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Discovery that Matters

Production of Caustic Soda from Natural Local Trona

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Abstract: **The aim of this study is the production of caustic soda from natural local trona ores(trisodium hydrogendicarbonate) ($Na_2CO_3.NaHCO_3.2H_2O$) from Atrun oasis.The sodium carbonate reacts with lime (causticization) to yield caustic soda and calcium carbonates .Trona ores from Atrun oasis in NW Sudan desert were collected from the local markets of Omdurman City and classified into two grades: (1) and (2) according to their constituents such as density, color and purity. The two grades were analyzed for estimation of sodium carbonate (Na_2CO_3) in addition to the other constituents. The sodium carbonate (Na_2CO_3) content was found to be 47.38wt %and 34.53wt% for the two grades respectively. The two samples were dissolved in water, filtered, evaporated calcined fallowed by leaching step with saturated sodium bicarbonate solution to upgrade the soda ash content to required grade limit. The results gave about 98.42% purity of Na_2CO_3 from grade (1) and 98.9% purity of Na_2CO_3 from grade (2) . After the carbonate is prepared with purity 98% a causticizing process is done by reacting the heated carbonated solution of proper strength with lime. The lime was made in unslaked condition in order to utilize the heat of the reaction. After agitation from 0.5 to 1.5 hours the suspension is allowed to settle for 0.5 hour. The caustic soda solution obtained from such reaction has a concentration of 81.99g/l and 119.66gm/l, with molarities, 2.05 M, 2.99 M respectively and the reaction yeilds were 81.71% and 81.74% respectively. The caustic solution so produced are very dilute and for need to concentrate the solution multiple effect evaporators are used .**

Index terms **–Trona ores, Soda ash, Sodium carbonate, Calcinations, Leaching, Causticization.**

I. INTRODUCTION

Trona is a naturally occurring mineral, known chemically as sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) or sodium hydrogen carbonate ($Na_3H(CO_3)_2.2H_2O$), it is an evaporative mineral occasionally encountered as a saline lake deposit .Crude trona ("trona ore") found in nature, consists primarily of 80-95 percent of sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) and in lesser amounts of sodium chloride (NaCl), sodium sulfate (Na_2SO_4) in general, in addition to organic matter and insoluble materials such as sand, clay and shales **[1]**. The mineral trona alone can be responsible for the increase of pH solution above 10 because of the presence of concentration of the carbonate ions **[2]**.

Natural trona is non –flammable, white, yellow, gray or brown crystalline solid with non-notable odor. Some important properties are melting point decomposition beginning at 70 Cº (158 F),solubility 13g / 100 ml at 0C, 42g /100 ml at 100 Cº .PH (%solution) is 10.5, specific gravity (H_2O=1)2.112 and the molecular mass 226.

In Sudan, trona deposits were found in many locations at Atrun oasis and other small basins around Atrun area at 18º 10´ 12º N and 26º 36´ 54º E. it's found at another location north of Nukheil Oasis at 19º 15´ 46º N and 26º 10´ 27º E. The deposit in all basins was found in many forms as hard beds at the middle and bottoms of the old lakes or disseminated through the sand in the upper part .Also it is found as efflorescence crust on the surface of the soil, and can be found in brine water at some basins as in Daleba and Atrun basin. After drilling, sampling and chemical analysis, the evaluation of the deposit at different basins was made by Geological Research Authority of Sudan . According to its estimates the total reserve is about 38,460,000 tons. The average quantity of sodium carbonate in the crude stocks is about 60%; the net expected sodium carbonate is 23,076,000 tons **[3]**. The deposit is recoverable depending on the availability of rainfall and underground water **fig (1,2)** **[4]**.

There is a reasonable market for sodium carbonate, and Sudan import considerable quantities for use in various industries such as textile, paper, soap and detergent, carbonated beverages, leather industry and water purification. **Table (1)** shows the amount of sodium carbonate imported from different countries (China, India, Romania .Egypt and others) during the period from 2000-2006, according to information received from the general administration of customs research and information department, report 2007, Republic of Sudan. Also **Table (2)** shows the amount of caustic soda imported from different countries according to Sudan customs statistics products imports, which is used in numerous industries, such as, textiles, industrial detergents, soap, edible oil refining and other industries which benefit from the characteristic of bleaching of the caustic soda.

Table 1
Amount of sodium carbonate imported from different countries **[5]**

year	2000	2001	2002	2003	2004	2005	2006
Na_2CO_3(tons)	32	800	414	686	567	786	236

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Table 2
Amount of Caustic soda imported from different countries

year	2008	2009	2010	2011	2012
NaOH(tons)	170	60	180	112	88

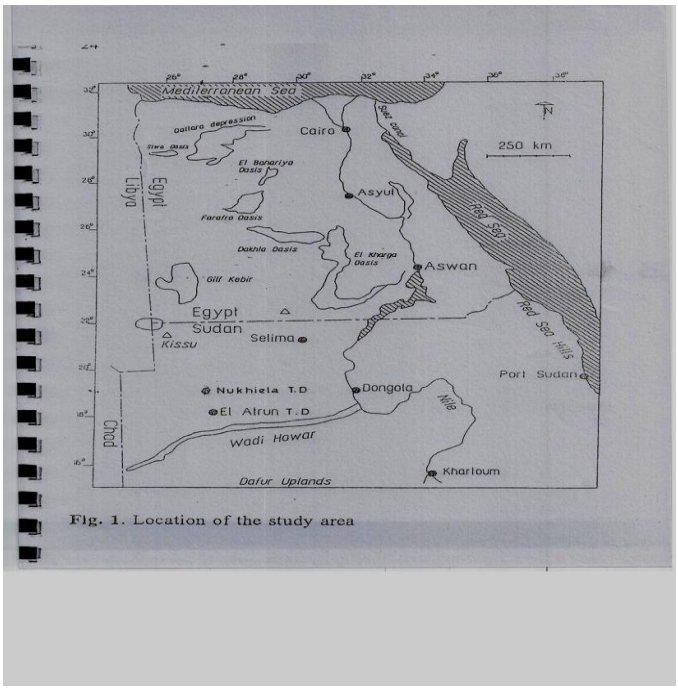

Fig. 1. Location of the study area

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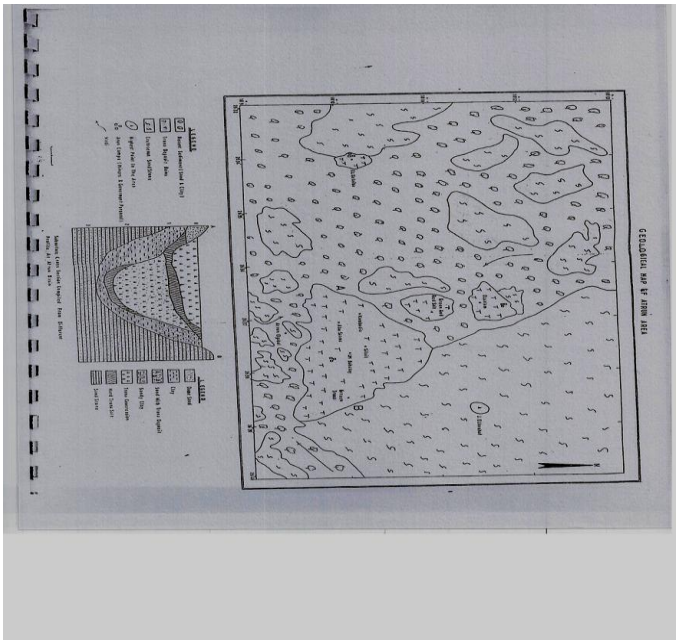

Fig (2) Geological Map of Atrun Area

Scope and limitation

The aim of this study is the production of caustic soda from natural local trona ores. The sodium carbonate reacts with lime (causticization) to yield caustic soda and calcium carbonates.

II. MATERIALS AND METHODS

Sample collection and preparation

About 2 kilograms of different trona ores of atrun area were collected from local markets of Omdurman state, the trona (Atroun) was brought from North Darfur state, from Historical sites of Atroun deposits such as Nukheil Oasis, Daleba and Atrun basin by the traditional traders for traditional uses.
Determination of the two grades samples of trona ores and the treated products was carried according to the standard methods of analysis.

Chemical analysis

During this research, the determination of the trona constituents was carried according to the standard methods of analysis, analytical reagent. Grades and standard solutions were used in addition to check synthetic samples standards.
The PH of the natural trona ores (1% solution), and crude soda ash of two samples were taken using PH meter**.** The content of sodium carbonate and sodium hydrogen carbonate were determined volumetrically using standard hydrochloric acid HCl (1M). Sodium chloride was determined volumetrically using silver nitrate ($AgNO_3$) and palintest photometer for measuring. The sodium sulphate was determined gravimetrically using barium chloride ($BaCl_2$) and palintest photometer for measuring. Insoluble matter was determined gravimetrically by dissolution, filtration and drying. **[6]**, results were shown in **tables (3, 4)**.

Trona purifications processes

Purification run was carried to purify two samples of trona ores; laboratory batch of 300 grams of the two grades was carried.

Filtration and Calcinations process

A quantity of 300 grams of each grade was crushed and dissolved in distilled water to produce saturated solutions, the solutions was clarified by decantation and filtration to remove silica and insoluble materials. The clear solutions were evaporated in a hot plate to produce crude sodium sesquicarbonate crystals; the crystals were calcined in an oven at 250 ºC for 3 hours to yield crude sodium carbonate. After calcinations, the crude soda ash was cooled.

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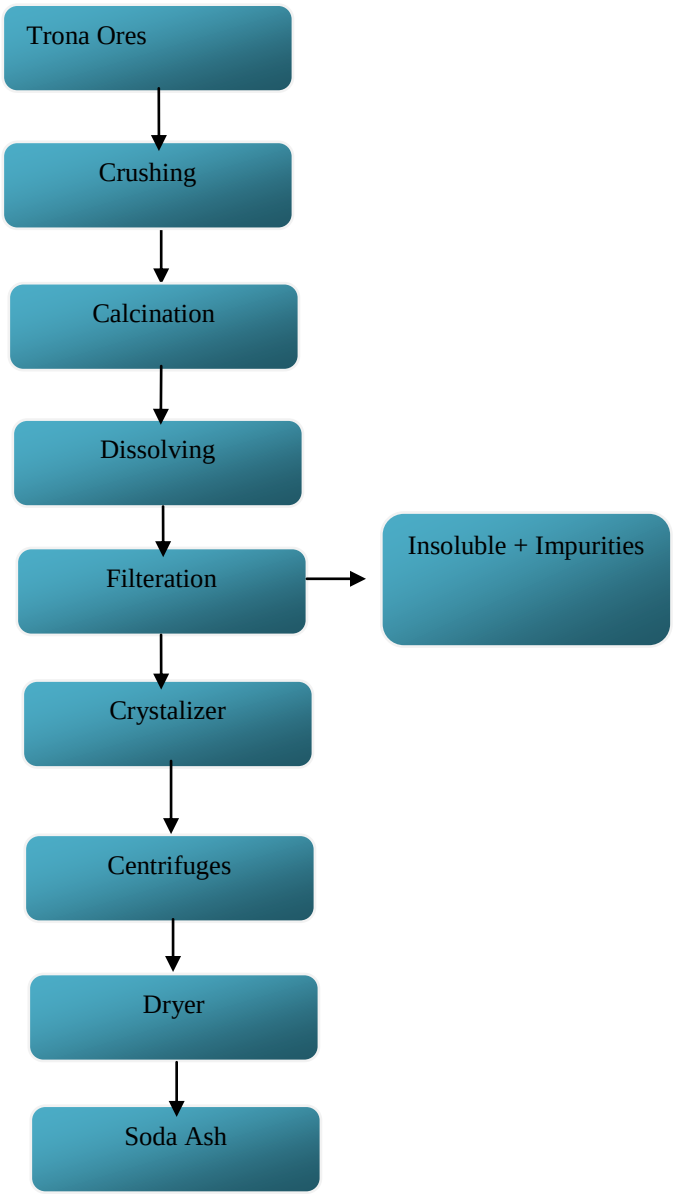

Fig (3) Soda Ash Production – Trona

Leaching process

Leaching is the process of extracting minerals from a solid by dissolving them in a liquid, either in nature or through an industrial process. A leaching solution was made up of saturated sodium bicarbonate solution.50 grams of the calcined solid sample of crude soda ash were ground, and added to the saturated sodium bicarbonate solution in a one litre beaker equipped with a mechanical stirrer at 75 ºC for 90 minutes. After the complete mixing, the mixture was allowed to stand for 4 hours at 20 ºC. The results were shown in **tables (5, 6)** **[7, 8]**.

Causticizing process

In this endothermic causticizing reaction, calcium hydroxide (slaked lime) Ca $(OH)_2$ reacts with the sodium carbonate (Na_2CO_3) in the green liquor. This reaction generates sodium hydroxide (NaOH) and calcium carbonate (lime mud) Ca CO_3.

$$Ca(OH)_2 + Na_2CO_3 \Rightarrow 2\,NaOH + Ca\,CO_3\downarrow$$

The object of the causticizing process is to turn inactive sodium carbonate (Na_2CO_3) into the active cooking chemical sodium hydroxide, and to make sure that the conversion efficiency of carbonate into hydroxide is as high as possible

In slaking lime (calcium oxide, CaO) reacts with the hot water (H_2O) mixed in green liquor, generating calcium hydroxide $Ca(OH)_2$ and heat (about 1 kJ/kg CaO)**[9]**.

$$H_2O + CaO \Rightarrow Ca(OH)_2 + heat$$

$$Na_2CO_3 + H_2O + CaO \rightarrow 2NaOH + Ca\,Co_3\downarrow$$

Sample 1

50 ml trona solution 10% was placed in 100 cm^3 beaker then it was heated gently. 6gm lime was added to it gradually with stirring for one to one & half hour, and then the solution was filtered through filter paper.

Sample 2

50 ml trona solution 10% was placed in 100 cm^3 beaker then it was heated gently. 8gm lime was added to it gradually with stirring for one to one & half hour, and then the solution was filtered through filter paper tables.
Results were shown in **table(7)**.

III. RESULTS AND DISCUSSION

Table 3

Chemical composition of the trona grade (1)

Test Description	Result%	Test Method
PH(1% solution)	10.36	ASTM D1293
Na_2CO_3	47.38	ASTM D513
Na_2SO_4	0.124	ASTM D516
NaCl	0.0378	ASTM D512
Si $O_{2+insoluble}$	42.189	-

Table 4

Chemical composition of the trona grade (2)

Test Description	Result%	Test Method
PH(1% solution)	10.45	ASTM D1293
Na_2CO_3	34.53	ASTM D513
Na_2SO_4	0.198	ASTM D516
NaCl	0.028	ASTM D512
Si $O_{2+insoluble}$	56.25	-

Results of the analysis showed that the sodium carbonate content in the ore is inversely proportional to the silica, insoluble materials and sand content, as shown in **Tables (3),(4)**.

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Trona calcining is a key process step in the production of soda ash (sodium carbonate anhydrate) from trona ore. The decomposition reaction occurs according to the following equation:

$$2Na_2CO_3.NaHCO_3.2H_2O\ (trona) + heat \xrightarrow{200\text{-}300^\circ C} 3Na_2CO_3 + CO_2 + 5H_2O$$

The calcinations process increased the sodium carbonate content of the raw trona, the increase was attributed to decomposition of sodium bicarbonate to sodium carbonate and the evaporation of water molecules from the sesquicarbonate crystals.

Decantation is a process for the separation of mixtures, by removing a top layer of liquid from which a precipitate has settled.

Decantation and filtration removed sand and insoluble material completely.

Crude soda ash from the calcination process above, showed an outstanding increase in the Na_2CO_3 content to the limits of 98.42 % and 98.9% for grade (1), (2) respectively, when treated with leaching solution. This upgrades the crude product to the limits near to that specified by some standards for industrial uses. The leaching process reduced Na_2SO_4 and the NaCl content. As shown in **Table (5) (6)**.

Table 5

Composition of grade (1) portions after leaching process

Test Description	Result%	Test Method
PH(1% solution)	11.33	ASTM D1293
Na_2CO_3	98.42	ASTM D513
Na_2SO_4	0.2	ASTM D516
NaCl	0.021	ASTM D512

Table 6

Composition of the grade (2) portions after leaching process

Test Description	Result%	Test Method
PH(1% solution)	11.93	ASTM D1293
Na_2CO_3	98.9	ASTM D513
Na_2SO_4	0.198	ASTM D516
NaCl	0.02	ASTM D512

causticizing process is carried on for the production of caustic soda as follows:

$$Na_2CO_3+H_2O+CaO \rightarrow 2NaOH + CaCo_3\downarrow$$

$$Na_2CO_3+ Ca(OH)_2 \rightarrow 2NaOH + CaCo_3\downarrow$$

Table 7

The sodium hydroxide obtained

Test	Sample 1(6gm)	Sample 2 (8gm)
Morality of the product	2.05 M	2.99M
Concentration as gm/L	81.99gm/l	119.6g/l
Yield	81.76%	91.74%

In this study local trona was used as starting raw material for obtain sodium hydroxide using a simple displacement reaction according to the equation:

$$Na_2CO_3+H_2O+CaO \longrightarrow 2NaOH+CaCO_3$$

Calcium Oxide is used in solid form and calcium carbonate which resulted from the displacement reaction can be used to regenerate CaO again by thermal decomposition (to above 840 °C).

$$CaCO_3 \xrightarrow{\triangle} CaO+CO_2$$

This proposition try to utilize the cyclic regeneration of one of the reaction ie CaO , hence an almost constant amount may be utilized in repeated cycles of production hence in parting a considerable cut of the raw material cost.

The above proposed reaction was carried out using two sample of trona purchased from the local market and the reaction is done using different quantity of CaO 8gm and 6gm.

The effect of temperature and mixing where examined and it was observed that 75C is optimum for thus reaction where higher %yield is obtained. Also gradual addition of reaction ingredients and vigorous mixing was found to positively affect the progress and percentage yield of the reaction.

Qualitative analysis of produced NaOH associated with careful selection of raw material (Trona) and purification of it.

IV. CONCULSIONS

In this study, local trona was used as starting raw material for production of caustic soda, the calcinations process increased the sodium carbonate content in the two grades, the leaching process showed high sodium carbonate content up to 98.0% ,sand and insoluble impurities were removed completely .The caustic solution so produced are very dilute that might be used if the demand and the supply were closed enough together but for the purpose of shipping it is necessary to concentrate the solution using multiple effect evaporators .

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