

Letter to Editor

**LEACHING MECHANISM OF SEMICONDUCTING MINERALS -
A HISTORICAL NOTE**

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Abstract

The mechanism of leaching of semiconducting minerals such as CuS, ZnS, UO₂, etc., has been the subject of intensive speculation by hydrometallurgy researchers in the early 1950s who assumed the formation of intermediate surface complexes that could be neither separated nor identified by physico-chemical techniques. The electrochemical theory of leaching introduced in the late 1960s resolved this problem by comparing the leaching process to a corrosion phenomenon similar to the corrosion of metals. A historical summary of these proposals is presented.

Keywords: Leaching; Semiconducting minerals; Hydrometallurgy; History.

1. Introduction

In the early 1950s researchers realized that kinetic studies for leaching ores are as important as thermodynamic calculations. It was also during this period that the concept of species adsorption on mineral surfaces has dominated the interpretation of the mechanisms of most reactions. This may have been due to the fact that many researchers of this period came from the mineral dressing sector and were influenced by flotation theories. However, when the knowledge of lattice defects and the semiconductivity of minerals became known and their importance in extractive metallurgy was realized, there was a need to explain the leaching reactions in light of these modern theories. Semiconductive minerals of importance in metallurgy are two categories: the sulfides such as those of copper, lead, zinc, and the oxides such as those of uranium.

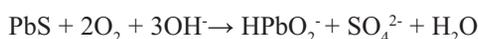
2. Leaching of semiconducting sulfides

The following mechanisms have been suggested for the leaching of semiconducting sulfides:

2.1 Adsorption complexes mechanisms

Leaching of lead sulfide

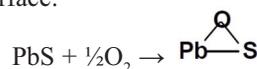
The reaction,



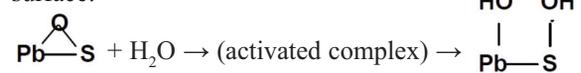
was suggested by Anderson et al. (1953) [1] to

take place according to the following steps:

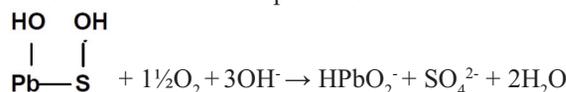
a) Adsorption and dissociation of oxygen on PbS surface:



b) Hydration of oxygen atom adsorbed on PbS surface:



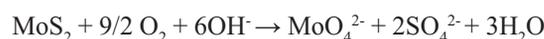
Formation of reaction products:



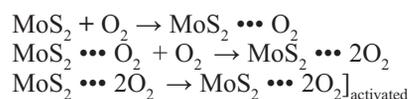
The rate-determining reaction was supposed to be step (b).

Leaching of molybdenite

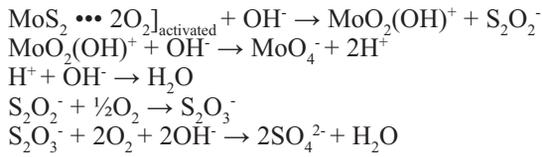
Similarly, the reaction,



was suggested by Drescher et al. (1965) [2] to take place according to the following steps:

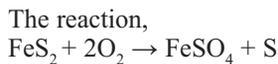


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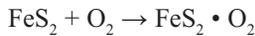
The symbol] was used to denote a surface site or product of reaction at the surface. Rate-determining steps are thought to be the second and third.

Aqueous oxidation of pyrite

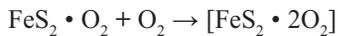


was suggested by McKay and Halpern [3] to follow the following steps:

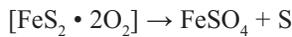
a) Oxygen is chemisorbed rapidly on the FeS_2 surface, which is thus always covered by a monolayer of oxygen, comprised of one O_2 molecule at each FeS_2 site:



b) A second O_2 molecule attacks on an O_2 -covered site:



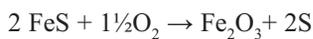
c) Formation of reaction products:



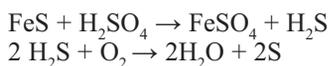
The rate-determining step was supposed to be step (b).

H_2S as intermediate product

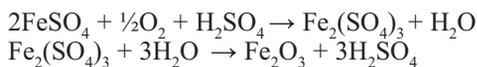
The aqueous oxidation of pyrrhotite:



was suggested by Downes and Bruce [4] to take place according to the following steps:



The ferrous sulfate formed is oxidized to ferric sulfate, which at about 100°C hydrolyzes rapidly, even at a pH as low as 1.5, to ferric hydroxide:

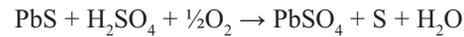


This mechanism was founded on the observation that an acid was essential in order that sulfur be liberated in the elemental form, and that a smell of H_2S could be detected in the reaction vessel. This

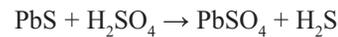
mechanism was also supported by Dobrokhotov [5] and by Gerlach *et al.* [6-7].

Aqueous oxidation of lead sulfide

Vizsolyi *et al.* (1963) also suggested a similar mechanism for the reaction:



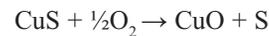
Namely, the first step is:



and H_2S is oxidized to elemental sulfur in the second step.

2.2 Oxide and elemental sulfur as intermediate products

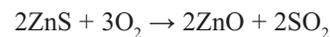
Rygaert *et al.* [8] suggested that the initial step in the dissolution of CuS at low temperature is the following reaction:



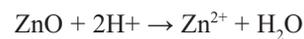
In an acid medium, sulfur is not oxidized, but CuO is continuously dissolved as soon as formed. In a neutral medium, sulfur is rapidly oxidized to H_2SO_4 , which dissolves CuO rapidly. In an ammoniacal medium, the oxidation of sulfur is highly accelerated, and CuO is complexed by the ammonia and goes into solution.

2.3 Oxide and SO_2 as intermediate products

Stranczyk and Rampacek [9] suggested that at high temperature, the initial step in the dissolution of ZnS , which is at the same time the slowest step, is the following reaction:



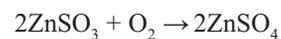
In an acid medium, the initially added acid dissolves ZnO :



while SO_2 is oxidized to H_2SO_4 :

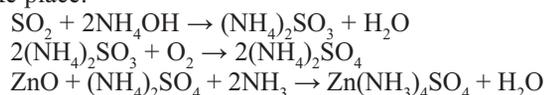


In neutral medium the reaction goes further, as follows:



In ammoniacal medium the following reactions

take place:

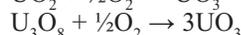
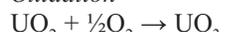


A similar argument was also suggested by the same authors [10] for the dissolution of CuS.

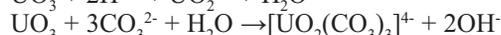
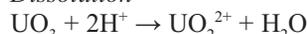
3. Leaching of semiconducting oxides

The fact that UO_2 and U_3O_8 dissolve in dilute sulfuric acid or sodium carbonate solutions only in the presence of an oxidizing agent while UO_3 readily dissolves without an oxidizing agent led some investigators (Mackay and Wadsworth [11], Pearson and Wadsworth [12], Peters and Halpern [13]) to believe that dissolution takes place in two consecutive steps:

Oxidation



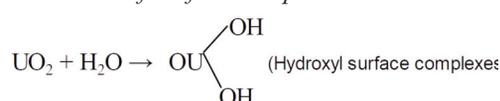
Dissolution



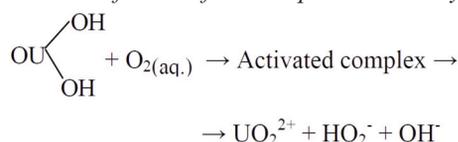
In other words, in order to dissolve either UO_2 or U_3O_8 it is necessary first to oxidize them to UO_3 and that is why oxygen or any other oxidizing agent were necessary for the process.

Another mechanism based on some active sites on UO_2 was suggested. These active sites react first with water to form a hydroxyl complex which reacts further with the dissolved oxygen to produce the uranyl ion, as follows:

a) Formation of surface complexes



b) Reaction of the surface complexes with oxygen

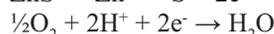
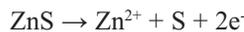


The difficulty with the first mechanism is that UO_3 cannot be formed by the aqueous oxidation of UO_2 and with the second mechanism is that many intermediate complexes were assumed.

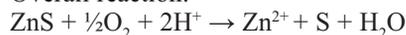
4. The electrochemical mechanism

In the above mechanisms many hypothetical

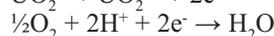
complexes or intermediate products which could not be confirmed or isolated were proposed. The suggestion that these reactions are electrochemical in nature similar to corrosion processes solved this problem (Habashi, [14-16]). For example, the aqueous oxidation of ZnS is considered to be an oxidation - reduction process:



Overall reaction:



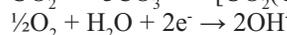
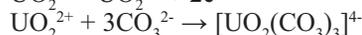
The same applies for the dissolution of UO_2 . For example in acid medium:



Overall reaction:



and in carbonate medium:



Overall reaction:



The electrochemical nature of these types of reactions has been demonstrated by embedding a piece of massive sulfide, e.g., pyrite in a salt gel containing few drops of phenolphthalein. After few days a red color formed at the sulfide-air interface thus indicating the liberation of OH^- ions where oxygen is reduced cathodically on the surface (Figure 1). To accelerate such process, OH^- ions formed at the cathodic region must be neutralized as soon as formed so that more oxygen can be reduced and more Fe^{2+} ions go into solution.

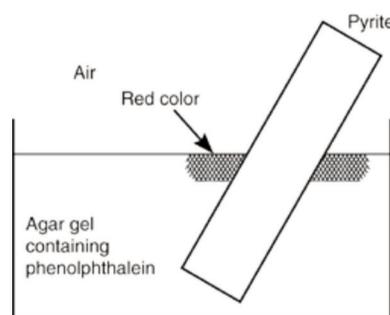


Figure 1. A piece of pyrite embedded in a gel containing phenolphthalein showed red color at the sulfide-air interface; an illustration of the formation of cathodic zone during leaching of sulfides (after Thornber [17])

5. Kinetics of electrochemical reactions

In electrochemical leaching processes involving transfer of electrons the rate will depend on one of the reagents only within a certain concentration region beyond which it will change its dependence to the second reagent. This has been demonstrated experimentally for metals as shown in Figure 2, for oxides as shown in Figures 3 and 4, and for sulfides as shown in Figure 5.

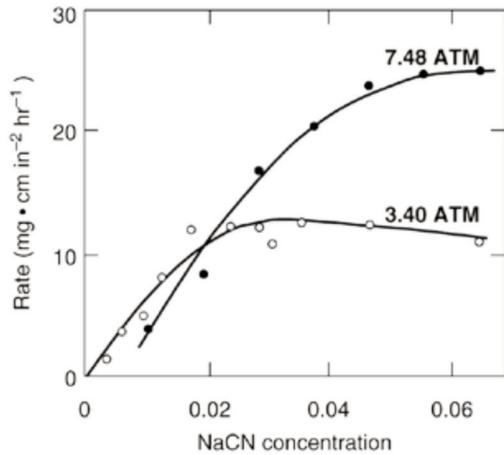


Figure 2. Dissolution of silver in cyanide solution (Deitz and Halpern [18])

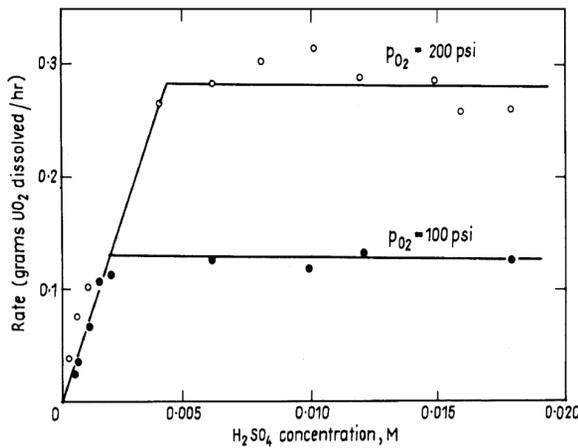


Figure 3. Dissolution of UO₂ in sulfuric acid (Habashi and Thurston [19])

This behavior can be explained as follows. When a metal or a semi-conductor comes into contact with an aqueous phase to which oxygen or any depolarizer is added, oxygen or the depolarizer takes up electrons at one part of the surface (the cathodic zone) while the solid gives them up at another (the anodic zone) as shown in Figure 6. The cathodic reduction of oxygen for example, at the surface of the solid may lead to the

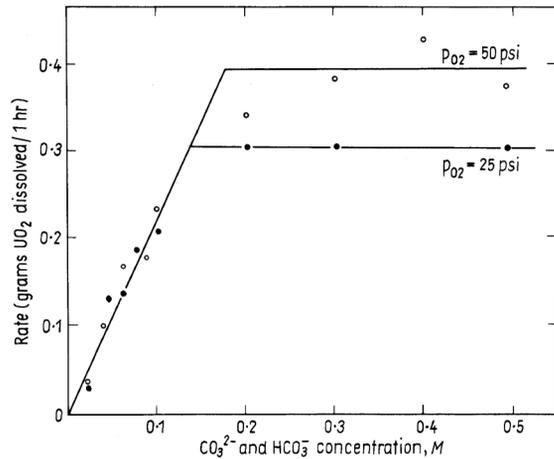


Figure 4. Dissolution of UO₂ in sodium carbonate solution (Habashi and Thurston [19])

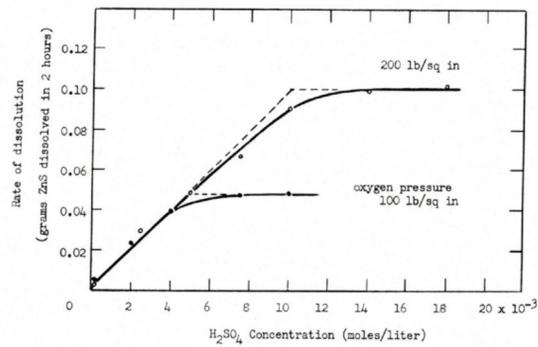
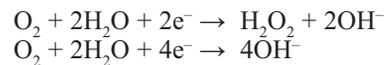


Figure 5. Dissolution of ZnS in sulfuric acid (Habashi [20])

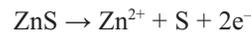
formation of either hydrogen peroxide or hydroxyl ions as follows:



The anodic reaction for a semiconducting oxide like UO₂ it would be:



and for a semiconducting sulfide like ZnS it would be:



The liberated metal ion would hydrolyze forming insoluble compounds that would block the anodic zone and the reaction would stop unless an acid or a complexing agent is present. An equation was derived theoretically that described such processes (Habashi, 1965) [14]:

$$\text{Rate of dissolution} = \frac{k_1 k_2 A [D][C]}{k_1 [D] + k_2 [C]}$$

Where A= surface area of the solid in contact with the liquid phase, [D] = concentration of the

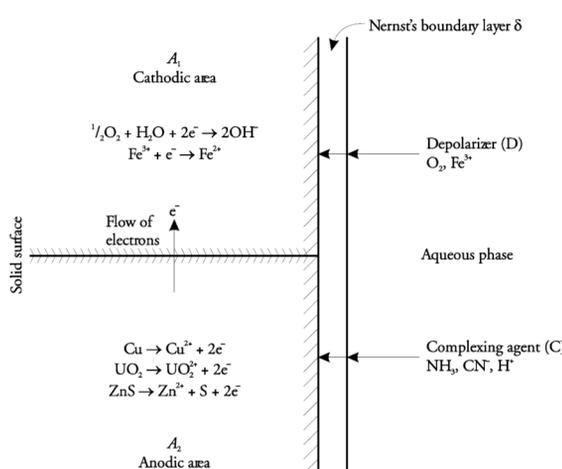


Figure 6. Mechanism of an electrochemical process in a solid-liquid reaction (Habashi [21])

depolarizer, $[C]$ = concentration of the complexing agent, k_1 and k_2 are velocity constants of the cathodic and the anodic reactions, respectively. It can be seen from this equation that if the first term in the denominator is negligible as compared with the second term the equation becomes:

$$\text{Rate of dissolution} = k_1 A [D]$$

And if the second term is negligible as compared to the first the equation becomes:

$$\text{Rate of dissolution} = k_2 A [C]$$

This agrees with the experimental data shown in Figures 2 -5.

6. Summary

The electrochemical mechanism of leaching semiconducting oxides and sulfides introduced in 1970 avoids the assumption of forming intermediate complexes that cannot be isolated or identified. The process can be considered like a corrosion process: oxygen or any oxidizing agent is reduced at the surface of the semiconducting mineral while the metal ion is liberated at the anodic zone where it may be complexed or kept in solution under certain conditions of acidity or basicity.

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