RECEIVED BY DHE OCT 9 1970

OPERATING EXPERIENCE USING SILVER
REACTORS FOR RADIOIODINE REMOVAL
IN THE HANFORD PUREX PLANT

OK
T
10/24/70

G.J. RAAB & R.E. VAN DER COOK

JUNE 17, 1970

MASTER

This Document was Prepared Under
AEC Contract AT(45-1)-2130

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY 9 HKahn/amb
DATE 10/27/70

Atlantic Richfield Hanford Company
Richland, Washington

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

P7062

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Atlantic Richfield Hanford Company
Richland, Washington 99352

LEGAL NOTICE

THIS REPORT WAS PREPARED AS AN ACCOUNT OF GOVERNMENT SPONSORED WORK. NEITHER THE UNITED STATES, NOR THE COMMISSION, NOR ANY PERSON ACTING ON BEHALF OF THE COMMISSION:

A. MAKES ANY WARRANTY OR REPRESENTATION, EXPRESSED OR IMPLIED, WITH RESPECT TO THE ACCURACY, COMPLETENESS, OR USEFULNESS OF THE INFORMATION CONTAINED IN THIS REPORT, OR THAT THE USE OF ANY INFORMATION, APPARATUS, METHOD, OR PROCESS DISCLOSED IN THIS REPORT MAY NOT INFRINGE PRIVATELY OWNED RIGHTS; OR

B. ASSUMES ANY LIABILITIES WITH RESPECT TO THE USE OF, OR FOR DAMAGES RESULTING FROM THE USE OF ANY INFORMATION, APPARATUS, METHOD, OR PROCESS DISCLOSED IN THIS REPORT.

AS USED IN THE ABOVE, "PERSON ACTING ON BEHALF OF THE COMMISSION" INCLUDES ANY EMPLOYEE OR CONTRACTOR OF THE COMMISSION, OR EMPLOYEE OF SUCH CONTRACTOR, TO THE EXTENT THAT SUCH EMPLOYEE OR CONTRACTOR OF THE COMMISSION, OR EMPLOYEE OF SUCH CONTRACTOR PREPARES, DISSEMINATES, OR PROVIDES ACCESS TO, ANY INFORMATION PURSUANT TO HIS EMPLOYMENT OR CONTRACT WITH THE COMMISSION, OR HIS EMPLOYMENT WITH SUCH CONTRACTOR.

UNCLASSIFIED

This document classified
by R. E. Van der Cook

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ARH-SA-67

OPERATING EXPERIENCE USING SILVER REACTORS
FOR RADIOIODINE REMOVAL IN THE HANFORD PUREX PLANT

G. J. Raab and R. E. Van der Cook

Separations Process Engineering
Operations Support Engineering Department
Chemical Processing Division

June 17, 1970

Work performed under Contract AT(45-1)-2130 between the
Atomic Energy Commission and Atlantic Richfield Hanford Company.

For presentation at the sixty-third National Meeting of the
American Institute of Chemical Engineers, Chicago, Illinois,
November 29 to December 3, 1970

ATLANTIC RICHFIELD HANFORD COMPANY
RICHLAND, WASHINGTON

Abstract

Silver reactors have been successfully employed to remove radioiodine from dissolver off-gas streams. Overall plant iodine release to the atmosphere are typically 0.1 percent with the reactors and 1 percent without the reactors of the iodine charged to the plant. Typical plant operating data are presented. Operation has been safe and reliable.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

UNCLASSIFIED

fly

OPERATING EXPERIENCE USING SILVER REACTORS
FOR RADIOIODINE REMOVAL IN THE HANFORD PUREX PLANT

INTRODUCTION

Silver reactors have been employed in the Hanford Purex Plant since startup in 1956 to remove radioiodine from gaseous waste streams before releasing the gases to the atmosphere. Operation, with two exceptions, has been reliable and safe. Recently, the cooling time of the nuclear fuels being processed in the plant has been long enough (radioiodine content low enough) so that the reactors are not routinely needed nor retained in a fully active condition. However, the reactors are still in the off-gas treatment system and only require regeneration to return them to full service. Meanwhile, they do provide limited protection by an isotopic exchange mechanism^[1] in the unlikely event that fuel containing a large quantity of radioiodine was dissolved by error. This change in plant operating mode offered an opportunity to gather additional information about the containment of iodine in the Purex Plant.

Individual silver reactors are employed to treat the off-gases from each of the three fuel element dissolvers and a fourth silver reactor is used to treat the vent gases from most of the rest of the process equipment pieces. Plant experience indicated that the reactors in the dissolver off-gas systems trap iodine more effectively than the reactor in the vent system. This prompted additional laboratory and

plant studies to better understand the chemistry of the vent system silver reactor.

This paper describes the possible iodine paths through the plant, the relationship of the reactors to the rest of the Hanford Purex Plant, the silver reactors, and regeneration methods and safety aspects of the reactors. It also presents the overall iodine containment capabilities of the plant with and without the reactors, the performance and operating conditions of the reactors in the two plant systems, and the results of plant and laboratory studies relating to reactor performance.

PATH OF RADIOIODINE IN THE PUREX PLANT

The relationships between the dissolver and vent system silver reactors is shown in Figure 1, along with the potential iodine paths in the Purex Plant. Only the major equipment systems are shown. Iodine enters the dissolvers with the irradiated fuel and the recovered acid solvent, and 50^[2] to 85^[3] percent of the iodine leaves the dissolver in the off-gasstream. The off-gas passes through a downdraft condenser, which removes most of the water and some oxides of nitrogen, a packed bed ammonia scrubbing tower (scrub liquid is only added during the decladding cycle), a steam heater, an electrical heater, which heats the gas to 380° F, and then enters the silver reactor. When active, these reactors remove 99 to 99.9 percent of the iodine.^[3] After passing through a glass fiber filter and flow control valves, the gas passes through another glass fiber filter outside the building before entering the backup recovery system which consists of bubble cap tray

towers. In these two towers, more oxides of nitrogen are recovered as nitric acid and up to 99 percent of the iodine is removed. The dilute acid is routed to an acid fractionator for concentration. The off-gas then passes through a steam jet which discharges into the lower part of the 200-foot-tall plant stack. Here, the gas blends with the nominal 120,000 CFM of building ventilation air.

Iodine enters the solvent extraction and acid recovery sections of the plant with the dissolved fuel element solution. Additional iodine is recycled by the iodine in the recovered acid (trapped by the backup recovery equipment). Some of the iodine volatilizes during solution transfers by steam jet and during solution concentration. All of the process equipment pieces in the solvent extraction and acid recovery system are serviced by one of three vent systems. Each system uses a steam jet to collect the gas and vapor from the various equipment pieces served. All three jets discharge into a common condenser where the water and most of the other vapors condense. Some of the iodine follows the condensate from the vent system condenser and recycles to a waste evaporator. The rest follows the gas stream, including a small amount of entrained liquid, into a steam heater where the gas is heated to about 320° F before entering a silver reactor which is similar to the dissolver reactors. After filtration through a glass fiber filter, the gas is mixed with the building ventilation air. This ventilation air is pre-filtered in a deep glass fiber bed, then passed through high-efficiency filters before entering the fans which discharge to the main ventilation stack.

Thus, there are two main routes for iodine to enter the building exhaust air: the off-gas from the dissolvers and the off-gas from the solvent extraction and acid recovery equipment. When the silver reactors in the dissolver off-gas system are charged with silver nitrate, they remove most of the iodine from the dissolver off-gas. The bulk of the remaining iodine is removed in the backup recovery facility. This iodine enters the acid fractionator along with the dilute acid. A portion follows the nitric acid through the vacuum fractionator into the recovered acid system. The recovered acid is used in the dissolvers as well as the solvent extraction system. When the dissolver silver reactors are not loaded with silver nitrate, a larger percentage of the iodine enters the recovered acid system and the solvent extraction system via the recovered acid. The increase in the amount of iodine entering the solvent extraction system is reflected by increased plant emissions. Thus, when the plant reactors are routinely regenerated, normally less than 0.1 percent of the iodine charged to the plant is found in the plant stack. This compares to a 1 percent release when the reactors are not regenerated.

PLANT EQUIPMENT

Silver Reactor Description

The silver reactor used in all four systems, as shown in Figure 2, is a stainless steel vessel, 4 feet 6 inches ID by 10 feet 6 inches tall. The silver nitrate coated 1/2-inch unglazed ceramic saddles are retained in two beds between grates and wire screens spaced

4 feet apart. A steam coil and insulation surround the packed reaction chamber to reduce heat losses. The preheated off-gas enters at the top of the reactor and flows downward through the beds and out the bottom outlet line. Regeneration or flush solutions are added via nozzles in the top head. Spent flush solutions are removed via the lower nozzle.

Regeneration and Operation

Plant experience indicates that after extended use the reactor begins to lose efficiency and requires regeneration. In the dissolver reactors this normally occurs after enough iodine has been charged to react with one-half of the silver. A similar correlation has not been developed for the vent system reactor.

To regenerate the reactor, the bed is cooled to about 140° F, 225 pounds of 55 weight percent silver nitrate solution is sprayed into the bed, and the bed is dried for two hours at 200° F and four hours at 250° F. A second silver nitrate addition of equivalent amount is then made and the bed is dried as before; however, an additional period of six hours at 380° F is maintained prior to use.

After several regenerations, the flow resistance of the reactor increases from the accumulated silver salts and the reactor requires flushing. Subsequent to disconnecting the reactor from the vapor system, it is filled with water and steam sparged to remove any residual soluble salts. This solution is drained out and the

reactor filled with a 6 weight percent sodium hydroxide - 24 weight percent sodium thiosulfate solution and steam sparged. The reactor is then drained and water flushed. In most cases the thiosulfate and water flushes are repeated. Prior to regeneration, the reactor flow resistance is measured and additional flushing is performed if needed.

EQUIPMENT PERFORMANCE

Operating Characteristics

Silver reactor operating performance has been routinely reliable. At no time has there been evidence that a used silver reactor has released from the inventory of trapped radioiodine as much as 1 percent of the AEC weekly release guide of 30 Ci/week through a tall stack.*

With only two exceptions, operation of the silver reactors has been routinely safe. Both of these exceptions are related to the presence of ammonia gas or solutions. One reactor was destroyed in February, 1958, by a rapid exothermic reaction.^[4] This reactor had been flushed with ammonium hydroxide solution and a thorough water flush to remove a plug of silver compounds which had accumulated from repeated regenerations. The investigating committee concluded that there was a probable relationship between flushing and the incident. Since that time, plugged reactors have been flushed with a sodium thiosulfate solution.

* Plant policy is to strive to keep releases at or below 10 percent of the guide.

The other potential problem noted in the Hanford Redox Plant involved a moderately exothermic reaction in silver reactors which resulted in an increased reactor outlet temperature. This effect was only noted when uranium dissolution off-gas (at 390° F) was passed through a reactor which had just previously processed ammonia-laden decladding off-gas at 250° F. [5] In particular, the exothermic reaction was not noted when the decladding off-gas was processed at a higher temperature (375° F). Since the reactions causing this energy release were not well understood, the piping in both the Purex and Redox plants was revised to include provision to divert the ammonia from the silver reactors. This change precluded the possibility of a sudden release of stored energy which could result in equipment damage.

Performance Comparison of Dissolver and Vent System Silver Reactors

The operating conditions for the two reactor systems are somewhat different as shown in Table I. Note that the water and NO_x contents of the two gas streams are markedly different and that the vent system temperature is lower. In addition, the predominant nitrogen oxide species in the dissolvers is nitric oxide (NO) whereas the vent system has predominantly nitrogen dioxide (NO₂).

For one operating period in 1968, the difference in performance between the dissolver and vent system reactors was estimated by obtaining Iodine-131 analyses on special samples of the vent system off-gas and acid recovery system acid. The results, shown in Table II, indicate that the vent system reactor was removing

little if any iodine and that the iodine concentration was relatively low in the vent gas. On the assumption that 50 to 85 percent of the iodine charged to the dissolver leaves the dissolver in the off-gas stream, the dissolver reactors were removing 90 to 95 percent of the iodine. During this run, two dissolvers were used and no difference in performance was detected between these two reactors. The lower than expected efficiency was probably caused by reactors which were not fully charged with silver nitrate.

REACTION CHEMISTRY AND RELATED STUDIES

The exact reactions which occur in the plant reactors between iodine and silver nitrate have not been determined. However, laboratory studies indicate that the reaction products change with gas composition and temperature. The various reactions proposed^[2,3,4,5,6] are presented in Figure 3. These indicate that one atom of iodine reacts with one atom of silver to form one molecule of silver iodide or iodate. Other products or reactants include oxygen, water, nitric acid, or oxides of nitrogen. All of these compounds could influence either the reaction rate or equilibrium relationships between silver nitrate and iodine. While insufficient quantitative reaction data are available to determine whether or not these differences in conditions are large enough to cause the difference in silver reactor performance, it is possible that the combination of conditions accounts for the poor performance. It is also possible that some trace impurity (organic vapor) or the specific form of the iodine might be interfering with the silver nitrate-iodine reaction.

To gain further insight into the problem, a laboratory program was conducted by personnel of the Pacific Northwest Laboratory in conjunction with additional plant studies. These studies showed that about 10 percent of the iodine passing through the vent system reactor could not be trapped in a sodium hydroxide solution but was trapped in an alkaline hydrazine solution. This indicates that about 10 percent of the iodine is in the organic form (methyl iodide for example). Similarly, about 10 percent of the iodine in samples of the plant stack is caught by charcoal after passing through a sodium hydroxide scrubber. In addition, while the measurements were not precise, the quantity of iodine passing through the vent system approximated the iodine measured in the gases leaving the stack.

Samples of the gas in the vent system were analyzed by gas chromatography. [7,8,9] The only organic iodide detected was methyl iodide. Other constituents found included carbon tetrachloride, NPH (normal paraffin hydrocarbon diluent) 60 μ g/ft³, and these alkyl nitrates: methyl, ethyl, 1-propyl, 2-propyl, and 1-butyl. The source of carbon tetrachloride in the vent system gas was at first unknown. However, it was discovered that the analytical laboratory did use a few grams of carbon tetrachloride per day and that this entered the solvent extraction system with the discarded analytical samples. About 5 percent of total quantity used was measured in the vent system off-gas both before and after the silver reactor. The concentration of organic nitrates was extremely low, and several of them are probably

decomposition products of the plant organic solvent (tributyl phosphate in NPH diluent). The butyl nitrate is the end product of tributyl phosphate (TBP) hydrolysis and again is an expected constituent.

VENT SYSTEM SADDLES

Saddles from a used vent system reactor were found to be coated with black solids which contained about 50 percent metallic silver, 25 percent silver chloride, and less than 5 percent silver iodide. The laboratory tests also indicated that either heat or gamma radiation can convert silver nitrate to silver. Thus, the metallic silver produced in the plant during continued usage may not be as reactive as silver nitrate. Other tests determined that ethyl iodide will react rapidly with silver nitrate at temperatures below the temperature of the vent system reactor.

CONCLUSIONS

In conclusion, dissolver off-gas system silver reactors have functioned efficiently. Exposure to ammonia may be hazardous. The vent system silver reactor, which has a more dilute feed stream, may be less efficient because of the lower operating temperature or from the competition of chloride for the available silver. It is also possible that the gas composition or silver form influences the reaction.

REFERENCES

- [1] USAEC Report HW-47676 (declassified), November 15, 1956, E. D. McClanahan, Jr., "Removal of Iodine-131 from Dissolver Off-Gas Streams by Isotopic Exchange"
- [2] USAEC Report DP-MS-66-78 (unclassified), March 28, 1967, S. R. Smith, "Suppression of Radioiodine Releases from a Radiochemical Separations Plant"
- [3] USAEC Report HW-49549 A (unclassified), April 10, 1957, W. C. Schmidt, "Treatment of Gaseous Effluents"
- [4] USAEC Report HW-57048 (declassified), September 15, 1958, E. R. Irish, "Separations Plant Silver Reactor"
- [5] USAEC Report HW-55974 (unclassified), May 7, 1958, G. L. Hanson, "Temperature Observations - Redox Plant Silver Reactors"
- [6] USAEC Report HW-38311 (declassified), July 1, 1955, L. L. Burger, "Thermodynamics of Iodine Removal with the Silver Reactor"
- [7] USAEC Report BNWL-CC-2048 (unclassified), 1969, L. A. du Plessis, "The Reaction of Gaseous Iodoethane with Silver Nitrate"
- [8] USAEC Report BNWL-CC-2188 (unclassified), 1969, L. A. du Plessis and Sue L. Sutter, "Analysis of Samples from the Purex Vessel Vent Silver Reactor"
- [9] USAEC Report BNWL-CC-2378 (unclassified), January 16, 1970, L. A. du Plessis, "Some Observations Concerning the Chemistry of the Purex Vessel Vent Silver Reactor"

TABLE I

OPERATING CONDITIONS

	<u>DISSOLVER REACTOR</u>	<u>VENT REACTOR</u>
TEMPERATURE, °F	380	320
FLOW, CFM	700	1,500
WATER, LB/LB OF DRY GAS	0.02	0.3
NO _x , VOL. O/O	25	2

TABLE II

PERFORMANCE

	<u>DISSOLVER REACTOR</u>	<u>VENT REACTOR</u>
INLET, $\mu\text{Ci}/\text{Ft}^3$	12 to 24	0.014
OUTLET, $\mu\text{Ci}/\text{Ft}^3$	1.2	0.014
INLET/OUTLET RATIO	10 to 20	1

IODINE PATHS IN THE PUREX PLANT

FIGURE 1

Figure 2— SILVER REACTOR

UNCLASSIFIED

FIGURE 3

REACTIONS

UNCLASSIFIED

ARH-SA-67
Page 15