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A Dynamic Study of the Extraction of Rare Earth Chloride - D2EHPA - ~~E~~HCl in a Multistage Mixer-Settler Extractor

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Gary Arnold Beetner

Ames Laboratory, USAEC
Iowa State University
Ames, Iowa 50010

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by

Gary Arnold Beetner

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Approved:

Ren G Bautista
In Charge of Major Work

Geo. Burnet
For the Major Department

Charlotte E Roderuck
For the Graduate College

Iowa State University
Ames, Iowa

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A DYNAMIC STUDY OF THE EXTRACTION OF RARE EARTH CHLORIDE - D2EHPA - HCl IN A MULTISTAGE MIXER-SETTLER EXTRACTOR

Gary Arnold Beetner

Under the supervision of R. G. Bautista
From the Department of Chemical Engineering
Iowa State University

ABSTRACT

The flow patterns within a pump mix mixer-settler extractor are studied photographically and visually. Dye is injected into the pump mixer and followed through the various portions of the equipment. These results are analyzed to give both a quanitative and qualitative measure of the flow within a single stage.

A mass transfer mechanism is derived based on a pseudo distribution constant and a pseudo first order rate constant. These constants are adjusted to give both the proper output concentrations, and stagewise concentrations of the proper form.

The results of both these studies are programmed on an IBM 360 model 65 digital computer. The results obtained by this computer simulation of startup to steady state are compared to experimental data. The comparison shows very close agreement.

A second simulation is then constructed and run to demonstrate that the model can be greatly simplified, and good results still obtained.

SUMMARY

The flow patterns within a pump mix mixer-settler extractor are studied photographically and visually. Dye is injected into the pump mixer and followed through the various portions of the equipment, photographically where possible. The study is divided into three parts. The settling chamber is studied first. Next the chamber surrounding the pump mixer (Prepump Chamber) is studied photographically, and finally the pump mixer is studied visually, and analytically.

For the study of the settling chamber, dye is injected into the pump mixer, and followed photographically through the settling chamber. The outlines of the dye in the photographs are plotted on graph paper, and the areas measured with a Keuffel and Esser Polar Planimeter. As the flow is essentially two dimensional, these areas are multiplied by the thickness of the settling chamber to give the corresponding volumes. These volumes are plotted against time to give a measure of the mixing taking place. A model is derived from these findings, for each phase, and simulated on the IBM 65, series 360 digital computer.

Photographs of the prepump chamber show the flow there to be pure plug flow. A hydraulic balance on the apparatus reveals that during an actual startup, the interface in the settling chamber will shift upward, slowing the flow in the prepump chamber. This is modeled as a prepump chamber larger

than the actual equipment, with constant flow rates.

The most difficult portion to study was the pump mixer. The material contained in it is whirled very rapidly, making it difficult to photograph. The flow here was observed visually, and found to be plug flow. The pump mixer is then modeled as a plug flow unit. A mass transfer mechanism is derived based on a pseudo distribution and a pseudo rate constant. These are adjusted to duplicate the output data of Casto et al. (5,6,7) and the stagewise data of Rahn(18).

The results of all these individual studies are then combined to form a detailed physical simulation of the mixer settler extractor. The simulation is then run and the results compared to experimental startup data. The simulation is found to closely duplicate the startup to steady state experimental data.

A second model is then constructed to test simplifying assumptions on the accuracy of the model. In the settling chamber, the organic phase is assumed to be in plug flow, and the aqueous phase is assumed to be well mixed. The prepump chamber is again modeled as pure plug flow, and the pump mixer is considered to be emptied each iteration of the computer.

The results of this simplified model are compared to the experimental data, and the detailed simulation. The simplified model is found to produce a simulation which is nearly as good as the detailed model. These results can be expected to apply to all similar systems, including opaque and liquid metal systems.

INTRODUCTION

The purpose of this study is to produce a computer simulation of the mixer-settler extractor which will model the startup and steady state data obtained by Casto(5) on this equipment. The accuracy of this model is intended to be sufficient to make it of value in future studies made with this and other similar apparatus.

The mixer-settler extractor used in these studies incorporates the improvements made on several previous versions of the equipment. The mixer also serves to pump the organic and aqueous phases from stage to stage. This pump mixer is equipped with an interface adjustment shaft on the inlet tube. This facilitates control of the interface level in the settling chamber. These and other improvenents are incorporated in a box like arrangement for the efficient use of space.

The chemical system studied is the extraction of rare earth chloride by D2EHPA in HCl. The organic phase consists of industrial grade di(2-ethylhexyl) phosphoric acid (D2EHPA) diluted to 0.5 M with Amsco Odorless Mineral Spirits(16). The aqueous phase was 0.1 N HCl prepared from reagent grade HCl and deionized water. The rare earth feed stock was a 2.7 M solution of Didymium Chloride. This system disengages rapidly in the settling chamber, producing two distinct phases.

"Didymium" refers to the mixture of rare earths obtained after removal of cerium and thorium from the naturally occurring mixture of rare earths found in ore. The manufacturer's stated typical composition was 46% lanthanum, 10% prasedymium, 33% neodymium, 6% samarium, 3% gadolinium, 1% cerium, and 2% other rare earths. Different lots of Didymium Chloride were found to vary in composition, but the cerium content was generally found to be higher than the stated typical composition.

Earlier work done by Casto(5), with the same system and apparatus indicated a response in the raffinate layer of a dead time of 80 minutes followed by an indeterminate order time constant response. Since this was the result of travelling through seven stages it might be expected that the dead time of the aqueous raffinate phase would be about 11 minutes for each stage. A dead time response is characteristic whenever plug flow occurs. A time constant response is characteristic of well-mixed zones of flow and may also arise due to mass transfer effects between the phases. Experimental work was done on a single stage to illuminate the correct flow characteristics.

The original data showed very little delay in the response in the organic extract phase. Only three stages were traversed by the rare earths from the feed inlet to the organic phase outlet, which would decrease the delay as compared with the aqueous phase which traversed seven stages.

The first sample was taken at 10 minutes after startup. The dead time in the organic phase is less than 10 minutes. Single stage experiments were performed to give further information concerning the correct flow characteristics.

Since analog machines capable of modeling a mixer-settler with this number of stages and duration of time delays are presently not available at Iowa State University, it was decided to use the IBM 65, 360 series digital computer. Early in the study it was decided to use an open-ended iterative calculation, with each iteration equal to one-tenth of a minute real time. This was judged to be a small enough time increment to give the desired accuracy. Because the raffinate phase showed a delay of about 11 minutes per stage, a one-tenth minute time increment would allow 110 iterations to simulate the flow through each stage. This was judged to be sufficient to allow for a simulation of the actual physical flow patterns. Since most of the runs made on the equipment took about 300 minutes, this time increment would only require 3000 iterations to simulate startup to steady state. It was judged that this would not consume an excess amount of computer time.

Single stage experiments led to the assumptions for the model. The model was constructed and run in its entirety and the startup data produced by the model was compared to the experimental data obtained by Casto(6). The results showed a very close correlation between the raffinate outputs of the apparatus and the model and a reasonable correlation between the extract outputs.

LITERATURE REVIEW

Sharp and Smutz(22), Sebenik et al.(21), and Bochinski et al.(3) performed stagewise calculations for a system using tributyl phosphate, rare earth nitrates, and nitric acid. Their work was for the steady state operation of an extraction column. Smith(23) reviewed a number of techniques of stagewise calculations for multistage systems, including those of Lewis and Matheson(14), Amundson and Pontinen(1), Amundson et al.(2), and Thiele and Geddes(24) for distillation. Other work done on the steady state stagewise compositions include the work of Goto and Smutz(9,10), and Lenz and Smutz(13). These and many other references in the literature dealt with the calculation of a column operating at steady state.

Lowe(15) studied the transient behavior of solvent extraction processes. He assumed that both phases were well mixed in the pump mixer, and in plug flow in the settler. Flow is cocurrent in each stage, but countercurrent overall. Provision is made in his simulation for the possible input and output of an extra organic and aqueous stream in each stage. His model is based on an ideal concept and the output compared to the outputs of a miniature mixer-settler.

Pollock and Johnson(17) reviewed the work presented in 46 various papers, books, and theses. Much work on stagewise contact processes has been done theoretically, numerically, and experimentally for both pulsed and Scheibel extraction columns. Little work has been done on mixer-settlers.

Burns and Hanson(4) studied the transient response of a multistage mixer-settler using the system tributyl phosphate in kerosene, water, and nitric acid. He studied the results of step and impulse changes in the nitric acid input to the system. He noted that the response lag in the raffinate was some 50% longer for a downward change than for an upward change. He explains this as being the result of nitric acid being transfered from the organic phase to the aqueous phase during a downward concentration change, maintaining a high concentration in the raffinate output. He states that during a period of increased nitric acid input such an interchange does not have nearly as marked an effect.

Halligan and Smutz(11) proposed several models for predicting the approach to steady state of a mixer-settler extractor. He simulated and recorded the results of several models of mixer-settler extractors and compares the results with experimental data. In all cases he assumed a well mixed pump mixer, and complete disengagement of the phases in the settler. In the case of the perfectly mixed model both phases are considered to be well mixed within themselves in the settling chamber. A plug flow model was considered with both phases in plug flow in the settling chamber. A hybrid model considered the organic phase as plug flow, and the aqueous phase as well mixed. A fourth model considered the mixer and settler as one vessel and each phase homogeneous. The models were programmed on the digital computer using the DIAN components of Farris and Burkhart(8). The results showed the most accurate model is the the hybrid model. It was also shown that the larger the number of stages, the more nearly identical the results of all the models.

Rahn and Smutz(19) and Rahn(18) designed and constructed a twenty stage mixer-settler extractor, in ten stage units. He made some preliminary runs with 1 M D2EHPA and 0.3 M HCl. He verified these results with a simulated column run using separatory funnels and a shaking machine. The simulated column allowed thorough mixing and ample time for phase separation, therefore approaching ideal stage efficiency. This confirmed the mixer-settler to be operating at nearly 100% stage efficiency.

Perry(16) continued the work of Rahn by studying the stagewise concentrations and compositions. As in the work of Rahn, he encountered trouble with emulsions forming in the pump mixer. Perry used a similar mixer-settler with a 6 M HCl scrub solution to strip rare earths from the organic extract product.

Casto _et_ _al_.(5,6,7) further refined the equipment and operating conditions. He changed the organic extract phase to 0.5 M D2EHPA. This eliminated the emulsion problem encountered in earlier work. The aqueous scrub solution was reduced to 0.1 M HCl. By adjusting the flow rates he was successful in obtaining a 97% lanthanum raffinate product.

Hoh(12) studied the stripping of rare earths from di(2-ethylhexyl) phosphoric acid with hydrochloric acid in a mixer-settler stripper. Experiments were run both with the pilot plant scale mixer-settler stripper and separatory funnels to find the amount of stripping accomplished as a function of HCl strength. A study was also made of the effects of changes of the various flow rates.

Hoh(12) also made a dynamic study. While operating the equipment at steady state, he introduced upsets and followed the return to steady state by titrations. Next, based on preliminary results by this author, Hoh studied the flow patterns in the stripper photographically. This was accomplished by injecting dye into the equipment, and photographing it as it advanced through the various portions of the equipment. These photographs were then analyzed to give a measure of the flow.

EXPERIMENTAL APPARATUS AND PROCEDURES

Description of Equipment

The mixer-settler used in this research was designed and constructed by Rahn and Smutz(19) and Rahn(18), and was successfully used to separate lanthanum from a rare earth chloride mixture by Casto et al.(5,6,7).

The mixer-settler is continuous, horizontal, box like and multi-stage. It was made in ten-stage units with adjacent stages having common walls. Figure 1 shows the detail of one stage and adjacent stages connected to it. Figure 2 shows the flow of the feed streams to the extractor, and the product streams from the extractor. Plexiglas was used as the construction material because it can withstand the HCl-D2EHPA environment and also because it is transparent and inexpensive.

Removable solid inserts were used in both the mixing and settling chambers to decrease the liquid holdup in the apparatus in order to attain steady state operation in a shorter time. The liquid volume in the settling chamber with the volume displacers in position is 1.02 l, divided equally between the organic and aqueous phases. The mixing chamber was divided into two parts, the pump itself containing 135 ml, and the chamber surrounding the pump containing 365 ml.

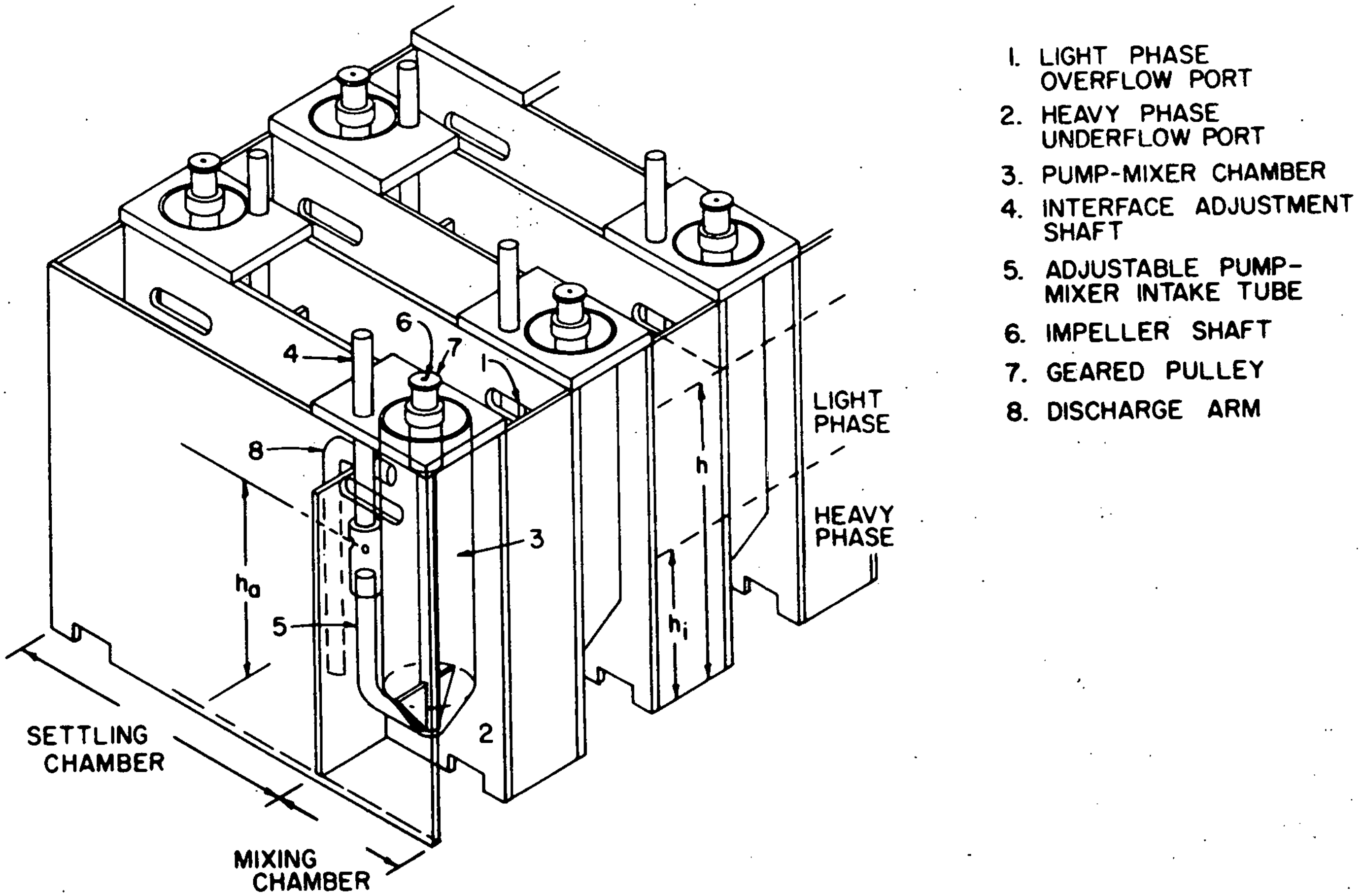


Figure 1. N-stage mixer-settler

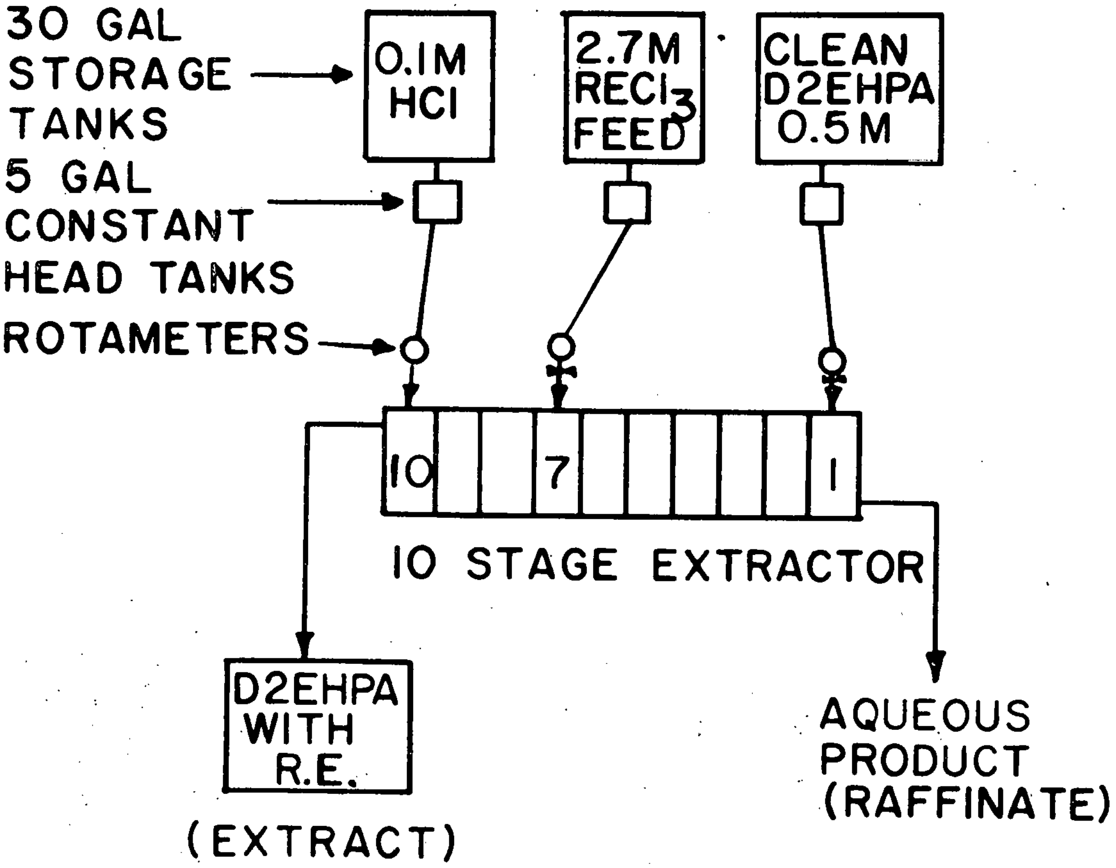


Figure 2. Flow to and from a ten stage extractor

The pump mixers used in this research were glass bodied. The bearings were stainless steel ball bearings. The shafts were made of Kel-F with a stainless steel insert, and the paddles of Teflon. The pump-mixers were driven simultaneously by employing a central shaft together with timing belts and sprocketed pulleys. The drive shaft was driven with a belt by a one-fourth horsepower motor with Minarik Speed Control.

A brief study of the equipment reveals that the simulation of each stage can readily be divided into four distinct parts. The settling chamber divides naturally into the aqueous and organic portions. The mixer is divided by the wall of the glass pump into the portion contained in the pump, and the portion in the chamber surrounding the pump.

Experimental Procedure

This mixer-settler proved to be ideal for the visual study of the flow patterns using dye as a marking material. For studies of the flow patterms in the settling chamber, narrow strips of paper were pasted on the side of the first stage settling chamber at intervals of 4 cm to form a grid. These were then graduated in cm with a pen. A "Precision Time It" digital timer was dismantled and the inner workings mounted on a portable stand such that the dial was exposed. This was placed adjacent to the settling chamber so that the face was clearly visible beside the chamber. The timer is graduated in hundredths of a minute. The pump mixer was removed from the second stage and the pump compartment drilled and tapped to allow the organic phase overflowing from the first stage to be drained from the equipment without flowing through the entire ten stages of the mixer-settler unit. A small hole was drilled through the cover plate of the pump chamber into the pump mixer. Both the organic and aqueous phases were introduced into the first stage pump chamber through the inlet port.

The pump mixer was turned on and the organic and aqueous feeds started. After about five minutes the rare earth feed was started, feeding directly into the pump mixer to insure total, complete, and immediate mixing. One-half ml of saturated alcoholic solution of Gentian Violet Dye was immediately injected through the opening in the coverplate. At the same time the timer was started. This was time zero. Pictures were taken through the side of the settling chamber with an Automatic 100 Polaroid Land Camera equipped with close up lens No. 583. Since a film cartridge contains only eight pictures, it was essential to use discretion as to what intervals to take pictures in order to capture all the flow patterns as they develop. Experience indicated the best times to take pictures to be 0.1, 0.2, 0.3, 0.4, 0.6, 1.0, 1.5, and 2.0 minutes.

A study was also made of the flow in the chamber surrounding the pump mixer. For this study the shaft and paddle were removed from the number six pump mixer and a vacuum line inserted. The timing belts were removed from all but the number seven pump mixer to render them inoperable. The number eight pump mixer was flooded with D2EHPA solution to above the level of the overflow port. This lowered the interface level of the number seven settling chamber to approximately 3 cm and helped to hold it constant during this experiment.

The aqueous phase and rare earth feed were introduced through the number seven pump mixer, as they had been introduced through the number one pump mixer in the settling chamber experiments. The organic phase was introduced into the number five settling chamber. The organic and aqueous phases were turned on and allowed to flow for about five minutes. Then the rare earth feed was introduced into the number seven pump mixer. At this time one-half ml of saturated alcoholic solution of Gentian Violet Dye was injected into the number seven pump mixer. Pictures were taken as the dye flowed into and through the chamber surrounding the number six pump mixer.

A study was also made of the flow inside the pump mixer. For this study the inlet port of the pump mixer was modified to allow the introduction of the rare earth feed stock and the dye through the inlet port. The pump mixer was turned on and the organic and aqueous phases introduced. Then the rare earth feed and the alcoholic solution of Gentian Violet Dye were introduced through the inlet port. The results were observed visually, as this was rather difficult to photograph.

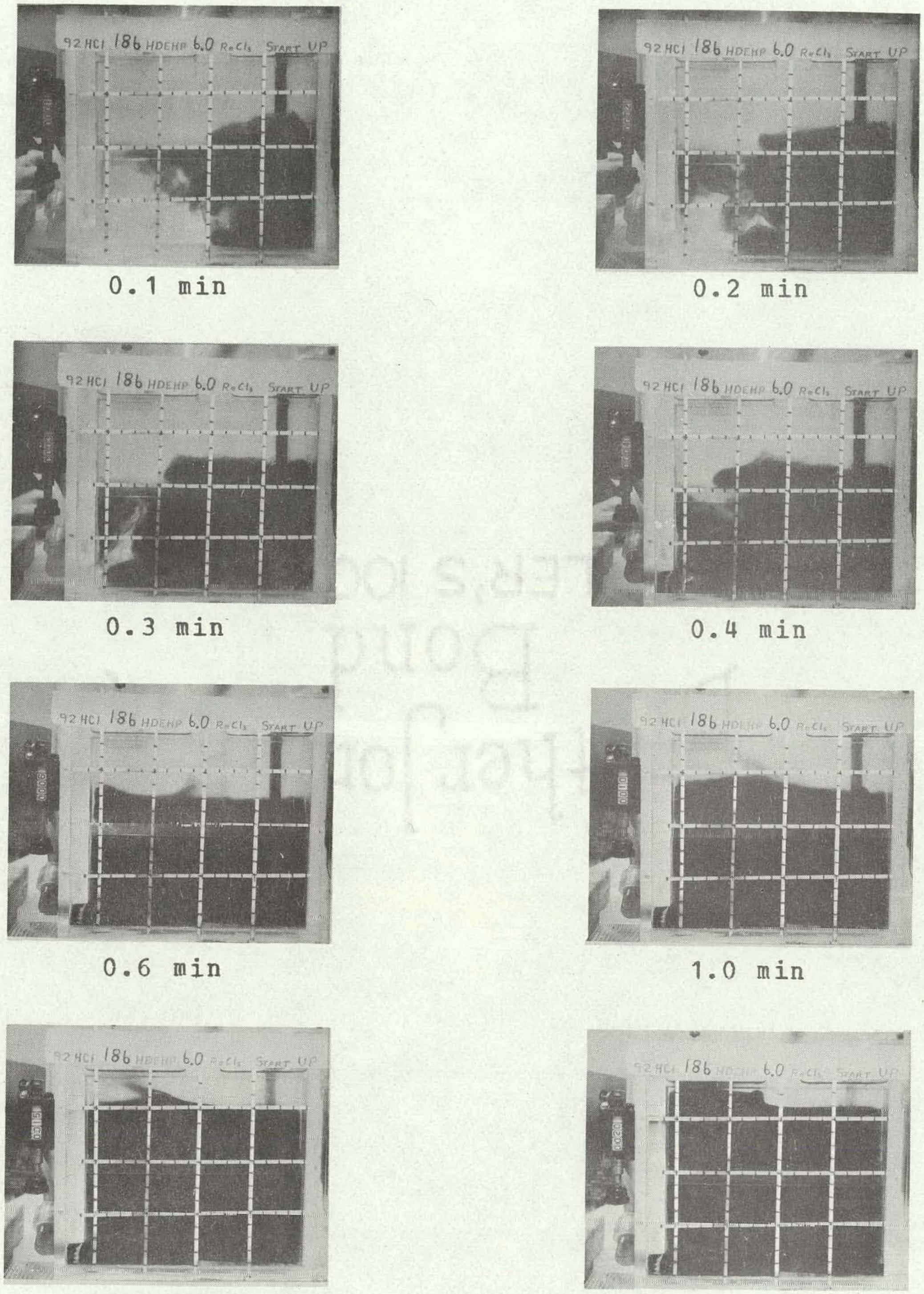
ANALYSIS AND SIMULATION

Settling Chamber

In observing the flow of the dye through the settling chamber it was noted that the flow was essentially two dimensional. Figure 3 shows photographs of the dye as it advances through the settling chamber. The outlines of the dye in the photographs are plotted in Figure 4. The areas contained by these outlines were measured with a Keuffel and Esser Polar Planimeter. Since the flow was two dimensional, these areas were then multiplied by the thickness of the settling chamber to give the corresponding volumes. These are listed in Table 1 and plotted against time in Figure 5 to give a measure of the amount of mixing actually taking place in the settling chamber.

Organic phase

As can be seen from Figure 5 the organic phase very nearly duplicates plug flow. It was also assumed that all of the volume that does not contain dye at the end of two minutes was dead space. In the pictures of the flow patterns (Figure 3) it is shown that the volume in the top right hand portion of the organic settling chamber was trapped by the heavier rare earth laden liquid below it and the partition support to the left. It was observed that this liquid remained trapped even after ten or more minutes of operation



0.1 min

0.2 min

0.3 min

0.4 min

0.6 min

1.0 min

1.5 min

2.0 min

Figure 3. Flow of dye in the settling chamber

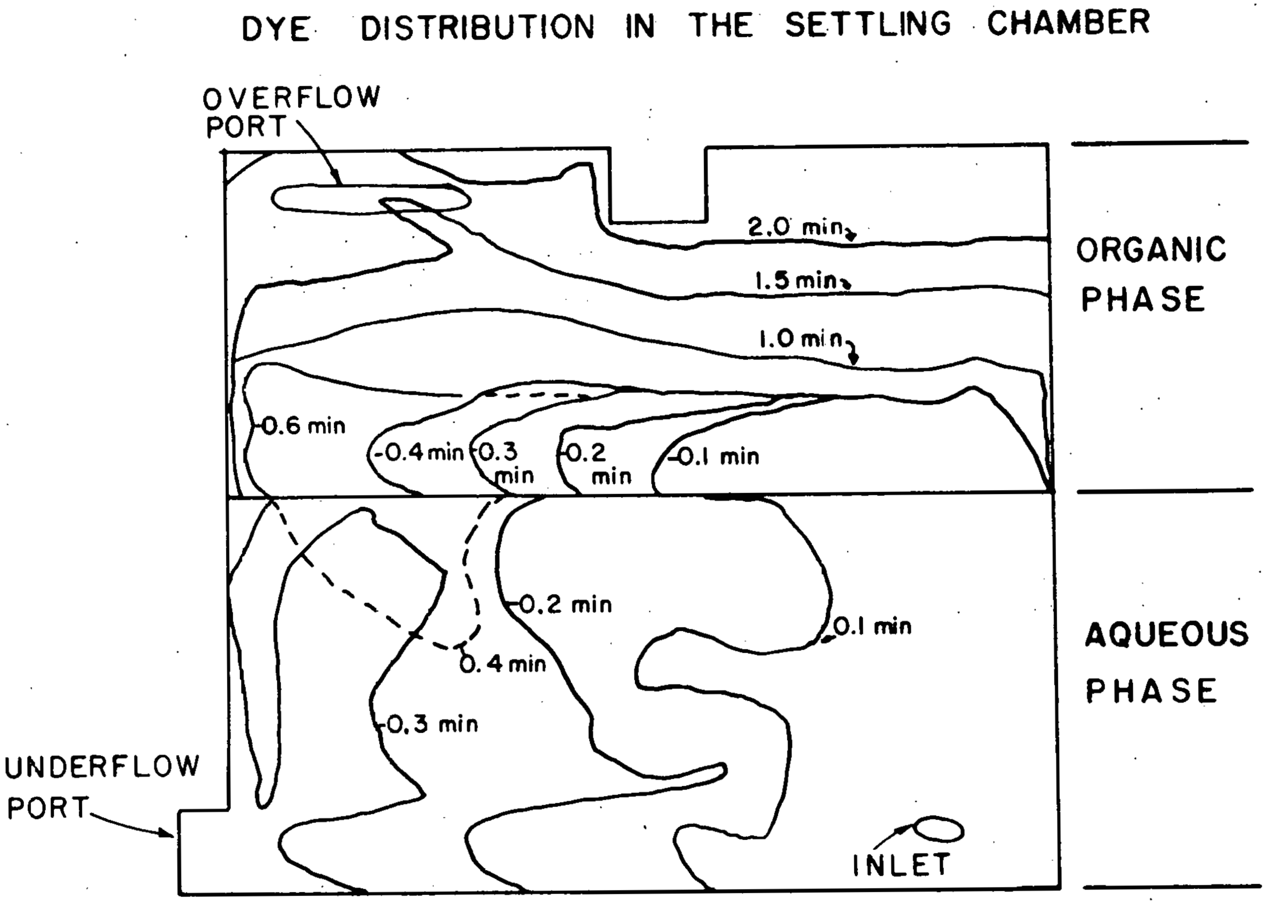


Figure 4. Outlines of the areas occupied by dye in the settling chamber

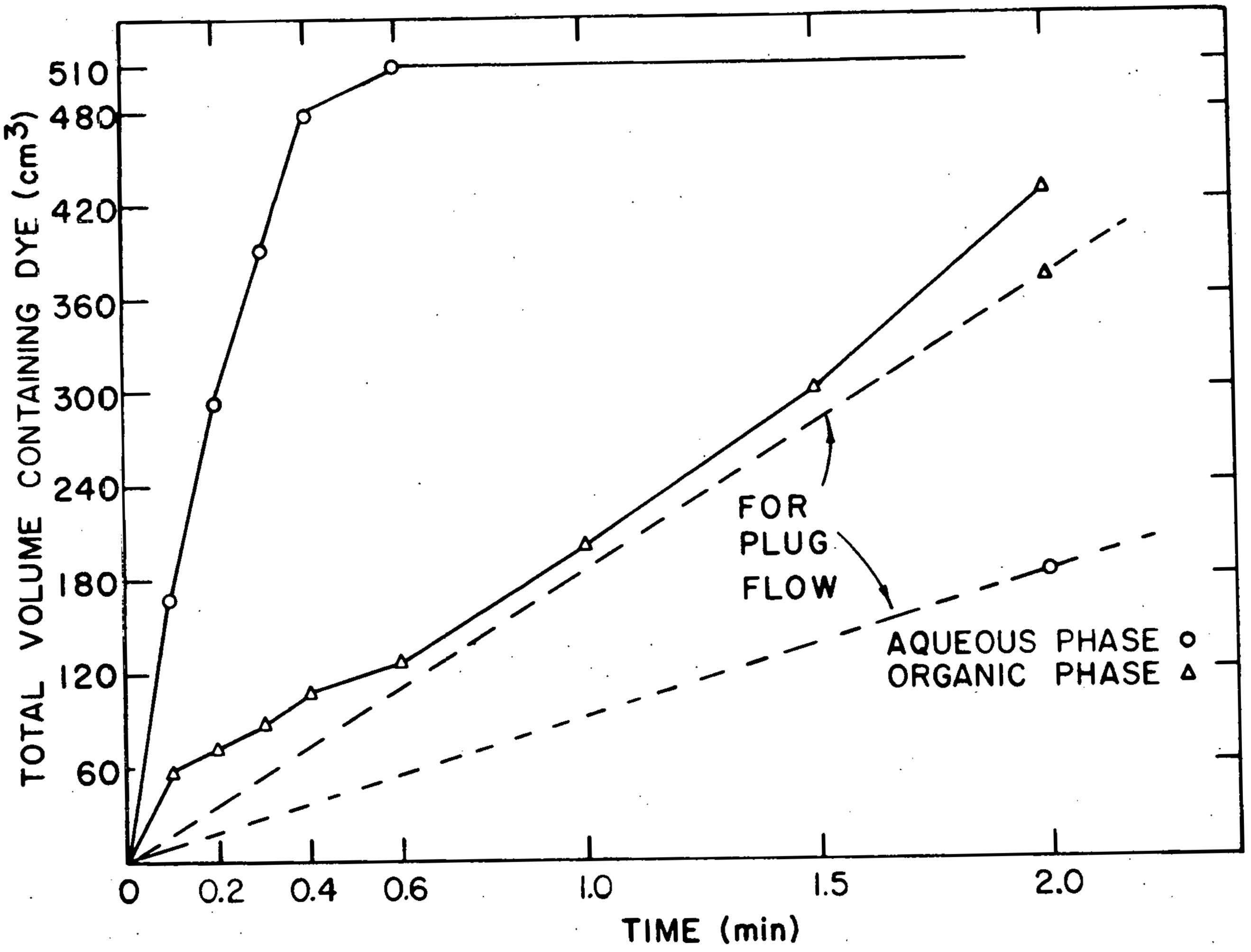


Figure 5. The volume occupied by dye in the settling chamber as a function of time

and hence was assumed to be dead space for this simulation.

Table 1. Volumetric flow in settling chamber

	Elapsed time in minutes	Change in dyed volume milliliters	Total dyed volume milliliters
Crganic phase	0.1	57	57
	0.2	15	72
	0.3	15	87
	0.4	20	107
	0.6	20	127
	1.0	73	200
	1.5	101	301
	2.0	127	428
Aqueous phase	0.1	169	169
	0.2	125	294
	0.3	97	391
	0.4	87	478
	0.6	32	510

To simulate this on the computer the organic portion of the settling chamber was assumed to respond like twenty small well mixed chambers. The dye took 2 minutes to fill the active portion of the chamber. Using a time increment of 0.1 minute, this requires twenty increments. This simulation is illustrated in Figure 6. It was assumed that plug flow was taking place in the second through the sixteenth volumes. The first volume is a well mixed volume twice as large as the remainder containing twice the time increment of the organic flow. This is the agitated entrance zone, as can be seen in

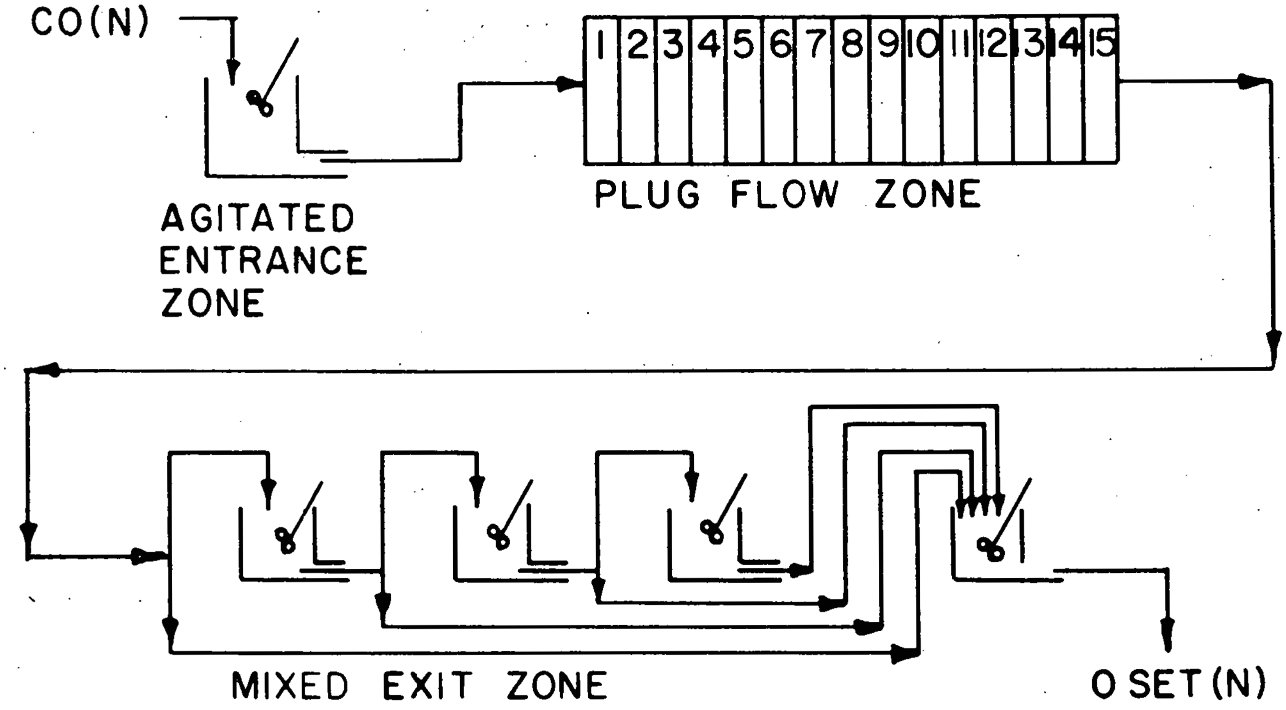


Figure 6. Model of the organic phase in the settling chamber

the first photograph of Figure 3. Figure 5 also shows that the first data point of the plot for the organic phase is twice as high as for plug flow. The exit stream from the settling chamber is drawn equally from each of the last four volumes. This is the exit zone of the settler where the flow ceases to be two dimensional.

Appendix A lists the Fortran program for a single stage simulation, and Figure 7 shows the response of this simulation to a step change in input. As shown in Figure 3, and in the simulated startup shown in Figure 7, the organic settling chamber does not begin releasing rare earths to the exit stream until 1.7 minutes after their entrance to the chamber. This does not contradict the results found by Casto as his first data was taken at the end of ten minutes.

Aqueous phase

Figure 5 indicates that the aqueous phase in the settling chamber is not in plug flow. It was observed while taking the pictures that while the dye advanced through the aqueous phase along the upper and lower boundaries, the nondyed portion flowed in the opposite direction in the center of the aqueous zone.

The photographs in Figure 3 show that the chamber took less than 0.6 minutes to become completely filled with dye. Since the time increment used is 0.1 minute, the simulation requires six well mixed chambers. It appeared that the flow

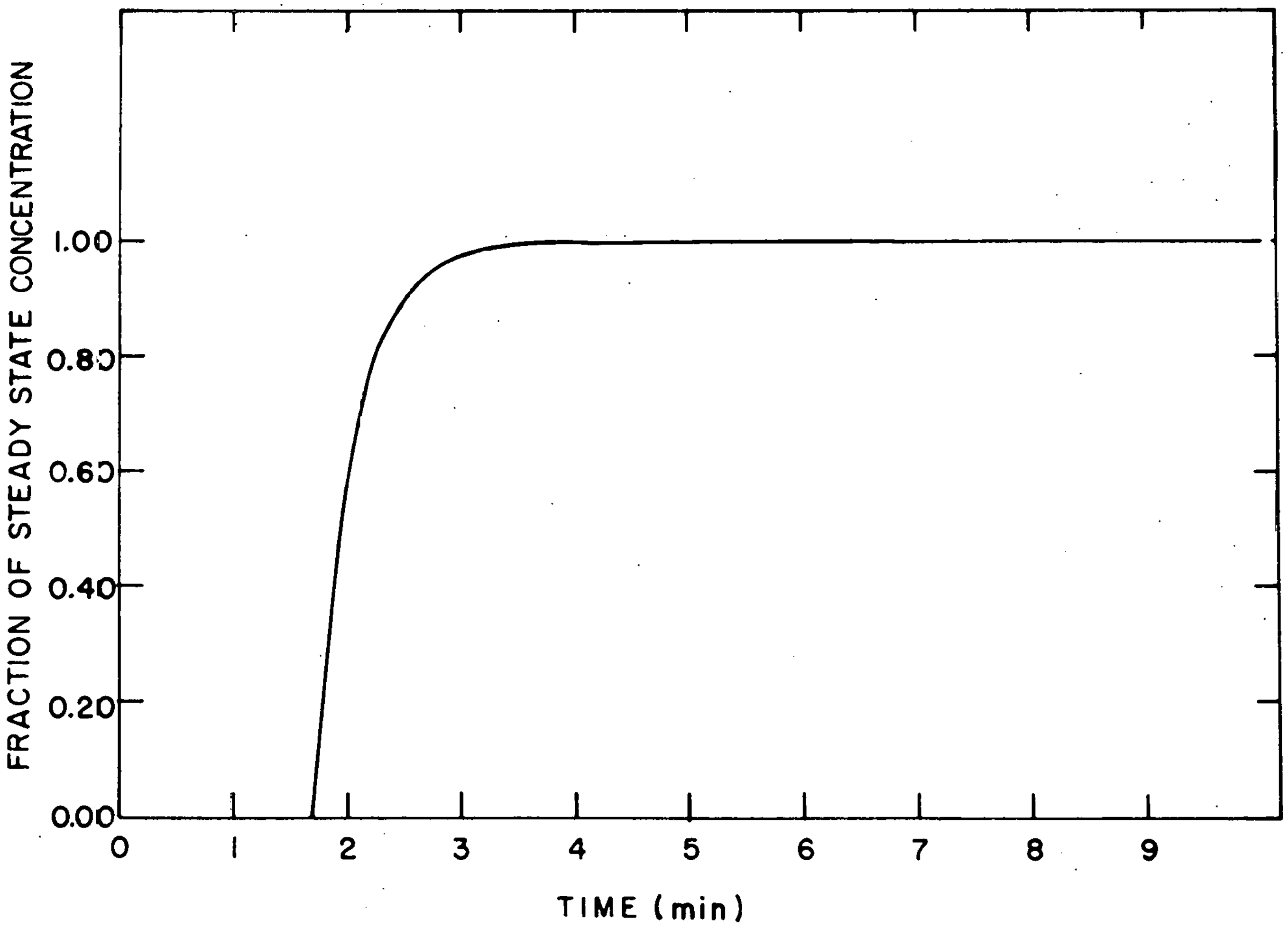


Figure 7. Response of the simulation of a single stage organic settling chamber to a step change

of organic phase through the aqueous phase increased the size of the apparent dyed aqueous volume in the first chamber of the model. This was partially due to the volume physically occupied by the organic material in this region. An even greater discrepancy is caused by the rapid upward flow due to the buoyancy of the organic material. This causes the dyed aqueous material to flow upward in a small column, rather than occupy the full thickness of the settling chamber. Hence the actual volume containing dye at the end of 0.1 minute is much less than that indicated by the photographs. Hence the volumes for the model were different from those given in Table 1.

The model for the simulation is illustrated in Figure 8. The material from the pump mixer enters the first well mixed zone, the first enters the second, et cetera. The material from the sixth flows back to the first. This rate of recycle is designated as ASR or Aqueous Circulation Rate. A portion of the material leaving the fourth chamber exits from the settling chamber and proceeds to the prepump chamber of the next stage. Appendix B lists the Fortran program for this simulation. Figure 9 is a plot of the response of a single stage aqueous settling chamber to a step change in input. In this plot six responses are shown for recirculation rates from 0 to 50 ml/min in steps of 10 ml/min.

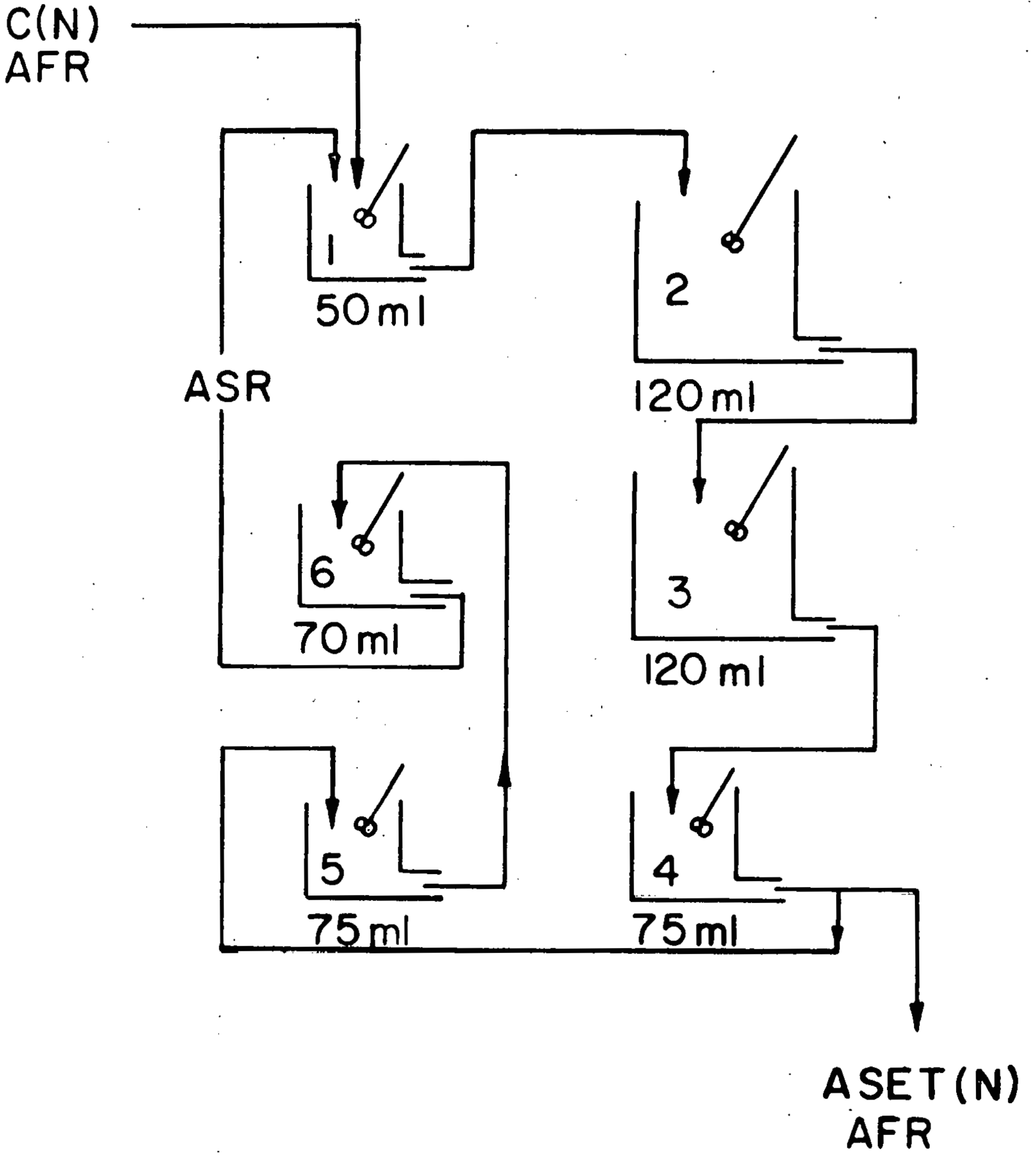


Figure 8. Model of the aqueous phase in the settling chamber

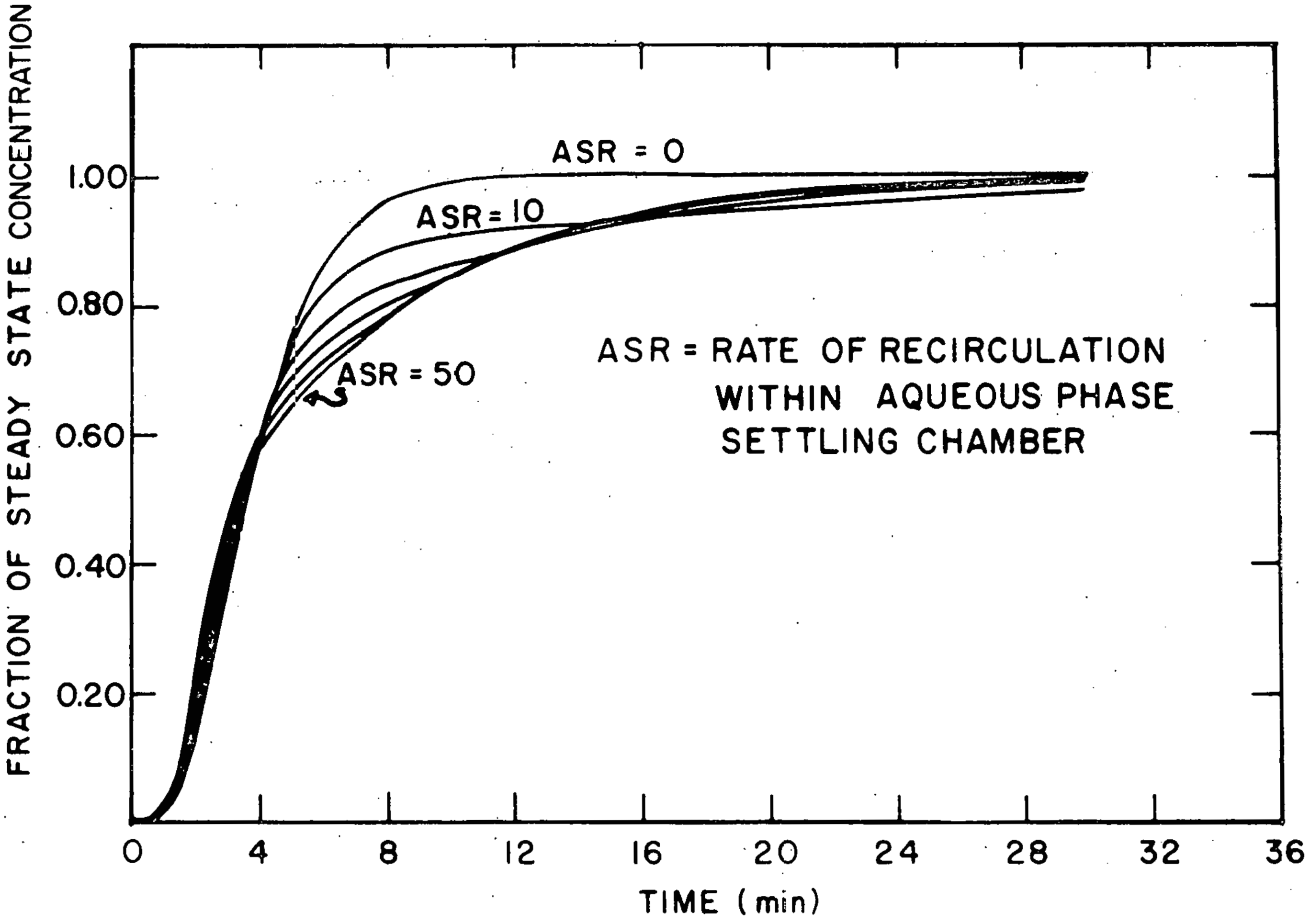


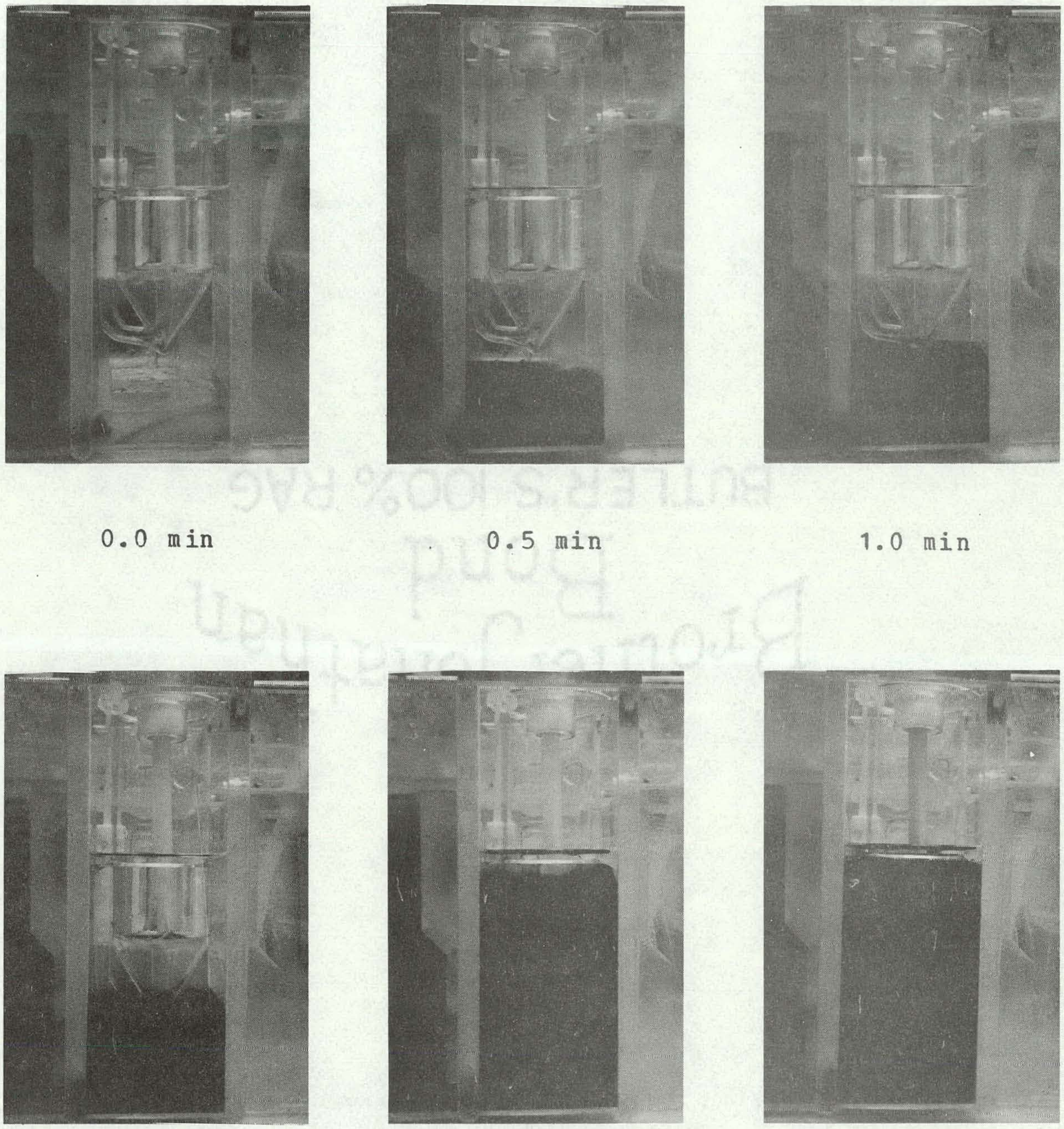
Figure 9. Response of the simulation of a single stage aqueous settling chamber to a step change

Prepump Chamber

The pictures taken of the chamber surrounding the pump mixer are shown in Figure 10. These photographs indicate that the flow is pure plug flow with a delay of 4 minutes. This added to the other delays is not enough to account for the 80 minute dead time in the raffinate phase shown in the original data. This apparent discrepancy is caused by the change in density of the material in the chamber. As the rare earth laden material enters the prepump chamber, the density of the material in the chamber increases, and the hydraulic pressure at the bottom of the chamber increases. To offset this increase the interface level rises in the settling chamber of the preceding stage. This causes a decrease in the flow rate of the aqueous phase entering the prepump chamber. This also effects the organic flow rates by an equal amount.

The height of the interface, shown as Hi in Figure 1, is equal to the density of the aqueous layer multiplied by the height of the aqueous layer minus the product of the density of the organic layer and the total height of the liquid in the settling chamber, all divided by the difference between the density of the aqueous and organic phases;

$$Hi = (Pa*Ha-Po*H)/(Pa-Po)$$



0.0 min

0.5 min

1.0 min

1.5 min

3.5 min

4.0 min

Figure 10. Flow of the dye in the prepump chamber

Where Pa is the density of the aqueous phase, and Po is the density of the organic phase. If it is assumed that the density of the aqueous phase increases from 1.0 to 1.06 grams per ml as the rare earths enter the system, it can be calculated from the hydraulic balance that the interface level will rise 1.6 cm, or the aqueous volume will increase 112 ml. This represents a time delay of 1.2 minutes.

For purposes of this simulation it was assumed that the prepump chamber was larger than the actual portion of the equipment, and that the flow rates were constant. A delay of 1.2 minutes was added based on the calculation of a hydraulic balance for a reasonable average increase in rare earth content of the aqueous phase during startup. Another 1 minute delay was added to account for the 90 ml displaced by the volume displacer in the prepump chamber, which was present in this work, but was not used by Casto(5,6) in his work. This chamber was then simulated by a delay of 6.2 minutes real time, or 62 iterations on the computer.

Pump Mixer

Hydrodynamic study

The pump mixer was rather difficult to study as the material in it was moving rather rapidly. When the dye was injected through the cover plate for the settling chamber studies, it was noted that the entire pump was colored by the dye almost instantly. This color remained in the pump for approximately five minutes before beginning to clear. This led to the assumption that the pump was well mixed. Initial simulations on the computer indicated that with a well mixed pump it was impossible to get as sharp a response as was obtained in the work of Casto(5,6). When the dye was added through the inlet port with the rare earth feed stock, a lightly colored boundary was observed to rise through the pump, followed by a darker colored boundary. This indicates that the phases are in plug flow, with the possibility that the residence times of the two phases may differ. For this simulation, the residence times are assumed to be identical.

From the observations of the type of flow present in the pump mixer, it is reasonable to calculate the pump volumes as follows.

The reactor volume involved in the mass transfer is equal to the time increment of the total liquid flow.

$$RV = dT*(OFR+AFR)$$

The volume of organic material involved in the mass transfer reaction is equal to the time increment of the organic flow rate.

$$OVP = dT*OFR$$

The volume of the aqueous material involved in the mass transfer reaction is equal to the time increment of the aqueous flow rate.

AVP = dT*AFR

These are the volumes used in the simulation as the volumes actually involved in the mass transfer process. The total volume in the pump mixer is known to be 135 ml. How much of each phase is contained in the pump is unknown. The remainder of each phase in the pump is estimated to be proportional to the flow rates. These remaining volumes are assumed to be in plug flow. As a time increment of one-tenth minute is used, a multiple of this must be used as the time delay caused by the plug flow. Four time increments (0.4 min) closely duplicates the delay for most of the flow rates used on this equipment. The model for the simulation of the pump mixer is illustrated in Figure 11.

Mass transfer derivation

In this simulation the rare earth equilibrium relationship used is as follows: At equilibrium, the concentration of rare earths in the organic phase is equal to a constant, K1, times the concentration in the aqueous phase. This is shown in Figure 12. If this were the only parameter used, the stagewise concentrations for the steady state operation would be as shown in Figure 13.

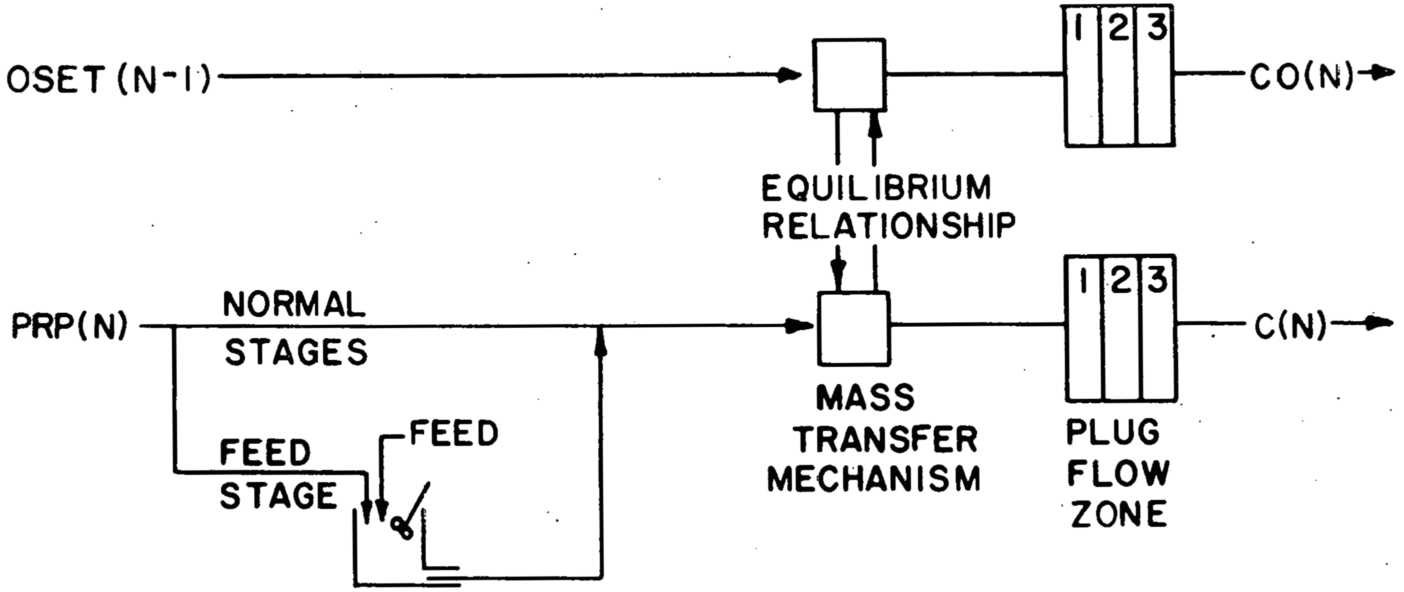


Figure 11. Model of the flow in the pump mixer

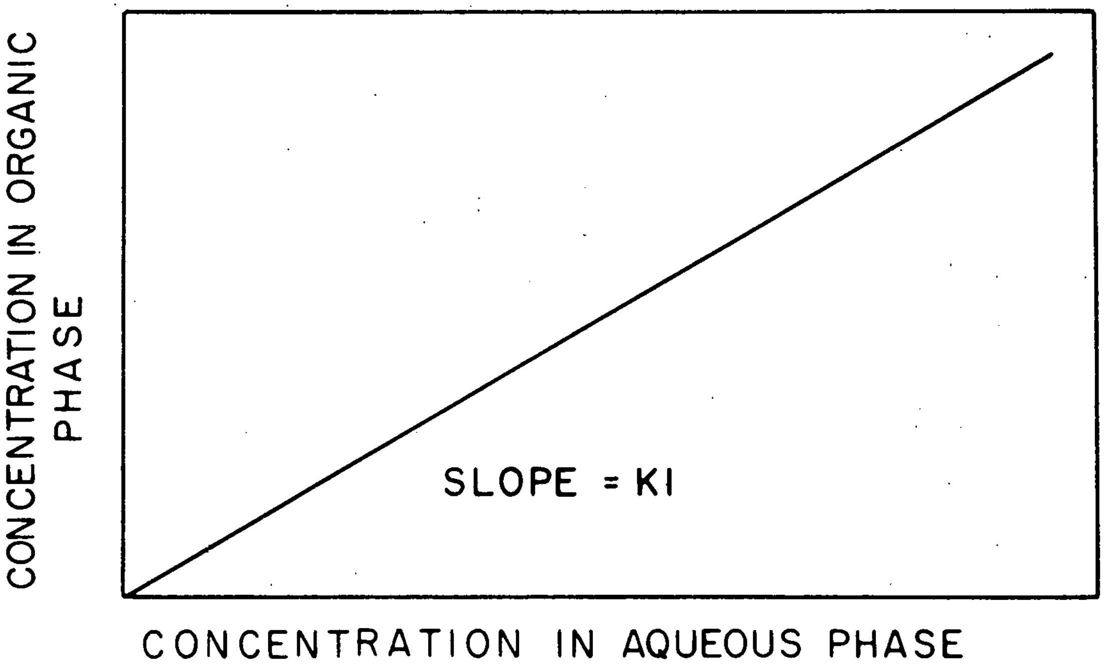


Figure 12. Pseudo equilibrium relationship between aqueous and organic phases

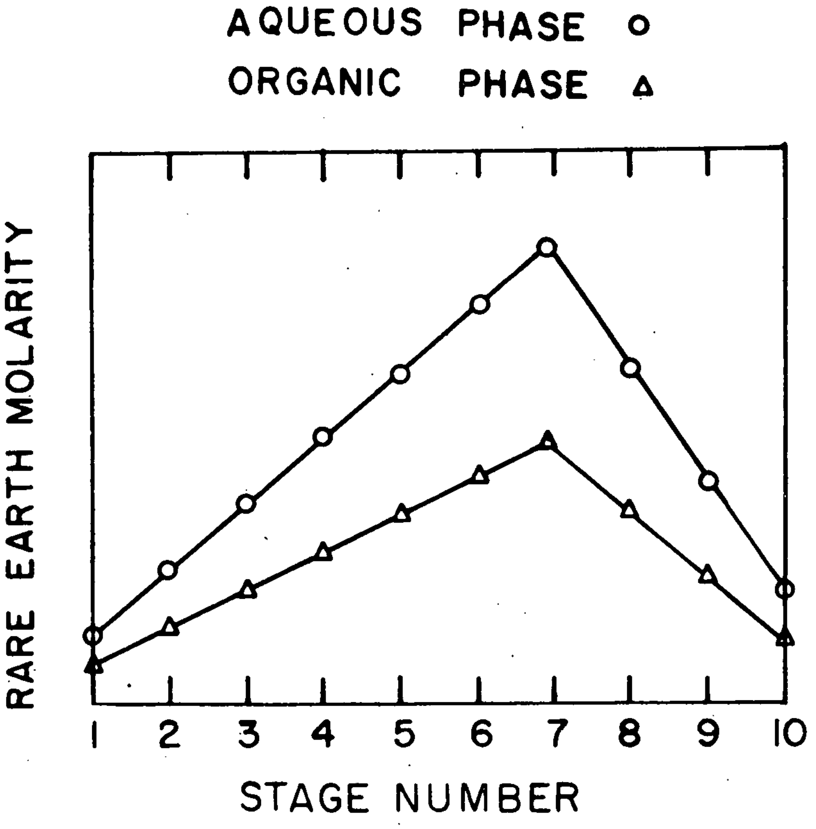


Figure 13. Stagewise concentrations for pseudo equilibrium stages

From the work of Rahn(18) the stagewise concentrations are known to be high in the aqueous phase in the extracting section only. In the stripping section the concentration in the organic phase is greater than that in the aqueous phase. Also the stagewise concentrations for each phase is relatively constant on either side of the feed stage. This is shown in Figure 14.

This is simulated as being the effect of poor stage efficency. This is known not to be the case from a simulated column run made with separatory funnels by Rahn(18). For a true simulation it would be necessary to use equilibrium data for each of the individual rare earths. This data is not yet available.

A first order rate constant, K2, was used for this simulation. This is defined as the rate at which rare earths are transferred between the phases, per unit volume, per molar difference between the concentration present in the organic phase and what would be present in equilibrium with the aqueous phase. The derivation of the equations for the programming of this concept follow. The notation used in this derivation is listed in Appendix E.

The rate at which rare earths are transferred between phases can be determined by a material balance on either of the phases. However the rare earth feed stream contributes liquid volume to the aqueous stream so that it is not con-

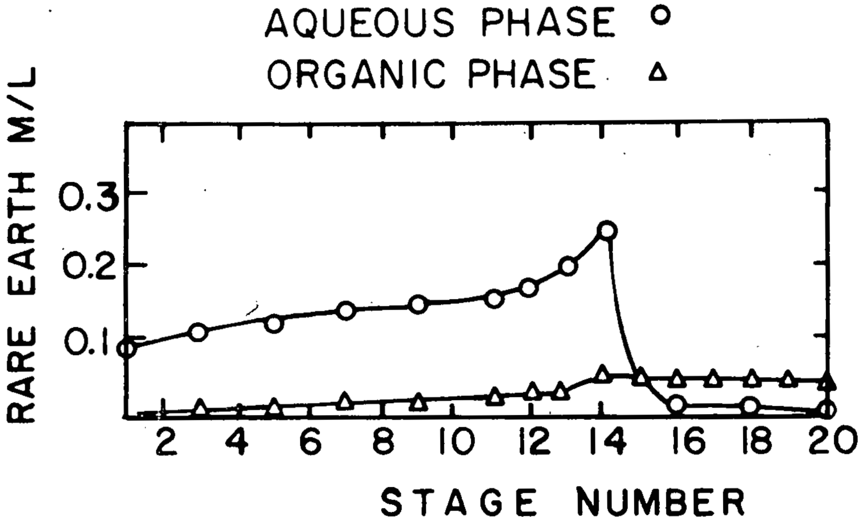


Figure 14. Experimental steady state stagewise concentrations of Rahn(18)

stant throughout the extractor. Hence it is more convenient to do the material balance on the organic phase. The rate of transfer is given by:

$$\text{Rate of transfer} = OFR*(CO(N-1)-CO(N))$$

This same rate of transfer can also be obtained by considering the concentration in the organic phase and the pseudo distribution concentration for the aqueous phase:

$$\text{Rate of transfer} = K2*RV*(CO(N)-K1*C(N))$$

Equating the two rate expressions and dividing by OFR:

$$CO(N-1)-CO(N) = (K2*RV/OFR)*CO(N)-K1*C(N))$$

Defining K3 = K2*RV/OFR and substituting:

$$CO(N-1)-CO(N) = K3*CO(N)-K1*K3*C(N)$$

Rearranging and factoring:

$$(K3+1)*CO(N) = CO(N-1)+K1*K3*C(N)$$

Dividing by (K3+1):

$$CO(N) = (CO(N-1)+K1*K3*C(N))/(K3+1) \tag*{1.}$$

By basic material balance:

$$\text{INPUT} - \text{OUTPUT} = \text{ACCUMULATION}$$

$$OFR*CO(N-1)+AFR*C(N+1)-OFR*CO(N)+AFR*C(N)) = (dCO(N)/dT)*OVP + (dC(N)/dT)*AVP$$

At steady state the time derivatives are zero. By collecting terms, factoring and rearranging we have:

$$C(N+1) = C(N)+(CO(N)-CO(N-1)*OFR/AFR \qquad 2.$$

$$C(N) = C(N+1)+(CO(N-1)-CO(N))*OFR/AFR \qquad 3.$$

Substituting 3 in 1 and solving for CO(N):

$$CO(N) = (CO(N-1)+K1*K3*(C(N+1)+CO(N-1)*OFR/AFR)) / (K3+1+K1*K3*OFR/AFR) \qquad 4.$$

Calculation of Pseudo Distribution and Rate Constants

From Casto's data the inlet and outlet concentrations are known at the ends of the column. It is possible to find the steady state stagewise concentrations throughout the column by successively applying equations 1 and 2 to the stage one aqueous phase concentration. Equations 1 and 2 contain two unknowns, K1 and K2. (K3 is a function of K2). By specifying a K2, a trial and error calculation is necessary to find K1.

The program to calculate K1 and K2 is listed in Appendix

C. This program initially reads in labels for graphs which will be produced by this program. Next it reads in the run number as designated by Casto(5,6). This is followed by the number of stages in the extractor, the feed stage number, and the input flow rates in ml per minute of the aqueous scrub solution, the organic extract solution and the rare earth feed solution. Next the composition of the feed, and the compositions of the aqueous raffinate product and the organic extract product are read. The program then performs a material balance calculation over the extractor to calculate the feed flow rate. The new calculated value is then output on the printout.

The program calculates the aqueous flow rate in the extracting section of the apparatus as the sum of the input aqueous flow rate and the feed flow rate. This seems reasonable as the feed stream is aqueous in nature. The aqueous flow rate in the stripping section is considered to be the same as the input aqueous flow rate. The extracting section and stripping section aqueous flow rates are stored in the computer as the variables AFRE and AFRS respectively. Then the aqueous flow rate is equated to the appropriate value as the calculations proceed from one end of the column to the other.

In this program the value of the pseudo rate constant is initially set to 5 and decreased to a value of 0.2 by increments of 0.2 to give a range of values for the pseudo distribution and rate constants. The value of the pseudo distribution constant is initially set to 0.0 at the beginning of each calculation for a new pseudo rate constant. Equations 1 and 2 are then applied successively to the output aqueous concentration until the other end of the column is reached. The input aqueous concentration is known to be 0.0. The calculated input concentration is then compared to 0.0. It it is less than 0.0, the pseudo distribution constant is increased first by tenths until the aqueous input is positive, then by hundredths, et cetera, until the input concentration is calculated to be less than one millionth. Then the stagewise concentrations are plotted to allow their comparison to known data.

The value of the pseudo rate constant is then incremented, the value of the pseudo distribution constant set to zero and the calculations repeated. When the calculations for the lowest desired pseudo rate constant have been completed, the program then plots a graph of pseudo rate constant versus pseudo distribution constant. Figure 15 shows a plot of K1 versus K2. The selection of the values of K1 and K2 used for the simulation was made by comparing the simulated steady state stagewise concentrations for various pseudo distribution and rate constants with the experimental steady state stagewise concentrations. Some of the simulated

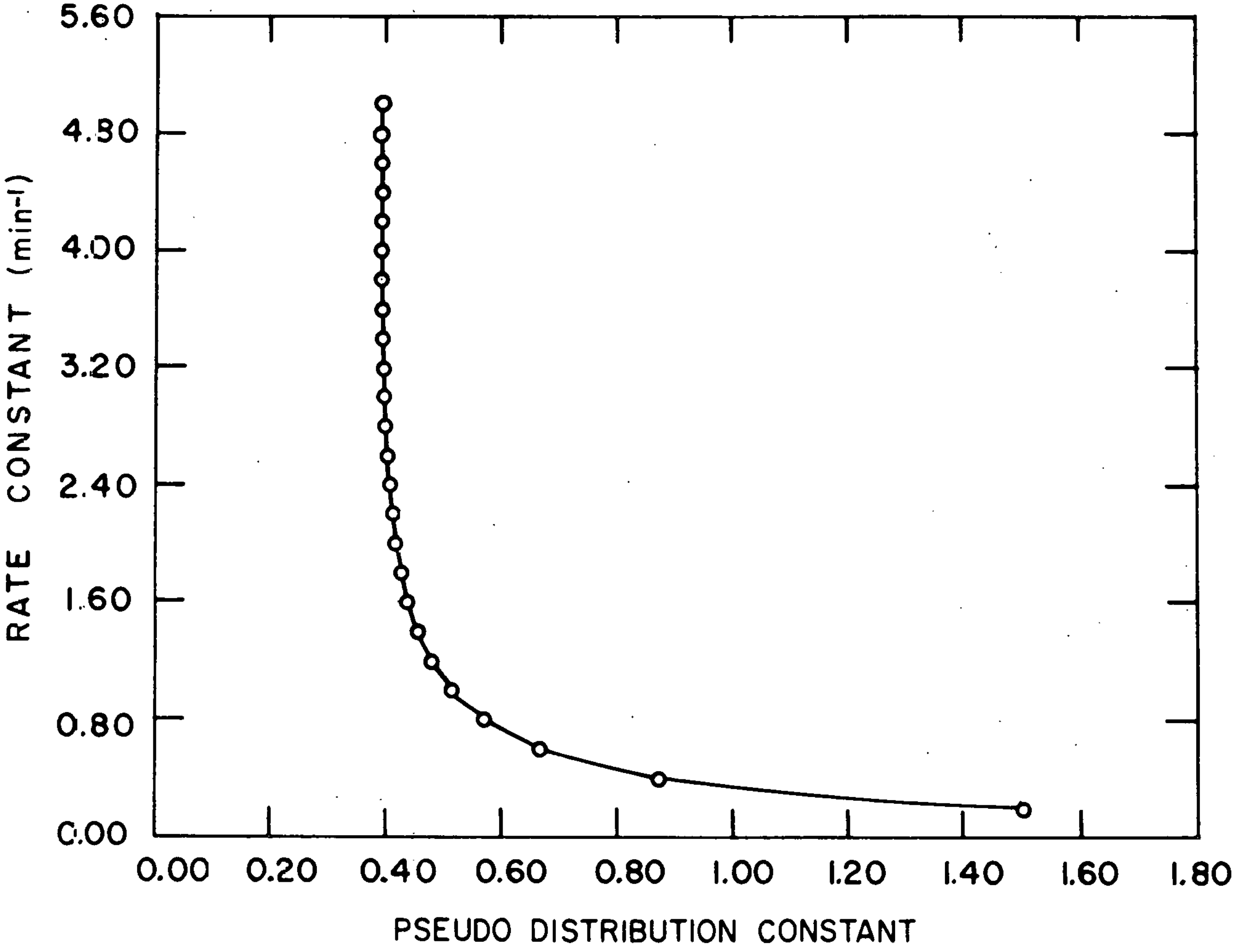
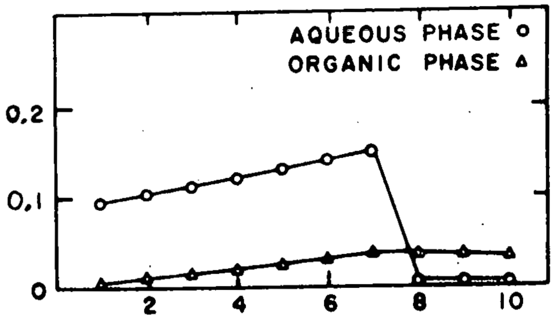
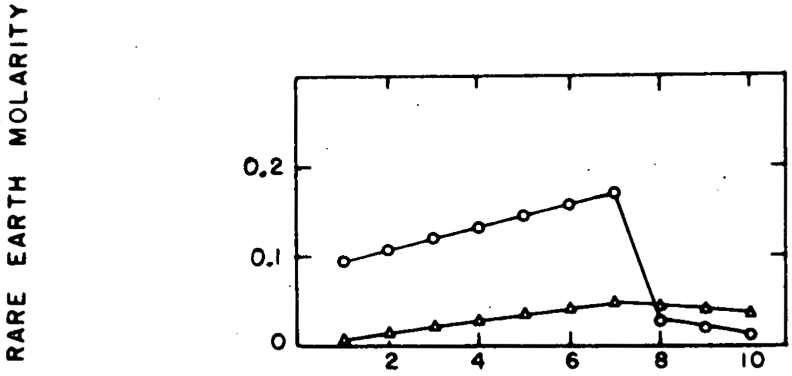


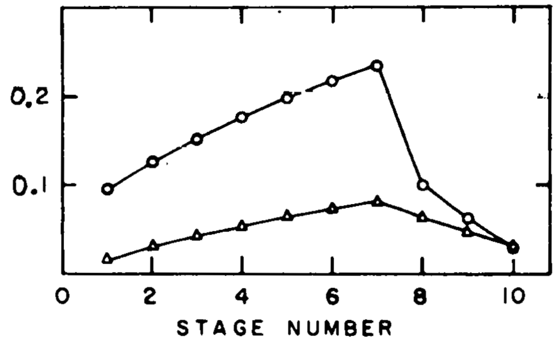
Figure 15. Relationship between pseudo distribution and pseudo rate constants



16a. Stagewise concentrations for rate constant of 0.2



16b. Stagewise concentrations for rate constant of 0.5



16c. Stagewise concentrations for rate constant of 1.0

Figure 16. Comparison of simulated stagewise concentrations for various values of pseudo constants

stagewise concentrations are shown in Figure 16.

Care must be taken in the trial and error calculation process, because for every K2 there are an undetermined number of K1's which will satisfy the end conditions. These are harmonics of the desired solution. The undesirable harmonic solutions produce negative concentrations in certain intermediate stages.

The convergence scheme used in this program is crude. However the inlet aqueous concentration as a function of pseudo distribution constant was found to be too highly irregular to allow the use of a more sophisticated convergence scheme.

Simulation of Mixer-Settler Extractor

When the proper values of K1 and K2 have been determined, Equations 3 and 4 are then used for the actual simulation. These are used as the pseudo equilibrium relationship in the simulation of the pump mixer. In deriving these equations it was assumed that the time derivatives were equal to zero. By using a two step calculation the total amount of material in the pump-mixer can be kept constant during the calculation of the mass transfer between phases. Hence although the individual derivatives are not equal to zero, the accumulation term of the material balance is indeed zero and the equations remain valid for this simulation.

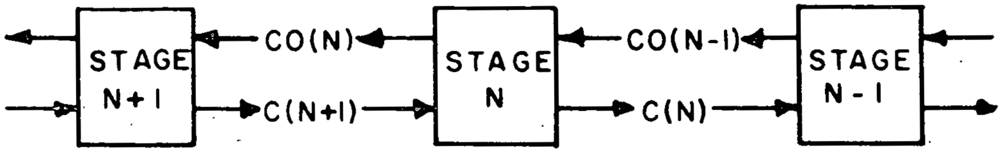
The program for the simulation was written so that it could simulate any of the runs made by Casto et al.(5,6,7), which did not involve upsets. All arrays in the program are dimensioned to handle an extractor as large as twenty stages. For a large change of flow rates, it is necessary to change the time delays in the plug flow zones. The program is written to continuously read in new paramaters and then simulate the startup of the specified extractor. The program is set to terminate if the number of stages is specified as less than five.

The program reads in all essential constants for a startup. It reads in graph labels for the plots which will be produced in the program. It next reads in the designated run number, the total number of stages in the extractor, and the feed stage number. These are followed by the flow rates of the organic and aqueous phases, and the feed. The steady state output concentrations of the organic and aqueous output streams and the feed composition are read in last. These are then output to the printer. A new feed flow rate is then calculated from a material balance on the extractor input and output streams. This value is then output to the printer. The values for the pseudo distribution and rate constants to be used in the simulation are then read.

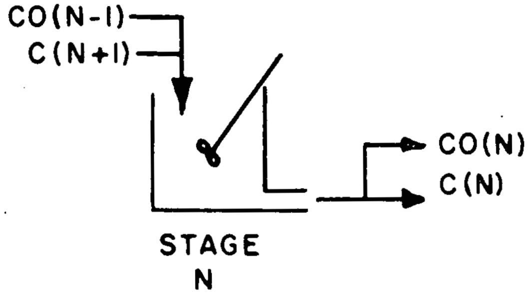
The program then initializes the arrays to zero. This is similar to cleaning the extractor before a run. The aqueous flow rate in the extracting section is calculated as the sum of the input aqueous flow rate and the feed flow rate as in the K1 and K2 calculations.

In this simulation, time is started at 17 minutes rather than at zero. This is because in the run by Casto that is being simulated, the feed was added to the prepump chamber, rather than being fed through the interface control tube. Casto(6) observed that the rare earth feed solution collected in the bottom of the prepump chamber. This layer increased in depth for about 17 minutes before reaching a constant level. It would seem reasonable that this layer would build up without an appreciable amount dissolving into the aqueous stream, until the depth was sufficient to partially block the underflow port leading to the feed stage prepump chamber. Then the layer extending into the underflow port would be exposed to the moving aqueous stream, and be dissolved at a rate equal to the feed flow rate. This is simulated simply by adding 17 minutes to the initial starting time.

The heart of the simulation consists of a master calling program and the simulations of the various parts of the equipment written as subroutines. The flow of material in the extractor is cocurrent within each stage, and countercurrent overall. This is illustrated in Figure 17. The simulation also uses this in its information flow pattern illustrated in Figure 18. The simulations of the prepump chamber, the pump mixer, the organic phase settling chamber,



17a. Interstage flow



17b. Intrastage flow

Figure 17. Flow scheme of materials within and about stage N

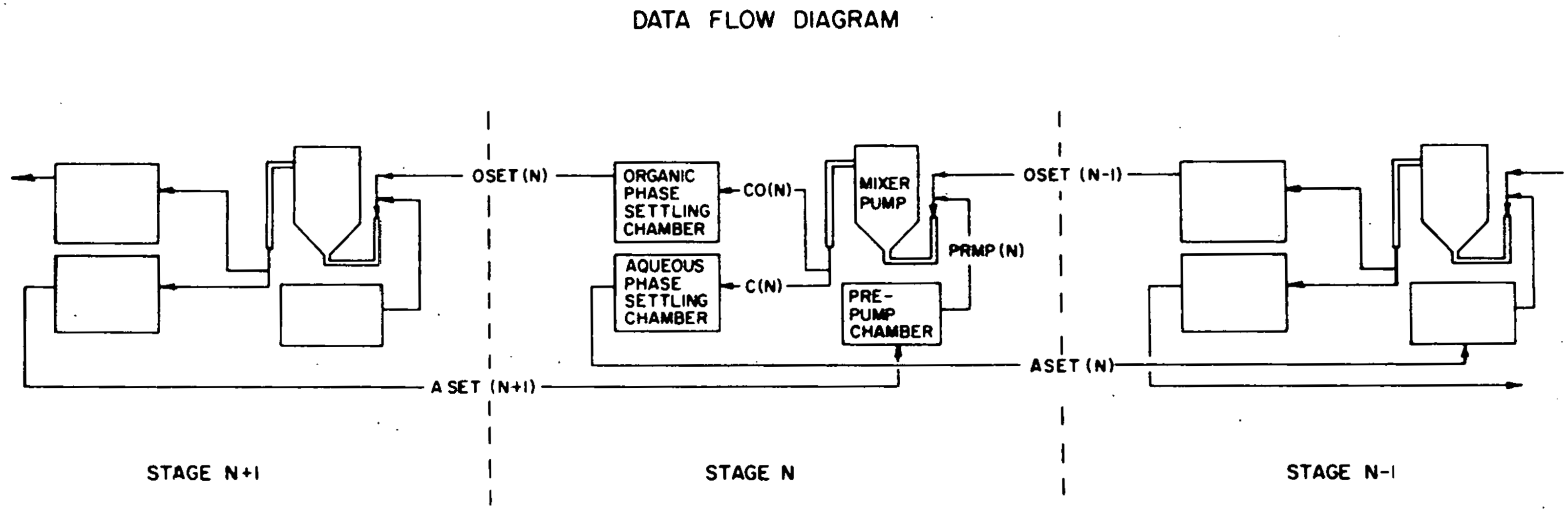


Figure 18. Information flow diagram for simulation of model

and the aqueous phase settling chamber are referred to as PRMP, PUMP, OSET, and ASET respectively. The simulation of the modified feed stage pump mixer is called FEED. As each of these subroutines are called by the master program, the fluid in them is incremented by one-tenth of a minute.

Since in the runs by Casto samples were usually taken every ten minutes, this simulation is written to output a data point every hundred iterations or every ten minutes real time. This continues for a total of 390 minutes real time. This is sufficient for the startup of even a twenty stage run.

After a startup is completed, the program plots the simulated startup along with the experimental data listed in Table 2, for comparison. The program reads first the number of the aqueous phase experimental data points for the startup, and then reads the aqueous concentrations and times for these points. This is then repeated for the organic phase. The data from the simulation is plotted as solid lines drawn between the data points produced by the simulation. The experimental data is plotted as points, circles representing the aqueous phase data, and triangles representing the organic phase data. A plot is also made of the stagewise concentrations for both phases. Both of these plots are made in two sizes, for convenience.

A second simulation was made to test the possibility of simplifying the model. For this simulation a time increment of one-half minute was chosen. The prepump chamber is again pure plug flow, but due to the larger time increment must be simulated as having a time delay of six minutes or twelve increments of one-half minute each. The organic phase in the settling chamber was simulated as pure plug flow with a time delay of two minutes. The aqueous phase is considered as well mixed. The pump is small enough to be considered to be completely emptied during each iteration. Hence the type of flow is unimportant.

For this simulation the programs described previously were modified to accept the new time increment. The values for the pseudc distribution and rate constants were recalculated, by changing the value of the reactor volume. The subroutines in the program for the simulation were replaced by the new, greatly simplified versions. This lessened the size of the arrays needed in the program. The number of iterations required to simulate the startup to steady state operation were reduced by a factor of five.

Table 2. Experimental data from Casto(6)

Aqueous phase		Organic phase	
Time in minutes	Rare earth molarity	Time in minutes	Rare earth molarity
10	0.00015	10	0.00126
40	-	20	0.00111
50	0.0001	30	0.00261
60	0.00015	40	0.00824
65	0.00116	50	0.01367
70	0.00548	60	0.01733
75	0.01407	70	0.0202
80	0.02497	80	-
85	0.03663	90	0.0230
90	0.04652	100	-
95	0.05486	110	0.0254
100	0.0624	120	0.0262
105	0.06757	130	0.0279
110	0.07285	140	0.0279
120	0.07938	150	0.0281
130	0.08440	160	0.0283
140	0.08817	170	-
150	0.09043	180	0.0299
160	0.09219	190	-
170	0.09345	200	0.0309
180	0.09395	210	-
190	0.09470	220	0.0322
200	0.09470	230	-
210	0.09445	250	0.0324
220	0.09470	303	0.0324
230	0.09470		
250	0.09520		
270	0.09495		
290	0.09446		
310	0.09546		

RESULTS AND CONCLUSIONS

The results of the pseudo distribution and rate constant calculation generally showed an inverse relation between the two. The program shown in Appendix C terminated with a pseudo rate constant of 0.2. It was found that further reduction of the pseudo rate constant produced pseudo distribution constants which were unreasonably large, without producing a significant change in the stagewise concentrations.

The use of a pseudo rate constant of 0.2 and the corresponding pseudo distribution constant produced a simulated startup which was close to the actual experimental data. This is shown in Figure 19. The aqueous phase data was extremely close. The simulated organic phase data gave a faster startup than was found experimentally. This is because the interface level was assumed to be constant. In the apparatus the interface actually rose during startup, producing a higher organic phase flow rate in the stripping section. The result was that the organic output stream was diluted during startup. As the extractor approached steady state the interface levels became constant, and the organic flow rate decreased until steady state was attained. Adding a simulation of this to the program would more closely approximate the experimental data.

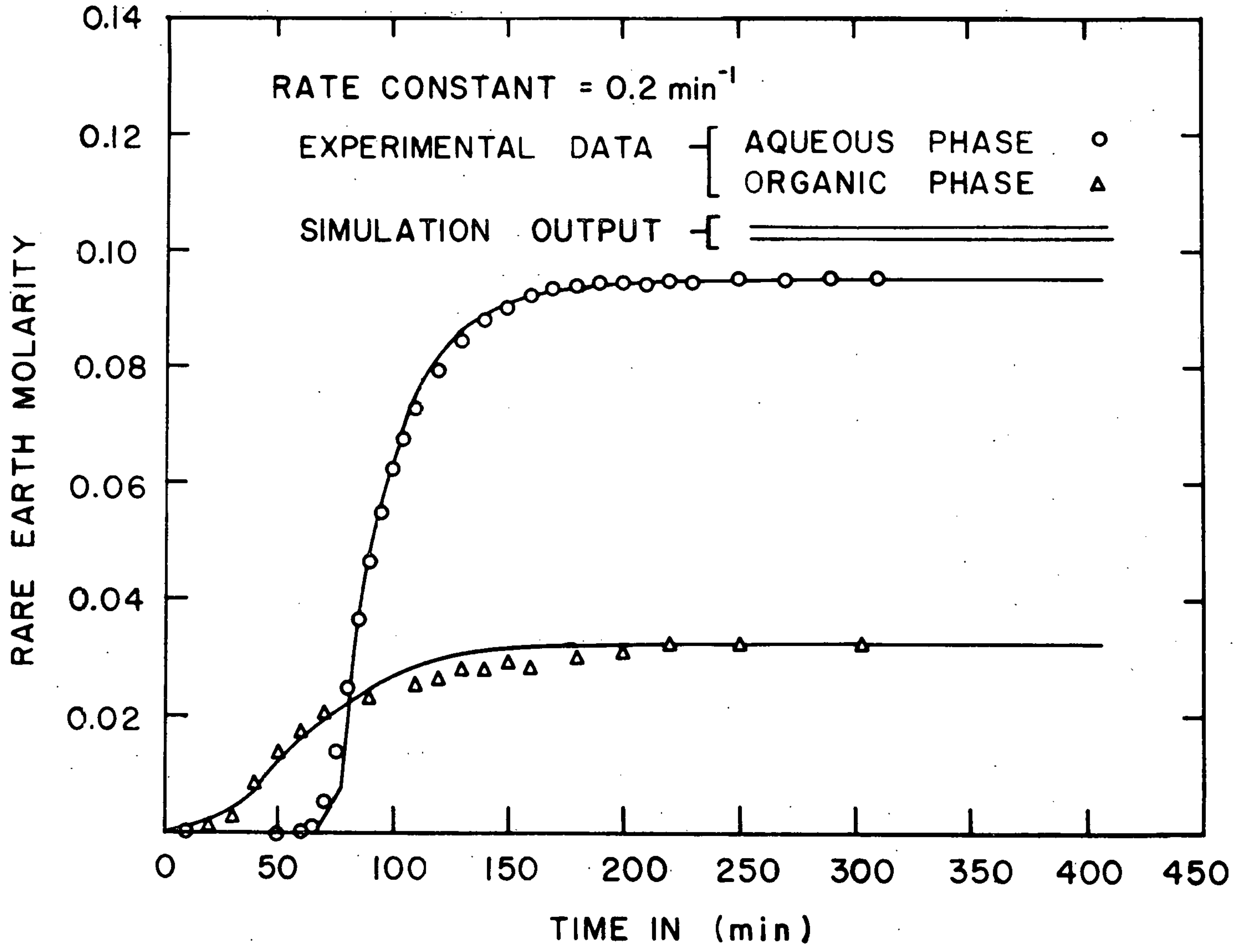


Figure 19. Comparison of simulated to experimental results

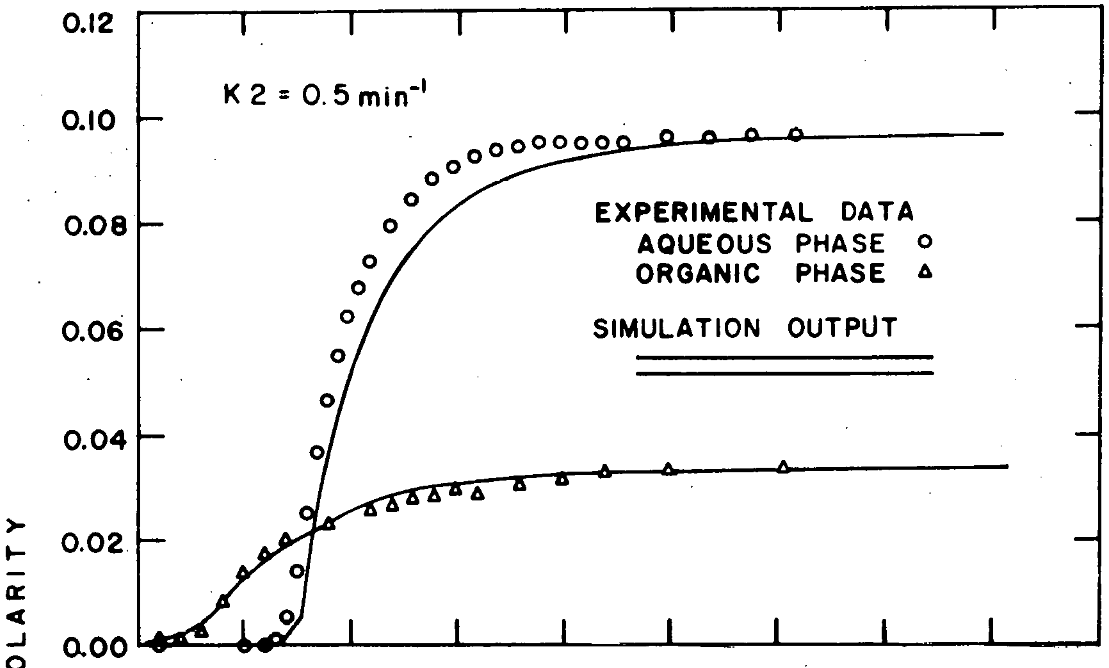
This parameter was not included to simplify programming. It should also be mentioned that the organic phase was very difficult to analyze chemically. Hence some error can be expected in the experimental data. Therefore the exclusion of this parameter can be justified.

As the pseudo rate constant is increased, the startup becomes more gradual. This is shown in Figure 20. This is because more material is being extracted in the extracting section, and stripped in the stripping section. As it is increased the entire extractor recirculates more and more material. In the limit, this approximates the time constant response of a well mixed zone.

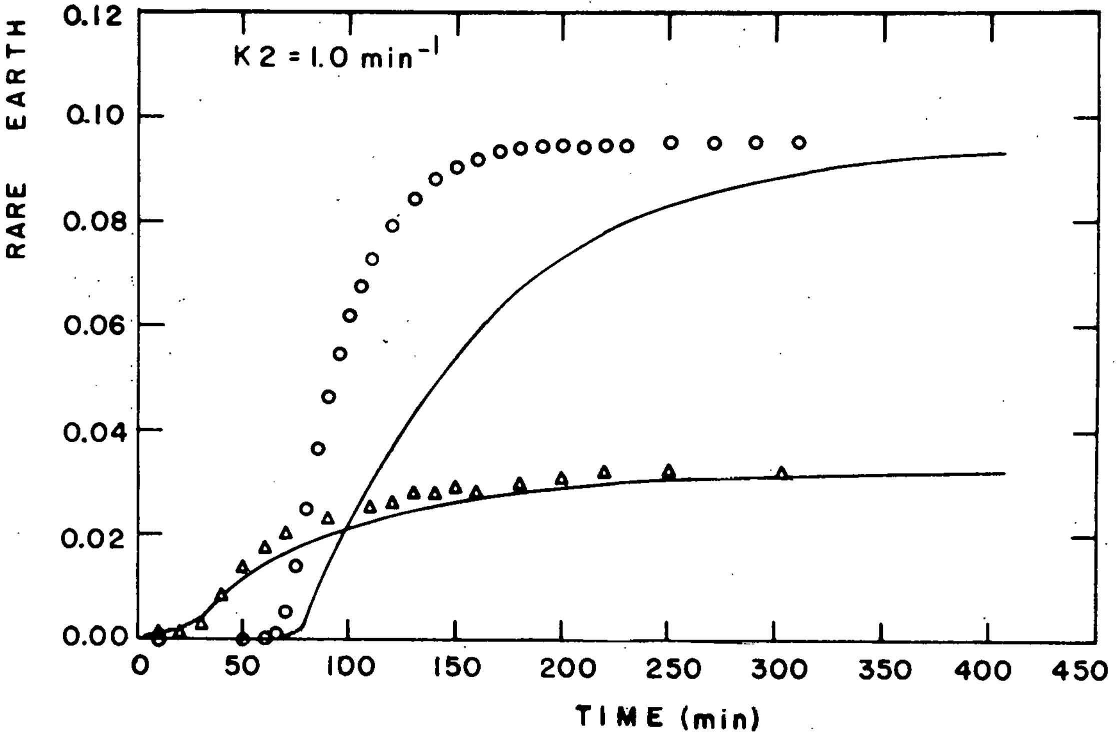
The time increment of 0.1 minute was chosen so that the physical flow patterns could be simulated in detail. However it can be seen from Figure 21 that nearly as good startup to steady state data can be obtained from the simpler model, simulated with a time increment of 0.5 minute. A simulation of this type would normally be more practical.

The simplification of the model and simulation produced a considerable savings in computer time and space. The central processing unit time required for the calculations was reduced from 133 seconds to 7 seconds. The region required was slightly reduced from 54K to 46K.

It should be emphasized that the model is for startup only. The flow patterns in the machine are highly dependent



20a. Startup to steady state for rate constant of 0.5



20b. Startup to steady state for rate constant of 1.0

Figure 20. Effect of change in pseudo rate and distribution constants

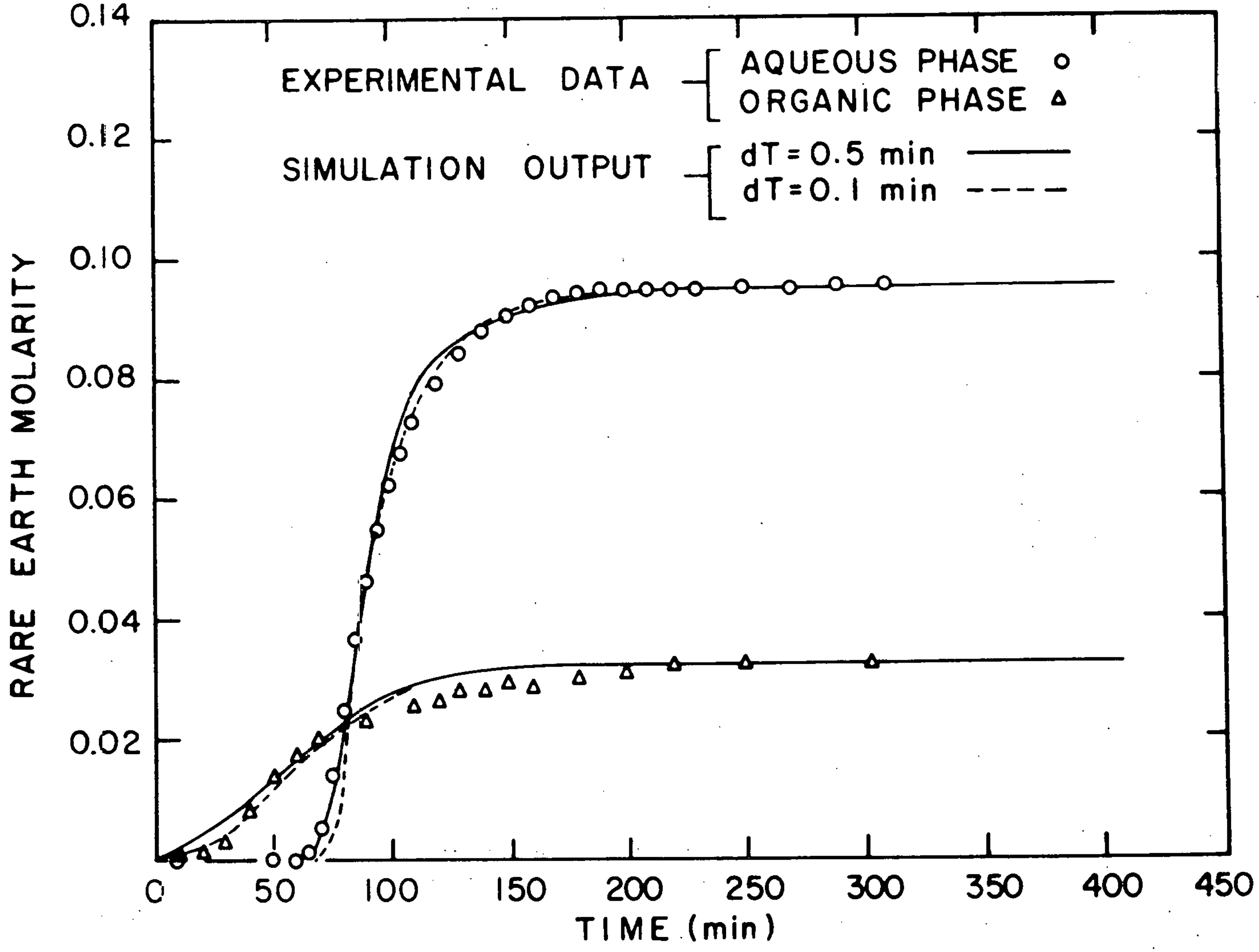


Figure 21. Comparison of detailed and simplified simulations

on density changes. During a startup, a more dense material is being added to each part of the equipment. This causes the plug flow in the prepump chamber and the organic phase settling chamber. During shut down, the situation is reversed. A lighter material is entering which immediately flows upward to the top of the chamber producing a partially shunted, partially mixed chamber. A similar situation exists in the pump mixer.

The aqueous phase settling chamber will always be agitated by the organic phase flowing through it. However if the material entering is much more dense than the residual material, the agitation will not be sufficient to produce an appreciable amount of mixing. A heavy layer will form on the bottom until the underflow port is covered. Then this layer will remain at a constant thickness until it is slowly mixed with the residual material. As the density becomes more nearly uniform, the mixing increases.

If the material introduced is much lighter than the residual material, the situation is reversed, and the lighter layer forms at the top of the aqueous phase settling chamber. The chamber then operates in essentially plug flow until the more dense material is pushed out.

These flow patterns could be expected to be present in all similar equipment. If the material enters the settling chamber at the interface level or lower, and is more dense than the residual material, the same forces will be present as were present in this system. This can be expected to produce a similar response in the settling chamber. Whether or not the mixer is plug flow or well mixed is a function not only of density, but also the basic equipment design. As noted earlier, the output of the computer simulation is strongly influenced by the mass transfer mechanism. These findings should be of value in studies of all similar equipment, including opaque and liquid metal systems.

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APPENDIX A:
SIMULATION OF
ORGANIC PHASE SETTLING CHAMBER

```
//D215OR JOB 'A0366,TIME=7,REGION=144K,LINES=2K,CARDS=300',BEETNER
//STEP1 EXEC FORTG,LINES=2,CARDS=300,REGION.GO=128K,TIME.GO=3
//FORT.SYSIN  DD  *
      DIMENSION XL(5),YL(5),GL(5),DL(5)
      DIMENSION X(100),Y(100),XOSET(20)
      DO 10 I=1,20
   10 XOSET(I)=0.0
      DO 30 I=1,100
      XTIM=I
      X(I)=XTIM/10.0
      Y(I)=XOSET(20)
      XOSET(20)=(XOSET(19)+XOSET(18)+XOSET(17)+XOSET(16))/4.0
      XOSET(19)=(3.0*XOSET(19)+XOSET(18))/4.0
      XOSET(18)=(XOSET(18)+XOSET(17))/2.0
      XOSET(17)=(XOSET(17)+3.0*XOSET(16))/4.0
      DO 20 J=1,15
   20 XOSET(17-J)=XOSET(16-J)
   30 XOSET(1)=1.0
      READ(5,100) XL,YL,GL,DL
      DO 40 I=1,100
      WRITE(6,110) X(I),Y(I)
   40 CONTINUE
      CALL ORIGIN(0,1.5,1)
      CALL GRAPH(100,X,Y,1,4,10.0,7.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
      CALL ORIGIN(15.0,2.0,1)
      CALL GRAPH(100,X,Y,1,4,05.0,4.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
      STOP
  100 FORMAT(20A4)
  110 FORMAT(' X(I)=',E20.10,'   Y(I)=',E20.5)
      END
//GO.SYSIN  DD  *
TIME IN MINUTES     FRACTION OF S S VAL START UP OF A SINGLESTAGE ORGANIC SETTLE
//GO.FT14F001  DD  DSNAME=&SM,UNIT=SYSDA,DISP=(NEW,PASS),               SMPLT1/3
// SPACE=(800,(120,15)),DCB=(RECFM=VS,LRECL=796,BLKSIZE=800)            SMPLT2/3
//SMPLTTR EXEC PLOT,PLOTTER=INCRMNTL,PARM.PLOT='TYPE 00 PAPER PLEASE'   SMPLT3/3
//
```

APPENDIX B:
SIMULATION OF
AQUEOUS PHASE SETTLING CHAMBER

```
//D215AQ  JOB 'A0366,TIME=5,REGION=96K,LINES=4K,CARDS=300',BEETNER
//STEP1 EXEC FORTG,LINES=2,CARDS=300,REGION.GO=96K,TIME.GO=2
//FORT.SYSIN  DD *
      DIMENSION TIME(300),Y(300),XL(5),YL(5),GL(5),DL(5),X(6)
      READ(5,100) XL,YL,GL
      READ(5,101) DL
      CALL ORIGIN(0,3.0,1)
      AFR=92.0
      DAFR=AFR/10.0
      ASR=-10.0
      C=1.0
      DO 200 J=1,6
      XTIM=0.0
      ASR=ASR+10.0
      DASR=ASR/10.0
      DSFR=(ASR+AFR)/10.0
      DO 5 I=1,6
    5 X(I)=0.0
      DO 99 IT=1,300
      XTIM=XTIM+0.1
      TIME(IT)=XTIM
      Y(IT)=X(4)
      SXPL=X(6)
      X(6)=((70.0-DASR)*X(6)+DASR*X(5))/70.0
      X(5)=((75.0-DASR)*X(5)+DASR*X(4))/75.0
      X(4)=((75.0-DSFR)*X(4)+DSFR*X(3))/75.0
      X(3)=((120.0-DSFR)*X(3)+DSFR*X(2))/120.0
      X(2)=((120.0-DSFR)*X(2)+DSFR*X(1))/120.0
   99 X(1)=((50.0-DSFR)*X(1)+DAFR*C+DASR*SXPL)/50.0
      IF(J.GE.2) GOTO 50
      CALL GRAPH(300,TIME,Y,1,4,10.0,7.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
      GOTO 200
   50 CONTINUE
      CALL GRAPH(300,TIME,Y,1,4,00.0,7.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
  200 CONTINUE
      STOP
  100 FORMAT(15A4)
```

```
  101 FORMAT(5A4)
      END
//GO.SYSIN  DD *
   TIME IN MINUTES  FRACTION OF SS VALUE AQUEOUS SETTLER
ASP=0 TO 50 BY 10
//GO.FT14F001 DD DSNAME=&SM,UNIT=SYSDA,DISP=(NEW,PASS),                  SMPLT1/3
// SPACE=(800,(120,15)),DCB=(RECFM=VS,LRECL=796,BLKSIZE=800)             SMPLT2/3
//SMPLTTR EXEC PLOT,PLOTTER=INCRMNTL,PARM.PLOT='TYPE 00 PAPER PLEASE'    SMPLT3/3
```

APPENDIX C:
PROGRAM FOR PSEUDO DISTRIBUTION AND RATE CONSTANT CALCULATIONS

```
//D215KK JOB 'A0366,TIME=7,REGION=144K,LINES=5K,CARDS=300',BEETNER
//STEP1 EXEC FORTG,LINES=4,CARDS=300,REGION.GO=128K,TIME.GO=3
//FORT.SYSIN  DD  *
C      PROGRAM TO CALCULATE K1 AND K2
C
C      DECLARATION OF VARIABLES
C
       IMPLICIT REAL*8 (A-H,O-Z)
       INTEGER FSN,RN
       REAL*8 K1,K2,K3
       DIMENSION C(22),CO(22),X(36),Y(36),Z(36),XK1(15,25),XK2(15,25)
       REAL*4 XL(5),YL(5),GL(5),DL(5)
       REAL*4 DL2(5)
       REAL*4 XK(5),YK(5),DK(5),GK(5)
       READ(5,130) XL,YL,GL,DL
       READ(5,130) DL2
       IG=0
C
C      READING PARAMETERS
C
    10 READ(5,120) RN,NS,FSN,OFR,AFR,FFR,FC,FAC,FOC
       WRITE(6,121) RN,NS,FSN,OFR,AFR,FFR,FC,FAC,FOC
       NPTS=-1*NS
C
C      RN=RUN NUMBER
C      NS=NUMBER OF STAGES
C      FSN=FEED STAGE NUMBER
C      OFR=ORGANIC FLOW RATE
C      AFR=AQUEOUS FLOW RATE
C      FFR=FEED FLOW RATE
C      FC=FEED COMPOSITION (RARE EARTH MOLARITY)
C      FAC=FINAL AQUEOUS COMPOSITION
C      FOC=FINAL ORGANIC COMPOSITION
C      CO(N)=RARE EARTH CONCENTRATION IN ORGANIC PHASE LEAVING STAGE N
C      C(N)=RARE EARTH CONCENTRATION IN AQUEOUS PHASE LEAVING STAGE N
C      K1=EQUILIBRIUM CONSTANT SUCH THAT AT EQUILIBRIUM CO(N)=K1*C(N)
C      K2=FIRST ORDER REACTION RATE CONSTANT
```

```
C     RV=REACTOR VOLUME (VOLUME OF MIXER PUMP)
C
      IF(NS.LE.5) GOTO 99
      IG=IG+1
      K2=5.0D0
      DK2=-0.2D0
      K2=K2-DK2
      AFRS=AFR
C
C     CALCULATING FEED FLOW RATE FROM RARE EARTH BALANCE
C
      FFR=(OFR*FOC+AFRS*FAC)/(FC-FAC)
      WRITE(6,300) FFR
  300 FORMAT(' FEED FLOW RATE CALCULATED FROM RARE EARTH BALANCE =',
     1E20.10,'ML/MIN')
C
C     BEGINING ITERATIVE CALCULATIONS
C
      AFRE=AFR+FFR
      CO(1)=0.0D0
      C(2)=FAC
      IZT=0
      CALL ORIGIN(0.0,3.0,1)
      DO 60 I60=1,5
      DO 59 I59=1,5
      IZT=IZT+1
      G=0.0D0
      DG=0.1D0
      K2=K2+DK2
      ICT=0
    1 CONTINUE
      ICT=ICT+1
      IF(ICT.GE.160) GOTO 45
      K1=G
C
C     STAGEWISE CALCULATIONS
C
```

```
C
C     EXTRACTING SECTION CALCULATION
C
      AFR=AFRE
      RV=(OFR+AFR)/10.0D0
      K3=K2*RV/OFR
      DO 30 I=2,FSN
      CO(I)=(CO(I-1)+K1*K3*C(I))/(K3+1.0D0)
      C(I+1)=C(I)+(CO(I)-CO(I-1))*OFR/AFR
   30 CONTINUE
C
C     FEED STAGE CALCULATION
C
      I=FSN+1
      CO(I)=(CO(I-1)+K1*K3*C(I))/(K3+1.0D0)
      C(I+1)=(C(I)*AFR+(CO(I)-CO(I-1))*OFR-FC*FFR)/AFRS
C
C     STRIPPING SECTION CALCULATION
C
      ID1=FSN+2
      ID2=NS+1
      AFR=AFRS
      RV=(OFR+AFR)/10.0D0
      K3=K2*RV/OFR
      DO 40 I=ID1,ID2
      CO(I)=(CO(I-1)+K1*K3*C(I))/(K3+1.0D0)
      C(I+1)=C(I)+(CO(I)-CO(I-1))*OFR/AFR
   40 CONTINUE
C
C     COMPLETION OF STAGEWISE CALCULATIONS
C     BEGIN CONVERGANCE SCHEME
C
      AQ=C(NS+2)
      ORG=CO(NS+1)
      IF(DABS(AQ).LE.1.0D-07)GOTO 50
      IF(AQ.LT.0.0) GO TO 5
      G=G-DG
```

```
      DG=DG/10.0D0
      IF(DG.LE.1.0D-10) GO TO 49
    5 G=G+DG
      GO TO 1
C
C     COMPLETION OF CONVERGANCE SCHEME
C     BEGIN PRINT OUT SCHEME
C
   49 CONTINUE
      WRITE(6,152) DG
   50 CONTINUE
      WRITE(6,150) G,AQ,ORG,ICT,K1,K2
      WRITE(7,101) RN,K1,K2
      XK1(IG,IZT)=K1
      XK2(IG,IZT)=K2
   59 CONTINUE
      DO 90 IK=1,NS
      X(IK)=IK
   90 Y(IK)=C(IK+1)
      WRITE(8,153) K1,K2
      REWIND 8
      READ(8,154) GL
      REWIND 8
      CALL GRAPH(NPTS,X,Y,1,103,05.0,4.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
      DO 91 IK=1,NS
   91 Y(IK)=CO(IK+1)
      CALL GRAPH(NPTS,X,Y,2,103,00.0,7.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL2)
      CALL ORIGIN(7.0,0.0,1)
   60 CONTINUE
      DO 61 IZT=1,25
      X(IZT)=XK1(IG,IZT)
   61 Y(IZT)=XK2(IG,IZT)
      READ(5,130) XK,YK,GK,DK
      CALL GRAPH(-25,X,Y,1,1,5.0,4.5,0.4,0.0,1.6,0.0,XK,YK,GK,DK)
      CALL ORIGIN(7.0,-2.0,1)
      CALL GRAPH(-25,X,Y,1,1,10.5,7.5,0.2,0.0,0.8,0.0,XK,YK,GK,DK)
      CALL ORIGIN(15.0,-1.0,1)
```

```
      GOTO 10
   45 CONTINUE
      WRITE(6,151)
      WRITE(6,150) G,AQ,ORG,ICT,K1,K2
      WRITE(6,140) (CO(IPT),IPT=1,ID2)
      WRITE(6,141) (C(IPT),IPT=1,ID2)
   99 WRITE(6,102)
      STOP
  101 FORMAT(I2,3E21.14)
  102 FORMAT('  EXECUTING CARD 99 OF PROGRAM')
  120 FORMAT (3I3,1X,6E10.5)
  121 FORMAT(1X,3I3,1X,6E15.5)
  130 FORMAT(20A4)
  140 FORMAT('0',21F5.2)
  141 FORMAT(' ',21F5.2)
  150 FORMAT('0  G=',E13.5,5X,'AQ=',E13.5,5X,'ORG=',E13.5,5X,'ICT=',I3,
     15X,'K1=',E13.5,5X,'K2=',E13.5)
  151 FORMAT('   CONVERGANCE FAILED  ICT=160')
  152 FORMAT(' DG STOPPED ITERATIONS DG=',D25.15)
  153 FORMAT('K1=',F10.7,'K2=',F4.1)
  154 FORMAT(5A4)
      END
//GO.SYSIN  DD  *                                                       03
STAGE NUMBER        RARE EARTH MOLARITY STAGEWISE CONCENTRAT AQUEOUS PHASE
 ORGANIC PHASE
  4 10  7      186.0       92.0       5.80      2.643    0.0950    0.0324
EQUILIBRIUM CONSTANT   RATE CONSTANT    RUN 4 BY CASTO
  0  0  0         0.0        0.0        0.0        0.0       0.0       0.0
//GO.FT08F001 DD UNIT=SPOOL,SPACE=(TRK,(1,1))
//GO.FT14F001 DD DSNAME=&SM,UNIT=SPOOL,DISP=(NEW,PASS),                SMPLT1/3
// SPACE=(800,(120,15)),DCB=(RECFM=VS,LRECL=796,BLKSIZE=800)            SMPLT2/3
//SMPLTTR EXEC PLOT,PLOTTER=INCRMNTL,PARM.PLOT='TYPE 00 PAPER'          SMPLT3/3
```

APPENDIX D:
PROGRAM TO SIMULATE
MIXER-SETTLER EXTRACTOR

```
//D215SM JOB 'A0366,TIME=7,REGION=144K,LINES=5K,CARDS=300',BEETNER
//STEP1 EXEC FORTG,LINES=5,CARDS=300,REGION.GO=128K,TIME.GO=3
//FORT.SYSIN  DD  *
C
C    THIS PROGRAM SIMULATES THE START UP OF A TEN STAGE MIXER-SETTLER
C    EXTRACTOR
C
C    THE PROGRAM CONSISTS OF A MASTER CONTROLING PROGRAM AND THE NECESSARY
C    SUBROUTINES TO SIMULATE THE VARIOUS PARTS OF THE APPARATUS
C
      REAL K1,K2,K3
      COMMON N,FC,FFR,K1,K2,K3,AFR,OFR,OVP,AVP,FVP,ASR,DAFR,DASR,DSFR
      COMMON PRP(21),XPRP(62,21),ASET(22),OSET(21),XOSET(20,21),DOFR
      COMMON XASET(6,21),CO(21),C(21)
      COMMON XOMP(4,21),XAMP(4,21)
      DIMENSION XL(5),YL(5),GL(5),DL(5),X(40),Y(40),Z(40)
      DIMENSION DLO(5)
      DIMENSION XK(5),YK(5),GK(5),DK(5)
      DIMENSION EXT(35),EXC(35),EXCO(35)
      DIMENSION EZT(35)
      INTEGER RN,FSN
      DIMENSION LABL(7)
      READ(5,110) XL,YL,GL,DL
      READ(5,110) XL,YL,GL,DLO
      READ(5,110) XK,YK,GK,DK
    6 CONTINUE
      READ(5,120) RN,NS,FSN,OFR,AFR,FFR,FC,FAC,FOC
      WRITE(6,121) RN,NS,FSN,OFR,AFR,FFR,FC,FAC,FOC
      IF(NS.LE.5) GOTO 99
      READ(5,111) GL
      AFRS=AFR
      FFR=(OFR*FOC+AFRS*FAC)/(FC-FAC)
      WRITE(6,300) FFR
      AFRE=AFR+FFR
      ASR=10.0
      DOFR=OFR/10.0
      READ(5,101) RN,K1,K2
```

```
C
C     INITIALIZING ARRAYS TO ZERO
C
      XICT=17.0
      Z(1)=0.0
      Y(1)=0.0
      X(1)=0.0
      DO 5  N=1,21
      PRP(N)=0.0
      DO 1  I=1,62
    1 XPRP(I,N)=0.0
      ASET(N)=0.0
      OSET(N)=0.0
      DO 2  I=1,20
    2 XOSET(I,N)=0.0
      DO 3  I=1,6
    3 XASET(I,N)=0.0
      CO(N)=0.0
      DO 4 I=1,4
      XOMP(I,N)=0.0
    4 XAMP(I,N)=0.0
    5 C(N)=0.0
      OSET(22)=0.0
      AFR1=AFR
      AFR2=AFR+FFR
      OVP=DOFR
C
C     MASTER PROGRAM
C
      DO 40 ICT=2,40
      DO 30 ITIM=1,100
C
C     EXTRACTING SECTION
C
      AFR=AFR2
      DAFR=AFR/10.0
      DASR=ASR/10.0
```

```
      DSFR=(ASR+AFR)/10.0
      AVP=DAFR
      RV=(OFR+AFR)/10.0
      K3=K2*RV/OFR
      DO 10 N=2,FSN
      CALL PRPMP
      CALL PUMP
      CALL OSETL
      CALL ASETL
   10 CONTINUE
C
C    FEED STAGE
C
      N=FSN+1
      CALL PRPMP
      CALL FEED
      CALL OSETL
      CALL ASETL
C
C    STRIPPING SECTION CALCULATIONS
C
      AFR=AFR1
      DAFR=AFR/10.0
      DASR=ASR/10.0
      DSFR=(ASR+AFR)/10.0
      AVP=DAFR
      RV=(OFR+AFR)/10.0
      K3=K2*RV/OFR
      ID1=FSN+2
      ID2=NS+1
      DO 20 N=ID1,ID2
      CALL PRPMP
      CALL PUMP
      CALL OSETL
      CALL ASETL
   20 CONTINUE
      XICT=XICT+0.1
```

```
30 CONTINUE
   X(ICT)=XICT
   Y(ICT)=ASET(2)
   Z(ICT)=OSET(11)
   WRITE(6,100) XICT,ASET(2),OSET(11)
40 CONTINUE
   WRITE(10,275) K1,K2
   REWIND 10
   READ(10,276) LABL
   REWIND 10
   READ(5,122) NPTS
   DO 50 INPTS=1,NPTS
50 READ(5,123) EXT(INPTS),EXC(INPTS)
   READ(5,122) NPTZ
   DO 51 INPTS=1,NPTZ
51 READ(5,123) EZT(INPTS),EXCO(INPTS)
   CALL ORIGIN(0.0,1.C,1)
   CALL GRAPH(40,X,Y,1,4,10.0,7.5,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
   CALL GRAPH(40,X,Z,2,4,0.0,0.0,0.0,0.0,0.0,0.0,XL,YL,GL,DLO)
   CALL GRAPH(NPTS,EXT,EXC,1,107,0.0,0.0,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
   CALL GRAPH(NPTZ,EZT,EXCO,2,107,0.0,0.0,0.0,0.0,0.0,0.0,
  1XL,YL,GL,DLO)
   CALL LETTER(2.0,7.C,0.1,LABL,0.0,28,0,0,0,0,0,0,0,0,0)
   CALL ORIGIN(15.0,2.0,1)
   CALL GRAPH(40,X,Y,1,4,05.0,4.5,0.0,0.0,0,0,0.0,XL,YL,GL,DL)
   CALL GRAPH(40,X,Z,2,4,0.0,0.0,0.0,0.0,0.0,0.0,XL,YL,GL,DLO)
   CALL GRAPH(NPTS,EXT,EXC,1,107,0.0,0.0,0.0,0.0,0.0,0.0,XL,YL,GL,DL)
   CALL GRAPH(NPTZ,EZT,EXCO,2,107,0.0,0.0,0.0,0.0,0.0,0.0,
  1XL,YL,GL,DLO)
   CALL LETTER(0.2,4.2,0.1,LABL,0.0,28,0,0,0,0,0,0,0,0,0)
   DO 90 I=1,10
   X(I)=I
   Y(I)=C(I+1)
90 Z(I)=CO(I+1)
   CALL ORIGIN(15.0,-2.0,1)
   CALL GRAPH(10,X,Y,1,103,10.0,7.5,0.0,0.0,0.0,0.0,XK,YK,GK,DK)
   CALL GRAPH(10,X,Z,2,103,00.0,0.0,0.0,0.0,0.0,0.0,XK,YK,GK,DLO)
```

```
      CALL LETTER(2.0,7.0,0.1,LABL,0.0,28,0,0,0,0,0,0,0,0,0,0)
      CALL ORIGIN(15.0,2.0,1)
      CALL GRAPH(10,X,Y,1,103,05.0,4.5,0.0,0.0,0.0,0.0,XK,YK,GK,DK)
      CALL GRAPH(10,X,Z,2,103,00.0,0.0,0.0,0.0,0.0,0.0,XK,YK,GK,DLO)
      CALL LETTER(0.2,4.2,0.1,LABL,0.0,28,0,0,0,0,0,0,0,0,0,0)
      CALL ORIGIN(15.0,-3.0,1)
      GOTO 6
   99 CONTINUE
      WRITE(6,155)
  155 FORMAT(' PROGRAM TERMINATED NS<5')
      STOP
  100 FORMAT(1X,3E20.8)
  101 FORMAT(I2,3E21.14)
  110 FORMAT (20A4)
  111 FORMAT(40X,5A4)
  120 FORMAT (3I3,1X,6E10.5)
  121 FORMAT(1X,3I3,1X,6E15.5)
  122 FORMAT(I3)
  123 FORMAT(F3.0,2F5.5)
  275 FORMAT('K1 = ',F10.8,'   K2 = ',F4.1,1X)
  276 FORMAT(7A4)
  300 FORMAT(' FEED FLOW RATE CALCULATED FROM RARE EARTH BALANCE =',
     1E20.10,'ML/MIN')
      END
```

```
C
C    CALCULATION OF MIXER PUMP
C
      SUBROUTINE PUMP
      REAL K1,K2,K3
      COMMON N,FC,FFR,K1,K2,K3,AFR,OFR,OVP,AVP,FVP,ASR,DAFR,DASR,DSFR
      COMMON PRP(21),XPRP(62,21),ASET(22),OSET(21),XOSET(20,21),DOFR
      COMMON XASET(6,21),CO(21),C(21)
      COMMON XOMP(4,21),XAMP(4,21)
      CO(N)=XOMP(4,N)
      C(N)=XAMP(4,N)
      DO 10 I=1,3
      XOMP(5-I,N)=XOMP(4-I,N)
   10 XAMP(5-I,N)=XAMP(4-I,N)
      XOMP(1,N)=(OSET(N-1)+K1*K3*(PRP(N)+OSET(N-1)*OFR/AFR))/
     1(K3+1.0+K1*K3*OFR/AFR)
      XAMP(1,N)=PRP(N)+(OSET(N-1)-XOMP(1,N))*OFR/AFR
      RETURN
      END
```

```
C
C    CALCULATION OF PLUG FLOW PRE PUMP CHAMBER
C
      SUBROUTINE PRPMP
      REAL K1,K2,K3
      COMMON N,FC,FFR,K1,K2,K3,AFR,OFR,OVP,AVP,FVP,ASR,DAFR,DASR,DSFR
      COMMON PRP(21),XPRP(62,21),ASET(22),OSET(21),XOSET(20,21),DOFR
      COMMON XASET(6,21),CO(21),C(21)
      COMMON XOMP(4,21),XAMP(4,21)
      PRP(N)=XPRP(1,N)
      DO 10 I=1,61
   10 XPRP(I,N)=XPRP(I+1,N)
      XPRP(62,N)=ASET(N+1)
      RETURN
      END
```

```
C
C    CALCULATION FOR ORGANIC PHASE IN SETTLING CHAMBER
C
      SUBROUTINE OSETL
      REAL K1,K2,K3
      COMMON N,FC,FFR,K1,K2,K3,AFR,OFR,OVP,AVP,FVP,ASR,DAFR,DASR,DSFR
      COMMON PRP(21),XPRP(62,21),ASET(22),OSET(21),XOSET(20,21),DOFR
      COMMON XASET(6,21),CO(21),C(21)
      COMMON XOMP(4,21),XAMP(4,21)
      OSET(N)=XOSET(20,N)
      XOSET(20,N)=(XOSET(19,N)+XOSET(18,N)+XOSET(17,N)+XOSET(16,N))/4.0
      XOSET(19,N)=(3.0*XOSET(19,N)+XOSET(18,N))/4.0
      XOSET(18,N)=(XOSET(18,N)+XOSET(17,N))/2.0
      XOSET(17,N)=(XOSET(17,N)+3.0*XOSET(16,N))/4.0
      DO 10 I=1,15
   10 XOSET(17-I,N)=XOSET(16-I,N)
      XOSET(1,N)=(XOSET(1,N)+CO(N))/2.0
      RETURN
      END
```

```
C
C    CALCULATION FOR AQUEOUS PHASE IN SETTLING CHAMBER
C
      SUBROUTINE ASETL
      REAL K1,K2,K3
      COMMON N,FC,FFR,K1,K2,K3,AFR,OFR,OVP,AVP,FVP,ASR,DAFR,DASR,DSFR
      COMMON PRP(21),XPRP(62,21),ASET(22),OSET(21),XOSET(20,21),DOFR
      COMMON XASET(6,21),CO(21),C(21)
      COMMON XOMP(4,21),XAMP(4,21)
      ASET(N)=XASET(4,N)
      SXPL=XASET(6,N)
      XASET(6,N)=((70.0-DASR)*XASET(6,N)+DASR*XASET(5,N))/70.0
      XASET(5,N)=((75.0-DASR)*XASET(5,N)+DASR*XASET(4,N))/75.0
      XASET(4,N)=((75.0-DSFR)*XASET(4,N)+DSFR*XASET(3,N))/75.0
      XASET(3,N)=((120.0-DSFR)*XASET(3,N)+DSFR*XASET(2,N))/120.0
      XASET(2,N)=((120.0-DSFR)*XASET(2,N)+DSFR*XASET(1,N))/120.0
      XASET(1,N)=((50.0-DSFR)*XASET(1,N)+DAFR*C(N)+DASR*SXPL)/50.0
      RETURN
      END
```

```
C
C     FEED STAGE MIXER PUMP CALCULATION
C
      SUBROUTINE FEED
      REAL K1,K2,K3
      COMMON N,FC,FFR,K1,K2,K3,AFR,OFR,OVP,AVP,FVP,ASR,DAFR,DASR,DSFR
      COMMON PRP(21),XPRP(62,21),ASET(22),OSET(21),XOSET(20,21),DOFR
      COMMON XASET(6,21),CO(21),C(21)
      COMMON XOMP(4,21),XAMP(4,21)
      CO(N)=XOMP(4,N)
      C(N)=XAMP(4,N)
      DO 10 I=1,3
      XOMP(5-I,N)=XOMP(4-I,N)
   10 XAMP(5-I,N)=XAMP(4-I,N)
      XAFS=(FFR*FC+(AFR-FFR)*PRP(N))/AFR
      XOMP(1,N)=(OSET(N-1)+K1*K3*(XAFS+OSET(N-1)*OFR/AFR))/
     1(K3+1.0+K1*K3*OFR/AFR)
      XAMP(1,N)=XAFS+(OSET(N-1)-XOMP(1,N))*OFR/AFR
      RETURN
      END
```

```
//GO.SYSIN  DD  *
     TIME           RARE EARTH CONC.    TEN STAGE SIMULATION AQUEOUS PHASE
     TIME           RARE EARTH CONC.    TEN STAGE SIMULATIONORGANIC PHASE
STAGE NUMBER        RARE EARTH CONC     STAGEWISE CONCENTRAT AQUEOUS PHASE
  4 10  7      186.0      92.0       5.8     2.643     0.095    0.0324
EQUILIBRIUM CONSTANT   RATE CONSTANT    RUN 4 BY CASTO
 4 0.87287400000000D 00 0.40000000000000D 00
 29
 1000015
 5000010
 6000015
 6500116
 7000548
 7501407
 8002497
 8503663
 9004652
 9505486
10006240
10506757
11007285
12007938
13008440
14008817
15009043
16009219
17009345
18009395
19009470
20009470
21009445
22009470
23009470
25009520
27009495
29009546
31009546
```

```
  19
  1000126
  2000111
  3000261
  4000824
  5001367
  6001733
  7002020
  9002300
 11002540
 12002620
 13002790
 1400279
 15002910
 16002830
 18002990
 20003090
 22003220
 25003240
 30303240
   0  0  C        0.0        0.0        0.0        0.0        0.0        0.0
//GO.FT10F001 DD UNIT=SPOOL,SPACE=(TRK,(1,1))
//GO.FT14F001  DD  DSNAME=&SM,UNIT=SYSDA,DISP=(NEW,PASS),                    SMPLT1/3
// SPACE=(800,(120,15)),DCB=(RECFM=VS,LRECL=796,BLKSIZE=800)                 SMPLT2/3
//SMPLTTR EXEC PLOT,PLOTTER=INCRMNTL,PARM.PLOT='TYPE 00 PAPER'               SMPLT3/3
```

APPENDIX E:
LIST OF SYMBOLS
AND ABBREVIATIONS

LIST OF SYMBOLS AND ABBREVIATIONS

CO(N)=Concentration of Rare Earths in the Organic Phase of Stage N

C(N)=Concentration of Rare Earths in the Aqueous Phase of Stage N

K1=Pseudo Distribution Constant such that at equilibrium CC(N)=K1*C(N)

K2=Pseudo First Order Rate Constant with the units minutes**-1

RV=Reactor Volume

OFR=Organic Flow Rate

AFR=Aqueous Flow Rate

AFRE=Aqueous Flow Rate in the extracting section of the mixer-settler

AFRS=Aqueous Flow Rate in the stripping section of the mixer-settler

FFR=Feed Flow Rate

FC=Feed Composition (rare earth molarity)

dT=Time Increment

OVP=Organic Volume in the Pump involved in mass transfer

AVP=Aqueous Volume in the Pump involved in mass transfer

K3=K2*RV/OFR

N=Stage Number

DAFR=Time Increment of AFR

DOFR=Time Increment of OFR

ASR=Rate of Recirculation within the Aqueous Settling Chamber

DASR=Time Increment of ASR

DSFR=DASR+DAFR

Prp(N)=The Output of the Prepump Chamber of Stage N

XPRP(I,N)=The Ith Volume of Fluid in the Stage N Prepump Chamber

ASET(N)=The Output of the Stage N Aqueous Phase Settling Chamber

XASET(I.N)=The Ith Volume of Fluid in the Stage N Aqueous Phase Settling Chamber

OSET(N)=The Output of the Stage N Organic Phase Settling Chamber

XOSET(I,N)=The Ith Volume of Fluid in the Stage N Organic Phase Settling Chamber

XCMP(I,N)=The Ith Volume of Liquid in the Organic Phase Portion of the Stage N Pump Mixer

XAMP(I,N)=The Ith Volume of Liquid in the Aqueous Portion of the Stage N Pump Mixer

XAFS=The concentration of Rare Earths in the Input Aqueous Stream to the Feed Stage Pump Mixer, after the Rare Earth Feed Stream has been added.