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Effects of ion strength and ion pairing on (plant-wide) modelling of anaerobic digestion processes

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Abstract: The objective of this study is to show the influence of ionic strength (as activity corrections) and ion pairing on (plant-wide) modelling of anaerobic digestion processes in wastewater treatment plants (WWTPs). Using the Benchmark Simulation Model No. 2 (BSM2) as a case study, this paper presents the effects that an improved physico-chemical description will have on the predicted effluent quality (*EQI*) and operational cost (*OCI*) indices. The acid-base equilibria implemented in the Anaerobic Digestion Model No. 1 (ADM1) are modified to account for non-ideal aqueous-phase chemistry. The model corrects for ionic strength via the Davies approach to consider chemical activities instead of molar concentrations. Also, a speciation sub-routine based on a multi-dimensional Newton-Raphson iteration method accounts for the formation of some of the ion pairs playing an important role in wastewater treatment processes. Results at high ionic strength demonstrate that corrections to account for non-ideal conditions lead to significant differences in predicted process performance. In addition, the paper describes: 1) how the anaerobic digester performance is affected; 2) the effect on pH and the anaerobic digestion products (CO₂, CH₄ and H₂); and, 3) how these variations are propagated from the sludge treatment to the water line.

Keywords: ADM1, BSM2, non-ideality, physico-chemical framework, weak acid-base chemistry modelling

1. INTRODUCTION

Anaerobic digestion is a proven waste stabilization technology, which is widely applied and studied because of its beneficial production of renewable biogas energy, making it a truly sustainable technology. From a systems engineering point of view, one of the major advances in the field of anaerobic digestion has been the development of the IWA Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.*, 2002). The ADM1 is a general structured model consisting of biochemical and physico-chemical processes, which is useful for the design, operation, and optimization of anaerobic digestion plants. In addition to organic municipal waste treatment, other applications of the anaerobic digestion process are the treatment of industrial waste, animal manure, landfill leachate, and brine from reverse osmosis (Batstone and Keller, 2003). Since the latter waste streams, in general, contain higher concentrations of ions than domestic wastewater, it is expected that significant physico-chemical effects will occur. It is believed that a key limitation of the ADM1, as applied to high-strength wastes, is the absence of corrections for ionic strength and ion pairing behaviour that occurs in such wastes (Batstone *et al.*, 2012, Tait *et al.*, 2012).

The work presented here fits within the activities of a broader IWA Task Group on a Generalised Physico-chemical Modelling Framework. The objective of the present study is to improve the physico-chemical description of the different phenomena taking place in an anaerobic digester during plant-wide modelling and simulation of wastewater treatment plants (WWTPs). Corrections are incorporated to account for ionic strength and ion pairing on top of the physico-chemical and bio-kinetic reactions of ADM1 implemented in the Benchmark Simulation Model No. 2 (Gernaey *et al.*, 2014). The paper presents simulation results for the above model modifications highlighting the significance of the corrections in a plant-wide context, particularly looking at the propagation of effects from the anaerobic digester aqueous phase through to final effluent quality and operational costs.

2. METHODS

2.1. WASTEWATER TREATMENT PLANT UNDER STUDY

The WWTP under study is the IWA BSM2 platform proposed by [Germaey et al. \(2014\)](#). The plant is treating an influent flow of $20,648 \text{ m}^3 \cdot \text{day}^{-1}$ and a total COD and N load of 12,240 and 1,140 $\text{kg} \cdot \text{day}^{-1}$, respectively. The activated sludge (AS) unit is a modified Ludzack-Ettinger configuration consisting of 5 tanks in series. The ASM1 is chosen as the biological process model ([Henze et al., 2000](#)). The double exponential settling velocity function of [Takács et al. \(1991\)](#) is selected as a fair representation of the secondary settling process, described by a one-dimensional model consisting of ten layers. The BSM2 plant further contains a primary clarifier (PRIM), a sludge thickener (THK), an anaerobic digester (AD), a storage tank (ST) and a dewatering unit (DW). The anaerobic digestion behaviour is described with the Anaerobic Digestion Model No. 1 (ADM1) ([Batstone et al., 2002](#)). Additional information about the plant design, operational conditions and process models of the BSM2 platform was previously reported by [Germaey et al. \(2014\)](#).

2.2. IMPROVED PHYSICO-CHEMICAL FRAMEWORK

The composition of the digester aqueous phase is represented as a set of chemical entities called species S_i ($\text{mol} \cdot \text{L}^{-1}$) and components S_j ($\text{mol} \cdot \text{L}^{-1}$). As applied here, components (S_j) are arbitrarily selected as the fully dissociated form of the species (S_i). For example, the fully dissociated form of inorganic carbon $S_{\text{CO}_3^{2-}}$ was selected as a component (S_j), while the partially dissociated $S_{\text{HCO}_3^-}$ and un-dissociated $S_{\text{H}_2\text{CO}_3}$ forms of inorganic carbon were species (S_i) in the model. **Table 1** summarizes all the considered species (rows) and how could be represented by a linear molar balance combination of the model components (columns) (more on this below).

2.2.1. Ionic strength corrections

In dilute wastewaters, ions in solution can be physically far apart (may not impose a chemical influence on one another), whereas when a wastewater becomes concentrated up to high strength, the chemical interactions between ions and with the solvent become significant and have an effect on equilibrium chemical reactions occurring in the aqueous phase. These interaction effects are commonly corrected for ([Stumm and Morgan, 1996](#)) by multiplying each concentration (S_i or S_j) with an activity coefficient (γ) with the product being called the chemical activity (a_i) as follows in **Eq. 1**:

$$a_i = \gamma S_i \quad \text{Eq. 1}$$

The ionic strength (I) of the aqueous phase empirically estimates the level of interactions between ions ([Hamann et al., 2007](#)) and is commonly calculated as in **Eq.2**:

$$I = \sum_{i=1} S_i z_i^2 \quad \text{Eq. 2}$$

where z_i is the valence of ion i . There are several correlations available which describe the relationship between activity coefficients (γ) and ionic strength for ions of different valences ([Batstone et al., 2012](#)). In the present work, the Davies approximation is used to calculate activity coefficients as shows **Eq. 3**:

$$\log \gamma_i = -A z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \quad \text{Eq. 3}$$

where A is a temperature dependent parameter and γ is calculated as a common activity coefficient value for monovalent, divalent and trivalent ions, respectively. The Davies approximation is said to be valid for ionic strengths up to $0.5 \text{ mol} \cdot \text{L}^{-1}$, but practically has been observed to deviate significantly from other valid activity coefficient correlations at lower ionic strengths ([Tait et al., 2012](#)).

Table 1. Stoichiometric matrix of the components (S_j) and species (S_i)

| i/j | formula | S_{Na+} | S_{K+} | S_{NH4+} | S_{Cl-} | S_{CO3-2} | S_{ac-} | S_{pro-} | S_{bu-} | S_{va-} | $\log K_i$ | ΔH^0 |
|---------------|----------------|-----------|----------|------------|-----------|-------------|-----------|------------|-----------|-----------|------------|--------------|
| S_{Na+} | Na^+ | 1 | | | | | | | | | 0 | 0 |
| S_{K+} | K^+ | | 1 | | | | | | | | 0 | 0 |
| S_{NH4+} | NH_4^+ | | | 1 | | | | | | | 0 | 0 |
| S_{Cl-} | Cl^- | | | | 1 | | | | | | 0 | 0 |
| S_{ac-} | $C_2H_3O_2^-$ | | | | | | 1 | | | | 0 | 0 |
| S_{pro-} | $C_3H_5O_2^-$ | | | | | | | 1 | | | 0 | 0 |
| S_{CO3-2} | CO_3^{2-} | | | | | 1 | | | | | 0 | 0 |
| S_{bu-} | $C_4H_7O_2^-$ | | | | | | | | 1 | | 0 | 0 |
| S_{va-} | $C_5H_9O_2^-$ | | | | | | | | | 1 | 0 | 0 |
| S_{H2CO3^*} | $H_2CO_3^*$ | | | | | 1 | | | | | 16.68 | -32 |
| S_{H-ac} | $C_2H_4O_2$ | | | | | | 1 | | | | 4.76 | 0.41 |
| S_{H-bu} | $C_4H_8O_2$ | | | | | | | | 1 | | 4.82 | 2.8 |
| S_{HCO3-} | HCO_3^- | | | | 1 | | | | | | 10.33 | -14.6 |
| S_{H-pro} | $C_3H_6O_2$ | | | | | | | 1 | | | 4.87 | 0.75 |
| S_{H-va} | $C_5H_{10}O_2$ | | | | | | | | | 1 | 4.84 | 2.8 |
| S_{K-ac} | $C_2H_3O_2K$ | | 1 | | | | 1 | | | | -0.27 | 4 |
| S_{KCl} | KCl | | 1 | | 1 | | | | | | -0.3 | -4 |
| S_{KOH} | KOH | | 1 | | | | | | | | -13.76 | 55.81 |
| S_{Na-ac} | $C_2H_3O_2Na$ | 1 | | | | | 1 | | | | -0.12 | 8 |
| S_{NaCl} | $NaCl$ | 1 | | | 1 | | | | | | -0.3 | -8 |
| S_{NaCO3-} | $NaCO_3^-$ | 1 | | | | 1 | | | | | 1.27 | -20.35 |
| S_{NaHCO3} | $NaHCO_3$ | 1 | | | | 1 | | | | | 10.03 | -283.3 |
| S_{NaOH} | $NaOH$ | 1 | | | | | | | | | -13.90 | 59.81 |
| S_{NH3} | NH_3 | | | 1 | | | | | | | -9.25 | 52 |
| S_{OH-} | OH^- | | | | | | | | | | -13.99 | 55.81 |

2.2.2. Ion pairing, acid-base reactions and formulation of the equilibrium equations

The aqueous phase reactions (weak acid-base and other ion pairing) are mathematically formulated by a set of non-linear algebraic equations including one law of mass-action for each species (i) (**Eq. 4**) and one molar contribution balance for each component (j) (**Eq. 5**) to guarantee the component conservation principle (that is, all species can be expressed as linear combinations of components). The mass action laws are commonly rearranged with the species (i) written as the product of components (j) and the equilibrium constant (see **Eq. 4**, note that the mass action law uses chemical activities rather than concentrations). This rearrangement allows substitution of the mass action laws into the molar contribution balances to eliminate the species from the equation set that has to be solved iteratively for the component concentrations. In **Eq. 4** and **Eq. 5**, a_i/S_i represents the activity/concentration of the i^{th} species, a_j/S_j is the activity/concentration of the j^{th} component, $v_{i,j}$ is the stoichiometric coefficient of the j^{th} component in the i^{th} species (see **Table 1**), γ is the activity coefficient (**Eq. 3**) and K_i is the equilibrium constant (see **Table 1**). In this case study the considered N_{sp} (number of species) and N_c (number of components) are 9 and 25, respectively.

$$a_i = K_i \prod_{j=1}^{N_c} a_j^{v_{i,j}} \quad i = 1, 2, \dots, N_{sp} \quad \text{Eq. 4}$$

$$S_{j,tot} = S_j + \sum_{i=1}^{N_{sp}} v_{i,j} S_i = \frac{a_j}{\gamma} + \sum_{i=1}^{N_{sp}} v_{i,j} \frac{a_i}{\gamma} \quad \begin{matrix} j = 1, 2, \dots, N_c \\ i = 1, 2, \dots, N_{sp} \end{matrix} \quad \text{Eq. 5}$$

The effect of temperature on the equilibrium constants (K_i) is corrected for by the constant enthalpy form of the van't Hoff equation (Stumm and Morgan, 1996).

The calculation of pH is performed using the charge balance approach, as originally proposed for ADM1 (Batstone *et al.*, 2002), and relies on the electro-neutrality principle. The electro-neutrality principle assumes that the charges of anions and cations in the aqueous phase are matched by the combined charge of anions in solution, resulting in a zero net charge, as shown in **Eq. 6**

$$\sum S_{cat} - \sum S_{an} = 0 \quad \text{Eq. 6}$$

where S_{cat} and S_{an} represent the total equivalent concentrations of cations and anions, respectively, which is the concentrations of respective ions multiplied by their valence..

Implementation details, numerical issues and model verification

The BSM2/ADM1 implementation is a very stiff system because some of the states react quickly (weak acid-base chemistry) whereas some states react sluggishly (different biological uptake processes). Stiff solvers are especially suitable to handle these kinds of problems. However, the BSM2 cannot be simulated using stiff solvers because stiff solvers in-turn are not tolerant to highly dynamic inputs and especially the noise and step changes frequently used in process control. As investigated in **Rosen *et al.* (2006)**, the stiffness of the ADM1 can be substantially reduced by re-writing some of the process equations as differential algebraic equations (DAEs) instead of ordinary differential equations (ODEs). Thus, in order to reach acceptable simulation speed, (1) the S_{H_2} state together with the (2) weak acid base chemistry are approximated by solving an implicit algebraic equation set using the iterative Newton-Raphson (NR) method:

$$Z_{i+1} = Z_i - J_F(Z_i)^{-1} G(Z_i) \quad \text{Eq. 7}$$

where Z_i is the vector of equilibrium states ($z_{1,i}, \dots, z_{n,i}$) obtained from the previous iteration step i , $G(Z_i)$ is a vector containing the values of the set of implicit algebraic equations ($g_1(z_1, \dots, z_n), \dots, g_n(z_1, \dots, z_n)$) which has to be zero in order to satisfy equilibrium. Nevertheless a major modification of the NR formula (**Eq. 7**) was necessary to simultaneously solve (2) i.e. the set of equilibria presented in Section **2.2.2** together with the algebraic equations for the charge balance (S_{H^+}) (**Eq. 6**), ionic strength (I) (**Eq. 2**) and activity corrections (**Eq. 3**). The full analytical Jacobian (J_F) was needed for calculation of the new state values, which requires symbolic manipulation of the algebraic equations in order to obtain the matrix of all first-order partial derivatives $\delta(G_1, \dots, G_m)/\delta(z_1, \dots, z_n)$. The iteration is repeated as long as the elements of the error function are larger than a predefined value, which in our case was set to 10^{-12} . The MINTEQ geochemical program (**Allison *et al.*, 1991**) was used as a reference for verification purposes.

VARIANTS AND MODEL TEST CASES

In this case study, three sets of model assumptions describing the physico-chemical processes taking place in the anaerobic digester are compared.

1. In the reference case (A_1), the default implementation of ADM1 (**Rosen *et al.*, 2006**) is implemented as is in the BSM2. Kinetic and stoichiometric parameters are defined for 35°C and reported in **Gernaey *et al.* (2014)**.
2. The second formulation (A_2) is an extension of the reference case (A_1), only upgrading the weak-acid base chemistry with iterative calculation of ionic strength (**Eq. 2**) and activity corrections (**Eq. 1** and **Eq. 3**) for the speciation of inorganic carbon (S_{IC}), inorganic nitrogen (S_{IN}), acetate (S_{ac}), propionate (S_{pro}), valerate (S_{va}), butyrate (S_{bu}) and protons (S_{H^+}) (**Table 1**).
3. The third approach (A_3) also included ion pairing reactions where S_{cat} is described as sodium (S_{Na}) and potassium (S_K) (strong bases) and S_{an} as chloride (S_{Cl}) (strong acid), respectively. These ions are also allowed to interact with other state variables and form new ion-pair species (see **Table 1**) in accordance with the principles of **Eq. 4** and **Eq. 5**. No sodium inhibition term was added to the ADM1 biokinetics.

All of the above approaches are subjected to identical influent flow rate and pollutant loads in terms of COD and N (**Gernaey *et al.*, 2011**), with the exception that a series of repetitions/scenarios (Sc_1, \dots, Sc_5) are carried out with progressively higher cationic load, in order to evaluate the effect of ionic strength ($I = 0.09-0.3 \text{ mol.L}^{-1}$). It is important to highlight that the added cations are unpaired with anions, hence having an impact on both raising the pH and adding ionic strength. This would be the case where a strong alkali (sodium hydroxide or a high alkalinity feed) is added to increase the alkalinity of the wastewater. Simulation results are evaluated dynamically during the last 364 days of simulation in accordance with BSM2 simulation principles (100 days simulation to reach steady state, then 609 dynamic influent data). The effluent quality index (EQI) is used to evaluate the (weighted) pollution load discharged to water bodies, and the operational cost index (OCI) is an approximate measure of the plant's operational costs (energy, sludge production, chemicals, etc.) (**Gernaey *et al.*, 2014**).

3. RESULTS

3.1. ADM1 STATE VARIABLES

Table 2 shows average values of the ADM1 state variables when the BSM2 is simulated with the different model approaches (A_1 , A_2 & A_3) and for different cationic loads (Sc_1 , Sc_2 , Sc_3 , Sc_4 , Sc_5). The rationale behind these scenarios is to increase the ionic strength. Simulation results show that at low ionic strengths (I), the differences between A_1 , A_2 and A_3 are not strong (compare the average state values for Sc_1 in **Table 2**). This is consistent with the original assumptions of ADM1 which applies to the majority of (dilute) domestic wastewaters. However, activity corrections of A_1 and A_3 do influence the species distribution in the inorganic carbon system (S_{IC}). More specifically, the concentration of deprotonated inorganic carbon (S_{CO3-2} , S_{HCO3-}) increases while the concentration of carbonic acid (S_{H2CO3^*}) decreases (see values for Sc_1 in **Table 2**). As a consequence, a higher concentration of free protons (S_{H+}) is required to uphold the electro-neutrality principle (**Eq. 7**) and the pH decreases from 7.21 (A_1) to 7.11 (A_2/A_3). In contrast, the relative distribution of the inorganic nitrogen species (S_{NH4+}/S_{NH3}) (pKa = 9.25) is driven by pH and then decreases the free ammonia (S_{NH3}) concentration. The lower S_{NH3} concentrations in-turn reduce acetoclastic methanogenesis inhibition ($K_{I,NH3} = 0.0018 \text{ mol.L}^{-1}$), which then results in a decrease in acetic acid concentration (S_{H-ac})/acetate (S_{ac-}) (see **Table 2**) and an increase in the concentration of acetate degraders (X_{ac}) with more uptake. Consequently, the level of ammonia inhibition was more pronounced for A_1 as compared to A_2/A_3 .

In Sc_2 , Sc_3 , Sc_4 & Sc_5 , the ADM1 system is evaluated by adding an additional stream ($Q_{add} = 5 \text{ m}^3.\text{day}^{-1}$) with different S_{cat} loads. In these scenarios, S_{cat} values (2, 4, 6 and 8 mol.L^{-1}) are distributed equally between S_{Na+} and S_{K+} , as would be the scenario where a strong alkali is dosed to increase the overall alkalinity of the wastewater. Results in **Table 2** show that high S_{Na+}/S_{K+} values result in a reduction of S_{H+} values (neutralized in effect), and consequently pH increases. Ionic strength (I) increases in a correlated manner with the applied cationic load (not necessarily linearly). Higher pH values increases S_{NH3} which then increases inhibition of acetate-degraders (X_{ac}), decreases acetate uptake and consequently influences the overall hydrogen (S_{H2})/acetate consumption (S_{ac}) (electron donors). Gas production (Gas_{CH4}/Gas_{CO2}) is then also reduced (see **Table 3**). At the high ionic strengths of Sc_4 and Sc_5 , S_{NH3} inhibition becomes very strong, leading to very notable accumulation of acetate (S_{ac}) in the digester and a substantial decrease in overall biogas production (see **Table 3**). Further accumulation of acetate can then decrease digester pH even further and influence many other processes, such as hydrogenotrophic methanogenesis and acetogenesis from different organics (**Batstone et al., 2002**). These are noted to be predominantly the effects of an overall rise in pH with increase S_{cat} loads (unbalanced sodium and potassium addition). However, importantly, the comparison between the results of A_1 , A_2 and A_3 provides a strong measure of the importance of ion activity and ion-pairing to correctly account for the progressive effects of salinity/pH.

The differences between A_1 and A_2/A_3 become more and more pronounced at higher ionic strengths ($I > 0.25$). The results (**Table 2**) show that up to Sc_3 , pH is less sensitive to S_{Na+}/S_{K+} variations in scenarios A_2 and A_3 (implemented as S_{cat} in A_2). The result is a lower pH in A_2 and A_3 as compared to A_1 , up to Sc_3 (that is, the increase in pH from Sc_1 to Sc_3 is less pronounced for A_2 and A_3 as compared to A_1). For this reason, the inhibition by free ammonia S_{NH3} is less for A_2 and A_3 as compared to A_1 , up to Sc_3 . Ion pairing would lower the effective concentration of free ions from A_2 and A_3 even further by converting the free ions into soluble ion-pairs (compare A_2 and A_3 in **Table 2**). This would be expected to provide further buffering of pH rise with the increased S_{cat} load. Nevertheless, compared to A_2 , the effects of ion pairing (A_3) is minor in both pH and species distributions (**Table 2**) and the resulting pH and species distribution are very similar in scenarios A_2 and A_3 . The implications are further discussed below.

Table 2. Average ADM1 state values with the different speciation/pH model implementations

| | Sc ₁ | | | Sc ₂ | | | Sc ₃ | | | Sc ₄ | | | Sc ₅ | | | Units |
|---------------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|---------------------|
| | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | |
| pH | 7.21 | 7.11 | 7.11 | 7.50 | 7.39 | 7.39 | 7.77 | 7.66 | 7.66 | 7.88 | 7.98 | 7.97 | 7.85 | 7.99 | 7.99 | - |
| S _{H+} | 6.16E-8 | 9.97E-8 | 9.96E-8 | 3.16E-8 | 5.40E-8 | 5.43E-8 | 1.72E-8 | 2.93E-8 | 2.97E-8 | 1.31E-8 | 1.43E-8 | 1.46E-8 | 1.42E-8 | 1.39E-8 | 1.39E-8 | mol.L ⁻¹ |
| S _{Na+} | | | | 0.027 | 0.027 | 0.026 | 0.054 | 0.054 | 0.052 | 0.076 | 0.081 | 0.076 | 0.088 | 0.096 | 0.094 | mol.L ⁻¹ |
| S _{K+} | | | | 0.027 | 0.027 | 0.027 | 0.054 | 0.054 | 0.054 | 0.081 | 0.082 | 0.081 | 0.104 | 0.105 | 0.099 | mol.L ⁻¹ |
| S _{NH4+} | 0.093 | 0.093 | 0.093 | 0.089 | 0.090 | 0.090 | 0.086 | 0.088 | 0.088 | 0.088 | 0.086 | 0.086 | 0.095 | 0.093 | 0.093 | mol.L ⁻¹ |
| S _{Cl-} | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 | 0.007 | 0.007 | 0.007 | mol.L ⁻¹ |
| S _{ac-} | 0.0013 | 0.0010 | 0.0010 | 0.0024 | 0.0014 | 0.0014 | 0.0075 | 0.0026 | 0.0025 | 0.0767 | 0.0168 | 0.0146 | 0.2216 | 0.2007 | 0.1920 | mol.L ⁻¹ |
| S _{pro-} | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00016 | 0.00017 | 0.00017 | 0.00017 | mol.L ⁻¹ |
| S _{CO3-2} | 0.00008 | 0.00013 | 0.00013 | 0.00024 | 0.00043 | 0.00043 | 0.00060 | 0.00118 | 0.00115 | 0.00069 | 0.00298 | 0.00287 | 0.00023 | 0.00121 | 0.00122 | mol.L ⁻¹ |
| S _{bu-} | 8.71E-5 | 8.71E-5 | 8.71E-5 | 8.93E-5 | 8.93E-5 | 8.93E-5 | 8.95E-5 | 8.94E-5 | 8.94E-5 | 9.04E-5 | 8.96E-5 | 8.96E-5 | 9.24E-5 | 9.21E-5 | 9.21E-5 | mol.L ⁻¹ |
| S _{va-} | 8.42E-5 | 8.42E-5 | 8.42E-5 | 8.65E-5 | 8.65E-5 | 8.65E-5 | 8.67E-5 | 8.66E-5 | 8.66E-5 | 8.79E-5 | 8.69E-5 | 8.69E-5 | 9.02E-5 | 8.98E-5 | 8.98E-5 | mol.L ⁻¹ |
| S _{H2CO3*} | 0.00947 | 0.00945 | 0.00945 | 0.00762 | 0.00756 | 0.00757 | 0.00553 | 0.00538 | 0.00539 | 0.00373 | 0.00302 | 0.00304 | 0.00146 | 0.00112 | 0.00113 | mol.L ⁻¹ |
| S _{H-ac} | 4.55E-6 | 3.37E-6 | 3.37E-6 | 4.33E-6 | 2.51E-6 | 2.49E-6 | 7.36E-6 | 2.44E-6 | 2.40E-6 | 5.77E-5 | 7.43E-6 | 6.59E-6 | 1.80E-4 | 8.55E-5 | 8.18E-5 | mol.L ⁻¹ |
| S _{H-bu} | 3.66E-7 | 3.62E-7 | 3.62E-7 | 1.93E-7 | 1.89E-7 | 1.90E-7 | 1.05E-7 | 9.85E-8 | 1.00E-7 | 8.08E-8 | 4.72E-8 | 4.82E-8 | 8.92E-8 | 4.66E-8 | 4.66E-8 | mol.L ⁻¹ |
| S _{HCO3-} | 0.0858 | 0.0867 | 0.0867 | 0.1344 | 0.1363 | 0.1354 | 0.1800 | 0.1861 | 0.1835 | 0.1590 | 0.2187 | 0.2154 | 0.0578 | 0.0842 | 0.0849 | mol.L ⁻¹ |
| S _{H-pro} | 7.27E-7 | 7.19E-7 | 7.19E-7 | 3.84E-7 | 3.76E-7 | 3.79E-7 | 2.09E-7 | 1.96E-7 | 1.99E-7 | 1.61E-7 | 9.41E-8 | 9.61E-8 | 1.79E-7 | 9.35E-8 | 9.34E-8 | mol.L ⁻¹ |
| S _{H-va} | 3.75E-7 | 3.70E-7 | 3.70E-7 | 1.98E-7 | 1.94E-7 | 1.95E-7 | 1.07E-7 | 1.01E-7 | 1.03E-7 | 8.31E-8 | 4.85E-8 | 4.95E-8 | 9.22E-8 | 4.82E-8 | 4.81E-8 | mol.L ⁻¹ |
| S _{K-ac} | | | 1.23E-5 | | | 4.33E-5 | | | 3.61E-4 | | | 5.7E-3 | | | 1.23E-5 | mol.L ⁻¹ |
| S _{KCl} | | | 4.02E-5 | | | 8.24E-5 | | | 1.27E-4 | | | 1.6E-4 | | | 4.02E-5 | mol.L ⁻¹ |
| S _{KOH} | | | 1.82E-8 | | | 6.66E-8 | | | 2.02E-7 | | | 2.6E-7 | | | 1.82E-8 | mol.L ⁻¹ |
| S _{Na-ac} | 5.45E-5 | 1.85E-5 | 1.77E-5 | 3.40E-4 | 6.66E-5 | 6.15E-5 | 4.89E-3 | 6.16E-4 | 5.06E-4 | 1.64E-2 | 8.67E-3 | 8.1E-3 | 5.45E-5 | 1.85E-5 | 1.77E-5 | mol.L ⁻¹ |
| S _{NaCl} | | | 3.68E-5 | | | 7.46E-5 | | | 1.14E-4 | | | 1.5E-4 | | | 3.68E-5 | mol.L ⁻¹ |
| S _{NaCO3-} | | | 5.31E-5 | | | 2.60E-4 | | | 9.12E-4 | | | 4.7E-4 | | | 5.31E-5 | mol.L ⁻¹ |
| S _{NaHCO3} | | | 8.57E-4 | | | 2.21E-3 | | | 3.72E-3 | | | 1.8E-3 | | | 8.57E-4 | mol.L ⁻¹ |
| S _{NaOH} | | | 1.34E-8 | | | 4.85E-8 | | | 1.45E-7 | | | 1.9E-7 | | | 1.34E-8 | mol.L ⁻¹ |
| S _{NH3} | 0.0032 | 0.0019 | 0.0019 | 0.0057 | 0.0034 | 0.0034 | 0.0075 | 0.0067 | 0.0066 | 0.0075 | 0.0076 | 0.0076 | 0.0032 | 0.0019 | 0.0019 | mol.L ⁻¹ |
| <i>l</i> | - | 0.09 | 0.09 | - | 0.14 | 0.14 | - | 0.20 | 0.20 | 0 | 0.25 | 0.25 | 0 | 0.30 | 0.29 | mol.L ⁻¹ |
| <i>γ</i> | 1 | 0.78 | 0.78 | 1 | 0.76 | 0.76 | 1 | 0.74 | 0.74 | 1 | 0.73 | 0.74 | 1 | 0.73 | 0.73 | - |

Table 3. H₂, CO₂ and CH₄ production values (gas phase) with the different speciation/pH model implementations

| | Sc ₁ | | | Sc ₂ | | | Sc ₃ | | | Sc ₄ | | | Sc ₅ | | | Units |
|-------------------------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|----------------------|
| | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | A ₁ | A ₂ | A ₃ | |
| Ga _{S_{H2}} | 0.0036 | 0.0036 | 0.0036 | 0.0034 | 0.0034 | 0.0034 | 0.0031 | 0.0031 | 0.0031 | 0.0024 | 0.0027 | 0.0027 | 0.0013 | 0.0015 | 0.0015 | kg.day ⁻¹ |
| Ga _{S_{CO2}} | 1525.7 | 1522.7 | 1522.7 | 1114.9 | 1106.9 | 1107.2 | 724.4 | 709.2 | 710.5 | 374.5 | 348.8 | 352.5 | 74.7 | 68.1 | 69.6 | kg.day ⁻¹ |
| Ga _{S_{CH4}} | 1058.3 | 1059.1 | 1059.1 | 1053.9 | 1056.5 | 1056.5 | 1039.3 | 1052.9 | 1053.0 | 842.3 | 1001.1 | 1007.0 | 434.7 | 509.7 | 517.9 | kg.day ⁻¹ |

3.2. WATER/SLUDGE LINE INTERACTIONS

In the reference case of Sc_1 , the simulation results show that differences in EQI and OCI within A_1 , A_2 and A_3 are minimal ($< 1\%$) (See **Figure 1**). The differences only become very pronounced at the higher ionic strength (I) of Sc_4 & Sc_5 where strong inhibition by free ammonia decreases the overall performance of the anaerobic digestion process (18% in EQI and 7% in OCI depending on whether one is using scenario A_1 or A_3). As a result, problems in the sludge line have an impact on the water line, which is then reflected in the EQI and OCI values. The result is much higher EQI and OCI values at Sc_5 as compared with Sc_1 , Sc_2 and Sc_3 (**Figure 1**). Interestingly, the effect of ammonia inhibition on EQI may be unrealistically high for A_1 at Sc_4 , when considering that the more comprehensive model approaches of A_2 and A_3 do not show the same influence on EQI at Sc_4 . Lastly, the differences between the EQI and OCI values of A_2 and A_3 is not pronounced, indicating that the influence of ion pairing is less important.

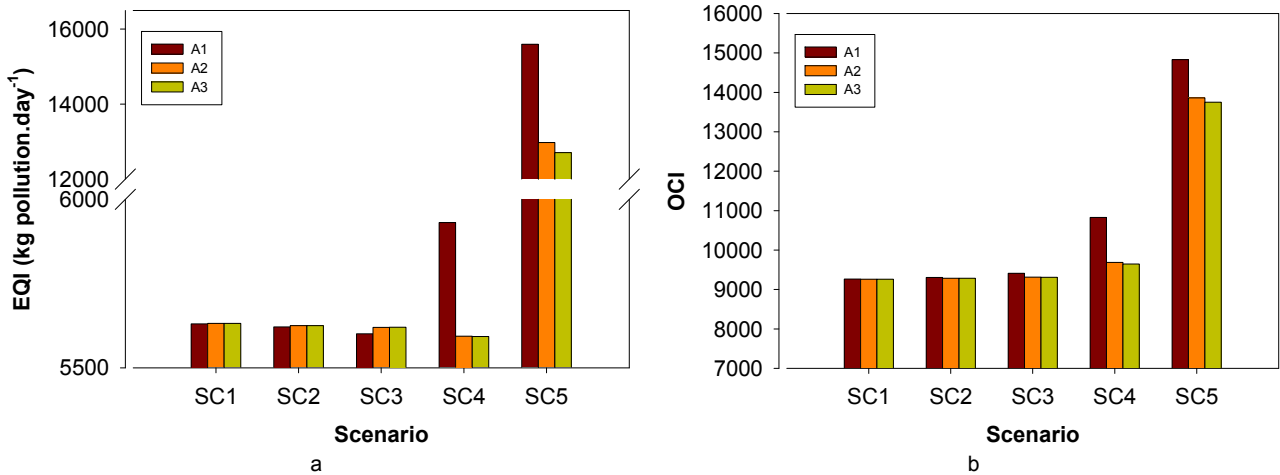


Figure 1. EQI (a) and OCI (b) variations in BSM2 using three different physico-chemical frameworks (A_1 , A_2 & A_3) and five different cationic loads (Sc_1 , Sc_2 , Sc_3 , Sc_4 & Sc_5).

The higher OCI values at Sc_5 is caused by reduced energy recovery from the AD system due to the substantial reduction in the biogas production (see the dynamic profiles of the normalized total biogas flow for the AD process in **Figure 2a, b**), especially Gas_{CH_4} (**Table 3** shows a reduction by up to 50%). Poor digester performance also affects the quantity/quality of the digester supernatant with a higher COD load returned from the sludge to the water line. This increased COD overloads the AS system and consequently results in a higher EQI for Sc_4 than for Sc_5 (See **Figure 1**).

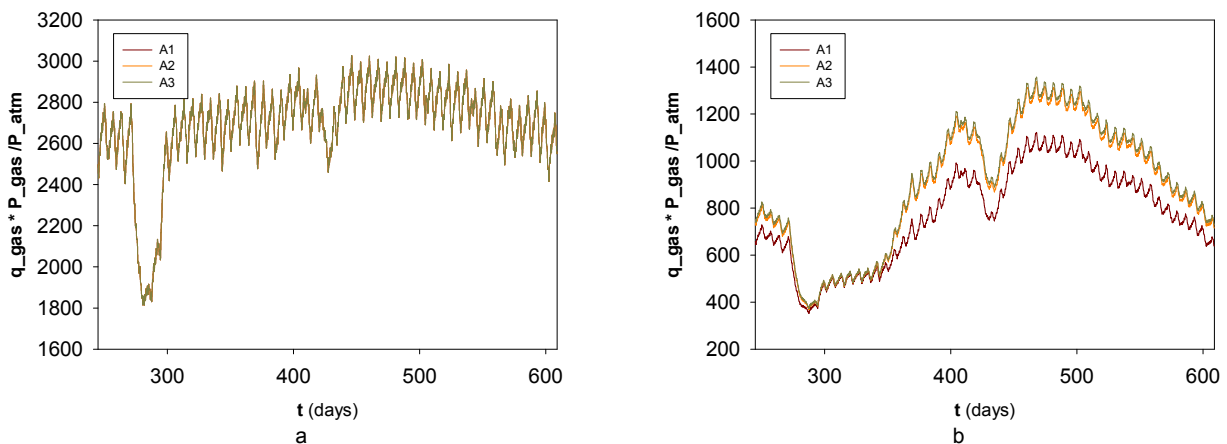


Figure 2. Dynamic profiles of the total biogas production in BSM2 using three different physico-chemical frameworks (A_1 , A_2 & A_3) and two different cationic loads (Sc_1) (a) and (Sc_5) (b).

DISCUSSION

The work that is presented above with an ADM1/BSM2 implementation highlights that simulation of dilute water systems such as drinking water, weak industrial wastewater and domestic wastewater (low ionic strengths, I) would likely not require activity style or ion-pairing corrections. This is seen by comparing the results for approaches A_1 (no corrections) with A_2 and A_3 (corrections applied) for cationic loads up to S_{C3} ($I < 0.2 \text{ mol.L}^{-1}$), showing that the plant performance indices (**Figure 1**) and overall biogas production (**Figure 2, Table 3**) are significantly similar without (A_1) and with corrections (A_2 and A_3). In contrast, the results above suggest that at $I > 0.2 \text{ mol.L}^{-1}$, such as with high solids digesters or manure digestion, proper activity (A_2) corrections would be required to ensure that the effects of increased salinity are correctly propagated throughout a plant-wide model such as BSM2. This is clearly seen in **Figure 1** at cation load S_{C4} , where A_1 (no corrections) predicts a substantial effect of cation load (added strong alkali) on plant performance indices, whereas both A_2 and A_3 (with corrections) buffered the increase in pH and the resulting increase in ammonia inhibition and consequently the propagation of poor digester performance through to overall plant performance indices (EQI and OCI). This is significant because, while local pH predictions (in an isolated model of an anaerobic digester) may be less sensitive to activity corrections (**Nielsen et al., 2008, Tait et al., 2012**), the present study shows that salinity effects at $I > 0.2 \text{ mol.L}^{-1}$ may not correctly propagate through a plant-wide model such as BSM2 without activity corrections. In such cases the inclusion of activity corrections is considered fully justified.

Also significant, the results of the present study suggest that ion pairing corrections are less important for BSM2, at least without precipitation. This is seen from the near identical results (**Table 2, Table 3, Figure 1 and Figure 2**) without ion pairing (A_2) and with ion pairing (A_3) across the entire cationic load range tested in the present study ($I = 0.09\text{-}0.3 \text{ mol.L}^{-1}$). In this regard, it is noted that predominantly monovalent ions are considered in the present study (the only exception is carbonate, which is low in concentration at the present pH range). It is important to note that ion pairing with divalent and trivalent ions heavily influence precipitation reactions. This is mainly due to the fact that the exponents in the activity coefficient corrections include the valence (see **Eq. 1**), so activity coefficients are much less than 1 for a higher valency (correction is stronger). This is important because, while pH is strongly influenced by the dominant weak acid-base species (bicarbonate), the thermodynamic driving force for precipitation reactions depends on the concentrations of the participating ions, which is often the less dominant form (such as carbonate in the case of calcium carbonate precipitation). This has previously led to the conclusion that ion pairing effects contribute as much as 50% of the overall effects of salinity on precipitation in high-strength wastewaters (**Tait et al., 2009**). For this reason, stronger differences should be expected when adding ionic strength/activity corrections on bivalent (S_{Ca+2} , S_{Mg+2}) or trivalent (S_{PO4-3}) ions for the purposes of modelling of precipitation. Nevertheless, in the modelling exercise presented in this contribution, it was preferred not to include such compounds because it would in that case have been necessary to (mathematically) properly model precipitation processes as well (**Musvoto et al., 2000; van Rensburg et al., 2003, Kazadi Mbamba et al., 2014**). This additional model complexity was considered not justified by the purpose of the baseline BSM2/ADM1 without precipitation. Further, consideration of metal ions and phosphate species without accounting for precipitation, amongst other factors, would result in a model that would probably estimate pH incorrectly (**Batstone et al., 2002**). In summary, in this specific case study, the effect of ion pairing was quite low and it is therefore proposed that baseline implementations of BSM2/ADM1 only include activity corrections and not ion pairing, unless precipitation reactions are under study.

As already noted, both activity and ion pairing corrections are of paramount importance when modelling minerals precipitation. Current research investigates upgrading the BSM2/ADM1 with phosphorus ($S_{H2PO4}/S_{HPO4-2}/S_{PO4-3}$) and sulphur (S_{SO4-2}/S_{H2S}) together with multiple metals (S_{Ca} , S_{Mg} , S_{Fe} and S_{Al}) and precipitation products (struvite, k-struvite, iron sulphide, calcium phosphate, calcium carbonate, magnesium carbonate, etc.). It is believed that the same framework as presented in Section 2 (with additional compounds and species and expanded biokinetics) can be used in such cases to correctly describe the behaviour of these new model add-ons.

5. CONCLUSIONS

The following is concluded from the findings reported in this manuscript:

1. Activity-style corrections influence the way that anaerobic digestion salinity/pH effects propagate throughout a plant-wide model such as BSM2, with a greater influence at higher ionic strength. These corrections significantly influence aqueous-phase species distribution, resulting pH predictions and consequently the overall process performance (water/sludge line). Accordingly it is recommended that activity-style corrections be applied with BSM2/ADM1 when ionic strengths (I) exceed 0.2 mol.L^{-1} (such as with manure and high-solids digestion)
2. Ion pairing effects on model performance are much less evident. This is attributed to 1) consideration of predominantly monovalent ions, and 2) relatively low level of complexity in the description of the aqueous phase as compared to studies of minerals precipitation. Accordingly, it is suggested that ion-pairing effects can be excluded from the baseline implementation BSM2/ADM1 without precipitation. Higher effects are expected with more ion rich systems and where (multiple) precipitation reactions are considered and this is an area of future work.
3. The (bio)chemical processes should be mathematically described as a combination of ODEs and DAEs in the baseline implementation BSM2/ADM1. Special solvers based on a multi-dimensional Newton-Raphson method are necessary to handle the algebraic interdependencies of such systems.

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