Modeling Electroplating Rinse Systems Using Equation-Solving Software

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Microcomputers are finding application in a vast array of academic and industrial settings, but are under-utilized in the electroplating industries. An often overlooked tool for computer simulation, for example, is equation-solving software. Such programs can predict the performance of a process system from basic mathematical relations without requiring the operator to have extensive knowledge of sophisticated programming and numerical solution techniques. A model of a multi-tank counter-current rinse system is described, then simulated with this software, and the results compared to actual plating facility rinse data, showing the excellent predictive qualities of this approach.

As the availability and sophistication of microcomputers has progressed, ever wider uses have been developing. A previous paper[1] demonstrated that these same microcomputers could be valuable tools in engineering and process analysis of electroplating operations. Specifically, Walton and Poppe addressed the use of programming languages (BASIC and FORTRAN) and spreadsheets for the efficiency analysis of rinse systems. As noted, programming languages require more detailed knowledge of mathematical methods of solving problems, but can be used to predict the behavior of very complex processing systems. On the other hand, spreadsheets are more easily used to solve simple engineering problems involving less programming effort, but are not easily applied to complex situations.

A third type of software that has appeared recently is the general purpose equation-solving package.* These programs combine the ease and intuitive qualities of spreadsheets with the power of programming languages, Users can apply the package in as simple or complex a way as they wish, depending on their own experience. The equation-solving package itself contains highly sophisticated mathematical methods for solving the information entered. This reduces the effort on the users' part tremendously. A user also has the option to study the details of the mathematical procedures and include additional methods of his own choice. Thus, these packages can be valuable tools for analyzing electroplating processes without need for sophisticated programming training, but with maintained flexibility.

*For example, TX!Solver Plus®, Universal Technical Systems, Inc., Rockford, IL.

Theory and Model Description

Models of typical rinse systems used in electroplating operations are presented here. Typically, pure water is fed to the rinse system. Once it has reached a set concentration, it is treated for reuse or disposal. A rinse system can be placed in a pseudo-closed loop with the plating bath and a recovery system. The rinse water, once contaminated, may be treated internally, the metals recovered and reused in the plating bath, and the water reused in the rinse system. This scheme can greatly reduce the amount of waste generated and materials used in a plating operation.

The more tanks utilized in a rinse system, the lees rinse water is required to obtain a specified part cleanliness. In a multi-tank counter current system, the concentration gradients are maintained at a higher level than for a single tank, which has an exponential decrease in effectiveness. By using two tanks, rather than just one, the water requirement can be reduced by nearly 99 percent.[2] Three countercurrent rinse tanks are a typically optimum number when considering the costs of water, waste treatment, capital equipment (tanks and pumps), and available floor space. Using multiple tanks not only saves money in water requirements but reduces the volume of treatable waste produced.

In a multi-tank rinse system (Fig. 1), the rinse and drag-out flow is arranged in a countercurrent configuration. The water is fed to the tank furthest from the initial dip tank. This tank has the lowest concentration of chemicals. The tank concentrations increase as the initial tank is approached. With this countercurrent configuration, a larger drillng force is attained with a correspondingly greater cleaning than exists in a single rinse tank with an equivalent resident; time.

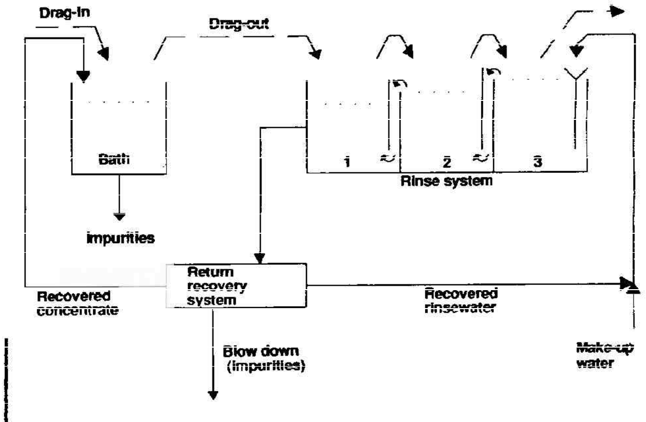


Fig. 1—Diagram of electroplating bath, rinse, and recovery system.

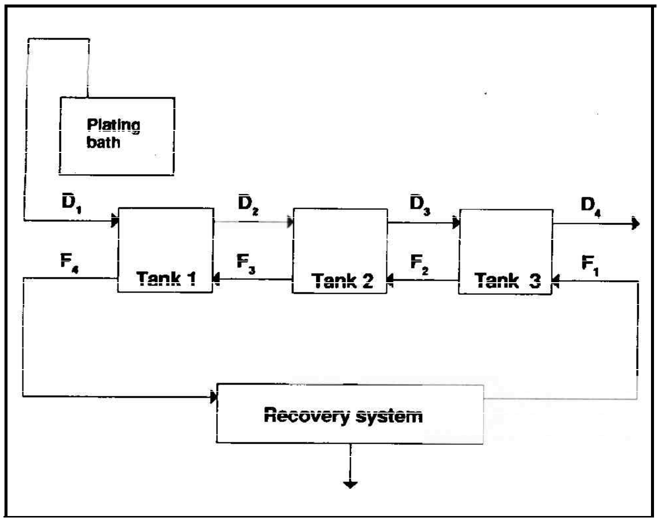


Fig.2—Schematic diagram of rinse and recovery system.

Rinse Ratio

A rinse system is characterized not only by the number of tanks, but the rinse ratio (R). The rinse ratio is defined as the volume of rinse used per volume of drag-out.[3]

$$F = R_D \times D \tag{1}$$

where F is the rinse volume, R_D is the rinse ratio, and D is the drag-out volume. The performance, or outlet concentration of plating chemicals on a part, is specified by this ratio. The larger the rinse ratio, the cleaner the part.

Process Model

Modeling a multi-tank rinse system involves solving the necessary material balances, which are mathematical descriptions of the material entering and leaving a system. These material balances are both coupled and simultaneous.

In Fig. 2, D represents the drag-out flow and F is the rinse flow. D, is the drag-out directly from the plating tank and F, is the pure rinse water.

As an example, consider a Watts nickel plating line. Analyzing a rinse system for this process involves four major components: Nickel (Ni^{2+}), sulfate (SO_2^{2-}), chloride (Cl-), and boric acid (H_3BO_3). These components come from three bath compounds, namely nickel sulfate ($NiSO_4$), nickel chloride ($NiCl_2$), and boric acid (H_3BO_3). Typical concentrations are: $NiSO_4$, 300 g/L; $NiCl_2$, 60 g/L; and H_3BO_3, 37.5 g/L. A useful model would describe the component concentrations at each stage of the rinse system under specified conditions.

Creating an accurate rinse system model requires solving the overall and component material balances. All such material balances must satisfy the conservation of mass law:[4]

$$\text{In} + \text{Production} = \text{Out} + \text{Accumulation} \tag{2}$$

For a rinse system at steady state, the Accumulation term is zero, that is, continuous operation of the system maintains a constant concentration in all tanks. Also, since there are no chemical reactions, the Production term is zero. Eq.(2) then reduces to

$$\text{In} + (0) = \text{Out} + (0) \tag{9}$$

This equation holds for all total and individual chemical component material balances.

The total material balances state that conservation of mass must hold about each rinse tank and the entire system. In terms of the flow variables in Fig. 2,

$$D_1 + F_3 = D_2 + F_4 \tag{4}$$

$$D_2 + F_2 = D_3 + F_3 \tag{5}$$

$$D_3 + F_1 = D_4 + F_2 \tag{6}$$

$$D_1 + F_1 = D_4 + F_4 \tag{7}$$

where D_i is the drag-outflow rate and F_i is the rinse flow rate (L/min) in this example, with an assumed constant density.

A similar set of material balances may be written for each chemical component in the Watts nickel plating rinse. The mass of each chemical component must be conserved about each tank A general equation that describes these balances maybe written as

$$D_i * C_{D_{i,j}} + F_{n+1-i} * C_{F_{n+1-i,j}} = D_{i+1} * C_{D_{i+1,j}} + F_{n+2-i} * C_{F_{n+2-i,j}} \tag{8}$$

where C_{Dij}, is the chemical component concentration in the drag-out (g/L); C_{Fij} is the chemical component concentration in the rinse stream (g/L); n is the number of rinse tanks; and j is the number of the chemical component (j = 1,2,...n). For a three-tank rinse system with the Watts nickel components, n = 3 and j = 4. This translates to four total material balances and 16 component material balances. Not all the balances, however, are independent. It is extremely important to isolate only the independent equations when modeling a system, especially when employing an equation-solving program.

Independent Equations

An independent equation is that which cannot be formed as a linear combination of others in the system. When considering the four total material balances, only three are independent, This also holds for each set of chemical component balances. A case in point, for stream total material balances, the overall balance, Eq. (7) is simply the sum of Eqs. (4), (5), and (6). One of these equations must not be used. The same holds within each set of component material balances. This leaves three stream balances and 12 component balances for a total of 15 independent equations.

Assumptions

At this point there are 15 equations and 40 variables in the rinse system model. Therefore, additional equations must be found in order to create a solvable system.

A reasonable approximation would neglect the small amount of evaporation from the tanks and treat the flow rates as constants. That is,

$$F_1 = F_2 = F_3 = F_4 = F \tag{9}$$

$$D_1 = D_2 = D_3 = D_4 = D \tag{lo}$$

Equations (9) and (1 O) represent only four dependent equations, however, because this *is* a requirement for steady-state operation. With these assumptions, the rinse ratio relation

$$F = R_D \times D \tag{11}$$

may be employed to relate rinse to drag-out flows. The system now consists of 20 equations and 43 unknowns, including F, D, and R_D.

Another assumption which adds supplemental equations is that the rinse tanks are perfectly mixed. Under this condition, the inlet tank streams are mixed well enough to produce a constant concentration of chemical components, which requires outlet rinse concentrations to be equal to drag-out compositions for each tank. In a general form, this corresponds to

$$C_{D_{i+1,j}} = C_{F_{n+2-i,j}} \tag{12}$$

where i = 1,2,...n. This introduces three new equations for each component. The system now consists of 33 equations and 43 unknowns. Ten variables must be specified.

The 10 specified variables are rather obvious. The inlet concentrations of the drag-out are known from the plating bath concentration, which fixes four variables $C_{D1,1}$, $C_{D1,2}$, $C_{D1,3}$, and $C_{D1,4}$. The inlet rinse stream can be assumed pure, which fixes its four component concentrations ($C_{R,1}$, $C_{P1,2}$, $C_{F1,3}$, and $C_{F1,4}$) as zero. Also, the drag-out flow rate, D_1, is known. The final variable that must beset is the rinse ratio, R_D. This variable maybe set at different values to determine optimum operating conditions. The three-tank rinse system model now consists of 43 equations and 43 unknowns. They may now be solved.

An Equation-Solving Program

Atypical equation-solving program is similar conceptually in its arrangement to a spreadsheet. The program is menu-driven and broken down into separate subdivisions or sheets.[5] Each sub-unit represents a different type off unction or procedure.

The two major sub-units are the rule (or equation) sheet and the variable sheet. The rule sheet is where the mathematical model equations are placed. A sample entry would appear as follows:

Rule Sheet

S Rule

D1 * CD1Ni + F3 * CF3Ni = D2 * CD2Ni + F4 * CF4Ni

This equation represents the nickel (Ni^{2+}) component material balance about the first tank in a three-tank rinse. The equation is entered just as it appears, as are all other system equations. Typically, no special arrangement of the equation is necessary, because the program will isolate and solve for any variable internally.

The variable sheet lii all the equation variables. For example:

Variable Sheet

St	input	Name	Output	Unit	Comment
	300	$NiSO_4$		g/L	Nickel sulfate concentration in bath
	60	$NiCl_2$		g/L	Nickel chloride concentration in bath
	37.5	H_3BO_3		g/L	Boric Acid concentration in bath

There are various subdivisions of the variable sheet. The status (St) portion allows the user to specify whether the variable is an input, output, a list, or whether an initial guess will be input by the program. The unit of the variable may also be specified, along with any needed comments. This is where moat of the action takes place. By changing the value of one variable, the program can recalculate an entire system of equations immediately. Anew unknown may also be solved for by simply blanking its input field. No rearrangement of equations in the rule sheet is necessary.

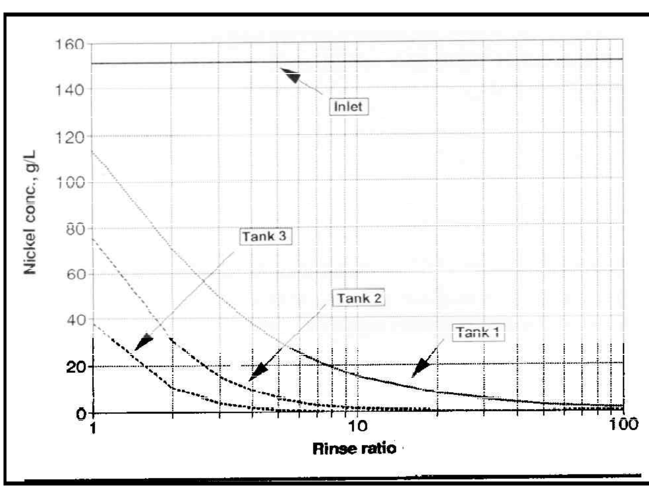
The equation-solving program is also broken down into other peripheral sub-units. They include procedures such as automatic unit conversions, subroutine functions, lists, tables, and plots. The sub-units may be used to specialize a system model to perform any number of tasks, including logical operations, list solving, and plotting.

Results of the Test Model

The systems examined consisted of a two- and three-tank counter-flow rinse system. The three-tank system was more complex and involved all the components discussed in the previous section. The two-tank system, however, was a scaled-down version of the three-tank model. It was created from the same basic format as the three-tank system, but consisted of fewer variables. The results of the two-tank system are compared to data taken from an actual nickel plating operation at the Lincoln Plating Company, Lincoln, NE.[6]

Three-Tank Model

The three-tank model produced component concentrations in each tank in the rinse system as a function of the rinse ratio. This rinse ratio was varied at a fixed inlet component



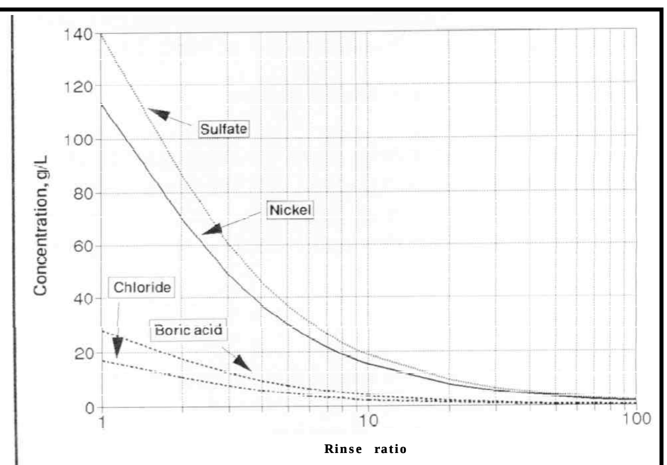
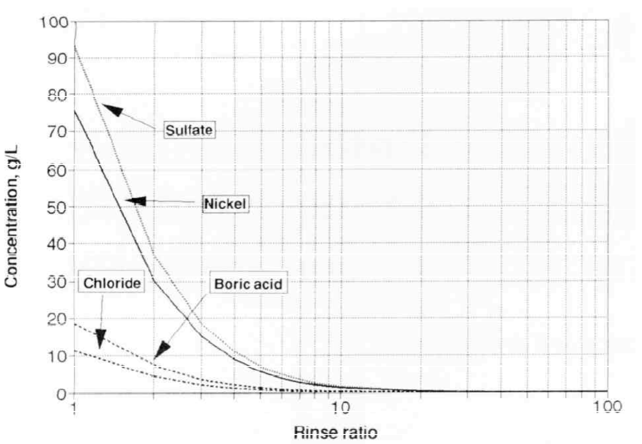
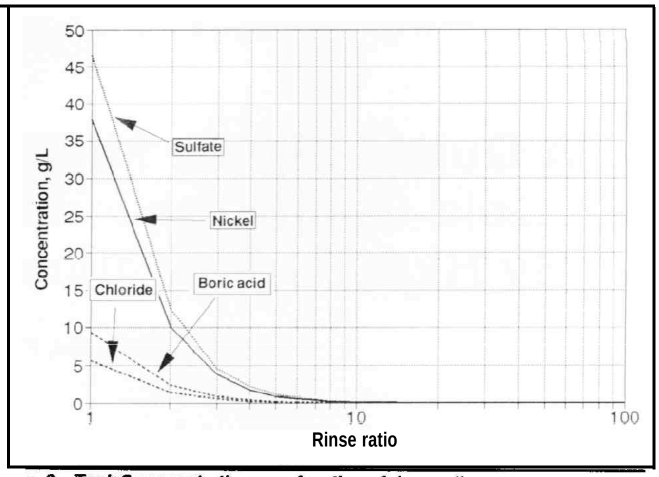


Fig. 4—Tank 1 concentration as a function of rinse ratio.



ig. 5—Tank 2 concentration as a function of rinse ratio



g. 6—Tank 3 concentration as a function of rinse ratio.

concentration. Figure 3 illustrates the variation in nickel (Ni^{2+}) as a function of the rinse ratio in each of the three tanks. It gives a glimpse of the effect of increased rinse ratio and tank number on chemical component purity. For example, a single tank requires a rinse ratio fives times larger than a three-tank system to reduce the nickel concentration from 150 to 10 mg/L. Figures 4, 5, and 6 illustrate component concentrations at various rinse ratios in all three rinse tanks.

' Two-Tank Model

A simplification of the three-tank system is a rinse operation involving two counterflow tanks. The two-tank system model is identical in form, but involving fewer equations and unknowns. The model was created to predict, for simplicity, only the nickel (Ni^{2+}) concentration in the rinse system. The results of this model at two rinse ratios are illustrated in the table.

The model predicts actual operation very well in the first tank The predicted concentration is significantly lower in the second tank than that described by the data. This phenomenon could be a result of deviations from the stated assumptions, such as imperfect mixing, tank evaporation, and changes in drag-out volume from each tank (because of changing viscosity and surface tension). In this particular case, drag-out volume was experimentally measured only for the plating tank and assumed equal from each rinse tank. Possibly, insufficient dwell time over the first rinse tank resulted in excessive drag-out to the second rinse tank. Additional experimental measurements are suggested to increase accuracy of this specific model.

Conclusions

An equation-solving program is a useful tool for modeling production systems in an electroplating operation. Immediate detailed knowledge of numerical methods is not required; one must only isolate the independent material and energy balances and describe mathematically the appropriate assumptions, A simple model, such as the one described, is quite powerful. It allows for prediction of rinse performance in a multi-tank system, which compares quite favorably with actual rinse operation data. The" model" would prove useful not only in process evaluation and performance, but in optimization and process control es well.

Comparison of Two-Tank Model With Plating Data

Rinse Ratio R_D	inlet Concentration ppm	Tank 1 Data ppm	Tank 1 Model ppm	Tank 2 Data ppm	Tank 2 Model ppm
138.3	3375	24.4	24.4	3.6	0.175
83.6	2953	35.3	36.3	2.3	0.417

Recommendations

A system model as described above is the first step to successful modeling of electroplating processes. Actual plating operations involve deviations from the ideal that must be considered. These involve non-steady-state operation, variation in drag-out, imperfect mixing, and tank evaporation-phenomana which can be described mathematically and included in a process model. With an equation-solving program, once the equations are isolated, the program performs the tedious calculations.

The electroplating industry must grasp current programming techniques and implement them in process analysis and development. Combining such systems with appropriate statistical quality control, today's electroplating processes can be run more efficiently and profitably.

Nomenclature

F Constant rinse stream flow rate, L/min
D Constant drag-out stream flow rate, L/min
R_D Rinse Ratio (R_D = F/D)
D_i Individual drag-out stream flow rate, L/min
F_i Individual rinse stream flow rate, L/min
C_{Dij} Component concentration in drag-cut stream, g/L
C_{Fij} Component concentration in rinse stream, g/L

Subscripts

i Counting variable for tank number
j Counting variable for chemical component number
n Number of rinse tanks

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Continued on page 102

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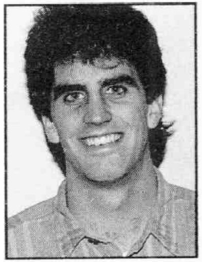

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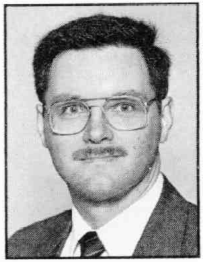

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