

SIMULTANEOUS REMOVAL OF CYANIDES AND COPPER IN AN ELECTROCHEMICAL REACTOR - EFFECTS OF AGITATION

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In our previous studies (Szpyrkowicz et al., 2000) the use of stainless steel electrodes for cyanide destruction from diluted wastewater was found to be technically and economically feasible. The rate of cyanide decomposition was favourably affected by a high bulk pH and the presence of Cu, due to an *in situ* deposition on the anode of a Cu oxyhydroxide electrocatalytic film. Though the formation of this film was observed to greatly depend on the mixing conditions in the reactor, this effect was not further investigated. As stirring may also influence the selectivity of electrochemical reactions (Szpyrkowicz et al., 2001), a study was undertaken to investigate its role in film formation and influence on the rates of the reactions competing for active sites on the anode during treatment of cyanide-bearing wastewater.

An undivided electrochemical reactor (0.7 l volume) with parallel plate stainless steel anode and cathode was used under isothermal conditions. It operated potentiostatically using different stirring modes and rates: mechanical ($0 < \omega < 210$ rpm), hydraulic ($46 < Re < 333$), and gas mixing. The pH, conductivity, Cu and N-NH₃, COD, and, for selected experiments, total cyanide concentration, were monitored. After electrolysis, the information on the morphology and composition of anode films was obtained by X-ray photoelectron spectroscopy (XPS) and electron microscopy (SEM) (Souto et al, 1997).

Conversely to the results of other studies (e.g., Hofseth & Chapman, 1999) indicating the existence of a limiting cyanide to copper molar ratio for the deposition of a stable anode film, under the conditions of our study, several factors concomitantly affected film formation. The absolute values of copper and cyanide concentrations, their relative ratio, and the stirring rate in the reactor were found to influence this phenomenon. The effect of stirring was two-fold. While no film was observed under stagnant conditions, if not for a very high Cu concentration, there was a certain range of turbulence under which film deposition could occur. Thus, a minimum degree of stirring was necessary for the build-up of the film but, exceeding a certain degree of mixing, shearing of the film from the supporting surface occurred. These two limiting situations have been quantified in terms of the shear rate $\dot{\gamma}$ and the shear stress τ acting on the anode surface. The shear stress during mechanical and hydraulic mixing was evaluated from the Blassius equation.

For mechanical mixing, the velocity of fluid outside the boundary layer was estimated on the basis of the blade tip velocity, using the experimental data for velocity distribution (Falk et al., 1998). For hydraulic mixing, the velocity was calculated assuming a uniform distribution of the fluid flow in the cross section of the reactor. For gas mixing, the shear rate was calculated, in analogy to a *G* factor, as a function of the power of mixing:

Shear rate and shear stress values calculated for different conditions are presented in Table 1. As it can be seen, the range of shear forces and rates under which the deposition of the anode film was achieved for mechanic and hydraulic mixing is within the same order of magnitude. Higher turbulence was necessary during gas mixing. XPS

data suggest that the catalytic effect is achieved through the formation of a highly porous surface film containing oxidation states +1 and +2 of copper. The relative Cu(II)/Cu(I) ratio in the films varies with the mixing conditions. No residues from cyanide oxidation were found.

Reactor performance was analysed in function of stirring rate and anode potential. Regarding elimination of cyanide, an increase of anode potential above 0.7 V caused a decrease in the reaction rate due to current consumption in a competing cyanate oxidation. In the paper an attempt to model the performance of the reactor using a first principles approach, considering the effect of stirring and other operational variables, is presented.

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