Report on the FLOWSHEET Model for the Electrochemical Treatment of Liquid Radioactive Wastes (U)

by

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Attached is the report prepared by the University of South Carolina under contract #AA00900T.
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**FLOWSHEET MODEL FOR THE ELECTROCHEMICAL TREATMENT
OF LIQUID RADIOACTIVE WASTES**

A Milestone Report Submitted To

**Dr. David T. Hobbs
Westinghouse Savannah River Company
WSRC/SCUREF Task Order # 112**

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Abstract

The objective of this report is to describe the modeling and optimization procedure for the electrochemical removal of nitrates and nitrites from low level radioactive wastes. The simulation is carried out in SPEEDUP™, which is a state of the art flowsheet modeling package. The flowsheet model will provide a better understanding of the process and aid in the scale-up of the system. For example, the flowsheet model has shown that the electrochemical cell must be operated in batch mode to achieve 95% destruction. The present status of the flowsheet model is detailed in this report along with a systematic description of the batch optimization of the electrochemical cell. Results from two batch runs and one optimization run are also presented.

1 Introduction

The objective of this project is to develop a dynamic flowsheet model for the electrochemical treatment of liquid radioactive wastes. The flowsheet includes the electrochemical reactor, an evaporator/crystallizer, gas recovery and processing for final disposal of the liquid wastes. The objective of the process is to destroy or remove the hazardous species. The current phase of the project involves optimization of the electrochemical reactor and evaporator operation so as to reduce material and energy costs. The final phase of the project involves a comprehensive study of the safety, and operability of the whole system design.

A schematic diagram of the flowsheet¹ is given in Figure 1. A brief description of the units in the flowsheet is given below.

- a) Electrochemical Reactor : The main purpose of this unit is to destroy the nitrates and nitrites. The flowsheet model has shown that the single pass undivided electrochemical cell gives a low conversion per pass, and therefore a divided cell operating in batch mode is required.
- b) Evaporator/Crystallizer : The main purpose of the evaporator is to concentrate the caustic (NaOH). The crystallizer separates the solids, that precipitate during evaporation. At present, single, double and triple effect evaporator models exist for the NaOH-H₂O system. They have been connected to Properties Plus, Aspen Tech's rigorous physical properties package. It will handle nitrates, nitrites and solids.
- c) Gas Treatment : This unit is used to treat the off gases (coming out of the EC reactor) if need arises, so that environmental regulations are met.
- d) Dissolution Tank & Waste Disposal : The solids separated in the crystallizer are dissolved in an appropriate solvent and sent to waste disposal facility.

The flowsheet model has been developed in SPEEDUP™, Aspen Tech's rigorous flowsheeting package. This model will provide the following.

- 1) A clear understanding of the process.
- 2) Determination of the boundaries of operation and identification of operating constraints.
- 3) Optimization of the system and its operation based on material and energy costs.

Figure 1: Process flowsheet for the electrochemical treatment of liquid radioactive wastes

4) Scale-up of the system.

5) Safety analysis.

In this report we summarize the present status of the flowsheet model and the methodology for the batch optimization of the electrochemical cell.

2 Outline of the Work Accomplished to Date

At present the flowsheet model comprises an electrochemical reactor and an evaporator as shown in Figure 2. Presently, optimization of the batch cell is being performed. The optimal operation of the cell will provide a much better estimate of the amount and composition of gases generated, after which the off-gas processing unit can be easily added. The outline below summarizes the work accomplished.

- a) Preliminary analysis with the flowsheet model indicated a necessity for using a divided cell in batch mode.
- b) The mass balances for the electrochemical cell were programmed into SPEEDUPTM and checked for consistency with the differential model developed by Coleman². These balances were for a cell operating at steady state and having constant current efficiencies.
- c) The development of a batch cell model based on a boundary layer approach has been completed. It includes diffusion and migration as the major flux components and has the capability of handling multiple reactions and rigorous thermodynamic calculations.
- d) Models for single, double, and triple effect evaporators have been developed for the NaOH-H₂O system. All of these are dynamic models. They produce a highly concentrated caustic stream.
- e) The dynamic evaporator models have been connected to Properties Plus (an Aspen Data Bank). Connection to Properties Plus provides quick and accurate evaluation of enthalpies and solubilities. This also allows handling of nitrates and nitrites along with solid phase calculations.
- f) An optimization strategy to minimize the capital plus operating costs for the batch electrochemical cell has been developed. It uses a Neural Net mapping to evaluate the optimal current at which the cell can be operated at each point in time.

Figure 2: Segment of the flowsheet that has been modeled

- g) A number of case studies have been run with the boundary layer electrochemical cell model studies accounting for the most of them. A few case studies aiming to validate the evaporator model have also been run.

The following sections describe the electrochemical cell and evaporator models and the batch optimization procedure. A discussion of the future direction of the flowsheet modeling studies is presented at the end of this report.

3 The Electrochemical Reactor Model

The electrochemical reactor is the heart of the flowsheet for the treatment of hazardous wastes. The objective of the reactor is to destroy or remove the hazardous species from the solution. The substances comprising the waste (decontaminated salt solution) simulant are tabulated in Table 1. The simulated feed¹ is assumed to consist only of nitrates, nitrites, and hydroxides.

3.1 Background

A number of parallel plate electrochemical cell models exist in literature. Parrish and Newman³ presented a model which considers the interaction of closely spaced electrodes and analyzes the current distribution, but they did not include multiple reactions. Sakellaropolous and Francis⁴ included multiple reactions in their model, which was used mainly to analyze product selectivity. Cabin and Chapman⁵ presented a model which focussed on using simpler techniques for the solution procedure. They used orthogonal collocation to solve for transport in the boundary layer, which gave them concentration profiles and current densities that agree well with rigorous calculations. Lee and Selman⁶ presented a similar model, but they also accounted for the effects of separator and electrode resistance. The model developed was for a Zn/Br₂ system.

White, Bain and Raible⁷ presented a complete electrochemical cell model that was used to model multiple reactions at the cathode. This model described the electrowinning of copper and used Newman's⁸ BAND algorithm to predict product selectivity and current efficiencies at different cell conditions. However, this model neither included a separator nor any gas evolving reactions. Mader, Walton and White⁹ made a modification to the above model that substantially reduced computational time. They suggested the one-step model which assumed that the axial concentration gradient is linear and is equal to the ratio of the change in concentration (from inlet to outlet) to the reactor length. This essentially changed the model from a two-dimensional model to a one-dimensional model. These

models form the basis for the differential model² which is a rigorous, divided cell model that effectively describes the nitrate system. It includes effects of separator, ionic migration, electrode resistances, multiple reactions and cell gap. The differential model uses the BAND algorithm to solve for the steady state continuity equation in the catholyte and anolyte regions with appropriate boundary conditions. This aids in evaluating the current efficiencies, current densities, concentration profile and the potential profile for a given set of operating conditions. This model, though highly accurate, is computationally intensive for optimization studies and for its use in the flowsheet simulation of the entire plant.

With a number of robust and complete electrochemical cell models existing in literature, the focus is now on devising solution procedures and strategies to reduce computer time. Cabin and Chapman⁵ used the orthogonal collocation technique in association with boundary layer approximations to solve for the continuity equation. Smeltzer and Fedkiw¹⁰ used an innovative technique to analyze the effect of periodic cell voltage control¹¹ on the reduction of nitrobenzene. They used the analytical solution to the Laplace equation in conjunction with the analytical solution to the transient diffusion equation of the reactant in the stagnant boundary layer, to model the reactor. In the present work, a boundary layer approximation is used to model the nitrate system, which results in a significant reduction of computer time. Henceforth, it will be referred to as the boundary-layer model.

Several models for the parallel plate electrochemical cell with recirculation have been developed^{12,13,14}. Most of the models assume that the reactor is in plug flow and include time dependence both in the reactor and the recirculation tank. In contrast, both Coleman's differential model and our boundary layer model assume that only the recirculation tank exhibits time dependency.

Preliminary studies^{1,15,16} on the nitrate system have suggested that in the range of operation of the electrochemical cell, the conversion per pass achieved is drastically low ($\approx 0.05\%$). Thus, the concentration profile in the bulk of the cell is relatively flat, with the only gradients existing in a small region in the vicinity of the electrodes. This supplements the validity of the boundary-layer model, which solves for the concentration profile only in the small region (δ) beside the electrodes. The differential model solves for the profile throughout the cell.

This report will delineate the development of an electrochemical reactor model based on the boundary layer approach, suitable for use in the process flowsheet model. It will also describe in detail, the systematic development of the batch optimization methodology formulated to minimize capital plus operating costs. Results from a few independent case studies (including one optimization run) are presented. The boundary layer model has been designed mainly to be used as a

module in the flowsheet and for optimization studies. The differential model, though precise, takes a significant amount of time to run. The boundary layer model can give accurate results much quicker.

Since the process stream is non-ideal (due to presence of polar species like water and a large number of gases), the use of rigorous thermodynamics is vital. The use of SPEEDUPTM as the programming environment further facilitates the use of rigorous thermodynamics. The rigorous VLE data is obtained by connecting the program to Properties Plus, which is Aspen Tech.'s property database.

3.2 Divided Cell in Batch Mode

Figure 3 shows the batch system. Most of the existing models assume that the cell is in plug flow and do not consider the effect of potential, electrode gap, ionic migration or electrode kinetics. Moreover, they do not consider flashing (separation of dissolved gases from the solution) of the gases produced in the reactor. All the above mentioned effects have been included in this work. The divided cell, two continuously recycling streams (anolyte and catholyte) and two recirculation tanks (one each for the two streams) are grouped together and treated as batch reactors with gas generation. The simulated feed composition of the anolyte and catholyte at the start of the batch run is given in Table 2. The divided cell is a parallel plate electrochemical reactor with an ion-exchange membrane separating the cathode and the anode. The reduction of nitrates and nitrites occurs at the surface of the cathode. The separator minimizes oxidation of the nitrites back to nitrates at the anode. The purpose of the reservoir is to thoroughly mix the incoming process stream with the reservoir contents. It also enables the gases trapped in the stream to flash.

The divided cell system is preferred over the undivided cell because of the very low conversion² per pass observed. Based on this low conversion per pass, it was estimated that the cost required to build the electrochemical cell (to attain 95% reduction of nitrates and nitrites) was prohibitive. The cost analysis indicated that the only viable configuration of the flowsheet would include a divided cell operating in batch mode.

Figure 3: Divided cell in batch mode

3.2.1 Model Assumptions:

The following assumptions have been made in developing the boundary layer electrochemical cell model.

1. The dynamics of the reactor are neglected in the presence of recirculation tank dynamics.
2. No homogeneous chemical reactions occur in the reactor.
3. Dilute solution theory applies.
4. The Nernst - Einstein equation ($u_i = D_i / RT$) applies.
5. The Butler-Volmer equation can be used to describe the reactions at the electrode surface.
6. Isothermal conditions exist.
7. The gases produced at the electrode surface stay in solution in the reactor and are flashed upon entering the recirculation tank.
8. The solution conductivity is uniform in each of the anolyte, catholyte, and separator regions.
9. Perfect mixing is achieved in the recirculation tank.
10. The physical transport parameters are constant.
11. Density of the process stream remains constant.
12. Concentration of gases in the anolyte stream is low.

Assumption 1 is valid because the volume of the reactor is small compared to the recirculation tank. Assumptions 2 through 6 are common to most parallel-plate electrochemical reactor models. Assumption 7 holds because the amount of gas produced at each pass is always below saturation limits, owing to the fact that the conversion per pass is quite low. Assumption 8 arises from the fact that the conductivity is a function of the sum of the species concentrations which remains almost unchanged (since all the species in the simulated waste carry unit charges and electroneutrality is maintained). Assumptions 9 through 11 are common in CSTR modeling. Assumption 12 is based on results from preliminary studies^{1,16}.

3.2.2 Batch Cell Model Development:

The function of the electrochemical reactor is to destroy the nitrates and nitrites. This is achieved by reducing them to gases such as nitrogen, ammonia and nitrous oxide. The main reactions presumed to be occurring inside the electrochemical cell are given below:

Reaction	$U^\theta(V)$	
$NO_3^- + H_2O_{(l)} + 2e^- \rightarrow NO_2^- + 2OH^-$	0.01	(1)
$NO_2^- + 5H_2O_{(l)} + 6e^- \rightarrow NH_{3(g)} + 7OH^-$	-0.165	(2)
$2NO_2^- + 4H_2O_{(l)} + 6e^- \rightarrow N_{2(g)} + 8OH^-$	0.406	(3)
$2NO_2^- - 3H_2O_{(l)} + 4e^- \rightarrow N_2O_{(g)} + 6OH^-$	0.15	(4)
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$	-0.828	(5)
$4OH^- \rightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$	0.401	(6)
$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O_{(l)} + 2e^-$	0.01	(7)

Due to assumption 12, the reverse rate of reactions (2) - (5) is low and hence reactions (1) - (5) occur at the cathode and reactions (6) and (7) occur at the anode. All the above reactions can be written in the following general format⁸.

In this format, the stoichiometric coefficient s_{ij} is positive for products and negative for reactants when the reaction is written as a reduction. The governing equations, based on the assumptions outlined, in catholyte section of the divided cell are:

Total Mass Balance:

$$\frac{d(\rho_c V_{ca})}{dt} = Q_c \rho_c - Q_c \rho_c \quad (9)$$

Species Molar Balance:

$$\frac{d(V_{ca} C_{i,b,c})}{dt} = Q_c C_{i,f,c} - Q_c C_{i,b,c} - \sum_j \frac{s_{ij} i_t A \epsilon_j}{n_j F} + R_i - A N_{i,s} \quad (10)$$

where, $N_{i,s}$ represents the net flux through the separator which is characterized by a MacMullin number¹⁷. The MacMullin number, denoted by N_m , is a function of the separator's porosity and tortuosity. The flux contains both diffusion and migration and its value is obtained by solving the following expression.

$$\frac{C_{i,b,a}}{C_{i,b,c}} = \left[\frac{N_{i,s} \kappa_s}{D_{i,e} z_i f C_{b,i}} \right] + \left[1 - \frac{N_{i,s} \kappa_s}{D_{i,e} z_i f C_{b,i}} \right] e^{\frac{z_i f i_t \Delta}{\kappa_s}} \quad (11)$$

where, $D_{i,e} = \frac{D_i}{N_m}$ and $\kappa_s = \frac{F^2}{2\mathcal{R}T} \sum_i z_i^2 D_i (C_{i,b,c} + C_{i,b,a})$

The summation term in equation (10) is the consumption term due to reaction at the electrode surface. The rate of any reaction is a function of the current associated with that reaction. ϵ_j is the fraction of the total current ($i_t A$) associated with reaction "j". To operate the cell in batch mode, it is essential to predict ϵ_j 's as a function of changing concentration. The subsequent section gives a brief description of the development of such a model.

The main purpose of the reservoir is to allow processing of a large system inventory. It also aids in the thorough mixing of process streams. The governing equations for the catholyte recirculation tank are:

Total Mass Balance:

$$\frac{d(\rho_c V_{res,c})}{dt} = Q_c \rho_c - Q_c \rho_c \quad (12)$$

Species Molar Balance:

$$\frac{d(V_{res,c} C_{i,f,c})}{dt} = Q_c C_{i,b,c} - Q_c C_{i,f,c} \quad (13)$$

Similar balances can be written for the anolyte section of the reactor. Since the dynamics of the reactor are neglected, it is reasonable to assume that the only time

dependence is in the recirculation tank and the reactor operates at steady state. Therefore, the derivatives in equations 10 and 11 are set to zero.

It is assumed in the batch model that, the gases produced remain in solution inside the electrochemical reactor. After passing through the reactor, a flash occurs (either prior to or in the reservoir). The flash calculations are performed by using a FLASH subroutine in the Speedup library. The program is connected to Properties Plus so that the physical properties and VLE calculations can be accurately determined. Properties Plus uses the UNIFAC approach to perform the VLE calculations.

In the differential model, the BAND algorithm is used to evaluate the concentrations everywhere (bulk and surface) and these values are used to verify the material balances. In contrast, the boundary layer model uses these balances to evaluate the outlet (or bulk) concentrations.

3.2.3 Current Efficiency Model Development:

During the batch operation of the electrochemical reactor, the current efficiencies are no longer constant. Hence, it is essential to develop a simplified model to predict the current efficiencies as a function of concentration.

The current efficiency (ϵ_j) indicates the fraction of the total current utilized by reaction "j". The Butler-Volmer equation gives a correlation between current (i_j) and the reference overpotential ($\eta_{ref,j}$).

$$i_j = i_{o,ref,j} \left[\left(\frac{C_{i,s}}{C_{i,b}} \right)^{p_{ij}} \left(\frac{C_{i,b}}{C_{i,ref}} \right)^{p_{ij}} e^{(1-\alpha_j)\eta_{ref,j}} - \left(\frac{C_{i,s}}{C_{i,b}} \right)^{q_{ij}} \left(\frac{C_{i,b}}{C_{i,ref}} \right)^{q_{ij}} e^{-\alpha_j\eta_{ref,j}} \right] \quad (14)$$

where, $\eta_{ref,j} = V_c - \phi_c - U_{ref,j}$ for reactions at the cathode.

$\eta_{ref,j} = V_a - \phi_a - U_{ref,j}$ for reactions at the anode.

$$\text{and, } U_{ref,j} = U_j^\theta + \frac{1}{n_j f} \sum_i \ln \left(\frac{1}{a_{i,ref}} \right) \quad (15)$$

In the above equation $a_{i,ref}$ refers to the activity of species "i" w.r.t reference conditions. It can be well approximated by the reference concentration of the species.

The flux of a species (N_i) is related to the current density (i_j) as follows:

$$N_i = -\sum_j \frac{s_{ij} i_j}{n_j F} \quad (16)$$

Since, both diffusion and migration contribute to the transport of species "i" to the electrode surface, N_i can be written as,

$$N_i = -D_i \frac{dC_i}{dx} + \frac{z_i D_i F i_t}{\Re T \kappa} C_i \quad (17)$$

where, $\kappa = \kappa_c = \frac{F^2}{\Re T} \sum_i z_i^2 D_i C_{i,b,c}$ for catholyte section.

and, $\kappa = \kappa_a = \frac{F^2}{\Re T} \sum_i z_i^2 D_i C_{i,b,a}$ for anolyte section.

Since N_i is a constant, the above ordinary differential equation (ODE) can be solved easily using the following boundary conditions (BC's).

$$BC \#1 : \quad @ x = 0, \quad C_i = C_{i,b}$$

$$BC \#2 : \quad @ x = \delta, \quad C_i = C_{i,s}$$

Solving the ODE using the above BC's, gives,

$$\frac{C_{i,s}}{C_{i,b}} = \left(\frac{N_i}{D_i \gamma_i C_{i,b}} \right) + \left(1 - \frac{N_i}{D_i \gamma_i C_{i,b}} \right) e^{\gamma_i \delta} \quad (18)$$

where,

$$\gamma_i = \frac{z_i F i_t}{\Re T \kappa} \quad (19)$$

Note that, $i_t = \sum_j i_j$

Using equation (18) to substitute for $(C_{i,s}/C_{i,b})$ in equation (14), a set of current densities and hence, a set of current efficiencies can be evaluated. These current densities and efficiencies are a function of bulk concentration, that varies with time in a dynamic run.

3.3 Results of Simulation and Optimization Studies

The physical and kinetic parameters, shown in Table 3, are used to perform batch runs (low voltage and high voltage runs). Single-pass studies are performed at various times during one batch run (low voltage run) in order to illustrate that an optimal current exists. The optimization objective function estimates the changes in this optimal current during the batch run. Some of the values such as exchange current densities are presently approximated due to lack of experimental data.

3.3.1 Batch Simulation Results:

The simulation of the batch cell provides a rough estimate of the energy consumed and time required for 95% reduction of nitrates and nitrites. Also, at the cathode, it is desirable to maximize the current efficiency of reactions 1 - 4 and minimize the current efficiency of reaction 5 (production of H_2). At the anode, it is desirable to maximize the efficiency of reaction 6 (oxidation of OH^-) and minimize that of reaction 7 (oxidation of nitrite to nitrate). Two test case batch runs were performed at cell voltages of 3.5 V (low voltage run) and 5.65 V (high voltage run). In each case, catholyte reservoir volume and anolyte reservoir volume were kept at 700 ml and 7000 ml respectively.

Low voltage run

Figure 4 shows a plot of the current efficiencies at the cathode vs. total coulombs passed for a batch run performed at a constant cell voltage of 3.5 V. The total coulombs passed is the time integral of the operating current. The cell current ranged from a maximum of 0.42 A/cm^2 (at startup) and a minimum of 0.3 A/cm^2 . Initially, nitrate reduction (reaction 1) has the largest current efficiency. It gradually decreases throughout the run as the nitrate concentration decreases. In contrast, the fraction of current going into reactions 2 through 5 increases through the first half of the run. The initial increase in the current associated with reactions 2 through 4 is due to an increase in nitrite concentration. However, towards the end of the run the nitrite concentration decreases and therefore the rate of reactions 2 through 4 decreases. By the end of the run, very little nitrate and nitrite remain and almost all the current is due to H_2 evolution (reaction 5). The current efficiencies at the anode are not shown since reaction 6 consumes nearly all of the current.

Figure 5 shows the ionic concentrations in the catholyte recirculation tank vs. coulombs passed. It can be seen that the concentration of nitrates and nitrites are reduced 95% over the course of the run. The nitrite concentration shows an initial

increase because the rate of production of nitrite from reaction 1 exceeds its destruction rate (reactions 2, 3, and 4) which is evident from Figure 4.

The catholyte off-gas compositions are shown in Figure 6. It can be seen that N_2 , N_2O , and H_2 are the major gases produced at the beginning of the run even though the current efficiencies for reactions 4 and 5 are lower than those of reaction 2 (NH_3 production). This is because the solubility of NH_3 is much higher than those of N_2 , N_2O , and H_2 . After most of the nitrates and nitrites are destroyed, hydrogen becomes the major off-gas.

The plot of total current vs. coulombs passed is shown in Figure 7. It decreases gradually during the course of the simulation.

Figure 8 shows a prediction of the total gas flowrate vs. coulombs passed. Around 500,000 coulombs, the curve shows an abrupt rise. This is due to the increase in H_2 generation.

High voltage run

Since the objective of the process is to destroy both nitrates and nitrites as quickly as possible, a batch run at 5.65 V was performed to investigate the consequence of operating at high destruction rates. The cell current ranged from a maximum of 1.38 A/cm^2 (at startup) and a minimum of 0.85 A/cm^2 . The rest of the parameters were left unchanged. The resulting plots are shown in Figures 9 through 11.

A plot of the cathodic partial current fractions vs. total coulombs passed is shown in Figure 9. It can be seen that, except for early in the batch when the NH_3 production rate is high, most of the cell current goes into H_2 production (reaction 5). The high H_2 partial current results because reactions 1-4 are under mass-transfer control during the entire batch run. This is the reason why no peaks (see Figure 4) are obtained. The large rate of H_2 production represents a significant amount of energy going into an undesired product. By the end of the run, very little nitrate and nitrite remain and hence the efficiency of reaction 5 is approximately 100%.

Figure 10 shows the ionic concentrations in the catholyte recirculation tank vs. coulombs passed for the high voltage run. The cell voltage is maintained constant at 5.65 V. Unlike the low voltage case, the nitrite concentration shows a constant decrease because the rate of nitrite destruction from reactions 2, 3, and 4 is much greater than the rate of production from reaction 1. This is due to the high current associated with reaction 2. The catholyte off-gas compositions are shown in Figure

11. It can be seen that H_2 and NH_3 are the major gases throughout the run as indicated by the high current efficiencies associated with their production.

Figure 12 shows a comparison of the nitrate and nitrite concentrations as a function of time for the two batch runs. It can be seen that the initial overall destruction rate (rate of destruction of nitrate and nitrite combined) is greater in the high voltage run than in the low voltage run. To obtain 95% conversion of the total concentration of nitrates and nitrites at 3.4 V requires approximately 7.4 hours, while at 5.65 V requires 6.4 hours.

3.3.2 Batch optimization:

The previous sections focused on batch simulations where the cell voltage was held constant. However there will likely be an optimal operational path in which the cell voltage (or cell current) is varied throughout the batch run. A methodology describing how the model can be used to determine optimal batch cell operation is presented.

Background

To minimize capital costs, it is necessary to maximize the amount of waste destroyed in a specific time period. This would, in turn, reduce the size of electrode area required. Maximizing the amount of waste destroyed during in a certain time period is equivalent to maximizing the destruction current (current going into reactions 1 to 4). Figure 13 shows a plot of destruction current vs. total current at different points in time (represented by total charge passed) during the low voltage batch simulation. A peak in the destruction current on each curve corresponds to an optimum total current. The formation of a peak is mainly due to the migration effect which repels the nitrates and nitrites away from the cathode, thereby increasing the current going into H_2 production (reaction 5). Note that the low voltage run operates at a very low destruction rate throughout most of the batch; the high voltage run operates near the maximum destruction rate at the start of the batch, but moves beyond the maximum after the start of the batch.

Clearly, adjusting the operating current to pass through these maxima throughout the batch will maximize the destruction rate and hence minimize the time to reach 95% conversion of nitrates and nitrites. However, such a strategy may generate an unacceptable amount of H_2 . For example, applying an operating current of 1.4 A/cm^2 (the peak destruction rate) at the start of the batch will result in 0.2 A/cm^2 going into H_2 production. Production of excessive amounts of H_2 causes high energy (electrical energy) losses resulting in increased operating costs. Thus,

operating at the maxima will lead to low capital but high operating costs. An optimization formulation which will provide a balance between capital and operating costs and lead to minimum overall cost is,

Minimize [Capital cost + Operating cost]

subject to 1) Nitrate and nitrite reduction ≥ 0.95

2) Processing time $\leq t_p$

3) Destruction efficiency $\geq \epsilon_d$

The destruction efficiency, ϵ_d , can be set to achieve a feasible optimum current which will bring about minimized overall costs. The choice of ϵ_d may depend on a number of factors like H_2 and NH_3 production, destruction rate of nitrates and nitrites, total processing time, and safety. To illustrate how the optimal current would vary in order to maintain an acceptable destruction efficiency, ϵ_d versus the total current is plotted in Figure 14. The symbol "o" indicates the maximum destructive current for which at least 98% efficiency is obtained. The symbol "x" in the figure corresponds to the maxima from Figure 13. Notice that operating at the maximum destruction current yields a slightly reduced efficiency (and increased H_2 evolution). By reducing the total current slightly from the maximum, much better efficiencies are attained while reducing the destruction rate only slightly. Also shown in Figure 14 is the efficiency during the low voltage run (indicated by the symbol "*"). Nearly 100% destruction efficiency was attained during the first half of the batch run and as a result very little H_2 was produced. The efficiency dropped to about 10% by the end. Unfortunately the overall destruction rate was low. By comparison, at the beginning of the batch, the high voltage case yielded very high destruction rates, but only 82% efficiency. Near the end the batch, this efficiency was around 2%.

Procedure

An examination of the batch cell governing equations and the optimization objective function shows that the optimum current (i_{opt}) is mainly a function of NO_3^- and NO_2^- concentration and destruction efficiency (ϵ_d). Therefore, several single-pass optimization runs were performed to obtain i_{opt} for different values of NO_3^- , NO_2^- , and ϵ_d . Figure 15 shows a 3-D plot of i_{opt} as a function of NO_3^- and NO_2^- at two different destruction efficiencies (0.98 and 0.82). It can be seen that operating at a lower ϵ_d yields higher currents. But from Figure 11, it can be seen that higher currents lead to significant H_2 evolution. The data obtained was used to train Neural Network. The purpose of the Neural Network is to obtain a mapping

between the output vector (i_{opt}) and input vectors (NO_3^- , NO_2^- and ϵ_d). A brief introduction to Neural Networks, followed by a description of the training and testing procedure is given in the next section. The Neural Net mapping function is used in conjunction with the batch cell model to perform a batch optimization run.

Function identification using a Neural Network

A Neural Network consists of a large number of simple processors called neurons¹⁸ that are reminiscent of biological nervous systems. The network function is determined largely by the appropriate weighted connections between these neurons. A typical network consisting of an input layer, a hidden layer and an output layer is shown in Figure 16. Each neuron in the input layer has one single external input. Each neuron in the hidden layer has an input from every neuron in the input layer and an additional input with a fixed value, termed as the bias. Finally, each neuron in the output layer has an input from every neuron in the hidden layer and a bias. The output layer provides the solution arising from the combination of the inputs. More complicated networks have additional hidden layers.

In this work, the purpose of the Neural Network is to obtain a mapping between the output vector (i_{opt}) and input vectors (NO_3^- , NO_2^- and ϵ_d) via the backpropagation learning rule¹⁹. This rule helps to adjust the weights and biases of the network so as to minimize the sum squared error of the network. Three neurons in the input layer, three in the hidden layer and one neuron in the output layer are being used for this work. The network was trained using 80% of the data generated through single-pass optimization runs. The plot of network prediction vs. training data is shown in Figure 17. The rest 20% of the data was used for testing the trained network. The plot of network prediction vs. test data is shown in Figure 18. From Figures 17 and 18 it is clear that the Neural Network with one hidden layer does a very good job of identifying the functional relationship between i_{opt} and NO_3^- , NO_2^- , ϵ_d .

Results of the optimization run

In the previous two batch runs, the cell voltage was fixed. In the optimization run, the optimal value of the cell current (and hence the cell voltage) at every point in time during the run is evaluated by the Neural Network mapping function, based on a value of ϵ_d (which is set at 0.98) and the concentrations of NO_3^- and NO_2^- existing at that time. The physical and kinetic parameters were unchanged.

Figure 19 shows a plot of the current efficiencies at the cathode vs. total coulombs passed for a optimization run. The cell current ranged from a maximum of 1.057 A/cm^2 (at startup) and a minimum of 0.062 A/cm^2 (at the end). Comparing with Figure 4, it can be seen that the current associated with reaction 5 (H_2 production) is very low throughout the run. This was one of the objectives of the optimization routine.

The catholyte off-gas compositions are shown in Figure 20. It can be seen that N_2 , and H_2 are the major components in the gas phase at the beginning of the run even though the current efficiency for reaction 5 is the lowest. This is because H_2 has the lowest solubility among NH_3 and N_2O . But in contrast to Figures 6 and 11, where the H_2 production increases towards the end, the optimization run produces significantly less H_2 . In fact, NH_3 and N_2O generation increases considerably.

Figure 21 shows a comparison of the nitrate and nitrite concentrations as a function of time for the two batch runs and the optimization run. It can be seen that the overall destruction rate (rate of destruction of nitrate and nitrite combined) is greatest during the optimization run. It takes the low voltage run approximately 7.4 hours, the high voltage run approximately 6.4 hours and the optimization run approximately 5.1 hours to reduce the total concentration of nitrates and nitrites by 95%.

A plot of how the optimal operating current changes during the course of the run is shown in Figure 22. It can be seen that the current follows an exponentially decreasing path.

4 The Evaporator Model

The outlet stream from the electrochemical reactor is mostly NaOH , but small amounts of nitrates and nitrites will be present. The function of the evaporator is to concentrate the NaOH , which can then be recycled back as the anolyte to the divided cell reactor. This is achieved by using steam to evaporate sufficient water to produce a more concentrated NaOH solution.

In order to achieve a significant reduction in the capital and operating costs, a dynamic triple effect evaporator (in feedforward configuration) was studied. Steam is used to provide the heat input to the first effect. The superheated vapor that is formed (due to evaporation) is then used to heat the liquor in the second effect and so on. For modeling purposes, it is assumed that the dissolved gases are stripped from the outlet stream (from the EC reactor) before feeding into the evaporator.

4.1 Model Assumptions

The assumptions below have been made to simplify the calculational procedure.

- 1) Perfect mixing is achieved.
- 2) Vapor holdup is negligible relative to the mass of holdup of thick liquor in the evaporator.
- 3) Vapor phase is pure water.
- 4) No heat losses.
- 5) Complete condensation of steam takes place in the heat exchanger section.
- 6) Heat transfer area and heat transfer coefficient are constant.
- 7) Energy holdup in the walls of the metal tubes is negligible.

4.2 Model Development

The governing equations are given below.

Total Mass Balance:

$$\frac{d(\rho V)}{dt} = Q_f \rho_f - Q_l \rho_l - Q_v \rho_v \quad (20)$$

Component Molar Balance:

$$\frac{d(V C_i)}{dt} = Q_f C_{i,f} - Q_l C_{i,l} - \frac{Q_v P}{R_g T} y_i \quad (21)$$

Energy Balance:

$$\frac{d(V \sum_i C_{i,l} H)}{dt} = Q_f \sum_i C_{i,f} H_f + E_{in} - Q_l \sum_i C_{i,l} H_l - \frac{Q_v P}{R_g T} H_v - E_{los} \quad (22)$$

Mass Equilibrium²⁰:

$$m(X_{i,l})T^{sat} + b(X_{i,l}) - Y = 0 \quad (23)$$

where, $X_{i,l} = \frac{C_{i,l}}{\sum_i C_{i,l}}$

The temperature inside the evaporator (Y) is superheated (due to boiling point elevation) and is related to the saturated temperature by means of equation (23). It might be noted here, that, the enthalpies in the energy balance are evaluated by Properties Plus, by use of the Soave-Redlich-Kwong (SRK) equation of state. E_{in} is the heat input to the heat exchanger section of the evaporator by means of steam. Hence, E_{in} would be equal to the heat transfer rate through the heat exchanger surface, which in turn would be equal to the heat given out by the condensing steam.

4.3 Results of Simulation Studies

The product solution left over after destruction of nitrates and nitrites is mainly a caustic (NaOH) solution. This solution is fed continuously to the triple effect evaporator. Superheated steam at 350 °C is passed through the first effect. The amount of evaporation taking place in each effect is monitored by plotting the change of mass fraction of NaOH in the solution with time. Figures 23 through 25 show the same. The operating conditions are tabulated in Table 4. The steady state predictions are tabulated in Table 5.

In the previous version of this report, the curves obtained indicated a drop in mass fraction initially, because those curves were plotted for startup conditions which were not completely correct. Hence, in the present version, an initial steady-state is taken as the starting point.

In order to study the optimization and control of the evaporator system, it is essential to understand the dynamics correctly. This is accomplished by giving a step change in one of the input variables and observing the response of the desired output variables. A 10% step change was given in the inlet concentration of NaOH and the responses of the desired output variables, viz., mass fraction of NaOH in each effect was observed.

The plot of the mass fraction of NaOH vs. time for the first effect is shown in Figure 23. The response is similar to first order dynamics. Figures 24 and 25 show the same plot for second and third effects respectively. Both the curves show a response comparable to first order dynamics plus dead time.

From the steady-state data, it can be seen that most of the evaporation takes place in the first effect. The plots are just an indication of the existence of a working model. The amount of evaporation can be changed by changing parameters like pressure, holdup, flowrate and steam properties. Further modifications, currently being implemented, include addition of nitrate, nitrite and solid phase calculations and determination of optimal flow configurations.

5 Future Work

The direction of future work for the flowsheet modeling studies are given below.

- 1) Include solid phase calculations in EC cell and evaporator models.
- 2) Complete optimization of the electrochemical cell which will minimize capital plus operating costs over a 15 year operating period.
- 3) Include the crystallizer in the evaporator model.
- 4) Include the dissolution tank, the gas processing unit and saltstone.
- 5) Perform optimization analysis on the flowsheet as a whole.

NOTATION

A	:	Electrode Area (cm^2)
$C_{i,\text{ave}}$	:	Concentration of species i in outlet stream (mol/cm^3)
$C_{i,\text{feed}}$	:	Concentration of species i in feed stream (mol/cm^3)
$C_{i,\text{ref},j}$	:	Concentration of oxidized species in reaction j at reference conditions (mol/cm^3)
$C_{i,s}$	:	Concentration of species i at the electrode surface (mol/cm^3)
$C_{i,b}$	:	Bulk concentration of species i (mol/cm^3)
E_{in}	:	Energy/heat input into the evaporator by means of steam (J/s)
E_{los}	:	Energy/heat losses from the evaporator (J/s)
F	:	Faraday's constant (96487 C/mol)
f	:	$F/(\mathcal{R}T)$ (C/J)
H	:	Enthalpy of the system (inside the evaporator) (J)
H_f	:	Enthalpy of the feed stream entering the evaporator (J/mol)
H_l	:	Enthalpy of the liquid stream leaving the evaporator (J/mol)
H_v	:	Enthalpy of the vapor stream leaving the evaporator (J/mol)
i_j	:	Current density of reaction j (A/cm^2)
$i_{0,\text{ref},j}$	:	Exchange current density of reaction j (A/cm^2)
i_t	:	Total current density (A/cm^2)
M_i	:	Species ' i ' indicator
N_i	:	Flux of species i ($\text{mol}/\text{cm}^2 \cdot \text{s}$)
N_m	:	MacMullin number
n_j	:	Number of electrons taking part in reaction j
P	:	Pressure maintained in the system (atm)
Q	:	Volumetric flowrate of a stream (cm^3/s)
$\mathcal{R}$	:	Universal gas constant (8.314 J/mol K)
R_g	:	Universal gas constant (82.06 $\text{cm}^3 \text{ atm}/\text{mol K}$)
R_i	:	Rate of generation of species i due to homogeneous reactions (mol/s)
s_{ij}	:	Stoichiometric coefficient of species i in reaction j
T^{sat}	:	Saturated temperature of water (K)
U_j^o	:	Thermodynamic potential of the reaction at standard conditions (V)
U_j^{ref}	:	Thermodynamic potential of the reaction at reference conditions (V)
V_a	:	Potential of the metal anode (V)
V_c	:	Potential of the metal cathode (V)
V_{ca}	:	Volume of the catholyte compartment of the cell (cm^3)
V_{res}	:	Volume of the catholyte reservoir (cm^3)
$X_{i,l}$	:	Liquid mole fraction of species i
y_i	:	Vapor mole fraction of species i
z_i	:	Charge carried by the species

Subscripts

ave	:	Average
f	:	Feed stream
i	:	Species
in	:	Inlet stream
j	:	Reaction
k	:	Stream ($\Rightarrow k \equiv \text{in, out, f, l, v}$)
l	:	Liquid stream
out	:	Outlet stream
ref	:	Reference conditions
s	:	Conditions at the electrode surface
v	:	Vapor stream

Greek

α	:	Cathodic transfer coefficient
δ	:	Diffusion length (cm)
Δ	:	Separator thickness (cm)
ε_d	:	Destruction efficiency to be specified for the optimization run
ε_j	:	Current efficiency of reaction j
η_i	:	Conversion (per pass) based on species i
$\eta_{\text{ref},j}$	:	Overpotential of reaction j at reference conditions (V)
$\nabla\Phi$	:	Potential drop through the electrolyte (V/cm)
κ	:	Conductivity of the electrolyte ($\Omega^{-1} \text{ cm}^{-1}$)
γ	:	Variable defined by equation (16)
ρ	:	Density of a stream (gms/cm^3)
T	:	Temperature inside the evaporator (K)

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Component	Concentration (M)
NaNO ₃	1.95
NaNO ₂	0.6
NaOH	1.33
NaAl(OH) ₄	0.31
Na ₂ SO ₄	0.14
Na ₂ CO ₃	0.16
NaCl	0.022
NaF	0.015
Na ₂ CrO ₄	0.0033
Na ₃ PO ₄	0.0085
Na ₂ SiO ₃	0.0038
NaB(C ₆ H ₅) ₄	0.0026

Table 1: Composition of the Decontaminated Salt Solution
Simulant

Species	Init. Catholyte Comp.(M)	Init. Anolyte Comp.(M)
NO ₃ ⁻	1.95	1.95e-3
NO ₂ ⁻	0.6	0.6e-4
OH ⁻	1.33	3.8797
Na ⁺	3.88	3.88

Table 2 : Simulated Feed Composition

<u>Exchange Current Densities²(A/cm²):</u>	
Reaction 1	8.0e-10
Reaction 2	8.5e-11
Reaction 3	3.0e-15
Reaction 4	1.5e-13
Reaction 5	3.0e-6
Reaction 6	1.9e-11
Reaction 7	1.0e-15
<u>Diffusion Coefficients(cm²/s):</u>	
Na ⁺	1.334e-5
OH ⁻	5.26e-5
NO ₃ ⁻	1.902e-5
NO ₂ ⁻	1.902e-5
N ₂	1.9e-5
NH ₃	2.168e-5
N ₂ O	1.801e-5
O ₂	2.151e-5
H ₂	2.322e-5
Catholyte volume	700 cm ³
Anolyte volume	7000 cm ³
Cell length	10.0 cm
Cell width	10.0 cm
Electrode gap	1.25 cm
Av. axial fluid velocity	10.5 cm/s
Separator thickness	0.05 cm
MacMullin number	5.0
Volumetric flowrate	63.0 cm ³ /s

Table 3 : Kinetic parameters, Physical parameters and Operating conditions

Parameter	Value Assigned
Feed Flowrate	1198.6 cm ³ /s
Feed Temperature	200°C
Feed Pressure	1 bar
Feed Comp.	
NaOH	0.38 w/w
H ₂ O	0.62 w/w
Steam Used	Superheated steam at 350°C
Holdup	
1 st effect	2000 moles
2 nd effect	1400 moles
3 rd effect	1000 moles
Ht. Tr. Area	
1 st effect	25000 cm ²
2 nd effect	25000 cm ²
3 rd effect	25000 cm ²
Ht. Tr. Coeff.	
1 st effect	0.4 W cm ⁻² °C ⁻¹
2 nd effect	0.35 W cm ⁻² °C ⁻¹
3 rd effect	0.3 W cm ⁻² °C ⁻¹
Pressure maintained	
1 st effect	3.5 bar
2 nd effect	1.0 bar
3 rd effect	0.06 bar

Table 4 : Operating Conditions for the Triple Effect Evaporator

Variable	S.S Value
Liquid flowrate	
1 st effect	345.653 cm ³ /s
2 nd effect	286.527 cm ³ /s
3 rd effect	213.825 cm ³ /s
Vapor flowrate	
1 st effect	108.812 gms/s
2 nd effect	12.392 gms/s
3 rd effect	16.093 gms/s
Comp. of NaOH	
1 st effect	0.42
2 nd effect	0.424
3 rd effect	0.43

Table 5 : Steady State Predictions for the Triple Effect Evaporator

Figure 4: Current efficiencies for the five cathodic reactions as a function of total coulombs passed for the low voltage run. Cell voltage is 3.5 V. Towards the end of the batch reaction 5 (H₂ production) increases rapidly. MC is an abbreviation for "Million Coulombs".

Figure 5: Ionic concentrations in the catholyte recirculation tank as a function of total coulombs passed for the low voltage run. MC is an abbreviation for "Million Coulombs".

Figure 6: Off-gas composition from the catholyte recirculation tank as a function of total coulombs passed for the low voltage run. N₂ is the main component of the off-gas during the initial phase of the simulation while H₂ evolution becomes significant during the terminal phase. NH₃ and N₂O are the other major components of the gas phase. MC is an abbreviation for "Million Coulombs".

Figure 7: Total cell current as a function of total coulombs passed for the low voltage run. It decreases gradually during the course of the run because of decrease in the concentration of nitrates and nitrites.

Figure 8: Volumetric gas flowrate as a function of total coulombs passed for the low voltage run. As the run proceeds, the solution gets saturated and hence more and more gas is evolved. The rise in the gas flowrate at around 500,000 coulombs is due to an increase in H_2 evolution.

Figure 9: Current efficiencies for the five cathodic reactions as a function of total coulombs passed for the high voltage run. It can be seen that most of the current goes into production of H_2 at this high voltage. MC is an abbreviation for "Million Coulombs".

Figure 10: Ionic concentrations in the catholyte recirculation tank as a function of total coulombs passed for the high voltage run. MC is an abbreviation for "Million Coulombs".

Figure 11: Off-gas composition from the catholyte recirculation tank as a function of total coulombs passed for the high voltage run. H_2 is the main component of the off-gas throughout the run while NH_3 evolution is significant during the initial phase. MC is an abbreviation for "Million Coulombs".

Figure 12: Comparison of nitrate and nitrite concentrations in the catholyte recirculation tank as a function of time for the low and high voltage runs. The slope of the curve corresponds to the destruction rate. It can be seen that the destruction rate of nitrates and nitrites combined is greater at the higher voltage.

Figure 13: Destruction current vs. total current from the low voltage run. The peaks represent the current which maximizes the destruction of nitrates and nitrites at each point in time. The symbols "+" and "x" denote initial conditions of the low voltage and high voltage runs respectively. MC is an abbreviation for "Million Coulombs".

Figure 14: Destruction current efficiency vs. total current from the low voltage run. The circles ("o") denote the optimal operating currents at which the reactor should be operated in order to maximize the destruction of nitrates and nitrites while preventing unacceptable levels of H_2 generation at each point in time. The "x's" denote the position of peaks from Figure 13. The "*"s" denote the destruction efficiency at various times during the low voltage run. MC is an abbreviation for "Million Coulombs".

Figure 15: 3-D plot of I_{opt} as a function of NO_3^- and NO_2^- at two different destruction efficiencies. Each point on the surface grid represents one single-pass optimization run.

Figure 16: Typical Neural Network Model

Figure 17: Plot of NN prediction vs. training data. The closer the points are to the diagonal, the better the prediction. A total of 115 data points were used for training the network.

Figure 18: Plot of NN prediction vs. test data. The closer the points are to the diagonal, the better the prediction. A total of 55 data points were used to test the trained network.

Figure 19: Current efficiencies for the five cathodic reactions as a function of total coulombs passed for the optimization run. The NN mapping function is used to predict cell voltage/current during the run. Compared to Figure 4, there is hardly any production of H_2 , because the current associated with reaction 5 is negligible.

Figure 20: Off-gas composition from the catholyte recirculation tank as a function of total coulombs passed for the optimization run. N_2 and H_2 are the major components in the gas phase at the beginning of the run even though the current efficiency for reaction 5 is the lowest. This is because H_2 has the least solubility among NH_3 and N_2O . But in contrast to Figures 6 and 11, where the H_2 production increases towards the end, the optimization run produces significantly less H_2 .

Figure 21: Comparison of nitrate and nitrite concentrations as a function of time for the two batch runs and the optimization run. It can be seen that the overall destruction rate (rate of destruction of nitrate and nitrite combined) is greatest during the optimization run.

Figure 22: Comparison of cell current profile for the two batch runs and the optimization run. The optimal current follows an exponentially decreasing path.

SPEEDUP Dynamic Simulation

Plot of massfraction of NaOH in the 1st effect vs. time

Fig 23

SPEEDUP Dynamic Simulation

Plot of massfraction of NaOH in the 2nd effect vs. time

Fig 24

SPEEDUP Dynamic Simulation

Plot of massfraction of NaOH in 3rd effect vs. time

Fig 25