Sodium Oxalate Salt Cake Degradation when Exposed to Natural Factors in the Disposal Area

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Abstract

In the course of processing tropical bauxites into smelter grade alumina, organic impurities accumulate in Bayer liquors, eventually degrading to sodium oxalate ($Na_2C_2O_4$). As a rule, in each Bayer cycle there is an imbalance between the oxalate formation rate and its further degradation to sodium carbonate (Na_2CO_3), resulting in oxalate accumulation. Since oxalate negatively affects the grain size of product alumina, refineries control oxalate concentration by removing it from their liquor. Sodium oxalate has a high hazard class so its disposal is expensive. Other useful components (notably Na_2CO_3), are disposed along with salt cake. To reduce alkali losses and environmental risks, some refineries convert sodium oxalate with lime to calcium oxalate (Na_2CO_3), recycling sodium to the Bayer process. Other methods are implemented, such as bacterial degradation of oxalate, but these methods are also expensive, and some do not entirely eliminate the risks. This paper presents a study on the impact of natural factors, including solar radiation and catalytic iron compounds in residue on the rate of sodium oxalate degradation to sodium carbonate in a disposal area. An economically feasible process for managing salt cake disposal is suggested that provides for alkali return to Bayer process and the reduction in the salt cake's hazard class.

Keywords: sodium oxalate; degradation; soda; solar radiation; bauxite residue; disposal area.

1. Introduction

At UC RUSAL refineries four methods are used for sodium oxalate ($Na_2C_2O_4$) removal from alkaline aluminate liquors:

1. Reacting of evaporated spent liquor with the sand fraction of lime. Calcium oxalate CaC_2O_4 is bound in its surface, and the residue, a mix of calcium oxalate CaC_2O_4, unreacted lime CaO, calcium hydroxide $Ca(OH)_2$, tri-calcium aluminate $3CaO.Al_2O_3.6H_2O$ or TCA, is filtered and disposed of in the residue area;

2. Reacting of wash water from the washing of hydrate seed or product with milk of lime under defined conditions including; the stoichiometric ratio of CaO : NaOx, the concentration of Na_2O_{total}, and temperature and reaction time to optimise formation of calcium oxalate. The soda in liquor is simultaneously causticized by ≥ 80%, while much of the aluminum is lost to TCA formation. The mud consisting of a mix CaC_2O_4, TCA and $CaCO_3$ is thickened and disposed in the residue area;
3. Precipitation of sodium oxalate from liquor supersaturated in NaOx, filtration and disposal of the salt cake in a specially equipped section of the residue area;

4. Precipitation of sodium oxalate cake from evaporated spent liquor (further concentrated by caustic addition), filtration, then dissolution of oxalate cake which is then reacted with milk of lime to convert sodium oxalate to calcium oxalate. The calcium oxalate mud is filtered and again disposed of in a specially equipped section of the residue area.

All four methods have advantages and shortcomings, but the criterion for assessment of effective management of this type of waste should be considered as follows:

1. the minimum quantity of disposed waste;
2. minimum losses in the main production process, and lowest cost of waste production;
3. avoiding accumulation of these wastes or reusing them.

Method 3 matches the first criterion since it produces the minimum amount of oxalate salt cake. Processing with lime leads to an increase in the disposed oxalate residue by 3 times and more.

The second criterion is satisfied by the 3rd and partially by the 2nd method. For the 3rd method, the main expenses are energy consumption for evaporation of part of the spent liquor flow, and its cooling to obtain sodium oxalate supersaturation. Expenses for evaporation are anyway justified in the broader process context since it is also closes the refinery water balance.

Repeated attempts have been made to develop processes avoiding disposal of oxalate waste having a certain class of hazard, and to process it immediately. Some of best known are listed below:

- Degradation of oxalate by various oxidizers including hydrogen peroxide (H_2O_2), ozone (O_3) or other strong oxidizers, strong ultra-violet radiation, etc., etc. These methods are widely known, but haven't been implemented due to their relatively high cost;
- Addition of calcium oxalate cake as a mix of CaC_2O_4, TCA and $CaCO_3$ to limestone supplied for roasting in shaft furnaces to produce CaO. This allows recycling most of the sodium and aluminum in the form of caustic alkali and sodium aluminate and the calcium as lime back to alumina production process. The main drawback of this method are restrictions in the operation of shaft limestone roasting furnaces;
- The experience of Worsley Alumina in microbiological decomposition of sodium oxalate with saline bacteria [1] at which the decomposition rate of Na_{Ox} may reach 2500 mg/l/hour in the lab. As a result of the reaction, sodium bicarbonate $NaHCO_3$ is formed which reacts with caustic alkali and is converted to sodium carbonate;
- The experience of Alcoa World Alumina in the microbiological decomposition of sodium oxalate with aerobic bacteria (at the pilot site of the Kwinana refinery), where they have managed to select conditions for the stable existence of biomass and to run the process in a continuous mode, making it more reliable and simpler to maintain. As with the Worsley process, oxalate is converted into sodium bicarbonate/carbonate which after a caustization, can be recycled back to the alumina production process.

Biological degradation of oxalate is undoubtedly a prospective direction, but has a number of drawbacks, including:

- The essential requirement to use a number of chemical reagents (fertilizers) for maintaining bacterial activity;
- the rather complicated control and management of the processes proceeding in biological reactors including maintenance of the set pH, concentration of liquor, temperature of the process, concentration of oxygen dissolved by aeration, etc.;

- utilisation or disposal of the biomass which is formed as a result;
- the installation itself is a rather complex technological facility (Figure 1).

Figure 1. The site of biological degradation of oxalate at Kwinana refinery (Australia).

Considering the complexity and cost of the known processes, our investigation was devoted to identifying a simpler process converting oxalate to soda at minimum cost.

2. Experimental

It is known that under the influence of a number of factors (including the dissolved oxygen in a NaOx containing solution, the action of ultra-violet solar radiation, the presence of fine iron oxides and oxy-hydroxides which act as catalysts, environmental temperatures ≥ 25 °C), the degradation of sodium oxalate NaOx proceeds at a rate of 1-4 mg/dm^3/hour. This process proceeds even under Northern European conditions where average annual temperatures are below 20 °C. Based on this reaction, an effort was made to make the NaOx degradation process controllable, as far as possible, at the Ewarton refinery located in tropical Jamaica.

For this work, oxalate mud from the Ewarton refinery was used. Chemical and phase composition of the mud sampled after deliquoring on the belt filter is presented in Table 1.

Table 1. Oxide contents in the oxalate cake sample from the Ewarton refinery (mass %).

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	V_2O_5	Cr_2O_3	MnO	C	H	S
<0.06	0.97	0.08	<0.05	<0.02	0.08	<0.025	41.4	<0.15	0.01	<0.02	<0.01	17.19	0.422	0.006

On the basis of the chemical analysis, oxalate content in the solid fraction of cake was calculated to be 96 mass% (as $Na_2C_2O_4$). The analysis agreed with the direct analysis of Na oxalate made using a Mettler-Toledo titrator. The X-ray phase analysis shows that salt cake consists of sodium oxalate with traces of gibbsite and Sodium Hydrogen Oxalate Hydrate $NaHC_2O_4 \times H_2O$.

Oxalate removed from the Bayer process by the Ewarton refinery technology of is generally much cleaner compared to other refineries. This is due to the concentration of caustic alkali

required for precipitation of Na oxalate being obtained by addition of concentrated NaOH, without the requirement of complete liquor stream evaporation.

2.1. Experiments on decomposition of sodium oxalate under the impact of solar radiation

To investigate decomposition of sodium oxalate under the influence of natural solar radiation, a long experiment was set-up which demonstrated that even during the typically cloudy rainy season, decomposition of sodium oxalate proceeds rather quickly. The experiment was carried out at the Ewarton site over 6 weeks.

The essence of experiment was as follows:

- oxalate cake was placed under the open sky in a cup (layer thickness of 1-2 cm);
- to monitor the degree and rate of destruction, once a week a sample was taken and total time of sample radiation was recorded (Figure 2).

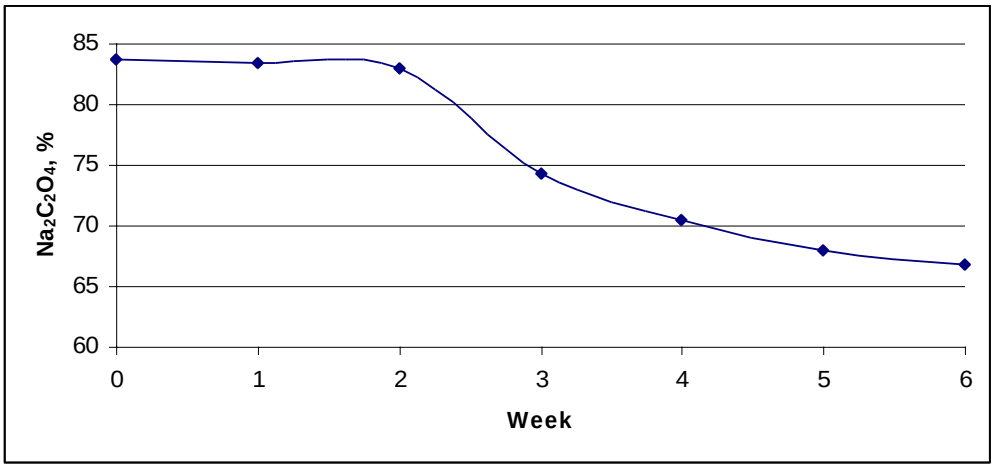

Figure 2. Photochemical destruction of sodium oxalate by solar radiation.

The above data demonstrates that within 6 weeks (taking into account 2 weeks of heavy rain when exposure wasn't conducted), photochemical destruction of the initial amount sodium oxalate was about 20%. Considering that this result was achieved during a monsoon season, this factor is expected to be higher under dry season conditions.

2.2. Experiments with an experimental cell

To obtain more reliable information, a pilot cell was built at the Ewarton site, which allowed tests to measure the degradation rate of oxalate depending on temperature, availability of the catalyzing additives (alumino-goethite mud) and composition of effluents, including pH, concentration and other characteristics (Figure 3).

Figure 3. Experimental cell for investigation of oxalate degradation rate by solar radiation.

The tests were carried out in a dry season at the maximum solar radiation. 280.014 kg of oxalate mud (on dry basis) were loaded into a cell. The mass of oxalate loaded into a cell in a humid state weighed 293.370 kg. The obtained data confirmed that oxalate degradation proceeds rather quickly, and in 3 weeks, sodium oxalate content reduced by 7%. The data continues to be collected.

3. Proposal for new technology for oxalate disposal

Arrangement of an experimental landfill cell in a residue area. On the basis of the obtained data, technical proposals were developed for arrangement of a site for sodium oxalate disposal. The site is prepared as a plain horizontal surface embanked with bulk limestone material of different size and covered with a layer of polymer film preventing leaks from the constructed banks. The height and the width of the embankment is determined on the basis of hydrodynamic calculations, and taking into account the high rainfall in the Monsoon season.

The order of storage and disposal of sodium oxalate. Sodium oxalate obtained from the belt filter is transported by motor transport to the site of disposal where it is unloaded and levelled off by mobile equipment in a layer of 8-10 cm (possibly with furrows, for increased working surface). Distribution on the surface as a layer enables an increased rate of drying and decomposition of sodium oxalate. At a layer thickness of 10 cm and dry sodium oxalate bulk density of ~1.2 g/cm^3, the recommended working area of the cell for oxalate disposal should be at least 600 m^2, which provides the period of contact of oxalate with natural ultraviolet of at least 1 month, and the degree of decomposition of oxalate to soda of at least 20%. The expenses for a bulldozer will also be minimized; being used only once a month for levelling the layer of material.

The second and subsequent layers of sodium oxalate are made only after full covering of a working horizontal surface of the site with a previous layer.

The order of storage is presented schematically, in Figure 4.

1 **16**	**2** **17**	**3** **18**	**4** **19**	**5** **20**
6 **21**	**7** **22**	**8** **23**	**9** **24**	**10** **25**
11 **26**	**12** **27**	**13** **28**	**14** **29**	**15** **30**

Figure 4 – The order of storage at the site of disposal of sodium oxalate.
Nos of landfill cells from 1 to 15 – 1st layer; Nos of landfill cells from 16 to 30 – 2nd layer

Thus, the maximum period of direct contact of sodium oxalate with natural ultraviolet and its maximum decomposition will be attained.

4. Conclusions

The proposed method is simple, and enables the minimization of the cost for sodium oxalate management, in particular to reduce the specific consumption of lime in alumina refining by at least 10% (the amount used to neutralize sodium oxalate cake).

The offered technology allows the arrangement of a landfill for continuous processing of oxalate mud to a soda solution for recycling into the alumina production process without waste volume accumulation.

5. References

1. R.A. Morton The Biological Degradation of Sodium Oxalate in an Alkaline Environment, *Proceedings of 3-rd AQW (New South Wales, Australia),* 1993, pp. 270-281.