APPLYING MICROCOMPUTERS TO THE ANALYSIS OF WASTE TREATMENT AND RECOVERY PROCESSES

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Abstract

The growing number of microcomputers appearing in plating and surface finishing companies are valuable and under-utilized tools for the analysis of plating process operations, including rinse, waste treatment, and recovery processes. Through the use of basic chemical engineering principles, the use of spreadsheet software is demonstrated by determining the performance of a typical rinse process. Also, the power of the use of programing languages, such as FORTRAN and BASIC, is demonstrated. These methods can be extended to evaluate the performance of new and existing treatment systems. With this information, management can make improved economic decisions.

1 Introduction

The electroplating industry is coming under increasing scrutiny as concern for the quality of the environment grows. This has resulted in growing regulation on the federal, state, and municipal levels. Federal laws, such as the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments of 1984, are forcing the plating industry to take an active role in pursuing and implementing solutions to the question of management of hazardous wastes [1,2]. The industry can no longer afford to wait for others to tell them the best means for plating waste management [3], they must develop the expertise to perform sophisticated analyses of these processes in order to make rational economic decisions.

The design, operation, and improvement of waste management facilities, whether treatment for disposal, recycle or recovery, requires significant technical knowledge of chemically reacting systems, chemical and physical separations, and fluid flow. These are all in the realm of knowledge of chemical engineers, exactly the type of technical personnel needed by the plating industry [3,4].

The complex decisions that must be made regarding the selection of a waste management system involve technical, legal, and economic considerations. The first step in a system design must begin with the determination of how plating wastes can be minimized, thereby reducing the need for expensive treatment or recovery equipment. Once wastes have been minimized, a decision on whether the waste

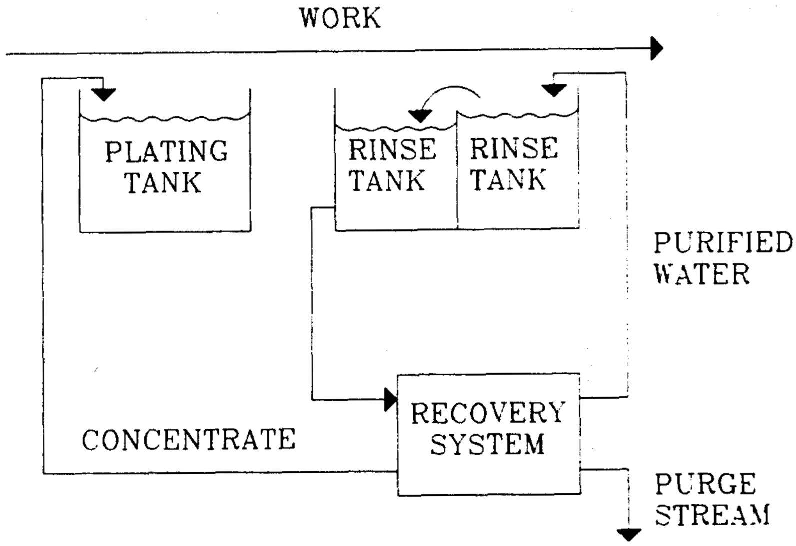

Figure 1: Basic schematic of a recovery system.

should be disposed of or recovered for reuse in some form must be made. With the increasing restrictions on land disposal, the trend is toward the effort to achieve, or at least approach, closed-loop operation; that is to say, that all chemicals which enter the plating process leave as part of the finished product. This is the ideal waste management system, one that is unlikely to be achieved since contaminates will accumulate in the plating system and result in poor finished product quality.

Waste recovery and recycling processes are inherently more complex than just simple, single rinse systems where the wastewater is treated to destroy hazardous materials and precipitate all the contaminates for subsequent land disposal. Figure 1 [5] shows a simple conceptual drawing of a recovery process. Even though recovery processes inherently require more capital equipment, changing economics are making them competitive with existing methods [6]. The obvious advantages of recovery include reduced chemical purchases, reduced treatment costs, and less sludge handling [5].

In order to evaluate these processes and identify reasonable options, a technical analysis of the processes must be made. This includes estimating actual performance by such things as mathematical modeling of the processes. This also includes the need to technically evaluate the conflicting claims made by vendors of environmental control equipment [4].

One major technical resource is the availability of microcomputers or "PC's" appearing in ever increasing numbers in the industrial environment. This convenient and inexpensive computing power provides a valuable opportunity for plating companies to do technical and economic evaluations of treatment and recovery processes in-house. This can be accomplished with such software packages as spreadsheets and programing languages, such as BASIC and FORTRAN. In the analysis of rinse process systems, basic chemical engineering principles (material balances and energy balances) can be incorporated into a spreadsheet or composed in a program using a language such as FORTRAN, to develop a computer model of a system. This computerized model can be used to analyze alternative systems for practicality without actually building a prototype of each system being considered. Computer models have the advantage that input data can be changed and new output is immediately generated, rather than having to deal with physically testing different conditions for different options, thereby saving tremendous time and expense. With these evaluations in hand, management will be in a position to make better decisions.

2 Objective

The object of this project was to demonstrate the capability microcomputers have for solving the complex engineering problems which plating processes can represent. This was accomplished by evaluating the performance of a simple rinse system by applying common and inexpensive spreadsheet and programing language software, and explaining how the procedures can be expanded to more complex systems.

3 Methods of Solution

3.1 Software Capabilities

Spreadsheet and programing language software provide the engineer with powerful tools to attack complex processing problems. They provide the means for doing quick comparisons, as well as detailed analyses of complex technical and economic options. The flexibility of programing languages, such as BASIC and FORTRAN, provide the capability of doing very sophisticated modeling of the performance of plating systems through the use of complex mathematical relationships. With the availability of inexpensive FORTRAN software (less than $500.00), as well as the nearly universal availability of BASIC on microcomputers, programing languages are a very accessible tool. Unfortunately, the ability to solve complex problems comes with a larger time commitment for the development of the program code and verifying proper program operation.

On the other hand, though spreadsheets were designed for doing accounting and other business related activities, they can be used to do some of the less complex engineering evaluations with little to no need for knowledge of programing. With extra effort, even complete plating and recovery systems can be analyzed using spreadsheet macro command capabilities. Macro commands are virtually short programs very much analogous to those written with traditional programing languages. An added benefit of most spreadsheets is their capability to make graphs. These graphs can aid in interpreting the performance predictions being made, making it easier to make the right choices. This is demonstrated by the graphs presented in this paper, which were generated with the spreadsheet software.

3.2 Software Training Resources

To make use of any tool requires proper training. Most engineers were exposed to using a programing language (usually FORTRAN) in college and today many community colleges and recreation programs offer instruction in basic and advanced programing on microcomputers (usually with BASIC). Many communities also offer classes in spreadsheet use.

Besides the availability of local resources, there is nearly a limitless supply of books, video tapes, and microcomputer-based training material available. Recently, an article appeared in *PC World* which listed the materials available for spreadsheet instruction [7]. The article included details on the contents of 37 video training programs, 27 computer-based programs, and 73 books. Books, and now some of the video and computer-based material, are readily available from most retail bookstores or computer dealers. Books on the BASIC programing language are also very common, but you may need to look further for books on the FORTRAN programing language, although they are readily available at most college bookstores. So, a lack of programing knowledge or familiarity with spreadsheets should not discourage you from making use of these powerful tools; much help is near at hand.

3.3 Chemical Engineering Principles

The performance of complex plating systems can be analyzed using material and energy balances, both basic principles of chemical engineering [8]. The material balance describes the relationship between material flow in and out of a process system and the rates of chemical reaction and accumulation in the process. This can be stated by the word equation

$$Accumulation = In - Out + Generation \tag{1}$$

where *Accumulation* is the rate of increasing material content in the process system, *In* is the total material flow rate into the system, *Out* is the total material flow rate out of the system, and *Generation* is the amount of material generated

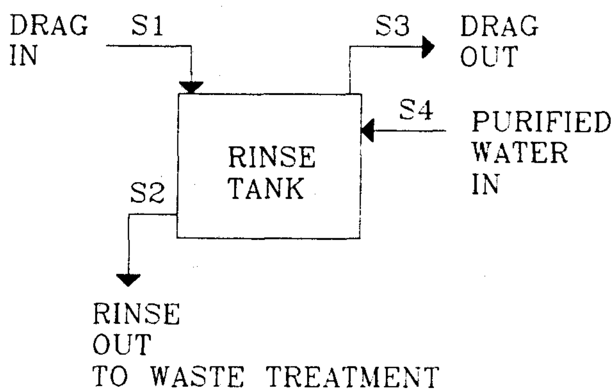

Figure 2: Single rinse tank block diagram.

by reactions. Using this relationship, the operating characteristics of a plating operation can be mathematically estimated in terms of such parameters as the rinse bath concentrations, rinse water flow rates, and plating bath and rinse drag-outs.

To demonstrate this, and how the resulting equations can be effectively solved on a microcomputer, a simple single-rinse system (Fig. 2), was studied, as applied to a typical Watts nickel plating line. The system contains one rinse tank with a drag-in stream ($S1$) from the plating bath, an outlet stream ($S2$) to some recovery system, a drag-out stream ($S3$) from the rinse bath, and a purified water inlet stream ($S4$). Evaporation was assumed to be negligible; however, including it in the analysis would not be difficult if its value were known or could be estimated.

Known information in the analysis included the volumetric flow rate of the drag-in to the rinse tank (stream $S1$: given the symbol D or F_{S1}), the concentrations of Ni^{2+}, SO_4^{2-}, Cl^-, and H_3BO_3 in $S1$ and $S4$, and the densities of $S1$ ($\overline{\rho}_{S1}$) and $S4$ ($\overline{\rho}_{S4}$). Typical bath compositions for a Watts nickel bath were used [9]. Unknown information included the volumetric flow rate of the purified water stream entering the rinse system (stream $S4$: F or F_{S4}), volumetric flow rates of $S2$ and $S3$ (F_{S2} and F_{S3}), the water concentration in $S1$ and $S4$ (C_{S1,H_2O} and C_{S4,H_2O}), and the species concentrations in $S2$ and $S3$. Finally, it was assumed that drag-out from the rinse tank equaled the drag-in from the plating tank, steady state operation as based on averaged flow rates, constant volume in the rinse tank, evaporation from the rinse tank is small compared to other flows, and the inlet water stream is assumed to be pure H_2O at $25°C$. Results for various values of the rinsing ratio, the ratio of the in-coming rinse water flow rate to the drag-in flow rate ($R_V \equiv F/D$ or F_{S4}/F_{S1}), were used to determine its effect on the species concentrations in the rinse.

The steps described below were based on initial information given in units of moles per liter (mol/l) because it was also desirable to have results in molarity. Concentrations in mol/l were converted into units of mass per volume (mg/l). It is **not** necessary to use a molar analysis if no output is desired with regard to moles—the analysis could have dealt only with mass and mass flow rates (e.g., mg/l or lb/hr). For the analysis, all flow rates are on a 1-hour basis (i.e., per hour).

Material balances, according to Eq. (1), were constructed to determine the relationships between the flow rates and concentrations in all of the streams. Using the known and assumed variable values, the necessary equations were formed and solved by using either a spreadsheet or a computer program written in FORTRAN. For example, the relationship between the four stream flow rates is found by applying Eq. (1) giving

$$(0) = (F_{S1} + F_{S4}) - (F_{S2} + F_{S3}) + (0) \tag{2}$$

which can be solved for F_{S2} since the drag-outs were assumed equal ($F_{S1} = F_{S3}$) and known, and the flow rate of the rinse water entering (F_{S4}) can be found from the chosen rinsing ratio and its definition. That is,

$$F_{S4} = R_V \cdot F_{S1} \tag{3}$$

To calculate the concentration of water in $S1$ and $S4$, the density of the respective streams was required. The exact density of the Watts nickel bath was unknown, so it was approximated by the density of a $NiSO_4$ solution of the same concentration as that of the Watts nickel bath. The density of $S4$ was assumed to be 1 g/ml, since it was assumed to be pure water. Then, on a 1 l basis,

$$C_{Si,H_2O} = \frac{\bar{\rho}_{Si} \cdot 1000 - \sum_{k \neq \mathrm{H_2O}}(C_{Si,k} \cdot \mathrm{MW}_k)}{\mathrm{MW}_{\mathrm{H_2O}}} \tag{4}$$

where MW_k is the molecular weight of species k.

Once the concentration of each species in the two inlet streams is known or calculated, determining the concentration in the two unknown (outlet) streams simply requires component material balances [8]. Also, since the concentrations of $S2$ and $S3$ are necessarily equal for a single rinse-tank system, the concentration of either stream can be calculated from the known information. For example,

$$C_{S2,j} = C_{S3,j} = \frac{\dot{n}_{S1,j} + \dot{n}_{S4,j}}{F_{S2} + F_{S3}} \tag{5}$$

Once the concentration of each species in each stream is known in mol/l, the concentration in any other units, such as mg/l, oz/gal, mole%, or mass% can be calculated by simple conversions.

Energy balances [8] can also be formulated to determine the need for heating or cooling of process flow streams. By inclusion of appropriate thermophysical property data, extensive thermal efficiency studies can be conducted. These analyses have not been demonstrated here for sake of brevity.

3.4 Application of Spreadsheet Software

Spreadsheets are easily used to organize numeric data in a systematic row and column structure, just like an accountant's ledger, where each block or space in this matrix is called a "cell." This organized form and computational ability of spreadsheets can be effectively used to solve chemical process problems [10]-[16]. Process variables (such as flow rate or concentration) are represented as one of these blocks or cells and their specific values, if known, are entered directly into the cells of the spreadsheet. The material and energy balance relations which describe the interrelationships of the process variables of the system to be analyzed are then entered into other cells using formulas based on the contents of the previously defined cells. When the formula for a group of cells has the same structure, they can be obtained by using the copy command of the spreadsheet to duplicate the formula into the remaining cells. When this is done the spreadsheet program will automatically adjust the cell identification information. Thus a complicated spreadsheet can be constructed rapidly.

In our test example of a single rinse system (Fig. 2), the known concentrations of the non-water species in $S1$ and $S4$ were entered into the spreadsheet as well as the volumetric flow rate of the drag-in stream (D or F_{S1}), the rinsing ratio (R_V), the estimated density of $S1$, and the assumed density of $S4$. The output (and computer screen appearance) for a sample run is given in Appendix A.1, a summary for various rinsing ratios is given in Appendix A.2, and a listing of the actual formula contents of each cell is given in Appendix A.3. For instance, Eq. (3) was entered as a formula in a cell to calculate the volumetric flow rate of the purified water stream, F_{S4}, and so on to determine the various flow rates and concentrations. An example of the appearance of one of these formulas is

$$(((\mathtt{B80} * 1000) - (\mathtt{B17} * \$\mathtt{B3} + \mathtt{B18} * \$\mathtt{B4} + \mathtt{B19} * \$\mathtt{B5} + \mathtt{B20} * \$\mathtt{B6}))/\$\mathtt{B}\$7) \qquad (6)$$

which is the spreadsheet's cell-address formula equivalent to Eq. (4).

Total molar flow was also calculated from the concentration in mol/l and the volumetric flow rate of each stream in l. Total molar flow was converted into total mass flow by using molecular weights. Conversion into other units would also be very easy, especially when aided by the ability of a spreadsheet to copy formulas.

Spreadsheets also make it very easy to produce graphs. Different values of rinsing ratio, R_V, were entered into the spreadsheet developed above, holding all other input parameters constant. New values were calculated instantly and then the results of interest that changed were copied into a tabular form onto a different part of the spreadsheet. The graph function of the spreadsheet was then employed to plot the data, resulting in the figures shown later.

3.5 Application of FORTRAN Program Software

Programing languages such as FORTRAN can also be used to construct mathematical models of process systems. This is done by converting the governing equations into the form required by the programing language, the construction of repetitive calculation sequences, and application of various numerical solution techniques, as needed [17,18]. For example, the volumetric flow rate of the purified water stream entering the rinse tank (F_{S4}) was converted from Eq. (3) into the FORTRAN code

$$\texttt{F(4)} = \texttt{D} * \texttt{Rv(i)} * 3600.0 \tag{7}$$

where `D` is an alternate variable symbol for the drag-in flow rate (F_{S1}), `Rv(i)` is a particular value of the rinsing ratio, and `3600.0` is a conversion factor from seconds to hours. The FORTRAN program listed in Appendix B.3 was developed to model the same single rinse system, shown in Fig. 2, as the spreadsheet listing given in Appendix A.3. During each repetitive calculation loop, similar formulas were used to perform the same calculations that were done in the spreadsheet. The calculated concentrations of the rinse outflow stream ($S2$) for each desired value of rinsing ratio were stored in a permanent array which can be printed in tabular form after all desired values of R_V have been evaluated. Finally, the desired data is printed out in tabular form, an example of which is given in Appendix B.1.

4 Example Results

Tabular results of the calculated concentrations and flow rates for the single rinse process shown in Fig. 2 are given in Appendices A.1 and B.1 for the spreadsheet and the FORTRAN programs, respectively. As would be expected, the results are the same for both methods. Three figures were generated to demonstrate the spreadsheet's graphics capabilities. Figure 3 shows the rapid drop in concentration which occurs as the rinsing ratio (R_V) rises from 5 to 1000. Recall that the rinsing ratio is the relation between the flow rate of the water fed to the rinse system (F_{S4}) to the drag-in flow rate (F_{S1}). Figures 4 and 5 show the same relationship for nickel and the other species in the rinse bath for a narrower range of rinsing ratio (5 to 100), respectively. These kinds of graphs are useful for determining the range of desired rinse bath operation.

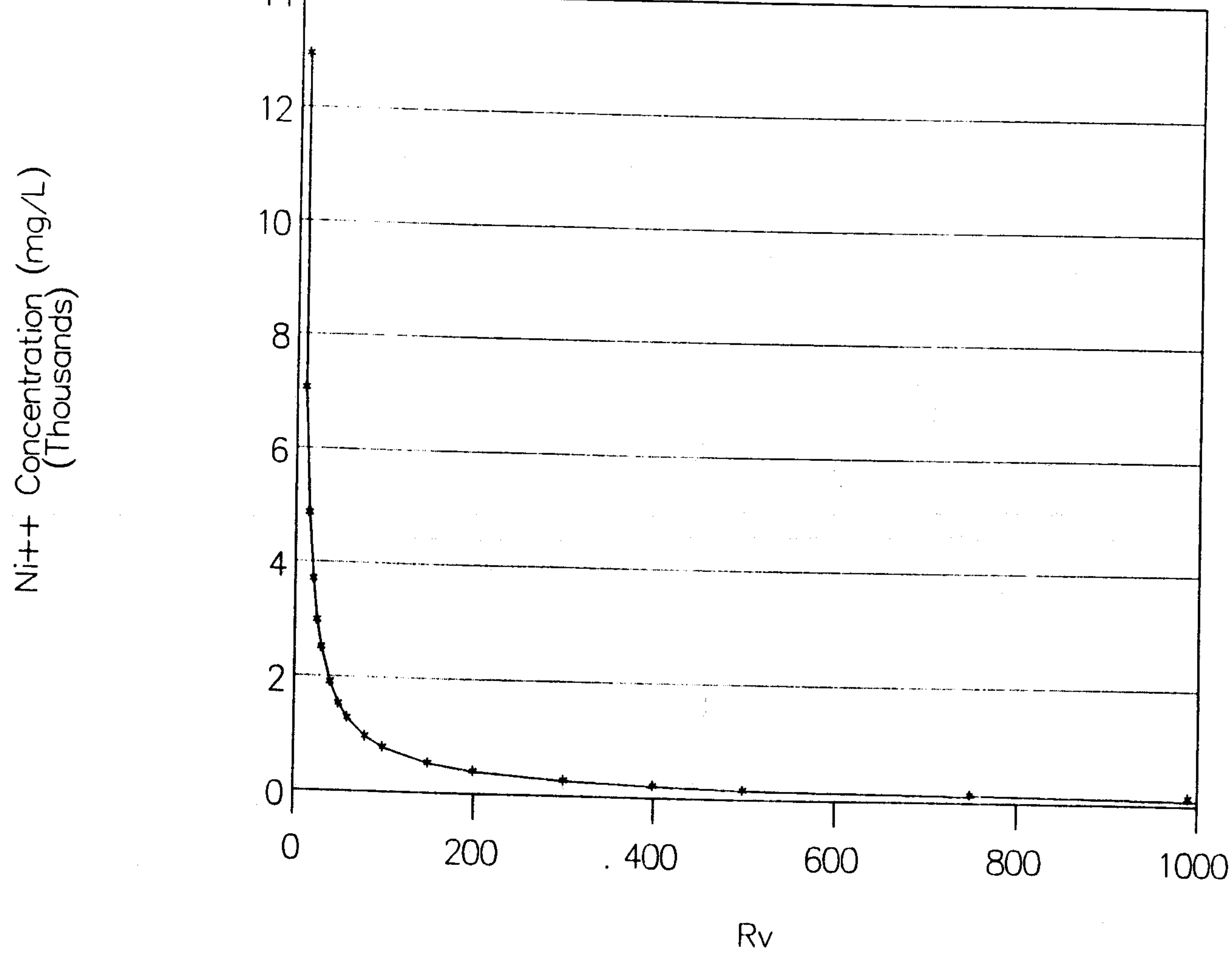

Figure 3: Concentration of nickel leaving a single rinse system as a function of the rinsing ratio, up to 1000.

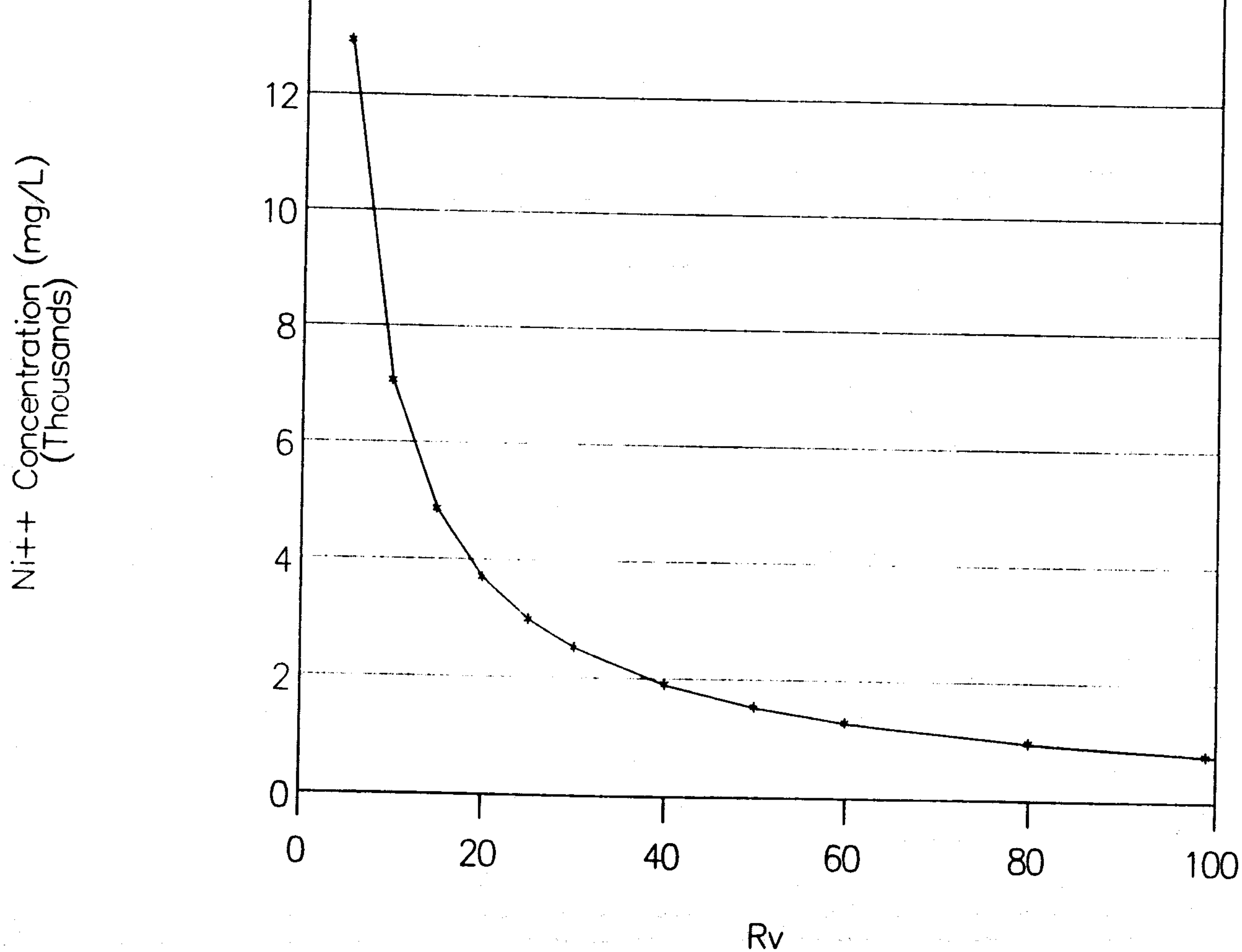

Figure 4: Concentration of nickel leaving a single rinse system as a function of the rinsing ratio, up to 100.

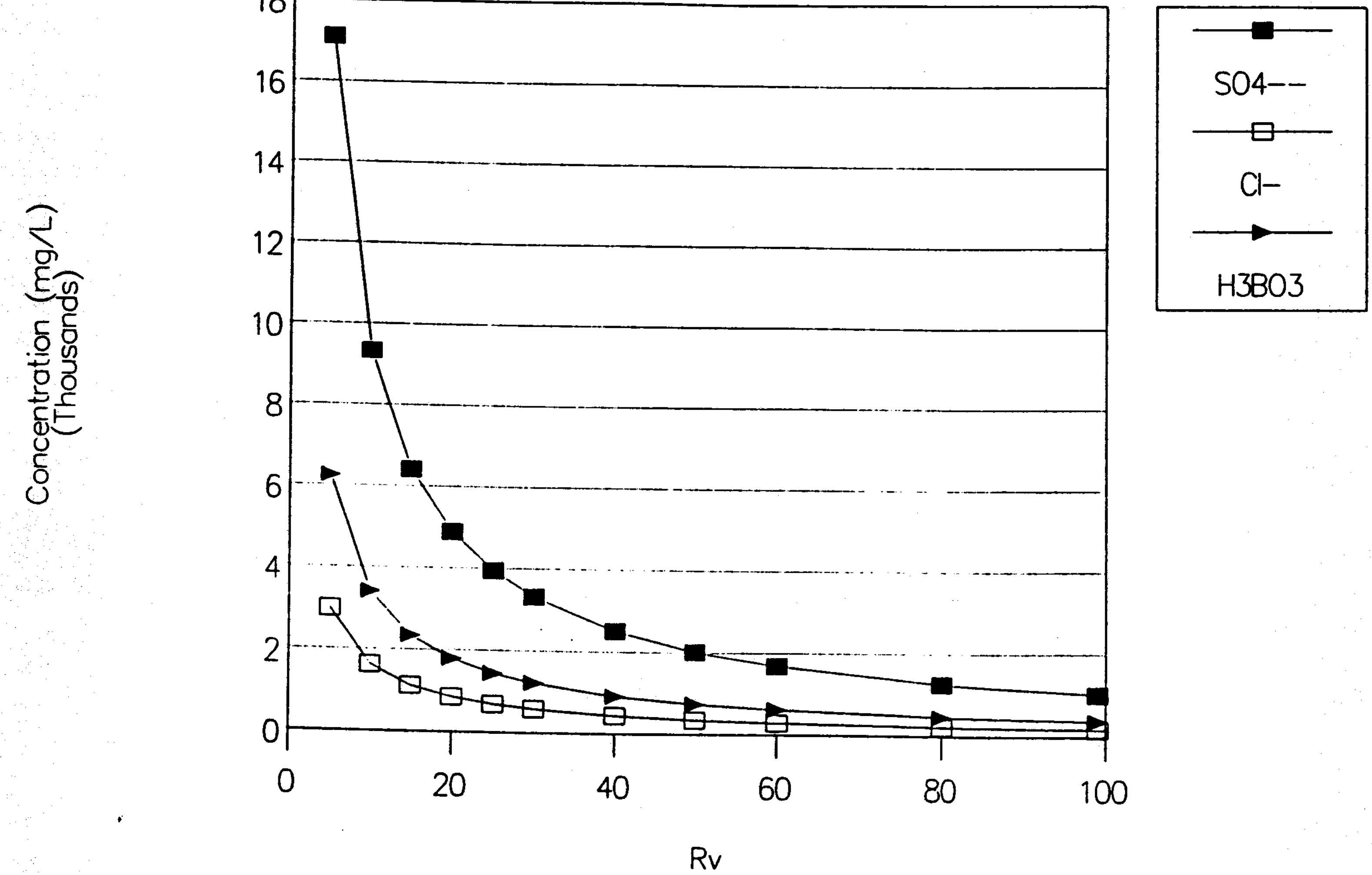

Figure 5: **Concentration of sulfate, chloride and boric acid leaving a single rinse system as a function of the rinsing ratio.**

5 Conclusions

The simple application of analyzing a single rinse system described in this paper demonstrates the use of spreadsheet and programing language software which is currently available for microcomputers. With the growing number of microcomputers available in the plating shop, it is only reasonable that they should be put to use in tackling the analysis of the increasingly complex processing problems in the electroplating industry.

Programing languages such as FORTRAN (or BASIC) provide a powerful tool to model electrochemical systems. Their use of loops, arrays, and subroutines, make repetitive operations quite simple. The major advantage of FORTRAN is its power with mathematical operations, which would be very useful in more complex systems with non-linear relationships. FORTRAN also allows the programer to define subroutines and functions that conveniently allow the same processes to be executed on different data by simply using the subprogram repeatedly. The disadvantage of programing languages lies in the time required to code, debug, and test the program.

Spreadsheets are also a useful tool in modeling electroplating systems. Their advantage lies in the ease of entering data and copying formulas, the immediacy of new results, and the time saved from coding or debugging; however, reliability testing is highly recommended. Spreadsheets are also capable of performing powerful calculations, such as finding solutions to non-linear equations, with the use of macros, which is basically a user-written program, not unlike FORTRAN or BASIC. The powerful and convenient graphing function of spreadsheets also provides a powerful visual aid for analyzing chemical process systems.

6 Recommendations

With the availability of powerful microcomputers, it seems only logical that they should be put to use. With either spreadsheet or programing language software, the increasingly complex waste treatment and recovery systems required to meet regulation standards can be analyzed and their economic performance evaluated. This can be done by starting with the simple example demonstrated here and expanding it to include multiple rinses and recovery process steps. As an example, the recuperative rinse configurations recommended by Stein [19,20,21], where the rinse stream from a series of rinses is returned to the plating tank, can be evaluated for the specific situation in a plating shop to determine feasible and optimum operating conditions. Also, these methods can be used for accounting in precious metal plating systems by allowing improved means of calculating expected recovery system performance. They can also be used to study the waste treatment section of the plating operation, permitting a rapid and cost-effective means for evaluating the effect of changing the operating conditions of the treatment facility. All together, the ability to rapidly evaluate these waste management options will permit management to choose the most economical options.

Acknowledgements

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Nomenclature

$C_{Si,j}$	Concentration of species j in stream Si, mol/l
D	Flow rate of the drag-in to the rinse tank ($\equiv F_{S1}$), l/s
F	Flow rate of incoming purified water stream to rinse tank ($\equiv F_{S4}$), l/s
F_{Si}	Volumetric flow rate of stream Si, l/s
MW_k	Molecular weight of species k, g/mol
$\dot{n}_{Si,j}$	Molar flow rate of species j in stream Si, mol/hr
R_V	Rinsing ratio ($\equiv F/D$), unitless
$\bar{\rho}_{Si}$	Average solution density in stream Si, g/ml

Subscripts

j	chemical species
k	chemical species
Si	process stream number (as in Fig. 2)

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Appendices

Sample program output and code for the spreadsheet and FORTRAN programming language software applications are found in Appendices A and B, respectively. These are available from AESF Headquarters or the authors.

A Spreadsheet Example for a Single Rinse

A.1 Sample Output

The following is the printout (as well as the general on-screen appearance) generated for the analysis of the single rinse tank shown in Fig. 2, for a rinsing ratio (R_V) of 10.

Component	MW
Ni^2+	58.700
SO4^2-	96.060
Cl^1-	35.453
H3BO3	61.830
H2O	18.015

D (L/s)	0.00283
Rv	10
F (L/s)	0.0283

Concentration (M)	S1	S2	S3	S4
Ni^2+	1.321	0.120	0.120	0.000
SO4^2-	1.068	0.097	0.097	0.000
Cl^1-	0.505	0.046	0.046	0.000
H3BO3	0.607	0.055	0.055	0.000
H2O	47.986	54.824	54.824	55.508

Conc. (mg/L)	S1	S2	S3	S4
Ni^2+	77513.4	7046.7	7046.7	0.0
SO4^2-	102592.1	9326.6	9326.6	0.0
Cl^1-	17903.8	1627.6	1627.6	0.0
H3BO3	37499.9	3409.1	3409.1	0.0
H2O	864490.9	987681.0	987681.0	1000000.0

Mole %	S1	S2	S3	S4
Ni^2+	2.565%	0.218%	0.218%	0.000%
SO4^2-	2.074%	0.176%	0.176%	0.000%
Cl^1-	0.981%	0.083%	0.083%	0.000%

H3BO3	1.178%	0.100%	0.100%	0.000%
H2O	93.202%	99.423%	99.423%	100.000%
Total	100.000%	100.000%	100.000%	100.000%

Mass %	S1	S2	S3	S4
Ni^2+	7.047%	0.698%	0.698%	0.000%
SO4^2-	9.327%	0.924%	0.924%	0.000%
Cl^1-	1.628%	0.161%	0.161%	0.000%
H3BO3	3.409%	0.338%	0.338%	0.000%
H2O	78.590%	97.878%	97.878%	100.000%
Total	100.000%	100.000%	100.000%	100.000%

Moles (gmole/hr)	S1	S2	S3	S4
Ni^2+	13.453	12.230	1.223	0.000
SO4^2-	10.881	9.892	0.989	0.000
Cl^1-	5.145	4.677	0.468	0.000
H3BO3	6.179	5.617	0.562	0.000
H2O	488.884	5585.496	558.550	5655.162
Total	495.063	5591.113	559.111	5655.162

Mass (g/hr)	S1	S2	S3	S4
Ni^2+	789.7	717.9	71.8	0.0
SO4^2-	1045.2	950.2	95.0	0.0
Cl^1-	182.4	165.8	16.6	0.0
H3BO3	382.0	347.3	34.7	0.0
H2O	8807.4	100624.9	10062.5	101880.0
Total	9189.5	100972.3	10097.2	101880.0

Flow rate (L/s)	0.003	0.028	0.003	0.028
Flow rate (L/hr)	10.188	101.880	10.188	101.880
Density	1.100			1.000
Temperature (deg.C)	60.000			25.000

A.2 Summary for Various Rinse Ratios (R_V's)

The following is a sample of results obtained by using four different rinsing ratios (R_V's).

D (L/s)	0.00283	0.00283	0.00283	0.00283
Rv	5	10	15	20
F (L/s)	0.01415	0.0283	0.04245	0.0566

COMPONENTS

Concentration (M)	S2	S2	S2	S2
Ni^2+	0.220	0.120	0.083	0.063
SO4^2-	0.178	0.097	0.067	0.051
Cl^1-	0.084	0.046	0.032	0.024
H3BO3	0.101	0.055	0.038	0.029
H2O	54.254	54.824	55.038	55.150

Conc. (mg/L)	S2	S2	S2	S2
Ni^2+	12918.892	7046.668	4844.584	3691.112
SO4^2-	17098.680	9326.553	6412.005	4885.337
Cl^1-	2983.961	1627.615	1118.985	852.560
H3BO3	6249.983	3409.081	2343.743	1785.709
H2O	977415.152	987680.992	991530.682	993547.186

A.3 Listing of Spreadsheet Cell Contents

The following is a list of the formula content of each of the cells in the spreadsheet that generated the results in Section A.1. The specific spreadsheet software used for this study was *Quattro*^{R} by the Borland Corporation, though any other spreadsheet software could have been used. The first letter number combination is the cell location. For example, B12: is the cell at the intersection of the second column (B) and twelfth row (12). The next information, which appears in "[...]" or "(...)," defines the width of the column and type of number format, respectively. Finally, the contents of the cell is given, for example for cell B12 it is "(B10*B11)," which means to multiply the number in cell B10 times the number in cell B11 and put the result in cell B12.

```
A1: [W19] ^Component
B1: [W12] ^MW
A3: [W19] '  Ni^2+
B3: (F3) [W12] 58.7
```

```
A4: [W19] '  SO4^2-
B4: (F3) [W12] 96.06
A5: [W19] '  Cl^1-
B5: (F3) [W12] 35.453
A6: [W19] '  H3BO3
B6: (F3) [W12] 61.83
A7: [W19] '  H2O
B7: (F3) [W12] 18.0154
A10: [W19] 'D (L/s)
B10: [W12] 0.00283
A11: [W19] 'Rv
B11: [W12] 10
A12: [W19] 'F (L/s)
B12: [W12] (B10*B11)
A15: [W19] '  Concentration (M)
B15: (F7) [W12] ^S1
C15: (F7) [W12] ^S2
D15: (F7) [W12] ^S3
E15: (F7) [W12] ^S4
A17: [W19] '  Ni^2+
B17: (F3) [W12] (B18+0.5*B19)
C17: (F3) [W12] (D17)
D17: (F3) [W12] ((B57+E57)/(C$78+D$78))
E17: (F3) [W12] 0
A18: [W19] '  SO4^2-
B18: (F3) [W12] 1.068
C18: (F3) [W12] (D18)
D18: (F3) [W12] ((B58+E58)/(C$78+D$78))
E18: (F3) [W12] 0
A19: [W19] '  Cl^1-
B19: (F3) [W12] 0.505
C19: (F3) [W12] (D19)
D19: (F3) [W12] ((B59+E59)/(C$78+D$78))
E19: (F3) [W12] 0
A20: [W19] '  H3BO3
B20: (F3) [W12] 0.6065
C20: (F3) [W12] (D20)
D20: (F3) [W12] ((B60+E60)/(C$78+D$78))
E20: (F3) [W12] 0
A21: [W19] '  H2O
B21: (F3) [W12] (((B80*1000)-(B17*$B3+B18*$B4+B19*$B5+B20*$B6))/$B$7)
```

```
C21: (F3) [W12] (D21)
D21: (F3) [W12] ((B61+E61)/(C$78+D$78))
E21: (F3) [W12] (((E80*1000)-(E17*$B3+E18*$B4+E19*$B5+E20*$B6))/$B$7)
A24: [W19] '  Conc. (mg/L)
B24: (F7) [W12] ^S1
C24: (F7) [W12] ^S2
D24: (F7) [W12] ^S3
E24: (F7) [W12] ^S4
A26: [W19] '  Ni^2+
B26: (F1) [W12] (B17*$B3*1000)
C26: (F1) [W12] (C17*$B3*1000)
D26: (F1) [W12] (D17*$B3*1000)
E26: (F1) [W12] (E17*$B3*1000)
A27: [W19] '  SO4^2-
B27: (F1) [W12] (B18*$B4*1000)
C27: (F1) [W12] (C18*$B4*1000)
D27: (F1) [W12] (D18*$B4*1000)
E27: (F1) [W12] (E18*$B4*1000)
A28: [W19] '  Cl^1-
B28: (F1) [W12] (B19*$B5*1000)
C28: (F1) [W12] (C19*$B5*1000)
D28: (F1) [W12] (D19*$B5*1000)
E28: (F1) [W12] (E19*$B5*1000)
A29: [W19] '  H3BO3
B29: (F1) [W12] (B20*$B6*1000)
C29: (F1) [W12] (C20*$B6*1000)
D29: (F1) [W12] (D20*$B6*1000)
E29: (F1) [W12] (E20*$B6*1000)
A30: [W19] '  H2O
B30: (F1) [W12] (B21*$B7*1000)
C30: (F1) [W12] (C21*$B7*1000)
D30: (F1) [W12] (D21*$B7*1000)
E30: (F1) [W12] (E21*$B7*1000)
A33: [W19] '  Mole %
B33: (F3) [W12] ^S1
C33: (F3) [W12] ^S2
D33: (F3) [W12] ^S3
E33: (F3) [W12] ^S4
A35: [W19] '  Ni^2+
B35: (P3) [W12] (B17/(@SUM(B$17..B$21)))
C35: (P3) [W12] (C17/(@SUM(C$17..C$21)))
```

```
D35: (P3) [W12] (D17/(@SUM(D$17..D$21)))
E35: (P3) [W12] (E17/(@SUM(E$17..E$21)))
A36: [W19] '  SO4^2-
B36: (P3) [W12] (B18/(@SUM(B$17..B$21)))
C36: (P3) [W12] (C18/(@SUM(C$17..C$21)))
D36: (P3) [W12] (D18/(@SUM(D$17..D$21)))
E36: (P3) [W12] (E18/(@SUM(E$17..E$21)))
A37: [W19] '  Cl^1-
B37: (P3) [W12] (B19/(@SUM(B$17..B$21)))
C37: (P3) [W12] (C19/(@SUM(C$17..C$21)))
D37: (P3) [W12] (D19/(@SUM(D$17..D$21)))
E37: (P3) [W12] (E19/(@SUM(E$17..E$21)))
A38: [W19] '  H3BO3
B38: (P3) [W12] (B20/(@SUM(B$17..B$21)))
C38: (P3) [W12] (C20/(@SUM(C$17..C$21)))
D38: (P3) [W12] (D20/(@SUM(D$17..D$21)))
E38: (P3) [W12] (E20/(@SUM(E$17..E$21)))
A39: [W19] '  H2O
B39: (P3) [W12] (B21/(@SUM(B$17..B$21)))
C39: (P3) [W12] (C21/(@SUM(C$17..C$21)))
D39: (P3) [W12] (D21/(@SUM(D$17..D$21)))
E39: (P3) [W12] (E21/(@SUM(E$17..E$21)))
A40: [W19] '  Total
B40: (P3) [W12] (@SUM(B35..B39))
C40: (P3) [W12] (@SUM(C35..C39))
D40: (P3) [W12] (@SUM(D35..D39))
E40: (P3) [W12] (@SUM(E35..E39))
A44: [W19] '  Mass %
B44: (F3) [W12] ^S1
C44: (F3) [W12] ^S2
D44: (F3) [W12] ^S3
E44: (F3) [W12] ^S4
A46: [W19] '  Ni^2+
B46: (P3) [W12] (B35*$B3/(B$35*$B$3+B$36*$B$4+B$37*$B$5+B$38*$B$6
+B$39*$B$7))
C46: (P3) [W12] (C35*$B3/(C$35*$B$3+C$36*$B$4+C$37*$B$5+C$38*$B$6
+C$39*$B$7))
D46: (P3) [W12] (D35*$B3/(D$35*$B$3+D$36*$B$4+D$37*$B$5+D$38*$B$6
+D$39*$B$7))
E46: (P3) [W12] (E35*$B3/(E$35*$B$3+E$36*$B$4+E$37*$B$5+E$38*$B$6
+E$39*$B$7))
```

```
A47: [W19] '  SO4^2-
B47: (P3) [W12] (B36*$B4/(B$35*$B$3+B$36*$B$4+B$37*$B$5+B$38*$B$6
+B$39*$B$7))
C47: (P3) [W12] (C36*$B4/(C$35*$B$3+C$36*$B$4+C$37*$B$5+C$38*$B$6
+C$39*$B$7))
D47: (P3) [W12] (D36*$B4/(D$35*$B$3+D$36*$B$4+D$37*$B$5+D$38*$B$6
+D$39*$B$7))
E47: (P3) [W12] (E36*$B4/(E$35*$B$3+E$36*$B$4+E$37*$B$5+E$38*$B$6
+E$39*$B$7))
A48: [W19] '  Cl^1-
B48: (P3) [W12] (B37*$B5/(B$35*$B$3+B$36*$B$4+B$37*$B$5+B$38*$B$6
+B$39*$B$7))
C48: (P3) [W12] (C37*$B5/(C$35*$B$3+C$36*$B$4+C$37*$B$5+C$38*$B$6
+C$39*$B$7))
D48: (P3) [W12] (D37*$B5/(D$35*$B$3+D$36*$B$4+D$37*$B$5+D$38*$B$6
+D$39*$B$7))
E48: (P3) [W12] (E37*$B5/(E$35*$B$3+E$36*$B$4+E$37*$B$5+E$38*$B$6
+E$39*$B$7))
A49: [W19] '  H3BO3
B49: (P3) [W12] (B38*$B6/(B$35*$B$3+B$36*$B$4+B$37*$B$5+B$38*$B$6
+B$39*$B$7))
C49: (P3) [W12] (C38*$B6/(C$35*$B$3+C$36*$B$4+C$37*$B$5+C$38*$B$6
+C$39*$B$7))
D49: (P3) [W12] (D38*$B6/(D$35*$B$3+D$36*$B$4+D$37*$B$5+D$38*$B$6
+D$39*$B$7))
E49: (P3) [W12] (E38*$B6/(E$35*$B$3+E$36*$B$4+E$37*$B$5+E$38*$B$6
+E$39*$B$7))
A50: [W19] '  H2O
B50: (P3) [W12] (B39*$B7/(B$35*$B$3+B$36*$B$4+B$37*$B$5+B$38*$B$6
+B$39*$B$7))
C50: (P3) [W12] (C39*$B7/(C$35*$B$3+C$36*$B$4+C$37*$B$5+C$38*$B$6
+C$39*$B$7))
D50: (P3) [W12] (D39*$B7/(D$35*$B$3+D$36*$B$4+D$37*$B$5+D$38*$B$6
+D$39*$B$7))
E50: (P3) [W12] (E39*$B7/(E$35*$B$3+E$36*$B$4+E$37*$B$5+E$38*$B$6
+E$39*$B$7))
A51: [W19] '  Total
B51: (P3) [W12] (@SUM(B46..B50))
C51: (P3) [W12] (@SUM(C46..C50))
D51: (P3) [W12] (@SUM(D46..D50))
E51: (P3) [W12] (@SUM(E46..E50))
```

```
A55: [W19] '  Moles (gmole/hr)
B55: (F3) [W12] ^S1
C55: (F3) [W12] ^S2
D55: (F3) [W12] ^S3
E55: (F3) [W12] ^S4
A57: [W19] '  Ni^2+
B57: (F3) [W12] (B17*B$78)
C57: (F3) [W12] (C17*C$78)
D57: (F3) [W12] (D17*D$78)
E57: (F3) [W12] (E17*E$78)
A58: [W19] '  SO4^2-
B58: (F3) [W12] (B18*B$78)
C58: (F3) [W12] (C18*C$78)
D58: (F3) [W12] (D18*D$78)
E58: (F3) [W12] (E18*E$78)
A59: [W19] '  Cl^1-
B59: (F3) [W12] (B19*B$78)
C59: (F3) [W12] (C19*C$78)
D59: (F3) [W12] (D19*D$78)
E59: (F3) [W12] (E19*E$78)
A60: [W19] '  H3BO3
B60: (F3) [W12] (B20*B$78)
C60: (F3) [W12] (C20*C$78)
D60: (F3) [W12] (D20*D$78)
E60: (F3) [W12] (E20*E$78)
A61: [W19] '  H2O
B61: (F3) [W12] (B21*B$78)
C61: (F3) [W12] (C21*C$78)
D61: (F3) [W12] (D21*D$78)
E61: (F3) [W12] (E21*E$78)
A62: [W19] '  Total
B62: (F3) [W12] (@SUM(B60..B61))
C62: (F3) [W12] (@SUM(C60..C61))
D62: (F3) [W12] (@SUM(D60..D61))
E62: (F3) [W12] (@SUM(E60..E61))
A66: [W19] '  Mass (g/hr)
B66: (F3) [W12] ^S1
C66: (F3) [W12] ^S2
D66: (F3) [W12] ^S3
E66: (F3) [W12] ^S4
A68: [W19] '  Ni^2+
```

```
B68: (F1) [W12] (B57*$B3)
C68: (F1) [W12] (C57*$B3)
D68: (F1) [W12] (D57*$B3)
E68: (F1) [W12] (E57*$B3)
A69: [W19] '  SO4^2-
B69: (F1) [W12] (B58*$B4)
C69: (F1) [W12] (C58*$B4)
D69: (F1) [W12] (D58*$B4)
E69: (F1) [W12] (E58*$B4)
A70: [W19] '  Cl^1-
B70: (F1) [W12] (B59*$B5)
C70: (F1) [W12] (C59*$B5)
D70: (F1) [W12] (D59*$B5)
E70: (F1) [W12] (E59*$B5)
A71: [W19] '  H3BO3
B71: (F1) [W12] (B60*$B6)
C71: (F1) [W12] (C60*$B6)
D71: (F1) [W12] (D60*$B6)
E71: (F1) [W12] (E60*$B6)
A72: [W19] '  H2O
B72: (F1) [W12] (B61*$B7)
C72: (F1) [W12] (C61*$B7)
D72: (F1) [W12] (D61*$B7)
E72: (F1) [W12] (E61*$B7)
A73: [W19] '  Total
B73: (F1) [W12] (@SUM(B71..B72))
C73: (F1) [W12] (@SUM(C71..C72))
D73: (F1) [W12] (@SUM(D71..D72))
E73: (F1) [W12] (@SUM(E71..E72))
A77: [W19] 'Flow rate (L/s)
B77: (F3) [W12] (B10)
C77: (F3) [W12] (E77)
D77: (F3) [W12] (B77)
E77: (F3) [W12] (B12)
A78: [W19] 'Flow rate (L/hr)
B78: (F3) [W12] (B77*3600)
C78: (F3) [W12] (C77*3600)
D78: (F3) [W12] (D77*3600)
E78: (F3) [W12] (E77*3600)
A80: [W19] 'Density
B80: (F3) [W12] 1.1
```

```
E80: (F3) [W12] 1
A82: [W19] 'Temperature (deg.C)
B82: (F3) [W12] 60
E82: (F3) [W12] 25
```

B FORTRAN Program for a Single Rinse

B.1 Sample Output

The following is the printed output generated by the FORTRAN program for analyzing the performance of the single rinse tank as shown in Fig. 2.

```
Rv =    5.000
Concentrations (mol/L):

                  S1         S2         S3         S4
Ni^2+          1.321      0.220      0.220      0.000
SO4^2-         1.068      0.178      0.178      0.000
Cl-            0.505      0.084      0.084      0.000
H3BO3          0.607      0.101      0.101      0.000
H2O           47.985     54.254     54.254     55.508

Concentrations (mg/L):

                  S1         S2         S3         S4
Ni^2+      77513.352  12918.892  12918.892      0.000
SO4^2-    102592.070  17098.678  17098.678      0.000
Cl-        17903.766   2983.961   2983.961      0.000
H3BO3      37530.813   6255.135   6255.135      0.000
H2O       864460.000 977410.063 977410.063 1000000.000



Rv =   10.000
Concentrations (mol/L):

                  S1         S2         S3         S4
Ni^2+          1.321      0.120      0.120      0.000
SO4^2-         1.068      0.097      0.097      0.000
Cl-            0.505      0.046      0.046      0.000
H3BO3          0.607      0.055      0.055      0.000
H2O           47.985     54.824     54.824     55.508
```

Concentrations (mg/L):

	S1	S2	S3	S4
Ni^2+	77513.352	7046.668	7046.668	0.000
SO4^2-	102592.070	9326.552	9326.552	0.000
Cl-	17903.766	1627.615	1627.615	0.000
H3BO3	37530.813	3411.892	3411.892	0.000
H2O	864460.000	987678.188	987678.188	1000000.000

Rv = 15.000

Concentrations (mol/L):

	S1	S2	S3	S4
Ni^2+	1.321	0.083	0.083	0.000
SO4^2-	1.068	0.067	0.067	0.000
Cl-	0.505	0.032	0.032	0.000
H3BO3	0.607	0.038	0.038	0.000
H2O	47.985	55.038	55.038	55.508

Concentrations (mg/L):

	S1	S2	S3	S4
Ni^2+	77513.352	4844.584	4844.584	0.000
SO4^2-	102592.070	6412.004	6412.004	0.000
Cl-	17903.766	1118.985	1118.985	0.000
H3BO3	37530.813	2345.676	2345.676	0.000
H2O	864460.000	991528.750	991528.750	1000000.000

Rv = 20.000

Concentrations (mol/L):

	S1	S2	S3	S4
Ni^2+	1.321	0.063	0.063	0.000
SO4^2-	1.068	0.051	0.051	0.000
Cl-	0.505	0.024	0.024	0.000
H3BO3	0.607	0.029	0.029	0.000
H2O	47.985	55.150	55.150	55.508

Concentrations (mg/L):

	S1	S2	S3	S4
Ni^2+	77513.352	3691.112	3691.112	0.000
SO4^2-	102592.070	4885.336	4885.336	0.000
Cl-	17903.766	852.560	852.560	0.000
H3BO3	37530.813	1787.182	1787.182	0.000
H2O	864460.000	993545.688	993545.688	1000000.000

B.2 Summary for Various R_V

Rv vs. Concentration (mol/L):

Rv	Ni^2+	SO4^2-	Cl-	H3BO3	H2O
5.000	0.220	0.178	0.084	0.101	54.254
10.000	0.120	0.097	0.046	0.055	54.824
15.000	0.083	0.067	0.032	0.038	55.038
20.000	0.063	0.051	0.024	0.029	55.150

Rv vs. Concentration (mg/L):

Rv	Ni^2+	SO4^2-	Cl-	H3BO3	H2O
5.000	12918.892	17098.678	2983.961	6255.135	977410.063
10.000	7046.668	9326.552	1627.615	3411.892	987678.188
15.000	4844.584	6412.004	1118.985	2345.676	991528.750
20.000	3691.112	4885.336	852.560	1787.182	993545.688

B.3 Program Listing

The following is the FORTRAN computer code for determining the performance of the single rinse bath shown in Fig. 2.

```
      PROGRAM Rinse
C     ***************************************************************
C                         Description of Variable Names
C     ---------------------------------------------------------------
C     Cmg(i,j)          Concentration of species j in stream i in mg/L
C     Cmol(i,j)         Concentration of species j in stream i in mol/L
C     C2molperm(i,j)    Concentration of species j in S2 for Rv(i)
C                                    in mol/L
C     C2mgperm(i,j)     Concentration of species j in S2 for Rv(i)
C                                    in mg/L
```

```
C       D                   Volumetric flow rate of S1 (Drag-in) in L/s
C       F                   Volumetric flow rate of S4 (water) in L/s
C       i,j,k               Loop control variables
C       mnonH20             Mass of non-water species per liter of stream
C       Moles(i,j)          Moles of species j in stream i
C       MW                  Molecular weight of each species
C       NRv                 Number of values of Rv to compute
C                               concentrations for
C       Nspec               Number of species in system
C       Rho                 Density of stream
C       Rv                  Rinse ratio = F/D
C       SpecName            Name of each species
C       ************************************************************
        REAL  D, Cmol, Rho, MW, Rv, mnonH20, F, Moles, Cmg, C2molperm,
     +        C2mgperm
        INTEGER  i, j, k, Nspec, NRv
        CHARACTER*8 SpecName
        DIMENSION  SpecName(25), Cmol(4,25), Rho(4), MW(25), Rv(100),
     +             F(4), Moles(4,25), Cmg(4,25), C2molperm(100,25),
     +             C2mgperm(100,25)

        OPEN (8, File = 'RinsePar.DAT', Status = 'Old')
        OPEN (9, File = 'RinseRv.DAT', Status = 'Old')
        OPEN (10, File = 'RinseCon.OUT', Status = 'New')
        OPEN (11, File = 'RinseRv.OUT', Status = 'New')

        READ (8,*) Nspec

        DO 5  i = 1,Nspec
          READ (8,7) SpecName(i)
    7       FORMAT (a8)
    5     CONTINUE

        DO 8  i = 1,Nspec
          READ (8,*) MW(i)
    8     CONTINUE

        READ (8,*) D

        DO 10  i = 1,(Nspec-1)
          READ (8,*) Cmol(1,i)
   10     CONTINUE

        DO 20  i = 1,(Nspec-1)
          READ (8,*) Cmol(4,i)
```

```
 20     CONTINUE

      READ (8,*) Rho(1)
      READ (8,*) Rho(4)

      DO 40  i = 1,100
        READ (9,*, END = 50) Rv(i)
 40     CONTINUE

 50   NRv = i - 1


C Iteration for different values of Rv.

      DO 170  i = 1,NRv

C Compute volumetric flow rate in L/hr.

        F(1) = D * 3600.0
        F(4) = D * Rv(i) * 3600.0
        F(2) = F(4)
        F(3) = F(1)

C Compute concentration of H2O for S1, S4.

        mnonH2O = 0.0
        DO 60  j = 1,(Nspec-1)
          mnonH2O = mnonH2O + (Cmol(1,j) * MW(j))
 60       CONTINUE
        Cmol(1,Nspec) = (Rho(1) * 1000.0 - mnonH2O) / MW(Nspec)

        mnonH2O = 0.0
        DO 70  j = 1,(Nspec-1)
          mnonH2O = mnonH2O + (Cmol(4,j) * MW(j))
 70       CONTINUE
        Cmol(4,Nspec) = (Rho(4) * 1000.0 - mnonH2O) / MW(Nspec)

C Compute moles of each species in S1, S4.

        DO 80  j = 1,Nspec
          Moles(1,j) = Cmol(1,j) * F(1)
          Moles(4,j) = Cmol(4,j) * F(4)
 80       CONTINUE

C Compute concentration of species in S3, S2.
```

```
        DO 90  j = 1,Nspec
          Cmol(3,j) = (Moles(1,j) + Moles(4,j)) / (F(2) + F(3))
          Cmol(2,j) = Cmol(3,j)
   90     CONTINUE

C Convert concentration of S1, S2, S3, S4 to mg/L.

        DO 110  j = 1,4
          DO 100  k = 1,Nspec
            Cmg(j,k) = Cmol(j,k) * MW(k) * 1000.0
  100       CONTINUE
  110     CONTINUE

C Store concentrations of S2 for each value of Rv in a permanent array.

        DO 120  j = 1,Nspec
          C2molperm(i,j) = Cmol(2,j)
          C2mgperm(i,j) = Cmg(2,j)
  120     CONTINUE

C Print concentrations of S1, S2, S3, S4 in mol/L.

        WRITE (10,124) Rv(i)
  124     FORMAT (////1x, 'Rv =', f8.3
     +              / 1x, 'Concentrations (mol/L):')
        WRITE (10,125)
  125     FORMAT (/13x, 5x, 'S1', 10x, 'S2', 10x, 'S3', 10x, 'S4')
        DO 140  j = 1,Nspec
          WRITE (10,130) SpecName(j), Cmol(1,j), Cmol(2,j),
     +                   Cmol(3,j), Cmol(4,j)
  130       FORMAT (1x, a8, 4f12.3)
  140     CONTINUE

C Print concentrations of S1, S2, S3, S4 in mg/L.

        WRITE (10, 144)
  144     FORMAT (/1x, 'Concentrations (mg/L):')
        WRITE (10, 145)
  145     FORMAT (/11x, 5x, 'S1', 10x, 'S2', 10x, 'S3', 10x, 'S4')
        DO 160  j = 1,Nspec
          WRITE (10,150) SpecName(j), Cmg(1,j), Cmg(2,j),
     +                   Cmg(3,j), Cmg(4,j)
  150       FORMAT (1x, a8, 4f12.3)
  160     CONTINUE
```

```
 170     CONTINUE

C Print table of Rv vs. concentrations in mol/L.

      WRITE (11,175) SpecName(1), SpecName(2), SpecName(3),
     +               SpecName(4), SpecName(5)
 175    FORMAT (1x, 'Rv vs. Concentration (mol/L):',
     +          // 4x, 'Rv', 5x, 5(4x, a8))
      DO 190  i = 1,NRv
        WRITE (11,180) Rv(i), C2molperm(i,1), C2molperm(i,2),
     +            C2molperm(i,3), C2molperm(i,4), C2molperm(i,5)
 180      FORMAT (f8.3, 5f12.3)
 190    CONTINUE

C Print table of Rv vs. concentration in mg/L.

      WRITE (11, 195) SpecName(1), SpecName(2), SpecName(3),
     +               SpecName(4), SpecName(5)
 195    FORMAT (///1x, 'Rv vs. Concentration (mg/L):',
     +          // 4x, 'Rv', 3x, 5(4x, a8))
      DO 210  i = 1,NRv
        WRITE (11,200) Rv(i), C2mgperm(i,1), C2mgperm(i,2),
     +               C2mgperm(i,3), C2mgperm(i,4), C2mgperm(i,5)
 200      FORMAT (f8.3, 5f12.3)
 210    CONTINUE

      STOP
      END
```