

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 ($\text{Na}_2\text{C}_2\text{O}_4$). 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 (CaC_2O_4), 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 ($\text{Na}_2\text{C}_2\text{O}_4$) 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 $\text{Ca}(\text{OH})_2$, tri-calcium aluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{CaO} : \text{NaOx}$, the concentration of $\text{Na}_2\text{O}_{\text{total}}$, and temperature and reaction time to optimise formation of calcium oxalate. The soda in liquor is simultaneously causticized by $\geq 80\%$, 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 NaOx 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.;

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

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