2 THE DEVELOPMENT OF THE RATE EXPRESSION

2.1 *THE RATE EXPRESSION*

The adsorption of gold cyanide onto activated carbon has been shown by Cho[11] and Fleming[8] to be reversible. The first rate expression used during this research project was a first order reversible rate expression, which had the form:

$$r = k_1 C_s - k_2 C_c \qquad 2\text{-}1$$

where k_1 and k_2 are the forward and reverse rate constants.

This rate expression was used to develop the model for gold adsorption by carbon. The pertinent points from this program of work are listed below:

* Using a batch mass balance and the rate expression, the batch test model was developed. The equation developed was shown to fit batch adsorption data from experimental results using Grootvlei pulp.

* The mathematics of the system stated that the rate parameters are constant for a particular pulp and carbon, irrespective of the carbon to solution ratio. Solution profiles of tests done at various ratios were obtained from Menne[13], and the rate constants were shown to be constant.

* The rate expression and a CSTR mass balance were used to describe the continuous operating system.

* Computer programs using numerical techniques were developed and the profiles predicted in this way were shown to fit an operating pilot plant at Western Areas Gold Mining Company.

The first order reversible rate expression was used during the initial phases of this project, but it was shown to have limitations. Testwork showed that both rate constants varied with particle size and with the rate of agitation, and a serious limitation of the rate expression was that it had no means of defining these physical parameters. A second limitation was the difficulty in obtaining the rate constants from a batch test. The forward and reverse rate constants differ by five orders of magnitude, and the solution concentration at the start of a batch test differs from the solution concentration at the end of a batch test by two to three orders of magnitude.

The first method of obtaining the rate constants was via linearization. The rate expression and the mass balance were manipulated to produce an expression from which a plot could be drawn to produce a straight line. Although this method was fairly accurate, it was not possible to obtain both rate constants from a single batch test, and batch tests at varying carbon to solution ratios were required for each physical parameter studied.

The second method of obtaining the rate constants was via non-linear regression. The equation describing the solution concentration was developed and programmed into

a subroutine of a program which used a "simplex hillclimber" and minimised the sum of the square of the errors. Although four different forms of the solution equation were tried, the difference in the order of magnitude between the rate constants proved to be a major stumbling block. It was possible to obtain numbers for the forward rate constant but not for the reverse rate constant.

Hence, although the first order reversible rate expression did give a good first approximation of the system, its drawbacks were such that it was rejected.

The second rate expression used during this investigation was based on the hypothesis that the rate controlling step is film diffusion. The classical rate expression for film diffusion was used, together with the equilibrium assumption of Nicol[7,19] and Fleming[8], that is, that the equilibrium between the gold in the solution and the gold on the carbon surface can be described by a linear isotherm. The resulting rate expression had the form:

$$r = (A_c/V_s)\ \rho_s\ k_1\ (C_s - K\ C_c) \qquad 2\text{-}2$$

The mathematics for the batch test were developed and were shown to fit observed data obtained from batch tests done at varying ratios of carbon mass to solution volume. The mass transfer coefficient (k_1) was linked to the carbon particle size and the solution linear velocity in columns by means of dimensionless correlations. Although this rate expression showed promise, it was rejected on account of the linear isotherm assumption. At equilibrium, the rate expression condensed to

$$K = C_s^e/C_c^e$$

This expression only holds at very low concentrations, and if the equilibrium is not in the region where the expression holds, the carbon concentration values predicted are greater than those observed. If the equilibrium is out of the linear region, difficulties are encountered in getting a single value of the equilibrium constant. These limitations did not produce serious errors in the concentration range encountered in the practical situation. However, the expression does have a serious limitation if it is to be used to establish optimum economic conditions on a theoretical operating plant. During an economic study, both extremes are considered in order to obtain the economic optimum. This rate expression has the capability of predicting much higher carbon loadings than are practically feasible, and therefore predicting incorrectly the economically optimal plant.

The third rate expression used during this project was similar to the second, in that it was based on the hypothesis that the rate controlling step in the range which is of practical interest is film diffusion control.

The classical film diffusion rate expression is derived from the following assumptions (Helfferich[12]):

* Interdiffusion in the film is treated as quasi-stationary, that is, it is assumed that diffusion across the film is fast compared with the concentration changes at the film boundary.

* The film is treated as a planar layer (one dimensional diffusion).

* The particles can be treated as equivalent spheres with a homogeneous outer surface.

If the rate is defined as the mass of gold adsorbed per unit volume of solution per unit time, the classical rate expression for film diffusion can be written (Perry[26]):

$$r = (A_c/V_s)\ \rho_s\ k_l\ (C_s^B - C_s^s) \qquad 2\text{-}3$$

where C_s^B is gold concentration in solution in bulk,

and C_s^s is gold concentration in solution at surface.

The majority of researchers in this field use the Freundlich isotherm to describe the equilibrium (Section 1.4). The Freundlich isotherm between gold in solution at the surface and gold on the carbon at the surface is

$$C_s^e = a\ (C_c^e)^b \qquad 2\text{-}4$$

As the adsorption is under film diffusion control, no concentration gradient exists in the carbon, and hence the rate expression is

$$r = (A_c/V_s)\ \rho_s\ k_l\ (C_s - a\ (C_c)^b) \qquad 2\text{-}5$$

2.2 THE MATHEMATICS OF THE BATCH TEST

The rate expression is

$$r = (A_c/V_s)\ \rho_s\ k_1\ (C_s - a\ (C_c)^b) \qquad 2\text{-}5$$

For a constant volume reactor (Barrow[27])

$$r = -\ \rho_s \frac{dC_s}{dt} \qquad 2\text{-}6$$

Combining 2-5 and 2-6

$$-\frac{dC_s}{dt} = (A_c/V_s)\ k_1\ (C_s - a\ (C_c)^b) \qquad 2\text{-}7$$

The mass balance on gold over a batch reactor is

$$m_s\ (C_s^o - C_s) = m_c\ (C_c - C_c^o) \qquad 2\text{-}8$$

Substituting 2-8 into 2-7

$$\frac{dC_s}{dt} = -k_1(A_c/V_s)C_s + k_1(A_c/V_s)a[C_c^o + (m_s/m_c)C_s^o + (m_s/m_c)C_s]^b \qquad 2\text{-}9$$

This expression describes the gold concentration in solution at any time in a batch reactor. It is unsolvable analytically and must be solved via a numerical technique.

2.3 OBTAINING THE RATE CONSTANTS IN THE RATE EXPRESSION

The equilibrium constant

The rate expression at equilibrium is in the form of the Freundlich isotherm, that is

$$C_s^e = a\ (C_c^e)^b \qquad 2\text{-}4$$

Taking the natural logarithm

$$\ln C_s^e = \ln a + b \ln C_c^e \qquad 2\text{-}10$$

Hence, plotting $\ln C_s^e$ against $\ln C_c^e$ should produce a straight line of slope b and intercept $\ln a$. To obtain the constants a and b, a series of batch equilibrium tests is required. When setting up the equilibrium tests, the factors affecting the equilibrium (discussed in Section 1.3) must be borne in mind.

The mass transfer coefficient

To obtain the mass transfer coefficient from a batch test, samples must be taken during the test to obtain the profile of the gold concentration in solution. The equation describing the gold concentration in solution was developed in Section 2.2. This equation (2-9) is unsolvable analytically, thus preventing the development of an expression from which a linear plot can be drawn to obtain the mass transfer coefficient. The following procedure is used to obtain the mass transfer coeffient:

1 A value of the mass transfer is estimated.

2 Equation 2-9 is solved numerically for this specific value, and predicted concentration profile obtained.

3 The predicted values are compared with the observed values by calculating the sum of the square of the errors.

4 The above three steps are repeated until the minimum sum of the square of the errors is obtained.

A program was written to complete the above task. A Runge-Kutta numerical method is used to solve the differential equation, and a golden section search technique is used to detect the mass transfer coefficient that corresponds to the minimum in the sum of the squares. The program is detailed in Appendix B.

3 EXPERIMENTAL PROCEDURES

3.1 INTRODUCTION

Batch adsorption tests were completed in three types of contactors, namely rolling bottle, fluidized bed and fixed bed.

The first set of tests was carried out to identify the rate controlling step. These tests included an interruption test in a fluidized bed and the varying of the agitation rate (rolling bottle speed) in a 5 litre bottle.

The second set of tests involved batch rolling bottle adsorption tests at different solution volume to carbon mass ratios.

The third set of tests was done using all three agitation systems at different carbon particle sizes and agitation rates to identify the effect of these parameters on the mass transfer.

Equilibrium tests were also performed in 2-litre rolling bottles.

3.2 SOLUTION AND CARBON PREPARATION

The make-up of the solution phase

The factors affecting adsorption were discussed in Section 1.3. Those relevant to the solution phase are:

* Pulp density
* pH value
* Ionic strength
* Free cyanide
* Solution concentration.

The solution was made up as follows for all the testwork:

* To nullify the effect of pulp density, a clear solution was used.

* To create a constant pH value and ionic strength, sodium hydroxide was initially added to the solution. This was found to be unsatisfactory, and a borax buffer was then used for this purpose.

  The conditions in solution were:
  0,165 g ℓ^{-1} H_3BO_3
  0,149 g ℓ^{-1} KCl
  0,094 g ℓ^{-1} NaOH
  Demineralized water was used to keep the effect of ionic strength variations to a minimum.

* Gold was added to the solution in the form of $KAu(CN)_2$. This had two advantages: firstly, that any desired solution concentration could be created, and secondly, that no free cyanide had to be added to dissolve the gold.

* On dump reclamation plants the solution concentration in the incoming feed varies from 0,2 p.p.m. to 1 p.p.m. On gold mines using the CIP process, the solution concentration in the feed varies from 2 p.p.m. to 8 p.p.m. Therefore a solution concentration of approximately 5 p.p.m. was chosen for all tests.

Carbon preparation

Because it is the carbon most commonly used on operating CIP plants, Le Carbone G210 AS was the carbon chosen for use in all tests. A bulk sample of carbon was split into size fractions by screening at different mesh sizes for one hour. This would be an excessive time for batch screening, but it was done to abrade the sharp edges off the virgin activated carbon. Each size fraction was then elutriated, to remove entrained carbon fines, and air-dried. The size fractions produced were -2,36 +2,00 mm; -2,00 +1,7 mm; -1,7 +1,4 mm; and -1,4 +1,18 mm.

3.3 *THE INTERRUPTION TEST*

The carbon particles and the solution containing gold cyanide were contacted in a column. The solution (gold concentration 4,5 p.p.m.) was made up in a 20 litre container and was kept well mixed during all stages of the experiment by means of an overhead stirrer. Solution was drawn off from the container, by means of a peristaltic pump, at a flowrate of 16,2 $\ell\ h^{-1}$, and pumped up through the column to fluidize the bed. The column (internal diameter 2,1 cm, height 23 cm)

contained 8 g of carbon in the size fraction -2,0 +1,7 mm. After passing through the bed of carbon, the solution was returned to the 20 litre container. A photograph of the equipment is shown in Figure 3.1.

The system was set up and the column fluidized. After a period of time the flow was interrupted and the solution entrained within the column was drained out and returned to the container. The system was left for two hours before the flow was started up again. Samples of the solution were taken before and after the interruption, and analysed for gold by atomic absorption spectrophtometry (AAS), using an Atomic Absorption Spectrophotometer Varian AA1275. The raw data from the tests appear in Appendix A, Table A1.

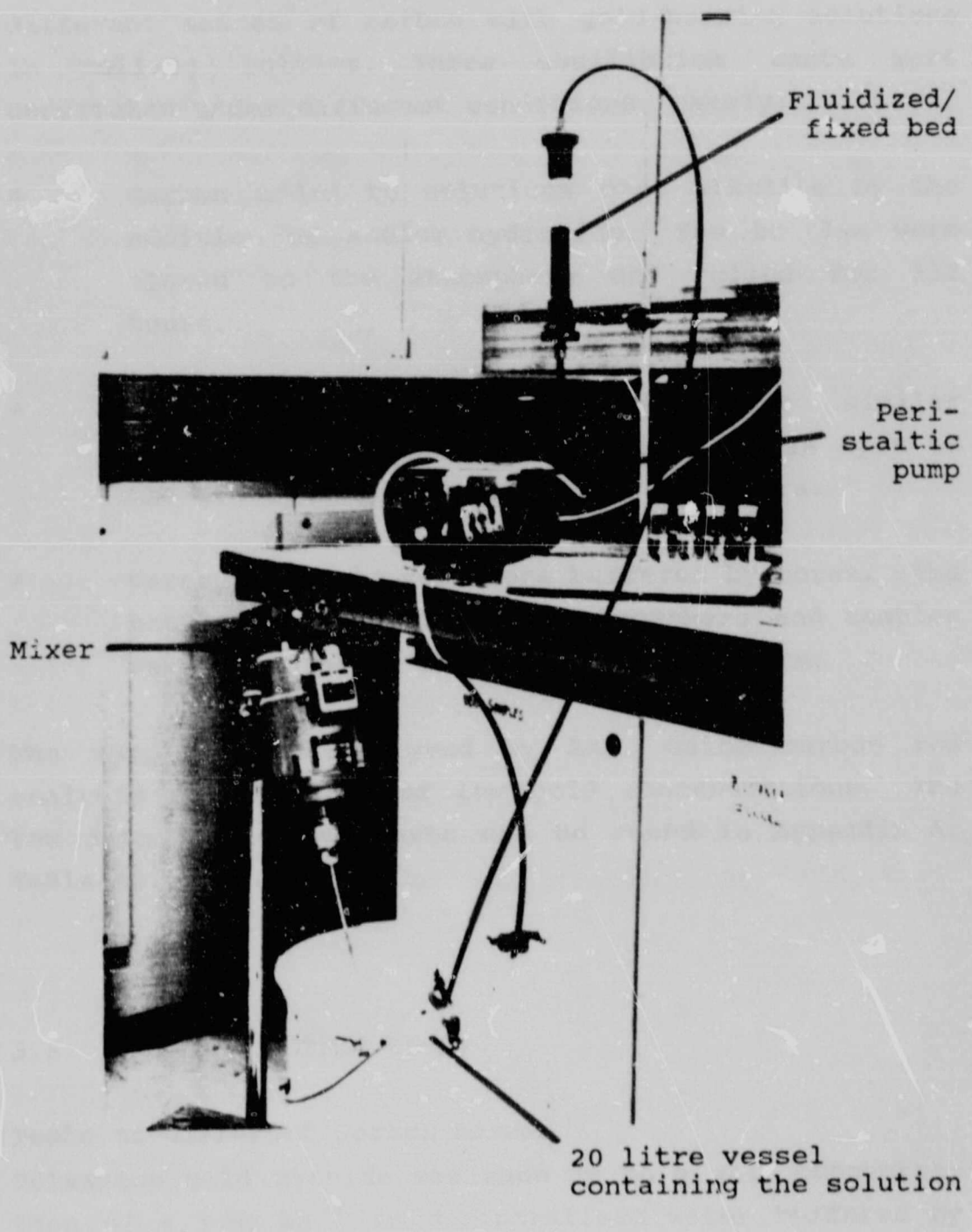

FIGURE 3.1 Photograph of equipment used in column tests

3.4 *EQUILIBRIUM TESTS*

Equilibrium tests were undertaken by contacting different masses of carbon with gold-bearing solutions in rolling bottles. Three equilibrium tests were undertaken under different conditions, namely:

* Carbon added to solutions made alkaline by the addition of sodium hydroxide. The bottles were closed to the atmosphere and rolled for 312 hours.

* Carbon added to solutions under similar conditions, except that the contact was open to the atmosphere, and rolled for 168 hours.

* Carbon added to solutions buffered by borax. The bottles were open to the atmosphere and samples were taken after 120 hours and 216 hours.

The samples were analysed by AAS, using carbon rod analysis in the case of low gold concentrations. The raw data from these tests can be found in Appendix A, Table A2.

3.5 *ROLLING BOTTLE TESTS*

Tests at different carbon masses

Potassium gold cyanide was made up to a gold concentration of 4,3 mg kg^{-1} in demineralised water buffered by borax. The pH value of the solution was 9,8. 500 ml of the solution was added to each two-litre bottle, and virgin carbon in the size fraction -2,0 +1,7 mm was

added. Five different ratios of carbon mass to solution volume were tested, namely 0,12; 0,25; 0,42; 0,71; and 1,21 g per litre of solution.

The bottles were rolled at 11,1 r.p.m. and, at predetermined times, samples were taken by means of a thin tube connected to a syringe. The pH value of the solution was checked and found to remain constant. The gold concentration of the solution was analysed by AAS. The contacting time for each adsorption test was six hours. The results are detailed in Appendix A, Table A3.

Tests at different speeds of rotation

Batch adsorption tests were conducted in two- and five-litre rolling bottles. Potassium gold cyanide was dissolved in demineralized water to give a gold concentration in solution of about 4,5 p.p.m. The pH value of the solution was brought up to 11,3 by the addition of sodium hydroxide; 0,5 litres of this solution was added to each bottle, with 0,77 g +1,7 -2,0 mm virgin carbon. Samples were removed from the bottles at predetermined times by means of a syringe, and analysed for gold by AAS. The duration of each run was seven hours.

3.6 *COLUMN TESTS*

Fluidized bed

The first system investigated was the fluidized bed. The equipment used for the fluidization tests was identical to that used for the interruption test (Section 3.3). Potassium gold cyanide was added to a

20 litre container filled with demineralized water buffered by borax, giving a concentration of approximately 4 p.p.m. The solution was agitated by an overhead stirrer. By means of a peristaltic pump, solution was withdrawn from the container and pumped up through a column consisting of a perspex tube (diameter 2,1 cm and height 23 cm), on either end of which was a unit with a detachable centre core, enabling the screen (aperture 0,5 mm) to be removed and carbon to be either loaded or unloaded from the column. After passing through the column, the solution was returned to the 20 litre container. Three different carbon size fractions were used. A photograph of the equipment is shown in Figure 3.1.

Samples of the solution were removed from the 20 litre container at predetermined times and analysed for gold by AAS.

Fourteen adsorption tests were completed using the fluidized bed, the duration of each run being 24 hours. The linear velocity in the column was varied from 0,009 m s^{-1} to 0,023 m s^{-1}. All three carbon size fractions were used. The temperature of the solution was not controlled, being ambient temperature. The raw data from these tests can be found in Appendix A, Table A5.

Fixed bed

The second system investigated was the fixed or packed bed. The equipment used, as well as the solution, carbon, and operating conditions, were the same as those for the fluidized bed tests. The only difference was that the peristaltic pump was reversed so that solution was drawn down through the column instead of up through

the column. The downflow mode of the solution packed the carbon against the screen at the bottom of the column.

In all, ten adsorption tests were completed using the fixed bed. The linear velocity in the column was varied from 0,009 to 0,017 m s^{-1}. All three carbon size fractions were used. The raw data from these tests can be found in Appendix A, Table A6.

4 RESULTS AND DISCUSSION

4.1 INTRODUCTION

The rate controlling step is discussed first with respect to the results obtained from the interruption tests. The results of the rolling bottle tests are also used as evidence during this discussion.

Next, the equilibrium isotherm is analysed and the Freundlich isotherm fitted to the data.

It is then shown that the model does simulate the adsorption of gold from batch tests done at varying carbon masses.

Dimensionless number correlations are used to fit the data obtained from varying the carbon particle size and agitation rates on the three systems tested, namely rolling bottles, fluidized beds and fixed beds.

4.2 THE RATE CONTROLLING STEP

Two sets of tests were undertaken to establish which control mechanism dominates. Interruption tests were carried out first, followed by bottle rolling tests carried out at different rotation speeds.

Under intraparticle diffusion control, film diffusion is so much faster that concentration differences in the

film are instantaneously levelled out (Helfferich[12]). Concentration gradients exist only in the particle. Under film diffusion control, intraparticle diffusion is so much faster that concentration gradients exist only in the film. The interruption test is done during a batch contact of gold in solution and carbon. The carbon particles are isolated from the solution for a period of time before being reimmersed. This pause gives time for the concentration gradients in the particles to level out. Thus, with intraparticle diffusion control, the rate of adsorption after reimmersion is greater than the rate prior to the interruption. With film diffusion control, there are no concentration gradients in the particles, and the rate depends on the concentration difference across the film. The interruption does not affect this difference and, hence, has no effect on the rate.

In all, four interruption tests were undertaken, being performed when the carbon had reached 25, 46, 59 and 94 per cent, respectively, of the equilibrium gold loading value. The results of these interruption tests are shown graphically in Figures 4.1 to 4.4, where asterisks indicate samples before the interruption and circles indicate samples after the interruption. As previously mentioned, if the system is under film diffusion control, the interruption has no effect on the rate of adsorption.

From examination of Figures 4.1 to 4.4, the conclusion can be drawn that, for the first three interruption tests, the system was under film diffusion control. When the carbon had reached 94 per cent of its equilibrium loading value (the fourth interruption test), the first slight indication of the influence of intraparticle diffusion control could be detected.

FIG 4-1 FIRST INTERRUPTION

CARBON LOADED TO 25% OF ITS EQUILIBRIUM VALUE

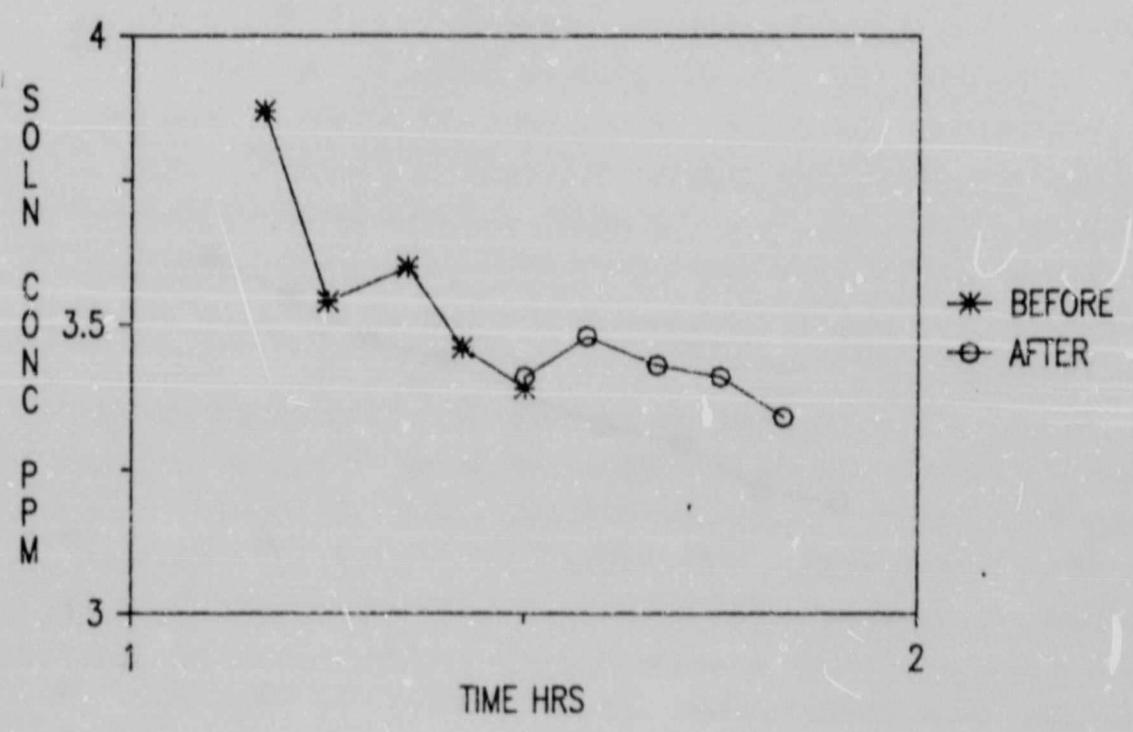

FIG 4-2 SECOND INTERRUPTION

CARBON LOADED TO 46% OF ITS EQUILIBRIUM VALUE