



A model for the zeta potential of copper sulphide



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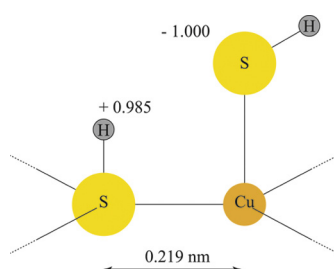
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HIGHLIGHTS

- A software to model the $p\zeta$ -pH curves with IPHREEQC in Matlab is available.
- The $p\zeta$ -pH curve of Covellite (CuS) is modelled with S-sites only.
- We transposed MUSIC to a sulphide.
- Partial surface charges were derived from Pauling's electrostatic valence.

GRAPHICAL ABSTRACT



Predominant species at the surface of covellite at pH 4

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ABSTRACT

A model is proposed for the zeta-potential versus pH curve of Covellite (CuS). The classical Gouy–Chapman–Stern treatment of the adsorption of protons is applied to a model surface derived from the crystallographic data. The surface charges are obtained by an original adaptation of the concepts from the MUSIC model to a sulphide, i.e. the analysis of the chemical bonding in Pauling's electrostatic valence framework to derive partial surface charges. The authors develop a software for the fitting of $p\zeta$ -pH curves using IPHREEQC for the calculation of the zeta potential at each pH point and Matlab to drive the calculation of the whole pH set and the optimisation of the parameters: capacitances of the double layer, site densities, charges and acidity constants. The model successfully reproduces the experimental data, considering only two sulphided surface sites: introduction of an elemental sulphur layer or consideration of hydroxyl surface sites is not required to explain the charging behaviour of Covellite when carefully precipitated under nitrogen.

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1. Introduction

1.1. Background

Acid Mine Drainage (AMD) has been one of the most prevalent sources of environmental pollution in regions of high mineral extraction activity “The low pH that characterises most AMD contaminated wastewater induces leaching of minerals which may lead to heavy impregnation of various metal ions” [1]. A conventional method of dealing with AMD has involved the use of lime which results in neutralisation of the waste water and

the simultaneous precipitation of the metal ions as hydroxides. According to Dyer et al. [2] and Charentanyarak [3], the minimal hydroxide solubility from AMD is achieved at an approximate pH range of 9.5–10. Consequently, this means that maximum metal ion removal from AMD using hydroxide precipitation is only possible in this pH range. In order to promote optimal metal hydroxide precipitation, large amounts of lime have to be added so as to attain this relatively high pH.

Metal sulphide precipitation has been proposed as an alternative to hydroxide precipitation due to several advantages over the latter that include: relatively lower solubilities which result in much lower downstream metal ion concentrations; potential selective recovery which would promote re-use of metal ions and a significant reduction in volume of the residual waste stream [4]. However, the same attributes that render metal sulphide

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precipitation superior to hydroxide precipitation also confer challenges to the overall viability of the process. The significantly low solubilities of metal sulphides result in the sulphide precipitation processes being inherently driven by high supersaturation. It has become generally accepted that the pre-requisite for the production of non-colloidal metal sulphide particles is to operate under mildly supersaturated conditions [5,6] and hence the high supersaturation conditions that characterise metal sulphide precipitation promotes the production of colloidal particulates. In a sedimentation or filtration based separation process the production of colloidal particles results in the sub-optimal solid–liquid separation of precipitated material which severely compromises the efficiency of the overall process.

Some electrochemical studies have shown that copper sulphide particles possess a highly negative zeta potential at pH values greater than 2, [7,8]. According to the DLVO theory, [9,10], this results in colloidal stability and a decrease in the absolute value of the zeta potential is required to promote aggregation and consequent enhanced separation. The exact value of this threshold zeta potential varies from one metal sulphide system to another largely due to the different Hamaker constants [11]. Other factors that also influence stability are ionic strength and solid fraction. According to Ottewill [12], aggregation should generally be dominant within a zeta potential range of -15 mV to $+15$ mV. This is consistent with results presented by Mokone et al. [7], the authors attributed the stability of a precipitated copper sulphide suspension to a highly negative zeta potential of about -38 mV at a pH of 6 while Vergouw et al. [13] also showed that the maximum settling velocity for PbS and FeS was observed roughly coincident to the isoelectric point.

It is from this background that the importance of electrochemical knowledge of metal sulphide particles is crucial in predicting and understanding suspension behaviour of metal sulphide systems. Work carried out by Moignard et al. [14] led to the initial development of a deduction that characterised the surface of metal sulphide particles of being composed of two functional groups, a sulphido- group ($>SH$) and a hydroxo- group ($>OH$). The charge on the surface of a metal sulphide particle, therefore, becomes dependent on the density and partial charge of the surface sulphido- and hydroxo- groups respectively. Surface density and partial charge of the surface groups depend on the crystal lattice structure and the interaction between the respective metal and sulphide ions. Hiemstra et al. [15] developed a charge distribution and multi-site complexation model (CD-MUSIC) which can be used to determine the surface charge of (hydr)oxide species. The model can predict the zeta potential–pH properties of oxide and hydroxide species and this knowledge is invaluable in various geological, agricultural and precipitation studies. In the current study the CD-MUSIC model will be used to develop a surface complexation model that is applicable to the surface of metal sulphides. This will be done by adapting the similarities that exist between the two systems and in certain cases proposing original ideas based on first principles of physical chemistry.

1.2. Modelling of $p\zeta$ –pH curves: state of the art

Because of the importance of oxide and hydroxide compounds in geochemistry, transport of metal ions in soils and industry (intermediates, pigments, fillers, catalysts, ceramics, etc.), their respective properties have been widely studied. The available literature is too extensive to be cited here and many good textbooks have been published (e.g. [16]). There is general consensus that the aqueous surface of (hydr)oxides is covered by $>O$ and $>OH$ sites (where $>X$ denotes a species X , bound to a surface, and can represent either Cu, S, O or any cation M) and this can be (i) lattice oxide or hydroxide ions with unsaturated coordination at the surface;

(ii) a result of the adsorption of water on coordinately unsaturated metal and oxide ions at the surface. The latter gives rise to different hydroxyl groups according to Eq. (1):



Consequently, even the simplest surfaces such as $MgO\{001\}$ bear at least two different hydroxyl sites. More complex structures with structurally different faces and several metal and/or oxide sites exhibit wide variation in the nature of surface hydroxyl groups [17]. The surface charge then arises from the protonation/deprotonation of these surface hydroxyl sites and this is classically ruled by pK_a acidity constants. Therefore, it follows that surface hydroxyl groups in different structural environments exhibit different acidity constants [18]. This means that the knowledge of pK_a values is crucial in predicting surface charge and rightfully so it has been the object of many studies, especially by ab-initio methods [19]. Currently the most successful approach is the straightforward MUSIC model, [15,20], which is based on two main original concepts: (i) an empirical relation between the geometrical environment and the pK_a ; (ii) a partial charge on the less or more protonated hydroxyl as derived from Pauling's electrostatic valence.

The calculation of the surface charge of a particle in an aqueous solution of known pH requires additional input of the electrochemical potential of surface species which is derived from the electrostatic potential which itself arises from the presence of charged surface species. A classical treatment to this challenge is the use of the Poisson–Boltzmann equation and its resolution in the framework of a double layer or triple layer, typically the Gouy–Chapman–Stern (GCS) theory. Derived from the same theory is the value of the potential at the (ill-defined) shear plane in the motion of charged particles in an electrostatic field: namely the zeta-potential ($p\zeta$) that is easily computed from the experimental electrostatic mobility measured by commercial “zetameters”.

A combination of non-integer surface charges, multiple surface pK_a s and the GCS theory are state of the art and implemented in software such as PHREEQC [21] to successfully model the $p\zeta$ of oxides in various environments [22,23]. GCS calculations but with “conventional” charges ($>S^-$, $>SH$, $>SH_2^+$) have been performed on some sulphides such as ZnS [24] and FeS [25], but no literature on CuS has been found except for a few raw $p\zeta$ –pH, mobility–pH or charge–pH curves [8,26,7].

2. Materials and methods

2.1. Reagents

All chemicals used in the investigation, $CuSO_4 \cdot 5H_2O$, $Na_2S \cdot 9H_2O$, KCl, NaOH and HCl were of analytical grade obtained from Sigma–Aldrich and these were used without further purification. Solutions were made up to the required concentration using Millipore de-ionised water. All gases used were obtained from Afrox and regulated to one atmosphere during use. Nitrogen was at a purity level of 99.999%.

2.2. Experimental set-up

Precipitation of copper sulphide was carried out at room temperature ($20^\circ C$) and atmospheric pressure. A 1 L glass vessel, fitted with baffles and operated as a continuously stirred tank reactor (CSTR) was used as a metal to sulphide contactor. The reaction vessel was covered at the top with a lid that had 7 ports for a sulphide resistant pH probe, Redox probe, overhead stirrer, reagent feed, nitrogen sparger and an acid base dosing port. Agitation in the vessel was achieved by a 45° pitched 4 blades impeller connected to an overhead variable speed motor operating at 650 rpm.

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