CHEMICALLY ENHANCED RECOVERY OF BICARBONATE FROM LAKESALT

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ABSTRACT

The application of carbon dioxide, acetic acid and hydrochloric acid to convert sodium carbonate to the bicarbonate and thereby enrich the bicarbonate in a mixture of both salts derived from lakesalt by fractional crystallization is reported. The CO_2 was bubbled through aqueous solutions of the salt mixture at various test temperatures in the range 0 - 90°C and the carbonate to bicarbonate conversion monitored by determining the bicarbonate to carbonate ratio of the crystals obtained under the various conditions. The ratio increased as temperature increased up to 90°C; hence the derivation of sodium bicarbonate from lakesalt was finished by bubbling CO_2 through solutions of derived salt mixtures heated to 90°C. Also acetic acid and hydrochloric acid were applied in stoichiometric amounts to achieve the conversion of the carbonate content of derived salt to bicarbonate. HCl was superior in performance to acetic acid and was applied regularly in the acid conversion. Bicarbonate to carbonate ratio increased 5.5-fold in the CO_2 process, 6.5-fold with acetic acid and 16.6-fold with hydrochloric acid.

INTRODUCTION

It has been highlighted that lakesalt has potential as a source of raw material[1] It has been recognised as a complex mixture of chemical substances yielding to possibilities of contamination and adulteration[2,3]. Sorted, hand-picked and purified samples have been shown to be rich in sodium and also contain low levels of potassium and traces of other elements[4]. Salts identified in samples include carbonates and bicarbonates, sulphates and chlorides[2,3,5]. The distribution and traditional uses of lakesalt in Nigeria have been broadly reported[3,6]. In its native state lakesalt has been shown to contain relatively higher levels of carbonate than bicarbonate[2,3,5]; hence it has been recommended as a source of sodium carbonate for industrial use. It has also been discovered that lakesalt may be enriched in bicarbonate in its beneficiation as a source of sodium bicarbonate[7] This article presents inexpensive, simple approaches to the enhancement of sodium bicarbonate content after isolating the carbonate/bicar-bonate fraction from lakesalt.

EXPERIMENTAL

Samples

Lakesalt samples were selected and bought from traders in Kano, Maiduguri and Malumfashi markets. For this work samples were selected to avoid adulteration, excluding those that possessed dark colours, which suggested the inclusion of vegetable matter. Each sample was ground using a mortar and pestle and stored in a stoppered bottle.

Reagents

Marble chips were obtained from a local source, a Company that manufactures marble ornamental stones from limestone. The hydrochloric acid used for generating carbon dioxide was of general purpose reagent grade (BDH) while that used for converting carbonate to bicarbonate in samples was of analytical reagent grade (M&B). The acetic acid used was of analytical reagent grade (M&B). All crystallizations were conducted in distilled water.

Generation of carbon dioxide

Some quantity of marble chips was taken in a two-necked CO_2 bottle. 20% aqueous HCl was

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poured into the bottle through a thistle funnel inserted in one neck while the CO_2 evolved from the reaction was delivered through a glass delivery tube adapted to the other neck.

Recovery of carbonate/bicarbonate from samples

50.0 g of a selected sample was dissolved in 800 cm^3 of water and the solution brought to boil and made to concentrate until crystals started to appear. The mixture was cooled in ice and the crystals separated were filtered out, washed with methanol and allowed to dry in air. The mother liquor was further concentrated to obtain other generations of crystals by fractional crystallization. All crystals were identified by qualitative analysis and any carbonate/bicarbonate containing crystals put together and recrystallized. Samples were considered pure when they tested negative for anions other than CO_3^{2-} and HCO_3^-. The pure carbonate/bicarbonate crystals were weighed and stored in a stoppered bottle as the recovered salt.

Determination of total carbonate and bicarbonate in samples

To determine the combined carbonate-bicarbonate content in either an unprocessed lakesalt sample or salt crystallized therefrom, a small mass (0.5 g) of the sample or salt was titrated against aqueous 0.1M HCl using methyl orange as indicator. The results of triplicate titrations were averaged and applied to calculate the combined percentage by mass of carbonate and bicarbonate in each sample as indicated in Table 1.

Determination of bicarbonate to carbonate ratios in samples

To determine the content of carbonate and bicarbonate respectively in a sample, 0.5 g of the sample was titrated against 0.1M HCl using phenolphthalein and methyl orange in a double end point titration[7]. While the titration result up to the phenolphthalein end point (x) was doubled to obtain the titre for the carbonate in the sample (2x), the result up to the methyl orange end point (y) was the titre for the carbonate and bicarbonate combined. The bicarbonate titre was obtained by difference (y-2x). Typical bicarbonate to carbonate ratios are indicated in Table 1 for raw lakesalt samples and carbonate-bicarbonate mixtures obtained by fractional crystallization from them, each value tabulated being the average of triplicate observations.

Enhancement of bicarbonate content of derived salt using carbon dioxide

3.0 g of the mixed carbonate/bicarbonate crystals obtained from the lakesalts was dissolved in each of six small beakers. In the first three beakers, carbon dioxide was bubbled continuously through the cold solutions for 30, 60 and 90 minutes (min) respectively. In the next three beakers, the carbon dioxide was bubbled for 30, 60 and 90 min respectively while heating each solution on a hot plate just below boiling. At the end of each duration, each solution was concentrated by boiling, cooled in ice and the crystals obtained filtered out, washed with methanol and dried in air. Thereafter each crystal was analysed for its

Table 1: Combined carbonate/bicarbonate content of typical lakesalt samples and recovered salt

Sample no.	Characteristics	% Carbonate/ bicarbonate	Bicarbonate to carbonate ratio
1	Pink, crystalline lakesalt	81.23±3.25	1.46
2	White, crystalline lakesalt	75.92±2.88	1.37
3	Greyish green powdery lakesalt	62.22±2.90	0.93
4	Recovered carbonate/bicarbonate fraction	95.29±3.03	1.17

Table 2: Effect of carbon dioxide on bicarbonate to carbonate ratio of recovered salt

Thermal state -CO_2 duration (min)	Cold-0	Cold-30	Cold-60	Cold-90	Hot-30	Hot-60	Hot-90
Bicarbonate to carbonate ratio	1.17	4.09	4.91	5.56	5.08	6.27	6.41

bicarbonate to carbonate ratio by the procedure already described. The results are presented in Table 2 for triplicate determinations.

Enhancement of bicarbonate content of derived salt using acids

5.0 g fractions of the mixed carbonate-bicarbonate crystals obtained from lakesalt samples were dissolved in water to obtain saturated solutions in separate beakers. To each of a set of three of these beakers, 2.10 cm^3 (0.0212 moles) of commercial HCl (10.10M) was added carefully with stirring. To each of another set of three of these beakers, 1.30 cm^3 (0.0212 moles) of commercial acetic acid (16.67 M) was added with stirring. Thereafter all six solutions were heated over a steam bath to clarify and concentrate. They were allowed to cool down to room temperature and the crystals formed in each case were filtered out, washed with methanol and allowed to dry in air before weighing. The average weight obtained from each set of three experiments was noted. The bicarbonate to carbonate ratio was determined in triplicate for each set of crystals using the double end point procedure already described. The results are presented in Table 3.

RESULTS AND DISCUSSION

Samples investigated were either white in colour or pink; these are the varieties of lakesalt widely used locally in cooking and medicines[3,6]. They appear clean and crystalline and are less likely to be adulterated. Though samples contained sulphate and chloride in addition to carbonate and bicarbonate, emphasis was on the carbonate/bicarbonate fraction. In successive recrystallizations of this fraction, the process of purification was stopped when both sulphate and chloride tested negative. Then the derived salt was assumed to be only a mixture of carbonate and bicarbonate of sodium which is known to be the dominant metal[2,3]. The conversion of carbonate to enhance bicarbonate was performed on this derived salt mixture.

The bicarbonate to carbonate ratio was applied to estimate the relative content of these two salts in samples and to evaluate the effect of both carbon dioxide passed and the extent of conversion of carbonate to bicarbonate achieved by the acid applied. The data of Table 1 show that there is a variation in the carbonate/bicarbonate content in different samples and that the bicarbonate content is not always less than carbonate. The bicarbonate to carbonate ratios

Table 3: Bicarbonate enhancement using acid to convert carbonate in recovered salt

Acid applied	% yield	Bicarbonate to carbonate ratio in product	% bicarbonate in product
HCl	34.47±3.95	12.91	88.44±1.05
CH_3COOH	41.93±2.76	5.05	74.94±1.39
Untreated (Control)		0.78	35.10±0.44

indicated for specific samples in Table 1 illustrate this point; the value shown in Table 3 for the pure salt finally derived by fractional crystallization and purification from various lakesalts and pooled together implies a lower content of bicarbonate than carbonate in the derived salt (control).

The results presented in Table 2 demonstrate that the carbonate content of the carbonate/bicarbonate fraction is converted to bicarbonate by the carbon dioxide passed. This produces a large increase in derivable bicarbonate at the expense of the carbonate. The CO_2 enhancement is promoted by heating; hence the bicarbonate enrichment was carried out heating to 90°C while bubbling the carbon dioxide. A 5.5-fold increase in bicarbonate to carbonate ratio is indicated in the process. A residual carbonate content of 13.5% is implied in the data of Table 2 for the bicarbonate-enriched salt. This could be further reduced by increasing either or both of the temperature and duration for which the CO_2 is bubbled to achieve the completion of the reaction

$$CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^-$$

Stoichiometric mole ratios were desired in the acid conversion reaction,

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

The acid conversion of carbonate to bicarbonate, as shown in Table 3, increased the 35.1% bicarbonate in the pooled derived salt to 88.4% in the acid modified product. While HCl increased the bicarbonate to carbonate ratio 16.6-fold, acetic acid yielded a 6.5-fold increase in the ratio. The performance of HCl commends it over acetic acid. A rigid control of the acid would permit a further reduction of the residual carbonate level and further enhance the bicarbonate level thereby.

CONCLUSION

The two procedures investigated offer inexpensive ways for deriving sodium bicarbonate from lakesalt. These procedures would widen the range of use of lakesalt which is a naturally occurring mineral in this country. Use as an industrial raw material is suggested herein.

REFERENCES

1. Ekanem, E.J. and Harrison, G.F.S., The raw material potential of lakesalt ('kanwa') - a poser for Nigerian industries, Paper presented at the 33rd Annual Conference of Science Association of Nigeria, Makurdi, 1992.

2. Ekanem, E.J., M.Sc. Thesis, Ahmadu Bello University, 1977.

3. Ekanem, E.J. and Harrison, G.F.S., Nig. Jour. Chem. Res., 1997, 2, 33.

4. Makanjuola, A.A. and Beetlestone, J.G., Jour. Min. Geol. (Nigeria), 1973, 10, 31.

5. Ako, P.A.E. and Harrison, G.F.S., Nig. Jour. Technol. Res., 1990, 2, 39.

6. Buchannan, K.M. and Pugh, J.C., Land and People in Nigeria, 8th imp., University of London Press, London, 1971.

7. Lambert, J. and Muir, T.A., Practical Chemistry, 3rd ed., Heinemann Educational Books, London, 1987.

8. Jatau, S.S., B.Sc. Dissertation, Bayero University, 1995.

accepted 19/5/99

received 17/3/99