CROATICA CHEMICA ACTA
CCACAA **80** (3-4) 333–343 (2007)

ISSN-0011-1643
CCA-3176
Original Scientific Paper

Influence of Impurities on Acid-base Data for Oxide Minerals – Analysis of »Observable« Surface Charge and Proton Affinity Distributions and Model Calculations for Single Crystal Samples*

Johannes Lützenkirchen

Institut für Nukleare Entsorgung Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany
(E-mail: johannes@ine.fzk.de)

RECEIVED NOVEMBER 30, 2006; REVISED JANUARY 5, 2007; ACCEPTED JANUARY 16, 2007

Acid-base data for oxide minerals are fundamental building blocks for adsorption models. Although the influence of impurities is often discussed in a qualitative way, a quantitative analysis is largely missing. A notable exception is the discussion of the possible effect of surface impurities on the results of mass titrations. In the present contribution potential contaminations are discussed in a generic way, with respect to their origin and their effects. Also dynamic aspects of such a contamination are considered in some detail. Besides, two examples are quantitatively analysed in more detail. In this analysis, one potential surface impurity (sulphate impurities on the iron oxyhydroxide goethite) and one possible source of »environmental« impurities (carbonate contamination on the iron(III) oxide hematite) are evaluated. The contaminant effect is a function of the ratio between the amount of contaminant and exposed surface area and also depends on the ionic strength of the sulphate-goethite system, since the adsorption of sulphate is sensitive to changes in ionic strength. While for a surface contamination like sulphate, the threshold ratio is mainly affected by the total amount of goethite at a given ionic strength, for an »environmental« contaminant like carbonate, the absolute value of the exposed surface area of the mineral is most important. From the hematite calculations the model surface potentials are obtained. These are of interest, because this most important quantity has recently been measured for a range of solids. One outcome of the calculations is that model surface potentials in the absence of a contamination are not in agreement with the measured values. The calculations for a contaminated system suggest that carbon dioxide adsorption will not significantly affect the surface potential contrary to the big effect obtained for the diffuse layer potential. The predictions like the ones in the present paper have the capability of avoiding experimental problems, if the calculations are carried out prior to the experimental work, or to evaluate potential effects a posterior for example in data selection for data base development.

Keywords
acid-base model
surface complexation
isoelectric point
proton affinity distribution
streaming potential
adsorption

INTRODUCTION

Surface charge on (oxide) minerals in electrolyte solutions is an important feature in governing the stability of suspensions,[1] the adsorption of inorganic ions,[2] small organic ligands[3] or polyelectrolytes.[4] The surface charge of these minerals is mainly governed by the affinity of protons (or hydroxyls) for the mineral surface functional groups. These are typically represented as hydroxyl groups. Thus the proton surface charge density can be

---

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

determined from acid-base titrations. Such acid-base titrations of minerals are the fundamental building block for surface complexation models of adsorption. These models can in principle be used to predict contaminant retention on such minerals.

Potentiometric titrations and the charging curves derived from these kinds of experiments can still be seen as the basis for any surface complexation model. They are typically backed up in comprehensive studies by electrokinetic investigations. Electrokinetics can yield the best estimate of the zero level (*i.e.* where the particle is net uncharged). This in turn is necessary to fix the reference level for potentiometric titration data. Without unambiguous access to the reference level titration data yield no more than relative charge on the surface and some assumption is required to recalculate the data to absolute surface charge. One assumption frequently used is the equality of a cip (common intersection point, *i.e.* the cross-over point from titrations at various levels of background electrolyte concentration) with the zero level. This is a dangerous procedure since such cips also appear in solutions of specifically adsorbing ions, which are known to shift points of zero charge.[5] Thus a combination of titrations and electrokinetics is far more useful to avoid ambiguities. As a consequence of the cip-ambiguity it should already be clear that the suggestion of Bourikas *et al.*[6] to use only one set of potentiometric titration data to estimate a point of zero charge is a dangerous one. Use of a single set of elektrokinetic data at low ionic strength is more useful in that respect. But it is recommended to collect as much information as possible to avoid avoidable errors. This includes for the titration also the control of solid dissolution or phase transformation. In particular solid dissolution may perturb the results of titrations in the pH-region where dissolution (kinetics) is such that proton balances are perturbed. If no phase transformation occurs, it is possible by measuring the dissolved amounts to correct the raw titration data for this effect (including the proton balance in solution due to the proton effects of aqueous species formation). In the case of phase transformation the situation is even more complicated. Phase transformations can be minimised by *e.g.* keeping the mineral in suspension for an extended time before starting the titration. This pre-equilibration should then be done at several pH-values and the samples pre-equlibrated at those pH-values should then be titrated and the results compared. The resulting samples should then be analysed in terms of specific surface area and XRD, and if possible by some surface spectroscopic technique that gives surface compositions (such as XPS). The same tests should be carried out on samples which have been titrated. Dissolution may of course also occur in such pre-equlibrated suspensions. Such extensive studies of these kinds of effects are not known to the present author.

Since the adsorption reactions governing retention of ions on minerals are very sensitive to the mean field electrostatic potential of the mineral, a feature which is becoming even more important when the Charge Distribution (CD) concept[7] is applied, the reliability of the final retention models will strongly depend on the quality of the acid-base data and the accuracy of the associated acid-base model. As such the underlying acid-base data and the model might be compared in terms of quality to the basis sets used in quantum chemical calculations. All subsequent modelling results and conclusions will depend on the quality of these acid-base data and the resulting acid-base model. While the determination of proton ad/desorption on minerals and their points of zero charge may appear as a trivial task, it was shown theoretically how the outcome of simple mass titrations may be affected by small amounts of contaminants, present on the surface.[8]

The point of zero charge fixes the absolute level of zero mean field electrostatic potential. As such it is a major property within the electrostatic parts of surface complexation models. With a point of zero charge mis-determination by one pH unit the electrostatic contribution to overall equilibrium constants (*i.e.* the product of the »intrinsic« and the electrostatic contribution) for proton ad- or desorption will be »wrong« by one log unit (for surface potential *vs.* pH slopes of around 59 mV per pH unit, which is the case for the currently popular models). This means that the inferred »intrinsic« equilibrium constants will be »wrong« by one log unit. For reactions involving metal ion or ligand adsorption, the »error« depends on the amount of charge transferred in the defined complexation reaction as well as on the charge distribution and the other (competing) surface chemical equilibria.

Contrary to work on mineral surfaces in suspensions, contaminants in aqueous solution studies are usually easily taken into account, since for example »dirt«-acids can be found and quantified even based on potentiometric data alone.[9] A similar procedure is more complicated in the case of suspensions, since the titration results usually will not show such problems due to the significant electrostatic mean field effects, which are included in the raw data. For example significant effort is necessary for mass titrations on solids with a contaminant present to obtain the true point of zero charge.[8] Without that effort and for the more common methods, if no systematic variation of experimental parameters is carried out, the resulting point of zero charge will be questionable. Unfortunately, it is precisely the point of zero charge condition which is required to define the zero level for interpreting potentiometric titration data, which in turn are the data used for the development of the acid-base model as mentioned above. It is also known that micro-electrophoresis for determination of the so-called isoelectric point (iep) is sensitive to contaminations. From this it is concluded that only a series of experiments and preferably from different set-ups has the potential to reveal problems or alternatively allow the development of a model that has to describe those data sets.

To conclude this introduction it is important to state that it requires some effort to obtain a contaminant free mineral (or rather a mineral free of significant contaminations) as will be detailed in the next section. One aim of the present contribution is to exemplify potential sources of contaminations. This is done in a generic way without attempting to quantify effects but rather pointing to the existing problems. The generic examples, which will be discussed, may yield an indication how difficult a critical evaluation of published acid-base data may be, in particular when only limited information has been published on procedures.

The other purpose of this paper is to use some well accepted state of the art models to study the effect of impurities on (i) potentiometric titration curves and the derivatives of charging curves of the iron(III) oxyhydroxide goethite and (ii) on experimental work on small surface area samples (single crystals) of hematite.

POTENTIAL SOURCES OF IMPURITIES

There are several groups of potential impurities which may affect potentiometric titrations. The following list is not meant to be complete. Overall three sources will be distinguished here for the sake of illustration. Note that contaminants like carbonate may originate from several sources.

Impurities due to Mineral Production Procedures. – Within this group of contaminations, various impurities may occur. When a mineral is produced in the laboratory the chemicals used may include impurities, which may then be incorporated into the solid. They may also be close to surface of that solid and create some kind of defect structure, which may in turn affect surface properties. They may also be enriched at the interface itself. It is often observed that residual amounts of ions involved in the preparation procedure are difficult to remove. Sometimes, history-dependency or some kind of »memory-effect«[10,11] have been invoked to discuss a preferential interaction between the solid and such ions. Due to this, such impurities are not only difficult to remove, they may also interact with the surfaces in a surprisingly strong way after having been removed (*e.g.* when being used as part of the »inert« background electrolyte). Another group of impurities would be »adventitious« chemicals, which intrude during the preparation from the environment (such as carbon dioxide), from reaction vessels (such as silica or organics from glass or plastic containers, respectively) from dialysis tubes *etc.*

Impurities due to Chemicals Added in the Course of a Potentiometric Titration. – Such impurities may be included in the background electrolyte itself. Generally the chemicals used to fix the »inert« background electrolyte concentration for a titration may include anionic or cationic impurities, which may be involved in aqueous acid-base reactions or adsorbed. Both effects will lead to errors in the »ideal« (*i.e.* the expected or assumed) proton balance, which will be applied to the raw potentiometric data to obtain surface charge data (the analysis of the raw data relies on the assumptions that there are no impurities). This can to some extent be avoided *via* blank corrections, but in case the impurity adsorbs and affects proton balances, the blank correction is incorrect. Similar problems are introduced *via* titrant solutions in case they have been adjusted to the same electrolyte concentration as the background electrolyte in the titration vessel to minimise changes in aqueous species activity coefficients (constant ionic medium). Furthermore, a potential source of carbon dioxide can be seen in base solutions used as titrants or as reagents to fix a basic starting point of the titration. Here, the introduced error in the data is twofold. Not only will carbonate typically adsorb to the mineral surface, but the OH concentration in the base solution will also be affected and the expected proton balance will not be valid. The overall effect will depend on the relative amount of the impurities, *i.e.* if the amount of impurities is sufficiently low the effect may be neglected, or if the impurity does not adsorb, the blank correction will allow a correct result.

Impurities due to Adventitious (»Environmental«) Intrusions During the Tirations. – Here, the contaminants may come from components of reaction vessels (titration vessels themselves, *e.g.* glass), material intruding into the suspension (such as electrodes) or from air or »inert« gas. In this class of contaminations, silica would be a potential problem, but the most important issue is typically carbon dioxide, since even the »inert« gas used to avoid carbon dioxide may include traces of it. Since the gas is usually continuously bubbled through or flowed over the suspension, it would provide a source of carbon dioxide and the titration vessel would then correspond to a system open to carbon dioxide. When the titration vessel itself is not entirely closed to the atmosphere, carbon dioxide may leak into the vessel and affect the results. In these intrusion reactions, kinetic aspects may interfere, *i.e.* it is usually not justified to assume equilibrium concentrations for example with respect to carbon dioxide concentrations or glass/silica dissolution.

The consequences of the various impurities are different. Their effects will depend on their relative abundance but also on the boundary conditions and the dynamics of the contaminant intrusion into the system. In the following some of these issues will be discussed.

Abundance of Impurities

This is a rather obvious issue, since the overall effect of an impurity will be related to its relative abundance with respect to other relevant reactants. In titration experiments the exposed surface area (the amount of reactive surface functional groups), the concentrations of titrant solutions and the concentrations of protons (hydroxyls) in solution are the crucial reactants. Of course the relative reactivities of all the components must also be considered.

Boundary Conditions

Boundary conditions can be discussed in terms of a carbonate contamination. If carbonate is present only due to an initially adsorbed or dissolved amount, which is then not removed from the system by purging with inert gas, carbonate should be treated as a component for which the total concentration is known. This is the case for a closed system such as streaming potential set-ups, where solutions are pumped back and forth. If on the other hand carbon dioxide intrudes only from a pollution of the titrant, the total concentration will change as a function of titrant addition. Finally, if the source of carbon dioxide is the gas phase, the free concentration of dissolved carbon dioxide would be constant (given the partial pressure of carbon dioxide remains constant) and this would result in variable overall contaminant concentrations as a function of pH. These effects may occur simultaneously in the case of carbonate. However, for the simulations presented later, either a constant total concentration of inorganic carbon or a constant partial pressure of CO_2 will be assumed. These are idealised boundary conditions, since the closed system with a total concentration of carbonate is not realistic for any titration set-up, since titrant solutions are added in the course of a titration.

Another potential contamination, which is not at constant concentration but where the concentration varies with the added volume of titrant in particular base titrant, might be silica which may be leached from a glass burette (*e.g.* assuming a glass burette is used).

Dynamics of Contaminant Intrusion

This issue is related to the kinetics of a process which may lead to the intrusion of a contaminant into a system. It has been shortly addressed above with respect to carbonate and the choice of boundary conditions. It is convenient to discuss silica as an example in this context. One possible source for silica contamination would be a glass vessel used as a titration reactor. A glass burette (either intruding the solution in the solution in a titration vessel or in contact with acidic and basic solution, which is added to the titration vessel) or the glass electrode itself would be other examples. Considering that the equilibrium solubility of quartz is 0.1 mmol dm^{-3} there is at least the danger that silica may dissolve from glass material in substantial amounts (although there is no mention of that in the literature with respect to titrations, but it is not clear whether someone has attempted to evaluate this experimentally). It is known that the kinetics of quartz dissolution at constant ionic strength depends on pH. However, dissolution rates are not very high, so that the extent of potential/possible silica in solution in such a system will be affected by the concomitant effect of the overall duration of the titration, exposure to extreme pH values and the ionic strength. Furthermore, the interaction of silica with the titrated mineral will be of importance, since silica adsorption will keep the gradient for glass dissolution high. Even silica adsorption is a function of pH, such that a very complex system is created. It would be highly interesting to study such a complex system systematically both from a modelling and an experimental point of view. The main question of course is whether dissolution of silica bearing material really occurs and if that will result in significant amounts (*i.e.* amounts that will affect proton balances).

Another »dynamic« aspect might be an impurity which is present at the mineral surface due to the synthesis and which was not or could not be removed in washing/cleaning procedures. As indicated above the »memory« effect may cause slow equilibration *e.g.* with respect to desorption of an ion. As an example to be discussed in more detail below, certain commercial goethites made from sulphate containing solutions include a sulphate impurity. Although based on equilibrium studies sulphate will desorb at high pH it may be difficult to remove such a sulphate impurity from goethite. This may explain the low points of zero charge, which are often reported for commercial samples. With respect to titrations the extent to which desorption from such samples (desorption at equilibrium is a function of pH and ionic strength) may interfere with proton balances may depend on the equilibration times chosen for the titration (steps), in particular if desorption is slow. Kinetic effects may also explain observed hysteresis in titration curves, which often are reported to disappear after some runs on the same sample, *i.e.* after repeated exposure to the extreme pH-values in such a titration. Inherited contaminations (in terms of excess ions) from the sample preparation are a puzzling issue. Theoretically, it is impossible to remove counter-ions quantitatively from a mineral except for the case where the mineral has a pristine point of zero charge of 7. In all other cases, there will be more or less significant residual charge on minerals when washing with distilled water is pursued. Although at the expected low ionic strength the charging curve around the point of zero charge (pzc) will become diffuse layer controlled and will have a very low slope, some residual counter-ions must be there to counter-balance that charge. Consequently, washing cannot remove this residual counter-charge. A most illustrative experiment would be washing of such a mineral in a column. At equilibrium the pH of the outlet solution must be that of the inlet solution (*i.e.* pH = 7). The mineral with say a pzc of 10 would be exposed to a pH = 7 solution in the column and therefore have some (residual) charge. Consequently, the counter-ions that assure the electro-neutrality of the system cannot be removed.

SYSTEMS CHOSEN FOR DETAILED QUANTITATIVE ANALYSIS

Based on the discussion of the above potential impurities, two examples have been chosen for more detailed discussion. One is an assumed surface impurity. As indicated above sulphate may be found on commercial goethite samples. Thus the sulphate-goethite-system may serve as a realistic example. The other case to be discussed is an adventitious contamination, namely carbon dioxide. Here the interaction of dissolved inorganic carbon with hematite is considered to be of interest. Over the last decade experiments with single crystals have gained importance. Single crystals are taken as the ideal substrates for studying mechanisms of adsorption, since they are expected to be best characterised in terms of surface structure. This is assumed based on known crystal structures, but in reality the presence of water may change the ideal surface structure. A variety of different techniques has been applied in studies on reactions at single crystal-electrolyte interfaces, ranging from X-ray absorption spectroscopy, over X-ray standing waves to sum frequency generation/second harmonic methods. Measurements of interaction forces between such single crystals or between a colloidal probe and a single crystal are another class of experiments. Streaming potential measurements[12] are capable of yielding classical electrokinetic data on such substrates.

Compared to streaming potential measurements with particles, where larger surface areas are involved, a potential problem with all the single crystal work is that a small surface area is exposed to the aqueous phase. The volume of the solution is usually not specified by authors of the relevant experimental work. Furthermore, the presence of carbonate is typically not discussed. In this context, it is worthwhile to mention a paper by Gan and Franks.[13] These authors studied charging of gibbsite basal planes with an AFM colloidal probe technique (force distance curves). As in streaming potential measurements these kinds of experiments involve very small surface areas. The solution volume in contact with the probes (the basal planes and the colloidal particle grafted to the AFM tip) is not given in the experimental part of the paper. However, Gan and Franks[13] explicitly discuss carbon dioxide contamination. They state that their solutions were not degassed, thus carbon dioxide was most probably present. As one potential consequence of this intrusion they mention small drifts of pH. They furthermore claim that since bicarbonate cannot »contribute a positive charge to the gibbsite surface«, the effect of carbon dioxide in the solution may be safely excluded. However, they do not discuss the possibility that the adsorption of carbonate species may contribute negative charge to the gibbsite and thus be able to shift isoelectric points, an issue which is documented for a number of systems.[14] This will obviously affect the elelctrostatics of the interfaces and consequently the results of force distance measurements.

For many experiments, which are sensitive to mineral surface charge, it is difficult to consequently exclude carbonate because the setup has simply not been designed for that purpose. Therefore, it is useful to apply some model calculations to evaluate the threshold of carbonate interference compared to a carbonate free environment. Boundary conditions have been discussed above and will be applied accordingly.

Sulfate on Goethite

As indicated above, sulphate is a potential impurity on commercial goethite. Sulphate adsorption on goethite has been studied on a sulphate-free goethite sample (synthesized from ferric chloride solutions) and a mechanistic model has been obtained[15] for the adsorption and proton-co-adsorption data. The model is not in conflict with a set of spectroscopic data available for that system. This model by Rietra[15] is used here to calculate titration curves in the absence and presence of sulphate. The purpose of the model calculations is to obtain an idea about typical threshold concentrations, at which the impurity will significantly affect measurement results, when compared to impurity-free conditions.

Carbonate on Hematite

As mentioned above carbonate may originate from all kinds of sources. It may already pollute the solid during its synthesis, *e.g.* when hydrous ferric oxide is precipitated it may be present in the base solution. This may lead to residual carbonate content in the solid. To what extent such contamination can be removed by washing and/or bubbling with pure gas is an open issue. Boily *et al.* recently conducted studies on such issues.[16] Thermodynamically it should be possible to remove the associated inorganic carbon from the system, but there will usually be kinetic constraints on reaching equilibrium. For the present study, hematite titration data and carbonate adsorption data were modelled using a 1-pK-1-site-Basic Stern model. Thus, a carbonate adsorption model for hematite was obtained (see Figures 1 and 2, and Table I). Figure 1 shows the model performance for the titration data of Kohler *et al.*[17] Based on this acid-base

Table I. Parameters for the surface complexation model pertaining to the carbonate-hematite system (specific surface area is 14.4 m^2 g^{-1}). All stability constants refer to zero ionic strength. Activity corrections were made using the Davies equation. The basic Stern model was used for the electrostatic corrections to the surface equilibria. H_2CO_3* corresponds to basis species (component, used in the equilibrium calculations) and is defined as the sum of H_2CO_3 and dissolved CO_2

Parameter/reaction	Parameter value/stability constant
Site density / sites nm^{-2}	8
C / F m^{-2}	1.71
$\equiv FeOH^{-1/2} + H^+ \leftrightarrow \equiv FeOH_2^{+1/2}$	9.4
$\equiv FeOH^{-1/2} + Na^+ \leftrightarrow \equiv FeOH^{-1/2\cdots}Na^+$	–0.11
$\equiv FeOH^{-1/2} + H^+ + NO_3^- \leftrightarrow \equiv FeOH_2^{+1/2\cdots}\ NO_3^-$	–0.11
$\equiv FeOH^{-1/2} + H_2CO_3^* \leftrightarrow \equiv FeOH_2^{+1/2\cdots}HCO_3^-$	6.45
$\equiv FeOH^{-1/2} + H_2CO_3^* \leftrightarrow \equiv Fe^{0.33}OCO_2H^{-0.33}$	4.97

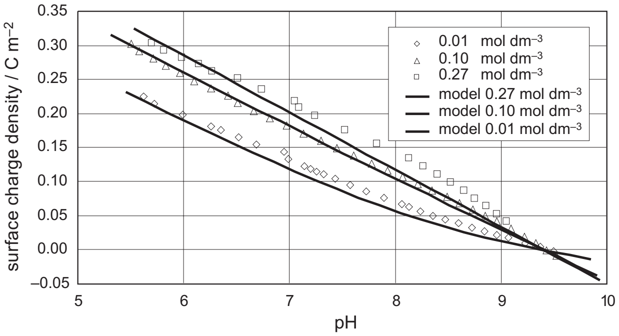

Figure 1. Acid-base model for the hematite system in comparison to experimental data from Kohler *et al.*[17]

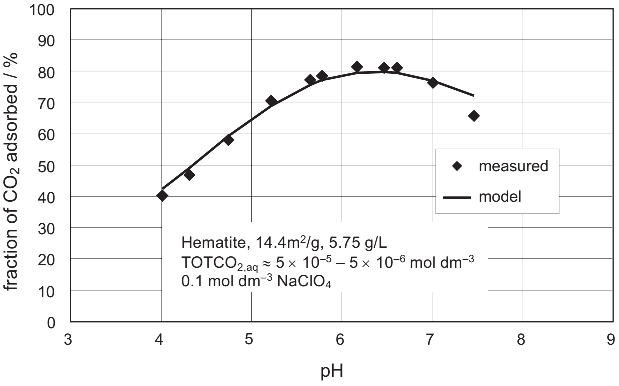

Figure 2. Carbonate adsorption model for the hematite system in comparison to experimental data from Kohler *et al.*[17]

model the carbonate adsorption data of Kohler *et al.*[17] were evaluated and the performance of the carbonate adsorption model is shown in Figure 2. The model was used subsequently to calculate potentials at the head-end of the diffuse layer to obtain the »would-be-observed« isoelectric points of hematite as a function of total carbonate concentration or carbon dioxide partial pressure. Also the sensitivity of surface potential measurements on hematite to carbon dioxide contamination may be evaluated in this way.

METHODS

Calculations were carried out using either a modified version of FITEQL2.1[18] or ECOSAT.[19] The former was used for inverse modelling of the hematite systems (*i.e.* parameter optimisation) and for forward modelling of hematite systems under conditions relevant to streaming potential measurements. ECOSAT was applied to the goethite system to first calculate »observable« surface charge density *vs.* pH curves. To this end, actually proton consuming or producing species were used. Then the results were used to compute proton affinity spectra by spline fitting the »observable« or »measurable« surface charge *vs.* pH curves and obtaining the first derivative curve of these. The terms »observable« and »measurable« indicate that the surface charge density in the output of ECOSAT calculations cannot be used directly since they also include surface charge contributed by the adsorbed sulphate ions. Instead proper proton balances have to be applied to surface and solution equilibria as indicated above.

RESULTS AND DISCUSSIONS

Sulphate on Goethite

Figures 3 and 4 show selected results for the sulphate – goethite system. Figure 3 shows the effect of sulphate on the »measurable« or »observable« surface charge of goethite at constant ionic strength. It is clear that for the conditions chosen (10 g/L goethite, 100 m^2/g, and ionic strength 0.01 mol dm^{-3} as fixed by sodium nitrate) a contamination of 0.1 mmol dm^{-3} will cause some deviation from the contaminant free titration curve. The »observable« surface charge is recalculated from the ECOSAT output by applying the appropriate proton balances. The »observable« surface charge does not include the surface charge originating from the charge of the adsorbed sulphate ions, whereas the proton effects induced by the adsorption of sulphate ions must be included. Whereas the effect is not that big in the surface charge curves, it is clearly seen in

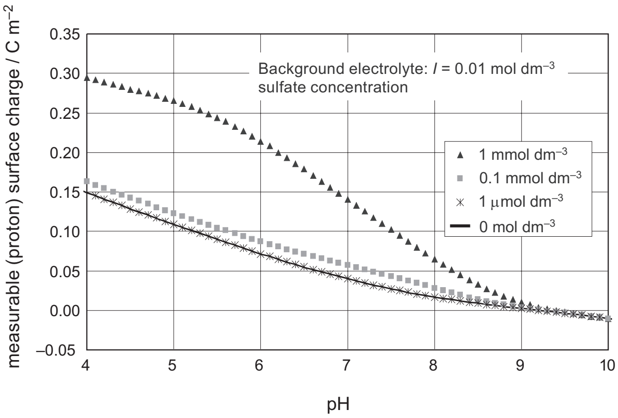

Figure 3. Effect of sulphate on the »observable« surface charge of goethite as a function of pH.

the derivatives of these curves as shown below (Figure 4). For a 1 mmol dm^{-3} sulphate solution a huge effect is obtained, although probably a contamination of 1 mmol dm^{-3} is not realistic.

Figure 4A shows the effect of background electrolyte on the observable surface charge. Since sulphate adsorption is sensitive to ionic strength, the changes in the shape of the resulting curves were expected. For the present conditions chosen (10 g/L goethite, 100 m^2/g, and sulphate concentration 0.1 mmol dm^{-3}) several issues can be discussed. At pH around 4 the curve with the lower ionic strength shows an increase with respect to the curve at higher ionic strength. This is due to the effect of sulphate adsorption, but also to the fact that the ionic strength varies because of the addition of acid required to lower the pH (which comes close to the nominal ionic strength fixed by sodium nitrate at 1 mmol dm^{-3}). This strong increase can be found in various sets of published experimental data. In this pH range experimental errors also tend to become more important, since the free proton concentration is close to the concentration of protons added to the system to lower the pH. Under these conditions for calculating the relative surface charge, the difference of two similar numbers is required. The threshold, at which these errors become significant, depends on the mineral surface area exposed in the titration vessel. As a rule of thumb at least 10 m^2 of solid should be in the reaction vessel: Dumont (Université Libre de Bruxelles, personal communication, 1994) claimed that it would be pointless to even start a potentiometric titration with less (reactive overall) surface area in a titration system. The important number is the (absolute) amount of surface sites in the system and (crystallographic) site densities do not vary that much between different minerals. Although a more detailed analysis may typically be advisable, for the present author this has become the number, which he tends to apply to published titration data in order to estimate their quality. Unfortunately, the value for literature data cannot always be calculated from the information given in the description of experimental procedures.

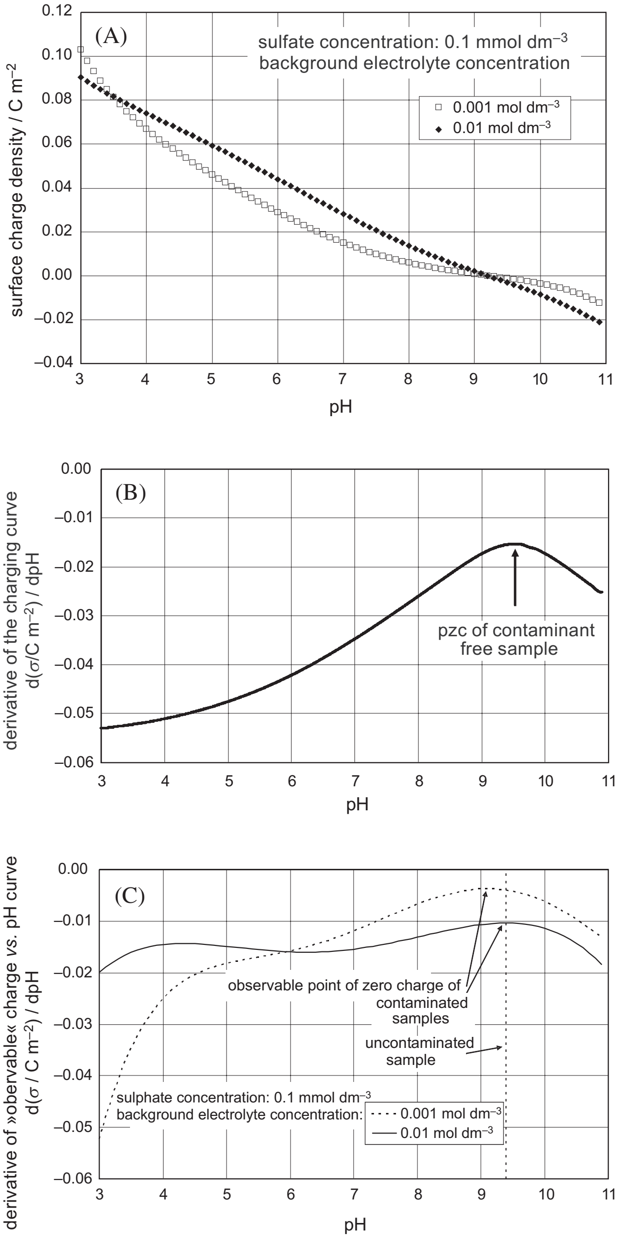

Figure 4. Effect of ionic strength on the »observable« surface charge of goethite as a function of pH and on proton affinity distributions (proton affinity spectra as described in the text). (A) Observable surface charge as a function of pH. (B) Proton affinity spectrum (*i.e.* derivative of the surface charge density with respect to pH as a function of pH) for the contaminant free goethite system. (C) Proton affinity spectrum (*i.e.* derivative of the surface charge density with respect to pH as a function of pH) of the sulphate containing goethite system pertaining to the data in Figure 4A. Arrows indicate extreme values (*i.e.* the »would be obtained« pzcs) for the two derivatives. Vertical dashed line corresponds to the pzc for contaminant-free sample (*i.e.* the »should be obtained« pzc).

Figures 4B and 4C show the proton affinity spectra for the contaminant-free system and the sulphate containing systems, respectively. The derivative for the contaminant free system yields the pzc in agreement with the suggestion of Bourikas *et al.*[6] However, the proton affinity spectra in the presence of the contamination (Figure 4C) show significant deviations from the master curve in Figure 4B. Therefore, the derivative may yield some indication on the quality of the titration data. The shift of the extremum close to the pristine point of zero charge of the sample is relatively small for the higher ionic strength. It is questionable whether this difference could be obtained experimentally. For the lower ionic strength a stronger shift is obtained and this shift makes it apparent that the measurement of just one titration curve is not enough to safely determine a point of zero charge no matter which method is used. If the presence of a contaminant is not known the derivative method as proposed by Bourikas *et al.*[6] may yield the wrong pzc (as would other methods if only one data set is collected) and if only one such curve is available there is no information that might help raise suspicion (except the shape of the derivative curve). It is noteworthy that the shapes of the curves in Figure 4C are quite similar to those of an experimental affinity spectrum published by Prélot *et al.*[20] on a commercial goethite. Compared to the sulphate-goethite-system chosen for illustration, the effect of a contaminant on the pzc would be much stronger if adsorption of the contaminant at the pzc were more important.

As a conclusion of the presented results, it is obvious that surface impurities may strongly affect experimental results. The present model calculations are in striking agreement with published experimental results on a commercial goethite sample. It is furthermore concluded, that such impurities are difficult to identify if a minimised approach to pzc determination is chosen. As discussed in the introduction a wrong pzc will have severe repercussions on a surface complexation model. Furthermore, the impurity will also interfere in other experiments such as metal ion adsorption experiments. Therefore, an extended acid-base study is recommended to (i) identify potential impurities and (ii) make sure a proper acid-base model can be developed.

Carbonate on Hematite

Figure 5 shows the diffuse layer potential of hematite as a function of pH for a closed system. The model used for the calculations corresponds to the parameters given in Table I. The conditions correspond to an experimental set-up for streaming potential measurements as described by Werner *et al.*[12] It becomes clear that carbonate will shift the observed isoelectric point. As expected, the more carbonate is in the system the stronger the shift will be. With a concentration of total inorganic carbon of 50 μmol dm^{-3} a significant shift is observed. Above it was stated that the derivative analysis of one titration curve as proposed by Bourikas *et al.*[6] bears the risk that a contamination cannot be discovered. The same is also valid for electrokinetic measurements. It is always advisable to carry out more than one experiment and to vary the conditions. This is the only way to make sure that the pristine point of zero charge can be found.

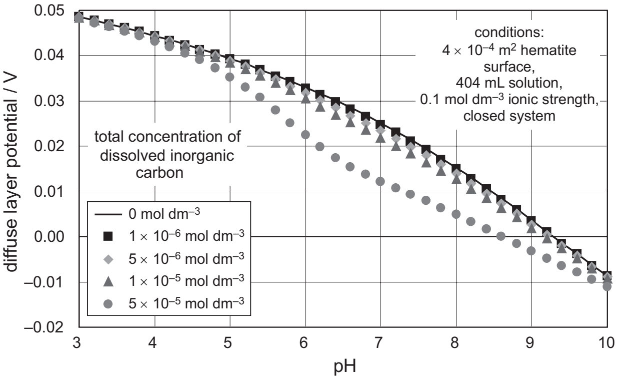

Figure 5. Diffuse layer potential of hematite as calculated from the model summarized in Table I for a closed system and a variation of the total carbonate content. Isoelectric points would correspond to zero diffuse layer potentials.

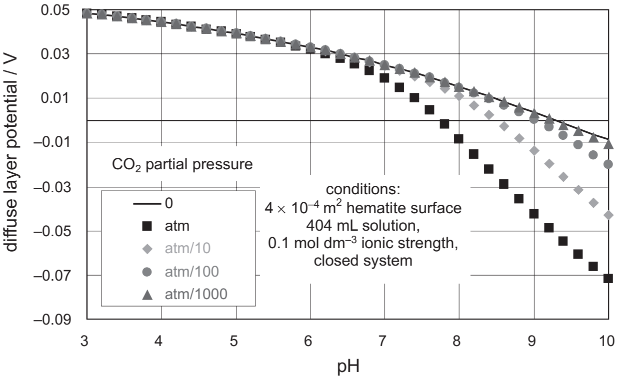

Figure 6. Diffuse layer potential of hematite as calculated from the model summarized in Table I for an open system and a variation of carbon dioxide partial pressure (atm pertains to atmospheric conditions). Isoelectric points would correspond to zero diffuse layer potentials.

Compared to the closed system, for an open system the situation becomes worse. Figure 6 indicates that for the system under consideration even at a partial pressure corresponding to a hundredth of the atmospheric partial pressure of carbon dioxide there is still a significant effect on the measured isoelectric point. For atmospheric pressure a decrease of the isoelectric point by 1.5 pH units is predicted. Again the effect is linked to the amount of dissolved inorganic carbon relative to the exposed surface area. For the open system the amount of dissolved inorganic carbon increases with pH. Already at pH = 10 this increase results in carbonate ion concentrations of 0.1 mol dm^{-3}, which will then dominate the ionic strength and additionally affect the zeta potential. The (additional) amount of hydroxide required to obtain such high pH values may accentuate the effect. From Figure 6 it can be seen that with increasing partial pressure the zeta potential pH relationships become steeper.

Recently a new approach to measuring surface potentials has been published and applied to hematite.[21,22] The situation for this kind of experiment with respect to potential contaminations compares to the streaming potential measurements: a small surface area is exposed to a solution (of usually unknown volume). Surface potential data are available for hematite. The experiments were carried out on a crystal sample, where the exposed crystal planes are not known. To be able to compare with experimental data on this system[21,22] the above calculations were repeated for 0.01 mol dm^{-3} ionic strength. The resulting surface potential is plotted as a function of the pH for a variation of the carbon dioxide partial pressure (Figure 7). Although compared to the carbonate-free system the resulting point of zero potential is slightly affected, the effects are nearly negligible in particular when compared to the dramatic effects carbon dioxide had on the diffuse layer potentials for the 0.1 mol dm^{-3} system. The shifts of the isoelectric point due to carbonate were clearly more important (*cf.* Figure 6).

The surface potential for the absence of carbonate is shown in Figure 8. As a comparison, experimental data from Preočanin *et al.*[22] are also shown for the same system. The model predicted absolute value of the slope of the surface potential *vs.* pH curve is lower than the Boltzmann-slope (which is typically obtained with these kinds of models, note that according to Cheng,[23] it is more appropriate to interpret these kinds of slopes in terms of a Boltzmann-slope instead of a NERNST slope). However, the model slope is not as low as the experimental values. Also the shape of the experimental curve is not linear and appears to follow rather the shape of a surface charge density curve at low ionic strength (Figure 9). This would suggest a linear relationship between the surface potential and the surface charge density and correspond to a constant capacitance model. With increasing ionic strength the curvature in the surface charge density *vs.* pH curves more and more disappears. The observation strictly contradicts the previously suggested range of application of the constant capacitance model. Also the capacitance would vary with pH.

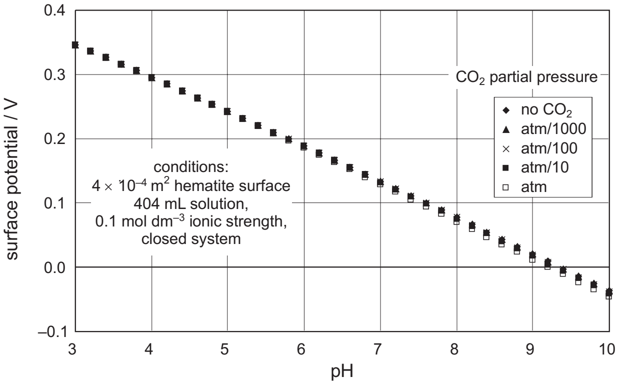

Figure 7. Surface potential of hematite as calculated from the model summarized in Table I for an open system and a variation of carbon dioxide partial pressure (atm pertains to atmospheric conditions).

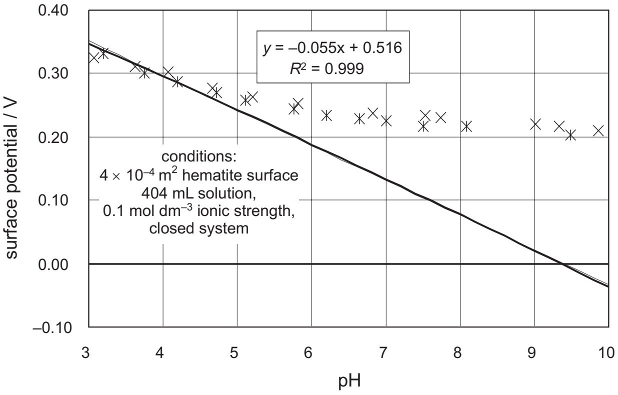

Figure 8. Calculated surface potentials of hematite according to the model in Table I and experimentally detemined values according to Preočanin *et al.*,[23] open system. The experimental values were shifted to coincide to the model values at pH = 3. The slope of the model curve is given on the plot.

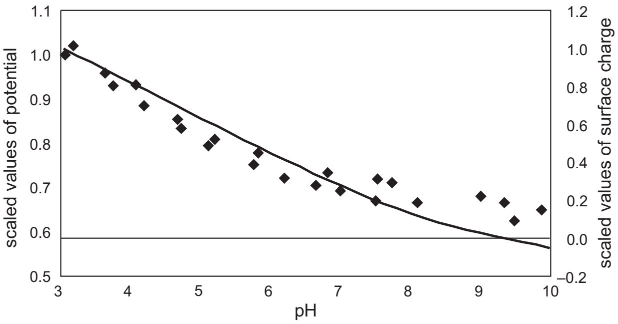

Figure 9. Comparison of the scaled experimental surface potential according to Preočanin *et al.*[23] and scaled surface charge density for hematite at 0.01 mol dm^{-3} ionic strength. Scaling was done in such a way that the values at the lowest pH would be unity, *i.e.* the values were all devided by the respective values at the lowest pH.

As a conclusion of the above calculation-results, it is clear that isoelectric points may be strongly affected through adventitious surface contaminations by carbon dioxide, in particular in experimental set-ups, where small surface areas are exposed. The same would hold for force distance measurements using *e.g.* the atomic force microscope or the surface force apparatus. It is crucial to exclude carbon dioxide in such experiments. The effect of carbon dioxide is predicted to be nearly negligible for surface potential measurements in the system discussed.

CONCLUSIONS

A range of potential contaminations relevant for experimental work with particles in suspension has been discussed. To what extent such a contamination may affect experimental results is usually dependant on the chemical system studied and on the experimental set-up used. Furthermore, the conditions chosen in the experimental work are crucial.

Boundary conditions, which may be important for model calculations and complicating time dependencies, respectively, and kinetic effects have also been discussed. Theoretically, one may imagine quite complex situations, with total contaminant concentrations varying as a function of pH and ionic strength.

Two systems have been analysed in more detail based on model calculations:

For the sulphate-goethite system it was found that a sulphate contamination on the order of 0.1 mmol dm^{-3} would have significant effects on the results of potentiometric titrations for the experimental conditions chosen (10 g/L and 100 m^2/g goethite). The impact of the sulphate contamination as visualized by the shape of the charging curve also depends on the ionic strength of the system (in terms of the background electrolyte used in the experiments). Derivatives of the charging curves significantly deviate from that of a sulphate free curve and are comparable to derivatives of curves published for a commercial goethite. Although they still display maxima, it is not advisable to equate such maxima from only one titration curve with the point of zero charge. Instead it is recommended to carry out the necessary variation of experimental conditions (ideally with various experimental set-ups) to avoid an erroneous determination of the most important property of the mineral sample (*i.e.* the point of zero charge). From one titration curve (or one set of micro-electrophoretic data) it is difficult if not impossible to identify potential contaminations. The shape of the derivative curve may give a hint. A comprehensive study avoids ambiguities and allows a consistent modelling of the acid-base properties of the mineral in question. Modeling of titrations of suspensions with a significant degree of contamination would have repercussions on the model parameters compared to an uncontaminated sample. First the pzc (*i.e.* in a 1-pK model the stability constant of the protonation reaction) and the electrolyte binding constants (due to the shape of the curves) and finally the capacitance values (due to the slope of the charging curves) would be affected.

For the carbonate-hematite system, experimental set-ups in which small mineral sample areas are typically exposed to large volumes of solutions have been analysed in terms of open or closed systems. As would be expected, carbonate may have dramatic effects on isoelectric points. For a typical streaming potential set-up small carbonate contaminations may significantly shift isoelectric points. The effect is quite pronounced even for a closed system because of the small sample surface area that is exposed to a potential contamination. Surprisingly for similar conditions in measurements of surface potentials, the effect of carbon dioxide/carbonate would be negligible. The contamination would not affect the surface potential to a significant extent.

As a by-product of the calculations, a comparison between the modelled surface potential for hematite and measured surface potentials was carried out and it became apparent that the model cannot describe the experimental surface potentials satisfactorily. The shapes of the experimental surface potential *vs.* pH data are quite similar to surface charge density *vs*. pH data. This might suggest a constant capacitance type of model. Estimations of that approach would result in a variation of the capacitance with pH at constant ionic strength.

Acknowledgements. – The author is grateful for the possibility to contribute to this »Festschrift«. He is very grateful for the far too rare possibilities to have met Professor Kallay and the occasions for discussions.

REFERENCES

1. N. Kallay and S. Žalac, *Croat. Chem. Acta* **74** (2001) 479–497.
2. N. Kallay and S. Žalac, *J. Colloid Interface Sci.* **230** (2002) 1–11.
3. D. Kovačević, I. Kobal, and N. Kallay, *Croat. Chem. Acta* **71** (1998) 1139–1153.
4. L. P. Weng, W. H. Van Riemsdijk, L. K. Koopal, and T. Hiemstra, *J. Colloid Interface Sci.* **302** (2006) 442–457.
5. S. Ardizzone, L. Formaro, and J. Lyklema, *J. Electroanal. Chem.* **133** (1982) 147–156.
6. K. Bourikas, C. Kordulis, and A. Lycourghiotis, *Environ. Sci. Technol.* **39** (2005) 4100–4107.
7. T. Hiemstra and W. H. Van Riemsdijk, *J. Colloid Interface Sci.* **301** (2006) 1–18.
8. S. Žalac and N. Kallay **149** (1992) 233–240.
9. S. L. Simpson, S. Sjöberg, and K. J. Powell, *J. Chem. Soc., Dalton Trans.* (1995) 1799–1804.
10. A. Breeuwsma, Ph. D. thesis, Agricultural University Wageningen, The Netherlands, 1973.
11. J. P. Chapel, *J. Colloid Interface Sci.* **162** (1994) 517–519.
12. C. Werner, R. Zimmermann, and T. Kratzmüller, *Colloids Surf., A* **192** (2001) 205–213.
13. Y. Gan and G. V. Franks, *Langmuir* **22** (2006) 6087–6092.
14. C. M. Su and D. L. Suarez, *Clays Clay Miner.* **45** (1997) 814–825.
15. R. Rietra, Ph. D. thesis, Agricultural University Wageningen, The Netherlands, 2001.
16. J. F. Boily, J. Szanyi, and A. R. Felmy, *Geochim. Cosmochim. Acta* **70** (2006) 3613–3624.
17. M. Kohler, B. D. Honeyman, and J. O. Leckie, *Radiochim. Acta* **85** (1999) 33–48.
18. J. C. Westall, FITEQL, A Computer Program for Determination of Chemical Equilibrium Constants, Version 2.1;

Report 82–02; Department of Chemistry, Oregon State University, Corvallis, OR, 1982.

19. M. G. Keizer, ECOSAT, Technical report, Agricultural University Wageningen, The Netherlands, 1998.
20. B. Prelot, R. Charmans, P. Zarzycki, F. Thomas, F. Villieras, W. Piasecki, and W. Rudzinski, *J. Phys. Chem. B* **106** (2002) 13280–13286.
21. N. Kallay, Z. Dojnović, and A. Čop, *J. Colloid Interface Sci.* **286** (2005) 610–614.
22. T. Preočanin, A. Čop, and N. Kallay, *J. Colloid Interface Sci.* **299** (2006) 772–776.
23. K. L. Cheng, *Microchem. J.* **59** (1998) 457–461.

SAŽETAK

Utjecaj nečistoća na kiselo-bazna svojstva mineralnih oksida – analiza »izmjerenog« površinskog naboja i distribucije afiniteta vezivanja protona te modelni računi za monokristalne uzorke

Johannes Lützenkirchen

Kiselo-bazna svojstva mineralnih oksida od temeljne su važnosti pri razradi modela površinskih reakcija. Utjecaj nečistoća na adsorpciju često je razmatran samo kvalitativno, dok kvantitativna analiza uglavnom izostaje, osim u slučaju utjecaja nečistoća na masenu titraciju. U ovom je radu utjecaj nečistoća razmatran općenito, s posebnim osvrtom na njihov izvor i dinamičke aspekte. Detaljno su i kvantitativno obrađena dva specifična slučaja: površinsko zagađenje (adsorpcija sulfata na getit) te zagađenje iz okoline (adsorpcija karbonata na hematit). Stupanj zagađenja je funkcija omjera količine zagađenja i izložene površine, a ovisi, kao i adsorpcija, o ionskoj jakosti. U slučaju adsorpcije sulfata, najznačajniji utjecaj ima ukupna količina getita pri nekoj ionskoj jakosti, dok na adsorpciju karbonata utječe apsolutna vrijednost izložene površine. Izračunat je površinski potencijal hematita u slučaju adsorpcije karbonata iz otopine i uspoređen s literaturnim eksperimentalnim vrijednostima. Izračunate vrijednosti površinskog potencijala u odsutnosti zagađenja karbonatom nisu u slaganju s izmjerenim vrijednostima. Rezultati računa za sustav zasićen otopljenim ugljikovim dioksidom sugeriraju, da adsorpcija ugljikova dioksida na površinu hematita ne utječe znatno na površinski potencijal, dok je utjecaj na potencijal difuznog sloja znatan. Prikazana razmatranja omogućuju izbjegavanje eksperimentalnih teškoća. Potrebno je provesti proračune prije samog eksperimenta ili moguće efekte uzeti u obzir prilikom selekcije mjerenih podataka.