MASTER

External Transmittal

Authorized

ORNL
CENTRAL FILES NUMBER59-3-94, Revision 2
(deleted)

COPY NO. 36

OAK RIDGE NATIONAL LABORATORY

Operated by

UNION CARBIDE NUCLEAR COMPANY

Division of Union Carbide Corporation

Post Office Box X
Oak Ridge, Tennessee

DATE: November 16, 1960

SUBJECT: Eurochemic Assistance Program: Comments by ICPP,
dated February 25, 1959, on Questions Listed in
ORNL-CF-59-1-75

TO: E. M. Shank, ORNL

FROM: M. E. Weech, ICPP

Acknowledgment

The attached comments were given by ICPP personnel to questions listed in ORNL-CF-59-1-75, ICPP Trip Report. The comments have been retyped at ORNL after official deletion and release. The original questions from ORNL-CF-59-1-75 are listed in Appendix I.

Revision 2 has been issued to include additional information given to clarify the original statement about TBP, DBP, and MBP analyses (page 2, section B).

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

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.

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.

ANSWERS TO QUESTIONS FROM DECEMBER 2, 1958 ICPP TRIP REPORT BY E. M. SHANK
(ORNL-CF-59-1-75)

B. Handling of Interface Jettings and Recycle

Interface liquids from columns are jettied to first solvent-wash mixer settler (weak nitric acid wash). Aqueous wash from this mixer settler normally is routed to the first cycle waste evaporator; however, if uranium is high the solution is routed to a holdup tank (G-108) where the material is blended with other solutions and rerun through the extraction system when schedules permit. Wash solutions from the second and third mixer settlers are routed to the PEW (warm) waste evaporator.

Organic from the mixer settler box goes on through the solvent treating system. This organic solvent is sampled once per week, and the amount of nitration the Amsco has undergone determined. Its determination is made by the direct analysis for TBP and the indirect analysis of DBP and MBP. The quantitative effects of DBP and MBP, which are a measure of their concentration, are measured by means of a "Z" and a "C" test. The Z (Zirconium Index Test)¹ gives a measure of the degradation products in uranium or plutonium process solvents. The C test,² described below, gives an indication of losses that may be incurred in the stripping column and of the general solvent quality. A 50-ml sample of the recovered solvent is submitted periodically for analyses, which consists of the following steps:

1. Adjust solvent to 30% TBP.
2. Wash solvent three times with equal volume of 1.0 M sodium carbonate.
3. Wash solvent three times with equal volume of distilled water.
4. Contact solvent with an equal volume of standardized 1 g/liter uranium (as the nitrate) solution.
5. After phase separation, centrifuge organic phase to remove entrained water.
6. Analyze the organic phase for uranium fluorimetrically.

Carbonate wastes from solvent washings are never recycled. They are routed directly to the low level waste system.

C. Availability of CPP, CPM, and RaLa As-Built Drawings

The vast majority of these drawings are unclassified and as such would be available.

¹DP-237, "A Test for Solvent Quality."

²Used by HAPO.

D. Availability of Copies of Monitoring Detection System

Drawings on the Jordon area monitoring system can be made available.

E. Decontamination Procedures used at CPP

The decontamination procedures used in the central decontamination facility are not routinely established but vary with the geometry, material to be cleaned, and with the nature of the contamination. We follow the procedures outlined by the Turco people more than any other and use their decontaminating solutions frequently. These procedures are outlined in their bulletin "Decontamination with Turco," Turco Products Incorporated.

Our contact with this company is with:

Mr. Kenneth W. Newman
Chief Process Engineer
Turco Products Incorporated
Terminal Annex 2645
Los Angeles 54, California

Our experience in this area would indicate that decontamination is still more of an art than a science.

The procedures used in plant decontamination are outlined in "CPP-601, Standard Operating Procedures Manual." A copy of the decontamination procedures is included. New procedures and new decontaminating solutions are continuously being tried in the plant on an experimental basis. A procedure being tried at present is as follows:

1. Flush lines and equipment free from uranium.
2. Treat with hot Turco solution 4501.
3. Flush solution out with water.
4. Treat with Turco 4502.
5. Flush out with water.
6. Flush with 10 w/o nitric acid solution.

The optimum time and temperature conditions for these steps are still being worked out.

Special facilities installed for decontamination include internal spray nozzles in all vessels. These nozzles are piped to the cold solution makeup areas so decontaminating solutions and steam can be added directly to the vessel. All vessels are equipped with air and steam spargers or jackets for steaming down vessel walls and heating-agitation of decontaminating solutions. Certain vessels are equipped with recirculation jets and sprays. However, due to dilutions and temperature limitations this system is not favored. In addition to these provisions, in-cell vessels are constructed under a specification that includes:

1. All metal for vessel fabrication is supplied in a solution annealed and pickled condition.
2. Internal and external welds are ground flush and free of pits and icicles.
3. A Number 1 finish is specified both inside and out.
4. Vessels are designed such that no crevices or cracks or other areas are present that decontaminating solutions cannot reach.

F. CPM Type Flowsheet for Processing MTR Fuels

We have processed MTR fuels in the CPM equipment; however, no complete official flowsheet was ever worked up for this. Preparation of such a flowsheet is on our agenda and can be forwarded to you when complete. This flowsheet will be unclassified.

G. Revised Stack Off-Gas Sampling System

The revised stack off-gas sampler is presently being designed by an architect engineer and will not be completed for some time. All that is currently available are the design specifications. When the design is complete, it will probably be unclassified and could be distributed.

I. Available Information on Off-Gas Handling

Reports pertaining to krypton, xenon, and iodine removal from dissolver off-gases are as follows:

ORNL-51-7-90	Unclassified
ORNL-51-11-16	Declassified
ORNL-51-10-55	Declassified

There is a little information in a Geneva paper UN-1986, Section 2.4, page 25, "Production of High Specific Activity Radioisotopes," by A. L. Ayers, C. E. Stevenson, and W. B. Lewis on this that may be some help.

J. Evaporator De-Entrainment

The evaporator system at ICPP has a number of evaporators in the first cycle such as feed evaporators in G cell (G-110), headend product evaporators in H cell (H-110), and waste evaporator G-114. In addition subsequent solvent extraction cycles have product evaporators in cells P, Q, and S. There are structural differences between these evaporators. The enclosed print 4272-301-25-1 is an as-built drawing on G-110. G-114 and H-110 were essentially identical to this. The P, Q, and S cell evaporators are shown in enclosed prints 4272-301-22-1 and 4272-301-24-1. The overhead from these evaporators is condensed and routed to the PEW evaporator (WL-113) where it is re-evaporated. Prints A-1257-A5 through A-9 give the details on WL-113 and the de-entraining column WL-112. Entrainment on the G, H, P, Q, and S cell evaporators is not measured, but tests on a similar evaporator gave de-entrainment factors averaging 10^4 . De-entrainment on WL-113-112 has averaged approximately 10^3 . Overall de-entrainment on the whole evaporator system is probably 10^7 to 10^8 .

K. Waste Calcining in a Fluidized Bed

Data on this system is given in the following reports:

IDO-14416	Unclassified	
IDO-14443	Unclassified	Quarterly Progress Report
IDO-14453	Unclassified	Quarterly Progress Report
IDO-14457	Unclassified	Quarterly Progress Report

A demonstration unit utilizing this system is currently being designed by the Fluor Corporation. This design will not be completed for some time.

The design criteria which was supplied to Fluor is given in PTR-177. This is a Phillips Petroleum Company internal document and is not readily available. Fluor is also preparing design and operating manuals on the calciner. The completion date on these manuals is indefinite now but you can be informed when they are ready if you desire. These manuals will probably be unclassified.

L. Information on Lapp Pulse Units

Enclosed is a set of the vendors prints, a copy of the specifications, and a copy of the installation and operating instructions. These instructions should answer your questions on filling the hydraulic system and phasing the diaphragms.

We have had some difficulty with these units mostly in getting the hydraulic system properly filled and in getting the diaphragms phased. The chief difficulty being inconsistency between shifts on the manner and methods to be used in these adjustments. As a result the pulse amplitude in the columns has been erratic at times. There has been some ruptures in the diaphragms both in the remote and accessible units on the pulsers and on pumps of similar design. These ruptures were attributed to dirt getting between the diaphragm and stop which causes fine holes to eventually appear in the diaphragm. Some of the dirty solutions have resulted from recycle of PEW wastes (i.e., warm wastes that have been concentrated but contain too much uranium to discard) which contain almost everything including concrete. With proper charging and cleanliness in the system, operation can be satisfactory. Depending upon the nature of the feed solutions, adequate cleanliness in the system may be difficult to achieve and maintain over long operating periods, so the type of solutions being handled may weigh heavily in the selection of a unit of this type.

Overall continuous dissolution has been very successful. The difficulties experienced have been largely due to mechanical failures and not process or flow-sheet difficulties.

The following operating advantages have been definitely proven in the runs to date:

1. Considerable increase in capacity if equivalent cell and equipment size limitations are considered between batch and continuous dissolution requirements.
2. Less severe criticality problems arise in a continuous dissolution process.
3. Continuous nature of the process makes it amenable to automatic control that is free of some possible operational errors such as double batching, solution transfer to wrong vessels, etc.
4. Greater percent utilization of equipment which would ultimately be reflected in lower processing costs.
5. Overall product decontamination has been better than that attained in the batch process. This may be due to the two solvent system used here, where the TBP-Amsco headend solvent gives a good decontamination factor on ruthenium but poorer decontamination factors on zirconium and niobium. The subsequent second and third cycles use a Hexone solvent which gives good decontamination on zirconium-niobium but poorer decontamination factors on ruthenium.

Disadvantages of continuous dissolution have been:

1. Solid fuel handling and charging equipment is more complex than for a batch system and subject to more mechanical and breakdown difficulties.
2. Equipment is usually under more continuous duty and thus must be more reliable to minimize shutdowns.

Specific difficulties that have arisen during CPP operations in dissolution are as follows:

1. Breakdown of mechanical handling equipment. Mainly manipulators that are used for loading fuel into transporting casks or that are used for charging fuel into the dissolver.
2. Failure of remote head column pulsers and pumps. Failure here occurred for a variety of reasons such as punctured diaphragms, loss of hydraulic fluid in linkage system, plugging or sticking of check valves in the pumps, air binding in the hydraulic linkages. Pump valve sticking was probably due to accumulations of compounds of zirconium fission products and degradation products of tributyl phosphate.
3. Accumulation of surface active materials at the column interfaces which ultimately causes stable emulsions to form in the columns and subsequent column flooding. This difficulty was attributed to silica which was a minor constituent of the fuel element. It was found that additions of nitric acid to the column interface zone broke up the emulsions and carried the surface active silica out with the column raffinate.

Due to the difficulties experienced with pumps in hot feed and waste lines, these pumps are being replaced or spared with air lifts.

The above difficulties are not peculiar to a plant employing continuous dissolutions, but would occur in any plant where running for extended periods is necessary.

Decontamination has been good. Product specifications (ratio of product beta count to beta count of uranium-235 of 30) can be readily met or exceeded from a fuel with better than 30 percent burnup and 120 days cooling. It appears that the two solvent system is an aid in getting these good decontamination factors.

Product losses are given over a specified operating period in "Comparison of Design and Operating Performance at the ICPP" by A. L. Ayers and F. M. Warzel. This will be given as a paper at the April 5-10 Fifth Nuclear Congress at Cleveland. A preprint of this paper is included for your information. You may find other information in it that will be of value to you.

Outside of the above general discussion several reports could probably be written on your question. If you have any more questions, I will be happy to attempt to answer them.

0. Expansion of Appendix I

The reports cited and included have a very extensive bibliography in them. I do not believe there are any pertinent reports not cited in these lists that I could call to your attention.

Appendix I. Basis for Comments

1. Three reports have been issued on sulfuric acid decladding, one each by KAPL, IDO, and Blaw-Knox. The report numbers are required along with permission to transmit copies of each to E. L. Nicholson. If the reports are classified, only the numbers and a statement as to the possibility of declassification are required now. (answer deleted)
2. How are the interface jettings handled for material recovery? Does ICPP have a rework system? How are off-specification products handled? What type of rework system would be recommended for a multipurpose plant? Are the solvent recovery carbonate wastes recycled? (answer partially deleted)
3. Can copies of the as-built drawings (Appendix I) for the CPP, CPM, and RaLa be made available to Eurochemic?
4. Can copies of a "Typical Radiation Monitoring Detection System" be made available (see N. J. Rigstad)?
5. Please provide the decontamination procedures as used in the central decontamination facility. What is the current decontamination procedure used in the plant and are any special facilities designed into the system to aid decontamination?
6. Please provide copies of the CPM flowsheet for MTR processing, including the second and third cycles (this should include the dual solvent recovery flowsheet). Can this information be sent to Eurochemic? (answer partially deleted)
7. Please provide information on the new (revised) stack off-gas sampling system. Can these be sent to Eurochemic?
8. All the information available on off-gas handling (including Kr, Xe, and I_2 removal) is requested. A list of reports and permission for transmittal is all that is required. (answer partially deleted)
9. Information on de-entraining equipment for evaporators, etc., is requested.
10. Information, including design data, is desired on the waste fluidized bed treatment system. (answer partially deleted)
11. Please provide drawings, specifications, and installation requirements on the large Lapp pulsing units. How well have these units performed? What are the special problems, if any, on installation, filling the hydraulic system or phasing the diaphragm?

12. Please provide design data and operating experience for the downdraft condenser (with O₂ addition). (answer deleted)
13. Please provide operating experience for continuous dissolution of fuels. (answer partially deleted)
14. Please expand Appendix I to include all reports and drawings pertinent to this trip report. Indicate which ones may be made available immediately to Eurochemic.

DISTRIBUTION

- 1-2. R. J. Sloat, via ORNL and DIA
- 3-4. F. L. Cuthbert, FMPC
- 5-6. I. G. Dillon, ANL
- 7-8. O. F. Hill, HAPC
- 9-10. B. Manowitz, BNL
- 11. E. M. Shank
- 12-13. V. R. Thayer, du Pont
- 14-19. M. E. Weech, ICPP
- 20-21. Central Research Library
- 22. Document Reference Section
- 23-32. Laboratory Records
- 33. Laboratory Records - RC
- 34. Technical Exchange Branch, DIA, via ORNL
- 35. Research and Development Division, ORO
- 36-50. TISE