SOLVENT IMPROVEMENT RESULTING FROM
THE USE OF NPH IN THE HANFORD PUREX
PLANT

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INTRODUCTION

The stability of a diluent to radiolytic and chemical degradation is an important consideration in nuclear fuels reprocessing by solvent extraction. The degraded diluent tends to form ligands which absorb fission products. These ligands are not easily removed by the normal solvent washing techniques. Therefore, fission products accumulate in the solvent until the final product is affected. Many years of laboratory testing have been spent trying to find diluents with a high resistance to chemical and radiolytic degradation.

BACKGROUND

Tests of radiolytic and chemical stability which were performed on candidates meeting the requirements of flashpoint, viscosity and density, indicated that normal paraffin hydrocarbons were more resistant than kerosene cuts, isoparaffins, olefins and aromatic hydrocarbons. Of the normal paraffin hydrocarbons which were tested, n-dodecane was the most stable. However, the cost of this diluent was considered excessive for solvent extraction in the Hanford Purex Plant.

In 1961, the Savannah River Plant (SRP) which has lower solvent losses than the Hanford Purex Plant, switched to Adakane-12* (approximately 93 wt. % n-dodecane) in their first cycle. Immediate improvements were observed in fission product decontamination and in the overall operating stability. The diluent previously used was a kerosene cut, Ultra-sene**.

The use of Adakane-12 was continued at SRP until December 31, 1963, when a less expensive normal paraffin hydrocarbon (NPH) mixture became available from the South Hampton Company. This mixture has the following typical composition:

*A product of Archer-Daniel Midland Company, Minneapolis, Minnesota

**A product of the Atlantic Richfield Company, Philadelphia, Pennsylvania

<u>Component</u>	<u>Weight %</u>
n-decane	3.2
n-undecane	29.9
n-dodecane	28.4
n-tridecane	23.6
n-tetradecane	14.9

The SRP blended the NPH into the process and a continuation of good process performance was reported.

At the Hanford Purex Plant, Soltrol-170 had been used as the diluent in the process since September, 1961. This diluent, a mixture of highly branched aliphatic hydrocarbons, is produced by the Phillips Petroleum Company as an alkylation process by-product.

The higher solvent losses at the Purex Plant, as compared with SRP, made the change from Soltrol to the more costly NPH less attractive. A subsequent increase in the demand for NPH in the manufacture of biodegradable detergents caused a reduction in price. This price, although higher than Soltrol, was acceptable since a significant improvement in plant operations was expected. On February 12, 1966, NPH was introduced into the plant on a test basis to evaluate its performance. The entire solvent inventory was changed from a mixture of 30 volume percent tributyl phosphate in a Soltrol-170 diluent to 30 volume percent tributyl phosphate in an NPH diluent.

BASIS FOR EVALUATION

The criteria considered in evaluating the NPH diluent were the solvent extraction performance as measured by fission product decontamination, product quality, product losses, recycle rates, column operability and solvent losses. Additional studies were made on the following factors which are indications of solvent quality: the fission product activity of the stripped solvent leaving the First Decontamination Cycle (feet for the No. 1 Solvent Treatment System); the decontamination factors* of the No. 1 Solvent Treatment System; and the fission product and plutonium retention analyses** of the solvent following solvent treatment.

*The factor by which the concentration of radioactive contaminants is reduced is termed the decontamination factor (DF) which can be expressed mathematically as follows:

$$DF = \frac{\text{Concentration of radionuclide initially present}}{\text{Concentration of radionuclide after processing}}$$

**The plutonium retention analysis is a reliable measure of solvent quality. In this analysis, a measured amount of plutonium is extracted in a solvent sample. The solvent sample is then contacted with 0.01 M nitric acid to strip the plutonium into the aqueous phase. The concentration of plutonium retained in the solvent after stripping is measured by alpha count. A high plutonium count-rate reflects poor solvent quality.

Characteristic periods of operation with Soltrol were then reviewed for comparison with NPH operations. The data from the 1961 period, immediately following the initial use of Soltrol, was reviewed but rejected. Prior to the initial use of Soltrol, a column in the Second Uranium Cycle was flushed extensively. A rapid increase in fission product activity and poor decontamination performance was noted upon resumption of processing operations. This poor initial performance is believed to be due to the pick-up of residual fission products by the solvent. The fission product activity of the solvent increased to values approximately a factor of 10 higher than the selected base period.

Solvent extraction performance was also poorer during initial Soltrol operations; the zirconium-niobium (Zr-Nb) decontamination factors across the uranium cycle were a factor of 5 low; the Zr-Nb decontamination factors across the plutonium cycle were a factor of 9 low. These decontamination factors gradually increased during processing operations to equal those values of the base period.

The period of December 1, 1965 to February 8, 1966 was selected as basis for comparison. The December-February operation was similar in most respects to the NPH operational period of February 16 - April 13, 1966. The operational periods were comparable in duration and in-plant processing rate. One slight inconsistency in the compared periods was a 30 percent of normal Zr-Nb activity in the first month of NPH operations. This was a result of the longer than normal aging of the fuel. However, the Zr-Nb activity of the fuel processed during the final month of NPH operations was comparable to the Zr-Nb activity during the base period.

RESULTS

The most significant results of the change in diluent were the increases in the overall ruthenium-rhodium arithmetic decontamination factor (Ru-Rh DF) by a factor of 13 to 15 for the uranium solvent extraction system and a factor of 7 to 14 for the plutonium solvent extraction system (Figure 1). The Ru-Rh contents of the uranium product was lower by factors of 18 to 24.

The data on the overall Zr-Nb DF is contradictory. A slight improvement in overall Zr-Nb DF of approximately 2 to 3 in the uranium and plutonium solvent extraction systems was noted during the latter part of the NPH test period when the fission product activity was high. This is contrasted with the slightly lower overall Zr-Nb DF during the early portion of NPH operations when the fission product activity was lower.

Column product losses and recycle rates during the test were approximately equal to or lower than those during the base period with the exception of plutonium recycle from the uranium scrub column (IBS column). This increase in plutonium recycle was not considered significant. Periods of comparable plutonium recycling have been observed in the past during Soltrol operation.

The operation of the uranium stripping column (1C column) improved considerably during the test. The improved operation allowed a reduction in the aqueous to organic ratio (a/o) from 0.9 to 0.83 and a corresponding decrease in the operation temperature of 7 F. Solvent losses with NPH diluent were comparable with short term solvent losses during Soltrol operation. However, the solvent loss during the test was 28 percent lower than the previous months of operation with Soltrol.

During the test, the solvent quality, as indicated by several different factors, showed a significant improvement. The fission product activity of the stripped organic leaving the 1C column was lower by a factor of 6 to 13 (Figures 2 and 3). This reduction and a 2 to 5 increase in the fission product decontamination factor in the No. 1 Solvent Treatment System resulted in a decrease in the fission product activity of the treated solvent by factors of 20 to 40 (Figures 4 and 5). The plutonium retention of the solvent with NPH was a factor of 2 lower during the early portion of the test period and a factor of 50 lower during the latter portion.

CONCLUSIONS

The use of NPH diluent in the Purex Plant provided a significant improvement in plant operation. Solvent quality, plant performance as measured by the Ru-Rh decontamination factors, and the 1C column operations all showed marked improvement during NPH operations. The Hanford Purex Plant has continued to use NPH as the diluent for all solvent extraction operations.

FIGURE 1
OVERALL RU-RH
DECONTAMINATION FACTORS FOR U PURIFICATION

FIGURE 2
1ST CYCLE SPENT ORGANIC Zr-Nb ACTIVITY

FIGURE 3
1ST CYCLE SPENT ORGANIC RU-RH ACTIVITY

FIGURE 4
THE Zr-Nb ACTIVITY OF THE SOLVENT AFTER SOLVENT TREATMENT

FIGURE 5
THE RU-RH ACTIVITY OF THE SOLVENT AFTER SOLVENT TREATMENT