

REVIEW OF BAYER ORGANICS-OXALATE CONTROL PROCESSES

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Since the mid-forties, the Aluminum Company of Canada Arvida Research Centre jointly with the Technical Departments of the Bayer Plants have been actively searching for suitable methods of controlling Bayer organics, in general, and sodium oxalate, in particular. Initially, these included such measures as electrolytic, chemical and high pressure air/oxygen oxidations, massive sorption of organics by carbon, alumina and ion exchange resins as well as hydrate seed washing and the subsequent precipitation of calcium oxalate with lime. None of these, however, was ever employed by us on a large industrial scale. The present paper reviews several of our older methods of industrial potential, namely, liquor calcination, ozonation, and precipitation of oxalate/organics through slight, medium and deep evaporation. It also describes recent processes designed for a speedy precipitation of large amounts of sodium oxalate from Bayer spent liquor destabilized with respect to sodium oxalate supersaturation by means of minute amounts of suitable adsorbents or cationic sequestrants.

Introduction

Most Bayer plants have to face the problem of organics control.

The organic carbon present in bauxite is by and large in the form of humic substances. On digestion in the Bayer process, over 50% of the organic carbon is extracted and its concentration in the recycled liquor gradually builds up to an equilibrium peculiar to each plant, typically, to 7, 10, 15 or, in extreme cases, to 25 g/l C.

During the digestion operation, the humic matter degrades to various lower molecular weight compounds. These have been recently characterized into the following three groups (1):

- a) the humics, consisting of the freshly extracted high molecular weight material and its initial degradation products of molecular weight greater than 500,
- b) the intermediate degradation products which constitute the "building blocks" of the large humic molecules, e.g. benzene carboxylic acids and phenolic acids,
- c) the low molecular weight aliphatics.

The most interesting compounds in the latter group is sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, often responsible for a number of operating problems such as a poor classification-settling of fine Bayer seeds and an excessive scaling of pipes and tanks.

The breakdown of organics through digestion-oxidation can be readily demonstrated in the laboratory. Thus, if Bayer spent liquor originally containing 12 g/l organic carbon, including some 4.5 g/l $\text{Na}_2\text{C}_2\text{O}_4$, is kept for 10 minutes at 300°C under air at 100 Kg/cm² pressure, the oxalate in the liquor will increase to about 6.5 g/l $\text{Na}_2\text{C}_2\text{O}_4$. Also, if a similar liquor is subjected to ozonation at room temperature for 2-3 hours, one obtains 6-8 g/l $\text{Na}_2\text{C}_2\text{O}_4$ precipitate while still leaving in the liquor about 3 g/l $\text{Na}_2\text{C}_2\text{O}_4$. On the other hand, if one were to subject the liquor to heat-pressure treatment at 100 Kg/cm² under the atmosphere of pure oxygen for one hour, then essentially all the organic matter would oxidize to CO_2 , carbonating an equivalent amount of caustic to Na_2CO_3 .

Under the Bayer digestion conditions, the formation of CO_2 proceeds at a much slower rate than the net buildup of organic carbon in the liquor. As a result, the yearly rate of organic carbon buildup in Arvida Bayer plants, employing a digestion temperature of 150°C, varies between 1.8 and 2.5 g/l C, depending on the amount and the type of the organic matter present in the processes bauxite.

It is not difficult to show experimentally that only the high molecular weight colored humic compounds are responsible for (i) liquor foaming, (ii) deactivation of Bayer hydrate and oxalate seed and (iii) an increased liquor stability with respect to alumina and

oxalate solubilities.

The stabilizing effect of the high molecular weight humics on the solubility of oxalate in Bayer spent liquor can be demonstrated by passing the liquor through a bed of activated carbon. Such a treatment removes only colored humic compounds, but leaves all the oxalate in solution, say, 5 g/l $\text{Na}_2\text{C}_2\text{O}_4$ or so. If such a partially purified liquor is left to stand overnight at room temperature, the oxalate will spontaneously precipitate out without any seeding, leaving in the solution about 2.5 g/l $\text{Na}_2\text{C}_2\text{O}_4$.

Schemes for Controlling Bayer Organics-Oxalate

Throughout the years, both the Arvida Research Centre and the Works Technical Departments investigated well over a dozen possible schemes for the control of Bayer organics.

Some of these never passed the laboratory scale experimentation stage and for various reasons were eventually abandoned, namely:

1. High pressure-high temperature oxidation under air and/or oxygen.
2. Electrolytic oxidation.
3. Use of powerful oxidizing agents (peroxides).
4. Adsorption on activated carbon, activated alumina, fine hydrate and ion exchange resins.
5. Seed washing followed by the precipitation of CaC_2O_4 .
6. Precipitation of sodium oxalate from non-evaporated spent liquor through seeding with over 50 g/l $\text{Na}_2\text{C}_2\text{O}_4$ seed.

The present paper discusses only those schemes that are either of a novel nature, have been tried on a large pilot scale or have been used in the actual industrial practice, namely:

1. Liquor calcination with added bauxite.
2. Liquor ozonation.
3. Precipitation of oxalates-organics mixtures in fluidized bed columns.
4. Precipitation of oxalate in packed spray-trickle columns.
5. Precipitation of oxalate from destabilized spent liquor.
6. Precipitation of Bayer organics from deeply evaporated spent liquors.

Description of Six Methods for the Control of Bayer Organics

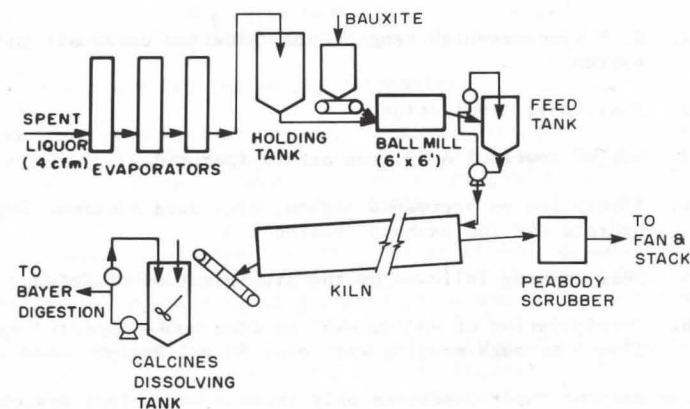
1. Liquor Calcination

For the past twenty five years or so, the control of Bayer organics in Arvida has been exercised through the calcination of pre-evaporated spent liquor, as indicated in Figure 1.

In the early stages of this process, the liquor was calcined without any additives which resulted in the carbonation of essentially all of its caustic. Later, the liquor was mixed with fine hydrate and, eventually, with a finely ground bauxite, as causticizing agents.

FIGURE 1

SCHEMATIC FLOW SHEET OF ARVIDA LIQUOR CALCINATION PLANT



The efficiency of organic carbon destruction is about 95% and the daily rate of organic carbon removal is around 1.2T C.

The liquor calcination process is neither simple nor cheap in operation. For this reason alternative methods have been sought.

2. Ozonation of Bayer Spent Liquor

Early in 1971, we found that when oxygen containing some 1.7-2.0% of ozone, O_3 , was bubbled through Bayer spent liquor containing 10-12 g/l organic carbon, the solid phase that crystallized out as in the form of relatively large needles of pure $\text{Na}_2\text{C}_2\text{O}_4$.

The liquor yielded up to 8 g/l of oxalate precipitate when treated with up to 8 g/l O_3 . Since the original liquor taken for ozonation contained 4.5 g/l of soluble $Na_2C_2O_4$ and that after treatment only 2.5 g/l $Na_2C_2O_4$, the net amount of $Na_2C_2O_4$ generated during ozonation was 6 g/l.

Concurrently with the generation of oxalate, the ozonation also resulted in the carbonation of about 10 g/l of caustic to Na_2CO_3 . As a result of these two effects the concentration of the organic carbon in the liquor decreased by about 2.5 g/l C. About one half of this reduction of the organic carbon in the liquor was due to the precipitation of oxalate whereas the other half was due to the generation of CO_2 .

The liquor ozonation also resulted in the following side effects:

- (i) The color of the liquor changed from dark-brown to straw-pale.
- (ii) The liquor became non-foaming.
- (iii) On deep evaporation, down to 560 g/l caustic concentration, the ozonated liquor yielded a coarse precipitate of excellent settling and filtering characteristics.
- (iv) The ozonated liquor gave 2-3% lower alumina productivity when digested with bauxite at $150^\circ C$, but it gave 2-3% higher Al_2O_3 productivity than the non-ozonated liquor when digested at over $200^\circ C$.

A suggested ozonation setup for treating $140\text{ m}^3/\text{day}$ Bayer spent liquor is shown in Figure 2.

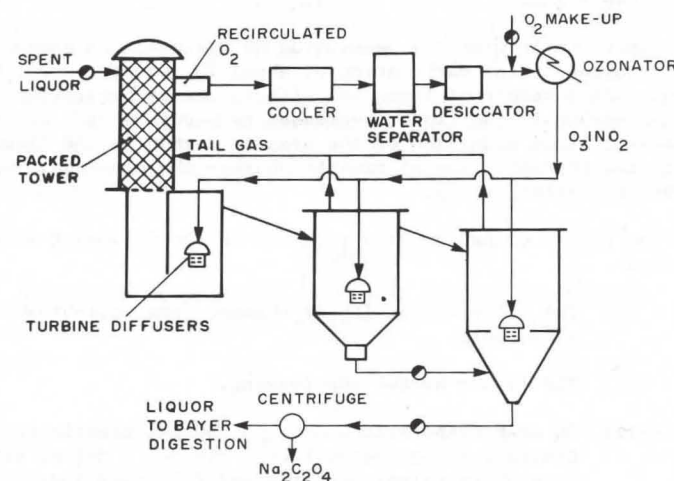
3. Precipitation of Oxalate-Organics Mixture in Fluidized Bed Columns

A continuous process for the precipitation of oxalate through seeding of non-evaporated spent liquor was tried on a large pilot scale in the early fifties. It proved to be quite troublesome in operation owing to the fact that the coprecipitating high molecular weight organics tended to inhibit oxalate seed. For this reason large quantities of fine oxalate (50-75 g/l $Na_2C_2O_4$) were required to effect satisfactory precipitation in a reasonable time. In addition, the final oxalate seed was difficult to handle in a fluidized bed column. The maximum rate of upward liquor flow in the column could not exceed 6 cm/hr, if a clear overflow were to be obtained.

Because of the difficulties described above, in 1964 we developed the so-called "oxalate column" that operated on a partially evaporated liquor of about 420 g/l TTS concentration.

FIGURE 2

SKETCH OF SUGGESTED OZONATION PLANT FOR TREATING 5000 cu.ft / DAY BAYER SPENT LIQUOR, (3 S.S. TANKS, 6' dia. x 8', 2 hrs. RETENTION TIME.)



The pre-evaporated liquor was cooled down to $70^\circ C$, and then contacted with very coarse Bayer organics seed kept under fluidized condition in a 60 cm diameter, 20 m high column. The actual plant setup is sketched in Figure 3.

A 30-minute contact of the evaporated liquor with coarse Bayer organics seed particles of between 4 and 10 mesh in size, reduced the liquor organic carbon by about 2 g/l C (evaporated basis). About one half of the precipitated carbon was in the form of oxalate, $Na_2C_2O_4$, whereas the other half represented several unidentified colored Bayer organic compounds. The product that was in the form of relatively soft spheres analysed: 32% $Na_2C_2O_4$, 12% total organic carbon, 15% free caustic, 10% Na_2CO_3 and about 5% Al_2O_3 .

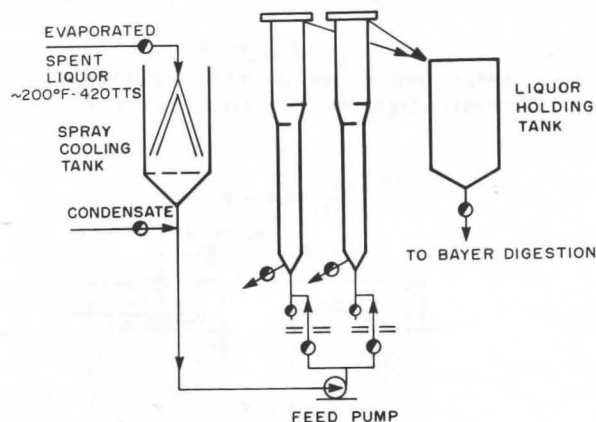
The seeding was self-sustaining, i.e. the column could be started on coarse or fine seed and in the course of normal operation a sufficient amount of new fine seed was formed. The nominal upward flow of the liquor through the column was between 60 and 90 cm/min. The fine seed at the very top of the fluidized bed contained -12+28 mesh particles.

Under normal operating conditions, the rate of build-up of solids in the column was between 30 and 45 cm/hr of column height. To maintain a continuous operation, coarse solids were removed from the bottom of the column at least four times per shift. Each dump yielded 0.15-0.20 T of spheres up to 1.25 cm in diameter.

For proper functioning of the column, both the degree of liquor evaporation and the liquor flow through the column have to be carefully controlled.

FIGURE 3

PRECIPITATION OF BAYER ORGANICS-OXALATE IN FLUIDIZED BED COLUMNS (2'x2.5'x70')



A more recent version of the process substitutes a stirred reactor-precipitator for the old fluidized bed column. This produces relatively fine but easy-to-dewater solids instead of large spheres that did not require any filtration.

4. Precipitation of Oxalate in Packed Spray-Trickle Columns

An interesting modification of the "oxalate column" technique was developed (2). The idea was to spray-trickle only a very slightly concentrated spent liquor, from 230 g/l TTS up to 290 g/l TTS, into a bed of steel turnings. After some small-scale tests, a pilot column of 1.7 m diameter and 5.5 m high was packed with mild steel turnings to a height of about 3.5 m. A flow of 283 l/sec. of spent liquor at around 70°C was sprayed onto the bed from a height of about 1 m by radially distributed 1.25 cm diameter series of nozzles.

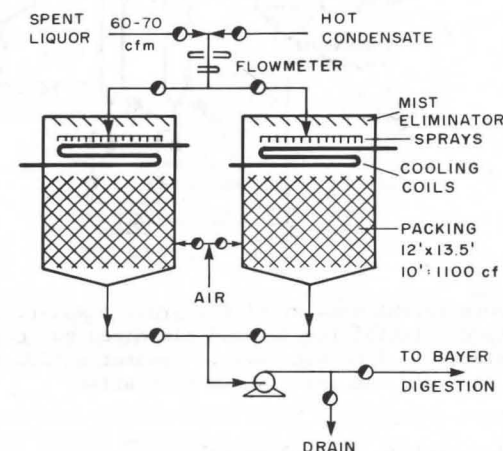
The column was in operation on a regular basis from December 1974 to March 1957, yielding some 180-230 Kg/day of essentially pure oxalate, deposited as a scale on steel packing.

The column could be operated on a continuous basis for at least seven days before washing the packing with hot condensate at 100°C. After seven days of operation, the deposited oxalate amounted to about 1.5 T and required 42.5 m³ of condensate to dissolve it, giving a wash solution of about 35 g/l Na₂C₂O₄. Following the successful pilot runs, a plant scale unit was built comprising two columns in parallel, each of 3.5 m diameter, 4.0 m high and containing some 30 m³ of steel turnings packing.

Initially, the sprayed liquor was at its usual plant temperature of 75-80°C. Later, however, a series of cooling coils were placed in the free space between the sprays and the packing to lower the liquor temperature by about 15°C. As a result, the columns were able to increase their oxalate pickup from the usual 1.0 T/day to 1.4 T/day. The modified plant setup is shown in Figure 4.

FIGURE 4

SPRAY-TRICLE SET-UP FOR THE ENCRUSTATION CRYSTALLIZATION OF BAYER OXALATE



The peculiarity of this system is that the liquor yields very minute amounts of oxalate precipitate; something of the order of 0.25 to 0.5 g/l Na₂C₂O₄. As a result, it is necessary to process large volumes of the liquor in order to remove the required 1.0-1.5 T/day Na₂C₂O₄.

5. Precipitation of Oxalate from Destabilized Liquor

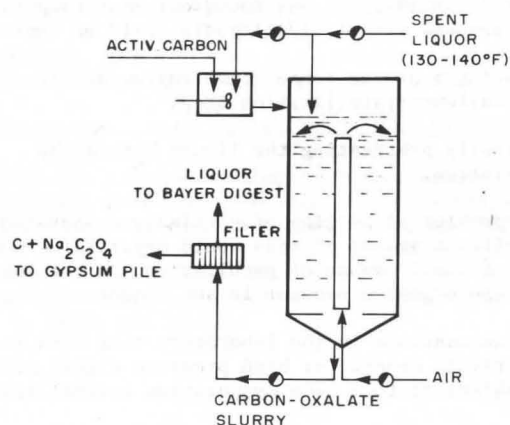
Bayer spent liquors normally tolerate over 100% supersaturation with respect to Na₂C₂O₄, before spontaneous precipitation of oxalate takes place. It is generally believed that the high molecular weight colored humic organics are responsible for this supersaturation.

Late in 1977, it was discovered that very small quantities of adsorbents, e.g. activated carbon, or cationic sequestrants such as "Arquads" or "Armosoft-L", (Quarternary ammonium compounds manufactured by Armaq Chemicals Ltd), when added to spent liquor supersaturated with respect to sodium oxalate, will destabilize the liquor by removing small amounts of the inhibiting organics, less than 0.5 g/l C. This allows the oxalate to autoprecipitate.

Additions of either 0.1-0.2 g/l Arquad or 0.25-0.5 g/l activated carbon were effective in reducing the $\text{Na}_2\text{C}_2\text{O}_4$ concentration of Arvida spent liquors from 4.5-5.5 g/l $\text{Na}_2\text{C}_2\text{O}_4$ to the solubility level of approximately 2.5 g/l. The closer the oxalate level is to the critical supersaturation level, where precipitation occurs spontaneously, the easier it is to induce the precipitation and the smaller the quantity of the destabilizing agent required.

For liquors containing 4-5 g/l $\text{Na}_2\text{C}_2\text{O}_4$, the addition of a small amount of active sodium oxalate seed, (around 0.2-0.5 g/l), helps considerably in inducing oxalate precipitation. On a large industrial scale, activated carbon, in amounts of 0.25-0.5 g/l, was used to induce oxalate precipitation in batches of 850 to 1,700 m^3 of spent liquor per day, as indicated in Figure 5.

FIGURE 5
AN INDUSTRIAL SET-UP FOR BATCH DESTABILIZATION-
PRECIPITATION OF OXALATE



Ideally, only liquors containing more than 4.5 g/l $\text{Na}_2\text{C}_2\text{O}_4$ should be used for the destabilization-precipitation. Such liquors yield some 2.0 g/l $\text{Na}_2\text{C}_2\text{O}_4$ precipitate when treated with only 0.25 g/l fine activated carbon. If one were to treat liquors of 4 g/l $\text{Na}_2\text{C}_2\text{O}_4$, it would be necessary to increase the carbon charge to 3.0-0.5 g/l while, at the same time, the amount of the precipitated oxalate drops to less than 1.5 g/l $\text{Na}_2\text{C}_2\text{O}_4$.

At Arvida, the oxalate-carbon mixture after precipitation is separated from the liquor by filtration and then trucked to disposal at an environmentally acceptable location.

The process is especially useful when there is a need to remove rapidly large quantities of oxalate from Bayer liquor. Patents are pending on this method.

The destabilization-precipitation readily lends itself to a continuous operation. Two different continuous-type systems are being presently worked out.

6. Precipitation of Bayer Organics from Deeply Evaporated Spent Liquor

In the late sixties, a considerable effort was put into the development of sodium carbonate-organics co-precipitation from deeply evaporated spent liquors (540-560 g/l caustic soda).

In the case of Arvida liquors, containing 12-15 g/l organic carbon, it was first impossible to obtain filterable solids through the evaporative crystallization. At caustic concentrations required for an effective removal of sodium carbonate, the liquor tended to gel and the increased viscosity of the resulting slurry was too high to permit efficient crystallization.

However, early in 1972, it was found out that evaporative crystallization process with Arvida liquors could be improved by:

- (i) Following a proper temperature regime of the evaporation-crystallization step.
- (ii) Chemically pretreating the liquor before the evaporation.

The Arvida problem of gelling of partially evaporated liquors, before any significant amount of soda would crystallize out, was primarily due to a small amount of peculiar and as yet not identified precipitable organics present in the liquor.

One way to demonstrate in the laboratory that this is so, is to either exhaustively ozonate or high pressure digest Arvida liquor and then subject it to a deep evaporation crystallization (3).

The ozonated liquor will not foam during the evaporation and the crystallized-out solids will be light-brown color containing only soda, sulphate and oxalate. The solids are easy to filter and/or centrifuge and the filter cake retains less than 20% moisture.

Subsequent tests on evaporative salting-out of sodium carbonate and organic mixtures from Arvida spent liquors, carried out in the laboratory and on a large pilot scale, showed that about 25% of the organic carbon present in the liquor precipitates out with soda. Typically, a 12 g/l organic carbon liquor gave over 3 g/l of precipitated carbon when the liquor was evaporated down to about 560 g/l caustic (as Na_2CO_3).

The precipitated organics contain about 30% of oxalate which corresponds to essentially complete removal of oxalate from the liquor while the remaining 70% of the precipitated carbon represents colored humic organics.

Unlike any other known method for the purification-rejuvenation of Bayer liquor, the evaporative crystallization technique removes objectionable organics, soda ash, some sodium sulphate and fluorides in one single-step operation.

Problems encountered in the process of a large-scale evaporation of Bayer aluminate liquors to 500-550 g/l caustic soda have been widely discussed in the published literature (3)(4)(5).

Acknowledgement

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