#### Minerals Engineering 95 (2016) 185-196

Contents lists available at ScienceDirect

**Minerals Engineering** 

journal homepage: www.elsevier.com/locate/mineng

## On the mechanism of the flotation of oxides and silicates

### F.K. Crundwell

CM Solutions (Pty) Ltd, Building T5 Pinelands, 1 Ardeer Road, Modderfontein, 1609, South Africa

#### ARTICLE INFO

Article history: Received 18 April 2016 Revised 11 June 2016 Accepted 15 June 2016 Available online 7 July 2016

Keywords: Flotation Mechanism Electrostatic mechanism Zeta potential Surface charging

#### ABSTRACT

The mechanism of flotation of oxide and silicate minerals was established long ago as being due to the electrostatic attraction between the charged surface and the charge of the collector. What is less well established is the mechanism of the charging of the mineral surface. Most researchers have postulated that the adsorption of  $H^+$  is the cause. However, the adsorption model and its derivatives (such as the amphoteric and multisite-adsorption models), do not successfully describe the data for the zeta potential as a function of pH. In particular, these adsorption models have the following features that are not observed: (i) they are symmetrical about the point of zero charge, whereas the data is asymmetrical, (ii) they have an inflection at the  $pK_a$  values, leading to an asymptotic approach to the point of zero charge, whereas such an inflection is not observed, and (iii) they only fit the data in its extremes, that is, when the pK<sub>a</sub> values differ by orders of magnitude, or are very close to one another. An alternative mechanism of charging is proposed here that is based on the dissolution of ions from and deposition of ions onto the mineral surface. It is shown that this model (a) fits the data, (b) is consistent with the thermodynamic model for reversible interfaces, (c) is consistent with the thermodynamics of the overall reaction and its solubility, (d) indicates reasons for the ageing of surfaces and (e) displays the observed features of zeta potential measurements as a function of pH, that is, it is pseudo-Nernstian and asymmetrical in nature. Application of the proposed theory is discussed for the flotation of quartz and corundum. © 2016 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Froth flotation, practiced for more than a century, is an enormously successful process treating billions of tons of material each year (Fuerstenau, 1999). The flotation of oxides and silicates at industrial scale includes rutile, mica, quartz, feldspars, and the iron oxides minerals (Miller et al., 2007).

The mechanism of flotation of these minerals is known to be dependent on the electrical properties and the solubility of the mineral, the charge and the chain length of the collector and the stability of the metal-collector salt (Miller et al., 2007). Depending on the predominance of any of these factors, flotation may occur by an electrostatic attraction between the surface and the collector (referred to as physical adsorption), or by a "specific" chemical interaction (referred to as chemical adsorption). In many instances, flotation is strongly influenced by electrostatic interactions because the surface of the mineral develops an electrical charge that attracts the charged "head" of the collector molecule (Miller et al., 2007).

The primary variable affecting the surface charge of oxide and silicate minerals is the pH (Fuerstenau and Pradip, 2005). This

charge can be measured using electrokinetic techniques and is reported as the zeta potential (or the electrophoretic mobility) (Hunter, 1981). As a result, the primary evidence for the electrostatic mechanism is the correspondence between the zeta potential and flotation recovery as a function of pH (Gaudin and Fuerstenau, 1955a,b). For example, Iwasaki et al. (1960) reported the results for the flotation of goethite (FeOOH) shown in Fig. 1. The flotation recovery using anionic collectors (dodecyl sulphate and sulfonate) increases as the pH decreases below the point of zero charge (pzc) where the zeta potential is zero. On the other hand, the flotation recovery using cationic collectors (dodecyl ammonium) increases as the pH increases above the pzc. The explanation of these results as follows. When the pH is less than the *pzc*, the surface has a positive charge, and when it is greater than the pzc, it has a negative charge. When the surface has a positive charge anionic collectors are able to attach to the surface. Thus flotation using anionic collectors occurs at pH values below the pzc. When the surface has a negative charge the anionic collector does not attach and no flotation occurs. On the other hand, when the surface has a negative charge cationic collectors are able to attach to the surface. Thus flotation using cationic collectors occurs at pH values above the pzc. This mechanism, shown in Fig. 2, clearly emphasises the importance of excess surface charge, pH and *pzc* as determining factors in flotation.







E-mail address: frank.crundwell@cm-solutions.co.za

#### Nomenclature

Latin symbols		
C <sub>d</sub>	electrical capacity across Stern layer, F	
$\vec{k}$	dissolution rate constant, mol/s	
$\overleftarrow{k}$	precipitation rate constant, mol m/s	
F	Faraday's constant, C/mol	
Ι	ionic strength, mol/L	
Κ	equilibrium constant, –	
Ns	total concentration of sites on surface, $m^{-2}$	
pzc	point of zero charge	
q	charge on an electron, C	
$r_M$	rate of removal of M from surface, mol/m <sup>2</sup> s	
r	rate of dissolution, mol/m <sup>2</sup> s	
R	gas constant, J/mol K	
t	stoichiometric coefficient, –	
Т	absolute temperature, K	
Greek symbols		
α	charge transfer coefficient, –	
60	permittivity of free space, F/m	
E <sub>rw</sub>	relative permittivity of water, –	
$\phi$	galvani (outer) potential, V	
$\mu$	chemical potential, J/mol	

The source of this excess surface charge is usually seen as being caused by one of two possible equilibrium mechanisms: (i) a result of differences in the affinity of the phases for ionic species, and (ii) a result of the ionisation (or hydrolysis) of surface groups (Hunter, 1981). The first mechanism envisages the equilibrium of one of the components of the solid with that component in solution, say Ag<sup>+</sup> in solution with AgI. If the silver ions in solution are in equilibrium with those of the solid, the electrochemical potential,  $\tilde{\mu}(Ag^+)$ , must be equal in both phases:



**Fig. 1.** The relationship between the flotation recovery and the zeta potential for the mineral goethite using anionic (dodecyl sulphate and dodecyl sulfonate) and cationic (dodecyl ammonium) collectors. Data from Iwasaki et al. (1960).

$\tilde{\mu}$	electrochemical potential, J/mol
$\sigma$	electrical charge, C
$\Gamma(\ldots)$	surface activity or concentration with respect to a particular surface species, $m^{-2}$

Additional symbols

- {...} thermodynamic activity, –
- [...] concentration or thermodynamic activity in solution, mol/L
- $\equiv$  M species M on surface
- $\equiv^{a-}$  surface vacancy with charge a-

#### Subscripts

- a aqueous
- s solid
- ohp outer Helmholtz plane
- $\infty$  bulk conditions

Superscripts

0 standard thermodynamic conditions of pressure and temperature

$$\tilde{\mu}_s(\mathbf{Ag}^+) = \tilde{\mu}_a(\mathbf{Ag}^+) \tag{1}$$

where the subscript *s* refers to bulk of the solid phase, and *a* to the bulk of the aqueous phase. (Refer to the list of symbols.) By expanding the electrochemical potential into its component parts, Eq. (1) can be written as Eq. (2) (Hunter, 1981):

$$\mu_{s}^{0}(Ag^{+}) + RT \ln\{\Gamma(Ag^{+})\} + F\phi_{s}$$
  
=  $\mu_{a}^{0}(Ag^{+}) + RT \ln(\{Ag^{+}\}) + F\phi_{a}$  (2)

where  $\mu^0$  is the chemical potential at standard conditions,  $\Gamma$  represents surface activity, {} represent the activity of the ion in solution,  $\phi$  represents the galvani potential, *R* is the gas constant (8.314 kJ/mol), *T* the absolute temperature (*K*), and *F* the Faraday constant (95,485 C/mol).

Eq. (2) can be rearranged to yield Eq. (3):

$$\Delta \phi = \phi_s - \phi_a = \frac{\mu_a^0(\mathsf{Ag}^+) - \mu_s^0(\mathsf{Ag}^+)}{F} + \frac{RT}{F} \ln\left(\frac{\{\mathsf{Ag}^+\}}{\Gamma(\mathsf{Ag}^+)}\right) \tag{3}$$

As a result of Eq. (3), silver ions in solution (and iodide ions, following an analogous treatment) are referred to as *potentialdetermining ions*. In addition, Eq. (3) is Nernstian, which means that the potential follows a logarithmic dependence on the concentration.

This mechanism has been widely accepted for *ideal reversible* surfaces, and it will be shown that the mechanism proposed in this paper is consistent the thermodynamic approach leading to Eq. (3).

A difficulty, however, arises in the case of minerals such as the oxides, silicates and indeed almost all other minerals. The measured zeta potential of these surfaces depends on the pH of the solution, implying that the potential-determining ion is  $H^+$  (or  $OH^-$ ). Since  $H^+$  is not a component of the solid, the application of the above thermodynamic analysis is not applicable (Berube and de Bruyn, 1968). In this case, the second mechanism of surface charging mentioned above is invoked. The adsorption of  $H^+$  (or equivalently, hydrolysis or ionisation of the surface) is envisaged as the cause of the excess surface charge. However, the adsorption of only  $H^+$  on the surface does not solve the conundrum, because the zeta potential will not change sign. With this in mind, Yopps and Fuerstenau (1964) proposed the "amphoteric model" (also

Download English Version:

# https://daneshyari.com/en/article/232722

Download Persian Version:

https://daneshyari.com/article/232722

Daneshyari.com