

INCREASING ALUMINA PRECIPITATION YIELD USING SODA CONTROL

Besida J* and Van Emden B

Technology Delivery Group, Alcoa World Alumina, Kwinana, WA, Australia

Abstract

The solubility of alumina in caustic soda is influenced by a number of factors of which the major two are temperature and caustic concentration. A novel approach towards extracting caustic soda from Bayer liquor, and increasing alumina precipitation yield, is presented in this paper. It has been demonstrated that Bayer liquor can be supersaturated without cooling, with respect to alumina solubility, by the extraction of soda using a solvent extraction technique. The technology is based on ion exchange principles whereby a weak acid, dissolved in a non aqueous solvent, is able to extract a sodium ion into the organic phase, with the concomitant transfer of a proton into the Bayer liquor, leading to neutralization of hydroxide. Unlike liquor carbonation, this technique reduces both the TC and the TA of the Bayer liquor. By choosing appropriate extractants having pK_a s in the range of ~ 9-13, caustic can be recovered from the organic phase, without the use of lime, by stripping with an aqueous solution of relatively low alkalinity.

Notation and units

TC = Total Caustic = $[\text{OH}^-] + [\text{Al}(\text{OH})_4^-]$ expressed as gL^{-1} of Na_2CO_3 .
TA = Total Alkalinity = $[\text{OH}^-] + [\text{Al}(\text{OH})_4^-] + [\text{CO}_3^{2-}]$ expressed as gL^{-1} of Na_2CO_3 .
A = Alumina Concentration = $[\text{Al}_2\text{O}_3]$ expressed as gL^{-1} .

1. Introduction

The Bayer process is widely used for the production of alumina from alumina containing ores such as bauxite. The process involves digestion of bauxite with recycled caustic aluminate solutions at elevated temperatures. After digestion and clarification, the aluminate solution is cooled to induce a state of super saturation and seeded to precipitate alumina as gibbsite. The precipitated gibbsite is then separated from the aluminate solution, now known as spent liquor (SL), with a portion of the gibbsite being recycled to be used as seed and the remainder calcined to produce smelter grade alumina. The spent liquor, which in most cases contains more than fifty percent of the alumina initially present in liquor to precipitation (LTP), is then recycled for further digestion of bauxite. The liquor cooling/seeding approach for alumina precipitation from Bayer liquor gives a product containing low levels of impurities, such as sodium and silicon, and also enables good control of alumina particle size and morphology, issues which are very important towards subsequent smelting operations. The theory behind the concept is shown in Figure 1 which displays a generic solubility curve for alumina at a given concentration of caustic.

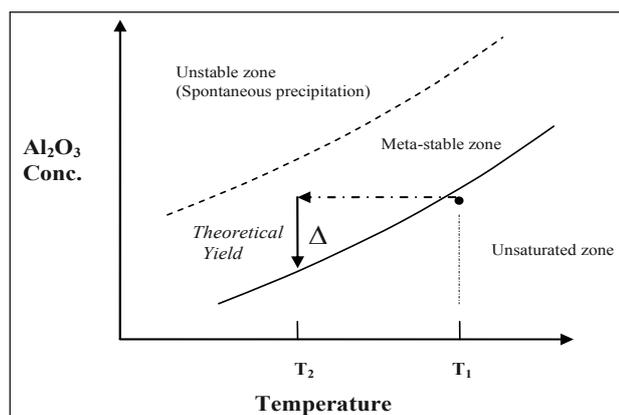


Figure 1. Alumina solubility curve showing the concept of liquor cooling to induce super saturation

By cooling the Bayer liquor from temperature T_1 to T_2 , the solution becomes supersaturated because the alumina concentration crosses to the left of the solubility curve. Once the solution is in the metastable region of the graph, precipitation can be induced and controlled by seeding.

The gibbsite precipitation reaction can be represented by the following equation:



Equation 1 signifies a chemical reaction, rather than a simple temperature related solubility of a compound in a solvent, because the soluble compound, sodium aluminate, is not what precipitates from solution. It also demonstrates that, even though current practice in Alcoa refineries makes use of temperature to create a state of supersaturation, supersaturation can also be achieved by reducing the level of causticity of Bayer liquor since, without the presence of "free" caustic, aluminate cannot stay in solution.

Indeed, the classical precipitation approach of Bayer liquor carbonation has been used widely in the past to precipitate alumina. Carbonation converts caustic to carbonate and, if taken to completion, can result in the precipitation of most of the alumina from Bayer liquor. However, it has a number of major drawbacks such as producing alumina of inferior quality both in terms of included impurities as well as inappropriate particle size and morphology, most of which are linked to lack of control of precipitation conditions. Furthermore, Bayer liquor carbonation requires large amounts of relatively expensive lime to convert carbonate back to caustic before the liquor can be reused for digestion.

The concept of liquor carbonation is shown in Figure 2. The entire alumina solubility curve, at a caustic concentration of TC_1 and at a given temperature T_1 , is shifted lower when the level of causticity is reduced to TC_2 . Hence, there is a concomitant decrease in alumina solubility and increase in liquor supersaturation as the solution becomes depleted in caustic. However, Bayer liquor carbonation reduces the total causticity (TC) of the liquor but not the total alkalinity (TA).

This paper reports on new technique which can be used to reduce the level of causticity in Bayer liquor leading to super saturation. Unlike liquor carbonation, the soda extraction technology reduces both the TC and the TA of the liquor.

1.1 Soda extraction as a means of inducing Bayer liquor super saturation

Grinstead (1971a, 1971b) patented a method for the selective recovery of caustic from waste solutions having a pH of at least 14. The soda extraction technology is based on cation exchange

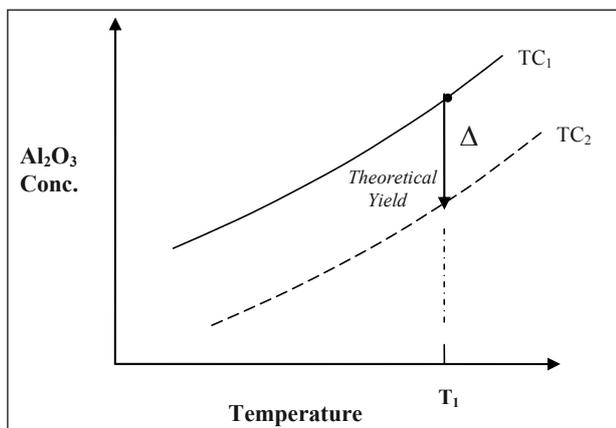


Figure 2: Alumina solubility curve showing the concept of reducing causticity to induce super saturation

principles. It involves the exchange of a proton from a weakly acidic lipophilic reagent (HA), dissolved in a non aqueous solvent, for an aqueous sodium ion at high pH according to Equation 2:



The reverse reaction occurs, and caustic is recovered in pure form, when the organic phase containing sodium is contacted with water. However, for hydroxide recovery to occur efficiently, HA has to have an aqueous $\text{pK}_a \sim 9-12$ so that contact with water readily regenerates the protonated form of the extractant. Use of the forward and reverse steps constitutes a cyclic process for the transfer of hydroxide equivalents (termed a pseudo hydroxide extraction because Na^+ is actually extracted). Grinstead advocated the use of a series of alkylated phenols as the weak acids in his patent.

Later, workers at Oak Ridge National Laboratory (Moyer 2001), expanded on the earlier work of Grinstead and replaced the alkylated phenol extractants with a series of fluorinated analogues. It was claimed that the fluorinated alcohols would have a greater stability towards degradation in highly alkaline media and would thus be more suited towards industrial application. This more recent modification of the soda extraction concept had as its ultimate aim the recovery of caustic soda from high level radioactive tank wastes.

Although developed solely for the recovery of caustic from waste solutions, it was envisaged that application of the above solvent extraction concept, towards extracting soda from Bayer liquor, would lead to increased levels of supersaturation of the liquor, with respect to alumina solubility, and therefore lead to increased precipitation yields. The key to this approach is that once extracted from Bayer liquor, the caustic soda can be recovered by water stripping of the organic phase, without the use of lime or other chemicals, and returned to the Bayer liquor prior to digestion of more bauxite.

2. Experimental

2.1 General

Two different soda extractants were tested in this study and their structures are shown in Figure 3.

1H, 1H, 9H - Hexadecafluorononanol (HDFN) was purchased from Novachem Pty Ltd and 4-*tert*-octylphenol (97%) (TOP) was purchased from Sigma-Aldrich.

The extractants were dissolved in 1-octanol (Sigma-Aldrich) which was used as a modifier and diluent.

All extraction experiments were performed using blended plant liquor from Alcoa's Kwinana Refinery, Western Australia.

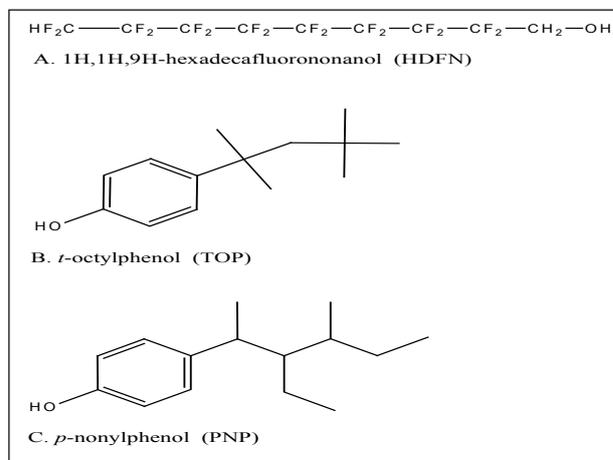


Figure 3. Weak acids used as soda extractants in this study

2.2 Caustic extraction and stripping experiments as a function of time

The kinetic experiments were performed at a temperature of 70 °C in a 3 litre capacity, water jacketed, stirred stainless steel reactor. The mixed liquids were periodically sub-sampled during each experiment. In the extraction experiment, pre-heated (70 °C) Bayer liquor and organic phase were contacted in the reactor. Sub-samples (up to 10 mL) of mixed liquid were isolated at different times. A sample of each contacted liquor was quickly isolated from the extractant phase, allowed to cool to ambient temperature and then analysed for TC, TA and Al_2O_3 .

The organic layer of mixed samples, at several different contact times, was isolated and analysed for sodium by ICP-OES.

To ensure the extraction of hydroxide had reached completion, mixing continued for 16 hours at 70 °C where after the bulk, mixed liquid was separated to provide a sufficient volume (> 500 mL) of Na loaded organic extractants for use in determining the kinetics of stripping.

The stripping kinetics experiments were performed by contacting de-ionised water (500 mL) with 0.50M *t*-OP and 0.50M HDFN loaded organic phase (retained from the extraction kinetic experiments and pre-heated to 70 °C) in a stainless steel reactor. Sub-samples (up to 10 mL) of mixed liquid were isolated at different times. A sample of the contacted strip solution was quickly isolated from the extractant phase, allowed to cool to ambient temperature and then analysed by ICP-OES to determine the sodium concentration.

2.3 Soda extraction and precipitation from Bayer liquor using varying concentrations of TOP.

In this set of experiments, plant liquor with an A/TC value of 0.5 was contacted with specified quantities of TOP, dissolved in 1-octanol. After a contact, the phases were separated and the treated plant liquor was then seeded with gibbsite and allowed to precipitate hydrate for 24 hours at 70 °C. The amount of treated liquor used in each seeding experiment was 200 ml, the added seed was 20 g of Alcoa C33 hydrate and the experiments were conducted in 250 ml polypropylene bottles placed in a rotating holder in a water bath to maintain temperature. After completion of the experiment the solids were collected and dried. The filtrates were analysed for TC, TA and Al_2O_3 . All solids were analysed by powder XRD.

2.4 Multiple stripping experiments to recover caustic soda from the TOP organic phase.

A bulk organic phase, generated by contacting 0.75 M *tert*-octylphenol in 1-octanol with plant liquor ex-precipitation, was used in these experiments. The organic phase was analysed for

Na content and found to contain 0.623 M of Na expressed as 33.0g/L of Na_2CO_3 . The stripping experiments were performed at 70 °C in a stirred 3 L capacity stainless steel reactor to affect phase contact. Prior to contact, the organic (initially 600 mL) and aqueous phases (initially 300 mL) were preheated to 70 °C. Following contact, the phases were separated and a sub-sample of the aqueous phase was withdrawn for analysis. The remaining aqueous phase was contacted with twice the volume of fresh loaded organic and the procedure repeated until a total of six independent contacts, using the same aqueous strip, had been conducted.

3. Results and Discussion

3.1 Soda extraction from Bayer liquor using HDFN and TOP.

Experiments were performed to establish the level of soda extraction, and also the time required to reach equilibrium, when Bayer liquor is contacted with 1-octanol containing 0.5 M of dissolved HDFN or TOP. The starting A/TC was 0.50 for these experiments and they were performed at 70 °C. The results are shown in Figure 4.

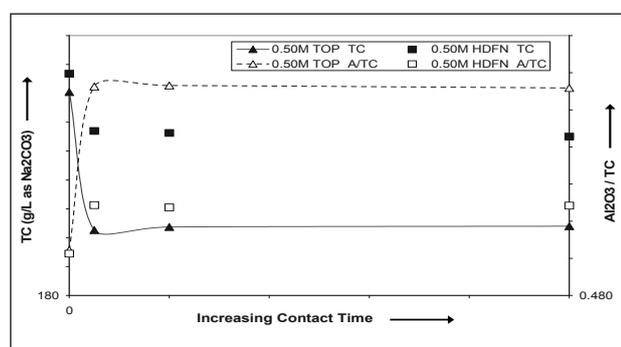


Figure 4. The extraction of soda from Bayer liquor using 0.5 M TOP or HDFN in 1-octanol.

The extraction of soda from Bayer liquor using either extractant reaches equilibrium relatively fast. There is a significant drop in the TC of the Bayer liquor, and also an increase in the level of supersaturation with respect to alumina as measured by A/TC, when either TOP or HDFN are used. However, TOP extracts much more soda than HDFN. The 0.5 M TOP phase extracted an amount of soda in excess for the amount of TOP used, assuming a maximum of 1:1 extraction of soda with the phenol. The extra Na extraction is due to the 1-octanol. Importantly, the A/TC ratio of the TOP contacted Bayer liquor increased to the point where significant amounts of additional alumina could be precipitated from this liquor if seeded.

The 0.5 M HDFN phase in 1-octanol extracts less soda than the 0.5 M TOP phase. Although the pK_a of HDFN is not reported in the literature, it is likely to be significantly higher than that of TOP, since the fluorine atoms in the structure would not have as great an electron withdrawing effect on the alcohol group as an aromatic ring, making it a weaker acid. Even though it is a weaker extractant for soda, it should strip more efficiently than TOP by releasing more soda from the organic phase when contacted with water. The results of contacting the Na loaded organic phases from the extraction experiments with water are given in Figure 5.

Equal volumes of organic phase and deionised water were used and the experiments were conducted at 70 °C. The recovery of soda from the HDFN organic phase is quantitative whereas that from the TOP organic phase is ~ 60 %. Nevertheless, the stripping kinetics appear to be as fast as the extraction kinetics and, in both cases, substantial amounts of caustic soda can be recovered from the organic phases of both extractants by contacting with water. It should also be possible to increase the causticity of the stripping solution by performing multiple contacts using freshly loaded organic phases of either extractant. This could provide an

aqueous caustic stream more suitable for recycle back into the Bayer process.

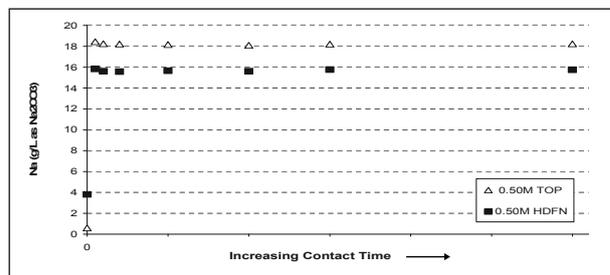


Figure 5. The recovery of caustic from the Na loaded organic phases

3.2 Soda extraction and precipitation from Bayer liquor using varying concentrations of TOP

TOP was chosen for further test work based on its ability to extract more soda, on an equimolar basis, than HDFN.

Bayer liquor was contacted with 1-octanol containing varying concentrations of TOP. After phase separation, precipitation experiments were performed on the soda extracted liquor using gibbsite seed at 100g/L loading for 24 hours at 70 °C. The results are shown in Figure 6 which displays the TC drop of the liquor after extraction and the yield of alumina obtained after precipitation based on liquor analyses. It was also found that it was not possible to investigate soda extraction with loadings of TOP above 1M because of the high viscosity of the solutions hindering phase disengagement.

From the data, there appears to be a linear correlation between TOP concentration, in the organic phase, and soda extraction from Bayer liquor. On a molar basis, 1 M of TOP extracts approximately 1 M of Na from the Bayer liquor with the concomitant neutralization of 1 M of hydroxide. This leads to a significant supersaturation of the liquor and precipitation experiments, with hydrate seeding, have demonstrated that substantial amounts of alumina can be precipitated from the treated liquor. Hence, it is possible to obtain significant yield increases of alumina over control experiments where no soda was extracted.

The precipitates were analysed by x-ray diffraction and shown to contain gibbsite only.

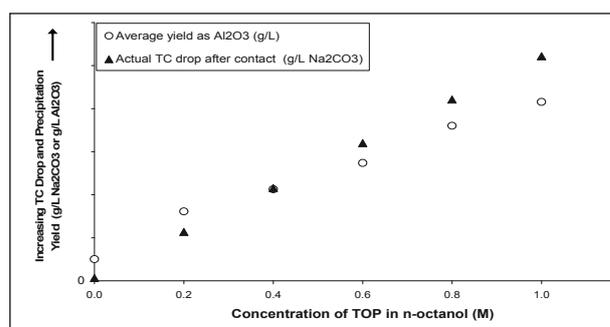


Figure 6. The extraction of soda from Bayer liquor using varying concentrations of TOP in 1-octanol and precipitation yields of alumina from the treated liquor

3.3 Multiple stripping experiments to recover caustic soda from the TOP organic phase.

It has been demonstrated that significant amounts of soda can be extracted from Bayer liquor, using an alkyl phenol such as TOP dissolved in 1-octanol, and that the supersaturated liquor can be seeded to precipitate substantial amounts of gibbsite. However, from a process point of view, it needs to be established that the extracted soda can be recovered in a form that enables it to be recycled back into the Bayer process at minimal cost.

A bulk organic phase, generated by contacting 0.75 M TOP in 1-octanol with plant liquor from ex-precipitation, was used in these experiments. The organic phase was analysed for Na content and found to contain 0.623 M of Na expressed as 33.0g/L of Na_2CO_3 . Stripping experiments were conducted, starting with de-ionised water which was contacted successively with fresh Na loaded organic phase. Details are given in the experimental section and the results are presented in Figure 7 which displays the caustic content of the aqueous phase as a function of the number of volume contacts with the soda loaded organic phase. The diagram also contains a theoretical line which shows the level of caustic in the aqueous phase which is representative of 100 % stripping efficiency.

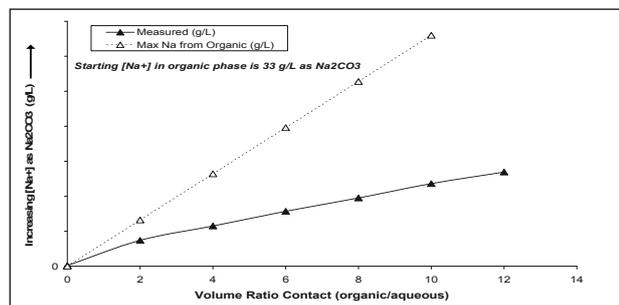


Figure 7: Recovery of caustic soda from *tert*-octylphenol (TOP)/ 1-octanol as a function of the number of volume contacts with the organic phase.

It is possible to extract soda from the organic phase to recover a reasonably concentrated stream of caustic by performing a number of sequential stripping steps using the same aqueous phase. However, as shown in the graph, the stripping is not complete and a substantial amount of soda still remains in the organic phase. From a process perspective, much of this remaining soda could be recovered utilizing a setup employing counter current stripping, where stripped organic phase is contacted further with fresh aqueous phase, which should increase the efficiency of the operation.

Importantly, these stripping experiments have demonstrated that a significant amount of caustic can be recovered from the organic phase, containing *tert*-octylphenol, which could then be recycled back into the Bayer process.

4. Conclusions

This study has demonstrated that Bayer liquor can be supersaturated without cooling, with respect to alumina solubility, by the extraction of soda using a solvent extraction technique. The technology is based on ion exchange principles whereby a weak acid, dissolved in a non aqueous solvent, is able to extract a sodium ion into the organic phase, with the concomitant transfer of a proton into the Bayer liquor, leading to neutralization of hydroxide. Unlike liquor carbonation, this technique reduces both the TC and the TA of the Bayer liquor and can provide increased alumina precipitation yields over conventional techniques. By choosing appropriate extractants having pK_a s in the range of ~ 9-13, caustic can be recovered from the organic phase, without the use of lime, by stripping with an aqueous solution of relatively low alkalinity. When this super saturation technique is combined with liquor cooling, as shown in Figure 7, it has the potential to increase alumina precipitation yields of Bayer liquor substantially compared to current practices.

References

- Grinstead, R. R., 1971a, 'Extracting sodium and potassium from aqueous solutions having a pH of 14 using phenols and an extractant additive', *US Patent 3,598,547*.
 Grinstead, R. R., 1971b, 'Extracting sodium and potassium from aqueous solutions having a pH of 14 using unhindered phenols', *US Patent 3,598,548*.
 Moyer, B. A. et al., 2001, 'Solvent and process for recovery of hydroxide from aqueous mixtures', *US Patent 6,322,702 B1*.

For example, following bauxite digestion, solid liquid separation and clarification, Bayer liquor is cooled and passed through a seeded precipitation loop to precipitate gibbsite. The spent liquor could then be treated by solvent extraction to create a further state of supersaturation and passed through a secondary precipitation loop to recover more gibbsite, thus increasing the overall yield of alumina per litre of Bayer liquor.

Work is now being undertaken within the Technology Delivery Group, of Alcoa World Alumina, to fully evaluate this technology for Bayer process application. A number of important issues need to be resolved which include precipitating alumina of acceptable impurity levels, particle size and morphology.

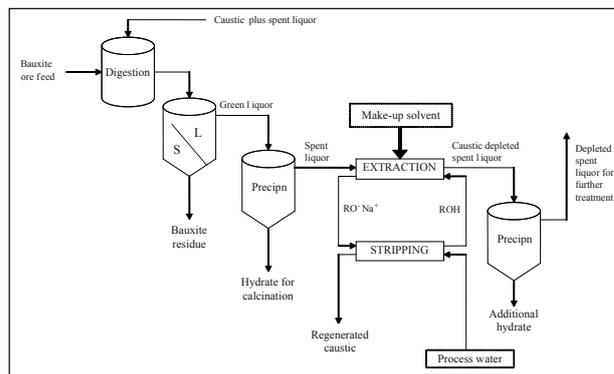


Figure 7. Flow sheet indicating incorporation of the soda extraction technology in the Bayer process

Nevertheless, this preliminary study has shown that substantial quantities of alumina can be precipitated from Bayer liquor of relatively low A/TC ratio with use of the solvent components reported in this paper.

Acknowledgements

The authors wish to express their appreciation towards Alcoa World Alumina for allowing publication of these results.