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Chemistry-Separation Processes
for Plutonium and Uranium
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Performance of the TBP Process for Aluminum Fuels
Idaho Chemical Processing Plant
1955-1956

K. L. Rohde

January 30, 1958

AEC RESEARCH AND DEVELOPMENT REPORT

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PHILLIPS PETROLEUM CO.
ATOMIC ENERGY DIVISION
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PERFORMANCE OF THE TBP PROCESS FOR ALUMINUM FUELS

IDAHO CHEMICAL PROCESSING PLANT

1955-1956

by

K. L. Rohde

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PERFORMANCE OF THE TBP PROCESS FOR ALUMINUM FUELS

IDAHO CHEMICAL PROCESSING PLANT
1955-1956

by

Kenneth L. Rohde

A B S T R A C T

Observations of the performance of the Idaho Chemical Processing Plant as modified for continuous dissolution and TBP 1st cycle extraction, as to process chemistry and process engineering are reported for the initial plant scale, full irradiation level operating run. As-operated flowsheets, the results of plant scale tests of the continuous dissolver, and fission product decontamination data are emphasized.

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PERFORMANCE OF THE TBP PROCESS FOR ALUMINUM FUELS

IDAHO CHEMICAL PROCESSING PLANT
1955-1956

by

Kenneth L. Rohde

1. INTRODUCTION1.1 Purpose of This Report

It is the intention of this document to make available at an appropriate classification level the bulk of the experimental, plant assistance, and process evaluation experience gained by the CPP Technical Branch from work with the Chemical Plant Modification (CPM) during the 1955-1956 period of startup and processing. It is anticipated that this record will be useful for evaluation of the TBP-Hexone process for enriched uranium-aluminum reprocessing. A somewhat more detailed document⁽¹⁾ has already been published which included some additional material which is not of general interest.

1.2 The Chemical Plant Modification

This new headend system designated as the CPM or Chemical Plant Modification System, which consists of continuous dissolvers, one TBP solvent extraction cycle, solvent wash system, and aqueous waste concentration facilities, was designed to provide the Idaho Chemical Processing Plant (ICPP) with an improved facility for processing enriched uranium-aluminum alloy fuels. The design flowsheet provided for the daily processing of the uranium associated with 370 kilograms of aluminum. Since the diluent metal; i.e., the alloying aluminum, cladding or structural pieces, actually determined the limiting processing rate*, the uranium rate varies with fuel composition and burnup.

The CPM system also involved two major innovations, the continuous dissolvers and the dual solvent (one TBP cycle and two Hexone cycles) extraction chain, and therefore offered opportunity for plant-scale evaluation of these processes.

The basic design data and operating procedures are given in the architect-engineers operating manual⁽²⁾.

*In some equipment geometry criticality may be significant, but in general the bulk and physical properties of aluminum and its compounds are capacity limiting.

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1.3 Outline of the Process

1.31 Continuous Dissolution and Feed Adjustment. Enriched uranium-aluminum alloy fuels are charged semi-continuously to the top of the dissolvers while acid and catalyst, metered separately, are pumped in the bottom. Operation is thus countercurrent with the full slug bed submerged in acid or foam. Product overflows at the top of the slug pack and the vapors are condensed and returned to the dissolver feed stream.

The density of the flowing stream of dissolver product is recorded continuously and this record is used to indicate the need for minor changes in dissolution rate, which are effected by changing the catalyst injection rate. The dissolver product is accumulated in either of two collection tanks where the batch density, acidity, uranium concentration, and volume are determined. From these tanks, the feed is jetted to the feed tank from which it is metered into the headend evaporator. In this headend evaporator, the scrub column raffinate, IBR, is blended with the fresh feed and these streams concentrated to column feed (IAF) specifications.

1.32 Solvent Extraction. The three major columns in the cycle are pulsed sieve-plate columns. A simple extraction column is used with 4-1/2 percent TBP in Amsco 125-90W solvent. The separate scrub column uses 0.7M aluminum nitrate scrub. Stripping is accomplished in the third column with dilute (0.02N) nitric acid.

A packed column is provided for washing the strip column product with Amsco diluent for the removal of traces of TBP from the product prior to evaporation. A steam stripper is also provided for removal of TBP and other organics. The uranium-bearing strip solution is concentrated in the first cycle product evaporator to make feed for the second cycle.

1.33 Process Solvent Recycle. The strip column organic raffinate, ICR, is washed in three successive mixer-settlers with dilute nitric acid, sodium carbonate solution, and dilute acid. The recovered solvent is recycled.

1.34 Aqueous Waste Concentration. The first cycle aqueous raffinate, IAR, and the spent washes from the first two solvent wash mixer settlers are concentrated together continuously and then transferred to permanent storage.

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2. PROCESS FLOWSHEETS

2.1 Introduction and Description of Flowsheets

There has been a series of process flowsheets (formal statements of the plant material balances) from which operating flows and stream compositions have been derived. The architect-engineers flowsheet was developed from the fundamental work done by ORNL and the CPP Technical Branch. This work is reported in the Operating Manual⁽²⁾, and various topical and summary reports of the CPP Technical Branch. Two topical reports⁽³⁾ ⁽⁴⁾ describe the development work for the continuous dissolver. The solvent extraction work is given in several summary reports.⁽⁵⁾ ⁽⁶⁾

The design flowsheet, Figure 1, and Tables 1A, 1B, and 1C have been the basis for the several actual operating flowsheets for the TBP process dissolution and first cycle. Typical of these is the solvent extraction flowsheet for processing MTR elements shown in Figure 2. Second and third cycle design and as-operated flowsheets for various materials are essentially identical and are represented by Table 2 and Figure 3.

2.2 Modifications of the Design Flowsheet

There were several modifications made in the design flowsheet prior to and during the early stages of operation. Each of these is discussed below.

2.21 Use of an Alternate Solvent Diluent. After the design flowsheet had been written, the superior stability of Amsco 125-90W dictated its substitution for the original diluent, Shell Spray Base. Because the former diluent has a density of 0.763 contrasted to 0.811 for Shell Spray Base, there was a minor change in column hydraulics. This factor may have contributed to some of the early difficulties which were experienced in obtaining inter-column flow. It was not felt that the change in diluent would be accompanied by any deleterious change in the chemical behavior of the system.

2.22 Reduction in the Scrub Column Flow Ratio and the Use of Acid-Deficient Scrub. Study of the scrub column design indicated that a scrub of 0.2N acid-deficient aluminum nitrate at one-half the design flow ratio would approximate the acid removal efficiency of the design scrub column. This change was successfully used for a cold processing run. With the first processing of irradiated feed, it was necessary to remove the ammonia from the scrub to avoid the storage of ammonium nitrate in the raffinate storage tanks. Therefore, the design scrub flow ratio was used (Table 1). Following the study of two sets of decontamination data,

FIGURE 1

DISSOLUTION AND SOLVENT EXTRACTION FLOW DIAGRAM FOR CPM FIRST CYCLE

Figure 2

FIRST CYCLE SOLVENT EXTRACTION FLOWSHEET FOR MTR ELEMENTS
BASIS: 1 kg OF URANIUM, 25% BURNUP

CPR-S-700

Figure 3

Table 1A

DISSOLUTION AND SOLVENT EXTRACTION FLOWSHEET FOR FIRST CYCLE

Fuel Charge (Nominal): 15,545 grams aluminum and 1042 grams uranium per hour

	Dissolver Reagent	Diss. Solution	Fresh Feed ⁽¹⁾	Evap. Feed	Evaporator Product to Extraction Column 1AF	Extractant 1AX	Solvent Product 1AU	Extraction Raffinate 1AR	Scrub 1BS	Scrubbed Solvent 1BU	Scrub Waste 1BR	Strip Reagent 1CX	Aqueous Product 1CU 1DU	Stripped Solvent 1CR	Diluent Wash 1DS	Waste Diluent 1DR	Concentrated Product 1LAF
Flow, Liters/Hour	500	480	503	756	501	501	501	499	251	501	253	201	201	501	20.0	20.0	2.95
Density, g/cc	1.177	1.223	1.213	1.18	1.27	0.811	0.822	1.27	1.11	0.816	1.11	1.0	1.009	0.812	0.804	0.805	1.488

Composition:

Uranium, g/l		2.17	2.07	1.38	2.07		2.07	$< 2 \times 10^{-4}$		2.07			5.20	$< 2 \times 10^{-4}$			353
Aluminum Nitrate, <u>M</u>		1.2	1.14	1.0	150			1.51	0.7		0.694						
Nitric Acid, <u>N</u>	5.60	1.0	0.95	0.70	1.05		0.0956	0.96		0.002	0.19		0.005				0.339
Mercuric Nitrate, <u>M</u>	0.005	0.005	0.005	0.003	0.005			0.005									
Tributyl Phosphate, Volume Percent						4.5	4.5			4.5					0	0.1	

(1) Jet dilution taken as 4 weight percent of stream transferred.

Table 1B

SOLVENT RECOVERY FLOWSHEET FOR FIRST CYCLE

	Stripped Solvent 1CR	First Wash	Second Wash	Third Wash
Flow, Liters/Hour	501.2	50.1	50.1	50.1
Density, g/cc	0.812	1.05	1.00	1.004

Composition:

Nitric Acid, <u>N</u>				
Sodium Carbonate, <u>M</u>		0.5		
Sodium Hydroxide, <u>N</u>				0.1
Tributyl Phosphate, Volume Percent	4.5			

Table 1C

RAFFINATE CONCENTRATION FLOWSHEET FOR FIRST CYCLE

	Extraction Raffinate 1AR	First Solvent Wash	Evap. Feed	Conc. Waste 1ARM	Conc. Waste As Stored
Flow, Liters/Hour	499.0	50.1	548	323	342 ⁽¹⁾
Density, g/cc	1.27	1.05	1.25	1.42	1.4
Freezing Point, °C.				35	30

Composition:

Nitric Acid, <u>N</u>	0.96		0.78	1.3	1.25
Aluminum Nitrate, <u>M</u>	1.51		1.37	2.3	2.2
Sodium Carbonate, <u>M</u>		0.5			
Sodium Nitrate, <u>N</u>			0.09	0.15	0.15
Mercuric Nitrate, <u>M</u>	0.005		0.005	0.008	0.008

(1) 4 weight percent jet dilution.

Table 2

SOLVENT EXTRACTION FLOWSHEET FOR SECOND AND THIRD CYCLES

	2nd Cycle Feed 11AF	2nd Cycle Solvent Product 11AP	2nd Cycle Aqueous Product 11BP	3rd Cycle Feed 111AF	3rd Cycle Solvent Product 111AP	3rd Cycle Aqueous Product 111BP	Concentrated Product	2nd-3rd Cycle Extractant 11AX 111AX	2nd Cycle Scrub 11AS	2nd-3rd Cycle Strip Reagent 11BX 111BX	3rd Cycle Scrub 111AS	2nd Cycle Aqueous Waste 11AR	3rd Cycle Aqueous Waste 111AR	2nd-3rd Cycle Waste Solvent 11BR 111BR
Flow, Liters/Hour	2.95	16.6	4.85	2.95	16.6	4.85	2.95	16.6	13.7	4.44	13.7	16.6	16.6	16.2
Density, g/cc	1.488	0.893	1.293	1.479	0.893	1.293	1.479	0.800	1.283	1.0024	1.271	1.236	1.224	0.800
<u>Composition:</u>														
Uranyl Nitrate, <u>M</u>	1.5	0.27	0.92	1.5	0.27	0.92	1.5							
Aluminum Nitrate, <u>M</u>									1.80		1.80	1.49	1.49	
Nitric Acid, <u>N</u>	0.34		0.033	0.055		0.033	0.055			0.04				
Ammonia, <u>N</u>									0.32		0.26	0.20	0.20	
Ammonium Nitrate, <u>N</u>												0.06	0.01	
Ferrous Sulfamate, <u>M</u>									0.05					

it was judged that the 1B scrub column was not contributing significantly to the decontamination in the first cycle and, therefore, the scrub column flow ratio was reduced to $A/O = 0.25$. Currently, it appears that this scrub ratio is adequate with the present 1B column chemistry.

2.23 Nitric Acid in the First Cycle C Column Extractant. Pilot plant data obtained after the initial flowsheet design demonstrated that the use of a very dilute acid strip solution (a ICX of 0.02N nitric acid instead of water) would both decrease the column HTU and help prevent the precipitation of interfacial crud. This change was made immediately at start-up.

2.24 Reduced Product Concentration. Early in the processing, it was discovered that the accumulation of insolubles in the first cycle product (IIAF) led to plugging of the outlet pumps from the evaporator. (Silica from the makeup water was identified as one component of the precipitate.) The use of a 0.55M uranium product instead of a 1.5M product was resorted to in order to decrease build-up and flush out the evaporator. This necessitated the use of more concentration scrub solution in the second cycle A column to maintain salting strength.

2.25 Change in Streams in the Solvent Wash System. Early in the operation, a precipitate formed in the first mixer-settler which plugged both the box inlet and outlet. When the precipitate was identified as containing basic compounds of aluminum (and iron) it was considered necessary to use the sodium carbonate wash in the second mixer-settler using only dilute (0.04N) nitric acid in the first. Dilute acid was also used in the third mixer-settler instead of 0.1N caustic. The underflow from the second mixer-settler was then routed to the raffinate evaporator and stayed in the system. Although the operating condition that led to this situation; i.e., the flow of process feed through a vent or interface jet line which drained to the mixer-settler manifold, was alleviated, the modified mixer-settler arrangement was maintained for the duration of the run.

2.26 Reduction in IARm Density and Freezing Point. The preparation of a concentration waste of 1.42 g/cc density (freezing point 35°C) as indicated in the design flowsheet was a significant departure from previous ICPP operating experience; most especially since the concentrate was to be removed from the evaporator by pumps rather than jets. In order to avoid plugging of the pumps, the evaporator density specification was placed at 1.35 g/cc at 25°C which would yield a freezing point of about 10°C.

2.27 Reduction in IDS Flow. The ID column, wherein the uranium containing strip solution is scrubbed with pure diluent to remove TBP, was found in an initial study to be considerably oversized on the basis of TBP removal. Therefore, when difficulty was experienced with the incinerator designed to burn the IDR stream, the flow ratio of the

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IDS was cut to 50 percent of the design value. Fundamental data on the behavior of the components other than TBP in this system are lacking and the most effective use of this column and the steam stripper is dependent on further development.

2.28 Evaporatorless Flowsheet. The feed evaporator indicated on the flowsheets shown in Figures 1 and 2 consists of a continuous evaporator to blend and concentrate IBR and fresh feed for IAF. Difficulties in operation of this evaporator caused by the maloperation of the associated feed and underflow pumps led to a trial of a flowsheet in which the evaporator was not heated in order to simulate the conditions which would exist in its absence. This flowsheet, while shown to be operable, was plant-tested for only 16 hours.

3. CONTINUOUS DISSOLUTION

3.1 Plant Performance

The continuous dissolver as used for the several fuels proved to be an exceptionally effective device. No difficulties were experienced in operation and the only equipment failure associated with the dissolver was the corrosion failure of the inadequately constructed catalyst feed pumps.

Control of dissolver solution concentration by variation in rate of catalyst injection into the constant acid feed stream was very successful. As will be shown later, the dissolution rate was slightly less sensitive to catalyst concentration in the plant processing than in the pilot plant studies; however, there was still ample dependency for control. In actual practice, the operating point on the dissolver solution continuous density recorder was selected by correlation with the analysis of grab or batch samples. Only minor and infrequent adjustments in catalyst rate were required to produce constant quality feed with constant metal feed composition. The average aluminum concentration of forty-one dissolver product batches collected during the earliest processing was 1.27M with extremes of 1.12M and 1.42M. This average was six percent greater than flowsheet indicating a small bias in the density control point. The extreme values, while representing a ± 12 percent deviation in aluminum concentration, were equivalent to a density deviation of only ± 0.02 g/cc.

The fuel level monitor, a partially shielded ion chamber which was designed to traverse the length of the dissolver and record the radiation level, proved very satisfactory. The device was calibrated by noting the trace developed when the large diameter portion of the dissolver was full of fuel. It was found that the midpoint of the uppermost drop off in radiation intensity represented the top of the fuel pack*.

*Analogous to the location of the half-wave potential in polarography.

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There was also a significant fall off in radiation at the bottom of the dissolver corresponding to the location of the less-irradiated cores of the fuel.

In general, rigid control of the pack height was not required during this processing since the flooded portion of the dissolver was operated full. Reduced catalyst was used instead of reduced surface area to control the rate. However, it was convenient to have an indication of fuel element height on those occasions when the precalculated charging rate diverged from the dissolution rate.

3.2 Operating Variables Studied in the Plant

The several variables involved in continuous dissolver operation have been studied in the pilot plant⁽³⁾. It has not been possible in the production plant to study each of the variables in great detail; however, enough runs were made under controlled conditions to show that the 7-1/2 inch diameter plant dissolver had operating characteristics similar to the 2-inch diameter⁽³⁾ and 5-inch diameter⁽⁴⁾ pilot plant dissolvers. Similar variation of dissolution rate with acid feed rate and catalyst feed rate were shown in the plant dissolvers as in the pilot plant. The scaleup factor was extended to include the plant dissolver by study of the dissolution of aluminum rod stock in all three sizes of dissolvers.

3.21 Dissolution Rate Scaleup from Pilot Plant Dissolvers. In order to confirm the reliability of the extrapolation of pilot plant data to the plant continuous dissolver, data from dissolution of extruded aluminum rod in the three dissolvers were compared as shown in Figure 4. The dissolvers were the 2-inch diameter⁽³⁾ and 5-inch diameter pilot plant dissolvers⁽⁴⁾ and the 7-1/2 inch diameter plant dissolver. All reagent feeds were 5.6N nitric acid and all the results were normalized to 0.005M mercuric nitrate catalyst concentration. Aluminum rod stock used extensively for dissolver startup testing is the only material which has been processed in all three dissolvers and thus represented the only opportunity for scale-up verification.

Analysis of the data from the three dissolvers at rates up to 16 kg of aluminum/(day)(in.²) indicates that there is no significant difference among the three dissolvers when rates are considered on the basis of cross-sectional area. The slopes of the curves for the two larger dissolvers differ by less than 2 percent. Therefore, properly normalized data from the several dissolvers may be compared on this basis.

3.22 Effect of Acid Feed Rate on Dissolution Rate. The pilot plant experience indicated that at constant catalyst concentration (m_f) (moles mercuric nitrate per liter), the dissolution rate for aluminum-uranium alloys (R_a , kg Al/(day)(in.²) was proportional to the 0.8 power

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of the acid feed rate (N, moles per hour). In the plant dissolver, it was shown that the dissolution rate was proportional to the 0.77 and 0.78 power of the acid feed rate for aluminum rod stock and unirradiated fuels, respectively. Irradiated cast alloy showed a rate dependent on the 0.7 power of the acid feed rate. It was concluded that this correlation was generally applicable to the plant dissolver. This information is shown in Table 3 with the applicable acid feed rate ranges.

3.23 Effect of Catalyst Concentration on Dissolution Rate. Similarly, the pilot plant data showed that at constant acid feed rate, the dissolution rate was proportional to the 0.33 power of the catalyst concentration. In the plant dissolver, it was shown that the dissolution rate was proportional to the 0.3 power, and to the 0.2 power, of the catalyst concentration for the dissolution of aluminum rod stock and unirradiated alloy, respectively. Irradiated cast alloy of composition B showed a rate proportional to the 0.2 power of the catalyst concentration. The agreement between the rate effect for the aluminum rod stock in the plant dissolver and the alloy in the pilot plant is excellent. The cast unirradiated alloy of composition A and cast irradiated alloy of composition B appear to be slightly less sensitive to catalyst than the other alloys. The range of catalyst concentrations used is shown in Table 3.

Table 3

Dependence of Dissolution Rate on Catalyst Concentration and Acid Feed Rate
Continuous Dissolution of Aluminum and Aluminum-Uranium Alloy in Nitric Acid

Metal	Dissolver	Catalyst Range M	Catalyst Dependency $Ra = K_1(m_f)^x$ Where x is	Acid Feed Rate Range moles/hour Per in. Cross-Section	Acid Feed Dependency $Ra = K_2N^y$ Where y is
Extruded Aluminum	Plant	0.0006 - 0.0013	0.3	32 - 48	0.8
Cast U-Al Alloy Composition A	Plant	0.0005 - 0.0028	0.2	29 - 64	0.8
Extruded U-Al Alloy Composition B	Pilot	0.0005 - 0.005	0.33	16 - 120	0.8
	Plant	0.005 - 0.1	0.0		
Cast U-Al Alloy Composition B	Pilot	0.005 - 0.015	0.33	16 - 120	0.8
	Plant	0.015 - 0.05	0		
Irradiated Cast U-Al Alloy Composition B	Plant	0.02 - 0.045	0.2	23 - 64	0.7

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3.24 Effect of Fuel Burnup on Dissolution Rate. It has been shown in previous work on batch dissolution that irradiated extruded and cast alloy dissolved significantly slower than the corresponding unirradiated material(7). To test this effect in the continuous dissolver, three batches of alloy fuel, each of limited burn-up range, were isolated and each batch dissolved continuously at the same nominal aluminum dissolution rate. Catalyst was metered in each case to produce 1.2M aluminum nitrate in the dissolver product. The variation in catalyst requirement is shown in Table 4.

TABLE 4

Catalyst Concentration Required for Continuous Dissolution of Cast Uranium Aluminum Alloy of Varying Nominal Burnup

<u>Percent of Standard Uranium Burnup</u>	<u>Mercuric Nitrate Catalyst Concentration M</u>
113	0.041
87	0.043
53	0.036
0	0.012*

*Pilot plant data.

Burnup does not apparently limit the dissolver capacity. Almost equivalent maximum rates were obtained with irradiated alloy as with the unirradiated alloy. This maximum rate was maintained with the irradiated alloy only through the use of significantly larger quantities of catalyst; i.e., 0.012M mercuric nitrate catalyst for unirradiated alloy as compared to of the order of 0.035M catalyst for irradiated alloy.

3.3 Dissolver Off-Gas Composition

The continuous dissolver off-gas composition is of interest for the following reasons:

1. The presence of some hydrogen in plant batch dissolution and pilot plant continuous dissolution off-gas has raised the question of off-gas flammability.

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2. The off-gas composition reflects the reaction stoichiometry and thus might yield some information on the dissolution reaction mechanism.

To date, the only off-gas samples taken were from aluminum rod dissolution at the rate of 140 kg of aluminum per day (Table 5). Air dilution was found to be very large and did prevent the hydrogen content of the off-gas from being in the flammable region. The dilution was too great to yield any precise information on the reaction stoichiometry except that the proportions of various reactions making up the overall reaction were equivalent to those found in the pilot plant(3).

TABLE 5

Continuous Dissolver Off-Gas Analyses

Metal: 2S Aluminum
Acid Feed: 5.6N HNO_3
Dissolver Solution: 2.0N HNO_3 , 1.02 $\text{Al}(\text{NO}_3)_3$

	Volume Percent H_2 Unadjusted	Volume Percent (Water and Air Free Basis)			
		N_2O	NO	NO_2	H_2
Maximum	1.6	37	66	8	6
Minimum	0.4	25	62	3	1
Average	0.9	30	56	5.4	2.8

4. SOLVENT EXTRACTION4.1 The Two-Solvent System

The use of one-solvent extraction cycle with TBP as the uranium extraction agent followed by two cycles using Hexone represents a considerable departure from previous practice. This innovation seemed justified for the CPM system at ICPP since the TBP headend would permit the use of acidic feeds and would yield more throughput for given size column. It was reasoned that the use of two solvents might make possible a broader attack on the problems of fission product decontamination, perhaps suggesting a means of processing more highly irradiated and shorter-cooled fuels in the traditional three cycles of solvent extraction. Historically, the principal decontamination problems in the three-cycle Hexone system involved ruthenium removal. Three Hexone cycles have dependably produced a decontamination factor of 2×10^6 for gross beta with no obvious increase in cases of high irradiation or shorter cooling. To date, the CPM system

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has shown little better performance in decontamination although as will be seen here, the products were generally very satisfactory. Reference to the various flowsheets used and the decontamination factors experienced also suggests that the first cycle scrub column was not being used at maximum effectiveness and that some improvement might be easily obtained.

4.2 Fission Product Decontamination

4.21 Plant Data

4.211 Sampling Scheme for Columns. The CPM first cycle was equipped with samplers on each of the feed vessels as well as the following flowing streams: IAR, IBR, ICR, and IDP. Referring to the design flowsheet, Figure 1, it may be seen that these samples were inadequate to give directly a complete picture of the efficiency of each of the systems components. Because it seemed highly desirable to evaluate separately the efficiency of the first cycle scrub column, the IAP uranium and fission product composition was obtained by material balance with the IBR, ICR, and IDP. This balance made possible the calculation of IB column decontamination factors. Similarly, with the IAF being a composite of the fresh feed and IBR, the IAF composition could be obtained by material balance. A problem of definition and interpretation enters here since a decontamination factor based on the ratio IAF/IAP, while revealing the efficiency of the column, would not show a correct process decontamination factor from the feed. Similarly, a decontamination factor based on the ratio fresh feed/IAP would give a correct value for the overall process but peculiar results in cases of high fission product reflux via the IBR. The latter method was used to yield a proper overall process picture; i.e., the overall and incremental decontamination factors are compatible, at the expense of some superficial misrepresentation of zirconium behavior in the extraction column.

4.212 Analyses of Plant Samples. Five sets of samples were taken in the course of the processing runs to define the decontamination efficiency of the system. The first set was taken somewhat early in the run and the samples were analyzed only for gross beta and gamma. The samples from later sets were analyzed for both total beta and gamma, as well as ruthenium and zirconium. In several sets, enough plutonium analyses were made to trace the course of plutonium through the system. The complete analytical results and calculations are given in Tables 6 through 10. Where quantitative results are given for zirconium and ruthenium analyses, the analytical procedures involved carrier isolation of the specific fission product and counting. Very frequently gamma scintillation spectrometer scans were used to indicate the relative amounts of ruthenium, zirconium-niobium, cerium, and cesium in the various streams. These results are reported qualitatively.

All columns were operated at 25-30°C.

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Table 6

ANALYSIS OF PLANT FLOWING STREAMS AFTER 4 DAYS OF OPERATION

Feed was prepared from irradiated uranium-aluminum alloy, > 300-day cooled

Stream	Relative Flow Rate	Uranium g/l	Beta Activity		Gamma Activity (Ion Chamber)	
			Cts/(Min)(ML)	Cts/(Min)(gU)	μg Ra Equiv/ML	μg Ra Equiv/gU
Fresh Feed	1.00	1.48	3.14×10^9	2.1×10^{12}	2820	1.9×10^6
1st Cycle Product	0.42	2.07	4.23×10^5	2.0×10^8	6.6	3.2×10^3
2nd Cycle Product	0.012	107	2.60×10^5	2.4×10^6	0.53	5.0
3rd Cycle Product	0.009	41	1.17×10^4	2.0×10^5	0.063	1.6

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Table 7

ANALYSIS OF PLANT FLOWING STREAMS AFTER 9 DAYS OF OPERATION

Feed was prepared from irradiated uranium-aluminum alloy, > 300-day cooled

Stream	Relative Flow Rate	Uranium g/l	Beta Activity		Gamma Activity				Ruthenium Beta		Zirconium Gamma	
			cts/(min)(ml)	cts/(min)(gU)	Scintillation Counter		Ion Chamber		cts/(min)(ml)	cts/(min)(gU)	cts/(min)(ml)	cts/(min)(gU)
					cts/(min)(ml)	cts/(min)(gU)	ug Ra equiv/ml	ug Ra equiv/gU				
Feed	1.00	1.76	3.75×10^9	2.13×10^{12}	1.21×10^9	6.8×10^{11}	1.84×10^3	1.04×10^6	1.15×10^8	6.54×10^{10}	1.17×10^8	6.65×10^{10}
1AR	1.04	1.6×10^{-3}	3.60×10^9		1.16×10^9		1.76×10^3		1.10×10^8		1.12×10^8	
1AP	1.04	1.89	4.67×10^7	2.47×10^{10}	4.87×10^7	2.57×10^{10}	1.67×10^2	8.82×10^4	1.20×10^4	6.34×10^6	2.54×10^7	1.34×10^{10}
1BR	0.52	0.40	9.27×10^7		9.69×10^7		3.20×10^2		1.64×10^4		5.02×10^7	
1DP	0.42	3.25	5.91×10^5	1.82×10^8	5.58×10^5	1.72×10^8	4.59	1.41×10^3	9.88×10^3	3.04×10^6	3.4×10^5	1.1×10^8
11BP	0.012	56.6	5.65×10^4	1.00×10^6	7.05×10^4	1.24×10^6	0.209	3.7	1.2×10^4	2.1×10^5	2.23×10^4	4.57×10^5
111BP	0.009	83.0	5.77×10^4	6.88×10^5	6.88×10^4	8.22×10^5	0.044	0.53	1.12×10^4	1.34×10^5	1.27×10^3	1.52×10^4

Table 8

ANALYSIS OF PLANT FLOWING STREAMS AFTER 47 DAYS OF OPERATION

Feed was prepared from irradiated uranium-aluminum alloy, > 300-day cooled

Stream	Relative Flow Rate	Uranium g/l	Beta Activity		Gamma Activity				Ruthenium Beta		Zirconium Gamma		Plutonium	
			cts/(min)(ml)	cts/(min)(gU)	Scintillation Counter		Ion Chamber		cts/(min)(ml)	cts/(min)(gU)	cts/(min)(ml)	cts/(min)(gU)	d/(min)(ml)	d/(min)(gU)
					cts/(min)(ml)	cts/(min)(gU)	µg Ra equiv/ml	µg Ra equiv/gU						
Feed	0.96	1.74	2.83×10^9	1.63×10^{12}	1.04×10^9	5.98×10^{11}	1.23×10^3	7.07×10^5	6.0×10^7	3.45×10^{10}	5.57×10^7	3.20×10^{10}	2.92×10^5	1.68×10^8
1AU	1.00	1.78	1.13×10^8	6.35×10^{10}	1.24×10^8	6.97×10^{10}	424	2.38×10^5	9.92×10^4	5.57×10^7	8.57×10^7	4.81×10^{10}	3.71×10^5	
1AR	1.00	5×10^{-5}	3.42×10^9		1.17×10^9		1.44×10^3		8.52×10^7		7.61×10^7		550	
1BR	0.25	0.43	4.28×10^8		4.74×10^8		1.61×10^3		2.6×10^5		3.29×10^8		4.43×10^5	
1DU	0.40	3.44	1.63×10^7	4.74×10^9	1.57×10^7	4.56×10^9	51.7	1.50×10^4	8.57×10^4	2.49×10^7	8.67×10^6	2.52×10^9	6.51×10^5	1.89×10^8
1CR	1.00	5×10^{-5}	2.53×10^5		2.66×10^5		0.97							
Recovered Solvent			1.65×10^3		1.61×10^3		0.0091							
11BU	0.012	124	3.90×10^5	3.14×10^6	5.13×10^5	4.13×10^6	2.07	16.7	5.37×10^4	4.32×10^5	4.37×10^5	3.52×10^5		
111BU	0.009	146	1.79×10^4	1.23×10^5	1.05×10^5	7.20×10^5	0.04	0.27	3.05×10^3	2.09×10^4	550	3.77×10^3		

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Table 9

ANALYSIS OF PLANT FLOWING STREAMS AFTER 67 DAYS OF OPERATION

Feed was prepared from irradiated uranium-aluminum alloy, > 300-day cooled

Stream	Relative Flow Rate	Uranium g/l	Beta Activity		Gamma Activity				Ruthenium Beta		Zirconium Gamma		Plutonium	
			cts/(min)(ml)	cts/(min)(gU)	Scintillation Counter		Ion Chamber		cts/(min)(ml)	cts/(min)(gU)	cts/(min)(ml)	cts/(min)(gU)	d/(min)(ml)	d/(min)(gU)
					cts/(min)(ml)	cts/(min)(gU)	ug Ra equiv/ml	ug Ra equiv/gU						
Feed	1.05	1.25	4.33×10^9	3.46×10^{12}	1.31×10^9	1.05×10^{12}	1.78×10^3	1.42×10^6	9.04×10^7	7.23×10^{10}	3.23×10^7	2.58×10^{10}	1.14×10^6	9.12×10^8
LAP	1.00	1.30	1.72×10^8	1.32×10^{11}	1.71×10^8	1.32×10^{11}	619	4.76×10^5	6.91×10^4	5.32×10^7	1.13×10^8	8.69×10^{10}	8.48×10^5	
LAR	1.00	2.2×10^{-4}	5.62×10^9		1.76×10^9		1.75×10^3		1.40×10^8		3.50×10^7		1.28×10^5	
LBR	0.25	0.29	6.75×10^8		6.77×10^8		1.97×10^3		2.24×10^5		4.50×10^8		6.41×10^5	
LDP	0.40	2.83	5.57×10^6	1.97×10^9	5.50×10^6	1.94×10^9	32.1	1.13×10^4	3.27×10^4	1.16×10^7	3.61×10^6	1.28×10^9	1.72×10^6	6.08×10^8
LCR	1.00	1.6×10^{-4}	2.32×10^5		2.23×10^5		1.14×10^2							
Recovered Solvent			3.32×10^3		2.49×10^3		0.045							
11BP	0.010	68.7	9.57×10^5	1.39×10^7	8.46×10^5	1.23×10^7	3.30	48.0	6.25×10^4	9.10×10^5	4.71×10^5	6.86×10^6		
111BP	0.0068	118	7.34×10^4	6.22×10^5	1.22×10^5	1.03×10^6	0.076	0.64	5.77×10^4	4.89×10^5	801	6.79×10^3		

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Table 10

ANALYSIS OF PLANT FLOWING STREAMS AFTER 100 DAYS OF OPERATION

Feed was prepared from MTR elements, 25 percent burnup and 300 days cooled

Stream	Relative Flow Rate	Uranium g/l	Beta Activity		Gamma Activity				Ruthenium Beta		Zirconium Gamma	
			cts/(min)(ml)	cts/(min)(gU)	Scintillation Counter		Ion Chamber		cts/(min)(ml)	cts/(min)(gU)	cts/(min)(ml)	cts/(min)(gU)
					cts/(min)(ml)	cts/(min)(gU)	µg Ra equiv/ml	µg Ra equiv/gU				
Feed	0.96	1.66	8.12×10^9	4.89×10^{12}	2.71×10^9	1.63×10^{12}	4.25×10^3	2.56×10^6	2.38×10^8	1.43×10^{11}	1.14×10^8	6.87×10^{10}
1AP	1.00	1.66	1.40×10^8	8.43×10^{10}	1.23×10^8	7.41×10^{10}	294	1.77×10^5	4.71×10^5	2.84×10^8	7.60×10^7	4.58×10^{10}
1AR	1.00	2.0×10^{-4}	8.75×10^9		2.97×10^9		6.13×10^3					
1BR	0.25	~0.26	5.45×10^8		4.81×10^8		1.13×10^3					
1DP	0.40	3.08	9.05×10^6	2.94×10^9	7.47×10^6	2.42×10^9	29.4	9.54×10^3	3.03×10^5	9.84×10^7	6.20×10^6	2.01×10^9
11BP	0.0186	35.6	6.07×10^4	1.70×10^6	1.06×10^5	2.98×10^6	0.3	8.4	3.44×10^4	9.67×10^5	3.40×10^4	9.55×10^5
111BP	0.0122	144.7	2.06×10^5	1.42×10^6	3.23×10^5	2.23×10^6	0.2	1.7	1.37×10^5	9.48×10^5	725	5.01×10^3

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4.213 Discussion of the Decontamination Data.

4.2131 Product Quality. The first criterion for judging plant decontamination performance is product quality. During the initial CPM operation with long-cooled alloy, products of exceptional quality were prepared. Beta ratios* of one or two were obtained consistently. The principal product contaminant was ruthenium with zirconium also being identified by spectrometer scans (Figure 5). Cerium and cesium were not detected. Inert impurities were typically quite low. However, when MTR feeds were processed, very high product beta ratios, up to 60, were experienced and product recycle was required. This phenomenon is discussed in paragraph 4.2134 on page 34.

4.2132 Gross Beta Decontamination. Three-cycle gross beta decontamination factors in excess of 10^6 have been indicated in each of the five sets of plant samples. (Tables 11 and 12). Because of the bias of the beta counts of the IIBP and IIIBP due to self-absorption in the uranium on the counting plant, the 2- and 3-cycle gross beta decontamination factors are likely to be biased high. Further, the third cycle decontamination factors are likely to be non-reproducible for the same reason.

This result for gross beta is essentially equivalent to the results experienced with three Hexone cycles and leads to the conclusion that the decontamination efficiency for the two-solvent system on this flowsheet has not been proven to be superior to the three Hexone cycle performance.

4.2133 Gross Gamma Decontamination. Gross gamma decontamination factors of the order of 10^6 were obtained for all samples. (Tables 11 and 12). The factors obtained by ion chamber measurement data were consistently slightly higher than those derived from scintillation counting data, reflecting slightly the relative behavior of the hard gamma-emitting zirconium-niobium and the ruthenium-rhodium.

Comparison of the overall gamma decontamination, as determined by ion chamber measurement, shows little difference between the three-cycle Hexone data and the two-solvent data. While this result is not immediately encouraging, the two-solvent system still offers considerable opportunity for the use of complexing agents and flowsheet manipulations to improve the removal of specific fission products.

* The ratio of the specific activity of the product to the specific activity of unirradiated uranium aged nine months. Since ICPP product is contaminated essentially only by ruthenium-106 at these cooling times, an empirical relationship between ion chamber gamma measurements and beta ratio is used with the gamma reading of the product to get the stated beta ratio.

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Figure 5

Gamma Scintillation Spectrometer Scan of CPP Product

Table 11

CPM TWO-SOLVENT DECONTAMINATION DATA SUMMARY

<u>Operation</u>	<u>Gross Beta</u>	<u>Log Decontamination Factor</u>			
		<u>Gross Gamma</u>		<u>Ruthenium</u>	<u>Zirconium</u>
		<u>Scintillation Counter</u>	<u>Ion Chamber</u>		
1A (Extraction)	1.7	1.1	0.9	3.0	0.0
1B (Scrubbing)	1.5	1.6	1.5	0.5	1.3
1 Cycle (TBP)	3.2	2.7	2.4	3.5	1.3
11A (Hexone)	2.6	2.5	2.7	1.7	3.1
2 Cycles	5.8	5.2	5.1	5.2	4.4
111A (Hexone)	0.7	0.7	1.3	0.4	2.5
3 Cycles	6.5	5.9	6.4	5.6	6.9

Table 12

CPM TWO-SOLVENT PROCESS DECONTAMINATION DATA

<u>Sample Set No.</u>	<u>Days from Start of Run</u>
1	4
2	9
3	47
4	67
5	100

Notes:

1. All cooling times were in excess of 300 days
2. After 9 days the first cycle scrub column flow ratio was reduced from A/O = 0.5 to A/O = 0.25

Cycle and Solvent	Sample Set	Log Decontamination Factors				
		For Gross Beta	For Gross Gamma by		For Ruthenium Beta	For Zirconium Gamma
			Scintillation Counter	Ion Chamber		
1A Column	2	1.9	1.4	1.1	4.0	0.7
	3	1.4	0.9	0.5	2.8	-0.2
	4	1.4	0.9	0.5	3.1	-0.5
	5	1.7	1.3	1.1	2.7	0.2
1B Column	2	2.1	2.2	1.8	0.3	2.1
	3	1.1	1.2	1.2	0.3	1.3
	4	1.5	1.5	1.3	0.5	1.3
	5	1.5	1.5	1.3	0.5	1.3
1 Cycle (TBP)	1	4.0	---	2.8	---	---
	2	4.1	2.1	2.0	4.3	2.8
	3	2.5	2.1	1.7	3.1	1.1
	4	3.3	2.7	2.1	3.8	1.3
	5	3.2	2.8	2.4	3.2	1.5
11A Column (Hexone)	1	1.9	---	2.8	---	---
	2	2.3	2.1	2.6	1.1	2.4
	3	3.2	3.0	3.0	1.8	3.9
	4	2.1	2.2	2.4	1.1	2.3
	5	3.2	2.9	3.1	2.0	3.3
2 Cycles	1	5.9	---	5.6	---	---
	2	6.3	5.8	5.4	5.5	5.1
	3	5.7	5.1	4.6	4.9	5.0
	4	5.4	4.9	4.5	4.0	3.6
	5	6.4	5.7	5.5	5.2	4.8
111A Column (Hexone)	1	0.9	---	0.5	---	---
	2	0.2	0.2	0.8	0.2	1.5
	3	1.4	0.8	1.8	1.3	2.0
	4	1.3	1.1	1.9	0.3	3.0
	5	0.1	0.1	0.7	0.0	2.3
3 Cycles	1	6.9	---	6.1	---	---
	2	6.5	5.9	6.3	5.7	6.6
	3	7.1	5.9	6.4	6.2	6.9
	4	7.7	6.0	6.3	5.2	6.6
	5	6.5	5.8	6.2	5.2	7.1

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4.2134 Ruthenium Behavior. While the above gross beta and gamma decontamination factors are indicative of the overall performance of the system and serve as convenient references, it is the behavior of ruthenium specifically which limits the performance of the whole system.

Historically, ruthenium has generally been the principal contaminant of product from the "25" process (three Hexone cycles). Therefore, flow-sheets have been designed to favor ruthenium removal but, even so, tail end processes or recycle has been required occasionally. It was anticipated that the TBP first cycle in the CPM system might yield enhanced ruthenium removal with the sacrifice of zirconium decontaminating efficiency. To date, this superior performance has not been demonstrated but the data from the process do help to suggest modes of improving the decontamination in the TBP system. In Table 11, the typical overall ruthenium decontamination factor, $\log D.F. = 5.6$, may be seen to be well below the gross beta value, which is admittedly biased, and equivalent to the value obtained by gamma scintillation counting. The excellent agreement among the factors for gross beta, gross gamma by scintillation counting and ruthenium over two cycles and in the third cycle indicate that beyond the second cycle ruthenium is the dominant species. A study of the analyses, Table 6 through 10, will also indicate this. The decontamination factor values for the first cycle extraction (IA) and scrub (IB) columns, Table 11 and 12 clearly indicate that a ruthenium species is present which has a very low distribution into TBP and under these conditions an excellent separation factor from uranium. The very low scrub column efficiency with respect to ruthenium; i.e., decontamination factors of 2 to 5, emphasizes first the completion of the separation of the unextractable ruthenium in the IA column; i.e., essentially none of it gets to the scrub column, and second, the failure of the scrub column to remove the extractable species. The extractable nature of the second ruthenium species is indicated by the second and third cycle decontamination data where decreasing decontamination factors are obtained from the second to the third cycle and the separation factor, ruthenium to uranium, approaches one in the third cycle. Further evidence relative to the behavior of extractable ruthenium was obtained at the end of the processing period when batch-dissolved MIR feed was processed in the two-solvent system. Although this feed was only about twice as active as the previously processed slug feeds, very poor products were obtained. Examination of the samples taken early in this portion of the run showed that the third cycle was producing no decontamination. Review of the operations schedule showed that this feed had been aged for from one to ten days prior to extraction and it was reasoned that the distribution of ruthenium species was altered unfavorably during this aging period. Subsequent aging of the contaminated product for several weeks and re-extraction through one Hexone cycle yielded adequate additional decontamination. These data are readily correlatable with other laboratory and plant experience with ruthenium, although none of this information is adequate to furnish an unqualified explanation of the phenomenon.

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Regardless of whether the overall three-cycle decontamination factor could be improved, it would still appear valuable to test flowsheet changes in the first cycle scrub column in anticipation that ruthenium decontamination might be improved there. One such change would be the use of a high acid scrub; i.e., 3N nitric acid, which might facilitate the conversion of extractable ruthenium to non-extractable ruthenium.

Another characteristic of the ruthenium data which was worthy of study was the lack of regularity in the performance of the first cycle extraction (IA) column. Fluctuations of more than an order of magnitude were shown in the extraction column and first cycle decontamination factors. Unlike the readily explained behavior of zirconium (paragraph 4.2135) there was no particular trend shown by the ruthenium factors. No firm explanation is available for this behavior although both solvent quality and feed aging might be suspected.

4.2135 Zirconium Behavior. Zirconium decontamination of the three-cycle product was excellent with decontamination factors approaching 10^4 . It would appear that 120-day cooled feeds, in contrast to greater than 300-day cooled fuels processed, of even higher burnup than experienced could be successfully decontaminated from zirconium by the present system and flowsheet.

Although overall zirconium removal was excellent, the fact that the TBP first cycle did not contribute appreciable decontamination; i.e., typical decontamination factor of 20, is of considerable process importance. Referring to the summary of the decontamination data, Table 11, it may be seen that fission product zirconium was significantly extractable in the IA column. The scrub column removed some zirconium (typical decontamination factor = 20) which was of course recycled to the IAF. This recycle resulted in a buildup of zirconium in the IA and IB column and the streams between. Although no direct evidences are available, the buildup might have been influenced by the accumulation of silica-containing solids in the equipment. The increase in zirconium content of the system with time is shown in Figure 6. Although this buildup did not have significant effect on product quality, it resulted in contamination of the first and second cycle equipment which would not have been as extensive if a reasonable zirconium removal could have been obtained in the IA extraction column. Presently, the use of complexing agents in the scrub is being considered to yield greater control of the zirconium in the first cycle.

4.3 Behavior of Plutonium

Plutonium analyses were made on appropriate flowing stream samples, Tables 8 and 9, to demonstrate the distribution of plutonium in the system. One feed sample was analyzed for plutonium (IV) and (VI) to determine what proportion of the plutonium in continuous-dissolver product was fully oxidized. It was found that more than 97 percent of the plutonium was present as Pu(VI).

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Figure 6

EFFECT OF REFLUX OF ZIRCONIUM IN THE TBP FIRST CYCLE
ON DECONTAMINATION

SAMPLE SET	DAYS FROM START OF RUN	ZIRCONIUM DECONTAMINATION FACTOR
(2)	9	620
(3)	47	13
(4)	67	20

THE TOTAL CURIES OF ZIRCONIUM IN EACH FLOWING STREAM AT EACH SAMPLING PERIOD ARE SHOWN AS NORMALIZED TO THE FRESH FEED ZIRCONIUM CONTENT.

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Figure 7 shows the plutonium material balance around the first cycle extraction and scrub columns. Greater than 99 percent of the plutonium appears in the first cycle product. As might be expected, plutonium reflux from the scrub column significantly exceeds that for uranium but is markedly less than the reflux for zirconium. In the "25" process the plutonium has been diverted to aqueous raffinate by the use of ferrous sulfamate in the second cycle scrub (IIAS). This practice has been continued when using the CPM system.

4.4 Process Engineering Performance

4.41 Macro Composition of the Flowing Streams. Analyses were made for the most pertinent major components of the flowing streams in the system in order to determine the adherence to the chemical flowsheet. This information is valuable in demonstrating the fit of the operating plant to the flowsheet and thus reflecting the validity of use of the flowsheet in predicting such factors as production rates, specific waste volumes, and the effects of the flowsheet on decontamination.

Table 13 shows the analyses of the inert components in the plant streams. In the analysis of the fresh feed stream; i.e., dissolver product plus one jet dilution, the excellent agreement of the dissolver product density and aluminum content to flowsheet value is illustrated.

The other stream compositions are essentially normal except that the second and third cycles were running exceptionally dilute with respect to uranium.

4.42 Column Losses, HTU and HETS. The accumulative column losses can serve as a guide to the evaluation of the design flowsheet and the effectiveness of operation. Each ICPP column and associated flowsheet was designed for a uranium loss of 0.01 percent or less. In the Hexone system, the stripping columns usually show no detectable losses while the extraction columns show about 0.01 percent each for the second and third cycle columns and 0.03 percent for the first cycle extraction column. During the series of processing runs in 1955-1956, the measured cumulative first cycle extraction and stripping column losses were slightly under 0.09 percent. The losses for the product wash column, ID, were of the order of 0.003 percent. At the same time, the two Hexone cycles produced measured extraction column losses of the order of 0.01 percent each. The only loss of any significance was the combined first cycle loss apparently due primarily to the extraction column. The fluctuations in the weekly cumulative first cycle losses (from 0.03 up to 0.16 percent) suggest that the various experimental programs being run in connection with processing, as well as equipment malfunction and the lack of experience with the system, contributed to this slightly excessive loss since pilot plant data indicate that the first cycle extraction column is overdesigned with respect to achieving a maximum loss of 0.01 percent.

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Figure 7.

CPM EXTRACTION-SCRUBBING COLUMN MATERIAL BALANCES
BASED ON ANALYSES OF TABLE 8

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Table 13

CONCENTRATIONS OF MACRO COMPONENTS IN PLANT STREAMS

<u>Stream</u>	<u>Concentration of Property</u>	<u>Flowsheet Value (Figure 2)</u>	<u>Value by Analysis</u>
Fresh Feed	Uranium, g/l	1.53	1.66
	Density, g/cc	1.288	1.290
	Nitric Acid, <u>N</u>	0.91	1.09
	Aluminum Nitrate, <u>M</u>	1.64	1.62
1AR	Uranium, g/l	2×10^{-4}	2×10^{-4}
	Density, g/cc	1.298	1.260
	Nitric Acid, <u>N</u>	0.88	0.82
	Aluminum Nitrate, <u>M</u>	1.74	1.48
1BR	Uranium, g/l	0.40	---
	Density, g/cc	1.126	---
	Nitric Acid, <u>N</u>	0.51	0.35
1CR	Uranium, g/l	2×10^{-4}	---
1DP	Uranium, g/l	3.67	3.08
11BP	Uranium, g/l	216	36
111BP	Uranium, g/l	216	145

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Since the IAR and ICR uranium losses are composited in the CPM system, it is not possible to use samples for the calculation of column efficiencies. However, several sets of flowing stream samples were taken and these data are suitable for such calculations. Since these flowing stream samples were only taken when the system appeared to be at equilibrium and no local upsets were present, they represent average operation and, therefore, the losses are lower than the accumulative losses discussed above. HTU and HETS values have been calculated which indicate the ability of the system to yield the design column performance. Since the lower limit of the analytical method for uranium is 5×10^{-5} grams per liter, the attainment and proof of about 0.01 percent loss with the existing feeds represent a practical optimum. In Table 14, it may be seen that extraction column transfer unit heights (HTU values) of 2.2 - 2.6 feet and calculated heights equivalent to a theoretical stage (HETS values) of 7.4 - 8.7 feet were produced from the three best samples. The values for HETS obtained by graphical interpolation on the operating diagram correspond to this. The error due to the fluor-photometric uranium analysis yields an error in HTU due to this cause alone of about ± 0.2 feet. The corresponding error in HETS is about ± 0.5 feet. The design stage height for the extraction column was 8.25 feet.

For the stripping column, the HTU was calculated as 1.4 feet with an HETS of 7.4 feet. The design stage height was 7.2 feet.

It is concluded that the design column performance has been realized in practice as illustrated by these samples although the cumulative data for the whole run are less favorable.

4.43 Column Flooding Data. Considerable preliminary pilot plant flooding data⁽²⁾ for the CPM system were available for the design of the system and these data were extended in start-up tests⁽⁹⁾ as shown in Figure 8. During plant startup there were numerous incidents of column instability which were temporarily interpreted as flooding. After instrumental and mechanical deficiencies were rectified, it became clear that these incidents of instability were not flooding due to either excessive volume velocity or pulse energy. With the mechanical deficiencies eliminated in the plant, a few flooding points were determined at full flood. These are shown as individual data points in Figure 8 wherein the pilot plant data are shown as smooth curves. Pumping rates and the capacities of other associated equipment limited the volume velocities attainable to relatively low values. Thus, fairly high energy inputs were required to attain flooding. The data of Figure 8 show rather good agreement between work with 2-inch columns in the pilot plant and 8- to 10-inch columns in the production plant. The slight restriction indicated for the extraction column is not serious in view of the considerable overdesign of the system. These data appeared adequate to indicate that the plant columns were not restrictive at any anticipated operating rates.

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Figure 8

Oil Column Flooding Curves

Table 14

EXTRACTION AND STRIPPING COLUMN HTU AND HETS CALCULATIONS

<u>Sample Set No.</u>	<u>Uranium Concentration, g/l. in</u>		<u>Loss, Percent</u>	<u>HTU</u>	<u>HETS</u>	<u>HETS (2) Graphical</u>
	<u>Feed</u>	<u>Raffinate</u>		<u>Calculated, (1) Feet</u>	<u>Calculated, (1) Feet</u>	
<u>Extraction Column (1A)</u>						
2	1.7	1.6×10^{-3}	0.09	3.2	11	12
3	1.7	$>5 \times 10^{-5}$	<0.003	<2.2	<7.4	<7.7
4	1.3	2.2×10^{-4}	0.017	2.6	8.7	8.5
5	1.7	2.0×10^{-4}	0.012	2.4	8.0	8.2
<u>Stripping Column (1C)</u>						
3	1.7	5×10^{-5}	<0.003	<1.3	<6.9	<7.0
4	1.3	1.6×10^{-4}	0.012	1.5	7.9	7.2

(1) Calculated by the Colburn equation⁽⁸⁾, neglecting curvature of the equilibrium lines.

(2) Operating diagrams given in the design manual⁽²⁾.

4.44 Pulse Energies. The design data⁽²⁾ were used to set up initial column energy input specifications. These were 50 cycles per minute at 1-inch amplitude for the extraction column and 60 cycles per minute at 1-inch for the scrub and strip column. The values were derived from the HETS calculations and the HETS versus energy input data. As plant operations progressed and high energy flooding was apparently experienced, it became desirable to reduce the energy input to the extraction and scrub columns to obtain more stable operation. These two columns, which are so interconnected through the headend evaporator that minor upsets are transmitted one to the other, were the least stable in the extraction chain. The strip column appeared to be relatively stable at high energy input. Ultimately, conditions of 30 cycles per minute at 1 inch, and in an extreme case 0.75 inch, were reached for the extraction and scrub columns and 40 cycles per minute at 1.25 inches for the strip column. With the several flowsheets used this reduced energy input did not adversely effect the extraction column performance. It is hoped that this low energy input for the extraction column will not be a requirement for future operations since it might seriously prejudice flowsheet design. Some device for directly indicating the column energy input at the column appeared desirable but it was not possible to introduce such a device into this operating system⁽¹⁰⁾.

4.45 Column Hydraulics. Several aspects of column hydraulics were studied during the initial operations of the CPM system. Some process lines were too small for design flows and apparently no precise knowledge was available of the pumping effect (undirectional) of the column pulsers in the system. Another only partially resolved problem associated with column hydraulics was the degree of head decrease experienced with increased organic content of an aqueous-continuous column.

At start-up it was impossible to maintain the extraction column liquid level or the scrub column interfaces at their normal levels and still get organic flow from the top of the IA, extraction column, to the bottom of the IB, scrub column. This experience prompted the calculation of the hydrostatics of the IA and IB columns. With the IB column filled with scrub, a head of approximately 12.9 feet of water exists (11.62 feet times 1.11 grams per cubic centimeter = 12.9 feet of water). The organic head from the IA column is about 12.45 feet of water (16.33 feet times 0.763 grams per cubic centimeter = 1.9 feet of water). With no pumping action from the pulser, solution would not be expected to be moved. An approximate 0.5 foot of water pressure drop was calculated for the fluid flow. At this time, the question of whether an aqueous continuous column was effectively less dense by the inclusion of substantial amounts of organic was investigated in the pilot plant. It was found that where an organic-free column showed a static head of 155 inches of water, the same column contained 16.5 percent organic showed a head of 153 inches of water. If the static head were proportional to the organic content, this measured head would be 147 inches. This experiment suggests that no allowance could be made for reduction of column head due to the inclusion of organic although certainly there might be some effect, especially with higher percentages of organic.

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Investigation of the sizing of the overflow line from the top of the IA column to the base of the IB column showed that there was inadequate large-diameter air disengaging length in the line and that very likely this line contained entrapped air which resulted in loss of static head. The enlargement of this line and the removal of certain high flow resistance piping improved the hydraulic system. Simultaneously, it was discovered that the IB column pulser was putting less than the indicated amount of energy into the system and, therefore, this pumping action, whatever its value, was being lost. With the correction of the pulse generator and the piping changes, the problem of IA-IB column hydraulics was partially solved. It became possible to operate the IB column with a normal interface level but the IA column organic liquid level remained very high; i.e., up to the emergency over flow, indicating that even with piping correction and under dynamic conditions, the hydraulic relationships of the columns were less than adequate.

4.5 Strip Product Wash Column

In the CPM system, a packed column is provided after the stripping column for the washing of strip product with pure hydrocarbon diluent. It is the purpose of this column to wash the TBP out of the strip product solution prior to evaporation. Equilibrium data for this scrubbing are given in the design data⁽²⁾.

TBP removal is required in the system to prevent the accumulation of TBP or DBP in the first cycle product evaporator and the second cycle. No data were taken to define the efficiency of this column for TBP removal. However, the column and the stripper combined were at least so effective that there was no indication of DBP in the IIB column stripping results. In practice, the mechanics of disposing of the spent diluent from this scrub column raffinate became so involved; i.e., the solvent incinerator was of inadequate design and construction, that the scrubbing process was examined theoretically to determine if flow ratio reduction were possible. These calculations are shown in Table 15. Calculations were first made of the effect of recycle of the spent diluent (IDR) to the wash column as IDS, on the possible second cycle strip column (IIBR) loss due to DBP. Next the essentially equivalent effect of reduced IDS/ICP flow ratio was considered. With TBP to DBP, hydrolysis rates approximating 10 percent per hour and holdup of 10 hours in the evaporator, the hydrolysis of a large portion of the TBP not scrubbed or stripped out seemed assured. Therefore, only a limited reduction in flow ratio seemed justified pending actual stream analyses. Actually, the flow ratio was reduced from $O/A = ICS/ICP = 1/10$ to $1/20$.

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Table 15

CALCULATED EFFECT OF LDR RECYCLE OR REDUCED 1D FLOW RATIO
ON 11BR URANIUM LOSSES DUE TO DBP FORMATION

1. TBP concentration of 1 g/l in the 1CP.
2. One theoretical stage in the 1D column.
3. Eighty-five percent efficiency for the steam stripper for the removal of TBP in the concentration range 0.0004 - 0.007 g/l TBP.
4. Typical exposure time in the evaporator of 10 hours at 100° C.
5. Design flowsheet compositions of major streams.
6. The DBP-uranium complex formed in a 1 : 1 mole ratio.
7. The only significant process effect of TBP hydrolysis after the 1D column is that of forming unstrippable uranium in the 11B column.

Number of Recycles of 1DR	1D Flow Ratio 1DS/1CP	Tributyl Phosphate in		Maximum 11BR Loss at 100 Percent Hydrolysis	Tolerable Percent of TBP Hydrolysis in the Evaporator to Give Less Than 0.01 Percent 11BR Uranium Loss
		1DP g/l	Evaporator Feed After Steam Stripper g/l		
0	1 : 10	0.0026	0.00039	0.008	100
1	1 : 20	0.0051	0.00076	0.015	67
2	1 : 30	0.0076	0.0011	0.021	48
10	1 : 100	0.025	0.0037	0.072	14

4.6 Solvent Quality (TBP System)

The hydrocarbon diluent for CPM solvent was required to satisfy the specifications shown in Table 16. Of these specifications the most important were specific gravity, flash point, viscosity, and chromyl chloride number⁽¹¹⁾. Amsco 125-90W was selected as being the most inert of the diluents tested, the material obtained for this run having a chromyl chloride number of 0.05 milliequivalents of chromyl chloride per milliliters of diluent.

Table 16

Hydrocarbon Diluent Specifications

Specific Gravity at 25°C	0.800 maximum
Flash Point - Tag Close Cup - °F	130 minimum
Viscosity at 25°C	2 centipoises maximum
Doctor Test	Negative
Acidity	Neutral
Color, Saybolt	+ 25 minimum
Aromatics	1% maximum
Chromyl Chloride Number	0.07 meg./ml, maximum

To help determine solvent life and to relate solvent quality to general column operation, a series of process solvent samples was taken during plant operation. Because of the low turnover of solvent and the gradual changes in quality anticipated, samples were taken only twice each week. Based on design rate, the solvent cycles through the system nine times each 24 hours.

The solvent samples which were drawn from the solvent holdup tank were subject to four different tests: (1) determination of coalescence and dispersion characteristics⁽¹²⁾, (2) determination of fission product retention by scintillation spectrometer gamma counting, (3) determination of the extent of nitration by following the absorbance at 340mμ, and (4) determination of unstrippable uranium by the "C" test. A check was also made on TBP content.

Table 17 presents a summary of the data obtained. The number of cycles each solvent sample received was calculated on the basis of new and recycled uranium processed through the plant. To compensate for irregularities during operation; e.g., startups and shutdowns, throughput was assumed to be increased by 10 percent for these calculations.

Table 17

SUMMARY OF PLANT SOLVENT QUALITY TESTS
TRIBUTYL PHOSPHATE DILUENT SYSTEM

<u>Days From</u> <u>Start of Run</u>	<u>Cycles</u>	<u>TBP</u> <u>Vol. %</u>	<u>Results of</u> <u>"C" Test</u> <u>mg/ml x 10³</u>	<u>Beta Activity,</u> <u>cts/(min)(ml) x 10⁻³</u>	<u>Absorbance</u> <u>at 340 mμ</u>	<u>Dispersion</u> <u>Time (Sec)</u>	<u>Disengaging</u> <u>Time (Sec)</u>
Standard	--*	4.5	5.0	0	0.00	57	50
11	31.5	4.3	--	5.1	0.292	52	70
16	45.0*	4.5	4.0	3.7	0.603	51	41
18	51.0	4.5	6.5	--	--	--	--
30	102	4.5	5.5	6.0	0.728	53	59
34	114	4.5	5.5	7.7	0.528	53	60
37	124	4.4	6.0	16.7	0.525	53	60
39	131	4.4	4.5	68.6	0.567	54	57
40	135	4.5	4.8	--	0.500	58	75
41	140	4.5	4.0	12.9	0.520	55	61*
44	6.3*	4.6	3.8	19.3	0.440	56	50
46	18.8	4.7	6.8	8.2	0.400	55	72
60	78	12.4	3.2	6.4	0.712	55	55
66	115	4.4	4.3	26.6	0.700	54	50

*Solvent additions to system

From Table 18 it may be seen that an unusually large amount of solvent was used during this run. At one time, for example, the solvent system was almost replaced with the addition of 75 percent of the initial charge. It is felt that these data on solvent usage are not typical. Allowing 13 percent for jetting of the mixer-settlers, 60 percent is still an unrealistic loss for approximately 100 cycles. A large part of this loss is undoubtedly due to entrainment during forced flooding tests which were conducted during this period. It was not possible, therefore, to determine the maximum useful life of the solvent.

Volume percent TBP (Table 17) does not vary much from the standard with the exception of the sample drawn after 60 days. This high percentage may perhaps be explained on the basis of inadequate mixing since the solvent is not mixed prior to addition to the system, but rather the Amsco and TBP are pumped separately to the mixer settlers.

As may be seen from the table, there is little evidence for solvent deterioration with respect to nitrated degradation products and unstrippable uranium, or dispersion and disengaging characteristics. Absorption measurements for synthetically nitrated diluents⁽¹³⁾ at 340 m μ are much higher than these. A slight decrease in dispersion time and a slight increase in disengaging time is typical for used solvent.

Table 18

Solvent Consumption

<u>Days from Start of Run</u>	<u>Liters</u>
Initial Charge	First cycle extraction system flushed and filled with 1500 liters of solvent.
12	200
14	200
43	1100
55	80
58	50

The gamma activities listed are not excessive with the exception of the one listed for 39 days. There is no explanation for this sudden peak of activity. The activity in the samples is essentially all zirconium with perhaps a trace of ruthenium and cerium.

Two sets of samples were taken during this run to check the efficiency of the solvent recovery system. Solvent recovery consists of successive washes with one-tenth volumes of 0.04M nitric acid, 0.5M sodium carbonate, and 0.04M nitric acid. Table 19 presents the beta and gamma activities for 1C column raffinate and recovered solvent. The data show a decontamination factor of approximately 100.

Table 19

Efficiency of the Solvent Recovery System

Days from Start of Run	Sample	β Activity Cts/(min)(ml)	γ Activity Cts/(min)(ml)
47	ICR (Raffinate)	2.53×10^5	2.66×10^5
	H-118 (Recovered solvent)	1.65×10^3	1.61×10^3
67	ICR	2.32×10^5	2.23×10^5
	H-118	3.32×10^3	2.49×10^3

5. EVAPORATOR OPERATION

5.1 General Experience

In the CPM system, three essentially identical thermo-syphon evaporators are used for first cycle feed, raffinate and product concentration. These evaporators were designed for a heat transfer rate of 660,000 BTU per hour. Although this boilup initially appeared adequate, the design temperature difference was not realized, partially due to restrictions on the steam chest pressure; i.e., maximum wall temperature was restricted to avoid excessive corrosion and TBP decomposition. This factor became limiting in the case of the raffinate evaporator which carried a disproportionate share of the boildown load. The restrictions imposed by boilup limitations were minor compared to difficulties in removal of the concentrate from the evaporators. This latter problem was the major operational difficulty in the CPM system.

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In the case of the two evaporators where the contents of the evaporator almost approached the crystallization point; i.e., the product and raffinate evaporators, there was numerous incidents of pump stoppages due apparently to a combination of evaporator density oscillation and pump faltering at high density peaks.

5.2 Feed Evaporator, G-110

There were two approaches considered for the operation of the feed evaporator (G-110). In one case where operation of the evaporator was necessary in order to give the required overall boildown; i.e., from dissolver solution to stored raffinate, it seemed advisable to give as much boildown as possible, compatible with proper column operation, in the feed evaporator. This lessened the load on the raffinate evaporator and yielded the maximum practical uranium content for column feed. This approach is suitable for fuels of either low percentage uranium content or extremely poor dissolution characteristics.

Alternatively, the desirability of eliminating this evaporator was considered. Where fuels of high percentage uranium content or very reactive composition are available, it is possible to prepare a dissolver solution of such uranium content that no head-end concentration is required to yield the required production rates without overloading the raffinate evaporator. The flowsheet of Figure 6 illustrates such operation. While this latter design concept was tested briefly, it was concluded that the necessary flexibility of the plant would be impaired by removal of the evaporator.

5.3 Product Evaporator, H-110, Flowsheet and Performance

The flowsheets for the Hexone second cycle require that a fairly concentration uranium solution, 1.5M be used for feed. Lower feed uranium concentrations require higher scrub flow or density. The design CPM flowsheet, as shown in Table 1 requires a 68-fold boildown of the strip column product. Experience indicated that this boildown was excessive with the quality of process solutions available. Precipitation of corrosion products and certain minerals in the makeup water appeared to occur in this evaporator which contributed to pump stoppages. Ultimately, a value of about 130 grams per liter uranium, 0.55M, was selected for the composition of the concentrate; i.e., the second cycle feed (IIAF). This approximately 25-fold boildown tended to yield less pumping trouble at this point in the system. The desire to prepare flowsheets having conservative uranium concentrations in the flowing streams and then also to operate the system dilute due to startup techniques and feed interruptions increases the severity of this problem. To overcome this difficulty, evaporator pump-out control was frequently switched from density actuation to fixed rate operation so that undesirable accumulations of non-uranium containing solids would be eliminated.

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5.4 Raffinate Evaporator, G-114

5.41 Performance. While the design flowsheet boilup for the raffinate evaporator was approximately 500 pounds per hour in contrast to the component design value of about 660 pounds per hour, this evaporator frequently failed to maintain the required density at design rate or less. While this evaporator was required to make up any boildown deficiency of the feed evaporator, the system was generally operated with a more concentrated feed (IAF) to favor the raffinate evaporator. It is concluded that either rapid scaling or inadequate circulation of the fairly concentrated solution impaired the heat transfer characteristics of the evaporator.

5.42 Raffinate Concentrate. There is continuing interest in the composition of the plant raffinate concentrates both for the purpose of defining the probable feed material for waste processing and to determine the efficiency of waste storage space utilization. In order to determine this composition, the composite density of the last 21 IARm batches accumulated during this processing period was determined. The composition was calculated from this density and the flowsheet proportions. This information is discussed here with respect to:

1. Solution composition.
2. Raffinate storage space economy.
3. Freezing of concentrate in the lines from the evaporator.

5.421 Chemical Composition. The density of the 21 raffinate batches averaged 1.331 grams per cubic centimeter at 25°C with extremes of 1.306 and 1.353 grams per cubic centimeter. Using the flowsheet proportions for the major components; i.e., aluminum nitrate, nitric acid, and sodium nitrate, and the plant mercuric nitrate inventory for the catalyst usage, the composition of Table 20 was calculated for the raffinate concentrate. The fission product concentration is based on the average burnup, the fuel composition, and flowsheet proportions. This composition is prior to any jet dilution required to transfer the raffinate from the evaporator holding tanks to permanent storage.

5.422 Storage Economy. The control point for the raffinate evaporator G-114 has been specified at 72 percent of the density recorder controller chart, nominally 1.31 grams per cubic centimeter at 100°C and 1.35 grams per cubic centimeter at 25°C. The typical density observed in the concentrate holdup tanks, G-115 and G-116; i.e., 1.331 grams per cubic centimeter at 25°C, indicates considerable care in the operation of the evaporator considering the continual pump failures and associated evaporator control problems. The difference in density between the flowsheet specification (1.35 grams per cubic centimeter at 25°C) and the value observed represents a use of 7 percent excess storage space. It may be assumed that an improved method of transferring the concentrate from G-114 to the holding

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tanks will allow closer control of the evaporator and stricter adherence to specifications. It may be possible to specify a higher density if air lifting of the material proves feasible. The incentive for use of a higher density is illustrated by the relative raffinate volumes accumulated at various densities (Table 21).

Table 20

Average Composition of Raffinate Concentrate

Aluminum Nitrate, <u>M</u>	1.81
Nitric Acid, <u>M</u>	1.44
Sodium Nitrate, <u>M</u>	0.11
Mercuric Nitrate, <u>M</u>	0.02
Uranium, g/l	$< 1 \times 10^{-3}$
Density, g/cc	1.331
Fission Product, g/l	0.25

5.423 Freezing of Concentrate. There is always some concern regarding the degree of protection of the concentration process against freezing; i.e., crystallization of the major component which in this case is aluminum nitrate. Consideration of the density-freezing point relationships of Table 21 indicates that at a specification of 72 percent on G-114 density recorder-controller (DRC) there is ample protection against freezing due to lack of evaporator control up to about 90 percent of G-114 density recorder-controller. Indeed the Blaw-Knox design flowsheet indicated that the evaporator should be operated at 1.42 grams per cubic centimeter at 25°C which is 86 percent on G-114 density recorder-controller. While there were occasional density swings up to 90 percent on the density recorder-controller it seems unlikely that material with a freezing point of 40°C pumped out during these swings could have been responsible for freezing of the pumps and adjoining lines if the flow through the lines were not interrupted at the same time by mechanical failure. Removal of the concentrate at a uniform rate will minimize the possibility of freezing.

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Table 21

Density - Freezing Point Relationships for Raffinate Concentrate

(Solution Proportions given in Table 20)

Density Recorder- Controller Setting G-114 %	Density at 100°C g/cc	Density at 25°C g/cc	Initial Crystallization Temperature °C	Relative Raffinate Volume
67	1.285	1.325	0	1.00
72	1.31	1.35	10	0.92
76	1.33	1.37	20	0.86
82	1.36	1.40	30	0.80
88	1.39	1.43	40	0.75
100	1.45	1.49	~ 60	

(1) Seidell, A., "Solubilities of Organic Compounds", 3rd edition, Vol. I, page 92.

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