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EUROCHEMIC ASSISTANCE PROGRAM: COMPILATION OF ORNL-ORIGINATED INFORMATION SENT TO EUROCHEMIC VIA TRANSMITTAL LETTERS (THROUGH TRANSMITTAL LETTER 87)

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ABSTRACT

ORNL-originated information sent to Eurochemic via transmittal letters is combined in this report to facilitate general distribution. The subjects covered include analytical, criticality, sampling systems, radiation safety and control, fabrication, corrosion, airlifts, head-end development, storage canals, fuel shipment, and waste disposal.

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1.0 INTRODUCTION

As part of the Eurochemic Assistance Program, information was sent and identified in transmittal letters. Specifically prepared information was generally issued with an identifying number and sent via the Division of International Affairs. Information needed quickly or small in quantity was included in the transmittal letters. The ORNL-originated information, which was not given the general distribution prescribed in the procedures for obtaining and transmitting information, is combined in this report.

2.0 DISCUSSION

2.1 Analytical (via transmittal letters 33 and 45)

Eurochemic Technical Reports Nos. 17 and 29 have been reviewed by E. J. Frederick, ORNL, with the following comments:

> "Although both plans appear functional, I am particularly impressed with the organization of the modified plan. The logic used in orientating the various areas is consistent with good radiochemical laboratory practices and reflects considerable thought. The only apparent shortcomings in the modified plan are the lack of analytical support facilities for the alpha, beta-gamma, and hot cell facilities and the small curie capacity of the hot cells. It has been our experience that analytical facilities located either at or near the areas specified greatly increase the efficiency of the operations carried out in the area itself and reduce the possibility of cross contamination and contamination spread. As for the shield capacity of the hot cell facility, past experience has shown that the trend in hot cell operations is to work with more highly irradiated and shorter decayed materials. I would strongly recommend increasing the shielding effectiveness to 48 in. of barytes concrete or its equivalent; the immediate additional cost can be more than justified on a long term basis."

The questions listed in the status report as of April 1, 1959, Section 5.0 (ORNL-CF-59-5-5) have been commented on by the Analytical Division personnel as follows:

Question: What is the status of the development of coulometry for uranium and plutonium analysis?

Answer: A complete status report on coulometry for uranium and plutonium analysis will be issued soon.

Question: Is X-ray fluorescence useful for very radioactive solutions of uranium and plutonium? Does this method have in-line instrumentation applications?

Answer: It might be possible to use this method if impurities were low or relatively constant in concentration. The high activity level might be circumvented by x-ray reflection optics and energy discrimination in detection. The inability to use an internal standard would be an inherent disadvantage in applying fluorescence to an in-line determination. Much would depend on the nature and variability of the chemical composition of the stream.

The use of x-ray absorption would avoid the need for internal standards and render the analysis essentially independent of changes in matrix composition.

Considerable development work would be necessary in order to incorporate either method into an in-line analytical instrument.

Question: The usual in-line gamma absorptometer uses an Am-241 source and direct scintillation counting. Consequently, it is not useful at > 5 μc/liter. Could one use a coincidence counting technique, with, for example, Na-22 and a shielded plate to reduce hardness, to make the method specific for heavy elements?

Answer: Reduction in "hardness" of 0.51-Mev annihilation radiation of Na-22 would give no well-defined energy, and the average, after great attenuation in a Compton-scatter medium like Al, would be ~ 0.2 Mev. Assuming one wished to count coincidences between pairs of annihilation photons, attenuation of the gammas reaching one detector would result in a low and uncertain coincidence rate - uncertain because of <u>random</u> coincidences between the radiations detected by the two counters. Recommended

approaches, using an Am source, in order of increasing freedom from interference by sample activity:

(a) (Good) Use an upper and lower "gate" on detector amplifier output, i.e., make it a manual single-channel spectrometer. Center "window" on 0.06 Mev radiation of Am. Further, use thin (3/32 in.) NaI crystal for detector. This should make tolerance nearer 5 μc/ml than 5 μc/liter.

(b) (Better) In addition to (a), provide a lead "screen" for sources; read transmission in terms of difference with source open and screened.

(c) (Probably best) Use a rotating "shutter" to screen source; amplify "A.C." (pulsed) current from photomultiplier, not the D.C. (steady) component resulting from sample activity.

Question: Am-241 is expensive; could one use bremsstrahlung from a beta emitter such as Sr-90 instead?

Answer: Bremsstrahlung (wide range of energies) should be minimized. Beta source may be mounted on, or covered with, material whose K x-rays have desired energy. Pm-147 would be better than Sr-Y-90 because lower beta energy would excite less "white" radiation. See Matlack et al., Anal. Chem. 30, 1753 (1958).

Question: No literature references have been found on the actual technique used for determination of very small amounts of uranium in concentrated plutonium solutions. Fluorometry seems dangerous because of the plutonium hazard; therefore, a wet method would be preferable. The lower limit of poloragraphy is not sufficiently sensitive to determine 10^{-2} gU/liter and analysis for even lower values seems to be necessary. Is there any information on this?

Answer: ORNL uses both fluorometric and polarographic methods. At present we are determining uranium in plutonium solutions by the fluorometric method. This is discussed in the ORNL Master Analytical Manual. We determine uranium to 10^{-2} g/l now by the polargraphic method and feel we can go to lower

limits if necessary. We have the polarographic method only in rough draft form, which we will be glad to furnish Eurochemic.

Additional information on the Am-241 sources for Eurochemic has been obtained. A 10-mg unshielded sample of Am-241 will produce about 2.3×10^{10} photons/min. After encapsulation, the activity through the 10-mil-thick stainless steel window will be about 0.95×10^{10} photons/min. The sample size will have to be increased to 21 mg to provide the 2×10^{10} photons/min specified in Mr. Goris's letter to the Research and Development Division. The sources now being built for ORNL will be increased to 21 mg Am-241 each. Mr. Vanderryn, ORO, has checked with the Washington AEC and has been informed that increasing the Eurochemic request to 42 mg of Am-241 will probably be approved. This request for the increase should be directed to T. R. Jones, Research and Development Division, Washington AEC. Reference should be made to Mr. Goris's letter of December 28, 1959.

2.2 Criticality (via transmittal letters 48, 70, and 86)

ORNL management has approved the use of geometrically safe settlers, followed by large-size catch tanks, for handling clad solution streams from the Sulfex and Darex dissolvers. The catch tanks will be equipped with means for detecting the accumulation of fissile solids. The core solution will be routed through a digestor-settler system and will be digested further in the catch tank. Soluble nuclear poisons are also approved as a primary control in the feed adjustment tank provided adequate procedural, analytical, and instrumentational safeguards exist to ensure the addition of the poison.

A geometrically safe centrifuge is being designed since it is fairly easy to do. A proposed design for one was previously sent.

Continuous instrument-controlled dilution might be considered an adequate safeguard provided two or three similar instruments were used independently or two or more independent variables were monitored.

Rocky Flats has used high-boron glass for poisons for a year without difficulty. Scouting experiments at ORNL, however, indicate the high-boron glass is subject to cracking and crazing; our preference is Pyrex glass. We have recently fabricated a non-geometrically safe storage container, which will be poisoned with Pyrex, and are fabricating a container to ship 50 kg of U-233 solution off-site.

Copies of EIR-49, "Pyrex Raschig Ring Poisoning of Enriched Uranium Solutions in Large Vessels," were sent to several people for review. ORNL has made the following comments:

(1) A spot check of the experimental data indicates that the calculational methods given permits adequate estimation of the critical concentration. For actual application, however, it is recommended that a concentration safety factor of about 2 be used and that a multiplication measurement be made during the initial filling.

(2) If precipitation in a tank is a possibility, it is desirable to have critical mass versa concentration curves (see ORNL-CF-60-8-58 sent in transmittal letter No. 74). These curves depict the estimated minimum critical mass in a vessel.

(3) Multiplication was negligible in the ORNL U-233 storage tank (see ORNL-CF-61-2-54 sent in transmittal letter No. 72) when 11 kg of U-233 at 100 g/liters was put into the tank. This tank is now used to store U-233 solutions. Most of our tests on the chemical and physical properties of packed rings are given in the above report.

2.3 Sampling Systems (via transmittal letter 53)

The information requested on sampling systems is being sent under separate cover. This information includes the nine drawings specified, eleven drawings for the MR Expansion II project, a report (ORNL-CF-59-11-26) which discusses improvements to the original Thorex sampler design, and two drawings for the 3019 building Darex facility. Some of the weak points of the Thorex sampler are:

(1) Sampler lines for concentrated solutions frequently plugged owing largely to insufficient slope. Elimination of all horizontal runs are mandatory and the use of the maximum slope is desirable.

(2) The present conveyor gives troubles which might be decreased by using a cable in place of the chain. Also, the cable will permit decreasing the height of the conveyor cavity.

(3) The needle-clip removal system, including the flush attachment, needs improving.

(4) The thermistor alarm system for the PRV stations never functioned. The liquid level system discussed in ORNL-CF-59-11-26 is preferred.

(5) Use of an all-welded installation in the cell is preferred to the tube fittings used originally. Radiation levels generally preclude direct maintenance at the PRV stations so that provisions for external flushing is very desirable.

(6) Tongs for transferring samples must be extremely rugged and simple.

2.4 Radiation Safety and Control (via transmittal letter 63)

All routine personnel monitoring film at ORNL is processed on a quarterly basis with no unusual difficulties from fading and fogging. There is considerable range in temperature and humidity here, but a comparison in this regard with the Eurochemic locality cannot be made for lack of pertinent information.

The quarterly period is probably the maximum time one can expect to use a film in the field without exchanging it and still be consistent with reliable results. Accordingly, to measure dose levels of 0.5 rem, it is necessary for one to measure a dose of 125 mr for thirteen weeks. With the type of film packets currently in use, DuPont 553, this is only a few percent above the minimum dose which can be measured with any accuracy.

In brief, if climatic conditions at Eurochemic are comparable with ORNL, films can be used to determine whether the dose rate exceeds 125 mr per quarter. The film currently in use at ORNL cannot be used to determine doses below this level.

2.5 Fabrication (via transmittal letter 64)

Two ORNL titanium welding specifications were previously requested. Since Eurochemic may be considering some titanium fabrication, these specifications and some pertinent comments are being sent now.

ORNL Comments on Specification HRP-7

This is a welding procedure and should be used for basic information only. It was not intended to be used as a specification with which a fabricator must comply. Experience indicates that the specification should be revised. Some requirements may be too conservative (example: Argon protection above 200°F) and others may not be restrictive enough (example: permissible x-ray porosity). In general, the specification gives many procedural rules that must be followed for satisfactory welding of reactive metals. However, many requirements might be questioned on an economic basis. Details of joint design, welding current, joint alignment could be changed providing inert-gas protection is adequate. Also, the specification should be more explanatory and definitive; many questions must now be answered by someone having background in titanium welding.

ORNL Comments on Specification RD 9.6-1

This specification may be used as an example of a type suitable for procurement. No equipment, however, was fabricated or purchased under this specification. The equipment to be fabricated was to be from relatively thin material, and some revision might be desirable to give it more general coverage.

The problem of on-the-job quality control checks for weld contamination is somewhat unresolved. The practicability of color criteria in Sect. 10.2.3 is questionable since it leaves much to judgment. The hardness test in Sect. 10.3.1 may give a more positive indication of weld quality. Problems arise in general application of portable hardness-test equipment, and has not been shown that the method is practicable and that test results can be correlated with performance of a welded structure.

Note that the specification requires the fabricator to "qualify" (prove by test) his welding procedure before fabrication. In the course of this, establishment of additional requirements might be found necessary.

2.6 Corrosion (via transmittal letter 65)

The most recently published corrosion data on Ni-o-nel and Hastelloy-F is in HW-61662, "Power Reactor Fuels Reprocessing Progress Report on Corrosion Studies," which was sent via transmittal letter 39. Some supplemental

information to that given in BMI-1375 has been obtained at ORNL. Actual corrosion rate data obtained in laboratory-scale experiments are available if you desire them. Corrosion rates of 1 mil/month or less are considered satisfactory at ORNL.

Sulfex. Five materials, Carpenter-20, LCNA (low-carbon nickel alloy similar to Ni-o-nel), Hastelloy C, Hastelloy F, and Titanium-45A, are currently being tested for low-temperature Sulfex clad solutions (multipurpose centrifuge); all materials showed corrosion rates less than 0.5 mil/month and are considered satisfactory.

ORNL data show a slightly lower corrosion rate for LCNA than for Hastelloy F when using an initial sulfuric acid concentration of 4.0 M or greater as the decladding solution. Neither material showed localized attack but both were higher (a factor of 2 to 4) than desired; however, the rates can be considered permissible. Dissolved stainless steel (about 35 g/liter) decreased the corrosion rate of LCNA by a factor of about 4 in 4 to 6 M H_2SO_4 and a factor of about 10 when chloride was present. If a Niflex head-end is used in the same dissolver, Hastelloy F is preferred but the maximum sulfuric acid concentration for Sulfex decladding should be limited to about 3.5 M.

Two Haynes experimental alloys have also been tested. The results are reported in the June CTD Chemical Development B monthly progress report. Neither material currently appears significantly better than LCNA or Hastelloy F.

Zirflex. The standard Zirflex decladding solution (6.0 M NH_4F-1.0 M NH_4NO_3) and a modified Zirflex solution (4.0 to 6.0 M NH_4F-0.5 to 1.0 M NH_4NO_3-0.01 to 0.03 M H_2O_2) has been evaluated. The same five materials tested with the low-temperature Sulfex decladding solutions were tested similarly with Zirflex decladding solutions. All materials except Titanium-45A were satisfactory.

Both single-pass and cyclic tests were made on Hastelloy F and on LCNA with no clearly significant differences in the corrosion rates. Neither is considered entirely satisfactory for the standard Zirflex decladding solution, but both have permissible rates with the Modified Zirflex solution. In this case Hastelloy F appears to have a slightly lower corrosion rate.

Purex IWW. The corrosion rates are excessive for both Hastelloy-F and LCNA in Purex IWW type solution evaporators.

2.7 Airlifts (via transmittal letter 65)

The three best documents on airlift design and performance are:

ORNL-2175, "Use of an Air Lift as a Metering Pump for Radioactive Solutions," which was taken by E. L. Nicholson.

IDO-14398, "Factors Affecting Capacity of Air Lifts," which was sent via transmittal letter 21.

Y-1304, "Air Lift Pumps - Characteristics and Application to Liquid-Liquid Extraction Systems," which was sent via transmittal letter 63.

Y-1304 contains design and performance information for sizes starting at 1/8 in. Since this document was not sent until October 28, 1960, and was sent via Seivering's office, it is possible that Eurochemic had not received it at the time of your letter. Some information on HAPO Semi-works experience with airlifts was included in HW-61848, "Eurochemic Questions--Preliminary Report," which was sent via DIA.

Some information from the Thorex pilot plant operation, taken by E. L. Nicholson, was used by Mr. Nicholson to prepare an evaluation of airlifts for metering and pumping low-flow-rate streams. This information was not formally given to Eurochemic, and for your information, is as follows: Return of the 2AD stream to the 1A-column requires a pumping rate of about 20 liters/hr. Thorex data indicate satisfactory performance of a 1/2-in.-dia pipe (15.8 mm i.d.) airlift with about 38% submergence for pumping 18 liters/hr of water or high density (1.65) thorium nitrate-aluminum nitrate solutions (2AF). This airlift was routinely operated at approximately 1/15 maximum capacity. A similar flow rate was obtained with the Thorex IAF stream airlift at 64% submergence; this airlift was operated at about 1/30 maximum capacity. The above information indicates a larger operating flow range than was previously anticipated. Assuming a flow range (minimum to maximum) of 20 for small airlifts the following rates for water may be expected.

3/8 in. (nominal) pipe, 65% submergence	max.	4.9 liters/min
	min.	0.25 liters/min (est.)

1/4 in. (nominal) pipe, 65% submergence	max.	1.59 liters/min (est.)
	min.	0.08 liters/min (est.)

We would expect the effect of dirt to be insignificant on airlift capacity, reproducibility, or reliability. No attention has been given at ORNL or the Y-12 Plant to pipe roughness, but the only effects expected would be a slight increase in pressure drop. Nozzle design does not appear too important on small airlifts. Of greater importance is the need for providing an air dampener to prevent large instantaneous oscillations in flow rate. Two dampeners are used at ORNL, one an orifice at the air inlet point to the airlift and the second a long run (several feet) of capillary tubing; our preference is the capillary tubing.

2.8 Head-end Development (via transmittal letter 66)

In response to your request for dissolving information (your letter 28), members of the ORNL Chemical Technology Division have reviewed ETR-72, "Proposal for Semi-Continuous and Continuous Dissolution in a Multipurpose Dissolver." The following comments, while not extensive, may assist Eurochemic. The comments refer to sections of the original report as indicated and are all based on ORNL experience and data.

One general impression from ETR-72 is that a semi-continuous dissolver allows a lower dissolvent acid concentration for a constant metal ion loading in the product. Dissolution data do not substantiate this; i.e., for a given loading a higher dissolvent acid concentration is required in a semi-continuous dissolver owing to the reduced dissolution rate from the metal concentration.

ETR-72

Section 5.4 (page 11)

The data given appear to be for batch dissolution conditions. The 12 mils/hr average attack rate seems high. The stainless steel concentration in the declad solution from a semi-continuous dissolver is expected to be about 30 g/liter as opposed to the 92 g/liter shown; consequently, a dilution step should not be required since a 30 g/liter stainless steel solution is expected to be stable. Based on laboratory-scale data, losses to the clad solution are independent of burnup up to

10,000 to 12,000 Mwd/t. Previously reported apparent losses were based on a high gamma activity; the high gamma activity resulted from cobalt activation in the stainless steel rather than from uranium dissolutions. This indicates that the clad solution will require "hot" storage or that low-cobalt stainless steel must be used in fuel fabrication.

Section 5.5 (page 11)

The zircaloy clad solution concentration indicated [0.45 M NH_4F, 0.48 M NH_4NO_3, 0.9 M $(NH_4)_2ZrF_6$] is unstable at room temperature.

Section 5.6

This section is somewhat confusing to us. The initial comment, above, appears to apply.

Section 5.7

The unit quoted for the average dissolution rate, g/min/g U, assumes a specific area/mass ratio. A value for such a unit will be conservative for whole pellets. The dissolution rate value will be much greater for fragmented pellets, which is to be expected.

Section 7.0

The 3-mm-dia holes in the removable crash plate (first paragraph) may result in frequent plugging. It is not clear which dissolution step, clad or core, is referred in the last paragraph of this section. Oxygen addition should not be used during the Sulfex decladding step owing to the quantity of hydrogen evolved. We assume the oxygen addition is proposed during core dissolution for increased acid utilization. We have found that hydrogen monitoring during stainless steel dissolution provides a good control indicator and permits accurate calculations of the percentage dissolved.

2.9 Storage Canals (via transmittal letter 73)

In answer to your question on contamination of crane hooks (your letter 32), the following information summarizes our experience. Contamination of the hook, hook housing, and cable will occur to the extent that gloves are required for handling. The highest radiation observed is less than 5 mr/hr, most of which probably comes from the grease on the hook bearing and the cable. Actually, this radiation

level is insignificant compared to the radiation from the sides of the canal. Stainless steel hooks have not been used and would not, in themselves, eliminate the contamination problem. Simple water flushing as the crane hook is raised has proven satisfactory. Also, the equipment being handled by the crane will be contaminated similarly, necessitating certain minimum precautions to maintain contamination control.

2.10 Fuel Shipment (via transmittal letter 70)

ETR-94 has been reviewed at ORNL. These comments are referenced to the various sections of ETR-94.

ETR-94

Section 3.1

IAEA 15.3.2.2.b. The use of a solid primary coolant may be worth considering. Loss of such a coolant may be less likely in case of an accident.

IAEA 15.3.3. A 10% safety factor may not be sufficient where geometry is used as the controlling factor. Further information will be included in the revised issue of TID-7016, and copies of this will be sent.

Section 3.2

IAEA 16.2.4. The heat generated within the container should not affect the container's efficiency in case of an accident as well as under normal conditions.

IAEA 16.2.4.4.b. The statements on excessive pressure and significant radioactivity should be clarified by specifying numerical values.

IAEA 16.2.5. This section is apparently based on earlier USAEC regulations. Recent information suggests that fuel element cladding may fail at temperatures lower than its melting point owing to other types of damage. Therefore, the 100°C below melting points limit on temperature is being revised. This has been discussed more in ORNL-CF-60-12-15 (see comment for section 7.4).

Section 3.3

IAEA 16.2.1. The cask should also be approved by the authorities of the countries through which it passes.

Section 5.4

The internal cask temperature should be noted, prior to release of

the overpressure, when the cask is received at the "cask decontamination" installation. The use of pure water will also reduce the quantity of radiolytic gas formed.

Detection of a ruptured slug may be inconclusive by analysis of the cask water sample. Per L. J. King (ORNL-CF-60-3-49, sent by transmittal letter 53), it is possible that as little as 4% of the crud on spent fuel elements could give indications of a ruptured element.

Section 5.5

The primary cooling water activity level may be difficult to pre-establish owing to the uncertainities existing from crud activity. The ASA Committee is considering levels of 10^{-2} β-γ curies/liter and 10^{-5} α curies/liter for liquid coolants.

Section 6.6

Cask attachment requirements are such that total times of 1 to 4 hours might be expected rather than the 10 min. indicated. An exposure limit, controlled by time control and self-reading personnel dosimeters, should be considered.

Section 7.4

As indicated in ORNL-CF-60-12-15, "Eurochemic Assistance Program: ORNL Comments on USAEC Regulation 10 CFR Part 72," (being sent via DIA), acceptable proof of structural integrity is a difficult problem to resolve. Such proof is necessary, however, and should be standardized.

2.11 Waste Disposal (via transmittal letter 80)

Mr. Moeken's letter of August 21, concerning the effects of tritium on waste disposal from a reprocessing plant was reviewed with the following comment.

> "There has been no work done at Oak Ridge to confirm the presence of tritium in fission. So far, implications of tritium as a waste problem in fuel processing have not been considered at ORNL. Using the yield reported by Savannah River, we agree it could be a source of concern in the processing of high-burnup fuel. The large-volume effluents from such processing are normally treated and discharged to the environment."

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