Environmental Impact

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$CaCO_3$ solubility in the process water of recycled containerboard mills

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Abstract: Water system closure in recycled containerboard mills may have reached a technical limit due to the accumulation of organic and inorganic contaminants in the process water. The specific water chemistry characteristics of recycled containerboard mills with restricted water systems were analyzed and a computer model was developed to simulate calcium carbonate solubility in the presence of volatile fatty acids under relevant mill conditions. A strong linear correlation between VFAs and calcium ions was found. The calcium carbonate dissolution mechanism, solubility, and precipitation were investigated. The reaction of VFAs with calcium carbonate results in the formation of bicarbonate and carbonic acid. By binding hydrogen ions, the carbonate has a pH buffering effect. The carbonic acid dissociates into water and CO_2. Gaseous CO_2 escapes from the water and leads to decarbonization. This mechanism is responsible for the uncoupling of pH from the concentration of VFAs, as well as from the concentration of dissolved calcium ions. The resulting lack of carbonates prevents the precipitation of calcium carbonate. The introduction of CO_2 contained in the biogas produced in anaerobic biological water treatment reverses the dissolution mechanism and causes the precipitation of calcium carbonate. Concentrating technologies such as membrane filtration and evaporation may therefore meet the specific requirements for complete water system closure in recycled containerboard mills better than current commonly used biological treatment.

Keywords: calcium carbonate; solubility; thermodynamic model; volatile fatty acids; water treatment.

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1 Introduction

Water system closure has been a long-standing goal for the water intense paper industry. Full closure means that no effluent is discharged from the process and fresh water is only added to make up for water that evaporates during thermal drying of the paper. Since the 1970s, the specific effluent discharge volume of paper and board mills has been reduced by approximately 80%, but water use has plateaued at slightly under an average of 10 m^3 per metric tonne of paper produced (Jung and Kappen 2014). According to the Industrial Emissions Directive for Integrated Pollution Prevention and Control, the average specific effluent discharge volume of European recycled containerboard mills is 5.5 m^3/t (Suhr et al. 2015). While water system closure is beneficial from a fresh water usage and water pollution perspective, it causes unwanted substances to build up in the mill's water system, due to material that enters the mill contained in the recycled paper and board. Research found that the concentration of organic and inorganic substances, measured as chemical oxygen demand (COD) and electrical conductivity (EC), respectively, accumulate exponentially in the water system as the proportion of process water recycled increases and the proportion of fresh water added and effluent discharged, decreases (Miranda et al. 2009).

In 2018, 59% of all paper and board produced worldwide was made from recycled fibres (Verband Deutscher Papierfabriken e.V. 2020). 76% of containerboard mills use recycled paper as their raw material (Valeeva and Li 2017). The water chemistry of recycled containerboard mills with restricted water systems is characterised by high concentrations of calcium species and volatile fatty acids (VFAs). Increasing recycling rates lead to a deterioration of the quality of the recycled paper grades because the fraction of virgin fibres decreases, while the content of non-fibrous additives such as calcium carbonate and starch increase. In general, the processed recycled paper is a heterogeneous raw material with varying composition of packaging and graphic paper grades. Recovered packaging paper grades contain up to 65 kg of starch per metric tonne (Auhorn 2006). Starch is used for sizing as well as when converting the base paper into corrugated boxes. The starch dissolves during repulping and contributes to the COD of the process water. In the repulping process, the starch hydrolyses to glucose and provides an abundant nutritional basis for anaerobic bacteria that generates VFAs as one of the key metabolic products (McCarty 1964). This causes acidification of the process water and odour issues with the final product (Jung and Kappen 2010). Graphic paper grades in the recovered paper contain up to 38% fillers and coating pigments (Holik 2006). Fillers and coatings are used to enhance optical properties and printability. 75% of pigments are based on calcium carbonate (Confederation of European Paper Industries 2019). Australian recycled containerboard contains a calcium carbonate content of approximately 10% (Milligan 2018). In the presence of VFAs from fermented starch, calcium carbonate dissolves and calcium ions contribute to higher electrical conductivity in the process water. These cations also interact with anionic surface charges of the fibres and lead to charge neutralisation. This reduces the effectiveness of cationic wet-end additives such as internal sizing agents and retention aids. As a consequence, product specifications may not be met, greater quantities of additives may be needed, and machine downtime may increase (Xu et al. 2017).

Only a small number of mills eliminated effluent discharges completely; either by recycling treated effluent or by integrated process water purification. Biological treatment, membrane filtration, and evaporation technologies have been investigated for water system closure in recycled containerboard mills. In the 1980s, biological water treatment using a combination of anaerobic and aerobic digestion began being employed in the pulp and paper industry (Meyer and Edwards 2014). Anaerobic reactors are capable of handling the high COD concentrations in the process water from recycled containerboard mills, and the subsequent aerobic stage is capable of meeting effluent requirements. In the first stage of anaerobic digestion, dissolved organic substances are fermented to VFAs (pre-acidification) and in a second stage these acids are further converted into biogas (methanogenesis) (McCarty 1964). Apart from methane, biogas from recycled paper mills contains around 20 vol% carbon dioxide (Bakraoui et al. 2020). Depending on temperature and pressure, water absorbs carbon dioxide. At atmospheric pressure and 40 °C, approximately 1 g/L of CO_2 can be absorbed (Dodds et al. 1956). The dissolved carbon dioxide can form bicarbonates that, in the presence of calcium ions, cause calcium carbonate to precipitate (Schabel et al. 2014). If calcium carbonate attaches to the anaerobic granular sludge, the reactive surface area of the biomass will be reduced and the efficiency of the fermentation process will also be affected. Furthermore, the diffusivity of the sludge bed is reduced when the affected granules settle (Habets 2003). This so-called 'cementing' of the sludge bed can make it necessary to decommission and reseed a bioreactor (Batstone et al. 2002). Consequently, research has focused on calcium-related issues (Pingen et al. 2000). One paper suggests that operational issues become inevitable at calcium ion concentrations beyond 400 mg/L (Hamm et al. 2001). Another researcher reported manageable calcium ion concentrations of up to 600 mg/L and cementing of the sludge bed beyond concentrations of 1200 mg/L (Van Langerak et al. 1998). Precipitation and mitigation using inhibitors and magnets have been investigated, but these results have not led to clear guidelines for the industry (Hamm et al. 2001). Biological methods for end-of-pipe wastewater treatment are therefore widespread, but very few mills have used anaerobic digestion for process water recycling that would allow complete water system closure. This is due to the uncontrolled calcium carbonate precipitation that occurs during biological treatment, rendering conventional anaerobic digestion theoretically unsuitable for the concentrated process water of recycled containerboard mills with a closed water system. In this context, research suggests that calcium related problems may prevent water system closure in recycled paper mills (Hamm et al. 2001; Schabel et al. 2014).

Membrane filtration which is used in many water treatment applications did not establish for water system closure of recycled paper mills. This is because the high concentration of organic substances in the process water quickly causes fouling of the membrane modules. This has been investigated for ultrafiltration at laboratory scale (Cainglet et al. 2021). Furthermore, fouling was found to be the limiting factor for a pilot plant in a municipal wastewater treatment plant using microfiltration, ultrafiltration, and reverse osmosis (Ordóñez et al. 2011). Another pilot plant using ultrafiltration, nanofiltration and reverse osmosis for biologically treated water from newsprint mill led to similar conclusions (Richardson et al. 2008). The attempt to use membranes to replace fresh water and eliminate effluent discharge also failed in a full scale application where a containerboard mill used membranes to recycle biologically treated water (Wirth et al. 2005).

Water treatment using evaporation is used in so called zero liquid discharge systems. Thermal separation allows to reclaim more than 90% of the water from designated water streams and eliminate effluent. Due to the high energy consumption, the implementation is mostly limited to applications such as power plants (Mickley 2008). In the 1990s the first Canadian mechanical pulp mills used evaporators to successfully eliminate liquid waste (Ward et al. 1993; Young 1994). However, as these mills process virgin fibres and not recovered paper, their water chemistry cannot be directly compared to recycled containerboard mills. Evaporators in recycled containerboard mills are rare. An evaporator with polymeric heat exchange surfaces was installed in a mill in Saudi Arabia to treat ground water and also water from production (Koistinen 1998). A mill in Mexico uses four multiple effect evaporators and an evaporative crystallizer to achieve zero liquid discharge (Rodden 2012). Research at laboratory scale showed that evaporation very effectively removes inorganic substances such as silica from paper mill process water (Huuha et al. 2010). Other researchers also reported efficient removal of organic compounds by evaporation (Güneysu and Aydın 2017). Evaporation therefore appears to be superior to biological treatment and membrane filtration as its principle allows high removal efficiency for both organic and inorganic constituents. However, both membrane and evaporation processes would be expected to be significantly affected by some form of fouling due to calcium carbonate precipitation. Fouling caused by the effluent of a mechanical pulp mill was investigated and found that the formation of mostly organic material reduced the heat transfer coefficient by more than 30% after only 40 h of operation (Li and Watkinson 2011). However, this study is not necessarily relevant to the water chemistry of recycled containerboard mills. Fouling of heat exchangers is, however, of wide spread concern in heat exchange technology in general and is accompanied by significant operational and economic consequences (Steinhagen et al. 1993).

In summary, the water chemistry of recycled containerboard mills with a restricted water system is characterised by high concentrations of calcium and the presence of VFAs that are due to the anaerobic fermentation of starch in the paper recycling process. Using data from three industrial mills with varying degrees of water system closure, this paper will show that there is a correlation between VFAs and calcium in the process water of all three mills. Although the dissolution of $CaCO_3$ in strong inorganic acid has been studied under a wide range of conditions (Schabel et al. 2014), the dissolution of $CaCO_3$ in the presence of weak organic acids that do not completely dissociate has not been reported in the context of industrial wastewater. This paper presents a model for this water chemistry which can be used to predict the dissolved and precipitated calcium species under various conditions. This model will explain the specific characteristics of the water chemistry and identify the technological principle that is most suitable to overcome the current technical limitation for advanced water system closure of recycled containerboard mills.

2 Recycled containerboard mills with restricted water system

Figure 1 shows a schematic of the water system of a recycled containerboard mill. The recovered paper is pulped, screened and cleaned in the stock preparation plant. The fibre stock suspension is passed on to the paper machine where it is dewatered and containerboard is produced. Water is used in a counter-current principle. This means that fresh water is only added to the paper machine and effluent is only discharged from the stock preparation. Approximately 1–1.5 m^3/t of water is evaporated in the dryer section of the paper machine (Auhorn 2006). Filtrate from the former section (white water 1, WW1) is directly reused at the paper machine to dilute the fibre stock from the stock preparation plant. Water from the former and the press sections of the paper machine (white water 2, WW2) is clarified and used for fibre stock dilution prior to the paper machine and as make-up water in the stock preparation plant. Clarified process water may further be used for certain showers or for lubrication water at the paper machine to further minimise fresh water intake. The process water samples that are described in the following sections are sampled from downstream of the process water clarifier, as shown in Figure 1.

The clarifier is designed to recover fibres from drainage and press water. It efficiently removes suspended solids, while dissolved substances remain in the filtrate. The suspended solids eventually leave the process with the paper product. Dissolved substances in the process water are either discharged with the effluent, or in the case of effluent restriction, they accumulate. Due to this build up and related

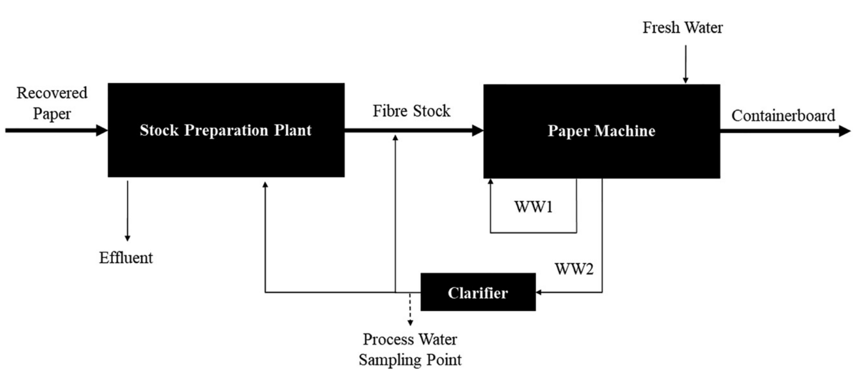

Figure 1: Simplified illustration of the water system of a recycled containerboard mill with internal water clarification.

problems, very few paper mills operate with a strongly restricted or even entirely closed water system. Accordingly, there is little data on the corresponding process water published. This paper compares data of two mills from literature and data from a mill specifically investigated for this study.

The quality of the process water from paper mills is commonly described using a number of broad parameters such as total suspended solids, total dissolved solids, and indicators to identify the individual organic as well as inorganic constituents. COD is commonly used as an indicator of the presence and concentration of organic compounds and EC as an indicator of inorganic constituents. The presence of VFAs is an indicator for anaerobic biological activity, and pH is a measure of acidification of the system. Water hardness and free calcium ions are evidence of calcium carbonate dissolution.

Table 1 gives an overview of the composition of the process water from recycled containerboard mills with specific effluent discharge volumes between 0 and 5.5 m^3/t. Data from published sources provides the water composition of a mill with a completely closed water loop (Smurfit Kappa, Zülpich, 'SKZ') and a mill with a restricted system that discharges 3.2 m^3/t (Julius Schulte, Düsseldorf, 'JSD') (Hamm and Schabel 2007). Experimental data from an Australian paper mill with a specific effluent discharge volume of 2.4 m^3/t (Visy Paper, Coolaroo, 'VPC'), collected specifically for this investigation, lies between the two published literature sources. The VPC mill can therefore be considered to have a strongly restricted water system. The average COD of European recycled packaging paper mills (Recycled fibre, 'RCF') with a discharge volume of 5.5 m^3/t is also provided for comparison with the restricted and closed water loop, and is designated as an open water system (Suhr et al. 2015).

Table 1 shows that the process water of the three containerboard mills with restricted or closed water circuit are highly loaded with organic as well as inorganic substances. The full set of reported parameters is provided in the supplementary data. The concentrations increase with reduced specific effluent discharge volume. Miranda et al. showed that the concentration of dissolved substances in the process water increases exponentially with lower fresh water intake (Miranda et al. 2009). However, their experimental data comes from laboratory trials using recycled graphical papers. Figure 2 illustrates the exponential increase of COD and EC, and confirms these results on an industrial scale for the recycled containerboard mills in Table 1.

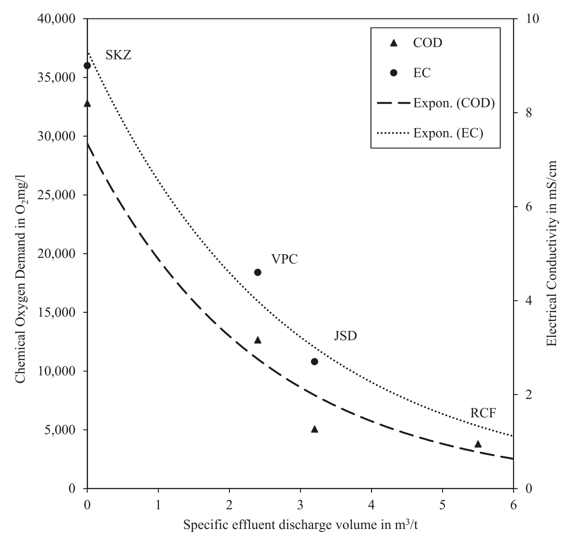

Figure 2: Exponential increase of COD and EC in the process water of literature data SKZ & JSD (Hamm and Schabel 2007), experimental VPC data, and average data from European mills (RCF) (Suhr et al. 2015).

Table 1: Water composition of recycled packaging paper mills with specific effluent discharge volumes varying from 0 to 5.5 m^3/t.

		Smurfit Kappa, Zülpich ('SKZ') (Hamm and Schabel 2007)	Visy Paper, Coolaroo ('VPC')	Julius Schulte, Düsseldorf ('JSD') (Hamm and Schabel 2007)	Average RCF Mill Europe (Suhr et al. 2015)
Water loop		**Closed**	**Strongly restricted**	**Restricted**	**Open**
Specific effluent discharge volume	m^3/t (AD)	0.0	2.4	3.2	5.5
pH		6.3	6.2	6.6	
Electrical conductivity	mS/cm	9.0	4.6	2.7	
Ca2+-ions	mg/L	2650	844	420	
Hardness as $CaCO_3$[a]	mg/L	6625	2110	1050	
Chemical oxygen demand	O_2 mg/L	32,800	12,655	5070	3800
Acetic acid	mg/L	6300	1627	760	
Propionic acid	mg/L	600	647	330	
n-butyric acid	mg/L	350	94	<20	
Sum of VFAs[b]	mg/L	7250	2368	1090	

[a]Calculated from the calcium-ion concentration (Ca2+ × 100/40). [b]Sum of propionic-, acetic- and n-butyric acid

The two trend lines in Figure 2 confirm the exponential accumulation of organic as well as inorganic constituents in the process water also for industrial scale. COD increases moderately between 5.5 m^3/t and 3.2 m^3/t, and strongly at discharge volumes of less than 3 m^3/t.

The high COD indicates that the process waters of these mills carry significant loads of organics, providing abundant nutrition for bacteria in the system. The bacteria metabolise the organic content and produce VFAs. These VFAs are short chained fatty acids such as acetic-, propionic- and n-butyric acid. Acetic acid is the predominant acid formed during anaerobic fermentation and typically makes up around 70% of all VFAs (McCarty 1964). This is confirmed for the restricted and strongly restricted systems presented in Table 1 for the closed water loop, acetic acid accounts for 86% of all the VFAs.

It was found that the performance of retention aid drops significantly when electrical conductivity increases from 2 to 3 mS/cm; for containerboard mills EC is usually below 5 mS/cm (Xu et al. 2017). The mills with restricted water systems in Table 1 are in this range. As EC in all cases presented here is beyond 2 ms/cm, an adverse impact on the efficiency of chemical additives is expected. This applies especially for the completely closed water loop with an EC of 9 ms/cm.

The calcium ion concentration of the three paper mills shows a strong linear correlation with the sum of the concentrations of acetic, propionic and n-butyric acids (Table 1) as can be seen in Figure 3a. Higher acid concentrations lead to an increase of calcium carbonate dissolution and consequently calcium hardness of the process water. As data from literature is limited, the correlation was further investigated experimentally for the Australian paper mill VPC. Figure 3b shows a good linear correlation between VFAs and calcium hardness also for experimental data from the strongly restricted water system of VPC. Both plots show that the correlation fits well the model of linear regression. A water hardness of 280 mg/L was assumed for all three mills.

Coto et al. compiled experimental data from publications and developed a model for the solubility of calcium carbonate in water under varying conditions such as temperature and pressure. This literature suggests a calcium ion concentration of 160–280 mg/L for a pH range between 6.2 and 6.6 and a temperature of 25 °C (Coto et al. 2012). However, the calcium ion concentration in the process water of the investigated mills is significantly higher in this pH range; between 420 and 2650 mg/L.

The data in Table 1 shows that an increase of VFA concentration does not lead to a reduction of pH. Furthermore, the concentration of calcium does not correlate with pH. In general, the concentration of calcium ions in the process water is higher than literature suggests at the given pH. These observations can be considered specific characteristics of the process water from recycled containerboard mills with restricted water systems. Due to the lack of publicly available complete data sets and in order to explore these observations further, a computer model of the dissolution of calcium carbonate in the mill water has been developed and is presented in the next section.

3 Water chemistry equilibrium models

The purpose of the water chemistry model is to simulate the dissolution of calcium carbonate in the process water of recycled containerboard mills with restricted water systems. Models were developed using VFAs and calcium carbonate at relevant conditions of temperature and pH to simulate the dissolution mechanism of calcium carbonate in the process water of recycled containerboard mills.

The models were developed using OLI Systems Inc. Stream Analyzer, which is the main interface to the OLI Studio V11 suite (OLI Systems Inc. 2021). This thermodynamic software calculates the multiphase properties of electrolyte and non-electrolyte streams to enable modelling of aqueous systems based on experimental data. The OLI aqueous thermodynamic framework is an electrolyte activity

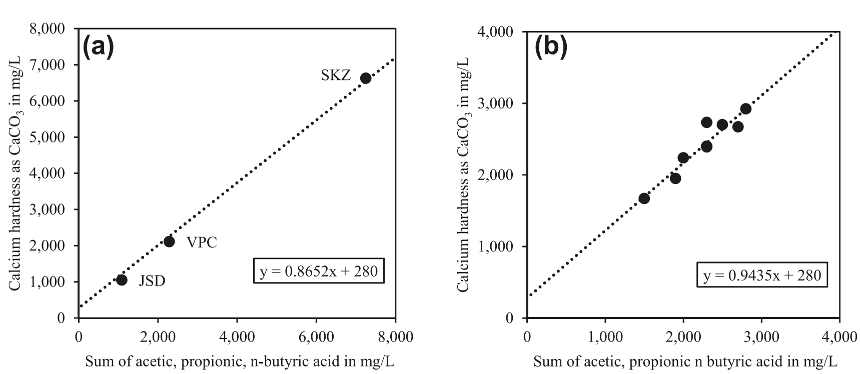

Figure 3: Correlation of calcium hardness and the sum of acetic, propionic and n-butyric acid of (a) three recycled containerboard mills with restricted, strongly restricted and closed water loop and (b) additional data for the VPC mill with strongly restricted water system.

coefficient model based on the Bromley-Zemaitis activity model (Linz et al. 2003). The database contains approximately 6000 species, including electrolytes and hydrocarbons. The software is used for single and multipoint calculations, as well as equilibrium calculations for electrolyte chemistry.

The dissolution of calcium carbonate in water is governed by the carbonic acid-carbonate equilibrium. Furthermore, calcium carbonate reacts with weak acids. In this section, these systems are presented separately and the accuracy of the modelling software is confirmed by comparison of data points with literature. The developed simulation model describes the dissolution mechanism of calcium carbonate in the process water of recycled containerboard mills as a combination of these two dissolution pathways.

3.1 The carbonic acid–carbonate equilibrium

The dissolution of calcium carbonate in water is a function of pH and depends on the equilibria between the various species of aqueous carbonates. Equations (1)–(4) describe the changes in equilibria and dissolved species in the carbonic acid–carbonate system in order of decreasing pH. Figure 4 presents the OLI model data that illustrates the system dependence on pH. The model is developed based on an atmospheric pressure of 1 bar and a temperature of 40 °C to simulate mill conditions.

Depending on pH different carbonate species dominate. At high pH (above 10.5), the lack of hydrogen ions lead to exclusively carbonate. In the presence of calcium ions, calcium carbonate is formed Eq. (1). Between pH 6.5 and 10.5, bicarbonate dominates Eq. (2) and at pH below 6.5 carbonic acid Eq. (3). Carbonic acid is not stable in water and decomposes into dissolved carbon dioxide and water Eq. (4).

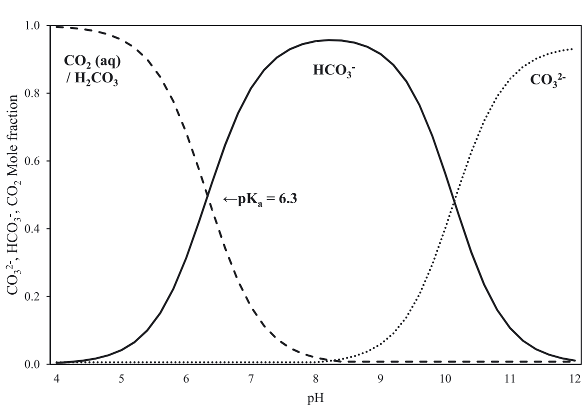

Figure 4: OLI model: Effect of pH on the carbonic acid–carbonate equilibrium.

When the saturation concentration of carbon dioxide in water at the prevailing temperature and pressure is exceeded, the carbon dioxide is released as gas.

$$CaCO_3\ (s) \leftrightarrow Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \tag{1}$$

$$H^+\ (aq) + CO_3^{2-}\,(aq) \leftrightarrow HCO_3^-\,(aq) \tag{2}$$

$$H^+\ (aq) + HCO_3^-\ (aq) \leftrightarrow H_2CO_3\ (aq) \tag{3}$$

$$H_2CO_3\ (aq) \rightarrow H_2O\ (l) + CO_2\ (aq/g) \tag{4}$$

Figure 4 shows a Bjerrum plot of carbonate species simulated with OLI to confirm the pK_a agrees with literature. The pH range of recycled containerboard mills process water is typically between 6 and 7. This is also the critical pH range for calcium carbonate dissolution and precipitation, because it is the transition between bicarbonate and carbonic acid/dissolved carbon dioxide as dominant species. The presentation of the transition area from bicarbonate to carbonic acid at a pH of 6.3 in the OLI model agrees well with literature, which suggests that carbonic acid has its pK_a of 6.35 (Tossell 2005).

3.2 Reaction of calcium carbonate with a weak acid

In the next stage of building the water chemistry model, the reaction of calcium carbonate with a weak acid is investigated. In recycled paper mills, the dominant VFA is acetic acid (Bakraoui et al. 2020). The reaction of calcium carbonate and acetic acid leads to the formation of either calcium acetate Eq. (5) or calcium acetate ions (Eq. 6). Both reactions lead to the release of carbon dioxide gas; Eq. (5) directly, and Eq. (6) via Eqs. (3) and (4) above.

$$CaCO_3\ (s) + 2CH_3COOH \rightarrow Ca\,(CH_3COO)_2\,(aq) + H_2O + CO_2\ (g) \tag{5}$$

$$CaCO_3\ (s) + CH_3COOH \rightarrow Ca\,(CH_3COO)^+\,(aq) + HCO_3^-\,(aq) \tag{6}$$

The degree to which calcium acetate or calcium acetate ions are formed, and the mechanism by which CO_2 is released, depends on the dissociation of the acetic acid (7).

$$CH_3COOH\ (aq) \leftrightarrow CH_3COO^-\ (aq) + H^+\,(aq) \tag{7}$$

Figure 5 shows that the dissociation of acetic acid depends on pH.

According to the OLI model acetic acid and acetic acetate are in equilibrium at a pH of 4.8. This agrees well with literature that suggests a pK_a of 4.76 (Serjeant and Dempsey 1979). In the pH range of the recycled paper mills (6–7), it is therefore expected that the acetic acid will exist predominantly as acetate ions. The other major VFAs have similar dissociation behaviour; the pK_a of propionic acid is 4.88 (Serjeant and Dempsey 1979) and n-butyric acid is 4.82 (Peldszus 2000).

4 Results

The combination of the carbonic acid–carbonate equilibrium and the reaction of calcium carbonate with acetic acid leads to a complex system, represented by Eqs. (1)–(7). The overall dissolution mechanism and its relationship to recycled mill process water conditions and compositions are presented in this section.

For the OLI model, the closure of a mill's water system is simulated by an increasing concentration of VFAs. Acetic acid makes more than 70% of acids from anaerobic fermentation. Other VFAs are by-products and can be found in minor concentrations. For the model used to investigate the dissolution mechanism of calcium carbonate in the process water (Figures 6 and 7), the sum of propionic-, acetic- and n-butyric acids is represented by acetic acid. This simplification is made to minimise the number of calcium species in the model. The impact of minor acids on the dissolution of calcium carbonate is further evaluated in Section 5.2.

The mills with restricted (JSD) and closed (SKZ) water loops had VFAs concentrations of 1000 and 7300 mg/L, respectively. The acetic acid concentration for the OLI model was therefore modelled from 0 to 10,000 mg/L. The model uses 8500 mg calcium carbonate to simulate a surplus of calcium carbonate over the entire VFAs concentration range. Literature on water system closure suggests a process water

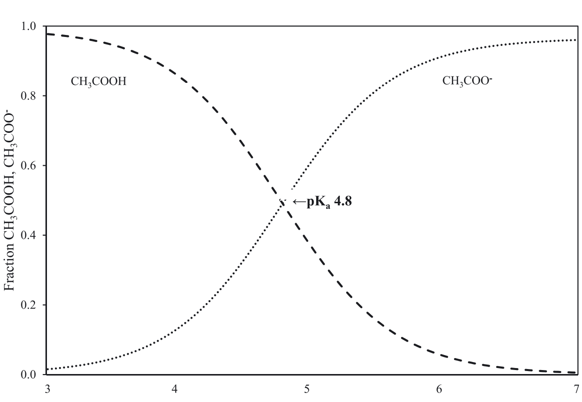

Figure 5: OLI model effect of pH on dissociation of acetic acid.

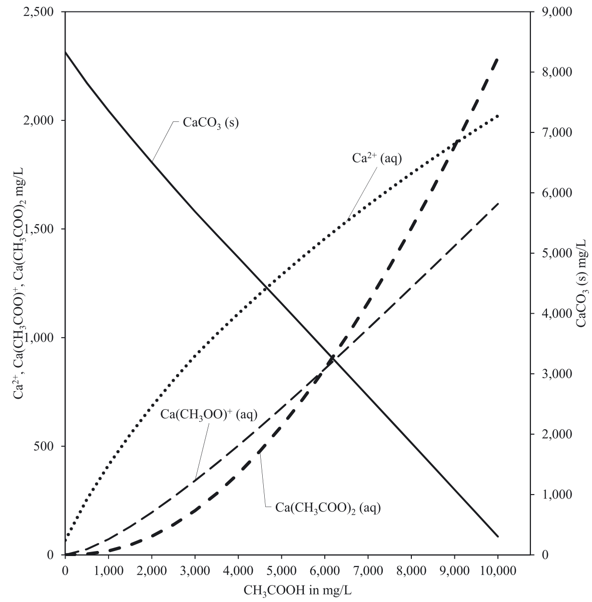

Figure 6: OLI model dissolution mechanism: Concentration of calcium species with increasing acetic acid concentration.

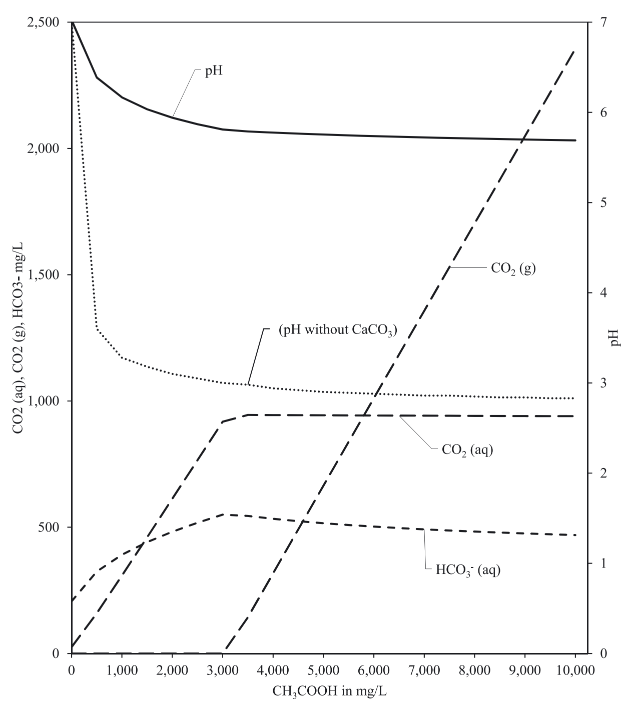

Figure 7: OLI model dissolution mechanism: Concentration of carbonate species with increasing acetic acid concentration.

temperature of 21–66 °C (Barton et al. 1996). In the model, the temperature is set to 40 °C, which is similar to the process temperature of VPC. The model parameters thus mimic the recycled containerboard mill process, and indicate potential impact of increasing VFAs on aqueous calcium species in mill process water.

It is expected that the carbonic acid-carbonate system and the reaction of calcium carbonate with the weak acid simultaneously affect the calcium carbonate dissolution mechanism. For low concentrations of acetic acid, it is expected that the carbonate system dominates the dissolution mechanism, while the reaction of $CaCO_3$ with the acetic acid is expected to dominate at higher concentrations. The phases of the mechanism are identified by the concentration of calcium and carbonate species. Calcium ions indicate dominance of the carbonic acid-carbonate equilibrium. Calcium acetate and calcium acetate ions indicate dominance of the reaction of $CaCO_3$ with acetic acid. Calcium bicarbonate ions and calcium hydroxide ions are neglected in the diagrams because their concentrations are relatively low in comparison to the dominant species. Figure 6 shows the illustration of the OLI computer model.

The model shows a linear correlation between acetic acid concentration and the dissolution of calcium carbonate. With increasing acetic acid concentration, the solid calcium carbonate dissolves, forming calcium ions, calcium acetate ions, and aqueous calcium acetate. At low acetic acid concentrations, calcium ions are the main species. The concentration curve of calcium ions follows an inverse exponential trend with increasing acetic acid concentration. Aqueous calcium acetate follows an exponential trend, while the curve for calcium acetate ion is nearly linear.

It can be seen that the species formed in reaction with the VFAs dominate the dissolution mechanism at higher concentrations, while at lower concentrations it appears to be mainly governed by the carbonate system. Figure 7 elaborates on this by presenting the concentrations of the carbonate species relevant for the carbonate equilibrium.

Figure 7 shows that the pH initially drops from 7 to 5.8 and the carbonate equilibrium shifts towards carbonic acid, as indicated by the increasing concentration of dissolved CO_2 (compare also Figure 4). The concentration of bicarbonate ions increases as calcium ions are released. At approximately 3000 mg/L of acetic acid, the saturation concentration of dissolved CO_2 is reached. In the model, this occurs at 944 mg/L of CO_2, which is in good agreement with literature values of up to 1 g/L at 40 °C (Dodds et al. 1956). Beyond a concentration of 3000 mg/L of acetic acid, CO_2 is released as gas. The reaction of calcium with acetic acid becomes dominant, and calcium acetate and calcium acetate ions become more prominent.

5 Discussion

When analysing the process water characteristics of the three recycled containerboard mills, it was found that pH does not decline with increasing VFA concentration, the calcium concentration does not correlate with pH, and the calcium concentration is higher than the carbonate system would suggest. Based on the developed dissolution mechanism, these observations will be explained in this section.

5.1 CO_2 release

The dissolution mechanism shows that the addition of acetic acid impacts the pH only until the CO_2 saturation concentration is reached. In the model, this occurs at 3000 mg/L of acetic acid. Beyond this concentration, additional acid does not impact pH significantly. This is due to the buffering effect of the carbonates binding hydrogen ions. Moreover, the model shows that CO_2 is released into the gas phase, causing decarbonization and an absence of counter ions for calcium to reform calcium carbonate.

The pH buffering effect can be explained by the fact that the hydrogen ion donated by acetic acid is bound by the carbonate ion of calcium carbonate to form carbonic acid. Carbonic acid in water dissociates into water and dissolved CO_2. Beyond the CO_2 saturation concentration of water, excess CO_2 is released and is no longer available to form carbonic acid; therefore it does not cause increasing acidity. This explains the plateauing of the pH in Figure 7 and also the observation from experimental data from the mills that pH does not correlate with the VFA concentration and dissolved calcium does not correlate with pH. For comparison, Figure 7 further shows the pH for an acetic acid solution without dissolved calcium carbonate. The figure shows that the pH of the solutions without calcium carbonate is acidic - around pH 3 compared to the solution with calcium carbonate with a pH near-neutral of around 6.

The release of CO_2 not only impacts the pH of the solution, but also causes the absence of carbonate ions. The absence of carbonate ions and CO_2 lead to the fact that calcium carbonate does not reach its saturation concentration, even when calcium concentrations are very high due to accumulation in restricted water systems. Also, neither elevated temperature nor pH cause precipitation beyond that which would usually be expected in the carbonate system. Thus, very high calcium ion concentrations can be found in the process water of recycled containerboard mills with restricted water systems.

This lack of carbonates was confirmed in the laboratory by increasing the pH of process water samples and measuring the impact on the calcium ion concentration. The carbonate system suggests that carbonate is the dominant species at a pH beyond 11 (Figure 4). Figure 8 shows the calcium ion concentration of three process water samples

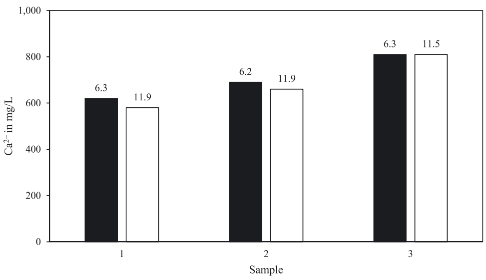

Figure 8: Calcium ion concentration of three process water (pH around 6.3) and after pH-adjustment to over pH 11.

before and after their pH was adjusted. It can be seen that the calcium ion concentration did not change notably at high pH, when all calcium carbonate should precipitate. The absence of carbonate ions therefore appears to prevent calcium carbonate precipitation, including at high calcium concentrations, at elevated temperatures or pH.

To utilise this specific characteristic of the process water in water treatment, the maximum CO_2 concentration in the water can further be minimised with the use of a vacuum system. This would avoid precipitation or fouling up to high concentration factors in concentrating technologies such as membrane filtration or evaporation. At atmospheric pressure the saturation concentration of dissolved CO_2 is around 1 g/L, at 0.5 bar (abs) it is approximately 0.4 g/L and at 0.1 bar (abs), it is less than 0.03 g/L (see supplementary data, Figure 11).

5.2 Correlation between model VFA concentration and calcium hardness

A strong linear correlation between VFA concentration and calcium hardness was observed in the process water of recycled containerboard mills (Figure 3). Furthermore, the dissolution model showed a linear decrease in solid calcium carbonate with increasing acetic acid concentration. In this section, the validity of the exclusive use of acetic acid to simplify the VFA composition in the OLI model is investigated.

Two models were developed; a single component model using only acetic acid (0.0–10,000 mg/L) and a three components model using acetic acid (0.0–10,000 mg/L), propionic acid (0.0–526 mg/L), and n-butyric acid (0.0–148 mg/L). Propionic acid and n-butyric acid are by-products of anaerobic fermentation, and the concentrations in the simulation are derived from the experimental data (Table 1). The acidity of the three organic acids vary slightly; the pK_as are 4.76 for acetic acid (Serjeant and Dempsey 1979), 4.88 for propionic acid (Serjeant and Dempsey 1979) and 4.82 for n-butyric acid (Peldszus 2000). In addition to the two OLI models, the JSD and SKZ literature data (Hamm and Schabel 2007) are shown, as well as multiple data points from VPC.

Figure 10 shows the regression of the two OLI models, experimental data points from literature (JSD and SKZ) as well as data points from VPC. The dotted lines are the trend lines of the OLI models. The dashed line is the linear trend of the mills.

As Figure 9 shows, the single component model (acetic acid only) and the three component model (propionic, acetic and n-butyric acid) are in very good agreement with the data points of the restricted mills. With increasing concentrations, propionic acid and n-butyric acid become more relevant and the three component model is in better agreement with the completely closed water loop compared to the single component model.

Other ions that are present in the process water such as Na^+, SO_4^{2-} and Cl^-, are not included in the models as their concentrations are not reported for the two mills from literature. The impact of these ions on the concentration of dissolved calcium carbonate was investigated based on the data from the VPC mill. Table 2 in the supplementary data shows that these ions impacted the resulting calcium hardness by a maximum of 5%.

The VFA/calcium correlation model developed in OLI is able to estimate calcium carbonate dissolution due to

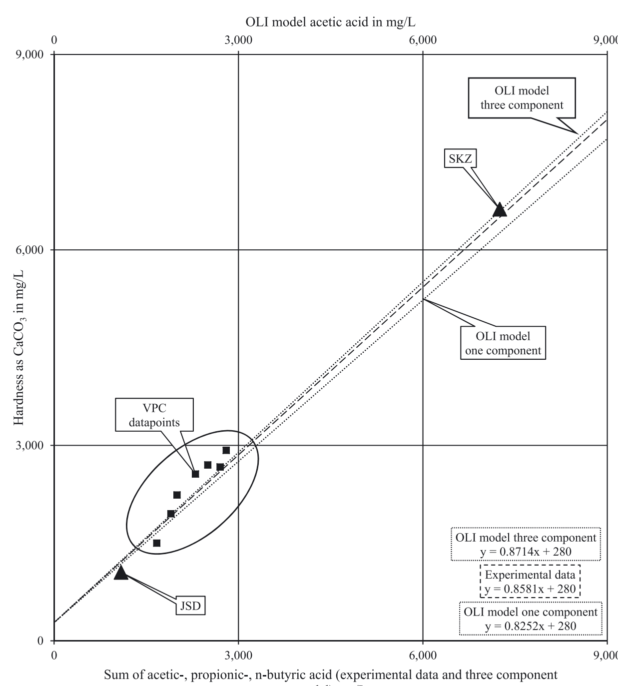

Figure 9: Similarity in the correlations between VFAs and calcium hardness for OLI models, process data, and experimental data from recycled containerboard mills with restricted to closed water circuit.

increased VFAs concentrations in process water with reasonable accuracy. Especially considering potential complexity of individual process waters. The single component model using only acetic acid appears to be of sufficient accuracy for restricted water systems. Multi component models considering minor by-product acids need to be designed to the individual chemistry of each mill. Based on the data presented, this approach may be useful for completely closed water systems.

5.3 Calcium carbonate precipitation

The dissolution model shows that the reaction of calcium carbonate with acetic acid results in the release of carbon dioxide gas. This allows high calcium concentrations to build up in restricted paper mill water loops without causing calcium carbonate to precipitate. However, the reintroduction of carbon dioxide potentially reverses the dissolution mechanism and shifts the equilibrium back towards calcium carbonate.

Anaerobic digestion of process water from paper mills is widely applied in the industry. Dissolved organic substances such as VFAs in the process water are converted to methane and carbon dioxide. Equation (8) shows this reaction exemplarily for acetic acid.

$$CH_3COOH\ (aq) \rightarrow CH_4\ (g) + CO_2\ (aq) \tag{8}$$

The dissolved carbon dioxide is in equilibrium with carbonic acid which potentially dissociates into bicarbonate at higher pH. The carbonate reacts with calcium ions to solid calcium carbonate and precipitates Eqs. (1)–(4). The first stage of biological treatment, acidification, requires a slightly acidic pH of 5.5–6.5 for acidogenesis (Kim et al. 2003). The bacteria in the following methanogenesis require a neutral pH of 6.8–7.2 (McCarty 1964). The increase of pH promotes the transition of carbonic acid to carbonate. These conditions inevitably lead to calcium carbonate precipitation of calcium ion rich process waters. It reverses the dissolution mechanism shown in Equations (1)–(3). This explains the calcium carbonate precipitation that is frequently observed in industry, and is frequently blamed on the presence of Ca^{2+}. However, as the model shows, a high calcium concentration alone does not cause calcium carbonate precipitation. The presence of calcium ions in combination with aqueous CO_2 or carbonate ions does.

Figure 10 simulates the reintroduction of CO_2 into concentrated process water. The model assumes a process water with a calcium acetate concentration of 4000 mg/L. For

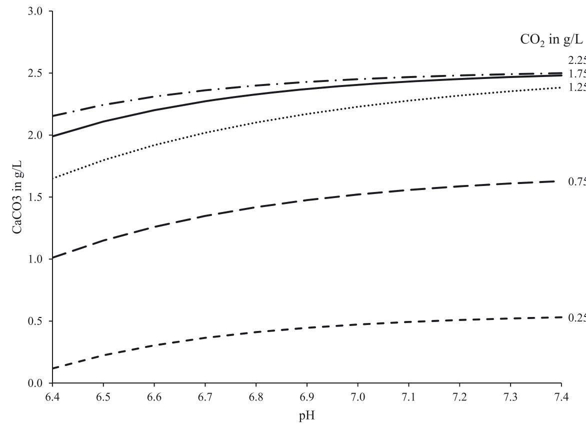

Figure 10: OLI model calcium carbonate precipitation from concentrated process water due to the introduction of CO_2.

simplification, it is assumed that all calcium is present as calcium acetate. The calcium acetate includes a calcium ion concentration of 1000 mg/L and an acetic acid concentration of 3000 mg/L. Acetic acid forms one third methane and two thirds carbon dioxide when being converted in an anaerobic digester. For 3000 mg/L acetic acid being converted to biogas this would result in up to 2250 mg/L of carbon dioxide. The temperature is set to 38 °C. Conversion of acids to gases lead to an increase of pH. This is considered by showing precipitation as function of pH. The impact of the partial pressure of gases is not considered in the model. The figure shows that the introduction of CO_2 reverses the dissolution mechanism and causes precipitation of $CaCO_3$. The concentration of solid $CaCO_3$ precipitate is shown in g/L for a pH range between 6.4 and 7.4. CO_2 is introduced from 0.25 to 2.25 g/L. The system is at atmospheric pressure.

The model shows the increase of calcium carbonate precipitation with increasing pH and CO_2 concentration. The higher the pH, or the more CO_2 is introduced with the biogas, the more calcium carbonate precipitates. However, operating at low pH to mitigate the formation of calcium carbonate leads also to a reduction in the efficiency of the anaerobic fermentation process (McCarty 1964). As biological treatment reintroduces CO_2, and therefore potentially carbonate ions, calcium precipitation is virtually unavoidable if calcium rich water is processed in conventional biological treatment plants.

Only few recycled containerboard mills realised strongly restricted or completely closed water systems. Data on process water of these mills is rarely published. This is the first paper to compare process water from three mills with restricted water systems and to identify as well as define their common characteristics. Their similarities verify the assumption that the mills are comparable. The analysis and comparison of the mills found that they share specific water characteristics. The pH appears to be decoupled from the concentration of VFAs and dissolved calcium carbonate. Furthermore, calcium ion concentrations in the process water exceed the maximum concentration that the carbonate system alone would suggest. A computer model showed that this is due to the dissolution mechanism of calcium carbonate in reaction with VFAs. The carbonate binds hydrogen ions and therefore buffers the pH of the water. As carbonic acid is formed it dissociates into water and CO_2. When the CO_2 reaches its saturation concertation it is released as gas causing decarbonization. This explains why the pH does not correlate with the concentration of VFAs or dissolved calcium. Moreover, it explains the observed high calcium ion concentrations in recycled containerboard mills.

As only little data is publicly available the generated general model contributes to a better understanding of the water characteristics from recycled containerboard mills and specific requirements for water treatment for water system closure. The simplification of the models is justified by their good agreement with experimental data. The absence of carbonates allows high calcium ion concentrations without calcium carbonate reaching its saturation concentration. The water treatment of recycled containerboard mills with restricted water system and concentrated process water can take advantage of these specific water characteristics. Conventional biological water treatment is widely used to reduce the high COD of the process water from recycled containerboard mills. However, this process introduces CO_2 with the generated biogas which reverses the dissolution mechanism and promotes the formation of calcium carbonate. Concentrating technologies such as membrane filtration and evaporation do not introduce carbon dioxide and therefore appear to comply better with the specific water characteristics shown here. The concept of CO_2 removal could be further developed by applying a vacuum to degas the process water prior to concentration.

Finally, in order to achieve a water quality that is suitable to substitute fresh water, either a reverse osmosis membrane process or an evaporation process would be required. However, due to the small pore size, reverse osmosis is very sensitive to biofouling and plugging. In contrast, the principle of evaporation is robust against high organic as well as inorganic concentrations, and provides a high removal efficiency based on boiling point. Therefore, based on evidence from both the experimental data and modelling of calcium dissolution presented in this study, there is a strong indication that evaporator technology could be the most suitable means for assisting with water system closure of recycled containerboard mills.

6 Conclusions

The specific water characteristics of recycled containerboard mills have been identified by analysing and comparing experimental data from three mills. It was demonstrated that there is a strong linear correlation between the concentration of VFAs and dissolved calcium. Therefore, it can be concluded, that the anaerobic fermentation of starch to VFAs in the process is the underlying reason for calcium carbonate dissolution.

A computer model was developed to study the dissolution mechanism and solubility of calcium carbonate in the process water. Results have shown to be in good agreement with the experimental data. The release of CO_2 gas from the process water during the dissolution of calcium carbonate in the presence of VFAs explains the pH-buffering effect and the absence of carbonates. Thus, pH does not correlate with the VFAs or dissolved calcium. It can be concluded that very high concentrations of calcium ions are possible without reaching the calcium carbonate saturation concentration; also at elevated pH or temperature.

However, the reintroduction of CO_2 into the process water causes the reversal of the dissolution mechanism and leads to calcium carbonate precipitation under mill conditions. Consequently, the principle of conventional biological water treatment does not appear to be ideal for water system closure of recycled containerboard mills with concentrated process water. The general assumption that high calcium ion concentrations are the cause for calcium carbonate precipitation is challenged. Concentrating technologies such as membranes or evaporation appear to be more suitable in regards of operating issues related to calcium carbonate precipitation; especially when carbonate concentrations are managed and minimised. Of the two options, evaporation technology would appear to be the more robust.

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Appendix: Supplementary data

Table 2 shows the process water data for two recycled packaging paper mills with restricted and closed water system as reported in literature.

Table 2: Process water data as presented in literature (Hamm and Schabel 2007).

		Smurfit Kappa, Zülpich ('SKZ') (Hamm and Schabel 2007)	Julius Schulte, Düsseldorf ('JSD') (Hamm and Schabel 2007)
pH		6.3	6.6
EC	ms/cm	9.0	2.7
Ca^{2+}-ions	mg/L	2650	420
Water hardness	dH	375	62
COD	O_2 mg/L	32,800	5070
Sulphate	mg/L	1350	360
Chloride	mg/L	430	215
Acetic acid	mg/L	6300	760
Propionic acid	mg/L	600	330
n-butyric acid	mg/L	350	<20
AOX	mg/L		0.34

Table 3 shows the element balance for the OLI model presented in results (Figures 6 and 7). The table shows only non-zero values of total, aqueous, vapour, as well as solid hydrogen, calcium, oxygen, carbon, and acetate ions with increasing concentration of acetic acid.

Table 3: Element balance of total, aqueous, vapour, and solid elements from OLI model dissolution mechanism.

CH_3COOH Total mg	H(+1) Total mg	Ca(+2) Total mg	O(−2) Total mg	C(+4) Total mg	Acetateion Total mg
0	1.11E+05	3403.66	8.85E+05	1047.35	0
500	1.11E+05	3403.66	8.85E+05	1047.35	491.608
1000	1.11E+05	3403.66	8.85E+05	1047.35	983.215
1500	1.11E+05	3403.66	8.85E+05	1047.35	1474.82
2000	1.11E+05	3403.66	8.85E+05	1047.35	1966.43
2500	1.11E+05	3403.66	8.85E+05	1047.35	2458.04
3000	1.11E+05	3403.66	8.85E+05	1047.35	2949.65
3500	1.11E+05	3403.66	8.85E+05	1047.35	3441.25
4000	1.11E+05	3403.66	8.85E+05	1047.35	3932.86
4500	1.11E+05	3403.66	8.85E+05	1047.35	4424.47
5000	1.11E+05	3403.66	8.85E+05	1047.35	4916.08
5500	1.11E+05	3403.66	8.85E+05	1047.35	5407.68
6000	1.11E+05	3403.66	8.85E+05	1047.35	5899.29
6500	1.11E+05	3403.66	8.85E+05	1047.35	6390.9
7000	1.11E+05	3403.66	8.85E+05	1047.35	6882.51
7500	1.11E+05	3403.66	8.85E+05	1047.35	7374.11
8000	1.11E+05	3403.66	8.85E+05	1047.35	7865.72
8500	1.11E+05	3403.66	8.85E+05	1047.35	8357.33
9000	1.11E+05	3403.66	8.85E+05	1047.35	8848.94
9500	1.11E+05	3403.66	8.85E+05	1047.35	9340.55
10,000	1.11E+05	3403.66	8.85E+05	1047.35	9832.15

Table 3: (continued)

CH_3COOH Total mg	H(+1) Aqueous Mg	Ca(+2) Aqueous mg	O(-2) Aqueous Mg	C(+4) Aqueous mg	Acetateion Aqueous mg
0	1.11E+05	69.2436	8.81E+05	48.0437	0
500	1.11E+05	273.092	8.81E+05	109.136	491.608
1000	1.11E+05	455.775	8.81E+05	163.885	983.215
1500	1.11E+05	629.93	8.81E+05	216.078	1474.82
2000	1.11E+05	798.872	8.81E+05	266.709	1966.43
2500	1.11E+05	964.1	8.82E+05	316.227	2458.04
3000	1.11E+05	1126.47	8.82E+05	364.888	2949.65
3500	1.11E+05	1279.36	8.82E+05	371.558	3441.25
4000	1.11E+05	1431.13	8.82E+05	369.486	3932.86
4500	1.11E+05	1583.48	8.82E+05	367.721	4424.47
5000	1.11E+05	1736.33	8.82E+05	366.195	4916.07
5500	1.11E+05	1889.6	8.82E+05	364.858	5407.68
6000	1.11E+05	2043.24	8.82E+05	363.673	5899.28
6500	1.11E+05	2197.22	8.82E+05	362.614	6390.89
7000	1.11E+05	2351.5	8.82E+05	361.66	6882.49
7500	1.11E+05	2506.06	8.82E+05	360.795	7374.1
8000	1.11E+05	2660.87	8.82E+05	360.005	7865.7
8500	1.11E+05	2815.92	8.82E+05	359.28	8357.31
9000	1.11E+05	2971.2	8.83E+05	358.611	8848.91
9500	1.11E+05	3126.68	8.83E+05	357.992	9340.52
10,000	1.11E+05	3282.36	8.83E+05	357.417	9832.12

CH_3COOH Total mg	H(+1) Vapor mg	O(−2) Vapor mg	C(+4) Vapor mg	Acetateion Vapor mg
0	0	0	0	0
500	0	0	0	0
1000	0	0	0	0
1500	0	0	0	0
2000	0	0	0	0
2500	0	0	0	0
3000	0	0	0	0
3500	0.523055	108.45	39.1498	6.70E−04
4000	1.15823	240.184	86.7055	1.71E−03
4500	1.79144	371.552	134.13	2.99E−03
5000	2.42325	502.668	181.464	4.50E−03
5500	3.05403	633.609	228.735	6.25E−03
6000	3.68407	764.436	275.966	8.23E−03
6500	4.31359	895.19	323.171	0.010441
7000	4.94273	1025.9	370.362	0.01287
7500	5.57162	1156.6	417.547	0.015519
8000	6.20034	1287.3	464.734	0.018382
8500	6.82897	1418.02	511.927	0.021456

Table 3: (continued)

CH_3COOH Total mg	H(+1) Vapor mg	O(−2) Vapor mg	C(+4) Vapor mg	Acetateion Vapor mg
9000	7.45758	1548.76	559.13	0.024738
9500	8.08618	1679.54	606.346	0.028223
10,000	8.71481	1810.35	653.578	0.031909

CH_3COOH Total mg	Ca(+2) Solid mg	O(−2) Solid mg	C(+4) Solid mg
0	3334.41	3993.36	999.303
500	3130.57	3749.23	938.211
1000	2947.88	3530.44	883.462
1500	2773.73	3321.87	831.269
2000	2604.79	3119.54	780.638
2500	2439.56	2921.66	731.12
3000	2277.19	2727.2	682.459
3500	2124.3	2544.1	636.64
4000	1972.53	2362.34	591.155
4500	1820.18	2179.88	545.496
5000	1667.33	1996.83	499.689
5500	1514.06	1813.27	453.754
6000	1360.42	1629.26	407.708
6500	1206.44	1444.85	361.562
7000	1052.16	1260.08	315.325
7500	897.6	1074.98	269.005
8000	742.787	889.575	222.609
8500	587.735	703.883	176.141
9000	432.461	517.923	129.606
9500	276.978	331.714	83.0085
10,000	121.298	145.268	36.3521

Figure 11 shows the saturation concentration of CO_2 in water as a function of pressure.

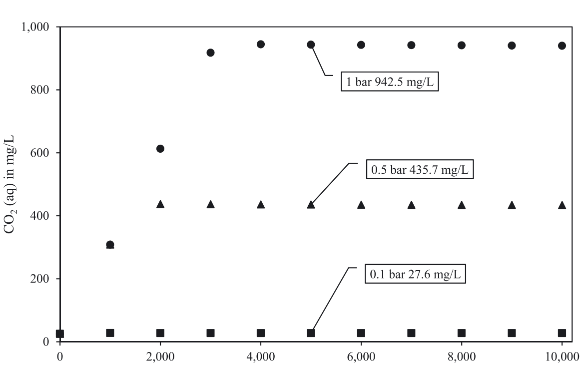

Figure 11: Saturation concentration of CO_2 as a function of pressure

Table 4 shows OLI models with different complexity in composition in comparison to experimental data.

Table 4: Comparison of experimental data with OLI models.

	Propionic acid	Acetic acid	n-butyric acid	Na	SO_4	Cl	Ca hardness	Discrepancy
VP5 experimental data	860	1840		590	340	360	2500	
OLI model assuming all acids can be represented with acetic acid and not considering ions		2700					2451	2%
OLI model assuming all acids can be represented with acetic acid and considering ions		2700		410	336	364	2634	5%
OLI model considering all acids and ions	860	1840		410	336	364	2496	0.02%

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