

# POISONS, POLYOLS AND PRECIPITATION

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## ABSTRACT

Polyols are organic compounds with a hydroxyl functional group at every carbon atom. They are related closely to the simple sugars, and are active in physiological processes, at least in part because of their ability to form strong complexes with multivalent cations. Their value to us is in the use of their complexation properties to probe the mechanisms of poisoning of gibbsite precipitation under strongly alkaline conditions.

Methods have been developed with which the effects of organic compounds on specific precipitation processes (gibbsite nucleation, agglomeration and growth) and their adsorption on a partially hydrated alumina (gibbsite-like) surface can be quantified. Data obtained from these studies have been supplemented by mechanistic information about their interactions with aluminate ions and with a gibbsite-like surface, obtained using NMR and vibrational spectroscopy.

The comparative results obtained are discussed in relation to the mechanisms by which polyols might interact with a gibbsite surface.

## **KEY WORDS:**

gibbsite precipitation, crystallization poisons, polyols, Bayer process

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### **1.0 INTRODUCTION**

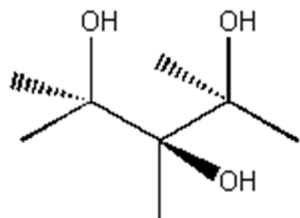
#### **1.1 Bayer Precipitation and Organics**

In the Bayer Process gibbsite in bauxite ore is dissolved in hot, sodium aluminate solution and then re-precipitated after unwanted solid materials such as aluminosilicates and iron-rich compounds have been separated from the solution. However, organic compounds derived from the ore, or added to improve the process, accumulate to quite high concentrations in the recycled plant liquor.

The organic compounds in plant liquors not only affect the yield and quality of the gibbsite product but also further inhibit (poison) an already slow precipitation process (Power, 1991). A number of correlations can be demonstrated when the results from several studies on the effects of specific compounds on gibbsite precipitation from plant and synthetic liquors are compared. For example, compounds which are adsorbed onto gibbsite are often those which cause a significant decrease in gibbsite yield as well as an increase in sodium content (Grocott and Rosenberg, 1988; Armstrong, 1993; Coyne *et al.*, 1994).

These inhibitory effects can be used to advantage in studies about the mechanisms of precipitation poisoning, by choosing model organic compounds, in this case selected polyols, rather than those compounds which occur naturally in plant liquors.

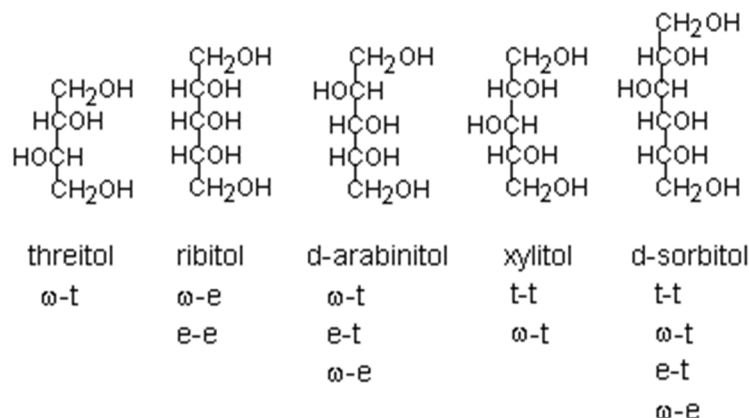
### 1.2 Useful Properties of Polyols



The ability of polyols to complex cations (at acid to neutral solution pH) and the role that stereochemistry plays in complexation have been collated by Angyal (1989) in a comprehensive review on complexes of metal cations with carbohydrates. Comparative data on the structures of complexes and their relative strengths reinforce his conclusion that polyols form complexes with metal cations in solution if they contain at least three hydroxyl groups in a favourable steric arrangement, the "M,P arrangement". The M,P arrangement is not naturally favoured but every polyol can take up the conformation by rotation around a C-C bond; however, the energy required varies with the configuration so that different polyols form complexes to a different extent under the same conditions. Tridentate bonding increases the stability of the complex, increasing the possibility of complex formation in alkaline solutions with metal anions, such as borate and ferrate (Angyal, 1989).

### 1.3 This Study

Threitol (C4), ribitol, arabinitol and xylitol (C5 stereoisomers), and sorbitol (C6) are five of a number of polyols which have been used for method development and to investigate correlations between poisoning of gibbsite precipitation, adsorption on a hydrated alumina surface and aluminate ion complexation in solution at high pH. Between them they exhibit the configurations which affect the rank order of polyol interactions (Angyal, 1989).



The tendency of three vicinal oxygen atoms in a polyol to form complexes with metal ions decreases in the following order:

t-t: threo-threo sequence  
 ω-t: threo pair next to primary hydroxyl  
 e-t: erythro-threo sequence  
 ω-e: erythro pair next to primary hydroxyl  
 e-e: erythro-erythro sequence

## 2.0 EXPERIMENTAL

### 2.1 Precipitation

Gibbsite was precipitated from seeded aluminate solutions at different supersaturations and temperatures. Organic compounds were dissolved into the solutions just prior to seeding with either C31 or Hydral-710. In this way it was possible to study their effects on nucleation (C200, A/C 0.7, 60°C), agglomeration (C200, A/C 0.7, 80°C), or growth (C200, A/C 0.55, 80°C), largely independently of the other processes. The effects of polyols on gibbsite morphologies were also investigated in parallel, unseeded precipitation tests (C200, A/C 0.7, 60°C).

### 2.2 Adsorption

Details of the methods for preparation of aluminate solutions (1.15 M  $\text{NaAl}(\text{OH})_4$  with 2.1 M NaOH excess), adsorption of polyols onto alumina and their quantification are described by van Bronswijk *et al.* (1999). The alumina surface on which adsorption took place was shown by vibrational spectroscopy to be partially hydrated and to have a surface-spectrum resembling that of gibbsite.

### 2.3 Spectroscopy

Stock solutions of aluminium in sodium hydroxide were prepared by dissolving aluminium wire in a 2 M sodium hydroxide solution. These were used to prepare a number of solutions having different polyol to aluminate ratios and a final hydroxide concentration of 1 M.

$^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were obtained with a Varian Gemini 200 MHz Nuclear Magnetic Resonance spectrometer at ambient temperature. Spectral acquisition was optimised dependant upon the solution. Raman spectra were obtained with a Bruker RFS100 FT-Raman spectrometer and a Nd:YAG (1064 nm) laser at 4  $\text{cm}^{-1}$  resolution. Infrared spectra were obtained with a Bruker IFS-66 FT-IR spectrometer and a Dipper-210 ATR solution probe at 4  $\text{cm}^{-1}$  resolution and corrected for water absorption by a scaled subtraction of an appropriate caustic solution spectrum.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Effects of Polyols on Gibbsite Precipitation

Threitol has the least effect on gibbsite crystal growth, the effect increasing with increased number of hydroxyl groups through the C5 isomers to sorbitol (Figure 1). Of particular interest is the variation across the C5 compounds, ribitol < arabinitol < xylitol.

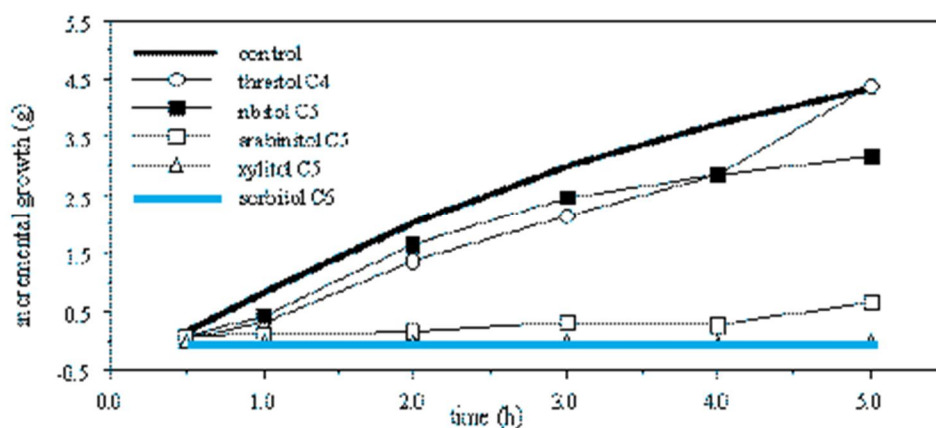


Figure 1

Comparative inhibition of gibbsite growth (low supersaturation, 80oC)

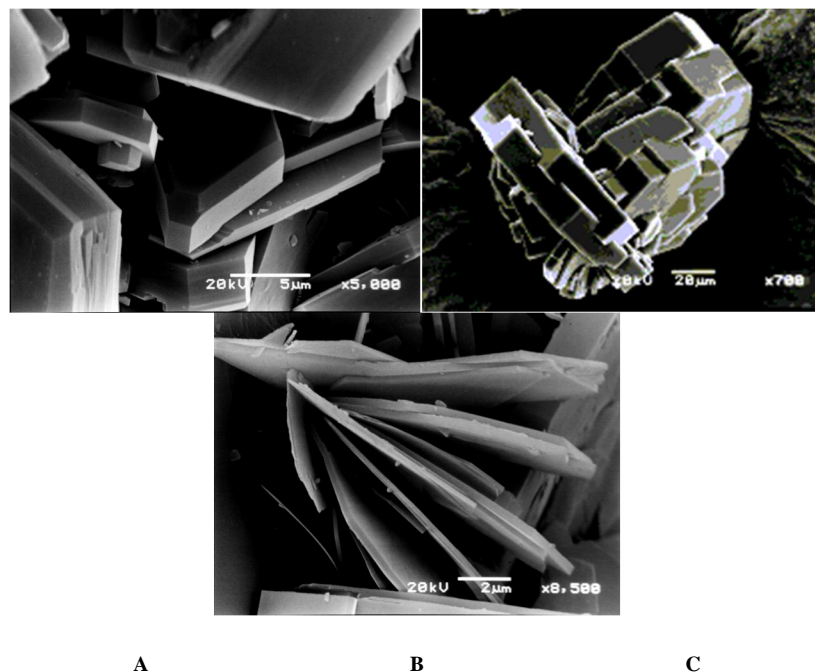
by polyols at a concentration of 6 mM.

In similar tests at intermediate supersaturation (agglomeration) and high supersaturation (nucleation), the polyols were found to decrease overall precipitation yield as a function of time, and to delay and inhibit both agglomeration and nucleation processes in the same rank order as found for growth.

Inhibition of precipitation was also found in parallel, unseeded tests and was accompanied by interesting changes in the morphologies of the gibbsite crystals formed. Gibbsite crystals grown from pure solutions are well-formed

hexagons with chamfered faces and smoothed surfaces. Similar crystals are formed in the presence of low concentrations of crystallization inhibitors (Figure 2).

In the presence of stronger inhibitors, chamfered faces are reduced or absent, crystals are thinner and/or needles may be formed. The morphological changes depend on both the strength of the inhibitor and the polyol concentration but are not predictable on the basis of either. They may occur without there necessarily being a reduction in precipitation yield and may be accompanied by roughening of crystal surfaces, a reduction in overall crystal size and an increase in fine material. Low concentrations of polyols promote scale formation.



**Figure 2**

Changed gibbsite morphologies in the presence of

(A) 4 mM xylitol; (B) 8 mM arabinitol; (C) 8 mM ribitol.

### **3.2 Adsorption on a Hydrated Alumina Surface**

The amounts of polyol adsorbed onto a high-surface-area, partially-hydrated aluminium oxide increased with increasing number of hydroxyl groups (threitol<arabinitol<sorbitol), illustrated for threitol and sorbitol, the two end-members of the ranked series (Figure 3). Adsorption reduces the imbalance of attractive forces that exist at a surface, reducing the surface free energy of a heterogeneous system. The free energies calculated from the first part of the Langmuir adsorption isotherms show that binding of threitol is weaker than that of sorbitol by 2-3 kJ mol<sup>-1</sup> for the initial adsorption. The second plateau in the isotherm may indicate the possible presence of more than one type of adsorption site.

Superimposed on this is the effect of stereochemistry; the C5 polyols exhibited the expected differences, ribitol<arabinitol<xylitol, in adsorption strengths.

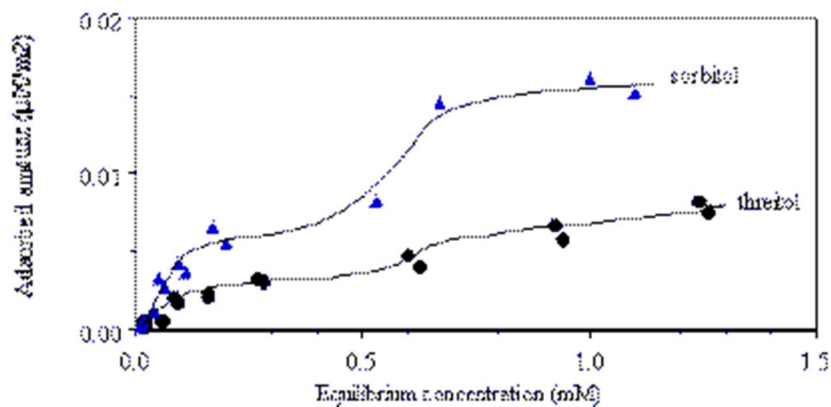


Figure 3

Adsorption isotherms for threitol (C4) and sorbitol (C6) adsorbed from aluminate solutions 2.75 M NaAl(OH)<sub>4</sub> and 1 M NaOH (pH 14) onto an alumina surface.

### 3.3 Complexation with Aluminate Ions

Differences in solution NMR and Raman spectra (illustrated for xylitol in Figures 4 and 5) indicate that polyol-aluminate complexes are formed in alkaline solutions to varying extents. The trend is towards greater complexation with increasing number of hydroxyl groups (threitol<arabinitol<sorbitol), with complexation among the C5 polyols increasing from ribitol<arabinitol<xylitol, as was found for both crystallization inhibition and adsorption.

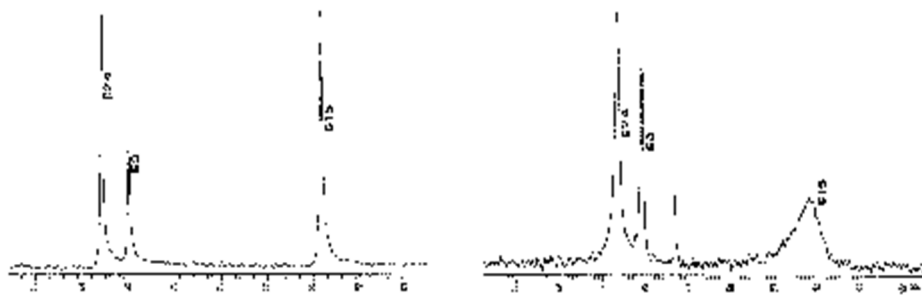


Figure 4

<sup>13</sup>C nmr spectra of alkaline-xylitol (left) and aluminate-xylitol (right).

(an unidentified impurity is not labelled)

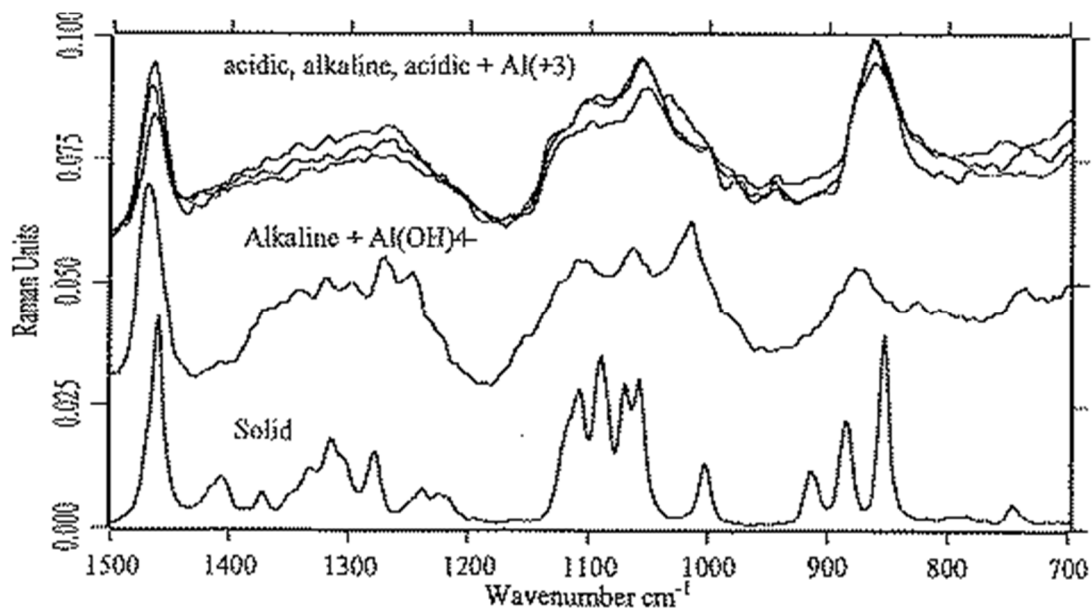


Figure 5

Raman spectra of xylitol in acidic (pH 2) and alkaline (pH 14) solution without aluminium ions; xylitol in acidic (pH 2) solution with  $Al^{3+}$ , and in alkaline (pH 14) with  $Al(OH)_4^-$  ions. A spectrum for crystalline xylitol is also shown.

For the three C5 polyols, the above outcomes can be predicted by the ease with which the M,P configuration is adopted. For xylitol the three C2-C4 hydroxyl groups are already in this configuration and rotation about the terminal carbon bonds aligns the C1 and C5 hydroxyls as well. Arabinitol can form the M,P arrangement by rotation about the terminal (threo-adjacent OH) bond to bring the terminal hydroxyl into the axial position. However, this introduces a gauche interaction in the chain and is an unfavourable configuration. Ribitol can only adopt the M,P arrangement by rotation about the erythro-erythro bond forming the so-called "sickle" arrangement, which results in a 1,3 parallel interaction as well as gauche interactions so that complex formation is not favoured.

Sorbitol has the structure of xylitol with an additional C-OH and so will adopt the M,P configuration with the same ease as xylitol. It is therefore not surprising to find its activity is similar to that of xylitol. These stereochemical factors help explain the correlation between the complexing ability of aluminate ions at high pH, slow gibbsite growth, increased adsorption and nucleation inhibition.

#### 4.0 DISCUSSION

Adsorption, complexation and inhibition of gibbsite growth can all be correlated to the increasing number of hydroxyl groups present and in the case of the C5 and C6 compounds the stereochemistry of the individual polyol (Table 1).

Table 1

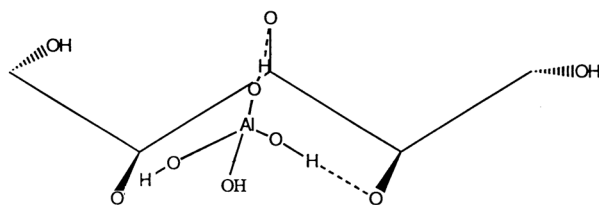
The comparative effects of five polyols on precipitation, adsorption and complex formation

Test	threitol	ribitol	arabinitol	xylitol	sorbitol
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seeded precipitation yield (expressed as a % of that in the control); 6 mM polyol	84	85	58	11	6
unseeded precipitation yield (as % of that in control); 10 mM polyol	89	100	30	<1	<1
adsorption on gibbsite-like alumina surface (mol g <sup>-1</sup> ) polyol concentration 0.075 mM	1.00 x 10 <sup>-7</sup>	0.27 x 10 <sup>-7</sup>	1.30 x 10 <sup>-7</sup>	2.20 x 10 <sup>-7</sup>	2.00 x 10 <sup>-7</sup>
evidence from spectroscopy of complex formation (additional bands and band shifts)	6	6	4	4 4	4 4

Preliminary data suggests that adsorption is particularly sensitive to polyhydroxy configuration and that it tends to parallel the trend observed for the inhibition of gibbsite precipitation under different conditions. Specifically, adsorption increases with increasing numbers of vicinal hydroxy groups and threo-threo sequences promote adsorption whilst erythro-erythro sequences have little effect.

From adsorption experiments it appears hydroxyl groups on the lower order, C4, polyols are possibly physisorbed via a weak Al-O(H)...H-O-C or Al-O-H...(H)O-C interaction whilst the higher order (more acidic) polyols are likely to be chemisorbed via stronger hydrogen bonding through an Al-O-H← -O-C interaction. As adsorption experiments were conducted at pH 14, it is expected that deprotonation of the more acidic protons of the hydroxyl groups occurs, supporting the chemisorbed hypothesis (Figure 6).



**Figure 6**

Possible binding of the aluminate ion with xylitol.

The strong correlation between adsorption and inhibition of crystallization for the polyols studied thus far is consistent with the view that adsorption is a factor in the mechanism of such inhibition. The correlation can be extended further to include their ability to form complexes with aluminate ions in strongly alkaline solutions.

The different complexing abilities of C5 stereoisomers (xylitol>arabinitol>>ribitol) is readily explained in terms of the ability of each to adopt the M,P arrangement and enter into tridentate complexation. Although it is a widely held view that aluminium complexes with hydroxy-organic compounds, but that these either do not exist or are unstable at

high pH, our results confirm the earlier data of Smith et al. (1996) that polyol-aluminate complexes can form readily, depending on steric factors, and are stable at high solution pHs.

These authors suggested that complexation occurred through oxo-bridges between aluminate ions and deprotonated polyol hydroxide groups releasing water via a condensation reaction. Our spectroscopic data tend to support an alternate mechanism (Figure 6), in which deprotonated polyol hydroxide groups are stabilised via hydrogen bonding with aluminate ions (C-O--H--O-Al). It is possible that complexation in solution and adsorption on a gibbsite-like surface may occur by a similar interaction.

## **5.0 SUMMARY**

Selected polyols of different carbon chain length and stereochemistry show a range of inhibitory effects on gibbsite nucleation, agglomeration and growth from caustic aluminate solutions. Parallel trends are observed for surface adsorption and solution complexation. They are thus excellent model compounds with which to probe the mechanisms of gibbsite precipitation. The combination of methods gives both solid and solution data which can be used to describe or quantify polyol-gibbsite and polyol-aluminate ion interactions.

Comparative data demonstrate strong correlations between the ability of different polyols to form solution complexes with aluminate ions in strongly alkaline (pH 14) solutions, to adsorb on a hydrated alumina surface, and to poison gibbsite precipitation, not only by reducing overall precipitation yield but also by affecting the quality of the product.

Clearly further research is needed, particularly in relation to surface adsorption and solution complexation, before we are in a position to describe the mechanisms by which polyols affect gibbsite precipitation. However, we believe our continuing studies using such model compounds should enable the mechanisms of gibbsite precipitation poisoning to be elucidated and, indirectly, should provide information on mechanisms of gibbsite growth.

## **ACKNOWLEDGMENTS**

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