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Determination of Carbonate and Bicarbonate in Specific Samples of Trona Deposit

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Abstract

Trona is one of the natural forms of sodium carbonate minerals, it is well known as (sesquicarbonate) or (trona) and is known in Arabic as (natron) or (atrun). The possibility of determining some constituents of trona ore was studied, using the methods of purification, separation, titration gravimetric analysis and calcination. The aim of this study is to determine the major chemical Constitutes of three types of trona from different locations in Sudan, A chemical analysis has been carried out on these samples to determine their major constituents, and their quantities, using different analytical techniques. From the results obtained, it was found that the percentage of carbonate and bicarbonate for Northen, Westen, and Southern Darfour, were (35.52%: 18.19%), (25.87%: 12.20%) and (16.82%: 6.24%) respectively. These results suggest that the use of trona deposits for soda ash production is promising and important. We can recommend the use of trona as a source for the production of sodium carbonate.

Keywords: Trona, Natrn, Atrun, Sesquicarbonate.

1. Introduction

1.1 Trona

Trona is one of the natural forms of sodium carbonate minerals, it is tri-sodium hydrogen di-carbonate dehydrate also sodium sesquicarbonate dehydrate,

$Na_3(CO_3)(HCO_3)\cdot 2H_2O$) is a non-marine evaporate mineral. It is mined as the primary source of sodium carbonate in the United States, where it has replaced the Solvay process used in most of the rest of the world for sodium carbonate production[1,2].

The word "trona" entered English by way of either Swedish (trona) or Spanish (trona), with both possible sources having the same meaning as in English [3]. Both of these derive from the Arabic, which in turn derives from the Arabic natron, and which comes from ancient Greek (nitron), derived ultimately from ancient Egyptian ntry (or nitry) [3]. Trona is a common source of soda ash, which is a significant economic commodity because of its applications in manufacturing glass, chemicals, paper, detergents, and textiles.

1.1.1 Trona Calcination

Trona calcination is a key process step in the production of soda ash (sodium carbonate anhydrate) from the relatively cheap trona ore. It is accomplished by heating trona to an appropriate temperature to remove CO_2 and H_2O. The calcination reaction may proceed in a sequence of steps. Depending on the conditions, it may result in the formation of sodium carbonate monohydrate ($Na_2CO_3.H_2O$), sodium sesquicarbonate (Na_2CO_3. $NaHCO_3$).

The rate of formation and subsequent decomposition of these compounds are vital in the overall efficiency of the calcinations stage of process. The decomposition reaction occurs according to the following equation:

$$2Na_2CO_3\cdot NaHCO_3\cdot 2H_2O \rightarrow 3Na_2CO_3+CO_2+5H_2O$$ [3]

The decomposition of trona starts at about 347 K ,the effect of the temperature has been investigated in the range from 373K to 600 K for two particle sizes Fig. (1.1). It is seen that the weight loss increases with increasing temperature [3].

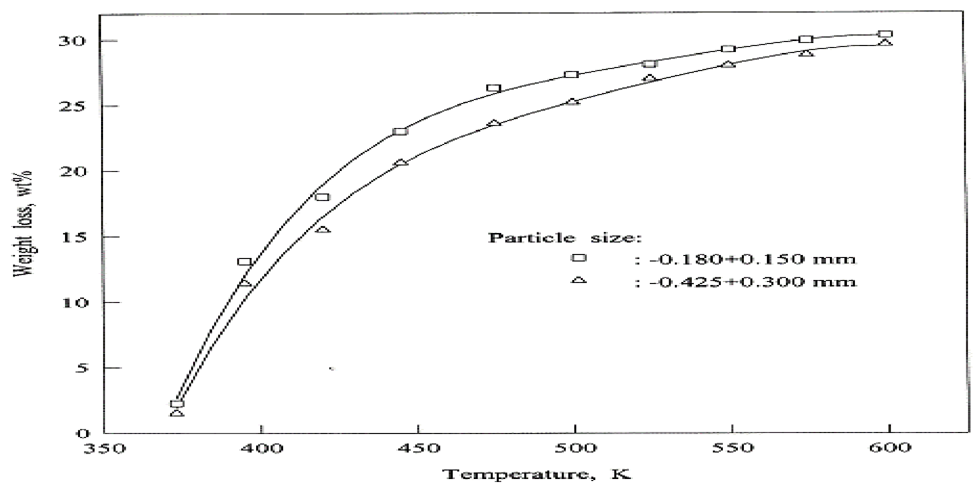

Fig (1.1): Effect of calcination temperature on the weight loss.

1.1.2 Uses of Trona

There are many uses for example [3]:

- Production of soda ash.
- Production of sodium carbonate.
- Applications in manufacturing glass, chemicals, paper, detergents.
- Many drugs in the industry.
- It is used to condition water.
- It is used to remove sulfur from both flue gases and coals.
- It is a product of carbon sequestration of flue gases.

1.2 Soda Ash

soda ash, the common name for sodium carbonate (Na_2CO_3), has significant economic importance because of its applications in manufacturing glass, chemicals, paper, detergents and many other products. It has been used since ancient times, it's a white, anhydrous, powdered or granular material containing more than 99% sodium carbonate (Na_2CO_3) [4].

Soda ash is an alkali that has a high pH in concentrated solutions. It can irritate the eyes, respiratory tract and skin. It is dangerous to be ingested because it can corrode the stomach lining [5].

-It is also used as a food additive [5].

Figure (1.2): Trona deposit in nature

Figure (1.3): Trona from local market

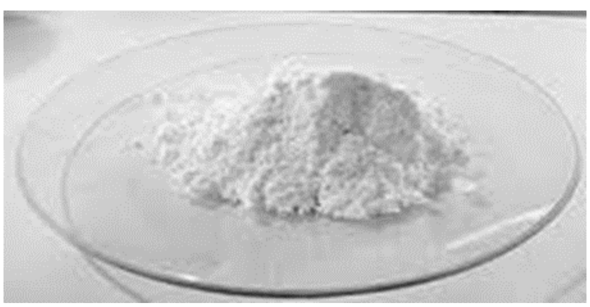

Figure (1.4): Sodium carbonate

Figure (1.5): Soda ash

1.3 Sodium Carbonate

Sodium carbonate (commonly known as soda ash) is one of the most important chemicals which is widely used in chemical and allied industries. Sodium carbonate forms transparent crystals as $Na_2\ CO_3.10\ H_2O$ and is known as washing soda. In contact with dry air it gradually parts with water of crystallization and turns into a white powder, Na_2CO_3. $7H_2O$ the salt also gives rise hepta-hydrate, $Na_2CO_3.7H_2O$. carbonate, deca-hydrate, on heating, gives first mono hydrate, which on prolonged heating gives the anhydrous salt. The latter is a stable compound. The salt is soluble in water, the aqueous solution being alkaline due to hydrolysis of carbonate ion:

$$CO_3^{-2} + 2H_2O \rightarrow 2OH^- + H_2CO_3$$

On contact with an acid, sodium carbonate gives effervesces due to carbon dioxide evolution, sodium bicarbonate is obtained when carbon dioxide is passed in to the solution of sodium carbonate (6).

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

1.4 Sodium Bicarbonate

Sodium bicarbonate is a white solid. It is stable in air at room temperature, but when heated it begins to dissociate at temperatures well below 100̊C to give water, carbon dioxide, and sodium carbonate (7)

$$2NaHCO_3 \rightarrow H_2O + CO_2 + Na_2CO_3$$

If it is heated to 250-300̊C for a short while the decomposition is complete and the pure anhydrous sodium carbonate so obtained is suitable for standing acids.

Sodium bicarbonates is soluble in water and 100 grams of water at 15C̊, dissolve 9 grams of salt. Although sodium bicarbonate is the acid salt of carbonic acid, the aqueous solution is alkaline owing to hydrolysis (5).

$$NaHCO_3 \rightarrow Na^+ + HCO^-_3$$

The removal of H^+ ions from dissociated water by the HCO^-_3 ions to from un dissociated carbonic acid, gives rise to preponderance of OH^- in the solution. The hydrogen ion concentration of the normal solution gives an alkaline reaction with methyl orange, but, the reaction with phenolphthalein is acid at temperatures

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approaching 0°C, if the aqueous solution is warmed decomposition occurs with the formation of sodium carbonate, the decomposition is complete on boiling. (7)

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

1.5 Uses

1.5.1 Sodium Carbonate

Sodium carbonate is used in the laboratory for neutralizing acids. Either the anhydrous salt or the monohydrate may be used for the preparation of standard alkaline solutions. The decahydrate, owing to its tendency to effloresce, is not suitable for this purpose. The anhydrous salt is used in analysis for opening up insoluble salt for bleaching textile fabrics, for softening water and for the preparation of other sodium salt. It is extensively used in glass, paper and soap industries (5).

1.5.2 Sodium Bicarbonate

Sodium bicarbonate is used in medicine and in making effervescent drinks, fruits salt, etc…A major commercial application is the preparation of baking powder and alum or potassium hydrogen tartrate (7). During baking of bread or cakes, carbon dioxide is evolved importing a porous or spongy texture to the baked products. Sodium bicarbonate is also employed. In fire-extinguishers (5).

1.6 Objectives

1. Develop the methodology needed for the investigation of an industrial significant process, namely the determination of some chemical constituents of trona, such as sodium carbonate and sodium bicarbonate.
2. Identification of the most promising deposit of trona samples
3. Optimization of process parameters that give the highest yield.
4. Production of soda ash.

2 Materials and Methods

2.1 Samples Collection

Trona deposit samples were collected from three different local location in Sudan Darfour

Table (2.1): Samples Locations

Sample No.	Location
1	Western Darfour
2	Southern Darfour
3	Northern Darfour

2.2 Extraction of Soluble Materials in Trona Samples

50 g of trona samples were taken, dissolved in distilled water, and the insoluble materials were filtered off and washed, the filtrate and washings from each sample were combined and divided into three portions:

These portions were treated as follows:

- The first portion was freeze-dried.
- The solvent in the second was removed by air.
- The third portion was dried by heating it in a water bath.

The total soluble produced was weighed, and the results were recorded following the previous method carried out [(8)].

2.3. Determination of Carbonate, Bicarbonate in Trona Samples

1 g of trona samples were taken and dissolved in a 400 ml beaker in about 100 ml of water heated and transferred to a 250 ml volumetric flask and made up with distilled water to the mark. 25 ml of solutions were titrated against standard 0.1M HCl from the burette using phenolphthalein as an indicator until the endpoint was reached. For

the same portion the titration was done using screened methyl orange as indicator. The volumes of HCl reacted with carbonate and bicarbonate was found as follows [8].

Stage 1- $NaHCO_3$+Na_2CO_3+ HCl → NaCl + 2$NaHCO_3$

Stage 2- 2$NaHCO_3$ + 2HCl → 2NaCl + 2H_2O + 2CO_2

When phenolphthalein was used as the indicator, the endpoint occurred at the end of stage one. In this stage, only half of the carbonate had been neutralized. When screened methyl orange was used as the indicator, the endpoint occurred at the end of stage two. In this stage, all carbonate and all bicarbonate had been neutralized [5,8].

2.4 Determination of Soluble:

2.4.1 Determination of Sulphate:

The method consists of slowly adding a dilute solution of barium chloride BaCl to a hot solution of the sulphate slightly acidified with hydrochloric acid.

$$Ba^{+2} + SO^{-2}{}_4 \rightarrow BaSO_4$$

The precipitate is filtered off, washed with water, carefully ignited at a red heat, and weighted as barium sulphate.

Barium sulphate has a solubility is increase in the presence of mineral acids, because of the hydrogen sulphate ion [8].

$$SO^{-2}{}_4 + 2H^+ \rightleftarrows H_2SO_4$$

Accurately 0.3 g of trona samples were weighted into a 400 ml beaker, provided with a stirring rod and clock-glass cover. The sample was dissolved in about 25ml of water, 0.3-0.6 ml of concentrated hydrochloric acid was added, and the solution was diluted to 250 ml, then was heated to boiling, 10-12ml of warm 5 percent barium chloride solution was added dropwise by burette, the solution was stirring constantly during the addition, the precipitate was allowed to settle for 2 min, few drops of barium chloride was added to test supernatant liquid for complete precipitation. The solution was boiled for one hour (volume of the solution should not be allowed to fall below 150ml. The precipitate was settled readily and was tested with a few drops of barium chloride solution for complete precipitation, then the solution was filtered off by filter paper Whatman No.4, and then the filtrate was collected in a clean breaker. The precipitate was washed with small portions of hot water. The moist paper was folded around the precipitate and placed in a porcelain crucible then cooled in a desiccator and weighed, the paper was dried above a small flame. Then the crucible and contents were weighted, and the percentage of SO^{-2}_4 was calculated [5].

2.5 Decomposition of Sodium Bicarbonate:

Decomposition of sodium bicarbonate by either dry or wet calcination is endothermic, and the heat in the wet calcination operation comes from steam, in wet calcination it takes heat to drive off CO_2 from the solution [21] Heat, is required to dissolve solid sodium bicarbonate (heat of solution), to heat up the solution, and to drive CO_2 out of solution. Moreover. The steam that was used serves two purposes, first to furnish the heat necessary for decomposition, second, to act as a distilled medium lowering the partial pressure of CO_2 above the solution.

Two types of process are used, first by dissolving trona ore in solution, second calcination of the trona, and dissolving the crude soda ash, as previously [15,21] used.

In the trona process the hot form dissolving trona is clarified by the removal of solids and organic matter, then calcinated to produce soda ash. In the monohydrate process the conversion of the sample to soda ash requires a temperature of about 200°C to achieve the following reaction within a reasonable length of time:

$$(2Na_2CO_3.NaHCO_3.2H_2O) \xrightarrow{\Delta} 3Na_2CO_3 + 5H_2O + CO_2$$

The washed sodium bicarbonate from the filters drops on to a belt conveyor which feeds the furnace in which the bicarbonate is decomposed by calcination. The reaction in the furnace is the decomposition of sodium bicarbonate into soda ash, carbon dioxide and water.

The process looks very simple, and it's so in the laboratory where the product can be stirred and no attempt is made to recover CO_2 gas in concentrated form. But in actual operation it is one of the most difficulty rises from the following facts:

Sodium bicarbonate has a tendency to cake onto lumps of balls, especially when it's moisture content is high. The un-decomposed lumps of bicarbonate on heating can be converted to carbonate.

Accurate amounts of extracted trona from different locations were calcinated to constant weights for different periods of time at different temperatures. Curves showing the increase of sodium carbonate, and the decrease of sodium bicarbonate during the calcination at different temperatures were plotted [(10)].

3. Results and Discussion

3.1 Soluble Contents of Trona Samples:

The soluble content of the trona samples was determined by three different methods as outlined in section (2.2). The data obtained are shown in table (3.1). These data show that the highest yields are obtained by freeze-drying, they also show that, irrespective of the method used, and of all the samples treated, sample No (3) from Northern Darfour deposit has the highest soluble contents (64%), while sample No (1) from Westen Darfour deposit has the lowest soluble contents (26.80%). The data show that the soluble contents of the samples from the different locations varied between (26.80%, 64%), and seen to divide the samples into three distinct samples: high, medium and low soluble contents, which are referred to as samples (1), (2) and (3), sample (3) has very high contents of soluble, presumably carbonates and bicarbonate, sample (3) has high contents of soluble (64%), sample (2) have medium contents (40%), sample (1) has very low contents of soluble (26.80%) The first sample (1) has, therefore it has been dropped from further Investigation.

The samples from Northern Darfour deposits seem to be the most promising, the standard deviation was calculated to determine the accuracy of the particular method, see table (3.1.1).

The heating in water bath method has a small standard deviation, although it gives the lowest yield compared with other methods tablet (3.1).

3.2. Insoluble Contents

Table (3.2) shows that the insoluble components of the trona samples vary between (27-63%) exceptions to this are the samples from Northern Darfour sample No (3), which have extremely low insoluble contents of (27%).

This probably reflects an environmental change in the nature of the deposit. Mobile dunes and sand migration may cause significant alternation in the composition of the accessible deposit.

The insoluble contents constitute an important factor in the suitability of a deposit for economic exploitation in this aspect, The Western Darfour deposit stands out as the deposit with the highest feasibility; deposits containing 63% insoluble are useless.

Complex carbonates and sulfates may not dissolve under the conditions adopted in this study, to isolate this from the presence of the detections SiO_2, the determination of the latter separately was performed using the procedure outlined in section (2.2).

The results are shown in table (3.2); and indicate that the silica contents of the trona deposit are generally high, notable exceptions are again sample No (1) from Western

Darfour, which gave 63.90%. insoluble solids contain salts in addition to SiO_2. In processing trona deposit this should be taken into consideration.

3.3. Determination of Carbonate, Bicarbonate Contents

The percentage of carbonate and bicarbonate contents in the trona sample were determined using the procedure given in section (2.3) the results are shown in table (3.3), the percentages of carbonate of more than 35.52% in sample (3), sample (2) has 25.87% and sample (1) has 16.82% percentages.

An exception is sample No (1) which recorded the lowest percentage (16.82%), sample No (3) also recorded high percentages of bicarbonate 18.19% and sample (1) 6.24%, and sample (2) 12.20% of bicarbonates, sample (1) was very poor and it may be removed.

3.4. Decomposition of Bicarbonate:

The rate of decomposition of bicarbonate depends on both the calcination temperature and time, results are shown in table (3.5).

At 160° C the bicarbonate is completely decomposed but requires longer time than at higher temperatures. The optimum working temperature was found to be between (175-200°C). Sodium bicarbonate decomposition gives in soda ash (Na_2CO_3) carbon dioxide and water. The decomposition of sodium bicarbonate by either dry or wet calcination is an endothermic reaction.

The percentages of calcination of the trona sample at 150°C obtained (26.9%), (40.64%)and (64.81%) respectively while the percentages of calcination at 200°C, give (29.78%), (43.16%), and 65.45%), sample No (3) contain a high percentage of bicarbonate, for this reason, decomposition of bicarbonate was studied using the procedure shown in section (2.5) sample No (1) contains smallest bicarbonate carbonate and took longer time more than other samples.

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The curves show an increase in carbonate, and a decrease in bicarbonate with time during calcination at different temperatures.

The results indicate that the level of sodium is relatively high in the trona deposits compared to other elements. This is apparently due to the existence of sodium in most ore rations, the elements (Ca, Fe, and K) recorded low concentrations, and it was not necessary to measure these trona elements in further work.

Table (3.1): Soluble in trona samples as a percentage of original solid

Sample No	Evaporation (water Bath)	Evaporation (air)	Freeze drying	Average
1	26.20%	25.25%	26.80%	26.083%
2	39.88%	38.82%	40.22%	39.64%
3	62.12%	60.89%	64.00%	62.14%

Table (3.1.1): Calculation of standard deviation

No Sample	**Method 1**	**Method 2**	**Method 3**
1	26.20%	25.25%	26.80%
2	39.88%	38.82%	40.22%
3	62.12%	60.89%	64.00%
Standard deviation	0.1813	0.1800	0.1884

Table (3.2): Soluble and insoluble in trona samples

Sample No	**Soluble**	**In soluble**
1	26.08%	63.90%
2	39.64%	58.30%
3	62.14%	27.40%

Table (3.3): Determination of carbonate, bicarbonate percentage in trona samples

Sample No	**CO^{-2}_3%**	**HCO^-_3 %**
1	16.82%	6.24%
2	25.87%	12.20%
3	35.52%	18.19%

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Table (3.4): Chloride and sulphate contents of trona samples (%)

Sample No	Chloride%	Sulphate%
1	8.4%	2.1%
2	9.4%	4.2%
3	12.12%	6.62%

Table (3.5): Calcination of trona at different temperature

Sample No	Percentage of calcination at 150̊C	Percentage of calcination at 200̊C
1	26.9%	29.78%
2	40.64%	43.16%
3	64.81%	65.45%

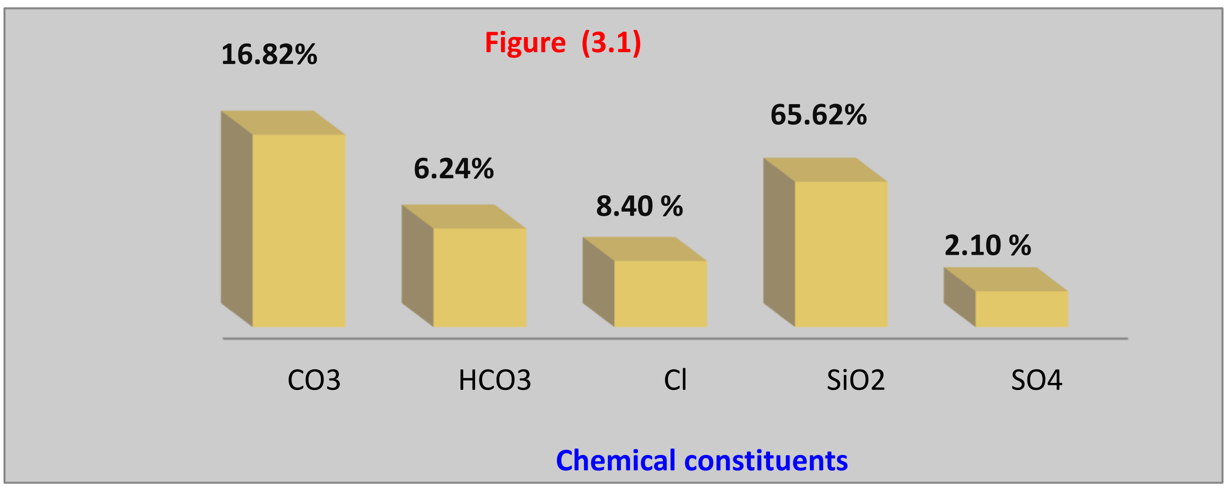

Figure (3.1): Chemical constituents of sample (1)

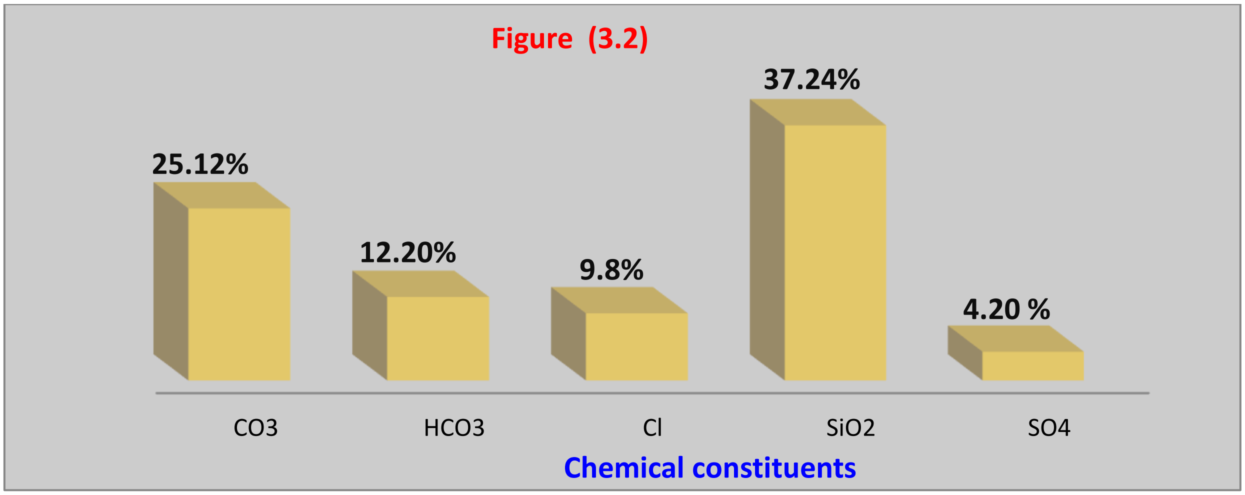

Figure (3.2): Chemical constituents of sample (2)

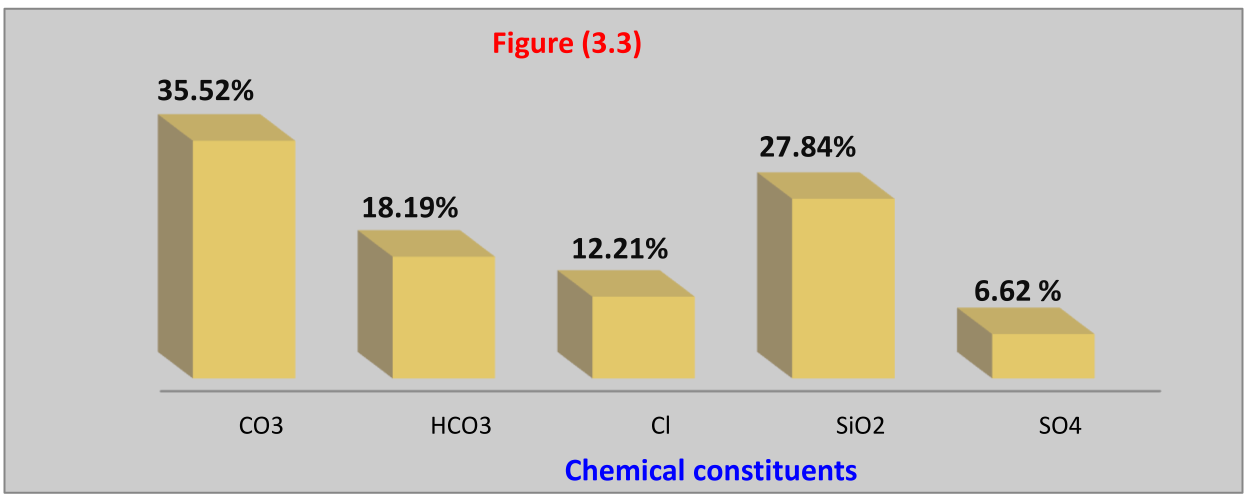

Figure (3.3): Chemical constituents of sample (3)

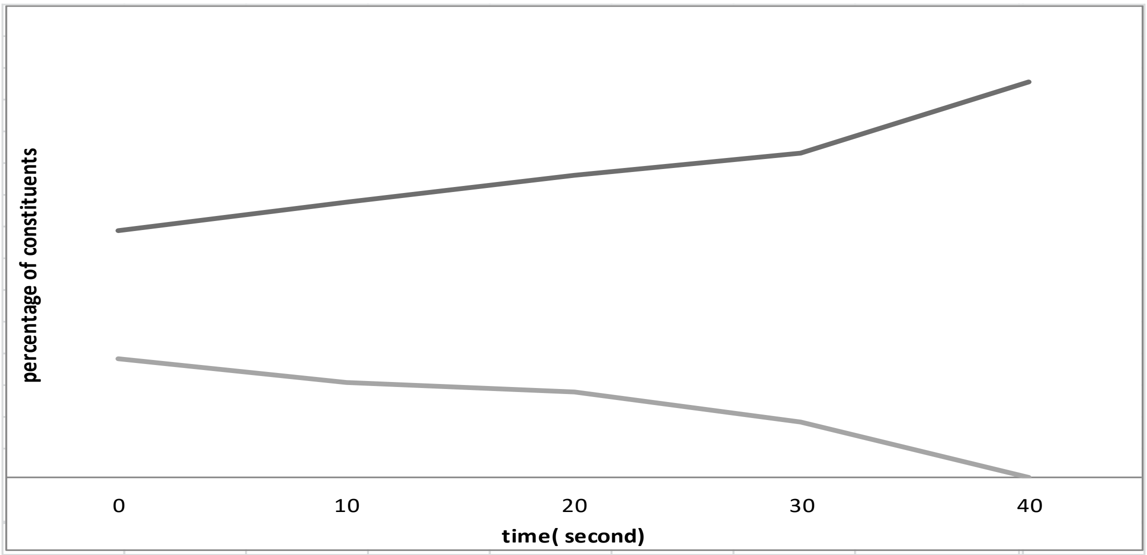

Figure (3.4): Calcination sample (1) at 200̊C

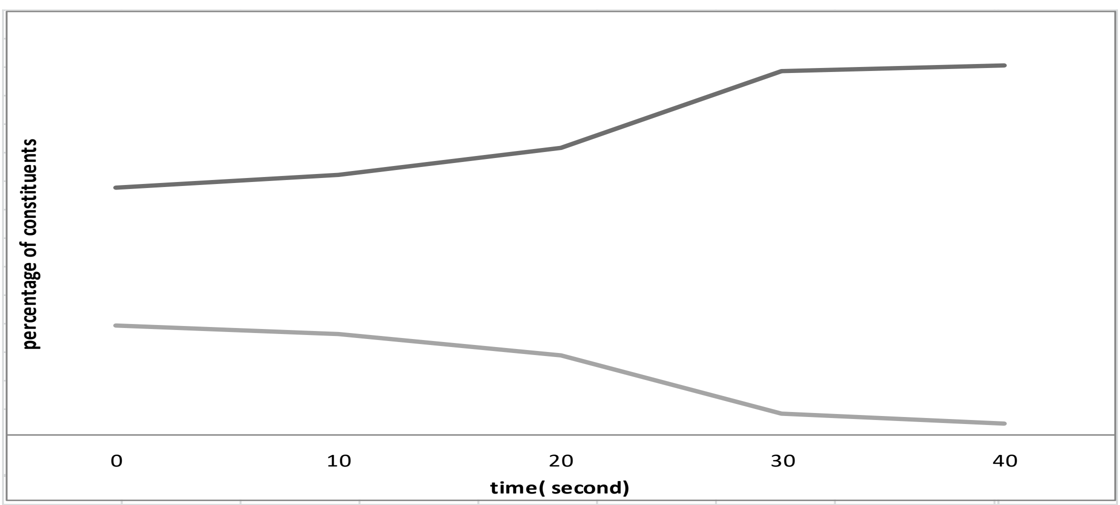

Figure (3.5): Calcination sample (2) at 200̊C

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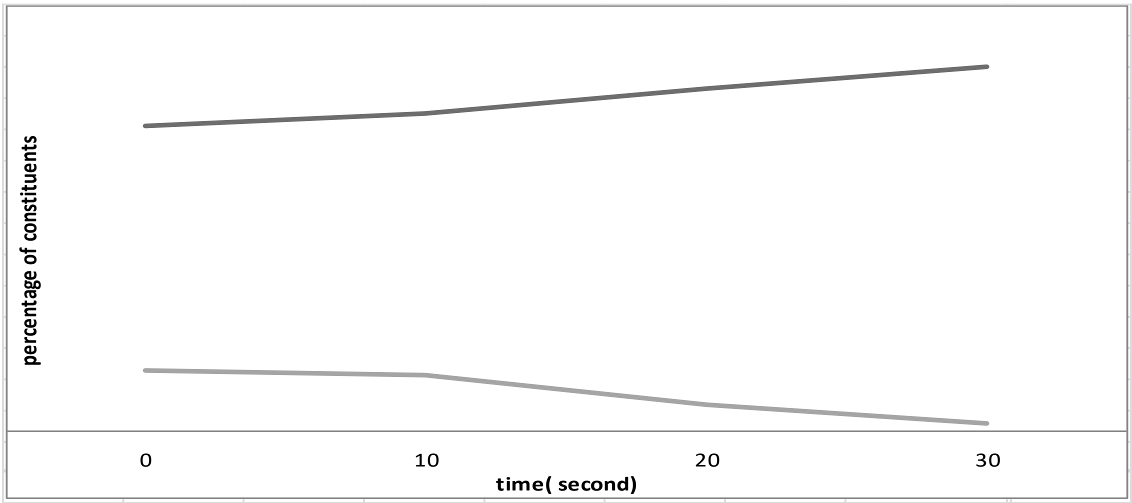

Figure (3.6): Calcination sample (3) at 200̊C

3.6 Conclusion and Recommendation

Trona deposits, limestone and gypsum, can be utilized to provide some important industrial chemicals. From the results obtained in this presented work, it is better to obtain the soda ash (sodium carbonate) Na_2CO_3, sodium bicarbonate $NaHCO_3$, by processing naturally available trona.

The results show that the main constituents of trona deposits are sodium carbonate (Na_2 CO_3), sodium bicarbonate ($NaHCO_3$), sodium chloride NaCl, sodium sulphate (Na_2 SO_4), silica (SiO_2) and trace elements (eg. Ca, K,Na and Fe). trona deposits are composed mainly of sodium carbonate and sodium bicarbonate, and the two deposits may be suggested for development and further study, sodium chloride was found to be of too high percentage in some samples.

It is recommended that to produce soda ash from trona, the deposit material should be purified by: separation of soluble matters like sulphate SO_4^{-2} and chloride Cl^-, then calcination of the yield to convert all bicarbonates to carbonates. In the monohydrate process, the conversion of trona to soda ash requires a temperature of about 200̊C to achieve the following reaction within a reasonable length of time $Na_2\ CO_3$.

$$2Na_2CO_3.NaHCO_3.2H_2O \rightarrow 3Na_2CO_3 + 5H_2O + CO_2$$

The solution derived from the crude soda ash is evaporated to produce mono-hydrate crystals, which are in turn heated to convert them to the anhydrous salt.

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