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ABSTRACT

The off-gas from the reprocessing of HTGR fuel elements is unique among ~~reprocessing~~ nuclear fuel reprocessing off-gases because of the large amount of CO_2 produced by the burning of the fuel element which contains about ten times as much graphite as heavy metals. The relatively high temperature of the burning process ($\sim 800^\circ\text{C}$) releases virtually all of the volatile fission products, and troublesome amounts of some which are normally solid. There exists filters to remove particulate solids and sorbtion methods for I_2 and $^3\text{H}_2\text{O}$ which have good potential for application to this off-gas, but no existing technology was found to remove and concentrate the Kr. The high concentration of CO_2 in the filtered gas stream ($\sim 90\% \text{CO}_2$, 10% light gases, 10-20 ppm Kr), and the similarity of CO_2 behavior to that of Kr preclude the use of commonly employed processes such as membrane permeation, sorption on charcoal or molecular sieves, and physical absorption by a third component. The removal of CO_2 before such an operation appears feasible, but undesirable. A process involving Kr absorption in liquid CO_2 (KALC), which exploits the fact that Kr is more soluble in liquid CO_2 than is O_2 , N_2 , or CO , appears to be a natural solution to this particular problem.

The solubility of Kr in liquid CO_2 has been experimentally determined by an in situ radioactive counting method using ^{85}Kr . This method avoided the problems usually associated with sampling systems of highly volatile components. Kr (a total content of about 100 ppm) and CO_2 were contained in a sealed stainless steel tube, brought to equilibrium by rocking in a constant temperature bath, and counted with the tube in a vertical position to measure the radioactivity in each phase. Data were obtained at various temperatures over almost the entire CO_2 liquid range.

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Engineering calculations, based on literature values for the solubility of O_2 , N_2 , and CO and the measured values for Kr, on a KALC system which employs a fractionator and a stripper as well as an absorber indicate that a decontamination factor for Kr of 1000 can be achieved and that the Kr can be concentrated such that it comprises several percent of the removal stream.

The Rare Gas Removal Pilot Plant at the ORGDP was used to explore the feasibility of operating a KALC system. In addition to demonstrating that feasibility, the initial pilot campaign provided encouragement that the KALC process will be a good way to decontaminate the HTGR reprocessing off-gases.

DECONTAMINATION OF HTGR REPROCESSING OFF-GASES*

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Off-gas from the reprocessing of HTGR fuel elements is unique among the processing plant off-gases because the graphite and other carbon components of the HTGR fuel must be burned. This means that the quantity of gas is larger than that evolved from LWR, or IMFBR processing and the composition is different since it is mostly CO_2 . While alternative processing schemes were suggested which proposed the separation of the graphite by physical methods to make burning unnecessary, problems were encountered (not the least of which was the storage of the contaminated graphite) which proved more difficult than the treatment of the burner off-gas. The burning operations are performed at temperatures between 700 and 1000°C with a slight excess of oxygen to avoid, in so far as possible, the formation of CO. Commercial oxygen would be used rather than air to avoid handling large quantities of N_2 , but some in leakage of N_2 is unavoidable. It has been found⁽¹⁾ that several of the normally solid fission products are volatile at combustion conditions. The most important of the ones reported are Cs, Zr, Nb, Ru, and Ce, of which only the Ru exceeded (by a small amount) 10% volatilization. A sintered metal filter, located above the burner was very effective in retaining all of these except Cs. About 2% of the Cs passed through a filter

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train, while the other metal fission products were retained with a decontamination factor greater than 10^3 . The T, Xe, and Kr were all quantitatively released in the burning operations. Data are not available on I_2 but it is also expected to come off during burning. A description of the gas stream after filtration is given in Table 1. For a one tonne per day plant, one hundred blocks would be processed per day and the given numbers would be multiplied by one hundred.

Since the removal and handling of Kr seemed to be the most difficult problem, our attention has been directed to it. The available technology was thoroughly assessed to establish whether there existed a process which would do the job. ⁽²⁾ The processes practical for removing Kr from streams similar to contaminated air, without seriously altering the composition of the bulk stream, are ineffective for streams containing large amount of CO_2 . Indeed, the insidious similarity of the behavior of Kr and CO_2 usually establishes tolerable limits of CO_2 concentration in such processes. Sorption on molecular sieves or other solid sorbants, selective absorption with halocarbons, and selective membrane permeation techniques are among the processes eliminated by this factor.

The expedient of removing the CO_2 from the gas stream was then considered. This could be done by several methods. Reaction of the CO_2 with a lime bed produces prodigious amounts of solid radioactive waste for storage, and was ruled out. Caustic scrubbers are effective but also produce unacceptable amounts of waste. Among the regenerable scrubbing systems, the hot potassium carbonate system seems most desirable; specifically, it is as effective and more economical than the amine sorbants. Finally, the possibility exists that the CO_2 could be removed by condensation. Because the triple point of CO_2

ESTIMATED BURNER OFF-GAS ANALYSIS*

MAJOR COMPONENT	POUNDS	SCF	MOLE FRACTION
CO ₂	1223	9976	0.897
O ₂	75	846	0.075
N ₂	24	312	0.028
CONTAMINANT	PPM (TOTAL)	PPM (RADIOACTIVE)	CURIES
⁸⁵ Kr	16	1.2	572.0
³ H	2.4×10^{-2}	2.4×10^{-2}	9.8
¹³¹ I	3	9.2×10^{-7}	0.2
Xe	61	-	-

* FOR HEAD-END REPROCESSING OF ONE FSVR FUEL BLOCK;
6-YEAR EXPOSURE, 150-DAY COOLING.

is -56.6°C at a vapor pressure of 5.1 atm, it is not feasible to completely remove the CO_2 as a liquid. In order to reduce the CO_2 content to a small fraction of the gas stream, desublimation temperatures of the order of -100°C are necessary even when the gas is compressed to several atmospheres pressure. In none of the methods considered is it certain that the CO_2 removed from the gas stream would be sufficiently decontaminated from Kr or other fission products to allow its discharge. Further, the removal of CO_2 does not reduce the volume of the off gas stream sufficiently to allow it to be stored, but only prepares it for Kr removal by other methods.

This rather unpromising review of existing technology led us into the development of a rather unique method for removing Kr from the HTGR burner off-gas. The process involves the selective absorption of Kr in liquid CO_2 and has been called the KALC process (for Krypton Absorption in Liquid Carbon Dioxide). The process operates at about 20 atms pressure and at temperatures from about -45°C to -20°C . The flowsheet, in simplified form, is shown in Fig. 1. The flowrates shown are those that might be used in a pilot facility and would be equivalent to processing of three blocks of Ft. St. Vrain fuel per day. The flow ratios shown are approximate, but more precise calculations, which continually change with incorporation of newly acquired data, show no qualitative differences.

The filtered burner off gas, before being fed into the system, is compressed and chilled so that part of the CO_2 is condensed. In the absorber-fractionator system virtually all of the Kr is selectively absorbed in the liquid phase while all gas components with solubility less than Kr,

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such as O_2 , N_2 and CO , are returned to the gas phase and discharged from the top of the absorber along with much of the CO_2 . Gases more soluble than Kr, like Xe, go with the liquid CO_2 to the stripper where the Kr is removed and concentrated. The CO_2 from the bottom of the stripper would contain components of low volatility. Xenon could either be allowed to accumulate in the CO_2 to the point where it eventually were discharged from the top of the absorber, or it could be removed by a separate distillation operation on the recycle CO_2 stream. A very high purity Xe product should be possible by this technique.

The scrubber may be expected to remove from the incoming gas most of the particulates that reach the process. At KALC conditions, water and all conceivable forms of iodine are essentially non-volatile components which, at the expected inlet concentrations, are soluble in the liquid phase. Solids and non-volatile components would tend to accumulate in the recycled liquid CO_2 . They could be removed by an evaporator which would return purified CO_2 to the process and concentrate the solids for discharge. When it is realized that the volatility of water and the iodine compounds is limited by the vapor pressure of the pure solid phases, one can imagine such an evaporator effectively operating with a thick slurry of crystals in the reboiler.

Development of the KALC process requires: (1) obtaining the necessary equilibrium and thermodynamic data for describing the system, (2) selecting, characterizing, and, in some cases, developing components required for a radiochemical application of the process, (3) selecting a good operating mode with its associated control system, and (4) demonstrating the performance of an integrated system. At this time problems 2 and 3 have received only

sufficient attention to assure us that appropriate solutions will be forthcoming. Work on problems 1 and 4 has already yielded significant results.

Solubility of Krypton in Liquid CO₂

A previous experimental determination of the solubility of krypton in liquid CO₂ was made at Jülich,⁽³⁾ but the results differed considerably from the calculated solubility assuming ideal behavior. We therefore made our own measurements using in situ counting of tracer ⁸⁵Kr distributed between equilibrated gaseous and liquid phases in a sealed container. The in situ technique eliminated the inaccuracies usually associated with sampling highly volatile systems.

The equipment used is shown schematically in Figure 2. Essential components were a cold bath, an equilibrating device, and counting equipment. The cold bath temperature was controlled to within $\pm 0.03^\circ\text{C}$ by circulating a slight excess of coolant from a dry ice-trichlorethylene reservoir and supplying heat as called for by a thermostat. The Kr-CO₂ mixture was contained in a stainless steel cylinder 1 in. diam by 11 in. long, which was rocked for at least one hour at temperature. We have determined that distribution equilibrium is attained by this procedure. The equilibrated system was then set upright and the ⁸⁵Kr activity counted in each phase, yielding raw data on a volume basis. Data reduction involved (a) correcting for internal attenuation and backscatter from the CO₂, and (b) recalculating the Kr activity on a mole (rather than volume) basis. The correction, sometimes as much as 25% depending upon the CO₂ density and the counting energy

- A - Counterweight
- B - Lead-shielded scintillation counter
- C - Cylinder in counting position
- C' - Cylinder in equilibrating position
- D - Controlled temperature bath
- E - Motor-driven oscillator

- F - Circulating pump
- G - Dry ice/solvent cold reservoir
- H - Temperature controller
- I - Sensing element
- J - 250 watt heater

range, was made by means of a calibration curve. This curve was prepared empirically by incrementally adding CO_2 to a fixed quantity of Kr. The recalculation merely required the use of the CO_2 density, which is well known.

The data were finally expressed as a separation factor, $Y_{\text{Kr}}/X_{\text{Kr}}$, where Y and X are the mole fractions of Kr in the gaseous and liquid phases, respectively. The total amount of Kr present (^{85}Kr plus cold Kr) was usually less than 1000 ppm, but since the separation factor is a ratio, it was not necessary to know the exact amount. The reduced data are shown in Figure 3. A total of 59 data points were obtained, covering the entire liquid range. The curve drawn through our data is linear over most of its length, showing a slight positive curvature near the triple point, and dropping off strongly toward a value of unity as the critical temperature is approached. Our curve has about twice the slope of the calculated ideal curve, and crosses it near 0°C . A more sophisticated calculated curve, which allows for non-ideality in both phases ⁽⁴⁾ falls below the ideal curve. The Jülich data tend to follow this latter curve, but show a minimum at about 20°C . The fact that no minimum was predicted favors our results. Further, in order to validate the method used here, the distribution of ^{85}Kr in a $\text{Kr-H}_2\text{O}$ system was determined and founded to agree with reported values obtained by other methods. ⁽⁵⁾ Our known errors (from uncertainties in counting, temperature, CO_2 density, and empirical calibration) are somewhat less than the total scatter shown in Figure 3.

Preliminary data indicate that the krypton distribution is not significantly altered either at much higher krypton contents or by the presence of added oxygen.

KRYPTON DISTRIBUTION BETWEEN GASEOUS AND LIQUID CO₂

Solubility of O₂, N₂, and CO in CO₂

The literature has provided some data on the solubility of O₂ in liquid CO₂,^(6,7,8) somewhat less on N₂ in CO₂,^(6,8,9) and a very small amount on CO in CO₂.⁽¹⁰⁾ Most of the available data are at high concentrations, and hence higher pressures than of interest to this work. When the light gases comprise less than 50% of the gas phase, at total pressures less than 50 atms, the liquid phase contains less than 10% dissolved light gases. As the light gas concentration decreases from this level, data become sparse with degenerating accuracy, but theory has given us some assistance in correlating and extrapolating the data in the low concentration regions.

Equilibrium data from the literature have been fitted to a model which, over the range of conditions of interest, describes the KALC system well. Of necessity the model is based on binary system data. The only ternary data close to the KALC system conditions were for the O₂-N₂-CO₂ system at pressures over 50 atm. Even though out of the proper range, these data and equilibrium numbers calculated from the model were in reasonable agreement. The model is most simply expressed in the form: given a liquid phase composition and a temperature, calculate the total pressure and the vapor phase composition.

The total pressure was found to fit the empirical relation,

$$P_t = P_{CO_2}^* + \sum a_i x_i + \sum b_i x_i P_{CO_2}^* + \sum_j \sum c_j x_i \quad (1)$$

Where P_t = total pressure (atms)

$P_{CO_2}^*$ = saturated vapor pressure of CO₂ at system temperature (atms)

x = mole fraction in liquid phase

i, j = index subscripts applied to all components except CO_2

a, b, c = empirically determined constants.

The compressibility of CO_2 vapor is such that correction for non-ideality is required. All other components have critical points sufficiently removed from KALC conditions that gas phase ideality can be assumed. A reasonable form for the gas phase composition then becomes

$$y_{\text{CO}_2} = (p_{\text{CO}_2}/Z)/[\sum p_j + (p_{\text{CO}_2}/Z)] \quad (2)$$

$$y_i = p_i/[\sum p_j + (p_{\text{CO}_2}/Z)] \quad (3)$$

where Z = the compressibility factor for saturated CO_2 at the temperature of the system

p = partial pressure

y = mol fraction in vapor phase.

The partial pressures are defined so that

$$P_T = p_{\text{CO}_2} + \sum p_i. \quad (4)$$

Because the concentration of the dissolved light gases is small, Raoult's law was applied to the CO_2 . It was necessary, however to make a Poynting-type correction to the CO_2 vapor pressure. As an expedient in getting a better fit, the molar volume of the liquid phase was not used, but instead a fictitious molar volume is about a factor of three times the real molar volume.

The partial pressure of CO_2 is then,

$$p_{\text{CO}_2} = p_{\text{CO}_2}^* (1 - \sum x_j), \quad (5)$$

where

$$P_{CO_2} = P_{CO_2}^* \exp[k (P_t - P_{CO_2}^*)/T], \quad (6)$$

and

P_{CO_2} = effective vapor pressure of CO_2 (atm),

T = absolute temperature ($^{\circ}K$),

k = a determined constant = $1.7^{\circ}K/atm$.

The partial pressure of the i th component is given by

$$P_i = \frac{x_i}{\sum x_j} [P_{CO_2}^* - P_{CO_2} (1 - \sum x_j)] + a_i x_i + b_i x_i P_{CO_2}^* + c_i x_i \sum x_j \quad (7)$$

For a binary system, equation 7 reduces to

$$P_i = P_t - (1 - x_i) P_{CO_2} \quad (8)$$

These equations comprise a set from which equilibrium can be calculated. The numerical values for the constants are given in Table 2 along with the expressions used in this study to compute the compressibility factor, Z , and the saturated vapor pressure of CO_2 , $P_{CO_2}^*$.

Henry's law constants consistent with the model, and defined as the limit of the ratio of the partial pressure to the mole fraction in the liquid phase, are shown in Figure 4. It is noted that carbon monoxide is predicted to be the most difficult component to separate from krypton, but only slightly more difficult than oxygen. The separation factor between krypton and carbon monoxide increases from 1.43 at $0^{\circ}C$ to 1.8 at $-20^{\circ}C$. These separation factors are sufficiently high that neither the required height of towers nor the control of flow rates for KALC will cause undue concern.

Table 2. Coefficients Correlating Equilibrium Data for the KAlC System

Component	a	b	c
O ₂	532.33	-2.7153	-494.72
N ₂	720.22	-5.9729	-553.88
CO	484.39	-1.8473	-395.10
Kr	188.0	2.80	—

$$\text{Total Pressure} = P_t = P_{\text{CO}_2}^* + a_i x_i + b_i x_i P_{\text{CO}_2}^* + c_i x_i \sum x_j$$

$$\text{Henry's Constant} = H_i = a_i + P_{\text{CO}_2}^* (1 + b_i)$$

Saturation Vapor Pressure of CO₂:

$$\ln(P_{\text{CO}_2}^*) = -8.175626 + 26.27742 \left(\frac{T}{600} \right) - 23.76839 \ln \left(\frac{T}{600} \right) - 8.62709785 \left(\frac{600}{T} \right)$$

$$\text{Compressibility of CO}_2 = Z = 3.21203 - .029634967T + 1.3757 \times 10^{-4} T^2 - 2.2960 \times 10^{-7} T^3$$

T = Absolute temperature (°K)

Fig 4.

HENRY'S CONSTANTS FOR MAJOR COMPONENTS IN KALC

Feasibility Demonstration of KALC

Despite the early stage of the development of KALC, the feasibility of the process has been demonstrated in a recent campaign conducted by ORNL at the ORGDP Rare Gas Removal Pilot Plant. The primary objective during these feasibility studies was to establish our confidence in operating a liquid CO_2 /light gas system. However, ^{85}Kr was used in tracer amounts during much of the operation.

The basic pilot plant, which has been used quite extensively over the past few years in the development of the fluorocarbon absorption processes, (11) is composed of three separate columns for carrying out the absorption, fractionation, and stripping operations. Each of the packed columns has a 9-foot section of packing, with the absorber and fractionator being 3-in. in diameter and the stripper being 10-in. in diameter.

A nominal gas flow to the absorber of 10 to 15 SCFM was used during the feasibility studies, with a counter-current flow of about 1.5 gpm of liquid CO_2 . Under these conditions and with about 20 atmospheres operating pressure, the column temperatures were in the predicted range of -20 to -40°C . The system operated very smoothly throughout the campaign period of three weeks.

In-line analyses were not possible for checking concentrations, etc., but estimates (which were later verified by mass spec analyses) leave little doubt that such a system, with controls and instrumentation suited specifically to the liquid CO_2 process, can effectively remove Kr from the burner-type off-gases. Spot checks on Kr behavior in the system at arbitrary run conditions indicated both absorber and process DF's on the order of 100, with process concentrations in excess of 1000.

Discussion and Conclusions

An economic evaluation of KALC has not yet been undertaken and specific costs are not yet available. The compressor and refrigeration requirements will be a major portion of the total system expense but the costs will not be severe. The capital and operating cost associated with the KALC system should be only a small fraction of those for the rest of the reprocessing plant. Corrosion in the basic KALC process should present no problems. More study is required, however, on corrosion in any special operation which concentrates iodine and tritium for removal.

There are still many unanswered questions of an engineering nature, primarily concerned with equipment design and performance but also including the selection of the operating mode most conducive to reliable control and system performance under transient loads. Preliminary analysis of the control problem indicated several alternatives which should work. A calculational model of the KALC process which can predict system performance will be valuable both in studying control and in interpreting the results of engineering experiments. Such a model is now partially complete.

Doubts about the feasibility of KALC have been dispelled by an actual demonstration in engineering equipment and by the accumulation and consideration of basic equilibrium and physical property data. Our determination of the distribution of Kr in the KALC system and/or the data on the other light gases reported in the literature would have to be in error by incredible factors to render the process unworkable. We have still to discover any supportable objection to its application to HTGR off-gas decontamination,

and the advantages of using one of the components of the stream as the solvent to effect its decontamination, the moderate operating conditions employed, and the general effectiveness of the process make KALC very attractive.

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