

RECOVERY OF SODA FROM BAUXITE RESIDUE BY ACID LEACHING AND ELECTROCHEMICAL PROCESSING

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Abstract

Caustic soda consumption is a significant production cost when high silica bauxite is processed in an alumina refinery. The authors have developed a new process to recover soda from desilication product (DSP) in bauxite residue (BR), which comprises the following steps: (1) leaching DSP by sulphuric acid to extract soda as sodium sulphate, (2) purification of the leached liquor and (3) splitting the sodium sulphate into caustic soda and sulphuric acid by electrochemical processing. The recovered NaOH is returned to the alumina refinery and sulphuric acid is recycled to the soda recovery leaching process.

Optimised acid leaching and liquor purification processes have been established for synthetic DSP, lime-free BR and lime containing BR using sulphuric acid without troublesome leaching of silica. A soda extraction extent of up to 80% was achieved by stoichiometric consumption of sulphuric acid to form sodium sulphate with DSP or lime-free BR. For the lime containing BR, ~1.6 times more acid was consumed in leaching because of lime-acid reactions. The resultant liquor contained 50~120 g/L Na₂SO₄ and <10 mg/L (each) of impurities (Al, Si, Ca, Mg, Fe, Ti).

Sodium sulphate solution (250 g/L), as model (recycled) liquor was dialysed by two-compartment system. 160 g/L NaOH was recovered with electric power consumption of less than 1500 kWh/t-NaOH.

The leached residues after soda recovery showed a low and stable pH and, of course, lower soda. This is expected to be of great benefit to long term residue management.

1. Introduction

A worldwide trend of declining bauxite grades underlines the importance of research into practical ways of processing high silica bauxites. The existing and potential processes for processing high silica bauxite have been reviewed by Smith (2009). He categorized options into three strategies – reduce reactive silica input, modify the process to produce lower soda DSP and recovery of soda from residue - this paper relates to the third strategy.

Treatment of BR with sulphurous acid (SO₂ absorption) can dissolve the DSP entirely, liberating soda and silica into acid solution. Amorphous silica can be precipitated from the leached solution, which is then causticized with lime to produce a caustic stream (recycled to refinery) and solid calcium sulphite (which is calcined to regenerate CaO and SO₂). The process has been patented by Comalco (Cresswell et al. 1987; 1992). However causticisation by lime and its recovery from CaSO₃ and dealing with the silica waste product all represent significant costs.

BR slurry is used to scrub SO₂ from stack gases (Yamada et al. 1979, 1982a, 1982b; Leoni et al. 2002). The reactions produce both sodium sulphite and sodium bisulphite which are rapidly oxidised to sodium sulphate. Yamada et al. reported that the soda extraction extent of 60~70% (Na₂O in DSP) was achieved and the resultant slurry contained about 40 g/L of sodium sulphate after oxidation. The concentration of silica and alumina were much less than 1 g/L. At the same time, it was supposed that the resultant DSP maintained the original cage structure of DSP after acid treatment such that alumina and silica were not substantially released to solution. This led to the possibility of substantial soda recovery without the problems associated with total DSP cage breakdown.

Recent advances in membrane technology have encouraged the use of electrochemical processing for the recovery of soda from industrial wastes containing sodium sulphate (Mani et al. 1988; Paleologou et al. 1997; Pinacci 2001; Huang et al. 2006; Davis et al. 2008). To date there is no practical application of acid leaching and membrane electrochemical processing to recover soda from DSP/BR. A possible reason is that the membrane electrochemical processing requires extremely purified liquor especially with respect to polyvalent cation such as Ca, Mg, Al and Fe ions to keep current efficiency high and to prevent fouling of the membrane by precipitation of alkali-earth salts, aluminium and iron hydrates.

The authors have developed a new process (CSIRO 2011) to recover soda from DSP in BR, which comprises the following steps: (1) leaching DSP/BR by sulphuric acid to extract soda as sodium sulphate, (2) purification of the leached liquor and (3) splitting the sodium sulphate into caustic soda and sulphuric acid by electrochemical processing. The recovered caustic soda is recycled to the alumina refinery and sulphuric acid is recycled to the soda recovery leaching process. The conceptual process is shown in Figure 1.

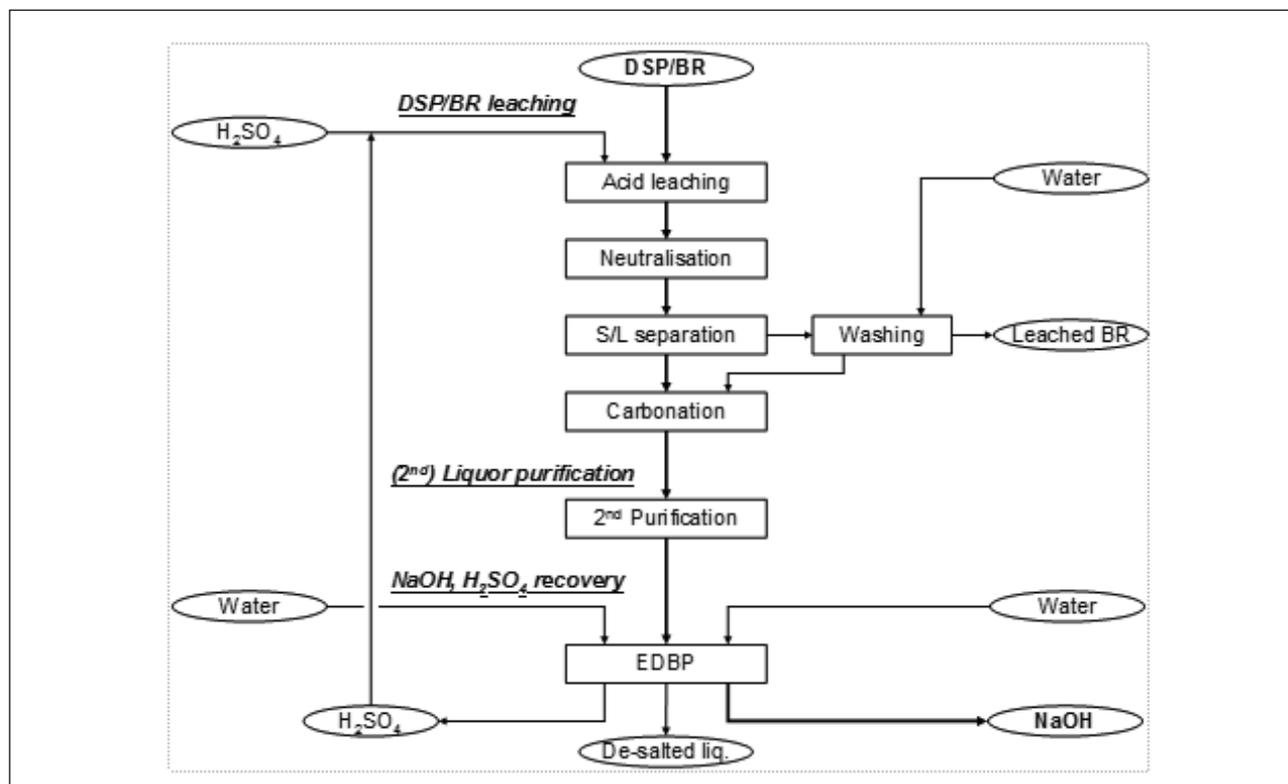


Figure 1 Conceptual process diagram of soda recovery from DSP/BR

In this paper we present results of acid leaching of DSP/BR and electro dialysis (EDBP) of sodium sulphate. Integration of EDBP into the whole recovery system and its economy are roughly considered. Some scientifically interesting issues such as dissolution of DSP with sulphuric acid [Na ion extraction mechanism, equilibrium of partially soda extracted DSP with hydrogen ion ($\text{Na}^+ \rightleftharpoons \text{H}^+$)] will be reported at a later date.

2. Experimental Method of Leaching

2.1 Materials

DSP was prepared from synthetic Bayer liquor and Eckalite kaolinite (ECC International) at 150°C (hereinafter DSP). Lime-free BR (Lf-BR) was synthesized from an Australian high silica bauxite (SiO_2 7.3%) under high temperature digestion conditions (250°C) without the addition of lime. A calcium containing residue received from an Australian refinery was de-liquored and washed several times with DI water and then dried in an oven at 100°C (Ca-BR). The chemical compositions were determined by XRF and are shown in Table 1.

Table 1 Chemical composition of DSP, Lf-BR and Ca-BR

Sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	P_2O_5	SO_3	TiO_2	LOI_{1000}
DSP	33.8	31.5	0.02	0.46	0.11	23.6	0.006	0.08	0.51	10.3
Lf-BR	22.7	23.5	0.03	21.6	0.14	15.7	0.17	0.16	7.66	8.28
Ca-BR	11.3	23.1	2.73	39.9	0.13	6.40	0.20	0.25	7.54	7.78

All leaching and neutralisation were performed using AR grade of NaOH, Na_2CO_3 and H_2SO_4 .

2.2 Procedure of acid leaching and neutralisation

Leaching was carried out with the following procedure: (1) DSP/BR slurry was prepared and heated to 60°C with stirring. (2) Acid was injected into the beaker by using an automatic titrator (Metrohm 857) until the targeted pH was achieved, and the slurry was kept at this pH for 0.5~4.0 hours. (3) The slurry was then neutralised by caustic soda. (4) Solid was separated by pressure filter (Supor membrane, pore diameter 0.45 μm) and washed with hot DI water. When Ca-BR was treated, further purification of Ca^{2+} was required and sodium carbonate was added to the filtrate after step (4). Samples of liquor and solid were taken at each step and sent to ICP and XRF analysis respectively.

3. Results and Discussion of Leaching Experiments

3.1 Soda extraction extent (Ex-Na₂O) from DSP/BR

Soda extraction extent (Ex-Na₂O) was calculated from the analysis data and shown in Figure 2.

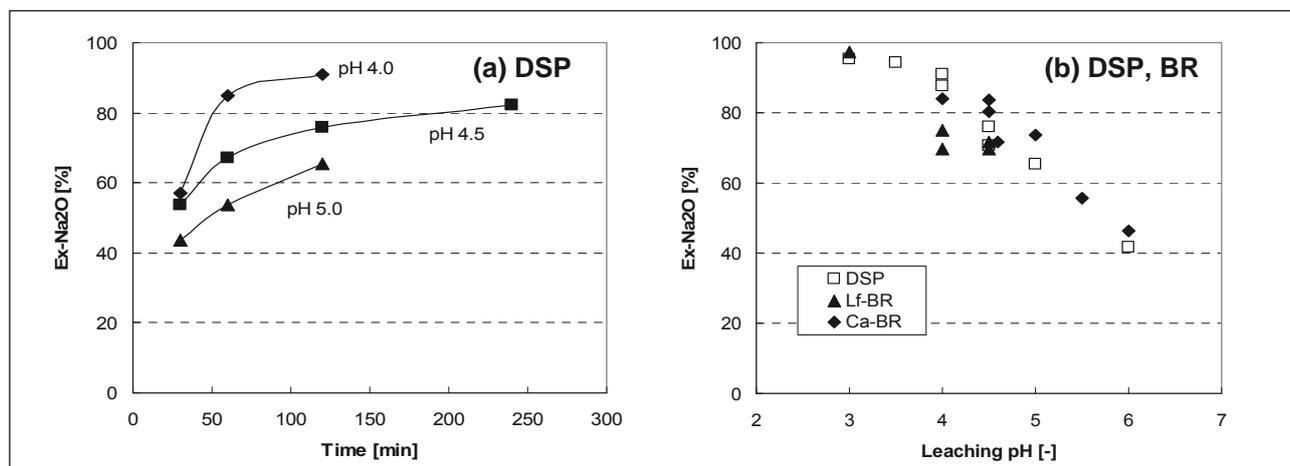


Figure 2 Soda extraction extent: (a) DSP, (b) DSP, Lf-BR, Ca-BR (leaching 120 minutes).

For DSP Ex-Na₂O of 90% can be achieved by acid leaching at pH 4.0 with a leaching time 120 minutes. At pH 4.5 over 80% of Ex-Na₂O was obtained but with a longer holding time. Figure 2(b) shows that Ex-Na₂O depends strongly on leaching pH. Ex-Na₂O for Lf-BR at leaching pH 4.0 appears to be slightly lower than DSP and Ca-BR. The extractability of sodium in DSP/BR may depend on the DSP/BR synthesis conditions.

3.2 Required acid for leaching

The acid consumed during leaching was expressed in two ways MR and A/N: [MR; feed acid to product salt (molar ratio of amount of H₂SO₄ added (A) per extracted amount of Na₂O), A/N ratio; N is the amount of Na₂O in feed DSP/BR] - both are shown in Figure 3. Leaching time was 30~240 minutes for this data.

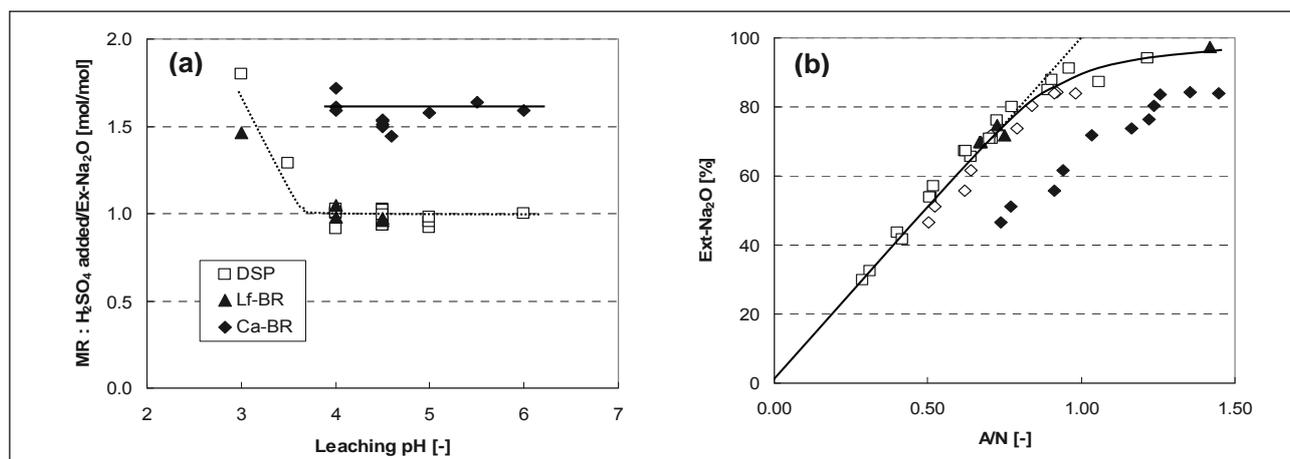
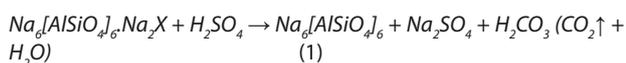


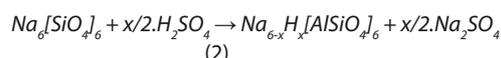
Figure 3 (a) MR vs. leaching pH, (b) Ex-Na₂O vs. A/N ratio [□ DSP, ▲ Lf-BR, ◆ Ca-BR; ◇ Ca-BR (N=Na₂O+ CaO)].

Extraction of soda from DSP is expected to proceed as follows:

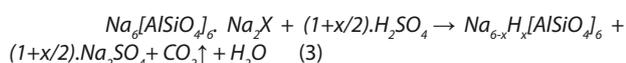
1st step; extraction of Na₂X (NB X assumed to be CO₃²⁻);



2nd step; extraction of sodium from DSP cage;



The whole reaction (1) + (2) can be written as:



Reaction equation (3) indicates that the feed acid to product salt ratio H₂SO₄:Na₂SO₄=1:1. Figure 3(a) shows that MR is 1.0 for DSP and Lf-BR at leaching pH 4~6 and shows that sulphuric acid is consumed for extraction of soda at 1:1 molar ratio. The MR

increased by lowering leaching pH. The MR for Ca-BR was high at ~1.6. Ca-BR contains 2.7% CaO and the calcium is expected to react with sulphuric acid to precipitate calcium sulphate.

Figure 3(b) shows that until Ex-Na₂O reaches 80% soda is extracted with the acid addition equivalent to potential extractable soda in DSP and Lf-BR. The correlation for Ca-BR (◆) was different from that of DSP and Ca-free BR. When the expression of N for Ca-BR is changed to (Na₂O+CaO) in BR, the correlation agreed well with other calcium free DSP/BR (◇).

3.3 Extraction behaviour of impurities (Al, Si, Ca, Mg and Fe)

It is expected that alumina and silica in BR dissolve readily into acid solution over a range of pH, whereas iron and titanium essentially remain in the solid over the same range. The extraction behaviour of impurities was measured. Figure 4 shows the concentration of impurities (Al, Si, Ca and Mg expressed as oxides) after 120 minutes leaching at various leaching pH. The solid concentration was fixed at 25 wt%.

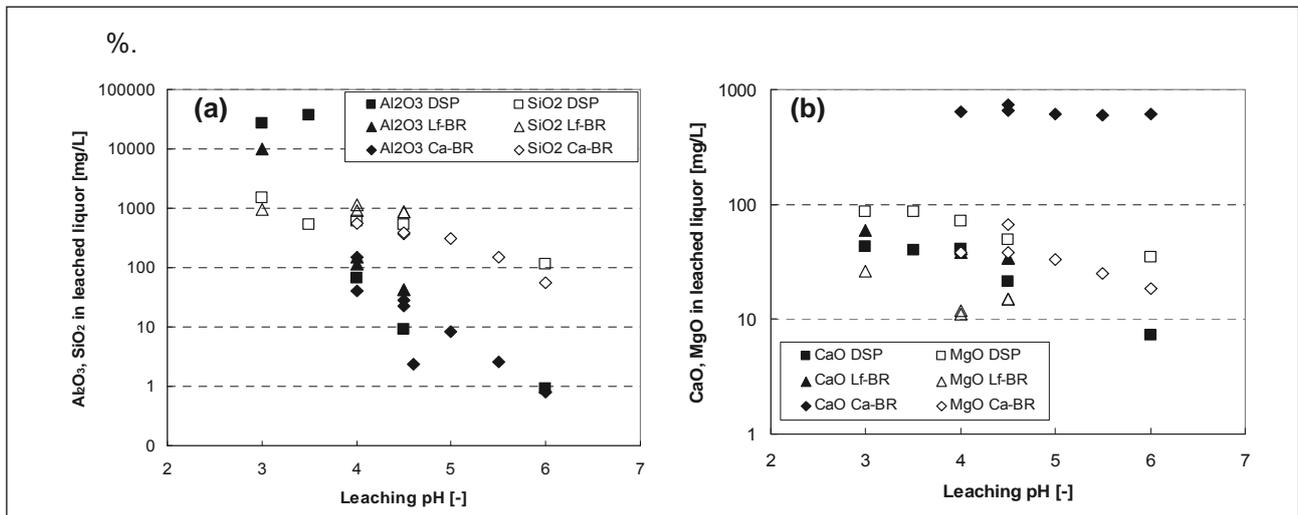


Figure 4 Concentration of impurities after leaching: (a) Al₂O₃, SiO₂; (b) CaO, MgO.

The amount of alumina and silica dissolved into liquor depends on the leaching pH. The concentration of alumina and silica at leaching pH of 4 was ~100 and ~1000 mg/L respectively for all DSP/BR. Dissolution of alumina increased by lowering the leaching pH, though the dissolution of silica plateaus. The dissolution extent of alumina from DSP at pH 4 was low at 0.1% and it increased very rapidly by decreasing pH. The reason for the difference of alumina and silica is not clear, but silica may dissolve and re-precipitate as amorphous silica.

The calcium concentration for Ca-BR was high at 650 mg/L and it did not depend on the leaching pH. On the other hand, it was low for DSP and Lf-BR. It is supposed that calcium compounds in residue dissolve and precipitate as calcium sulphate in the leaching step. The solubility of calcium sulphate (CaSO₄·1/2H₂O) in water at 60°C is about 0.15 g/100 g solute (about 580 mg/L as CaO), and it is supposed that the precipitated calcium sulphate re-dissolves up to its solubility.

The concentration of magnesium (MgO) was 10~100 mg/L at pH 4. Iron concentration (Fe₂O₃) was lower than the detectable limit of 0.3 mg/L by ICP at leaching pH 4, increasing to 10~30 mg/L at a leaching pH 3.5~3.0 (respectively).

It can be concluded that the optimum leaching pH is ~4.0 from the view point of soda extraction extent, acid consumption and dissolution of impurities. The leached liquor contains impurities Al₂O₃ 100; SiO₂ 1000; CaO 40 (DSP/Lf-BR), 1000 (Ca-BR); MgO 10~70 [all as mg/L] at a leaching pH of 4.

3.4 Purification of leached liquor

3.4.1 Purification by caustic neutralisation

It is expected that Al, Si, Ca, Mg and Fe in the leached liquor are precipitated as their hydroxyl-gel analogs or adsorbed onto precipitated Al or Si gel when the liquor is neutralised by caustic soda (leached slurry was neutralised at pH 6~10 by using sodium hydroxide).

Alumina was purified to <5 mg/L by neutralisation within the pH of 7.0~9.0, but it increased at pH >9.5. It is supposed that dissolved and re-precipitated alumina (basic aluminium sulphate Al(OH)SO₄) or aluminium

gel) are in solution at higher pH. Silica, magnesium and iron were also purified to less than 10 mg/L by neutralisation of the leached slurry. For Ca, the liquor obtained from DSP or Lf-BR was purified less than 10 mg/L by neutralisation - but the neutralised liquor from Ca-BR still contained a high concentration of ~600 mg/L CaO.

A decrease of soda extraction extent by 5~15% was found on neutralisation depending on both leaching and neutralisation pH. We call this "reversion of sodium." Process modification to avoid this reversion and accompanied silica issues have been investigated but it is omitted from this report in favour of a better understanding of the whole recovery process.

3.4.2 Purification of Ca by sodium carbonate (carbonation)

Purification of liquor was carried out by using sodium carbonate to change the lime precipitates to a low soluble material (calcium carbonate CaCO₃). This operation should be applied after S/L separation of residue as shown in Figure 1.

The filtrate that contained CaO 640 mg/L after neutralisation by caustic soda at pH 7.5 was carbonated. This was reduced to CaO 6 mg/L by the addition of three times the stoichiometric amount of sodium carbonate to form CaCO₃.

3.4.3 Integrated leaching experiment comparing DSP and Ca-BR

An experiment integrating neutralisation/carbonation with leaching was carried out comparing DSP (as a typical residue of the highest Na₂O content and almost Ca-free) and Ca-BR (small Na₂O content and high Ca content residue) by the process as shown in Figure 1.

DSP (27 g) and Ca-BR (100 g) were suspended in DI water (300 mL) separately, leached by sulphuric acid (pH 4.0, 120 minutes, 60°C), neutralised by caustic soda (pH 7.5, 60 minutes) and separated by filtration. The filtrate of Ca-BR (200 mL) was then carbonated by sodium carbonate. The amount of residue charged for leaching was set as the same amount of Na₂O is contained in the slurry (both 6.4 g Na₂O). Experimental results are summarised in Table 2 and 3.

Table 2 Experimental results of integrated leaching comparing DSP and Ca-BR

	Unit	DSP	Ca-BR
Required acid for leaching H ₂ SO ₄ (47.1%, 6.72mol/L) H ₂ SO ₄ per extracted soda	[mL] [mol/mol]	13.3 1.12	22.5 1.88
Required NaOH for neutralisation NaOH (10%, 1.12mol-Na ₂ O/L) NaOH per extracted soda	[mL] [mol/mol]	13.7 0.19	22.4 0.28
Required Na ₂ CO ₃ for carbonation Na ₂ CO ₃ (10%, 0.943mol-Na ₂ O/L) Na ₂ CO ₃ /CaO	[mL] [mol/mol]	-- --	7.5 3.0
Ex-Na ₂ O after neutralisation/carbonation	[%]	77.7	78.1

Table 3 Liquor analysis

Sample		Na ₂ O [g/L]	Al ₂ O ₃ [mg/L]	SiO ₂ [mg/L]	CaO [mg/L]	MgO [mg/L]	Fe ₂ O ₃ [mg/L]	SO ₃ [g/L]
DSP	After neutralisation	20.0	1.7	5.3	1.9	2.3	<0.3	26.8
Ca-BR	After neutralisation	20.4	1.2	5.1	661	11.1	<0.3	28.2
	After carbonation	21.4	1.7	5.6	7.8	5.7	<0.3	28.0

About 80% of soda extraction was achieved after neutralisation/carbonation. The loss of extracted soda by reversion was about 9%. The liquor after neutralisation contained <10 mg/L of (each) impurity. In the case of the liquor from Ca-BR, CaO was very high (660 mg/L) but it was purified by the following carbonation using sodium carbonate.

By this operation, purified liquor of sodium sulphate concentration about 50 g/L was obtained. Solid charge for these experiments was 8.3% (DSP) and 25.0% (Ca-BR). Na₂SO₄ concentration obtainable at the leaching step can be increased by increasing the solid charge.

3.4.4 Characteristics of leached residue

Dry leached residue (DSP 5 g, Lf-BR 7.5 g, Ca-BR 20 g) was resuspended in 100 mL of DI water. The solid content was chosen to ensure equal soda content in residue before leaching. The pH change of the leached residue suspension was observed and is shown in Figure 5.

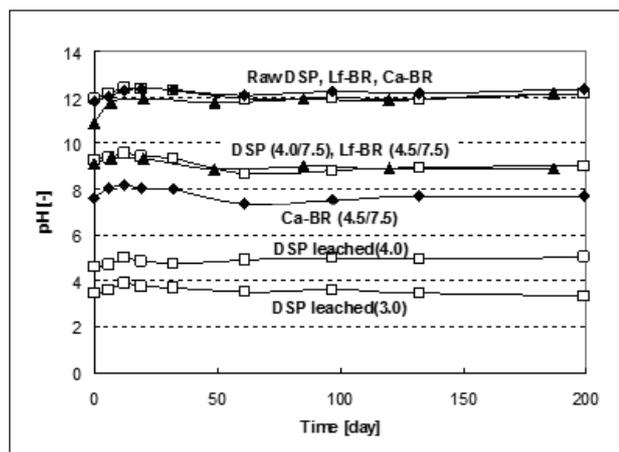


Figure 5 pH change of leached residue suspension [(X/Y) shows leaching and neutralisation pH respectively].

There is some initial fluctuation, but after 100 days the pH has stabilized. Slurries of raw DSP and both BRs showed a pH of 12 after 200 days. It can be concluded that the leached residue shows stable and low pH, and when the residue is neutralised it shows stable and safe pH of 7~9.

4. Experimental method of EDBP

There are two ways for membrane electrochemical splitting of sodium sulphate into caustic soda and sulphuric acid; electrolysis and electro dialysis with bipolar membrane (EDBP). The main difference involves the ion-formation mechanism of hydrogen ion (H⁺) and hydroxide ion (OH⁻). With electrolysis, these ions are generated on both electrodes, but with EDBP, both ions are generated on the border of the bipolar membrane (BPM). The theoretical potential to achieve the water splitting capability is 0.83V. This equates to a theoretical energy consumption of 600-700 kWh/t-NaOH (Pourcelly, 2002). Generally one electro dialysis plant includes many dialysis units, perhaps >100~200 units. The generation of oxygen and hydrogen on both electrodes is small compared to electrolysis. Plant investment cost for EDBP will be much lower than electrolysis because it does not require expensive electrodes. We expected for the present application, electro dialysis has some particular advantages compared to electrolysis and have therefore used EDBP.

There are some reports on the performance of EDBP for recovering caustic soda from sodium sulphate (Mani et al. 1988, Paleologou et al. 1997, Pianacci 2001). According to these reports, power consumption is in the range of 1450~3300 kWh/t-NaOH and caustic soda concentration is 40~240 g/L. There is no clear explanations of the differences in power consumptions and caustic concentrations achievable. We therefore decided to investigate the application of EDBP from a fundamental perspective.

4.1 Materials, equipment, procedure and conditions

All EDBP tests were performed using AR grade of Na₂SO₄, NaOH and H₂SO₄. EDBP test using actual liquor recovered from refinery BR will be reported at a later date.

EDBP experiments were carried out using electro dialyzer unit "ACILIZER EX3B". A flow diagram of the equipment is shown in Figure 6(a). The dialysis cell was composed of 10 units (just two dialysis units are shown in Figure 6(b)) using ten Neocepta CMB cation-exchange membranes (CEM), ten Neocepta ACM anion-exchange membranes (AEM) and eleven Neocepta BP-1E bipolar membranes (BPM) (electro dialyzer and membranes: ASTOM, Japan). The available area of each membrane was 55 cm². The distance between the membranes was 0.75 mm. Three-compartment EDBP system (3C-EDBP) is shown schematically in Figure 6. Caustic soda and sulphuric acid is recovered into separate compartments. In the two-compartment system (2C-EDBP), an electro dialysis unit is composed of salt/acid- (S/A-) compartment

and base-compartment without AEM. Caustic soda is recovered into the base-compartment and a mixture of acid (sulphuric acid) and diluted sodium sulphate is recovered at S/A-compartment.

EDBP operation was carried out batch-wise at a constant current of 5.50 A (operational voltage is controlled automatically by the power unit to keep current constant: current density 100 mA/cm²). Temperature was controlled manually as close to the maximum recommended 40°C as possible. Liquor samples were taken from each tank periodically and analysed by ICP. In the case of 3C-EDBP, dialysis operation was terminated at 10 mS/cm. At the end of dialysis, liquor volume was measured using a measuring cylinder.

Current efficiency for NaOH generation (CE) and power consumption (PC) were calculated as follows:

$$\text{NaOH (g-eq)} = [\text{current (A)} \times n \times \text{time (sec)} \times \text{CE}] / [96500(\text{A}\cdot\text{sec/g}\cdot\text{eq})] \quad (5)$$

$$\text{Unit power consumption} = \text{current (A)} \times \text{unit-cell voltage (V)} \times \text{time (h)} / [\text{generated NaOH}] \quad (6)$$

Here, Equation (5) is Faraday's law; $n=10$ (number of units). PC is shown as an integrated power required to generate NaOH from starting time $t=0$ to a definite time (t_1). CE for NaOH was defined for the definite sampling time periods (time: $t_n \sim t_{n+1}$).

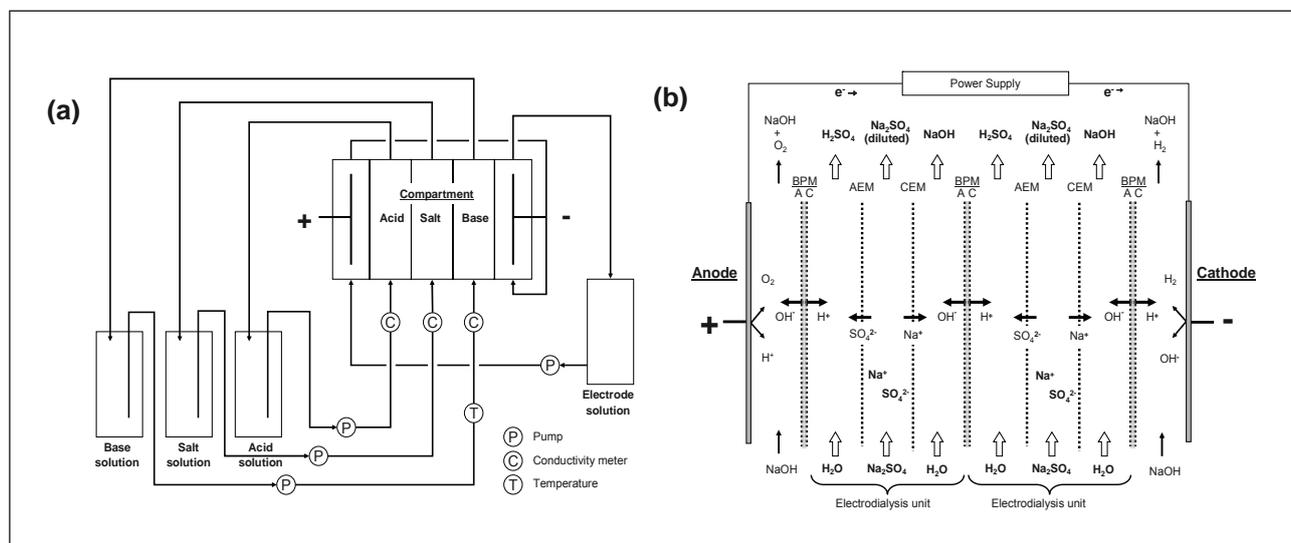


Figure 6 (a) A simplified process flow diagram of 3C-EDBP configuration for batch-wise operation, (b) EDBP dialysis mechanism of Na₂SO₄ into H₂SO₄ and NaOH by 3C-EDBP.

5. Results and Discussion of EDBP Experiments

5.1 Preliminary EDBP experiments

In order to compare 2C- and 3C-EDBP, Na₂SO₄ liquor (100 g/L, 700 mL) was dialysed with base-compartment liquor (NaOH

40 g/L, 700 mL) and acid-compartment liquor (H₂SO₄ 24.5 g/L, 700 mL: only for 3C-EDBP experiment).

Operating conditions, concentration changes of products and feed with time are shown in Figure 7.

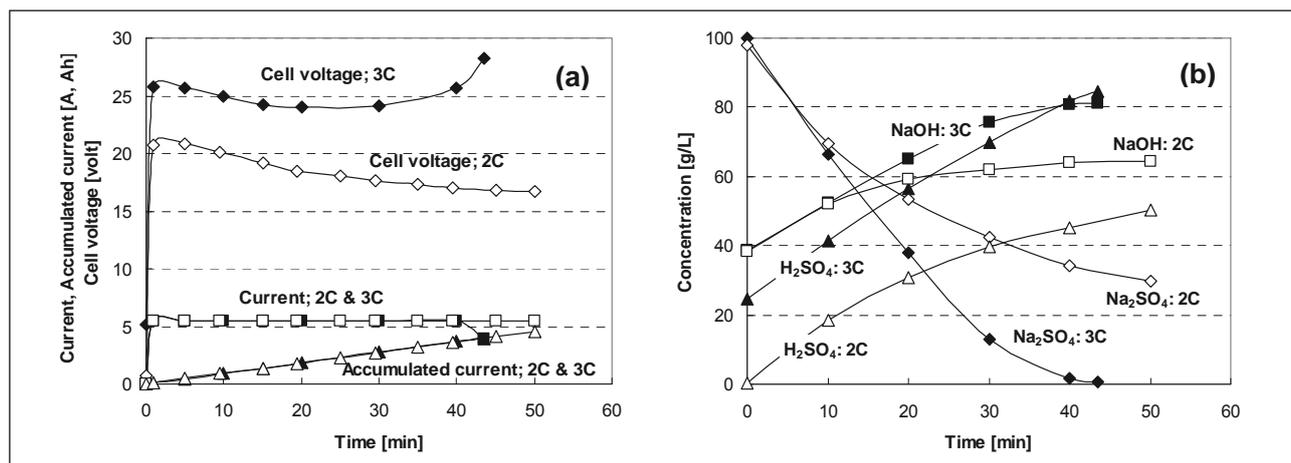


Figure 7 (a) Operation conditions of 3C- and 2C-EDBP, (b) Concentration change with time.

When dialysis operation starts, voltage goes up abruptly to keep current at 5.5A, and the integrated current is accumulated linearly with time. The cell voltage of 3C-EDBP was much higher than that of 2C-EDBP. In 3C-EDBP caustic soda concentration increased steadily with time, but in 2C-EDBP it has reached plateau soon after 10 minutes. Acid concentration increase lasted a little longer

than caustic soda increase. The decrease of Na_2SO_4 concentration is similar to caustic concentration change with time. Over 98% of de-salting extent was achieved in 3C-EDBP, but it was not more than 70% in 2C-EDBP.

CE and PC are shown in Figure 8(a).

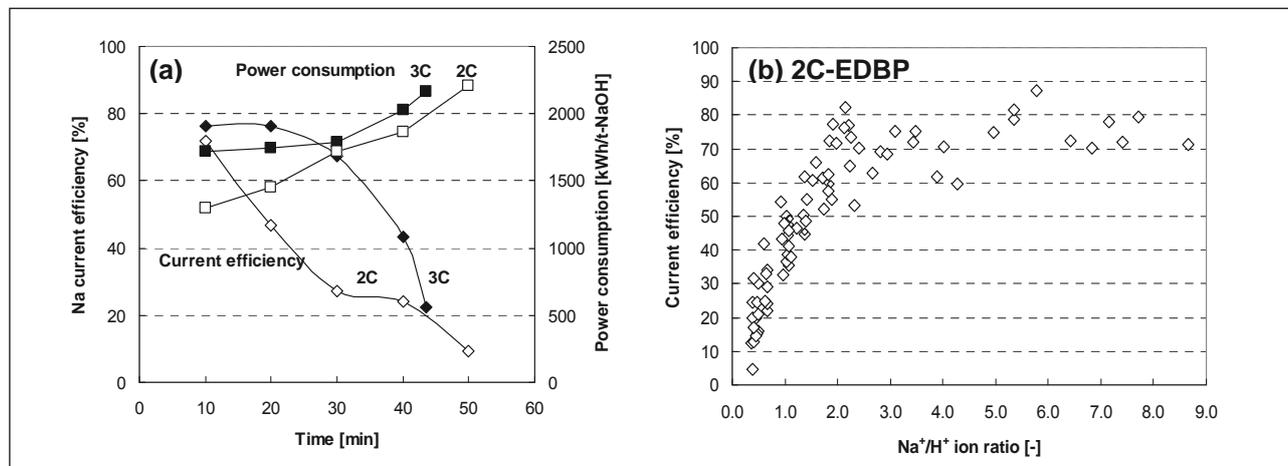


Figure 8 (a) Change of CE and PC with time comparing 2C- and 3C-EDBP; (b) Effect of Na^+/H^+ ion ratio on current efficiency in 2C-EDBP [Starting Na_2SO_4 100~300 g/L, Base-NaOH 20~140 g/L].

CE in 3C-EDBP was 76~60% until 30 minutes and then it decreased abruptly to 20%. In 2C-EDBP CE was high of 71% at first 10 minutes, but it decreased almost linearly with time to 10% (after 50 minutes). Despite CE was low in 2C-EDBP, PC was lower in 2C-EDBP than in the 3C-EDBP in the whole range of the experiment because of lower cell voltage in 2C-EDBP.

Can the soda recovery process be cost competitive with other commercial processes?

To compete with commercial production of NaOH by brine electrolysis, 2C-EDBP is significantly more suitable than the three compartment system from the view points of running cost (electric power consumption) and capital cost. Experimental results in Figure 8(a) indicate that the power consumption of less than 1500 kWh/t can be achieved by limiting the dialysis operation to within 20 minutes (de-salt extent ~40%).

The effect of concentration of Na^+ and H^+ ion and the ratio of these ions (Na^+/H^+) in the S/A-compartment on CE in 2C-EDBP were measured with varying starting Na_2SO_4 concentration in the range of 100~300 g/L. The result is shown in Figure 8(b). There are some fluctuations in the data, but it is found that while the Na^+/H^+ ratio is higher than 1.0, CE is kept fairly high (>50%).

In batch-wise operation in 2C-EDBP, the concentration of Na^+ ions decreases in the S/A-compartment. Consequently the concentration of H^+ ion in the compartment will increase with time which will increase the unfavourable H^+ migration through CEM to the base-compartment. As long as sodium sulphate remains in the liquor, the generated H^+ will favour the formation of sodium bisulphate rather than transfer to the base-compartment (competitive reaction/transport). When sodium sulphate is exhausted and hydrogen ion concentration increases, the transfer of hydrogen ion through CEM exceeds the transfer of sodium ions, and current efficiency will decrease drastically.

This conclusion agrees well with reports by Pinacci (2001) and Paleologou et al. (1997). Pinacci indicated that Na^+/H^+ ratio should be maintained as high as possible to obtain high CE and obtained 3.5 M (140 g/L) of NaOH from a 1 M feed (40 g/L) NaOH and 2.5 M (355 g/L) Na_2SO_4 with a current efficiency of 60%, though their PC was high at 3300 kWh/t. Paleologou et al. reported that 1.08 M (44 g/L) NaOH was consistently obtained with current efficiency 78% (power consumption 1986 kWh/t) by keeping S/A-compartment liquor composition $\text{Na}_2\text{SO}_4:\text{NaHSO}_4$ ratio nearly 1:1 (Na^+/H^+ ratio = 3.0).

Power consumption difference in these reports including our results, while CE is at the same level, is thought to be caused by the difference of cell voltage which will depend on the characteristics of membranes (CEM and BPM) and the voltage drop of liquors (liquor conductivity and clearance between membranes). But what concentration of product NaOH can be obtained at high current efficiency is not clear from these papers. The effect of starting liquor concentration in S/A- (100~250g/L) and base-compartment (30~130g/L) on Na^+ transfer rate was measured by changing these concentrations - Figure 9(a) and (b). In Run 2C-3 & 4, starting S/A-compartment liquor (a mixture of Na_2SO_4 200g/L and H_2SO_4 50g/L) was employed as a liquor roughly equivalent to the 20% de-salted liquor of Run 2C-2.

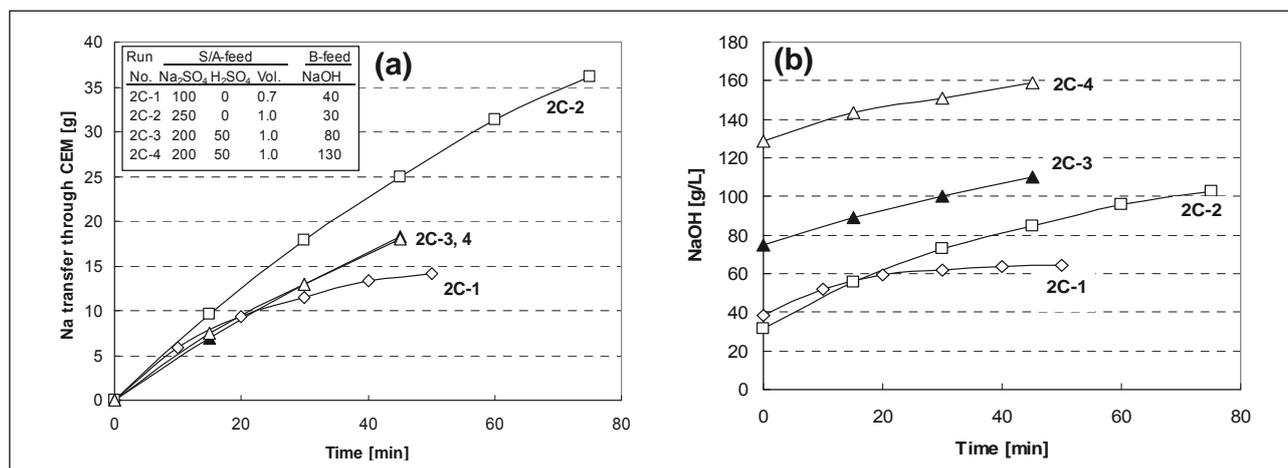


Figure 9 (a) Amount of Na⁺ transferred through CEM with time; (b) NaOH concentration change with time.

It was found that the starting Na₂SO₄ concentration (Run 2C-1, 2) does not affect the initial Na⁺ transfer rate (<10 min). In Run 2C-3 and 4, Na⁺ transfer rate was a little slower compared with Run 2C-1 and 2 because of H⁺ ion concentration in the starting liquor. But Run 2C-3 & 4 in Figure 9(a) show that the Na⁺ transfer rate was not affected by the initial base NaOH concentration. As a result, 160 g/L of NaOH was obtained after 45 minutes dialysis (Figure 9(b)) with a final point CE 45% and additional de-salt extent of 28% (total de-salt extent; ~42%). PC for the dialysis was 1320 kWh/t. Total energy consumption from pure liquors (Na₂SO₄ 250 g/L) will be less than 1300 kWh/t. After dialysis the de-salted liquor composition in S/A-compartment was Na₂SO₄ 150 g/L and H₂SO₄ 95 g/L.

Notably, this EDBP study was carried out using reagent grade Na₂SO₄, and impurities effect on the performance, especially the effect of organics, should be investigated further.

6. Integration of EDBP into Whole Recovery System and Economy of This Recovery System

6.1 Integration of EDBP

When 3C-EDBP system is integrated into this recovery system (Figure 1), de-salted liquor (de-salt extent >90%) will be used for washing of leached residue and as feed water for acid compartment. This will ensure the system is a self-sustained in regard to water balance.

For 2C-EDBP, recovered acid at S/A-compartment at low de-salt extent (~40%) results in a high Na₂SO₄ content recycle liquor in the system. Preliminary experiments confirmed that the salt did not affect leaching and impurities purification performance. One disadvantage is the increasing loss of any Na₂SO₄ adsorbed onto the leached residue which should be recovered by washing after S/L-separation. Wash water for the leached residue should be removed from the whole recovery system to maintain the water balance. One advantage is the increased salt concentration will make EDBP batch-wise operation easier even by using liquor obtainable from low Na₂O BR.

6.2 Economy of this recovery system

When this recovery system is applied to Bayer alumina refinery handling high silica bauxite, the cost of recovered caustic soda should be approximate to (or lower than) the commercial production cost, notwithstanding some reduction of BR-management costs which are expected. Nowadays, almost all new commercial plants for the production of caustic soda employ membrane electrolysis of brine. The caustic recovery cost by this process (2C-EDBP) is therefore compared to membrane brine electrolysis.

Capital cost

Liquor preparation: Slurry tanks for leaching DSP/BR and neutralisation is not so large, but S/L-separation, washing after neutralisation and evaporation will be needed. The cost will be more expensive than the brine dissolution and its primary purification process. Secondary liquor purification cost by e.g. chelating resin will be at the same level.

Electrochemical process: EDBP capital cost is expected much cheaper than brine electrolysis because of the need for expensive and exotic metal electrodes.

Total capital cost is expected to be, overall, cheaper in DSP/BR soda recovery system than brine electrolysis.

Running cost

Liquor preparation: Acid leaching will be more expensive than the brine dissolution because of sulphuric acid losses which need to be replenished. Additionally low Ca-content BR is preferred to maximise the efficiency of this process.

Electrochemical process: Electric power consumption is much lower in 2C-EDBP (~1500kWh/t) than in the brine electrolysis (~2500kWh/t). The difference will amount to 1000kWh/t. But the life of membrane for EDBP seems to be shorter than brine electrolysis and the cost may be significant for running cost. Fouling will control the life of membranes.

Additionally there should be a cost saving associated with a lower soda, lower pH and more stable residue. Although a very rough and qualitative cost comparison, this caustic recovery process offers the prospect of caustic at a cost competitive to caustic from brine electrolysis.

7. Conclusions

A new process to recover caustic soda from DSP/BR is outlined. The process consists of leaching DSP/BR with sulphuric acid, purification of the liquor by neutralisation and electrodialysis to split Na_2SO_4 into NaOH and H_2SO_4 . By this method 80% of soda in DSP/BR was recovered as Na_2SO_4 . When 2C-EDBP is applied for salt splitting, 160 g/L NaOH was recovered at a current efficiency >50% and power consumption <1500kWh/t-NaOH. By using 2C-EDBP, the cost of recovered caustic soda compares favourably to alternative commercial methods.

Optimisation of acid leaching and liquor purification (neutralisation), study of membrane fouling on EDBP are future development issues.

8. Acknowledgements

The authors are grateful to the CSIRO PSE's analytical group at Waterford.

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