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INTERFACIAL PHENOMENA IN HYDROMETALLURGY

Hydrometallurgical systems are often controlled by processes that take place at interfaces. A complete understanding of interfacial phenomena is therefore necessary for identifying the optimum operational conditions of processes in hydrometallurgy. This paper presents various concepts of interfacial phenomena that are relevant to hydrometallurgy, and discusses some examples in hydrometallurgical practice where interfaces play a significant role in determining the success or failure of a given operation.

INTRODUCTION

Hydrometallurgical processes, like all separation processes, are by nature heterogeneous. At the boundaries where the phases meet, the interfacial region, several phenomena take place including transfer of reactants and products, adsorption, wetting and some or all of the chemical reaction steps involved in these interfacial phenomena. It is now widely recognized that the physical and chemical characteristics of interfaces control the performance of many operations in hydrometallurgy. Therefore, knowledge of the fundamental concepts of interfacial phenomena is vital for having a better understanding of the principles involved in these operations.

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A number of interfaces that exist in several hydrometallurgical processes has been identified. These include two-phase as well as three-phase systems. Solid/liquid interfaces are encountered in leaching, precipitation, solid-liquid separations, adsorption and ion exchange. Liquid/liquid interfaces control solvent extraction systems. Solid/solid/liquid interfaces are present in the cementation of copper onto scrap iron or in the leaching of complex sphalerite/pyrite systems, while solid/liquid/gas boundaries form during flotation or when oxygen or hydrogen evolves from electrodes. Flotation is used in hydrometallurgy to recover CuS in oxidized copper leaching and to recover copper by the leaching-precipitation-flotation process. The interfaces commonly encountered in hydrometallurgical systems are summarized in Table 1.

Table 1. Interfaces in Hydrometallurgical Systems

S/L	L/G	L/L
leaching solid-liquid separation adsorption and desorption ion exchange electrowinning precipitation	pressure leaching froth formation dissolution of gaseous oxidants or reductants	solvent extraction liquid-liquid separation
S/S/L	S/L/G	L/L/S
cementation leaching of complex ores passivation solid product layer formation	flotation gas evolution during electrowinning and electrolysis	liquid (or molten) product layer formation

Since the interfacial behavior of both solid and liquid particulates is critical in many instances in controlling the success of an operation, in this paper a few examples of typical systems that exist in hydrometallurgy will be presented to illustrate the vital role played by interfacial phenomena in hydrometallurgical practice.

INTERFACIAL PHENOMENA

When two homogeneous phases meet, a non-homogeneous transition or interfacial region is formed between them with properties that differ greatly from those of the bulk of either phase. Some general concepts of interfacial phenomena associated with various interfaces in hydrometallurgical systems will be discussed in the following paragraphs.

The Electrical Double Layer

The electrical nature of the interface can play an important role in determining the performance of processes involving charged species. When a solid or a non-polar liquid comes into contact with the molecules of a polar liquid, the interface can acquire an electric charge. The mechanism by which solid or liquid surfaces become charged include polarization of the interface by an applied external potential, transport of ions constituting the crystal lattice of the liquid phase across the interface, ionization of the ionogenic surface groups, specific adsorption of surface-active ions, and isomorphous substitution of ions in the lattice of minerals. Since the system must remain electrically neutral, the surface charge is compensated by the charge of a diffuse layer of all ionic species in solution. These so-called counterions spread out into the polar medium. The surface charge and the region of counterions constitute the electric double layer. Since water is the most common polar liquid used in hydrometallurgical operations, the mechanisms responsible for the development of a charge at surfaces in contact with aqueous solutions may involve not only the dissociative adsorption of water molecules, but also preferential dissolution of ions.

In solid-liquid systems, the surface charge density, σ_0 , of the solid is defined as

$$\sigma_0 \equiv zF (\Gamma_+ - \Gamma_-) \quad (1)$$

where z is the valence of the ion, F is the faraday constant, and Γ_+ and Γ_- are the adsorption densities in mol/cm^2 of the positive and negative potential

determining ions. These ions have the ability to control both the magnitude of the surface charge and the surface potential, ψ_0 , which is the potential difference between the solid surface and the bulk solution. Since absolute potentials across the interface cannot be measured, the potential of the bulk aqueous phase is generally assigned a value of zero [1].

The point of zero charge (PZC) of a solid is the single most important parameter describing the electrical nature of its surface in contact with polar solutions. The PZC is the value of the activity of the potential determining ions in solution at which the surface charge density is zero. At the PZC, and in the absence of specific adsorption, the surface potential is zero. The surface potential is given by the Nernst equation.

$$\psi_0 = \frac{RT}{F} \ln \frac{a}{a_{pzc}} \quad (2)$$

where R is the gas constant, T is the absolute temperature and a is the activity of the potential determining ion. The importance of the PZC is related to identification of the solution conditions under which the surface is positively or negatively charged. Knowledge of the sign of the surface charge is essential in understanding ionic adsorption phenomena, particularly the adsorption of counterions. The closest distance of approach of the center of counterions to the surface is called the Stern plane or plane δ .

Two opposing processes maintain the concentration profile of counterions against the charged surface: the electrostatic attraction by the surface charge and the Brownian motion diffusion flux away from the high concentration zone near the surface. When these two opposing fluxes are just in balance, the system is in equilibrium and steady state profiles of concentration and potential are established. The potential at any point at the interface varies considerably depending on such parameters as the ionic strength, the nature of counterions and the concentration in solution of potential-determining ions. In the absence of specific adsorption, for example, the potential drop from the surface to the Stern plane is linear, and from this plane on out into the solution it falls off gradually to zero in the bulk solution. The interfacial

potential at the plane δ is termed the Stern potential, ψ_δ .

Electrical double layer phenomena involving solid particles or liquid droplets suspended in polar liquids have been investigated by measurements of electrokinetic effects, which are the result of the relative motion between the solid particles (or liquid droplets) and the polar liquid in a charged system. This relative movement of one phase with respect to the other causes transport of counterions in the diffuse layer outside the slipping or shear plane and allows one to evaluate the electrokinetic or zeta potential, ζ . The exact position of the shear plane, however, has not been unequivocally located. Detailed studies with micelles indicate that the slipping plane occurs very close to the surface so that taking ζ as a measure of ψ_δ is a reasonably good approximation [2].

Perhaps the most commonly used technique to measure the zeta potential is electrophoresis. This technique allows study of the movement of dispersed particles, droplets or bubbles when the suspension is placed in an electric field. Electrophoretic mobilities, E , are converted into zeta potentials using the following expression [3].

$$E = \frac{e\zeta}{4\pi n} \quad (3)$$

where n is the viscosity of the liquid and e is the dielectric constant of the polar liquid. To accurately determine zeta potentials with very small particles, however, one must use the functional relation for particle radius and the inverse of the thickness of the diffuse layer of counterions given by Wiersema et al. [4].

Counterion adsorption at the interface may arise from simple electrostatic attraction or a combination of electrical and specific adsorption mechanisms. If the only driving force for the adsorption of the ions of a particular compound is electrical in nature, this chemical reagent is called an indifferent electrolyte. Some ions, however, exhibit surface activity in addition to electrostatic interaction, and they can adsorb through

such mechanisms as covalent bond formation, hydrogen bonding, hydrophobic adsorption and solvation effects. Under certain conditions, these surface-active counterions may be able to reverse the sign of the zeta potential. The condition where ζ reverses sign has been termed the iso-electric point or simply the point of zeta potential reversal (PZR) [5]. Figure 1(a) shows how the zeta potential of silica can change with pH in the presence and absence of a hydrolyzing metal salt [6]. The reversal of the zeta potential of silica in the presence of an indifferent electrolyte is the PZC of the silica itself. However, in the presence of cobaltous nitrate, the reversal of the zeta potential at about pH 7 results from specific adsorption of the Co(II) hydroxo complex ions. The third reversal represents the PZC of the metal hydroxide, and the Co(OH)₂-coated silica. The electrophoretic behavior of oxides in aqueous ammoniacal solutions of copper, nickel and cobalt has been investigated in detail by Osseo-Asare and Fuerstenau [7], and they observed

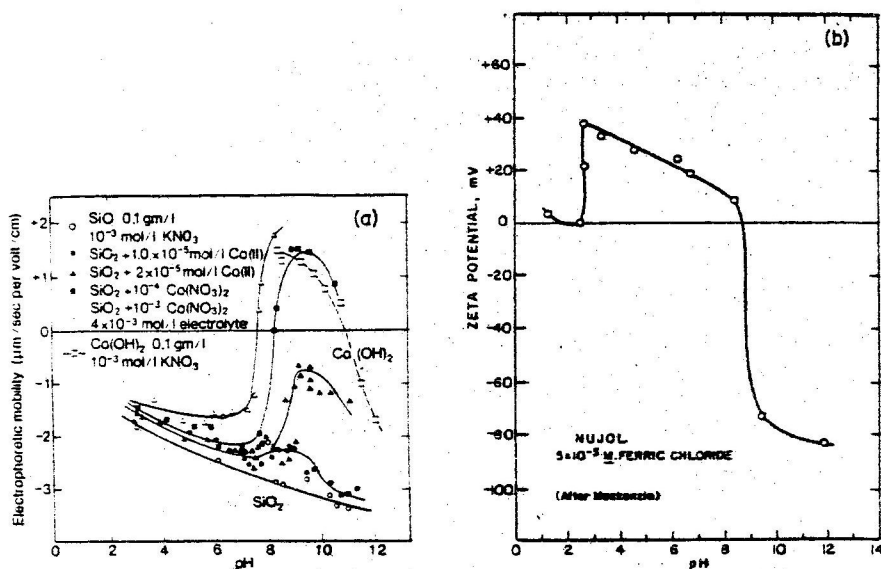


Fig. 1 - a) The electrophoretic mobility of silica, in 10^{-3} M KNO_3 as a function of pH in the absence and presence of various added concentrations of $\text{Co(NO}_3)_2$. Also shown is the electrophoretic mobility of precipitated Co(OH)_2 [6], and b) the zeta potential of oil (nujol) droplets as a function of pH in the presence of 5×10^{-3} M $\text{Fe(NO}_3)_3$ [9].

five points where the zeta potential of the oxide changes sign in these systems.

Double layer potentials can be controlled either by changing the concentration of potential-determining ions or by finding conditions where inorganic or organic ions can specifically adsorb at the interface. Fuerstenau [3] has recently described in detail the close relationship between adsorption phenomena and the electrical double layer at the mineral/aqueous solution interface.

In systems involving water and a liquid immiscible in it, the interface is composed of two non-rigid phases and the electrical double layer can be considered to be of a double diffuse type [8]. This double diffuse electrical layer is the consequence of the extension of both charged layers over a certain distance into their corresponding liquid phases. Figure 1(b) shows the zeta potential of oil (nujol) droplets as a function of pH in the presence of ferric chloride [9]. These results indicate that metal hydroxo complexes are surface-active on oil droplets also.

Thermodynamics of Adsorption at Interfaces

The free energy change for the adsorption of species i at an interface, $\Delta G_{\text{ads},i}$, can be considered to be the sum of a number terms:

$$\Delta G_{\text{ads},i} = \Delta G_{\text{coul},i} + \Delta G_{\text{solv},i} + \Delta G_{\text{chem},i} + \Delta G_{\text{CH}_2} \quad (4)$$

where $\Delta G_{\text{coul},i}$ is due to electrostatic interaction between the charge of the adsorbing species and the potential difference across the electrical double layer, $\Delta G_{\text{solv},i}$ is the change in solvation energy of the ion on moving from the bulk solution to the interfacial region, $\Delta G_{\text{chem},i}$ is a specific energy term that allows for contributions due to chemical bond formation, and ΔG_{CH_2} accounts for the contributions due to the association between hydrocarbon chains of adsorbed organic species. If ϕ is the fraction of the surface covered by the adsorbed species, then the fractional coverage at a given solution concentration (for an aqueous system) is given by:

$$\phi/(1-\phi) = \frac{C}{55.5} \exp (-\Delta G_{\text{ads}}/RT) \quad (5)$$

The adsorption of hydrolyzable metal ions by oxide adsorbents in aqueous ammoniacal solutions has been modeled by Osseo-Asare and Fuerstenau [10] in terms of a mechanism involving the competitive adsorption of all aqueous species. They expressed the total adsorption density Γ_T as

$$\Gamma_T = \frac{\sum_i \Gamma_{m,i} K_i [M_i]}{1 + \sum_i K_i [M_i]} \quad (6)$$

where $\Gamma_{m,i}$ is the monolayer coverage (in mol/m²) of species i , $[M_i]$ is the activity of species i in the bulk solution and K_i is the equilibrium constant of the surface reaction.

Since chemical species are transferred from one phase into another in solvent extraction systems, the transport of material from the bulk of the phases to the boundary that separates them and through the interface is a critical aspect of the operation. Extracting reagents possess molecules that have a hydrophilic-hydrophobic nature and therefore exhibit surface activity (through ΔG_{CH_2}). As a result, these molecules concentrate at the interface and they favor the occurrence of interfacial reactions. Chemical reactions at the organic/polar liquid interface in solvent extraction involve two mechanisms [11].

a) formation of an interfacial complex between the adsorbed molecules of the extractant and the extraction metal species.

b) transfer of the complex from the interface to the bulk organic phase and simultaneous replacement of the interfacial vacancy with bulk organic molecules of the extractant.

Thermodynamics of Wetting

Phenomena involving wetting, spreading and adhesion are determined by the surface tensions at the respective interfaces. Changes in surface or interfacial tensions can be evaluated as a function of adsorption densities

using the Gibbs adsorption equation that relates the interfacial tension between two phases to the temperature T of the system, the chemical potential of species i in the bulk, μ_i , and the surface excess or adsorption density of species i at the interface, Γ_i . At constant pressure, the Gibbs adsorption equation has the following form:

$$d\gamma = -S_s dT - \sum_i \Gamma_i d\mu_i \quad (7)$$

where S_s is the surface entropy. Since $d\mu_i = RT d \ln a_i$, where a_i is the activity of species i in the bulk aqueous solution, the Gibbs equation can be rewritten for constant temperature conditions as

$$\Gamma_i = - \frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln a_i} \right)_T \quad (8)$$

Since a necessary condition for foaming is that there be a surface tension concentration gradient, solutions foam when $d\gamma/da$ is not zero.

Interfacial tensions control the wetting of solids by liquids or the attachment of bubbles to solids, and this is expressed thermodynamically in terms of the equilibrium conditions that control the formation of a three-phase line. This situation is defined by the Young-Dupre equation that relates the interfacial tensions between the three phases and the contact angle, θ .

$$\gamma_{12} \cos \theta + \gamma_{23} - \gamma_{13} = 0 \quad (9)$$

When a gas bubble is attached to the surface of a solid immersed in a liquid, the contact angle is defined as the angle measured across the liquid at the bubble-solid contact. The free energy change for the attachment of fluid phase 2 to a solid phase 3, all immersed in fluid phase 1, is given by

$$\Delta G_a = \gamma_{23} - \gamma_{12} - \gamma_{13} \quad (10)$$

and with the Young-Dupre equation,

$$\Delta G_a = \gamma_{12} (\cos \theta - 1) \quad (11)$$

If θ is finite, then air bubbles attach to a solid during flotation or sulfur droplets to sphalerite in leaching systems.

Precipitation from Aqueous Solutions

Supersaturation can be considered to be the driving force for precipitation from solution to occur. In addition, the spontaneous formation of a stable solid phase from dissolved species must be accompanied by a decrease in the free energy of the system [12]. Precipitation phenomena for the recovery of dissolved metals in solution involve such processes as nucleation, crystal growth and particle agglomeration. The rate of homogeneous nucleation, B , has been derived by Burkhart and Voigt [13] from classical nucleation theory. Their expression for spherical nuclei is

$$B = K \exp \left[- \frac{16 \pi \gamma^3 M^2}{3(kT)^3 \rho N \ln^2(S)} \right] \quad (12)$$

where γ is the solid/liquid surface free energy, M is the molecular weight of the solid, ρ is its density, N is Avogadro's number, k is Boltzman's constant, K is a coefficient of the order of $10^{30} \text{ ml}^{-1} \text{ sec}^{-1}$ (which is a function of the temperature and supersaturation), T is the absolute temperature, S is the supersaturation, and B is the nucleation rate in nuclei/ml/s. The second step in precipitation is the growing of the nuclei through the reaction of ions, molecules or clusters at the interface. These surface reaction products will then become incorporated into the crystal lattice which results in crystal growth. Surface nuclei are built up by a two-dimensional nucleation process that requires an activation free energy [14]. For a spherical nuclei, the free energy of formation of the critical two-dimensional nucleus, ΔG^* , is given by [15].

$$\Delta G^* = \frac{s \sqrt[3]{\frac{2}{3}} \gamma^2}{\Delta \mu} \quad (13)$$

where $\Delta \mu$ is the chemical potential difference per neutral growth unit of ionic species, V_m is the molar volume of the solid phase, and γ is the surface tension.

Because of the presence of a number of nuclei during precipitation in many hydrometallurgical systems, the process of crystal growth in these systems is strongly affected by particle aggregation. Electrical double layer phenomena control the state of aggregation of colloids. If two particles have extensive diffuse double layers that overlap, there is a sufficient energy barrier that prevents the particles from coming close enough together. The attractive van der Waals forces can cause them to aggregate. In the simplest case, for two spherical particles the energy of repulsion, V_R , and the energy of attraction, V_A , are given by:

$$V_R = 2\pi a \epsilon \zeta^2 \exp(-\kappa h); \quad V_A = -Aa/12h \quad (14)$$

where h is the closest distance between two particles of radius a , and A is the Hamaker constant. The expression of the repulsive energy shows that it changes with the square of the zeta potential, and also with the thickness of the double layer ($1/\kappa$). As a general approximation, the aggregation of particles occurs when the zeta potential drops below about 20 or 30 mV.

A wide range of hydrometallurgical processes demonstrate the significance of interfacial phenomena in hydrometallurgy. A few of these processes are reviewed in the following discussion.

Cyanidation of Carbonaceous Ores

Carbonaceous materials in gold and silver ores have been known to inhibit extraction by cyanidation. Dorr and Bosqui [16] correctly attribute this refractoriness to losses of gold and silver cyano complexes by their uptake on the carbonaceous matter. Numerous deposits have been identified to be

refractory by virtue of their carbonaceous matter content. These include the California mother lode [17], the Carlin-type deposits of Nevada [18-20], and the McIntyre-Porcupine and Addison mines in Canada [21]. Similar deposits are found in Russia [21] and Africa [22,23].

The recent interest on the adsorptive properties of activated carbons brought about by the success of the Carbon-In-Pulp (CIP) process has provided a useful tool to analyze the problem. It is believed that the carbonaceous matter in these ores contains active carbons that have large surface areas for adsorption, and active sites made up of oxygen-containing functional groups like phenolic and carboxylic acids. Abotsi and Osseo-Asare [23] suggested that the adsorption of gold-cyanide complex on the carbonaceous material arises from a specific chemical interaction, possibly by hydrogen bonding between the nitrogen in the aurocyano complex and the organic functional group on the ore.

Radtke and Scheiner [24] correlated low cyanidation recovery with the humic acid content of the ore. Removal of the humic acid from the ore by dissolution in a hot NaOH solution resulted in higher gold recovery. On the other hand, the addition of 5 grams of humic acid to 100 grams of non-carbonaceous ore prior to cyanidation reduced extraction from 95 to 21 percent. Humic acid itself abstracted gold from cyanide solutions. Radtke and Scheiner proposed that gold cyanide interacts with humic acids by forming stable metal chelates with the functional groups in the humic acid, a mechanism that is equivalent to that proposed by Abotsi and Osseo-Asare.

Several treatment procedures have been used or suggested for the processing of carbonaceous ores [20,21,25]. They include flotation for the removal of carbon, coating the carbonaceous matter with surfactants, use of CIP or RIP (Resin-In-Pulp) processes, use of alternative chelating or complexing agents, and oxidation by roasting or by chemicals. Flotation would be a simple procedure if no gold is contained in the carbonaceous matter and if either the gold or the organic carbon is easily liberated. The carbonaceous material may be floated and discarded prior to cyanidation. Alternatively the gold/sulfides may be floated while the carbonaceous matter is depressed [21,26].

Adsorption of the gold and silver cyano complexes on carbonaceous material may be prevented by pretreating the ore with organic surfactants that preferentially adsorb on the carbonaceous material. These reagents make the carbon inactive by reducing the surface area directly in contact with the solution. The rest of the ore is left amenable to cyanidation. Examples of these agents are: kerosene and/or oil used by Kerr Addison Mines [21], RV-2 or para nitro benzol azo salicylic acid reportedly used in Russia [20], and heavy machine oils [16]. Other organic reagents like phenols and pyridines are potentially useful because of their irreversible adsorption on active carbons. This method is of course inapplicable to Carlin-type ores where the carbonaceous component has a high gold content. Also, the method may not be appropriate if the ore is to be subsequently treated by the CIP process because any excess surfactant will poison activated carbon.

The introduction of activated carbon during cyanidation of carbonaceous ore was suggested by T. G. Chapman [27] and Crabtree et al. [28]. The method is based on the idea that activated carbon should be more reactive to gold cyanide than the carbonaceous material in the ore. Newmont Exploration Limited [20] extended this idea and applied it to Carlin ores in which the carbonaceous material is high in gold. The objective was to be able to pull the gold out of the carbonaceous material into a hot NaOH/NaCN solution (similar to elution solutions in the CIP process) and adsorb the resulting cyano complex onto the added granular activated carbon. The rest of the procedure is the same as in the regular CIP scheme. Again the assumption is that activated carbon has a considerably higher adsorption power than the carbonaceous materials. The solution conditions are adjusted such that desorption on one happens simultaneously with adsorption on the other. The method worked on mildly refractory ores tested by Newmont Exploration but only with limited success on the most refractory ores which contain pyrite in addition to the organic carbon.

Gold and silver form complexes or chelates with compounds other than cyanide. Each compound represents a potential lixiviant [29]. Malononitrile, one of these compounds, was found to be more effective with carbonaceous ores

than cyanide [30]. Nitriles certainly merit further investigation, to understand how they react with gold and silver and thereby fully assess its usefulness and address such issues as their toxicity.

Extraction of gold from refractory ores by cyanidation may be improved by preroasting. The carbonaceous material is burned to CO_2 and CO while pyrites are oxidized to iron oxides. Although roasting liberates any gold values contained in the carbonaceous materials, it does not always leave the occluded gold accessible to the cyanide solution. The temperature of roasting must be carefully controlled in order to produce a porous iron oxide residue [16,31,32].

Chemical oxidation of refractory ores by various oxidizing agents has been successfully used. The ore from the Homestake McLaughlin Mine in Northern California is somewhat refractory due to its carbon and complex sulfide content, and it is oxidized in autoclaves with oxygen in a sulfuric acid medium at elevated temperatures and pressures. Chlorine or hypochlorite, which was found to be effective in tests done by the U.S. Bureau of Mines [33,34], has been used at the Freeport McMoran Gold Company in Elko, Nevada, where chlorine gas is introduced into an agitated pulp via gas spargers [35]. Guay [19] developed a process in which both oxygen and chlorine are used to oxidize pyrites and carbonaceous material in the ore at 80 to 86°C.

The Carbon-in-Pulp Process

Activated carbon has been used extensively for the recovery of gold and silver from cyanide solutions since the introduction of the CIP process at the Homestake Mine in 1973 [36]. In spite of this industrial success, the nature of the interaction between the cyano complexes and the activated carbon is still not very well understood. Numerous investigators have forwarded postulates that relate the adsorption of a species with its solvated radii [37-40], or propose that the adsorbed species is reduced to the metallic state [41], or attribute the adsorption to the overlapping of the double layers in the narrow pores of the carbon [42]. McDougall et al. [43,44] proposed what is perhaps the most widely accepted theory. It involves the adsorption of an

ion pair $M^{n+}[Au(CN)_2]^-_n$, where M^{n+} may be H^+ , K^+ , Na^+ , Li^+ , Mg^{2+} , Ca^{2+} , etc., followed by a partial reduction of Au^+ to an oxidation state of about +0.3 and a change of the adsorbed form from $Au(CN)_2^-$ to a $(AuCN)_x$ cluster.

Activated carbons commonly used in the CIP process are gas adsorbent coconut carbons with specific surface areas of about $1000 \text{ m}^2/\text{g}$ arising from slitlike pores in the micropore range. They are believed to contain irreversibly adsorbed oxygen in the form of phenolic-type and carboxylic acid functional groups [45]. Quinone type carbonyl groups, carboxylic acid anhydride, cyclic peroxide, normal and fluorescent-type lactones are also believed to be present.

The chemistry of adsorption of metal cyano complexes on activated carbon has been the subject of a research investigation in our laboratories [46]. The activated carbon used has a specific surface area of $1220 \text{ m}^2/\text{g}$ (CO_2 -Dubinin-Polanyi Equation). It contains 0.51 meq/g total surface acid, 0.49 meq/g of which is phenolic in functionality (by methods outlined by Brooks and Sternhell [47]). At pH's above about 2, the zeta-potential of the activated carbon is negative as shown in Figure 2. Cyanide solutions of Ag, Cu, Hg, Cd, and Zn were contacted with this carbon as a function of pH [46]. Figures 3(a) and 3(b) show the copper cyano species distribution diagram and the copper

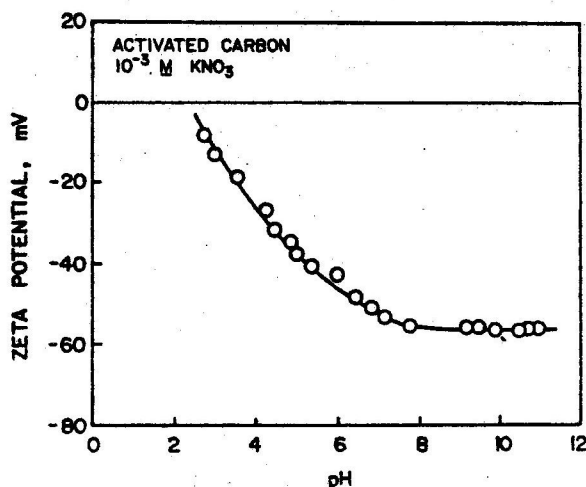


Fig. 2 - The zeta potential of activated carbon in 10^{-3} M KNO_3 as a function of pH [46].

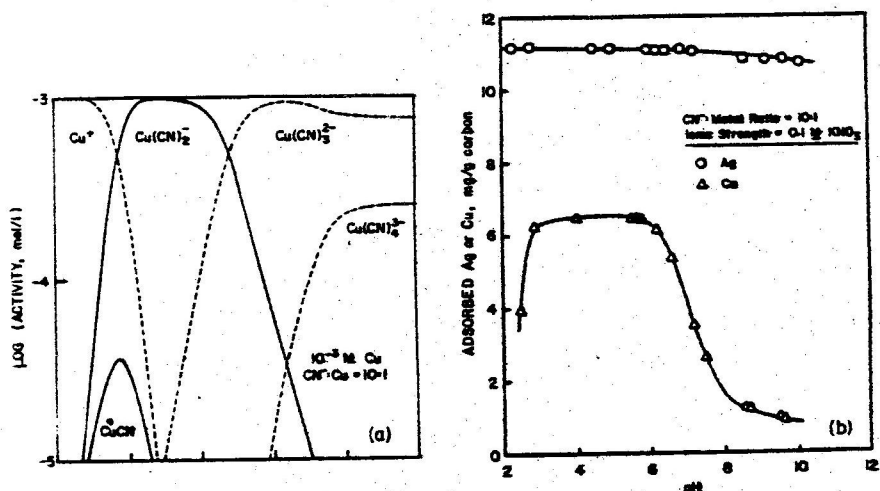


Fig. 3 - a) Logarithmic distribution diagram for Cu(I) cyano complexes at $\text{CN}^- : \text{Cu} = 10$ showing the predominance lines for CuCN and Cu(CN)_2^- , and b) the adsorption of Ag(I) and Cu(I) cyano complexes on activated carbon as a function of pH at an initial metal concentration of 10^{-3} M [46].

uptake by the activated carbon as a function of pH, respectively. The adsorption of Cu(I) from cyanide solutions shows marked pH dependence that corresponds closely with the predominance profile of the Cu(CN)_2^- and CuCN species. This means that whereas CuCN and Cu(CN)_2^- adsorb on activated carbon, Cu(CN)_3^{2-} and Cu(CN)_4^{3-} do not. On the other hand, the uptake of Ag(I) cyano complexes by activated carbon is essentially complete throughout the pH range of the experiment, as also shown in Figure 3(b). In the same pH range, the predominant form of the Ag(I) cyano complexes is Ag(CN)_2^- , evidence that the adsorbing species is the Ag(CN)_2^- complex. Thus a trend in adsorption is seen based on the charge carried by the cyano complexes. Neutral and singly-charged complexes seem to be the active species during adsorption. Apparently, the negative charge on the carbon surface repels the more highly charged species, preventing them from adsorbing. The effect of the charge of the aqueous species is also seen in the adsorption of Zn(II) from cyanide solutions from activated carbon, Figure 4(b). Comparison of the adsorption

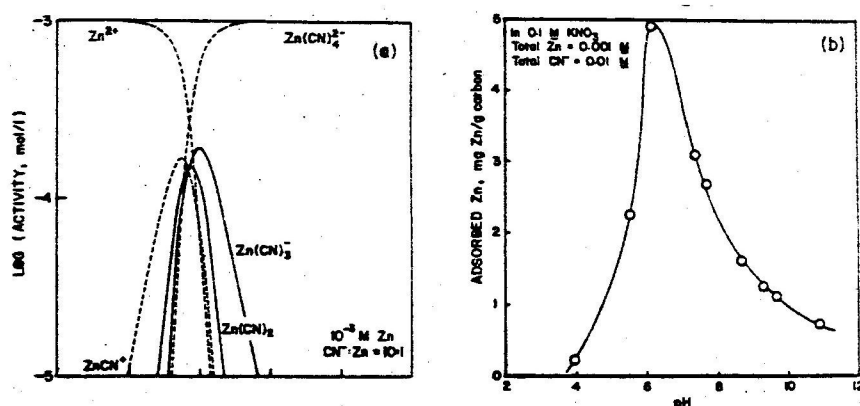


Fig. 4 - a) Logarithmic distribution diagram for Zn(II) cyano complexes at $CN^- : Zn = 10$ showing the predominance lines for $Zn(CN)_2$ and $Zn(CN)_3^-$, and b) the adsorption of Zn(II) cyano complexes on activated carbon as a function of pH at an initial metal concentration of 10^{-3} M [46].

curve and the predominance lines for the Zn(II) cyano species, Figure 4(a), indicates that the active species are $Zn(CN)_2$ and $Zn(CN)_3^-$ and that the species $Zn(CN)_4^{2-}$ does not adsorb.

The sensitivity of the carbon to the charge of the species indicates that the adsorbing species do not form neutral salts with the co-adsorbing cations. The carbon actually behaves as if the species were negatively charged or it should indiscriminately adsorb all the cyano complexes regardless of their charge. Furthermore, the selectivity of activated carbon for gold and silver may be attributed to the greater preference of these metals to form the dicyano complex compared to the rest of the metals in Groups I-B and II-B [48]. This allows prevention of Cu(I) adsorption in plant operations by maintaining high pH values and cyanide-to-copper ratios to ensure that Cu(I) exists as the non-adsorbing tri- and tetracyano complex forms.

Adsorption Losses in Ammonia Hydrometallurgy

One of the major problems encountered in the ammoniacal leaching of

laterite ores is the low recovery of cobalt. Various workers have recognized the cause of the low extraction to be the coprecipitation of dissolved cobalt with iron hydroxide and adsorption on the high surface area precipitate [49-51] or residue [52,53].

Osseo-Assare and Fuerstenau [7,53,10] made a detailed study of the uptake of copper, nickel and cobalt by alumina, hematite, quartz and rutile as a function of, among other parameters, pH and ammonia concentration. The effect of the adsorbent on adsorption was determined as a function of pH with the total ammonia concentration fixed at 0.5 M, the total metal concentration at 10^{-3} M, and the amount of adsorbent such that the surface area of the solids was $160 \text{ m}^2 \text{ dm}^{-3}$. As can be seen in Figure 5, the order of adsorbability appears to be titania > hematite > alumina > quartz for Cu and Ni, and titania = hematite > alumina >> quartz for Co. The role of the substrate does not appear to be as significant at high pH (>10.5) as it does at low and intermediate pH values. Increasing the total ammonia concentration reduced the adsorption losses. The positions of the humps and valleys seem to be a characteristic of the metal rather than the substrate, and they must result from competition between hydroxyls and ammonia as ligands in forming complexes. These observations indicate that the electrical double layer does not play an overriding role in the uptake of metals from ammoniacal

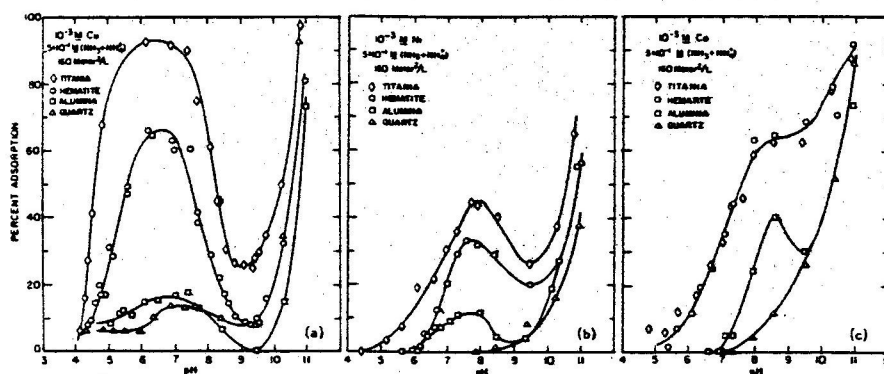


Fig. 5 - Adsorption of (a) copper, (b) nickel, and (c) cobalt onto various substrates in aqueous ammoniacal solutions containing 10^{-3} M total metal ion and 0.5 M total ammonia as a function of pH [53].

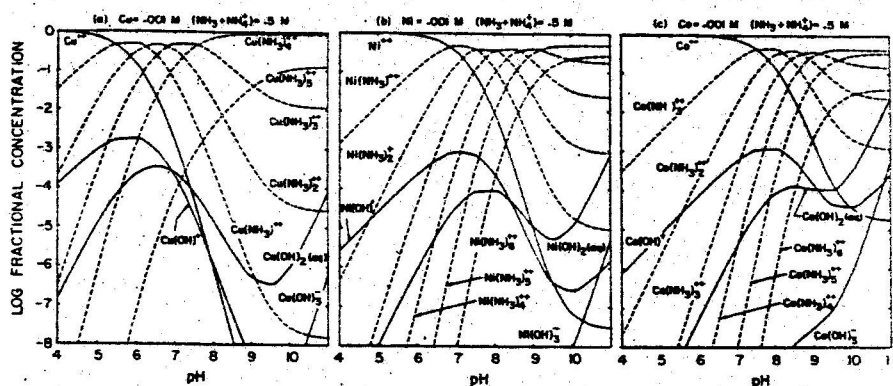


Fig. 6 - The distribution of aqueous species as a function of pH in a solution containing 0.5 M total ammonia and 10^{-3} M (a) Cu (II), (b) Ni(II), and (c) Co(II) [53].

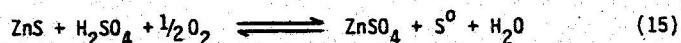
solutions. However, the solid substrates do play a role, as evidenced by their effect on the amount of metal uptake at a given pH.

In order to delineate the mechanism by which a dissolved metal species is withdrawn from ammoniacal solutions, Osseo-Asare and Fuerstenau [53] computed the species distribution in 0.5 M total ammonia and 10^{-3} M total metal concentration. The results are presented in Figure 6 for Cu(II), Ni(II), and Co(II), respectively. These diagrams imply that the ammine complexes have a strong regulating effect on adsorption because they control the distribution of $M(OH)_2(aq)$, which most closely resembles the hump and valley profiles. Although the concentration of this species is so small, they have been shown to adsorb readily against electrostatic repulsion forces [54-57]. Osseo-Asare and Fuerstenau [7] attributed the adsorption to field induced precipitation [58]. The high electric field in the interfacial region causes a substantial decrease in the dielectric constant of water in the interfacial region from its value in the bulk aqueous solution [59,60]. Thus the interfacial dielectric constant of water may be as low as 6 compared to the bulk value of about 78. Under these circumstances, the metal concentration needed for interfacial precipitation is much less than that necessary for bulk precipitation.

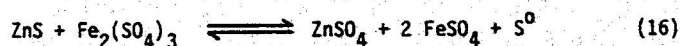
Acid Pressure Leaching of Sphalerite

The acid pressure leaching of zinc concentrates is based on the oxidation of sulfur in sphalerite by oxygen according to the following reaction [61]:

The mechanism by which quebracho and lignin sulfonate cause dewetting has



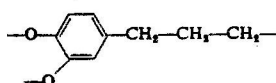
This reaction proceeds at practical rates in the presence of acid soluble iron which, in effect, breaks down the reaction into two [62]:



The formation of elemental sulfur is a distinct advantage because it reduces the necessity to produce sulfuric acid as would be the case when sulfur dioxide is formed. Elemental sulfur, however, markedly reduces the leaching rate by forming a product layer, particularly when the temperature is high enough that the sulfur is molten and wets the sphalerite. Earlier, the working temperature had to be kept below the melting point of sulfur. One or more regrinding operations during the course of leaching can offset the effect of the solid sulfur product layer, but the low reaction rate still called for 6 to 8 hours retention time [63].

A crucial factor in the development of the acid pressure leaching process is the addition of surfactants to the leaching system. The surfactants inhibit the wetting by molten sulfur of unleached or partially leached zinc sulfide. The optimum working temperature was found to be about 150°C which corresponds to the minimum viscosity of molten sulfur [62]. Typical surfactants used are quebracho and/or calcium lignin sulfonate at a dosage of 500 to 1500 g/t. The retention time is reduced to 20 to 60 minutes with a recovery of 96 to 98 percent [64].

barely been studied. Clearly, the effect is due to modification of the surface tensions at the three-phase contact between the mineral M , water W , and sulfur S . Water rather than sulfur wets the mineral if $\gamma_{MW} + \gamma_{SW} < \gamma_{MS}$. A surfactant will therefore be effective if it adsorbs at the mineral/water interface or the sulfur/water interface or both. Osseo-Asare [65] suggested that organic surfactants adsorb on sulfur by orienting their nonpolar groups towards the bulk of the sulfur phase and the ionic polar groups towards the aqueous phase. In the case of ZnS , he suggested that lignin sulfonates adsorb by the interaction of the polar groups with the positively-charged surface and the subsequent adsorption of a second layer by hydrophobic interaction. The probable structures of quebracho and lignin sulfonate, however, suggest that Osseo-Asare's model may be too simplistic. The most important building block of most lignin components is the dioxiphenyl propyl unit which has the following structure [66]:



Simple combinations of this unit will result in compounds that are truly heteropolar and will be useful in the reduction of the surface tension of molten sulfur as suggested by Osseo-Asare. As the degree of complexity of the structure increases and with the addition of polar groups by methods such as sulfonation and saponification, the compound becomes replete with functional groups so that it is effectively polar all throughout. This is probably the reason why addition of lignin sulfonate does not always result in the reduction of the particle size of the sulfur droplets as observed by Doyle et al. [64].

Quebracho is a tannin extract composed of very complex mixtures of polyphenols and their derivatives [66]. Figure 7 shows the structures of the components of hydrolyzable and condensed tannins. The presence of large number of hydroxyls cause quebracho always to be hydrophilic. These anionic polar groups make it a good depressant in flotation with anionic collectors, for example, in the depression of calcite, carbonaceous matter and sphalerite

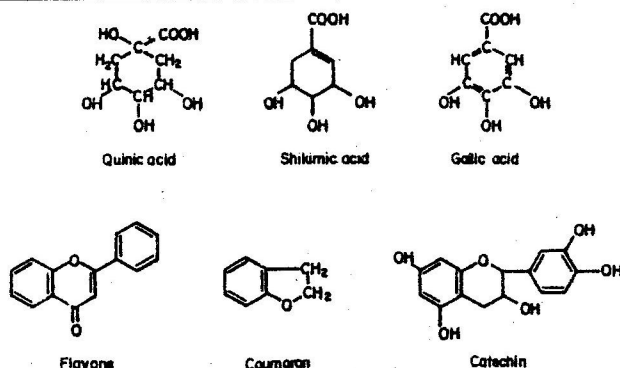


Fig. 7 - Chemical structure of the components of hydrolyzable and condensed tannin molecules [66].

[66]. The dewetting effect of quebracho in acid pressure leaching of sphalerite could therefore take place by the same mechanism found in depression during flotation. Quebracho adsorbs on sphalerite by the interaction of ionized phenolic and carboxylic groups with the cationic surface sites. The remainder of the polar groups that are oriented towards the aqueous phase renders the sphalerite surface hydrophilic.

Flotation Processes in Hydrometallurgy

The Leaching-Precipitation-Flotation (LPF) process is a hydro-metallurgical process that incorporates a surface-based operation, namely flotation, as a separation step. Leach-precipitation-flotation has been long used for the recovery of copper from oxidized copper ores [67]. In this process, oxidized copper is dissolved by acid leaching techniques and the copper is precipitated by cementation with powdered iron sponge. The resulting copper particles are recovered by flotation, using a xanthate to make the copper particles hydrophobic.

Kuhn et al. [68] published a detailed article on the recovery of copper from oxidized copper leach circuits at Anaconda. In that operation, copper was precipitated with H_2S gas, forming Cu_2S which was hydrophobic and could be recovered by flotation without adding a collector. Only a frothing agent is necessary to create the froth for flotation. Close control of the amount of

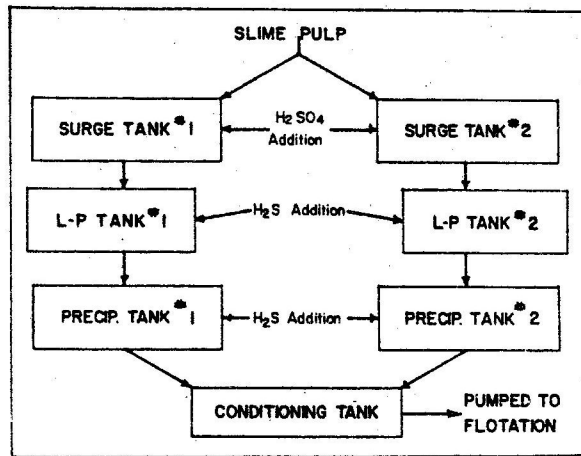


Fig. 8 - Flowsheet of the Anaconda LPF process [68].

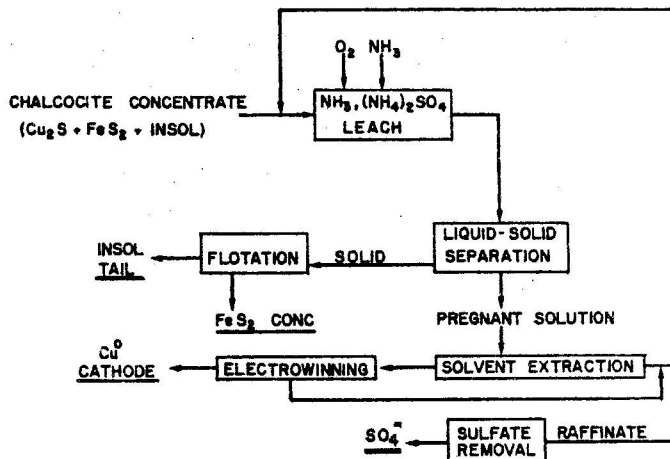


Fig. 9 - Schematic representation of the Arbiter process for the recovery of copper from copper sulfide concentrates [69].

H₂S was necessary, however, since adding too much sulfide ion would disperse the particles. The flocculated colloidal particles, by being large aggregates, float at a more rapid rate. Figure 8 shows the general flowsheet of the Anaconda LPF operation.

The Arbiter process, which is an oxidizing ammonia leach process, is of interest in recovering copper and other metals from concentrates while rejecting iron and sulfur [69]. Figure 9 schematically illustrates the

flowsheet for recovering copper from chalcocite concentrates, where flotation is an integral part of the operation.

Harmful Effects of Surfactants

Surfactants are not always welcome in hydrometallurgical processes. Collectors used to preconcentrate an ore by flotation, for example, have been shown to inhibit cyanidation of gold [70-72]. The surfactant apparently stabilizes gold with respect to the cyanide lixiviant by tying up the reactive sites on the surface. Alternatively, it can be considered to be acting as a dewetting agent, inasmuch as the collector makes the surface more hydrophobic. Frothers have also been known to poison activated carbon in the CIP process. Results of experiments on the effect of a series of aliphatic alcohols on the adsorption of silver from cyanide solutions onto carbon are

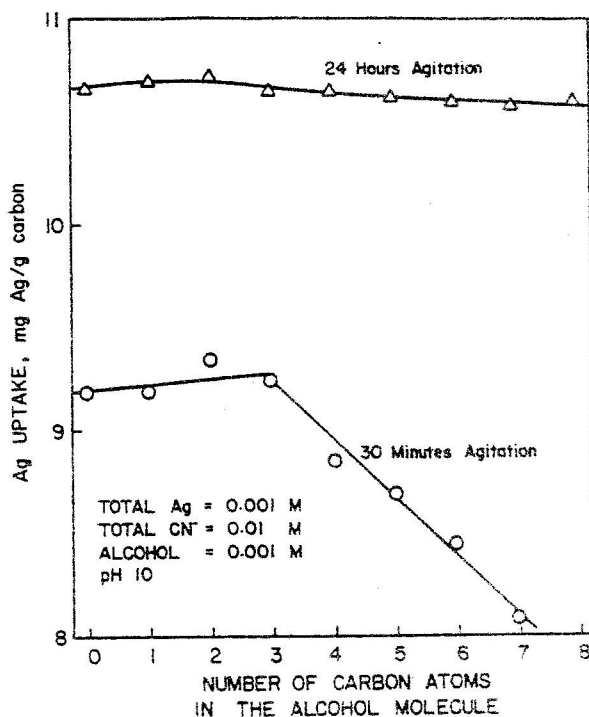


Fig. 10 - The effect of alcohol chain length on the adsorption of $\text{Ag}(\text{CN})_2^-$ on activated carbon at two different agitation times at pH 10 and 0.1 M KNO_3 [46].

given in Figure 10 [46]. These results show that although the alcohols did not affect the equilibrium amount of silver adsorbed, their effect on the initial loading was strong. In plant operations, where equilibrium conditions are rarely attained, a kinetic effect like this is significant. The presence of frothers must therefore be avoided or at least limited to those that do not show surface activity towards activated carbon.

In the acid pressure leaching of zinc, quebracho may have counter-productive effects as shown by Arauco and Doyle [73]. It seems that quebracho can coat sphalerite extensively and tenaciously to the point of hindering direct contact of the surface with the leaching solution. Flocculants that are used to aid filtration may also reduce the leaching rate of sphalerite. Adding the flocculant before leaching results in even better filtration characteristics [74]. However, the cost of this advantage is a reduction of the leaching rate [75].

SUMMARY

Interfacial phenomena that are important in controlling hydro-metallurgical processes have been discussed. These include the formation of the electrical double layer and its properties, adsorption phenomena, surface tension and precipitation. In many instances, the control of interfacial phenomena is crucial in the success of an operation. Losses due to adsorption were observed in the ammoniacal leaching of laterite ores and the cyanidation of carbonaceous gold ores. These losses are minimized by direct or indirect intervention in the adsorption process. Adsorption, if selective, can be beneficial, as in the CIP process. The acid pressure leaching of zinc concentrates at molten sulfur temperatures is made feasible by the addition of dewetting agents to prevent sulfur coating. Precipitates or solid impurities may be separated by flotation as in the LPF process and in the removal of carbon from carbonaceous gold ores. The amount and type of surfactants to be used must be chosen judiciously to prevent passivation of surfaces during leaching and adsorption.

ACKNOWLEDGEMENT

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STRESZCZENIE

Fuerstenau D.W., Herrera-Urbina R., Ibrado A.S., 1987. Zjawiska międzyfazowe w hydrometalurgii. Fizykochemiczne Problemy Mineralurgii 19; 53-82.

Procesy hydrometalurgiczne są często kontrolowane zjawiskami zachodzącymi na granicach fazowych. Dlatego poznanie tych zjawisk jest niezbędne dla określenia optymalnych warunków zachodzenia procesów hydrometalurgicznych. Artykuł ten opisuje różne zjawiska międzyfazowe ważne dla hydrometalurgii. Przedyskutowano w nim niektóre przykłady z praktyki, gdzie odgrywają one znaczącą rolę i decydują o sukcesie lub niepowodzeniu w przeprowadzanych operacjach hydrometalurgicznych.

СОДЕРЖАНИЕ

Д.В.Фирстенау, Р.Херрера, А.С.Ибрадо, 1987. Междофазовые явления в гидрометаллургии. Физикохимические вопросы обогащения, 19; 53-82.

Гидрометаллургические процессы часто контролируются явлениями, происходящими на фазовых границах. Поэтому ознакомление с этими явлениями необходимо для определения оптимальных условий происхождения гидрометаллургических процессов. Эта статья описывает различные междофазовые явления для гидрометаллургии. Обсуждены некоторые примеры из практики, где они играют значительную роль и решают об успехе или неудаче в проводящихся гидрометаллургических операциях.