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Design of a slurry electrode reactor system*

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A 'slurry electrode' is a suspension of particles with large double-layer capacity, such as activated carbon, in an electrolyte solution. These particles transfer charge from an electrochemical cell to an external reactor, where a substance is oxidized or reduced, and are recharged in the cell. The circulated particles must be separated from the solution of the reaction product. Various aspects of a system consisting of an electrochemical cell, a reactor, and a sedimentation vessel for separation are discussed.

For the reactor the following aspects are considered: rate of influx, residence time in the reactor, size of the reactor, concentration of particles in the suspension, rate and degree of conversion, flow rate of particles and single or cascade reactors.

The transport of charge by the particles determines the current flowing in the electrochemical cell as well as the rate of conversion, or, for a given degree of conversion, the maximum initial concentration. Specific, and yet unsolved, problems of the cell are examined. These result from the contact between the particles and the feeder electrode, of which either the duration is too short or the resistance is too great.

Possible application of a slurry electrode working in steady state conditions is considered.

List of symbols

A	feeder electrode area (m^2)
A_R	total area of particles in reactor (m^2)
c	concentration ($mol\,dm^{-3}$)
c_{in}	inlet concentration ($mol\,dm^{-3}$)
c_{ex}	outlet concentration ($mol\,dm^{-3}$)
C_p	capacity of a particle ($A\,s\,V^{-1}$)
C^*	specific capacity ($A\,s\,V^{-1}\,g^{-1}$)
D	diffusion coefficient ($m^2\,s^{-1}$)
ΔE	potential difference (V)
F	Faraday constant ($A\,s\,mol^{-1}$)
g	gravitational constant ($m\,s^{-2}$)
i	current (A)
j	current density ($A\,m^{-2}$)
k	rate constant (s)
m_p	mass of a particle (g)
n	amount of substance (mol)
r	radial coordinate (m)
r_p	radius of a particle (m)
R_c	contact resistance (Ω)
R_E	resistance of external electrolyte (Ω)
R_p	resistance of pore electrolyte (Ω)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
u_p	velocity of particles ($m\,s^{-1}$)
u_{liq}	velocity of liquid flow ($m\,s^{-1}$)
u_{sed}	sedimentation velocity ($m\,s^{-1}$)
v_{in}	inlet flow rate ($dm^3\,s^{-1}$)
v_p	flow rate of particles ($dm^3\,s^{-1}$)
v_{sp}	flow rate of suspension ($dm^3\,s^{-1}$)
V_R	reactor volume (m^3)
z	cell reaction number

Greek letters

β	mass transfer coefficient ($m\,s^{-1}$)
γ	liquid fraction in suspension
δ	diffusion layer thickness = D/β (m)
η	viscosity of liquid ($kg\,m^{-1}\,s^{-1}$)
κ_{liq}	conductivity of liquid ($S\,m^{-1}$)
κ_{sol}	conductivity of solid matter ($S\,m^{-1}$)
ξ	degree of conversion
ρ_{dry}	density of dry particle ($g\,cm^{-3}$)
ρ_{liq}	density of liquid ($g\,cm^{-3}$)
ρ_p	density of flooded particle ($g\,cm^{-3}$)
ρ_{sol}	density of massive solid ($g\,cm^{-3}$)
τ	residence time (s)
τ_c	charging time constant (s)

1. Introduction

The term 'slurry electrode' refers to a suspension of particles in an electrolyte solution. The suspension accepts charge by contacting a 'feeder' electrode; it then carries the charge to a reactor where the charge is transferred to a substrate to be oxidized or reduced. It has been shown earlier [1] that particles of acti-

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vated carbon, due to their large double-layer capacity, are suitable for this purpose. In particular, a process was developed applying slurry electrodes for machining solid workpieces by metal oxidation [2, 3].

In this paper cases are considered in which the substance to be oxidized/reduced is present in dissolved form, for example, a toxic substance in waste water. The applicability of a slurry electrode has been demonstrated for cyanide removal from waste water by oxidation [4].

Figure 1 shows a diagram of a reactor system with a slurry electrode. The particles are separated from the liquid by sedimentation in this scheme. However, no major modification of the following considerations is necessary if a different separation technique is applied.

The solution to be treated ('in') and the charged particles (from 'E') are introduced into the reactor 'R' where the particles are held in suspension by stirring. From 'R' the suspension is pumped (pump 'P') into a sedimentation chamber 'S' where the solution and the particles are separated. The solution then flows out of the system ('ex') while the particles are transported (e.g., by sliding downwards by gravity) to the electrochemical cell 'E'. Here, the voltage 'U' between the feeder electrode and the counter electrode serves to recharge the particles. In order to avoid short-circuiting, the particles must not contact the counter electrode. This contact can be prevented by placing a diaphragm or membrane between the feeder and counter electrodes, or by sedimentation.

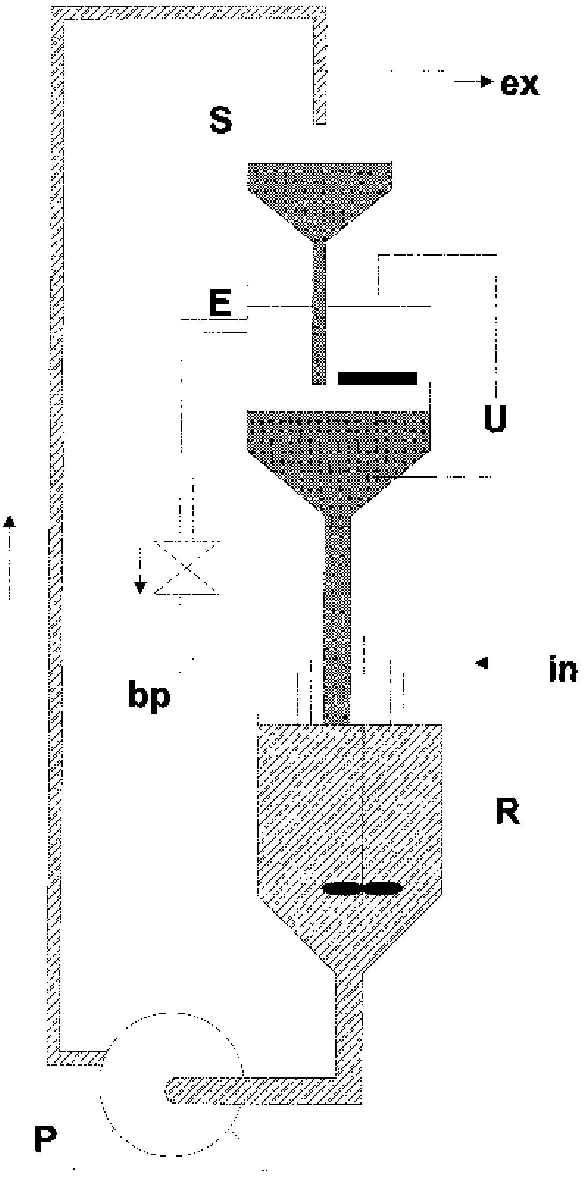

Fig. 1. Schematic diagram of the device. (S) sedimentation chamber; (E) electrochemical cell; (R) reactor; (P) pump; (U) cell voltage; (bp) bypass; (in) inlet; (ex) outlet; (light hatch) suspension; (dark hatch) sedimented bed.

2. Reactor

A fraction γ of the reactor volume is occupied by the solution while a fraction $1-\gamma$ is occupied by particles. Under steady-state conditions the flow rates are correlated as follows:

$$v_{\mathrm{in}} = \gamma\, v_{\mathrm{sp}} \quad \text{and} \quad v_{\mathrm{p}} = (1-\gamma)\, v_{\mathrm{sp}} \tag{1}$$

The residence time of the solution in the reactor is given by

$$\tau = \frac{V_{\mathrm{R}}}{v_{\mathrm{sp}}} = \frac{\gamma V_{\mathrm{R}}}{v_{\mathrm{in}}} \tag{2}$$

The concentration c_{ex} of the substance to be treated in the liquid part of the suspension and also in the effluent is obtained by balancing the amounts of substance introduced via the inlet, reacting in the reactor, and discarded with the effluent:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{v_{\mathrm{in}}}{\gamma V_{\mathrm{R}}} c_{\mathrm{in}} - k\, c_{\mathrm{ex}} - \frac{\gamma v_{\mathrm{sp}}}{\gamma V_{\mathrm{R}}} c_{\mathrm{ex}} = 0 \tag{3}$$

Hence, the degree of conversion is given by

$$\xi = 1 - \frac{c_{\mathrm{ex}}}{c_{\mathrm{in}}} \tag{4}$$

The rate constant k results from the rate-determining step which may be either the heterogeneous charge transfer or mass transport. Assuming that the potential is sufficiently positive or negative, respectively, only mass transport to the external surface of the particles must be considered regardless of whether easily accessible macro pores are involved. Mass transport is most efficient if the particles are held in suspension and prevented from sedimentation. The rate constant can then be calculated from the mass transfer coefficient, the area of the surface on which reaction takes place, and the volume from which the reactant is supplied. If spherical particles are applied, then the area and the volume can be expressed by the particle radius:

$$k = \frac{A_{\mathrm{R}}\beta}{\gamma V_{\mathrm{R}}} = 3\frac{1-\gamma}{\gamma}\,\frac{D}{r_{\mathrm{p}}\delta} \tag{5}$$

Spherical particles of activated carbon display nearly frictionless gliding and little clogging. This accounts for the satisfactory behaviour during pumping as well

Table 1. Properties of spherical activated carbon particles and other parameters entering in and resulting from Equation 5

Pore volume	57%
Density of solid matter, ρ_{sol}	$2\,\text{g cm}^{-3}$
Density of dry particle, ρ_{dry}	$0.86\,\text{g cm}^{-3}$
Density of H_2O-flooded particle, ρ_{P}	$1.43\,\text{g cm}^{-3}$
Particle radius, r_{P}	0.25 mm
Specific capacity of particles, C^*	$100\,\text{A s V}^{-1}\,\text{g}^{-1}$
Density of solution, ρ_{liq}	$1.0\,\text{g cm}^{-3}$
Viscosity of liquid, η	$0.9\,\text{g m}^{-1}\,\text{s}^{-1}$
Gravitational constant, g	$9.8\,\text{m s}^{-2}$
Sedimentation velocity, u_{sed}	$6.5\,\text{cm s}^{-1}$
Liquid flow velocity, u_{liq}	0.65 to $6.5\,\text{cm s}^{-1}$
Reynolds number, *Re*	3.6 to 36
Schmidt number, *Sc*	900
Sherwood number, *Sh*	5 to 43
Mass transfer coefficient, β	3 to $9\,\mu\text{m s}^{-1}$
Diffusion coefficient of substrate, D	$1 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$
Diffusion layer thickness, δ	12 to 33 μm
Rate constant, k	0.09 to $0.25\,\text{s}^{-1}$

as during sedimentation and other separation techniques. Some properties of such material (BAC.MP, supplier Kureha Chemical Industry, Tokyo/Japan) are listed in Table 1.

The velocity of sedimentation is calculated from the properties of the particles and of the liquid, for which the data of pure water have been applied, by balancing gravitational and frictional forces:

$$u_{\text{sed}} = \frac{\frac{4}{3}\pi r_{\text{p}}^3(\rho_{\text{p}} - \rho_{\text{liq}})g}{6\pi\,\eta\,r_{\text{p}}} \tag{6}$$

The velocity of the liquid relative to the particles, required to prevent sedimentation, is estimated to be lower than u_{sed} but at least 10% of u_{sed}. The Sherwood number is calculated from the relation [5]

$$Sh = 2 + 0.23\ (Re\ Sc)^{0.5} \tag{7}$$

In calculating the rate constant a value of $\gamma = 0.8$ is assumed for the fraction of liquid in the suspension, because the volume fraction of particles must not considerably exceed 25%, otherwise clogging and unwanted settling will occur [6].

In a trial experiment, Fe^{3+} was reduced under conditions similar to those assumed in the above consideration. A rate constant of $k = 0.06\,\text{s}^{-1}$ and strictly first order kinetics throughout almost the entire experiment were obtained. The electron transfer reaction at the interface [7] is by orders of magnitude faster than the observed rate. Also, were the heterogeneous reaction rate-determining, the rate constant would decrease upon the consumption of charge from the particles because of the resulting positive shift of the particles' potential, thus abolishing first order kinetics. Hence, transport kinetics must have been controlling in these experiments. The slight discrepancy of the experimental and estimated (Table 1) rate constants is partly due to the diffusion coefficient of Fe^{3+} being somewhat lower ($0.6 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$) than the data underlying the above estimate. Besides, hydrodynamic conditions in these experiments had not been optimized.

The extent to which a substance can be converted in the reactor depends on the residence time of the solution in the reactor (Equation 2). If a residence time of $\tau = 40\,\text{s}$ is chosen [8], the conversion is merely 78 to 91% complete (Equation 4). Generally, a larger degree of conversion is required. Employing a cascade of reactors (two or three) may in such cases be more economical than applying a longer residence time and dealing with a considerably larger reactor volume requiring a correspondingly larger mass of particles and more expensive stirring.

In further considerations an influent rate of $v_{\text{in}} = 1\,\text{m}^3\,\text{h}^{-1} = 0.28\,\text{dm}^3\,\text{s}^{-1}$ will be assumed. According to Equation 2, the reactor volume must then be $V_{\text{R}} = 14\,\text{dm}^3$. The flow rate of particles is $0.056\,\text{dm}^3\,\text{s}^{-1}$ corresponding to a throughout of particles of about $10^6\,\text{s}^{-1}$.

3. Conveyance of liquid, particles and charge

Attention must be paid to the balance of electrolyte in the passage of liquid and the circulation of particles. The flow rate of particles, from 'S' to 'E' and from 'E' to 'R' is $v_{\text{P}} = 0.07\,\text{dm}^3\text{s}^{-1}$. The sedimented particles, regarded as close packed spheres, still contain about 26% of liquid, apart from the liquid in the pores which is neglected here and will be considered for a particular case below. In experiments using a conveyor spiral for transporting particles from the electrolytic cell to the reactor, a liquid portion of 35% by volume accompanied the particles. Therefore, at least $0.025\,\text{dm}^3\,\text{s}^{-1}$ of the treated solution is transferred into the electrolytic cell. A corresponding amount of electrolyte is also transferred from the cell into the reactor, the bypass 'bp' of Fig. 1 being closed.

The effluent will contain some electrolyte, the amount of which depends on the electrolyte content of the influent, on the transfer of electrolyte from 'E' to 'R', and on the consumption or production of ions in the particular process. In general, the influent will not contain an electrolyte concentration as large as that required in the electrolytic cell. Supply of electrolyte to the cell will then be necessary to maintain the concentration.

The amount of charge that can be transported by the particles determines the maximum concentration of the substrate to be treated in the influent if the degree of conversion (see Equation 4) is to be fully exploited. Further it determines the charging current in the electrochemical cell. This amount results from the specific charge capacity, from the difference between the potentials of the charged particles and the particles leaving the reactor, and from the rate of particle transport:

$$i = v_{\text{P}}\ \rho_{\text{sol}} C^* \Delta E \tag{8}$$

A typical value of the specific capacity is given in Table 1 [9]. The available range of potentials is approximately 1 V. The potential actually depends on the pH value, for example, in acid solutions it ranges from −0.1 to +0.9 V vs SHE. The potential at which the oxidation (reduction) takes place must be located between these limits, with sufficient distance to the positive (negative) limit. Taking $\triangle E = 0.5\,\mathrm{V}$, a current of 2000 to 3000 A is calculated. The upper limit of the equivalent concentration of the substrate in the influent results from Faraday's law

$$c_{\mathrm{in}} = \frac{i}{zFv_{\mathrm{in}}\xi} \tag{9}$$

to be $zc_{\mathrm{in}} = 0.08$ to $0.15\,\mathrm{mol\,dm^{-3}}$. If the concentration exceeds this limit, the maximum attainable degree of conversion is not reached, at least not in the first chamber of a cascade system.

4. Sedimentation chamber

The construction of the sedimentation chamber 'S' is not discussed in detail. It raises no major problems because the particles exhibit a satisfactory sedimentation behaviour. Introduction of the suspension at some intermediate position in a sufficiently high tube will allow for a clear effluent. Particularly after applying a new charge of carbon material, the effluent will contain a black colloidal dust resulting from abrasion.

5. Electrochemical cell

5.1. *General construction of cell*

The construction of the electrochemical cell 'E' is much more critical because the entire charge necessary for the conversion of the substrate must be transferred to the particles while they are present in the cell at a suitable position.

As long as the transfer of some electrolyte, accompanying the particles, from the electrolytic cell into the reactor will not cause problems, the electrolyte and the geometry of the cell can be chosen in order to establish favourable conditions in the cell. Since merely negligible amounts of the substrate are transferred into the cell, an undivided cell can be used in most cases, if the particles are prevented from contacting the counter electrode.

A cell in which the particles were charged by flowing the suspension past the feeder electrode [2, 3] proved useful for the purpose of etching metals, particularly for the etching of printed circuit boards. A comparatively large electrode area is permissible due to the high value of the product. Charging of suspended particles at a rotating feeder electrode turned out to be insufficient for carrying out homogeneous chemical reactions [10] due to the small amount of charge transferred during a single encounter with the electrode. This drawback results from the short duration of the contact, which was found to be about 5 to 10 μs when the suspension was sprayed onto the feeder electrode at a relative velocity of about $1\,\mathrm{m\,s^{-1}}$ [11]. More than 10^4 encounters would be necessary to charge the particle. Lower impact velocities, technically more easily realizable, are inefficient, because the contact resistance increases more rapidly than the duration of the contact:

$$R_{\mathrm{c}} \sim u_{\mathrm{p}}^{-0.8} \tag{10}$$

$$\tau_{\mathrm{c}} \sim u_{\mathrm{p}}^{-0.2} \tag{11}$$

It is therefore more reasonable to keep the particles in a position where charging can take place until complete. The design of a corresponding electrochemical cell may resemble that shown in Fig. 1: Partly discharged particles are replenished to a bed of particles on the feeder electrode, while freshly charged particles drop off. The maximum current density or the minimum electrode area is determined by the adjustment of the duration of the contact and the time needed for charging.

5.2. *Charging of a layer of particles*

The time required for charging a particle, exhibiting a capacity of about $C_{\mathrm{P}} = 0.0056\,\mathrm{F}$, is determined by the resistance of the transfer of electrons between the feeder electrode and the solid particle, and by the resistance of the exchange of ions with the external electrolyte. Although the former resistance causes particular problems (see below), it is neglected in the following considerations.

The effective electrolyte resistance consists of contributions, in series, by the external and by the pore electrolyte. The pore resistance can be estimated from a simple geometric model. Assuming a porosity of 57% and cylindrical pores pointing to the centre of the sphere, almost 90% of the particle's volume is included when integrating between $r = r_{\mathrm{p}}$ and $r = 0.5r_{\mathrm{p}}$:

$$R_{\mathrm{p}} = (4\pi r_{\mathrm{p}}\kappa_{\mathrm{liq}}0.57)^{-1} \tag{12}$$

The external electrolyte resistance, applying to a single sphere, between the upper surface of the bed (facing the counter electrode) and the plane comprising the centres of the top layer (closest packing), is approximately given by:

$$R_E \approx (\kappa_{\mathrm{liq}}r_{\mathrm{p}})^{-1} \tag{13}$$

Taking $r_{\mathrm{p}} = 0.25\,\mathrm{mm}$ and $\kappa_{\mathrm{liq}} = 50\,\mathrm{S\,m^{-1}}$ (approximately corresponding to the conductivity of 10% aqueous sulfuric acid or sodium hydroxide solution), the values determined from these equations are $R_{\mathrm{p}} \approx 11\,\Omega$, $R_{\mathrm{E}} \approx 80\,\Omega$, and $\tau_{\mathrm{c}} = 0.5\,\mathrm{s}$*.

Due to the resistance R_{E}, a potential drop will develop across the electrolyte adjacent to the particle. To avoid potentials beyond the limit where faradaic

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* A charging time constant of somewhat less than one second has also been observed experimentally upon clamping a particle between two connecting wires thus keeping the contact resistance low [12]. The resistance of the external electrolyte is considerably smaller under these conditions [11] where the particle is not embedded in a layer of other particles. The actual pore electrolyte resistance may be somewhat larger than estimated because the conductivity in the pores is somewhat smaller due to the narrowness of the pores.

processes occur, the current must be restricted to approximately 2 mA per particle. Charging then requires 1.5 s. If no time is required for replacing a given batch of particles, then 1.5×10^6 particles must be charged simultaneously. A feeder electrode area of $0.3\,\mathrm{m}^2$ is required. Since the current (for $\Delta E = 0.5\,\mathrm{V}$) is about 2800 A, the current density is almost $10\,\mathrm{kA\,m}^{-2}$. For several reasons (e.g., inhomogeneous current distribution, time required for replacing a batch of particles, heat developed in the cell, contact resistances) it is doubtful whether such a large current density could be applied under technical conditions. Actually, it will be necessary to reduce the current density by a factor of 2 to 3 (or even more) and to expand the electrode area correspondingly.

5.3. *Multilayer beds of particles*

The question arises whether the electrode area can be kept lower by applying a multilayer bed of particles charged simultaneously. Again, however, the potential drop across the layer due to the electrolyte resistance must be considered. Under technical conditions, electrochemical cells are in general operated at constant current. The top layers, which reach the required potential first, will continue to be charged while the lower layers are still below the required value. Table 2 displays data obtained by digital simulation, assuming $\Delta E = 0.5\,\mathrm{V}$ and allowing for a potential drop of not more than 50 mV in order to avoid faradaic currents. An electrolyte resistance of $160\,\Omega$ between two particles of adjacent layers has been applied in these calculations.

As demonstrated in Table 2, it is unreasonable to use beds containing more than two or three layers, otherwise the cost of the cell would increase due to the increase in electrode area.

5.4. *Contact resistance*

The solid material exhibits good conductivity ($\kappa_{\mathrm{sol}} = 10^3\,\mathrm{S\,m}^{-1}$[13]). Hence, the resistance across the particle (several ohms) may be neglected if the current per particle does not exceed several milliamperes. The contact resistance between the feeder electrode and the particle, however, which has been neglected in the preceding sections, deserves particular consideration and proves to be the most critical item in the entire system.

Table 2. Conditions for charging a multi-layer bed ($i = 2800\,A$; particle throughput $10^6\,s^{-1}$)

Number of layers	*Charging time,* τ_c /s	*Particles per layer*	*Current density,* j /Am^{-2}	*Feeder electrode area,* A /m^2
1	1.5	1.5×10^6	9000*	0.3*
2	4.5	2.3×10^6	5600*	0.5*
3	15	5×10^6	2500	1.1
4	32	8×10^6	1600	1.7
5	50	1×10^7	1300	2.2
7	115	1.6×10^7	800	3.6

* These data must be corrected (lower current density, larger area) for the reasons given in Section 5.2

The potential difference by which the feeder electrode potential may exceed that potential to which the particles must be charged, depends on the material but will in general not exceed some hundred millivolts. Hence, at a current of about 2 mA (see Section 5.2), the contact resistance must be restricted to the order of $R_c < 100\,\Omega$.

The contact resistance developing merely under the particle's own gravitational force is very large, typically of the order of $R_c = 1\,\mathrm{M}\Omega$ [12]. Under such conditions, very small currents would be permissible so that impractical large electrode areas would be required. If the particle is pressed onto the feeder electrode with sufficient force, the contact resistance may be reduced to a few ohms. This is realized if the particle collides with the electrode at sufficient velocity [11], but the contact time is too short under these conditions. A low contact resistance is also realized by clamping the particle between two contacting wires [12].

Finding an effective procedure for charging the particles under technically reasonable conditions is, therefore, a priority task. Possibly, positioning a stirrer within a packed bed of particles lying on the feeder electrode, or rotating or vibrating a feeder electrode within the packed bed, or periodically pressing a layer of particles onto the feeder electrode may be successful. This problem has not yet been satisfactorily solved.

6. Example of potential application

The electrolyte concentrations in the various components of the system will now be considered for a model process, viz. the detoxification of an aqueous solution of SO_2 using aqueous sulfuric acid in the electrolytic cell. Quite similar considerations would apply to the oxidation of cyanide using sodium hydroxide as an electrolyte in the cell.

In the following formulas, the subscript P will indicate that the respective species is supplied by or transferred to the particles, while CE indicates the same for the counter electrode. Species without an index leave or enter the external electrolyte.

The overall reaction is

$$SO_2 + 2H_2O \longrightarrow H^+ + HSO_4^- + H_2 \qquad (14)$$

In the reactor,

$$SO_2 + [SO_4^{2-}]_P + 2H_2O \longrightarrow 2HSO_4^- + 2H^+ + [2e^-]_P \qquad (15)$$

In the electrochemical cell,

$$H^+ + HSO_4^- + [2e^-]_P \longrightarrow [SO_4^{2-}]_P + \underbrace{2H^+ + [2e^-]_{CE}}_{H_2} \qquad (16)$$

Let the influent be a pure 0.05 M aqueous solution of SO_2 (3% of saturation at room temperature). The effluent is then aqueous sulfuric acid. The electrolyte in the electrochemical cell shall be 1 M sulfuric acid ($\kappa_{\text{liq}} = 40\,\text{S}\,\text{m}^{-1}$) and is maintained by supplying concentrated H_2SO_4 to the cell.

Disregarding side reactions, the current must be 2600 A if $v_{\text{in}} = 1\,\text{m}^3\,\text{h}^{-1}$. The size of the reactor ($V_R = 14\,\text{dm}^3$), the flow rates ($v_{\text{sp}} = 0.35\,\text{dm}^3\text{s}^{-1}$, $v_p = 0.07\,\text{dm}^3\,\text{s}^{-1}$), and the first order rate constant ($k = 0.1\,\text{s}^{-1}$, diffusion-limited) are assumed as in the above calculations. According to Equation 6, the degree of conversion is $\xi = 80\%$, and the concentration of SO_2 in the effluent is $c_{\text{ex}}(SO_2) = 0.01$ M. For achieving a lower effluent concentration, a cascade system is presumably more reasonable than an extended residence time.

In balancing the amount of sulfate

$$n = n(\text{HSO}_4^-) + n(\text{SO}_4^{2-}) \qquad (17)$$

in the reactor, the following must be considered: (i) the carry-over of 26% electrolyte with the particles from the electrolytic cell ($0.26 \times 0.07\,\text{dm}^3\,\text{s}^{-1}$, 1 M H_2SO_4); (ii) the production by reaction (15) (80% conversion of $1\,\text{m}^3\,\text{h}^{-1}$ 0.05 M SO_2); and (iii) the liquid part (80% by volume) of the outflow, subsequently forming the effluent ($0.8 \times 0.35\,\text{dm}^3\,\text{s}^{-1}$ at a concentration c_{ex}(sulfate)).

The assumption made in Equation (16), that the electronic charge supplied by the particles is balanced by a corresponding amount of sulfate entering the particles, is derived from an investigation of the ionic part of the double layer of carbon [9]. Re-entry of some solution, with the sedimented particles, into the electrochemical cell is disregarded in this rough estimate. The balance then reads as follows:

$$\begin{aligned}(\mathrm{d}n/\mathrm{d}t)\,/\,\text{mol s}^{-1} = {} & 0.26 \times 0.07 \times 1 + 0.80 \times (1/3600) \\ & \times 50 - 0.8 \times 0.35 \\ & \times (c_{\text{ex}}(\text{sulfate})/\text{M}) = 0 \qquad (18)\end{aligned}$$

Hence, the concentration in the effluent is c_{ex}(sulfate) = 0.1 M. Under these conditions, the effluent contains twice as much sulfate as the influent contains SO_2. For maintaining the acid concentration in the electrolytic cell, $1.5\,\text{cm}^3\,\text{s}^{-1}$ concentrated sulfuric acid must be replenished. This amount, and the sulfate content of the effluent, can be reduced if a lower concentration of acid is applied in the electrolytic cell; this would require a corresponding increase of the electrode area.

7. Conclusion

A slurry electrode, especially a suspension of activated carbon particles, is a conceivable means for the oxidative or reductive processing of solutions comprising waste water treatment and, possibly, chemical synthesis also.

Particular advantages in comparison with direct treatment in an electrochemical cell result from the fact that the solution to be treated does not enter the cell and is essentially separated from the cell electrolyte. The latter may, therefore, be rather concentrated while an additional loading of the effluent with salt is kept low. Also, possible fouling of the electrode by reaction products is avoided.

The necessary contact between the particles and the charging feeder electrode still raises some problems. While the contact time is too short if moving particles are applied, the contact resistance is too large with particles resting on the electrode. Though concepts for overcoming this problem exist, the construction of an adequate electrochemical cell for technical application remains a priority task.

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