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PUREX IBX - IBS COMBUSTION STUDIES, 1964

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PUREX IBX - IBS COLUMN STUDIES, 1964INTRODUCTION

The pilot plant pulse column runs described in this report had three objectives: to develop a high-capacity cartridge for the Purex IBX column, to demonstrate the use of this cartridge under flow conditions typical of a proposed Thorex process flowsheet, and to determine the behavior of sodium formaldehyde sulfoxalate (SFS) and uranium-IV in the IBX-IBS system. SFS, available commercially as Discolite^R, is a strong reductant which under IBX column conditions is capable of quantitatively reducing uranium to U-IV and plutonium to Pu-III.

SUMMARY

Stable operation at volume velocities as high as 1620 gph/ft², sum of flows, was demonstrated in the IBX column under both Purex and Thorex flow conditions. A mixed-plate cartridge containing 2-in.-spaced stainless-steel nozzle plates with fluoroethene sieve plates inserted at 8 to 12-in. intervals was used in this demonstration. The relatively coarse dispersion obtained at the higher rates was estimated to give transfer unit heights of about 2 to 3 ft (raffinate-film basis). Up to 70% dispersed phase holdup in the column midsection was measured at maximum apparent efficiency.

The path of SFS, and of the U-IV produced by its reaction with uranyl ion, was followed as a function of the SFS introduction point. The SFS was apparently completely reacted within a few inches of its feed point; uranium-IV was detected from about 6 ft below the SFS feed point to the top of the column, the concentration being nearly constant above the feed point. Thus, the optimum point of introduction of either SFS or U-IV reductant should be about 6 ft above the bottom of the cartridge.

The use of SFS as a plutonium reductant in the IBX column is not recommended at this time because of its variable and unpredictable corrosion behavior. Stainless steel has been reported to corrode at rates on the order of 1 in/month at 60°C in synthetic IBX column solutions containing SFS, although such a vigorous corrosion was observed in only one of the pilot plant runs.

EXPERIMENTAL CONDITIONS

The pilot plant runs were carried out in three 3-in.-diameter glass pulse columns arranged in cascade series as shown in Figure 1. The first two columns simulated the Purex IBX-IBS system, the third was used to replenish the uranium in the IBU stream so it could be recycled as IBF. Typical stream compositions and flow rates for the Purex steady-state runs are presented in Table 1.

FIGURE 1

SCHEMATIC PULSE COLUMN LAYOUT - 3-IN. DIAMETER COLUMNS

TABLE 1

Stream	M U	M HNO ₃	M Fe ⁺⁺⁺	M SFS	M Sulfamic Acid	Flow Rate, Ml/min ^(a)
"HAF"	0.9	2.9	0.095 ^(b)	0	0	100
IBF	0.32	0.19	0	0	0	3560
IBXF	0.31	0.22	0	0	0	3770
IBU	0.31	0.13	0	0	0	3770
IBX	0	0.20	0	0	0.1	165
IBXP	0.12	2.25	(c)	(0.06)	(0.1)	170
IBXP-HNO ₃	0	10	0	0	0	55
IBS	0	0	0	0	0	207
IBSU	0.098	0.70	0	0	0	210
IBP	1.3×10^{-5}	3.4	(c)	(0.045)	(0.07)	225
IB-SFS	0	0	0	2.0	0	5.1

(a) These flow rates correspond to volume velocities of 1270 gph/ft² in the IBX column and 140 gph/ft² in the IBS column.

(b) Ferric ion was added to oxidize residual uranium-IV in the IBU before recycling it as IBF.

(c) Approximately 0.0025 M iron was found in representative column samples.

Two plate cartridges were used in the IBX column. The first simulated the present plant column and contained 19 ft of 4-in-spaced, 33% free area stainless steel sieve plates with 3/16-in holes. The cartridge also contained four 28% free area louver plates at about 4-ft intervals; each louver plate had six inches of free space on each side.

The second IBX cartridge contained 23% free area stainless-steel nozzle plates with 23% free area fluorothene plates inserted at intervals ranging from 8 inches at the bottom to 12 inches at the top. All plates contained 3/16-in-holes and were spaced 2 inches apart. (Four 28% free area louver plates were also inserted at 3.2, 6.7, 11.2, and 15.3 ft from the bottom; each had 6 inches of free space bounded by fluorothene plates on each side.) Both the top and bottom plates of the cartridge were fluorothene. If each section of plates bounded by a plastic plate is considered as a unit, the cartridge contained, in series from the bottom, four 8-in-long units followed by a louver plate, three 10-in-long units followed by a louver plate, four 10-in units followed by a louver plate, three 12-in units followed by a louver plate, and three 12-in units.

The IBS column contained a 10-ft-long cartridge of two-inch-spaced, 23% free area stainless steel sieve plates with 1/8-in holes, similar to that used in the Purex Plant.

Pulse amplitudes were 0.85 inches in the IBX column, 1 inch in the IBS and IIA columns. All columns were operated with top interface (organic phase dispersed) unless otherwise noted. The IBX column was operated at $50 \pm 5^\circ\text{C}$. The other columns were operated at ambient temperatures. A total of thirteen runs were made, including three with either the IBX or the IBS column operated alone. The runs were normally about six hours long.

CARTRIDGE DEVELOPMENT - PUREX CAPACITY STUDIES

A summary of the Purex capacity studies is presented in Table 2, below:

<u>Cartridge</u>	<u>TABLE 2</u>	
	<u>Flooding Threshold</u>	
	<u>Volume Velocity,</u> <u>GPH/Ft²</u>	<u>Frequency,</u> <u>Cycles/Min.</u>
Plant-type	680	55 ± 5
	960	45 ± 5
	1100 ± 110	40
New, mixed-plate	1000	90 ± 5
	1210	82 ± 5
	1620	77 ± 5

The flooding threshold obtained with the Plant-type cartridge was about 30% lower in this series of runs than previously reported^(1,2,3,). The discrepancy was attributed to poor solvent quality in the present series of runs. (The initial HAP used in these runs had been prepared from unwashed solvent several weeks prior to these runs.)

Flooding began near the bottom of the Plant-type cartridge. This observation, also reported for an ungraded, mixed-plate cartridge⁽²⁾, led to the design of the new graded, mixed-plate cartridge. The addition and variable spacing of the plastic plates resulted in moving the point of incipient flooding from the bottom to slightly above the middle of the column and permitted stable operation at flow rates at least 35% greater than allowed by the present Plant cartridge.

- (1) G. A. Nicholson, "Purex Pulse Column Studies with Hydrocarbon Diluent." HW-40550, July, 1956. (SECRET)
- (2) M. D. Alford, "Purex IBX Column Studies." HW-51931, Aug., 1957 (SECRET)
- (3) G. Jansen and G. L. Richardson, "Purex Pulse Column Studies-1960." HW-68846, Feb. 1961.

The performance of the new cartridge was characterized by very high dispersed phase holdup. In one stable run (made at 58 cycles/min, 1300 gph/ft²), the organic holdup increased from 20% at 3 ft from the bottom to 40% at 6 and 9 ft and to 70% at 12 and 16 ft. The magnitude of the holdup tended to cycle, a possible disadvantage because of its effect on static or differential pressure monitors. The cycling began at frequencies as much as 20 cycles/min from the assumed flooding threshold, increasing in severity as the flooding frequency was approached. It may have been accentuated or caused in part by over-reaction of the interface controller, which automatically controlled the position of the interface by controlling the IBXP flow rate.

The quality of the dispersion produced by the mixed-plate cartridge was only fair at high rates (≤ 1200 gph/ft²). The dispersed organic phase tended to coalesce into 1/4 to 1/2-in drops at the plastic plates. Most of the large drops were broken up into 1/8-in or smaller drops after passing through two nozzle plates, but a few of the larger drops could be seen throughout the column. At least part of the loss in efficiency due to large drop sizes should be recovered by the recurrent coalescing action of the plastic plates.

An attempt to measure the efficiency of the mixed-plate cartridge at high rates was made in Run 12. The flowsheet was adjusted to permit complete stripping of the uranium from the solvent (approximate IC column conditions: A/O flow ratio = 1, 52°C, 0.18M U in the feed, 0.01M HNO₃ in the strip). The overall uranium loss at 1835 gph/ft² was 4.3%, corresponding to an HTU of 4.6 ft; however, intermediate column samples gave HTU's in the range of 2 to 3 ft, indicating the presence of unstrippable uranium in the solvent. It would appear likely from the results of this test and from observations of nitric acid and uranium-IV behavior described later that HTU's of 3 ft and possibly as low as 2 ft are attainable.

THOREX CAPACITY STUDIES

The mixed-plate cartridge was also tested for use with a Thorex Flowsheet (uranium used as a stand-in for thorium). The feed to this run was the same as that used in the Purex IBX column runs. The IBX stream was water and the IBIX (entering 6 ft below the top of the cartridge) was 0.24 M HNO₃. The flow rates of the IBF, IBX, and IBIX streams were, respectively, 3230, 350, and 1360 ml/min, giving volume velocities of 1160 gph/ft² in the top section and 1600 in the bottom section of the column.

The column flooded at a frequency of 72 ± 4 cycles/min at 50C. Profile samples taken at 60 cycles/min showed dispersed phase holdups increasing from 40% at the 3 ft level to a maximum of 70% at the 12 ft level (just below the IBIX introduction point) and decreasing to 25% holdup at the top. The dispersion was relatively coarse; however, the water scrub effectively reduced the nitric acid concentration from 0.18M in the feed to 0.0005M in the IBU. The acid analysis in the IBU is of doubtful accuracy; but assuming it to be correct, this would correspond to a nitric acid HTU of 2 ft or less in the top six feet.

SFS AND URANIUM-IV BEHAVIOR IN THE IBX COLUMN

The path of SFS as a function of addition point to the IBX column was followed indirectly by U-IV analyses. The reaction

has been reported to proceed quantitatively with a sulfoxylate half-life of about 6 minutes under conditions of the pilot-plant runs⁽⁴⁾; however, no more than 30% of the SFS could be accounted for by this reaction from U-IV analyses of end stream and profile samples. (The samples were analyzed for U-IV within two hours of sampling by spectrophotometric techniques, and there was no evidence of concentration change on standing as long as 20 hours.) The poor material balance was assumed to be caused by side reactions of the SFS with impurities in the system. The uranium-IV analyses appeared to be consistent, despite the poor stoichiometry; and it is believed that the profiles shown below are representative of U-IV behavior in the IBX column.

TABLE 3U-IV PROFILE IN THE IBX COLUMN

	SFS Addition Point (a)				
	3 Ft	6 Ft		12 Ft	19 Ft
	50C	42C	53C	50C	52C
G/L U-IV in Aqueous at 0 Ft.	1.5	0.43	<0.1 ^(b)	<0.1 ^(b)	<0.1 ^(b)
" " " " " 3 "	1.5	0.96	0.35	<0.1	<0.1
" " " " " 6 "	0.15	2.3	1.8	<0.1	<0.1
" " " " " 9 "	0.15	0.37	0.49	1.1	<0.1
" " " " " 12 "	0.16	0.29	0.41	1.6	0.12
" " " " " 16 "	0.22	0.39	0.36	0.8	1.7
" " " " " 19 "	0.18	0.50	0.55	1.3	3.4
G/L U-IV in IBU	<0.01 ^(b)	0.11	0.12	0.20	0.12
% SFS accounted for:	(11) ^(c)	17	19	30	19

(a) Heights are measured from the bottom of the cartridge.

(b) Approximate lower limits of U-IV detection were 0.1 and 0.01 g/l in the aqueous and organic phases, respectively.

(c) Based on U-IV found in the IBXP. Other values based on U-IV in the IBU.

(4) J. E. Mendel, Unpublished data.

It is evident from the above data that the effect of SFS penetrated no more than about 6 ft below its addition point at the normal operating temperature of 50-53C. It was concluded that introduction of either SFS or U-IV at the 6-ft level would provide plutonium reduction power throughout the IBX column without excessive carryover of U-IV into the IBS column. The nine-ft level would be preferable for SFS addition at operating temperatures much below 50C.

U-IV HTU's of 1.5 to 2 ft were estimated from the U-IV profile analyses and U-IV distribution ratios measured in two of the runs. These distribution ratios ranged from 0.1 to 0.45 and averaged 0.22, a value that agrees well with published values(5).

A bottom-interface run was so made but is not included in the summary above. The SFS was introduced at the 9-ft level and U-IV concentrations of 0.018, 0.038, and 0.10 g/l were found in the solvent phase at 3, 6, and 9 ft from the bottom, respectively. An HTU of 3 ft or less was estimated from these analyses and from the IBXP analysis of <0.1 g/l U-IV. The dispersion was quite poor up to the flooding frequency of 105 cycles/min, and this type of operation is not recommended.

URANIUM-IV BEHAVIOR IN THE IBS COLUMN.

Under the operating conditions shown in Table 1, very little, if any, U-IV was found in the IBP - except under conditions in which appreciable U-IV was carried into the IBS column with the IBXP. The total amount of uranium found in the IBP (with the SFS added at or above the 6-ft level in the IBX column) varied from 0.0017 to 0.0055 g/l, corresponding to 0.007 to 0.04% of the total uranium in the IBXP and U-VI HTU's of 1.0 to 1.2 ft. About 0.1 g/l U-IV were found in the IBP with the SFS introduced at the 3-ft level.

The results, above, would not necessarily be typical of Plant runs because of the low pilot-plant volume velocity. To overcome this handicap, a separate IBS column run was made at flow rates more nearly corresponding to the Plant's operating volume velocity. The IBXP for this run contained 0.15M U, 4.2M HNO₃, and 0.1M sulfamic acid. The IBXP was divided in half and 0.05M SFS added to the second portion several hours before the run was made (0.039M U-IV was found by analysis). The column was operated at a volume velocity of 1560 gph/ft², an A/O flow ratio of 1.3, a temperature of 45-50C, and a frequency of 40 cycles/min. These operating conditions were near the limiting throughput rate for this cartridge, and mild cyclic local flooding occurred throughout the run. The total uranium in the IBP increased from 0.04 to 0.5% of the IBXP uranium when the SFS-containing portion of the feed was introduced. The uranium in the latter IBP was essentially all U-IV and amounted to 2.1% of the U-IV in the feed. The corresponding HTU's for U-IV and U-VI were estimated to be 1.6 and 1.3 ft, respectively, assuming an average U-IV distribution ratio of 2.6(5).

(5) H. A. C. McKay, R. J. W. Streeton, A. G. Wain, "Mixer-Settler Runs to Study Uranium (IV) as a Reductant in Uranium/Plutonium Separation." AERE-R-4381, 1963.

SFS CORROSION OF STAINLESS STEEL

An unsuspected corrosion problem was discovered in Run 9, the first attempt to run a bottom-interface IBX column. After running about one hour, a vigorous reaction was observed at or just above the SFS feed point. The reaction was characterized by greatly accelerated U-IV production and the evolution of a colorless, odorless gas. The reaction subsided as soon as the SFS flow was stopped and started again within ten minutes after the SFS flow was resumed. Subsequently, the stainless steel plates and spacers were found to be severely pitted and stainless steel components - iron, chromium, and nickel - were identified in the highly colored IBXP. The run was repeated several days later with no evidence of the corrosion reaction.

The pilot plant results have been confirmed by J. E. Mendel. He has reported stainless steel corrosion rates at 60C on the order of about 1 in/month (and as high as 3.6 in/month) in contact with IBXP containing SFS⁽⁴⁾. The reaction proceeded at about the same rate in the presence or absence of uranium and sulfamic acid. Corrosion is believed to be induced by SFS reduction of the passive oxide film. The unprotected stainless steel would then be attacked by acid, liberating hydrogen. The active metal should also be effective in reducing uranyl ion, as observed in the pilot plant run.

At this time, the variable and unpredictable nature of SFS corrosion prohibits its use in stainless steel equipment.