The Impact of EDTA and Sodium Hexametaphosphate Habit Modifiers in the Production of Quality Soda Ash Crystals

Zukiswa S. Raditladi*, Jane C. Ngila, Boitumelo V. Kgarebe†
and W. Ddamba
University of Botswana, Private Bag UB 0074, Gaborone. Botswana
E-mail: zraditladi@netscape.net;   Fax: (267) 355 2836

The impact of two sequestering agents, namely, ethylenediamine-tetraacetic acid (EDTA) and sodium hexametaphosphate (SHMP) on the morphology, size and purity of soda ash was studied. Analysis of soda ash crystals, precipitated by bubbling carbon dioxide through the brine solution, was done using various techniques including powder X-ray diffraction (XRD), differential thermal analyses/thermogravimetric analyses (DTA/TGA), environmental scanning electron microscope (ESEM) and ion chromatography (IC). Crystals produced in the presence of SHMP resulted in spherical shapes which is a more desirable morphology compared to the needle-like shapes observed for the control sample. On the other hand, the presence of EDTA maintained the undesirable needle-like shapes. Each sequestering agent had an optimum concentration (EDTA = $1.09 \times 10^{-2}\%$ w/v and SHMP = 2.13×10^{-2}–$2.17 \times 10^{-2}\%$ w/v) that gave the best product purity as demonstrated by minimum impurities in the final product. The particle size distribution (PSD) results show that the soda ash grown in the presence of SHMP had the largest particle sizes ranging between 180 and 500 microns while that of both the control and EDTA samples had particle sizes between 0 and 180 microns.

Key Words: Soda ash. Brine solution, Sodium hexametaphosphate, Ethylenediaminetetraacetic acid, Crystal morphology and purity.

INTRODUCTION

Sodium carbonate, industrially known as soda ash, is a basic and important chemical used in glass manufacturing, metallurgical applications, textiles, printing, foodstuff, medication, detergent industry and chemical manufacture[1]. The world consumption of soda ash, which stood at 35 million tons as at the end of 1996[2], is indicative of the scale and importance of this chemical feed. Soda ash which is produced by carbonation of an alkaline-rich brine tends to crystallize as small, needle-shaped crystals which break easily producing a lot of fines. These fines have an adverse effect on downstream filtration processes, drying and compaction, thus greatly complicating the handling and processing of the resulting product[3]. Equally important is the purity of the soda ash produced. The starting solution, brine, contains sodium chloride impurity that contributes to the

†National Food Technology Research Centre, Private Bag 008, Kanye, Botswana.

small crystals that are also susceptible to entraining occlusions. In order to improve the purity, size and morphology of the soda ash crystals, the use of impurities was employed because "of the many factors controlling a crystallization process, none can cause a more spectacular change than the addition of certain impurities to the crystallizing liquor"[4]. The presence of the impurities results in a selective adsorption of an impurity that alters the normal rate and pattern of growth. Adsorption of the impurity on the crystal surface changes the normal surface-energy relations, besides blocking certain sites and promoting others to be favoured[5], resulting in a change in morphology. When impurities are intentionally added specifically to produce a desired morphological effect, they are referred to as additives[6].

In this study, we have investigated the influence of two commonly used additives, namely EDTA and SHMP additives, on the morphology, purity and size of the industrially produced sodium bicarbonate. EDTA was used because of its ability, as a chelating agent, to sequestrate metal ions[7], thereby preventing their interference while SHMP was chosen because of its relatively large molecules. It has been reported[8] that when added into the crystallizing solution, SHMP exerts its influence through selectively enhancing or retarding growth of certain faces of the resulting crystal. This study is a continuation[9] of investigations of different types of additives (inorganic and organic compounds) as habit modifiers in the production of crystals.

EXPERIMENTAL

Brine sampling and crystal growing

At Sua Pans (Botswana), carbonate-rich brine found under the saline sands is pumped into solar evaporation ponds. The extraction process starts with partial evaporation of the brine solution from the solar ponds to a concentration just prior to trona crystallization. The resulting brine, henceforth referred to as T-brine, was used in this work.

The conditions used in the industrial process[1] were simulated in the laboratory. Various amounts of SHMP (8.29×10^{-3} to 3.41×10^{-2}% w/v) obtained from BDH Chemicals (England) and EDTA (1.63×10^{-3} to 2.52×10^{-1}) from Saarchem (RSA) were added to the brine prior to carbonation. T-brine solution (1000 mL) containing an additive was heated on a hot plate to about 54°C to ensure optimal growth of $NaHCO_3$ after which 800 mL was transferred into the carbonation unit. The unit comprised of an electronic stirrer (Heidolph RZR 2051) equipped with a two-blade propeller for the efficient mixing or dispersion of the CO_2 gas, a baffle whose function was to prevent the formation of a vortex and a spurger used to allow even distribution of the CO_2 gas. The agitator was set to 1100 rotations per min (rpm) and the rotameter to 80%. Carbon dioxide gas was bubbled through the mixture until the pH dropped to 7.40 after which the sodium bicarbonate crystals were separated from the mother liquor by vacuum filtration and purified by washing using 100 mL Na_2CO_3 solution (0.100 M)[10]. The sodium bicarbonate crystals were then heated in an oven at 220°C for 4.5 h so as to convert sodium bicarbonate to sodium carbonate.

The x-ray powder diffraction studies to determine the mineral phases were carried out using a Philips PW 3710 diffractometer, operated at 40 kV and 45 mA with a copper source (Cu-K$_\alpha$, λ = 1.54056 Å) and a graphite monochromator. The soda ash samples were scanned for 2θ values from 0–70° and the diffractograms recorded. The sodium chloride impurity content in the precipitated sodium carbonate was determined by integrating the peak characteristics of halide, *i.e.*, sodium chloride at d spacing 2.82 Å and 1.99 Å.

For morphological analyses, the carbonate samples were examined under low vacuum using a Phillips XL 30 ESEM microscope (Fei & Phillips) fitted with a tungsten filament and a gaseous secondary electron detector. Samples were mounted on aluminium pin type mounts (3 mm) using carbon tape. A thin coating of carbon was applied to the sample to ensure that no charging occurs in the low vacuum mode during analysis, as charging effect interferes with the analysis.

The chloride impurity content in the resulting soda ash crystals was determined using ion chromatography (IC). About 1 g of each soda ash sample was dissolved in a 100 mL volumetric flask and made up to the mark with deionized water and the resulting solution was analyzed for chlorides using a DX-100 IC system which is interphased with a Dionex 4400 integrator and auto sample unit (Dionex, USA). The IC pump was set to a cut-off pressure of 2700 psi.

Thermogravimetric analyses were performed on a STD 2960 DTA-TGA thermal analyser (TA Instruments, USA) using 5–10 mg samples in Pt pans under nitrogen atmosphere at a heating rate of 10.0°C per min from ambient temperature to 1400°C.

RESULTS AND DISCUSSION

In the control sample, crystallization of soda ash was attained from a carbonation of 800-mL T-brine solution with no habit modifier added. An electronic stirrer ensured homogeneity of the crystallizing solution as CO_2 was bubbled through. Results obtained on the crystals produced in the presence of the two additives (EDTA and SHMP) were compared with those obtained from the control experiments.

XRD and IC analyses

While XRD was used in the preliminary investigations to identify the crystalline phase composition of soda ash crystals formed in both the control experiment and in the presence of the two modifiers (EDTA and SHMP), IC was used to quantify the sodium chloride impurity.

XRD distinctly identified two mineral phases, namely soda ash, which is the main salt and sodium chloride as an impurity. The diffractogram pattern (trace not included) of the EDTA and SHMP-modified soda ash samples revealed presence of prominent soda ash peaks that displayed no distortion, along with smaller peaks of sodium chloride impurity. Therefore, the crystalline components, soda ash and sodium chloride, retained their separate phase individuality. It was further observed that the sodium chloride impurity level decreased in the soda ash crystals formed as the habit modifier increased until the optimum concentra-

tion was attained beyond which the impurity content started to increase. The optimum modifier concentration for which the sodium chloride peak was non-detectable was between 2.13×10^2–2.17×10^2 % w/v for SHMP and 1.09×10^2 % w/v for EDTA. These observations were also confirmed by IC studies. Fig. 1 presents plots of sodium chloride concentration as a function of the habit modifiers: (a) [SHMP] and (b) [EDTA] concentration.
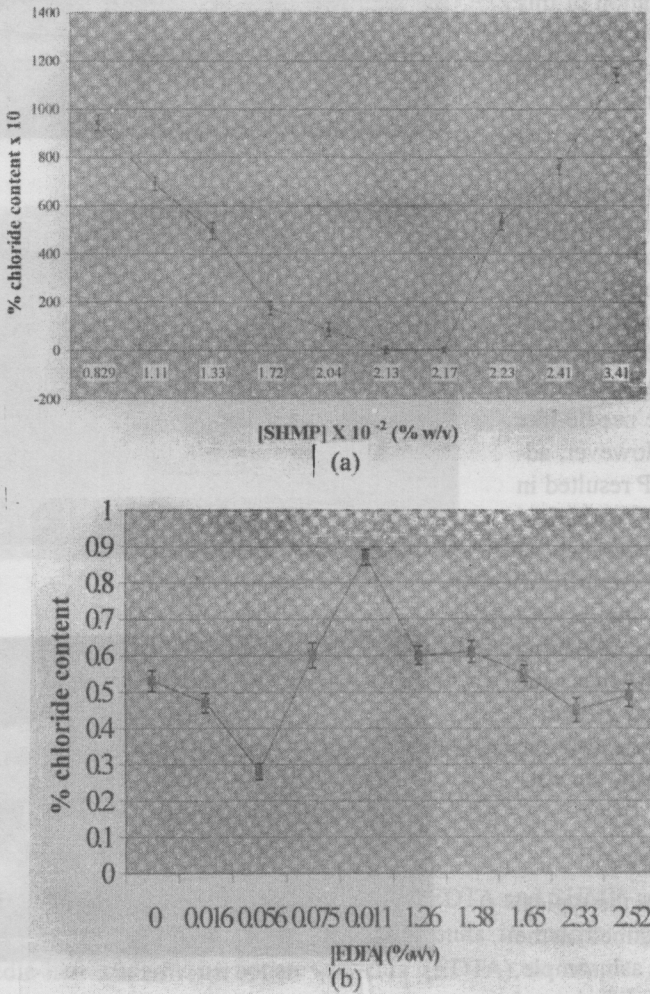

Fig. 1.   Levels of chloride (expressed as mean ± standard deviation for n = 3 samples) determined in the soda ash crystals produced in the presence of (a) SHMP and (b) [EDTA]

It has been suggested that the mechanism by which each of these two habit modifiers lowers the sodium chloride impurity content, at the optimum concentration, is through sequestration of the sodium ions (from sodium chloride). SHMP which has niches in its ring structure, attracts and holds the sodium ions in sodium chloride so tightly that they lose their normal characteristics such as the ability to form sodium chloride precipitate[11]. This process, known as sequestration, leads

to the lowest amount of chloride impurity content in the crystals formed. In a similar manner, EDTA sequestrates the sodium ions to produce EDTA disodium salt. Formation of this salt prevents the occlusion of chloride ions thus minimizing its interference.

ESEM analyses

In the absence of habit modifiers, precipitation of sodium carbonate crystals from brine solution resulted in the expected fine and needle-like structures[3]. Addition of EDTA maintained the undesirable needle-like morphology. However, addition of SHMP resulted in a spectrum of spherical crystals. The presence of SHMP induces significant alterations of the crystal morphology by blocking surface growth sites and impeding crystal growth[12], resulting in a different morphology from the control sample.
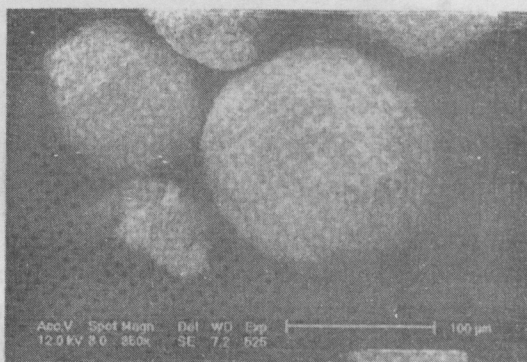
Thermal analyses

Fig. 3 shows the typical TGA traces obtained on the reference soda ash sample, the EDTA-modified and the SHMP-modified samples that exhibited minimum chloride impurity content.

(a)

(b)

(c)

Fig. 2. ESEM images of soda ash: (a) control sample, (b) grown in the presence of SHMP, (c) grown in the presence of EDTA
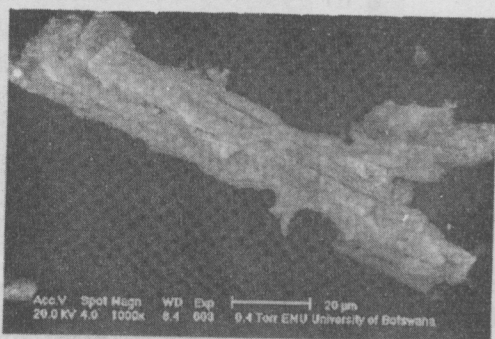
The TGA traces for the control sample (Fig. 3b) and the SHMP-modified soda ash (Fig. 3c) closely overlap up to point X, the onset of the thermal decomposition of the habit modifier. This close similarity in the thermal decomposition characteristics of the

two TGA traces indicated soda ash, sodium chloride and the SHMP modifier to have maintained their phase individualities in the modified sample, as evidenced by the XRD diffractogram pattern (XRD trace not included). Further, the melting point of soda ash in the SHMP modified sample as revealed by the DTA traces, was 851.57°C compared to the control sample with 857°C. Fig. 3a represents the TGA trace for the EDTA-modified soda ash, clearly exhibiting distinct thermal decomposition behaviour from the reference TGA trace (Fig. 3b). This difference arises due to the formation of products released by high temperature reactions between EDTA and soda ash. The investigation of these reactions is outside the scope of this study.
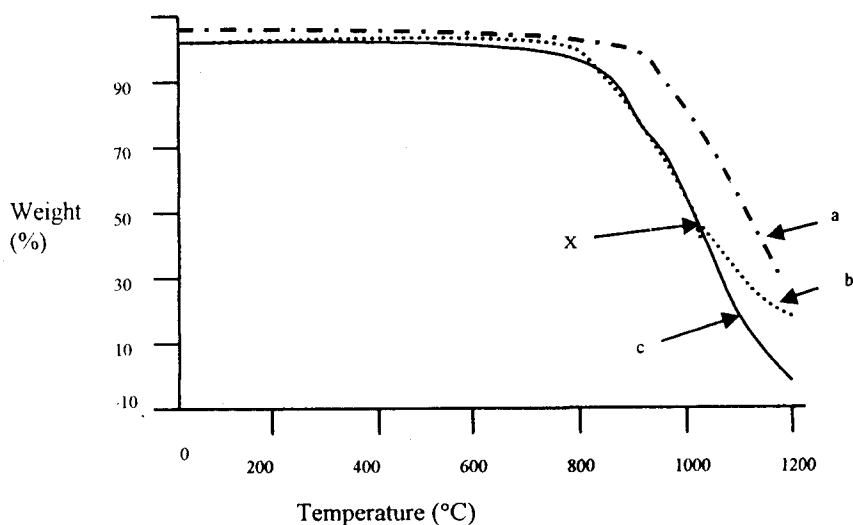

Fig. 3.   TGA traces for soda ash: (a) EDTA-modified sample, (b) control sample, (c) SHMP-modified sample

Conclusions

It has been shown that the presence of EDTA and SHMP, as additives, has an effect on the purity of soda ash and results in morphologies ranging from needle-like sodium carbonate crystals (EDTA) to single spherical crystals (SHMP). Each additive had an optimum concentration at which the chloride purity was minimal. Of the two sequestering agents studied, SHMP at an optimum concentration range of $(2.13–2.17) \times 10^2 \%$ w/v was shown to be the most effective, resulting in larger spherical soda ash crystals that are industrially desirable as they would be easier to handle and transport. The crystals were found to have a low chloride impurity content. The presence of phosphate (from SHMP) in the crystallizing solution was found to have no significant effect on the thermal properties of the soda ash such as melting point, as was shown by TGA results.

ACKNOWLEDGEMENTS

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