

Towards a Generalized Physicochemical Framework: WWTmod Workshop Position Paper

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Abstract

Process models used for activated sludge, anaerobic digestion and in general wastewater treatment plant process design and optimization have traditionally focused on important biokinetic conversions. There is growing realization that abiotic processes occurring in the wastewater (i.e. “solvent”) have a fundamental effect on plant performance. These processes include weak acid-base reactions (ionization), spontaneous or chemical dose induced precipitate formation, chemical redox conversions, which influence pH, gas transfer, and directly or indirectly the biokinetic processes themselves. There is a large amount of fundamental information available (from chemical and other disciplines), which, due to its complexity and its diverse sources (originating from many different water and process environments), cannot be readily used in wastewater process design as yet. The authors of this position paper are participants of the WWTmod2010 Physico-Chemical workshop and other active contributors. Their objective was to outline the need, the methods, available knowledge and the fundamental approaches that would help to focus the effort of research groups to develop a physico-chemical framework specifically in support of whole-plant process modeling. The findings from the workshop, as well as the position paper are that in general, existing models such as produced by IWA for biological processes are limited by omission of key corrections such as non-ideal acid base behaviour, as well as major processes (e.g., ion precipitation). While the underlying chemistry is well understood, its applicability to wastewater applications is less well known. This justifies activities by a dedicated Task Group, with both experimental and model development activities to clarify an approach to modeling of physiochemical processes.

Keywords: physico-chemical framework, pH calculation, chemical equilibrium, precipitation

Introduction and Problem Statement

This is a position paper that reports outcomes from the Physico-chemical Workshop at the WEF and IWA sponsored WWTmod2010 seminar at Mt St. Anne, in Quebec, Canada. The objective of the workshop was to identify the scope, need, and current capacity to develop and disseminate a common basis for implementation and solution of physicochemical models within the current IWA modeling framework.

Physicochemical processes are those which commonly occur in biochemical systems, but which are not directly mediated by microbes. Such processes can act as stand-alone treatment (e.g., coagulation), have an impact on biochemical processes (e.g., pH, gas transfer), or be intimately linked to the underlying biochemical process (e.g., anaerobic digestion (AD) hydrogen transfer or bioelectrochemical systems). Physicochemical sub-models in existing standardized biochemical models are often rudimentary, empirical, or both. The ASM series contains only the alkalinity state, and a single film gas transfer model, while more complex models such as the pH system in the ADM1 are only valid for dilute systems, and do not include mechanistic (pH-based) precipitation. We address limitations in models specifically further in this position paper. Issues around modeling of physicochemical processes in wastewater systems were originally raised in a two page position paper (Batstone 2009), which mainly identified technical issues across the range of wastewater treatment systems. This also identified that different models take different approaches, even though the basic processes are the same. This was emphasized during the workshop, with the additional discussion that modeling approaches were moving towards plant-wide models, and a common physicochemical system across the whole model is a favored approach.

The workshop had 10 participants, with excellent technical knowledge, and diverse backgrounds, including representatives from three major environmental modeling software development companies (in alphabetical order, EnviroSim, developing BioWin, Hydromantis, developing GPS-X, and MOSTforWATER, developing WEST), as well as consultants and researchers. The workshop had a topic based approach. Topics as presented here were discussed in detail during the meeting, some were removed as a specific topic (e.g., bioelectrochemical systems), and others added (e.g., impact of temperature, organics buffering, implementation, weak acid-base reactions, and case studies). As a final step from the workshop, the group classified and sorted the topics into the report structure that forms the outline of this paper.

Current wastewater models

The focus of this analysis is on standardized IWA models, and it is noted that other models (published or commercially available) may be more complete and/or address specific requirements, e.g. Sötemann et al. (2005) included two-phase (aqueous-gas) mixed weak acid base chemical and physical processes for non-ideal conditions in ASM1 to predict reactor pH. Also, the focus of this discussion is wastewater treatment process models (e.g., ASM series, ADM1) and excludes other environmental models. Some of these models such as the RWQM No. 1 (Reichert et al. 2001) use the same structured modeling approach as the ASM series, and include chemical reactions (calcium carbonate precipitation as well as phosphate sorption and desorption on organics in RWQM No1). This can be a useful source of information for the wastewater process modeling industry.

Existing IWA models contain a targeted but limited approach with regard to inclusion of the three major classes of physicochemical reactions: acid-base, gas transfer, and precipitation. No models include chemical oxidation/reduction. The approaches of the major models are given in Table 1.

Table 1: Current approaches to physicochemical systems in IWA models.

Model	Acid-Base	Gas-Liquid	Solid-Liquid
ASM1/ASM3 ¹	alkalinity state	Liq film controlled ($k_L a$)	None
ASM2/ASM2D ¹	alkalinity state	Liq film controlled ($k_L a$)	Empirical P complex
ADM1 ²	pH calculated	Liq film controlled ($k_L a$)	None
RWQM1 ³	pH calculated	Liq film controlled ($k_L a$)	Empirical

1. (Henze et al. 2000)
2. (Batstone et al. 2002)
3. (Reichert et al. 2001)

Acid-base. The ASM models utilize a global alkalinity state (S_{ALK}), which is impacted by acid or base producing (or consuming) dynamic processes. In the approach advocated in ASM it is not considered that the acids/bases considered are weak and therefore only partially contribute to the alkalinity dynamics. For instance at pH around 8, the nitrification of one mole of ammonia only produces 0.9 mole of acid since 10% of the total ammonia is in fact free ammonia (Gernaey et al., 2002). Processes such as nitrification (acid producing) will decrease alkalinity, while processes such as ammonia release (base producing) will increase it. The alkalinity state provides an approximation that indicates whether pH is near neutrality, or well below it (Henze et al. 2000). It is assumed that when alkalinity is depleted, pH will drop dramatically, a situation which the models cannot predict directly. A switch may be used to stop processes when alkalinity is low (e.g., alkalinity limitation on biological processes in ASM2-3). The advantage of this approach is its simplicity – however it has fundamental limitations: a) it is not generally possible to correlate alkalinity and pH, and b) the alkalinity state cannot be mass balanced (i.e. during the combination of two streams).

Processes such as anaerobic digestion or nitrification-denitrification of high-strength wastewater streams require explicit pH calculation using a charge balance, with either differential, or algebraic calculation of speciation between the different forms of the acids and bases. The ASM approach is computationally much faster and simpler, while the ADM approach allows prediction of pH. None of the IWA models include non-ideal behavior (i.e., activity, ion pairing etc). Examples of nitrification-denitrification models with pH calculation using the charge balance approach, (but not taking into account non-ideal behavior) are: Hellinga et al., 1999; Volcke, 2006; Ganigué et al., 2010.

Solid-liquid. The ASM2D contains empirical relationships for precipitation or redissolution of metal phosphate complexes. The metal is nominally ferric ions ($Fe(OH)_3$), but the basic process can also be used for alum or calcium, with appropriate stoichiometry. Because pH is not calculated, the metal hydroxide is used as driver for the forward (precipitation) process. The ADM1 does not consider metal ion precipitation, due to its complexity, though a potential approach is provided, based on calcium precipitation (Batstone et al. 2002)

Gas-liquid. The ASM series use liquid film controlled mass transfer for oxygen transfer during aeration. Stripping of CO_2 or NH_3 (and other gases) during aeration is not considered. Gas phase depletion (as bubbles rise, partial pressure and therefore driving force decreases) is also ignored. The ADM1 likewise uses liquid film controlled mass transfer to the headspace. The impact of pH on CO_2 speciation is considered. None of the models consider impact of non-ideality on gas dynamics or equilibrium. None of the models consider all the important greenhouses gases (i.e. N_2O).

Discussion and Outcomes. The general consensus, within the workshop was that the limitations of existing models were significant. In particular, pH prediction is a key limitation in the ASM series, while the lack of ion activity correction (at low conductivity), ion pairing (at high conductivity), precipitation and phosphorus modeling are a limitation of the ADM1. Implementation in commercial packages has already started to address this issue in response to engineering demand.

Case studies

A full report addressing a generalized framework should provide case studies demonstrating how standardized models can fail to predict specific situations, and updated models that provide improved predictions. Such examples may include:

(a) Failure of ASM1 to predict free acid inhibition during activated sludge nutrient removal (impact on nitrification and/or phosphorus removal). Calculation of pH is required.

- (b) Failure of ADM1 or nitrification models to predict pH correctly due to lack of activity corrections. Ganigué et al. (2010) noted an underprediction of the pH value during nitrification of landfill leachate and mentioned the effect of salinity as a possible cause for this deviation.
- (c) Failure of ASM2D to predict P precipitation kinetics driven by pH dependence.

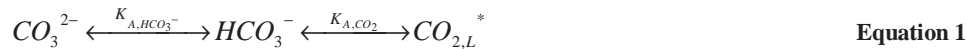
Processes

This section outlines the various physicochemical reactions that may be included. As is inherent in the name, physicochemical reactions are spontaneous (not biochemically mediated). The basic classes include:

Type	Reaction speed	References
Acid-base	very fast: time constants <1 s ⁻¹	(Stumm and Morgan 1996)
Gas-liquid	medium: time constants < 0.1 min ⁻¹	(Paus et al. 1990)
Amorphous precipitation	fast or medium: time constants <1 min ⁻¹	(Szabo et al, 2008)
Crystalline precipitation	slow – time constants > 0.2 d ⁻¹	(Musvoto et al. 2000a; Musvoto et al. 2000b; Tait et al. 2009)
Chemical oxidation - reduction	not well characterized, variable	

Acid-base reactions

Acid-base reactions are extremely rapid reactions, occurring in the liquid phase between a weak acid and its conjugate base. Examples include the carbonate, bicarbonate, and carbonic acid/carbon dioxide species within the inorganic carbon system, ammonium/ammonia system, sulfide species within the inorganic sulfide system, the various phosphate species within the inorganic phosphorus system, and the acidic analogues for nitrite. Weak organic acids (acetate, etc.) also play a role. The reactions for the inorganic carbon system, where each reaction is governed by equilibrium, are as follows (with equilibrium constant K_A):



Where CO₃²⁻ is the weak base carbonate, HCO₃⁻ is the weaker base/weaker acid bicarbonate, and CO_{2,L} is the liquid phase concentration of the weak acid carbon-dioxide. CO_{2,L} represents the combined concentration of CO_{2,L} and H₂CO₃, since reaction between these is rapid, and equilibrium strongly favors CO_{2,L} (Stumm and Morgan 1996).

Another example is the nitrite reaction to nitrous acid:



The concentration of the acid can be related to the concentration (or, more correctly, the activity) of the base from the equilibrium relationship (as an example, for free nitrous acid):

$$K_{A,HNO_2} = \frac{[NO_2^-][H^+]}{[HNO_2]} \tag{Equation 3}$$

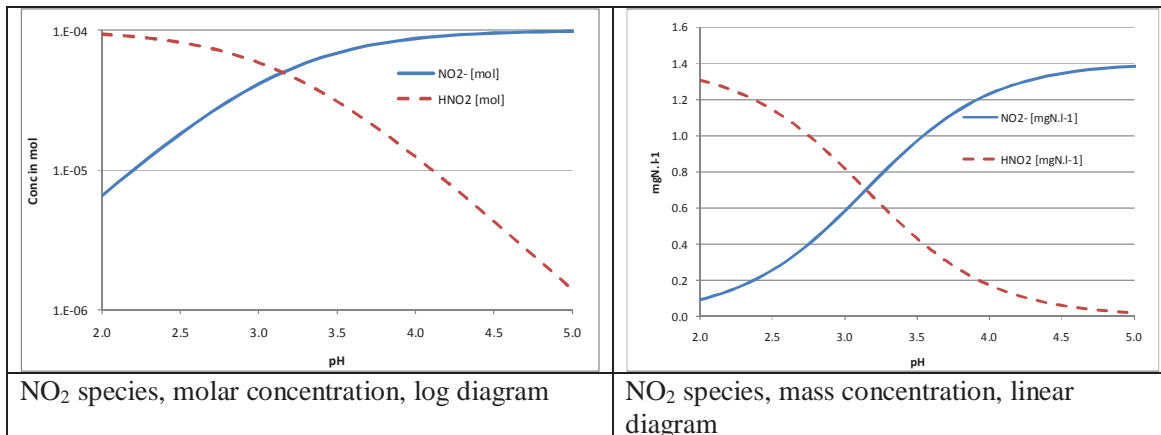


Figure 1. $\text{HNO}_2 - \text{NO}_2^-$ concentrations of a solution containing 1.4 mgN.l^{-1} (0.0001 mol) total NO_2 ($\log K = -3.15$)

If the total (acid+base) concentration is known for each component present, the concentration of each acid and base can be solved. An example for nitrous acid – nitrite ion pair can be seen in Figure 1. The equations can be formulated either as (a) the equilibrium equations + mass balance equations + electroneutrality condition, known as charge balance (Stumm and Morgan 1996) or (b) as a set of allocated mass balances, known as the Tableau method (Morel and Hering, 1993; Loewenthal et al., 1989). This provides a solvable set of non-linear implicit algebraic equations. These equations can then be solved as a set of stiff differential equations (DE approach), or as a set of algebraic equations to be solved in a non-linear algebraic equation solver (DAE approach) (Batstone et al. 2002). The equations can also be solved simultaneously with other differential equations in a DAE solver.

Discussion and Outcomes. This topic was not originally a part of the workshop plan (since approaches are well developed), but was added as one, since the acid-base approach so heavily impacts the remainder of the model framework. Solving the acid-base system is required to calculate pH, and this was regarded as a minimum requirement for a generalized physicochemical model. It was also discussed that the rest of the modeling framework would depend heavily on the approach to solving the acid-base system (and pH). The generally favored approach to formulation was the charge balance approach (Stumm and Morgan 1996), since it is easier to understand and represent in general terms. The favored approach to solution was the DAE approach. This is (a) so that non-stiff solvers can be used to solve the biochemical system (with the algebraic system solved algebraically), and (b) because adding complex ion activity and precipitation behavior in the DE approach causes an exponential increase in the number of state variables. This can be controlled in the DAE approach by calculating many elements as algebraic variables. While a DAE on charge balance approach was favored by the majority, it was by no means a consensus, and there was a large amount of discussion on this topic. Any future work should develop a well justified and common approach to solving the acid-base system that is compatible with the rest of the physicochemical system.

Gas-liquid transfer

Gas-liquid transfer is important across the whole wastewater collection, treatment, and discharge process. Some important gas transfer mechanisms are (least soluble to most soluble gases):

- H_2 transfer
- Aeration during aerobic stages.

- Nitrogen gas. Most of “air” is nitrogen gas and most liquids in the plant are saturated with it. Its supersaturation status may play an important role in phase separation processes.
- Methane and N₂O supersaturation and environmental stripping causing GHG impacts.
- Carbon-dioxide and methane transfer during AD (carbon-dioxide is a weak acid).
- Transfer and odors, and occupational health and safety (OH&S) concerns caused by sulfide stripping (H₂S is a weak acid).
- Loss, odors, and OH&S caused by ammonia stripping (NH₃ is a weak base).
- Detection and odors caused by organic acid and volatile organics stripping.

Note that many of the dissolved gases are also acids or bases, and hence the acid-base subsystem is vitally important to calculate gas transfer, while gas transfer has a significant impact on the acid-base subsystem through its effect on pH.

Transfer of material from the liquid to the gas phase (and vice versa) is described by dynamic mass transfer:

$$r_{\text{gas,t}} = k_{L,G}A([S_{\text{gas}}]_L - K_H[S_{\text{gas}}]_G) \quad \text{Equation 4}$$

Where $r_{\text{gas,t}}$ is the gas transfer rate, $[C]_L$ and $[C]_G$ are the gas and liquid concentrations, and K_H is the gas solubility (Henry’s Law coefficient). A is the gas transfer area. The parameter $k_{L,G}$ is a combination of resistance in the gas phase and resistance in the liquid phase:

$$\frac{1}{k_{L,G}} = \frac{1}{k_L} + \frac{1}{k_G \cdot K_H} \quad \text{Equation 5}$$

Depending on the relative ratio of k_G/k_L and the value of K_H the relative contribution of gas and liquid phase resistance can be estimated. The ratio of k_G/k_L depends on the type of gas-liquid transfer apparatus, the specific compound under consideration and temperature (Munz and Roberts, 1989). The typical reported values of k_G/k_L are in the range of 100-150. Munz and Roberts (1989) also suggest that, liquid phase resistance control can be assumed when it accounts for more than 95% of the total resistance. Thus, assuming a k_G/k_L ratio of 100, it can be estimated that the K_H value has to be higher than 0.19 for liquid phase resistance to be governing. The value of Henry’s constant for H₂S is 0.36 (Munz and Roberts 1989) estimated a K_H value of 0.55 assuming a k_G/k_L value of 30-40) and place it in a range where both liquid and gas phase resistance may be required in overall transfer resistance calculation depending on the ratio of k_G/k_L . On the other hand, for ammonia Henry’s constant being of the order of 0.000561, makes the gas film resistance governing.

Therefore the gas transfer is limited by either the liquid phase or the gas phase, depending on which k value is lowest. Compounds with high solubility will be gas film limited, while compounds with low solubility will be liquid film limited. We believe the cross-over point between liquid and gas film limiting is H₂S but this needs to be tested experimentally.

Both gas and liquid film controlled compounds will be influenced by ion activity via influence on $[C_{\text{gas}}]_L$. For liquid film controlled processes, k_L will also be impacted by non-ideal behavior.

A relatively large and not well characterized impact in gas transfer is the effect the (surface active) organic compounds in the wastewater exert on the transfer rate. This is empirically described through an alpha factor (Painmanakul and Hébrard, 2008).

Discussion and Outcomes. The workshop participants agreed that this was a very important topic, with an impact across all areas, with good suitability to be addressed in a generalized model. The

current approaches are quite standardized and effective, with the similar basic relationship across all models. In diffused aeration, separate models of aerators are used to determine k_LA . One of the key issues raised was determination of the transfer area of different gaseous phases in contact with water. These could be free liquid surface in contact with atmosphere, air supply in aerated reactors, gas generated by biochemical processes e.g. anaerobic digesters and anoxic systems, where the gas composition can be atmospheric or enriched with oxygen, etc.). The calculation of the gas composition and the contact area A for each one of these phases (several gas phases in contact with the liquid in the reactor!) will have an important effect in the acid-base and biochemical processes, particularly in systems where gas is generated (e.g., anaerobic digesters and anoxic systems). The impact of activity on gas solubility can be independently addressed by ion activity corrections, but specific corrections are required to determine the impact of non-ideal behavior on k_L . In summary, the current k_LA approach is effective (first order equilibrium driven transfer), particularly if general activity corrections are applied to solubility but work should be done to better assess the impact of non-ideality on dynamics. A unified approach to estimate K_LA values of different gases relative to the K_LA value of oxygen based on physical properties of gases would be useful.

Precipitation

Metal ion precipitation and coagulation are similar processes, resulting in transfer of metal ions and associated anions from liquid to solid phase. The first term generally refers to formation of hard metal precipitates such as calcium carbonate and calcium phosphate (e.g., Musvoto et al. 2000b), while the second generally refers to formation of soft flocs from primary precipitates, commonly by ferrous or alum phosphate coagulation for wastewater treatment (e.g., Takacs et al. 2006). Common precipitants include:

- (a) Metal (Ca, Mg, Fe, Al) ion phosphates and related compounds (e.g., struvite)
- (b) Metal (Al) ion hydroxides.
- (c) Metal (Ca, Mg) carbonate (CO_3^{2-})
- (d) Metal (Fe, heavy metal) sulfides.

Precipitation processes are critical in modern wastewater treatment. They describe the behavior of phosphorus in all stages, as well as calcium and magnesium scaling. The presence of precipitates provides a slow buffer to changes in pH, and emerging processes (e.g., phosphorus recovery, Kim et al. 2007) are highly dependent on metal ion precipitation.

Of the IWA models, only ASM2/2D contains precipitation, and in this case, it is an empirical 1st order pseudo-equilibrium process (Henze et al. 2000).

Approach 1

A common method of modeling precipitation is a pseudo-equilibrium approach, with a first order coefficient (Batstone and Keller 2003; Henze et al. 2000; Takacs et al. 2006; van Langerak and Hamelers 1997). As an example, the formation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) is modeled as:

$$r_{stru} = k_{emp} \left([Mg^{2+}] [NH_4^+] [PO_4^{3-}] - K_{SP} \right) \quad \text{Equation 6}$$

Where r_{stru} is the crystallization rate, k_{emp} is a kinetic coefficient, K_{SP} is the solubility product, and is approximately $10^{-12.6}$. A continuous or discrete switch is needed to prevent negative struvite concentrations. This is a simple method to model precipitation processes, but is almost entirely empirical.

Approach 2

An alternative is the approach by UCT (Musvoto et al. 2000b, Ekama et al. 2006), which is also equilibrium driven, but is closer to fundamental relationships used for crystallization (Tait et al. 2009). A modified (more generalized) form of this for struvite is

$$r_{stru} = k \left(\left(\frac{[Mg^{2+}][NH_4^+][PO_4^{3-}]}{K_{SP}} \right)^{1/3} - 1 \right)^3 \quad \text{Equation 7}$$

Where the exponent is normally related to the stoichiometry of the crystallisation reaction (Musvoto et al. 2000a; Tait et al. 2009).

The actual process of crystallization is complicated by several issues:

- (a) Impact of non-ideal behavior; ions engaged in precipitation are divalent and trivalent. These are most influenced by non-ideal behavior, and ions form soluble ion pairs at elevated concentrations prior to precipitation.
- (b) Crystallization is a two-step process of nucleation followed by crystallization. Either can be rate limiting. This can be adjusted for by including the existing solid product in the crystallization reaction, but adds another layer of complexity to the model.
- (c) Specific compounds can both promote or inhibit both reactions. This can be general (through ion pairing, activity etc), or specific (poisoning or promotion).

Multiple precipitates

Equilibrium or dynamic conditions in concentrated liquid solutions such as digester centrate may lead to multiple precipitates forming. Finding the right combination of precipitates forming, particularly if the precipitation potential needs to be determined directly from solubilities for each combination of solids is not trivial. The supersaturation index (SSI) for each potential precipitate can provide guidance. If the product of the activities of ions participating in a precipitate is larger than the solubility constant, the solution is supersaturated for the specific precipitate. However, for “n” precipitates, 2ⁿ solutions must be considered. In reality some of these solutions may not be physically feasible. From chemical equilibrium tables (NIST, 2001) about 30 potential precipitates can be identified. 2³⁰ large equation systems are beyond the scope of practical applicability. A mixture of kinetic and equilibrium expressions can significantly simplify the computational demand. The specific species and the best way of their handling should be investigated by the Task Group.

Discussion and Outcomes. The workshop generally agreed that precipitation was critical to include in most modern wastewater treatment processes, and that a generalized approach was preferable. With the exception of the UCT group, and specific precipitants, a generalized approach to precipitation had been placed in a “too hard” basket by wastewater researchers. The effective simulation of precipitation kinetics depends on a good overall framework, including acid-base description, as the pH dependency is vital to proper precipitation prediction. The common opinion was that while some precipitation processes may be represented by algebraics (e.g., FeS), dynamic equations were generally required, since time constants for certain process rates are similar to biological rates. Any Task Group report should be backed by experimental validation to improve confidence in the models used, and address common examples. This can be done by relatively simple batch precipitation experiments in different matrices and there are good examples in the literature (Musvoto et al. 2000b, Szabó, et al, 2008). Some phenomena (e.g., scaling) are likely very difficult to predict, but in general, describing precipitation is a highly important component of a generalized model. The two approaches were not evaluated at the workshop (only the 1st model), and should be discussed in this position paper review.

Chemical oxidation-reduction

Spontaneous chemical reactions apart from those involving ions or gases are relevant to wastewater processes. They involve oxidation or reduction of specific chemicals, which can have an impact on the biochemical and physicochemical system. Important pairs in the wastewater environment that act as spontaneous mediators include:

- (a) S^{2-}/S^0
- (b) Fe^{2+}/Fe^{3+}
- (c) O_3, ClO^-
- (d) Others

These chemicals will react spontaneously with each other as well as other normally non-reactive chemicals (e.g., O_2 , NO_3^- , organics). The importance in an overall model is (a) accounting for the oxidation and reduction in the overall COD balance, and (b) accounting for modified state of the reactive chemicals during other physicochemical and biochemical reactions.

Discussion and Outcomes. It was discussed that this was a lower priority, as even though these chemicals are widespread in wastewater treatment, the impact of spontaneous redox reactions was low as compared to other biochemical reactions. The key compound which may be important is Fe^{2+}/Fe^{3+} , as this will reduce under anaerobic conditions, and oxidize under aerobic conditions consuming oxygen. Both reactions will alter its behavior towards anions, particularly OH^- , PO_4^{3-} and S^{2-} . This may make it difficult to simulate phosphate and sulfide. There are two approaches. The specific approach is to assume that all Fe is as Fe^{2+} under anaerobic conditions, and Fe^{3+} under aerobic conditions. This would describe transformation of precipitates. The generalised approach is to fully model redox reactions, with an overall “redox” output, analogous to pH. It was noted that redox probes were generally relative in their measure of redox, even when recently calibrated.

Corrections

The chemical processes themselves are influenced by a number of factors such as non-ideality, temperature, atmospheric and hydraulic pressure. Corrections to the physicochemical system have been largely neglected in standardized models, though the principles are generally well understood. While there are additional corrections (e.g., gas non-ideality) the major impacts are solution non-ideality and temperature as discussed further below. The impact of complex organic buffers is really related to acid-base processes, but we have included it as a correction here.

Non Ideality

Solutions begin to behave non-ideally when not infinitely dilute. By non-ideality, the activity of a component is lower than its concentration. Solution non-ideality is often referred to (but not fully defined as) ionic strength, or ion activity. Non-ideality has an impact on both ionic and non-ionic species within the solution. The deviation is caused by changes in hydration of molecules, changes in surface properties of solid and gas boundary layers, and chemical interactions in the solution as a whole. Specific chemical interactions (ion pairing) need to be handled separately. None of the IWA models represent non-ideal ion behavior, while commercial software is ahead of standardized models by inclusion of simple ion activity. Simplified ion activity correction is included in the UCT models (Musvoto et al. 2000a), together with some ion pairing behavior.

In non-ideal solutions, a calculations relating to an ion (e.g., pH, acid-base equilibrium etc) are done using the ions activity (a_i), rather than molal concentration. Activity is analogous to molal concentration in an ideal solution. Activity can be calculated as shown below:-

$$a_i = \gamma_i C_i^{z_i} \tag{Equation 8}$$

Where a_i is the activity of the ion, γ_i is the activity coefficient for ion i , and $C_i^{z_i}$ is the molar concentration for ion i . In simple cases relevant equations can be corrected directly and the molal concentration used in place of the activity. The level of non-ideality can be estimated by calculation of ionic strength (Hamann et al. 2007; Stumm and Morgan 1996):

$$I = \frac{1}{2} \sum_{i=1} C_i z_i^2 \tag{Equation 9}$$

Where I is the ionic strength, C_i is the molar concentration of ion i , and z_i is the valence of ion i . There are then a number of corrections to calculate activity coefficients for ions of different valencies. The simplest is the Debye-Hückel equation (Hamann et al. 2007):

$$\log(\gamma_i) = -A z_i^2 \sqrt{I} \tag{Equation 10}$$

A is a solvent specific constant. Therefore, for this simple equation, there will be common γ_i values for monovalent, divalent, and trivalent ions. Obviously higher valency ions will be more influenced. There are many more complex corrections available (Hamann et al. 2007; Langmuir 1997; Morel and Hering 1993; Stumm and Morgan 1996), but one to highlight in particular is the extended Debye-Hückel equation (Langmuir 1997) as used in PhreeqC, (Parkhurst and Appelo 1999), which allows correction of non-valent compounds:

$$\log(\gamma_i) = \frac{-A z_i^2 \sqrt{I}}{1 + B \alpha_i^0 \sqrt{I}} + b_i I \tag{Equation 11}$$

Where A and B are solute and temperature specific, while α_i^0 and b_i are ion specific. For non-valent compounds (z_i being zero), activity correction becomes linear with ionic strength (Setchenow equation (Langmuir 1997)). In principle, the whole process of calculation should be iterative since the concentration of ions depends on activity, which depends on strength, which depends on concentration in an implicit loop. This obviously becomes more complex with higher levels of correction.

The correction required depends on ionic strength. Ionic strength and necessary components in the model to control errors in pH to <5% are summarised in Table 2 (this is based on our initial calculations and needs to be tested).

Table 2: Required non-ideality corrections to achieve pH error of <5%

Level	Ionic Strength (M)	Wastewater type	Approach
1	<0.001	Drinking water, clean natural fresh water	No correction required – assume ideal
2	<0.1	Weak industrial WW. All domestic WWTP.	Non-iterative simple correction $K_{a,corr} \approx \gamma K_a^{-1}$
3	<1 (only ion activity)	Sea water, anaerobic digesters	Full iterative calculation of ion activity using appropriate activity calculation.
4	<1 (activity with non-valents)	As above, with gas transfer	As above, with use of non-valent equation (e.g., equation 10).
5	<5	Strong industrial, landfill leachate, RO brine	As for level 4, but inclusion of specific ion pairs.

1. γ is the activity correction for single valency ions suitable for K_a (generally monovalent for simple corrections).

Based on our experiments at ionic strength of 1-5 in landfill leachate, approximately 50% of non-ideality can be explained by inclusion of non-specific activity (levels 3-4), while the other 50% can be explained by specific ion pairing (level 5) (Tait et al. 2009).

Discussion and Outcomes. While adding ion activity does add some complexity to the model, coefficients associated with all models have been well established in the literature. Level 2 activity correction should be regarded as the minimum for low strength and/or non-precipitating systems. The main barrier to implementation of level 3 and above is that it generates an algebraic loop, and practical implementation requires a differential algebraic equation (DAE) approach to solution of the weak acid-base system. In general, however, to properly correct for the impact of activity on precipitation equilibrium, a level 3 or higher approach is required. Level 4 could also enable replacement of the current empirical approach to gas-liquid transfer corrections for salinity in aeration systems.

Temperature

Temperature has a strong impact on all physicochemical processes. The largest impact is change in equilibrium, due to a change in free energy of reaction. This will generally cause gases to decrease in solubility, acidity coefficients to decrease, and may cause solids to increase or decrease in solubility. The IWA ASM series does not put an emphasis on the effect of temperature, and the priority in that case has been on biochemical processes anyway. The ADM1 contains correction of gas solubility and acidity coefficients. Basic correction is described by the van't Hoff equation, which describes the change in free energy with temperature, based on enthalpy of reaction (Puigdomenech et al. 1997; Stumm and Morgan 1996). In the ADM1 scientific and technical report (Batstone et al. 2002), the use of the constant enthalpy form of the van't Hoff equation is recommended:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Equation 12}$$

Where K_1 and K_2 are equilibrium coefficients at temperatures T_1 and T_2 (K) respectively, ΔH^0 is the enthalpy of reaction, and R is the universal gas law constant. This relationship holds true for most acidity coefficients and gas solubilities in wastewater treatment. It needs to be assessed for its applicability to solids.

Reaction rates will generally increase with temperature according to the Arrhenius equation. A review also needs to be done to assess Arrhenius law constants.

Discussion and Outcomes. Impact of temperature needs to be included in any generalized model. In general, it was agreed that a single, fundamental relationship was preferable to empirical relationships. As part of Task Group activities, a review should be conducted to validate application of the van't Hoff law against the wide range of coefficients to be used. This should be done against (a) acidity coefficients, (b) gas solubilities, (c) solids solubilities, (d) activity coefficients, and (e) ion pairing coefficients. A wide temperature range for consideration could be 0°C-60°C. Constants will be classified either as (i) not varying substantially with temperature; (ii) following van't Hoff constant enthalpy equation; (iii) following van't Hoff with variable enthalpy; or (iv) must be represented empirically. A review should also be done to assess applicability of the van't Hoff equation, as well as parameters for temperature dependency of kinetics.

Reactions with organic solids

While it is well known that organic solids (particularly microbes) are reactive (Madigan et al. 2000), their impact on the physicochemical system has not been considered in models that we are aware of. A search in the literature returns a few results (Van Vooren et al., 1999, Szabó et al, 2008). Microbes and organic solids may act as acidity buffers, with negatively charged sites at high pH, and neutrally charged sites at neutral and low pH. They may also act as complexing agents for cations. It is not known whether anaerobically digested solids behave differently from activated sludge, primary sludge, but given the different nature of the solids, it is likely. We have preliminary results that indicate the impact is quite strong at high solids (>3% anaerobic digestate), with an error of 2 pH units after titration with 7 mL of 0.2M HCl (Figure 2).

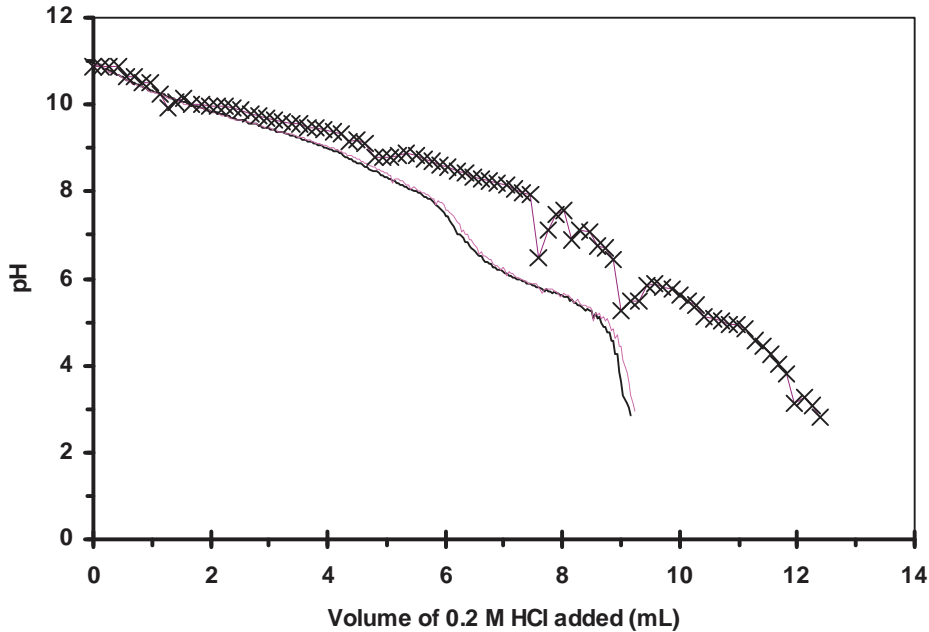


Figure 2: Titration in the presence of (x) and without organic solids (line). Solids concentration was approx. 3% anaerobic digestate. The solid blue line is an automated on-line filtration and analysis, while the purple line is an off-line filtration and analysis. This indicates that CO₂ stripping during analysis has no impact. Data generated at UQ, not otherwise published

This can be viewed in the light of a simulated titration of pure ammonia solution without organics or suspended solids as shown on Figure 3 (Fairlamb et al, 2003). In this model simulated and “theoretical” pH shows a good agreement.

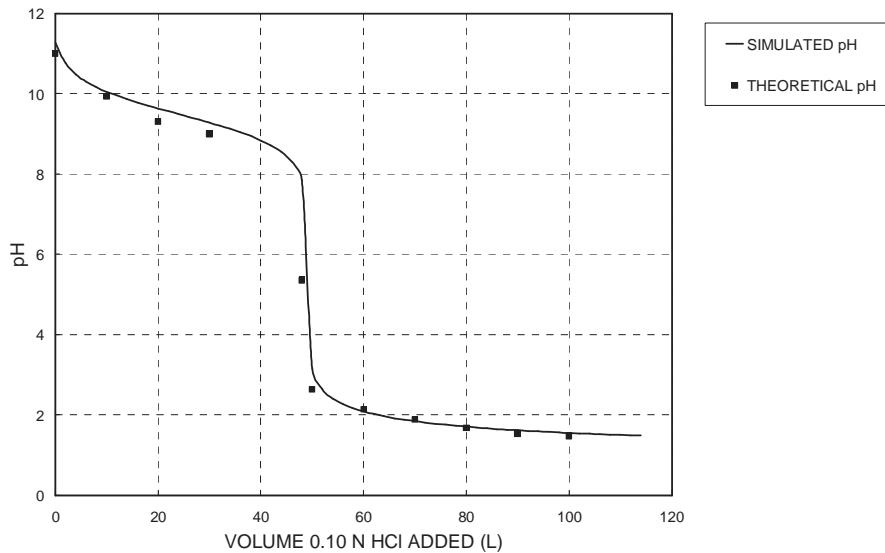


Figure 3: Pure solution: 0.10 N NH₃ titrated with 0.10 N HCl (Fairlamb et al, 2003) .

Discussion and Outcomes. This was a topic raised during the workshop. Given the lack of literature, it is important to quantify this issue. There were many anecdotal references to the impact of organic solids on pH buffering, but again, almost no literature references.

Implementation and solution

Implementation and solution

Methods for solving the acid-base and physicochemical system have been well established. As discussed in the acid-base reaction section, equations can either be formulated as fast dynamic equations, or it can be assumed that the equations are at equilibrium (Hellinga et al, 1999). These are addressed individually below. The ADM1 proposed equations to solve the pH according by both systems (Batstone et al. 2002), and given the speed of acid-base reactions, if appropriately fast kinetic coefficients are chosen for the acid-base system (Stumm and Morgan 1996), the results should be the same (Musvoto et al. 2000a). Gas-liquid and solid-liquid reactions may be represented as differential or algebraic equations depending on the speed of the process. More complex systems only are addressed here, but an alternative for very simple models is simplifying acid-base reactions into the biochemical systems. This is the method used in the ASM models (via alkalinity), but it is also possible to extend this method to calculate pH (Siegrist et al. 2002). This method is inherently limited to very simple models, and still induces model stiffness.

The differential approach represents the mass balance of each acid and base as a differential equation, and requires a modification of the acid base equations (equation 3) to represent them as rates (impacting the states of nitrite and free nitrous acid respectively in this case). These rates are naturally high (Musvoto et al. 2000a; Stumm and Morgan 1996), and must be maintained at a high level ($>10^8 \text{ d}^{-1}$) to avoid model artifacts (errors), particularly in discrete systems such as biofilms. When there are both fast and slow processes in a model, the model becomes more difficult to solve for explicit differential solvers. Essentially, the step length and numerical solution stability is controlled by the rapid process, whilst the dynamic behavior is determined by the slow process (Hangos and Cameron 2001). As such, implicit stiff solvers (backward Euler, DASSL, ODE15s, Gear' Stiff, CVODE) need to be used to solve such models. These inherently include a non-linear algebraic solver as part of the differential system, and providing the algebraic acid-base equations

as differential equations is mainly for convenience on the part of the user. Essentially, almost all stiff solvers are also DAE solver. Stiff solvers are excellent for stiff differential equations, but they are inherently slow or unstable when inputs or disturbances are dynamic or where the model is discontinuous (including derivatives). This strongly limits application of the model. Finally, as an additional negative of the DE approach, an algebraic solver is still needed to represent complex activity, and where ion pairs are to be represented, each pair must be represented by an additional differential state. Therefore, as physicochemical model complexity increases, the number of states increases dramatically.

In a DAE approach, the acid-base equations are represented as algebraics (equation 3), and formulated such that the left hand side is zero, and individual acids and bases are calculated as implicit algebraic equations. For each acid and base couple, there is a differential state representing the sum of the two (acid+base), as well as two algebraic variables to represent concentration of the acid and base. Slow processes (e.g., biochemical, precipitation, gas-liquid transfer) only affect the differential state. The two algebraic equations are the acid-base equation (eq. 3), as well as the mass balance. In addition to the acid-base couples of algebraics, there is also the charge balance equation (to calculate $[H^+]$). There are therefore generally a large number of non-linear implicit algebraic equations to be solved, using a capable algebraic solver.

For simple systems, it is possible to manually reformulate the equations such that they are explicit. For complex systems automated symbolic manipulation is also possible. However, as model complexity increases, the complexity of the explicit solution increases dramatically such that it is generally faster to solve the implicit equations (normally 2-3 steps) than to calculate the right hand side of a very complex explicit solution. This is especially true in the context of a differential model, where the initial estimate is taken from the previous time step, and is likely very close to the solution.

An algebraic approach also allows further analysis of the model, and if necessary, solution of other fast reactions (e.g., some gas transfer and precipitation, or even biochemical) within the algebraic subsystem (Rosen et al. 2006). This can be used to further optimize the model solution speed when used with a non-stiff solver.

Discussion and Outcomes. The workshop agreed that in general, an algebraic approach should be taken towards acid-base equations and a default approach of differential equations for gas transfer and precipitation. Acid-base systems should be formulated as algebraics because (a) solving as differential equations mandates the use of stiff solvers, which limits application and formulation of the model, and (b) it reduces the numbers of states with more complex models, by calculating many variables as algebraics. Algebraic solvers are widely used already – for example to calculate the impact of hydraulic recycles. It was discussed that many solid-liquid and gas-liquid processes could be represented by algebraic equations, and that this may be required to avoid excessive model stiffness. The final report should attempt to provide rates for individual processes (under those specific sections), which would allow determination as to whether the process should be solved by a differential or algebraic equation. There should also be an attempt to minimize algebraic equation non-linearity and/or differential equation stiffness.

Other software outside the wastewater field

There are a range of packages that predict speciation under different conditions. Most are equilibrium only, and orientated mainly towards prediction of speciation. Taking only open source or freely available examples, examples are:-

- (a) PhreeqC– USGS. Orientated towards geology (Parkhurst and Appelo 1999).
- (b) MINTEQA2– USEPA. Developed to describe environmental interactions (Allison et al.

1991).

These packages are designed to describe chemical equilibria within their specific application. This may have direct application to wastewater modeling. They are generally designed to be very expandable, have ion activity and other corrections applicable to most situations (e.g., up to level 5 non-ideality correction), and are open source. Obviously if these packages are directly applicable or easily modified to wastewater applications, this would avoid much of the effort involved in developing a new framework. Both packages are complex, and solve most reactions (including gas transfer and precipitation) using an algebraic approach.

Discussion and Outcomes. Both of these packages (as well as a number of commercial alternatives) are oriented towards algebraic solutions with long time scales compared to wastewater systems. Even biological reactions are normally solved algebraically. As such, they are not directly applicable to wastewater systems. However, the databases associated with these models will be extremely valuable as a source of data, and the models may be used in virtual experiments to conduct sensitivity analysis, validate a wastewater physicochemical model, as they are very comprehensive, with excellent predictive capability within their area of application.

Conclusions and Future Work

Important issues

It was generally agreed that the two critical issues (compared to the basic requirement of plant-wide pH prediction) were adding precipitation as a process, and an integrated approach for handling non-ideal behavior. This can also be seen in the approaches by commercial developers. Properly handling non-ideal behavior will address other issues (such as the impact of salts on gas-liquid transfer). Finally, it should be noted that topics have already been filtered, and all topics presented here were regarded as worthy of addressing, and in the structure as presented.

Need for an IWA Task Group and technical report

Motivation and interest in physicochemical systems was strong in both the workshop, and subsequent conference-wide presentation. The fact that there have been a number of different approaches taken, despite the underlying reactions being the same, indicates that the field can benefit from a common approach. This can have a (limited) number of levels of complexity, depending on the application. In general, the default would be capable of plant-wide domestic wastewater prediction, including correction of non-ideal behavior, and simple precipitation. This can be supported by reference implementations in common languages, including (if necessary), solvers.

Approach and future steps

The recommendation of the workshop is to form a Task Group, and work towards a scientific and technical report. One point made was that experts in aquatic chemistry be approached to contribute to the Task Group (thus enlarging from the current group of engineers, engineering academics and programmers). The current report structure should follow that of this position paper, following feedback. This position paper will be circulated to interested parties, modified, and then released for general comment. Following this, a Task Group will be formed, with production of a scientific and technical report planned within two years of Task Group formation.

The Task Group would need to address a number of components:

- (a) The basic elements of a generalized model need to be formed, mainly by literature review, discussion, and workshops.
- (b) Some specific elements may need experimental analysis. The Task Group should have a mechanism to readily conduct, discuss, and disseminate experiments as required.
- (c) The different generalized models need to be formulated, implemented, and verified.

- (d) Models need validation against other complex models (e.g., those referenced in this paper), as well as experiments.
- (e) Two types of batch experiments can be done as standard – automated titrations, and crystallization experiments. Titrations if performed with care (such as shown in Figure 2) are “relatively” straightforward, and require minimal equipment. Crystallization experiments are more complex, and generally require access to ion chromatography.

While the experimental work adds minor complexity to the Task Group, it would provide an additional level of validation to the Task Group outcomes, specifically orientated towards the target application.

Acknowledgements

Leendert Vergeynst, Agnieszka Zak, Chirag Mehta, Stephan Tait, David Ikumi, and Chris Brouckaert were also involved in aspects of this work. We also thank the organizers of WWTmod 2010, and particularly Leiv Rieger for facilitating this activity. Acid-Base work at UQ was funded by the Australian Research Council (ARC-Linkage Grant LP0669527). Ion precipitation work at UQ was funded by the Grains Research and Development Corporation Australia (Nutrients from Waste Project Number UQ00046). Peter Vanrolleghem holds the Canada Research Chair in Water Quality Modelling

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