Mathematical Optimization of plating processes

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Abstract

The operations of a plating process including the degreaser and acid system together with the plating tank is subject to various constraints. These include chemical makeup, temperatures and operational factors. The efficient use of plating and related chemicals is crucial to cost effectiveness and environmental impact. It has traditionally proven difficult to optimize the various processes as the levels of variability have been high. Recent studies have successfully modeled the individual process but have not been extended into optimization. This paper focuses on the application of the acid, degreaser and plating models , developed to date, to predict optimal operations. The models indicate optimum concentrations temperatures etc based on the factorial models developed in previous experimentation.

1. Metal finishing

The electroplating industry, like most other industries generates waste, which is potentially harmful to humans. The electroplating industry is regarded as one of the most polluting industries worldwide.[1-3] Electroplating processes continuously generates huge amounts of hazardous or toxic waste which range from volatile organics, acid/alkali fumes, wastewater containing metal/cyanide, sludge with high metal contents, oil/grease, paint residue etc. Most important to the profitability of the company is the fact that waste generated implies profit losses. This is mainly due to poor plant operations, which result in the wastage of raw materials. This waste material has to then be treated at the wastewater treatment plant, resulting in further costs. It can be stated that the most effective means of dealing with waste is by curbing the production of waste.

The application of cleaner production in the metal finishing sector has resulted in significant reductions in waste generation. This has been achieved by firstly identifying the source of waste generation. Cleaner production systems are then applied to reduce/eliminate the wastage at source. Typical systems include closed loop operations, chemical substitution and improved housekeeping. Success in the application of cleaner production in the metal finishing sector has been well documented. [4-11]

Cleaner production systems to date have focused on waste reduction from plating facilities. Further improvements to processes would include process optimization that would ensure optimum use of raw materials. This would include improved process efficiencies.

The cleaner production models developed to date by Telukdarie[11] has focused on statistical models. These models have been used to facilitate cleaner production operations at metal finishers. This paper extends the use of these models to be used in optimization of plating processes. This papers now details a basic introduction to these model development together with the application of these to process optimization.

For the purpose of this study the plating line would be divided into three sections. The zinc plating section, degreaser section and the acid cleaning section. Models were established for each section independently.

2. Zinc plating

The zinc plating section would be considered first. The model would be based on the operations of the zinc plating tank.

For the purpose of this study, the zinc model has been developed using the alkali zinc plating process. The electrolyte consists of zinc metal in a caustic solution. The solution contains many supplier specific components such as brighteners etc. These components enhance the cosmetics of the final product.

The zinc plating tank reactions[12-15] can be separated into anode and cathode reactions. Reactions are complex but the main reactions can be represented as:

Anode reaction:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \tag{1}$$

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \tag{2}$$

Cathode reactions:

$$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^- \tag{3}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{4}$$

These equations can be used to determine the mass balance for the plating tank.

2.1. The mass balance in the plating tank

The change in concentration of zinc metal in the plating tank is dependent on the rate of dissolution at the anode and the rate of deposition at the cathode. The rate of deposition is dependent on various influences on the system. Chemical composition and temperature are the two main variables influencing anode dissolution and cathode deposition. The impact on each component has to be investigated. The impact of interaction of the different components is also essential.

The rate of change of dissolved zinc metal in solution can be related to the cathode and anode efficiency i.e. R_c and R_a. The net change in dissolved zinc in the plating tank can be represented by:

$$V_P \frac{dC_{Zn_P}}{dQ} = \frac{R_a^{Zn} - R_c^{Zn}}{2F} \tag{5}$$

where:

V_p=Volume of plating tank (L)

R_a=Cathode efficiency

R_a=Anode efficiency

F=Current(Faradays)

C_{Zn}=Zinc concentration in plating tank(g/l)

From the anode and cathode reactions (Eq 3-4) above it can be seen that the caustic is also consumed during the reaction. The rate of change of caustic is directly related to the anode and cathode efficiency since it can be considered to be the main side reaction.

$$V_P \frac{dC_{OH_P}}{dQ} = \frac{-2R_a^{Zn} - (100 - R_a^{Zn}) + (100 - R_c^{Zn}) + 2R_c^{Zn}}{F} \tag{6}$$

C_{OH}=Caustic concentration in plating tank(g/l)

From the above the anode and cathode efficiency needs to be determined.

2.2.The determination of the cathode and anode efficiencies

Wery *et al*[5] developed a model of cathode efficiency based on the impact of the five main chemicals in an alkali zinc solution. The chemicals that were considered by Were[16] were considered restrictive. For the Alkali zinc plating process for this study, the plating temperature[16] has been identified to have a very substantial effect on the plating efficiency; hence the investigating variables were modified.

Table 1: Table of variable limits for degreaser experiment, Actual

	Min	Max	Optimum
	Mol/l		
Zinc	0.15	0.27	0.21
Sodium carbonate	0	0.65	0.32
NaOH	2.5	4	3.25
Brightener	10 ml/l	20 ml/l	15 ml/l
Temp	22	28	34

The above variables were investigated using the fractional factorial method. The experimental method proposes that the maximum and minimum limits of the variables being investigated be investigated in a specified sequence. The experimental results were manipulated to develop the model equation, Equation 7.

$$R_c = 81.15 + 6.36250.C_{Zn}^E + 10.2125C_{Zn}^E * C_{Na_2CO_3}^E + 8.6 * C_{Zn}^E * C_{OH}^E - 5.9 * T^E * C_{Bright}^E - 5.1125 * C_{Zn}^E - 4.475 * C_{Na_2CO_3}^E * T^E \tag{7}$$

Where:

C_{Zn}^E: Zinc concentration (mol/l)

C_{OH}^E : Caustic concentration(mol/l)

T^E: Temperature of Zinc tank(Degrees Celsius)

C_{Bright}^E : Brightener concentration(ml/l)

$C_{Na_2CO_3}^E$:Sodium carbonate concentration (mol/l)

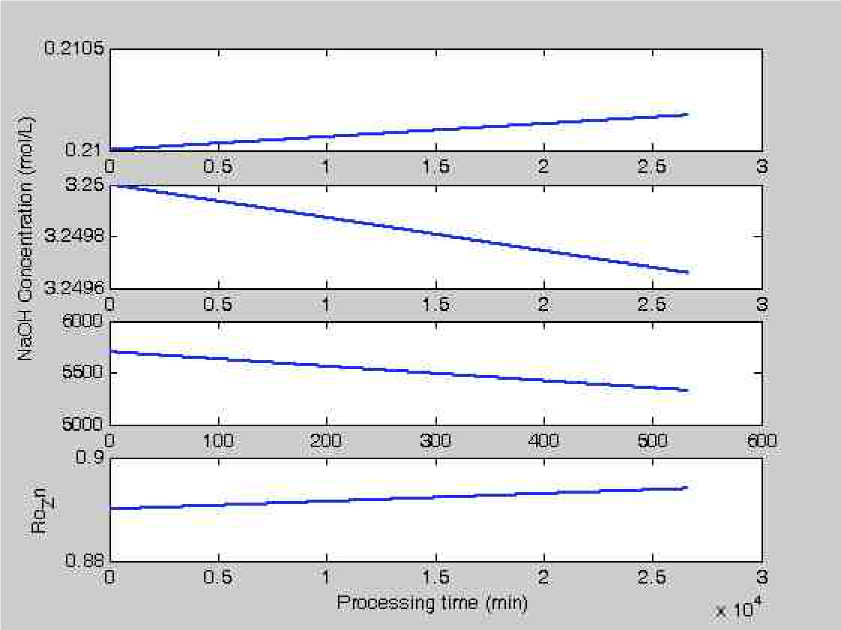
The model above together with the mass balance equations is used to establish a Mat Lab model for alkali zinc plating. This model can then be used to illustrate the different operating conditions for the zinc plating system.

2.3. Model application

For the purpose of illustrating the benefits of process optimization the following company's operating conditions would be used in the Mat Lab model.

The company under consideration plates in a 5700 liter zinc tank. The company operates on a 24 hour day seven days a week. The plating area is approximately $2m^2$/ barrel or 535 barrel /week. The current drag-out at the company was determined to be $0.35 l/m^2$. Figure 1 illustrates a typical result of the current plant.

Figure 1: Current operation of plating line

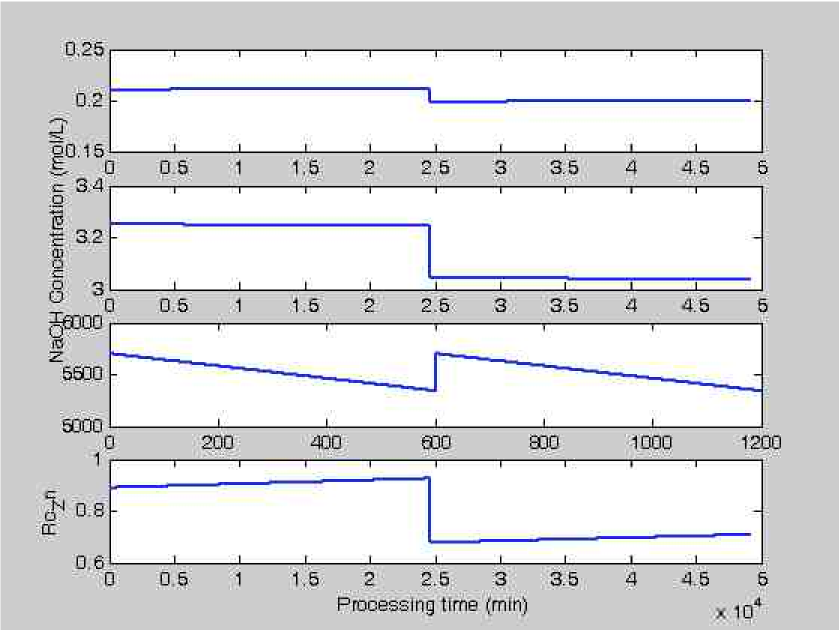


From the figure above it is noted that the concentration of the reactants taking part in the plating reaction can be monitored. The plating efficiency increases with an increase in zinc concentration. Key is the fact that after one week the amount of liquid dragged out is

374 liters or 7% of the plating solution. Conducting the same simulation with a dragout of 0.15 results in 161 l being lost. More importantly is the top up operation after the week is over. It is noted that if top up occurs inaccurately the plating solution may evolve into an inefficient system.

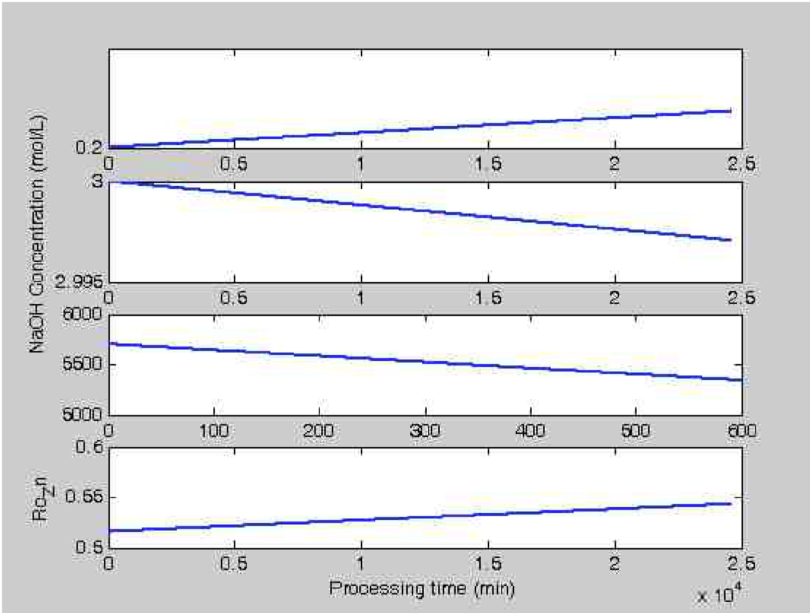
The operation of a zinc tank without chemical corrections can result in significant efficiency reductions. From Figure 2 below it can be seen that an intermediate top up without chemical corrections results in an efficiency reduction of almost 20 %. It is further noted that the caustic concentration has decreased from 3.24 to 3.04 moles/l.

Figure 2: Tank operation with water to up only



To investigate the impact of running a zinc bath with less than recommended operating conditions the zinc plating system was run with a lower temperature and high contamination, with low caustic and zinc concentrations. The anode efficiency is in the region of 55%. It can be further noted that the zinc concentration evolution is very slow, from 0.2 to 0.2017 moles/l, indicating low dissolution of the anode.

Figure 3: Process with less than optimum operation



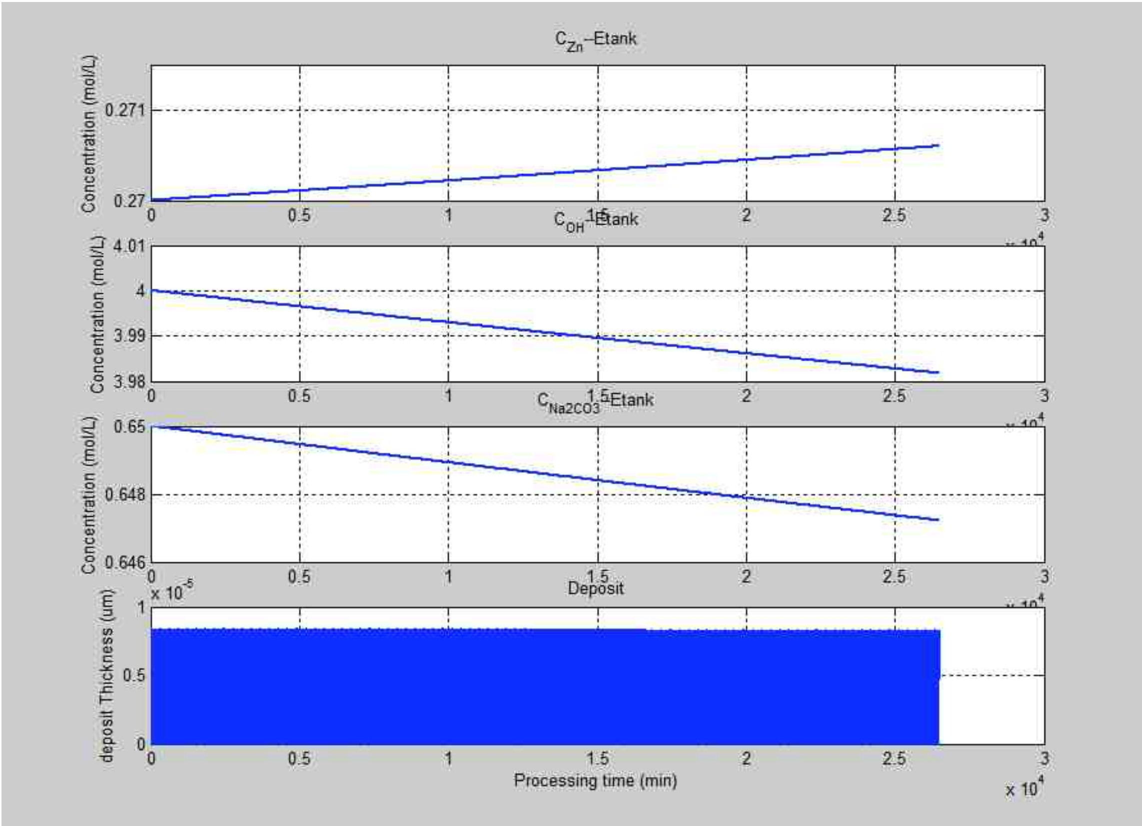
The above investigations are on a system is considered to be less than optimum. Since there is an equation relating the variables an the key output it is possible to find the optimum operating condition for the zinc plating system. For this optimization the model was inputted into excel together with the operating range for the different variables of the zinc plating system. Solver was used to find the optimum operating condition.

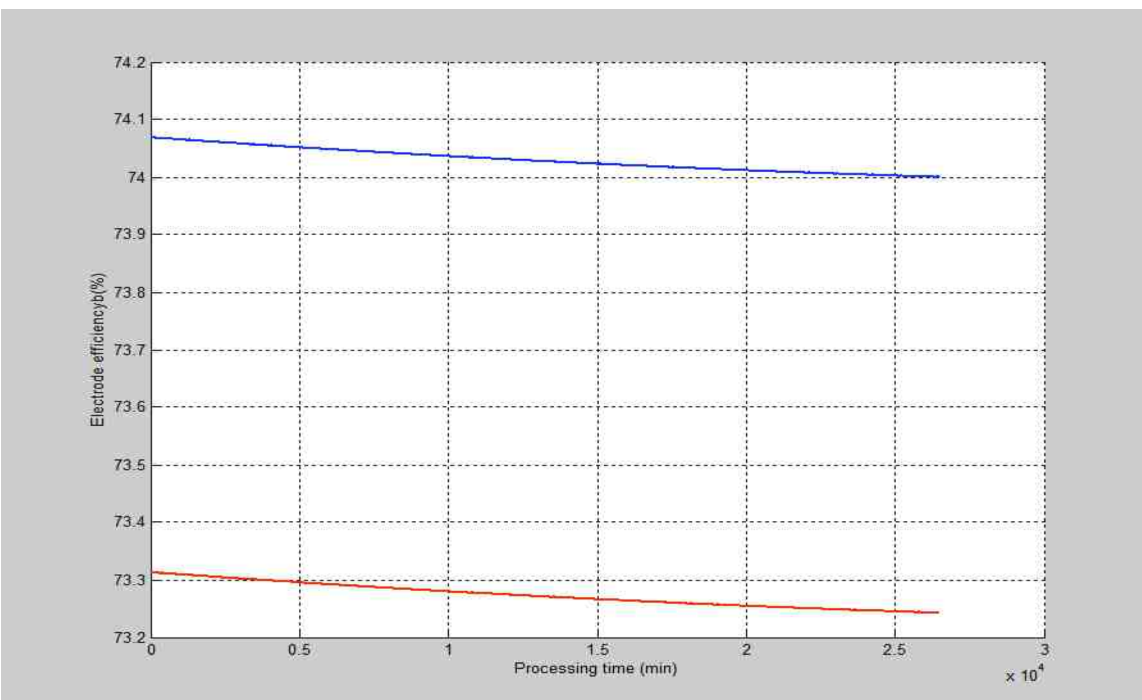
Table 2: Optimization of zinc system

Zinc	Carbonate	Hydroxide	Temp	Brightener	efficiency
1	1	1	-1	1	73.3125
1	1	1	1	1	42.3375
1	-1	1	1	1	30.8625
-1	-1	-1	1	-1	60.5875
-1	-1	-1	-1	-1	29.6125

The optimum operation of a plating system implies zero or near zero wastage. Thus the zinc system was modeled with a three stage counter current rinse system which ensures recovery of drag out. Using optimum operation and a three stage drag-out the plating tank would operate as follows.

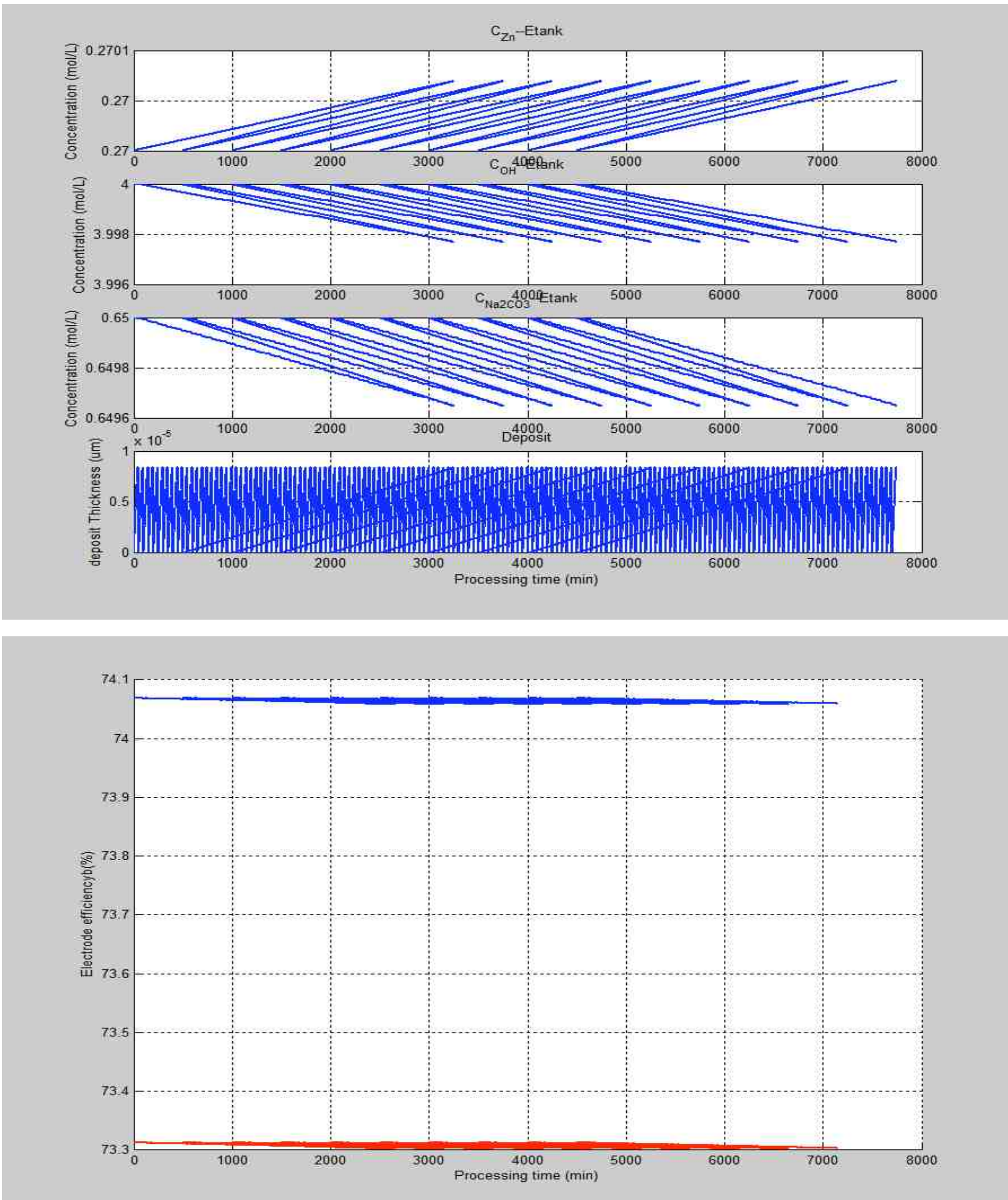
Figure 4: Zinc tank operation with closed circuit operation





The plating system can only be considered optimal if it continuously operates in a small band around optimum operation. This implies continuous dosing and management of the zinc tank. This operation is illustrated in Figure 5.

Figure 5: Closed circuit operation with continuous top up



From figure's 4 and 5 it is clear that there is a significant loss in efficiency when the plating system is not maintained at optimum.

3. The Acid model

The model development was carried out using a similar experimental design as the zinc model. The variables investigated together with the constraints are detailed below.

Table 3: Trial data values for factorial experiments

Variable	**Minimum Value (-1)**	***Maximum Value(+1)***
Acid	60 g/l	120 g/l
Temperature	25 ^oC	45 ^oC
Iron contaminant	0	1 g/l
Inhibitor (Actipret BTS 40)	0	5 g/l
Time	180 s	600 s

The experimental results based on the fractional design was manipulated to establish an equation representing the effect of all the above variables on mass of rust removed. The factorial methodology is able to convert the impact of different variable changes into a representative equation. The statistical significance of the effects and interactions were evaluated. At 95% confidence, the interaction between, acid+contaminant, contaminant+time, temperature+inhibitor, time+temperature, acid+inhibitor, inhibitor+contaminant, contaminant+temperature, inhibitor+time were found to be statistically insignificant. Removing this from the overall factorial equation representing the metal depletion results in the following equation:

$$M_D = 136.27 + 9.02 * C^A_{H2SO4} + 17.44 * C^A_{Fe} - 10.4 * T^A - 18.97 * IN^A - 23.66 * t^A$$
$$+ (17.14 * C^A_{H2SO4} * C^A_{Fe}) - (16.85 * C^A_{H2SO4} * \mathrm{IN}^A) - (25.384 * T^A * \mathrm{IN}^A) \quad (8)$$

Where:

C^A_{H2SO4} =Concentration of acid(g/l)

C^A_{Fe} =Concentration of Iron(g/l)

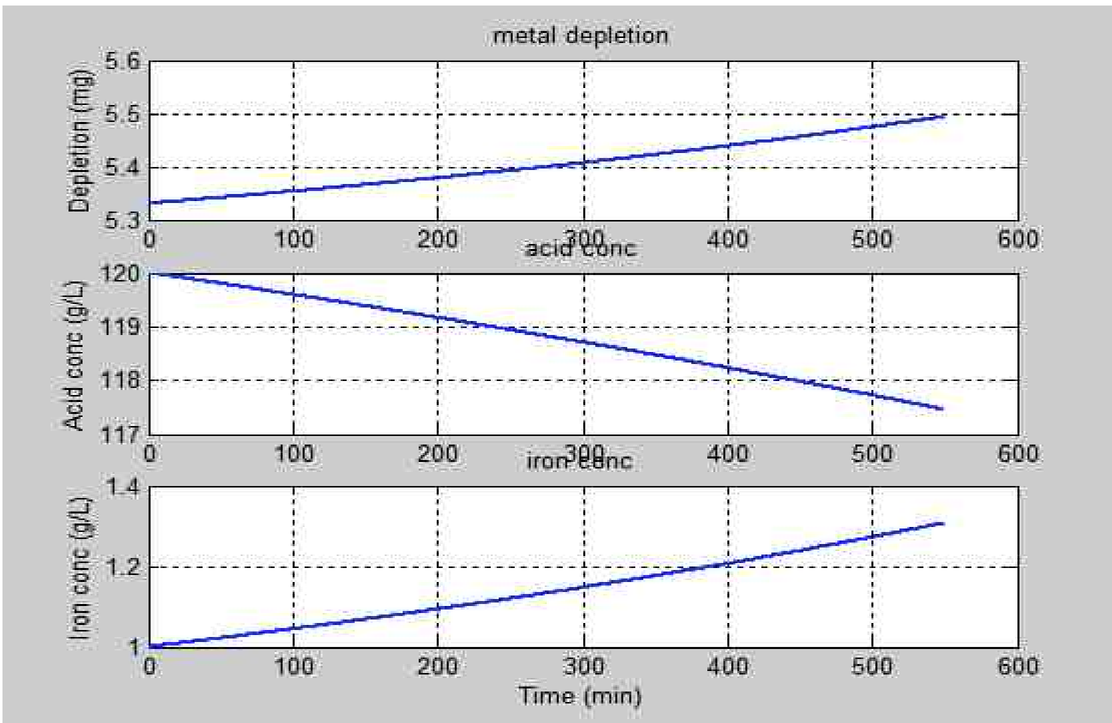
T^A =Temperature of bath(C^0)

IN^A =Inhibitor concentration (g/l)

t^A =Time(s)

This equation is to be model the operation of the acid tank at a plating facility. A typical acid tank operated as per the conditions for the zinc tank is illustrated in Figure 7.

Figure 7: Operation of acid tank-Non optimum



The optimum operation of the acid tank is determined from the mass depletion model. Similar to the zinc the degreaser concentration can then be optimimised using Newton's method. This is carried out in Excel and the optimum metal removal is determined. The results are illustrated in Table 4. The results indicated the optimum acid efficiency occurred at high temperatures, low contamination levels and low inhibitor levels.

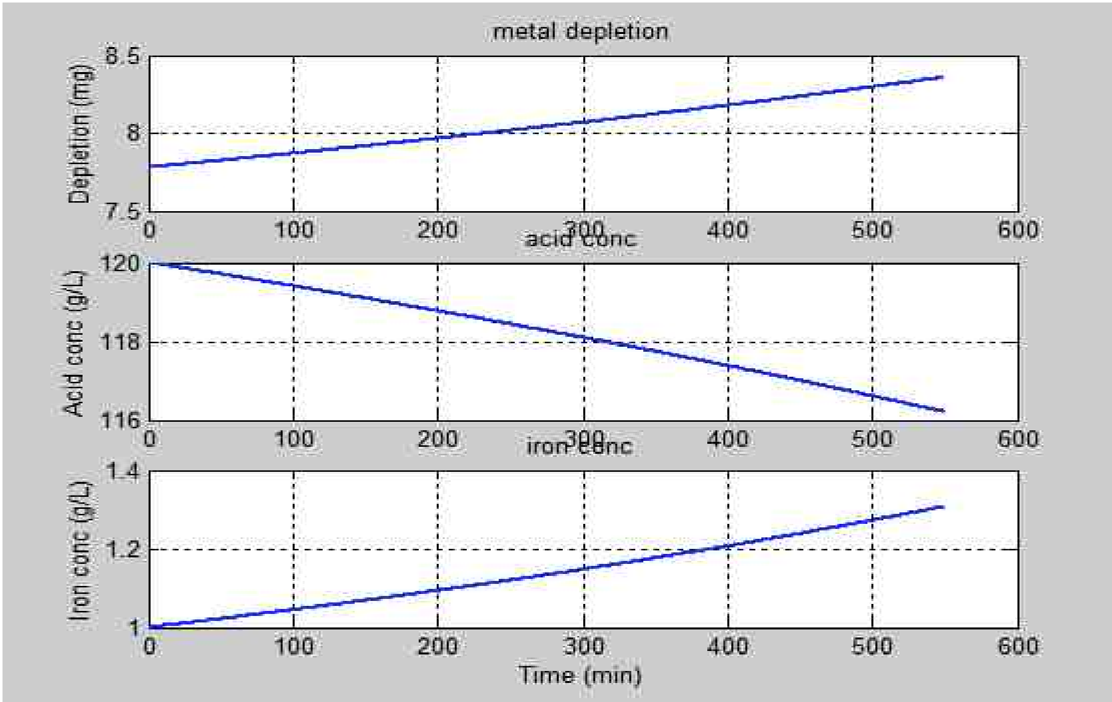
Table 4: Optimization of acid model equation

Acid	Iron	Temperature	Inhibitor	Time	Mass depletion

1	1	1	1	1	288.537
1	1	1	1	1	104.643
1	1	1	1	0	106.496
1	1	1	0	1	151.977
1	1	0	1	1	125.137
1	0	1	1	1	57.966
0	1	1	1	1	66.003
1	1	1	1	-1	108.349
1	1	1	-1	1	199.311
1	1	-1	1	1	145.631
1	-1	1	1	1	11.289
-1	1	1	1	1	27.363

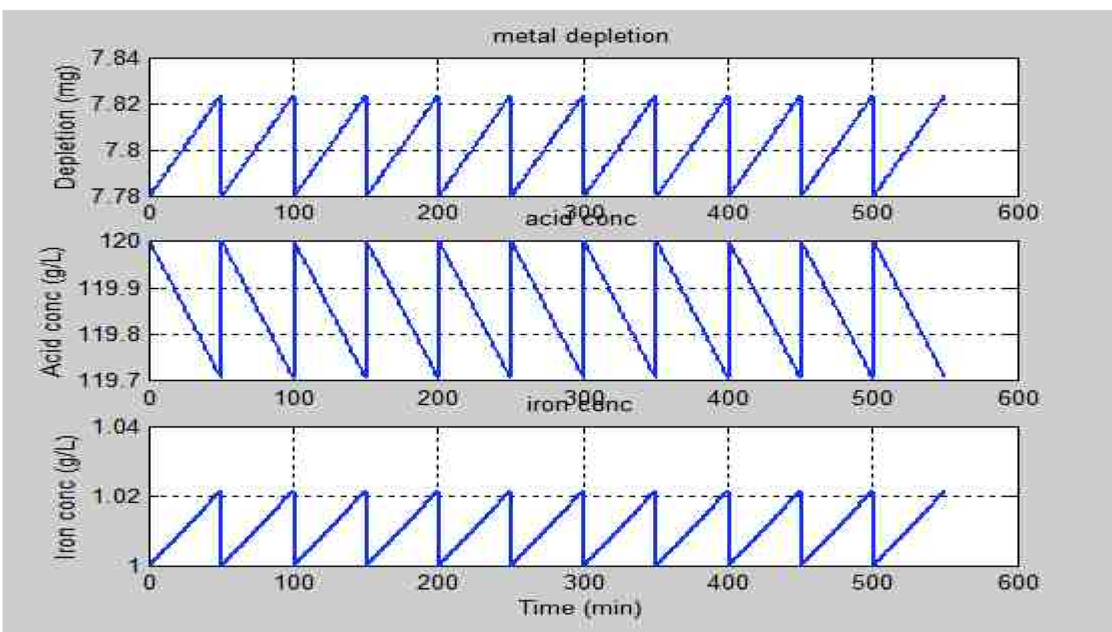
Conducting the Mat Lab simulation at these parameter setting results in a significant improvement to the acid effectiveness. This improvement is illustrated in the Mat Lab simulation illustrated below.

Figure 8: Optimum operation of acid tank



In the above simulation it can be seen that the acid reacts faster with the metal as the contaminant increases. The experiments were carried out with a contaminant of 1g/l. It has been noted that a low iron concentration actually improves the acid effectiveness.

Figure 9: Continuously refreshing the acid results in



The optimization was then set up in Mat Lab to determine the impact of operating away from the optimum. Figure 9 illustrates the benefit of maintaining the acid solution at optimum. It has to be noted that the efficiency is not at its highest sue to metal contamination been at a max of 1g/l for the experiments used to set up the model.

4. Degreaser model

Similar to the acid model the degreaser model was constructed based on the variables that effect degreaser efficiency. The experimental model is detailed below.

$$O_R = S_A * (182.457 - (5.1612 * C_{Oil}^D) - (10.818 * O_{Oil}^D) - (24.505 * t^D) + 10.7581 * (C_{Oil}^D * T^D) - (8.7055 * O_C^D * T^D) + 7.60675 * (C_{Oil}^D * A_M) + 29.5501 * (O_C * A_M) - 8.1726 * (T^D * A_M) \quad (9)$$

Where:

O_R=Oil removal(g)

C_{Oil}^D = Concentration of degreaser(g/l)

O_C^D = Concentration of oil in solution(g/l)

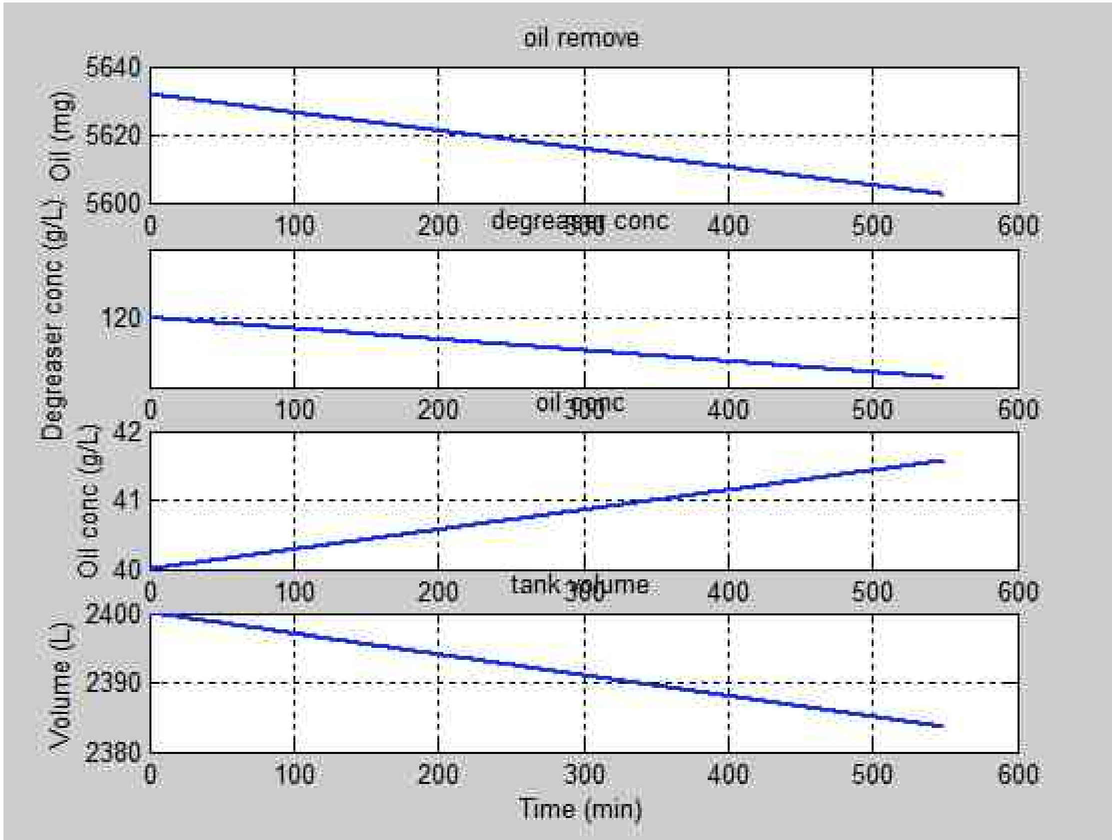
T^D =Degreaser temperature (^{0}C)

A_M^D =Power into bath(Amps)

t^D =Time in bath(s)

Running the above model for oil removal in a typical plating line results in a prediction of the current degreaser concentration and oil levels.

Figure 10: Typical degreaser tank operation



The degreaser operation can then be optimimised using Newton's method. This is carried out in Excel. Conducting the Mat Lab simulation at these parameter setting results in a significant improvement to the acid effectiveness. This improvement is illustrated in the Mat Lab simulation illustrated below.

Figure 11:Degreaser tank operation -optimum

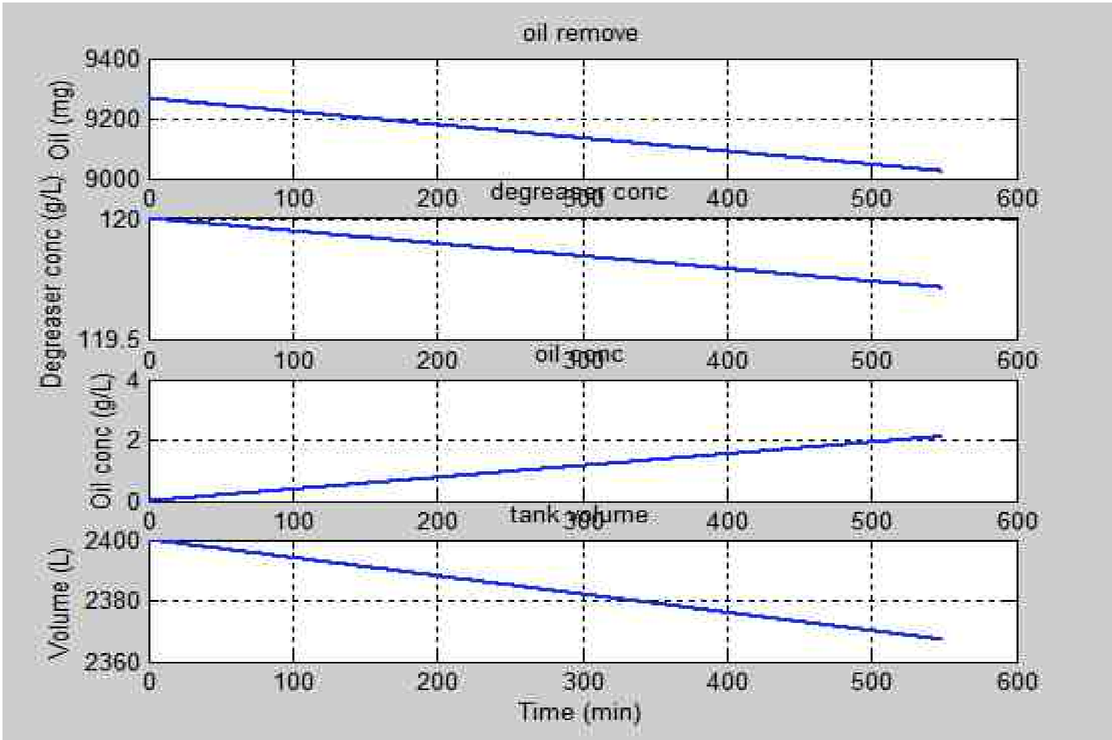


Figure 12: Degreaser tank operation with continuously refressing solution

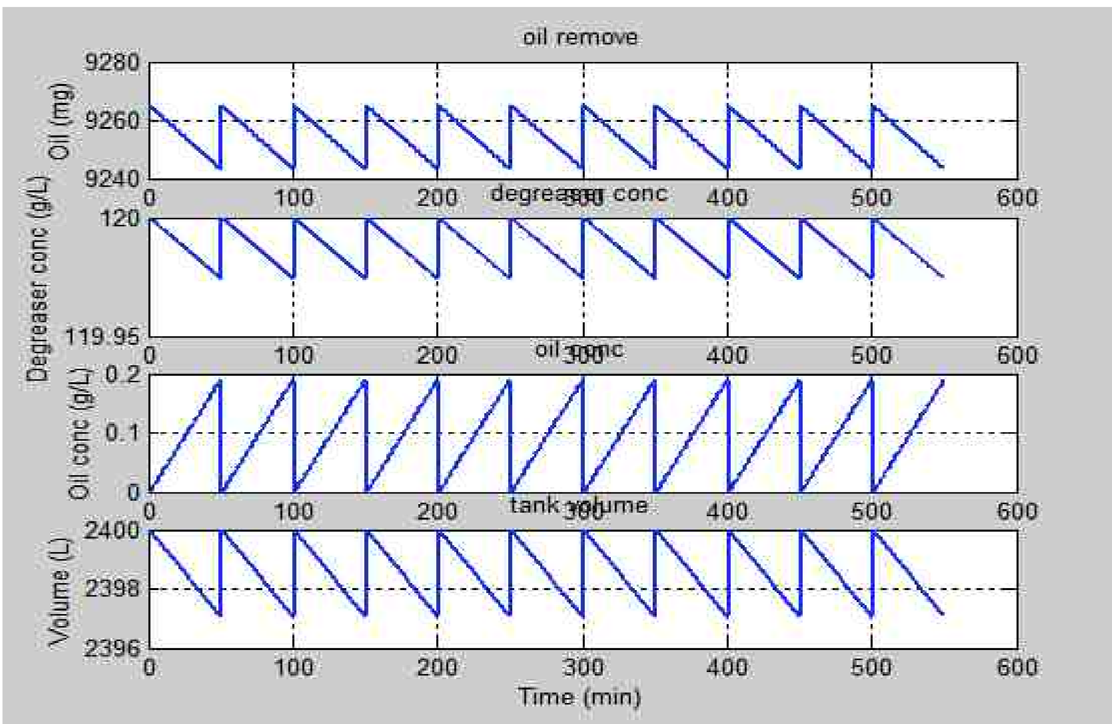


Figure 12 illustrates the benefits of operating the degreaser at optimum operating conditions. It is clearly seen that the degreaser effectiveness is maintained.

5. Conclusion

The models developed and applied have facilitated the successful modeling of the three major components to a plating process. These optimization models help to indicate to electroplating companies the optimum operating range. Operating at optimum implies effective cleaning and plating. This results in minimization of resources used. It is acknowledged that in some instances the maintaining the various process tanks at optimum could prove to be a challenge.

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