

Extension and application of the three-phase weak acid/base kinetic model to the aeration treatment of anaerobic digester liquors

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Abstract

The kinetic model for the carbonate (inorganic carbon) system in three phases and the phosphate, short chain fatty acid and ammonia mixed weak acid/base systems in single phase, based on modelling the kinetics of the forward and reverse dissociation processes of the weak acid/base species, is extended to model the three-phase mixed weak acid/base chemical reactions in anaerobic digester liquor aeration. The kinetic reactions for ion pairing, precipitation of struvite, newberyite, amorphous calcium phosphate, calcium and magnesium carbonate and stripping of NH_3 gas are added to the model. A preliminary validation of the model was done by comparing model predictions with an equilibrium based struvite precipitation model; and equilibrium experimental results from the literature on simultaneous precipitation of calcium and magnesium carbonate and phosphate minerals. To collect data to validate the non-steady state behaviour of the model, aeration batch tests were conducted on liquor from a spent wine upflow anaerobic sludge bed (UASB) digester and a sewage sludge (SS) anaerobic digester. In the batch tests pH, Ca, Mg, Total $\text{PO}_4\text{-P}$ (P_T), free and saline ammonia (FSA, N_T) and H_2CO_3^* alkalinity (from which inorganic carbon C_T is calculated) with time were measured over 24 to 56 h. To simulate the batch test results, solubility product and ion pairing constants were obtained from the literature and the mineral precipitation and CO_2 and NH_3 gas stripping rates calibrated by minimising the error between the predicted and measured results. A very good correlation was obtained for all the measured parameters in six out of the seven batch tests, four on SS and three on UASB anaerobic digester liquors (ADL).

From the model results the masses of the different calcium and magnesium carbonate and phosphate minerals that precipitated and the CO_2 and NH_3 stripped via the gas phase could be calculated. Comparing the results from the two liquors it was found that:

- the minerals that precipitated were very similar in both, viz. in decreasing proportion of precipitate mass formed, struvite (MgNH_4PO_4) (82 to 89%), amorphous calcium phosphate (ACP) (5 to 15%), calcium carbonate (CaCO_3) (0-6%), magnesium carbonate (MgCO_3) (0 to 5%) and newberyite (MgHPO_4) (0.1 to 0.3%);
- the solubility product values for these minerals were the same in both liquors and within the range of literature values, but
- the specific precipitation rates were different;
- the rates of struvite and ACP precipitation were 9 and 2 times faster in the UASBDL than in the SSADL respectively;
- in contrast, the rate of CaCO_3 precipitation was 140 times faster in the SSADL than in the UASBDL;
- the rates of MgCO_3 and MgHPO_4 precipitation were approximately the same in both liquors; and
- the stripping/dissolution rates of oxygen (O_2), carbon dioxide (CO_2) and ammonia (NH_3) increased with increased aeration rate in the batch tests.

The kinetic modelling approach allows the determination of the specific precipitation rates for a number of minerals simultaneously in an integrated manner from a single batch test.

Introduction

Musvoto et al. (1997) describe the development of an integrated kinetic model to simulate the chemical-physical processes of the carbonate¹ system in three phases (solid-aqueous-gas); and the mixed water², carbonate, phosphate¹, short chain fatty acid (SCFA) and ammonia weak acid/base systems in single (aqueous) phase. The model was validated for the steady state (time independent) condition by comparing predicted equilibrium results with predictions from well established equilibrium chemistry based models in the literature, such as Stasoft I (Loewenthal et al., 1988) and Stasoft III (Friend and Loewenthal, 1992) for the three-phase carbonate system in pure water; and Loewenthal et al. (1989, 1991) for the single aqueous phase behaviour of the water², carbonate, phosphate, SCFA and ammonia mixed weak acid/base systems.

¹ In this paper, as in the earlier paper on the same subject (Musvoto et al., 1997), the term "carbonate system" refers to the inorganic carbon system. The term "carbonate system species" refers to all the species making up the total inorganic carbon (denoted C_T), viz. H_2CO_3^* comprising dissolved CO_2 and H_2CO_3 , bicarbonate HCO_3^- and carbonate CO_3^{2-} , and the term "carbonate species" refers to the CO_3^{2-} species only. The same nomenclature applies to the term "phosphate system", "phosphate system species", denoted P_T and "phosphate species".

² In aqueous single or mixed weak acid/base systems, the water always is present and acts as an additional weak acid/base system because of its dissociation to H^+ and OH^- . It is included here for completeness. In mixed weak acid/base systems, the water system is one of several weak acid/base systems that contribute to the total alkalinity and acidity mass parameters (Loewenthal et al., 1989).

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