

Modeling for Rinse Water Reduction

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Regulatory and cost drivers have brought a new focus on rinse water management. The first step in making rinse water use reductions is to determine the required amount of water for any specific process. The difference between common current practices and how much water is needed account for over half of the potential rinse water reduction obtainable.

Incoming water flow rates can be estimated by developing mathematical models by means of mass balances. Methods of determining model constituent values are discussed. Models for double counter current and single heated rinse tanks are provided for steady state and transient conditions. Methods to determine uncertainty values are provided.

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Introduction

Until recent years there has not been much incentive to reduce the amount of water consumed with tankline operations. The advent of the Environmental regulations on the horizon, such as the Endangered Species Act (ESA) and Pollution Prevention initiatives require tankline operators to bring a new focus on methods to reduce the amount of water used. Additionally, rising cost for water use, treatment and disposal provide substantial economic incentives.

Since, almost all tanklines use more water than is actually needed (reference 14), for rinsing operations, the first step is to determine the quantity of water required. Performing mass balances is a useful tool to develop mathematical models for both single and double counter current (DCC) immersion rinsing systems. Model development is based on the assumptions of uniform chemical concentration or complete mixing in the rinse tank (references 5, 6).

Steady State Mass Balance

Mass flux can be simply viewed as flow rate times concentration:

$$dM/dt = FC \quad (1)$$

where F is flow rate; C is concentration and $M = (\text{concentration})(\text{volume})$.

Figure 1 illustrates the streams that adequately describe the parameters of concern for a simple system, such as for a single, heated rinse tank.

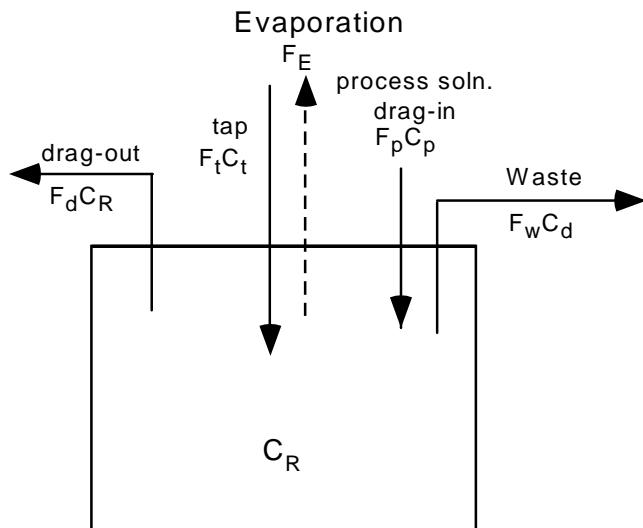


Figure 1 - Single heated rinse tank

The setup equation that follows is:

$$d(C_R V)/dt = C_R dV/dt + V dC_R/dt = F_p C_p + F_t C_t - F_d C_R - F_w C_R \quad (2),$$

where,

C_R = concentration of the rinse tank

V = volume of the rinse tank

t = time

F_p = flow rate of the process solution into the rinse tank (drag-in)

F_t = tap water flow rate into the rinse tank

F_d = drag-out of rinse water from the rinse tank

F_w = flow rate of rinse water to waste hold sump

C_t = concentration of the tap water

C_p = concentration of the process solution.

At this point, since we are only interested in the steady state (SS) solution, we can also write:

$$dV/dt = F_p + F_t - F_E - F_d - F_w = 0 \quad (3).$$

Substituting, it follows then that the General solution for this system is:

$$F_t = (F_p(C_R - C_p) - F_E C_R) / (C_t - C_R) \quad (4).$$

Further simplification of equation (4) can be achieved if $C_p \gg C_R \gg C_t$, resulting in

$$F_t = F_p(C_p/C_R) + F_E \quad (5).$$

These last two simple expressions then determine the amount of fresh water needed to keep a single heated rinse tank at a constant level of "dirtiness".

However, most tankline rinsing systems employ DCC tanks. This type of rinsing system is so named since the parts flow in the opposite direction that the water flows and accounts for huge improvements in rinse water savings over a single rinse tank (references 3, 6). Figure 2 display streams that will enter into a mathematical model.

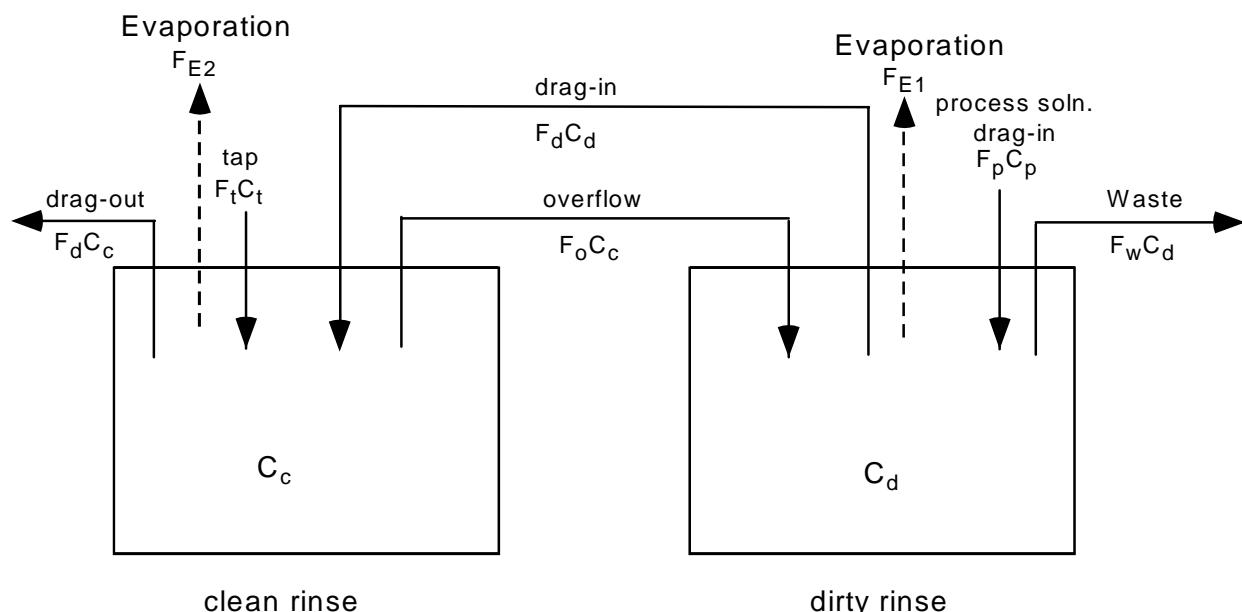


Figure 2 - Double Counter Current Rinse Tank

Set-up equations involve performing balances around both the dirty rinse and the clean rinse.

$$\begin{aligned} d(C_d V)/dt &= C_d dV/dt + V dC_d/dt \quad (6), \text{ for the dirty rinse and} \\ d(C_c V)/dt &= C_c dV/dt + V dC_c/dt \quad (7), \text{ for the clean rinse.} \end{aligned}$$

With additional terms, the algebraic derivation is more complicated and the general solution is the positive root of a quadratic,

$$F_t = \{-b \pm \sqrt{b^2 - 4ac}\}/2a \quad (8)$$

Where,

$$a = (C_c - C_t)$$

$$b = C_c(F_p - F_{E1} - 2F_{E2}) - C_t(F_p - F_{E1} - F_{E2})$$

$$c = F_d F_p (C_c - C_p) - C_c [F_{E2}(F_p - F_{E1} - F_{E2}) + F_d F_{E1}].$$

The subscripts are the same as for those defined for equation (2) and the 1, 2 subscripts of the evaporation flow rate represent the dirty rinse and clean rinse respectively. From equation (7), a new term, C_d , is the concentration of the dirty rinse, since nomenclature changes have the C_R of equation (2) now being C_c .

The overall general solution can be shortened if evaporation rates (F_{E1} , F_{E2}) are considered negligible. Additional simplification can be made if: 1) the process solution concentration (C_p) is considered much greater than the clean tank concentration (C_c), and 2) the b term is ignored if it is concluded to be much less than the c term from the positive root of equation (8).

$$F_t = (F_d F_p C_p / (C_c - C_t))^{0.5}, \quad (9)$$

Further simplification can be made if the solution removal rates (F_p) out of the process tanks are the same as that out of the rinse tanks (F_d). Equation 9 is the same as reported in earlier documentation (reference 4). Testing revealed that this is a fairly good assumption for rinses following acid solutions but not for rinses following alkaline process solutions such as emulsion degrease and caustic etch due to differing rheologies, affecting surface tension and thus how the parts "hold onto" the rinse water or process solution.

If DCC rinse tanks are heated it is clear that equation (8) must be used over that of equation (9). However, it is worth noting that evaporation rates can be significant when the required tap water flow rate (F_t) is small. This was found to be the case of DCC rinses after Boric Sulfuric Acid Anodizing (BSAA) and for tanklines that have limited part flow.

Transient Models

Non-steady state conditions occur when the rinse concentration is allowed to change with time. For the following model development, tank volumes are kept constant. Situations where this type of modeling is necessary can be many. As an example, downstream process interruptions can restrict the amount of wastewater sent to the hold sump. The obvious question becomes: How long can we continue to operate? The cheap answer is: Until the rinse water becomes too dirty – "we'll monitor that for you". If that answer is inadequate, an engineered estimate is needed. Determining the general solution for such a problem now involves first order ordinary differential equations (ODE). The use of LaPlace transforms helps convert these types of problems back into algebraic form.

Back to the single heated rinse tank example (Figure 1), from equation (2) the differential equation is:

$$dC_R/dt = -C_R(F_p + F_t - F_E)/V + (F_p C_p + F_t C_t)/V \quad (10),$$

which can be more simply expressed as:

$$C_R' = aC_R + b \quad (11).$$

Converting to LaPlace and solving, results in a general solution than can be manipulated to an expression that solves directly for time.

$$t = -(V/(F_p + F_t - F_E)) \ln(1 - ((F_p + F_t - F_E)C_R / (F_p C_p + F_t C_t))) \quad (12).$$

This model is applicable at less than steady state F_t values and more than the low levels needed to makeup for evaporation, so that the rinse tank volume is not changing. Given values other than that for fresh water flow rate, time can be plotted against F_t .

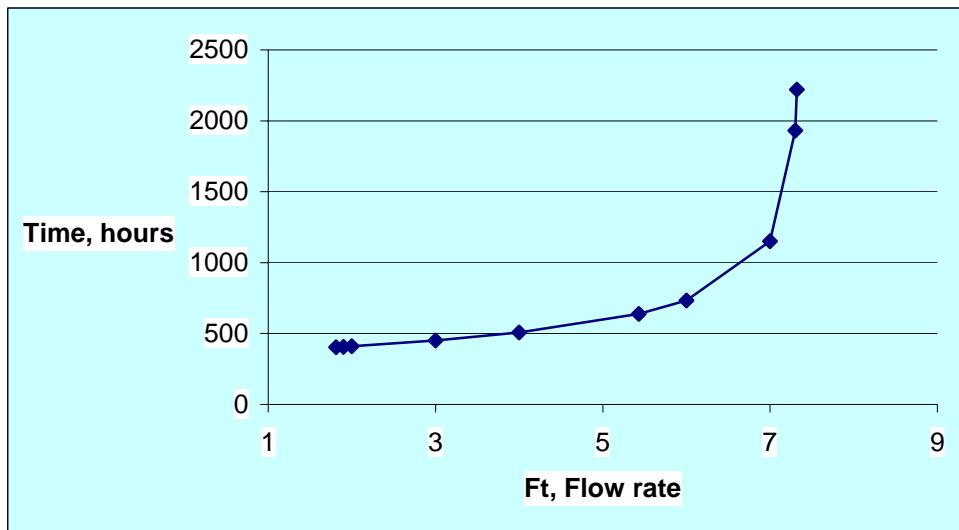


Figure 3 - Single heated rinse tank flow versus time

As shown in Figure 3, the model depicted by equation (12) behaves predictably, with time going to infinity as the value for F_t approaches the flow rate that would maintain steady state.

Just as the steady state solutions were much more complex when going from a single rinse to a DCC rinse, so it is true with the difficulty in deriving the transient solution. The ODE's of equation (6) and (7) must be solved simultaneously through the use of LaPlace transforms and Linear Algebra. Partial fractions techniques are used to determine the general solution eigenvalue coefficients, which also incorporate the initial conditions. The final solution is too complicated to write out in predefined concentration and flow rate terms. Solving for time then is best performed iteratively.

$$C_c, C_d = A_{1,2}(\lambda_1 e^{\lambda_1 t} - \lambda_2 e^{\lambda_2 t}) / (\lambda_1 - \lambda_2) + B_{1,2}(e^{\lambda_1 t} - e^{\lambda_2 t}) / (\lambda_1 - \lambda_2) + C_{1,2}(((e^{\lambda_1 t} - 1) / \lambda_1) - ((e^{\lambda_2 t} - 1) / \lambda_2)) / (\lambda_1 - \lambda_2) \quad (13).$$

In practice, use of an Excel spreadsheet proved to be very useful; thereby you can simply enter units of time (loads), and quickly close in on the final rinse concentration of concern. In one case, the dirty rinse was of more importance, since the pH of the dirty rinse is required to be above 1.5. The pH and concentration relation was predetermined and was expressed as a regression equation within the Excel spreadsheet.

Model Components

These models can only be as good as the components used to describe them (reference 5).

- Process solution carry-over

- Process solution concentrations
- Rinse water drag-out
- Water loss due to evaporation

Determining drag-in rate from the process solution is perhaps the one component fraught with the most error (reference 14). Not only does it change with each load but also the measurement method options are not altogether straightforward. Three options that were considered are: 1) gravimetric, 2) conductivity, and 3) tracer. Weighing the parts and load rack dry and then wet, after a set drip time is the most direct method. Unfortunately, unless the parts are very large, scales need to be custom made to provide the accuracy required. Estimating total dissolved solids (TDS) via conductivity is a decent means of determining concentration changes for salt solutions in a laboratory environ but has proved unreliable in production settings, especially for acid rinses due to buffering effects of incoming water supply (reference 11). Therefore, the method chosen was tracing elemental markers measured by ICP (Inductively Coupled Plasma). Specifically, the process solution drag-in (C_p) is the tank volume times the concentration difference quotient, involving measures before and after a load has been processed.

$$F_p = V(C_B - C_A)/(C_A - C_p), \quad (14)$$

Where,

F_p = volume of process solution drag-out

C_B = concentration of rinse tank before drag-in

C_A = concentration of rinse tank after drag-in

C_p = concentration of process tank

V = volume of rinse tank

ICP measures are also used to determine the concentration of the process solutions. Drag-out values can be determined by using equation (14) from the dirty rinse to the clean rinse. There should be very little difference between drag-in (F_p) and drag-out (F_d) for acid processes. However, due to surface energy properties of many alkaline solutions F_p and F_d can be expected to significantly different.

As noted earlier, evaporation rate is important to consider for heated rinse tanks but also becomes an important factor for rinses that require minimal amounts of incoming water. Evaporation rates can easily be measured directly for each condition but a theoretical expression would be most useful to save time. A literature search (reference 1) revealed that instantaneous evaporation rates can be estimated by simply measuring: 1) relative humidity, 2) air temperature, 3) air speed, 4) water temperature and 5) tank surface area;

$$E = 1.857 T_o^{-0.4} v^{0.5} ((P_s(T_w)/T_w) - (H P_s(T_o)/T_o)), \quad (15)$$

Where,

E = evaporation rate, mg/cm²-min

T_o = ambient air temperature, K

T_w = water surface temperature, K

$P_s(T_w)$ = saturated vapor pressure at T_w , N/M²

$P_s(T_o)$ = saturated vapor pressure at T_o , N/M²

v = air speed at water surface , m/s

H = relative humidity

The biggest source of error for this calculation seems to be the anemometer (air speed) measures at low levels. When tested, in a production setting, equation (15) provided very good estimates of direct measures.

If sparge air is used for tank mixing there will be additional evaporation to account for. However, equation (15) cannot be used to estimate the additional evaporation, due to air sparging. Equation (15) is a model for evaporation of water from a vessel, not for bubbles rising through a column of water. It is worthwhile to estimate evaporation rate contributions due to air sparging. A simple approach is to measure relative humidity differences, at the tank surface, with the sparge air on and the sparge air off. An estimate for mass airflow rate is estimated to be 0.22–0.45 m³/minute of air per m² per tank surface area (reference 12). Use of psychometric charts (reference 13) enables one to determine the amount of water picked up by the rising bubbles via the measured relative humidity and ambient temperature data. Having performed this exercise, the sparge air, when full on, is estimated to provide an additional ~75% evaporation as compared to the evaporation rate calculated values from equation (15).

Uncertainty Analysis

After arriving at a steady state model, the next question becomes how accurate is it? An uncertainty analysis can be performed on the simplified form of the steady state model (equation 9), which incorporates an uncertainty for the process solution drag-out (equation 14). To perform this type of analysis you must execute a partial derivative of the model with respect to each component, in conjunction with estimating the +/- values (ω) of each component.

$$\omega_{F_p} = (((dF_p/dV)\omega_v)^2 + ((dF_p/dC_B)\omega_{CB})^2 + ((dF_p/dC_A)\omega_{CA})^2 + ((dF_p/dC_p)\omega_{C_p})^2)^{0.5}, \quad (16)$$

$$\omega_{F_t} = (((dF_t/dF_d)\omega_{Fd})^2 + ((dF_t/dF_p)\omega_{F_p})^2 + ((dF_t/dC_p)\omega_{C_p})^2 + ((dF_t/dC_c)\omega_{C_c})^2 + ((dF_t/dC_t)\omega_{C_t})^2)^{0.5}, \quad (17)$$

Equations 16 & 17 then provide the process solution drag-outs (F_p) and fresh water (F_t) uncertainty values that should be added to these calculated flow rates.

Uncertainties (ω values) were estimated as +/- 5% for C_t , C_p , and C_c . A 90% confidence value was used for F_d . The tank volume uncertainties were estimated as +/- 2%. Again, using an Excel spreadsheet to calculate partial derivatives and uncertainty values is most useful. The purpose of this exercise is to develop an estimated accuracy of the calculated incoming water required and then use the higher extreme.

Implementation

Once the required incoming water flow rates have been determined, ($F_t + \omega_{F_t}$) there are issues to consider before implementation. Setting steady state flow rates so that the clean rinse is at or near the specification limits may mean that the dirty rinse will exceed criteria (e.g. pH) set for sending wastewater to waste treatment. Thus, studying pH vs. process solution dilution is needed to establish a new rate-controlling factor. Performing a regression analysis can be used to develop expressions that predict the pH of a rinse that follows a specific process solution. Selecting the data in the ranges of interest the regression sum of squares values (R^2) are all over 0.9, which indicate good predictive value by the regression models (1.0 is perfect).

The first application of these techniques was to that of a ~8200 liter (2166 gallon) anodize line. In order to be exceedingly cautious, the new incoming water flow rates were changed in phases. The initial phase was for the upstream alkaline rinses followed sequentially by the acid rinses. This manner of implementation and increased Quality Assurance (QA) measures of rinse tank TDS values allowed a subjective analysis of whether there were any chemistry effects on the downstream process tanks and whether there were any resultant part defects. Since implementing these reductions in the amount of incoming water into rinse tanks there have been no deleterious consequences.

For the 2000 gallon anodize line, an approximate water savings of 330,000 gallons per year is being realized. This reduction represents a 48% improvement. A smaller conversion coating, 3785 liter (1000 gallon) line is estimated to realize a 186,000 gallon/year reduction (~71%). The current annual cost

savings are only modest. However, with anticipated severe price increases for incoming water and waste disposal the savings will be more substantial. Best of all, the cost of implementation involves only the engineers time, perhaps some flow meters and the labor to reset automated timers.

After this initial step of determining only the amount of water required there are numerous other well known techniques for obtaining further rinse water reductions (references 7, 10). These methods mainly focus on techniques to either reduce the volume or the concentration of the process solution drag-in:

- Spray rings
- Extended hang time
- Basket/Rack redesign
- High frequency vibration
- Withdraw rate
- Double dipping
- Common first rinse

Spray rings over the process tanks will reduce the drag-in concentration and has been known to be successful in many applications (reference 8). Specifically, this has proved successful over deoxidizer tanks but is problematic over conversion coating tanks due to a “streaking” phenomenon (uneven coating).

Extended hang time will reduce the amount of drag-in volume and is effective for non-heated process solution. However, it can be detrimental for many treated surfaces (reference 8). For example, extended hang time is after conversion coating should not be done since it would impact the effective immersion time and thus coating weight.

A recent University study (reference 2) concluded that basket redesign can contribute up to an ~40% reduction in drag-out. However, the cost for redesign and construction of new baskets can easily exceed acceptable ROI (return on investment) figures.

A high frequency vibrator will also reduce the volume of drag-out. However, there would need to be sufficient “wiring” of small parts to a rack so that they would not be dislodged and lost to the bottom of the tank.

Slower withdraw rates may reduce the drag-out volume (reference 14) but would require a variable speed crane.

Double dipping (reference 3) the part load will likely improve the process solution being thoroughly mixed into the dirty rinses and would be most effective if the residence time in the first rinse is necessarily short, such is the case after a caustic etch on aluminum.

Finally, depending on tankline configuration a “common rinse” can be employed where DCC rinses are not available. This practice is known to be successful, especially for acid solutions.

Summary

The unchecked use of rinse water can no longer be ignored in the wake of forthcoming environmental regulations and increasing prices for use and disposal of water. With little or no capital expense an ~50% rinse water reduction can be achieved by simply establishing rinse water cleanliness criteria (references 9, 10) and determining the quantity of incoming water required to maintain those levels.

The first step is to determine what are the needs of any particular rinsing. An excellent tool for calculating the amount of water required is by mass balance.

Although steady state models provide answers for normal operation, transient models provide a means to predict how long processing can continue under defined process interruptions.

Careful model component estimates are crucial in calculating end results. Process solution drag-out can be adequately determined via the elemental tracer technique. Evaporation rates can be quickly and sufficiently calculated using a theoretical expression that includes relative humidity, air & water temperature, and air speed measures.

Further rinse water use reductions can be achieved by employing well known techniques that focus on limiting the amount or concentration of process solution drag-out.

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