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1.0 SUMMARY

A Darex flowsheet is presented wherein dissolution of stainless steel-type fuel elements in dilute aqua regia, stripping of chloride from spent dissolver solution, adjustment of stripper product composition and rectification of HNO_3 - H_2O vapors are accomplished in a completely continuous relatively simple loop process. Product from the loop needs only dilution with water to be made suitable as feed for a solvent extraction processing plant. The proposed scheme differs from earlier concepts⁸ in that:

(1) A continuous, pot dissolver (well-mixed liquid phase) is utilized rather than a trickle type dissolver.

(2) A strip vapor slightly lower in HNO_3 concentration than the azeotrope is used.

(3) A feed adjustment tank serves not only to recover HNO_3 - H_2O vapor, but also to dehydrate any silica present and to adjust the product composition such that upon water addition the material is ready for feed to solvent extraction. In most previous concepts, separate, batchwise feed adjustment was contemplated.

The Unit Operations Section proposes to continue an engineering development program yielding the necessary design information for the above described process.

2.0 INTRODUCTION

The Darex process is a method undergoing development for dissolving spent stainless steel-U fuels in dilute aqua regia, removing chloride ion from the dissolution product and adjusting nitrate preparatory to a solvent

extraction process of the Purex type. The chloride removal is accomplished by the stripping of the spent dissolver solution with concentrated nitric acid vapor. Adjustment to provide feed for solvent extraction processing is accomplished by boiling off nitric acid and water from the stripped solution and returning water to the concentrated product if necessary. Overhead vapors from the feed adjustment tank may be rectified to remove water and the liquid product recycled to the nitric acid boiler for reuse as stripping vapor.

The principal areas of work in the Unit Operations Section in support of the Darex process have included dissolution, stripping, feed adjustment tank, and rectification studies. The dissolution studies have yielded data needed to design a flooded type dissolver in which aqua regia dissolution of stainless steel-Uranium fuel types can be carried out.¹ These data showed the effect of aqua regia composition, feed rate, and surface area on dissolution rate. The stripping studies showed the effectiveness of chloride removal and the effect of V/L and stripping vapor composition on various column parameters.^{1,2,3} The feed adjustment tank (FAT) studies showed to what degree and in what concentration the nitric acid could be recovered from the stripped product and indicated the degree of stability of the concentrated solutions.^{4,5} The rectification studies showed that water removal would have to be accomplished in a chloride free portion of the system.^{6,7}

Guthrie⁸ presented a Darex flowsheet wherein a stripper, a rectifier, and a trickle dissolver were combined in a loop operation utilizing azeotropic $\text{HNO}_3 - \text{H}_2\text{O}$ vapor as stripping medium. Adjustment of product composition for feed to a solvent extraction processing plant was to be accom-

plished batchwise. Irvine⁹ advanced the concept of an integral reboiler for feed adjustment but without operational details. The scheme proposed herein (Fig. 1) combines the advantageous features of these previous concepts along with a simplified control system. The resulting flowsheet is a compact, relatively simple, completely continuous loop producing a solution which, after water dilution, can be fed directly to solvent extraction. The newly proposed loop utilizes a continuous, overflow type dissolver and a strip vapor whose nitric acid concentration is slightly below that of the azeotrope. The feed adjustment tank accomplishes nitric acid recovery as well as producing product of the desired concentration.

The original concept of the Darex process flowsheet is shown in Fig. 2. Had the process worked, the product would have been further treated in a continuous feed adjustment tank, possibly the reboiler itself, with nitric acid vapor being recycled directly to the stripper. When the rectification of the mixed acid $\text{HCl} - \text{HNO}_3 - \text{H}_2\text{O}$ system proved infeasible, it appeared logical to rectify the chloride-free nitric acid vapor recovered in the feed adjustment step. This necessitated an additional vessel for feed adjustment and another condenser. The rectifier in Fig. 1 is the same size as the one shown overhead in Fig. 2.

3.0 PROCESS DESCRIPTION

For comparison purposes both the revised and original flowsheets are presented (Figs. 1 and 2 respectively). The original is similar to the Guthrie proposal⁸, while the revised flowsheet represents the new proposal. Both flowsheets involve dissolution, the feeding of spent dissolver solution

Figure 1 Revised Darex Flowsheet

Figure 12 Original Darex Flowsheet

to the top of a continuous stripper, and the production of stripping vapor in an $\text{HNO}_3 - \text{H}_2\text{O}$ boiler. Make-up HCl is added directly to the dissolver while water is removed overhead in a rectifying column. Table I lists the assumptions used in making the material balances shown in the flowsheets.

The principal difference between the two flowsheets is that in the revised form, rectification is carried out in a Cl^- free system. Since rectification in the presence of useful amounts of Cl^- was not feasible, this was believed to be the only practical solution. The flowsheet in Fig. 2 uses azeotropic (15.3 N) stripping vapor and produces a highly acidic product, which the flowsheet in Fig. 1 operates at 15.0 N HNO_3 and yields a product with much lower acidity and higher metallic ion concentration. The product from the Fig. 2 flowsheet process would be assumed to go through an additional feed adjustment step. Although both flowsheets indicate the dissolution of stainless steel alone, the systems approximate those resulting from the dissolution of APFR-type stainless steel fuels containing approximately 10% UO_2 .

The original system would have had certain advantages, but the revised scheme has other advantages in addition to appearing feasible at the present state of development. The obvious disadvantage of the new system is that it requires at least one condenser not necessary in the other scheme. The chloride removal efficiencies and HNO_3 consumptions of both systems should be essentially equal. An advantage of the revised system is its flexibility and ease of operation. The equilibrium data for the rectification of $\text{HNO}_3 - \text{H}_2\text{O}$ are well known. Surge storage can be added in the lines feeding both boilers to stabilize flows. There is no chance for Cl^- contamination of

Table I Assumptions Incorporated in Material Balance Calculations

1. Steady-state operation.
2. A basis of 1.00 l containing 5 moles HNO_3 and 2 moles HCl entering the dissolver.
3. Composition and volume of dissolver product,* density and HNO_3 content of stripper product.*
4. One mole (55.4) g of 304SS combines with 2.85 moles NO_3^- .*
5. In flowsheet 2 the composition of the vapor generated in the feed adjusted tank.*
6. Loss of 35% of Cl^- entering the dissolver,* 0% of the NO_3^- entering the stripper.
7. Pure H_2O overhead in the rectifier.*
8. Densities of HCl and HNO_3 are additive in the mixed-acid streams.
9. Gaseous decomposition products not considered in calculating V/L.

*

Assumptions based on interpolation and extrapolation of experimental data.

the product concentrator on shut down or in case of column upset.

The Fig. 1 flowsheet indicates the use of a downdraft condenser. This design should allow the absorption of gaseous decomposition products with a minimum volume of non-recoverable vent gases and maximum acid recovery.

Feed adjustment following stripping is necessary because solvent extraction requires a feed of 3 N H^+ while the stripped product is 13 N; if adjustment were made by water dilution alone, the metals concentration would be prohibitively low. An additional step is therefore required to remove and recover nitric acid and to concentrate the metallic salts.

It is also necessary in reducing the volume of the stripper product to dehydrate the silica present. Silica dehydration will be partially accomplished in the dissolver and continued to some extent in the stripper. It must be completely dehydrated prior to entry into the solvent extraction system since the use of feed containing undehydrated silica may cause the formation of gelatinous material in both the aqueous and organic phases.¹⁰ It has been shown that dehydration can be accomplished by digesting at a sufficiently high temperature. The severity of conditions necessary to bring about silica dehydration in Darex product has yet to be established, however.

The solution in the feed adjustment tank would partially crystallize if its temperature were lowered to room temperature; however, in any other scheme such conditions would have to prevail somewhere in the process in order to accomplish silica dehydration. If crystallization does occur the material can be returned to the liquid state by reheating, but to avoid any

possible difficulties the hot product should be diluted immediately upon withdrawal.

Materials of Construction

Based on subcontract work at Battelle, Clark¹¹ states that Ti is a suitable material of construction for all the components of the Darex system. In the revised flowsheet there is no longer any possibility that a nitrate-free chloride system could be encountered due to mis-operation of the rectifier.

Materials of construction under evaluation in the Unit Operations' equipment are tantalum, titanium, and Haynes 21 (a high Co alloy). It is suspected that "ultimate" materials such as these will be necessary only in the dissolver, the top section of the stripper and the downdraft condenser. In normal operation the boilers in both flowsheets could be SS but a more resistant material is recommended since Cl^- contamination is possible due to column upsets and shutdown procedures.

Instrumentation and Control

Figure 3 presents a possible system of control for Flowsheet 1. Selection of stripping vapor composition leaves only one independent variable; this variable may be taken as the amount of heat supplied to the nitric acid boiler. Fixing the heat input determines the throughput of the apparatus and controls the magnitude of flow in all streams.

The temperature within the rectifier would be used to control the H_2O removal in the rectifier, thus stabilizing the HNO_3 content of the regenerated acid. A Cl^- analyzer on the dissolver product stream would control HCl

Figure 3 System of Control for Flowsheet 1

Legend

- C - Liquid Level Control
- TRC - Temperature Recording Control
- FRC - Flow Recording Control
- CRC - Concentration Recording Control

make-up to the dissolver. Level and composition are to be maintained in the feed adjustment tank by discharging under temperature control and regulating heat input on level control.

Areas of Uncertainty in the Proposed Process

There are still uncertainties at this stage of the process development. The performance of the down-draft condenser has not been established. Gaseous decomposition products from the dissolver and stripper will flow through the condenser; some may be dissolved at operating temperatures, others will not. An off-gas system will be necessary to treat those gases not absorbed in the condenser. Any chloride lost must be replenished by an HCl make-up stream.

The compositions of streams entering and leaving the stripper and feed adjustment tank are based on interpolations and extrapolations of experimental data gathered in separate studies mentioned earlier. The values shown should not be taken as exact but are consistent throughout, reasonable, and certainly of the right order of magnitude. The feed adjustment tank has not yet been run continuously at the conditions indicated but batchwise boil-downs to these high concentrations suggest the conditions indicated. Operating conditions may have to be changed somewhat or the final dilution of the concentrated product may require dilute nitric acid rather than water to obtain the required 3 N H^+ feed strength.

It has been reported that colloidal silica which is likely to be present in the Darex system may coagulate in the solvent extraction system and render it ineffective.¹⁰ It is believed that conditions in the feed adjustment tank will dehydrate the silica resulting in precipitation of the colloid, but more work is required on this problem. The conditions required for complete silica

dehydration must be determined. If a long hold-up time and hence a large vessel is required, safety from the standpoint of criticality in any proposed application must be guaranteed.

The liquid overhead in the rectifier is shown as pure H_2O ; it should be possible to obtain this goal in a reasonable number of stages with the nitric acid-water system and a minimum of Cl^- contamination. This water withdrawal stream can be returned as part of the diluent to the concentrated product and thus not constitute another external waste stream.

4.0 UNIT OPERATIONS PROGRAM - STATUS AND RECOMMENDATIONS

Apparatus was assembled to study flowsheet 2; but when rectification of the mixed acids proved infeasible, it was modified to the boiler, stripper, dissolver, and downdraft condenser portion of flowsheet 1. After this equipment has been operated successfully, the feed adjustment tank and rectifier will be added and run separately. The two units will then be tied together and operated with full instrumentation. Corrosion specimens of Ti, welded Ti, tantalum, and Haynes 21 were placed in the system during construction in the top, middle, and bottom sections of the stripper and in the dissolver in both the liquid and vapor phases.

It is anticipated that the Unit Operations Darex program will yield design information applicable to a Pilot Plant or to larger units. From the evaluation of Flowsheet 1 specific information should be obtained pertaining to:

1. The operation and control of an integrated loop.
2. The operability of the rectifier.

3. Chloride removal and recovery.
4. Silica deposition on surfaces of equipment.
5. Corrosion rates of various materials of construction.
6. Effect of SS/U ratio of fuel on loop operation.
7. Silica dehydration.
8. Operability of the feed adjustment tank.
9. Volume reductions obtainable on Darex waste.

It is recommended, therefore, that development work directed toward the operation of the complete Flowsheet 1 be pursued vigorously. This work should include:

1. The determination of conditions necessary to accomplish silica dehydration.
2. The demonstration of the operability of a continuous feed adjustment tank using fuels of both APPR and Yankee Atomic types.
3. The development of instrumentation capable of maintaining a 2 N Cl^- concentration in the stream leaving the dissolver (determination of Cl^- in dissolver product and HCl addition).
4. Development of methods of determining composition and flow rate of system off-gas.
5. Dissolution studies with Yankee Atomic type fuel.

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