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R. A. Leonard[a]
[a] Chemical Technology Division Argonne National Laboratory Argonne, Illinois

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Use of Electronic Worksheets for Calculation of Stagewise Solvent Extraction Processes

R. A. LEONARD

CHEMICAL TECHNOLOGY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439-4837

ABSTRACT

The electronic worksheet, a powerful new tool for engineering analysis, is used to calculate flowsheets for stagewise solvent extraction processes. The algorithms presented give the component concentration of each stage at steady-state conditions and an estimate of the time to reach steady state. Any number of inlet and exit streams can be included and a different distribution ratio can be specified for each stage. The procedure is illustrated using a nuclear waste flowsheet. Although this paper deals with stagewise solvent extraction, it shows the utility of the electronic worksheet for many types of scientific and engineering calculations.

INTRODUCTION

Equations for solvent extraction calculations have been summarized by Alders (1) and Lawrowski et al. (2). Alders, in particular, focuses on stagewise solvent extraction calculations, giving equations for every occasion including continuous countercurrent operation, batch countercurrent operation, and the approach of these operations to steady-state conditions. The equations are especially useful when there is no more than one intermediate feed point and the distribution ratio of the component being analyzed is constant. More recently, following the work of Lowe (3), Groenier (4) developed a FORTRAN program called SEPHIS for solvent extraction processes. This model uses a solvent consisting of an extractant, tributyl phosphate (TBP), in a diluent, normal paraffinic hydrocarbon (NPH), and an aqueous phase containing nitric acid, uranium, and plutonium. For these components, SEPHIS can handle a range of extractant concentrations and process temperatures, a variety of side streams in the process flowsheet, and can calculate the distribution ratios of the components as they vary from stage to stage. The SEPHIS model has proven to be quite useful and has been expanded (e.g., to include a fourth component, thorium) and modified in various ways in the past 13 years to make it even more useful. In this paper, procedures and algorithms for doing these types of calculations, albeit of a more general nature, on an electronic worksheet are explored. The ease with which electronic worksheets can be set up for these calculations makes their use very attractive.

Electronic worksheets, or "spreadsheets" as they are more often called in the popular literature, have been around for seven years now (5). Because of the more popular name and because of what they were first used for, business applications, the spreadsheet did not seem to have any utility for engineers and scientists. However, this is not true. The electronic worksheet program can do complex engineering calculations involving material balances (6,7), heat transfer (8), and chemical reactors (9). In this paper, the electronic worksheet is applied to flowsheet calculations in stagewise solvent extraction processes.

For those not familiar with electronic worksheets, a quick overview is in order. Each worksheet is a table or matrix of cells, each cell designated by the row and the column in which it is located. The individual cells can contain text, numbers, equations, or logical expressions. The equations and logical expressions can use numbers or, for the logical expression, text located in other cells. The structure of the equations is similar to those found in the FORTRAN and BASIC languages. Some worksheets can do iterative calculations. For example, if there are equations in both cells A and B, and the equation in cell A uses the value of cell B and the equation in cell B uses the value of cell A, the worksheet will recalculate the values of these cells until the difference between the last two values in a cell is less than an amount specified by the user.

Quite a variety of worksheets exist to choose from; these include MULTIPLAN, EXCEL, CRUNCH, JAZZ, DIGICALC, C-CALC, VISICALC, SUPERCALC, and LOTUS 1-2-3. The work reported here was first done using a DIGICALC worksheet on a VAX computer. It was later checked using MULTIPLAN and EXCEL on a 512K Macintosh computer. If it is large enough, any electronic worksheet should be able to perform the calculations described here. The time to recalculate a worksheet depends both on the number of cells to be calculated and the worksheet program. With the 5000-cell worksheets evaluated for this report, the recalculation time for the DIGICALC worksheet was 7 minutes; for the MULTIPLAN worksheet, 30 seconds; and for the EXCEL worksheet, 10 seconds.

The electronic worksheet has been called a fourth-level programming language because of its power and ease of use compared with third-level languages such as FORTRAN, BASIC, PASCAL, C, etc. (The first- and second-level languages are machine language and assembly language, respectively.) One of the criticisms leveled at worksheets is that they are not as structured as third-level programming languages. Thus, one can get into trouble with complex worksheet programs. One must always be careful that a program is written correctly. Also, of course, the end result is only as good as the model available for use in the program.

ALGORITHMS FOR STAGEWISE SOLVENT EXTRACTION PROCESSES

An electronic worksheet that has been set up for calculating stagewise solvent extraction processes is described. Besides outlining the appropriate algorithms, a general philosophy of worksheet organization is presented, and features unique to the use of electronic worksheets are noted.

Worksheet Organization

The first step in worksheet organization is to determine the required size of the worksheet. To prepare a worksheet that could accommodate up to 25 contactor stages, a 50-column worksheet was specified. The 50 columns have letter designations, from A to Z and AA to AX. To allow calculations to reach steady-state conditions, a 128-row worksheet was specified. The rows have number designations, from 1 to 128. The cell in the upper left-hand corner of the worksheet is referred to as A1; the cell in the lower right-hand corner is referred to as AX128. For example, to specify a range of cells that includes the entire worksheet, the convention A1..AX128 is used. These conventions are used throughout this paper.

The second and final step in worksheet organization is to assign various work areas within the worksheet. For the solvent extraction process, three areas are used: the summary, aqueous-phase, and organic-phase sections. The summary section is placed in the upper left corner of the worksheet so that, if the number of rows or columns needs to be increased, the worksheet can be enlarged without overrunning the summary section. The summary section is designed so that it fits entirely on the display screen of seven columns by 20 rows (A1..G20). The space allocated for the aqueous-phase section is below the summary section on the worksheet, using 25 columns and the rest of the rows (A21..Y128). The space for the organic-phase section is to the right of the aqueous-phase section, occupying the other 25 columns and using the rows from 21 down to the bottom (Z21..AX128). The remaining range of cells (H1..AX20) is not used. The overall worksheet organization is depicted in Fig. 1.

The location of the aqueous- and organic-phase sections was chosen carefully, based on the way that the worksheet does its calculations. In the worksheet used, DIGICALC, the cells are calcu-

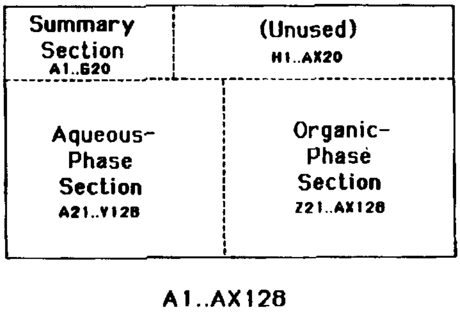

Fig. 1. Overall Worksheet Organization

lated row by row starting at the top of the worksheet. Within each row, the cells are calculated left to right. Thus, because the aqueous-phase concentrations are needed for the organic-phase calculations, the organic-phase concentrations within each row are placed to the right of the aqueous-phase concentrations in that row. Because of this calculation order, the worksheet must be recalculated twice so that the calculated values in the summary section are correct.

Some electronic worksheets, e.g., MULTIPLAN, 1-2-3, and EXCEL, can evaluate the cells with equations and see that they are calculated in their proper order. If there are circular references between cells, these programs indicate this and provide iterative calculational routines. For such worksheet programs, the strict attention to worksheet organization and order of calculation given here is unnecessary.

Summary Section

The summary section contains information about the process being evaluated, the input data, and the calculated results. A typical summary section for a worksheet is shown in Table 1. The first three rows contain general process information that is not used in the calculations. In these rows, the component being extracted, the temperature at which the distribution ratios were measured, and the number of contactor stages in each section are indicated.

The middle section of this table, rows 6 through 8, contains input data from the process flowsheets. The codes for the various input streams are as shown in Fig. 2, which describes stream flows in a 14-stage contactor used in studies of actinide extraction and recovery from waste solutions (10). Note that DX and FP are shown in a single column in Table 1. This is because the organic effluent (FP) is recycled and, so, becomes the organic feed (DX). Although the concentration for DX-FP is a calculated value, it is shown here

TABLE 1
Summary Section of the Worksheet

Row	A	B	C	D	E	F	G
1			Number of Stages				
2	Component	Temp, C	Extraction	Scrub	1st Strip	2nd Strip	
3	Am	30	5	2	4	3	
4							
5							
6			DX, FP	DF	DS	EF	FF
7	Relative Flow		150	400	50	150	75
8	Concentration, mmM		0.0001247	6.000	0.000	0.000	0.000
9							
10	Distribution Ratios (D)					Calculated Values	
11	16	16	17	17	17	R(extr)	0.333
12	8.8	6.5	0.87	0.13	0.11	R(scrub)	3.000
13	0.11	0.1	0.1	0.1		R(strip1)	1.000
14						R(strip2)	2.000
15						q(DW)	450
16				Conc(DP)	16.00	Conc(DW)	0.000879
17				Conc(EP)	0.01946	Conc(EW)	15.978
18				Conc(FP)	0.0001247	Conc(FW)	0.039
19							
20							

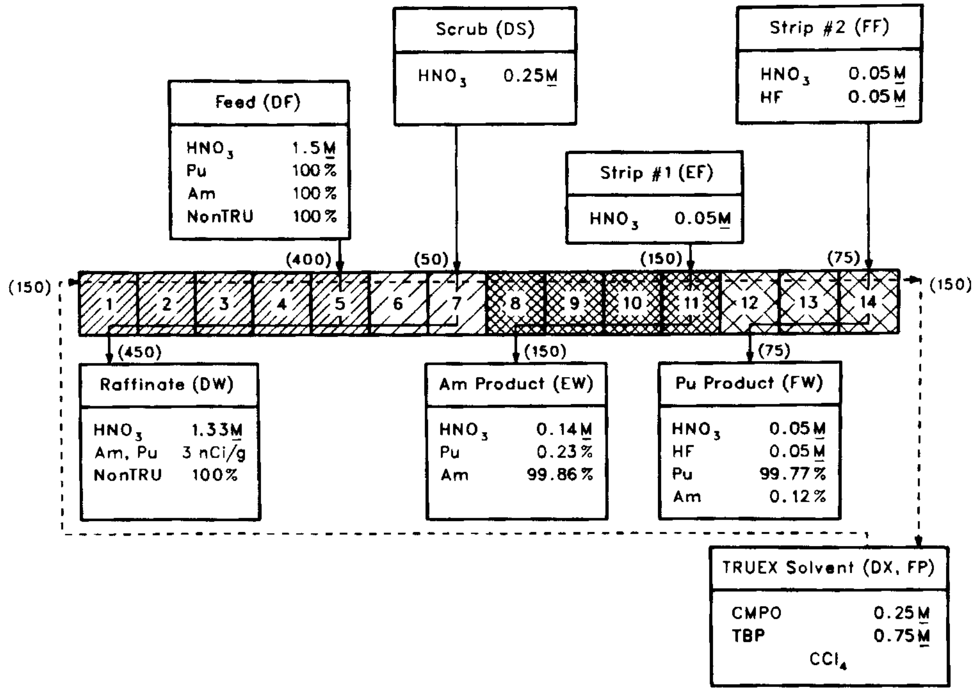

Fig. 2. Flowsheet for Actinide Recovery from a Nuclear Waste Effluent. (Parenthetical entries indicate stream flow rates in mL/min.)

for completeness. Because of the limitations of the worksheet character set, the americium concentration in μM is typed out as "mmM".

Additional input data, the component distribution ratios (D) for each stage, are given in the lower left section of Table 1, in rows 11 through 15. The distribution ratios for stages 1 through 5 appear in cells A11..E11, those for stages 6 through 10 in cells A12..E12, etc. As there are only 14 stages (see Fig. 2), the ratios end in cell D13.

Calculated results in Table 1 are to the right and below the distribution ratios. In cells F11..G15 are the flow ratios (R) for each process section and the flow rate for the aqueous raffinate, q(DW). In cells D16..G18 are the calculated americium concentrations (in the same units as those of the input values, μM) in each of the organic and aqueous effluents from each section of the flowsheet shown in Fig. 2. These effluents include two not shown in Fig. 2:

the organic effluent (DP) from the extraction/scrub section, which goes directly from stage 7 to stage 8, and the organic effluent (EP) from the first strip section, which goes directly from stage 11 to stage 12. Each of these concentrations is taken from the appropriate column in row 128 of the worksheet.

Aqueous-Phase Section

In the aqueous-phase section of the worksheet, the component concentration in the aqueous effluent of each stage is calculated for successive intervals of time where each time interval is the residence time of one phase in a stage. For these calculations, the residence time ($t_{R,k}$) for one phase (k) in a stage is assumed to be the same as that for the other phase in the same stage. In addition, it is assumed that the residence time for a phase in a stage is the same for all stages. Because the residence time for a phase in a stage is given by

$$t_{R,k} = V_k/q_k \qquad (1)$$

where V_k is the volume of phase k in the stage and q_k is the volumetric flow rate of phase k, these assumptions are equivalent to assuming that, for a given residence time, the volume of each phase in each stage is given by Eq. 1. In addition, one further assumption is made; namely, that this movement of phase liquid from stage to stage in discrete volumes is a reasonable approximation to continuous countercurrent liquid flow. With these assumptions, each row of the aqueous-phase section will represent a time interval corresponding to the residence time of one phase in a stage. Time will then be increasing with each row by the amount calculated using Eq. 1.

This nonsteady-state model is strictly valid only for batch countercurrent operation. For all other cases, it is only an approximation. However, even if the above assumptions are not realized, this model will give the appropriate concentrations for both phases in all stages at steady state.

A part of the aqueous-phase section of the worksheet (A21..N42) is shown in Table 2. In row 21, the columns are labeled xi to indicate x_i, the aqueous-phase concentration of the component (in this case, Am) in the effluent from stage i. The units for x_i are the same as those used in the summary section of the worksheet. In row 22, the initial concentration of the effluent from each stage at time zero is given; for the case shown in Fig. 2, the americium concentration is taken to be zero at all 14 stages, the liquid flows are assumed to be at steady-state conditions, and americium is introduced into stage 5 of the contactor.

To account for component movement through the contactor, a material balance about each contactor stage is made. In the calcula-

TABLE 2
Aqueous-Phase Section of the Worksheet

	Americium Concentration in the Aqueous Effluent of Each Stage, μM													
Row	A	B	C	D	E	F	G	H	I	J	K	L	M	N
21	x1	x2	x3	x4	x5	x6	x7	x8	x9	x10	x11	x12	x13	x14
22	0	0	0	0	0	0	0	0	0	0	0	0	0	0
23	0.00000	0.0000	0.000	0.000	0.80	0.00	0.0	0.0	0.0	0.00	0.000	0.000	0.0000	0.00000
24	0.00000	0.0000	0.000	0.120	0.80	1.49	0.0	0.0	0.0	0.00	0.000	0.000	0.0000	0.00000
25	0.00000	0.0000	0.018	0.120	0.93	1.49	1.9	0.0	0.0	0.00	0.000	0.000	0.0000	0.00000
26	0.00000	0.0028	0.018	0.154	0.93	1.80	1.9	6.7	0.0	0.00	0.000	0.000	0.0000	0.00000
27	0.00045	0.0028	0.025	0.154	0.96	1.80	2.3	6.7	5.1	0.00	0.000	0.000	0.0000	0.00000
28	0.00045	0.0044	0.025	0.166	0.96	1.87	2.3	10.8	5.1	0.60	0.000	0.000	0.0000	0.00000
29	0.00069	0.0044	0.028	0.166	0.97	1.87	2.4	10.8	8.8	0.60	0.060	0.000	0.0000	0.00000
30	0.00069	0.0051	0.028	0.170	0.97	1.90	2.4	13.1	8.8	1.09	0.060	0.011	0.0000	0.00000
31	0.00080	0.0051	0.030	0.170	0.98	1.90	2.4	13.1	11.0	1.09	0.108	0.011	0.0018	0.00000
32	0.00080	0.0053	0.030	0.172	0.98	1.91	2.4	14.4	11.0	1.39	0.108	0.021	0.0018	0.00030
33	0.00084	0.0053	0.030	0.172	0.98	1.91	2.5	14.4	12.3	1.39	0.138	0.021	0.0038	0.00030
34	0.00084	0.0054	0.030	0.172	0.98	1.91	2.5	15.1	12.3	1.57	0.138	0.028	0.0038	0.00063
35	0.00086	0.0054	0.030	0.172	0.98	1.91	2.5	15.1	13.0	1.57	0.155	0.028	0.0053	0.00063
36	0.00086	0.0055	0.030	0.172	0.98	1.91	2.5	15.5	13.0	1.67	0.155	0.033	0.0053	0.00088
37	0.00087	0.0055	0.030	0.172	0.98	1.91	2.5	15.5	13.4	1.67	0.165	0.033	0.0062	0.00088
38	0.00087	0.0055	0.030	0.172	0.98	1.91	2.5	15.7	13.4	1.72	0.165	0.035	0.0062	0.00104
39	0.00088	0.0055	0.030	0.172	0.98	1.91	2.5	15.7	13.6	1.72	0.170	0.035	0.0068	0.00104
40	0.00088	0.0055	0.030	0.172	0.98	1.91	2.5	15.8	13.6	1.75	0.170	0.037	0.0068	0.00113
41	0.00088	0.0055	0.030	0.172	0.98	1.91	2.5	15.8	13.8	1.75	0.173	0.037	0.0071	0.00113
42	0.00088	0.0055	0.030	0.172	0.98	1.91	2.5	15.9	13.8	1.77	0.173	0.038	0.0071	0.00118

tion, the extraction efficiency[a] of a stage (stage efficiency) is assumed to be 100%. This is a reasonable assumption for well-designed annular centrifugal contactors, which allows the concentration (y_i) of the organic effluent from stage i to be related to the concentration (x_i) of the aqueous effluent from stage i by the distribution ratio (D_i) for stage i as

$$D_i = y_i/x_i \tag{2}$$

Then, for stage i, with flows into and out of the stage as shown in Fig. 3, a material-balance equation can be written for the stage that, when combined with Eq. 2, gives

$$x_i = \frac{x_{i+1} + R_j y_{i-1}}{1 + R_j D_i} \tag{3}$$

where R_j, the organic/aqueous (O/A) flow ratio for process section j, is given by

$$R_j = q_{o,j}/q_{a,j} \tag{4}$$

In Eq. 4, $q_{a,j}$ is the aqueous flow rate in process section j and $q_{o,j}$ is the organic flow rate in process section j.

Equation 3 is used in each cell in row 23 of the aqueous-phase section of the worksheet. The values of R_j and D_i are obtained from the summary section of the worksheet. The x_{i+1} and y_{i-1} values are obtained from their appropriate columns, but one row up from the row being calculated; in this case, row 22. (The location of the y_i values is discussed later.) At the end stage of a process section, the x_{i+1} or y_{i-1} value is replaced by the value of a feed stream. For example, for stage 1 in Fig. 2, y_0 is replaced by y_{DX}, the americium concentration in the organic feed (DX). For once-through solvent operation, this value will be listed in the summary section. For complete solvent recycle as shown in Fig. 2, y_0 is y_{14}, the americium concentration in the organic product effluent (FP) from stage 14. In a second example, for stage 7 in Fig. 2, x_8 is replaced by x_{DS}, the americium concentration in the aqueous scrub (DS) to stage 7.

Special attention is necessary where there are two liquid feeds of the same phase into a process section, as at stage 5 in Fig. 2. For this stage, x_{i+1} (where i = 5) must be replaced by an average value, $\bar{x}_{i+1}$, of the two streams being fed to stage i; i.e., the effluent from stage i+1, which has an americium concentration of

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[a] Extraction efficiency is the ratio of the amount of a component extracted from one phase into the other to the amount that would be extracted if the two phases were at equilibrium. The extraction efficiency is expressed either as a fraction or as a percentage.

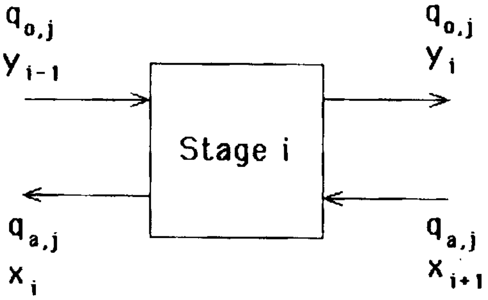

Fig. 3. Liquid Flows to and from Contactor Stage i in Section j

x_{i+1} and an aqueous flow rate of $q_{a,j+1}$, and the aqueous feed, which has an americium concentration of x_{DF} and an aqueous flow rate of $q_{a,DF}$. A material balance gives $\bar{x}_{i+1}$ to be

$$\bar{x}_{i+1} = \frac{q_{a,DF}x_{DF} + q_{a,j+1}x_{i+1}}{q_{a,DF} + q_{a,j+1}} \tag{5}$$

When Eq. 5 is substituted into Eq. 3 for x_{i+1} and noting that when $q_{a,j+1}$ and $q_{a,DF}$ merge they form $q_{a,j}$, Eq. 3 becomes

$$x_i = \frac{R_{ex}y_{i-1} + \left(1 - \frac{R_{ex}}{R_{sc}}\right) x_{DF} + \frac{R_{ex}}{R_{sc}} x_{i+1}}{1 + R_{ex}D_i} \tag{6}$$

for the feed stage where R_{ex} is the O/A flow ratio in the extraction section and R_{sc} is the O/A flow ratio in the scrub section.

Thus, Eq. 6 is used for stage 5 in cell E23, and Eq. 3 is used for all other stages (cells) in row 23 of the aqueous-phase section shown in Table 2. Once the cells of row 23 are filled in, "fill down" worksheet commands are used to copy the equation in each cell of row 23 to those in the corresponding cells in rows 24 to 128. Thus, all cells in A23..D128 and F23..N128 contain Eq. 3. Those in E23..E128 contain Eq. 6.

Organic-Phase Section

In the organic-phase section of the worksheet, the component concentration in the organic effluent of each stage, y_i, is calculated using Eq. 2 where x_i is the corresponding aqueous-phase value for the same stage during the same time interval; i.e., in the same row as the y_i value. A part of the organic-phase section of the worksheet

(Z21..AM42) is listed in Table 3. In row 21, the columns are labeled yi to indicate y_i, the organic-phase concentration of the component in the effluent from stage i. The actual y_i values, calculated using Eq. 2, start in row 22. This equation is used for the entire organic-phase section. The use of Eq. 2 assumes that the stage efficiency is 100%, as mentioned above. Also, within the assumptions discussed above in the aqueous-phase section, increasing row numbers denote increasing time. As before, even if the assumptions are not realized, the steady-state concentrations for the y_i values will be correct.

DISCUSSION

With the algorithm for stagewise solvent extraction operations developed above, a wide variety of processes can be evaluated, both for steady-state operation and during startup. In the following discussion, a flowsheet proposed for processing nuclear waste is so evaluated. Then the electronic worksheet is compared with similar FORTRAN programs, possible worksheet modifications are outlined, and the double-diamond nature of the worksheet algorithm is explained. Finally, the application of the electronic worksheet to calculations for other stagewise separation processes is discussed.

Steady-State Operation

Whether or not the residence times of the two phases in all stages are equal, as assumed in the algorithm, the steady-state concentrations predicted by the algorithm will be unaffected. These steady-state concentrations can be seen in the lower rows of Tables 2 and 3, where the concentration values in most stages have reached constant values.

For the nuclear waste processing flowsheet discussed in Ref. 10, the reference flowsheet (Fig. 2) was modeled using an electronic worksheet as discussed above; the results are partially listed in Tables 1, 2, and 3. Based on these results, the process was tested in the laboratory. After the test, the americium distribution ratios (D) were found to be higher than expected because of evaporative losses of the CCl_4 diluent in the solvent. The new, higher D values were used in place of those shown in Table 1, and the americium profile was recalculated. The measured and calculated americium concentrations in the aqueous phase exiting each stage are listed in Table 4 and plotted in Fig. 4. The calculated value of americium concentration and the americium concentration in each effluent sample taken during the test run agree quite well. Agreement is not as good, at least not in the extraction/scrub section, for the samples taken from each stage after the test run. This deviation occurred because the liquid feed pumps to the contractor were stopped five seconds before the rotors were turned off. In addition, the rotors continued to spin for 10 to 15 seconds after they were turned off. This allowed internal liquid flow to continue after external liquid flow to the contactor had stopped. The results of this are seen most clearly in the measured stage concentrations near the feed stage,

TABLE 3
Organic-Phase Section of the Worksheet

	Americium Concentration in the Organic Effluent of Each Stage, μM													
Row	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM
21	y1	y2	y3	y4	y5	y6	y7	y8	y9	y10	y11	y12	y13	y14
22	0	0	0	0	0	0	0	0	0	0	0	0	0	0
23	0.0000	0.000	0.00	0.0	13.6	0.0	0.0	0.0	0.00	0.000	0.0000	0.0000	0.00000	0.000000
24	0.0000	0.000	0.00	2.0	13.6	13.1	0.0	0.0	0.00	0.000	0.0000	0.0000	0.00000	0.000000
25	0.0000	0.000	0.31	2.0	15.8	13.1	12.5	0.0	0.00	0.000	0.0000	0.0000	0.00000	0.000000
26	0.0000	0.045	0.31	2.6	15.8	15.8	12.5	5.8	0.00	0.000	0.0000	0.0000	0.00000	0.000000
27	0.0072	0.045	0.43	2.6	16.3	15.8	15.0	5.8	0.67	0.000	0.0000	0.0000	0.00000	0.000000
28	0.0072	0.070	0.43	2.8	16.3	16.5	15.0	9.4	0.67	0.066	0.0000	0.0000	0.00000	0.000000
29	0.0111	0.070	0.48	2.8	16.5	16.5	15.7	9.4	1.15	0.066	0.0066	0.0000	0.00000	0.000000
30	0.0111	0.081	0.48	2.9	16.5	16.7	15.7	11.4	1.15	0.120	0.0066	0.0011	0.00000	0.000000
31	0.0128	0.081	0.50	2.9	16.6	16.7	15.9	11.4	1.44	0.120	0.0119	0.0011	0.00018	0.000000
32	0.0128	0.085	0.50	2.9	16.6	16.8	15.9	12.5	1.44	0.153	0.0119	0.0021	0.00018	0.000030
33	0.0135	0.085	0.51	2.9	16.6	16.8	16.0	12.5	1.60	0.153	0.0152	0.0021	0.00038	0.000030
34	0.0135	0.087	0.51	2.9	16.6	16.8	16.0	13.2	1.60	0.172	0.0152	0.0028	0.00038	0.000063
35	0.0138	0.087	0.51	2.9	16.6	16.8	16.0	13.2	1.69	0.172	0.0171	0.0028	0.00053	0.000063
36	0.0138	0.088	0.51	2.9	16.6	16.8	16.0	13.5	1.69	0.183	0.0171	0.0033	0.00053	0.000088
37	0.0140	0.088	0.51	2.9	16.6	16.8	16.0	13.5	1.74	0.183	0.0182	0.0033	0.00062	0.000088
38	0.0140	0.088	0.51	2.9	16.6	16.8	16.0	13.7	1.74	0.189	0.0182	0.0035	0.00062	0.000104
39	0.0140	0.088	0.51	2.9	16.6	16.8	16.0	13.7	1.77	0.189	0.0188	0.0035	0.00068	0.000104
40	0.0140	0.088	0.51	2.9	16.6	16.8	16.0	13.8	1.77	0.192	0.0188	0.0037	0.00068	0.000113
41	0.0140	0.088	0.51	2.9	16.6	16.8	16.0	13.8	1.79	0.192	0.0191	0.0037	0.00071	0.000113
42	0.0140	0.088	0.51	2.9	16.6	16.8	16.0	13.8	1.79	0.194	0.0191	0.0038	0.00071	0.000118

TABLE 4
Concentration of Americium in the Aqueous Phase of Each Contactor Stage

Stage				Aqueous Americium Concentration, μM		
				Measured		
Section	No.	Feed	Effluent	Effluent	Stage (after run)	Calculated[a]
Extraction	1	DX	DW	0.000145	0.00052	0.000144
Extraction	2				0.00078	0.00128
Extraction	3				0.0048	0.0099
Extraction	4				0.034	0.072
Extraction/Feed	5	DF[b]			0.42	0.64
Scrub	6				0.84	1.28
Scrub	7	DS			0.94	1.40
Strip 1	8		EW	13.6	13.1	14.0
Strip 1	9				50.0	40.0
Strip 1	10				13.6	19.3
Strip 1	11	EF			6.2	3.5
Strip 2	12		FW	2.3	1.83	1.45
Strip 2	13				0.68	0.60
Strip 2	14	FF	FP		0.20	0.168

[a] Corrected D values used in the electronic worksheet.

[b] x_{DF} = 5.81 μM americium.

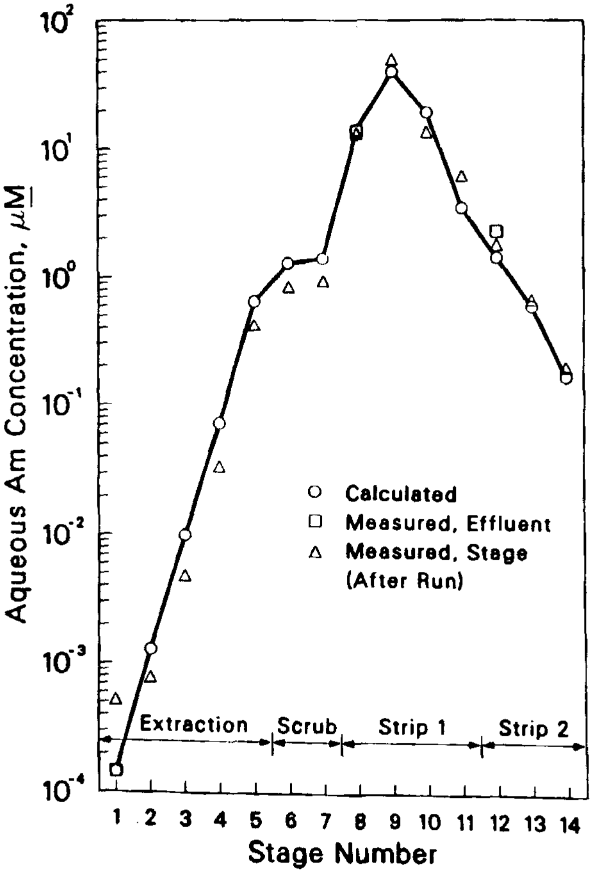

Fig. 4. Americium Profile through the Contactor Stages

stage 5. These americium concentrations are lower than the predicted values because of the loss of americium entering the contactor when the feed pump for DF was turned off. The shutdown effect also shows up in stage 1, where the organic feed is no longer entering and the concentration of americium is 3.6 times higher than both its measured and calculated values in the effluent.

In calculating the americium concentrations for the laboratory test shown in Fig. 4, one other change had to be made. Recycle of the solvent was expected; this was included in the worksheet calculations for the reference flowsheet. However, because of the large volume in the recycle system, none of the solvent fed to the contactor contained americium. Thus, when the flowsheet was calculated for the actual test, the organic solvent feed (DX) was specified to contain no americium.

Once the worksheet is set up, each of the components in the flowsheet, indicated in Fig. 2, can be calculated. The only changes that need to be made are in the summary section of the worksheet: the component name, the component concentration in each incoming liquid feed, and the distribution ratio for the component in each stage. Worksheet calculations for components, such as nitric acid, that can affect the D values of other components are made first. If there is sufficient storage capacity available, a worksheet can be saved for each component. Otherwise, one worksheet can be used over and over until all the component concentrations have been calculated.

Process Startup

During process startup, the americium concentration in each stage gradually builds up and approaches a steady-state value. This can be seen by looking down each column of Tables 2 and 3. This approach to steady state should be fairly accurate if the residence time of each phase in each stage is the same. There will be some loss in accuracy because, in the model, liquid movement from stage to stage occurs as discrete volumes. In the contactors, the actual liquid movement from stage to stage is continuous.

A further loss in the ability of the worksheet to predict the component concentration during process startup will occur if, as is usually the case, the residence times of the two phases in a stage and from stage to stage are different. For the test reported in Ref. 10, the stage residence times for the two phases varied from 7 to 34 seconds. The residence time for each phase in each stage is shown in Table 5. Assuming that the phase with the longer residence time will limit concentration changes and assuming the residence times between the feed point and the effluent point are most important, a time of 30 seconds was assigned to each row of the worksheet for the analysis of the americium concentration in the organic effluent (FP). The results, plotted on Fig. 5, show that agreement between experimental and calculated values is quite good, even though (1) the organic-phase residence times in the extraction section were quite a bit less than 30 seconds and (2) the residence times of the aqueous phase were less than 30 seconds in all but one stage. Thus, as a first approximation, the worksheet can be used to predict the rate at which steady-state conditions will be approached. The results will often be quite good, as in this case.

Based on the electronic worksheet calculations in Tables 2 and 3 and 30 seconds per time interval (row) for the organic effluent (the last effluent to reach steady-state conditions), the americium concentration in the organic effluent had been expected to reach 99% of its steady-state value within 12 to 14 minutes, not 25 to 30

TABLE 5
Flow Rates, Volumes, O/A Ratios, and Residence Times in the Contactor Stages

Stage Number	Flow Rate, mL/min		Volume after Test, mL			O/A Ratio		Residence Time, s	
	Aqueous	Organic	Aqueous	Organic	Total	Flow	Volume	Aqueous	Organic
1	450	150	55	40[a]	95	0.333	0.73	7.3	16.0
2	450	150	54	46	100	0.333	0.85	7.2	18.4
3	450	150	50	53	103	0.333	1.06	6.7	21
4	450	150	52	50	102	0.333	0.96	6.9	20
5	450	150	52[a]	48	100	0.333	0.92	6.9	19.2
6	50	150	28	70	98	3.0	2.5	34	28
7	50	150	23[a]	70	93	3.0	3.0	28	28
8	150	150	35	67	102	1.0	1.91	14.0	27
9	150	150	32	65	97	1.0	2.0	12.8	26
10	150	150	30	67	97	1.0	2.2	12.0	27
11	150	150	33[a]	65	98	1.0	1.97	13.2	26
12	75	150	29	70	99	2.0	2.4	23	28
13	75	150	29	68	97	2.0	2.3	23	27
14	75	150	28[a]	70	98	2.0	2.5	22	28

[a] This value is assumed to be somewhat low because this phase was being fed externally into this stage and its flow was stopped as much as 20 seconds before the rotors stopped turning. The turning rotors provide internal pumping for the liquids inside the contactor.

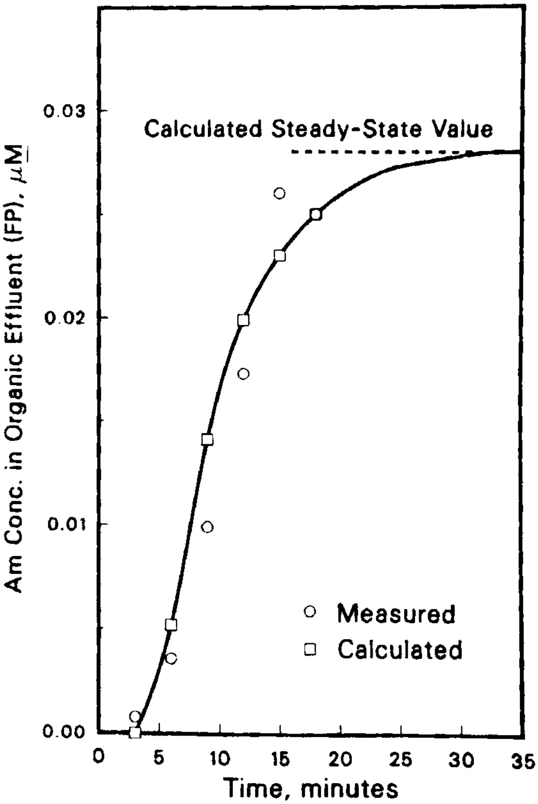

Fig. 5. Approach of the Americium Concentration in the Organic Effluent to its Steady-State Value

minutes as seen in Fig. 5. The slower approach to steady state was the result of americium distribution ratios that were higher than expected during the experimental run. New worksheet calculations using the higher ratios showed it would indeed take 25 to 30 minutes for the americium concentration in the organic effluent to reach its steady-state value, in good agreement with the experimental results. The cause of the slower approach was determined by reviewing the stage-to-stage americium concentrations. As the D values increase, the already high americium concentrations in the scrub and first strip stages become even higher. Thus, the americium in the aqueous feed (DF) must accumulate in these stages before steady-state operation is established. This buildup is limited by the rate at which americium is being brought into the contactor. As other components have different D values, so each component will approach its steady-state concentration at a different time.

Comparison with FORTRAN Programs

When the electronic worksheet is compared with FORTRAN programs such as SEPHIS (4), both techniques are found to have their strong points. The SEPHIS program has at least three advantages. First, the program is well developed and documented so that, once it is up and running, it is ready to use. Second, if the system used consists of uranium, plutonium, tributyl phosphate, normal paraffinic hydrocarbon, nitric acid, and water, the program will calculate their D values. Third, if the number of stages needs to be varied, it can be more easily done using the SEPHIS program.

The electronic worksheet also has several advantages. First, each of the components in a process can be evaluated as long as its D value is known. In addition, variation of D values from stage to stage can be accommodated easily. Second, once electronic worksheet operation is learned, worksheets such as the one described here can be set up from scratch in a few hours. Third, input and output data are displayed simultaneously; thus, results are obtained quickly and can be reviewed with respect to the input data. In addition, process sensitivity to variations in the input data can be evaluated easily. Finally, worksheets can be modified to include many special problems. Some of these modifications are discussed below. Advanced worksheet programs, such as Lotus 1-2-3 and Microsoft EXCEL, are especially useful when worksheets need to be modified.

Worksheet Modifications

Special problems always seem to arise, requiring the worksheet to be modified. The number of stages in a process section and the location of the feed stage are normal process variations that require worksheet modifications. As mentioned above, the worksheet must be modified depending on whether or not the organic solvent is recycled. These modifications are a normal occurrence in using the described algorithm. Other process sections and additional feed points can also be handled in a straightforward manner using this algorithm for stagewise solvent extraction calculations.

Interactive distribution ratios between components.

For systems with two components, in which the D values of each depend on the concentration of the other component, two worksheets of the form outlined in Fig. 1 could be set up on a single larger electronic worksheet. Currently unused areas, e.g., H1..AX20 in Fig. 1, could be used to calculate D values for each stage based on the concentration of the other component. A number of recalculations or iterations would be needed so that the values for D and for concentration can converge to their steady-state values. A more sophisticated approach would be to have the equation for D incorporated in each cell of the component worksheet that uses a D value and have this equation get the required concentration of the other component from the appropriate cell (same stage and time) of the worksheet for the other component.

Extraction efficiency. For a stagewise solvent extraction process where the extraction efficiency, E, is significantly less than 100%, the distribution ratio for stage i, D_i, should be replaced by the effective distribution ratio for stage i, $D_{eff,i}$. Thus, $D_{eff,i}$ replaces D_i in Eq. 2:

$$D_{eff,i} = y_i/x_i \qquad (7)$$

When extraction efficiency for stage i, E_i, becomes 1.0 (100%), the concentrations of the exiting aqueous and organic phases are denoted as x_i^* and y_i^*, respectively. Therefore, D_i now becomes

$$D_i = y_i^*/x_i^* \qquad (8)$$

An expression for E_i can be written as

$$E_i = \frac{x_{i+1} - x_i}{x_{i+1} - x_i^*} \qquad (9)$$

using the nomenclature developed here and shown in Fig. 3. Finally, the countercurrent concentration ratio for stage i, S_i, is given by

$$S_i = y_{i-1}/x_i \qquad (10)$$

Equations 7-10, when combined with a material balance about stage i, give the following expression for $D_{eff,i}$:

$$D_{eff,i} = \frac{D_iE_i + R_jD_iS_i(1 - E_i) + S_i(1 - E_i)}{1 + R_jD_i(1 - E_i)} \qquad (11)$$

This expression replaces D_i in Eqs. 2, 3, and 6 when they are used in the aqueous- and organic-phase sections of the electronic worksheet.

Batch countercurrent operation. In batch countercurrent operation of a solvent extraction process, e.g., an operation carried out using separatory funnels, the initial rows of the aqueous-phase section of the worksheet are more tedious to set up. However, either Eq. 3 or Eq. 6 is still used for each stage, as appropriate, and the O/A flow ratio for section j, R_j, is the same as the O/A volume ratio. These two ratios will be identical for batch countercurrent operation as long as all of both phases are separated and transferred at one time. The first calculational row of the aqueous- and organic-phase sections of the worksheet has equations only for those stages where the component is being introduced into the system, i.e., at the feed stage. The second row has equations in the cells on either side of the feed stage, as well. The third row has equations in the two adjacent cells on either side of the feed stage. In each successive row, two more stages are included until the full number of stages available is used. Each of the feeds at the end of a process section for any given calculational row is introduced into the corresponding cell farthest from the feed stage that has an equation in it. Thus, the cells with equations expand in a triangular shape from the feed stage until the full complement of process stages is reached.

Transient operation. Any type of transient operation can be accommodated using the electronic worksheet. A worksheet column (or columns) can be set up for the variable (or variables) in a feed stage (or stages). Either the flow rate or the component concentration can vary. In either case, the equations would be revised so that, when the varying flow or concentration is called for, the value of a cell in the proper row in the new column is used rather than the constant value in the summary section. In this way, all types of process variations can be incorporated into the worksheet.

Unequal residence times of the phases in a stage. Although the present worksheet algorithm seems to work fairly well in predicting process startup, there may be cases where startup conditions are important and, perhaps, somewhat unusual. To provide a better model for this case, as well as to model process variations, the worksheet must be expanded to twice as many columns. Between each worksheet column for a stage equilibrating zone would be a column for a stage holding zone. A material balance would be written for the holding zone, and the volume of the holding zone would be chosen to give the proper stage residence time for each phase in a stage. Data on the liquid going to the next stage equilibrating zone would come from the holding zone of the previous stage.

In most cases, this more complex procedure will not be needed, for two reasons. First, the simple procedure usually gives a good indication of how the process will approach steady-state conditions. Second, in many cases, only the steady-state concentration profile will be needed; this profile will be the same regardless of which model is used.

Double-Diamond Structure

One of the features of the worksheet algorithm given here is that the cells in the aqueous-phase section have a double-diamond structure; i.e., a cell never refers to the cell immediately above it. Rather a cell in column i refers to the cells above it but in the columns to the left (i-1) and to the right (i+1). Imagine the cells colored red and black in a checkerboard pattern. The calculations in the red cells and in the black cells are completely independent. Thus, the equations could be removed from one set of cells and the other cells would do the job. In practice, this is not worth the effort. However, one must remain aware of the properties of the worksheet algorithm presented here; otherwise, mistakes could be made when modifying the worksheet for the batch countercurrent or transient operation.

Application to Other Stagewise Separation Processes

The algorithm for application of electronic worksheets to stagewise solvent extraction processes can be extended to other stagewise separation processes where two phases are present and where component concentrations in the two phases are related in some fashion. This relationship, plus a material balance around each stage, can be used to set up a worksheet where the two sections for the phases of the new process replace the aqueous-and organic-phase sections shown in Fig. 1.

CONCLUSIONS

The algorithm developed here allows electronic worksheets to be used for the calculation of component concentrations in stagewise solvent extraction processes. The model was tested with a solvent extraction process that cleans up nuclear waste liquids and was found to work well, not only for predicting steady-state concentrations, but also for predicting concentrations during process startup. The algorithm is easy to set up and to use. It has a flexibility that allows it to be adapted for a wide variety of process conditions, and it can be modified to model other stagewise separation processes.

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