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DATE: March 26, 1959
SUBJECT: Eurochemic Assistance Program: Comments
by HAPC, dated March 12, 1959, on Questions
by E. L. Nicholson
TO: E. M. Shank
FROM: L. P. Bupp, HAPC

Acknowledgment

The attached comments were given by HAPC personnel to questions directed to HAPC by E. L. Nicholson, USAEC Contractor Advisor to Eurochemic. The comments have been retyped at ORNL after official deletion and release. The original questions are given in Appendix I.

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ANSWERS TO QUESTIONS ON OFF-GAS TREATMENT

Reference: Letter, E. L. Nicholson to W. C. Schmidt &
A. G. Blasewitz, O/Ref. ELN/ys-No. 988,
dated February 17, 1959.

The referenced letter requests information relative to the performance and operation of silver reactors. Mr. W. C. Schmidt of our Purex Technology Operation, Chemical Processing Department, has provided answers to the questions submitted and these are presented below for your transmittal to Mr. Nicholson. The numbers refer to the questions in the referenced letter.

1. The regeneration of silver reactors using the technique of spraying 5 molal silver nitrate on the column packing appears to be inefficient, but the cost of equipment and silver nitrate inventory necessary to effect a complete flooding of the column is out of proportion to the gains to be realized. A study made in the development laboratory, HW-41053, "Regeneration of Silver Reactors", by L. G. Amos, indicated that the spraying technique was quite adequate.

The washing of a tower with dilute nitric acid might release a large quantity of the captured iodine. The substitution of 2 M $\text{Na}_2\text{S}_2\text{O}_3$ - 0.1 M NaOH should not only eliminate the hazard of evolution, but should also give a more efficient flush. After the thiosulfate flush, copious quantities of water should be used to flush the reactor. Following the aqueous flush the reactor packing should be dried, regenerated with 5 molal silver nitrate, and then redried.

2. Two old reactors were operated in series in a group of tests. Data from these tests are presented in HW-38872, "Technological Performance of Backup Silver Reactor", by W. C. Schmidt. (In its present form this report does not appear to be declassifiable.) Although the first reactor was known to be operating at an impaired efficiency (75% removal) the two reactors in series removed only 99.8 percent of the radio-iodine. From theoretical calculations of the partial pressure of iodine above silver iodide, one would believe that this performance is representative.

3. A reactor with two new beds in series has been installed in the Purex Plant with the following operating philosophy:

A continuous sample of the gas between the two beds would be monitored for radio-iodine concentration. Whenever the initial bed indicated a breakthrough, the unit would be shut down and the initial bed would be regenerated. With this type of operation the second bed would afford a decontamination factor to prevent bursts of radio-iodine to the atmosphere when the initial bed failed. It is this combined unit that has run for over a year with a 99.99 percent removal of the radio-iodine.

4. A material balance of radio-iodine around the dissolver has been very difficult to obtain. The data indicate that the amount of radio-iodine leaving via the off-gas lines varies between 50 and 85 percent

of the total iodine present in the dissolver. This split is influenced a great deal by the sparging of the dissolver solution with air during the dissolution period. Air sparging increases the amount of radio-iodine which leaves via the off-gas lines from the 50 percent to the 85 percent range. Sparging is quite desirable in the dissolver during dissolution to promote a faster, yet more controllable dissolving reaction, and also to drive the iodine out the off-gas system which has the best equipment for removal.

5. The reaction between silver nitrate and iodine at elevated temperatures was examined in our laboratories. With our operating procedure, air in-bleed to supply oxygen for the oxidation of NO and entrance gas temperature to the silver reactor at 375°F, the best overall equation appears to be:

A series of experiments were run in the laboratory to further verify this equation. Considerable difficulty was encountered in controlling the variables which resulted in erratic data. However, the trend of the data seemed to substantiate the above equation. With the validity of this equation established, you can see that the amount of iodine passing the bed is proportional to the square of the NO₂ concentration. All of this work is reported in HW-42408, "Chemistry of the Silver Reactor", by G. B. Barton and E. D. McClanahan, Jr.

6. Our experience has been that a vent system with some type of iodine removal facility is a necessity. At the Purex Plant a silver reactor is installed on the vessel vent system, but, for some unexplained reasons, the reactor does not function as well as those on the dissolver off-gas system. The largest contributor to the release of radio-iodine downstream of the dissolvers appears to be the feed clarification step.

In this step the dissolver solution is centrifuged at 1500 G's for the removal of the undissolved solids associated with the uranyl nitrate solutions. Addition of mercuric nitrate (5×10^{-4} M) to the dissolver solution after its removal from the dissolver vessel depresses this evolution of radio-iodine by a factor of 2 - 3. Addition of mercury at this concentration appears to have no measurable effect upon either column performance or corrosion of the stainless steel equipment.

7. There are some particulates in the dissolver off-gas which necessitated the installation of a Fiberglas filter. The exact chemical composition of these particulates is not too well defined, but ruthenium is one of them. The Fiberglas filter, however, does an excellent job of removing these particulates, including ruthenium, and as a result practically no ruthenium is found in the off-gas system downstream of the filter.

The same is true of the vessel vent system, and again an in-cell Fiber-glas filter is required. In addition, the vessel vent system is discharged into the main ventilation air filter for further decontamination. If you are going to use a head-end oxidation step with KMnO_4 , as is done in the Redox process, additional equipment would be needed for ruthenium decontamination.

8. The progress of the development program for better silver reactors has been slow with the main emphasis being placed on flushing techniques and studying the effect of ammonia gas in silver reactors. As a result we do not have any data to report on higher efficiency silver reactors but my personal belief is that if a new packing of elemental silver were used, higher operating temperatures could be maintained, and as a result higher iodine DF's could be obtained.

It is our collected opinion that serious consideration should be given radioactive decay as a method of removing significant quantities of the radio-iodine. The technology of iodine suppression by chemical means is expensive, complicated, and incompletely defined. Although the decay method for sufficient decontamination involves larger capital investment for uranium inventory, there are no qualifying factors to guarantee any desired decontamination factor.

Reports HW-41053 and HW-42408, referenced above, were commented on in my letter of February 3, 1959. Additional HAPD references relating to off-gas handling, some of which you may already be aware, and which may be of some value to the Eurochemic Program, are as follows:

HW-20803, HW-21103, HW-21865, HW-21957. These reports are classified SECRET. In our opinion they are declassifiable.

HW-50259. This report is classified CONFIDENTIAL. In our opinion it is declassifiable.

HW-20847, Parts I and II. These reports are UNCLASSIFIED.

TID-7534, "Treatment of Gaseous Effluents", W. C. Schmidt, presented in Brussels, Belgium, 1957.

Air Repair, Vol. 4, No. 4. "Filtration of Radioactive Aerosols by Glass Fibers, A. G. Blasewitz and B. F. Judson, Feb., 1955, p. 223.

L. R. Michels, "Design and Operating Consideration for Off-Gas Systems in Nuclear Processing Plants", to be presented at 1959 Nuclear Congress in Cleveland, Ohio, April 5-10, 1959.

Additional data which you requested by questions in your trip report and in your letter to me of December 15, 1958 (ORNL-CF-58-12-54) have been collected. These data are being reviewed and edited and will be forwarded to you shortly. It is probably that the material will be sent as classified, with a simultaneous request for declassification.

Appendix I. Basis for Comments

Letter, E. L. Nicholson to A. G. Blazewitz and
W. C. Schmidt, HAPCO, dated February 17, 1959.

A health physics evaluation of the hazards generated here by a proposed fuel reprocessing plant revealed a questionable situation when an average removal of 99.5% of the I-131, as per your report, was assumed from dissolver off gases. In addition, the survey assumed 50% volatilization of I-131 from the dissolver which had a downdraft condenser.

I should like to ask the following:

1. Could a silver reactor be designed to be regenerated in such a way as to result in substantially "new" performance with each regeneration. For example, the tower might be washed with dilute warm nitric acid, dried, filled with nearly saturated AgNO_3 , drained and dried. Could you suggest any improved procedure?
2. Would a series installation of two silver reactors, each sized as per your recommendations, be expected to result in significantly improved performance (factor of 10 to 100 better) over a single tower? Is 99.7 to 99.9% removal considered the maximum, regardless of reactor length, for this system?
3. Can you give the reason why one reactor gave the exceptionally good performance? (99.99% removal of I_2 for approximately 1 year).
4. Is a 50% escape of iodine in the off gases from the dissolver's downdraft condenser probable?
5. We envision operating the dissolver with the usual downdraft condenser followed by a liquid scrubber tower for recovery of traces of NO as nitric acid. With this fumeless dissolving system, we expect to have a low NO content in the effluent gas and to get rather good control of air inleakage to the dissolver and of the dissolution reaction. Would you expect any improvement in silver reactor performance under these conditions?
6. Is the evolution of iodine from head end operations such as steam jet transfers, air sparging, and evaporation generally sufficient to require a silver reactor for the vessel off gas system? We do not envision use of MnO_2 precipitation as a head end operation.
7. In Geneva Paper 394, Mr. Schwendiman and others from Hanford mentioned automatic instrumentation for measurement of ruthenium and iodine in a gas stream. Is ruthenium to be expected in more than tracer amounts in dissolver off gases and the vessel off gas? Is any data available for removal of ruthenium by fiber glass filtration, by caustic scrubbing, or by other methods? (answer partially deleted)

8. Your paper mentions a future program for developing higher temperatures, ultra-high efficiency silver reactors. Is any data available on this at this time? In case answers to questions 1, 2, and 5 are negative, we would be very interested in even preliminary data on the development to give us an idea of whether we can eliminate iodine as a hazard when processing 90-120 day cooled fuel.

The preceding questions are part of the cooperative program between the USAEC and Eurochemic. You may receive an official request later for the same information by Mr. E. M. Shank at Oak Ridge to Mr. L. P. Bupp of the Chemical Processing Department. I am writing directly to you, with a copy to Shank in Oak Ridge, so the information can be forwarded as quickly as possible if it can be made available to me.

Thank you very much for any assistance you can give us on this problem.

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