Essential Readings in Light Metals: Alumina and Bauxite.
Edited by Don Donaldson and Benny E. Raahauge.

OXALATE REMOVAL BY OCCLUSION IN HYDRATE

Valérie Esquerre, Philippe Clerin, Benoît Cristol
Alcan B&A Technical Assistance; Route de Biver P.O. Box 54, 13541 Gardanne Cedex, France

Keywords: Oxalate, Occlusion, Alumina trihydrate

Abstract

Occlusion in hydrate plays a significant role in the removal of oxalate at Alcan's Gardanne refinery. Up to 50% of the oxalate purge can be achieved by occlusion.

This study investigates the occlusion phenomenon and identifies the action parameters that facilitate the control of the occlusion process.

Successive precipitation cycle laboratory tests have been conducted in different operating conditions to ascertain the key factors. Having a high level of precipitated oxalate doesn't ensure a high level of occluded oxalate. The addition of CGM appears to completely inhibit oxalate occlusion, whereas an increase in caustic concentration enhances the process. An increase in temperature also tends to increase occlusion. Possible mechanisms are proposed.

A new operating instruction to maintain a high caustic concentration in the spent liquor has led to a high and lasting level of occluded oxalate.

Introduction

The removal of oxalate is a key issue in Bayer plants, where specific units, such as a side stream of evaporated liquor, are sometimes necessary to cope with this impurity.

At Alcan's Gardanne refinery, oxalate is allowed to precipitate along with part of the precipitated gibbsite (referred to below as 'hydrate'), by adapted temperature conditions in one precipitation line. The oxalate is then removed by hydrate washing on a belt filter. However, a significant amount of oxalate is eliminated by occlusion in hydrate, a no-cost purge that is innocuous for hydrate in the context of Gardanne refinery.

Only a few studies in the literature refer to occlusion. Grocott and Rosenberg [1] mention the increase in soda impurity by incorporation of sodium oxalate needles in hydrate. Occlusion is also thought as leading to additional particle breakage in calciners, which is not observed at Gardanne's plant.

This paper investigates the occlusion phenomenon in order to improve its control.
After presentation of the experimental method, the effect of different process parameters is described. An attempt towards a better understanding of the occlusion phenomenon is then proposed and the paper ends with the industrial application made of the results of this study.

Experimental

Successive precipitation recycling tests have been conducted in the laboratory to ascertain the key factors impacting occlusion.
Precipitation experiments have been performed in a rolling water bath in PVC bottles. Precipitation tests have lasted 48h typically, with a change in temperature at mid-time to reproduce a temperature profile (60°C then 50°C). Plant pregnant liquor has been seeded with oxalate-free hydrate, at a concentration of 400gAl_2O_3/L, lower than the industrial value, in particular to accelerate the inclusion of impurities. The hydrate produced in one test has been used as seed for the following test, and so on, until a sufficient number of cycles was available to answer the question regarding occlusion.

Different operating conditions have been tested:
- Addition of CGM (Crystal Growth Modifier – Nalco 7837) to pregnant liquor. Experiments with CGM were also aimed at validating the operating mode in the laboratory, by verifying the effect of CGM to reduce occlusion, as observed in the plant. A dosage of 50ppm of CGM (volume/volume in liquor) has been introduced.
- Caustic soda concentration. The liquor has been concentrated so as to reach a caustic concentration of 180g/L (expressed as Na_2O) in the spent liquor (compared with 165g/L in the blank test).
- Temperature. The temperature has been changed from 60-50°C to 65-55°C.

Effect of process parameters on occlusion

Occlusion has to be enhanced to maximize oxalate purge of Gardanne Bayer circuit. This demands knowledge of the action parameters to better control the occlusion process.
The results are illustrated by the level of occluded oxalate as a function of the number of precipitation cycles.

Effect of CGM

The effect of CGM is shown on figure 1.
The occlusion is inhibited by the presence of CGM. The level of occluded oxalate remains stable at a low value of around 40gC_{ox}/tAl_2O_3, even after 35 precipitation cycles.

The level of precipitated oxalate is also compared on figure 1. The precipitation of oxalate is lowered by CGM, but still reaches a significant level (only around 15% less than without CGM).
Little black balls are visible after a few cycles. The adsorption of CGM on oxalate crystals could poison the surface for further occlusion. The inhibited activity of oxalate as a seed surface for gibbsite nucleation [2] could be part of the explanation for reduced occlusion.

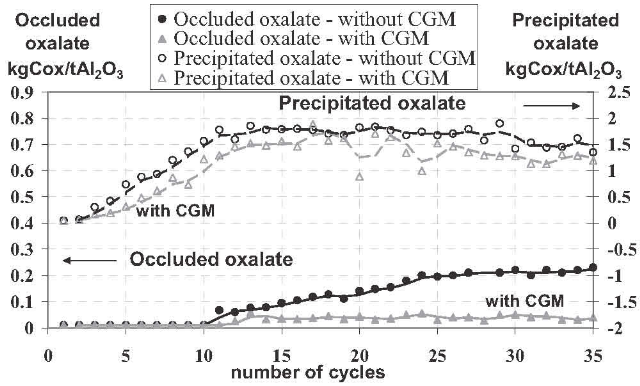


Figure 1. Precipitated and occluded oxalate - Effect of CGM

At Gardanne's plant, this detrimental effect on occlusion excludes the use of CGM to coarsen the circuit.

Effect of caustic soda concentration

The level of occluded oxalate is compared for two caustic soda concentrations (normal plant concentration and concentrated liquor) on figure 2.
Occlusion is clearly enhanced by high caustic soda concentrations: the phenomenon is faster and of greater intensity.

A higher caustic concentration leads to higher oxalate precipitation: the apparent solubility of oxalate is indeed lowered, as is the Critical Oxalate Concentration (COC).
However, a high level of precipitated oxalate is not a sufficient condition for a high level of occlusion, as it will be demonstrated in the following section.

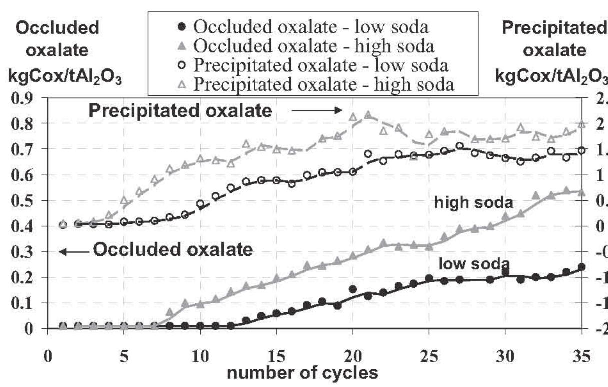


Figure 2. Precipitated and occluded oxalate - Effect of caustic soda concentration

Effect of temperature

The effect of temperature has been measured by increasing the temperature from 60-50°C to 65-55°C in cycle n°37.
The complete evolution of the occluded oxalate is reported in figure 3 for two experiments:
- "blank test" (normal plant soda concentration)
- high caustic soda concentration

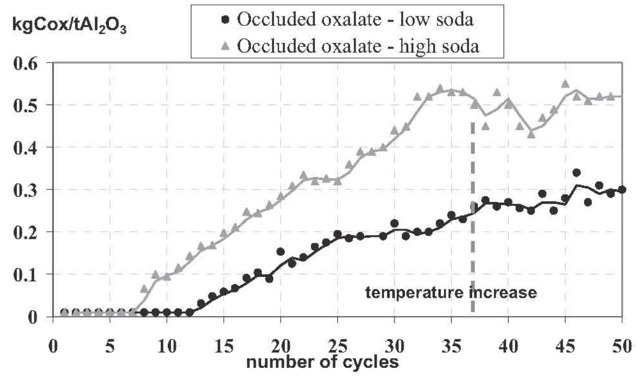


Figure 3. Occluded oxalate - Effect of temperature

When the temperature is increased, the precipitation of oxalate (ie oxalate lost by the liquor) is reduced. The occluded oxalate appears however to increase, with a clearer trend in the blank test. The change in conditions during processing of cycles implies that the effect is only visible after a few cycles, time for the seed to be renewed.

This result on the effect of temperature is also visible on the analysis of industrial data (see last paragraph).

Decorrelating the occluded oxalate from the amount of precipitated oxalate and the hydrate growth (which would both act in the opposite sense of the observed results), the effect of temperature is suggesting a type or size of oxalate crystals easier to occlude.

Comprehension of the occlusion process

Laboratory experiments enabled identification of one powerful actuator on occlusion, which is a major result for Gardanne's plant (see last paragraph). The discussion below intends to give hints for a better understanding of the occlusion phenomenon.

Link with precipitated oxalate

One test has been conducted with a higher oxalate concentration in the liquor to increase supersaturation, and then enhance precipitation. This test should answer the question about a relationship between the level of occluded oxalate and the level of precipitated oxalate.
The test liquor has been doped with a synthetic oxalate solution (average Cox=0.23%Na2Otot vs 0.205%Na2Otot).

In the oxalate-enriched liquor, an enhanced precipitation is effectively measured, as well as a higher occlusion (figure 4).

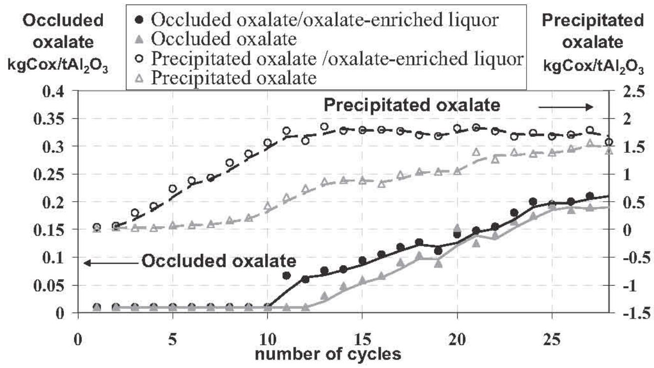


Figure 4. Precipitated and occluded oxalate - Link between precipitated and occluded oxalate (1)

When the enrichment in oxalate is stopped (21st cycle), the two curves join each other after a few cycles.

Similarity between both tests and results (caustic concentration, granulometry, hydrate production) suggest that the difference in occlusion in this case is only due to the difference in the level of precipitated oxalate.

However, this test with oxalate-enriched liquor makes it possible to further comment on the link between precipitated oxalate and occluded oxalate.
Indeed, the level of precipitated oxalate obtained in the oxalate-enriched system is similar to the one obtained in the test conducted at high caustic soda concentration. The evolution of precipitated oxalate and occluded oxalate are compared for both tests in figure 5.

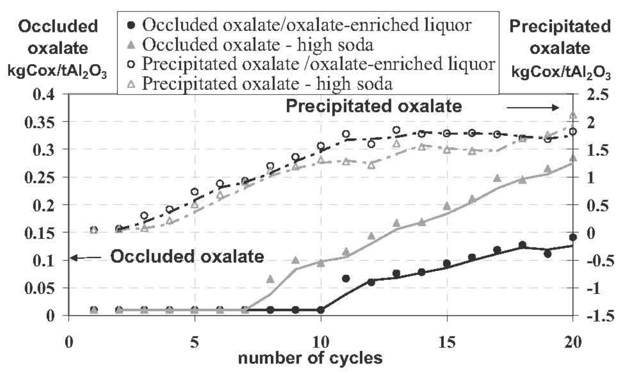


Figure 5. Precipitated and occluded oxalate - Link between precipitated and occluded oxalate (2)

Despite a similar precipitation, the occlusion is significantly different, with a ratio of two between the two conditions.
On the basis of these results, there is no direct relationship between precipitated and occluded oxalate.

Link with productivity and hydrate growth

One could suppose that a higher productivity or alumina supersaturation leads to a higher oxalate inclusion, considering the higher hydrate growth.
However, productivity is less at high caustic concentration, where the occlusion is at a maximum. The hypothesis of a higher potential to occlude related with a higher productivity is here dismissed, as had already been suggested by the study of the effect of temperature.

Link with type of oxalate crystals

Occlusion cannot be directly correlated to a high level of precipitated oxalate or to a high hydrate growth. A difference in the type or size of oxalate crystals as a function of conditions could be an explanation for the different behaviors towards occlusion.

In the presence of CGM, oxalate does not precipitate as individual fine needles, but more as "bunchs" of many needles. One of this crystal morphology is visible on figure 6. These larger crystals are more difficult to occlude.

Figure 6. Oxalate crystals on hydrate with CGM

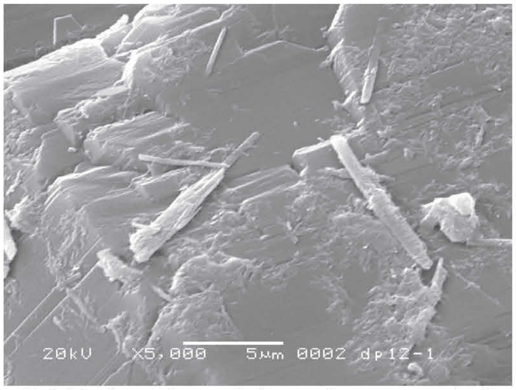
Considering the effect of high caustic soda concentration, one could link the enhanced occlusion with an oxalate liquor concentration closer to the Critical Oxalate Concentration.
Indeed, a high caustic concentration reduces the COC.
Extra experiments following oxalate precipitation during hydrate precipitation for two caustic concentrations and comparing oxalate concentrations to COC values (obtained via models) support this idea. Indeed, in the case of concentrated liquor, oxalate liquor concentration is running closer to the values of COC and even goes above the COC at the end of precipitation (see table I).

One possible explanation to the enhanced occlusion observed in precipitation cycles at higher soda concentration could be then a finer oxalate product generated by spontaneous nucleation above the COC.

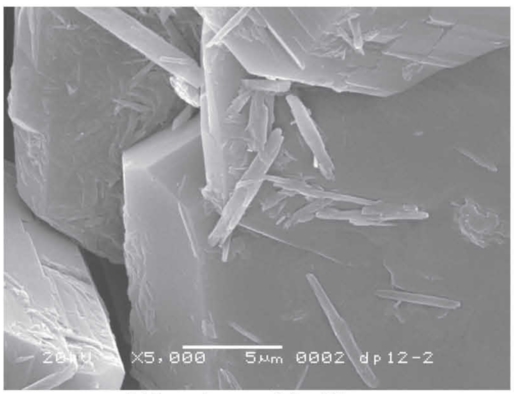
Table I. Oxalate precipitation kinetics during hydrate precipitation for two caustic concentrations - Difference between oxalate liquor concentration and COC

Time (h)		0	1	3	5	7	22	25	28	30	48
Cox liq - COC	low soda	-0.031	-0.053	-0.050	-0.041	-0.050	-0.071	-0.049	-0.013	-0.006	-0.018
(%Na2Otot)	high soda	0.003	-0.009	-0.019	-0.017	-0.020	-0.030	-0.007	**0.017**	**0.035**	**0.020**

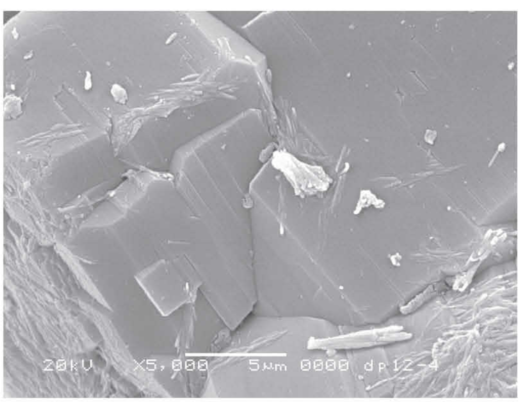
Photographs for three conditions of precipitation cycles are visible on the following figure 7. It looks as if big oxalate needles are less numerous for the test at high soda concentration.



7.a) blank test (normal plant soda concentration)



7.b) oxalate-enriched liquor



7.c) high soda concentration

Figure 7. Oxalate crystals on hydrate in different conditions

However, observations made on the effect of temperature don't support this hypothesis, since a higher temperature increases the COC, and should have lead to a decrease in occluded oxalate. The growth of oxalate crystals may also play an important role here. The reduced growth at lower temperature could lead to an easier product to occlude.

A clear mechanism is not proven yet, but proposals made here could give leads for further consideration.

Process control in the plant

The caustic concentration has been identified as a powerful control parameter on occlusion. In the plant, the operating instruction is now to maintain a high caustic concentration in the spent liquor.

Figure 8 below illustrates the good correlation between the caustic concentration and the oxalate occlusion. Each time the soda concentration is reduced, the level of occluded oxalate decreases.

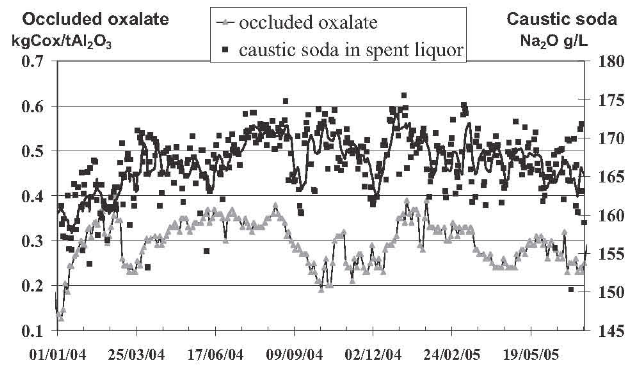


Figure 8. Industrial data: caustic soda concentration in spent liquor and level of occluded oxalate

The effect of temperature is overwhelmed by the effect of caustic concentration. However, the temperature, as illustrated in figure 9, can explain some inconsistent evolutions between caustic concentration and occlusion.

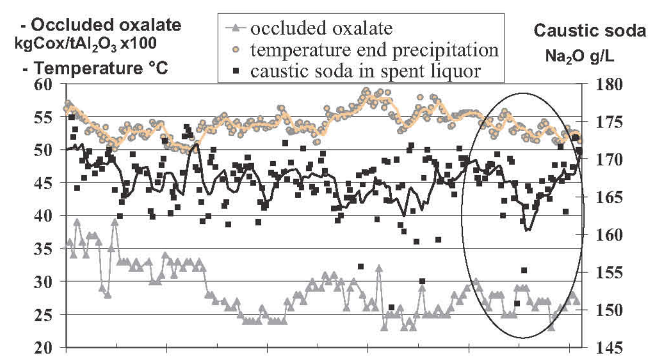


Figure 9. Industrial data: caustic soda concentration in spent liquor, temperature at the end of precipitation and level of occluded oxalate

The September 2005 period shows a hesitating level of occluded oxalate, despite a caustic soda concentration close to 170g/L. It is associated with a decreasing temperature, which is likely to counteract the effect of a high soda.

Periods maintaining a caustic concentration of around 170g/L in the spent liquor, with a temperature relatively high, ensured a good value of the occluded oxalate of $350 gC_{ox}/tAl_2O_3$.

Conclusion

The complexity of the occlusion phenomenon is underlined in this study. Although no clear mechanism for the occlusion of oxalate has been obtained, the type and size of oxalate crystals is supposed to play a major role in the occlusion, and should be considered for further study.

Moreover, the impact of different process parameters on occlusion has been evaluated, which constitutes an answer to plant concerns.

- The addition of CGM completely inhibits the occlusion of oxalate.
- The temperature is considered as a second-level action parameter, since the higher the temperature, the higher the occlusion, but the lower the productivity.
- The caustic soda concentration is a powerful actuator on occlusion; a high level of caustic soda is necessary to guarantee a high occlusion of oxalate.

Finally, this work has given the Alcan Gardanne refinery a solution for increasing the occlusion of oxalate in hydrate, thus purging oxalate at a lower cost.

Acknowledgements

Many thanks to Jean-Pierre Macario, for his significant contribution to this work.

References

1. S.C. Grocott and S.P. Rosenberg, "Soda in Alumina. Possible Mechanisms for Inclusion", *Proceedings of the First International Alumina Quality Workshop (Gladstone, Australia)*, 1988, 271-287.

2. M.M. Reyhani et al., "Gibbsite nucleation at sodium oxalate surfaces", *Proceedings of the Fifth International Alumina Quality Workshop (Bunbury, Australia),* 1999, 181-191.

Recommended Reading

Abboud, H.I. Successful side stream causticization in an alumina plant (1963, pp. 265–271).

Addai-Mensah, J., et al. Microstructure and uranium adsorption behavior of sodium aluminosilicate polytypes in caustic aluminate liquors (2005, pp. 171–176).

Addai-Mensah, J., et al. Reduction of sodium aluminosilicate scale in Bayer plant heat exchangers (2001, pp. 13–18).

Addai-Mensah, J., et al. The precipitation mechanism of sodium aluminosilicate scale in Bayer plants (1997, pp. 23–28).

Addai-Mensah, J., A.R. Gerson, and R.S.C. Smart. Continuous plug flow precipitation of sodalite scale on steel heat transfer surfaces (1998, pp. 21–28).

Benito, J.L.M. Control of process liquor impurities at San Ciprian (1984, pp. 53–62).

Boily, H.L., F. Campa, and K. Theisen. The chemistry of solid-liquid calcination (SLC) (1999, pp. 49–54).

Bouzat, G., and G. Phllipponneau. Physical chemistry models of oxalate and gibbsite solubilities in Bayer solutions (1991, pp. 97–102).

Breuer, R.G., L.R. Barsotti, and A.C. Kelly. Behavior of silica in sodium aluminate solutions (1963, pp. 133–157).

Brown, N. The heat of crystallization of aluminum trihydroxide derived from equilibrium solubility data (1973, pp. 807–814).

Buttery, J.H.N., et al. Thermodynamics of hydrocalumite formation in causticisation (2002, pp. 185–190).

Chin, L.A.D. Chemical additives in Bayer process (1991, pp. 155–158).

Cousineau, P.G., and G.D. Fulford. Aspects of the desilication of Bayer liquors (1987, pp. 11–17).

Cousineau, P.G., and K.I. The. The transformation of Bayer sodium oxalate to oxalic acid by the ion exchange process: Pilot plant tests (1991, pp. 139–143).

Deabriges, J., M. Noble, and R. Magrone. Purification of Bayer liquors by baryum salts (1977, pp. 15–21).

Duncan, A., et al. An investigation of desilication kinetics in spent Bayer liquor (1995, pp. 37–44).

East, F. Analysis of bauxites by x-ray fluorescence using the fused sample technique (1985, pp. 239–248).

Eyer, S.L., et al. Removal of organics from Bayer liquor and wet oxidation (2000, pp. 45–51).

Fulford, G.D. Scavenging non-filterable iron from Bayer liquors using activated Bayer digester sands (1989, pp. 77-89).

Fulford, G.D. Use of conductivity techniques to follow A12O3 extraction at short digestion times (1985, pp. 265–278).

Gee, A.R., A.D. Stuart, and T.B. Ashcroft. Assessment of Bayer liquors treated with manganese dioxide ore (1992, pp. 123–130).

Grocott, S.C., and L. McGuiness. Residence-time distributions in Bayer process vessels-development of a suitable liquor tracer (1990, pp. 95–102).

Hudson, L.K. Evolution of Bayer process practice in the United States (1988, pp. 31–36).

Hudson, L.K. Recent changes in the Bayer process (1963, pp. 59–69).

Kjar, A.R., and A.J. Crisp. Plant layout and preassembly concepts for alumina plant construction (1986, pp. 3–10).

Lalla, A., and R. Arpe. 12 Years of experience with wet oxidation (2002, pp. 177–180).

Landi, M.F., and G. Ricci. Changes in the composition of the sodium salts precipitated from Bayer process liquors in the presence of sulphates (1979, pp. 163–170).

Lepetit, J.G. Autoprecipitation of alumina in the Bayer process (1986, pp. 225–230).

Libby, S.C. The effects of lime/limestone characteristics on causticization (1983, pp. 275–293).

Loh, J., et al. The effects of wet oxidation on hydrate yield inhibitors in alkaline aluminate solutions (2008, pp. 181–186).

Matocha, C.K. Analytical instruments for available alumina and soluble soda (1985, pp. 249–263).

Matocha, C.K. Automated laboratory liquor analyzer--ALLA--for analysis of Bayer liquor (1984, pp. 101–114).

Mercier, H., and M. Noble. Optimization of the alkaline treatment of the different bauxite varieties (1974, pp. 777–786).

Muller-Steinhagen, H., M. Jamialahmadi, and B.J. Robson. An investigation into the formation of DSP on heat transfer surfaces (1993, pp. 159–165).

Overbey, T.L., and C.E Scott. An improved method for determining boehmite and gibbsite in bauxite and red muds by x-ray analysis (1978, pp. 179–193).

Owen, D.O., et al. Evaluation of downstream effects of specialty chemicals in the Bayer process (1991, pp. 173–176).

Perrotta, A., and F. Williams. Electrocatalytic oxidation of organics in Bayer liquor (2009, pp. 215–218).

Perrotta, A.J., and F. Williams. Hydrocalumite formation in Bayer liquor and its promotional effect on oxalate precipitation (1995, pp. 77–87).

Perrotta, A.J., and F. Williams. Layered double hydroxide formation in Bayer liquor and its promotional effect on oxalate precipitation (1996, pp. 17–28).

Perrotta, A.J., F.S. Williams, and L. Stonehouse. Layered double hydroxides for treatment of Bayer process lake water (1997, pp. 37–48).

Roach, G.I.D. The influence of mineralogy on the dissolution kinetics of gibbsite (1985, pp. 183–196).

Ruecroft, G., D. Hipkiss, and M. Fennell. Improving the Bayer process by power ultrasound induced crystallization (sonocrystallization) of key impurities (2005, pp. 163–169).

Sato, C., et al. New process for removal of organics from Bayer liquor (1982, pp. 119–128).

Sato, C., and S. Kazama. Behavior of organic matter in aluminate solution (1971, pp. 63–74).

Schooler, L.N., and G. Ruiz. Residence time distribution studies in predigestion desilication (1985, pp. 117–123).

Shibue, Y., et al. Liquor burning process-its modification and increase in capacity (1990, pp. 35–40).

Smith, P.G., et al. The composition of DSP formed under predesilication and high temperature Bayer digestion conditions (2001, pp. 5–11).

Solymar, K., et al. Co-processing of different types of bauxite with high efficiency (2001, pp. 105–111).

Solymar, K., and J. Zoldi. Lime in the Bayer process: Present state and future trends (1993, pp. 185–194).

Stahl, W., H. Reinsperger, and W. Stockhausen. Application of disc filters in the Bayer process (1979, pp. 131–149).

Stuart, A.D. Removal of organics from Bayer spent liquors using manganese dioxide (1988, pp. 95–102).

The, K., et al. A new method of sodium oxalate destruction (1990, pp. 53–56).

The, K., and R. Roussel. Application of ion chromatography to the analysis of Bayer and aluminum process liquors (1984, pp. 115–125).

The, K.I. A novel approach to post-desilicating Bayer process liquor (1992, pp. 117–122).

The, P.J. Removal of copper and zinc from Bayer liquor by process filtration (1982, pp. 129–141).

The, P.J., and J.F. Bush. Solubility of sodium oxalate in Bayer liquor and a method of control (1987, pp. 5–10).

The, P.J., and T.J. Sivakumar. The effect of impurities on calcium in Bayer liquor (1985, pp. 209–222).

Tizon, E., P. Clerin, and B. Cristol. Effect of predesilication and digestion conditions on silica level in Bayer liquor (2004, pp. 9–14).

Wahnsiedler, W.E. The kinetics of bauxite digestion in the Bayer process (1985, pp. 145–182).

Wehrli, J.T., and A.R. Kane. Application of differential scanning calorimetry for characterization of Bayer process solids (1993, pp. 175–184).

Williams, F.S., and A.J. Perrotta. Enhanced oxalate removal utilizing the multi-functional Purox process (1998, pp. 81–87).

Xu, B., et al. The effect of anatase and lime on the transformation of sodalite to cancrinite in Bayer digestion at 250 C (2010, pp. 81–86).

Xu, B., C. Wingate, and P. Smith. The kinetics of quartz dissolution in caustic solutions and synthetic Bayer liquors (2008, pp. 157–161).

Yamada, K., T. Harato, and Y. Furumi. Removal of iron compounds from the Bayer liquor (1974, pp. 713-722).

Yamada, K., T. Harato, and H. Kato. Oxidation of organic substances in the Bayer process (1981, pp. 117–128).

Yamada, K., T. Hashimoto, and K. Nakano. Behavior of organic substances in the Bayer process (1973, pp. 745–754).

Zambo, J. Structure of sodium aluminate liquors; molecular model of the mechanism of their decomposition (1986, pp. 199–215).

Zhonglin, Y., and G. Songqing. The influence of lime addition amount on scaling rate in preheating process of diasporic bauxite slurry (2001, pp. 139–142).