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CHLORINE RECOVERY AND RADIOIODINE
BEHAVIOR IN THE SALT CYCLE PROCESS

L. K. Mudge
J. R. Lundquist

J. Mishima 30634 325 DEC 1 1966
Seolhem for 60013 271-4 DEC 1 2 1966
O. J. Hill 60838 2704-E DEC 14 1966
M. J. Szulinski 60169 703 DEC 14 1966

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THE SALT CYCLE PROCESS

By

L. K. Mudge
Chemical Development Section

and

J. R. Lundquist
Chemical Research Section
Chemistry Department

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PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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THE SALT CYCLE PROCESS

INTRODUCTION

The Salt Cycle process* for reprocessing irradiated $\text{UO}_2\text{-PuO}_2$ reactor fuels makes use of large quantities of chlorine and hydrogen chloride as dissolving and melt-conditioning agents, and produces chlorine as a by-product of the electrolysis steps. A study of the factors influencing the economic attractiveness of the process has pointed to the desirability of recycling the chlorine and hydrogen chloride in the off-gas stream. This need arises from two considerations. First, treatment by neutralization is uneconomic because of the production of large quantities of radioactive waste caustic solution for each ton of uranium processed. And second, the processing of short-cooled fuel from power reactors will require high decontamination factors for iodine-131, which may be difficult to achieve by conventional techniques such as caustic scrubbing. In considering the problem, it was concluded that low-temperature liquefaction might be an attractive means of recovering the chlorine, for subsequent re-use. In addition to permitting a large reduction in caustic scrubber waste volumes and in chlorine costs, the technique was believed to have the merit of providing an effective means of iodine-131 removal from the off-gas, namely scrubbing with liquid chlorine. Hence, a short-term study was made of the concept, with the results described below.

*The Salt Cycle process was conceived and developed at Hanford as one phase of the Plutonium Recycle Program. It is based on the use of molten chloride salts as reaction media for the dissolution of the oxide fuels and the electrolytic deposition of crystalline, reactor-grade $\text{UO}_2\text{-PuO}_2$ solid solutions and UO_2 .

SUMMARY

Engineering-scale tests of chlorine recovery by liquefaction at -100°C showed it to be nearly 100 percent of that theoretically obtainable (as calculated from vapor pressure measurements). Caustic usage in the down-stream caustic scrubber was reduced by a factor of ten by operation of the chlorine liquefier, and can be further decreased by reduction of the air in-leakage to the system.

In operation of the pilot plant apparatus, it was observed that the volatility of an iodine compound was limiting the removal of iodine-131 from the gas stream by the action of the liquid chlorine scrubber. A laboratory investigation of the vapor pressure of iodine over liquid chlorine showed that the observed volatilization of iodine in the pilot plant apparatus was due to part of the iodine not reacting with the liquid chlorine. Reaction of iodine with liquid chlorine forms a precipitate of ICl_3 , which subsequently volatilizes with decomposition to form ICl vapor. Estimation of the equilibrium constants for vaporization at 0°C and -45.2°C indicated that much greater iodine decontamination of the off-gas could have been obtained if good contact of the off-gas with the liquid chlorine had been made.

DISCUSSION

The pilot plant equipment arrangement with radioiodine sample locations indicated is illustrated in Figure 1. Chlorine is metered through a flowmeter into the salt pot, which contains 65 pounds of molten chloride salt at 550°C . A vacuum of about 0.05 inches of water is maintained on the salt pot. Air in-leakage through the top lid results in a total flow of about 20 liters per minute when a chlorine flow rate of 4 liters per minute is used. The off-gas from the salt

FIGURE 1

Demonstration Equipment

pot is pulled through a disengagement and safety trap which collects entrained salt and prevents solution from the auxiliary caustic scrubber from running back into the salt pot should an off-standard condition arise. A 4-inch diameter by 4-foot-length glass column packed with a 2-foot-depth of magnesium perchlorate dries the off-gas before it enters the low temperature trap where the chlorine is condensed at -100°C . The Hastelloy C[®] condenser has a chlorine capacity of 200 pounds and is cooled with a two-stage Cincinnati Sub-Zero unit powered by two 1-1/2 hp Copeland compressors. The condenser is illustrated in Figure 2. From the condenser the off-gas flows through a 1-inch deep by 4-inch diameter activated charcoal bed for removal of I^{131} , and a caustic scrubber for determination of chlorine losses.

The apparatus for sampling radioiodine is shown in Figure 3. A portion of the off-gas from the points indicated on Figure 1 is pulled through this arrangement at the rate of 250 ml/min at points 1 and 2 and 1000 ml/min at point 3. The radioiodine is collected on an activated charcoal impregnated filter paper and a -6 +10 mesh activated-charcoal bed; activity was never found in the downstream caustic bubblers. The fact that the charcoal sampler removed greater than 99 percent of the radioiodine from the sample stream was proved by placing two samplers in series.

Chlorine Recovery

The recovery of chlorine by conventional techniques of compression and cooling has the disadvantage in the handling of Salt Cycle off-gas of having a radioactive gas stream under pressure. A preferred technique for handling a radioactive gas stream is to keep the stream at a lower

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FIGURE 2

Chlorine Condenser

FIGURE 3

Sampler Arrangement

pressure than that of the surroundings. This requires condensation of the chlorine from the off-gas stream near the freezing point of chlorine at less than atmospheric pressure.

The chlorine introduced into the molten salt mixes with the air that leaks in through the salt pot lid, and the mixture cools to ambient temperature. After drying it is drawn through the chlorine condenser which is maintained at -100°C .

The results of several runs at varying chlorine flow rates are shown in Table I. The efficiency of removal was determined by absorbing the unremoved chlorine in the exit stream into a known volume of caustic solution. Theoretical chlorine recoveries were calculated from the vapor pressure of chlorine at -100°C (12 mm Hg) with the condenser pressure at 1 atm, which gives the concentration of chlorine to be expected in the exit gas stream. The actual conditions were less than 1 atm pressure (730 mm) and greater than -100°C (up to -90°C) which would reduce the actual theoretical recoveries below those shown in the table. The recovery of chlorine is directly dependent on its concentration in the condenser inlet gas stream. Improvement in chlorine recovery will require design changes in the salt pot that will reduce air in-leakage. With the present design, chlorine recovery by condensation during typical operation (3-5 l/min Cl_2) reduced caustic usage from about 2000 to 200 gal/T.U.

Radioiodine Behavior in the Pilot Plant Equipment

The radioiodine was prepared for addition to the salt pot by pipetting 50 λ of solution containing one millicurie of I^{131} into a 15 ml vial, adding carrier iodine in the form of potassium iodide, and filling the vial half full of U_3O_8 to simulate the addition of

TABLE I
CHLORINE RECOVERIES

<u>Percent Chlorine in Total Flow</u>	<u>Chlorine Flow Rate, Liters Per Minute</u>	<u>Total Flow Rate, Liters Per Minute</u>	<u>Percent Recovery</u>	<u>Percent Theoretical Recovery at -100°C, 1 atm</u>
3.3	0.5	15	48	54
4.8	1	21	65	68
8.7	2	23	76	83
11.1	2	18	84	87
15	3	20	90	91
15.8	3	19	89	92
15.8	3	19	85	92
16.6	3	18	90	92
20	3.6	18	91	94
22.6	4.3	19	93	94
22.7	3.4	15	89	95

feed material containing I^{131} . The vial with its contents was dropped into the molten salt through a 2-inch opening which was immediately closed after the admission. The chlorine sparging through the molten salt at 550°C caused immediate volatilization of the carrier and radioactive iodine, probably in the form of I_2 and $ICl^{(3,4)}$.

The iodine removal efficiency of the chlorine condenser was determined by sampling at the inlet and outlet points indicated in Figure 1, and the removal efficiency of the charcoal adsorber was determined similarly. The radioiodine in the samples was counted on a multichannel analyzer using three geometric configurations which were calibrated with known amounts of I^{131} such that the counting efficiency of each configuration was known.

The results in Table II show the decontamination factors and the experimental release rates of I^{131} from the chlorine condenser. The data are erratic with a strong memory effect from run to run. Single slugs of introduced iodine were followed through the system and iodine compounds were found to adsorb strongly at various places in the piping and desorb slowly over a period of time when conditions are changed.

After an initial increase in the decontamination factor there appeared to be no significant effect of adding carrier iodine. The data show that submergence of the condenser inlet (i.e., filling the container above the inlet skirt as shown in Figure 2) gave no significant reduction of the I^{131} release rate. With the inlet open, solid ICl and $ICl_3^{(5)}$ could deposit on the walls of the container without entering the liquid chlorine. Extrapolation to -100°C of the data of Cornog and Bauer⁽⁶⁾ for the vapor pressure of ICl , which

TABLE II

RADIOIODINE DECONTAMINATION FACTORS*

Run Number	Off-gas Inlet	Grams Carrier Iodine per Millicurie I^{131}	Decontamination Factor			Experimental I^{131} Release Rate Millicuries per Hour
			Condenser	Charcoal	Total	
4	Open	< 0.01	66	----	66	1.4×10^{-3}
5	Open	< 0.01	4	----	4	4.6×10^{-3}
6	Open	0.8	23	----	23	1.4×10^{-3}
10	Open	1.5	4	> 1000	> 4,000	9.6×10^{-4}
8	Open	3.0	111	29	3,220	1.1×10^{-4}
7	Open	6.0	26	----	26	2.1×10^{-3}
9	Open	6.0	27	65	1,750	4.1×10^{-4}
2	Open	12	690	----	690	7.4×10^{-5}
3	Open	12	120	----	120	6.4×10^{-4}
1	Open	70	2760	----	2,760	$< 10^6$
11	Submerged	1	119	46	5,500	6.42×10^{-4}
12	Submerged	1	1080	49	52,700	1.29×10^{-4}
13	Submerged	1	48	123	5,900	2.16×10^{-3}
14	Submerged	1	245	11	2,700	3.02×10^{-4}
15	Submerged	1	2045	17	35,000	1.26×10^{-4}

* Nominal air-inleakage flow rate through the system was 20 liters per minute.

is the most volatile of the iodine-chlorine compounds, gives an I^{131} release rate of 1.34×10^{-4} mc/hr at -100°C and 8.83×10^{-4} mc/hr at -90°C with a ratio of one gram carrier iodine per millicurie of radioiodine. The release rate of I^{131} from the condenser should decrease if submerging the inlet causes the iodine compounds to dissolve in, be reacted with, or precipitate from the liquid chlorine. Since higher decontamination factors were not found, apparently the method of submerging the inlet did not allow efficient absorption of the solid iodine compounds into the liquid chlorine. The activity passed into the charcoal adsorber was not high enough to demonstrate high decontamination factors across this unit.

The mechanism by which the radioiodine was released from the chlorine condenser was checked by passing an inert gas through the unit at a known flow rate at temperatures ranging from -30°C to -100°C and collecting the radioiodine in the stream on charcoal samplers. The results indicated that the release was caused by the volatility of iodine or an iodine-chlorine compound as shown by the approximate linear plot of inverse temperature versus log activity in Figure 4 with the least square line and 95% confidence limits shown. Heat of vaporization (8000 ± 1400 cal/gram mole) was calculated from the slope of the line. This corresponds approximately to the values of the heat sublimation for ICl (11,000 cal/gram mole)⁽⁵⁾ or I_2 (7400 cal/gram mole). If all of the ICl had reacted with the liquid chlorine to form ICl_3 , volatilization of this ICl_3 would have given a slope of 25,000 cal/g

FIGURE 4

Iodine-131 Release from Liquid Chlorine

mole. Since this was not observed, at least part of the ICl did not contact the liquid chlorine, or else other volatile iodine-containing compounds such as methyl iodide may have been formed. Uncertain experimental control of any of the following three conditions could have caused error in the data: (1) incomplete and inconsistent saturation of the inert gas streams; (2) inaccurate temperature measurements by the uncalibrated copper-constantan thermocouples; and (3) a varying ratio of radioiodine to carrier iodine between different parts of the equipment caused by poor initial mixing of the iodine.

Liquid Chlorine-Iodine Equilibria

Since pilot plant studies showed that the quantity of iodine in noncondensable gases from the liquefaction unit exceeded theoretical values in the literature, the vapor pressure of iodine compounds over liquid chlorine as a function of temperature was investigated.

The vapor pressure of iodine (as iodine monochloride, ICl) over liquid chlorine saturated with iodine was estimated. A precipitate of ICl_3 is formed in the presence of excess chlorine. The prevailing reaction is:

Equilibrium constants for the prevailing reaction were estimated at 0 and -45.2°C , and found to be in good agreement with the constants calculated from data obtained by Nies and Yost⁽⁷⁾ at 25 and 35°C .

Experimental

The gas-saturation technique was used to estimate the vapor pressure of ICl_3 in liquid chlorine. Slush baths (0°C -water;

-45°C chlorobenzene) were used to hold the system at constant temperature. Dry argon was used as the carrier gas and an equilibrium sample of the gases was collected in a 1 liter bulb. The equilibrium mixture was then passed through 20 cc of 20% NaOH using a glass frit for assuring good gas-liquid contact for trapping out the halogens. The iodine was previously spiked with a known quantity of I^{131} ; thus the amount of ICl formed could be determined by gamma ray spectroscopy assuming no dimers are formed, which is consistent with the literature. The amount of NaClO was determined by controlled potential coulometry after reduction with hydroxylamine hydrosulfate.

Results and Discussion

A precipitate of ICl_3 is formed in the presence of excess chlorine in an iodine-liquid chlorine system. Equilibrium constants have been previously determined at 20°C and 35°C for the following reaction:

for which $K_p = P_{ICl} P_{Cl_2}$.

Equilibrium constants for lower temperatures were extrapolated from the above data and compared with experimental results in Table III below.

TABLE III

Temp., °C	P_{ICl} (mm)	P_{Cl_2} (mm)	K_p (mm) ² literature	K_p (mm) ² found
0	2.6	5.5	1.0×10^1	1.4×10^1
-45.2	$\geq 2.8 \times 10^{-6}$	360	1.0×10^{-3}	$\geq 1.0 \times 10^{-3}$
-95	1×10^{-11} (calc)	18 (lit)	2.0×10^{-10}	----

As shown in the above calculations, the vapor pressure of ICl_3 at -95°C is about 1×10^{-11} mm in a liquid chlorine system.

CONCLUSIONS AND RECOMMENDATIONS

Chlorine Recovery

Recovery of chlorine by condensation from a gas stream has been demonstrated on a pilot plant scale for the Salt Cycle process. Present operating conditions would reduce caustic requirements by a factor of 10. The amount of chlorine recovered could be increased by sealing the salt pot so as to reduce the amount of noncondensable gases leaking into the off-gas stream. The ultimate would be no in-leakage and 100 percent recovery of the chlorine.

Difficulty was encountered with plugging of the condenser inlet by moisture that passed through the drying column. Additional study of drying techniques is necessary to alleviate this problem.

Anhydrous hydrogen chloride recovery by low temperature condensation should be feasible, but demonstration of this is needed to finalize an off-gas system design for the Salt Cycle process. In the operation of plant equipment, radioiodine will not be present in the molten salt when HCl sparge gas is used, so that a study of radioiodine behavior with HCl is not necessary.

Iodine Behavior

The data indicate that the release mechanism for iodine from the low temperature condenser in the pilot plant equipment is by volatilization of an iodine compound, the most volatile apparently being ICl or possibly CH_3I . Using a value of 1.5×10^{-5} mm Hg for the vapor pressure of $\text{ICl}^{(3)}$ at -100°C permits calculation of the I^{131} concentration in the condenser off-gas. This is 0.0143 curies per liter of air for radioiodine undissolved in the liquid chlorine with no carrier and the system at 1 atm pressure. With this information

the operating limits are defined by the allowable discharge rate of I^{131} in a populated area, which is about 1.5 curies per week from a 150 foot stack with no farms within three miles. Figure 5 illustrates the release rate of radioiodine and the decontamination factor across the chlorine liquefaction unit, obtained as a function of noncondensable gas flow rate, while processing one ton per week of 15-day-cooled fuel irradiated to 10,000 Mwd/t. In this figure it is assumed that only 24 hours of condenser operating time are required each week to remove all the radioiodine from the system. After the 24 hour period the off-gas would be diverted to a second condenser. The decontamination factor needed under these conditions is 1.2×10^5 which corresponds to a release rate of 0.0625 curies/hr and an air in-leakage rate of 4.4 liters/hr. The air in-leakage rate in the present equipment is about 1200 liters/hr which gives a decontamination factor of only 420. This emphasizes the need for a well-sealed salt pot.

The results obtained in the equilibrium experiments show that it is possible to get decontamination factors high enough from this technique to let off-gas escape to the atmosphere. However, there still remains the problem of designing the proper equipment so that the gas stream makes good contact with the liquid chlorine, since the pilot plant experiment showed that all the iodine in the system did not react with the liquid chlorine to precipitate ICl_3 . Also, one must make certain that I_2 or ICl is the only species present in the off-gas as the vapor pressure of other iodine compounds may be considerably higher. If for some reason all of the liquid chlorine is separated from the ICl_3 precipitate, the amount of I^{131} in the

FIGURE 5

Effect of Off-Gas Flow Rate on the Radioiodine Release from the Chlorine-Liquefaction Unit

off-gas will increase several orders of magnitude.

The plant-scale equipment units required for I^{131} removal with an air in-leakage rate of 400 liters/hr are a chlorine condenser operated at -100°C (d.f. > 100), a charcoal adsorber (d.f. > 100) and a caustic scrubber (d.f. > 10), which should give an overall decontamination factor greater than 10^6 . The schematic equipment diagram in Figure 6 illustrates the type of equipment that would be required to handle the Salt Cycle off-gas stream. In addition, a means of withdrawing the liquid chlorine and HCl from the condenser into a pressure vessel for storage and subsequent reuse should also be provided.

FIGURE 6

Projected Off-Gas System for Salt Cycle Process

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