REGENERATION OF FERROUS*EDTA IN AN SO_2/NO_x SCRUBBER SYSTEM

BY ELECTROCHEMICAL METHODS

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Prepared for presentation at AICHE 1995 Summer National Meeting, July 31, 1995; NO_x and SO_x Removal from Gaseous Systems II

July, 1995

Unpublished

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Regeneration of Ferrous*EDTA in an SO₂/NO_x Scrubber System by Electrochemical Methods

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ABSTRACT

The decay of iron-chelate absorbent used in an wet scrubber system of SO₂/NO_x is regenerated by electrochemical cell. The concept of electrochemical regeneration of iron*EDTA along with the kinetics information is described in this paper. Electrode materials, electrolyte concentration, applied current level and the operating potential range of the regeneration are the decisive parameters to affect the cell performance.

INTRODUCTION

Iron chelate reagent was used as an absorbent in a wet scrubber system to simultaneously remove SO₂ and NO_x from the gas effluent. It was demonstrated to be very effective in removing the NO_x[1]. However, the removal rate decay dramatically after several hours operation of the wet scrubber system. It is due to the oxidation of the effective absorbent Ferrous-EDTA to the ineffective absorbent Ferric-EDTA by the oxygen in the aqueous[2]. Since it is economically

¹ Work supported by the U.S. Department of Energy, Assistant Secretary for Fossil Energy, under contract W-31-109-Eng-38

unfavorable by adding the Ferrous-EDTA continuously into the system, due to the high price of the EDTA chemicals, in-situ regeneration of the iron chelate becomes practically not only in simplifying overall process but also in economical favorate. Electrochemical regeneration is one of the potential methods have been proposed[3][4]. The followings are the results from laboratory-scale electrochemical kinetic study of the regeneration process which is part of the bench-scale process development.

TECHNICAL BACKGROUND

In principle, the main electrochemical reactions involving in the regeneration are as follows.

The process is carried out in a membrane separation electrochemical cell. An anion-exchange membrane was used as the separator. Schematic of the ionic flow in the anion-exchange membrane cell is shown in Fig.1. The regeneration rate depends on the applied current level and the cathod current efficiency. In general, the current efficiency is function of the applied currents. The loss of current efficiency is caused mostly by the simultaneous reaction of other species on the same electrode surface and the reverse reaction of the acting species.(see Fig. 1) The increase of the applied current will increase the overpotential (see Fig. 2) of the electrode reaction. This will

increase the overall cell voltage to the potential level which the other electrode reactions can occur thus results a loss of current efficiency. (See Fig. 3) The possible electrode reactions, which can significant influence the current efficiency, in the cathode compartment are the followings.

Therefore, reducing the overpotential of the electrode reactions of interested is the key to increase the current efficiency. The overpotential of the electrode reaction is determined mainly by two factors; electrode kinetics, such as the electrode materials; and mass transfer, such as flow rate, concentration and applied current modulation. The applied current density is determined by the mass transfer limitation of the ions, the reactants on the electrode surface and the species moving through the membrane.

In summary, the parameters which affect the cell performance are: electrode materials; flow rate; concentration of reactant and electrolyte (i.e., conductivity); applied current modulations; membrane properties.

The results presented here show the effect of system parameters on the current efficiency as well as the regeneration ratio of ferrous-EDTA to ferric-EDTA.

EXPERIMENTAL SETUP

The catholyte contains ferric-sodium-EDTA, sulfurous and sulfate species. Sodium sulfate was used as anolyte. The electrochemical kinetics study of the regeneration was carried out in a three-electrodes H-cell from Electrosynthesis Inc. A laboratory bench-scale flow-cell with 100 cm² electrodes surface and membrane area was used for process demonstration. Anion-exchange membranes were used in the electrochemical cell. Through out the paper, the current density is defined as the total current passing through the fixed surface area of cathode electrode.

RESULTS AND DISCUSSION

The main objective of the first series experiments is to investigate the cathode electrode reactions with respect to the applied potential (or current). As mentioned early, there are three major competitive cathodic electrode reactions, i.e., reaction (1)-(3). To increase the cathodic current efficiency of reaction (1), it requires to minimize the occurrence of the reaction (2) and (3) during electrochemical regeneration. Since the electrode equilibrium potential of reaction (2) is very close to reaction (1), it is almost impossible to avoid the reaction (1) and (2) simultaneously occurring on the cathodic electrode surface. However, because of the low solubility of oxygen in the water (i.e., around 19 ppm), reaction (2) can be limited to a minimum level by purging the electrolyte with nitrogen during the pretreatment step. Figs. 4 and 5 show the current efficiency (C.E.) of ferrous regeneration in different electrolytes. Without nitrogen purging, the current efficiency is less than 100 % (Fig.4). With nitrogen purging, the C.E. of ferrous regeneration reaches 100% at the begining of operation. (Fig. 5)

The difference of equilibrium potential of reaction (1) and (3) is around 1.0 V (i.e., 0.3 V and -0.7 V vs. standard hydrogen potential respectively). Therefore, as long as the potential on the surface of cathodic electrode is maintained above -0.7 V, reaction (3) can be avoided (i.e., near 100% C.E.). However, the effects of kinetics and mass transfer on the electrochemical reaction will decrease the cathodic potential in negative direction (i.e., to the potential regime of reaction (3)). This potential is called overpotential. Reducing the overpotential of reaction (1) during operation is a decisive effort of the regeneration process and it is influenced by several factors. It is a function of applied current density, electrode material, flow rate and concentration of the reacting species.

At the current density above 1 mA/cm^2 , the overpotential of reaction (1) on graphite electrode surface is relatively high and causes a low C.E. (Fig. 6) When the graphite electrode was replaced with platinum electrode, the improving of overpotential results very high C.E. (Fig. 5) Fig. 7 shows the cathode potential of reaction (1) on the stainless steel and on the platinum electrode surface. With the same applied current density (1 mA/cm^2), the overpotential of reaction (1) is higher on the S.S. electrode than on the platinum electrode.

Increasing the current density will increase the overpotential which may cause the loss of current efficiency. Fig. 8 shows the current efficiency when the applied current density is increased to 3.75 mA/cm^2 . Current efficiency dropped below 100% while the regeneration only reached 50%. It is also found that the ferrous-EDTA regeneration is a mass-transfer control process. Therefore the convection will influence the cathodic overpotential dramatically. An example is observed

during the large cell operation (flow cell). At 1.5 mA/cm^2 applied current density, increasing catholyte flow rate from 0.4 gallon per minute (GPM) to 0.5 GPM, the overpotential decrease 240 mV.

The kinetic information of ferrous regeneration above obtained from the laboratory H-cell was applied to the large scale flow cell. The expected 100% current efficiency was obtained (Fig. 9).

CONCLUSION

Electrochemical regeneration of iron-EDTA is investigated using laboratory-scale H-cell. The kinetics information obtained via the H-cell was applied in the regeneration process on a bench-scale flow cell. Electrode materials, electrolyte flow rate, iron-EDTA concentration and the conductivity of the electrolyte are four important process parameters. The cathode electrode material is important for a successful operation of the regeneration process. To avoid significant cathodic current efficiency loss, the applied current density (with respect to electrode surface) should be controlled below 3.0 mA/cm^2 , for an initial 0.03 M concentration of the iron-EDTA. Convection significantly reduce the overpotential of iron-EDTA reduction reaction.

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Fig. 1 Schematic of ionic flow in electrochemical cell

Figure 2. Potential Distribution Cross the Cell Under Current Loading

Figure 3. Equilibrium Potential of Electrode Reaction

Figure 4 Cathodic Current Efficiency of Ferrous EDTA (without Nitrogen Purging)

Figure 5 Current Efficiency of Ferrous EDTA Regeneration (with nitrogen purging)

Figure 6 Current efficiency of Ferrous EDTA Regeneration on Graphite Surface

Figure 7A Cathodic Potential on Platinum Electrode

Figure 7B Cathodic Potential on Stainless Steel Electrode

Figure 8 Current Efficiency of Ferrous EDTA Regeneration
(current density = 3.75 mA/cm^2)

Figure 9 Current Efficiency of Ferrous EDTA Regeneration in a Flow Cell