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SUBJECT: SOLVENT EXTRACTION APPLIED TO REACTOR FUEL
PROCESSING - FIRST QUARTER CO-OP REPORT

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ABSTRACT

The solvent extraction of thorium with 42.5% TBP in a Decalin diluent was studied in a compound pulse column. The HETS for the extraction section of the column was 4.7 feet. A discussion of the method of graphical calculations of a compound column is included.

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1.0 INTRODUCTION

One of the immediate goals of the atomic energy program is to provide electrical power cheaply enough to compete with conventional power costs. It is expected that at least 10% of the cost of power provided by atomic reactors will be for the reprocessing of fuels.

At first, one may think that the fuels could be left in the reactor until all the fissionable material is used up. However, since the fission products formed in a chain reaction are good neutron absorbers, the reaction cannot be self-sustaining after a certain point. Consequently, the fuel must be periodically taken from the reactor and the fission products removed.

Fuel burnup per cycle runs from a fraction of a per cent to about half of the total amount of fissionable material. Hence, many cycles of burnup and reprocessing operations are necessary to utilize the total equivalent of a single fuel charge. A separation process for fuel recovery must therefore be capable of low losses and low costs per cycle. Moreover, processing should be accomplished in a short time to avoid a large inventory of fissionable material.

The principal metal recovery method presently being used is a solvent extraction process. Solvent extraction has the benefit of a long period of development with both conventional and radioactive materials and has been brought to a high degree of flexibility and efficiency for certain types of fuels. In the interest of improving the existing solvent extraction processes, new techniques concerning operation and design are being developed. Perhaps more important, theories concerning the basic properties of the system are being sought.

Oak Ridge National Laboratory (ORNL) is engaged in the operation of small extraction columns for development and pilot plant scale columns for development and production.

2.0 PREPARATION FOR EXTRACTION

If solvent extraction is to be used as the process for the recovery of the valuable metal (uranium, plutonium, or thorium), there are a few steps which must be carried out to prepare the fuel element for the process.

At all times an accumulation of a critical mass must be avoided. These steps may be summarized as follows:

<u>Processing Step</u>	<u>Method</u>
1. Radiation Cooling	Storage for 60-120 days, generally underwater, to allow radioactive decay of short-lived isotopes. Organic solvents used in solvent extraction are unstable when exposed to high level radiation.
2. Cladding Removal	Mechanical separation or chemical dissolution of the cladding only. Extraneous material is removed. The specific process varies with geometry and composition of the element and its metallurgical structure.
3. Fuel Dissolution	Dissolution involving HNO_3 , HF , HCl , or H_2SO_4 or mixtures thereof. Choice of reagent depends upon fuel composition. Can be done batchwise or continuously.
4. Feed Adjustment	Concentration adjustments and addition of suitable chemical reagents, dependent upon the chemistry of the desired separation, to prepare for solvent extraction.

3.0 EQUIPMENT

Figure 1 shows a flowsheet for a continuous solvent extraction process. There are three columns: the extraction or A column, the strip or B column, and the solvent clean-up column. All three are sieve plate pulse columns.

The A column is 2 inch diameter glass pipe with stainless steel plates, perforated with $1/8$ inch holes to give 23% free area, spaced every 2 inches for 26 feet. The top and bottom of the column flare out to 4 inches. (The

Fig. 1. Continuous Solvent Extraction Process.

4 inch sections do not have any sieve plates.) The feed stream may be introduced at 8, 14, or 22 foot levels. The column is run aqueous continuous with the interface at the top of the column. The interface level is controlled by an instrument which converts the pressure differential developed by two bubbling air probes, one above and one below the interface, to units on a scale. An automatic valve in the AW line is controlled by this instrument. Thus the interface level is kept constant during an extraction run. A pulser whose frequency can be varied and whose amplitude is set to give 0.8 inch in the 2" column is connected to the bottom of the column.

During an extraction run, an emulsion forms at the interface at the top of the column. This emulsion can become quite large and sometimes works its way down the column into the stainless steel plate section. For this reason the column is flared out at the top so as to give a large interfacial area and residence time. Thus it will be easier for the solvent globules to coalesce. An outlet is located at the interface. Here the emulsion is withdrawn, broken into the aqueous and organic phases, and returned to their respective phases in the column.

The B column is shown as one column for simplicity. Actually, it consists of two interconnected columns placed side by side. This type of design, a concatenated column, conserves overhead space. There are 24 feet of the same type of stainless steel plates as in A column. Similarly, this column is 2 inches in diameter, flared at the top and bottom, and run aqueous continuous with a top interface controlled with the same type of instrument as A column. The pulser on B column has a frequency of 27 1/2 cpm and an amplitude of 0.8 inch.

Lastly, the solvent cleanup column is 6 inches in diameter and has stainless steel plates with 1/8 inch holes spaced every 2 inches throughout its 16 foot height. The ends of the column are again flared. This column is run organic continuous with a bottom interface. The pulse frequency is 44 cpm, and the amplitude is 1.0 inch.

4.0 FLOODING STUDIES

Prior to an extraction run, flooding studies are made with the A column. These data yield the maximum throughput for the column at any given A/O (aqueous/organic) flow ratio and pulse frequency.

In a countercurrent type apparatus, such as the A column, there are two immiscible phases, each of a different density. The organic is the light phase and makes its way up the column while the heavy aqueous phase goes down the column. These two streams are countercurrent and the flow rates of each can be increased only to a certain point. This point is called the flooding point. It is characterized by a buildup of the discontinuous phase in the column. In other words, more organic is being put into the column than is taken out. Fortunately this buildup can be conveniently measured, and consequently the flooding point can be determined.

The following flooding procedure has been adopted: flow rates are set and the column is run for 30 minutes. At the end of this time all streams are shut off simultaneously, and all of the solvent in the column is pulsed up to the top. The total solvent holdup is measured by the resulting interface drop. Runs are made with increased feed rates until flooding occurs. A plot of units of interface drop and feed rate is made for a given pulse frequency. The plot is linear up to the flooding point. At this point at which flooding occurs there is a constant solvent buildup in the column, (independent of pulse frequency), and the interface drops more rapidly with an increased feed rate. (See Fig. 2a)

At those frequencies which are suitable for extraction, higher throughputs can be obtained as the frequency is lowered. However, at these low frequencies, extraction is not as efficient as at higher ones. At higher frequencies the solvent is beaten up into small droplets which gives a large surface area for mass transfer.

Flooding runs were made at several frequencies. It was found that the log of the flooding rate was inversely proportional to the pulse frequency. (See Fig. 2b) Total throughput (aqueous + organic) is divided by the column cross section and expressed gal/ft²/hr.

The flooding rate is a function of: density difference between the aqueous and organic phases, A/O, surface tension, viscosity and pulse frequency. It would be desirable to find some empirical relation expressing the flooding rate as a function of these variables. At the present time flooding information is only in the form of experimental data.

5.0 SOLVENTS

Tributyl phosphate (TBP) is currently one of the most popular extracting agents. The density of pure TBP alone is often too close to that of the feed

Fig. 2a. Interface Drop vs Aqueous Feed Rate
42.5 % TBP-Decalin and H₂O. Flow ratio A/O
=0.40, Pulse frequency 70 cpm.

Fig. 2b. Flooding Rate vs Pulse Frequency
42.5 % TBP-Decalin and H₂O. Flow ratio A/O=0.40

solution to make the separation of phases feasible for a practical process. A diluent such as kerosene, Decalin or Amsco is mixed with the TBP so that the resulting density is low enough to allow separation. Recently comparisons have been made of TBP-Decalin and TBP-Amsco systems. Experimental results with thorium extraction runs indicated that the Amsco system was superior to Decalin in terms of flooding rates and extraction efficiency.

6.0 THORIUM EXTRACTION RUN

Before an extraction run was made, several flooding runs were made using the actual feed, scrub, and solvent solutions. Flow rates were then set at about 80% to 90% of flooding. A 5:1:1 flow ratio of solvent to feed to scrub was maintained.

The feed solution was 1.5 M Th^{+4} and 0.7 M Al^{+3} . The scrub solution was 0.5 M Al^{+3} and the stripping solution 0.008 M HNO_3 . In the case to be described the solvent was 42.5% (vol.) TBP-57.5% Decalin.

Feed was introduced into the A column at the 14 foot level, and the scrub entered at the 26 foot level. Solvent was pumped in to the bottom of the column and pulsed upwards. As the solvent and feed solutions contact each other the thorium is transferred to the solvent because the metal is more soluble in the organic phase. The extraction probably is

At NO_3^- concentrations above 2.5 M a polymerization reaction occurs.

Any fission products which also may have been transferred to the solvent are removed when contacted by the scrub solution. Fission products and the scrub and depleted feed solutions are taken off as aqueous waste. This waste is analyzed to determine thorium loss in the extraction. The product, which consists of the metal dissolved in the solvent, is taken off at the top of the column.

The A product then entered the bottom of the strip column. Here the solvent was contacted by the stripping solution which was introduced at the top of the column. In this operation the metal was stripped from the organic back into the aqueous phase. The final product, $\text{Th}(\text{NO}_3)_4$ was taken off at the bottom of the column.

The solvent, which contained practically no thorium, was pumped to the main solvent holdup tank S-1. From S-1 the solvent was sent to the Na_2CO_3 column to be cleaned. In this step the solvent was contacted by 0.1 M Na_2CO_3 . The purpose of this step was to remove any of the decomposition products of TBP. TBP decomposes into dibutylphosphate and monobutylphosphate. These two products are undesirable because they are emulsion formers. It has been established that the greater the tendency of the solvent to form an emulsion the lower the flooding rates.

The cleaned solvent was gravity fed into two other holdup tanks S-2 and S-3 before it was recycled.

7.0 HETS CALCULATIONS

The height equivalent to a theoretical stage (HETS) is a good indication of the extraction efficiency of a column. For analysis, an extraction column can be approximated by assuming it is equivalent to a sequence of stages each of which is performing the function of a theoretical stage. A theoretical stage is defined as a stage which discharges separated phases which satisfy the equilibrium relationship.

A simple graphical procedure has been developed for HETS determinations. (See example, Fig. 3) An "equilibrium line" is first established. The coordinates of the points on the equilibrium line are determined by allowing the thorium to reach an equilibrium distribution between the two phases in an agitated flask, allowing the phases to separate, and determining the thorium concentration of each. An "operating line" is constructed by means of a material balance around the section of the column being considered. The slope of this line is A/O , where A is the aqueous and O the organic flow rate.

In the case under consideration, two operations take place in the column. The feed enters approximately at the middle of the column (at the 14' point) and the scrub solution at the top (26' point). Hence, the thorium extraction into the organic phase takes place in the bottom 14', while there is some transfer of thorium from the solvent back into the aqueous scrub solution in the 12' scrub section.

Fig. 3. HETS Determination.

The coordinates of point P_2 in Fig. 3 show the concentration in each phase at the bottom of the column. To determine P_2 the column is run until steady state is reached; then the aqueous waste stream is sampled and analyzed for thorium. (Steady state occurs when the concentrations of all streams level out.) The entering solvent is assumed to contain no thorium.

Point P_3 represents the conditions at the bottom of the scrub section. Since the concentration in the organic phase at the feed point represents the conditions at both the bottom of the scrub section and the top of the extraction section, a horizontal line from P_3 intersects the extraction section operating line at a point P_4 , representing conditions at the top of the extraction section. The number of stages in the extraction section can be determined by drawing a horizontal line from this point until the extraction equilibrium line is intersected. A vertical line is drawn from this intersection down to the operating line. This "stepping off" procedure is continued until the aqueous waste concentration is reached. The total number of stages is counted and the HETS is calculated by dividing the extraction height by the number of stages. In this case, the extraction HETS = $14\frac{1}{3}$ stages = 4.7'.

Point P_3 is determined by internal sampling or a knowledge of the number of stages in the scrub section. In this case, previous work indicated the scrub HETS = $\sim 6'$. Since the scrub section was 12' long, point P_3 was located by stepping off 2 steps from point P_1 using the scrub operating and equilibrium lines. Point P_1 represents the conditions at the top of the scrub section; the ordinate is the thorium concentration in the organic product from the column and the thorium concentration in the fresh aqueous scrub solution is 0.

HETS values are helpful in the design of a solvent extraction column. The active length of column required can be estimated if the HETS is known and the maximum allowable concentration in the waste is specified.

8.0 PROPOSED CHANGE IN OPERATION

A possible change in this process would be to run the A column as a "zebra" column. Instead of having all stainless steel sieve plates, a "zebra" column has a section of stainless steel plates followed by a section of teflon or polyethylene plates. Since stainless steel is preferentially wetted by the aqueous phase and teflon or polyethylene by the organic phase, bands of aqueous continuous and organic continuous form on the stainless steel and plastic plates respectively. Hawford Works has been operating a 2 inch

"zebra" column and reports a satisfactory HETS. By running a "zebra" column the interface may be maintained at the bottom of the column. At the interface, an emulsion containing contaminants collects, and in the present process the product is taken off just after it passes through the interface where it may be recontaminated. If the bottom interface were to be maintained merely by running the conventional stainless steel plate column organic continuous, HETS values would be higher, due mainly to two factors, both contributing to reduced interfacial area: (1) Dispersing the aqueous phase, which has considerably lower flow rate than the organic phase, gives less material to be dispersed, and (2) Dispersing the aqueous phase, which preferentially wets the stainless steel plates, causes poorer drop formation.

This report dealt mainly with thorium extraction. It should be noted that the solvent extraction process for fuel reprocessing is by no means limited to thorium. Processes for uranium, plutonium, (the two fissionable materials) and fission product separation are being used in production operations.

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