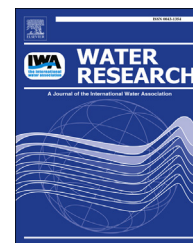


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Effects of ionic strength and ion pairing on (plant-wide) modelling of anaerobic digestion

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ABSTRACT

Plant-wide models of wastewater treatment (such as the Benchmark Simulation Model No. 2 or BSM2) are gaining popularity for use in holistic virtual studies of treatment plant control and operations. The objective of this study is to show the influence of ionic strength (as activity corrections) and ion pairing on modelling of anaerobic digestion processes in such plant-wide models of wastewater treatment. Using the BSM2 as a case study with a number of model variants and cationic load scenarios, this paper presents the effects of an improved physico-chemical description on model predictions and overall plant performance indicators, namely effluent quality index (EQI) and operational cost index (OCI). 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. A speciation sub-routine based on a multi-dimensional Newton–Raphson (NR) iteration method is developed to address algebraic interdependencies. The model also includes ion pairs that play an important role in wastewater treatment. The paper describes: 1) how the anaerobic digester performance is affected by physico-chemical corrections; 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. Results at high ionic strength demonstrate that corrections to account for non-ideal conditions lead to significant differences in predicted process performance (up to 18% for effluent quality and 7% for operational cost) but that for pH prediction, activity corrections are more important than ion pairing effects. Both are likely to be required when precipitation is to be modelled.

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| Nomenclature | | | |
|-----------------|---|------------------|--|
| γ | activity coefficient | S_{an} | anions concentration (mol L ⁻¹) |
| ΔH^0 | enthalpy change of the reaction | S_{bu} | butyrate concentration (kmol COD m ⁻³) |
| A_1, A_2, A_3 | physico–chemical framework 1, 2 and 3 | $S_{Ca^{+}}$ | calcium concentration (mol L ⁻¹) |
| AD | anaerobic digestion | S_{cat} | cations concentration (mol L ⁻¹) |
| ADM1 | Anaerobic Digestion Model No. 1 | S_{Ci} | ith scenario |
| a_i or a_j | activity of the species (i) or component (j) | S_{Cl} | Chloride concentration (mol L ⁻¹) |
| BSM2 | Benchmark Simulation Model No. 2 | $S_{CO_3^{2-}}$ | carbonate concentration (mol L ⁻¹) |
| COD | chemical oxygen demand | S_{Fe} | iron concentration (mol L ⁻¹) |
| CSTR | continuous stirred tank reactor | $S_{H^{+}}$ | proton concentration (mol L ⁻¹) |
| DAE | differential algebraic equation | $S_{H_2CO_3}$ | carbonic acid concentration (mol L ⁻¹) |
| EQI | effluent quality index (kg pollution day ⁻¹) | $S_{H_2PO_4^-}$ | dihydrogen phosphate concentration (mol L ⁻¹) |
| Gas_{CH_4} | methane gas production (kg day ⁻¹) | S_{H_2S} | hydrogen sulfide concentration (mol L ⁻¹) |
| Gas_{CO_2} | carbon dioxide gas production (kg day ⁻¹) | $S_{HCO_3^-}$ | bicarbonate concentration (mol L ⁻¹) |
| Gas_{H_2} | hydrogen gas production (kg day ⁻¹) | $S_{HPO_4^{2-}}$ | hydrogen phosphate concentration (mol L ⁻¹) |
| GISCOD | general integrated solid waste co-digestion | S_i | species concentration (mol L ⁻¹) |
| $G(Z_i)$ | vector containing the values of the set of implicit algebraic equations ($g(z_1, \dots, z_n), \dots, g(z_1, \dots, z_n)$) | S_{IC} | inorganic carbon (kmol m ⁻³) |
| I | ionic strength (mol L ⁻¹) | S_{IN} | inorganic nitrogen (kmol m ⁻³) |
| IWA | International Water Association | S_j | component concentration (mol L ⁻¹) |
| J_f | analytical Jacobian of first order partial derivatives $\delta(G_1, \dots, G_m)/\delta(z_1, \dots, z_n)$ | S_K | potassium concentration (mol L ⁻¹) |
| K_i | equilibrium constant | $S_{Mg^{+}}$ | magnesium concentration (mol L ⁻¹) |
| N | nitrogen | S_{Na} | sodium concentration (mol L ⁻¹) |
| N_C | number of components | S_{NH_3} | ammonia concentration (mol L ⁻¹) |
| NR | Newton–Raphson | $S_{NH_4^{+}}$ | ammonium concentration (mol L ⁻¹) |
| N_{sp} | number of species | $S_{PO_4^{3-}}$ | phosphate concentration (mol L ⁻¹) |
| OCI | operational cost index | S_{pro} | propionate concentration (kmol COD m ⁻³) |
| PCM | physico–chemical model | $S_{SO_4^{2-}}$ | sulphate concentration (mol L ⁻¹) |
| ODE | ordinary differential equation | S_{va} | valerate concentration (kmol COD m ⁻³) |
| R | universal gas constant (bar L mol ⁻¹ K ⁻¹) | T | temperature (K) |
| S_{ac} | acetate concentration (kmol COD m ⁻³) | UASB | upflow anaerobic sludge blanket |
| S_{Al} | aluminium concentration (mol L ⁻¹) | WWTP | wastewater treatment plant |
| | | z_i | of ion i |
| | | Z_i | vector of equilibrium states ($z_{1,i}, \dots, z_{n,i}$) |

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 International Water Association (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 (Batstone et al., 2006). The adoption of the ADM1 in popular systems analysis tools, such as the plant-wide benchmark simulation model for wastewater treatment plants (BSM2), and its use as a virtual industrial system can stimulate modelling of anaerobic processes by researchers and practitioners outside the core expertise of anaerobic processes (Jeppsson et al., 2013).

Anaerobic digestion models are still being extended to include: i) improved biodegradability predictions (Astals et al., 2013); ii) inhibition factors (Wilson et al., 2012; Zonta et al., 2013); and, iii) microbial diversity (Ramirez et al., 2009). The ADM1 has been successfully implemented into multiple tank configurations: continuous stirred tank reactors (CSTRs) (Rosen et al., 2006), upflow anaerobic sludge blanket (UASB) reactors (Batstone et al., 2005; Hinken et al., 2014) and biofilm reactors described by 1D (Batstone et al., 2004) and 2D/3D models (Picioreanu et al., 2005). Important aspects about modelling frameworks and methodologies for parameter estimation and model validation in the field of anaerobic digestion processes can be found in Donoso-Bravo et al. (2011). In addition to municipal wastewater treatment, other applications of the ADM1 have been hydrogen production (Penumathsa et al., 2008), blue-algae digestion (Yuan et al., 2014) or co-digestion processes using the general integrated solid waste co-digestion (GISCOD) model interface (Zaher et al., 2009). Along this line of thinking, the ADM1 could potentially be applied to the treatment of industrial waste, animal manure, landfill leachate and brine from reverse

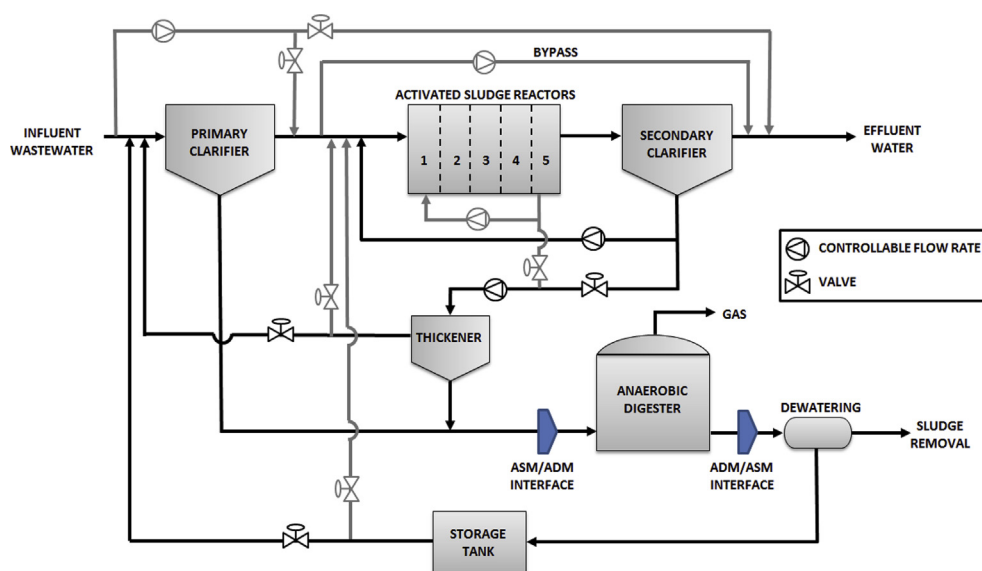


Fig. 1 – Schematic representation of the BSM2 plant (Gernaey et al., 2014).

osmosis (Batstone and Keller, 2003). Since the latter waste streams, in general, contain substantially higher salinity than domestic wastewater (ionic strengths of various waste streams can be found in Batstone et al. (2012)), it is expected that there will be significant physico-chemical effects, which may need to be accounted for in a model. 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 to account for non-ideal physico-chemical behaviour that occurs in such wastes (Batstone et al., 2012; Tait et al., 2012). The IWA Task Group on Generalized Physico-chemical Framework is developing a structure to better understand and represent these non-ideal behaviours in the frame of wastewater treatment modelling. By gathering complex knowledge from different disciplines and combining this in a general framework, a guideline on how to approach modelling of physico-chemical processes will be developed. The work presented here fits within the scope of work of this task group, and as such, the authors propose an extension of the ADM1 (BSM2 implementation) to include: i) ionic strength correction via the Davies equation; ii) ion pairing of inorganic carbon, inorganic nitrogen and volatile fatty acids with different cations (K^+ , Na^+) and anions (Cl^-); and, iii) a new solving routine that accounts for the increased number of implicit algebraic variables without the use of an implicit differential algebraic equation (DAE) solver.

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). The paper describes: i) how the anaerobic digester performance is affected; ii) the effect on pH and the anaerobic digestion products (CO_2 , CH_4 and H_2); and, iii) how these variations are propagated from the sludge treatment to the water line.

The paper details the development of the new physico-chemical framework, the connection between the bio-kinetic and physico-chemical models, how numerical/stiffness

issues have been handled and finally the differences in the predicted effluent quality (EQI) and operational cost (OCI) indices. The authors illustrate the performance of this new approach with a number of case studies. These case studies investigate the overall WWTP performance for different physico-chemical model (PCM) frameworks and cationic loads.

The main novelty of this paper relies on developing a new ADM1: i) with a physico-chemical framework implementation to describe non-ideal behaviour; ii) taking into account the interactions between biotic and non-biotic processes when mathematically describing the usefulness of control/operational strategies; and, finally iii) by integrating all the different models (physico-chemical/biochemical) in one single software.

This paper contributes to the field of wastewater engineering by filling some of the gaps which previous studies did not handle. For example model compatibility, simulation input–output transferability, ionic strength and ion pairing assessment, and WWTP and control strategy/operational procedure performance assessment. Once these models are codified, the developed platform will be an excellent tool to further analyse/evaluate the behaviour of additional compounds (phosphorus, sulphur, etc.) and for developing different chemical/recovery processes (precipitation). Indeed, the correct description of the precipitation processes in wastewater treatment system requires the consideration of non-ideal conditions (Musvoto et al., 2000; van Rensburg et al., 2003; Barat et al., 2011; Kazadi Mbamba et al., 2014).

2. Methods

2.1. Wastewater treatment plant (WWTP) under study

The WWTP under study is the IWA BSM2 platform proposed by Gernaey et al. (2014) (Fig. 1). The plant is treating an influent

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

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

flow of 20 648 m³ day^{–1} and a total COD and N load of 12 240 and 1140 kg day^{–1}, respectively, following the principles outlined in Gernaey et al. (2011). The activated sludge unit is a modified Ludzack–Ettinger configuration consisting of 5 tanks in series. Tanks 1 and 2 are anoxic, while tanks 3, 4 and 5 are aerobic. Tanks 1 and 5 are linked by means of an internal recycle. The ASM1 is chosen as the biological process model (Henze et al., 2000) and the double exponential settling velocity function of Takács et al. (1991) as a fair representation of the secondary settling process described by a one-dimensional model divided into ten layers. The BSM2 plant further contains a primary clarifier, a sludge thickener, an anaerobic digester, a storage tank and a dewatering unit. The ADM1 (Batstone et al., 2002) is the dynamic model implemented in this platform to describe the anaerobic digestion (AD) process. Detailed information about the plant design, operational conditions and process models of the BSM2 is reported by Gernaey et al. (2014).

2.2. Improved physico–chemical framework of the anaerobic digester

The composition of the digester aqueous phase is represented as a set of chemical entities called species S_i (mol L^{–1}) and components S_j (mol L^{–1}). As applied here, components (S_j) are selected as the fully dissociated form of the species (S_i). For example, the fully dissociated form of inorganic carbon $S_{CO_3^{2-}}$ was selected as a component (S_j), while the partially dissociated $S_{HCO_3^-}$ and undissociated $S_{H_2CO_3}$ forms of inorganic carbon were species (S_i) in the model. Table 1 summarizes all the considered species (rows) and how each of the species can be

represented by a linear molar balance combination of the model components (columns). More details will be provided 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. These interaction effects are commonly corrected for in a model (Stumm and Morgan, 1996) by multiplying each concentration (S_i or S_j) with an activity coefficient (γ), the product being called the chemical activity (a_i or a_j) as shown in Eq. (1):

$$a_i = \gamma_i S_i \quad (1)$$

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):

$$I = \frac{1}{2} \sum_{i=1} S_i z_i^2 \quad (2)$$

where z_i is the valence of ion i . There are several correlations available that 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 shown in Eq. (3):

$$\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (3)$$

where A is a temperature-dependent parameter and γ_i is calculated as common activity coefficient values for monovalent, divalent and trivalent ions, respectively. The Davies approximation, which is mostly used in geochemical models, is said to be valid for ionic strengths up to 0.5 mol L^{-1} (Stumm and Morgan, 1996).

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

The aqueous phase reactions (weak acid-base reactions and ion pairing) are mathematically formulated by a set of non-linear algebraic equations (Stumm and Morgan, 1996; Morel and Hering, 1993) including one law of mass-action for each species (i) (Eq. (4)) and 1 M 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 (Eq. (4)) with the species (i) written as the product of components (j) and the equilibrium coefficient (K_i), where v_{ij} is the stoichiometric coefficient for each respective aqueous phase reaction. This rearrangement allows substitution of the mass action laws into the molar contribution balances to eliminate the species from the equation set, which then has to be solved iteratively for the component concentrations. To illustrate, in the present study the number of species (N_{sp}) is 24, but by substitution, is reduced to 9 components to be solved implicitly (N_c).

$$a_i = K_i \prod_{j=1}^{N_c} a_j^{v_{ij}} \quad i = 1, 2, \dots, N_{sp} \quad (4)$$

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

The effect of temperature on K_i is corrected for by the constant-enthalpy form of the van't Hoff equation (Stumm and Morgan, 1996). In Eq. (6), K_1 and K_2 are the equilibrium constants at temperatures T_1 and T_2 (in K), respectively, ΔH° is the enthalpy change of the reaction and R is the universal gas constant.

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

Full specification of the algebraic equation set requires an additional equation, which can be resolved by the charge balance (Batstone et al., 2002), as shown in Eq. (7):

$$\sum S_{cat} - \sum S_{an} = 0 \quad (7)$$

where S_{cat} and S_{an} represent the total equivalent concentrations of cations and anions, respectively, which are the concentrations of respective ions multiplied by their valence. An alternative is the use of the proton balance (Morel and Hering, 1993), which generates the same equation set, but with a different structure.

2.2.3. Implementation details, numerical issues and model verification

The ADM1 implementation in the BSM2 framework is a very stiff system with some of the states reacting quickly (weak

acid-base chemistry) while other states are reacting sluggishly (different biological uptake processes). Implicit numerical solvers are especially suitable to handle this type of system, and can inherently solve DAE problems such as this, but cannot be used for the BSM2 because they are intolerant to highly dynamic inputs, controller numerical characteristics, noise and step changes used in the modelling of process control scenarios. In the past, this has been resolved by solving pH and the S_{H_2} state through independent algebraic equations (Rosen et al., 2006) with the use of a forward Runge–Kutta solver for the remaining ordinary differential equations (ODEs). This approach is not applicable due to algebraic interdependencies, and was extended to a full gradient search method as follows (Eq. (8)):

$$Z_{i+1} = Z_i - J_F(Z_i)^{-1} G(Z_i) \quad (8)$$

where Z_i is the vector of equilibrium variables ($z_{1,i}, \dots, z_{n,i}$) obtained from the previous iteration step i , $G(Z_i)$ is a vector containing the values of the set of implicit algebraic equations ($g_1(z_1, \dots, z_n), \dots, g_n(z_1, \dots, z_n) = [0]$). The iteration is converged to a tolerance of $g_{max} < 10^{-12}$. The full analytical Jacobian (gradient) (J_F) was required for this approach, which requires symbolic manipulation of the algebraic equations in order to obtain the matrix of all first-order partial derivatives $\partial(G_1, \dots, G_m)/\partial(z_1, \dots, z_n)$ and the matrix inverted using the decomposition method in LinPack. The MINTEQA2 geochemical program (Allison et al., 1991) was used to verify the approach.

A global sensitivity analysis was not included in this study but could be considered in future work. Parameters related to ion pairing behaviour are found to have well-established values from literature eliminating the need for a sensitivity analysis in this regard. On the other hand, variations in ion activity-related parameters' values could have a significant effect on numerous model outputs thus, performing a global sensitivity analysis would be interesting to see the highly sensitive parameters, as well as their contributions to variations in the model outputs.

2.3. Variants and model test cases

The performance of the improved ADM1 model was tested with three model variants:

1. A base case (A_1) using the default ADM1 (Rosen et al., 2006) with kinetic and stoichiometric parameters at 35°C from Germaey et al. (2014).
2. A variant (A_2) with an ionic strength correction: iterative ionic strength and activity corrections for inorganic carbon (S_{IC}), inorganic nitrogen (S_{IN}), acetate (S_{ac^-}), propionate (S_{pro^-}), valerate (S_{va^-}), butyrate (S_{bu^-}) and free reactive protons (S_{H^+}).
3. A variant (A_3) with ionic strength correction and ion pairing: the ion activity corrections of A_2 and in addition, S_{cat} replaced by sodium (S_{Na^+}) and potassium (S_{K^+}) and S_{an} replaced by chloride (S_{Cl^-}). These monovalent ions are permitted to form soluble ion pairs (see Table 1) modelled with Eq. (4) and Eq. (5). The methanogenesis step during anaerobic digestion could be inhibited by the presence of sodium ions, and it could be expected that this inhibition

Table 2 – Average ADM1 state values with the different physico-chemical framework implementations (using BSM2 influent data).

| | S_{C_1} | | | S_{C_2} | | | S_{C_3} | | | S_{C_4} | | | S_{C_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 | 9.95E-8 | 9.96E-8 | 3.16E-8 | 5.40E-8 | 5.43E-8 | 1.71E-8 | 2.92E-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 |
| $S_{NH_4^+}$ | 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 | 0.0768 | 0.0168 | 0.0146 | 0.2216 | 0.2009 | 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 |
| $S_{CO_3^{2-}}$ | 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 | 0.00121 | 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^-} | 5.90E-5 | 5.90E-5 | 5.90E-5 | 6.05E-5 | 6.05E-5 | 6.05E-5 | 6.06E-5 | 6.06E-5 | 6.06E-5 | 6.14E-5 | 6.07E-5 | 6.07E-5 | 6.28E-5 | 6.26E-5 | 6.26E-5 | mol L ⁻¹ |
| $S_{H_2CO_3}$ | 0.00947 | 0.00945 | 0.00945 | 0.00762 | 0.00757 | 0.00757 | 0.00553 | 0.00538 | 0.00539 | 0.00373 | 0.00302 | 0.00304 | 0.00146 | 0.00112 | 0.00112 | mol L ⁻¹ |
| S_{H-ac} | 4.55E-6 | 3.37E-6 | 3.37E-6 | 4.33E-6 | 2.51E-6 | 2.50E-6 | 7.36E-6 | 2.44E-6 | 2.40E-6 | 5.78E-5 | 7.45E-6 | 6.60E-6 | 1.80E-4 | 8.56E-5 | 8.19E-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 |
| $S_{HCO_3^-}$ | 0.0858 | 0.0867 | 0.0867 | 0.1344 | 0.1363 | 0.1354 | 0.1800 | 0.1861 | 0.1835 | 0.1590 | 0.2187 | 0.2154 | 0.0577 | 0.0840 | 0.0847 | mol L ⁻¹ |
| S_{H-pro} | 7.27E-7 | 7.18E-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 | 9.60E-8 | 1.79E-7 | 9.35E-8 | 9.34E-8 | mol L ⁻¹ |
| S_{H-va} | 2.63E-7 | 2.60E-7 | 2.60E-7 | 1.38E-7 | 1.35E-7 | 1.36E-7 | 7.51E-8 | 7.07E-8 | 7.17E-8 | 5.81E-8 | 3.39E-8 | 3.46E-8 | 6.43E-8 | 3.36E-8 | 3.35E-8 | mol L ⁻¹ |
| S_{K-ac} | | | | | | 1.23E-5 | | | 4.33E-5 | | | 3.61E-4 | | | 5.8E-3 | mol L ⁻¹ |
| S_{KCl} | | | | | | 4.02E-5 | | | 8.24E-5 | | | 1.27E-4 | | | 1.6E-4 | mol L ⁻¹ |
| S_{KOH} | | | | | | 1.82E-8 | | | 6.66E-8 | | | 2.02E-7 | | | 2.6E-7 | mol L ⁻¹ |
| S_{Na-ac} | | | | 5.46E-5 | 1.86E-5 | 1.77E-5 | 3.40E-4 | 6.66E-5 | 6.15E-5 | 4.89E-3 | 6.17E-4 | 5.07E-4 | 1.64E-2 | 8.68E-3 | 8.2E-3 | mol L ⁻¹ |
| S_{NaCl} | | | | | | 3.68E-5 | | | 7.46E-5 | | | 1.14E-4 | | | 1.5E-4 | mol L ⁻¹ |
| S_{NaCO_3} | | | | | | 5.31E-5 | | | 2.60E-4 | | | 9.13E-4 | | | 4.7E-4 | mol L ⁻¹ |
| S_{NaHCO_3} | | | | | | 8.57E-4 | | | 2.21E-3 | | | 3.72E-3 | | | 1.8E-3 | mol L ⁻¹ |
| S_{NaOH} | | | | | | 1.34E-8 | | | 4.85E-8 | | | 1.45E-7 | | | 1.9E-7 | mol L ⁻¹ |
| S_{NH_3} | 0.0017 | 0.0011 | 0.0011 | 0.0032 | 0.0019 | 0.0019 | 0.0057 | 0.0034 | 0.0034 | 0.0075 | 0.0068 | 0.0066 | 0.0075 | 0.0076 | 0.0076 | mol L ⁻¹ |
| 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 |
| γ | 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 | – |

will be influenced by ion activity and ion pairing. However, [Omil et al. \(1995\)](#) have shown that adapting the biomass to the high salinity levels could eliminate such inhibition and/or toxicity effects. It is assumed in this study that the biomass is adapted to high salinity levels and therefore, no sodium inhibition term was added to the ADM1 biokinetics.

Also, each of the model variants are tested for increases in ionic strength by adding another minor influent stream ($Q_{add} = 5 \text{ m}^3 \text{ day}^{-1}$) with different S_{cat} loads to progressively increase the ionic strength of the overall plant influent ($I = 0.09\text{--}0.3 \text{ mol L}^{-1}$). This leads to five test scenarios, S_{C1} , S_{C2} , S_{C3} , S_{C4} and S_{C5} , with additional S_{cat} loads of 0, 2, 4, 6 and 8 mol L^{-1} , respectively. In model variant A_3 , the added S_{cat} is distributed equally between S_{Na^+} and S_{K^+} . It is important to highlight that the added cations are unpaired with anions, so that a higher cation load also increases pH. This represents a scenario where a strong alkali is added (e.g. sodium hydroxide or a high alkalinity feed) to increase the alkalinity of the wastewater. All other model conditions, including influent flow rate, COD and N loads are kept identical for the three model approaches.

Simulation results are evaluated dynamically during the last 364 days of simulation in accordance with the BSM2 simulation principles, namely 200 days simulation to reach steady state followed by 609 days of 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 and discussion

3.1. Influence of physico–chemical corrections on ADM1 state variables

[Table 2](#) shows average values of the ADM1 state variables for the three model variants (A_1 , A_2 and A_3) and the five cationic load scenarios for increased ionic strengths (S_{C1} , S_{C2} , S_{C3} , S_{C4} and S_{C5}). At low ionic strengths (S_{C1}) the average ADM1 state values for A_1 , A_2 and A_3 seem to be similar ([Table 2](#)). However, activity corrections of A_2 and A_3 do influence the species distribution in the inorganic carbon system (S_{IC}), with deprotonated inorganic carbon ($S_{CO_3^{2-}}$, $S_{HCO_3^-}$) being up to 62% higher for A_2 and A_3 than for A_1 ([Table 2](#)). As a consequence, more reactive free protons (S_{H^+}) are required in A_2 and A_3 and are released to uphold the charge balance and thus the predicted pH is lower in A_2 and A_3 (pH 7.11) than in A_1 (pH 7.21). This release of protons is facilitated by the shift in inorganic species from protonated to deprotonated form. The lower pH in A_2 and A_3 results in a lower free ammonia (S_{NH_3}) concentration and this in turn reduces the level of free-ammonia-inhibition of acetoclastic methanogenesis ($K_{i,NH_3} = 0.0018 \text{ mol L}^{-1}$). Consequently, free-ammonia inhibition is more pronounced for A_1 as compared to A_2 and A_3 . A lower level of free-ammonia inhibition results in lower total acetic acid ($S_{H-ac} + S_{ac-}$) concentration, more acetate degraders (X_{ac}) and

Table 3 – H_2 , CO_2 and CH_4 production (gas phase) with the different physico–chemical framework implementations.

| | S_{C1} | | | S_{C2} | | | S_{C3} | | | S_{C4} | | | S_{C5} | | | 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 | |
| G_{asH_2} | 0.0036 | 0.0036 | 0.0036 | 0.0034 | 0.0034 | 0.0034 | 0.0031 | 0.0031 | 0.0031 | 0.0025 | 0.0027 | 0.0028 | 0.0013 | 0.0015 | 0.0015 | kg day^{-1} |
| G_{asCO_2} | 1526.6 | 1523.6 | 1523.6 | 1116.0 | 1107.8 | 1108.3 | 725.8 | 710.4 | 711.8 | 376.1 | 350.2 | 353.9 | 77.6 | 70.4 | 71.9 | kg day^{-1} |
| G_{asCH_4} | 1059.3 | 1060.0 | 1060.0 | 1054.9 | 1057.4 | 1057.4 | 1040.4 | 1053.8 | 1054.0 | 8434.0 | 1002.4 | 1008.3 | 442.0 | 518.7 | 527.1 | kg day^{-1} |

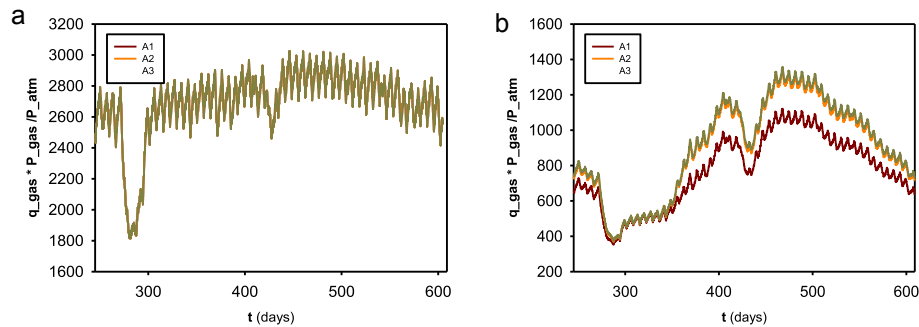


Fig. 2 – Dynamic profiles of the total biogas production in BSM2 using three different physico-chemical frameworks (A_1 , A_2 and A_3) and two different cationic loads (S_{C1}) (a) and (S_{C5}) (b).

higher acetate uptake (Table 2). These effects are depicted in the Graphical Abstract.

Increasing influent values of S_{Na^+} and/or S_{K^+} (Table 2, comparison between S_{C1} to S_{C5}) values result in a reduction of S_{H^+} values (neutralized in effect), and consequently pH increases. Ionic strength (I) increases in a correlated manner (not necessarily linearly) with the applied cationic load. Higher pH values increase S_{NH_3} which then increases inhibition of acetate degraders (X_{ac}), decreases acetate uptake and consequently influences the overall hydrogen (S_{H_2})/acetate (S_{ac^-}) (electron donors) consumption. Gas production (Gas_{CH_4} , Gas_{CO_2} , Gas_{H_2}) is then also reduced (Table 3). At the high ionic strengths of scenarios S_{C4} and S_{C5} , free-ammonia inhibition becomes very strong, leading to very notable accumulation of acetate (S_{ac^-}) in the digester (Table 2) and a substantial decrease in overall biogas production (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 in S_{cat} loads.

Importantly, the comparative results of A_1 and A_2 indicate the significance of ion activity corrections to account for the effects of increased salinity/pH. The results show that when cationic load is increased up to S_{C3} , digester pH is higher with case A_1 than with case A_2 . As noted above, these model differences are caused by the reactive free protons released through ion activity of inorganic carbon species in case A_2 ,

which counteracts the alkali effect of the added cationic load and buffers the overall increase in pH. The lower pH of case A_2 causes less ammonia inhibition than in case A_1 and therefore digester performance (biogas production) is better with case A_2 than with case A_1 (more on this below).

Theoretically, ion pairing would further shift the inorganic carbon species towards their deprotonated forms, causing the release of even more free reactive protons than in case A_2 . These free reactive protons would further buffer increases in pH with increasing cationic load with similar effects as noted above for ion activity. The comparative results of cases A_2 and A_3 show that the effect of ion pairing (A_3) is minor in both pH and species distributions (Table 2) and that the resulting pH and species distribution are very similar in both cases. These results thus indicate that ion pairing is less important to account for the effects of increased salinity/pH.

3.2. Water/sludge line interactions

In the reference scenario S_{C1} , the simulated values of EQI and OCI are very similar for cases A_1 , A_2 and A_3 (within 1%) (Fig. 4). Any differences between the results for cases A_1 , A_2 and A_3 only become pronounced at the higher ionic strengths of scenarios S_{C4} and S_{C5} . At these high ionic strengths, free ammonia inhibition substantially decreases the anaerobic digestion performance (see previous section) and consequently the overall process performance (18% in EQI and 7% in OCI depending on whether one is using scenario A_1 or A_3 as depicted in Fig. 4).

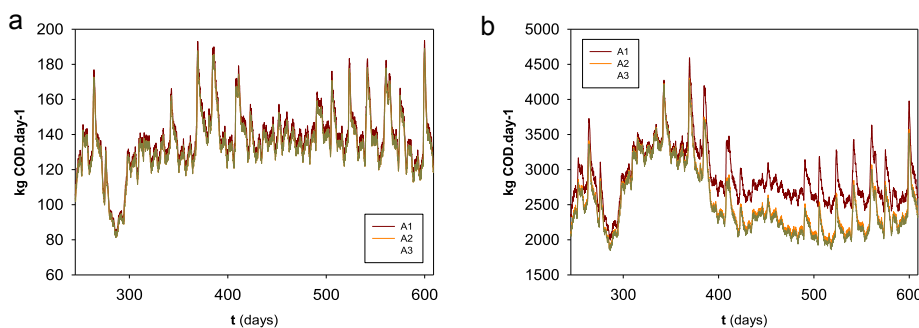


Fig. 3 – Dynamic profiles of the total COD loading returning to the water line in BSM2 using three different physico-chemical frameworks (A_1 , A_2 and A_3) and two different cationic loads (S_{C1}) (a) and (S_{C5}) (b).

This deterioration in simulated digester performance decreases biogas recovery and especially Gas_{CH_4} (Fig. 2, also Table 3 shows a reduction of up to 50%), which in turn increases the overall operational costs (OCI values), because less renewable energy is being recovered from biogas.

Poor digester performance also affects the quantity/quality of the digester supernatant with a higher COD load returned from the sludge line to the water line. Fig. 3 shows the dynamic profiles of the total organic load leaving the AD unit and returning to the water line ahead of the primary clarifier.

This additional COD load can overload the activated sludge process and influence effluent quality as reflected in EQI. The overall result of these effects is much higher EQI and OCI values for scenario SC_5 as compared with scenarios SC_1 , SC_2 and SC_3 (Fig. 4). Interestingly, the effect of ammonia inhibition on EQI may be unrealistically high for case A_1 and scenario SC_4 , when considering that the more comprehensive model approaches of cases A_2 and A_3 do not show the same influence on EQI for scenario SC_4 . Further, it is worth noting that the differences between the EQI and OCI values of A_2 and A_3 are not so pronounced (Fig. 4), indicating that the influence of ion pairing is less important. The implications are further discussed below.

3.3. Selection of appropriate physico–chemical framework

Overall, the results of the present study with ADM1 in BSM2 demonstrates that ion activity or ion-pairing corrections are not required when simulating anaerobic digestion of dilute wastewaters, such as weak industrial wastewater, in a plant-wide context. This is shown by the similar plant performance indices (Fig. 4) and overall biogas production for case A_1 (no corrections) and cases A_2 and A_3 (with corrections) up to cationic load SC_3 ($I < 0.2 \text{ mol L}^{-1}$) (Fig. 2, Table 3). In contrast, in scenarios SC_4 and SC_5 ($I > 0.2 \text{ mol L}^{-1}$, which are typical for high solids digestion and manure digestion), ion activity corrections are required to correctly propagate salinity and pH effects throughout the plant-wide model. This is seen from the results for cationic load SC_4 , where base case A_1 (no corrections) predicts a substantial effect on the plant performance indices (Fig. 4), which is not reflected in the results from the more comprehensive case A_2 (with ion activity corrections). This is significant because, while local pH predictions in an isolated model of anaerobic digestion may be

less sensitive to activity corrections (Nielsen et al., 2008; Tait et al., 2012), the present study results suggest that activity corrections are required for a plant-wide model such as BSM2 at $I > 0.2 \text{ mol L}^{-1}$. In such cases the inclusion of activity corrections is fully justified and even necessary.

In the present study, the Davies approximation to ionic activity is used because it is valid for the ionic strengths that are being tested. The Davies approach is also widely used in other industry-standard aqueous equilibrium models, predominantly because it is relatively simple to implement with single respective activity coefficients for mono, di- and tri-valent ions. In general with a model using the Davies approach, the equilibrium coefficients can be readily corrected directly by multiplying/dividing with activity coefficients as is relevant, and the iteration can calculate ion concentrations rather than activities. However, at higher ionic strengths of $I > 0.3 \text{ mol L}^{-1}$, activity coefficients of the Davies equation unexpectedly approaches unity with further increases in ionic strength (Tait et al., 2012). Accordingly, for $0.4 < I < 1 \text{ mol L}^{-1}$, the WATEQ Debye–Hückel approach (Parkhurst and Appelo, 1999) is recommended, for which activity coefficients continue to approach zero with increasing ionic strength (as expected) up to its validity limit of 1 mol L^{-1} .

The results of the present study with ADM1 in BSM2 suggest that ion pairing corrections are less important in the plant-wide context than ion activity corrections. This is seen from the near identical results (Table 2, Table 3, Figs. 2–4) for cases A_2 (without ion pairing) and A_3 (with ion pairing) for all the tested cationic load scenarios ($I = 0.09\text{--}0.3 \text{ mol L}^{-1}$). It is however necessary to note that predominantly monovalent ions are considered in case A_3 , whereas ion pairing with divalent and trivalent ions is known to be strong and influential in minerals precipitation (Tait et al., 2012). This is important because, while digester pH is strongly influenced by monovalent ions (such as bicarbonate), the thermodynamic driving force for minerals precipitation is determined by other participating ions, which commonly include divalent and trivalent ions. It has been suggested that ion activity and ion pairing contribute equally in high-strength wastewater, and can increase the effective saturation coefficient by an order of magnitude (Tait et al., 2009). When required for precipitation studies, an aqueous phase can be modelled with DAEs and precipitation reactions as ODEs with dedicated kinetic relationships (Batstone and Keller, 2003; Musvoto et al., 2000; van Rensburg et al., 2003; Kazadi Mbamba et al., 2014).

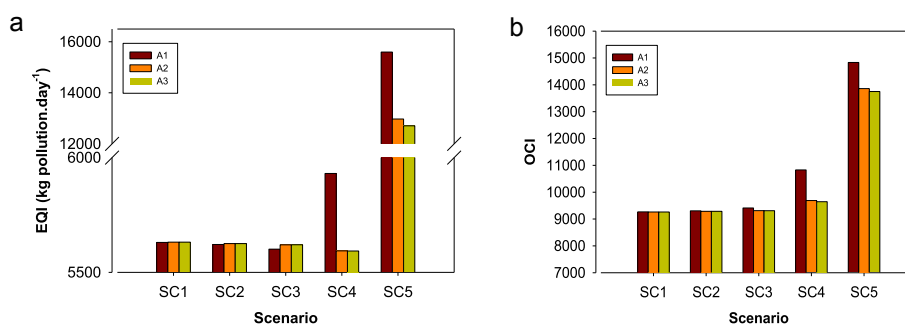


Fig. 4 – EQI (a) and OCI (b) variations in BSM2 using three different physico-chemical frameworks (A_1 , A_2 and A_3) and five different scenarios with increasing cationic loads (SC_1 , SC_2 , SC_3 , SC_4 and SC_5).

Current research investigates upgrading the ADM1 with phosphorus ($S_{H_2PO_4^-}/S_{HPO_4^{2-}}/S_{PO_4^{3-}}S_{PO_4^{3-}}$) and sulphur ($S_{SO_4^{2-}}/S_{H_2S}$) together with multiple metals ($S_{Ca^{2+}}$, $S_{Mg^{2+}}$, S_{Fe} and S_{Al}) and precipitation products (struvite, k-struvite, iron sulphide, calcium phosphate, calcium carbonate, magnesium carbonate). 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.

4. Conclusions

The findings of this study are:

- Ion activity corrections influence salinity/pH effects in a plant-wide model such as BSM2, showing a greater influence at higher ionic strengths (I). Accordingly, it is recommended that activity corrections be applied with ADM1 at $I > 0.2 \text{ mol L}^{-1}$ (manure and high-solids digestion).
- Monovalent ion pairing is much less influential and much less important than ion activity corrections. Thus, ion pairing effects can be excluded from ADM1 when minerals precipitation is not under study.
- The (bio)chemical processes in ADM1 should be described mathematically as a combination of ODEs and DAEs, and a multi-dimensional Newton–Raphson method should be used to handle algebraic interdependencies.

5. Supplementary material

The MATLAB/SIMULINK code containing the implementation of the physico-chemical modelling framework in ADM1 using BSM2 as a case study is available upon request to Prof. Ulf Jeppsson (ulf.jeppsson@iea.lth.se).

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