

# **A CASE STUDY IN DOWNSTREAM TESTING OF BAYER PROCESS ADDITIVES**

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## **ABSTRACT**

The use of chemical reagents to enhance the productivity of alumina refineries has become widespread in a number of areas of the Bayer process. Additives such as flocculants to assist in mud separation have been extensively used for some time, but reagents are now being used in such diverse areas as mud filtration, aluminium hydroxide precipitation and classification, product dewatering and mud disposal. With the ever increasing complexity of the Bayer process, it is important to recognise the possibility that some additives which are beneficial in one area of the refinery, may adversely affect other down-stream processes. Alternatively, there may be undesirable interactions between two or more additives used for different purposes. In order to avoid such potential problems a thorough understanding of both additive chemistry and Bayer process chemistry is required. One way of achieving this is for supplier and customer to work in close partnership to develop, test and implement new reagents.

In developing a range of reagents for the control of oxalate in Alcoa's refineries, the effects of the reagents on downstream processes have been carefully investigated. As well as developing a number of tests to assist in the full assessment of the reagents, the interactions of both the reagents and their degradation products with other additives in the system were considered. The cooperative research leading to the development of these reagents, their downstream testing and plant implementation are presented as a case study.

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## **1.0 INTRODUCTION**

The use of chemical reagents to enhance the productivity of alumina refineries has become routine in a number of areas of the Bayer process. The use of synthetic flocculants has been part of the operation of many refineries for more than two decades and the use of additives to improve the efficiency of other unit operations is becoming more widespread. In an effort to maximise productivity many plants are pushing for greater efficiency from existing plant capital and the use of chemical additives is seen as a simple way of achieving this end. However, the possible impact of additives on the downstream operations of the Bayer process must be duly considered so as to minimise risk to plant operations. The effects of downstream impacts for some additives are well known and have been previously documented [Owen *et al*, 1991; Graham and Davies, 1988]. While a product may have a favourable impact in one part of the plant it is imperative that no detrimental effects are observed if the same product enters a downstream process. Therefore proper implementation of a new chemical program requires that not only should product addition result in the desired process benefits, but that it should also NOT impact in any detrimental way on other parts of the process. In the implementation of new oxalate stabiliser technology in Alcoa's Western Australian refineries we have come across a number of interesting and difficult problems which were not predicted in standard laboratory tests. In light of this, a number of developments in the testing of a new product have been introduced.

The development of an effective liquor oxalate stabiliser has been the subject of joint research by Alcoa of Australia and the Nalco Chemical Company over a number of years. The outcome of this work has been the successful development of a reagent based on quaternary ammonium compounds which can effectively inhibit oxalate precipitation in the Bayer hydrate precipitation circuit at very low doses [Farquharson *et al*, 1995a, 1995b, 1996]. Laboratory testing of a variety of quaternary amine compounds initially focussed on, (a) identifying the best stabiliser under a variety of process conditions and (b) the impact of such materials on a number of downstream processes. Some of the conclusions obtained from this initial work include:

- (a) The oxalate stabiliser reagent is effective over a range of process and slurry conditions including temperature, liquor concentration and hydrate solid concentrations, which may be experienced in plant precipitation circuits.
- (b) The active component of the stabiliser is "neutralised" by degradation at high temperatures to give an inert by-product which has no stabilising activity.
- (c) The stabiliser has no negative impact on trihydrate particle sizing or yield and the reagent does not partition preferentially to the hydrate in the hydrate precipitation circuit.

These conclusions are the result of substantial downstream testwork, some of which is beyond what was regarded as standard testing for a new reagent. Despite the care taken in the downstream testing, a number of unforeseen and significant problems have developed as a result of implementation of this

technology onto Bayer plants. The fact that, despite some new recent concerns, these problems have been substantially overcome is both a triumph and a relief. The lessons learnt during the testing and implementation of the stabiliser are a useful guide for the implementation of other reagents into process streams and have been documented in this paper.

## **2.0 BACKGROUND**

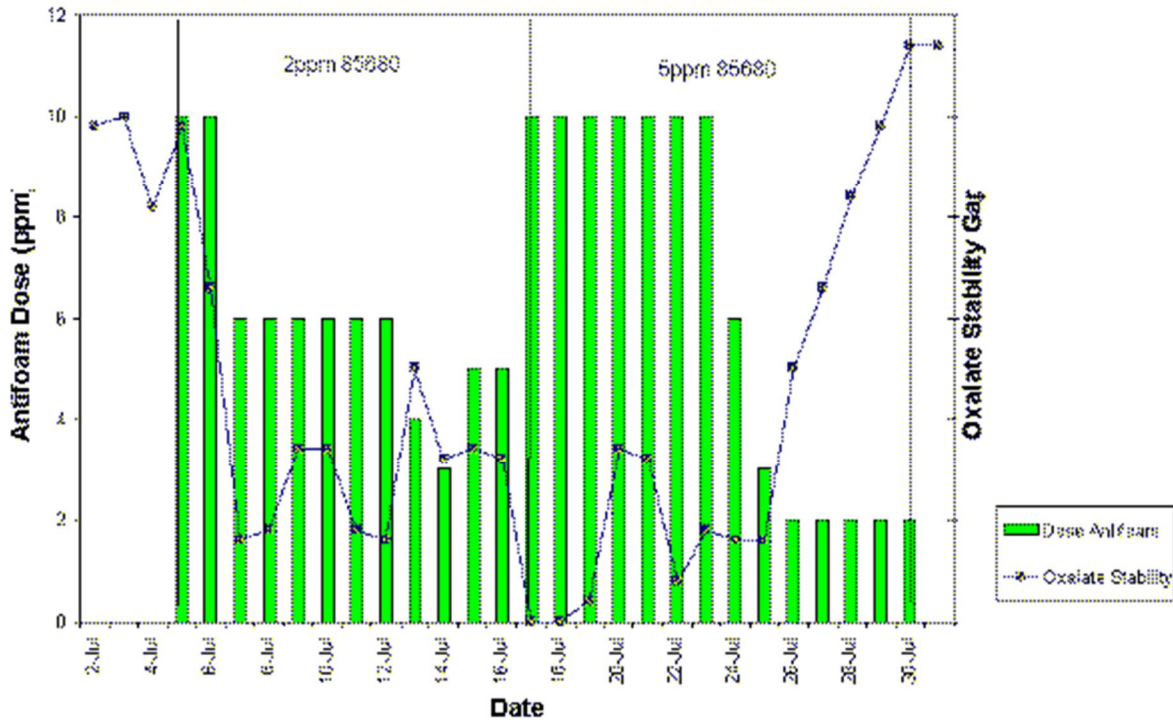
As well as the direct impact (both positive and negative) of reagents on plant operations, the cyclic nature of the process and the severe conditions experienced often results in chemical breakdown and/or buildup of additives. Therefore the downstream impact of the degradation products of chemical additives is also an important aspect of the risk assessment process. While many Bayer plant operators understand the implications of the downstream effects of the degradation products of reagents, the full implications of the subtleties of these effects were demonstrated in a plant crisis which occurred prior to any stabiliser plant trials. The root cause of this severe process problem was eventually tracked to increased addition of a certain chemical additive. However, the detrimental downstream effects of this reagent were only evident under (a) elevated additive concentration when (b) the digestion products of one component of the initial reagent was (c) recycled in a process stream where (d) it was not initially added. Unless these four criteria were met, no detrimental impact was observed.

Testing of the degradation products of this additive using the standard screening tests would not have predicted the problem, nor would they be expected to do so. It is only under a more stringent testing regime that these interactions became evident. In light of this result, consideration of such interactions, and the subtle impacts which may occur, have broadened the scope of downstream testing with a wider range of tests now being part of the product development phase for new reagents.

## **3.0 STABILISER IMPLEMENTATION**

### **3.1 Synergistic effects**

Initial use of the synthetic oxalate stabiliser Nalco 85680 (also known as Nalco 138) resulted in substantial and uncontrolled foaming in the liquor. While a number of conventional antifoam formulations were available to control this foam, the use of these resulted in stability loss rather than the desired stability gain because of an adverse interaction between the stabiliser and the antifoam. Figure 1 shows the dosing rates of the stabiliser and a conventional antifoam during a single bank trial and their combined impact on oxalate stability gap. It can be seen that during low antifoam dosing periods the oxalate stability gap is relatively high, however during higher antifoam dosing periods stability is substantially reduced. As a result of this interaction between the stabiliser and antifoam the development of a non-interacting antifoam or "liquor conditioner" was required. A range of such reagents were developed and these have since been incorporated into the stabiliser formulation to address the foaming issue.



**Figure 1.0**

Impact of antifoam dose on oxalate stability gap

The key issue in the interaction of the stabiliser and antifoams is that the antifoam components interact to make the stabiliser adsorb to the solids. Previous work [Farquharson *et al*, 1995a] has shown that the stabiliser does not partition to the hydrate solids under precipitation tank conditions but rather remains in the solution. However, with the addition of conventional antifoams, the stabiliser preferentially partitions to the hydrate solids. Table 1 shows the percent of stabiliser recovered in spent liquor in tests where stabiliser has been added to a slurry under simulated precipitation conditions. The analysis of stabiliser in the liquor showed that greater than 70% of the stabiliser can be removed from solution by addition of some types of antifoams. The removed stabiliser was consequently measured on the trihydrate solids. In contrast to this it can be seen that other, more compatible, "liquor conditioners" do not reduce stabiliser recovery below the control value.

**Table 1.0**

Recovery of 85680 stabiliser from liquor with the addition of conventional and newly developed antifoams after simulated precipitation conditions

Treatment	% Stabiliser recovered in spent liquor
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Control (85680 alone)	> 85
85680 + Antifoam	<30
85680 + Liquor Conditioner	> 85

In addition to the direct measurement of loss of stabiliser onto hydrate, the interaction between stabiliser and antifoams can also be assessed by the impact of both reagents on oxalate precipitation in the absence of trihydrate. The oxalate stabiliser is a known oxalate "poison" whereby it reduces the ability of oxalate crystals to grow by adsorbing to the crystal surface. This effect is significantly increased in the presence of an interacting material such as a conventional antifoam. Table 2 shows the impact of the stabiliser and antifoams on oxalate yield. The impact is measured in a test which simulates the precipitation of oxalate in the removal process used by Alcoa with the measure of yield being proportional to the final oxalate concentration of the liquor. It can be seen in Table 2 that the stabiliser itself causes the final liquor oxalate concentration to be elevated compared to the control due to the poisoning of the seed, however, this effect is significantly increased in the presence of incompatible antifoam. This impact has particularly important consequences for plants which practice oxalate side-stream removal since the interaction of the two reagents could result in substantial "poisoning" and therefore inefficient removal of oxalate from the liquor stream. The detrimental downstream impact of such events are well known to many alumina refineries.

**Table 2.0**

Enhancement of the poisoning impact of stabiliser with conventional antifoams

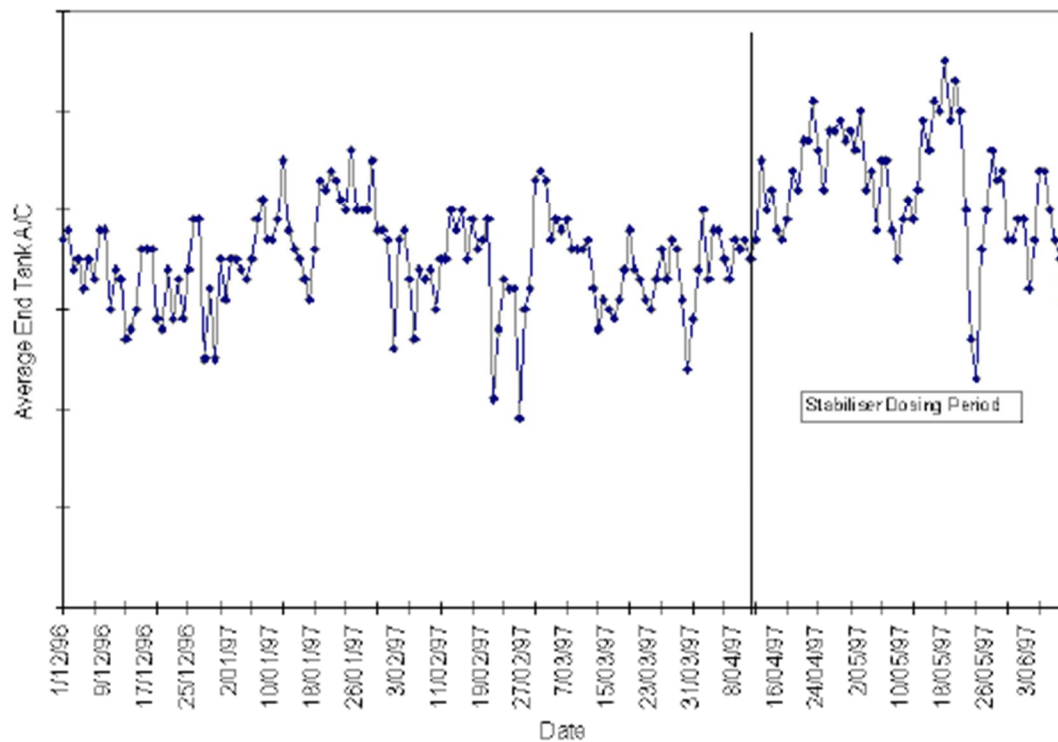
<b>Treatment</b>	<b>Final Liquor [Oxalate] (g/L)</b>
Control	2.21
85680	2.34
85680 + Antifoam	3.01
85680 + Liquor Conditioner	2.34

This clearly demonstrates that not only must the downstream impacts of individual reagents be tested but also the combination of reagents. In many cases laboratory testing may not be required but at the very least careful consideration of possible synergistic effects is recommended.

An example of more desirable synergy can be found in the use of crystal growth modifiers (CGM's) in the Bayer industry. These reagents have been used for well over a decade and substantial documentation and experience has shown how the impact of these reagents can be managed to enhance plant productivity [Roe, Owen and Jankowski, 1988]. However, it is also well known that the individual components of CGM formulations have a reduced impact compared to the formulated products [Owen *et al*, 1991]. In this case, a synergistic effect has been utilised to enhance a desired impact. The complex nature of synergistic effects in the Bayer process is an area that requires some thought so as to maximise the effectiveness of process additives and minimise risk during plant trials.

### **3.2 Suspected trihydrate yield impacts**

With the experience of such complex interactions in mind, and with the lessons learnt from these problem episodes, the full plant implementation of the oxalate stabiliser technology commenced in early 1997. The stabiliser was dosed to the precipitation stream of an entire plant. Shortly after dosing began a significant and sustained loss of trihydrate yield was observed in the process. Figure 2 shows a graph of the average end tank alumina to caustic ratios prior to and during the stabiliser dosing period. From this graph it appears that there is a correlation between the yield loss and the commencement of stabiliser dosing. Ultimately, through intensive laboratory and plant investigation, the cause of this loss was identified as having no relationship to the stabiliser, and hydrate yield has subsequently improved. Prior to this event, extensive laboratory and individual plant precipitation bank trials had shown no adverse effect on hydrate yield or sizing. Therefore this latter investigation focussed on reagent interactions and the impact of breakdown products.



**Figure 2.0**

End tank A/C ratio during non-dosing and stabiliser dosing periods

(Y axis is marked in increments of 0.010)

### **3.2.1 Assessment of possible trihydrate yield impacts**

Tests were conducted using liquor (undosed with stabiliser) from one of the Alcoa Western Australian refineries so as to obtain suitable baseline data. Two types of test were employed:

(a) Precipitation test. A precipitation bottle test was conducted by seeding stabiliser dosed liquor with coarse plant seed and mixing in a rotating water bath. The start liquor had a relatively high A/C so as to simulate the start of the precipitation process and A/C analyses were taken at intervals (typically 4 and 24 hours) to assess the progress of precipitation. It is important to note that end A/C values are not end tank values but rather an indicator of precipitation efficiency.

(b) Recycle Test. The conditions used for this test were the same as for the precipitation test above but the seed used was "preconditioned" by allowing the adsorption of an additive to its surface. This was done by adding the reagent to a trihydrate slurry in spent liquor and equilibrating in a rotating water bath over night. The slurry was then filtered and the solids collected (unwashed) and used as seed in a precipitation tests.

The range of reagents tested include:

- 85680 - liquor oxalate stabiliser
- 96AUS042 - liquor conditioner
- 96AUS085 – combined stabiliser and liquor conditioner
- 85705 - hydrate flocculant
- 94AUS046 - antifoam known to interact with stabiliser
- Component Z - a component in a process input stream suspected to be a problem

Initial work concentrated on the recycle impact of the various reagents being tested since all previous downstream testing on the impact of these reagents on trihydrate yield and sizing had been conducted using only "single cycle" precipitation tests. Table 3 shows the impact of reagents "adsorbed" onto the seed and tested in a recycle test. (Note that the adsorption of the reagents onto the seed is not proven in these tests. The use of the term adsorption merely indicates the opportunity for such an effect rather than a definitive statement of the phenomenon.) Duplicate samples for each dosing condition were taken with two parallel series of tests being conducted. In the first series the liquor in the precipitation run was undosed while in the second series it was dosed with 5ppm of oxalate stabiliser 85680. The data show that in all cases there was no apparent impact on trihydrate yield since end A/C ratios remain unchanged for the stabiliser dosed samples.

Further tests on these reagents were conducted at lower preconditioning step doses (20ppm for stabiliser and 50ppm for conditioners/antifoams) and addition to undosed liquor in the precipitation step. No impact on trihydrate yield was observed so the test was repeated with addition to the precipitation step of the same reagent mix and dose as that of the adsorption step. That is, 20 or 50ppm of the same reagents to both preconditioning and precipitation phases. Again, no impact on final A/C ratio was observed when compared to undosed control samples.

The possibility of an interaction of the stabiliser with an unknown component in the plant liquor was tested by addition of the stabiliser and conditioner to a precipitation test using liquor from the refinery where the hydrate yield problem was observed. Table 4 shows the results for some single cycle precipitation tests which indicate, as previously, no detrimental effect on hydrate yield since the end A/C ratios for the dosed tests are similar to the control.

**Table 3.0**

Treatment and end liquor A/C for two series of tests. Series A was run under conditions of no additive addition to the start liquor and series B used liquor which was dosed with 5ppm of oxalate stabiliser (85680). Start A/C = 0.599

Seed Treatment (Dose used in precondition step)	Average A/C (A) Undosed Liquor		Average A/C (B) Dosed Liquor	
	T = 4hrs	T = 22 hrs	T = 4hrs	T = 22hrs
Control	0.567	0.451	0.566	0.452
85680 (100ppm)	0.567	0.453	0.565	0.452



96AUS085 (150ppm)	0.566	0.451	0.564	0.447
85680/94AUS046 (100/200ppm)	0.565	0.451	0.564	0.444
85680/96AUS042 (100/200ppm)	0.565	0.450	0.562	0.448

**Table 4.0**

Treatment and end test A/C for test 4. Start A/C = 0.600

Treatment	A/C at T = 18hrs	
	Sample 1	Sample 2
Control	0.452	0.451
85680 (20ppm)	0.452	0.452
85680 (20ppm) + 96AUS042 (50ppm)	0.452	0.451

While the digestion products of the stabiliser are well characterised and their impact on oxalate precipitation thoroughly investigated in previous work, tests of their impact on hydrate precipitation, specifically under recycle conditions, had not been fully examined. Although the chemical nature of these reagents and their degradation products were not expected to influence hydrate yield, laboratory tests were carried out to confirm this.

Table 5 shows the results for the precipitation tests carried out with addition of digested and undigested stabiliser. The tests were designed to assess the effects of stabiliser digestion products, antifoams and the hydrate flocculant 85705 on hydrate precipitation. The hydrate flocculant had been used in the plant without issue for a considerable period prior to the introduction of the stabiliser. The tests reported here were also designed to address any synergistic effects between the digestion products of the stabiliser and the hydrate flocculant. The reagents were added to a high A/C liquor and digested (in liquor only) then transferred to precipitation test bottles and seeded as normal. In addition to the bomb digestion of the stabiliser, a tertiary amine which is the major known digestion product of the active component in the stabiliser formulation, was also added to an undigested liquor sample in the precipitation test stage for comparison. A lower liquor volume in this test was used due to size restrictions on the digestion bombs and this led to poorer replication in the data. Nonetheless, there appears to be no significant impact on precipitation yield of the digestion products or a combination of digested reagents.

While these reagents have no significant impact on trihydrate yield directly, their interaction with other process input streams was also tested. In particular, one process input stream (not a specialty chemical) contained one component (Z) which was suspected to have some impact on trihydrate precipitation. Tests were conducted using this component in combination with both stabiliser and conditioner. Table 6 shows the results from this testwork. The data indicate that no synergistic effect is found with the stabiliser and component Z at low doses but that component Z by itself acted as a hydrate poison at high doses. This was confirmed in further testing in a recycle test (refer to Table 7).

**Table 5.0**

Treatment and end liquor A/C. Bottles 1-10 were subjected to digestion.

Bottles 11-20 were not digested. Start A/C = 0.603.

Doses used were: 85680 = 20ppm; 85705 = 20ppm; 96AUS042 = 50ppm

Bottle	Treatment	A/C at T = 20hrs	
		Sample 1	Sample 2
1/6	Control	0.443	0.443
2/7	85680	0.446	0.444
3/8	85680 + 96AUS042	0.440	0.445
4/9	H152	0.443	0.444
5/10	85680 + 85705	0.445	0.441
11/12	Control	0.450	0.453
13/14	10ppm 85705	0.452	0.452
15/16	20ppm 85705	0.453	0.456
17/18	50ppm 85705	0.457	0.451
19/20	20ppm Amine	0.453	0.451

**Table 6.0**

Treatment and end liquor A/C from a standard precipitation test. In the last batch of this test doses used were: Z = 200ppm; 85680 = 20ppm; 96AUS042 = 50ppm

Treatment	A/C at T = 3hrs		A/C at T = 15hrs	
	Sample 1	Sample 2	Sample 1	Sample 2
Control	0.584	0.584	0.492	0.491
Z (200ppm)	0.584	0.585	0.495	0.497
Z (2000ppm)	0.599	0.598	0.512	0.515
Z/85680/96AUS042	0.580	0.581	0.493	0.492

Further confirmation of the impact of component Z on hydrate yield was afforded by a dose response test using the precipitation test method. The data shown in Table 8 indicates a clear impact with increasing dose as end liquor A/C increases by up to 0.3. As a result of this work, further investigation into the impact of the process stream containing component Z and the minimisation of this impact was undertaken.

**Table 7.0**

Treatment and end liquor A/C from recycle tests. Doses used were:

Z = 200ppm; 85680 = 20ppm; 96AUS042 = 50ppm

Adsorption/Precipitation Treatment	A/C at T = 19hrs	
	Sample 1	Sample 2
Control	0.475	0.476
Z	0.483	0.485
Z/85680	0.474	0.475
Z/96AUS042	0.479	0.476
Z/85680/96AUS042	0.476	0.477

**Table 8.0**

Treatment and end liquor A/C from precipitation test

Treatment	A/C at T = 17hrs	
	Sample 1	Sample 2
Control	0.468	0.468
Z (500ppm)	0.482	0.481
Z (1000ppm)	0.487	0.487
Z (2000ppm)	0.496	0.496

While these laboratory tests indicated no impact of the stabiliser or conditioner on hydrate yield, more comprehensive testing together with plant trials of the stabiliser technology were subsequently conducted to assess the impact of the additive on hydrate yield under true plant conditions. A series of stabiliser on/off trials were conducted on a single precipitation unit with close monitoring of the final end tank ratios. These trials were conducted over a period of two months. While quantification of the effects of the stabiliser were difficult it was nonetheless concluded from this work that, rather than inhibiting yield, use of the stabiliser has a significant, but small, positive effect on precipitation yield [Thomas, 1997]. That is, use of the stabiliser resulted in a small yield increase. Further laboratory tests [Harrison, 1998] also indicated a small but statistically significant increase in precipitation yield in the presence of the stabiliser. The magnitude of this impact on the plant in this case is not sufficient to justify use of the stabiliser for this purpose alone, however, the positive nature of this effect highlights the fact that not all downstream impacts of chemical reagents may be negative.

#### **4.0 CONCLUSIONS**

When developing new technology and implementing it in operational plants there will always be a certain amount of risk involved. These risks can never

be eliminated completely by laboratory testing since it is currently not possible to exactly mimic plant processes on the laboratory scale. However, significant minimisation of the risks can be achieved through laboratory test work combined with proper downstream testing and a thorough consideration of any likely impacts. This involves not only consideration and/or testing of the reagents themselves, but also their digestion products. In addition, the interaction of new products with other reagents or species in the process must be considered. The combination of these two paths leads to consideration of the interaction of digestion products of one reagent with the digestion products of another (or others). The possible laboratory testing regime could be considerably large however a knowledge of both reagent chemistry and process conditions can limit the workload to an acceptable sub-set of tests which adequately assess the risk. The cooperative research efforts afforded by the investigation into the new oxalate stabiliser technology has allowed a blending of both process knowledge and reagent understanding such that the stabiliser has been implemented in an alumina refinery with maximum effect and minimal risk to plant operations.

## **ACKNOWLEDGMENTS**

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