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CHEMISTRY TECHNOLOGY DEPARTMENT

RECOMMENDATIONS FOR DESIGN OF RADIOACTIVE SOLVENT EXTRACTION UNITS

D. G. REID

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CHEMICAL TECHNOLOGY DEPARTMENT

RECOMMENDATIONS FOR DESIGN OF RADIOACTIVE SOLVENT EXTRACTION UNITS

D. G. Reid

DATE ISSUED

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1.0 Abstract

Suggestions are presented for design of simplified radioactive solvent extraction units based on Oak Ridge National Laboratory Hot Pilot Plant processing experience.

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2.0 Summary

Experience obtained in the ORNL Pilot Plant development work on solvent extraction processes at all available levels of radioactivity has shown this type of processing to be operationally simple. Standard industrial techniques can be used and many of the expensive features previously considered essential may be eliminated. The processing steps can be sufficiently well developed on a small scale to permit operation by non-technical personnel with only a minimum of technical supervision.

Operational experience shows that a simple, one operating level building, housing all working areas essential to the process operation is possible and is definitely preferred from an operating standpoint. The use of a building of this type is possible by providing an adequate working area on all sides of the cell block. This simplified structure is possible by reducing the quantity of process equipment, remote maintenance facilities, and eliminating the active pipe trench, and making minor modifications in process operation. The use of commercially available instruments and materials of construction have been found to be adequate in most cases. The arrangement of equipment to permit gravity flow of process solutions has also been found to be extremely desirable. The unit operations performed in solvent extraction processings have shown that equipment design simplifications are possible.

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3.0 Introduction

Organic solvents ordinarily thought of as being used only for the extraction and purification of organic compounds have in recent years proven to be useful in the purification and separation of certain specific metallic inorganic salts. The unit process, solvent extraction, has received such a large amount of interest in radioactive separation development work that this type of operation has been developed to the point where the design and construction of large scale separation plants are being considered.

Solvent extraction experience at Oak Ridge National Laboratory includes five years on the laboratory and semi-works scales at moderate levels of fission product activity and two years of pilot plant investigations using the highest levels of fission product activity obtainable. The four solvent extraction processes investigated on the laboratory and semi-works scale for the past five years are: recovery of U_{235} from the Materials Testing Reactor fuel assemblies, recovery of Hanford waste uranium, U_{233}-Th separation, and Redox U-Pu separation. The pilot plant spent twelve months testing and proving the Materials Testing Reactor U_{235} recovery process using the highest specific activity of Hanford irradiated uranium obtainable, and is scheduled to process Hanford irradiated U_{235}/Al alloy for two months starting September, 1949. Eleven months of testing of the Redox process have just been completed in the Pilot Plant at 5% the mass throughput and up to 100% of the fission product activity level of the proposed Hanford production plant.

The purpose of this report is to assist in simplifying the design, construction, and operation of solvent extraction units by summarizing the operational experience in solvent extraction development work at ORNL. A discussion of the overall building and general equipment design are given in one section followed by another section discussing design of the individual pieces of processing equipment. Specific examples for these discussions have been chosen from the operating experience obtained developing the Redox uranium-plutonium and U-235 separations processes. More detailed information can be obtained from reports ORNL-109 and ORNL-463.

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4.0 Building and General Equipment Design

A general solvent extraction processing building is envisioned in elevation cross section as a t laid on its side, with the cell structure being the crossarm of the t containing all of the radioactive processing equipment with the essential service facilities and operating areas surrounding the cell structure. A number of the previously considered necessary facilities such as active material pipe trench, service pipe trench, and remote maintenance facilities can be either reduced or eliminated. One side of the cell block should contain the operating area, necessary solution makeup facilities, office and laboratories; the other side of the cell block should contain the isolated sampling area. Such a building design, shown schematically in Figs. 1 & 2, permits all normal operations to be performed on one floor level, is convenient for personnel, and simplifies design and operation.

4.1 Service Facilities

The active pipe trench, a normal adjunct to all previous high level radioactive processing buildings, can now be eliminated. The solvent extraction processes are, or can be, sufficiently developed to be extremely reliable eliminating the need for extreme flow flexibility. Also, the decontamination obtained in a single extraction step is so great that all process material transferred thereafter is at a low activity level. These attributes permit process solutions to flow directly through adjoining cell partitions with facilities for re-processing material consisting of only simple return lines.

Service mains for steam, water, electricity, and air are of a relatively small size and can be installed in a conventional industrial manner.

4.2 Remote Maintenance Facilities

Remote maintenance facilities have been found in pilot plant operation not to be justifiable, on the ORNL radiation exposure basis, except in the first cycle equipment. This includes only the dissolving, feed makeup, and first extraction column equipment. Radiation readings in the pilot plant show that 100 gallons of 2 M UNH from full Hanford level irradiated uranium after processing through one cycle of Redox extraction, read only 300 mr through a 1/16" thick stainless steel tank wall. This low level of radiation permits minor maintenance to be carried on directly in all first cycle product catch tanks and subsequent equipment with process materials still in the tanks. If maintenance is to be of long duration, the material is removed from the tanks and a simple decontamination performed.

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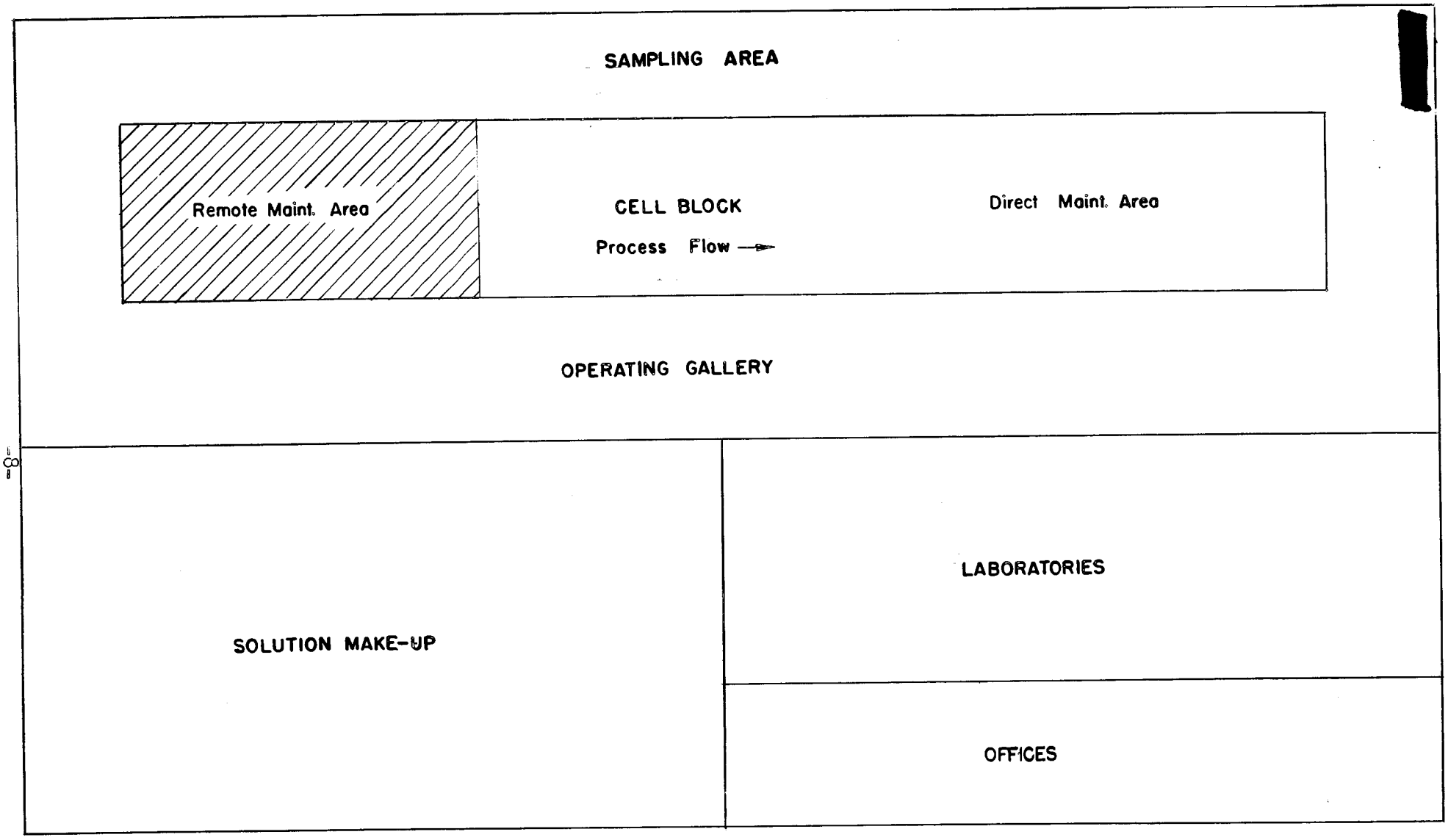
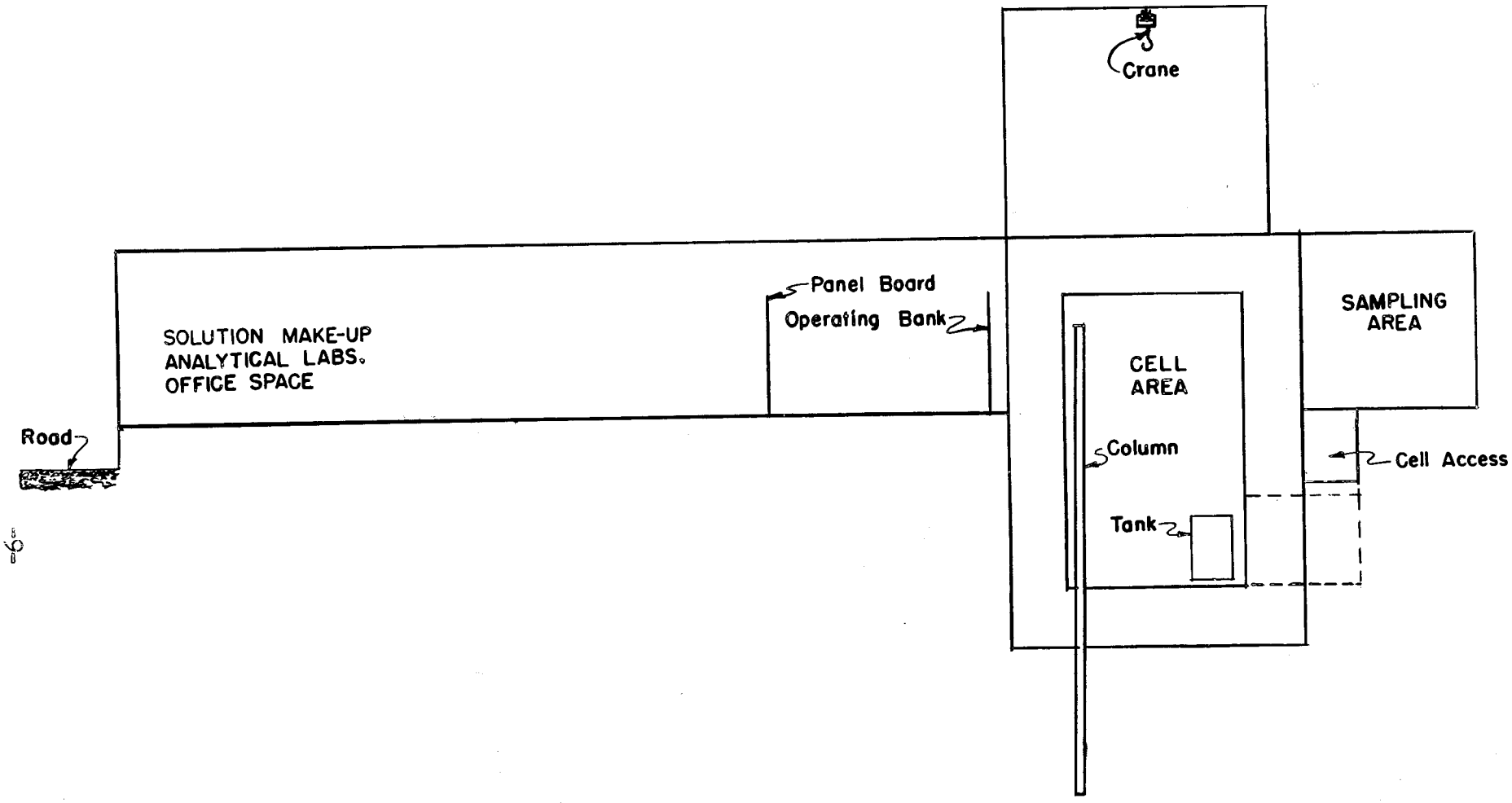


SCHEMATIC PLAN OF A TYPICAL RADIO ACTIVE SOLVENT EXTRACTION PLANT

FIGURE 1



SCHEMATIC ELEVATION OF A TYPICAL RADIO ACTIVE SOLVENT EXTRACTION PLANT

FIGURE 2

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4.3 Waste Disposal

Wastes from the pilot plant have been disposed of in the conventional manner of sending the liquid waste to a tank farm, and the gaseous activity to the atmosphere via a 200 foot stack without any facilities for particulate removal.

The method used for satisfactory disposal of the active gaseous waste has been to provide three independent ventilation systems that are kept at a pressure negative to that of the immediate surroundings. These systems include a large throughput of air for ventilating the cells housing the active equipment, a process ventilation system for ventilating all process vessels except the dissolver, and another process ventilation system for the exclusive use of the dissolving vessel. This system has been quite successful in retaining all the activity within the confines of the process vessels and ducts and has reduced airborne contamination to a low level, permitting and greatly simplifying direct maintenance.

Disposal of the airborne activity to the atmosphere by the pilot plant has resulted in no unusual difficulties at ORNL. Short lived gaseous fission product discharge is low because the material processed must usually decay to eliminate undesirable short lived heavy element isomers, such as U_{237} from U_{235} irradiation. The jetting of extremely radioactive materials is infrequent in solvent extraction processing so that the active material discharged to ventilating ducts by steam jets running "dry" has been greatly reduced. This dry running of the steam jets has been further reduced in the pilot plant by the use of ordinary manually operated valves supplying steam to the jets. This eliminates the gang valve type operation where air is blown through these jets as one of the operation sequences causing some of the residual activity to be discharged to the stack. In spite of these improvements, 20 to 50 millicuries of activity are discharged to the atmosphere during the entire processing of a 400 pound batch of 100 day old Hanford metal through two cycles of the Redox process.

The use of gravity flow for transporting radioactive liquid waste in lines from the plant to the storage area has been very successful. Experience in other parts of the plant site has shown that transporting active waste up even slight slopes or over long distances is to be avoided if at all possible because of solution run back, low transporting capacity of the lines, or making operation of the motivating steam jet unreliable or difficult.

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4.4 Materials of Construction

Materials of construction found to be applicable in the pilot plant are those easily obtained and used in ordinary industry. The recommended material of construction for pipe, tanks, etc. is stainless steel, using ordinary gasketing material, and serviced in most cases by standard industrial instrumentation.

The majority of the tanks in the ORNL pilot plant are of special 309 SCb stainless steel reclaimed from the former precipitation pilot plant. These tanks have shown excellent corrosion resistance, but those tanks which were constructed by the ORNL Maintenance Department out of the cheaper, commercial 347 stainless steel and which were not heat treated, have given service equally as good. This indicates that under ordinary operation type 309 SCb stainless steel is usually unwarranted. However, the body of the dissolver used in the pilot plant was manufactured of 309 SCb and heat treated after fabrication. It has given excellent service and since Type 347 stainless steel has not been plant tested for this service its utility is questionable.

Type 347 stainless steel pipe is used throughout the pilot plant and has given excellent corrosion resistance. Dissolver dip tubes fabricated of type 347 stainless steel seamless pipe were inspected with respect to corrosion after 3000 hours of dissolving operation and found to be only mildly attacked while those made of butt welded pipe were heavily corroded at the welds.

The gasketing material used has been teflon and polythene. Teflon gaskets are used where high temperature and pressures are encountered such as in steam lines, etc. Since Teflon has a tendancy to cold flow it has been necessary to replace some of the Teflon gaskets with the more satisfactory teflon-stainless steel type gaskets. Polythene has been found to give excellent results where no warm (above 50° C) temperatures are encountered.

The five foot thick concrete walls have proven more than adequate for shielding the dissolver when it contained 1200 pounds of Hanford irradiated uranium decayed 100 days. Radioactivity spilled and absorbed in concrete has been far harder to remove than the radioactivity in the stainless steel equipment. A number of impervious concrete coatings, which should eliminate these difficulties, are now being developed.

Radioactive processing equipment structural supports for a plant with a relatively long expected life should be fabricated of stainless steel and not of ordinary structural iron. Decontamination experiences have shown that radio activity spills are extremely difficult to remove from structural members made from iron but those made of stainless steel are relatively easy to cleanse. The stainless steel used for fabrication of these structural members can be of the relatively inexpensive types.

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4.5 Overall Instrumentation

Standard industrial and comercially available instruments have been found to be satisfactory in the pilot plant.

Placing of the process control instruments across the aisle from the operating valves makes a simple installation and is satisfactory from both an operating and maintenance standpoint. Elimination of the instruments immediately next to, or over, the operating valves is possible because of the lack of any operations requiring very close control such as centrifuge loadings.

The pilot plant was constructed using a large number of indicating instruments, such as manometers, in preference to the recording type, because of a slightly larger initial cost of the latter. Experience with the few recording instruments used has shown that recording instruments are not only preferable, but justified from an operational standpoint. If greater accuracy is needed for material balances than is possible with a standard recording instrument, an auxiliary indicating instrument such as a manometer of suitable length in parallel with the recording instruments is warranted.

Special flow recording instruments used for the 1/3 to 4 gallons per hour flows in the pilot plant have, as a general rule, been unsatisfactory. Recent and preliminary tests of newly developed flow meters indicate that a suitable instrument for use in these flow ranges may now be available. The need of flow recordings between cascading columns has proven to be unnecessary.

Radiation instruments have been found to be useful operation indicators, but they are not yet sufficiently developed to be used for process control.

5.0 Processing Equipment Design

The unit operations performed in solvent extraction processings are identical to those performed in normal industry with the mode of operation slightly altered. All of the unit operations in this type processing have been mechanically satisfactory but a number of design simplifications are possible.

5.1 Dissolution

The current method of converting the uranium metal slugs to a solution has been found to be mechanically and chemically satisfactory.

The charging of the slugs by crane methods for large scale processing, or the dropping of individual slugs for small scale operation are well suited to the respective scale of operation but a large number of minor mechanical improvements are possible depending on the specific application. Aluminum jackets, which encase the uranium to prevent activity from entering the cooling medium during irradiation, are removed by the extremely satisfactory standard $NaOH - NaNO_3$ method.

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Dissolution (Continued)

The dissolution of the uranium metal by nitric acid has been found to be extremely satisfactory. The ORNL Pilot Plant dissolver capacity is less than desired so that a more involved operating procedure than normal is necessary for uranium dissolution but completion of the reaction is determined to conform to rather narrow limits of free acidity by a recording specific gravity instrument.

Adjustment of the acid concentration of any of the radioactive process streams to rather narrow limits is easily made by direct addition of acid or base. This has been found to be more satisfactory than high temperature vaporization or the use of second degree chemical reactions. It is done in a moderately, but not violently, agitated auxiliary feed preparation vessel.

5.2 Feed Filtration

Clarification of the ORNL Pilot Plant active column feed solution is accomplished with moderate operational success by drawing the active feed through a sintered stainless steel plate. This mode of solution clarification, while satisfactory for small scale operation of the order of 100 gallons, is questionable for adaptability to 1000 gallon batches because of the low filtering capacity of the units, and the inherent complexity if used on a large scale. Tests at Hanford Engineering Works indicate centrifugation to be very promising. The entire question as to the degree of clarity of the column feed solution necessary for satisfactory operation is definitely open to question in as much as solutions of Hanford irradiated aluminum-silicon bonded uranium have been processed through cracked sintered stainless steel elements with no deliterious effects on column operation even over an extended period of time.

5.3 Column Operation

Extremely satisfactory remote operation of solvent extraction columns processing radioactive material has been proven. There has been no evidence of column fouling, the displacement method of pumping active feed is suitable for small installations although gravity may be preferred, cascading of columns is definitely desirable, and remote maintenance procedures are not justified except in the first column.

Simple construction techniques have shown that excessively high shielded areas for column work are unnecessary and ordinary construction techniques can be used for column construction. The first column can be made to twice the height of the cell, even if two or three columns are cascaded in series if the columns are put into sumps in the floor of the cell. Three columns have been operated in cascade in the pilot plant without difficulty except when the flow rates were increased to 200% of design capacity causing the hydraulic pressure drop through the equipment to exceed the elevational differences between the Pilot Plant columns. Access to the base of the columns, which is difficult if in a sump, has been found to be unnecessary. The chemical

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Column Operation (Continued)

reactions in columns are usually of a type wherein corrosion is not serious and all welded columns can be constructed of such a quality as to preclude the possibility of any trouble due to corrosion. This is the case with tanks where weld corrosion is not considered to be hazardous.

Column control and feeding have been very satisfactory using ordinary industrial equipment. Automatic remote control of column interfaces has been very satisfactory by the use of pneumatic Taylor Full Scope Recorder Controllers. The addition of all streams to the columns at the very low flow rates of 1/3 to 4 gal/hr has been very satisfactorily maintained with a variation in flow rate of less than 2% by the use of Milton-Roy piston pumps. The feeding of active material to extraction columns has been done by displacement pumping which consists of displacement of the radio active material from a feed tank by an immscible liquid. While this type pumping has been very satisfactory on a small scale a number of auxiliary tanks are needed and may make direct pumping of radioactive solutions preferred in large scale plants. Direct pumping, however, involves a large amount of mechanical and maintenance difficulties which are yet unsolved for any known pump. Another method of introducing active feed into columns would be by gravity but this type operation may require tall shielding structures. Inconclusive operational experience with modifications of this mode of column feeding has not been satisfactory.

The operation of up to three columns in direct cascade has shown that although the control of any subsequent columns is affected by variables in the preceeding column the method of interface controllers has been entirely adequate under all conditions. The use of intermediate hold up tanks to avoid possibility of criticality or for material balances is unnecessary.

The hexone after being processed and recovered has been found to give as good or better decontamination and yields than does new solvent. There has been no evidence of radiation decomposition under operating conditions. This substantiates laboratory tests that hexone decomposes only after prolonged contacting at high levels of radiation. The formation of solids (crud) at organic-aqueous interface, if it occurs, has caused no operating difficulties during the 5000 hours the columns have operated. It is known that particles enter the column via the non-radioactive solution streams as evidenced by plugging of a 5 micron porosity sintered stainless steel element one-half sq. ft. in area within eight hours. The filters were removed with no change in solution make up and column operating difficulties were encountered.

All columns past the first extraction column have been available for direct maintenance with little or no decontamination. During the 30% Hanford Redox investigation a first cycle extraction column leak caused by cold flow of a teflon gasket was repaired by direct maintenance procedures after three days of intermittent decontamination.

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5.4 Volume Reduction

The uranium product solutions are usually reduced in volume by evaporation. Adequate process control has been found to be easily attained using either the continuous or batch evaporating techniques.

Evaporation is a well known unit operation and sufficient industrial experience is available to design an evaporator that will give adequate operation and low entrainment losses. The evaporator in use in the pilot plant is a simple, cylindrical, 250 gallon, jacketed tank provided with a 4" vapor line and condenser. The tank is extremely crude but tests performed showed that batch wise volume reduction gave suitable performance with entrainment losses of less than .01%. The activity of this stream is such that remote operating technique is used but remote equipment maintenance procedures are unnecessary.

Work done during 25 process development with a continuous evaporator showed that this type of equipment gave extremely good performance with respect to losses, control, and general operability. Its incorporation into the 25 recovery plant would eliminate four tanks.

5.5 Sampling

Sampling of radioactive process streams has always been the greatest source of operating area contamination and personnel overexposure irrespective of the process and should, therefore be done in a special isolated area. The sampling of dilute solutions containing moderate levels of non-gaseous activity (10^5 beta cts/min/ml) is moderately satisfactory with the usual air motivated recirculating jet type sampler. Concentrated solutions containing high levels of fission product activities are far more difficult to sample but have been sampled by modifying and supplementing the low level equipment. Streams containing high levels of alpha activity can be satisfactorily sampled using sealed containers and hypodermic pharmaceutical techniques.

5.6 Solvent Recovery

Operation of the solvent recovery equipment for hexone has shown that this operation is relatively simple and straight forward using ordinary industrial techniques, and requires very little or no radioactive shielding. Activity, essentially ruthenium, was pronounced in the solvent in the early stages of developing a process but this activity was found to be satisfactorily reduced by the use of a simple dilute caustic wash. This washing, if found to be necessary in any process, could be carried out in a shielded tank, and the solvent then transferred to the unshielded tanks of the solvent recovery equipment.

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