

TABLE 1

Effect on precipitation particle size and yield
of supplier products and known chemicals

Supplier/ Product	Dose ppm	Component Identification			Relative Change in +7.5um %	Yield Change %
		Compound known	Generic Group	Compound Unknown		
A A1	50			X	-5	-10
A A2	50			X	-71	-93
A A3	50			X	-10	-15
A A4	50		X		-2	-5
A A5	50			X	-11	0
A A6	50			X	0	-9
A A7	50		X		-32	n.d.
A A8	50		X		-25	n.d.
A A8.1	25			X	-9	n.d.
A A8.2	25			X	-6	n.d.
A A9	50			X	0	0
B B1	50	X			0	0
B B2	50		X		0	0
B B3	50		X		-9	0
B B4	50		X		+8	-8
B B5	50			X	-43	-5
B B6	50			X	-28	-3
B B7	50		X		+1	0
B B8	50		X		+20	-2
C C1	50		X		+7	0
C C2	50			X	-19	0
C C3	50		X		-10	0
C C4	50			X	-7	0
C C5	50			X	-12	0
C C6	50			X	-12	0
D D1	50		X		-9	-9
D D2	50			X	-17	-11
D D3	50			X	-20	-11
E E1	100		X		-20	n.d.
E E2	100			X	-32	n.d.
E E3	100		X		-62	n.d.
E E4	100			X	-37	n.d.
E E5	100	X			+3	n.d.
E E6	50			X	+24	+3
E E7	100			X	-12	-10
E E8	100			X	-19	-7

n.d = not determined

TABLE 1
Effect on precipitation particle size and yield
of supplier products and known chemicals
(continued)

Supplier/ Product	Dose ppm	Component Identification			Relative Change in +75um %	Yield Change %
		Compound known	Generic Group	Compound Unknown		
E	E9	50		X	-21	-10
	E10	50		X	+7	-3
	E11	50		X	+27	0
	E12	50		X	+22	0
	E13	50		X	+7	0
	E14	50		X	+8	-2
	E15	50		X	-4	0
	E16	50		X	-77	+4
	E17	50		X	-42	0
	E18	50		X	+4	-6
	E19	50		X	-6	-6
E20	50		X	-54	-18	
F	F1	50		X	-59	-4
	F2	50		X	-41	-4
	F3	50		X	-59	-4
	F4	50		X	-24	-8
OTHERS	50	X			+9	0
	50	X			+3	0
	100	X			+19	-13
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	100	X			0	0
	50	X			-68	n.d.
	50	X			-72	n.d.
	50	X			+9	n.d.
	50	X			+7	n.d.
	50	X			+3	n.d.
50	X			+8	n.d.	

n.d. = not determined

OPTIMISATION OF YIELD FROM CONTINUOUS ALUMINA HYDRATE PRECIPITATION

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ABSTRACT

The yield in the Bayer precipitation circuit is affected primarily by the alumina supersaturation, caustic concentration, temperature profile, seed surface area, holding time and impurities.

Optimisation of the precipitation yield requires a knowledge of the interaction of these various factors, and is best handled by computer simulation using rate data obtained in the laboratory.

Batch experiments were carried out over a range of conditions on Plant and synthetic liquors to derive rate constants and equilibrium relationships. The synthetic liquors were organic free, but contained similar levels of other impurities as Plant liquors.

The rate constants were used in a continuous precipitation model with results matched to actual Plant performance using a seed effectiveness factor.

The model was then used to determine the optimum temperature and caustic concentration for the continuous precipitators. The model is also a useful tool for quantifying the benefit of other strategies such as additional holding time or reduction in the organic level in Plant liquors.

The model assists with the optimisation of precipitation to extract the best yield performance while maintaining or improving product quality. Further project development on particle balances and product soda content is required to determine the limitations these product quality values place on yield in Plant liquors and liquors in which the organics are controlled to a low level.

OPTIMISATION OF YIELD FROM CONTINUOUS ALUMINA HYDRATE PRECIPITATION

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1.0 INTRODUCTION

In the continuous precipitation process, alumina trihydrate is precipitated from green liquor by seeding with fine hydrate. In the American Bayer process, slurry holding times are typically 30-40 hours. The goal of the precipitation section is to maximise alumina yield while still maintaining product quality and seed balance.

Control of the precipitation process relies on a number of variables of which the important ones and their typical effect on particle size and yield are summarised below:

<u>Control Variable</u>	<u>Change</u>	<u>Yield</u>	<u>Particle Size</u>
Temperature	raise	lower	raise
Starting A/C ratio	raise	raise	raise
Surface Area (seed charge)	raise	raise	lower
Caustic concentration	raise	raise	lower
Holding time	raise	raise	raise

An additional factor that has a major effect on the yield and alumina quality is the impurity level, particularly organics.

High organic levels lower the yield, and sodium oxalate is considered to have a particularly adverse effect on particle size (Bird et al, 1983; Lever 1983; Bush and The, 1987).

To quantify the effects on yield of the more important control variables and organics, batch experiments on Plant and synthetic liquors were carried out over a range of conditions to establish rate and equilibrium data. These relationships when substituted in a computer model of a continuous precipitation circuit allow the parameters for maximum yield to be determined.

2.0 EXPERIMENTAL PROCEDURE

Plant liquors from the precipitation circuit were used. Reagent grade NaOH was added as required to raise the caustic concentration while keeping the other impurities constant.

Synthetic liquors were made by dissolving hydrate (i.e. $\text{Al}(\text{OH})_3$ from the Plant) in caustic liquor to the required initial A/C ratio* and adding the main inorganic impurities (Na_2SO_4 , Na_2CO_3 , NaCl) to the same concentrations as in the Plant. The synthetic solutions were thus equivalent to an organic free Plant liquor.

- * A = Al₂O₃ concentration, gpl
 C = Sodium hydroxide + sodium aluminate concentration, expressed as
 gpl Na₂CO₃

Product aluminum hydroxide was washed and dried for use as seed.

The batch laboratory precipitation tests were carried out by rotating the required slurries end-over-end in plastic bottles in a water bath held at constant temperature. The A/C ratio of the liquor and the soda content (Na₂O) and particle size of the solids were measured regularly over 24 hours.

To obtain equilibrium relationships, Plant or synthetic liquors at high charges of fine seed (>400 g/kg) were used and the A/C ratio measured after 3 days.

Typical equilibrium results obtained for Plant and synthetic liquors are shown in Table 1.

Table 1
 Equilibrium A/C Ratios

Liquor Type	Temperature °C (T)	Caustic Concentration gpl (C)	A/C Equilibrium (A/C _e)
Plant	55	209.5	0.298
"	55	277.6	0.392
"	73	204.2	0.384
"	73	284.1	0.480
"	73	249.5	0.432
"	85	199.5	0.468
"	85	245.6	0.509
Synthetic	55	209.2	0.254
"	55	262.1	0.303
"	73	210.2	0.359
"	73	203.8	0.352
"	73	265.4	0.415
"	85	202.4	0.434
"	85	251.6	0.488

The data from Table 1 can be correlated as a function of temperature (T) and caustic (C) as follows:

Plant Liquor :
$$A/C_e = \exp \left(\frac{3.792 + (-1846 + 1.0095C)}{(T + 273.15)} \right) \quad \text{----- (1)}$$

$$\text{Synthetic Liquor} : \quad A/C_e = \exp (5.098 + (-2337 + 1.0193C) / (T + 273.15)) \quad \text{----- (2)}$$

3.0 YIELD MODEL

Pearson's second order rate equation (Pearson, 1955) is the starting point for the model:

$$-\frac{dX}{dt} = k A_t [X_t - X_{\infty}]^2 / [a_{\infty} + X_{\infty}]^2 \quad \text{----- (3)}$$

where: k = kinetic rate constant
 A_t = area of seed surface at time t , m^2/l of liquor
 X_t = molar concentration of $NaAlO_2$ at time t , g mols/l of liquor
 X_{∞} = molar concentration of $NaAlO_2$ at equilibrium, g mols/l of liquor
 a_{∞} = molar concentration of $NaOH$ at equilibrium, g mols/l of liquor

Scott converted the rate equation to the usual terminology for the Bayer process (Scott, 1977) as follows:

$$\frac{-2 C}{102} \frac{dA/C}{dt} = k A_t \frac{(106)^2 (A/C_t - A/C_e)^2}{(102)^2} \quad \text{----- (4)}$$

where: C = caustic concentration, g/l as Na_2CO_3
 A/C = alumina to caustic ratio
 A/C_t = A/C ratio at time t
 A/C_e = A/C ratio at equilibrium

Based on the procedure outlined by Overby and Scott (Overby and Scott, 1978), the following substitution is made for A_t :

$$A_t = A_o (M_t / M_o)^{2/3} \quad \text{----- (5)}$$

where: A_o = initial area of seed surface, m^2/l liquor
 M_o = initial concentration of seed, g/l
 M_t = concentration of seed + precipitate at time t , g/l

Neglecting changes in C concentration,

$$M_t = M_o + (A/C_o - A/C_t) \times C_o \times 1.53 \quad \text{----- (6)}$$

where: A/C_o = initial A/C ratio
 C_o = initial caustic concentration, g/l

Substituting (5) and (6) in (4) and rearranging:

$$\frac{dA/C}{dt} = \frac{-k 106^2 A_0}{2C 102} \left(1 + \frac{(A/C_0 - A/C_1) C_0 1.53}{M_0} \right)^{2.3} \times (A/C_1 - A/C_2)^2 \quad \text{----- (7)}$$

3.1 Rate Constant

To obtain the rate constant k for each experiment, equation (7) was integrated by a 4th Order Runge Kutta equation and the value of the rate constant varied to obtain the curve of best fit for the data points.

A typical set of decomposition curves is shown in Figure 1 for Plant and synthetic liquors.

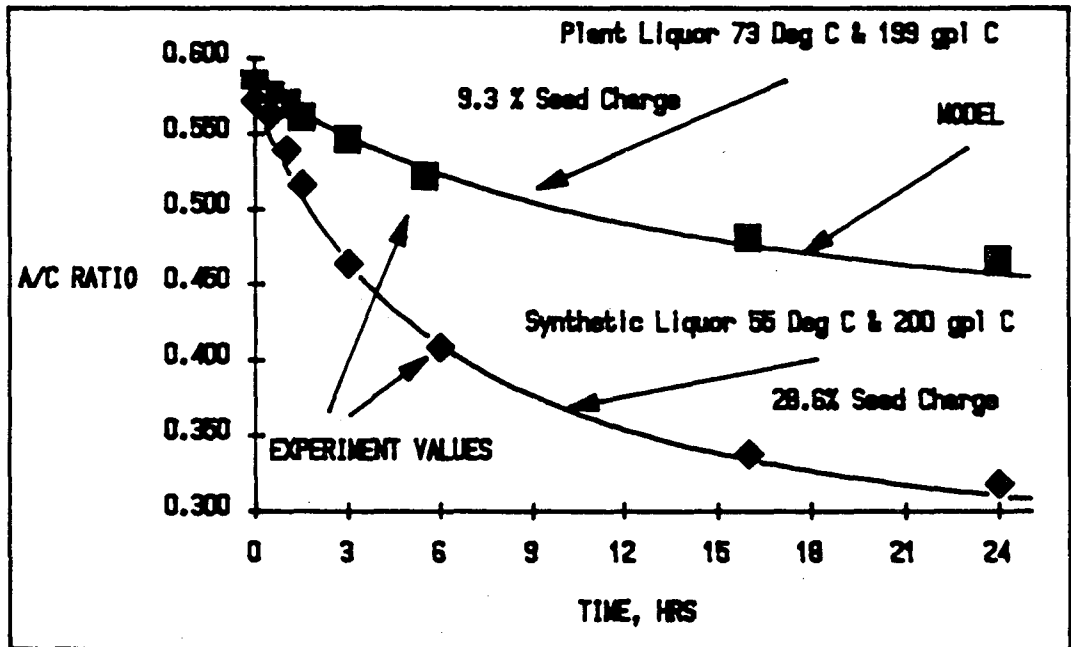


Figure 1
Decomposition Curves for Plant and Synthetic Liquors

A set of rate constants matched to the laboratory results are shown in Table 2.

Table 2
Rate Constant, k

Liquor Type	Temperature °C (T)	Caustic Concentration gpl (C)	Rate Constant (k)
Plant	55	199.8	0.14
"	55	268.6	0.06
"	73	199.0	0.40
"	73	242.3	0.21
"	85	198.8	0.70
"	85	243.5	0.50
Synthetic	55	199.6	0.14
"	55	247.6	0.12
"	73	202.3	0.40
"	73	255.3	0.35
"	85	198.5	0.60
"	85	250.6	0.50

The rate constant can be correlated as follows:

$$\begin{aligned} \text{Plant :} \quad k &= 0.229\text{E}8 \exp(-0.588\text{E}4/(T+273.15)) \quad \text{---- (8)} \\ \text{Liquor} &\quad \times (0.783 - 0.191\text{E}-2C) \end{aligned}$$

$$\begin{aligned} \text{Synthetic:} \quad k &= 0.661\text{E}7 \exp(-0.518\text{E}4/(T+273.15)) \quad \text{---- (9)} \\ \text{Liquor} &\quad \times (0.276 - 0.512\text{E}-3C) \end{aligned}$$

3.2 Continuous Precipitation Model

The equation for the A/C ratio leaving a continuous precipitator can be obtained by integrating equation (4) with the appropriate end points and solving the quadratic obtained for the outlet A/C ratio (Scott, 1977). The resulting equation is:

$$A/C_{\text{out}} = (B_2 + (B_2^2 - 4B_3)^{0.5}) \times 0.5 \quad \text{---- (10)}$$

where:

$$\begin{aligned} B_1 &= 2C / (k A t 110.16) \\ B_2 &= 2 A/C_e - B_1 \\ B_3 &= A/C_e^2 - B_1 A/C_{\text{in}} \\ A/C_{\text{out}} &= \text{outlet A/C ratio} \\ A/C_{\text{in}} &= \text{inlet A/C ratio} \\ t &= \text{residence time of liquor, hrs} \\ A &= \text{solids surface area, m}^2/\text{l of liquor} \end{aligned}$$

By substituting the appropriate equilibrium and rate correlations (equations 1, 2 and 8, 9), the yield from a single continuous precipitator can be obtained.

The A/C profile of a precipitation circuit can then be built up by starting from the 1st tank and allowing the outlet of one precipitator to be the inlet to the next and so on.

3.3 Plant Data

The Worsley precipitation circuit is described in detail elsewhere (Newchurch and Moretto, 1990). It consists of 3 sections - agglomerators, intermediates and finals - with 2 cooling stages, one after the agglomerators and one after the intermediates.

The model was matched to Plant data by determining an effectiveness factor, f_A , for the solids surface area as measured by Microtrac (Overby and Scott, 1978).

Although the model is applicable only to linear growth regimes, it was found that reasonable agreement could be obtained for the agglomeration section also by choosing the surface area exiting the final agglomerator to represent the average in-tank solids surface of the agglomeration section.

Effectiveness factors for each of the sections were obtained for one set of Plant conditions. These factors were then used to predict the decomposition profile for other periods and the results compared with actual Plant data. An example of the reasonable data fit is shown in Figure 2.

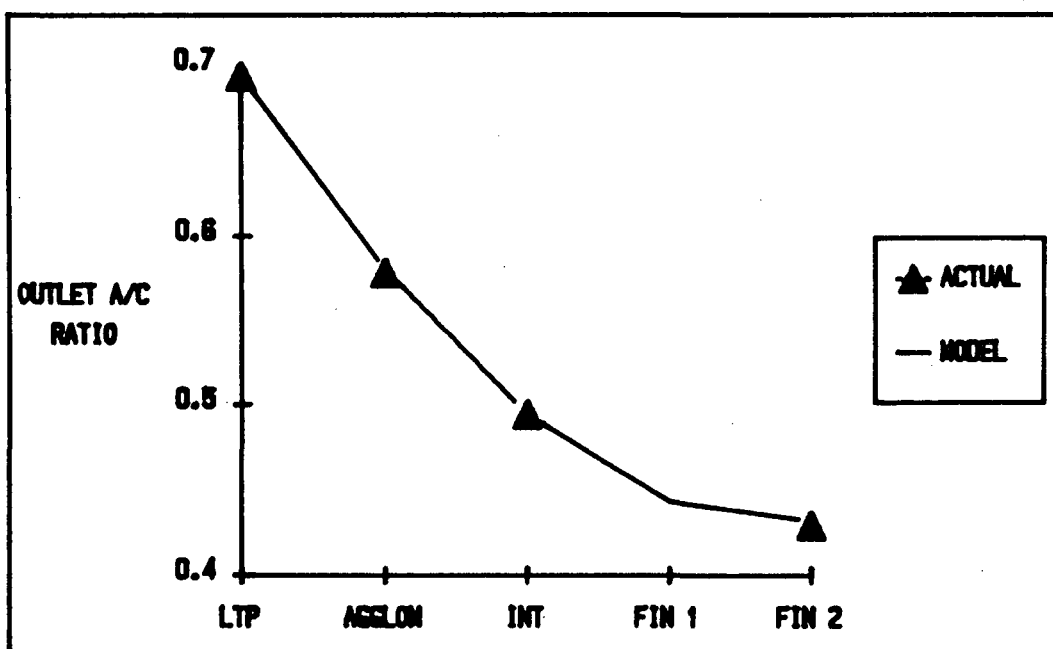


Figure 2
Comparison of Model and Plant Data

4.0 EFFECT OF PROCESS VARIABLES

4.1 Optimum Temperature Profile

There are references in the literature to an optimum temperature profile in the precipitation circuit (Kanehara, 1971; Davidov et al, 1983; White et al, 1984; Chaubal, 1990).

The continuous model can be used to determine the optimum temperature profile for the Worsley circuit by varying the temperature at each stage and using the Plant correlations in the continuous model. The results are shown in Figure 3, and confirm that an optimum temperature exists at each stage in the circuit.

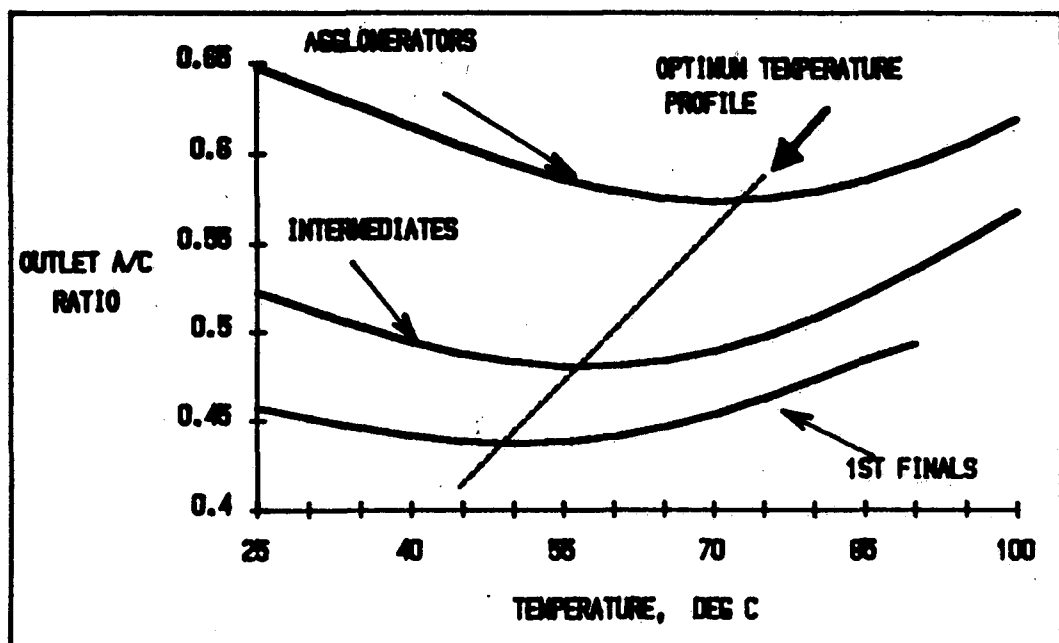


Figure 3
Optimum Temperature Profile

The practical use of the graph is that it allows a loss in yield to be determined at each stage when the desired temperature is not obtained.

Capital cost constraints determine how close to the optimum temperature profile the Refinery is initially designed.

4.2 Effect of Caustic Concentration

It is well known that raising caustic concentration in the precipitation circuit raises yield. (White, 1988; Audet et al, 1989).

The model can be used to predict the effect of raising caustic. The results are shown in Figure 4.

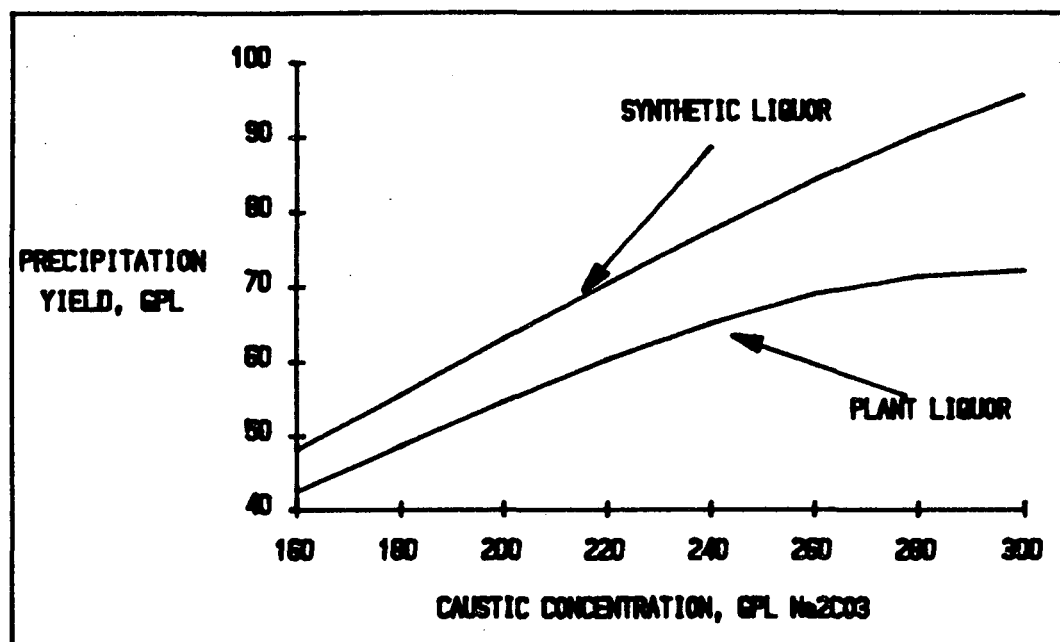


Figure 4
Precipitation Yield v/s Caustic Concentration

Allowance was made in the yield predictions for the rise in the starting A/C ratio, which a rise in caustic allows. In the current Worsley Plant liquor, the yield increases with rise in caustic concentration, within the practical limits of caustic concentration.

Other factors, particularly soda in product, particle size and seed balance, may limit the caustic rise in the circuit. In these experiments on Plant liquors in the growth regime, it was found that the soda content of the solids showed very little variation with caustic rise (see Table 3).

Table 3
% Na₂O on Hydrate (Plant Liquors)

T, °C	73	73	85	85
Caustic, gpl	199	244	199	244
Time, hrs				
0	0.46	0.45	0.44	0.43
16	0.44	0.46	0.40	0.40
24	0.45	-	0.42	0.43

4.3 Holding Time

The model can also be used to predict the production increase from adding more precipitators to the circuit, and to determine the optimal locations for them.

It has been found that maximum yield occurs when tankage is added at the end of the circuit, as expected. However, other considerations, such as the need to increase agglomeration to control seed balance, can dictate location of additional precipitators.

4.4 Organics

Reduction in organics can increase yield (Zoldi et al, 1989).

By using the relationships for synthetic liquors (in which all inorganic impurities were the same as Plant liquors except for organics which were nil), the yield increase in precipitation from removing all the organics was plotted in Figure 4 at various caustic concentrations. However, the starting A/C ratio in Figure 4 has not been adjusted for the effect of organics on alumina solubility in the digestion circuit. This relationship can be derived from breakpoint determinations in which the allowable A/C in digestion is measured as a function of organic concentration in the liquor.

There were indications from the soda analyses of the hydrate that product soda quality might be improved by reducing the organic content of Plant liquors. The soda contents of the solids for Plant and synthetic liquors are shown in Table 4. A larger reduction in % Na₂O on hydrate occurred for the synthetic liquors compared to Plant liquors.

Table 4
% Na₂O on Hydrate

Liquor Type	Plant	Synthetic	Plant	Synthetic
T, °C	73	73	85	85
Caustic, gpl	199	244	199	244
Time, hrs				
0	0.46	0.45	0.44	0.44
16	0.44	-	0.40	0.43
24	0.45	0.40	0.42	0.39

5.0 CONCLUSIONS

A relatively simple model suitable for running on a PC, can be obtained for both Plant and synthetic liquors, based on a limited number of batch precipitation experiments.

The model can be used to quantify the effects of changes in temperature, caustic concentration, holding time and organic levels. The model predicts an optimum temperature profile exists, confirming the benefit of the Worsley strategy of 2 cooling steps rather than 1 in the precipitation circuit.

Within the growth regime, raising caustic concentration did not appear to have a significant effect on product quality (% Na₂O and particle size). There were indications that liquors with reduced organics may result in lower product soda.

6.0 ACKNOWLEDGEMENT

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