DPSPU 69-30-1

Conf-690609--30

EVALUATION OF CENTRIFUGAL CONTACTORS

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June 1969

Synopsis of a presentation to the 15th Annual Meeting of the American Nuclear Society to be held in Seattle, Washington, June 15-19, 1969.

Publisher is requested to include this acknowledgment.

Information in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

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Introduction

Generally, pulse-columns and mixer-settlers have been the normal contactors used in solvent extraction processes for recovery of materials from reactor fuels. By comparison with fuels processed to date, fuels from power reactors will be highly active as a consequence of economic incentives for irradiation to high burnout and for processing at minimum cooling time. There is concern that highly active solutions may degrade the organic solvent sufficiently to cause poor performance in conventional contactors. Several types of contactors with short residence time have been studied in attempts to reduce solvent exposure.

Centrifugal contactors were developed by Savannah River Laboratory, and a bank of 18 stages was placed in service in 1966 as the 1A bank of the Purex solvent extraction system at the Savannah River Plant. These units were installed specifically to test their capabilities in plant service. Experience during the past three years provides information on mechanical performance, control requirements, recovery efficiency, decontamination from fission products, and solvent degradation. Further, the differences in fission product behavior in the mixer-settlers and centrifugals stimulated laboratory tests that have clarified the mechanism involved.

Discussion

The contactors and the plant installation will be reviewed briefly. A schematic of an individual contactor is shown on the first slide. Organic and aqueous phases enter at the bottom, are mixed and discharged to the bowl. The phases leave at the top of the bowl, the aqueous at the periphery and the organic next to the center shaft. The organic-aqueous interface level is controlled by back air pressure on the aqueous.

Characteristics of the unit are shown on slide 2. As shown on slide 3, the Purex first cycle has three banks, the first for extraction and scrubbing of uranium and plutonium, the second for plutonium partition, and the third for uranium recovery. The slide also shows some comparisons between the mixer-settlers and the centrifugal banks: 24 stages instead of 18; 12 to 16 scrub stages instead of 9; 5000 gallons total volume instead of 90.

To summarize maintenance experience, the service has been good for a new installation. There have been three specific equipment failures since the few miscellaneous corrections of the run-in period. The motors on two stages failed at 27 and again at 30 months, and a shaft seal developed an excessive air leak after 25 months. The units had been designed for remote maintenance and the failed parts were replaced expeditiously in each case.

Control

Close control of aqueous and organic flows is essential for proper operation. At nominal throughput rates of 25 to 50 gallons per minute of solvent in the 1A bank, small errors in flow ratios obviously can lead rapidly to imbalances in a bank with 4 gallons per stage. A certain minimum organic/aqueous flow ratio must be maintained to limit losses of uranium and plutonium, and a controlled degree of uranium concentration must be maintained in the middle of the bank to saturate the solvent with uranium and attain good decontamination.

These control requirements have been met satisfactorily by flow ratio and specific gravity instruments connected to automatic controllers. The system has functioned reasonably well, and satisfactory control also has been maintained with manual operation when necessary.

Startup Characteristics

Rapid flushing and turnaround are desirable features in any contactor for power fuels. The centrifugals have demonstrated that they can be started and stopped rapidly; they have been shut down many times since

installation. The ranges of shutdown and startup are shown on slide 4. At the minimum flush time shown, the bulk of the activity that surges through at startup is past in 8 hours, as shown on slide 5. The integrated difference between the activity surges with the long and short flushes is about a factor of six. We have not resolved the questions of how much activity is due to solvent degradation in the bank during shutdown, and how much to the initial low uranium saturation.

Solvent Behavior

An evaluation of solvent degradation and decontamination performance requires a review of our previous experience. In the Purex plant, the diluent for the tributyl phosphate was changed from the original mixed kerosene to n-dodecane in 1961 in an effort to counteract serious solvent degradation effects seen with highly active feeds in the large mixer-settlers. Since then, solvent losses have been made up with commercial normal paraffins with some distribution of chain lengths, but primarily dodecane. Solvent makeup has been about 2% per month, which means the solvent changes its identity quite slowly. With the straight-chain solvent and the big banks the decontamination factors from fission products were initially high, but decreased markedly over several years as shown on slide 6. Operating methods gradually were worked out to compensate for high radiation exposure in the big banks, and decontamination performance improved. In the period before the centrifugals were installed decontamination was in the range of 5000 to 7000 for zirconium and ruthenium, which are the fission products of concern and usually the limiting activities in the product streams.

This same solvent remained in use and allows some comparison between the performances of the two types of contactors. Unfortunately, a direct comparison of absolute decontamination is not valid because of the different number of stages in the banks. We can compare, however, the influence of residence on solvent degradation by other measures: the amount of zirconium and ruthenium bound in the solvent and the stability of operation as a function of feed activity.

In a continuous process such as we have, a steady state is reached between the input of degradation products in the extraction system and their removal in the solvent washing system. This steady state shifted with the change in contactors, and both the ruthenium and zirconium in the circulating solvent dropped markedly, as shown on slide 7.

With respect to stability of operation, the large mixer-settlers had an upper limit on fission product activity in the feed at about 150 Ci/l beyond which decontamination performance deteriorated rapidly with time as the input of solvent degradation products overtaxed the washing system. The centrifugals have operated with feed up to 225 Ci/l with no evidence that a limit has been reached; we have not tried to establish the upper limit.

Now to consider the decontamination performance. As mentioned previously, the actual decontamination in the centrifugal contactors is poorer than in the mixer-settlers in spite of the lower solvent degradation. This effect can be partially credited, for both zirconium and ruthenium, to the fewer scrub stages and also to the limited time for some relatively slow chemical reactions to proceed toward equilibrium.

A comparison of the nominal distribution of Zr-Nb activities through the first cycle is shown in slide 8. The activity coming from bank 1A in the organic stream was considerably higher with the mixer-settlers, but this activity remained in the solvent and less total activity transferred to the aqueous product streams. Since the centrifugals were installed, numerous analyses also have been made of the distribution of dibutyl phosphate (DBP) through the cycle; slide 9 shows typical results. Whereas most of the zirconium activity ended in the 1BP stream, most of the DBP follows the solvent from the bank. It is obvious that the DBP does not alone determine the decontamination.

Numerous laboratory tests have sought explanation for differences in Zr behavior between the slow mixer-settlers and the rapid centrifugal contactors. Most of these tests have been multiple extractions and scrubs. The technique has shown some different species and has clarified zirconium behavior.

At least three factors have significantly influenced overall differences between the centrifugals and mixer-settlers. An important factor was the change in the amount of DBP produced in the 1A bank. The larger quantity of DBP in the solvent from the mixer-settler caused more Zr to extract and follow the product to the 1B bank; however, the DBP-complexed Zr was less easily stripped from the solvent than uncomplexed Zr, so that the actual effect of the DBP on product contamination was slight.

The second factor is the slow rate with which Zr approaches equilibrium between the solvent and the aqueous phases. Laboratory measurements show that with 15 seconds of very vigorous mixing, which is much longer than in the centrifugal contactors, the distribution is only about 80% of its equilibrium ratio. In the extraction end of the bank, the successive stages still help zirconium approach the equilibrium characteristic of the extraction conditions. In the scrub end, every stage removes less than indicated by the equilibrium distribution coefficient, and the lower removal rate is compounded to give a large difference between actual decontamination and that calculated at equilibrium conditions.

The third factor is the conversion of the normal species of zirconium in the solvent to a tightly bound species. The data may be interpreted as shown in slide 10. The tightly bound species has no aqueous counterpart, exchanging only with the "normal" solvent form. The conversion of the tightly bound species back to the normal species is illustrated in slide 11. Solvent was scrubbed numerous times with 1.18N HNO_3, and activity of ^{95}Zr in the solvent and aqueous was determined after each scrub. After the fourth scrub, the solvent was allowed to stand for 72 hours, then scrubbed further. (The long period was not required for conversion; it was used to explore the equilibrium between "A" and "B".) Each of the curves resolves into two straight lines, indicating two separate chemical forms. The original solvent had 7.2% "B" form. After four scrubs the solvent Zr was 98.5% "B" form. After standing 72 hours it was 79% "B". The distribution coefficients of each form are functions of the slopes of the straight lines. Although the conversion of "B" to "A" is slow, it is fast enough to give an apparent distribution coefficient of 10 ± 5 when the scrubbing time is 2 minutes on 5-minute intervals. At shorter

intervals the value increases. The value of this apparent distribution coefficient does not vary greatly with aqueous acidity over the range of 0.6 to 4.6N through the fraction of "B" decreases with increasing aqueous acidity. The tests suggest that acid is not a reactant in the formation of "B" but does influence the abundance of one of the reactants, free tributyl phosphate (that not holding extracted nitric acid).

The net effect of the two Zr rate effects is given in slide 12, in which solvent was scrubbed both rapidly and slowly at 1A bank acid conditions and then stripped. We couldn't achieve sufficient speed to fully simulate the centrifugals; however, slow scrubbing is clearly superior. Also, it is noteworthy that the rate of stripping in these tests is consistent with present plant operation in distribution of activity and confirms other tests which show the current low level of DBP has little effect on the rate of Zr stripping in the 1B bank.

Ruthenium Behavior

Some comments also may be made on ruthenium behavior. When the centrifugals replaced the mixer-settlers, the decontamination factor for ruthenium increased by slightly less than a factor of two, from near 7000 to a range of 10,000 to 15,000. And, as stated previously, the bound ruthenium activity in the solvent decreased from over 100,000 c/m/ml to less than 20,000 c/m/ml.

In many studies during the past decade, ruthenium behavior in the Purex system has been shown to depend generally on the equilibria in a series of nitrato-nitrosylruthenium complexes. In addition, the long-term behavior of ruthenium with old solvent in the mixer-settlers pointed to a second mechanism for the transport of ruthenium — by ligands whose relative abundance in the solvent could be measured by the steady-state activity level of bound ruthenium.

Early laboratory development work on miniature centrifugal contactors had shown that decontamination with short residence times was determined by the characteristics of the trinitrato-nitrosylruthenium species

specifically. This behavior included a high dependency on temperature, with a large improvement in operating at 60°C instead of 40°C. However, changing temperature had little difference on ruthenium decontamination in the plant centrifugal units.

A self-consistent explanation of the various observations would be that less degradation of the solvent in the centrifugal contactors gives a lower steady-state concentration of ruthenium-carrying ligands, hence better decontamination. However, the decontamination still is less than was seen in the mixer-settlers when they had solvent containing the current bound ruthenium level, and this effect results from the fewer scrub stages. The small effect of temperatures on decontamination would indicate that the ruthenium carried by solvent degradation products contributes more activity to the product streams than the straightforward trinitrato-nitrosylruthenium extraction, which should be temperature dependent.

Conclusions

Plant performance and laboratory studies together point to factors that should be considered in the design of a plant.

- Short-residence times indeed reduce the degree of solvent degradation and increase permissible feed activity.
- Maximum decontamination demands an adequate number of scrub stages; 12 to 16 is not excessive, whether the units have long or short residence times.
- Nine short-residence extraction stages are probably the minimum for adequate recovery of plutonium and uranium, and one or two additional stages would be a distinct help. With our nine stages, plutonium losses still are quite sensitive to any increase in the uranium saturation in the bank.
- The best compromise between solvent degradation effects and the benefits of longer scrub residence times would be an extraction section of 10 to 12 short-residence stages, a scrub section of perhaps 8 short-residence stages, and perhaps 4 long-residence scrub stages (for slow equilibria).

- The continuing evidence that ultimate decontamination potential is determined by a steady state between solvent degradation and cleanup means that good solvent washing facilities must be provided for stable operation if the potential of short-residence contactors in processing highly active fuels is to be realized.

CENTRIFUGAL MIXER-SETTLER

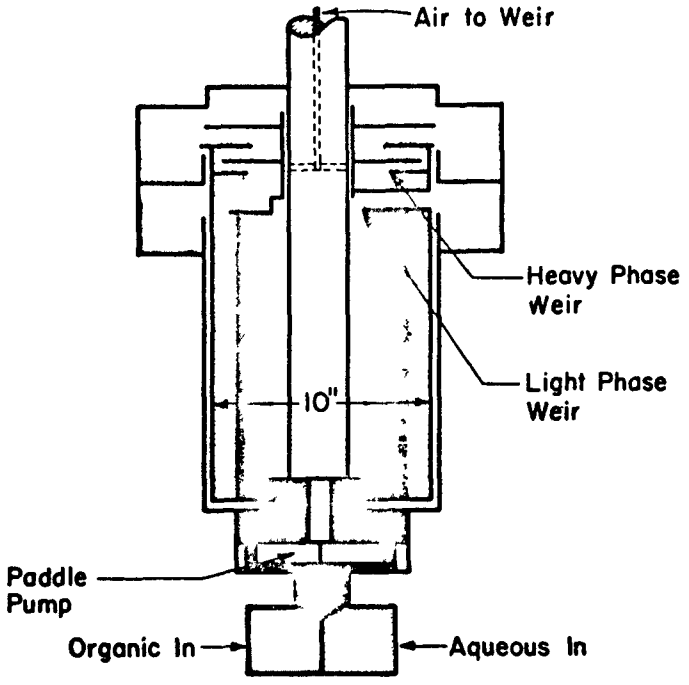


FIGURE 1.

CENTRIFUGAL CONTACTOR OPERATING DATA

ROTATIONAL SPEED	1745 rpm
CENTRIFUGAL SEPARATION FORCE	300-500 g
DYNAMIC LIQUID VOLUME	4 gal/stg
TOTAL LIQUID FLOW	20-65 gal/min

FIGURE 2.

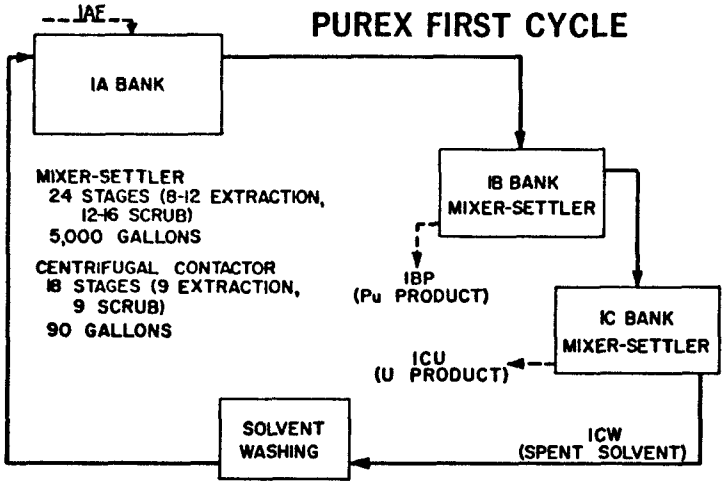


FIGURE 3.

SHUTDOWN AND STARTUP FLUSH CONDITIONS

MINIMUM	MAXIMUM
SHUTDOWN	
15 MINUTES CONTINUATION OF SCRUB AFTER STOPPING FEED	45 MINUTES CONTINUATION OF SCRUB AFTER STOPPING FEED
STARTUP	
NONE. ALL STREAMS NORMAL, NO DELAY OF FEED	FEED COLD U SOLUTION TO SATURATE SOLVENT, ABOUT ONE HOUR

FIGURE 4.

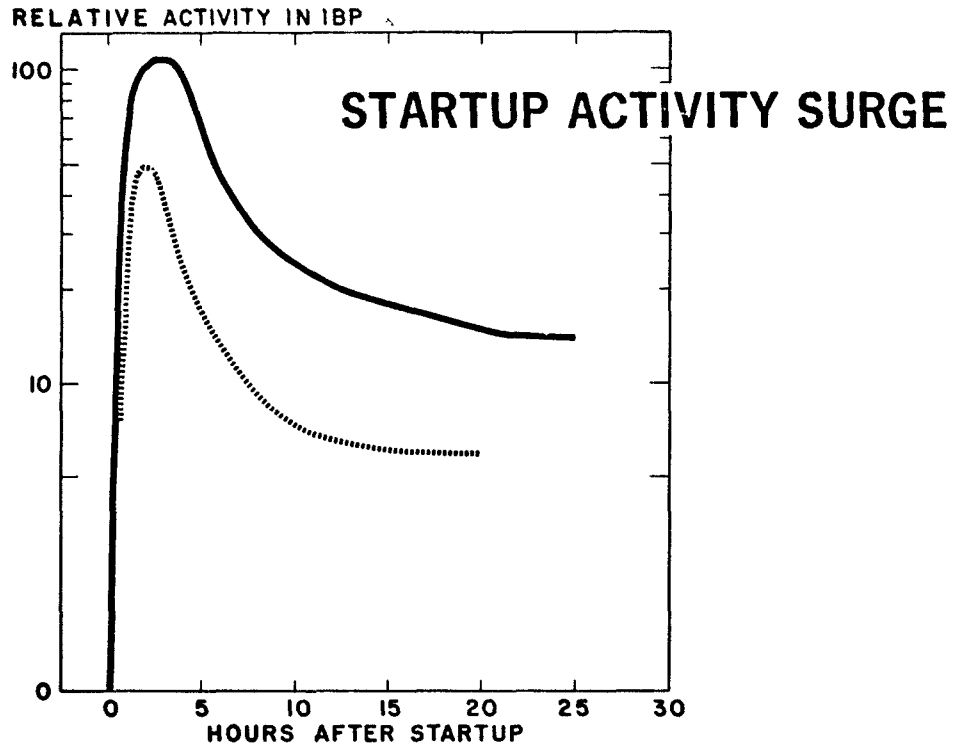


FIGURE 5.

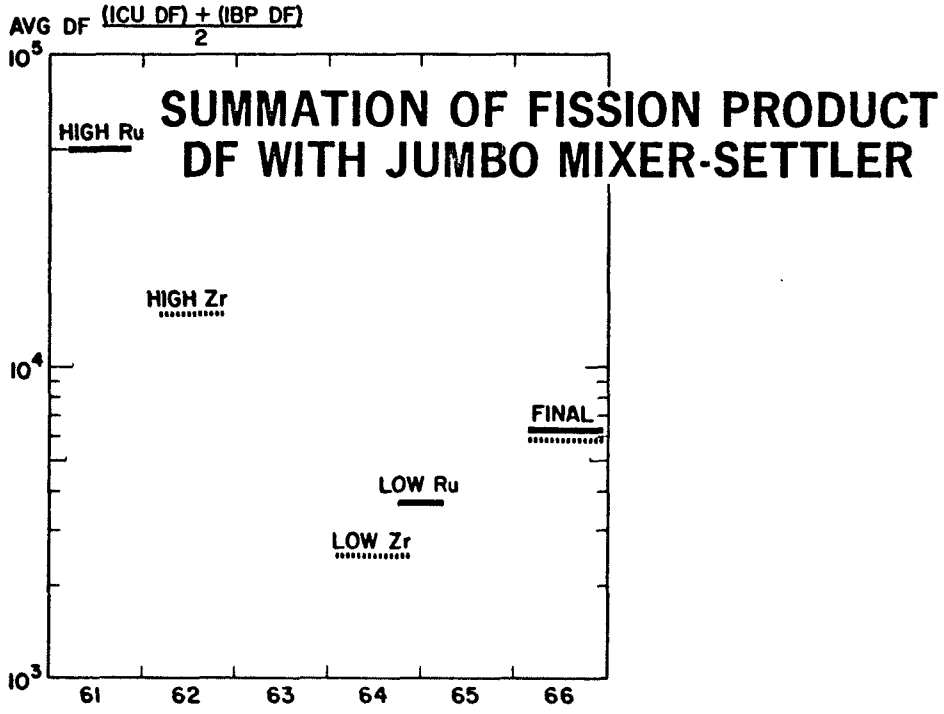


FIGURE 6.

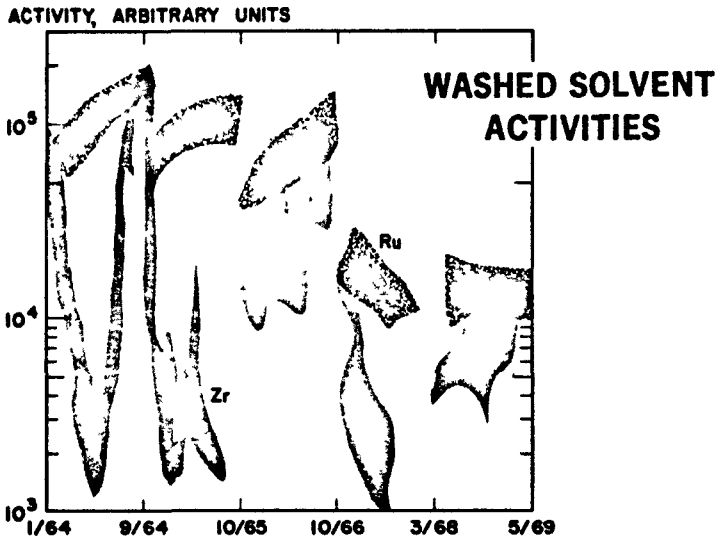


FIGURE 7.

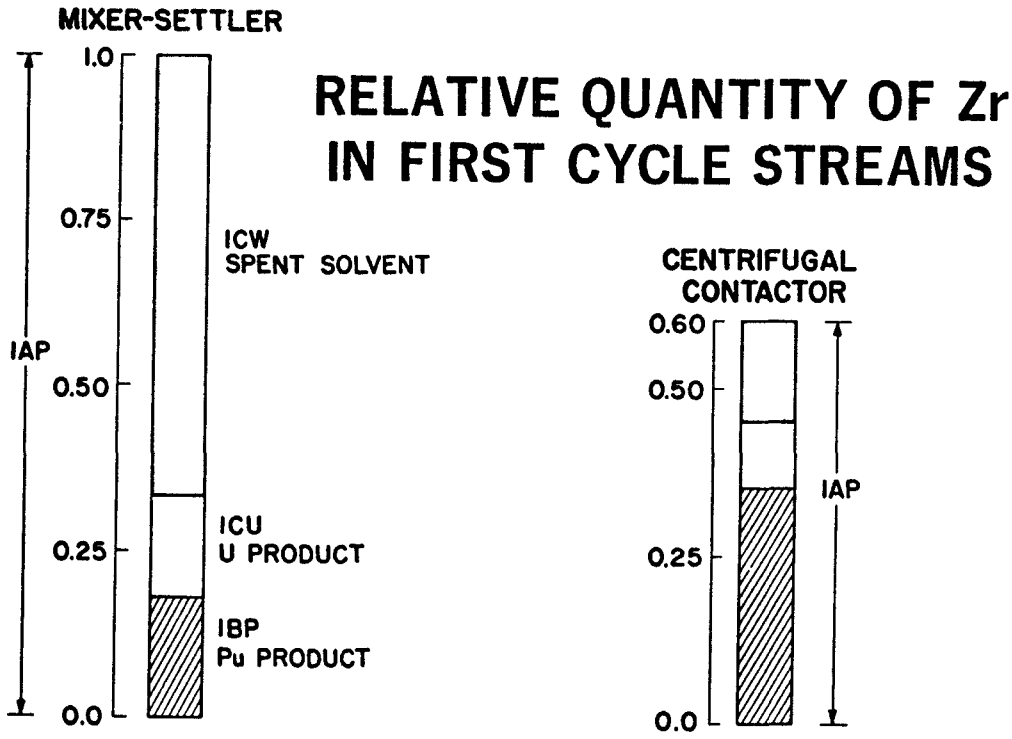


FIGURE 8.

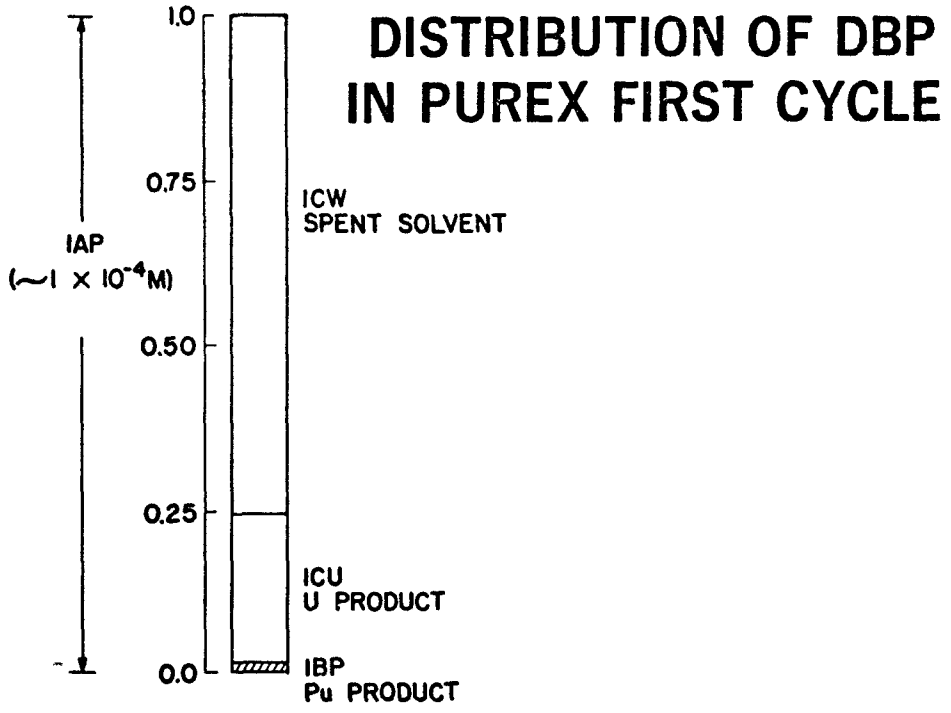
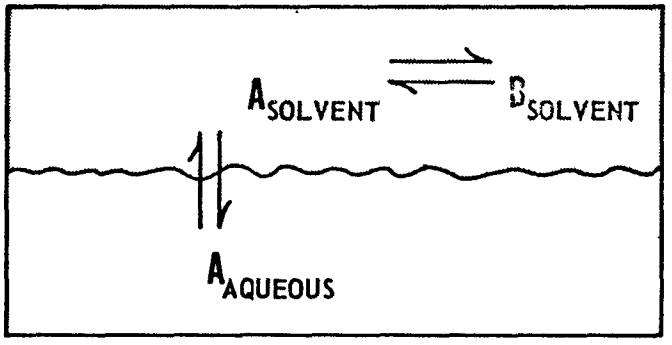


FIGURE 9.



WHERE: $A_{AQUEOUS} = Zr(OH)_x^{+(4-x)}$

$A_{SOLVENT} = Zr(NO_3)_4 (TBP)_3$

$B_{SOLVENT} = ?$

FIGURE 10.

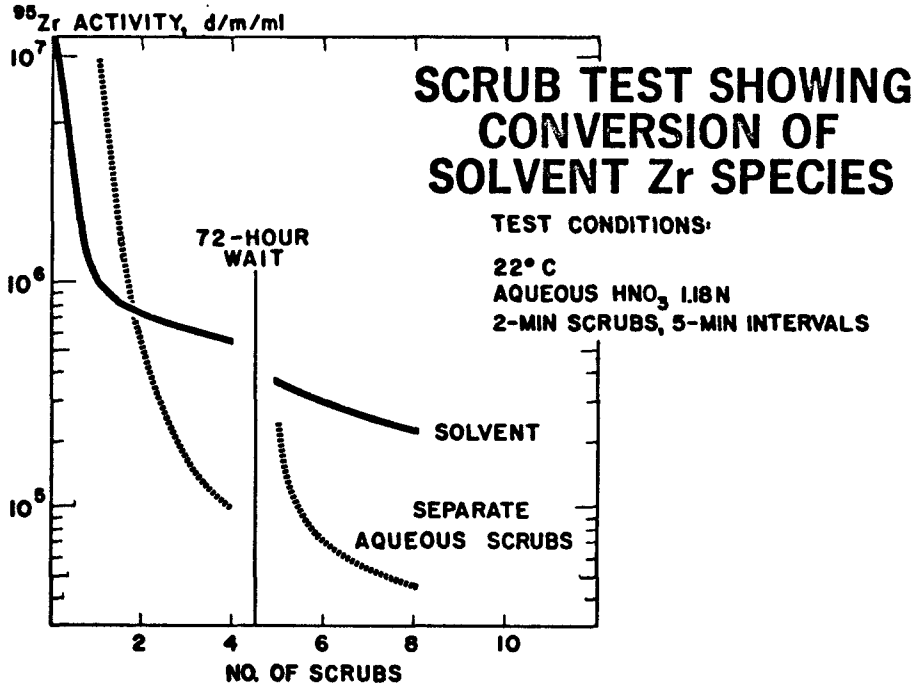


FIGURE 11.

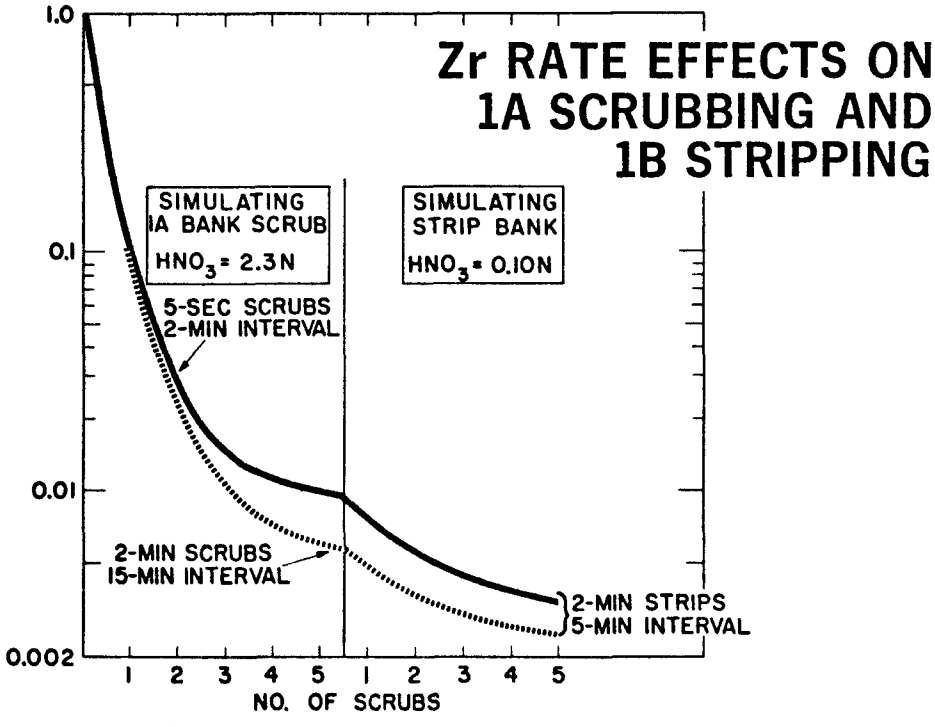


FIGURE 12.