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**Theoretical Analysis and Preliminary
Experiments on the Feasibility of
Removing CO₂ Containing ¹⁴C Selectively
with a Ca(OH)₂ Slurry from a
⁸⁵Kr-Contaminated HTGR Reprocessing Plant
Off-Gas Stream**

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MASTER

OAK RIDGE NATIONAL LABORATORY

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CHEMICAL TECHNOLOGY DIVISION

Thorium Utilization Program
Reprocessing Development - Task 200

THEORETICAL ANALYSIS AND PRELIMINARY EXPERIMENTS ON THE
FEASIBILITY OF REMOVING CO₂ CONTAINING ¹⁴C SELECTIVELY
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THEORETICAL ANALYSIS AND PRELIMINARY EXPERIMENTS ON THE
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ABSTRACT

Exploratory experiments were conducted to find methods of removing ¹⁴C-contaminated CO₂ with a Ca(OH)₂ slurry from off-gas streams without removal of ⁸⁵Kr. Purging the product CaCO₃ slurry, created by reacting CO₂ and Ca(OH)₂, with a small amount of gas appears effective in the removal of any residual krypton from the CaCO₃. It therefore appears feasible to remove ¹⁴C-contaminated CO₂ before removal of ⁸⁵Kr from HTGR off-gas streams and hence reduce the volume flow rate to the ⁸⁵Kr removal equipment with significant cost savings.

1. INTRODUCTION, SUMMARY, AND CONCLUSION

A preliminary experimental and theoretical investigation was conducted on an alternative flowsheet to remove radioactive ¹⁴C and ⁸⁵Kr from the off-gas stream of an HTGR fuel reprocessing plant. The present flowsheet removes ⁸⁵Kr first with the KALC (Krypton Adsorption in Liquid Carbon dioxide) process, followed by the removal of the ¹⁴C by reaction of all the carbon in the form of CO₂ with a Ca(OH)₂ slurry to yield solid CaCO₃. The existing flowsheet was developed before the hazards of ¹⁴C were fully recognized; hence, it was thought feasible to release all the ¹⁴C-contaminated CO₂ to the atmosphere. The CO₂ removal equipment for ¹⁴C was added to the existing flowsheet upon recognition of ¹⁴C as a possible health hazard. The proposed new flowsheet would remove all CO₂ first by reaction with a Ca(OH)₂ slurry, followed by krypton removal

with the FASTER (Fluorocarbon Adsorption System for the Treatment of Effluents from Reprocessors) process or some other process.

The two krypton removal systems, KALC and FASTER, are very similar. In each system, a scrub liquid absorbs krypton from the off-gas stream semiselectively. The krypton-rich liquid is sent to a fractionator where oxygen and other coabsorbed impurities, excluding krypton, are boiled out of the solution and recycled to the absorber feed gas so that any residual krypton may be recovered. The krypton-rich liquid is sent to a stripper column which separates the krypton from the liquid. The liquid is recycled to the absorber. In the KALC process, the liquid is liquid carbon dioxide. The KALC process is only practical with CO₂-rich streams because the high vapor pressure of liquid CO₂ results in large losses of CO₂ from the adsorber. Incoming CO₂ in the feed gas can compensate for these losses. The FASTER process uses liquid fluorocarbon-12, which has a low vapor pressure and, hence, a low loss rate from the adsorber. The FASTER process cannot be used for CO₂-rich streams because fluorocarbons adsorb CO₂ more readily than krypton.

The off-gas stream to be treated for ¹⁴C and ⁸⁵Kr removal contains about 95% CO₂ with 10 to 15 ppm krypton and about 60 ppm xenon. After CO₂ removal, the stream is primarily O₂ and N₂.

The advantages of the new proposed flowsheet include the following:

1. If the krypton removal occurs after CO₂ removal, the gas flow is about one-twentieth of the gas flow before CO₂ removal. This greatly reduces the size and cost of the krypton removal system.

2. If the FASTER process for krypton removal is used rather than KALC, the experience expected to be gained from using FASTER in LWR and LMFBR fuel reprocessing plants will also be applicable to HTGR plants. The KALC process would only be used for HTGR fuel reprocessing plants; hence, no practical experience can be gained from other plants concerning its operation.
3. It is expected that the FASTER process should be more stable with respect to unusual operating conditions compared with KALC. Any small heat leakage into KALC can easily vaporize the liquid CO_2 , resulting in a process upset. The fluorocarbon-12 does not vaporize as easily; hence, process upsets are less likely.
4. The inventory of CO_2 in FASTER is much less than that of KALC with its liquid CO_2 . In case of an accident or upset process condition, the FASTER process would release less ^{14}C -contaminated CO_2 .
5. The ^{14}C appears to be a greater health hazard in the long term than ^{85}Kr . Removal of CO_2 first allows the FASTER process to act as a backup CO_2 removal system for small breakthroughs of CO_2 .
6. If the CO_2 removal equipment breaks down, the plant must be shut down since it is not feasible to store the large volumes of off-gas being generated. If only the krypton removal equipment fails after CO_2 removal, it may be possible to store untreated off-gas for limited periods of time while making repairs. This is possible because the rate of production of the off-gas, excluding the CO_2 , is quite small.

The proposed process has several potential disadvantages. These include:

1. The system is presently undeveloped; hence, less assurance about its feasibility exists.
2. With krypton normally in the CO_2 removal equipment, this equipment may require additional radiation shielding.
3. If CO_2 removal with $\text{Ca}(\text{OH})_2$ precedes krypton removal, there is the risk of incorporating ^{85}Kr in the product CaCO_3 .

This probably cannot be allowed for two reasons:

- a. Krypton is an inert gas. If it is incorporated into CaCO_3 , there is the risk that it will escape later.
- b. The largest volume of radioactive wastes generated from an HTGR fuel reprocessing plant is the CaCO_3 from CO_2 removal. The ^{14}C is a low energy beta emitter with no gamma activity; hence, shipment of ^{14}C -contaminated CaCO_3 to a waste disposal site requires no shielding. If ^{85}Kr is incorporated into the CaCO_3 , its relatively high-energy gamma activity will require shipping the CaCO_3 with some shielding, which increases the difficulty and the cost of handling the CaCO_3 waste.

Uncertainties about the degree of incorporation of ^{85}Kr in the CaCO_3 are the prime reasons why CO_2 removal followed krypton removal in the original basic flowsheet.

A series of experiments and theoretical calculations were conducted. Since other experimenters have shown that each individual component in

the proposed process works,^{1,2} the study was directed at determining how to prevent ^{85}Kr from being incorporated into the CaCO_3 when the CO_2 reacts with the $\text{Ca}(\text{OH})_2$ to form CaCO_3 . The experiments consisted of: (1) reacting a slurry of $\text{Ca}(\text{OH})_2$ with CO_2 to form CaCO_3 in the presence of krypton, (2) treating the product slurry by some technique to remove krypton, and (3) destroying the slurry with HCl to convert the solid CaCO_3 to soluble CaCl_2 . During each step, the krypton concentration of the liquid and gas phase was measured. The following results were obtained:

1. Most of the krypton found in the product CaCO_3 slurry was dissolved in the water, not incorporated into the solid.
2. Purging the slurry with a gas (steam, air, etc.) will remove most of the krypton from the slurry.

Based on the present evidence, including laboratory-scale experiments, it appears feasible and desirable to remove CO_2 containing ^{14}C before removing ^{85}Kr in an HTGR fuel reprocessing plant off-gas stream. Additional work on an engineering scale would be needed to confirm these results and to obtain reasonable assurance that the process is indeed workable.

2. PROCESS FLOWSHEETS

Recent evaluations^{3,4} indicate that the long-term hazard from ^{14}C is significantly greater than the hazard of ^{85}Kr . This improved understanding of these gaseous radioactive wastes will certainly be reflected in future environmental regulations; hence, it is appropriate today to consider alternative off-gas flowsheets for HTGR fuel reprocessing plants

which can better meet the expected environmental regulations within present economic constraints.

This section reviews the present flowsheet and the newly proposed flowsheet for removal of ^{14}C and ^{85}Kr . An analysis is also made of the amounts of ^{85}Kr which can be tolerated in the CaCO_3 waste product produced when removing ^{14}C in the form of $^{14}\text{CO}_2$ with a $\text{Ca}(\text{OH})_2$ slurry. Section 3 reports on preliminary bench-scale experiments, and Sect. 4 addresses the capabilities of various flowsheets.

2.1 Present Flowsheet

Figure 2.1 shows the basic process flowsheet for the HTGR fuel reprocessing plant off-gas stream developed before ^{14}C was recognized as a significant health hazard. With the recognition that ^{14}C in the form of CO_2 could probably not be released to the atmosphere,³ a CO_2 removal process, consisting of reacting CO_2 with $\text{Ca}(\text{OH})_2$ to yield CaCO_3 , was added just before discharge to the stack. The initial paper study⁵ on this CO_2 removal process indicated that the process should be located at the end of the off-gas processing stream because location elsewhere in the flowsheet raised the problem of other radioactive materials being incorporated into the CaCO_3 waste, thus creating difficulties in disposal of CaCO_3 .

The present method removes krypton from the CO_2 -rich off-gas stream using the KALC² (Krypton Adsorption in Liquid Carbon dioxide) process. The KALC process (Fig. 2.2) selectively absorbs krypton from the off-gas at a concentration of 10 ppm while maintaining liquid CO_2 at a pressure of 2.4×10^6 Pa (24 atm) and a temperature of -22°C . The liquid

Fig. 2.1. Schematic flow diagram of off-gas system for HTGR prototype fuel processing facility and approximate material balance (TBV).

Fig. 2.2. Selective absorption system for krypton removal.

CO₂ containing the krypton is passed through a fractionator at 2.2×10^6 Pa (22 atm) and -20°C which selectively strips off other gases, primarily O₂. These gases are recycled to the absorber column feed since they contain traces of krypton. The krypton-rich liquid is then sent to a stripper at 2.0×10^6 Pa (20 atm) and -18°C which separates the krypton from the CO₂. The krypton-depleted liquid CO₂ is recycled to the absorber. The process can remove in excess of 99% of the krypton from the off-gas and concentrate it by a factor of 1000. The initial off-gas must be primarily CO₂ to replace the CO₂ lost out of the top of the absorber due to the high vapor pressure of liquid CO₂ under the above conditions.

It has also been proposed that KALC be used as a backup system for removal of other radioactive contaminants (³H₂O and I₂) from the off-gas. These impurities would be scrubbed out by liquid CO₂ and trapped by either filters or absorbers from the liquid CO₂.

After the removal of the krypton, the off-gas should contain only one radioactive material, ¹⁴C in the form of CO₂. The process to remove CO₂ in the present flowsheet and the newly proposed flowsheet are discussed in the next section. Note again, the difference between the flowsheets is that the old method removes krypton, then CO₂, whereas the new proposed method removes CO₂, then krypton.

2.2 Proposed Alternative Flowsheet

Figure 2.3 shows the proposed process to remove CO₂ containing ¹⁴C before removal of the krypton from the off-gas stream without incorporation of significant amounts of krypton into the CaCO₃. The off-gas stream is

Fig. 2.3. CO₂ removal system.

sent through two stirred tank reactors in series containing Ca(OH)_2 slurry. The Ca(OH)_2 slurry (1 M) reacts with the CO_2 to form CaCO_3 . Both Ca(OH)_2 and CaCO_3 are nearly insoluble in water; hence, the liquid is a slurry of Ca(OH)_2 and CaCO_3 . The off-gas flows countercurrent to the Ca(OH)_2 - CaCO_3 slurry through the tanks; hence, with proper control of flow rates, it is possible to ensure negligible CO_2 leakage from the system and nearly pure CaCO_3 slurry from the bottom of the system. Experiments² are still being conducted and analyzed on the reaction of CO_2 with Ca(OH)_2 slurry. The actual number and size of stirred tanks required in series and the optimum operating conditions cannot be determined until these parametric studies are completed.

From the stirred tank reactors, the CaCO_3 slurry product is sent to a stripping tank where a purge gas is used to strip dissolved krypton from the liquid slurry. The krypton-rich purge gas is combined with the feed gas and sent to the second stirred tank reactor. The slurry, minus the krypton, is sent to a liquid-solids separation facility (filters and/or settling tanks) where the solid CaCO_3 is separated and packaged for shipment and disposal. The liquid is recycled to make new Ca(OH)_2 slurry. Experimental and theoretical evidence (Sects. 3 and 4) indicates that the purge gas could be air, steam, or perhaps even the off-gas itself.

Air is the easiest purge gas to use, but any dilution of the off-gas stream will increase the gas flow to the downstream krypton-removal system. Steam will work and has two advantages: it can be condensed to minimize off-gas flow, and the higher temperatures available with steam reduces the solubility of krypton in the slurry. The off-gas itself

may work. Its krypton concentration is very small before CO_2 is removed. If additional krypton removal is required, the stripper tower can be operated at low pressure. Numerical details are given in the following sections. The final selection of purge gas will depend upon detailed economic analysis.

The off-gas, after CO_2 removal, is sent to the krypton removal system. Here the FASTER⁶ process could be used for krypton removal. This process (Fig. 2.4) is identical to the KALC process in principle, except that fluorocarbon-12 is used as the solvent rather than liquid CO_2 . In the FASTER process, fluorocarbon-12 at 7.91×10^5 Pa (115 psia) and -32°C scrubs the off-gas absorbing the krypton. The krypton-rich liquid is sent to a fractionator at 7.91×10^5 Pa (115 psia) and 32°C where other coadsorbed gases, such as O_2 and N_2 , are fractionated off. This gas stream is recycled to the front end of the absorber to remove any residual krypton. The krypton-rich solvent is then sent to a stripper at 2.05×10^5 Pa (30 psia) and -12°C where krypton gas is separated from the solvent. The solvent is recycled to the absorber, and the krypton is sent to a bottling or zeolite encapsulation station. This process is being developed to remove krypton from LWR and LMFBR fuel reprocessing plants. It cannot be used with CO_2 -rich off-gas streams because the solvent adsorbs CO_2 more readily than krypton.

The advantages of this new flowsheet compared with the standard flowsheet are:

Fig. 2.4. Simplified FASTER process system.

1. The gas flow through the krypton removal system will be reduced by at least 95%, with resultant large reductions in equipment size and cost.
2. The proposed flowsheet allows the use of the same krypton removal system found in LWR and LMFBR fuel reprocessing plants. Design and operating experience gained in other plants will be applicable to HTGR off-gas streams.
3. The fluorocarbon process reliability and ease of operation should be higher than for KALC due to smaller refrigeration requirements and lower pressure operation.

The fluorocarbon in the adsorber is used below its boiling point, whereas the liquid CO_2 is near or at its boiling point. Slight changes in system pressure or temperature will not significantly affect the fluorocarbon but will cause the CO_2 to flash to a gas. Control of KALC is much more difficult.

4. The fluorocarbon process should be safer than KALC during a serious process upset. If there is a refrigeration failure, the equipment can easily take the pressure generated by warming the fluorocarbon to room temperature. It is not practical to design equipment to take the pressure generated if the liquid CO_2 is heated to room temperature; hence, it must be vented. The much larger inventory of CO_2 plus the higher probability of its escape present problems in preventing accidental release of ^{14}C .

5. The ^{14}C appears to be a greater health hazard than ^{85}Kr .³
Removal of CO_2 first allows the FASTER process to act as a backup CO_2 removal system for small breakthroughs of CO_2 .
6. If the CO_2 removal equipment breaks down, the plant must be shut down since it is not feasible to store the large volumes of off-gas being generated. If just the krypton removal equipment fails after CO_2 removal, it may be possible to store krypton-rich off-gas for limited periods of time while making repairs. This is possible because the rate of production of the off-gas, excluding the CO_2 , is quite small.

The disadvantages of this system are: a stripper tank is required to remove the krypton from the CaCO_3 slurry, some of the CO_2 removal equipment may require additional radiation shielding, and detailed knowledge about the process does not exist. The proposed process appears attractive, but until it is demonstrated on a larger scale, no assurance of its feasibility can be given.

2.3 Radiation Hazards of Product CaCO_3

Each spent HTGR fuel block is expected to contain about 500 Ci of ^{85}Kr and <0.5 Ci of ^{14}C . The ^{14}C is a pure beta emitter and would produce negligible radiation levels when packaged as a barrel of CaCO_3 for waste disposal. The ^{85}Kr emits a higher energy beta and also gamma radiation. Consequently, if even a small fraction of the total ^{85}Kr is incorporated into the CaCO_3 , the ^{85}Kr will determine the radiation hazard of the CaCO_3 . The following problems would result from ^{85}Kr in the CaCO_3 .

1. By volume, the CaCO_3 containing ^{14}C from an HTGR fuel reprocessing plant will probably exceed all other radioactive wastes combined. The cost of shipping the CaCO_3 to a waste disposal site becomes very significant. The ^{14}C -contaminated CaCO_3 can be shipped with very little or no radiation shielding, whereas wastes containing ^{85}Kr will require shielding, thus increasing the cost of shipment.
2. Since krypton is a chemically inert gas, it is very difficult to ensure that krypton incorporated into the CaCO_3 will not escape from the CaCO_3 .

Calculations were made by Croff⁵ on the radiation levels at the surface of a 55-gal shipping drum filled with ^{14}C -contaminated CaCO_3 containing various amounts of ^{85}Kr . These data are shown in modified form in Fig. 2.5; Table 2.1 lists the assumptions and conditions used in making the calculations. The amount of ^{85}Kr per fuel block is well known (~ 500 Ci/block); however, the amount of ^{14}C is not and, consequently, the graph plots the calculated radiation level versus fraction of ^{85}Kr from the fuel block incorporated into the CaCO_3 for different amounts of ^{14}C per fuel block. The present best estimate of ^{14}C content per fuel element is 0.1 Ci.

The basic conclusion derived from Fig. 2.5 is that in most cases, the radioactive ^{85}Kr content of the CaCO_3 determines the radiation dose and the amount of shielding required. This results from two facts: (1) the expected number of curies of ^{85}Kr is 5000 times larger than the

Table 2.1. Assumptions and conditions used in calculation
in Figure 2.5

Assumptions/Input Data

CaCO₃ product density after dewatering is 102.2 lb/ft³.

CaCO₃ product is 60% CaCO₃ and 40% H₂O.

Dose rate calculations done with ANISN code.

Bremsstrahlung spectrum and intensity based on refs. 7 and 8.

Original calculations by A. G. Croff.⁵

Expected ⁸⁵Kr content per fuel element block = 531 Ci.

Best estimate of ¹⁴C per fuel element block = 0.1 Ci.

Initial Results (Radiation surface dose rates of CaCO₃ product)

Radiation dose at surface of drum per curie ⁸⁵Kr in drum

$$= 23.5 \frac{\text{mrem}}{\text{hr}} / \frac{\text{Ci}}{\text{drum}} .$$

Radiation dose at surface of drum per curie ¹⁴C in drum

$$= 0.511 \frac{\text{mrem}}{\text{hr}} / \frac{\text{Ci}}{\text{drum}} .$$

Radiation dose at surface of drum per curie of ⁸⁵Kr in fuel element

$$= 4.21 \frac{\text{mrem}}{\text{hr}} / \frac{\text{Ci}}{\text{fuel block}} .$$

Radiation dose at surface of drum per curie of ¹⁴C in fuel element

$$= 0.0917 \frac{\text{mrem}}{\text{hr}} / \frac{\text{Ci}}{\text{fuel block}} .$$

Fig. 2.5. Dose rate at surface of 55-gal drum containing CaCO_3 product with ^{14}C and ^{85}Kr .

expected number of curies of ^{14}C and (2) the radiation hazard per curie of ^{85}Kr is about 46 times larger than for one curie of ^{14}C . The radiation hazard herein refers to the penetrating radiation dose received from standing next to a drum containing ^{14}C or ^{85}Kr incorporated in the CaCO_3 .

In a practical transport scheme, assuming that a dose rate of 10 mrem/hr at 6 ft is tolerable for truck or train, transport of the waste CaCO_3 in drums encased by about 3 in. of iron shielding would be required if all the ^{85}Kr is incorporated in the CaCO_3 . The shielding would weigh about the same as the product CaCO_3 , and half the "transport charge" would be for carrying the shielding. The regulations do not presently address transportation requirements for ^{14}C -contaminated CaCO_3 incorporating ^{85}Kr ; hence, precise answers are not available.⁵

3. EXPERIMENTAL WORK

Two series of preliminary bench-scale experiments were conducted to determine the technical feasibility of removing radioactive krypton gas from a CaCO_3 slurry made by reacting a feed gas containing CO_2 , O_2 , and krypton with a Ca(OH)_2 slurry. These experiments were conducted using available equipment designed for a series of molecular sieve experiments;⁹ hence, many of the experimental conditions do not match conditions expected in a nuclear fuel reprocessing plant. These exploratory experiments suggest that CO_2 can be removed from a CO_2 -rich off-gas stream with a Ca(OH)_2 slurry without incorporating significant krypton in the product CaCO_3 slurry.

3.1 Experimental Procedure

For most experiments, the following procedure was used:

1. A 1 M slurry of $\text{Ca}(\text{OH})_2$ was reacted with a feed gas of 93.07% CO_2 , 5.43% O_2 , and 1.48% krypton with a ^{85}Kr tracer at 0°C and 1 atm of pressure. The batch reaction combined $\text{Ca}(\text{OH})_2$ with CO_2 to yield CaCO_3 precipitate, and water. Sufficient gas was fed to convert all the $\text{Ca}(\text{OH})_2$ to CaCO_3 .
2. The CaCO_3 slurry was treated by various techniques to remove krypton dissolved in the water or incorporated in the solid. These techniques tested included: purging the slurry with air or steam, boiling the slurry, and placing the slurry under vacuum.
3. The slurry was allowed to settle, and a small sample of the clear liquid over the settled CaCO_3 slurry was taken. The krypton content of the liquid sample was determined with a liquid scintillation counter.
4. The CaCO_3 slurry was titrated with 1.0 N HCl to yield a clear liquid containing CaCl_2 . The reaction of HCl with CaCO_3 yields CaCl_2 and CO_2 . The CO_2 evolved by this titration was sent through a krypton beta cell where the krypton content in the gas was determined.
5. The clear remaining liquid containing CaCl_2 was analyzed for its krypton concentration by a liquid scintillation counter.

This procedure was repeated many times with only Step (2) changed.

By comparing the amounts of krypton found in the liquids and in the CO_2

evolved during different runs, preliminary evaluation of the best techniques for krypton removal from slurries could be made.

3.2 Experimental Design

A simplified drawing of the experimental apparatus is shown in Fig. 3.1. Most of the equipment was from an earlier experiment⁹ and, except for the stirred tank reactor and Drierite dryer, was constructed of stainless steel. The feed gas was premixed and stored in a standard gas cylinder.

The stirred tank reactor consisted of a 250-ml Erlenmeyer flask with a magnetic stirrer. In all runs, unless otherwise specified, the reactor was kept in an ice bath when the $\text{Ca}(\text{OH})_2$ was reacted with the CO_2 , and a 1 M slurry of $\text{Ca}(\text{OH})_2$ containing 5.55 g of $\text{Ca}(\text{OH})_2$ and 75 ml of distilled water was used. Completion of the reaction to form a CaCO_3 slurry was determined by monitoring the krypton concentration exiting the reactor. When the krypton concentration exiting the reactor equalled the feed concentration, the reaction was assumed to be complete.

Two types of analytical equipment were used. For on-line krypton detection in the gas phase, a beta radiation cell was used. This cell¹⁰ was developed for the KALC process and can accurately determine the krypton concentrations when calibrated with a standard known gas, such as the feed gas in this experiment. For liquid samples, krypton concentrations were determined by a Packard Automatic Tri Carb Liquid Scintillation Spectrometer. The scintillation fluid consisted of 0.5 cc of the sample and 12 cc of the fluid. The scintillation fluid used consists of 12 g 1,4-bis-2-(5-phenyloxazolyl)-benzene (PoPoP), 0.3 g

Fig. 3.1. Experimental layout.

2,5-diphenyloxazole (PPO), 2010 ml toluene, and 990 ml tritium X-100. The liquid scintillation counter was used for relative count rates but was not calibrated to an absolute standard.

3.3 Experimental Results

Two series of experiments were conducted. The first series was a scoping experiment; the second was further evaluation of the best methods for krypton removal.

3.3.1 Initial experiments

The first seven experiments were conducted as described in Sect. 3.1. Table 3.1 lists the various methods used in Step (2) to remove the krypton from the slurry. Note that experiments 1 and 2 followed a slightly different procedure, and their purpose was to calibrate experimental equipment by determining such things as background count rate of the beta radiation detectors.

The results of these experiments are shown in Table 3.2. Column 2 shows the krypton decontamination factors (DF_L) found for various methods of krypton removal from CaCO_3 slurries. The DF_L is defined as the concentration of krypton in the liquid of the CaCO_3 slurry before any effort, such as purge or vacuum, was made to remove the krypton divided by the concentration of krypton in the liquid of the CaCO_3 slurry after krypton removal from the slurry was attempted. The krypton concentration measurements were made with a liquid scintillation counter. The product slurry was allowed to settle, and samples of the clear supernatant were analyzed for krypton content.

Table 3.1. Methods of krypton removal

Experiment	Method of krypton removal from product CaCO_3 slurry
1	Baseline experiment, measure background radiation, distilled water only, no Ca(OH)_2 , no feed gas used.
2	Baseline experiment; determination of feed gas dissolved in water; distilled water only, no Ca(OH)_2 .
3	Baseline experiment, slurry <u>not</u> treated for krypton removal.
4	Gas pressure over CaCO_3 product slurry lowered for 1 min to -20 in. Hg, vacuum treatment for krypton removal.
5	CaCO_3 product slurry purged with 1300 cc of O_2 .
6	CaCO_3 product slurry heated to boiling and cooled.
7	Gas pressure over CaCO_3 product slurry lowered for 1 min to -20 in. Hg. Slurry purged with O_2 and pressure raised to 1 atm; gas pressure lowered for 1 min to -20 in. Hg; gas pressure increased with O_2 to 1 atm.

The data in Table 3.2 clearly show that the most promising method of removing krypton from the liquid of the slurry is the purging of the liquid with a gas. A DF of 50 was easily obtained.

Column 3 shows the krypton decontamination factors ($\text{DF}_{\text{I.T}}$) of the liquid obtained after the slurry was titrated with HCl to produce a clear liquid solution of CaCl_2 . The DF is defined as the concentration of krypton in the liquid of the CaCO_3 slurry before any effort, such as purging or vacuuming, was made to remove the krypton divided by the concentration of krypton in the titrated liquid solution after correcting

Table 3.2. Results of initial experiments

Experiment No.	Slurry liquid decontamination factor, DF_L	Liquid DF after titration $CaCO_3$ to $CaCl_2$, DF_{LT}	CO_2 gas decontamination factor after titration, DF_g	Slurry krypton removal method
1	0	0	0	Baseline, background radiation count determined, distilled water only, no feed gas, no $CaCO_3$
2	1.2	$>1000^a$	1.09	Baseline, solubility feed gas in distilled water, experiment with no $CaCO_3$
3	1.0 (By definition)	193	1.0	Baseline, no krypton removal attempted
4	13.5	>1000	13.6	Krypton removal, -20 in. Hg vacuum
5	50.7	>1000	60.9	Krypton removal, O_2 purge
6	22.5	>1000	19.2	Krypton removal, light boil
7	61.2	>1000	674.4	Krypton removal, vacuum, purge, vacuum

^aLiquid was purged with a volume of CO_2 equivalent to that evolved in other experiments.

the volume of the titrated solution for the extra water added with the HCl. The process of titration evolves large amounts of CO_2 , and clearly this CO_2 has effectively purged the krypton from the liquid.

Column 4 shows the krypton decontamination factor (DF_g) for the CO_2 evolved from titrating each slurry. This DF_g is defined as follows: the maximum krypton concentration of the evolved gas from a slurry in which no effort was made to remove krypton divided by the maximum krypton concentration of the evolved gas from the slurry in question. These DF_g s are relative decontamination factors because there is no accurate way to calibrate this type of experiment. Note that the gas evolved mixes with the gas above the slurry before proceeding onto the beta detector. In addition, flow rates through pressure variations affect beta counter rates; hence, only relative numbers can be easily obtained by carefully conducting each experiment in an identical manner.

If the DF_g s of Column 4 are compared to the DF_L s of Column 2, they are seen to be nearly identical. The liquid DF_L measures relative krypton concentrations when CaCO_3 solid exists; the gaseous DF_g measures relative krypton concentrations when CaCO_3 is being destroyed. The single exception, experiment 7, is believed to be a result of experimental error. The krypton measured in this experiment comes from three sources — the gas space above the liquid, krypton adsorbed in the liquid, and krypton incorporated into the solid. It would be expected, due to the high-speed magnetic stirrer, that the liquid and gas phases are in equilibrium. Note that the total volume of the stirred tank reactor, 250 ml, is much less than the approximately 1800 cc of feed gas needed to convert the Ca(OH)_2 to CaCO_3 . The fact that

the liquid and gaseous DFs are equal implies that either the gas, liquid, and solid (CaCO_3) phases are in equilibrium with each other with respect to krypton or that the amounts of krypton incorporated in the solid are small. Either conclusion suggests that stripping krypton from a CaCO_3 slurry should be successful.

3.3.2 Set II experiments

A second set of experiments was conducted in an identical manner to those in Sect. 3.3.1, except for the method of krypton removal. In this series of experiments, various methods for purging krypton out of the CaCO_3 slurry were investigated. The methods of krypton removal are described in Table 3.3. The DFs for the liquids from the CaCO_3 slurry for all techniques exceeded 500. The DFs for the CO_2 gas evolved from titrating the CaCO_3 with HCl to yield CO_2 and CaCl_2 in all cases exceeded 500. Decontamination factors greater than 500 are reported as "greater than 500" because the experimental procedures used are not believed accurate for DFs in that range.

3.4 Experimental Conclusions

The experiments conducted herein are in many ways more qualitative than quantitative. The equipment accurately measured DFs, but measurements of the amounts of purge gas used, stirred tank reactor conditions, and other conditions were crude. Within these constraints, the conclusions are as follow:

1. The amount of krypton incorporated permanently into the solid when CaCO_3 is formed in the presence of krypton is $<1/1000$ of

Table 3.3. Methods used to remove krypton in set II experiments

Experiment	Method of krypton removal from product CaCO_3 slurry
1	Base case, no krypton removal method used.
2	Purged flask for 10 min at ~ 100 cc/min with steam.
3	Purged flask for 10 min at ~ 100 cc/min with O_2 and boiled slurry simultaneously with condensor to return liquid water to slurry.
4	Lowered pressure over slurry to -20 in. Hg; raised pressure to atmospheric pressure and purged for 5 min with O_2 at 100 cc/min; lowered pressure over slurry to -20 in. Hg.
5	Special case. When reacting CO_2 feed gas with slurry, slurry was boiled violently with condensor to return water to slurry. Boiling stopped shortly after feed gas was stopped. No measurement of relative gas flows of feed gas vs steam was made. Note: Ca(OH)_2 reaction with CO_2 took 50% longer. No separate krypton removal step.

the krypton in the feed gas. This conclusion is the result of two observations. Experiments 2 and 3 in the first set of experiments were identical in setup and results, except that experiment 2 used distilled water and experiment 3 used a Ca(OH)_2 slurry. About 1800 cc of feed gas is required to convert the 5.55 g of Ca(OH)_2 in these experiments to CaCO_3 . With a flask size of 250 ml, a maximum of about 14% of the feed gas in either of these experiments could be trapped in the flasks. Since both flasks were shown to have the same amount of krypton, the maximum amount of krypton in the feed that could conceivably

be in the CaCO_3 was 14%, assuming no krypton was in the gas or liquid (a very unlikely condition). This implies a DF of 7; that is, $<1/7$ of the krypton in the feed gas remaining in the CaCO_3 slurry. In addition, it was shown that the DFs for the liquid (DF_L) for various krypton removal techniques equalled the DFs of the CO_2 gas (DF_g) evolved when the CaCO_3 was dissolved to determine its krypton concentration. These DFs exceeded 500. Even allowing for experimental noise, it is unlikely that any of the DF_g s measured for CO_2 gas exceeding 500 could have a real value below 250. This implies that the amount of krypton incorporated in the CaCO_3 solid can only be $<1/250$ of the krypton originally in the flask. A DF equal to 7 and a DF equal to 250 imply that less than 1 part in 1750 of the krypton would be incorporated in the CaCO_3 .

2. It is technically feasible to remove krypton from a CaCO_3 slurry by purging the slurry with some gas.

3.5 Experimental Uncertainties/Future Experimental Work

No additional experiments are presently planned. If future work is done, the following areas of uncertainty, generated in part by the limits of the experimental apparatus used, should be investigated.

1. These experiments were conducted with a feed gas of 1.48% krypton, 5.43% O_2 , and 93.09% CO_2 . The expected HTGR fuel reprocessing plant off-gas system contains about 10 ppm krypton, and studies at this concentration should be made.

It is not certain that krypton will behave the same way in bulk concentrations as in near tracer quantities.

2. The experiments herein used reagent-grade Ca(OH)_2 . Actual plants would use a cheaper, less pure form of Ca(OH)_2 for economic reasons. Further investigations into the effect of Ca(OH)_2 impurities on incorporation of krypton in CaCO_3 are needed.
3. These experiments did not accurately measure the amount of purge gas required per unit of CaCO_3 slurry to obtain a desired DF. Future experiments would be required to investigate the effects of variables before design of a facility would be possible.
4. The experiments herein were designed to examine briefly krypton gases when CO_2 is reacted with Ca(OH)_2 to form CaCO_3 . No measurements were made of the ability of Ca(OH)_2 to remove CO_2 . Before the process herein can be adopted, a realistic experiment would have to be conducted which could simultaneously study CO_2 removal from an off-gas stream while keeping the krypton out of the CaCO_3 waste product. It is not feasible to treat the ^{85}Kr and ^{14}C removal problems separately.

4. THEORETICAL ESTIMATES OF KRYPTON DECONTAMINATION FACTORS WITH VARIOUS KRYPTON STRIPPING TECHNIQUES

The exploratory experiments showed that krypton was not incorporated into the CaCO_3 product and that krypton gas could be stripped from a slurry. With these verified assumptions, one can calculate how much krypton is removed by various krypton stripping techniques. Information

on the solubility of krypton in water is reviewed in Sect. 4.1. Decontamination factors (DFs) for krypton for various krypton stripping techniques are calculated in Sect. 4.2. Some engineering parameters for a full-scale plant are calculated in Sect. 4.3.

4.1 Solubility of Krypton in Water

Numerous measurements of the solubility of krypton in water, as shown in Fig. 4.1,¹¹ have been made.¹²⁻¹⁶ Using these measurements, it is possible to calculate the effectiveness of various techniques for removing dissolved krypton gas from a water solution. The following assumptions shall be used in these calculations:

(1) Henry's law applies:

$$P_i = HX_i, \quad (4.1)$$

where

P_i = Partial pressure of gas component i ,

H = Henry's law constant, and

X_i = Mole fraction (m.f.) of liquid component i .

(2) Ideal gas law applies:

$$P_i = Y_i P_t, \quad (4.2)$$

where

Y_i = Mole fraction of gas component i ,

P_t = Total gas pressure.

Equations (4.1) and (4.2) can be combined to yield:

$$K = \frac{H}{P_t} = \frac{Y_i}{X_i}, \quad (4.3)$$

Fig. 4.1. The solubility of krypton in water.

where

K = distribution coefficient.

The solubility data for krypton is given in the form of the Bunsen adsorption coefficient (α), which is defined as:

$$\alpha = \frac{V_o}{VP_{Kr}} = 22,414/(18H) , \quad (4.4)$$

where

V_o = Volume of gas (krypton) adsorbed at STP in liquid (H_2O)

$$= (\text{moles of water})(X_{Kr}) \left(\frac{22,414 \text{ cm}^3 \text{ gas}}{\text{mole of krypton}} \right) ,$$

V = Volume of liquid

$$= (\text{moles of water}) \left(\frac{18 \text{ g}}{\text{mole of water}} \right) \left(\frac{1 \text{ cm}^3}{\text{g of } H_2O} \right) ,$$

P_{Kr} = Partial pressure of krypton

$$= HX_{Kr}.$$

Combining Eqs. (4.3) and (4.4) yields:

$$K = \frac{22,414}{18 \alpha P_t} . \quad (4.5)$$

For future sample calculations, a representative value of K will be used. It will be assumed that the solubility of krypton in water (α) is 0.04 (see Fig. 4.1) and that system pressure is equal to 1 atm when K is equal to 3.11×10^4 . If α equals 0.03, then K equals 4.15×10^4 ; if α equal 0.05, then K equals 2.49×10^4 .

4.2 Expected Krypton Concentration in $CaCO_3$ Product Slurry

There are a variety of techniques to contact a CO_2 -rich gas stream with a $Ca(OH)_2$ slurry. For the discussions herein, however, only the

stirred contactor will be considered. Experimental experience² shows this to be a reliable solid-liquid-gas contactor. In this system, the reaction of CO_2 with Ca(OH)_2 produces solids. These solids can easily plug more complex mass transfer systems which contain packings, nozzles, or columns. The calculations will assume that each stirred tank reactor has ideal mixing.

The simplest configuration of stirred tank reactor is shown in Fig. 4.2. The CO_2 in the off-gas stream is reacted with the Ca(OH)_2 slurry in the reactor.

It is necessary to determine the fraction of krypton in the original off-gas stream which is carried away with the product CaCO_3 . The mole flow balance for krypton around the reactor can be written as:

$$Y_{\text{out}} V_{\text{out}} + L_{\text{out}} X_{\text{out}} = Y_{\text{in}} V_{\text{in}} , \quad (4.6)$$

where

Y_{out} = krypton m.f. out in gas phase,

V_{out} = total molar flow of gas out,

L_{out} = total liquid molar flow out,

X_{out} = krypton m.f. out in liquid phase,

Y_{in} = krypton m.f. in gas phase in, and

V_{in} = total molar flow of gas in.

If F_R equals the fraction of the incoming gas reacting with the Ca(OH)_2 , then

$$V_{\text{out}} = (1-F_R)V_{\text{in}} \quad (4.7)$$

and

$$L_{\text{out}} = F_R V_{\text{in}} C , \quad (4.8)$$

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Fig. 4.2. Stirred tank reactor.

where

C = moles of water out of reactor per mole of CO_2 reacted.

The value of C depends only upon the concentration of the incoming slurry and the fraction of the Ca(OH)_2 reacted to form CaCO_3 . For example, if a 1 M slurry of Ca(OH)_2 is used with 55.5 moles H_2O /liter and the slurry is completely reacted to CaCO_3 before leaving the reactor, C would equal 56.5. One mole of the water came from the reaction of the Ca(OH)_2 , and the other 55.5 moles came from the water used to slurry the Ca(OH)_2 . If only half of the Ca(OH)_2 was reacted, then C would equal $(2 \times 55.5 + 1)$, or 112. The value of C cannot be <1 because of the water produced by the chemical reaction. The value of C is determined by the design of the reaction.

If the gas phase leaving the reactor is in equilibrium with the aqueous phase leaving the reactor, then:

$$Y_{\text{out}} = KX_{\text{out}} \quad (4.9)$$

The krypton DF for the product CaCO_3 is defined as the total krypton into the system divided by the krypton in the product slurry:

$$DF = Y_{\text{in}} V_{\text{in}} / (X_{\text{out}} L_{\text{out}}) \quad (4.10)$$

Combining Eqs. (4.6) through (4.10) yields:

$$DF_1 = \frac{K(1-F_R) + F_R C}{F_R C} \quad (4.11)$$

In Fig. 4.3, DF_1 is plotted as a function of the fraction of gas adsorbed, F_R , and various values of C , the moles of water out for each mole of CO_2 reacted. A DF of about 30 is obtained for a nominal design

Fig. 4.3. Krypton decontamination factor for stirred tank reactors vs fraction off-gas adsorbed.

condition of $C = 56.5$, $K = 3.11 \times 10^4$, and $F = 0.95$. These conditions correspond to total CO_2 removal and complete reaction of a 1 M $\text{Ca}(\text{OH})_2$ slurry when the feed gas is 95% CO_2 . Two conclusions can be drawn from Fig. 4.3.

1. The DF decreases as the concentration of CO_2 in the feed gas increases, assuming that all of the CO_2 is reacted. This results because increased CO_2 implies a higher concentration of krypton in the gas phase leaving the reactor at equilibrium.
2. The DF increases with decreasing values of C . Decreasing C implies less water per unit of product CaCO_3 . If there is less water, less krypton can be dissolved in the water.

If the DF obtained by the stirred tank reactor in Fig. 4.2 is not sufficient, additional krypton can be removed from the CaCO_3 slurry by sending the slurry through a second stirred tank reactor and purging the slurry with a purge gas containing no krypton. Figure 4.4 shows such an arrangement.

The additional DF provided by this second reactor can be calculated by modifying Eq. (4.11) for the stirred tank reactor conditions of no gas reaction ($F = 0$) with the slurry. In this case:

$$\begin{aligned} \text{FC} &= L/V \\ &= \left(\frac{\text{moles } \text{CO}_2 \text{ reacted}}{\text{moles total gas to reactor}} \right) \left(\frac{\text{moles of water out of reactor}}{\text{moles } \text{CO}_2 \text{ reacted}} \right), \quad (4.12) \end{aligned}$$

where

L = liquid flow rate, moles/sec, and

V = gas flow rate, moles/sec.

Fig. 4.4. Complete CO₂ removal system.

Or rewriting Eq. (4.11),

$$DF_2 = K \left(\frac{V}{L} \right) + 1 . \quad (4.13)$$

This DF depends only on the values of K and V/L. For ease of understanding, Fig. 4.5 shows DF vs V/L. As a point of comparison, a V/L molar ratio of 0.0005 is obtained for the fluids exiting the stirred tank reactor described previously when the reactor is fed a 1 M slurry of Ca(OH)_2 and a feed gas containing 95% CO_2 . This assumes that all of the CO_2 and all of the Ca(OH)_2 is converted to CaCO_3 ; thus, only CaCO_3 slurry exits the reactor.

As shown in Fig. 4.4, stirred tank No. 1 removes all the CO_2 from the off-gas, thus creating a pure CaCO_3 product slurry. A purge gas is passed through stirred tank No. 2 to remove dissolved krypton from the slurry. In tank No. 1, the inert gas acts as a purge gas as the CO_2 reacts with the Ca(OH)_2 . The calculated krypton DF of stirred tank No. 1 is 30. If it is assumed that the volume of purge gas for stirred tank No. 2 nearly equals the volume of the off-gas from stirred tank No. 1, then the krypton DF for stirred tank No. 2 will also be 30. The total krypton DF for the system is then 30 times 30, or 900.

An alternative flowsheet (Alternative A, Fig. 4.4) in which the purge gas from stirred tank No. 2 is diverted to stirred tank No. 1 will double the purge gas flow rate to tank No. 1. The DF for this arrangement can be calculated. The purge gas flowing into tank No. 1 is equivalent to dilution of the off-gas with an inert gas. In such a case:

$$F_R = F / [I(1-F) + 1] , \quad (4.14)$$

Fig. 4.5. Stirred tank krypton decontamination factors.

where

F = moles of gas reacted per moles of off-gas feed, and

I = moles of purge gas per moles of off-gas not reacting

= ratio of inert purge gas to inerts in off-gas feed.

Substituting into Eq. (4.11) yields the DF for tank No. 1:

$$DF_{\text{tank 1}} = \frac{K(I+1)(1-F) + FC}{FC} \quad (4.15)$$

The DF for tank No. 2 can be derived from Eq. (4.13) with the following substitution:

$$\begin{aligned} \frac{V}{L} &= \frac{I(1-F)}{FC} \\ &= \frac{\left[\frac{\text{moles purge gas}}{\text{moles inert off-gas}} \right] \left[\frac{\text{moles inert off-gas}}{\text{moles off-gas feed}} \right]}{\left[\frac{\text{moles reactive off-gas}}{\text{moles off-gas feed}} \right] \left[\frac{\text{moles liquid out}}{\text{moles reactive off-gas}} \right]} \end{aligned} \quad (4.16)$$

This yields the DF for tank No. 2:

$$DF_{\text{tank 2}} = \frac{KI(1-F) + FC}{FC} \quad (4.17)$$

The total DF for alternative A is then equal to:

$$DF_3 = \left(\frac{K(I+1)(1-F) + FC}{FC} \right) \left(\frac{KI(1-F) + FC}{FC} \right) \quad (4.18)$$

For the conditions given earlier ($F = 0.95$, $C = 56.5$, $K = 3.11 \times 10^4$), this yields a DF of 1770 compared with a DF of 900 when the purge gas from stripper stirred tank No. 2 does not enter the main stirred tank reactor. Theoretically, a third tank would be used to obtain another DF of 30. In principle, any desired DF can be obtained with a sufficient number of tanks and purge gas streams.

If the control problems can be resolved, a fourth and highly attractive system for CO_2 removal would consist of two stirred tanks,

such as the ones shown in Fig. 4.6. Tank No. 1 would contain very high concentrations of Ca(OH)_2 to ensure the complete removal of all CO_2 . In tank No. 2, nearly pure CaCO_3 would exist, with the feed gas being used to ensure nearly complete conversion of Ca(OH)_2 to CaCO_3 in order to minimize CaCO_3 disposal problems. In such a configuration, the feed gas would act as a purge gas in tank No. 2 and provide a considerable DF for krypton.

The following equations can be written for the system shown in Fig. 4.6. The krypton molar flow balances for the system are:

$$Y_{\text{out}} V_{\text{out}} + LX_{\text{out}} = V_{\text{in}} Y_{\text{in}} , \quad (4.19)$$

$$Y_{\text{out}} V_{\text{out}} + LX_{\text{m}} = V_{\text{m}} Y_{\text{m}} . \quad (4.20)$$

For simplification of the calculations, the liquid flow rate through the system (L) is assumed to be constant. Since the reaction of Ca(OH)_2 and CO_2 yields water, the assumption that the liquid flow rate is constant is not strictly true; however, it changes only slightly. The vapor molar flow balances for the system are:

$$V_{\text{out}} = (1-F_R)V_{\text{in}} , \quad (4.21)$$

$$V_{\text{m}} = (1-F_R)V_{\text{in}} + RFV_{\text{in}} , \quad (4.22)$$

where

F_R = m.f. of gas reacting with liquid in system,

R = m.f. of gas that reacts with the liquid which reacts in stirred tank reactor No. 1.

The krypton equilibrium relationships between the gas and liquid phase are:

$$Y_{\text{out}} = K X_{\text{m}} , \quad (4.23)$$

Fig. 4.6. Carbon dioxide removal using the feed gas for krypton gas stripping.

$$Y_m = K X_{out} . \quad (4.24)$$

The liquid and gas flow rate can be related by the equation:

$$L = F_R V_{in} C , \quad (4.25)$$

where

$F_R V_{in}$ = the amount of CO_2 to be reacted with the $Ca(OH)_2$,
 C = the conversion factor relating the CO_2 reacted to
the liquid flow, mole of liquid per mole CO_2 reacted
with $Ca(OH)_2$.

The value of C depends on stirred tank reactor conditions. If 1 M $Ca(OH)_2$ is used as a feed and it is assumed that the $Ca(OH)_2$ is completely converted to $CaCO_3$, then C is nearly equal to 56.

The krypton DF for the overall system is defined as:

$$DF = V_{in} Y_{in} / L X_{out} . \quad (4.26)$$

If Eqs. (4.19) through (4.26) are combined, the DF can be shown to equal:

$$DF_4 = 1 + \frac{K^2}{FC} \frac{(1-F)(1-F+RC)}{FC + K(1-F)} . \quad (4.27)$$

Equation 4.27 is plotted in Fig. 4.7 for various values of R - the fraction of the CO_2 reaction with $Ca(OH)_2$ that occurs in reactor No. 1. For this calculation, $K = 3.11 \times 10^4$, $C = 56.5$, and $F = 0.95$.

The theoretical DF possible by this approach is very high, as shown in Fig. 4.7, but in all cases is limited by the krypton content of the feed gas.

The limits of decontamination for Fig. 4.7 result from the krypton concentration of the feed gas. Lower DFs can be obtained by

Fig. 4.7. Decontamination factor versus fraction of reaction of CO_2 with Ca(OH)_2 in stirred tank reactor No. 1.

adding a stripper section to the system as shown in Fig. 4.8. In such a case, the DF for the stripper section, tank No. 3, is identical to that derived in Eq. (4.17).

$$DF = \frac{KI(1-F) + FC}{FC} \quad (4.17)$$

The DF for tanks 1 and 2 can be obtained by modifying Eq. (4.27) with Eq. (4.14) derived earlier for the addition of a stripper system to a CO₂ removal system:

$$F_R = \frac{F}{1+I(1-F)} \quad (4.14)$$

Substituting Eq. (4.14) into Eq. (4.27) and combining the DF from stirred tank No. 3 with that from stirred tanks 1 and 2 yield:

$$DF_5 = \left[1 + \frac{K^2}{FC} \left(\frac{(1+I)(1-F)\{(1+I)(1-F) + RC[1+I(1-F)]\}}{FC + K[(1+I)(1-F)]} \right) \right] \left(\frac{KI(1-F) + FC}{FC} \right) \quad (4.28)$$

Figure 4.9 plots Eq. (4.28). As can be seen, very high DFs are obtainable.

Figure 4.10 compares alternative reactor configurations with identical flow rates. Which configuration is used ultimately depends upon the DF required. The simplest system which meets requirements will be used. Configuration 5 shows the highest DF. Higher DFs are obtainable with more stripper stirred tank reactors. Configuration 5, consisting of two reactors for CO₂ removal and a stripper reactor for krypton removal, is the most probable configuration since its multistage design with a stirred tank reactor above and below the main reactor allows for recovery from off operations. Other configurations do not have as much versatility.

Fig. 4.8. CO₂ removal system with 2 stirred tank reactors, 1 stripper stirred tank reactor.

Fig. 4.9. Krypton decontamination factor for slurry in three-tank system versus fraction of reaction in reactor No. 1.

Fig. 4.10. Alternative stirred tank reactor configurations.

4.3 Full-Scale Plant Design Considerations

No detailed HTGR fuel reprocessing plant design has been completed. A preliminary estimate of the size of the CO_2 removal system using the Ca(OH)_2 slurry system can however be made with the existing preliminary data. This information is very preliminary but can indicate the order of magnitude of the equipment needed. For this calculation, a single stirred tank reactor is used. All presently existing design information is based on using a single reactor.

Given the design numbers in Table 4.1 and assuming that a full-scale plant operates 300 days/year, the active volume of the stirred tank reactor would be about 2300 ft^3 , a 13-ft cube.² The power requirements to stir the slurry would be about 1300 hp.² With added margins for various design conditions, actual facilities are likely to be larger and/or consume more power. Within limits, horsepower and size requirements can be traded off against each other.

The above facility would produce about $9 \times 10^5 \text{ lb/day}$ (460 tons/day) of waste if it is assumed that the waste is 60 wt % CaCO_3 and 40 wt % H_2O . The tonnages of the waste involved show the necessity of minimizing radioactivity in the CaCO_3 product so that the necessity of heavily shielding the waste during transport to the final disposal site may be avoided.

This report has addressed methods designed to keep the krypton from contaminating the CaCO_3 . There is a second possible source of radioactivity. If upstream equipment fails, other fission products, such as I_2 , could be present in the off-gas stream. If this type of equipment

Table 4.1. Full-scale reprocessing plant parameters

General Plant	
No. of power plants served (1000 MW(e)/each)	50
Fuel elements processed/year	50,000
Off-gas flow/fuel element, scf	15,833
Off-gas composition	
% CO ₂	95
ppm Kr	10-15
CO ₂ Removal Equipment Parameters	
Assumed CO ₂ DF	300
Feed gas composition	
% CO ₂	95
% inerts	5
Gas flow/volume Ca(OH) ₂ slurry, scfm/ft ³ liquid	0.81
Reactor power requirements, hp/ft ³ of slurry	0.58

failure is considered a likely event, a small water scrubber upstream may be added with appropriate additives (e.g., sodium thiosulfate for I₂) for the removal of contaminants. This problem is basically one of economic trade-offs — the cost of one more off-gas cleanup system vs a higher cost of transporting and disposing of higher radioactivity CaCO₃ product slurry. The massive volumes of Ca(OH)₂ used are likely to catch most other chemically reactive gases and particulates which pass through the system.

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