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Recovery of Sodium Hydroxide from Trona Ore and Calcium Carbonate as Raw Materials

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Abstract: ***The possibility for the production of sodium hydroxide from raw materials of national occurring trona ore and calcium carbonate was investigated. This was occurred by precipitation reaction of sodium carbonate which was produced from trona ore and calcium hydroxide obtained by calcination of calcium carbonate. This process called causticization in which an aqueous solution of sodium hydroxide and solid precipitate of calcium carbonate are produced. The starting raw materials for production of sodium carbonate and calcium hydroxide were crushed trona ore and calcium carbonate respectively. The crushed trona ore was leached with warm water to remove silica and other water insoluble materials and then the solution was filtered to obtain a clear solution of sodium carbonate and bicarbonate. Calcium hydroxide was obtained by adding water to calcium oxide that obtained by calcination of calcium carbonate. The chemical analysis of cations Na, Ca, Fe, K, Mg and anions*** $CO_3^{-2}, HCO_3^{-1}, OH^{-1}, Cl^{-1}, SO_4^{-2}$ ***for trona ore, produced sodium carbonate, calcium hydroxide and sodium hydroxide were studied. Also the purity of produced sodium carbonate, calcium hydroxide and sodium hydroxide were calculated and are found to be 95.80 %.%, 92.97 %.% and 87.60 % respectively.***

Keywords: Trona ore- Calcinations- Causticization- Sodiumsesquicarbonate-Hydrate lime

1. Introduction

Precipitation and crystallization refer to unit operations that generate a solid from a supersaturated solution. In both precipitation and crystallization processes the same basic steps occur: super saturation, nucleation and growth. Nucleation does not necessarily begin immediately on reaching a supersaturated condition, except at very high super saturation, and there may be an induction period before detection of the first crystals or solid particles. Nucleation can occur by both homogeneous and heterogeneous processes. The super saturation for a solution of a salt can be obtained by evaporation of water using solar energy which considered to be an older and simpler technique used commercially throughout the world.(Coulson, 2002).

Trona, (sodiumsesqui carbonate) is a solid material that is found in nature in a form of double hydrate salts of sodium carbonate and bicarbonate having chemical formula $Na_2CO_3.NaHCO_3.H_2O$. It can be found in many parts of theworld,like Kenya,Sudan, Turkey, Mexico and United States.(Garrett, 1992)

Trona ore deposit is a body of rock, which contains metallic compounds or native metals in sufficient quantities that have an economical values, that is to say from which one or more metals can be profitably extracted.(Thomas,**et al,**1909)

Carbonate rocks represent about 20% of all sedimentary matter. The sands and clays of certain places in a deserts often show substantial deposit of reasonable pure sodium carbonate sesquicarbonate are found in a forms which geologists now term evaporates (Park and MAC Diarmid,1975)

The natural sodium carbonate deposits, consist of trona or sodium bicarbonate as solid material in crystalline forms of natural carbonate brines. The equilibrium between bicarbonate and carbonate ions in an aqueous solution is achieved via desorption of carbon dioxide to the air or due to the absorption of atmospheric carbon dioxide(Garrett, 1992). As shown in equation (1).

$$2HCO_3(aq) \overset{\Delta t}{\leftrightarrow} CO_3 = (aq) + H_2O(1) + CO_2(g) \quad (1)$$

This equilibrium is affected by temperature. That means the formation of carbonate increases with increasing temperature, while decreasing in the temperature results in the formation of bicarbonate. favored as the solubility of carbon dioxide increase with decreased in temperature. The equilibrium solution composition for atmospheric carbon dioxide partial pressure has actually nahcolite as stable solid phase till about 90 °C(Gärtner**et al,** 2005)

Depending on temperature and composition, sodium carbonates can exist as trona, as well as sodium bicarbonate or as sodium carbonate in various hydration states (Na_2CO_3. nH_2O)such as anhydrous, monohydrate, heptahydrate or decahydrate, (Linke, 1965)(Monnin, **et al,** 1984)
The characteristic constituent of the so-called ‘natron lakes’ is sodium carbonate; but this compound is always accompanied by sodium chloride and sodium sulfate. The deposits of such lakes are of peculiar character and often include natron (Na_2CO_3), tronaand few amount of Gaylussite ($CaCO_3.NaCO_3.5H_2O$).(Aldoma, 2003). Due to the activity of sodium, it is found in nature combined with oxygen, silicon and other metals in the form of double silicate of these ore of the commonest is feldspar $NaAlSiO_8$. By the action of water and carbon dioxide, feldspar and similar rocks become weathered to yield sodium carbonate, clay and silica as shown in equation (2).

$$NaAlSiO_8 + 2H_2O + CO_2 \rightarrow Na_2CO_3 + H_4Al_2Si_2O_9 + 4Si \quad (2)$$

The soluble sodium carbonate is washed out of the weathered rock by rain and it may accumulate inland seas where, at intense evaporation, the solid salt may be deposited, it probable that the deposits of sodium sesquicarbonate. National trona is non- flammable , white-yellow-gray or brown crystalline solid with non-odor, it is solubility13g/ 100ml of water at 0 ^{0}C and 42g / 100 ml of water at 20 ^{0} C, pH solution is 10.5 (Lirk, 1963)

Sodium carbonate (Na_2CO_3) or soda ashis manufactured from sodium sesquicarbonatewhich known as mineral trona or sodium carbonate bearing brines (both referred to as 'natural soda ash', or from one of several chemical processes. Sodium carbonate is a white, crystalline solid, hygroscopic powder have atomic weight of 106 g, it is solubility in water is 22 gram/100 ml water at 25 ^{0} C. It is consider to be important raw material for glass manufacturing, soap and detergent, chemicals, paper and water treatment industries. The current sodium carbonate manufacturing process is Solvay Process which uses salts, limestone, coke as raw materials and sand ammonia solution as acyclic reagent. Before this method was developed, the Leblanc process was universally used. Solvay Process produces about 45% of the world sodium carbonate while 24% is produced by natural trona reserves. Many methods for obtaining sodium carbonate from trona has been employed. The recovery of trona from mineral resources generally involves extraction by underground mining methods (Kostick, **et al** 1998).

The sodium carbonate is converted from trona in a multi-stage purification process; calcination, dissolution, clarification, filtration, and crystallization(O. Ozdemir a,b, A. Jain a, V. Gupta a, X. Wanga, J.D. Miller, Evaluation of flotation technology for the trona industry, Minerals Engineering 23 - 2010).The processes for the recovery of sodium carbonate from trona deposits and other sodium bicarbonate containing sources of sodium carbonate was reported(Robert **et al**- 2007) . This was carried out by using a mixed solvent containing ethylene glycol and water, the stability of trona ore is decreased due to increasing of the boiling point of the solution, that it spontaneously recrystallized to anhydrous sodium carbonate and ($Na_2CO_3{\cdot}3NaHCO_3(s)$). The sodium bicarbonate content was decomposed thermally in the mixed solvent into sodium carbonate and crystallized as pure anhydrous sodium carbonate. Calcining any of sodium carbonate source yields sodium carbonate with various physical properties, crystal size, shape and bulk density (Sommers, 1960) .Production of sodium carbonate from trona solution can be achieved by a spray dryer reactor (Dogan, **et al**1997). The production of sodium carbonate from trona deposits by processes of leaching and crystallizationcan also be applied by researchers (Martins and Martins, 1997). (Nasu**et al** 1996).

Sodium hydroxide (caustic soda) is one of the most widely used chemicals in the chemical industry. It is often used as a raw material for manufacturing of soaps, detergents, textiles, paper, water treatment, drilling mud in oil field, and petroleum refinery products. It is also used as an aid to manufacture other chemicals. Pure anhydrous sodium hydroxideis a crystalline, odorless, white, translucentsolid material of an atomic weight of 40, a density of 2.13 g/cm^3, and a solubility of 111g/100 ml of water at 20 ^{0}C. Solid sodium hydroxide has strong moisture absorption; it is easily mixed with water and heat is evolved.

Calcium hydroxide or hydrate lime $Ca(OH)_2$ traditionally called slaked lime, it is odorless, colorless crystal or white powder. It is solubility in water is only 0.19 g/100 ml of water at 0 ^{0}C and it is solubility decrease with increasing temperature (lowest at 100 ^{0}C), strong base have pH values of above 12 in a saturated solution. Stable under ordinary conditions but absorbs carbon dioxide from air to form calcium carbonate. is easily handled, and is cheap, it is refined from limestone ($CaCO_3$). The calcium hydroxide products are used in water treatment, pH control, paper manufacture, cement manufacture and leather tanning industries, it is also used an additive in petroleum industry.Calcium carbonate (lime stone) it is used as kiln feed to produce calcium oxide. The goal of the kiln operation is to produce lime from "perfectly calcinated limestone". (Thomas , 1997).

Trona ore in North Western Sudan is essentially sodium carbonate mixed with impurities such as silica and ions of iron, magnesium, calcium and potassium in form of chloride, sulphate and nitrate (Idris.**et al** 1996). Sodium hydroxide is an important compounds of a variety uses which are mentioned above. The availabilityand high quality ofraw materials of trona ore and calcium hydroxide in generals are more economical, in the same time the production of sodium hydroxide by Solvay process isexpensive. Therefore to have the optimum and proper use of trona ore and calcium carbonate they should be purified to minimum level of impurities and then used to recover pure sodium hydroxide.

The objective of this study is to recover sodium hydroxide from raw materials of trona ore and calcium carbonate by using solar energy. This is done through the chemical analysis of trona ore, calcium carbonate, and calcium hydroxide. Based on the results of this analysis, the suitable method for the purification and recovery of pure sodium hydroxide is to be used.

2. Materials and Methods

2.1. Materials

The sample of trona ore collected from north western Sudan. Before running the experiment, trona ore and calcium carbonate were analyzed to determine their composition.The main techniques used in chemical analysis of these samples is quantitative analysis and the methods used are gravimetric and titrimetric to determine the values of silica, carbonate, bicarbonate, chlorides and sulphate ions.(Bassett **et al**1978). To detect the cations of sodium, potassium, magnesium, calcium and ferrous, Atomic Absorption Spectrophotometer, Perkin Elmer model 3110, with accessories provided with integrator to give direct concentration in ppm is used. First of all, the samples of trona ore and calcium hydroxide are crushed finely using wood hammer and then prepared in a suitable form of a solution for the analysis, all reagents used in chemical analysis are of analytical grade. The glassware are carefully cleaned and rinsed with distilled water

Manufacturing of sodium hydroxide from raw materials of trona ore and calcium carbonate involves three steps and several processes. The first step is to manufacture sodium carbonate from trona ore deposits, which is based on leaching, evaporation crystallization and drying. The second step is to produce calcium hydroxide from calcium carbonate, which is based on calcinations of calcium carbonate to form calcium oxide and then reaction with water to form calcium hydroxide. The third step is to react sodium carbonate with calcium hydroxide solution in a precipitation reaction, this process is called causticizing (Deming, 1925), which produces a solution of sodium hydroxide and calcium carbonate as a precipitate according to Equation (3).

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_{3(s)\downarrow} + 2NaOH(aq) \quad (3)$$

2.2. Production of Sodium carbonate from trona ore

The solid raw material of trona ore is crushed into fine particles, leached with warm water (at 30-40 ^{0}C), and then filtered to remove silica and other water insoluble materials in order to obtain a clear solution. To separate the undesirable soluble matter from the clear solution and obtain pure sodium carbonate, the solution is sent to a pilot plant which consists of a storage reservoir, an evaporation reservoir, a crystallization reservoir and a dry reservoir units. These units are ordered as illustrated in Fig. 1. In this pilot plant, sodium carbonate solution is concentrated in the evaporation reservoir by solar energy until the concentration reaches 30%, then the solution is sent to the crystallization reservoir. At the crystallization stage, the yield of sodium carbonate crystals increases. With a proper drainage of sodium carbonate crystals followed by washing with distilled water, pure crystals of sodium carbonate are obtained. Thereafter, the crystals are dried to 150-160 ^{0}C for 48 hour to remove water of crystallization and to convert the traces of sodium bicarbonate into sodium carbonate.

2.3. Production of calcium hydroxide from calcium carbonate

Pure limestone is to be crushed to reduce its particle size in order to be fed to kiln step. In the kiln,the crushed limestone is heated to about 900^{0}C using wood fire. This is called the calcinations process as shown in Fig. 2. The calcium carbonate decomposes into calcium oxide (also known as quicklime) and carbon dioxide as shown in equation (4). This decomposition reaction is reversible in the presence of carbon dioxide gas.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \quad (4)$$

When calcium oxide is added to water at 30-50 ^{0}C, it is converted to calcium hydroxide (slaked lime) in an exothermic reaction as shown in Equation (5).

$$CaO(s) + H_2O(1) \rightarrow Ca(OH)_2(s) + Heat \quad (5)$$

The main disadvantage of calcium hydroxide, however, is that it is partially soluble in water. But the ionization of calcium hydroxide in an aqueous solution gives calcium cations (Ca^{+2}) and hydroxyl group (OH^{-1}) as shown in Equation (6).

$$Ca(OH)_2(s) \leftrightarrow Ca^{2+}(aq) + 2OH(aq) \quad (6)$$

2.4. Recovery of sodium hydroxide from produced sodium carbonate and calcium hydroxide

The sodium carbonate produced from the purification process is reacted with the calcium hydroxide produced in the calcinations process according to the precipitation reaction shown in Equation (7). The result of the reaction is a solid precipitate of calcium carbonate and an aqueous solution of sodium hydroxide which is more alkaline than sodium carbonate. The solution is separated from precipitate and then concentrated using solar energy evaporation asshown in Fig. 3.

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow 2NaOH(aq) + CaCO_3(s) \quad (7)$$

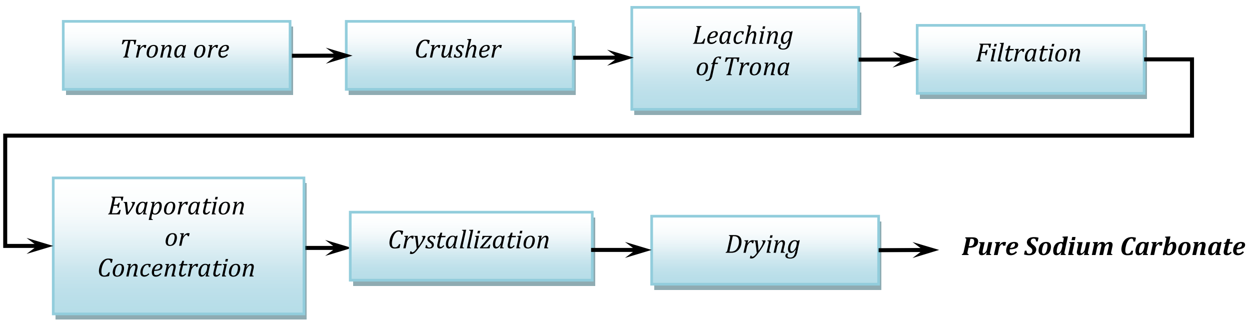

Figure 1: The flow diagram for the recovery of sodium carbonate from trona ore.

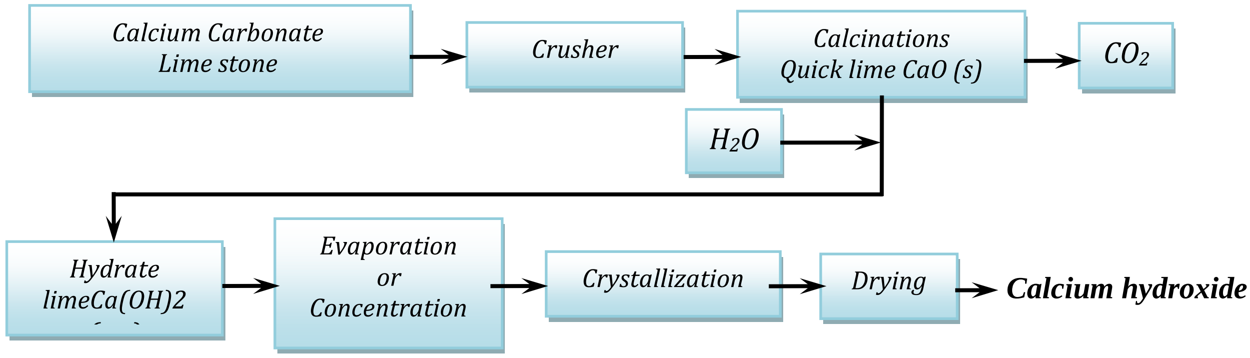

Figure 2: The flow diagram for the production of calcium hydroxide from calcium carbonate.

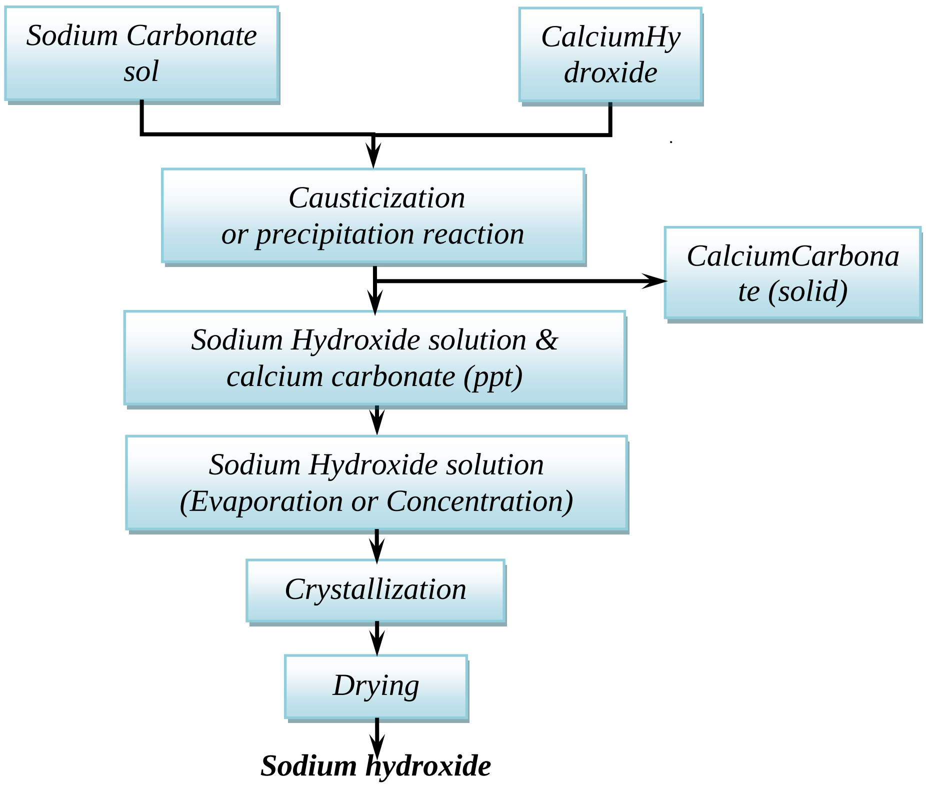

Figure 3: The flow diagram for production of sodium hydroxide from sodium carbonate and calcium hydroxide

3. Results

The results of the chemical analysis of trona ore are given in Table 1.

Table 1: percentage of sodium, potassium, magnesium, calcium, ferrous, carbonate, bicarbonate, chloride, sulphate and silica in sample of trona ore:

Cations & anions	Percentage %
Sodium	28.55
Potassium	00.55
Magnesium	00.02
Calcium	00.05
Ferrous	00.05
Carbonate	35.74
Bicarbonate	16.27
Chloride	06.80
Sulphate	00.42
Water insoluble (silica and others)	10.75
Other	00.80
Total	**100.00**

The results of the chemical analysis of produced sodium carbonate are shown that.

Table 2: percentage of sodium, potassium, magnesium, calcium, ferrous, hydroxide,carbonate, bicarbonate, chloride, sulphate in produced sodium carbonate

Cations & Anions	Sodium	Potassium	Magnesium	Calcium	Ferrous	Hydroxide	Carbonate	Bicarbonate	Chloride	Sulphate	Others	Total
Percentage %	42.1	0.3	0.02	0.2	0.3	ND	53.7	1.1	1.15	0.2	0.93	100

Table (3) shows that the results of the chemical analysis of produced calcium hydroxide

Table 3: percentage of calcium, potassium, magnesium, sodium, ferrous, hydroxide, carbonate, chloride and sulphate in sample of produced calcium hydroxide

Cations & Anions	Calcium	Potassium	Magnesium	Sodium	Ferrous	Hydroxide	Carbonate	Chloride	Sulphate	Others	Total
Weight in g	50.27	00.41	00.34	00.27	00.67	42.70	01.49	01.42	00.41	02.02	**100.00**

Table (4) shows that the results of the chemical analysis of produced sodium hydroxide

Table 4: percentage of sodium, calcium, magnesium, potassium, ferrous, hydroxide, carbonate, chloride, sulphate in produced sodium hydroxide.

Cations & anions	Sodium	Calcium	Magnesium	Potassium	Ferrous	Hydroxide	Carbonate	Chloride	Sulphate	Others	Total
Percentage %	50.1	1.6	0.25	0.3	0.55	37.5	2.7	1.25	0.3	5.45	**100**

4. Discussion

The results of chemical analysis of trona deposits shows that high percentage of sodium, carbonate and bicarbonate ions which represent the desirable materials in trona ore sample which is reached 80.56 %. whereas the undeniable soluble materials such as potassium, magnesium,calcium,ferrous, chloride sulphate ions and silica equal 19.44%. Table (1).In this work the leaching was carried out at low temperature which agree with previous work reported for trona from Turkey (Gu¨lhayat, 2003),who showed that the rate of dissolution increased slightly with temperature as it is apparently a more important factor at low solution concentrations than at higher concentrations

The purity of sodium carbonate which is produced from trona ore deposits of is equal to 95.80 %. Table (2)

The purity of calcium hydroxide produced from calcinations of calcium carbonate is equal to 92.97 %.Table (3)

The purity of sodium hydroxide which is recovered from produced sodium carbonate and calcium hydroxide is equal to 87.60 %.Table (4)

5. Conclusion

This work is study the availability of production of sodium hydroxide from raw material of trona ore and calcium carbonate by using solar energy. It can be concluded that this method is seems to be achieve option for production sodium hydroxide.
The chemical analysis of raw materials of trona ore and calcium carbonate shows the high percentage of sodium, carbonates and bicarbonates ions.

The yield and the quality of produced sodium hydroxide from raw materials of trona ore deposits and calcium carbonate by using solar energy depend on:

- The climate condition such as temperature, humidity of air, winds, rain and dust
- The feeding and leaving the solutions of trana ore, produced sodium hydroxide to different stages of the processes at different concentration
- The growth of sodium carbonate , and sodium hydroxide crystals

Solid raw materials of trona ore and calcium carbonate are very hard there-fore mechanical mining could be used to increase the extraction rate and reduce the time. The production of calcium hydroxide from calcium carbonate depend on the temperature of calcinations. The partial solubility of calcium hydroxide is consider to be the main problem in production of sodium hydroxide.

References

[1] Bassett J Denny J C Jeffery G H Mendham J. (1978) Vogel's Text Book of Quantitative Inorganic Analysis. William Clowes Limited London pp 827-830.
[2] D.S. Kostick, in: D.D. Carr, Sr (Ed.), Soda Ash in Industrial Minerals and Rocks, 6th ed., SME, Littleton CO, 1994. D.S. Kostick, Mining Eng. (June, 1998) 54.*
[3] Deming, Horace G. (1925). General Chemistry: An Elementary Survey Emphasizing Industrial Applications of Fundamental Principles (2nd ed.). New York: John Wiley & Sons, Inc. p. 452.
[4] F. Linke, Solubilities of Inorganic and Metal_/Organic Compounds, vol. II, 4th ed., American Chemical Society, Washington, DC, 1965.. C. Monnin, J. Schott, Geochim. Cosmochim. Acta 48 (1984) 571*
[5] G. Nasu¨ n-Saygili, H. Okutan, Application of the solution mining process to the Turkish trona deposit, Hydrometallurgy 42 (1996) 103–113.
[6] Garrett, D.E., 1992. Natural Soda Ash—Occurrences, Processing and Use. Van Nostrand -Reinhold, New York.
[7] Gärtner, R.S., Seckler, M.M., Witkamp, G.J., 2005. Reactive recrystallization of sodium bicarbonate. Ind. Eng. Chem. Res. 44, 4272–4283.
[8] Gu¨lhayat Nasu¨n-Saygılı, Effect of temperature on dissolution of Turkish trona, Hydrometallurgy 68 (2003) 43–49
[9] H.A. Sommers, Soda ash from trona, Chem. Eng. Prog. 56 (1960) 76–79.

[10] Idris. M.A, Abaker .M and Tagedin (1996).S.R. Evaluation and Geological Research Authority of the Sudan(G.R.A.S) Khartoum pp9-18

[11] J. F. Richardson and J. H. Harker J. R. Backhurst, Coulson and Richardson's Chemical Engineering volume 2 fifth edition 2002 ParticleTechnology and Separation processes pp 827-846

[12] J.P. Martins, F. Martins, Soda ash leaching of scheelite concentrates: the effect of high concentration of sodium carbonate, Hydrometallurgy 46 (1997) 191–203.

[13] M. Dogan, C¸. Gu¨ldu¨ r, G. Dogu, T. Dogu, Soda ash production from trona in a spry dryer, J. Chem. Technol. Biotechnol. 68 (1997) 157–162.

[14] Mubarak .A. Aldoma. production of soda ash from Sudanese trona deposite .university of Gezira MSC.sep 2003.

[15] O. Ozdemir a,b, A. Jain a, V. Gupta a, X. Wanga, J.D. Miller, Evaluation of flotation technology for the trona industry, Minerals Engineering 23 (2010) 1–9

[16] Other Lirk (1963) Encyclopedia of chemical technology. Volume one. Second edition, John Wiley and son inc, new York

[17] Park and MAC Diarmid (1975) Ore deposit. Third Edition. Freeman and Company. San Francisco pp1-2

[18] Robert S. Gärtner , Geert-Jan Witkamp, Mixed solvent reactive recrystallization of trona (sodium sesqui-carbonate) into soda (sodium carbonate anhydrate), Hydrometallurgy 88 (2007) 75–91.

[19] Thomas W. Swaddle. April 1997. Inorganic Chemistry An Industrial and Environmental Perspective . Elsevier Science & Technology Books pp205-215.

[20] Thomas H-H. M. M_{AC} Alister.D.A and AssocR.S.M(1909). The geology of ore deposits. Arnold's geological series London pp1-2