

Dissolution of Chalcopyrite with Hydrogen Peroxide in Sulphuric Acid

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Abstract. The dissolution of chalcopyrite with hydrogen peroxide in sulphuric acid solution was investigated. The influence of temperature, stirring speed, concentrations of hydrogen peroxide and sulphuric acid, as well as the particle size of chalcopyrite were studied. Increase in the concentration of sulphuric acid had a positive effect on the dissolution of the chalcopyrite. Stirring speed had a negative effect on the dissolution of chalcopyrite as it enhanced the decomposition of hydrogen peroxide. The dissolution process was found to follow a shrinking-core model, with surface chemical reaction as the rate determining step. This is in agreement with the activation energy of 39 kJ/mol, and a linear relationship between the rate constant and the reciprocal of the particle size. The dissolution process was postulated to be electrochemical in nature.

Keywords: hydrogen peroxide, chalcopyrite dissolution, chalcopyrite, electrochemical dissolution, shrinking-core model

Introduction

It is possible in principle to roast the sulphide ore of copper to the oxide, and then reduce it by carbon in blast furnace. However, since the concentrates also contain iron sulphide, iron oxide will be formed. In fact, oxidation of copper sulphide does not occur until iron sulphide is fully oxidized to ferric oxide. This ferric oxide is difficult to remove by slagging. Moreover, the matte smelting is carried out easily without the use of any reductant. Therefore, blast furnace smelting is not suitable for the extraction of copper (Gosh and Ray, 1991). With the gradual depletion of rich ore deposits, it is becoming increasingly difficult in many situations to apply the conventional pyrometallurgical methods for metal extraction. If there is too much gangue in a mineral ore, then the processing of the ores at high temperature causes wastage of energy. The disposal of slag and the release of gaseous pollutants into the environment are serious problems (Gosh and Ray, 1991). The siliceous gangue in the ore is unaffected by most leaching agents, whereas in the pyrometallurgical smelting processes, thermodynamically stable mattes are formed which reduce the extraction of the metals. Hydrometallurgical processes are suited for lean and complex ores.

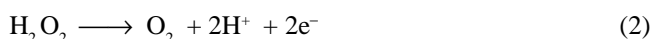
In most hydrometallurgical processes, high level of extraction of the base metals is achievable. In these cases, high oxidation potential is required (Ekinici *et al.*, 1997). The dissolution of mineral ores in aqueous solution may be a physical, chemical or electrochemical process, or a combination of these processes. The crystalline nature of the mineral, its state or subdivisions, its defect structures, and other factors play an

important role in the dissolution (Copur, 2001). Chalcopyrite usually occurs together with other sulphide minerals to constitute complex sulphide ores (Gomez *et al.*, 1997).

Hydrogen peroxide is a good oxidizing agent as depicted by the redox potential of 1.77 V in acid medium (Cotton and Wilkinson, 1980; Alimarin *et al.*, 1976; Wood and Holliday, 1967). The oxidative action of hydrogen peroxide in acidic medium is based on its reduction according to the following equation:



However, hydrogen peroxide can also act as a reducing agent in accordance with equation (2) below :



Hydrogen peroxide has been used as a leaching agent for uranium ores (Jiang *et al.*, 2002), and its use has been also studied with a zinc-lead bulk sulphide concentrate (Antonijevic *et al.*, 1997), as well as with the concentrate of pyrite (Balaz and Ebert, 1991) and sphalerite (Copur, 2001).

In the present study was investigated the dissolution of chalcopyrite in hydrogen peroxide acidified with sulphuric acid under various variables, such as temperature, concentrations of hydrogen peroxide and sulphuric acid, stirring speed, and the chalcopyrite particle size.

Materials and Methods

A sample of chalcopyrite concentrate from a Nigerian deposit was crushed, ground into fine powder, and sieved through standard ASTM sieves to obtain fractions of 100, 200, 250 and

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300 μm . The analysis of the ore sample for some elements and oxides was carried out using standard methods (Furman, 1963), which has been reported in Table 1.

The dissolution experiments were carried out in a 250 ml reactor made up of a 3-necked Pyrex glass vessel in a thermostatic heating mantle. The reactor was equipped with a condenser and an overhead mechanical stirrer. The reactor was charged with 50 ml hydrogen peroxide and 50 ml sulphuric acid. When the desired temperature was attained, 1.0 g of the chalcocopyrite was added to the acidified peroxide solution, stirring was continued, and the desired temperature of the reaction mixture was maintained constant. Two ml of the solution was withdrawn from the reactor at various time intervals and diluted with distilled water to 25 ml in a volumetric flask. The study of reaction kinetics was based on the amount of copper leached in the solution as a function of time. The amount of copper was determined using atomic absorption spectrophotometer.

For calculation of the fraction of copper leached, the equation developed by Papangelakis and Demopoulos (1990) was used, which includes within itself the correction factors to account for the volume and mass losses due to sampling and handling procedures. The fraction was calculated by dividing the amount of solubilized copper at the time of sampling by the amount of copper contained in the chalcocopyrite at the beginning of the reaction.

Results and Discussion

Dissolution process. There are many studies related to the dissolution of chalcocopyrite in various media (Jena and Brocchi, 1992). Direct chlorination of complex sulphides of copper, nickel and iron has been investigated by several authors (Smith and Iwasaki, 1985; Pilgrim and Ingrahm, 1967; Hohn, 1958). Jackson and Strickland (1958) studied the kinetics of dissolution of some common sulphide minerals,

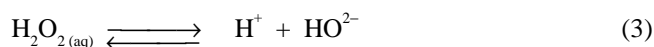
Table 1. Elemental composition of chalcocopyrite ore from a Nigerian deposit

Element/ oxide	Weight (%)
Cu	32.49
Fe	17.04
SiO ₂	13.97
S	11.91
Al ₂ O ₃	5.98
MgO	0.78
CaO	0.60

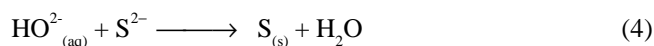
including chalcocopyrite, pyrite, sphalerite and galena in chlorine-saturated water. Dissolution of sulphide in oxidizing medium has been investigated by other researchers, who have reported that the sulphide is oxidized in two stages. In the first stage, sulphide is converted to elemental sulphur, and in the second stage the elemental sulphur is converted to sulphate (Copur, 2001).

At low temperature, most of the strong oxidising agents studied oxidise sulphide to elemental sulphur, whereas at temperature above 180 °C sulphate is formed (Ekinci *et al.*, 1997).

In aqueous solution, hydrogen peroxide dissociates to very reactive radicals (Moore *et al.*, 1978):



The peroxide radicals react with sulphide ion, as shown in equation (4):



the base metal, copper, reacts with sulphate, as shown in equation (5):



The effect of initial concentration of hydrogen peroxide.

Investigations on the effect of initial concentration of H₂O₂ on chalcocopyrite dissolution were carried out in the concentration range of 10-30%, conducted at 323 K and 1.0 mol/litre H₂SO₄. The results showed that concentration had a positive effect on the dissolution of chalcocopyrite. It was observed that there was a linear relationship for the range between 10 and 15%. As the concentration increased, deviation from linearity was noted (Fig. 1). The deviation might be due to the decomposition of hydrogen peroxide at higher concentrations which resulted in a slight reduction in the reaction rate. This means that H₂O₂ decomposition was faster at higher concentrations, leading to a significant lowering of its concentration.

The effect of sulphuric acid concentration. The effect of initial sulphuric acid concentration was investigated at the concentration range of 0.1- 6.0 mol/litre at 323 K and 20% H₂O₂. The dissolution curves are illustrated in Fig. 2. It was observed that increase in the concentration of the acid resulted in a significant increase in the dissolution of chalcocopyrite. Thus, dissolution rose to about 80% in 30 min of the leaching time at 6.0 mol/litre. This suggests that sulphuric acid had a significant effect on the oxidation of sulphide in order to release the copper ion. The effect of the acid was due to the increase in the redox potential of the oxidant (Cotton and Wilkinson,

1980; Alimarin *et al.*, 1976). The hydrogen ion concentration increases the redox potential of hydrogen peroxide, which consequently increases the rate of the reaction.

The effect of reaction temperature. For noting the effect of temperature, experiments were conducted in the temperature range of 303-353 K with the initial H_2O_2 and H_2SO_4 concentrations of 20% and 0.1 mol/litre, respectively. The dissolution curves are shown in Fig. 3, from which it may be noted that dissolution of chalcopyrite increased with increasing temperature. The curves for the temperature at 343 K and 353 K showed a levelling off at 90 min, indicating that dissolution at this stage had almost ceased. This might be due to the decomposition of H_2O_2 at the higher temperatures, which was particularly evident at the temperatures above 333 K.

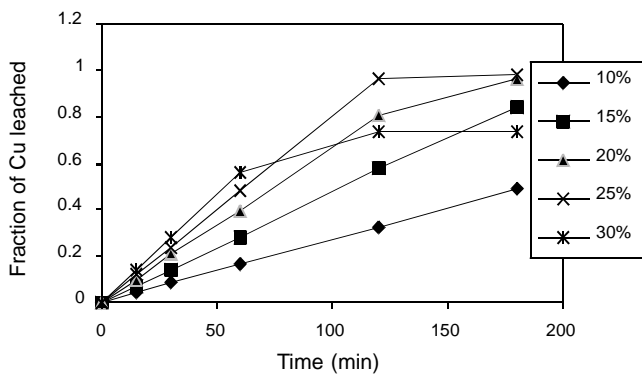


Fig. 1. The effect of different concentrations of H_2O_2 on the dissolution of chalcopyrite; the fraction of Cu was calculated by dividing the amount of solubilized Cu at the time of sampling by the amount of Cu contained in chalcopyrite at the beginning of the reaction in accordance with Papangelakis and Demopoulos (1990).

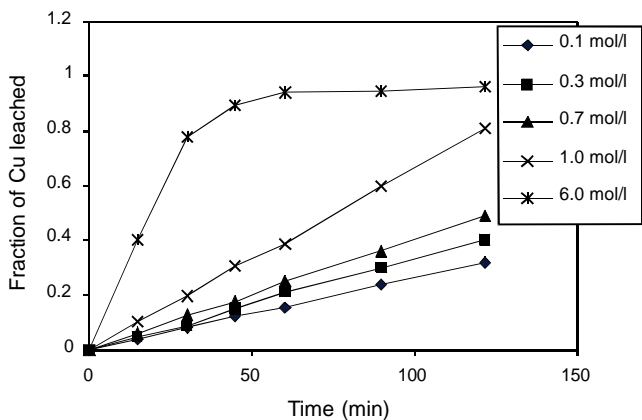


Fig. 2. The effect of different concentrations of H_2SO_4 on the dissolution of chalcopyrite with H_2O_2 (20%) at 323 K; the fraction of Cu was calculated as noted in Fig. 1.

The effect of stirring speed. The effect of stirring speed on the rate of dissolution of copper from chalcopyrite was carried out at the speeds of 300, 400 and 700 rpm at the concentrations of 20% H_2O_2 and 0.10 mol/litre H_2SO_4 at 323 K. The experiment was also examined without stirring, other conditions having been kept constant. The results revealed an irregular pattern (Fig. 4). The values obtained at 400 rpm were higher than those obtained at 700 rpm, the least values were obtained at 300 rpm. The highest dissolution rate was observed when there was no mechanical stirring. This observation showed that better contacts were made when there was no mechanical stirring. Similar observation has been reported for pyrite oxidation (Dimitrijevic *et al.*, 1999). As a result of stirring, decomposition of H_2O_2 takes place faster, which is accompanied by the evolution of molecular oxygen that got adsorbed onto the chalcopyrite particle surface, thus hindering in the particle contact with peroxide. Based on these observations, other experiments were carried out with occasional stirring. It has been already pointed out that as a result of the dissolution of particles by hydrogen peroxide, mixing of particles occurs, optionally termed 'self-mixing' caused by oxygen bubbles rising in the solution. These bubbles are produced by hydrogen peroxide decomposition, which is often catalysed by the solid particles as well as by the generated Fe^{3+} and Cu^{2+} ions (Cotton and Wilkinson, 1980; Wood and Holliday, 1967). The catalytic decomposition by the particles and the ions were suppressed by the addition of H_2SO_4 and acetanilide to stabilize hydrogen peroxide (Wood and Holliday, 1967).

The effect of particle size. The effect of particle size on the rate of chalcopyrite dissolution was studied using four particle size fractions (100, 150, 200, 300 μm) at 323 K in solutions of 20% H_2O_2 in 0.1 mol/litre H_2SO_4 . The results as shown in Fig. 5 reveal that smaller particles had a faster rate of dissolution than larger particles. The kinetic curves were linearised by applying equation (6).

$$1 - (1-X)^{1/3} = \frac{bkC_A}{\rho_B R} t \quad (6)$$

where:

X = the reacted fraction

t = the time (sec)

ρ_B = the average molar density of ore (mol/m^3)

R = the radius of the solid particle (m)

b = the stoichiometric coefficient of the solid reacting with 1 mol of hydrogen peroxide

k = the rate constant for surface reaction ($m^{-1} s^{-1}$)

D = diffusion coefficient ($m^2 s^{-1}$); see equation (8)

C_A = the concentration of hydrogen peroxide ($mol m^{-3}$)

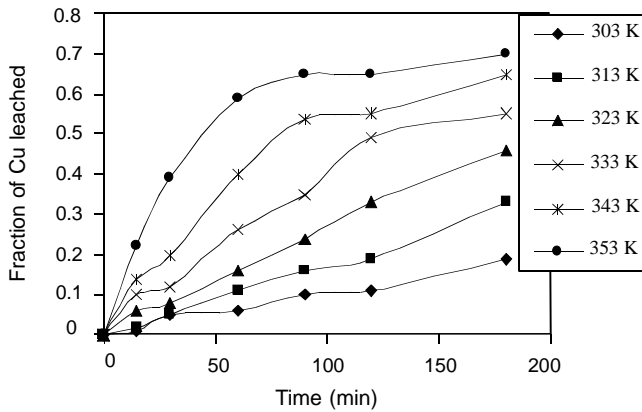


Fig. 3. The effect of different temperatures on the dissolution of chalcopyrite with H_2O_2 in H_2SO_4 , respectively, 20% and 0.1 mol/litre; the fraction of Cu was calculated as noted in Fig. 1.

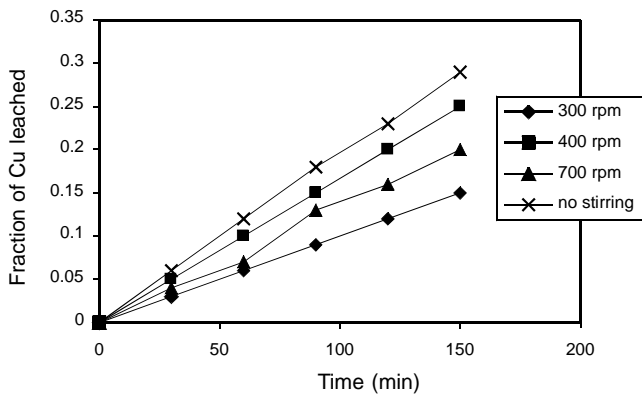


Fig. 4. The effects of different stirring speeds on the dissolution of chalcopyrite with H_2O_2 in H_2SO_4 , respectively, 20% and 0.1 mol/litre at 323 K. The fraction of Cu was calculated as noted in Fig. 1.

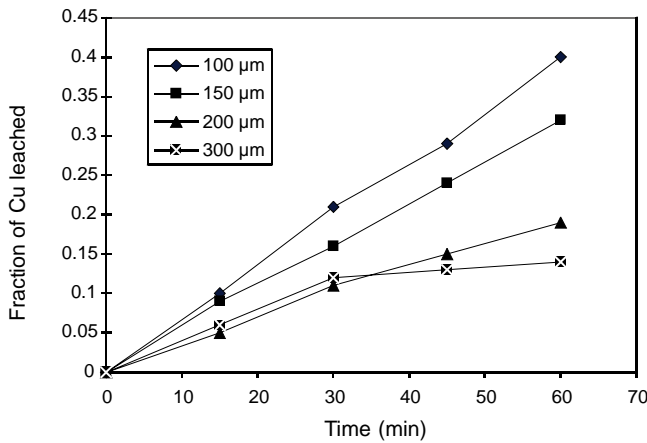


Fig. 5. The effect of different particle sizes of the chalcopyrite, ore on the leaching of copper with H_2SO_4 , respectively, 20% and 0.1 mol/litre at 323 K and occasional stirring; the fraction of Cu leached was calculated as noted in Fig. 1.

The apparent rate constants k_x were drawn as a function of the inverse of the particle radius (Fig. 6). A linear relationship between k_x versus $1/r_0$ confirms the chemical reaction on the chalcopyrite surface as the rate-controlling step (Gosh and Ray, 1991; Levenspiel, 1972).

Kinetics analysis: shrinking-core model. Two simple, idealized models are available for the analysis of non-catalytic reaction of particles in a surrounding fluid, namely, the progressive conversion model and the unreacted-core model. The progressive conversion model can be described by a particle, which is undergoing some form of a continuous conversion at all the locations within the material. The unreacted-core model is a progression of the reaction from the outer surface of the particle inward. The reaction zone moves into the solid, leaving behind completely converted and inert residue. At any given time there will exist an unreacted core of material, which is progressively reduced with the extent of reaction and time (Mgaidi *et al.*, 2004; Levenspiel, 1976).

The kinetic analysis was tested according to the unreacted-core model, if a reaction such as the following occurred:



The reaction is controlled by diffusion through the product layer; the integrated rate equation is thus given as:

$$1 - 3(1-X)^{2/3} + 2(1-X) = \frac{6bDC_A}{\rho_B R^2} t \quad (8)$$

If the reaction given in equation (7) is chemically controlled, then the integral rate expression becomes:

$$1 - (1-X)^{1/3} = \frac{bkC_A}{\rho_B R} t \quad (6)$$

On comparing equations (6) and (8), by plotting the experimental values of the dissolved copper versus time, the plot of equation (6) gave the best straight line as shown in Fig. 7. The rate constants were calculated as slopes of the straight lines. By using the value of the slopes, the Arrhenius plot in Fig. 8 was obtained, from which the apparent activation energy of 39 kJ/mol was calculated. Such a value of the activation energy obtained, suggested a chemical reaction at the chalcopyrite surface (Gosh and Ray, 1991; Biswas, 1987) and was the rate-determining step in the dissolution of chalcopyrite by hydrogen peroxide in sulphuric acid.

Electrochemical mechanism. Many dissolutions by oxidation reactions are electrochemical in nature. Direct leaching of sulphide minerals has been presumably argued to follow an elec-

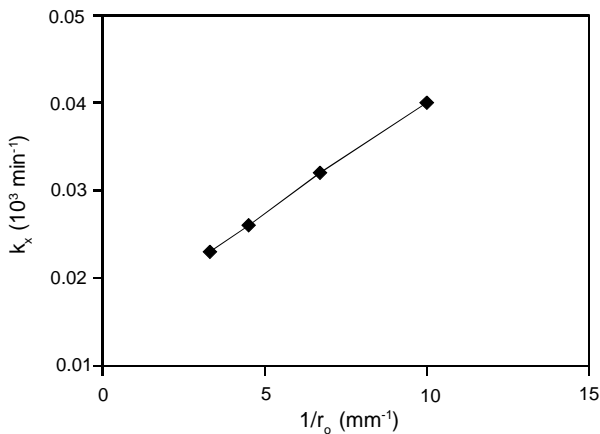


Fig. 6. The linear relationship of apparent rate constant (k_x) versus inverse of the chalcopyrite particle radius ($1/r_o$).

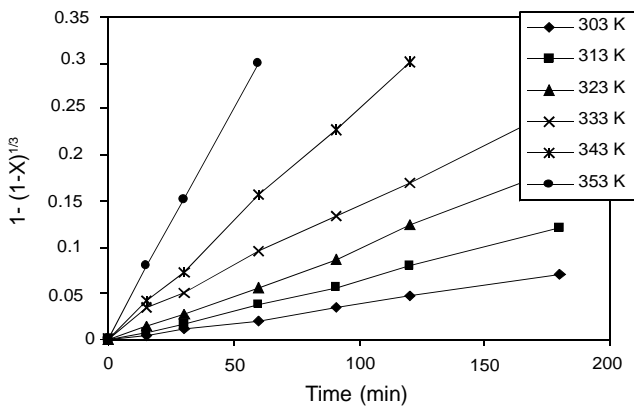


Fig. 7. The variation of $1-(1-X)^{1/3}$ (the integral rate expression) as related with various temperatures at different reaction periods; X = the reacted chalcopyrite fraction.

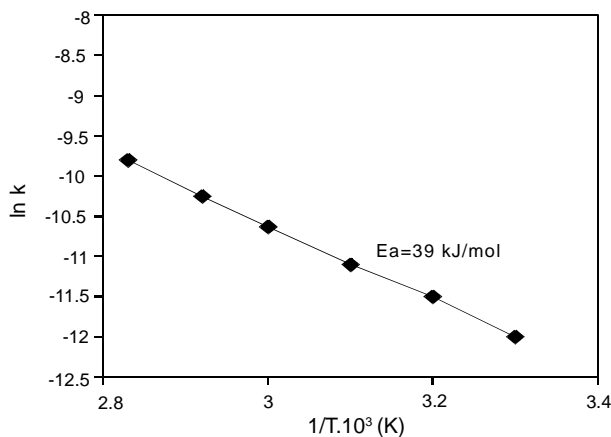
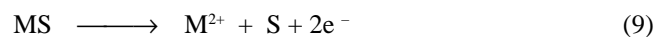


Fig. 8. Arrhenius plot for dissolution of chalcopyrite with H_2O_2 in H_2SO_4 , respectively, 20% and 0.1 mol/litre; E_a = apparent activation energy, K = absolute temperature, k = the rate constant for surface reaction ($m S^{-1}$, where m = radius of the solid particle).

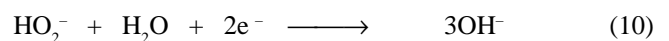
trochemical mechanism by many authors (Verbaan and Crundwell, 1986; Bobeck and Su, 1985; Warren *et al.*, 1985; Hiskey and Wadsworth, 1981; Rath *et al.*, 1981; Dutrizac and McDonald, 1978; Demopoulos, 1977). The pressure oxidation of both pyrite and arsenopyrite has been well established to be electrochemically controlled (Bailey and Peters, 1976). Similarly, the pressure leaching of sphalerite and chalcopyrite has also been shown to follow electrochemical mechanism (Harvey *et al.*, 1993; Lin *et al.*, 1987; Price and Warren, 1986).

During the oxidation of sulphide ore, the electrons produced are not restricted to any particular location but are free to move through the system, provided that the system is electronically conducting (Gosh and Ray, 1991). Thus, equivalent number of electrons may be released to the oxidizing media anywhere on the surface. Under these conditions, the mineral would be oxidized in some areas (anodic areas). At some other areas, electrons would be transferred to the oxidizing agent. Since such reactions are electrochemical in nature, these can be accelerated through the application of suitable potential on the ore body. Overall, the reaction for the dissolution of sulphide in acid media is a reaction which is sensitive to applied potential.

Hydrogen peroxide is a compound of oxygen. As such, in its chemistry it is close to the oxidation behaviour of oxygen. The hydrogen peroxide undergoes heterolytic fission according to equation (3) to produce very reactive superoxide radicals (Cotton and Wilkinson, 1980; Alimarin *et al.*, 1976). The hydrogen peroxide-chalcopyrite surface contains both cathodic and anodic reaction sites. The superoxide radical (cathodic) is adsorbed on the mineral surface followed by an electron exchange, as the reduction of the radicals and oxidation of the sulphide is carried out simultaneously. The principal reaction at the electrodes being:

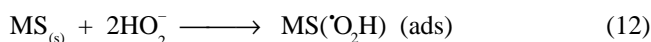


The reduction of the superoxide to hydroxide and subsequent neutralization are as below:

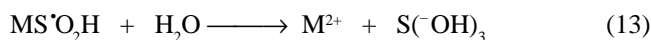


Each of these reactions (equations 9-11) has a unique electrode potential associated with it. The reduction of superoxide may proceed either by a two-electron process to hydroxide ion or decomposition to produce oxygen and hydroxide ion (Cotton and Wilkinson, 1976). The reaction path hypothesis being:

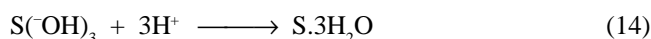
(a) the adsorption of the HO_2^- on the surface of the particles as below:



(b) the electron transfer occurs as:



(c) the neutralization of the hydroxide occurs as:



The redox reaction is usually a slow process and so the reduction of the superoxide at the mineral surface is most probably the rate-controlling step in the dissolution process. The actual rate-controlling step is most likely the one-half electron transfer stage.

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