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, Na₂C₂O₄, 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 Na₂C₂O₄, 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 Na₂C₂O₄. Also, if a similar liquor is subjected to ozonation at room temperature for 2-3 hours, one obtains 6-8 g/l Na₂C₂O₄ precipitate while still leaving in the liquor about 3 g/l Na₂C₂O₄. 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 CO₂, carbonating an equivalent amount of caustic to Na₂CO₃.

Under the Bayer digestion conditions, the formation of CO₂ 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 Na$_2$C$_2$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 Na$_2$C$_2$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$_2$O$_4$.
6. Precipitation of sodium oxalate from non-evaporated spent liquor through seeding with over 50 g/l Na$_2$C$_2$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 causticising 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 1.2 T 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 Na$_2$C$_2$O$_4$. 279