

# MECHANISMS OF DEGRADATION OF HYDRATE YIELD INHIBITORS BY WET OXIDATION

Loh J\*, Brodie G, Power G and Vernon C

CSIRO Light Metals Flagship / Parker CRC for Integrated Hydrometallurgy Solutions  
(CSIRO Minerals), WA, Australia

## Abstract

Organic compounds with adjacent hydroxyl groups inhibit gibbsite ("hydrate") precipitation. These hydrate yield inhibitors can be degradation products from the breakdown of larger organic molecules extracted from bauxite ore in digestion. It has been shown previously that yield inhibitors are readily destroyed at high temperature with or without oxygen.

This study investigates the reaction mechanisms of degradation of a set of known hydrate yield inhibitors in alkaline aluminate solutions by aerobic and anaerobic thermal degradation. The appearance of reaction products was monitored. Sodium oxalate was found to be the main organic degradation product from wet oxidation of the hydrate yield inhibitors studied. A reaction mechanism involving base-catalysed oxidation by water is proposed. This mechanism explains the formation of the degradation products observed. It also explains oxidation of organics in the absence of oxygen, and why it is that hydrogen is produced even in the presence of oxygen.

## Notation and Units

Standard North American terminology is used: C is the caustic concentration as g Na<sub>2</sub>CO<sub>3</sub> L<sup>-1</sup>, S is the total soda concentration as g Na<sub>2</sub>CO<sub>3</sub> L<sup>-1</sup> and A is the alumina concentration as g Al<sub>2</sub>O<sub>3</sub> L<sup>-1</sup>

## 1. Introduction

It is well known that there are organic compounds present in Bayer liquor that contribute to the inhibition of gibbsite growth by acting as seed poisons (Sato and Kazuma 1971; Norman *et al.* 1997; Smeulders *et al.* 2001). These compounds (referred to as hydrate yield inhibitors) are found in the degradation products of organic matter originating in the bauxite ore. Hydrate yield inhibitors have been observed in a single digestion pass with bauxite (Anderson *et al.* 2001). It has been established that hydrate yield inhibitors are characterised by adjacent hydroxyl groups and that some require only millimolar amounts to completely arrest gibbsite precipitation (Alamdari *et al.* 1993; Armstrong 1993; Coyne *et al.* 1994; Smith *et al.* 1996; Watling 2000; Watling *et al.* 2000).

Wet oxidation is an organics removal technique which involves exposing Bayer liquor to high temperatures and pressures in the presence of oxygen, causing oxidative degradation of the organic compounds. In principle, it is possible that the application of wet oxidation to Bayer liquor could contribute to the formation of hydrate yield inhibitors which could negate the benefits of a reduction in total organic carbon. Our recent investigations into the effect of wet oxidation on hydrate yield inhibitors (Loh *et al.* 2008) indicated that all of the yield inhibitors investigated were destroyed at 280 °C. Wet oxidation at 165 °C destroyed yield inhibitor compounds with more than 5 carbon atoms while compounds with 4 carbon atoms were stable under those conditions.

The mechanisms by which these compounds are destroyed under wet oxidation conditions are not well understood. There is generally more than one degradation pathway which is possible in the oxidation of a single organic compound forming several intermediate species which themselves may have various degradation pathways. Some of these pathways involve oxygen and a reactant, but oxidation also occurs in the absence of oxygen. The mechanisms of wet oxidation are further complicated in alkaline solutions because of possible reactions of the starting organic compound and the oxidised organic compound (intermediate species) with alkali. The complexity of this process is apparent in the degradation of cellulose by alkaline oxidation (Golova and Nosova 1973).

Published degradation mechanisms of wet oxidation reactions of Bayer organics (eg Tardio 2002; Tardio *et al.* 2004) account for the observed degradation products, but they fail to explain the following observations in the Bayer process:

### Oxidative reactions occur in the absence of oxygen

Sodium oxalate is a common degradation product of larger Bayer organics and is the result of an oxidative process. The majority of the sodium oxalate present in Bayer liquor is formed during the digestion process (Grocott 1988; Power and Tichbon 1990) which is generally acknowledged to occur under predominantly anaerobic conditions. The formation of oxalate (and carbonate) was also observed after the digestion of bauxite ore under nitrogen atmospheres (Yamada *et al.* 1981; Armstrong and Healy 2006) or low oxygen atmospheres (Sato and Kazama 1971; Gnyra and Lever 1979; Calalo and Tran 1993). Yamada *et al.* (1981) suggested that goethite present in bauxite ore may act as an oxidant in the absence of oxygen in an attempt to explain the apparent anomaly. However Power and Tichbon (1990) showed that the presence of goethite was not necessary to produce sodium oxalate.

### Hydrogen gas is produced under wet oxidation conditions

The production of hydrogen gas is commonly acknowledged in the alumina industry (Brown 1989; Anderson *et al.* 2001; Arnsward *et al.* 1991), but no reaction mechanism to describe its formation has been given. Hydrogen gas production has also been reported under oxidative conditions in non-Bayer solutions; for example, the degradation reaction pathway of the wet oxidation of glyoxalic acid included the formation of hydrogen gas under high oxygen partial pressures (Shende and Levec 1999), and the gas phase oxidation of formic acid can occur via a decarboxylation reaction which also produced hydrogen gas as a product (Ruelle *et al.* 1986).

The present work is a continuation of our studies of the effect of wet oxidation on Bayer organics (Loh *et al.* 2008). An additional four hydrate yield inhibitor compounds have been investigated to probe the apparent stability to wet oxidation of inhibitor compounds with less than 5 carbon atoms. The main focus of the work described here is the development of reaction mechanisms which explain the products formed in the degradation of yield

inhibitor compounds by wet oxidation. These mechanisms are based on standard organic reactions and also explain the common observations that oxidation reactions can occur under anaerobic conditions and that hydrogen gas can be produced.

## 2. Experimental

The experimental procedure has been reported in more detail elsewhere (Loh *et al.* 2008).

Two types of experiments were carried out for each yield inhibitor; with and without heat treatment. The heat treatment experiments were carried out at 165 °C and 280 °C in nitrogen and oxygen atmospheres. These two experiments were also carried out on sodium aluminate solution without the addition of an inhibitor compound (Control).

The effectiveness of wet oxidation and heat treatment in destroying yield inhibitors was determined using a standard precipitation test, in which seeded precipitation of gibbsite is carried out under strictly controlled conditions. These precipitation tests are used as an indirect measure of the inhibitors as direct analytical measurement of all of the organic compounds investigated is not generally available. It has been found that inhibitor effects are readily observed in a 2-hour test under conditions favouring nucleation over agglomeration and growth (Watling 2000; Watling *et al.* 2000). These conditions were therefore used in the current work, but it should be noted that the results are not directly comparable to the previous studies because of differences in the seed material and solution compositions.

### 2.1. Seed Material and Yield Inhibitors

The main chemical and physical characteristics of the high-purity gibbsite (OP25 hydrate, Rio Tinto Alcan Bauxite and Alumina, Canada) used to prepare the synthetic solutions and as the seed for precipitation tests are given in Table 1.

**Table 1. Characteristics of Gibbsite Material<sup>a</sup>**

Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO
66.7%	0.055%	0.016%	0.060%	0.004%
TOC	LOI <sup>b</sup>	SA <sup>c</sup>		D <sub>v</sub> , 0.5 <sup>d</sup>
0.0%	35.5%	0.19m <sup>2</sup> g <sup>-1</sup>		39.0µm

<sup>a</sup> elemental composition by XRF

<sup>c</sup> measured by 5 point N<sub>2</sub> BET

<sup>b</sup> measured by thermo-gravimetry

<sup>d</sup> measured by laser diffraction

Yield inhibitor compounds used in the current work were selected from a group of known yield inhibitors (Watling 2000; Watling *et al.* 2000; Smith *et al.* 1996) (Table 2).

**Table 2. List of yield inhibitors used in the current work.**

Yield Inhibitor	Molecular Formula
Glycerol	HOCH <sub>2</sub> CHOHCH <sub>2</sub> OH
Glyceric Acid	HOCH <sub>2</sub> CHOHCOOH
Threitol <sup>a</sup>	HOCH <sub>2</sub> (CHOH) <sub>2</sub> CH <sub>2</sub> OH
Threonic Acid <sup>b</sup>	HOCH <sub>2</sub> (CHOH) <sub>2</sub> COOH
Erythritol <sup>a</sup>	HOCH <sub>2</sub> (CHOH) <sub>2</sub> CH <sub>2</sub> OH
Erythronic Acid <sup>b</sup>	HOCH <sub>2</sub> (CHOH) <sub>2</sub> COOH
DL-Tartaric Acid	HOOC(CHOH) <sub>2</sub> COOH
Xylitol	HOCH <sub>2</sub> (CHOH) <sub>3</sub> CH <sub>2</sub> OH
Mannitol	HOCH <sub>2</sub> (CHOH) <sub>4</sub> CH <sub>2</sub> OH
Mannonic Acid	HOCH <sub>2</sub> (CHOH) <sub>4</sub> COOH
Sorbitol	HOCH <sub>2</sub> (CHOH) <sub>5</sub> CH <sub>2</sub> OH
Gluconic Acid	HOCH <sub>2</sub> (CHOH) <sub>5</sub> COOH
Gallic Acid	C <sub>7</sub> H <sub>6</sub> O <sub>5</sub>

<sup>a</sup> Threitol and Erythritol are structural isomers

<sup>b</sup> Threonic and Erythronic acids are structural isomers

Xylitol, sorbitol, glyceric and gluconic acids have been identified in water soluble organic compounds extracted from three plant species indigenous to the locations of bauxite deposits (Ellis *et al.* 2002). Gallic acid (3, 4, 5-trihydroxybenzoic acid) was included because it has the structural characteristics of hydrate yield inhibitors (adjacent hydroxyls) and was also found in the plant extracts (Ellis *et al.* 2002).

### 2.2. Experimental Procedure

Supersaturated sodium aluminate solutions were prepared by dissolving high-purity gibbsite (OP25 hydrate) in hot sodium hydroxide (AR) solution at atmospheric pressure. Sodium carbonate (AR) was dissolved separately in hot water and then added to the sodium aluminate solution. The solution was pressure filtered through a 0.45µm Supor membrane before dilution to volume with deionised water. Stock solutions were prepared for each of the selected yield inhibitors at a concentration of 300 mM. 1 mL of the stock solution was diluted to 50mL with sodium aluminate solution, to give a solution of 6 mM of the inhibitor. The initial concentration of the sodium aluminate mixtures (with and without the addition of an inhibitor) was 200 C, 240 S and 0.75 A/C. These solutions were used for precipitation tests directly (without heat treatment) or subjected to heat treatment prior to the precipitation tests.

Heat treatment of the solution was carried out in 250mL "bombs" (made from Inconel 600) with 50mL of the sodium aluminate solution. The headspace (200mL) of the bomb was filled with nitrogen or oxygen at atmospheric pressure using a glove box (1.4 mmol O<sub>2</sub> per mmol organic compound). The bombs were then sealed and heated by an external gas flame, and were continuously rotated during the reaction. The solution was held at the desired temperature (± 5 °C internal temperature) for 1 hour and then cooled rapidly by quenching with water. The solution was filtered through a 0.45µm Supor membrane and an aliquot (10mL) of filtrate was removed for analysis. The remainder of the filtrate was used immediately for the standard precipitation test without further adjustment.

The standard precipitation tests used 40mL of supersaturated sodium aluminate solution in 25mL Nalgene polypropylene bottles (as described elsewhere (Watling 2000)). The filtrate was analysed for aluminate, caustic and carbonate concentrations by titration (Connop and Morton 1997) and for five low molecular weight organic compounds (formate, acetate, oxalate, malonate and succinate) by ion chromatography. The solids were washed with hot deionised water, dried and weighed.

It is well known that hydrogen gas may be produced under alkaline digestion conditions (Arnsward *et al.* 1991) and it is likely that hydrogen gas may be produced under conditions of wet oxidation. Hydrogen production and oxygen consumption values from previous work on the digestion of Bayer liquor (Smith *et al.* 2000) were used here to estimate the H<sub>2</sub>:O<sub>2</sub> molar ratio for the solutions used in the present work. An organics loading of 6mM has been calculated to have a maximum H<sub>2</sub> production potential below the explosive range of 4 to 94% (Arnsward *et al.* 1991).

## 3. Results

Table 3 lists the yields from the standard precipitation tests for the blank and heat treatment experiments of the Control and hydrate yield inhibitor solutions. The extent of inhibition was determined by comparing the yields from a solution with yield inhibitor to the corresponding Control solution under the same experimental conditions. A decrease in the percentage yield inhibition after wet oxidation experiments is an indirect indication that the concentration of the yield inhibitor has decreased and also includes any possible inhibition effect of the degradation products.

**Table 3. Precipitation test yields (g Al<sub>2</sub>O<sub>3</sub> L<sup>-1</sup>) and % Yield Inhibition as a function of yield inhibitor compound with and without heat treatment.**

Yield Inhibitor	Without Heat Treatment (Precipitation Test Only)		With Heat Treatment							
			N <sub>2</sub> Atmosphere				O <sub>2</sub> Atmosphere (Wet Oxidation)			
			165 °C		280 °C		165 °C		280 °C	
	Yield	% Yield Inhibition	Yield	% Yield Inhibition	Yield	% Yield Inhibition	Yield	% Yield Inhibition	Yield	% Yield Inhibition
Control (None)	49.9	-	50.1	-	52.9	-	51.2	-	53.1	-
Glycerol	47.1	6	48.5	3	51.1	3	47.7	7	49.6	7
Glyceric Acid	37.9	24	45.5	9	49.9	6	45.2	12	51	4
Threitol	47.6	5	45.5	9	51.8	2	48.0	6	51.3	3
Threonic Acid	27.2	45	42.5	15	51.2	3	44.4	13	51.1	4
Erythritol	45.5	9	48.2	4	50.3	5	48.9	4	53.3	-
Erythronic Acid	41.8	16	43.2	14	50.5	5	44.1	14	51.2	4
DL-Tartaric Acid	33.0	34	31.8	37	53.8	3	32.4	36	52.5	1
Xylitol	27.7	44	44.0	12	53.4	0	48.7	5	52.4	1
Mannitol	29.2	41	33.4	33	49.6	6	49.4	4	51.8	2
Mannonic Acid	25.8	48	33.4	33	52.6	0	48.5	5	50.7	5
Sorbitol	0.0	100	25.2	50	48.1	9	48.9	4	51.4	3
Gluconic Acid	0.5	99	39.1	22	52.0	0	51.9	0	51.9	2
Gallic Acid	36.1	28	43.5	13	50.1	5	51.2	0	51.7	3

Experimental error (1σ) is estimated at 1.6 g Al<sub>2</sub>O<sub>3</sub> L<sup>-1</sup> for the precipitation yields.

The yield inhibition of the added inhibitor compounds in the tests without heat treatment ranged from 5% to 100% (i.e. no precipitation at all) when compared to the yield obtained from the Control solution (no yield inhibitor added). The inhibition effects were reduced by variable amounts by treatment at 165 °C under nitrogen, from essentially no reduction for threitol, erythronic and tartaric acids to 70% reduction (i.e. from 99% yield inhibition to 22% yield inhibition) for gluconic acid. Increasing the temperature to 280 °C removes almost all of the inhibition effects irrespective of the composition of the atmosphere. At 165 °C in the presence of oxygen, only those with > 5 carbon atoms were destroyed, but for C3 or C4 inhibitor compounds, the reduction in yield inhibition was independent of the atmosphere indicating that those inhibitors can be destroyed thermally in the absence of oxygen.

Figure 1 outlines the relative distributions of the low molecular weight degradation products observed for each yield inhibitor under the different conditions. Formate was produced at 165 °C under nitrogen and oxygen atmosphere (Figure 1A and 1C) while oxalate was the main organic degradation product at 280 °C in the presence of oxygen (Figure 1D). Formate, acetate and oxalate were the main degradation products at 280 °C under a nitrogen atmosphere (Figure 1B). Succinate was not observed as a degradation product. Malonate was observed only from the degradation of tartaric acid.

#### 4. Discussion

The overall ranking of the extent of gibbsite yield inhibition in the blank experiments agrees well with previous investigations (Watling 2000; Smith *et al.* 1996; Coyne *et al.* 1994; Alamdari *et al.* 1993). Our results also indicate that yield inhibition increased with the acidity of the inhibitor compounds (compare threonic acid and threitol, Table 3), consistent with previous observations (Watling 2000).

The inhibition effects of the yield inhibitors investigated were almost completely removed at 280 °C in both oxygen and nitrogen atmospheres. This demonstrates that oxygen is not necessary for the degradation of these inhibitors at this temperature (Table 3). Inhibitor compounds with > 5 carbon atoms were degraded

to some extent at 165 °C with nitrogen, but required oxygen for essentially full destruction at this temperature.

The apparent stability of C4 compounds observed previously (Loh *et al.* 2008) at 165 °C was observed here for erythritol and erythronic acid and also for C3 compounds (glycerol and glyceric acid). The reductions in yield inhibition effects observed for erythritol, glyceric and threonic acids were similar under oxygen and nitrogen atmospheres, indicating a common mechanism not involving oxygen. For glycerol, threitol, tartaric and erythronic acids, the lack of change in the inhibition effect relative to the blank experiment (no wet oxidation or heat treatment) indicated that these compounds were stable to at 165 °C even in the presence of oxygen.

Information about the degradation reaction mechanisms can be derived from the types of degradation products observed and the conditions under which they were formed. The proposed reaction mechanisms for the degradation of yield inhibitors are based on standard organic reactions. However, the conditions under which the wet oxidation and heat treatment experiments in the present work have been carried out (165 °C and 280 °C at pH 14) are considered "extreme" when compared to the conditions usually used for organic syntheses. The current experimental conditions therefore increase the probability of occurrence of reaction pathways that would not be favoured under milder conditions. The mechanisms proposed here account for the observed degradation products under the experimental conditions investigated, and incorporate the overall observations from the current investigation as well as standard organic reactions which occur in alkaline solution. The mechanisms proposed explain the occurrence of oxidation under anaerobic conditions, and also how hydrogen gas is produced under even in the presence of oxygen.

The proposed mechanisms are illustrated for the case of the reactions of tartaric acid (present in alkaline solutions as the tartrate anion). Oxidative reactions were observed under a nitrogen atmosphere; oxalate was observed as a degradation product at 280 °C (Figure 1B). This is in agreement with previous reports (Yamada *et al.* 1981; Armstrong and Healy 2006). In the absence of oxygen, oxidation via a free radical reaction is

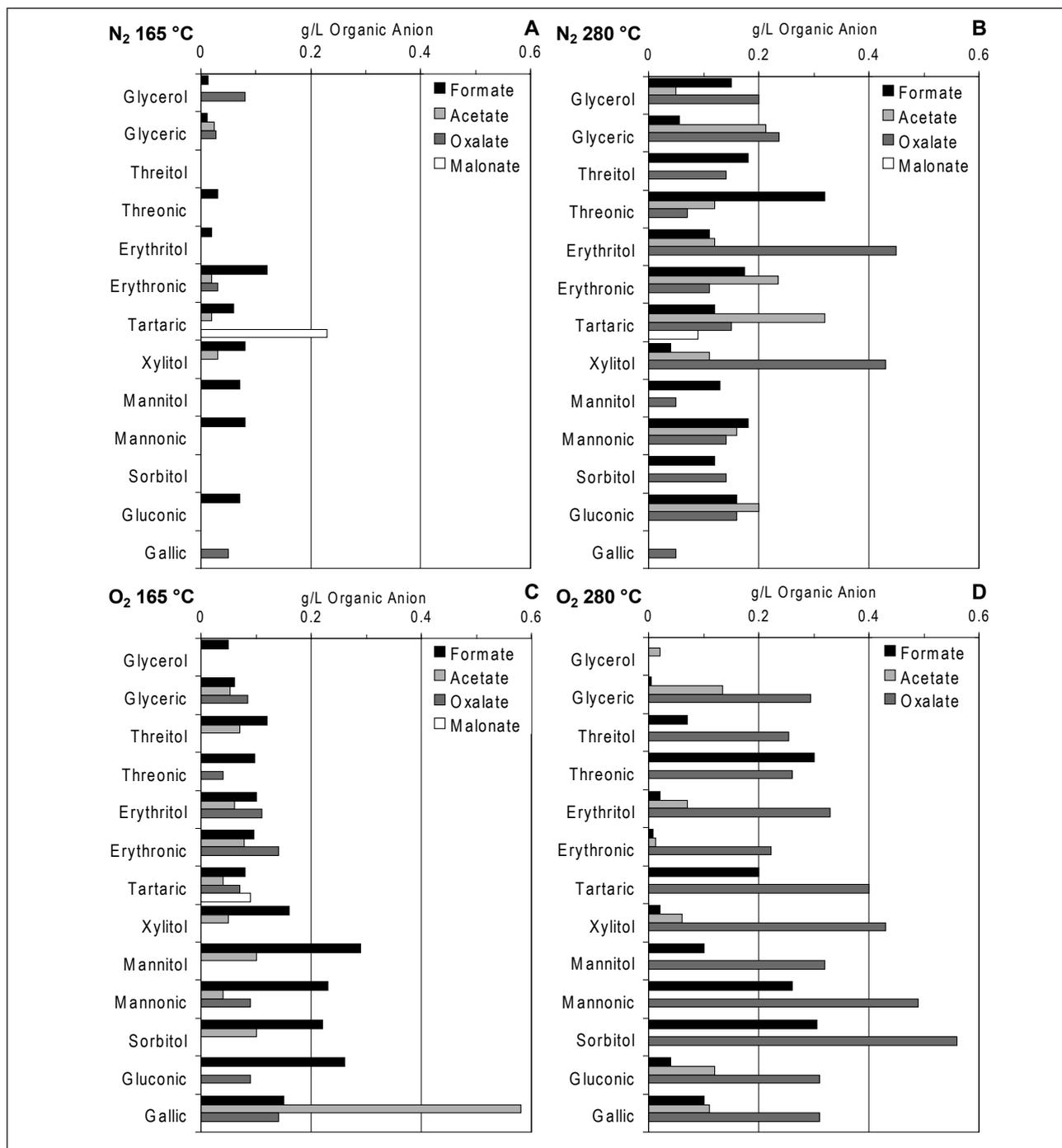


Figure 1. The distribution of low molecular weight degradation products of hydrate yield inhibitors after wet oxidation ( $O_2$ ) or heat treatment ( $N_2$ ) at 165°C and 280°C.

unlikely to occur and so oxidation is more likely to be via an ionic reaction.

#### 4.1. Base-catalysed oxidation by water

The proposed ionic reaction mechanism for an oxidation reaction in an anaerobic atmosphere (nitrogen) can be described as a **base-catalysed oxidation by water** (Reaction 1, Scheme 1). It involves a nucleophilic attack by a hydroxyl ion on a carbonyl carbon followed by a hydride transfer to a water molecule, producing hydrogen gas and regenerating the hydroxyl ion. The proposed mechanism is similar to the Cannizzaro reaction (Reaction 2, Scheme 1).

The degradation of tartrate produced formate, acetate, malonate and oxalate as degradation products (Figure 1). Scheme 2 describes the proposed degradation reaction mechanisms of tartrate which lead to the formation of formate (6) and oxalate

(9). Cleavage of tartrate can be initiated by the removal of the hydrogen of the hydroxyl group (Reaction A).

The alkene species (2) undergoes a hydrogenation of the double bond to form a primary alcohol (4) (Reaction B). Decarboxylation of 4 produces formaldehyde (5) and hydrogen gas (Reaction C). Nucleophilic attack on the carbonyl carbon of the formaldehyde forms species 6 (Reaction D). Species 6 can undergo a base-catalysed oxidation by water (Reaction E) to produce formate (7) and hydrogen gas (similar to Reaction 1, Scheme 1). Species 6 may also undergo a Cannizzaro reaction to produce formate (7) and methanol (8) (Reaction F) (similar to Reaction 2, Scheme 1).

The initial cleavage reaction (Reaction A) also produces species 3. Nucleophilic attack on the carbonyl carbon of 3 results in the intermediate species 9 (Reaction G). This intermediate

undergoes a base-catalysed oxidation by water (Reaction H) forming oxalate (**10**), hydrogen gas and hydroxyl ion.

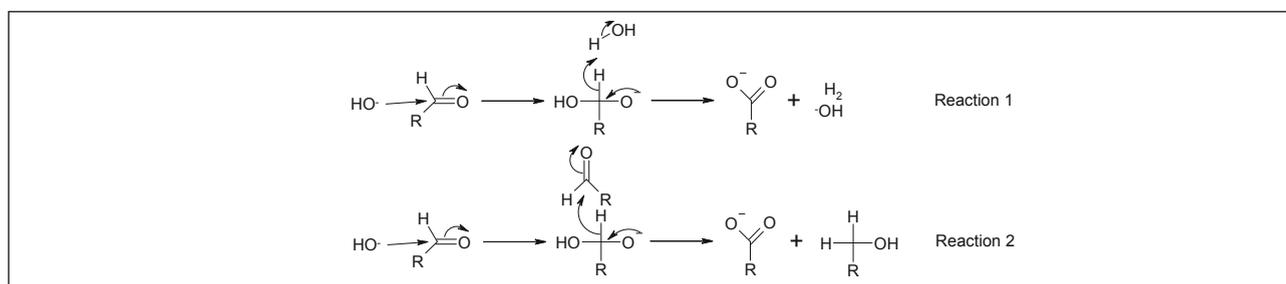
Scheme 3 describes the proposed degradation reaction mechanisms of tartrate (**1**) to form acetate (**15**). Decarboxylation (Reaction I) produces an enol species (**11**) which is in equilibrium with the keto form (**12**). Decarboxylation of the keto form (**12**) (Reaction J) and hydrogenation of the double bond (Reaction K) produces acetaldehyde (**13**) and hydrogen gas. [Acetaldehyde has been tentatively identified in a sample of non-condensable gas from a Worsley digestion heater (Forster *et al.* 2005).] Nucleophilic attack on the carbonyl carbon of acetaldehyde forms the species **14** (Reaction L). This intermediate undergoes a base-catalysed oxidation by water (Reaction M) to form acetate (**15**), hydrogen gas and hydroxyl ion.

Malonate was only observed as a product of reaction of tartaric acid (Figure 1A-C). This occurs under all conditions except 280 °C

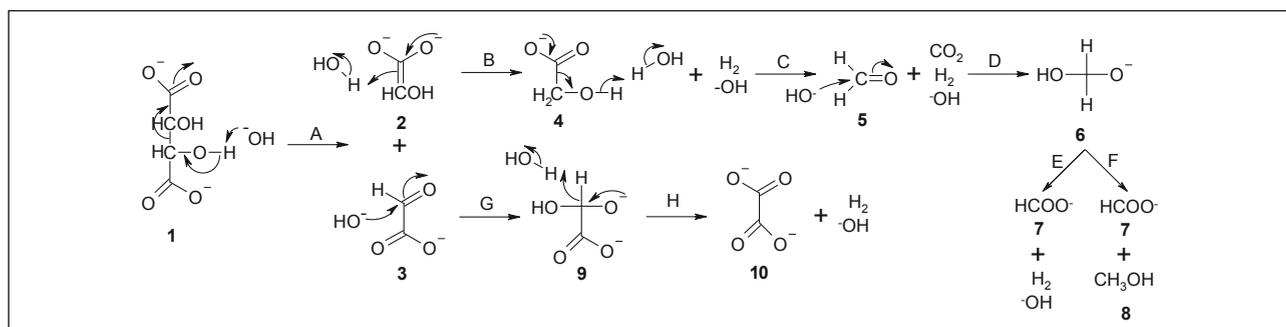
with oxygen, under which conditions malonate itself is destroyed. Tartaric acid is the only yield inhibitor compound investigated with two carboxylic groups present in the molecule.

*This observation implies that oxidation of a primary (terminal) alcohol did not occur under these conditions, and that oxidation of secondary alcohols after a cleavage reaction is preferred.*

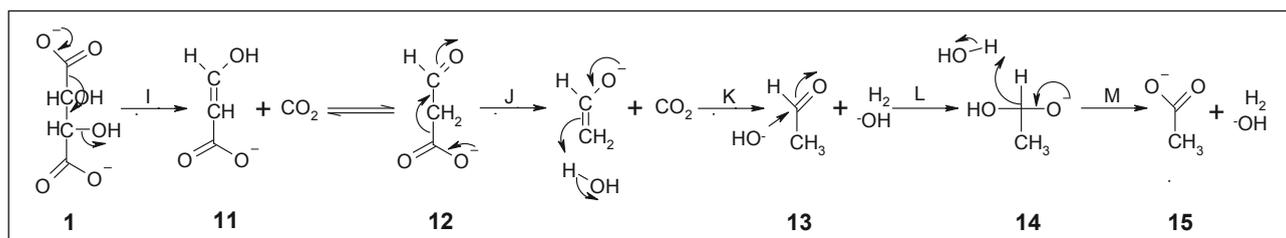
In the degradation of tartrate (**1**) to form malonate (**19**) (Scheme 4), decarboxylation of the carbanion and the elimination of a hydroxyl ion occur first (Reaction N). The resulting enol species (**17**) is in equilibrium with the keto form (**18**). Nucleophilic attack on the carbonyl carbon of the keto form by hydroxyl ion then occurs (Reaction O) which then undergoes a base-catalysed oxidation by water to produce malonate (**19**), hydrogen gas and hydroxyl ion (Reaction P). This reaction is an example of the oxidation of a secondary alcohol after a cleavage reaction; in this case, a decarboxylation reaction, Reaction N). Malonate



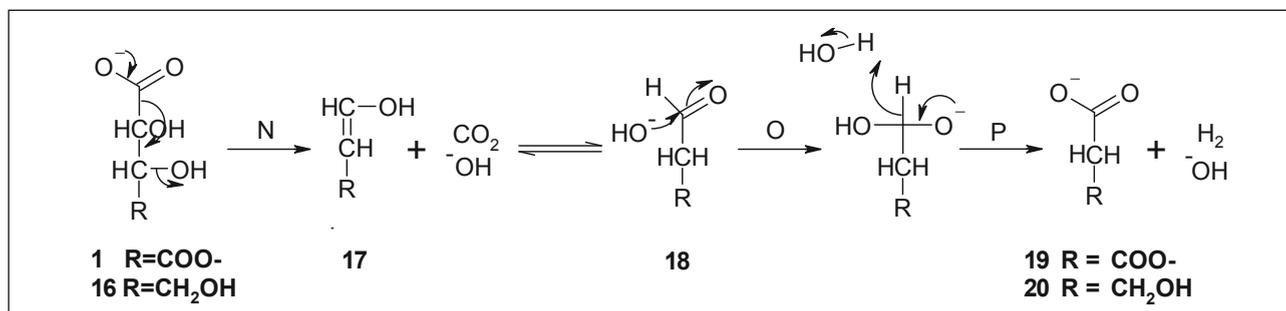
Scheme 1. Reaction mechanisms depicting base-catalysed oxidation by water producing hydrogen gas (Reaction 1) and a standard Cannizzaro reaction (Reaction 2).



Scheme 2. Proposed degradation reaction mechanisms for tartrate (**1**) to produce formate (**7**) and oxalate (**10**).



Scheme 3. Proposed degradation mechanisms for tartrate (**1**) to produce acetate (**15**).



Scheme 4. Proposed degradation reaction mechanisms of tartrate (**1**) to produce malonate (**19**) with the formation of hydrogen gas.

was not observed from other yield inhibitors (e.g. **16**, erythronic acid) indicating that oxidation of the terminal hydroxyl group to a carboxylic group does not occur under these conditions, resulting in a final product similar to **20**.

The degradation reaction mechanisms proposed here can also explain other reactions such as acetate and oxalate being preferentially produced from acidic yield inhibitors (Figure 1B and 1C).

The present work has confirmed the apparent stability of C4 hydrate yield inhibitor compounds to wet oxidation at 165 °C, and this stability was also observed for C3 inhibitor compounds. Reaction mechanisms for the degradation of hydrate yield inhibitors have been proposed. The proposed reaction mechanisms can be described as base-catalysed oxidation by water and explains how oxidation reaction can occur under anaerobic conditions, and how hydrogen gas can be produced even in the presence of oxygen.

## 5. Conclusions

This work has shown that the hydrate yield inhibitors investigated were not stable when exposed to 280 °C for one hour in oxygen or nitrogen atmospheres. *It is therefore unlikely that wet oxidation treatment of Bayer liquors will result in an increase in yield inhibitors at this temperature.* The apparent stability of hydrate yield inhibitor compounds with 4 carbon atoms to wet oxidation at 165 °C has been confirmed, and this behaviour was also observed for C3 inhibitor compounds. *It is therefore possible that some low molecular weight yield inhibitor compounds may be produced by wet oxidation at low temperature.*

The solutions after oxidation were analysed for five potential low molecular weight products (formate, acetate, oxalate, malonate and succinate). Of these, the main degradation produced at 165 °C and 280 °C were formate and oxalate respectively.

Ionic reaction mechanisms have been proposed for the degradation of the hydrate yield inhibitor compounds by heat treatment under aerobic (wet oxidation) and anaerobic conditions. The mechanisms involve base-catalysed oxidation by water, similar to the Cannizzaro hydride transfer reaction. They account for the observed degradation products and explain the well established observations that oxidative reactions occur under anaerobic conditions, and that production of hydrogen gas is produced even in the presence of oxygen.

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