



## Reactive extraction of sodium hydroxide from alkali solutions for the separation of sodium and aluminum—Part II. Effect of diluent



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### ABSTRACT

Enhancing the precipitation of  $\text{Al}(\text{OH})_3$  from supersaturated sodium aluminate solution has been a challenge for the alumina industry for decades in its effort to increase the productivity. However, limited by the thermodynamic equilibrium of alumina solubility in caustic solutions, the processes that are available to date for promoting the precipitation of  $\text{Al}(\text{OH})_3$  are unsatisfactory. An acid–base reactive solvent extraction method is proposed to enhance the separation of sodium hydroxide from sodium aluminate mother liquor by creating a condition for re-precipitation. The extraction process has been reported in Part I of this study by the present authors. In this paper the effects of diluents on sodium extraction when using 2-tert-butyl-4-methylphenol as the main organic extractant were systematically investigated. According to the classification of diluents, the capabilities for extracting sodium in different types of diluents were compared, and the protonic polar diluents were identified as being the most effective diluent. In the absence of alkyl phenol organic extractant, the sodium extraction equilibrium in 1-octanol and 2-ethyl hexanol, and the co-extraction of water in each of them were compared. In the presence of alkyl phenol, the extraction capabilities for sodium in different C8 alcohols, including 1-octanol, 2-ethyl hexanol and 2-octanol, were compared and analyzed. The results showed that 1-octanol is the most effective diluent among the three that are studied in this project. Furthermore, inert diluents including kerosene, octane and heptane, were used to dilute the pure 1-octanol solvent in different proportions in order to decrease the viscosity of the organic phase. The effects of the inert diluent on sodium extraction and water co-extraction were studied. Finally, the particle size distributions in the equilibrated organic phases and the Margules ternary 2-suffix equations were introduced to discuss the mechanisms of sodium extraction by 1-octanol and 2-ethyl hexanol. The results of this systematic research are expected to provide valuable guidance for the selection of diluents.

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### 1. Introduction

The Bayer process is the principle method for the production of alumina from bauxite worldwide (Smith, 2009). The Bayer process consists of four main steps: digestion, desilication, seeded precipitation, and evaporation. In spite of the significant improvements that have been made to the process over more than five decades, the precipitation ratio of  $\text{Al}(\text{OH})_3$  from supersaturated sodium aluminate solution remains very low, and improving the precipitation remains a key challenge for the industry.

The reaction during the precipitation of  $\text{Al}(\text{OH})_3$  can be described as follows.



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To measure the extent of the precipitation reaction, the molar ratio (MR) between  $\text{Na}_2\text{O}$  to  $\text{Al}_2\text{O}_3$  is often used. The precipitation ratio is defined as the percentage of changes of MR before and after the precipitation. Before precipitation, MR is typically around 1.5; after precipitation, it should be approximately 3.0. Hence, one way to increase the throughput of alumina production is to seek means to obtain higher MR value after precipitation.

There are a number of methods for enhancing the precipitation, including adding active  $\text{Al}(\text{OH})_3$  seeds while stirring to promote the crystallization of  $\text{Al}(\text{OH})_3$ , or decreasing the temperature of the pregnant sodium aluminate solution to increase the level of the supersaturation, or adding surfactants, and introducing ultrasound or magnetic field (Chen et al., 2003). However, even when those techniques were employed, the maximum precipitation ratio that can be achieved is no higher than 55%, which is very low and leads to the futile cycle of almost equal quantity of the output of alumina in key units, such as digestion, precipitation and evaporation, and the precipitation is thus a bottleneck of the alumina production process.

This is attributed to the thermodynamic equilibrium limitation of the solubility of alumina in the supersaturated solution. Another avenue for increasing the precipitation ratio is to reuse the spent liquor of the precipitation by decreasing its MR, recreating supersaturation state for the re-precipitation. Based on the definition of MR and the assumption that NaOH and NaAl(OH)<sub>4</sub> are the two main species in sodium aluminate solution, the following Eq. (2) can be obtained, where *n* represents the mole number.

$$MR = \frac{n_{\text{Na}_2\text{O}}}{n_{\text{Al}_2\text{O}_3}} = \frac{n_{\text{NaOH(total)}}}{n_{\text{NaAl(OH)}_4}} = \frac{n_{\text{NaOH(free)}} + n_{\text{NaAl(OH)}_4}}{n_{\text{NaAl(OH)}_4}} = 1 + \frac{n_{\text{NaOH(free)}}}{n_{\text{NaAl(OH)}_4}} \quad (2)$$

From Eq. (2) it can be deduced that if 50% of the total sodium hydroxide (or 75% of the free sodium hydroxide) can be captured and separated from the spent liquor, the MR of the mother liquor will decrease from 3.0 to 1.5, rendering the solution capable of precipitation reaction again, i.e. a second round of precipitation from the same original supersaturated solution based on Eq. (1). In effect the alumina productivity will be increased by having two cycles of precipitation from the same supersaturated solution. This process, however, requires the use of highly-selective method to capture NaOH rather than aluminum-bearing species.

Liquid–liquid extraction separation technology is one of those methods with high throughput and high selectivity (Chambliss et al., 2002; Zhu and Li, 2008). As stated, the purpose of the extraction process is to remove the sodium species to decrease MR of the spent liquor and make it useable again for precipitation. Even though the extraction of sodium hydroxide from the strong alkali system is a very challenging task, the pseudo-hydroxide extraction process has been proposed initially by Kang and Moyer (2006) for reducing the quantity of radioactive-bearing alkaline waste water and for recycling the alkaline solution. The principle of this technology can be explained by Eq. (3). Because of the equivalents of hydroxide, rather than actual extraction of OH<sup>-</sup>, the term “pseudo-hydroxide extraction” was used to describe the process (Kang and Moyer, 2006). Taking advantage of high separation factor of sodium relative to aluminum, Gu et al. (2006a,b,c) adopted this method to process high-alkaline sodium aluminate solution, including the pregnant Bayer liquor and the spent liquor. C12–C18 alkyl phenols were demonstrated as effective extractants. Besida et al. from Australia (Besida and Van Emden, 2008) also carried out similar work by adopting HDFN, TOP, and PNP as the weak acids. However, the parameters of the main factors affecting the extraction were not specified in detail due presumably to the proprietary nature of their work.



It is well understood that the effectiveness of the solvent extraction process depends on both extractant and diluent that are used. Sometimes, a modifier that is different and considered a part of diluent may be used to prevent the formation of third phase. In this case, the effects of extractant have been studied and reported in Part I of this article (Zhang et al., 2015). 2-tert-butyl-4-methylphenol was found to be one of the most effective extractant for removing sodium species from the spent liquor of the precipitation unit. This article, Part II, focuses on the diluents. In general, the diluents can have the following functions in solvent extraction (Ma, 2009). First, the concentration of the extractant can be adjusted by the diluents so as to control the extraction and separation ability for the objective. Second, the diluents can increase the solubility of extracted complex in the organic phase. Third, the diluents can play the role of optimizing the physical properties of the organic phase, such as reducing its viscosity and changing its density. Lastly, the diluents have the effects of solvation.

Examples of the effects of diluents include the following. (1) 3,5-DtBP is a typical acidic phenol, which can be used to extract sodium from alkaline solution. While Isopar L is chosen as the main diluent, the addition of C8 alcohols with various structures as the modifiers

has significant effect on the distribution ratio of sodium. The distribution ratio is 40% higher than with 1-octanol adopted, compared to that with Exxal® 8 applied (Arm et al., 2007). (2) Alamine® 336 is a water insoluble tri-octyl/dodecyl amine which is capable of extracting many metal ions and carboxylic acids from acid solutions when combined with synergistic reagents. However the distribution ratio has close relationship with the types of diluents used, depending on the interactive force between the formed complex and diluent (Inci, 2002).

It is clear from the above that the structure of different diluents and the physical and chemical properties of diluents have strong effects on the extraction process. However, there is a lack of comprehensive understanding on how the properties of diluent affect the extraction process, especially the extraction of sodium from the spent liquor. This research was thus designed to compare the effects of diluents in order to gain insights on the effects of the structure of those organic compounds. This work will also examine the interaction of the diluent with water molecules and the sodium species. The findings of this work are expected to provide an understanding as well as guidance for selecting and optimizing the extraction process.

## 2. Experimental

### 2.1. Materials

Alkyl phenol, 2-tert-butyl-4-methylphenol (CAS Number 2409-55-4) was selected as the extractant and purchased from Alfa Aesar without further purification. The water-immiscible alcohols, 1-octanol, 2-ethylhexyl alcohol, and 2-octanol, were obtained from Beijing Chemical Works and chosen as active diluents to provide a suitable solvation media for organic sodium salts. Kerosene, octane and heptane were used as inert diluents. The water used in this study was purified using Milli-Q (Millipore Corp.) high-purity water generator before use. Sodium hydroxide solutions of different concentrations were prepared by dissolving predetermined amounts of NaOH in high-purity water. The sodium aluminate solutions of different concentrations were prepared by dissolving predetermined amounts of aluminum hydroxide into hot sodium hydroxide solution, followed by filtration and diluting with different amounts of hot water in a polytetrafluorethylene (PTFE) vessel. The chemical compositions of the prepared solutions were determined before use, by ICP-OES and titration. All reagents were RG/AR grade.

### 2.2. Extraction procedures

The same volumes of initial organic and aqueous phases were equilibrated in a temperature-controlled shaker bath for 0.5 h, which had been demonstrated to be sufficient for equilibrium during preliminary tests. Then the mixture was transferred into a separation funnel, and the funnel was placed in a temperature-controlled oven for phase separation. The separated aqueous and organic phases were transferred into the sealed containers, which were preserved in a water bath with the same temperature as that for equilibrating, waited for dilution and analysis.

It should be pointed out that the risk of autoprecipitation of the sodium aluminate solution is near none during dilution for preparing caustic solutions with various NaOH concentrations and for preparing samples for analysis, as well as after extraction due to the decrease of the MR, for the following reasons. First, the sodium aluminate solution has very strong supersaturation stability. Although dilution without changing MR will weaken its stability, the relatively high MR of approaching 3 will protect the solution from autoprecipitation in a short time. Second, the one-stage extraction was carried out to obtain the extraction equilibrium. The MR of the alkaline solution does not decrease significant enough (from 3 to 1.5) to cause faster precipitation. Even when MR of the alkaline solution reaches 1.5, it will take a

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