MOBILITY OF INCLUDED SODA IN SODALITE

Smith P*, Wingate C and De Silva L

*Parker CRC for Integrated Hydrometallurgy Solutions
(CSIRO Minerals Light Metals Flagship), WA, Australia*

Abstract

Bayer sodalite is the main form of desilication product. Its zeolite type cage structure contains included ions, and the leaching of these ions is a possible way to recover "fixed soda". The ions leach through the windows of the sodalite cage structure and thus recovery should be restricted to those anions that are smaller than the cage openings. This paper examines the mobility of different ions within the structure of sodalite by water washing and re-digestion of the sodalite in water.

Whether dominated by sulphate, carbonate or hydroxide, soda leaches from sodalite with cold water washing only sparingly, and to a maximum of ~15% under a "standard" washing procedure used. When re-digested in water the sodalites leached soda more extensively. In particular all included soda can be removed from a hydroxide dominated sodalite by re-digestion and washing. Both "standard" washing and enhanced washing by re-digestion showed evidence of carbonate leaching despite the carbonate ion being too large to pass through the sodalite cage window. In addition, washed samples sometimes showed an imbalance of included soda and total included anions. This has led to the proposal that neutral CO_2 forms from carbonate during washing, a portion of which can exit through the sodalite cage openings.

Notation and units

Standard North American Bayer notation A= gL^{-1} Al_2O_3, C= gL^{-1} sodium hydroxide and sodium aluminate (as Na_2CO_3) and S=C + sodium carbonate (all as Na_2CO_3).

1. Introduction

"Desilication Product" (DSP) is a collective term used to describe several silica containing compounds that precipitate as a result of the dissolution of "reactive silica" from bauxite into Bayer liquor, - mostly during the operations of pre-desilication and digestion. Bayer sodalite is the main desilication product, consisting of a caged aluminosilicate structure (a feldspathoid) with charge balancing sodium cations. Included in the cage structure are sodium salts of the common anion impurity ions in Bayer liquor (Riley *et al.* 1999). This distinguishes Bayer sodalite from the natural form of the mineral which contains only chloride. The process of desilication has positive and negative aspects. It scavenges significant quantities of inorganic impurities from the liquor but also results in the loss of caustic soda (NaOH) from the same liquor. Since in almost all cases, DSP is discarded with the red mud residue, the loss of this caustic (fixed soda) is a major cost for refineries processing bauxites with high levels of reactive silica.

In refineries processing low reactive silicas, sodalites contain a variety of included anions, including sulphate, chloride, carbonate and aluminate. Previous work from our laboratory (unpublished) has shown that while included soda can inadvertently be washed out of sodalites by "over-washing", the sulphate and chloride ions of these sodalites do not leach and remain in the solid phase. This immobility indicates that the sodalite cages remain intact, and that any anions that are released must come from ions migrating through the sodalite cage openings (windows). Both sulphate and chloride are large ions (~5 and ~3.6 Å respectively) compared to the cage openings (~2.3 Å) and therefore would not be expected to be released.

In refineries processing high silica bauxites, concentrations of sulphate and chloride in the process liquor are generally low. Consequently sodalites formed from such liquors tend to be dominated by carbonate, aluminate and possibly hydroxide. Carbonate is also a large ion (~3.7 Å) and thus would not be expected to leach, but the aluminate ion is of comparable size to the cage window and the hydroxide ion even smaller (Figure 1). Sodium aluminate and sodium hydroxide are thus expected to be the ions released when sodalites are washed.

From the discussion above, the extent to which included soda is recoverable will be related to the distribution of anions in the sodalite as it is formed and the mobility of these ions during the extraction process. Before any soda recovery process can be considered it will be important to understand the relative leachability of anions from sodalite, particularly those typical of refineries processing high reactive silica bauxites.
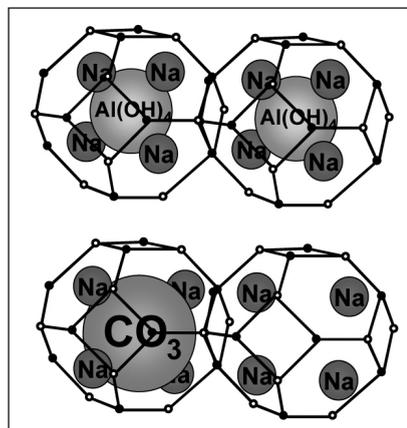

Figure 1. Unit cell of sodalite DSP (two aluminosilicate cages) showing full aluminate occupancy (upper) or full carbonate occupancy (lower). The carbonate ion is larger than the cage opening and should not be exchanged/washed out. The aluminate is roughly the same size as the opening.

2. Aims and Methodology

This paper reports the preparation of sodalite with three different inclusion distributions:

1. Inclusions of sulphate, chloride, aluminate and hydroxide
2. Inclusions dominated by carbonate
3. Inclusions dominated by hydroxide.

The paper compares the effect of a "standard" washing procedure on the release of included ions (both cations and anions) by examining the elemental composition before and after washing. Extensive washing was simulated by re-digesting these sodalites in water at 150°C and washing again.

3. Experimental

3.1 Materials

All reagents used were AR grade, with the exception of gibbsite (C31 hydrate, Alcoa) and kaolin (Eckalite 1a, English China Clay company). The Eckalite was found to contain a quartz impurity, quantified by an industry standard wet chemical method to be 2.5%. When this was taken into account, the kaolin in Eckalite had a calculated molar Al:Si ratio of 1.00.

Synthetic Bayer liquors and other solutions were prepared by dissolving reagents in deionised water (sometimes with heating). Once solutions had cooled to room temperature they were made up to volume using deionised water. Final liquors and solutions were titrated for A, C and S where applicable using the Connop titration method (Connop 1996). A 1:10 dilution in water was also prepared for ICP analysis (Si, Al, Na).

3.2 Formation of sodalites

Kaolin (4 g) was digested in caustic solution or synthetic Bayer liquor (100 mL) at 150°C for 30 minutes in a sealed bomb using a gas fired reactor capable of heat-up rate of ~35°C.min^{-1} and a faster cool-down rate. The start liquor composition varied depending on which test series was being carried out.

3.3 Filtration and washing

Digested slurries were filtered through a Supor membrane (0.45μm) using a pressure filter. The exit liquor was collected, weighed and titrated for A, C and S where applicable. A 1:10 dilution was prepared for ICP analysis (Si, Al, Na). A fixed amount of pure caustic solution (C = 170g/L) was used to rinse the remaining contents of the reaction vessel into the filter press.

The residue was then subjected to a sequential "standard" water wash program that involved:

i. Re-suspending the residue in approximately 40 mL of deionised water (equivalent to roughly 10 mL per gram DSP).
ii. Stirring the suspension for 10 minutes using a magnetic stirrer, then filtering through a Supor membrane (0.45 μm) using a pressure filter.

In most cases this digestion/washing procedure was repeated 4 times, giving a total of 5 sequential washes.

3.4 Re-digestion of sodalites

For some experiments a bulk sodalite was prepared under the same experimental conditions as above but using a Parr reactor. This resulting sodalite (caustic and singly water washed) was re-digested in water in the gas fired reactor (4g 100 mL^{-1}) and then re-washed according to the procedure above.

3.5 Analyses

In each case the washed residues were collected and dried in an oven at 100°C overnight. Samples were submitted for XRF analysis and total carbon measurements with appropriate standards. Selected residues were also analysed by a Philips X'Pert XRD analyser using Co K$_\alpha$ radiation.

4. Results

4.1 Presentation of results

The majority of results in this paper are presented as cage occupancies of sodalite DSP as prepared or as subsequently washed. These are calculated from the elemental composition of the residues as follows.

Sodalite is assumed to be the only mineral in the residue[1] and have the stoichiometry $Na_6[AlSiO_4]_6.Na_2X.6H_2O$, where the

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1 The kaolin used has a minor quartz impurity and this concentration is taken into account when performing the calculation of sodalite composition.

Na$_2$X represents the cage contents with a variety of anions (X). "Occupancy" is defined as the fraction (or %) of Na$_2$X that is associated with a particular anion. For example the occupancy of sulphate can be calculated from measured composition of sodalite using the expression:

$$Occupancy = 100 * \frac{moles\ SO_4}{6 * moles\ SiO_2}$$

Occupancies of soda (as Na$_2$) and X (the total of all anions) should match to ensure charge balance. Consequently, occupancies of Na$_2$ (or X) less than 100% indicate the presence of empty cages.

Previous work by our laboratory (Riley et al. 1999) has indicated a problem using the measured alumina content of the sodalite to calculate an aluminate occupancy. This may be due to problems associated with co-precipitation of an extraneous alumina containing phase, or with our assumption of the Al:Si molar ratio for the aluminosilicate cage. These problems surfaced again in the early stages of this work and thus in the following results an assumption has been made that the difference of soda occupancy and total measured anion occupancy indicates the presence of non-measurable anions. In this work non-measurable anions are defined as aluminate and hydroxide.

4.2 Sodalite DSP formed from synthetic liquor containing carbonate, sulphate and chloride

The inclusion composition of sodalite formed from a solution of C=260, A/C$_{exit}$=0.65, Na$_2$CO$_3$=50 gL^{-1}, Na$_2$SO$_4$=30 gL^{-1} and NaCl=25 gL^{-1} then washed 5 times is given in Figure 2.
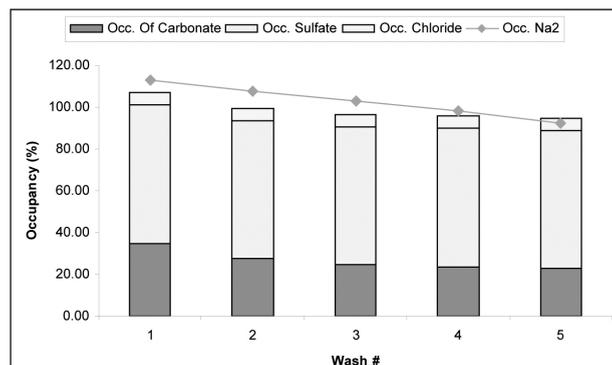
Figure 2. Distribution of included ions in sodalite and the change in distribution on washing.

Figure 2 shows ~ 100% occupancy and that anion inclusions are dominated by sulphate and carbonate[2]. In fact the total aluminate and hydroxide inclusions (indicated by the difference in soda and total anion occupancy) is very small. Washing this sodalite does not show a change in either sulphate or chloride (as expected). The decrease in included soda is shown to come from not only the aluminate / hydroxide but surprisingly, the carbonate. As indicated previously, this ion should not leach because of its size.

To focus attention on mobile rather than immobile ions, sulphate and chloride were excluded from further tests. In addition, and to circumvent the problems of defining aluminate inclusions, sodalites were formed in aluminate free caustic solutions. Kaolin provided only enough aluminium to form the sodalite cage structure thus effectively forcing the aluminate inclusions to zero. These changes to the liquor composition restricted the inclusions to carbonate and hydroxide, a model of a sodalite formed from high reactive silica.

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2 Other work from our laboratory (Lowe et al. 2002) has indicated these ions are "preferred" (ie more energetically stable than others (aluminate, hydroxide and perhaps chloride).

4.3 Sodalite formed from caustic-carbonate solution

Sodalite was formed from a caustic-carbonate solution containing no aluminate - C=260, S=300 (Na_2CO_3=40 gL^{-1}). The result is given in Figure 3 which shows not only the washing of the sodalite (3a), but the re-digestion of a duplicate sample (labelled "0" in 3b) and its subsequent washing.
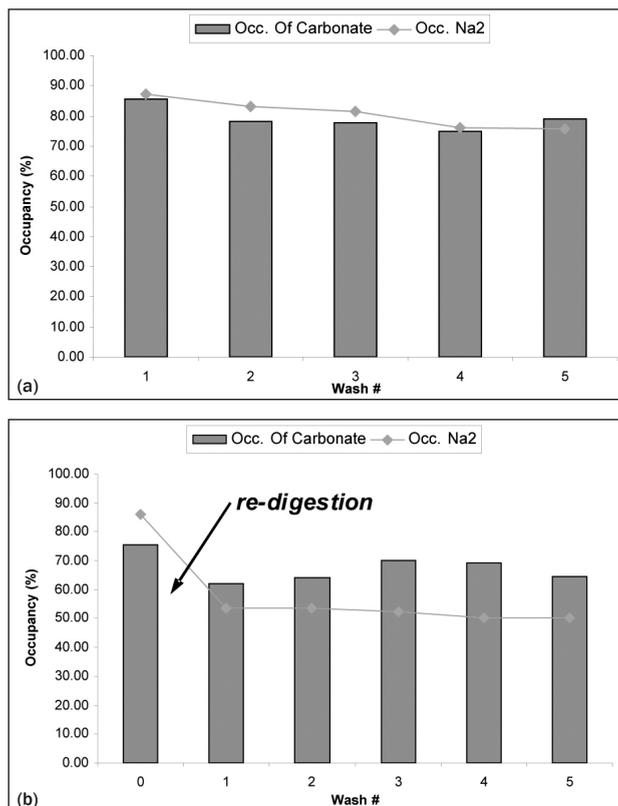

Figure 3. (a) Washing of sodalite formed caustic-carbonate solution (b) The re-digestion of this sodalite (labelled (0) in water and its subsequent washing.

In the absence of sulphate and chloride, this sodalite is dominated by carbonate, although the total inclusion level (now ~ 85-90%) indicates some empty cages. Whether this represents cages that were never occupied, or ions that were removed during the first wash is not clear. In common with Figure 2, the reduction of included soda is matched by a reduction in carbonate and non-measurable anions (this time exclusively assigned to hydroxide).

More extensive leaching conditions provided by a re-digestion of this sodalite in water shows a greater drop in both soda and carbonate. Thereafter washing appears to have little effect. The most significant aspect of Figure 3b is that soda occupancy has fallen below total anion occupancy. This implies that there is no remaining hydroxide, but more importantly, that there is insufficient soda to charge balance the remaining carbonate.

4.4 Sodalite formed from caustic only solution

Sodalite was formed from a caustic solution only (C=260, no carbonate or aluminate). This should produce a sodalite with substantial hydroxide which, so far, has been largely excluded by more dominant ions. The result is given in Figure 4a. Carbonate is present in the caustic solution as an impurity in the caustic soda used to prepare it, and also from CO_2 pickup. This carbonate has preferentially concentrated in the sodalite, but to a level below that in Figure 3. Hydroxide inclusions are significant, and the total inclusions are now restricted to ~70%. The standard washing has produced a reduction of soda of equivalent extent to the two previous figures (~15% of the Na_2X sites).
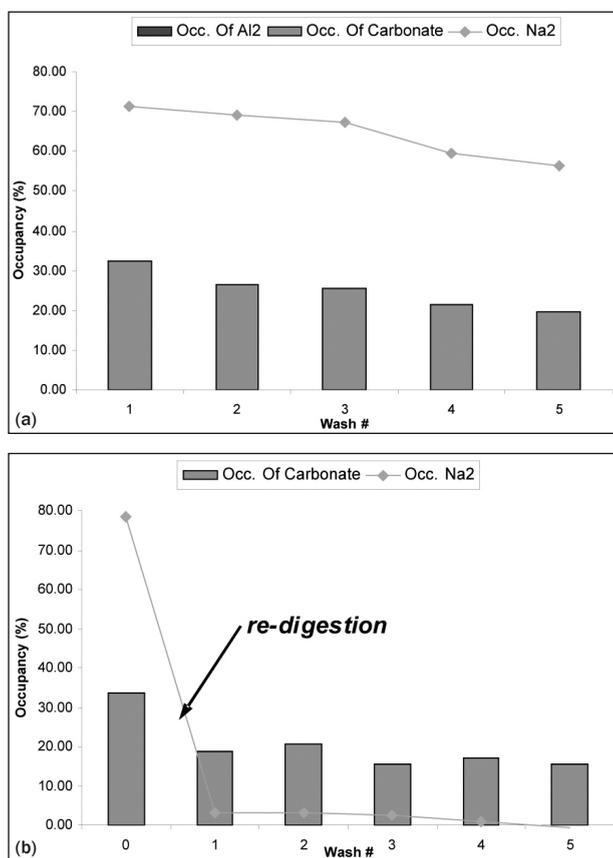

Figure 4. (a) Washing of sodalite formed caustic only solution (b) The re-digestion of this sodalite in water and its subsequent washing.

Re-digestion of this sodalite (Figure 4b) shows a most dramatic reduction in soda. A ~90% reduction in included soda is accompanied by a ~50% reduction of carbonate. Washing doesn't appear to significantly reduce carbonate further, but the soda is effectively reduced to zero after 5 washes. This corresponds to a sodalite with a molar soda to silica = 0.5 (i.e. cage soda only). Zero included soda should imply no associated anions (ie the total removal of the hydroxide and the carbonate).

The evidence from both Figure 3 and Figure 4 therefore implies that carbonate can be removed from sodalite cages, and that some of the residual carbonate does not have adequate charge balancing soda.

The change in sodalite cage contents affects the structural properties of the sodalite crystal which is reflected in changes to the XRD pattern. Figure 5 shows detail from the XRD patterns of sodalites from Figure 2 (full anion occupancy) and Figure 4b (minimal anion occupancy).
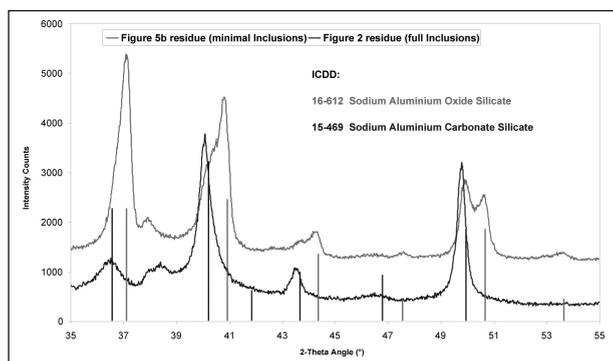

Figure 5. Detail of the XRD pattern of washed residues from Figure 2 (full cage occupancy, lower) and from Figure 4b (minimal cage occupancy, upper).

The figure shows a reasonable match of Figure 2 sodalite trace to ICDD card 15-469 (a synthesized carbonate rich sodalite) whereas the Figure 5b trace shows evidence of both this sodalite and 16-612 which is described as a synthesized sodalite molecular sieve with no reported inclusions.

5. Discussion

The data in the preceding figures demonstrate a number of features for sodalite with different inclusions and the reaction of these compounds to washing. It appears that whether dominated by sulphate, carbonate or hydroxide, washing can reduce the soda content by up to ~15% under our "standard" washing conditions.

Sodalites containing carbonate or hydroxide exhibit included soda contents <100% after an initial wash. Since these soda contents are either stable or exhibit very slow leaching with continued washing it is likely that the cages are empty (of ions) during the formation rather than leached during the first wash. Although this implies that these sodalites remove less soda from Bayer process liquors it is apparent that they leach soda during washing at much the same rate as those that have a full complement of included ions.

Re-digestion of the sodalites has resulted in enhanced leaching. Significant reduction in included soda has been only partially offset by a reduction in total anion inclusion leading to an apparent charge imbalance. In particular the re-digestion of hydroxide-dominated sodalite has shown an almost total removal of included soda whilst some residual carbonate remains.

One possible explanation of the leaching of carbonate or continued presence of carbonate without charge balancing soda is the formation of neutral CO_2 within the cages. The following reaction produces sodium hydroxide which, as has been demonstrated, can be washed out of the cage openings. The proposal is that CO_2 can either remain within the cage or be (partially) removed through the cage window depending on the extent of washing:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH \rightarrow CO_2 + 2NaOH$$
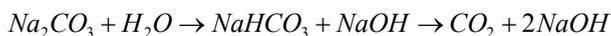
This reaction assumes some enhanced stability of the CO_2 within the cage structure[3]. In fact it is likely that if some CO_2 is removed through the window in this way, it recombines with NaOH to form sodium bicarbonate / carbonate in the washings. A similar mechanism could be postulated for aluminate inclusions, leaving neutral $Al(OH)_3$ in the cages. It should be pointed out that this concept is purely speculative and would require further work to evaluate.

6. Conclusions

The main conclusions of this work therefore are:

i. Under mild washing conditions, sodalites that are dominated by sulphate, carbonate, or hydroxide all leach soda at an equivalent (slow) rate. It is presumed that this release is via ion migration through the sodalite cage openings.
ii. Carbonate can be removed from sodalite despite the size of the ion being greater than the cage window.

iii. Under more extreme leaching conditions (re-digestion), all ion inclusions are more leachable. In particular hydroxide inclusions can be (totally) removed from sodalite.
iv. In some cases after re-digestion there is residual carbonate present with insufficient charge balancing soda.
v. A mechanism has been proposed whereby during leaching carbonate disproportionates into hydroxide and hydrated CO_2. The CO_2 thus formed can either stay within the sodalite or leave with the associated hydroxide through the cage openings.

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3 Caged zeolites have been used to sequester neutral CO_2 from the gas phase for many years. A recent study examines the stability of CO_2 in faujasites, Plant et al. (2006).

References

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