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A study of the production of glyoxylic acid by the electrochemical reduction of oxalic acid solutions

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An investigation has been made of the formation of glyoxylic acid by the electrochemical reduction of oxalic acid/sulphuric acid aqueous solutions at various temperatures and cathode potentials using lead electrodes.

It has been found that for a given quantity of electricity passed greater current efficiencies are obtained at higher electrode potentials and lower temperatures. The current efficiency decreased with increasing quantity of electricity passed.

A simple analysis for the process has been made in which glyoxylic acid is assumed to be reduced to glycollic acid. By incorporation of a variable factor f, to take into account electrochemical parameters for the two reactions, satisfactory predictions of the current efficiency have been obtained. The electrokinetic interpretation of the f-factor is also briefly discussed.

Nomenclature

C_A, C_B, C_C	Molar concentrations of species A, B, and C respectively	(mol cm^{-3})
C_{A_0}	Initial concentration of A	(mol cm^{-3})
F	Faraday = 96 500 Coulombs	(As)
f	Current efficiency correction factor	($= i_A/i_B$)
I	Cell current	(A)
i_A, i_B	Current densities for reactions A $\longrightarrow$ B and B $\longrightarrow$ C respectively	(A cm^{-2})
i_{0_A}, i_{0_B}	Exchange current densities for reactions A$\rightleftharpoons$B and B$\rightleftharpoons$C respectively	(A cm^{-2})
Q	Quantity of electricity passed ($= It$)	(As)
t	Time	(s)
V	Catholyte volume	(cm^3)
α_A, α_B	Transfer coefficients for reactions A$\longrightarrow$B and B$\longrightarrow$C respectively	
η_A, η_B	Overpotentials associated with reactions A$\longrightarrow$B and B$\longrightarrow$C respectively	(V)
η	Cathode overpotential	(V)
γ	Current efficiency for reaction A$\longrightarrow$B	

1. Introduction

The formation of glyoxylic acid by the electrochemical reduction of aqueous oxalic acid solutions has been investigated by many workers. The earliest references appear to be to a patent by Royer [1] and a study by Tafel and Friedrichs [2]. More comprehensive studies were made by Baur [3] and in particular by Mohrschulz [4] who patented a process which employed a graphite cathode and an oxalic acid/sulphuric acid mixture in ethanol and water. A yield of 60% by

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weight at a current density of 0·02 A cm^{-2} at 5–10°C was reported. Operation with lead and mercury cathodes gave yields of 79% and 82·5% respectively. An almost identical process to Mohrschultz's was described by Nakata [5], who used a mercury cathode and claimed a 90% yield.

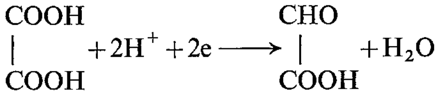
Much of the more recent work has been concerned with the mechanism of oxalic acid reduction. Listopadov and Antropov [6] used a variety of cathodes including lead, cadmium, thallium amalgam and mercury and considered that the rate determining step was the reduction of hydrogen ions activated in the double layer. Contrary opinions were held by Florianovich and Frumkin [7] and Florianovich [8] who proposed that the slow step was the addition of an electron to an oxalic acid molecule. Smialowski and Jarmolowicz [9] reported investigations with a lead cathode and stated that the reduction of oxalic acid was dependent on the hydrogen overpotential, the yield of glyoxylic acid being raised by the addition of sodium sulphate to the electrolyte to increase the hydrogen overpotential. Further studies on lead cathodes [10] indicated a two-electron mechanism for the process, and in neutral electrolytes with a cadmium cathode [11] a two-electron mechanism involving an oxalic acid molecule was also postulated.

A good deal has been mentioned about side reactions accompanying the formation of glyoxylic acid. Reduction to glycollic acid appears to be a major source of inefficiency especially at temperatures about 15°C, and formaldehyde, tartaric acid and dioxytartaric acid formation have all been reported. A Japanese patent [12] claimed a reduction in side reactions by using a cation exchange membrane as diaphragm, ostensibly to have a constant hydrogen ion concentration in the catholyte. The concentration of hydrogen ions appeared to have little influence on the glyoxylic acid current efficiency, however, which was in the region of 55–70%.

Despite the above information, little detail was available for the purposes of process evaluation. This paper reports an investigation using lead cathodes to attempt to find the best operating conditions, namely temperature and cathode potential, for the batch production of glyoxylic acid. The results are interpreted by a simple model for the process in which glycollic acid formation is considered to be the only side-reaction.

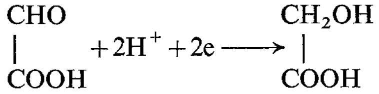
2. Analysis

Oxalic acid is reduced to glyoxylic acid by a two-electron process



$$\begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix} + 2H^+ + 2e \longrightarrow \begin{matrix}\mathrm{CHO}\\ |\\ \mathrm{COOH}\end{matrix} + H_2O \quad \text{(I)}$$

The production of glycollic acid then takes place by the further two-electron process:



$$\begin{matrix}\mathrm{CHO}\\ |\\ \mathrm{COOH}\end{matrix} + 2H^+ + 2e \longrightarrow \begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{COOH}\end{matrix} \quad \text{(II)}$$

The literature [13] reveals very little thermodynamic data on reactions (I) and (II), but estimates [14] of the free energy changes for both reactions are small (<20kJ mol^{-1}) so that at a given cathode potential both reactions probably occur simultaneously.

To model the system, other possible side reactions together with hydrogen evolution are ignored and for simplicity the two reactions will be denoted by the scheme

$$A \xrightarrow{2e} B \xrightarrow{2e} C \qquad \text{(III)}$$

where A, B, and C denote oxalic, glyoxylic and glycollic acids respectively.

In an electrolyte cell having a cathode compartment of volume V and assumed to be operating at a constant cathode potential and current, the rate of production of B is given by

$$\frac{V\mathrm{d}C_B}{\mathrm{d}t} = \frac{I\gamma}{2F} - \frac{I}{2F}(1-\gamma)$$

$$= (2\gamma-1)\frac{I}{2F} \qquad (1)$$

Equation 1 assumes that mass transfer effects are absent and sufficient hydrogen ions are available from the indifferent electrolyte. γ is the current efficiency of the reaction A⟶B, and $1-\gamma$ of the reaction B⟶C.

If both reactions have the same exchange current densities, overpotential relationships and are solely charge transfer dependent, then the current efficiency γ will be proportional to the concentration of A and B at the electrode and

$$\frac{\gamma}{1-\gamma}=\frac{C_{\mathrm{A}}}{C_{\mathrm{B}}} \tag{2}$$

The above assumptions are obviously highly idealized, so that a factor f is incorporated into Equation 2 which is then re-defined as

$$\frac{\gamma}{1-\gamma}=f\frac{C_{\mathrm{A}}}{C_{\mathrm{B}}} \tag{3}$$

f incorporates the exchange currents and overpotentials and will be discussed more fully later. At a fixed total current the sum of the combined concentrations of C_{A} and C_{B} at the electrode surface must be equal to $C_{\mathrm{A_0}}$, the initial concentration of A so that

$$\frac{\gamma}{1-\gamma}=f\left(\frac{C_{\mathrm{A_0}}-C_{\mathrm{B}}}{C_{\mathrm{B}}}\right) \tag{4}$$

Incorporation of Equation 4 into Equation 1 allows expression of the variation of C_{B} with time to be expressed by the differential equation

$$\frac{V\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t}=\frac{I}{2F}\left\{\frac{fC_{\mathrm{A_0}}-(1+f)C_{\mathrm{B}}}{fC_{\mathrm{A_0}}+(1-f)C_{\mathrm{B}}}\right\} \tag{5}$$

Integration of Equation 6 enables the concentration of B to be related to the quantity of electricity passed, Q, by

$$\frac{Q}{2VF}=\frac{2fC_{\mathrm{A_0}}}{(1+f)^2}\ln\frac{fC_{\mathrm{A_0}}}{fC_{\mathrm{A_0}}-(1+f)C_{\mathrm{B}}}-\frac{(1-f)}{(1+f)}C_{\mathrm{B}} \tag{6}$$

It is important to note that Equation 6 will only be an approximation for the bulk electrolyte where the total concentrations of each species are related by

$$C_{\mathrm{A_0}}=C_{\mathrm{A}}+C_{\mathrm{B}}+C_{\mathrm{C}} \tag{7}$$

However, if f is substantially constant at any given potential and temperature and with experimental conditions such that $C_{\mathrm{A_0}}$ is large and conversion through to C small, Equation 6 should give a useful prediction of the extent of the reaction to B.

3. Experimental

The cell, shown in Fig. 1, was made from two pyrex glass tubes separated by a sintered glass disc fused in between them to act as a diaphragm. The larger (cathode) compartment had a drainage tap and two side tubes were attached to give provision for a Luggin capillary and stirrer. The anode compartment also had a drainage tap and a side tube for a thermometer. The electrodes were made from AnalaR lead foil and were circular pieces 53 mm in diameter with connecting strips to allow for electrical connection. These electrodes were cemented with Araldite to neoprene rubber stoppers which fitted in the tubes. The Luggin capillary was connected to a saturated calomel electrode via a salt bridge. The stirrer was made from glass rod and was connected to a vertical variable speed electric motor.

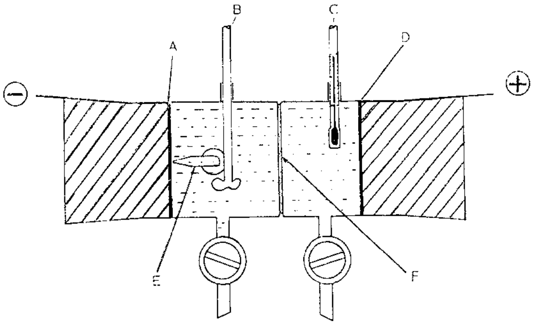


Fig. 1. Electrolyte Cell (A – lead cathode, B – Stirrer, C – mercury in glass thermometer, D – lead anode, E – Luggin capillary, F – sintered glass diaphragm).

Electrical supply was from a Coutant LA 200.2 stabilized power unit with a maximum current of 2 A. Cell current was measured using a Model 8 Mark 4 Avometer and the electrode potential with an EIL electronic voltmeter model 23A. Temperatures of operation other than ambient were achieved by immersing the cell in a perspex water bath which could be thermostatically controlled.

4. Procedure

Electrolyte solutions were made up using AnalaR oxalic and sulphuric acids and distilled water. The same solutions were used for anolyte and catholyte. Saturated solutions of oxalic acid in 1 M sulphuric acid were made up at ambient temperature (20°C). The resulting solution was also used in experiments at 45°C. For operation at low temperature (6°C), the electrolyte was cooled to 6°C and allowed to stand and the supernatant liquid used in the cell. Standardization was by means of potassium permanganate and the actual concentrations used were 0·68 M at 20°C and 45°C, and 0·33 M at 6°C.

Both electrodes were first degreased with carbon tetrachloride, then treated with 30% nitric acid followed by washes with water and ethanol. Fresh electrodes were used for all polarization data determinations and production runs.

Steady state polarization data were obtained by measuring the cell current at 50 mV potential increments until hydrogen was copiously evolved. Before each measurement two minutes were allowed for the attainment of steady state. The influence of mass transfer on polarization was investigated by runs in which the electrolyte was stirred and unstirred, and ones in which 1 M sulphuric acid alone was the electrolyte.

For the production runs, the cell was maintained for periods of time up to eight hours at constant cathode potentials in the range −1·15 to 1·40 V with respect to the saturated calomel electrode. Periodically samples of catholyte were withdrawn using a 0·2 ml micropipette and analysed. The glyoxylic acid was determined spectrophotometrically using the formation of a blue colour produced by 2,3,4-trihydroxybenzoic acid in the presence of sulphuric acid under carefully controlled conditions [14]. The absorptions produced were compared with those from a set of standard glyoxylic acid solutions in oxalic acid. Since the major source of current inefficiency attending this process has been reported as glycollic acid formation [12], determinations of this compound or of any other side products were not made. The number of coulombs passed were calculated from current values measured over one-minute intervals. These quantities of electricity passed were corrected approximately by using the polarization curves to estimate the current associated with hydrogen formation. Visual evidence indicated that the above procedure was not too unreasonable. The rates of gas evolution at a given cathode potential appeared to be the same both in the presence or absence of oxalic acid. The actual quantity of hydrogen produced was not measured due to the difficulty of gas collection in the cell during operation. Experimental procedures were the same for all three operational temperatures mentioned above.

5. Results and discussion

Fig. 2 presents typical polarization curves at 20°C for 0·68 M oxalic acid–1 M sulphuric acid for both stagnant and stirred electrolyte together with data for 1 M sulphuric acid under the same conditions. For the oxalic acid it can be seen that the relationship between the logarithm of the current density and the cathode potential is linear over much of the range, and although some influence of mass transfer is demonstrated, this appears small. There are significant differences in current densities between the oxalic and sulphuric electrolytes at any particular potential. Visual observation detected bubbles of hydrogen around −1·1 V with oxalic acid but a significant rate of discharge did not occur until −1·4 V. The slopes of the Tafel portions of the corresponding oxalic and sulphuric plots show a slight but perceptible

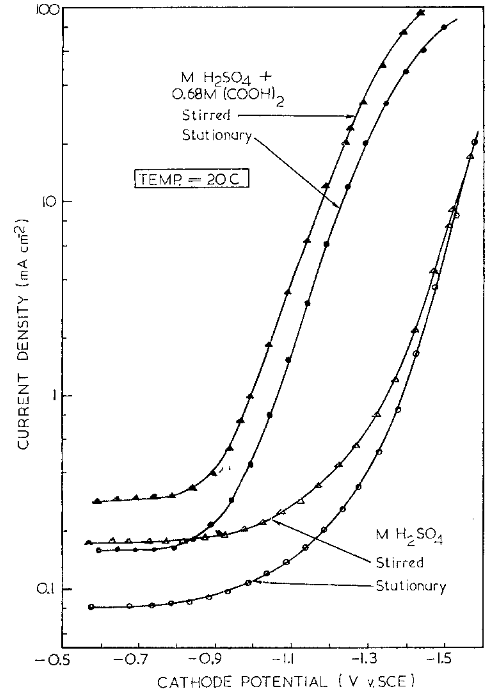


Fig. 2. Cathode polarization data at 20°C for oxalic/sulphuric and sulphuric acids.

difference, possibly due to adsorbed oxalic acid molecules, although no evidence exists for such a supposition.

Around $-1{\cdot}3$ V the slope of the oxalic acid curve decreases, corresponding to the start of quantitative hydrogen evolution. Polarization curves for stirred catholyte at 6°C and 45°C are compared with the corresponding plot at 20°C in Fig. 3. At a given potential there is approximately a tenfold increase in current density on raising

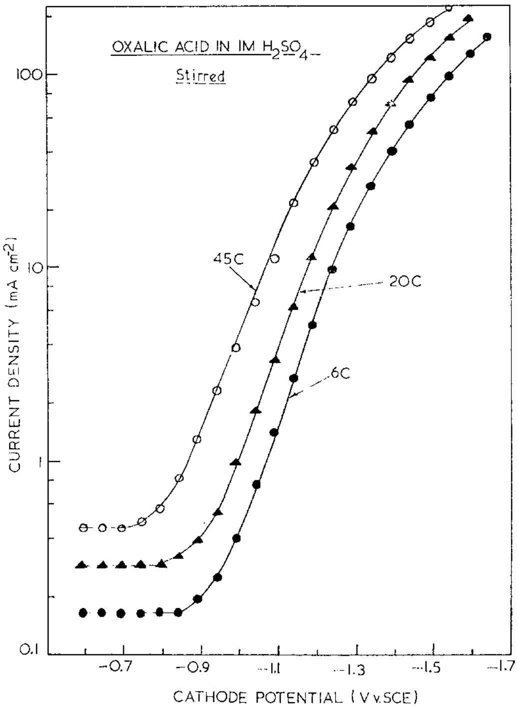


Fig. 3. Comparison of polarization data for oxalic acid at 6°C, 20°C and 45°C.

the temperature from 6°C to 45°C. Such an increase is far greater than could be expected by the enhancement of mass transfer and is in accord with observations made above on the minor role of mass transfer. Little differences in Tafel slopes at the three temperatures are discernable. There is a slight increase (about 15%) in slope from 6°C to 45°C at cathode potentials below about $-1{\cdot}3$ V. At potentials above $-1{\cdot}3$ V all the curves show a similar deviation from Tafel behaviour.

Data from the production runs are given in Figs. 4, 5 and 6 for 6°C, 20°C, and 45°C respectively, the points being current efficiencies calculated from catholyte sample compositions. In order to be consistent with Q and γ as defined in the analysis, both axes of all the graphs have been adjusted by subtracting the current associated with hydrogen formation from the total measured current. For example, from Fig. 2 the current density at $-1{\cdot}2$ V is about 0·4 mA cm^{-2} without the organic acid and 15 mA cm^{-2} with

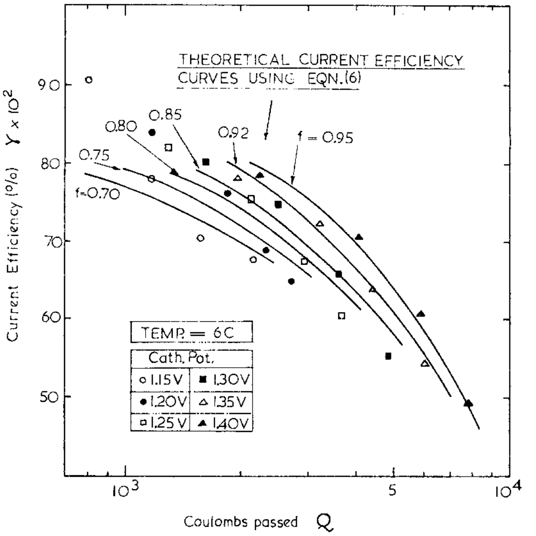


Fig. 4. Current efficiency versus coulombs at 6°C for various cathode potentials, compared with predictions using various f values in Equation 6.

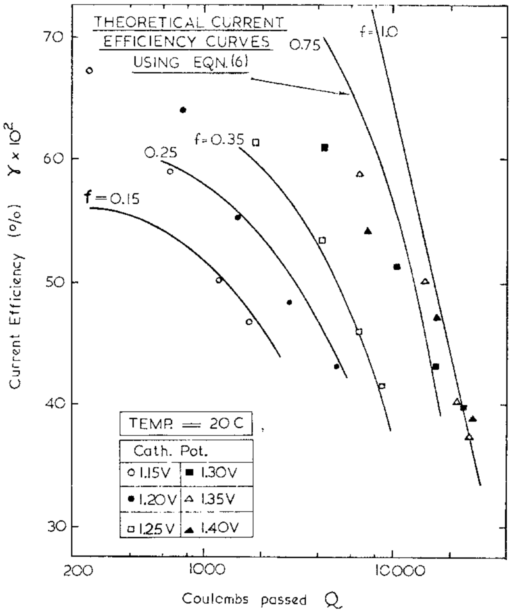


Fig. 5. Current efficiency versus coulombs at 20°C for various cathode potentials, compared with predictions using various f values in Equation 6.

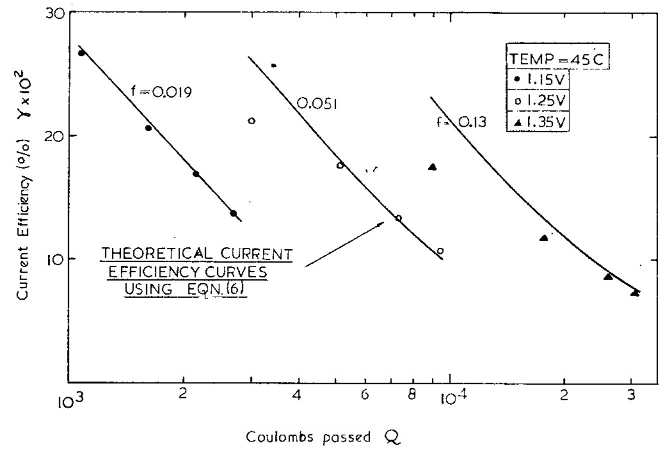


Fig. 6. Current efficiency versus coulombs at 45°C for various cathode potentials, compared with predictions using various f values in Equation 6.

the organic acid. The current efficiency for hydrogen production is thus about 3%. Under these conditions γ (the plotted current efficiency) is equal to the true current efficiency divided by 0·97 and the plotted Q is 0·97 of the total measured current. At higher potentials it will be seen that γ is even closer in value to the true current efficiency. It can be seen that for a given quantity of electricity passed, production of glyoxylic acid is most efficient at low temperatures (6°C), and at the higher electrode potentials (up to $-1{\cdot}4$ V). At 6°C and 20°C the current efficiencies are not much altered by potential variation between $-1{\cdot}3$ V and $-1{\cdot}4$ V. The series of lines accompanying the experimental points are current efficiency/coulombs curves predicted from Equation 6 for various values of the factor f. For a given temperature and potential the experimental points appear to lie reasonably close to a constant f curve except for those points at lower coulombs and for data for $-1{\cdot}3$ V to $-1{\cdot}4$ V at 20°C where a value of f, close to unity, embraces much of the data. The divergences of the curves from experiment at low coulombs correspond to stages in the production runs where the current fluctuated with time. At the later stages the current stayed appreciably constant and nearly fulfilled the assumption of constant current inherent in Equation 6. Overall higher values of the factor f are required to approximate the data as the electrode potential is increased up to $-1{\cdot}4$ V and the temperature is decreased to 6°C. Values of f which best approximate the data are plotted as log f against cathode potential in Fig. 7. Two approximate straight lines of equal slope occur for 20°C and 45°C, but at potentials close to $-1{\cdot}35$ V the 20°C line changes slope and approximately coincides with that for the 6°C data which is approximately a straight line but of much smaller gradient.

A number of observations of a somewhat tentative nature can be made of the significance

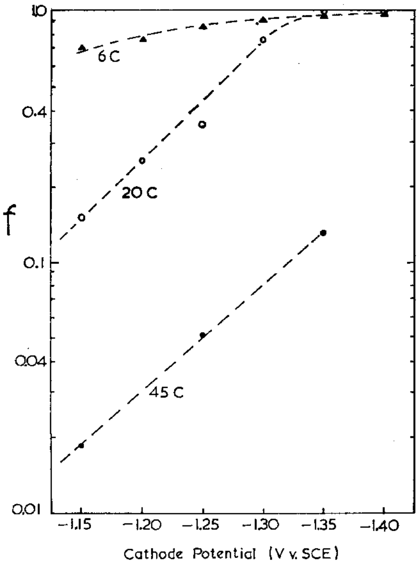


Fig. 7. Plot of f factors versus cathode potential at 6°C, 20°C and 45°C.

of f by expressing it in terms of exchange currents and overpotentials by the relation

$$f=\frac{i_{\mathrm{A}}}{i_{\mathrm{B}}}=\frac{i_{0\mathrm{A}}}{i_{0\mathrm{B}}}\cdot\frac{e^{-2\alpha_{\mathrm{A}}F\eta_{\mathrm{A}}/RT}}{e^{-2\alpha_{\mathrm{B}}F\eta_{\mathrm{B}}/RT}} \tag{8}$$

If the reactions are both subject to equal overpotential η, then

$$\log f = 2{\cdot}303\log\frac{i_{0\mathrm{A}}}{i_{0\mathrm{B}}}+\frac{4{\cdot}606\,(\alpha_{\mathrm{B}}-\alpha_{\mathrm{A}})}{RT}F\eta \tag{9}$$

If Equation 9 has any validity then $(i_{0\mathrm{A}}/i_{0\mathrm{B}})$ increases with decreasing temperature which is feasible and the values of α_{A} and α_{B} change markedly between 6°C and 20°C, except at high potentials which suggests that the rate determining step in the electrode reaction is substantially independent of temperature. At 45°C, this behaviour is not seen although the polarization data are similar. There is, however, insufficient fundamental data for further discussion and evaluation of the above postulates. Nevertheless, despite the lack of basic information concerning the reaction and in particular the formation of glycollic acid, the experimental data for the f factor, given in Fig. 7, together with the polarization data in Figs. 2 and 3 and Equation 6 should provide useful design information for this process. Indeed the only other requirements for batch cell evaluation are knowledge of the anodic polarization data and electrolyte ohmic resistance. The optimum electrode spacings for a given production rate would then be established by material and energy balances round the unit.

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