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ABSTRACT

The dilute aqua regia (Darex) system for processing stainless steel fuel elements in the Head-End Plant (HEP) design study consists of a continuous dissolution and chloride distillation system followed by a batch feed adjustment. The preliminary design is presented along with an outline of the development work required before a final design is possible.

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1.0 SUMMARY

The HEP design of the Darex head-end for stainless steel fuel elements consists of a continuous dissolution system followed by a batch feed adjustment system. The dissolution system contains a rectifying column (to recover acid from the dissolver off-gas), a trickle-type dissolver, and a stripping column (to remove chloride from the dissolver product); these three pieces of equipment are placed in series with a single reboiler and condenser. The feed adjustment system contains three batch evaporation tanks in parallel and is similar in operation to the Thorex FAT cycle. Both systems, as set up, should be easy to control.

The dissolver system design is based on preliminary and extrapolated data, and the feed adjustment system design on no data. They may, therefore, require modification after further development work is done. Unless some unexpected difficulty occurs in development, however, the process appears to have sufficient merit so that work on alternate processes for stainless steel fuel elements need not be pursued. An outline of the work required before final design of an aqua regia system is possible:

A. Dissolution System Studies Required

1. Vapor liquid equilibria data in the dilute region of the $\text{HCl-HNO}_3\text{-H}_2\text{O}$ system.
2. Chloride removal in stripping column as a function of number of stages.
3. Dissolution of various element types, including NaK bonded, to determine:
 - a. Dissolution rates
 - b. Operability, safety, and control of system
 - c. Off-gas composition and quantities.
4. Materials of construction.

B. Feed Adjustment System Studies Required

1. Decomposition rates of chloride in 15 M HNO_3 containing metal salts.
2. Solubility of appropriate metal nitrates in 15 M HNO_3 .
3. Demonstrate operability of system.
4. Determine effect on solvent extraction.

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2.0 DISCUSSION

2.1 Introduction

The Head-End Plant (HEP) design is a preliminary study to determine the order of magnitude of power reactor fuel processing costs for the AEC. This study offers an excellent opportunity to evaluate the many head-end processes currently under investigation here in the Laboratory to indicate what further work is required on the process and to point out where alternate processes should be developed.

The main problems connected with head-end processes are finding a dissolution reagent, converting the dissolver solution into a system compatible with the TBP extraction and waste systems, and finding materials of construction.

Dilute aqua regia is an excellent dissolution reagent for stainless steel and the uranium alloys. The chloride present in the dissolver solution, however, would interfere with the solvent extraction and corrode stainless steel extraction equipment and waste tanks. Preliminary laboratory data have shown that it should be possible to remove the chloride by stripping the dissolver solution with 15 M HNO_3 . This results in a nitrate system compatible with solvent extraction and stainless steel equipment. Preliminary data also indicate that titanium can be used as a material of construction for the dissolver and distillation equipment where the chloride is present. The only alternate dissolution reagent, at present, is sulfuric acid. The sulfate system, however, is not compatible with solvent extraction and would entail large waste volumes, since it cannot be removed by evaporation. In addition, a suitable material of construction is not available for the dissolver. For these reasons the dilute aqua regia (Darex) process was chosen for dissolution of stainless steel elements in the HEP design. In designing the system from sketchy or nonexistent data, several assumptions have been made that must be tested. An outline of further development work required is presented along with the design.

With the exception of sizing for criticality safety, the systems for handling either blanket or core elements of stainless steel and uranium, uranium alloy, or UO_2 will be the same. The design for the APDA Detroit Edison radial blanket element has been used as an example.

2.2 Process Description

2.2.1 Dissolution System. The dissolution system has several functions: (1) dissolution of the fuel elements (with $\text{HNO}_3\text{-HCl}$), (2) stripping the chloride from the dissolver solution, (3) removing the heat of reaction, and (4) recovering acid from the dissolver off-gas. The system has been designed to operate continuously in order to limit the reaction rate by the amount of acid present (this is particularly important in $\text{UO}_2\text{-SS}$ fuel elements, since the UO_2 is very reactive in acid) and to provide a distillation system that is easy to control.

In the proposed design (see Fig. 1) three major equipment pieces are involved: the acid rectifier, the dissolver, and the chloride stripper.

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These are arranged in series with a single reboiler and condenser. Operation of the system is as follows: 15 M HNO_3 (constant boiling) is added continuously to the reboiler of the chloride stripper. The acid vapors from the reboiler countercurrently contact the rich liquor from the dissolver, stripping the chloride (and some water) from the liquid. The vapors from the chloride stripper combined with the dissolver vapors (off-gas and acid vaporized from heat of reaction in the dissolver) flow to the acid rectifier, where the acid is condensed and separated from the off-gasses and water. The condensed acids from the rectifier (2 M HCl , 4 M HNO_3) flow through the dissolver, where they are consumed in dissolving the fuel element. The rich liquor from the dissolver is stripped of chloride, as previously described, and then overflows continuously to one of the feed adjustment tanks. The chloride recycles in the system (it is vaporized in the stripper and condensed in the acid rectifier) and HCl addition is required only to replace the amount decomposed by HNO_3 oxidation. Water, which is formed by the reaction of the nitric acid with metal, is removed from the top of the acid rectifier.

Control of the system is simple and well adapted to remote operation. The flow of acid to the dissolver, and thus the dissolution rate, is controlled by the flow of steam to the chloride stripper reboiler. Since the system operates at total reflux (with the exception of the small water bleed and the off-gas) the L/V in the stripping column does not change with acid boilup and does not require control. The concentration of HNO_3 in the dissolver is controlled by the rate of water removal from the top of the acid rectifier. (This could probably be automatically controlled by the temperature on the bottom of the rectifying column.) The HCl concentration would be controlled by batch additions (probably at the same time a fresh fuel element is charged) of HCl to replace chloride decomposition. The concentration of metal ions in the solution to the feed adjustment system is controlled by the ratio of acid feed to acid boilup in the stripper reboiler.

2.2.2 Feed Adjustment System. A system to adjust the uranium and acid concentrations to those desired for solvent extraction will be common to any aqua regia system since the removal and/or destruction of the chloride requires a higher acid concentration than is desirable in solvent extraction. To date no development has been done on a feed adjustment cycle for this system. This design assumes that a batch cycle similar to the Thorex feed adjustment will be satisfactory. This appears to be the least complicated of several alternates. Demonstration of the system and its effect on solvent extraction will be required.

The equipment consists of three parallel feed adjustment tanks each with a steam coil (or jacket) a condenser, and a condensate drum (see Fig. 1). Batch continuous operation over a cycle of 36 hours (12 hours filling and 24 hours for feed adjustment) has been assumed. One of the three tanks would always be connected to the overflow of the stripping tower.

The operational steps involved in the feed adjustment cycle are:
(1) refluxing to decompose any remaining chloride, (2) removing the excess

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15 M HNO_3 by distillation (the liquid temperature would be used as a control point, (3) dilution with water to desired uranium concentration for solvent extraction, (4) sampling, (5) addition of water or acid, as required, and (6) transfer to solvent extraction feed surge tank.

2.3 Development Required

2.3.1 Dissolution System. The only place in the system where equilibrium data on pure $\text{HCl-HNO}_3\text{-H}_2\text{O}$ is applicable is in the acid rectifying tower. The data available at present¹ on this system cover the range of 2 to 10 mole % acid. Basic data on this system below 2 mole % acid concentration is required to determine the number of trays required in the rectifier to obtain essentially acid-free water overhead and to determine the acid conditions in the tower for material of construction studies.

There are two methods of removing chloride from the dissolver solution: stripping with nitric acid-water vapors and oxidation with concentrated HNO_3 . It is desirable to strip as much of the chloride as possible, since it is then recycled to the dissolver. It is doubtful, however, if the chloride concentration can be reduced to the desired concentration (≤ 20 ppm) entirely by stripping. The design assumes that a major portion of the chloride can be recovered by stripping, with the remainder destroyed by refluxing in the feed adjustment tank. Laboratory demonstration is required to determine the amount of chloride stripped in a reasonable number of stages (three to four) and the time required to decompose the remaining chloride in the feed adjustment tank. This decomposition will take place in boiling 15 M HNO_3 with metal salts present. The existing data¹ on chloride decomposition covers the range of 1 to 5.5 M HNO_3 without metal salts present. If extrapolated to 15 M HNO_3 (see Fig. 2), these data would predict a chloride concentration decrease by a factor of ~ 350 every minute in the feed adjustment tank. If realized, this would be a fast enough rate so that negligible chloride would remain even with no stripping of the dissolver solution and should assure a solvent extraction feed free of chloride. The above figure, however, is a wild extrapolation; firm figures are required on chloride decomposition in 15 M HNO_3 with metal salts present.

Titanium has been assumed as a material of construction in this design. It is reported to be resistant to attack by boiling aqua regia². Explosions have been reported³ with titanium in contact with fuming nitric acid. This should not be of concern in this system, however, since it is impossible to concentrate to fuming acid from dilute aqua regia because of an azeotrope (at 15 M HNO_3). The corrosion resistance of titanium should be determined over the wide variations in acid concentrations and metal ion concentrations that will be encountered in the system. In addition, decontamination reagents and procedures should be determined for titanium equipment.

There are several questions regarding both the mechanics of dissolution and the operation of the dissolver that can only be answered by operating prototype dissolvers in the laboratory and unit operations. The effect on dissolution rate of the following variables should be studied: (1) HCl and

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HNO₃ acid concentrations, (2) the presence of more than one material in the dissolver (e.g., stainless steel and UO₂), and (3) position in the dissolver (may be important for long fuel elements). The operability, safety, and control of the system should be demonstrated especially when dissolving dissimilar materials and NaK bonded elements. In addition, the off-gas compositions and quantities should be determined for dissolution of the different element types.

2.3.2 Feed Adjustment System. The feed adjustment system is the largest uncertainty, since no data are at present available on its operation.

In addition to the problem of chloride decomposition discussed previously, there is the problem of precipitation and possible hydrolysis of the metal salts during the cycle. Studies are, therefore, required to determine the solubility of the appropriate metal salts (U, Fe, Cr, Mo, Ni, etc.) in boiling 15 M HNO₃ and to determine if the salts, once precipitated, can be redissolved when water is added to adjust to feed concentration. The uranium content of any insoluble product should be determined.

A very important part of the program should be to determine if the feed adjustment cycle has any adverse effect on decontamination factors in solvent extraction.

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- ¹ D. T. Morgan and G. W. Bond, Jr., MIT Engineering Practice School Report, KT-230.
- ² L. B. Golden, et al, Ind. Eng. Chem., 44, 1930 (1952).
- ³ Contract No. AF 33(616)-3066, Jet Propulsion Laboratory, California Institute of Technology.

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Fig.2. Chloride Decomposition Rate vs. Nitric Acid Concentration; Based on data in KT-230.

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