MASTER

WORKSHOP ON INSTRUMENTATION AND ANALYSES
for a
NUCLEAR FUEL REPROCESSING HOT PILOT PLANT

May 5-7, 1980

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WORKSHOP ON INSTRUMENTATION AND ANALYSES FOR A NUCLEAR FUEL REPROCESSING HOT PILOT PLANT

I. INTRODUCTION

In order to assist in the study of instrumentation and analytical needs for reprocessing plants, a workshop addressing these needs was held at Oak Ridge National Laboratory on May 5-7, 1980. The idea of the workshop arose from discussions held within the Subcommittee for Nuclear and Radiochemistry of the Committee on Chemical Sciences of the National Research Council. The purpose of the workshop was to incorporate the knowledge of chemistry and of advanced measurement techniques held by the nuclear and radiochemical community into ideas for improved and new plant designs for both process control and inventory and safeguards measurements. The workshop was attended by experts in nuclear and radiochemistry, in fuel recycle plant design, and in instrumentation and analysis. A list of workshop participants is included in Appendix A.

ORNL was a particularly appropriate place to hold the workshop since the Consolidated Fuel Reprocessing Program (CFRP), a national R&D program aimed at developing and demonstrating processes, equipment, and systems for reprocessing spent nuclear reactor fuels is centered there. This program includes research and development associated with mechanical and chemical processes required in fuel reprocessing, instrumentation and control systems required for the processes, and potential impacts on the environment of the processes. In addition, requirements for safeguarding the special nuclear materials involved in reprocessing, and for their timely measurement within the process, within the reprocessing facility, and at the facility boundaries are being studied. Because these requirements are becoming more numerous and stringent, attention is also being paid to the analytical requirements for these special nuclear materials and to methods for measuring the physical parameters (e.g., liquid flow rates, densities, and interface levels) of the systems containing them.

In order to provide a focus for the consideration of the workshop participants, the Hot Experimental Facility (HEF) being designed conceptually by the CFRP was used as a basis for consideration and discussions. The HEF has been designed as a versatile hot pilot plant which is expected to be built sometime in the last decade of this century. It is to provide a versatile facility for testing and evaluating reprocessing techniques for various kinds of nuclear reactor fuel, but with emphasis on liquid metal fast breeder reactor (LMFBR) fuel. A number of its fundamental design features have been determined.

There was no intent or expectation that the workshop would provide an in-depth exploration of the analytical or instrumentation needs of a facility as complex as a fuel reprocessing plant. This is clearly impossible in a 2 or 3 day meeting. Rather, the hope was that a wide range of experience and talents could be brought into a focussed effort for a few days of study and discussion of a very complex problem. People whose research and development interests normally keep them apart, and yet who have something to offer each other, become acquainted and aware of each other's accomplishments and problems. Several insights to solutions to the problems being addressed came out of the workshop. Major benefits of the workshop probably lie in the future, when the participants, because of familiarity with the problems and their acquaintance with one another, devise useful improvements to existing solutions and new solutions to the problems.

The workshop was cosponsored by the Subcommittee on Nuclear and Radiochemistry and by Oak Ridge National Laboratory. Oak Ridge National Laboratory was responsible for administration of the workshop and for the publication of this report.

II. GENERAL CONCLUSION

An important conclusion of the workshop is that the substantial attention being paid to the development and testing of instrumental and analytical methods for accountability, process control, and safeguards in the proposed HEF is worthwhile and should be continued. While features for experimenting with and testing a variety of measurement techniques may not be incorporated into a large-scale commercial plant design, such features are desirable in a developmental facility such as HEF. Many of the instruments and techniques described in this report have been developed for specific applications. For application to the HEF, and to subsequent plants, even well developed techniques will require extensive modifications to tailor the techniques to a specific application. For example, a K-edge densitometer has been designed for on-line plutonium assay at Savannah River. Because radiation levels and uranium and plutonium concentrations are different in the HEF from those at Savannah River, and because process equipment configuration is different, additional research and instrument development is required to adapt the methods to use in the HEF.

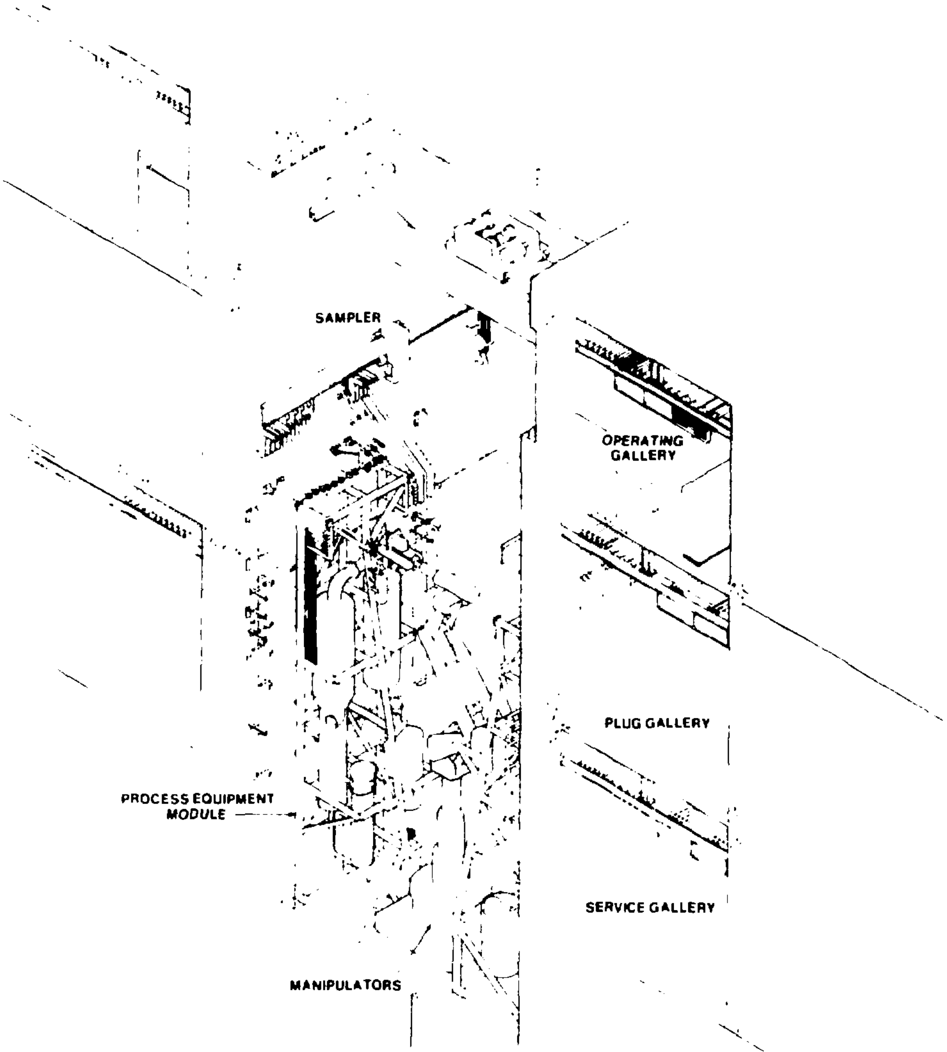
Considerable attention has been paid in the HEF design to incorporation of flexibility to permit a variety of fuel reprocessing techniques to be investigated for a wide variety of nuclear reactor fuel types. Included as an important goal is demonstration of totally remote operation of the HEF using highly advanced remote operating and maintenance equipment and techniques which virtually eliminate the need for human entry or direct interaction with in-cell equipment, and thus, also, with special nuclear materials. A basic design feature proposed for safeguards purposes is minimization or elimination of penetrations of shielding walls between areas accessible to people and areas which contain reprocessing equipment, especially equipment containing relatively pure plutonium. Restricting access to plutonium is one of the reasons for developing and demonstrating the totally remote operating and maintenance features mentioned above.

Access to process streams is important in the development of measurement and analytical technology, and the design should provide access points for instrumentation and control development that do not compromise the development of a safeguarded facility concept.

The organizers of the workshop recognize that the introduction of a totally remote concept for a fuel reprocessing plant poses new problems in instrument and control development. While this workshop did not produce solutions to the problems of truly remote measurements, it did provide a start in that direction.

A basic design feature of HEF is the location of equipment in replaceable modules in large "canyon"-type hot cells. The equipment is to be serviceable by advanced-design manipulators which travel back and forth in central aisles in the canyons. Extensive use is to be made of TV cameras to permit operator viewing of cell interiors. Such direct operator manipulations as are performed are to be made with force reflecting manipulators to provide bilateral direct operator involvement in operations.

An isometric view of a cross section through one of the HEF process cells is shown in Figure 1. It is expected that future plants for commercial power reactor fuel reprocessing would be similar. Of particular significance is the presence of the operating



PROCESS CELL ISOMETRIC

Fig. 1

gallery, plug gallery, and service gallery. One or more of these galleries might be appropriate as locations for developmental instruments for inventory, safeguards, and process control. These galleries have restricted access, and yet are areas of low radiation levels. Thus, people could carry out experiments on the developmental equipment for making the various required measurements.

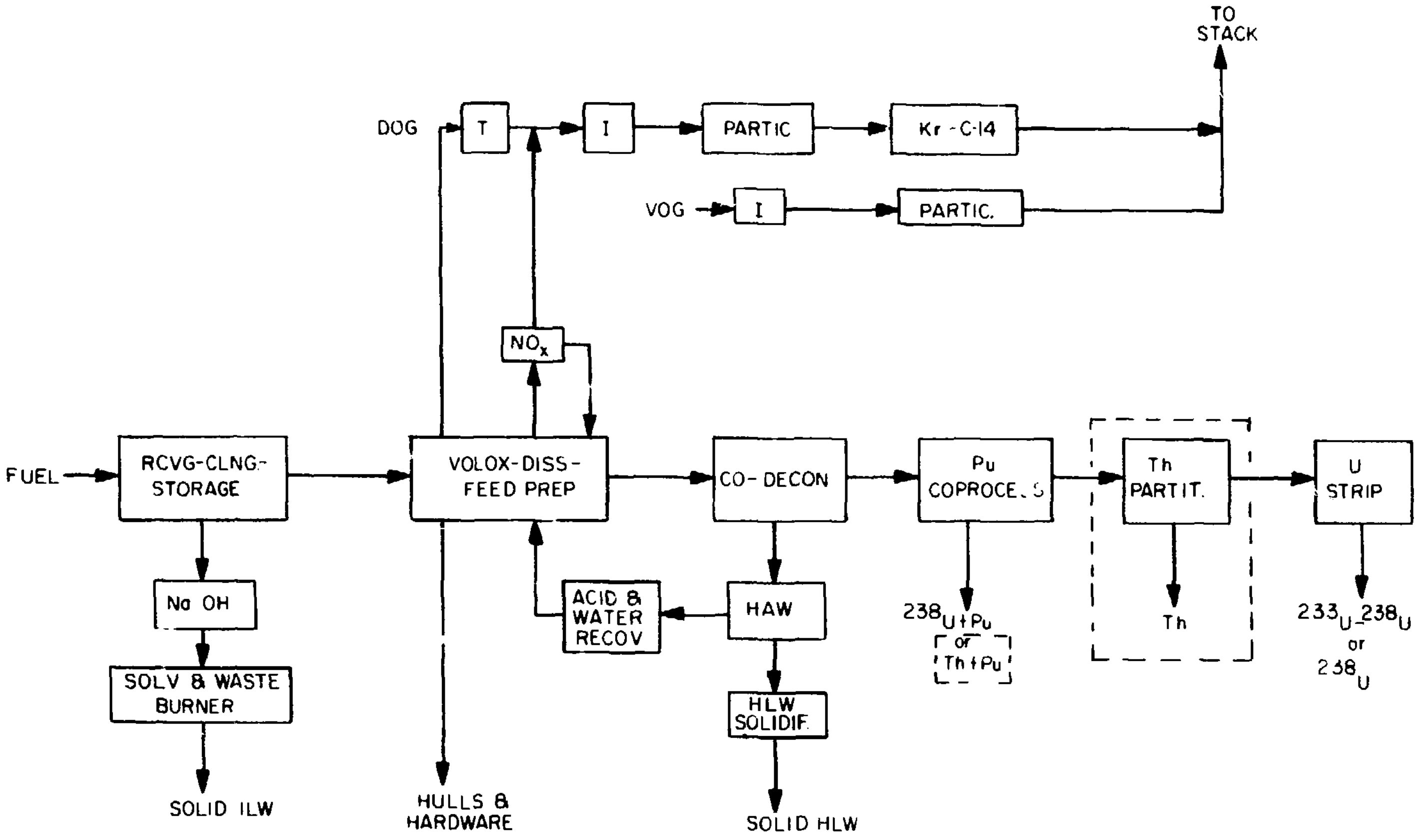
III. PROCESS DESCRIPTION

Fuel reprocessing in present plants (and in any future plants) is carried out using the steps outlined in Figure 2. Reprocessing entails fuel receiving and storage, fuel disassembling and/or shearing, voloxidizing (a process step which may be used for removing tritium), fuel dissolving, solvent extracting to separate uranium and plutonium from fission products, and converting the separated fissile material to a usable product.

A process option is purification of separated uranium and plutonium streams. Ancillary operations include concentrating and solidifying high-level liquid waste, concentrating and packaging low-level liquid and solid radioactive wastes, and converting the uranium-plutonium nitrate solutions to oxide for use in fuel fabrication. In addition, cleanup and disposal methods are employed for handling the radioactive off-gases from the processing steps. Each process step requires measurements, either on-stream or on samples removed from the process.

IV. GENERAL ANALYTICAL REQUIREMENTS

Analytical requirements for HEF as well as for future plants include chemical, nuclear, and physical property measurements. The functional needs are for process control, inventory, and safeguards. The measurement requirements vary widely throughout the process, from measurements of the fissile material content of the spent fuel assemblies which enter the plant to measurements of these materials in the product and waste streams which leave the plant. These measurements include determination of the compositions of flowing streams within the plant as well as of solutions stored at various process points. Uranium and plutonium must be measured at both high and low concentrations, and in both aqueous and organic media in the presence of varying degrees of fission product contamination.



HEF
MAJOR PROCESS SYSTEMS

Fig. 2

The HEF (and any subsequent commercial-scale plant) should meet both domestic and international safeguards criteria. Current US safeguards requirements are specified in 10CFR70 of the Code of Federal Regulations; International Atomic Energy Agency (IAEA) requirements for nations which have signed the non-proliferation treaty are defined in INFCIRC 153. However, both the US and the IAEA safeguards criteria are under review, with improvements in sensitivity for detecting diversion of fissile material in a timely manner as a major objective. The potential for more stringent safeguards and environmental pollution control criteria imposes measurement requirements not addressed for previous facilities. Safeguards criteria will require more frequent and more accurate measurements of volumes and concentrations in batches and in flowing streams than are currently obtained. International safeguards measurements must be independently verifiable by IAEA inspectors. Thus, instruments must be accessible for calibration in order to minimize systematic errors and to permit IAEA verification of their integrity and accuracy. It is hoped that development and testing of new instruments and techniques in HEF will provide a measure of just how good and accurate accountability can be made. More stringent requirements on environmental pollution will require lower detection limits for fissile material and contaminants of both gaseous and aqueous effluents.

At present, plants in the US and Europe are operating satisfactorily with limited on-line analytical instrumentation for process control. The bulk of the necessary analytical information comes from laboratory analyses of samples taken during processing. However, this system does not provide current information on inventories or on the movement of fissile materials. For normal operation, measurements of liquid levels and densities, flow rates, flow ratios, conductivities, neutron fluxes (and a few other parameters) give adequate process control information. Information on process performance requires additional measurements such as of losses to waste streams, of fission products in the product streams, and of the concentrations of plutonium and uranium in the product streams. Plutonium at low concentrations can be measured by in-line alpha counters in streams where extensive knowledge of the plutonium isotopic distribution is required.

Improper operation of the process would be characterized by gross fission product contamination in the uranium-plutonium product stream, or in solvent wash solutions; by not obtaining the desired separation of uranium and plutonium; or by the presence of mixed phases or emulsions in the normally-separate aqueous and organic streams. Other process problems are characterized by loss of uranium and plutonium to waste streams.

Valence control of the plutonium is of major importance because it is the major mechanism for uranium-plutonium separation. Process control would be improved if the necessary concentrations of the chemicals used for plutonium valence adjustments could be shown by direct measurement to be present.

The extractant quality (as indicated by the efficacy of the tributyl phosphate-diluent extraction) could be better defined and controlled if there were ready means for measuring dibutyl and monobutyl phosphate concentrations, and for checking emulsifying tendencies of the solvent.

The presence of neutron poisons in solutions where they are necessary to maintain nuclear safety has been monitored by neutron absorption measurements. This technique can be considered demonstrated, though further work could improve sensitivity and accuracy.

V. GENERAL CONSIDERATIONS FOR MEASUREMENTS IN THE PLANT

Several of the workshop participants identified and defined four different types of process stream measurements,based on where the measurements could be made. Although these are somewhat arbitrary, they have been adopted here as a matter of convenience. They are (1) in-line, measurements made within the process on the flowing process streams; (2) on-line, measurements on a fraction of the total stream, as for example on a by-pass stream; (3) at-line, measurements on samples physically taken from the stream and immediately analyzed at the site; and (4) off-line, measurements on samples removed and sent to a laboratory for analysis.

The HEF reference design specifies little or no penetration of the cell walls for process control or inventory. It appeared to the workshop participants that non-penetration of the hot cell shielding wall is not completely attainable in a practical sense. Two alternative approaches were suggested for consideration:

(1) Appropriate process stream lines could be brought to the plug (or other) gallery for at-line analysis or for laboratory analysis. This could allow a flexible approach to measurement problems, and permit new ideas to be tested. Controlled access to special nuclear materials could still be maintained with this alternative.

(2) On-line samples from appropriate streams (or tanks) could be brought to the cell shielding wall where they could be analyzed by remote instrumentation located outside or in the wall, making use of small-diameter, covered penetrations through the wall for transmission of interrogating signals to the streams and return of response signals to the sensors.

These modifications would permit making the necessary chemical and physical measurements with techniques that are presently developed or under development.

Material Composition Measurements

The conceptual design for the HEF calls for large "canyon"-type hot cells, with modular equipment arranged inside the cell so that it can be serviced by remote manipulation. The cells will be highly radioactive (with some areas having a radiation level of $\sim 10^5$ R/hr). Equipment to be used for the various required analyses must, therefore, be able to survive and operate properly under these conditions. Maintenance requirements should be minimized for instrumentation which is located in-cell.

It would be highly desirable from an instrumentation standpoint to locate many of the detectors outside the cell. This could be accomplished without having actual penetrations through the cell walls by having collimation "holes" through the walls. These could be sealed by stainless steel plates or caps or thick glass. Samples of the process streams could then be routed to the inside wall, adjacent to the penetration, and the detectors could be placed appropriately outside. This technique is especially applicable to gamma-ray detectors.

For dynamic analyses of the contents of tanks it was recommended that the measurement point be installed in the line from which solutions are withdrawn for subsequent laboratory analysis for inventory. Independent, off-line analyses were recommended to calibrate in-line instruments. For γ spectroscopy, an in-cell calibration source could be an advantage. For important accountability measurements, two or more reliable, independent measurement techniques are desirable.

Physical Measurements

Measurements of flow rates, liquid levels, and liquid densities will be important both for process control and for materials accountability systems. The majority of the tanks and liquid-liquid contactors will employ level detection as a part of the control instrumentation.

Accurate measurements of level and flow combined with accurate density measurements are essential to nuclear material accountability systems. Several constraints operate to make the choice of instruments and sensors for these measurements important. The constraints are: equipment must be relatively immune to radiation damage; environmental and safeguards considerations require few or no penetrations through the biological shield into the hot-cell area; equipment must be compatible with corrosive process fluids and be able to withstand decontamination procedures; equipment must be remotely maintainable or replaceable through the use of devices such as manipulators and remotely operated wrenches; and finally, the equipment should be minimally influenced by extremes in environmental effects (temperature, pressure, humidity, etc.)

Liquid flow measurement involving head-type meters are not suitable for low-flow, gravity-feed systems because of inadequate sensitivity and because of the possible necessity for wall penetrations for the sensing lines. Flowmeters with moving parts are generally unsuitable from a maintenance standpoint, and because of the possibility of plugging. Certain types of ultrasonic meters can be adversely affected by bubbles in the flowing stream. Types which may be developed include nuclear-magnetic-resonance and angular-momentum flowmeters.

Liquid level measuring devices which are commercially available include air- and liquid-measuring ultrasonic and capacitance devices. An ultrasonic level probe which can also detect the aqueous-organic interface and measure the organic layer thickness has been developed at Harwell, England, for use in British reprocessing plants.

Suitable liquid density meters currently available include the vibrating tube and the vibrating vane types. A waveguide-type ultrasonic level and density probe is under development. The microwave resonance cavity device perhaps could also be developed for level measurements.

VI. SUGGESTED MEASUREMENT TECHNIQUES AND INSTRUMENTS

In order to facilitate the activities of the workshop participants, their considerations were divided into three general areas: (1) applications of existing technology, (2) extrapolations of existing technology, and (3) new concepts.

(1) Applications of Existing Technology

Instrumentation is required to produce a near-real-time* mass balance across the process system(s) because of the long delay expected between sample withdrawal for off-stream analysis and availability of the subsequent analytical results. Near-real-time data availability is needed for process control and product quality assurance, for accountability and safeguards, and for safety. On-line determinations of plutonium and uranium with the degree of accuracy required for safeguards and accountability is probably beyond current available technology. Off-line laboratory analyses are still required.

Some of the instrumentation required for on-stream special nuclear materials (SNM) measurements must be applicable to uranium and plutonium in mixtures containing fission products and nitric acid. The SNM isotopic ratios must be known fairly accurately; many of the techniques available or being considered measure total elemental concentration but do not provide information on isotopic concentration. Isotopic information is needed to determine fissile content for both accountability (inventory) and safeguards purposes.

A distinction may be made between (1) information necessary to monitor the normally operating process, and (2) information necessary to identify and correct causes of abnormal operation. For normal operation, liquid levels, densities, absolute flow rates, flow ratios, conductivities (for low acid), neutron monitors, and a few other

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*Within 15 seconds to 30 minutes.

measurements give adequate process control information. Information on process performance requires additional measurements of losses to waste streams, fission products in the product streams, and concentrations of plutonium and uranium in various streams. Plutonium at low levels can be measured by in-line alpha counters in streams without excessive fission product activity; however, accurate determination of total plutonium requires knowledge of the isotopic composition. Gross gamma measurements are sufficient to show that adequate decontamination is being obtained from fission products. Colorimetric and gamma absorption techniques have been used for medium to high concentrations of uranium and plutonium, and appear satisfactory for semi-remote operation. There remains a set of process control measurements, such as of plutonium losses to high-level fission product streams, plutonium accumulations in solvent wash tanks, and uranium losses to waste streams that are not monitored now, and for which instruments are not immediately available.

For both liquid and solidified product, gamma spectroscopy provides the best method for quantitative determination of uranium and plutonium. Thickness of sample and subsequent attenuation of the signal strength could be a severe problem, especially in the bulk solids measurements.

Spontaneous fission/coincidence-neutron counting can be used for material quantity verifications with bulk solids such as oxides if the isotopic composition is known (supposedly determined in prior, pre-oxide conversion equipment). Also, active neutron interrogation methods can be used to give an approximate total fissile quantity.

Existing technology for nondestructive analytical measurements of U and Pu can be applied for in-line and on-line stream accountability measurements of process solutions. K-absorption edge densitometry and x-ray fluorescence can be evaluated for application to accountability measurement problems. These techniques can be optimized for minimum sensitivity to sample background emission. X-ray generators with high currents can be used with restrictive sample collimation to reduce the "passive" count rate relative to that for the transmitted gamma rays or fluorescent x-rays.

Three techniques are recommended for accurate in-line or on-line determination of U and Pu in the product solution streams. These are (1) passive gamma-ray spectroscopy,

(2) absorption edge densitometry, and (3) x-ray fluorescence (XRF). The first of these gives some Pu isotopic compositions and can be used to provide the total Pu concentration as well. K-edge densitometry and XRF will give a simultaneous determination of total U and Pu (and/or Th). The K-edge and XRF techniques can be applied using x-ray generators or radioisotopic sources for transmission and excitation, respectively. Solid-state detectors are essential for these measurements.

For accountability measurements downstream from the first extraction, the gamma-ray techniques recommended for product solution analysis might be also applied, either in-line or on-line. The active techniques (absorption edge densitometry or XRF) are well-suited for those cases with appreciable fission product contamination (>0.1 mCi/g Pu). Furthermore, K-edge measurements can be used for improved precision at the lower concentrations. Coincidence counting of spontaneous fission neutrons can be used to monitor Pu concentrations in flowing streams where isotopic fractions are relatively constant.

Neutron interrogation with delayed neutron counting is sensitive to the fissile Pu isotopes in low-level wastes. Uranium-235 can be determined by XRF (if the uranium enrichment is known). The latter technique can also be used for uranium in waste stream measurements or to determine the ratio of U to Pu in waste streams. (Active neutron interrogation must be explored to determine if this technique can be implemented with sufficient sensitivity for measurement of Pu concentration in the high-level waste streams. This measurement must be performed in the presence of high-spontaneous fission neutron backgrounds due to Cm in this stream.)

A combination of three nondestructive analysis techniques can be used to determine quantitatively the total Pu and U content of a batch of mixed oxides (MOX). The three are calorimetry, passive gamma-ray spectrometry, and XRF. XRF can be used to quickly determine the U/Pu ratio. Gamma-ray spectrometry provides some isotopic abundance ratios of U and Pu. The total power output of the sample can be measured by calorimetry. This, together with the other two measurements, can give an accurate assay of the total U and Pu.

Analysis of U and/or Pu in a flowing stream could be accomplished by several techniques. (In fact, redundant measurements on the same stream by different instrumental techniques are desirable.) The most promising appear to be spectrometry and measurement by either line absorption or by molecular excitation.

Gamma spectrometry is currently being used for uranium measurements. The uncertainty in any determination is expected to be $\leq 1\%$. It is limited by the time required for accumulating the total count and by fission product levels. The detector could be placed in-cell, but shielding around the detector would be required. (NaI/Tl should not be used for gamma spectroscopy; Ge detectors are acceptable. The reliability and availability of commercial γ-detectors have improved recently.) Associated supporting electronic equipment could be operated and maintained outside the cell. An in-cell check source could be used for calibration.

The potential use of fiber optics could be an advantage in the spectrophotometric and molecular excitation methods,but the possibility of leakage at the optics/sample interface must be addressed.

Although accountability tanks may have associated high radiation levels, a small shielded recirculation loop could be made available with a shielded detector designed for measuring the flowing stream. Careful resolution of the measured gamma spectrum is important for isotopic concentration determination. Interference from fission products is expected to be substantial. Better measurement of plutonium and uranium (elemental only) could be obtained by x-ray absorption or molecular excitation.

For high-level aqueous waste (HAW), there is no adequate technique for accurate determination of the fissile element content. For other liquid wastes it appears that the presence of fissile material could be determined qualitatively with currently available α-scintillation, cerium-glass, and photomultiplier detectors. These determinations provide a "gross-alpha" measurement, and when coupled with γ-spectroscopy, and/or neutron counting, could furnish quantitative measurements.

Abnormal operation would be characterized by gross fission product contamination of waste streams, plutonium or uranium in solvent wash solutions, plutonium in the uranium product, mixed phases or emulsions in the normal separated aqueous and organic streams, etc. The causes usually are related to chemical problems in the systems or to excessive degradation of the organic solvent. The chemical analyses for acid, reducing agents, and oxidizing agents could help resolve these problems. However, the systems would be required to handle a few more samples than needed for normal process control. The problem of solvent quality simply has not been addressed from the point of view of remote analyses. The pertinent measurements include dibutyl phosphate and monobutyl phosphate concentrations, emulsifying tendency, and fission product extraction characteristics. Adaptations of laboratory techniques might be possible, but off-line analyses in a hot analytical cell appear more feasible.

(2) Extrapolations of Existing Technology

The general feeling of the workshop group is that concepts for physical measurements are pretty well in hand, although some work is still probably needed. Accuracy does not appear to be a problem for process control application. The problem of obtaining the accuracy required for safeguards and accountability is more acute, but not insurmountable. It is quite clear that physical measurements suitable for safeguards and accountability will also serve for process control if response time is reasonable.

Spectrometric techniques are potentially useful for process control. Ultra-violet and visible spectrophotometry have been shown to be applicable to uranium analysis. (Infra-red spectrophotometry is useful for gas-phase analysis.) Molecular excitation followed by photon emission is being investigated and shows potential. Although there is no spectrometric technique ready for immediate application, these techniques could be made available in time for demonstration in HEF.

A flow measurement based on the ultrasonic tracking of a bubble introduced into the system is known. There also exists a low-flow-rate device based on a variable resistance/temperature sensor and a thermal generator.

Neutron interrogation of incoming spent fuel using neutrons from a suitable neutron source and methane-filled proton recoil detectors has been demonstrated in the laboratory to yield a nominal 1-5% accuracy. The analysis is comparatively rapid. If interfering quantities of spontaneous-fission-neutron emitters are present, their contributions to the counting rate will have to be corrected for. Adequate calibration standards would have to be provided. A spare interrogator may have to be provided as a backup against failure.

All alpha, beta, and gamma counting techniques are dependent on their respective detectors. Although the techniques are sound and well established, there are continuing advances in the various detector systems. Specific areas that could be greatly improved are resistance to radiation damage and better cryogenic systems (including the possibility of eliminating them altogether). Improvements in solid-state technology undoubtedly will play an important role and should be encouraged.

Most detectors that require low temperatures depend on liquid nitrogen for temperature control. However, there are some semiconductor cryogenic systems that may be applicable to current detectors. Also, new detectors (such as those using mercuric iodide and cadmium telluride) which do not require very cold temperature should be evaluated. Mercuric iodide detectors can be operated either at room temperature or cooled, and can be used to detect x-rays. Current available detectors have a resolution of 300 eV at 5.9 keV. The detector is very small, and its resolution decreases rapidly with increasing x-ray energy; nonetheless, it may have application for measuring or monitoring certain streams by looking at the low-energy L-series x-rays of Pu or U at ~ 15 keV, or at K-series x-rays at ~ 100 keV.

It may be possible to use Digiquartz pressure transducers for liquid level and density measurements. Such devices have good sensitivity (1 ± 0.0002) and reliability.

For off-gas monitoring, a catalytic converter can be employed to oxidize all tritium-containing compounds to HTO, and all ^{14}C compounds to $^{14}CO_2$. The tritiated water can be collected on silica gel for off-line analysis or, possibly, passed through a semi-permeable membrane and counted on-line with a gas counter. The ^{14}C can be collected on zeolite and analyzed off-line after conversion to a carbonate. Any ^{129}I can be collected on a charcoal cartridge for off-line analysis either in a counting facility or remotely using an automatic changer. Residual ^{85}Kr can be analyzed using a flow-through chamber and a beta counter. Particulates can be collected and analyzed off-line. Sensitivities for the detection of all these activities are currently adequate for monitoring needs.

(3) New Concepts

High-activity waste (HAW) will contain the bulk of the fission products and transplutonium actinides such as curium. A small fraction of the plutonium and uranium will also be present. It is desirable for accountability purposes as well as for process control to measure the fissile content of the HAW. Such a measurement would not necessarily have to be highly accurate since this stream will contain only a small amount of the total plant throughput. However, any quantitative measurement of the HAW will be extremely difficult due to the exceedingly high gamma activity of the fission products, the high neutron background due to spontaneous fission of even-numbered heavy isotopes such as ^{242}Cm and ^{244}Cm, and the relatively small concentrations of fissile nuclides relative to the high backgrounds. Techniques usually used in gamma spectroscopy measurements are not feasible. Measurements of a fission product gamma "line" or of the passive neutron background may be made, but it will be difficult, if not impossible, to relate these measurements to the amount of fissile material present. However, neutron-capture prompt γ-ray activation analysis should be applicable to the HAW as well as to the dissolver solution and to solid wastes. This non-destructive technique allows measurement of uranium and plutonium in the presence of fission products. The energy spectrum of the exciting neutron source (e.g., ^{252}Cf) could be thermalized to optimize the measurement. Fast mass spectrometric analyses could be used in conjunction with such a system for plutonium and uranium isotopic analyses. Since this technique can provide bulk measurements, it may be suited for use in determining the presence of fissionable isotopes in solid wastes. It is, however, bulky and expensive.

If in-line or on-line methods are employed for measurements on the HAW, it would be best to measure the material as it flows through a small line into a waste tank. By combining fissile concentration values with integrated liquid flow rates or with total liquid mass measured in a waste tank, the total fissile content may be calculated. A "rabbit" sampling system could be used to obtain small samples from limited-access or "hardened" areas of the plant.

Once the HAW has been solidified, it may be beyond present NDA technology to quantitatively measure the fissile material content. In addition to the background problems, neutron measurements would be hampered by the presence of neutron poisons such as boron. (It should be noted that it is also desirable to measure the amounts of the neutron poisons themselves.) A careful study should be made to determine accountability needs as they relate to the HAW and to the feasibility of measuring fissile material content nondestructively.

In order to perform continuous material balances, it will be necessary to perform inventory measurements on a real-time basis on all components within the plant as well as on the input and output streams to these components. Such measurements are feasible for components such as tanks where a single sample may be representative of the material in the tank. Analyses of samples, when combined with a measurement of the volume in these components, give the total inventory. It may be possible to employ non-destructive assay for these measurements.

Inductively-coupled plasma atomic emission spectrometry has been used to measure trace amounts of elements in a variety of matrices. The material to be analyzed is injected into a plasma arc where the sample is volatilized and optically excited. The subsequent photon emissions can be recorded using standard spectrophotometric methods. The method has considerable appeal for measuring plutonium, uranium, and other elements in the dissolver solution. To obtain quantitative results, it would probably be necessary to add appropriate spikes and to dilute the initial sample before it is injected into the arc. The advantages of the technique are: it is a non-nuclear technique and therefore is not sensitive to the intense radioactivity of the sample; it performs a complete analysis in seconds; it is a multi-element analysis; and it is very sensitive, requiring only a small sample. Some consideration should be given to the possibility of using tunable dye lasers to optically excite the specific isotopes of an element (e.g., plutonium), thereby permitting determination of isotopic as well as elemental abundances. Some disadvantages are: the method is destructive; full automation may be difficult; it will be quite expensive and sophisticated; it may never be more accurate than 1 - 2%; and considerable research and development will be required to demonstrate its utility. The resulting spectrum is also very complex, and interferences may be a problem.

Mass spectrometric measurements may also be used to measure isotopic abundances and provide quantitative analyses using the technique of isotopic dilution. Although this entails removing and analyzing a sample, the sample may be small (e.g., a single loaded bead of ion exchange resin), and the time required is short (5-6 minutes). Under certain conditions, accuracies of ± 1% may be achieved.

It should be noted in passing that the vast quantity of data from analytical equipment in HEF and in large-scale plants will be far too much for manual handling. Computer analysis and evaluation will be necessary. A team including computer programmers, mathematicians, chemists, and engineers will be necessary to develop adequate computer software for the necessary data management.

VII. THINGS TO KEEP IN MIND

Use of laser beams should have considerable advantage over conventional light sources for use in spectrophotometric measurements because they can be made much more intense, the wavelength may be selected, they are monochromatic, and they can be optically reflected and directed to the measurement point. The use of this light source should be considered when absorption and spectrophotometric techniques are planned or can be used.

It is well known that there are certain correlations that exist between fission product yields and plutonium isotope abundances. Of particular interest would be the possibility of correlating Xe and Kr isotopic abundances with plutonium isotopic abundances, since the isotopes of Xe and Kr can be measured easily by on-line gas mass spectrometry.

APPENDIX A.

WORKSHOP PARTICIPANTS

NAME	ORGANIZATION
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