8005140057

K-GD-1398

DEVELOPMENT OF THE FASTER PROCESS FOR REMOVING KRYPTON-85, CARBON-14, AND OTHER CONTAMINANTS FROM THE OFF-GAS OF FUEL REPROCESSING PLANTS*

M. J. Stephenson and R. S. Eby
Union Carbide Corporation
Nuclear Division
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

Abstract

The Oak Ridge Gaseous Diffusion Plant has the primary responsibility for the development of the FASTER (Fluorocarbon Absorption System for Treating Effluents from Reprocessors) process for application to LMFBR and LWR fuel reprocessing plants. Krypton-85 removals in excess of 99.9% and carbon-14 as carbon dioxide removals greater than 99.99% have been obtained in a development pilot plant. So far, pilot plant tests show that the presence of other reprocessing plant off-gas components does not appreciably affect the general operability or removal efficiency of the process. Tests also indicate that the one process designed for krypton and carbon removal may be even more effective in removing other fission products and objectionable chemical contaminants such as nitrogen dioxide. Elemental and organic iodine removals in excess of 99.99% and nitrogen dioxide removals over 99% were recently achieved. Higher process decontaminations are possible. Trapping studies show that 13X molecular sieves are very effective in removing the fluorocarbon vapor from the process product stream.

I. Introduction

Stringent emission standards are being formulated to limit the release of various volatile fission products from nuclear fuel cycle facilities. At this time, the viability of the nuclear fuel cycle rests, in part, on how well the industry can effectively manage all the associated nuclear wastes. The long-lived isotopes of krypton and carbon are of particular concern because the control technology has not yet been adequately demonstrated for removing either of these two fission products from the off-gas of commercial nuclear fuel reprocessing plants. The generally straightforward problem of off-gas decontamination is greatly complicated in this case by the presence of other common reprocessing plant off-gas components such as nitrogen oxides (NO, N_2O, NO_2), carbon dioxide, water, iodine, various organics, ruthenium tetroxide, and particulates. In the case of carbon-14, it is generally assumed that the volatile form of carbon will be carbon dioxide, although admittedly, quantities of carbon monoxide and light organics such as methane could also be present.

Figure 1. Schematic of the ORGDP Selective Absorption Pilot Plant

exchangers, and several refrigeration compressors. Physical and chemical traps are also installed for solvent recovery and final product separation and purification. Details of the process and development pilot plant are available in several program reports[3,4,5].

III. Experimental Program Plan

As currently envisioned, the krypton-85/carbon-14 removal process will be the final step in an integrated chain of processes designed to collectively decontaminate fuel reprocessing plant off-gas. The integrity and reliability of any off-gas decontamination system will undoubtedly be the subject of much scrutiny. Legitimate concern will be expressed not so much about how well the off-gas train will function in a normal operation, but about the overall conse-quences of abnormal operation and the capability of the individual processes to meet the challenges imposed by irregular or otherwise uncontrolled feed conditions. In this context, several fundamental questions need to be answered: (1) what happens in the event the upstream primary removal equipment fails and large amounts of other fission products and chemical contaminants inadvertently pass down-stream; (2) can the downstream process(es) be relied upon as a short-term backup system to remove the other radioactive components from the reprocessing plant off-gas in case of such a failure; and (3) how well can the fluorocarbon process function as the primary removal facility for iodine and other fission products. including ruthenium oxides, and chemical contaminants such as nitrogen dioxide. Pilot plant work is currently being directed toward exploring these points by establishing the general process behavior of feed gas components such as nitrogen oxides, iodine, methyl iodide, and water, and defining the effects of these components on the general operability and overall performance of a process designed for krypton-85 and carbon-14 removal.

Figure 3 gives the relative solubilities of various volatile feed gas components in the process solvent, refrigerant-12. Xenon and carbon dioxide are the most soluble of this group, while helium is the least. Figure 4 gives the predicted distribution coefficients of important feed gas components that are classified as high boiling components relative to the solvent. Those components more volatile than refrigerant-12 end up in either the process vent with the less soluble components, such as nitrogen and oxygen, or in the process product stream with the more soluble volatile components, such as krypton and carbon dioxide; while the less volatile components, i.e., iodine and nitrogen dioxide, collect in the solvent still reboiler. Water, not shown in figure 4, is more volatile than iodine but significantly less volatile than methyl iodide. Because krypton and xenon removals in excess of 10^3 were achieved previously, high process removals were projected for the even less volatile feed gas components.
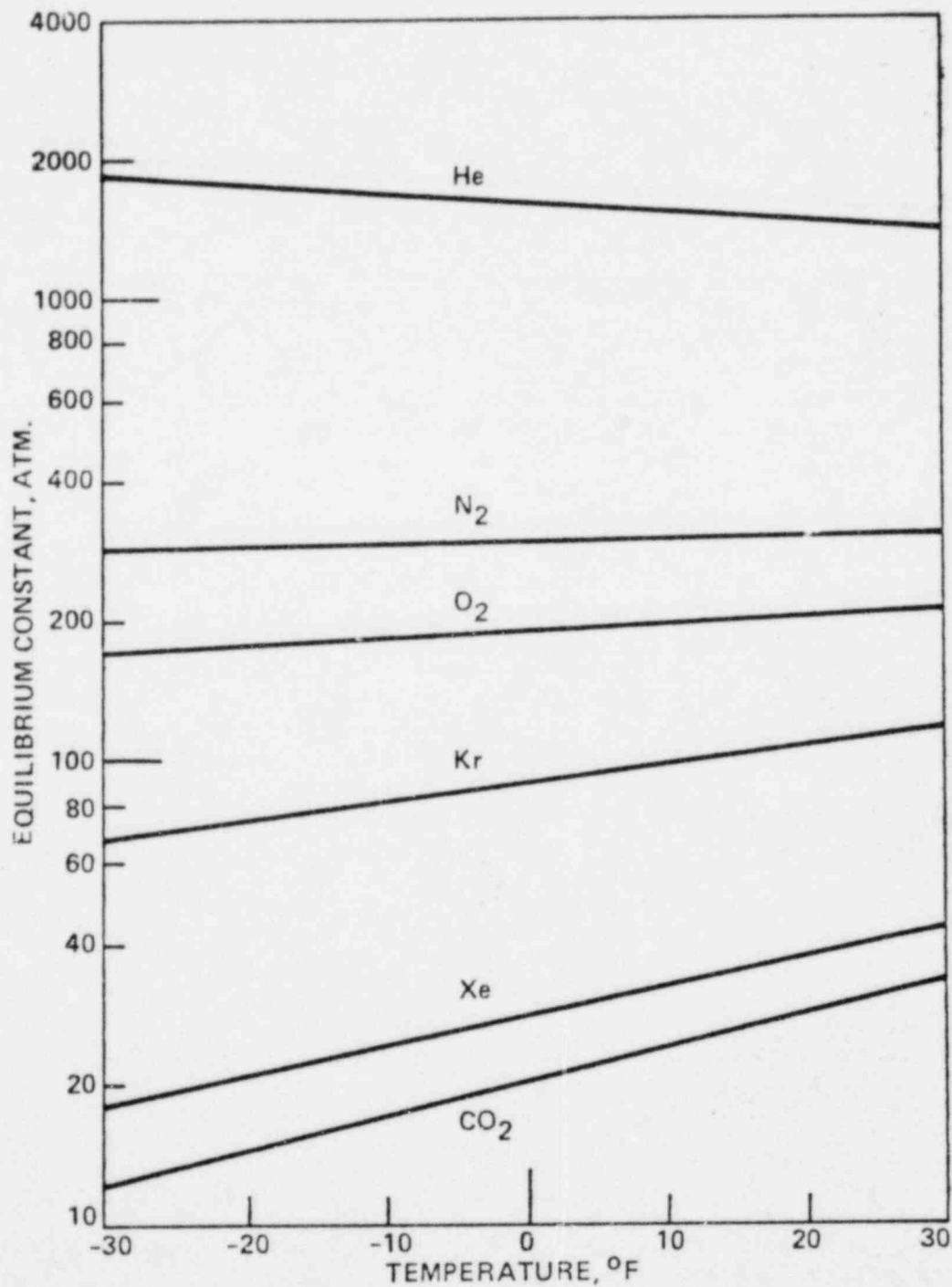
DWG. NO. G-76-671

Figure 3.   Equilibrium Distribution Coefficients of Various
Feed Gas Components in Refrigerant-12 (CCl_2F_2).

8005140057

K-GD-1398

DEVELOPMENT OF THE FASTER PROCESS FOR
REMOVING KRYPTON-85, CARBON-14, AND OTHER CONTAMINANTS
FROM THE OFF-GAS OF FUEL REPROCESSING PLANTS*

M. J. Stephenson and R. S. Eby
Union Carbide Corporation
Nuclear Division
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

Abstract

The Oak Ridge Gaseous Diffusion Plant has the primary responsibility for the development of the FASTER (Fluorocarbon Absorption System for Treating Effluents from Reprocessors) process for application to LMFBR and LWR fuel reprocessing plants. Krypton-85 removals in excess of 99.9% and carbon-14 as carbon dioxide removals greater than 99.99% have been obtained in a development pilot plant. So far, pilot plant tests show that the presence of other reprocessing plant off-gas components does not appreciably affect the general operability or removal efficiency of the process. Tests also indicate that the one process designed for krypton and carbon removal may be even more effective in removing other fission products and objectionable chemical contaminants such as nitrogen dioxide. Elemental and organic iodine removals in excess of 99.99% and nitrogen dioxide removals over 99% were recently achieved. Higher process decontaminations are possible. Trapping studies show that 13X molecular sieves are very effective in removing the fluorocarbon vapor from the process product stream.

I.   Introduction

Stringent emission standards are being formulated to limit the release of various volatile fission products from nuclear fuel cycle facilities. At this time, the viability of the nuclear fuel cycle rests, in part, on how well the industry can effectively manage all the associated nuclear wastes. The long-lived isotopes of krypton and carbon are of particular concern because the control technology has not yet been adequately demonstrated for removing either of these two fission products from the off-gas of commercial nuclear fuel reprocessing plants. The generally straightforward problem of off-gas decontamination is greatly complicated in this case by the presence of other common reprocessing plant off-gas components such as nitrogen oxides (NO, N_2O, NO_2), carbon dioxide, water, iodine, various organics, ruthenium tetroxide, and particulates. In the case of carbon-14, it is generally assumed that the volatile form of carbon will be carbon dioxide, although admittedly, quantities of carbon monoxide and light organics such as methane could also be present.
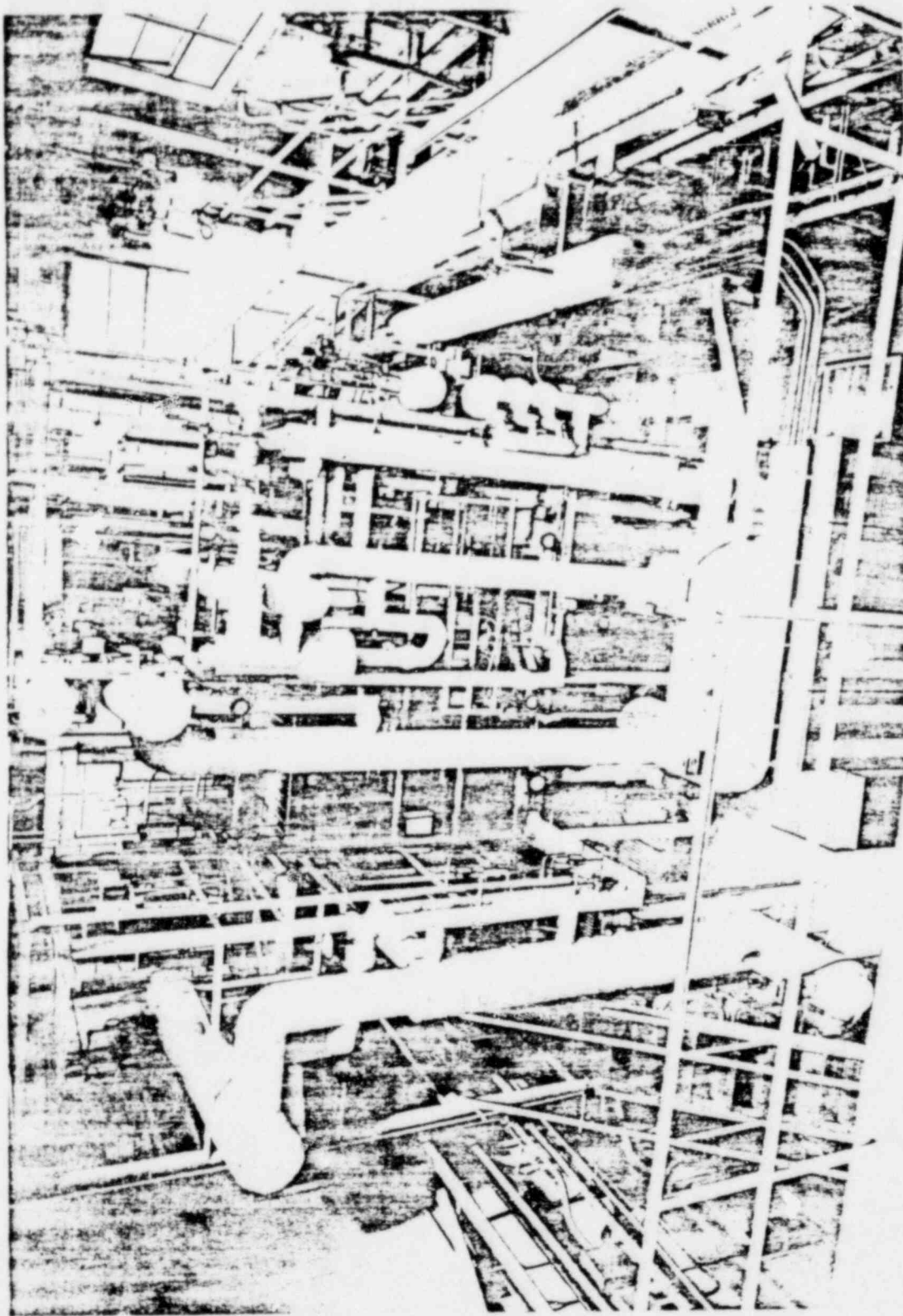

Figure 2.   Overall View of the ORGDP Selective Absorption Pilot Plant
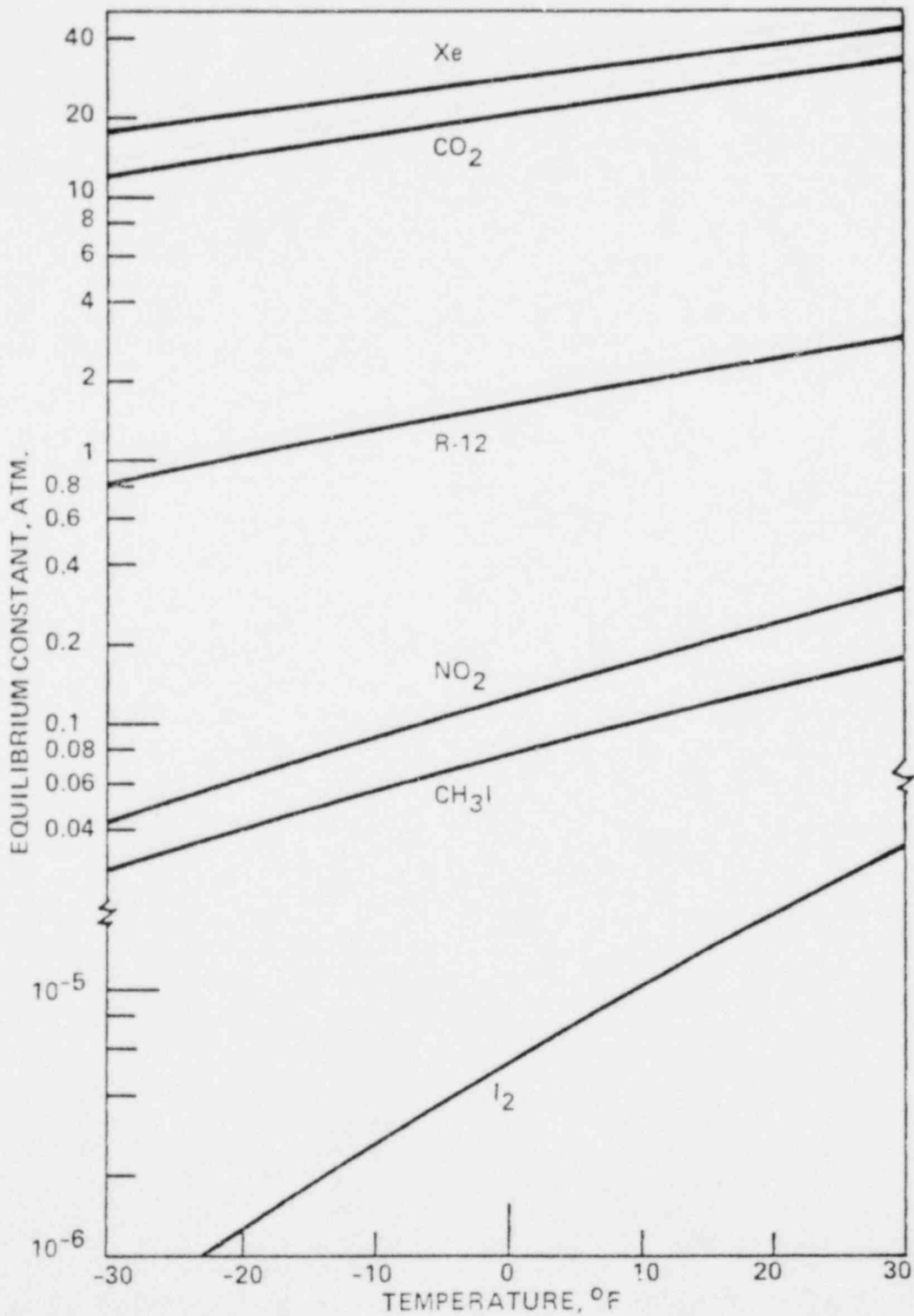
DWG. NO. G-76-670

Figure 4. Predicted Distribution Coefficients of High Boiling
Feed Gas Components in Refrigerant-12 (CCl_2F_2).

IV. Pilot Plant Test Results

Krypton absorption data were obtained several years ago and mass transfer correlations developed to describe the absorption phenomena[1,2]. Most of these tests, however, were conducted with a nitrogen feed gas containing only krypton. Recent pilot plant tests have been made with nitrogen feed gases containing (1) 0.1 ppm Kr, (2) 0.1 ppm Kr and, in addition, between 1000 and 3000 ppm CO_2 and between 6000 and 7000 ppm N_2O, (3) 0.1 ppm Kr and no feed gas cooler, (4) 0.1 ppm Xe, and (5) up to 6% carbon dioxide. The results of these tests are summarized in figure 5. Krypton tests were performed with 1 to 1.5 curies of Kr-85 and gamma scintillation techniques were used to analyze krypton process performance. Xenon tests were performed with 1 to 2 curies of Xe-133. Refrigerant-12, carbon dioxide, and nitrous oxide analyses were performed with an in-line infrared analyzer. Oxygen, nitrogen, and refrigerant-12 determinations were made with an in-line gas chromatograph and laboratory mass spectrometer. All tests were conducted at an absorber pressure of 300 psig, temperature between -25 and +10°F, solvent flow of 0.75 or 1.0 gpm, and feed gas flow between 7.5 and 22 scfm.

Pilot plant tests made with only krypton and nitrogen were repeated with high concentration of carbon dioxide and nitrous oxide (N_2O) to identify the effects of these very soluble feed gas components on krypton distribution in the system. The results of these tests suggest that, at least for the absorption step, the presence of other soluble feed gas components has no discernible effect on the process removal of krypton. Of course, the soluble components concentrate with the krypton and thereby dilute the krypton product. This problem, however, is not a very difficult one because the process product flow is only a small fraction of the reprocessing plant off-gas and can be handled in relatively small-scale equipment. Several product purification options are currently being evaluated to separate and isolate the krypton-85 and carbon-14[5].

Hot-gas feed is being considered as an alternative to desublimation of certain feed gas components such as iodine and water in the process gas cooler. In absence of the gas heat exchanger, the bottom of the absorber column will serve as the cooling section for the incoming feed gas and will allow the condensable and desublimable components to pass directly into solution. Comparison of plant tests with and without the feed gas cooler shows that the overall effect of the hot-gas feed on the process performance is small.

Xenon and carbon dioxide removals in excess of 99.99% were measured in pilot plant tests conducted at the same absorber conditions that yielded around 99% krypton removals. Carbon dioxide removals were a little higher than those measured for xenon. This is consistent with component solubilities given in figure 3. Based on pilot plant data, H_{OG} values for Xe and CO_2 were 6 to 10 inches. Significant amounts of carbon dioxide and xenon were found in the recycle solvent for those tests where final stripper molar L/V ratios above 2.0 existed. The absorber performance was noticeably affected by the recycle concentration in those cases where process removals exceeded 99.99%. Substantially better carbon dioxide removals were obtained in runs where higher stripper vapor upflows were maintained.
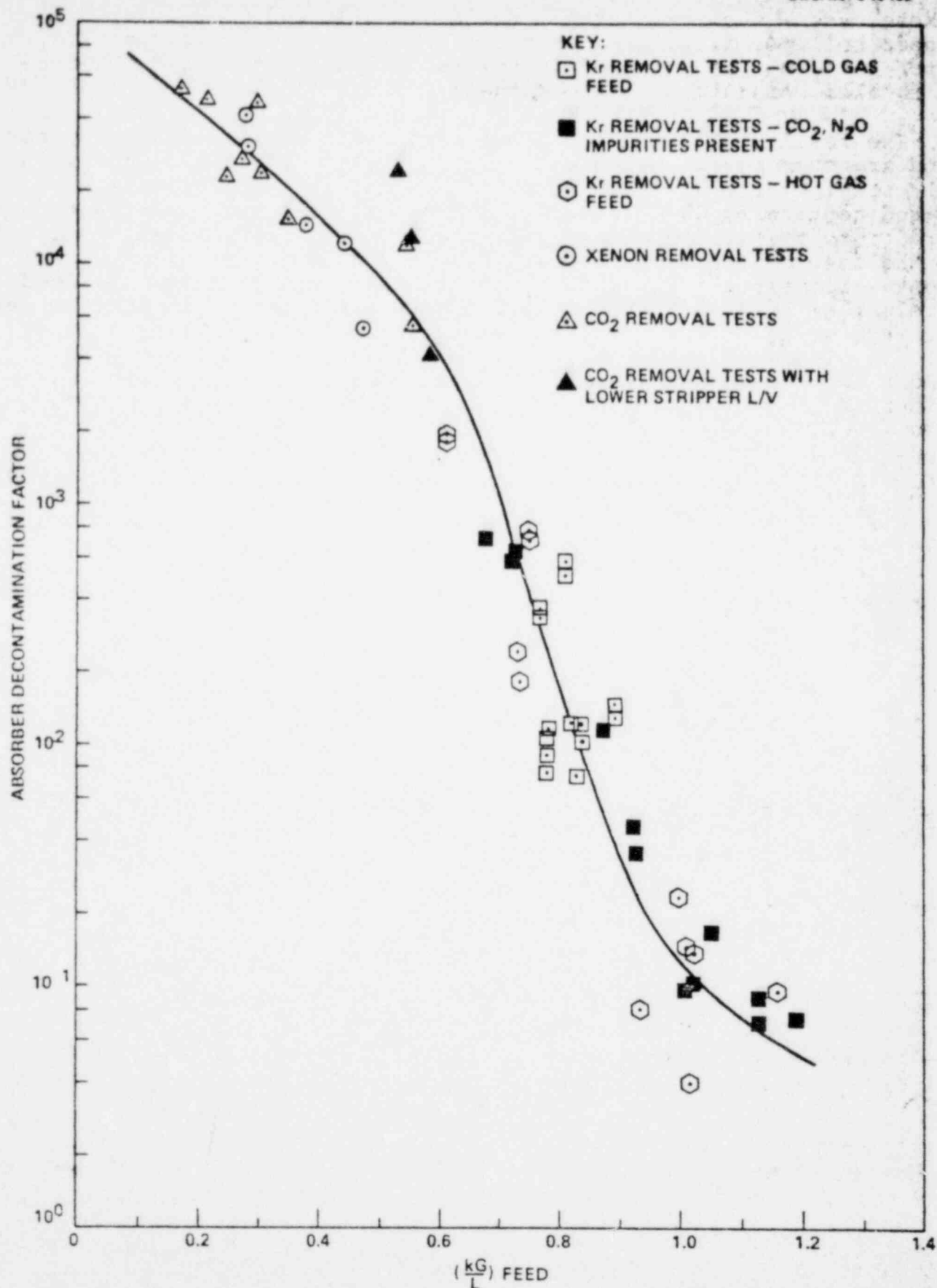
Figure 5.   Summary of Pilot Plant Tests with
             Krypton, Xenon, and Carbon Dioxide

In these cases, the stripper L/V ratio was near 1.8. At lower stripper boilups, i.e., even when the L/V ratio was as high as 3.0, krypton could not be detected in the recycle solvent. This observation is also consistent with component solubilities.

The results of the pilot plant tests with elemental and organic iodine are summarized in table I. The methyl iodide tests were relatively straightforward to perform and evaluate. A gas mixture was prepared containing CH_3I traced with 5 mc of I-131 and subsequently metered into the absorber feed gas line in the amount necessary to give the desired feed gas composition. No transport problems were evident. Elemental iodine, on the other hand, was difficult to feed and reluctant to move through the feed gas circuit even though the gas lines were heated. For these tests, solid iodine containing 5 mc of I-131 was placed on a finely divided support screen inside a feed cylinder and a pickup sweep gas flow was then diverted through the cylinder and routed to the absorber. Upon contacting the solvent, I_2 became mobile until collected in the solvent still reboiler. Elemental and organic iodine removals in excess of 10^4 were achieved. Gamma scintillation analytical techniques were again used to evaluate process performance. The small amount of activity relative to the plant size and long duration of the tests largely limited the quantitative capability of the counting equipment, since process removals were quite high and the off-gas in most cases contained an undectable amount of iodine. In some cases, the absorber performance could be calculated from the amount of activity in the recycle solvent by assuming that the absorber off-gas was in equilibrium with the incoming solvent.

The test results clearly show that the efficiency of the process to remove methyl iodide is definitely established by the performance of the solvent purification still. Elemental iodine, on the other hand, was much easier to remove from the recycle solvent. At the conditions of the still, i.e., -10°F, the volatility of refrigerant-12 relative to methyl iodide is 24. This value is greater than 10^5 for elemental iodine. Increasing the reflux ratio in the solvent still from 0.13 to 0.34 (tests 7 and 8) resulted in a significant reduction in the amount of methyl iodide in the recycle solvent and improved the process removal efficiency by a factor of 4. The effect of any recycled iodine on the process removal efficiency could not be determined because the iodine recycle concentrations were below the level of detection. The test data clearly indicate that higher reflux ratios and more rectifying stages will significantly improve the recovery capability of the process. It is important to point out that water and elemental iodine are significantly less volatile than methyl iodide, and consequently, these two components are much easier to remove from the solvent. Therefore, a process designed to achieve a methyl iodide decontamination factor of 10^6 should be capable of even higher elemental iodine and water removals.

The results of the nitrogen dioxide removal experiments are summarized in figure 6. More than 2 months of the recent test series was devoted to studying the long-term process behavior of NO_2. A spectrophotometric analyzer having the capability of detecting from 1 to more than 6,000 ppm NO_2 was used for direct in-line concentration determinations. Process removal efficiencies between 97 and 99.9%

Table I. Summary of Iodine Removal Tests*

Test Number	Iodine Form	Solvent Recycle	Still Reflux Ratio	Absorber Feed Gas Concentration, ppm	Measured Decontamination Factor†	Measured Decontamination Factor§
1	I_2	No	–	∿ 0.01	> 10^4	–
2	I_2	Yes	**	∿ 0.01	> 10^3	–
3	I_2	Yes	0.01	∿ 0.01	> 10^4	–
4	CH_3I	No	–	136	> 6×10^4	–
5	CH_3I	Yes	0.01	7	> 2×10^3	1.5×10^4
6	CH_3I	Yes	0.34	248	> 2×10^4	5.9×10^4
7	CH_3I	Yes	0.34	28	> 2×10^3	4.0×10^4
8	CH_3I	Yes	0.13	28	> 2×10^3	1.0×10^4

* General Test Conditions: Absorber Pressure, 300 psig; Absorber Temperature, -10°F; Solvent Flow, 1 gallon/minute.

† Based on absorber gas inlet and outlet stream I-131 analysis.

§ Based on absorber gas inlet and recycle solvent stream I-131 analysis and assumption that the absorber off-gas is in equilibrium with the recycle solvent.

** Solvent still partially by-passed.
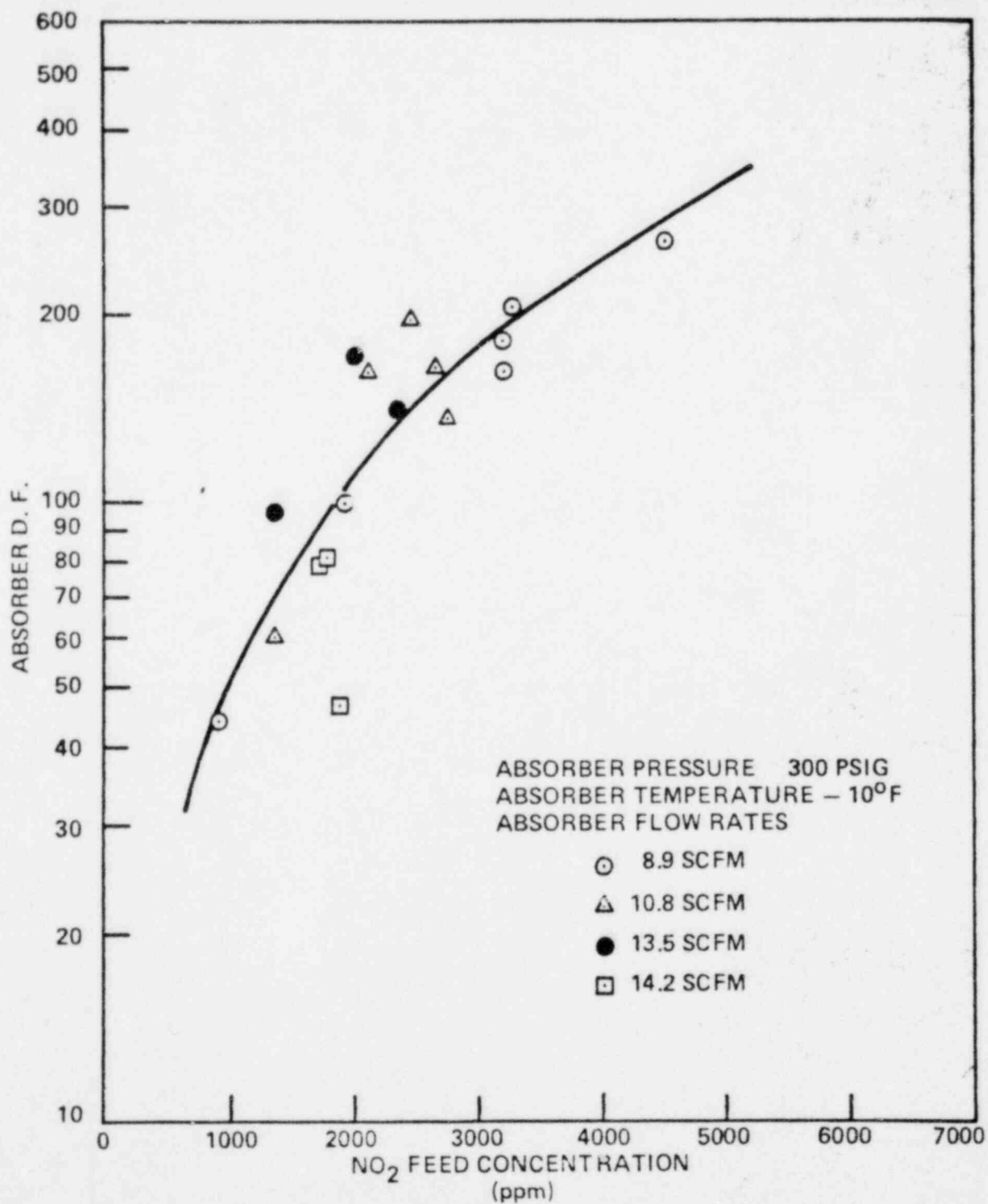
DWG. NO. G-76-658

Figure 6.   Fluorocarbon Process Removal of Nitrogen Dioxide
as a Function of Feed Gas Composition.

were achieved. No feed problems were encountered, and process effects due to the presence of the NO_2 in the feed gas and solvent lines were not observed. The data suggest that the removal of NO_2 is strongly dependent upon the feed concentration. This is contrary to previous experience with the less volatile components, I_2 and CH_3I, and the more volatile components, krypton and xenon. For one series of tests, the concentration of NO_2 in the absorber off-gas remained around 20 ppm regardless of the absorber feed gas flow or inlet concentration. This, of course, again indicates inadequate removal of high boiling components from the recycle solvent. The absorber off-gas concentration did decrease with an increase in the solvent still reflux but not to the extent that was found for the methyl iodide tests. This was not surprising since NO_2 is more volatile than CH_3I and thereby more difficult to remove from the solvent.

Another important part of the overall ORGDP development program is evaluation of process auxiliary subsystems. As part of this work, trapping studies were initiated to evaluate solid adsorbents for removing refrigerant-12 vapor from the process vent and krypton product. The results of these tests are given in table II. An ideal sorbent was identified as one that could reduce the refrigerant concentration in the process off-gas from a nominal 10% to less than 1 ppm. Three sorbent materials were initially considered: 5A molecular sieve, 13X molecular sieve, and H-151 alumina. Tests were conducted with 3-inch-diameter traps filled to a height of 4 feet with the test material. Initial bed temperatures were generally around 70 to 80°F. Tests were conducted with a total gas flow (R-12 and N_2) of 1934 sccm (0.02 ft/sec superficial velocity), 11,670 sccm (0.08 ft/sec), and 120,000 sccm (0.8 ft/sec). The 5A molecular sieve material proved to be unsatisfactory. Trap effluent contained 8.2 ppm before breakthrough, and the sorbent loading was only 0.5% at breakthrough. The alumina bed still could not achieve the desired refrigerant vapor removal. The trap effluent contained 10 ppm before breakthrough and refrigerant loading on the alumina varied between 2.2 and 2.9%. On the other hand, the 13X molecular sieve proved to be an excellent trapping material for the process solvent. The trap effluent contained less than 1 ppm R-12 and the 13X sieve loaded up to 30%. External cooling of the sorbent bed improved the loading capacity of the sieves. Regeneration studies showed that the loaded 13X sieves could be completely regenerated with a 350°F nitrogen sweep flow of 194 lpm in 6 to 7 hours.

V. Solvent Chemistry

The laboratory support work is being performed at ORNL by L. M. Toth, J. T. Bell, and D. W. Fuller. The initial program is designed to evaluate distribution coefficients of the various feed gas components in refrigerant-12, look at component interactions in a multicomponent system, and identify possible corrosion conditions that could develop. Undoubtedly, this important effort will be expanded as the program progresses. Work in this area was only initiated recently but a substantial amount of data has already been obtained. Several aspects of the physical and chemical behavior of I_2 in R-12 have been examined by absorption spectrophotometry in a high pressure optical cell. Iodine in R-12 has an electronic absorption band in the visible light region at 520 nm arising from a solvated I_2 molecular species.

Table II. Summary of R-12 Adsorption Studies for the Product Purification and Solvent Recovery Subsystems

Test Number*	Adsorbent	Cycle	Total Feed Flow, sccm	Feed Composition†, % R-12	Bed Temp., °F Initial	Final	Breakthrough Time hr	% R-12§	R-12 in Effluent Before Break, ppm	Regeneration Scheme Temp., °F	Time, hr
1	5A Sieve	1	1,934	9.5	65	~65	0.45	0.40	8.2	375	2.2
2	H-151 Alumina	1	1,934	9.5	75	~75	2.50	2.3	10.1	440	3.6
3	H-151 Alumina	2	1,934	9.5	69	~69	2.00	1.9	10.7	430	1.7
4	H-151 Alumina	3	11,670	10.0	77	88	0.30	1.7	19.0	420	1.5
5	13X Sieve	1	1,934	9.5	75	98	19.50	25.9	< 1	375	4.0
6	13X Sieve	2	11,670	10.0	78	127	2.67	22.3	150**	330	6.0
7	13X Sieve	3	11,670	10.0	85	139	2.67	22.0	< 1	350	7.7
8	13X Sieve	4	11,670	10.0	68	86††	2.92	24.8	< 1	360	6.5
9	13X Sieve	5	1.2 × 10⁵	3.1	73	85††	1.17	30.6	< 1	350	6.0
10	13X Sieve	6	1.2 × 10⁵	3.1	73	87††	1.12	29.5	< 1	360	6.0
11	13X Sieve	7	1.6 × 10⁵	2.3	88	145	0.5	13.3	< 1	360	6.0
12	13X Sieve	8	1.6 × 10⁵	2.3	75	113††	0.7	18.4	< 1	340	6.0

* All tests except 11 and 12 conducted at 4.5 psig in a nominal 3-inch-diameter trap with 0.0513 ft² (47.6 cm²) cross section. Tests 11 and 12 were made at 21 psig.

† The bulk gas is nitrogen.

§ R-12 loading defined as [(lb R-12 adsorbed)/(lb adsorbent)] × 100.

** The previous regeneration of 375°F for 4 hours was not sufficient to regenerate the 13X sieve loaded during the previous test; hence, the high concentration of R-12 in the effluent.

†† These tests conducted using external bed cooling.

In the absence of any added water, dilute solutions of iodine in refrigerant-12 are not expected to chemically react with either the solvent or stainless steel containment. There is some indication, however, that refrigerant-12 solutions of iodine containing excessive amounts of free water might interact with stainless steel. The solubility and distribution coefficient of iodine is currently being measured as a function of temperature. Later, the solution effects of free water will be determined.

VI. Conclusions

Recent and more detailed pilot plant tests continue to support hypotheses drawn from earlier scoping tests and performance calculations[2]. In short, the fluorocarbon-based process is versatile, has a high tolerance for feed gas impurities, and can function in a multiplicity of ways to clean up reprocessing plant off-gas and isolate the many contaminants for long-term storage and disposal. Tests show that a process designed to remove krypton-85 and carbon-14 can also achieve high iodine, methyl iodide, water, and nitrogen dioxide decontaminations. A comprehensive pilot plant testing program and an exhaustive solvent chemistry laboratory effort are continuing to fully define the capability and limitations of the FASTER process. If the process development program proceeds according to schedule, sufficient information will be available within 3 years to begin final design of an LMFBR or LWR demonstration plant. So far, no detrimental effects due to the presence of the various feed gas components in the fluorocarbon process have been uncovered except maybe a possible corrosion problem that could develop in a stainless steel system if free water is present. Materials of construction will be selected after the solvent chemistry work has been completed and possible corrosion mechanisms identified. Substantially more testing is required at this point before the process can be fully evaluated.

VII. References

[1] J. R. Merriman, Analysis of a Multicomponent Gas Absorption System with Carrier Gas Coabsorption, U.S.E.R.D.A. Report KY-G-300, Paducah, Kentucky (1975).

[2] M. J. Stephenson, et al., "Experimental demonstration of the selective absorption process for Kr-Xe removal", Proceedings of the Twelfth AEC Air Cleaning Conference, 11-27 (1973).

[3] M. J. Stephenson, et al., "Absorption process for removing krypton from the off-gas of an LMFBR fuel reprocessing plant", Proceedings of the Thirteenth AEC Air Cleaning Conference, 263-275 (1975).

[4] M. J. Stephenson, et al., Fluorocarbon Absorption Process for the Recovery of Krypton from the Off-Gas of Fuel Reprocessing Plants, U.S.E.R.D.A. Report K-GD-1390, Oak Ridge, Tennessee (1976).

[5] M. J. Stephenson and R. S. Eby, ORGDP Selective Absorption Pilot Plant for Decontamination of Fuel Reprocessing Plant Off-Gas, U.S.E.R.D.A. Report K-1876, Oak Ridge, Tennessee (In Progress).