

SIZING AN ORGANIC CONTROL SYSTEM FOR THE BAYER PROCESS

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Abstract

Organic materials are introduced to the Bayer process by almost all bauxites. Over time, the accumulation of organic matter in some Bayer liquors decreases liquor and plant productivity. The organics level can be limited by some form of liquor purging, or by operating an organics control system. This paper presents a Mass-Balance Model for predicting the rate of increase and decrease of organic concentration levels in response to changes in bauxite, purge rate and/or the commissioning of an organic destruction system. Correct selection and sizing of the organic destruction unit is the key to improved Bayer plant productivity and environmentally acceptable operation.

The first Solid-Liquid Calcination (SLC) plant for organic destruction has just been installed at Alumina Espanola, Spain. The performance criteria of this technology will be highlighted.

1. Introduction

The choice and justification of an Organics Control System for a Bayer plant is a complex issue. The quantity and quality of the organics input varies with the bauxite. The impact of the organics on the process varies from plant to plant. Prediction of the effect of a change in organics level on plant operation is not easy. There are a number of techniques available to modify the organic load, of varying efficiency. Any change in the organic content of a Bayer circuit will be exponential rather than immediate. From this catalogue of opportunities the engineer must produce a pattern of cash flow which will satisfy the economic criteria used by his company to evaluate investments.

This paper is intended to provide information which will enable an engineer to prepare such justifications.

2. Background

Origin of Organic Carbon

Organic matter is a component of all soils. Its concentration can vary between 0.05% and 90% depending on location and depth. Fortunately, the geochemical processes which give rise to 'bauxitisation' of soil tend also to deplete the soil of organic matter. Typical levels of organic matter in bauxite are 0.03% - 0.5% as Organic Carbon. The lower values are associated with

underground mining of geologically old karstic bauxites in Europe, Russia and China. The higher values occur in surface mining of younger lateritic bauxite in South America, Africa and Australia. Subsequent mining and beneficiation of bauxite ore is organised to further minimise the amount of organic matter in the ore supplied to plants for processing. Nevertheless, a small but significant level of Organic Carbon invariably reports as part of the bauxite feedstock to an Alumina Refinery.

Dissolution of Organic Carbon

Organic matter in bauxite consists principally of amorphous anionic high molecular weight polyelectrolytes termed humic acids. These are readily soluble in a strong base such as caustic. Under bauxite digestion conditions, 60-90% of humic matter dissolves as sodium humate. The remainder of the humic matter is unextracted due to bonding or adsorption by insoluble inorganic components in the bauxite. The hydrolysed humate is immediately subjected to a degradation process within digestion [1]. Large humate molecules are broken via cracking to yield their lower molecular weight 'building blocks' such as salts of benzene carboxylic and phenolic acids. Further cracking or oxidation of these intermediates yields a range of progressively lower molecular weight stable compounds such as sodium succinate, sodium formate and sodium lactate. The final oxidation products of the stable group are sodium oxalate and sodium carbonate. Digestion liquor is a cocktail of the above organics in various degrees of degradation.

Accumulation of organic carbon in plant liquor

For purposes of calculation this cocktail can be considered as a mixture of three chemicals:

(1) *Sodium oxalate*

This is the breakdown product of most importance. It is the only stable product with a low solubility under Bayer process conditions. It exists in a supersaturated state in most Bayer precipitation circuits. Its controlled removal and disposal are critical to the successful operation of a modern Alumina Refinery. Fortunately there are a number of satisfactory methods of control, and hence it is not the major focus of this paper.

(2) Sodium organics

It is analytically convenient to characterise the level of sodium organics by the 'Total Organic Carbon (TOC)' content. Liquor TOC, determined by oxidation or combustion to CO₂, is thus a blanket measure of the various types of organic compounds described above. Within this broad band, individual sodium organics exhibit specific properties such as hydrate kinetics inhibition, flocculation inhibition and foam generation. As the most negative side effects of organics are associated with the higher molecular weight humates, some plants attempt to quantify this fraction of organics by its colouring effect. However, for the moment, liquor TOC remains the principal descriptor of liquor organics.

(3) Sodium carbonate

This is a final oxidation product of sodium humate as well as being the principal inorganic impurity in liquor. The input from oxidised bauxite organics is the most significant contribution with smaller inputs from bauxite inorganic carbon and air carbonation.

The quantity of organic Carbon dissolved during digestion depends principally on the chemical composition of the precursor humic acid matter in the bauxite. The degree to which this sodium humate degrades to intermediate and stable compounds depends on digestion temperature and the presence of oxidising agents or catalysts in the bauxite. It is generally accepted that the bulk of organic degradation to intermediate and stable compounds occurs during the first pass of digestion [2].

Partitioning of bauxite 'Organic Carbon'

A typical breakdown of bauxite organic C in digestion is as follows :

Bauxite organics C -	Na-Carbonate	15%
	Na-Oxalate	10%
	Dissolved Na-organics (TOC)	55%
	Non extracted (with mud)	20%

Other process additives such as flocculants and antifoams contribute to the input of organic carbon and so influence the generation of TOC, oxalate and carbonate. However, their contributions are relatively small.

Because sodium organics, with the notable exception of sodium oxalate, are quite soluble in Bayer liquor, they accumulate over time to an equilibrium level where output rises to equal input. This affinity for Bayer liquor limits the scope to remove them and often results in disruptively high liquor TOC levels.

3. The Cost of Organic Carbon

Reynolds [5] calculated in 1980 that the physical effects of organic carbon (boiling point elevation, specific gravity, viscosity, specific heat) increased the cost of production of alumina by 5-13 cents per tonne per gpl of organic carbon.

In addition organic carbon in Bayer liquor reduces the rate of precipitation, raises the equilibrium end ratio and has no effect on the digestion ratio. In any plant, the net effect is a loss of productivity.

The impact of individual chemicals is known. Typical Alcan data is given in Table 1.

Caustic Concentration (gpl)	180	214
Organic Compound		
Sodium Formate	.65	.72
Acetate	.33	.46
Succinate	.20	.33
Lactate	1.21	1.35
2.5 Dihydroxy Benzoic Acid	.19	.42
1.2.4 Benzene Tricarboxylic Acid	.24	.31
1.2.4.5. Benzene Tetra Carboxylic Acid	.19	.16
Benzene Penta Carboxylic Acid	.33	.25

These figures were determined for a short precipitation (24 hours) with temperature ramped down from 70°C to 55°C during precipitation.

However data on individual chemicals is not particularly helpful in dealing with the cocktail in a mature Bayer liquor.

If mature plant liquor is available, the effect of a reduction in the organic carbon loading is easy to determine experimentally: dilute the plant liquor with caustic, carbonate and water to bring the organic carbon to its new level, and run precipitation tests simulating the installed circuit. In the absence of mature liquor (e.g. during the design of a greenfields plant) the problem is more difficult.

In 1971 Showa Denko KK [3] extracted organic matter from liquor by acidification and n-butanol extraction, and found that this matter reduced liquor productivity by 0.725 gpl per gpl of organic carbon at 46.5 hours precipitation time, and by 0.875 gpl at 22.5 hours.

Sumitomo found in 1973 [4] that 1 gpl organic carbon raises the end ratio by 0.0066 at 48 hours precipitation time, 55°C, 214 gpl caustic and 300gpl seed (units have been converted to a North American basis).

Reynolds [6] examined the effect of several impurities in 1983, and found that, unlike other liquor impurities (Na₂CO₃, NaCl and Na₂SO₄), organics have no effect on the Digestion ratio. They reported that 1 gpl organic soda changes the productivity by

0.195gpl Al_2O_3 at 65°C and 200 gpl caustic for precipitation times between 24 and 72 hours.

In the same year Pechiney [7] presented models which allow us to calculate a productivity loss "at the end of precipitation" of 0.31 gpl per gpl of organic soda at 273 gpl caustic, 380 gpl seed and 55°C.

Alcan would normally model the effect of organic carbon on precipitation, but for quick calculation purposes would assume 0.40 gpl productivity loss per gpl organic carbon.

(4) Methods of removing O.C. from Liquor

As already discussed, accumulation of TOC in liquor causes operating and process inefficiencies. Plants generally learn to operate within the constraints imposed by accumulated TOC until some development forces a more positive solution. These 'developments' can be an increase in plant caustic, a sudden jump in TOC due to improved soda loss control in the mud circuit or the decision to enter a higher specification hydrate market. Historically, the preferred methods of TOC control in liquor have been:-

Liquor Purging (Dawsonite Process)

Liquor Calcination

Wet Oxidation

Barium salt crystallisation

Partial Removal by Adsorption

Liquor Purging (Dawsonite Process)

Dumping liquor, in the form of spent liquor or in the form of a selected organics-rich stream, is the oldest and simplest technique available. The Dawsonite process allows partial recovery of Na and Al by precipitating sodium-aluminate-carbonate (dawsonite) via neutralisation with CO_2 . [14] These solids are removed, deliquored and calcined to produce sodium aluminate. The carbonated liquor containing other soluble impurities is rejected. While this process is quite efficient at controlling soluble impurities, it also leads to a significant loss of process caustic and alumina, and so its viability is closely linked to caustic prices. Additionally, disposal of solubilised impurities in this manner is not desirable from an environmental viewpoint.

Liquor Calcination

The basic process is well known and variations of it have been in existence since the early 1900's. The concept is that a side stream of liquor containing the accumulated organics is evaporated and calcined in the presence of available alumina to form sodium aluminate. 99%+ of the TOC is burned off and the Na from sodium-organates plus Na_2CO_3 is recovered. The product clinker is leached in spent liquor and any insoluble residue reports to the mud circuit. The attributes are complete destruction of TOC in the stream, recovery of Na and absence of an environmental waste disposal problem. The main drawbacks have been operational difficulty combined with an unsavoury working environment,

coupled with a high cost. These problems have now been overcome with the development of the SLC process. [12] [13]

Wet Oxidation

This method of organics destruction is a commercially proven Industrial process. It has been implemented successfully in the Bayer circuit by VAW at its Stade Refinery. [8] Here, oxygen injection into a high temperature tube digester yields a satisfactory rate of TOC oxidation. The main disadvantages of this system are the potential for an explosion, and also the difficulty in achieving adequate conversion rates at lower temperatures and as the TOC level reduces. The end product is sodium carbonate in solution, which must be controlled by appropriate means. The action of manganese dioxide on the system [9] is also an oxidation process.

Barium Salts

Both Barium-organics and Barium-inorganics can be precipitated from Bayer Liquor by the addition of soluble Barium salts such as Barium Oxide or Barium Aluminate.[15] The normal process application involves 2 stage crystallisation of Barium. In the first step, an excess of soluble Barium is added to precipitate all the inorganics followed by the organics. This is necessary because Ba-organics form only after all the inorganics have been precipitated. The salted-out Ba-products are removed and the Barium rich liquor is then contacted with more spent liquor in a second crystalliser to precipitate the remaining available Barium. The combined Ba-salts are mixed with an alumina source to yield a slurry of molar ratio 1.05 $\text{Al}_2\text{O}_3:\text{BaCO}_3$. This cake is calcined to yield a Barium Aluminate clinker that is recycled to the 1st stage crystalliser. The process is workable but involves Crystallisation, S/L Separation and Calcination. In addition, handling of Barium is potentially dangerous.

Partial Removal by Adsorption

Some long chain organics can be removed by adsorption on quaternary amines [11] or by magnesium hydroxide [10]. This can dramatically improve the colour of the process liquor and subsequent hydrate, but does little to address the productivity losses caused by the remaining organics. The cost of the reagent, coupled with the destabilisation of soluble oxalate on its use, limits its application to special cases.

5. TOC Accumulation and Required Liquor Purification Capacity

To establish the organic balance in a Bayer circuit we propose a simplified approach. Table II gives the basic data required.

Table II
Basic Plant Assumptions

	Units	Symbol	Quantity
Alumina production	T/y	A	1.4m
Bauxite factor	TBx/TAI ₂ O ₃	B	2.0
Organic carbon in bauxite	%	O _B	0.15
Extraction of organic carbon in bx.	%	O _I	65.0
Flour consumption	kg/TAI ₂ O ₃	F	1.0
Organic carbon in flour	%	O _F	44.0
Flour extracted to liquor	%	D	10.0
Salt cake produced	kg/T Al ₂ O ₃	S	13.0
Organic carbon in saltcake	%	O _S	8.0
Organic carbon with hydrate (as.Al ₂ O ₃)	%	O _H	0.04
Concentration of caustic in plant liquor	g/L	C	225.0
Caustic loss with effluents	kg/TAI ₂ O ₃	E	5.0
Plant liquor inventory	m ³	V	220,000

TOC Liquor Input to Process

(In all these calculations the zeros associated with kg/T, T/Y, g/L and % have been cancelled for simplicity in presentation)

From Bauxite: $A * B * O_B * O_L * 100$
 $\equiv 2730$ T. Organic Carbon/year

From Flour: $A * F * O_F * D/10$
 $\equiv 62$ T Organic Carbon/Year

Total Input (Ti) = 2792 T Organic Carbon/Year

TOC Output from Process Liquor

There are three main output streams. Let x (g/L) be the concentration of organic carbon in the liquor at any moment. Then:-

With Salt Cake (SC) $S * A * O_S * 10$
 $\equiv 1456$ T. o.c. /year

With Hydrate (H) $A * O_H * 10,000$
 $\equiv 560$ T o.c./year

With Effluent (L) $(A * E * X/C) * 1000$
 $\equiv k X$
 $\equiv 31.1 X$

Steady State Balance

At steady state inputs will be balanced by outputs.

Ti = SC + H + 31.1 X
 Hence X = 24.8 g/L TOC in liquor

The time (t) to reach steady state can be calculated as follows:-

Accumulation = Input - Output
 $VdX = Ti * dt - (SC-H-k*X)*dt$

$Vdx = (Ti-SC-H-k*X)dt$
 $dt/V = dX/(Ti-SC-H-k*X)dt$
 $dt/V = dX/(Ti-SC-H-k*X)$
 Let $X^1 = (Ti-SC-H-k*X)$
 Then $dX^1 = k * dX$
 $dt/V = dX/X^1$
 and $dX^1/kX^1 = dt/V$
 Integrating from $t_i=0$ gives
 $Ln X^1_{fin} - Ln X^1_{in} = -kt/V$ or
 $X^1_{fin}/X^1_{in} = exp(-kt/V)$
 Substituting for X^1 yields:
 $X^1_{fin} = (Ti-SC-H)/k (1-exp(-k t/V))$

The attached Fig. 1 shows the exponential accumulation of TOC in liquor over time. We have set out earlier the impact that this accumulation can have on costs and productivity. Suppose we wish to control the organic carbon at a level below the natural equilibrium level. We can set a target level and then calculate the costs of attaining it.

Assume for the above case the target TOC is set at 10g/L. The revised TOC balance with the additional liquor purge of Ym³/hour is:-

$Ti = SC + H + 31.1 * 10 + Y * 24 * 365 * 10/1000$
 Hence Y = 5.3m³/hour of spent liquor

i.e. the organics in the equivalent of 5.3 m³/hr of plant spent liquor must be removed from the circuit. If this spent liquor can be pre-concentrated, the volume will reduce accordingly. Liquor burning is a practical possibility for this volume, and at the same time, it also makes sense to calcine the relatively dry saltcake from the evaporative crystallisation to recover the sodium aluminate values. Once liquor burning is operational, the TOC balance at t' years after liquor burning becomes:

$Vdx = (Ti-SC-H-k^1 * X)*dt$, where
 $k^1 = 31.1 + (5.3 * 24 * 365/1000)$

and the solution is obtained as before as

$X_{fin} = (Ti-SC-H)/k^1(1-exp(-k^1 t/V))$

The impact of this exponential reduction in organics concentration is also shown in Fig. 1.

TOC accumulation and Depletion in plant liquor

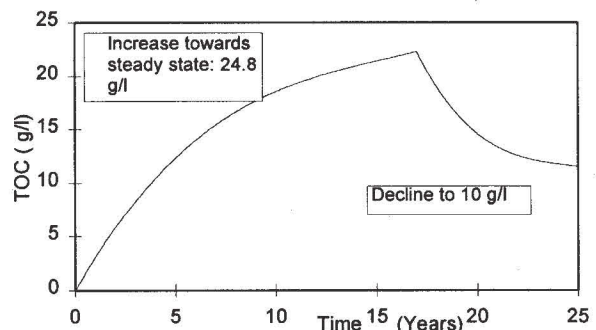


Figure 1

6. Costs of Removal of Organic Carbon

Calculations can be complicated because the methods described earlier can be used in combination. For example, liquor burning can be pursued alone, or in combination with an evaporative step, with or without separation of a crystalline "salt-cake". The costs given below are generalised and cover a broad range because of the complexity of the possible permutations. It is essential that real figures be worked out for each proposed location.

Capital Costs

Evaporation: US\$ 10-20/annual tonne of evaporation (lower range for simple evaporators, higher range for complete evaporator crystalliser systems, both including all ancillaries.)

Drying - Calcination: US\$ 200-400/annual tonne of calcine (lower range for large units operating on concentrated feedstocks. Higher range for small units operating on more dilute feedstocks).

Operational Costs

The operating cost variables are:

- Energy (fuel & power)
- Process Consumables
- Operation/Control
- Maintenance
- Soda and alumina recovery

Energy

A nominal 120T/D calcine prototype unit will be started at San Ciprian early in 1998. Success of this unit will be determined by achievement of the criteria set out in Table III.

At 120 MTPD figures of 1350 kcal/kg and 114 kWh/mt can be expected. The heat consumption can be translated into 0.13 tonnes fuel oil per tonne clinker, which at \$180/tonne is equivalent to \$24/tonne clinker.

At \$50/MW hour the power cost will be \$5.7/tonne clinker.

Consumables

The most significant consumables are filters for the bag-house and periodic filter aid charging. Estimated consumptions are:-

- \$30k/year for bag replacement
- \$30k/year for filter aid
- \$60k/year, = \$1.6 per tonne clinker.

Operations & Control

The robustness of the SLC process makes it amenable to a high degree of automation. At a conservative estimate, the headcount will increase by 1/shift (4 total).

Operations = 4* \$50k / (120*365*0.85)
= \$ 5.4/ton clinker

Maintenance

This is estimated at 2% of installed cost per annum
= \$300/annual tonne x 0.02
= \$6/tonne clinker

**Table III.
Criteria for Technical Success**

Performance Parameter	Depends on	Success Criteria	Remarks
Availability	Process Equipment & Design	>85% of available time	During 30 days out of first six (6) months
Organics Destruction	Particle size, Calcination Temperature and Residence time.	>95%	
Dust emission	Dust fineness	<50 mg.m3 (dry, 11% O2)	150 ppm at 11% O2
TOC emission	Temperature	Odor free	
Recovery of Na & Al	Calcination temperature and residence time	Rna*Ral>0.85	
Capacity		1) Consuming all salt cake produced during the commissioning period 2) 80 MTPD Clinker	30 days period
Specific heat consumption		2025 kcal/kg Clinker	
Specific Power consumption		170 kWh/Mt Clinker	

Caustic and Alumina recovery

The scope for material savings depends on the nature of the feedstock. For the case in hand a combination of bauxite, saltcake and concentrated spent liquor is being treated. To a first approximation, assume that only the chemicals in the saltcake can be claimed to be 'recovered'. 35% of the soda in the sinter comes from the saltcake, together with 8% of the alumina. Further assume 36% Na₂O and 59% Al₂O₃ in clinker, and 95% overall recovery.

Net soda recovery: $0.36 * 0.35 * .95 * 80/62$
 = 0.15T NaOH/ton clinker @ \$200/T
 = \$31/T clinker

Net alumina recovery: $0.59 * 0.08 * .95$
 = 0.045T Al₂O₃/ton clinker @ \$ 100/T
 = \$4.5/T clinker

Total chemical recovery = \$ 35.5/T clinker.

Costs/Benefits

Item	Saving/(Cost) \$/ton clinker
Energy: fuel	(24.0)
power	(5.7)
Consumables	(1.6)
Operation/Control	(5.4)
Maintenance	(6.0)
Soda and alumina recovery	35.5
Total	(7.2)

Thus it can be seen that the SLC operation largely covers its operating costs from the value of the chemicals recovered when the price of caustic approaches \$200/tonne. Of course, the overall Bayer process economics improve substantially due to increased plant productivity/production. A typical mature Australian alumina plant can easily increase its production by 10% by reducing the organic carbon content of its liquor. This could mean an additional 200,000 tonnes of production, which, at an incremental profit of \$100/tonne would be valued at US\$20M before tax.

If a new liquor burner alone is under consideration, this will be the primary justification for the installation. There may be other economic considerations in specific cases, such as elimination of the costs of disposal of saltcake, additional production by-passing the Bayer digester unit (for a bauxite slurry mix), or recovery of ESP dust which would otherwise be discarded.

7. Environmental aspects

Simplification of the liquor burning process by the SLC development introduces a number of environmental advantages.

Separation of the drying and calcination steps means that pre-dried granules can be transferred directly from a temperature range where organics do not vapourise to a high temperature zone where organics destruction is rapid and complete. In this way, volatile organic carbons are destroyed as they are formed, and it is possible to control stack gas TOC and odours to low levels.

The very efficient agglomeration mechanism in the GSD facilitates fine particle capture and so reduces carry over to the dust collection system. By containing the bulk of fine material in the dryer via an internal circulation mechanism, and under negative pressure, handling and transport of dusty material is minimised with consequent benefit to the working environment.

The use of ESP dust as a component of the feedstock can lead to better alumina quality, and hence a better working environment in the smelters.

8. Conclusions

This paper has outlined the calculations which go into the justification of an impurities control system. As the reader can see, the result will depend on the local circumstances peculiar to each case.

One more rule of thumb may be helpful. If the equilibrium organic carbon level is over 15gpl, it is very likely that a control system can be justified. Below 10gpl a control system is unlikely to be profitable. Between 10 and 15 gpl a sharp pencil is needed, and the justification may turn on specific local factors, such as environmental requirements, or a low cost capacity increment.

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