SODIUM OXALATE IN THE BAYER PROCESS:
ITS ORIGIN AND EFFECTS

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ABSTRACT

The presence of solid sodium oxalate in the precipitation circuit affects product quality by a number of mechanisms. Laboratory tests aimed at defining and quantifying these are described, and a case study of the effect of humate removal from the Plant liquor stream is given.

It is well known that the presence of solid sodium oxalate dramatically inhibits agglomeration. It also tends to promote nucleation of aluminium hydroxide. The effects of oxalate on hydrate classification are complex, and impact product quality by affecting the particle size distribution. The presence of other organic compounds in the liquor is critical in determining the nature and extent of sodium oxalate effects.

The phenomena so far mentioned impact the particle size distribution of the product.

Sodium oxalate can also affect the soda content of the product. Because sodium oxalate accounts for only a small proportion of the total organic content of the liquor, this is usually only significant if solid sodium oxalate is physically included with the product.

The sodium oxalate in Bayer liquor originates in digestion, primarily by degradation of organic compounds in the bauxite. The remainder arises by degradation of compounds already in the liquor. The magnitudes of these effects are examined for the case of the Worsley Refinery.

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1.0 INTRODUCTION

Numerous articles have been written on the subject of sodium oxalate (generally referred to as "oxalate" in the following) in relation to the Bayer process. There appears to be general agreement on the following points:

1. Most of the oxalate entering the liquor is generated in Digestion by degradation of higher molecular weight organic compounds, both directly from the bauxite and from the recirculating liquor (Grocott, 1988).

2. The presence of crystalline sodium oxalate in Precipitation increases the rate of fines generation (Brown and Cole, 1980; Verghese, 1987; Lever, 1978).

3. The presence of crystalline oxalate on the seed interferes with agglomeration (Verghese, 1987; Lever, 1978; Minai et al, 1978).

4. The extent of oxalate effects in Precipitation is dependent upon the presence of higher molecular weight organic compounds in the liquor (Verghese, 1987; Minai et al, 1978).

5. Oxalate effects depend on the size and shape of the oxalate crystals or crystal clusters (Minai et al, 1978).

6. The presence of crystalline sodium oxalate has a detrimental effect on seed classification (Verghese, 1987; Lever, 1978).

In addition, it should be noted that:

7. Rates of growth of aluminium hydroxide scale in the Precipitators are greatly increased by co-precipitation of oxalate.

2.0 CASE STUDY - EFFECT OF HUMATE REMOVAL

The damaging impact of oxalate on Precipitation was highlighted at the Worsley Refinery in late 1987. In October of that year it was decided to trial the use of polydiallyl dimethyl ammonium chloride (p-DADMAC) as a removal agent for the sodium salts of humic

acids (humates). A variety of undesirable effects (higher liquor viscosities, boiling point rise, reduced precipitation yield) have been ascribed to the presence of humates which enter the liquor from the bauxite (Pohland and Tielens, 1983; Romanov, et al 1975).

These effects are minimal, however, compared with the stabilisation of oxalate (Lever, 1983; The and Bush, 1987). The presence of humates reduces oxalate precipitation rates in seeded solutions, and also stabilises unseeded solutions in relation to oxalate nucleation (spontaneous precipitation).

Removal of humates from an already heavily contaminated Plant liquor stream therefore has the effect of not only increasing oxalate precipitation rates where oxalate is already crystallising, but also of causing oxalate to precipitate in hitherto oxalate-free parts of the circuit.

That p-DADMAC is an effective humate remover is shown in Figure 1, in which the humate concentration (determined spectrophotometrically) is plotted as a function of time.
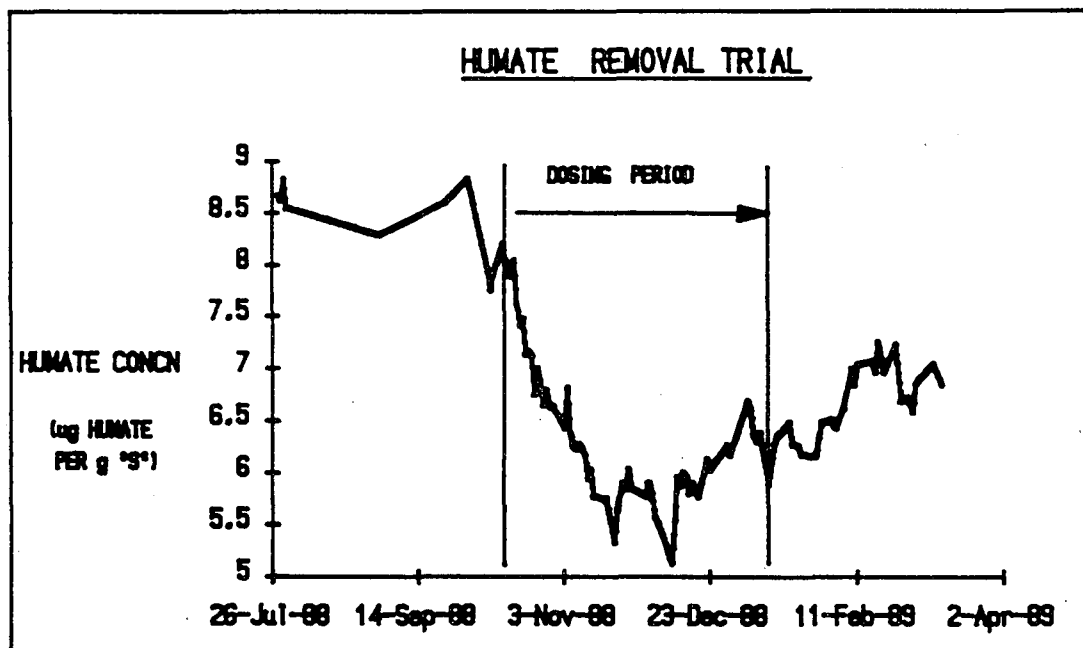

Figure 1

During the trial, an extensive program of analysis was conducted. Of particular interest here are the levels of Solid Phase Oxalate (SPO, expressed as a percentage of the dry solids) present in the overflows at the three stages of Precipitation. (The Worsley

precipitation circuit consists of three stages of precipitation, with heat interchange between stages. Agglomeration is followed by the Intermediate and Final stages (Newchurch and Moretto, 1990). The results are summarised in Figure 2.
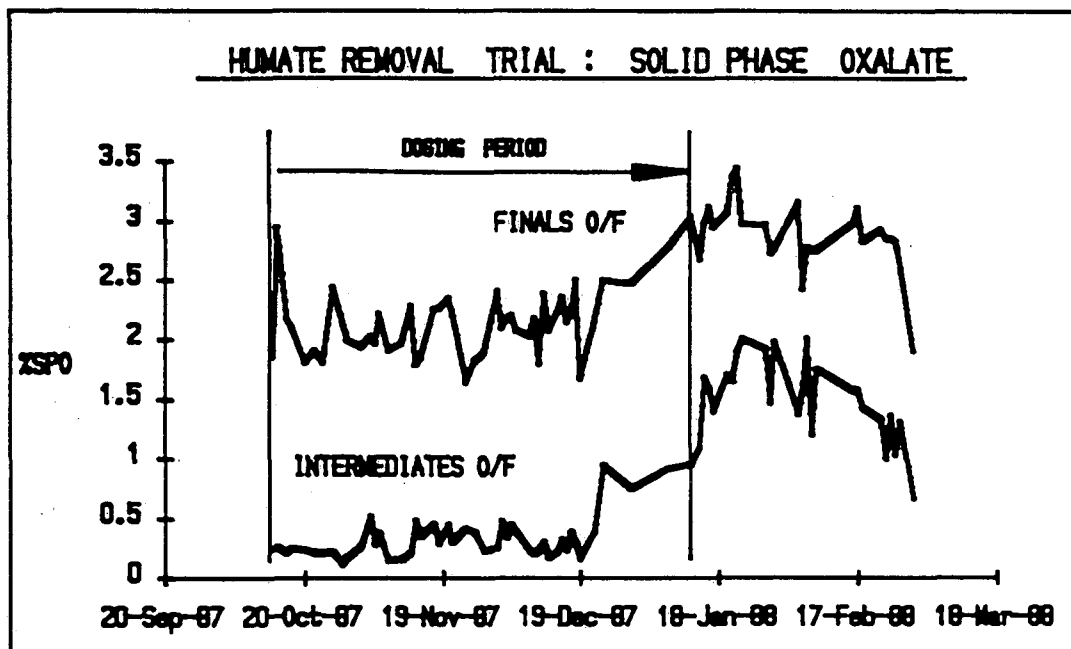

HUMATE REMOVAL TRIAL : SOLID PHASE OXALATE

Figure 2

Under normal operation, there are very low levels of SPO in the Agglomerator Overflow (0.01 to 0.05%), and less than 0.5% SPO in the Intermediate Overflow. The SPO in the Agglomerator Overflow is essentially that which was present on the seed. Ideally, no oxalate is precipitated in the Intermediate stage, the higher SPO being a result of elutriation.

Oxalate removal from the circuit depends upon co-precipitation of oxalate in the Finals and elutriation of this oxalate with the Final overflow, which reports to the Seed Thickeners (Newchurch and Moretto, 1990). The % SPO typically varies between 1.5 and 3%, depending on the mass of hydrate present (under normal conditions, the tonnes per hour of SPO is essentially constant).

By early December, the humate concentration had been reduced by 30% (Figure 1). This occasioned a sharp increase in the SPO in the Intermediate Overflow (Figure 2), indicating the onset of oxalate precipitation at the Intermediate temperature. As there was no change in the green liquor oxalate concentration, this was a direct result of destabilisation of oxalate by humate removal.

The increased extent of oxalate precipitation caused a progressive deterioration in Plant operation and performance, as follows:

1. Aluminium hydroxide scaling rates were greatly increased. This hampered operation by increasing the requirement for line cleaning. It also meant that the normal precipitator cleaning schedule was no longer adequate. This resulted in a reduction in effective precipitator volume.

2. A marked increase in the mass of fine (-45 um) aluminium hydroxide in the Precipitation circuit.

3. Particle breakdown in calcination increased.

4. Product soda increased.

Because most of the extra oxalate precipitation reported as scale, it was not available to the oxalate removal system. The only way out of the problem was therefore to allow the liquor to restabilise. Dosing was discontinued at the end of December. As the liquor restabilised, and an intensive cleaning program was carried out in Precipitation, the Plant quickly recovered, and by March 1988 was exceeding previous best production and product quality.

3.0   **OXALATE AND SEED BALANCE**

Following the p-DADMAC trial, a program of research aimed at achieving a better understanding of oxalate behaviour and control was established. Just as the trial demonstrated dramatically the limitations that oxalate puts on production, so improvements in oxalate removal have shown that lower oxalate levels bring relief. An improved operating strategy in the oxalate removal system instituted in mid 1989 (Morton, 1988), enabled reduction of the green liquor oxalate concentration from 3.5 g/l to 3.0 g/l. This improved operating flexibility, and was a key to enabling lower precipitation temperatures and higher flows than previously achievable.

3.1   Elutriation Behaviour

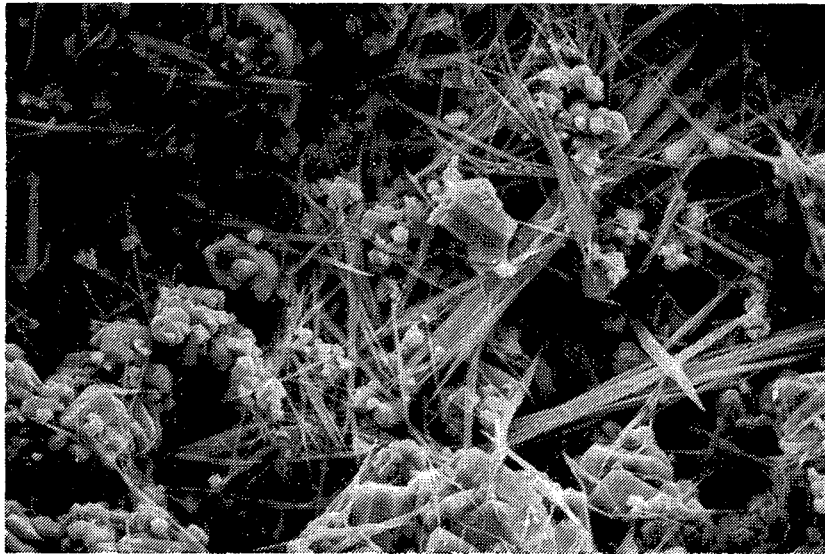Oxalate nevertheless remains a major factor limiting production.

The Finals were designed to operate as classifiers as well as precipitators (Newchurch and Moretto, 1990). The presence of crystalline oxalate has a complex and dominating effect on classification behaviour. This is because

oxalate, in liquor contaminated with other organics, readily attaches to hydrate. The more heavily organic contaminated the liquor, the longer and thinner the oxalate needle crystals tend to be, and the more readily they attach to aluminium hydroxide.

The oxalate-aluminium hydroxide interaction leads to the formation of aggregates, as shown in Figure 3. This effect has a marked influence on the classification behaviour of hydrate. At very low rising velocities, the oxalate behaves as a flocculant, increasing the settling rate of fine hydrate and improving supernatant clarities. This occurs in the seed thickeners.

In the Final Precipitators, however, the higher rising velocities mean that the desired preferential elutriation of fines is disturbed by the presence of oxalate.
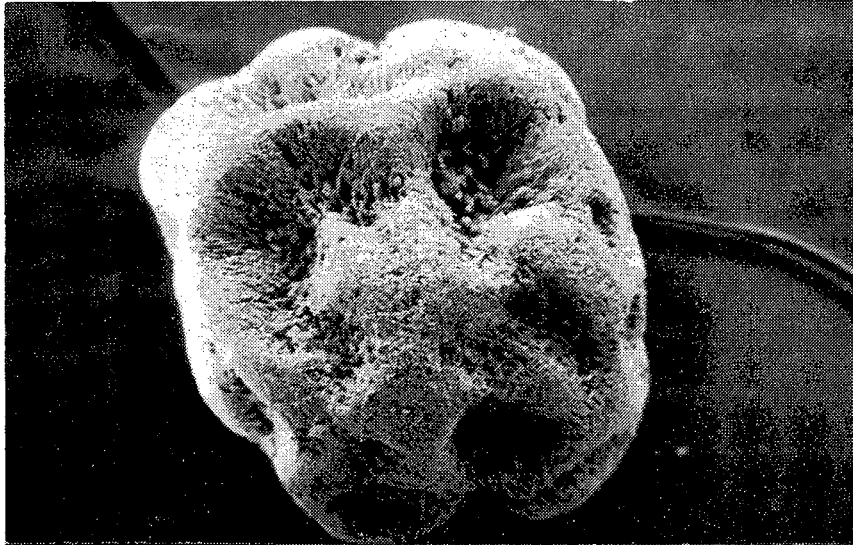
The open sodium oxalate-aluminium hydroxide aggregates have low apparent densities, and so fine and coarse aluminium hydroxide alike are elutriated, bound together by filamentous oxalate webs.

I I
10 um

Figure 3

Control strategies under consideration include the use of fatty acid surfactant based Crystal Growth Modifiers (CGM) (Nalco, 1988). It has been found that it is possible to change the degree of sodium oxalate-aluminium hydroxide interaction, and, in the limit, to promote the formation of spherulitic oxalate in preference to the filamentous form. An example of an oxalate ball formed in Precipitation during a trial application of a CGM is shown in Figure 4.

I I

100 um

Figure 4

3.2 Fines Generation

A number of authors have indicated that the presence of crystalline oxalate during precipitation stimulates the generation of hydrate fines. Minai et al (Minai et al, 1978) noted in 1978 that oxalate present on seed greatly reduces agglomeration efficiencies. Others have referred in more general terms to fines generation in the presence of solid oxalate (Verghese, 1987; Lever, 1978; Brown and Cole, 1980) ascribed increased fines generation to periods of increased oxalate crystallisation, in their study at the Burntisland Plant. The increased rate of fines generation corresponding to accelerated oxalate precipitation during the humate removal trial at Worsley has been referred to above.

Our laboratory studies at Worsley have demonstrated that oxalate does indeed play a key role in fines generation, and that this is catalysed by the presence of other organic impurities. This is another example of the "oxalate-humate" interaction referred to by Lever (Lever, 1983).

3.2.1 Effect of oxalate on agglomeration

The effect of oxalate is most marked in agglomeration as previously noted by Minai et al (Minai et al, 1978). The successful agglomeration of hydrate particles requires a high rate of precipitation. Agglomeration is therefore favoured by the combination of high supersaturation (high driving force), high temperature (high rate constant), and high seed surface area. The first of these conditions also favour nucleation, which will therefore occur if the seed surface area is not sufficient. Nucleation can happen as a result of undercharging, by poisoning of the seed, or by the introduction of spurious nucleation sites.

The presence of solid phase oxalate in the agglomeration stage can be very detrimental, because hydrate readily nucleates on oxalate surfaces contaminated with other organics adsorbed from the liquor. This is illustrated by the following laboratory test results. Agglomeration was carried out at 82°C. Green liquor was seeded to an initial charge of 35 g/l seed (dry hydrate basis) in 250 ml plastic bottles which were tumbled end-for-end in a water bath for 5 hours. Plant green liquor was used for Tests 1.1 to 1.3, while synthetic green liquor was used for Tests 1.5 to 1.6. The synthetic liquor was of the same composition as the Plant liquor, except that the organic impurities were omitted. The same level of dissolved oxalate was present in both liquors, and the conditions of the test were such that no fresh oxalate precipitation occured. Crystalline oxalate was present on the unwashed seed, or was added as clean, reagent grade sodium oxalate.

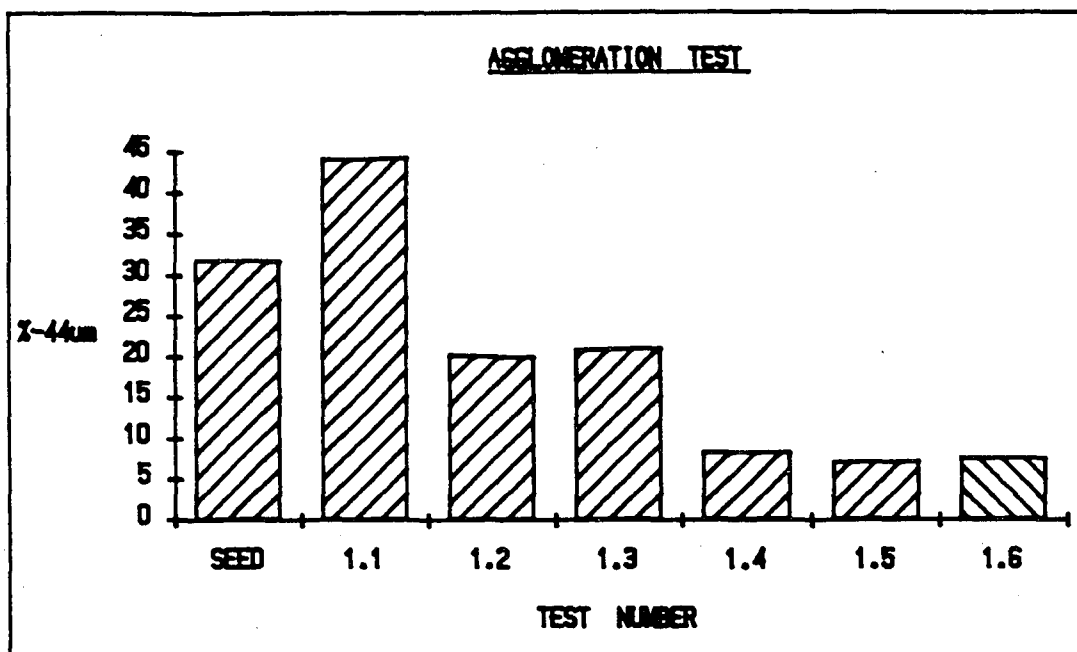The test parameters and main results are summarised in Figure 5.

AGGLOMERATION TEST

X-44um

45
40
35
30
25
20
15
10
5
0

SEED 1.1 1.2 1.3 1.4 1.5 1.6

TEST NUMBER

Figure 5

A. Plant Liquor

   Test #   Aluminium Hydroxide Seed

   1.1   Unwashed seed (1.5% crystalline oxalate)
   1.2   Washed Seed
   1.3   Washed seed + 1.5% reagent grade $Na_2C_2O_4$

B. Synthetic Liquor

   1.4   Unwashed seed (1.5% crystalline oxalate)
   1.5   Washed seed
   1.6   Washed seed + 1.5% Reagent grade $Na_2C_2O_4$

It can be seen that the combination of oxalate crystals and liquor contaminated with other organics causes nucleation to dominate agglomeration. Interestingly, oxalate crystals which have not formed in the contaminated liquor do not have this effect, nor does contaminated oxalate in synthetic liquor.

3.2.2 Oxalate effects during growth

To investigate the effects of oxalate during the growth stage of precipitation, a coarse seed was introduced to a partially spent liquor (C = 197 g/l, A/C = 0.579), and held at 55°C for 24 hours. Agitation was as for the agglomeration test (above).

The bottles were charged to 11% solids initially. In Tests 2.1 to 2.3, the initial liquor was first stripped of oxalate so that it was below saturation at 55°C. Normal supersaturated Plant liquor was used in Tests 2.4 to 2.6.

The results (Figure 6) show that nucleation occurred in all cases, irrespective of oxalate precipitation. The degree of nucleation was increased in the case of oxalate precipitation in the presence of contaminated oxalate seed (Test 2.6), but the effect was slight in comparison to the impact of contaminated oxalate on agglomeration.

Figure 6

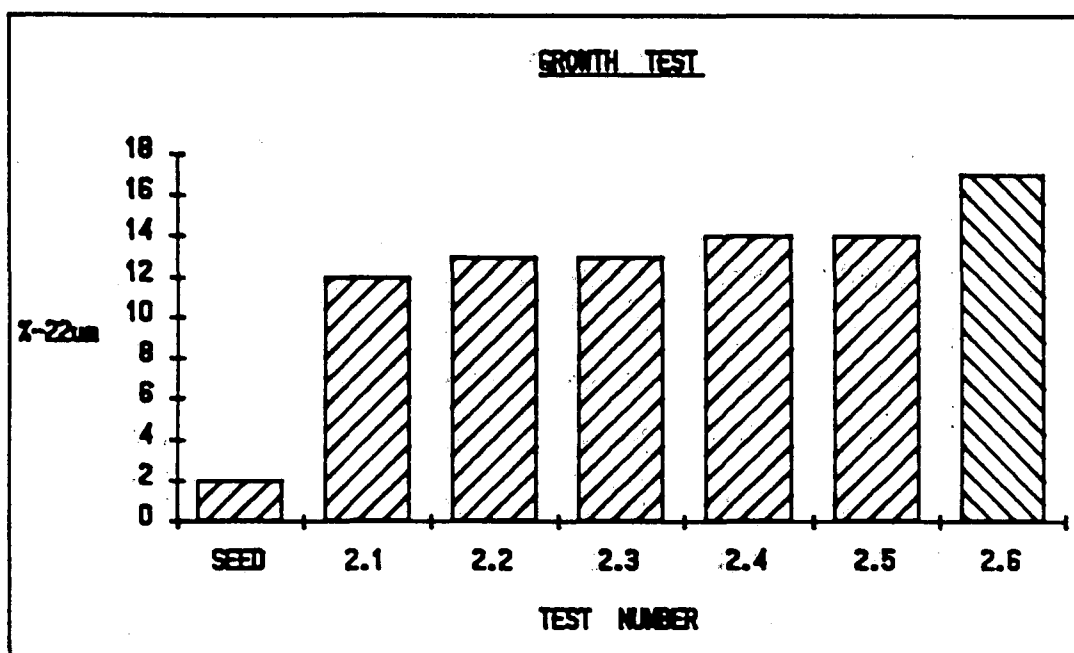A.   Low Oxalate Liquor (below saturation)

Test #   Oxalate Seed

2.1   Nil
2.2   Reagent grade $Na_2C_2O_4$
2.3   Plant oxalate cake

B.   High Oxalate Liquor (supersaturated)

2.4   Nil
2.5   Reagent grade $Na_2C_2O_4$
2.6   Plant oxalate cake

Thus, while the presence of contaminated oxalate crystals can accelerate nucleation during the growth stage, it is not the dominant factor.

In fact, we have observed cases in which, by binding fine particles to the surfaces of coarse particles, oxalate can assist in the incorporation of the fine particles onto the larger structures. The presence of oxalate crystals in these circumstances enables a mechanism of fines consumption.

4.0 OXALATE GENERATION

It has been suggested in the literature that up to half of the oxalate entering the Process from Darling Range bauxite was present as oxalate in the original bauxite (Grocott, 1988; Ellison, 1984). We have tested a range of bauxites, including Darling Range samples from both the Worsley and Alcoa leases. The bauxites tested are as listed in Table 1 (below). The tests were done by boiling a sample of the bauxite in deionized water for one hour, and analysing the resulting liquor for oxalate by ion chromatography. In all cases the level of oxalate present naturally in the bauxite was below the detection limit of 0.003 kg/t. We therefore conclude that the amount of native oxalate in bauxite is in general negligible. A sample of topsoil from the Worsley mining area was also included as background data for the digestion experiments described below. It gave an oxalate recovery of 0.03 kg/t.

It therefore follows that essentially all of the oxalate introduced to the liquor circuit is produced in the Process.

It is generally accepted that the only significant oxalate generation occurs in Digestion (Grocott, 1988).

We have accordingly studied oxalate generation in Digestion as follows:

4.1 Mechanism of Oxalate Formation in Digestion

It has previously been shown that dissolved molecular oxygen is not an effective oxidant under normal Digestion conditions, and that even if it were there would be insufficient dissolved oxygen present to account for the sodium oxalate and sodium carbonate produced in Digestion (Grocott, 1988).

- 109 -

It therefore follows that another oxidant must be present. It has been suggested that goethite is the principal oxidant in these circumstances (Grocott, 1988; Yamada et al, 1981).

To test these statements in relation to Worsley bauxite, the following solids were prepared:

1) A typical Worsley bauxite.

2) A sample from the topsoil stockpile.

3) A typical Worsley digester mud, which was further treated by leaching with alkaline dichromate to remove residual organics.

4) Bauxite from 1., which had been roasted for 30 minutes at 500°C.

Digestions were carried out by reacting the ground solids in 10 ml stainless steel bombs for 40 minutes at 175°C, with rolling. After digestion, the whole slurries were diluted to 250 ml, and then further diluted as appropriate for oxalate analysis by ion chromatography. Triplicate analyses were carried out, and the results were calculated back to the original liquor basis.

The analyses of the original solids samples are shown in Table 1.

Table 1
Initial Solids Samples

SAMPLE I.D.	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Carbon	CO_2
Worsley Bauxite	39.5	4.8	31.1	2.7	0.36	0.05
Roasted Worsley Bauxite	48.8	5.8	38.7	3.4	0.03	-
Topsoil	37.6	14.5	31.1	2.4	2.37	0.07

SAMPLE I.D.	MINERAL PHASES PRESENT (XRD)
Bauxite	Gibbsite, goethite, haematite, quartz, anatase, kaolinite
Roasted Bauxite	Haematite, anatase, quartz
Topsoil	Quartz, gibbsite, haematite/maghemite, anatase

Bombs were charged with 0, 2 or 3 grams of solids (see Table 2), and with either pure caustic solution at 190 g/l "C", or with Liquor to Digestion (LTD) from the Plant. The results are summarised in Table 2.

Table 2

Results of Bomb Digests

TEST #	BOMB SOLIDS	BOMB LIQUOR	g/l $Na_2C_2O_4$
	No bomb	Original LTD	3.0
OD1.1	Nil	LTD	3.1
OD1.2	2g bauxite	LTD	3.5
OD1.3	2g roasted bauxite	LTD	3.1
OD1.4	2g topsoil	LTD	4.1
OD1.5	2g topsoil + 1g mud	LTD	4.2
OD1.6	1g mud	LTD	3.2
OD1.7	2g bauxite	190 "C" NaOH	0.4
OD1.8	2g mud	190 "C" NaOH	0.0

From Table 2, the following observations can be made:

1.   Oxalate is produced in digestion by conversion of organic compounds in the bauxite and in the LTD.

2.   Of the 3.5 - 3.0 = 0.5 g/l oxalate produced in a digest of bauxite in LTD (Test # OD1.2), 3.1 - 3.0 = 0.1 g/l is from organics in the liquor (Test # OD1.1), and 3.5 - 3.1 = 0.4 g/l comes from organics in the bauxite (Test # OD1.2, 1.1 and 1.7).

3.   Roasted bauxite contributes no oxalate to the liquor, nor does it affect the break down of liquor organics to oxalate (Tests # OD1.3 and 1.1).

4.   The presence of goethite (suggested as an oxidant in the production of oxalate in digestion (Grocott, 1988; Yamada, et al 1981), is not required for oxalate formation to occur. This is confirmed in the tests using topsoil,

which is goethite free. Comparing Tests # OD1.4 and 1.1, 2 g of topsoil contributes 1.0 g/l oxalate to the liquor. Addition of 1 g of mud to the topsoil contributes a further 0.1 g/l (Test # OD1.5).

As the mud itself does not contribute any oxalate (Test # OD1.8), the presence of goethite, while not essential for oxalate formation, does appear to slightly increase the amount of oxalate produced. This is true in the presence of fresh organics (Test # OD1.5) or of LTD only (Test # OD1.6).

Note that the precision of the analytical determination of the oxalate is limited to 0.05 g/l at 95% confidence.

From the above, approximately 20% (confidence range +10%) of the oxalate formed in digestion is by breakdown of organics in the liquor, the remaining 80% coming from the bauxite. The proportion of Total Organic Carbon which is converted to oxalate for each pass of the liquor through digestion is of the order of 0.05%. These comments apply to the current, highly contaminated, Worsley Plant liquor.

4.2 Survey of Bauxites

In order to compare the degree of oxalate generation from a range of bauxites, a set of International and Australian Standard Bauxites was examined. A standard test was applied to each, in which 2.5 grams of dry bauxite was reacted with 10 ml of fresh caustic at 190 g/l "C". The samples were bombed at both 143°C and 230°C for 30 minutes, and the resulting liquor analysed for oxalate by ion chromatography. Full details of the method are given elsewhere (Power and Tichbon, 1990).

The results are summarised in Table 3. From the table, it is clear that there is a wide range of oxalate generation rates among bauxites. The highest generation rates tend to be with the Australian bauxites, on a kg/t bauxite basis.

Table 3

Oxalate Generation in Digestion:

Survey of Bauxite Types

SAMPLE I.D.	SOURCE	OXALATE GENERATED			
		kg $Na_2C_2O_4$/t bx		kg $Na_2C_2O_4$/tA*	
		143°C	230°C	143°C	230°C
NBS:					
NBS 69B	Arkansas	0.5	0.5	1.4	1.4
NBS 696	Suriname	0.6	0.9	1.2	1.8
NBS 698	Jamaican	0.4	1.9	0.9	4.1
ISOTC 129:					
MT/12/1	Gove	1.5	1.6	3.3	3.4
MT/12/3	Weipa	1.5	1.6	3.3	3.1
MT/12/5	Kimberleys	0.4	0.5	1.0	1.3
MT/12/6	Darling Range	0.9	0.6	2.7	2.1
MT/12/7	Wagina Island	1.1	2.0	2.7	4.7
MT/12/9	Jamaica	0.6	0.8	1.4	1.7
MT/12/12	USSR (diaspore)	0.1	0.2	1.7	0.5
MT/12/13	USSR	0.2	0.3	2.1	0.7
MT/12/14	USSR	0.2	0.2	2.1	0.7

* kg $Na_2C_2O_4$ per tonne of available Al_2O_3 basis.

5.0 CONCLUSIONS

1. Crystallization of sodium oxalate in the Precipitation section of the Bayer Process can severely disrupt the precipitation operation by:

   i)   reducing agglomeration efficiency
   ii)   increasing fines generation
   iii) interfering with particle classification

2. Oxalate is introduced to the liquor stream by degradation of more complex compounds. This occurs in the Digestion step. The majority of the oxalate arises directly from compounds in the bauxite and the balance from compounds in the liquor. There is virtually no oxalate as such in any of the bauxites surveyed.

- 113 -

3.   'Oxalate behaviour and effects can be modified by the addition of specific chemicals, generally known as "crystal growth modifiers". This is a developing technology with high potential for the industry.

6.0   ACKNOWLEDGEMENTS

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