EVALUATION OF SODA ASH PRODUCTION PARAMETERS FROM BEYPAZARI TRONA ORE

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ABSTRACT

EVALUATION OF SODA ASH PRODUCTION PARAMETERS FROM BEYPAZARI TRONA ORE

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This study was carried out with Beypazarı trona ore having a grade about 85 % trona ($Na_2CO_3.NaHCO_3.2H_2O$). The main target of the study is the determination of calcinations and leaching parameters, which are the two main unit operations in the production of soda ash (Na_2CO_3) from trona ore. Calcination parameters; calcination duration, calcination temperature and particle size were determined by using three different heat treatment systems, namely laboratory type muffle furnace, up draught furnace and microwave oven. As an alternative, wet type microwave-induced calcination which completes the decomposition of trona in solution was also investigated. Thirty minutes of calcination time was sufficient for complete calcination of –6.35 mm trona sample at 175 °C with the muffle furnace. Calcination of trona with microwave treatment was completed in a shorter time. The nature of thermal reactions and structural changes of trona during calcination were elucidated by TG (Thermogravimetry), DTG (Derivative Thermogravimetry), SEM (Scanning Electron Microscope) and XRD (X-ray diffraction) analysis. The effect of heat treatment on grindability, specific surface area and decrepitation of trona were also investigated. In the last stage of the study, leaching parameters; leaching time, leaching temperature and pulp density were determined for both uncalcined and calcined samples. 80 % leach recovery was obtained in 4 minutes for –6.35 mm particle size of uncalcined sample in 25 % pulp density while 100 % leach recovery was reached for the calcined samples under the same conditions.

Keywords: Soda ash, Trona, Calcination, Leaching

ÖZ

BEYPAZARI TRONA CEVHERİNDEN SODA KÜLÜ ÜRETİM KOŞULLARININ SAPTANMASI

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Bu çalışma, yaklaşık % 85 trona ($Na_2CO_3.NaHCO_3.2H_2O$) tenörü olan Beypazarı trona cevheri ile yapılmıştır.Bu çalışmadaki ana hedef, trona cevherinden soda külü (Na_2CO_3) üretimindeki önemli iki işlem olan kalsinasyon ve liç parametrelerinin belirlenmesidir. Kalsinasyon parametreleri olarak kalsinasyon süresi, kalsinasyon sıcaklığı ve tane boyu üç değişik ısısal işlem; laboratuvar tipi fırın, yukarı akımlı fırın ve mikrodalga fırın kullanılarak belirlenmiştir. Alternatif olarak mikrodalga yaş kalsinasyon yöntemi ile çözelti içindeki tronanın tamamen bozunması incelenmiştir. –6.35 mm tane boyundaki trona numunesinin tamamıyla kalsinasyonu için laboratuvar tipi fırında 175 °C de 30 dakikalık kalsinasyon süresi yeterli olmuştur. Tronanın kalsinasyonu mikrodalga ile ısısal işleme tabi tutularak daha kısa sürede tamamlanmıştır. Tronanın kalsinasyon sırasındaki ısısal reaksiyonları ve yapısal değişimleri, TG (Termal gravimetrik), DTG (Diferansiyel termal gravimetrik), SEM (Taramalı elektron mikroskobu) ve XRD (X-ışını kırınımı) analizleri ile aydınlatılmıştır. Isısal işlemin trona cevherinin öğütülebilirliği, spesifik yüzey alanı ve patlayarak ufalanması üzerindeki etkileri de araştırılmıştır. Çalışmanın son aşamasında, liç parametreleri; liç süresi, liç sıcaklığı ve pülp yoğunluğu kalsine edilmiş ve kalsine edilmemiş numuneler için belirlenmiştir. -6.35 mm tane boyundaki kalsine edilmemiş numune ile % 25 pülp yoğunluğunda gerçekleştirilen liç işleminde 4 dakikalık liç süresinde % 80 lik liç verimi elde edilirken, kalsine edilmiş numunelerele aynı koşullarda % 100 lük verime ulaşılmıştır.

Anahtar Kelimeler: Soda Külü, Trona, Kalsinasyon, Liç

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CHAPTER 1

INTRODUCTION

Sodium carbonate (*soda ash*) is the neutral sodium salt of carbonic acid. It is one of the most important raw materials used in the chemical industry. Sodium carbonate had many uses even then (cleaning and glass manufacture) for which it is still indispensable. Production of the alkaline materials sodium carbonate and potassium carbonate (which were recognized rather late as chemically distinct) was carried out from ancient times until the 1800s by the combustion of marine and land vegetiation, followed by calcination at red heat and leaching of the ash. The term soda ash originates from this process. Whereas the production of sodium carbonate from the ashes of plants in salty soil near the sea is only of historical interest, extraction from soda-containing minerals, especially *trona*, is of increasing importance.

Developed countries have higher per capita consumption of soda ash but lower growth rates than developing countries. However, the end-use patterns are basically the same for both. Glass production accounts for half of global soda ash consumption with commercial and residential construction driving flat glass demand. The second-largest market for soda ash is the chemicals sector, where it is used as an alkali source in numerous chemical processes and as a feedstock in the production of sodium chemicals. The third major use for soda ash is in formulated detergents and cleaners as a builder and also as a feedstock in the production of other builders, such as synthetic zeolites.

Today, world's supply of soda ash is derived occasionally. This demand is met by three ways; production from natural soda reserves, production from lake waters and production synthetically by Solvay method. One third of total world production is supplied from natural soda reserves (Thieme, 1993).

Trona is a relatively rare, non-metallic mineral, $Na_2CO_3.NaHCO_3.2H_2O$. The pure material contains 70.39 % sodium carbonate and by calcination the excess CO_2 and water can be driven off, yielding natural soda ash.

Soda ash can also be produced synthetically by the Solvay ammonia soda process. It uses common salt (sodium chloride) and limestone (calcium carbonate) as raw materials. Synthetic soda ash was first produced in the latter part of the 18th century, but it was not until 1863 that an economical and efficient method of production was discovered. The production of soda ash from trona is economically more attractive than the production of synthetic soda ash, and environmental problems associated with the ammonia-soda process, principally the disposal of by-product $CaCl_2$, are avoided. Hence natural soda ash gradually replaced synthetic soda ash produced domestically until the last ammonia-soda plant in the United States was shut down in 1986 (Eggman, 2001).

At the present time, trona deposits are normally mechanically mined. The method uses conventional, continuous or longwall mining technique or combination thereof. Then, the raw trona can be processed by different methods: sesquicarbonate process, monohydrate process, alkali extraction process and carbonation process. There are dominantly two processes, sesquicarbonate process and monohydrate process, used to convert mined trona into pure soda ash, or sodium carbonate (Na_2CO_3). In the sesquicarbonate process, the trona ore is dissolved in aqueous solution and after separation of the resulting solution from the insolubles, sodium sesquicarbonate is crystallized from solution by cooling. The sesquicarbonate crystals are then separated from the mother liquor and finally, calcined to recover soda ash (anhydrous sodium carbonate). In the monohydrate process, the trona ore is first calcined to convert its bicarbonate content to sodium carbonate and is then dissolved in water. After the resulting solution is separated from the insolubles, sodium carbonate monohydrate is precipitated by evaporative crystallization. The monohydrate crystals are then separated from the mother liquor and dried to recover soda ash.

While relatively effective, these processes suffer from several inherent disadvantages, which seriously affect the efficiency and commercial viability of the processes. For example, because of the need for calcination steps, the processes are energy intensive, requiring the use of large amounts of coal, fuel oil, natural gas or mixtures thereof. This is especially disadvantageous because of the high cost and scarcity of hydrocarbon fuels. Furthermore, these procedures are not readily adapted for removal of soda ash from uncalcined trona values in dilute aqueous streams, as for example solutions obtained via direct solution mining, mine waters, or from calcined trona values in aqueous process streams such as pond liquors or crystallizer mother liquor purges.

In the process of making sodium carbonate from trona involving the steps of crushing the trona, calcining the crushed trona, dissolving the calcined trona to obtain a solution comprising sodium carbonate and insoluble impurities contaminated by soluble silicates and soluble carbonaceous matter. Contamination of the sodium carbonate solution with soluble carbonaceous matter is reduced by the improvement, which comprises calcining the crushed trona at the temperature of 90-150 °C.

The largest known deposits of trona found in prehistoric alkaline lakebed in the southwest Wyoming and now called Green River Basin. The other important resources are Magadi Lake in Kenya and Texaco brines in Mexico. Natural soda ash sources (either trona or sodium carbonate-rich brines) found primarily in the U.S.A, Mexico, Russia, Kenya, China and Turkey (USGS Mineral Information, 2002).

The Turkish trona deposit was discovered by Mineral Research and Exploration Institute in 1979. Beypazarı trona deposit is the second largest trona ore having a total reserves about 300 million tons of trona. The average grade is 84 % trona. Although Beypazarı trona reserve has a worldwide economic importance, there is limited number of studies about having investigation of Turkish trona (Saygılı, 1996).

The main target in this study is to determine the production parameters of soda ash from Beypazarı Turkish trona ore by monohydrate process.

Calcination as a thermal treatment is the first step of this process. The mechanism is based on thermal treatment of the ore that affects its decomposition and the elimination of gangue minerals. Thermal treatment of trona was the core of this thesis. Thermal treatment was conducted in three different methods: conventional thermal treatment in a metallurgical furnace, designed up draught heating and microwave heating. The calcination parameters; particle size, calcination duration and calcination temperature have been investigated for all three heating types. Since microwave heating has found many uses in chemical and thermal engineering, microwave treatment of trona was also investigated. Due to high heating cost, an alternate possibility, wet calcination, which completes the decomposition of trona in solution, was performed in microwave.

CHAPTER 2

SODA ASH

2.1. Soda Ash (Sodium carbonate)

Soda ash is a white, anhydrous, powdered or granular material containing well above 99 % sodium carbonate (Na_2CO_3) when shipped. The accepted commercial standard for soda ash is expressed in terms of the total equivalent sodium oxide (Na_2O) content. In other words, commercial 58 % soda ash contains an equivalent of 58 % Na_2O. The conversion equation is % Na_2O x 1.71 = Na_2CO_3 %; 58 % Na_2O is thus equivalent to 99.2 % Na_2CO_3.

2.1.1. Definitions, Grades, Specifications

The terms soda ash and sodium carbonate are used interchangeably. Soda ash is an alkali, and because of the high pH of concentrated solutions, it may be irritating to the eyes, respiratory tract and skin.

Soda ash is produced in two principal grades, known as light soda ash and dense soda ash. These grades differ only in physical characteristics such as bulk density and size and shape of particles, which influence flow characteristics and angle of repose. Dense soda ash has a bulk density of 950 to 1100 kg/m^3, may command a slightly higher price than the light variety, and is preferred for glass manufacture because the lighter variety leads to frothing in the glass melt. Light soda ash having a bulk density at 520 to 600 kg/m^3, is the normal production item direct from the calcining furnace and is preferred by the chemical and detergent industries. Other physical properties, as well as chemical properties and properties of solutions, are common to both grades of soda ash.

All commercial grades are chemically similar. As density differences are the main distinguishing feature, Table 1 shows the typical market specifications of dense soda ash.

Table 1. Market specifications of dense soda ash

Chemical composition		
Sodium Carbonate (Na_2CO_3)	≥	99.8 %*
Sodium Oxide (Na_2O)	≥	58.4 %
Sodium Sulfate (Na_2SO_4)	≤	0.10 %
Sodium Chlorite (NaCl)	≤	0.03 %
Iron (Fe)	≤	0.0005% (5 ppm)
Bulk density		(0.96-1.04 g/cm^3)
Particle size		75 micron - 850 micron
		-75 micron < 10 %

*ANSAC: American Natural Soda Ash Corporation

2.1.2. Physical Properties and Hydrates of Sodium Carbonate

The three known hydrates exist in addition to anhydrous sodium carbonate, Na_2CO_3.

1. *Sodium carbonate monohydrate* ($Na_2CO_3.H_2O$), which contains 85.48 % Na_2CO_3 and 14.52 % water of crystallization. It separates as small crystals from saturated aqueous solutions above 35.4 °C, or it may be formed simply by wetting soda ash with the calculated quantity of water at or above this temperature. It loses water on heating, and its solubility decreases slightly with increasing temperature. In contact with its saturated solution it is converted to Na_2CO_3 at 109 °C.

2. *Sodium carbonate heptahydrate ($Na_2CO_3.7H_2O$),* which contains 45.7 % Na_2CO_3 and 54.3 % water of crystallization. It is of no commercial interest because of its narrow range of stability, which extends from 32 °C to 35.4 °C.

3. *Sodium carbonate decahydrate ($Na_2CO_3.10H_2O$),* commonly called “sal soda” or “washing soda” which usually forms large transparent crystals containing 37.06 % Na_2CO_3 and 62.94 % water of crystallization. It may be crystallized from saturated aqueous solutions below 32.0 °C and above -2.1°C or by wetting soda ash with the calculated quantity of water in this temperature range. The crystals readily effloresce in dry air, forming a residue of lower hydrates, principally the monohydrate.

The physical properties of these compounds are listed in Table 2.

Table 2. Solubility of the hydrates of sodium carbonate (Thieme, 1993)

Solid Phase	**T, °C**	**Solubility, gNa_2CO_3/100 g solution**
ice + $Na_2CO_3.10H_2O$	-2.1	5.93
$Na_2CO_3.10H_2O$+ $Na_2CO_3.7H_2O$	32.0	31.26
$Na_2CO_3.10H_2O$+ $Na_2CO_3.H_2O$ (metastable)	32.96	33.35
$Na_2CO_3.7H_2O$+ $Na_2CO_3.H_2O$	35.37	33.21
$Na_2CO_3.H_2O$+ Na_2CO_3	105 ± 5	31.15

2.1.3. Chemical Properties of Sodium Carbonate

Sodium carbonate is hygroscopic. In air at 96 % R.H. (relative humidity) its weight can increase by 1.5 % within 30 minutes. If sodium carbonate is stored under moist conditions, its alkalinity decreases due to absorption of moisture and carbon dioxide from the atmosphere. Water vapor reacts with sodium carbonate above 400 °C to form sodium hydroxide and carbon dioxide. Sodium carbonate is readily soluble in water and the resulting solutions are alkaline, as expected a salt formed from a strong base and weak acid. At 25 °C the pH of 1, 5 and 10 wt % solutions are 11.37, 11.58 and 11.70 respectively (Eggman, 2001). Sodium carbonate reacts exothermically with chlorine above 150 °C to form NaCl, CO_2, O_2 and $NaClO_4$.

2.2. Uses of Soda Ash

Soda ash is an important raw material for the chemical industry. Its sodium content results in fluxing properties that make it essential in the glass and silicate industries. Soda ash reduces the viscosity and acts as a fluxing agent in glass melting [soda-lime glass (flat and container glass), fiber-glass, specialty glass (e.g. borosilicate glass)]. Soda contributes alkalinity so it is used as an alkali in various pulp and paper industries; soap and detergents industries. Figure 1 represents the consumption areas of soda ash by end uses. Light and intermediate grades of soda ash are preferred for some of these applications where surfactant carrying capacity and dissolution are important.

Aqueous soda ash solutions are used to remove sulfur dioxide from combustion gases in steel desulfurization, flue gas desulfurization (FGD) systems, forming sodium sulfite and sodium bicarbonate.

$$Na_2CO_3 + SO_2 \Rightarrow Na_2SO_3 + CO_2 \qquad (1)$$

$$CO_2 + Na_2CO_3 + H_2O \Rightarrow 2NaHCO_3 \qquad (2)$$

$$2Na_2CO_3 + SO_2 + H_2O \Rightarrow Na_2SO_3 + 2NaHCO_3 \qquad (3)$$

These reactions are also important in the production of paper pulp by the sulfite process.

Commercial interest in production of sodium hydroxide by the lime soda process has been revived because of imbalances in the chlorine and caustic markets. Similar chemistry is used in green liquor recovery section of the Kraft pulping process and their bauxite digesters used in the production of alumina.

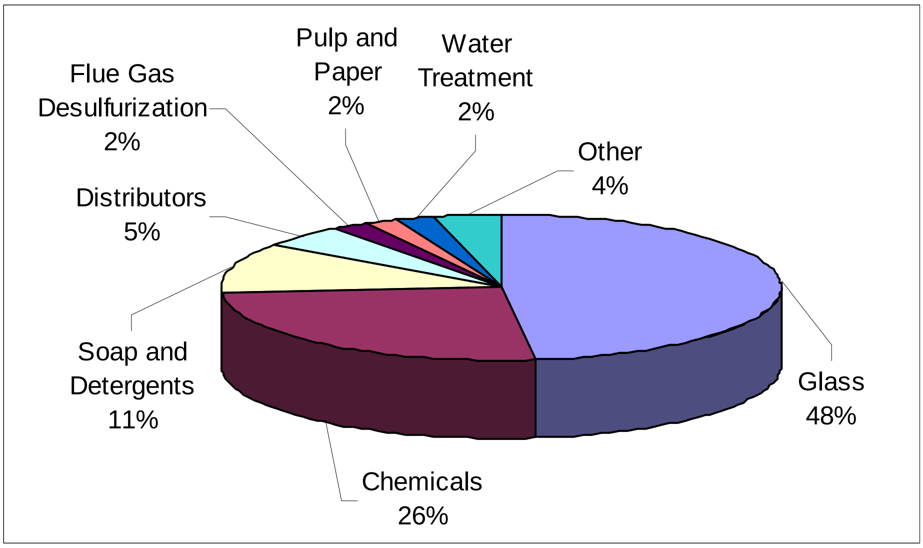

Figure 1. Distribution of soda ash by end use in 2001 (USGS Mineral Information, 2002)

2.3. World Trona Reserves

World Resources: Soda ash is obtained from trona and sodium carbonate-rich brines. The world's largest deposit of trona is in the Green River Basin of Wyoming. About 47 billion metric tons of identified soda ash resources could be recovered from the 56 billion tons of bedded trona and the 47 billion tons of interbedded or intermixed trona and halite that are in beds more than 1.2 meters thick. About 34 billion tons of reserve base soda ash could be obtained from the 36 billion tons of halite-free trona and the 25 billion tons of interbedded or intermixed trona and halite that are in beds more than 1.8 meters thick. Underground room-and-pillar mining, using a combination of conventional, continuous, and shortwall mining equipment is the primary method of mining Wyoming trona ore. The method has an average 45 % mining recovery, which is higher than the 30 % average mining recovery from solution mining. Improved solution mining techniques, such as horizontal drilling to establish communication between well pairs, could increase this extraction rate and enable companies to develop some of the deeper economic trona. Wyoming trona resources are being depleted at the rate of about 15 million tons per year (8.3 million tons of soda ash). Searles Lake and Owens Lake in California contain an estimated 815 million tons of soda ash reserves. There are at least 62 identified natural sodium carbonate deposits in the world, some of which have been quantified. Although soda ash can be manufactured from salt and limestone, both of which are practically inexhaustible, synthetic soda ash is more costly to produce and generates environmentally deleterious wastes.

Events, Trends, and Issues: The domestic market for soda ash for the first half of the 2002 was virtually identical to that of the corresponding period in 2001. Despite major price increase attempts that were initiated in late 2001, the estimated average annual value for 2002 was relatively unchanged. The U.S. soda ash industry was optimistic that the projected increase in exports in the last two quarters could bolster soda ash sales and revenue.

Global production of soda ash in 2000 is estimated at 34.7 million metric tons, equivalent to an 83% utilization of effective production capacity. Global consumption is estimated at 34.5 million metric tons and is projected to increase at an average annual rate of 2 % over the next five years, reaching 38.1 million metric tons in 2005. Trade among the major geographic regions is estimated at 5.5 million metric tons and is expected to increase at an average annual rate of 5 % to reach 6.9 million metric tons by 2005. The top five exporters in 2000 were the United States, China, Western Europe, Russia and Bulgaria. Global soda ash production is projected to grow at an average annual rate of 2 % from 2000 through 2005. The three years of the five-year period are expected to be above trend line growth. Projected regional average annual growth rates range from highs of 3.4 % for Asia and 2.7 % for Eastern Europe down to 0.8 % for North America and 0.4 % for Western Europe (USGS Mineral Information, 2002).

World Review: The largest consumers of soda ash were, for the most part, developed nations; these countries, however, also usually had lower growth rates compared with developing countries, which usually have greater demands for consumer products. Although the production and consumption quantities varied among the countries, the end-use patterns were basically the same; glass, chemicals, and detergents were the major sectors. Estimated values of world soda ash poduction are represented in Table 3. Nine countries had the capacity to produce more than 1 million metric tons per year (Mt/yr). They are, in descending order, the United States, China, Russia, India, Germany, France, Italy, Poland, and the United Kingdom. Bulgaria, Romania, and Ukraine had production installations that were rated at about 1 Mt/yr; adverse economic conditions, however, had caused these nations to produce below their design capacities. Recent acquisitions or joint ventures with major European soda ash producers that have soda ash manufacturing expertise should reverse this situation in the next few years. Most of these sodaash-producing countries have large populations that require consumer products made with soda ash. The less developed nations tend to have higher soda ash demands and higher growth rates as soda-ash-consuming industries are developed.

Table 3. World soda ash production, reserves and reserve base (USGS Mineral Information, 2002)

	Production		**Reserves**	**Reserve Base**
Natural	**2001**	**2002**		
United States	10 300	10 300	23 000 000	39 000 000
Bostwana	270	270	400 000	NA
Kenya	260	300	7 000	NA
Mexico	-	-	200 000	450 000
Turkey	-	-	200 000	240 000
Uganda	NA	NA	20 000	NA
Other Countries	-	-	260 000	220 000
World Total, natural (may be rounded)	10 800	10 900	24 000 000	40 000 000
World Total, synthetic (rounded)	24 300	22 100		
World Total,(rounded)	35 100	33 000		

2.4. Beypazarı, Turkey Trona Deposit

The Turkish natural trona deposit was found in Beypazarı by Mineral Research and Exploration Institute (MTA) in1979 during coal exploration studies. Field tests related to geology and hydrology were completed by MTA. The studies showed that trona is present in 130-400 m deep, in layers, which are thicker, and richer in quality compared to the ones in Wyoming (USA). The deposits are accumulated in two disconnected levels, and have several strata in the upper and lower levels. The minerals of the enclosing sedimentary rocks of the trona levels mainly consist of dolomite, analcite, potassium feldspar, quartz and clay minerals. Generalized stratigraphy of Beypazarı trona formation is given in Figure 2. The average grade is 84 % trona. The results obtained from only such a limited area indicated the presence of nearly 200 million tons of trona. This reserve may be small in comparison to 50 billion tons reserve in Wyoming (USA). However, exploration activities in the same area show that discovery of new ore bodies is possible (Ataman et.al., 1986).

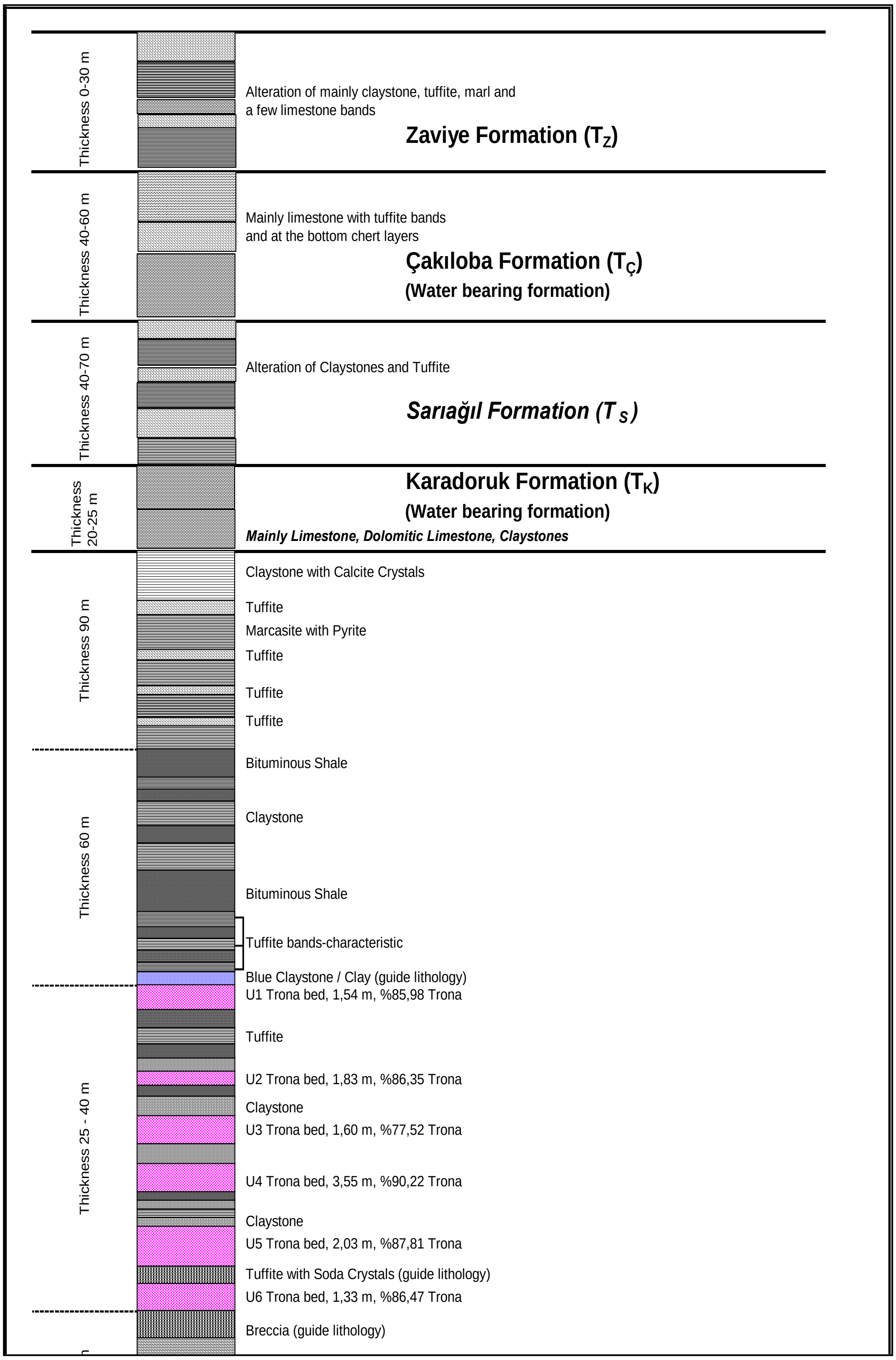

Figure 2. Generalized stratigraphy of Beypazarı trona formation (Ataman et.al., 1986)

2.5. Sodium Carbonate Minerals

Whereas the production of sodium carbonate from the ashes of plants in salty soil near the sea is only of historical interest, extraction from soda-containing minerals, especially trona, is of increasing importance. The natural soda minerals occurred in the world is given in Table 4.

Table 4. Natural soda minerals occurred worldwide (Eggman, 2001)

Mineral	**Chemical Name**	**Chemical Composition**	**% Na_2CO_3 content**
Trona	natural sodium sesquicarbonate	$Na_2CO_3.NaHCO_3.2H_2O$	70.3
Nahcolite	natural sodium bicarbonate	$NaHCO_3$	63.1
Bredeyit	natural sodium bicarbonate		47.1
Gaylusitte	natural sodium bicarbonate	$Na_2CO_3.CaCO_3.5H_2O$	35.8
Pirrsonite	natural sodium bicarbonate	$Na_2CO_3.CaCO_3.2H_2O$	43.8
Thermonatrite	sodium carbonate monohydrate	$Na_2CO_3.H_2O$	85.5
Natron	sodium carbonate decahydrate	$Na_2CO_3.10H_2O$	37.1
Burkeit	-	$Na_2CO_3.2Na_2SO_4$	27.2
Dawsonit	-	$NaAl(CO_3)(OH)_2$	35.8
Hankcite	-	$Na_2CO_3.9Na_2SO_4.KCl$	13.5
Sortite	-	$Na_2CO_3.2CaCO_3$	34.6

Only trona is of commercial interest. These Na_2CO_3-containing minerals were formed from the original rock by the erosive action of, air, water, heat, and pressure, followed by chemical changes caused by the action of atmospheric carbon dioxide. The carbonate-containing salts formed were leached by water and then concentrated and crystallized by evaporation.

2.6. Trona Mineral

Trona is a relatively rare, non-metallic mineral, $Na_2CO_3.NaHCO_3.2H_2O$. The pure material contains 70.3 % sodium carbonate and by calcination the excess CO_2 and water can be driven off, yielding natural soda ash.

Trona is the type mineral so-to-speak for several sodium carbonates that form in non-marine evaporate deposits. Other sodium carbonates include gaylusitte, natron, pirssonite, nahcolite and thermonatrite. Trona is probably the most common and well known of these minerals. They are all difficult to tell apart from each other except when good crystal form is present or when optical or X-ray techniques can be used. All are subject to dehydration and/or hydration to one degree or another and should be stored in sealed containers for this reason. All may form as efflorescent crusts on the walls of caves and mines or in soils in arid regions. Trona gets its name from a discarded Arabic word for native salt, "tron", which is derived from the word "natrun".

Chemical composition : $Na_2CO_3.NaHCO_3.2H_2O$

or

$Na_3H(CO_3)_2.2H_2O$

$$\left.\begin{array}{l}46.9\ \%\ Na_2CO_3\\ 37.17\ \%\ NaHCO_3\\ 15.93\ \%\ H_2O\end{array}\right\}\text{ gives }\ 41.15\ \%\ Na_2O$$

Crystal structure	: Monoclinic
Crystal habit	: Prismatic to blocky crystals, but usually massive, fibrous or columnar
Cleavage	: Perfect in one direction and poor in two others
Fracture	: Subconchoidal to uneven
Hardness	: 2.5-3.0
Specific weight	: 2.11
Color	: Colorless, grayish white, pale yellow or pale brown
Tranparency	: Transparent, semi-transparent
Luster	: Vitreous
Other characteristics	: Has an alkaline taste

The probable main products are given in Table 5.

Table 5. Trona products

Various Forms of Sodium Carbonate	Formula
Anhydrous sodium carbonate Sodium carbonate monohydrate Sodium carbonate heptahydrate Sodium carbonate decahydrate	Na_2CO_3 $Na_2CO_3. H_2O$ $Na_2CO_3 .7H_2O$ $Na_2CO_3 .10H_2O$
Caustic Soda	(NaOH)
Sodium Bicarbonate	($NaHCO_3$)
Sodium Derivatives	

2.7. Soda Ash Production from Trona Mineral

Trona deposits show deviations in geological and chemical characteristics. Geographical location and site characteristics such as environmental matters, specific energy resources, distribution methods, and trade barriers are key elements in a selection of processing method. Soda ash is readily produced from either natural deposits or trona or by synthetic pathways. Soda ash production methods are given below in historical sequence.

1. Le Blanc Process (synthetic soda ash)
2. Solvay Process (synthetic soda ash)
3. DUAL and NA Processes (synthetic soda ash)
4. Monohydrate Process
5. Sesquicarbonate Process
6. Carbonation Process
7. Alkali Extraction Process

2.7.1. Le Blanc Process

Large-scale production was possible only after the development of a new process, named after its inventor LEBLANC (1742-1806). This method was the first conventional method in which salt, sulfuric acid, coal and limestone were used. This is the synthetic soda as production method. In 1970, the first plant was built in St. Denis, France. Initially, production was 300 kg per day. In the following years, the soda industry developed rapidly in England due to the increasing demand for soda ash to clean cotton from the colonies (Thieme, 1993). In this process, sodium chloride reacts with sulfuric acid to produce sodium sulfate and hydrochloric acid. The sodium sulfate is then roasted with limestone and coal and the resulting sodium-carbonate-calcium sulfide mixture (black ash) is leached with water to extract the sodium carbonate. Poor economics and excessive pollution caused by the hydrochloric acid and calcium sulfide by-product led to the eventual demise of the Le Blanc process. The Leblanc process, which is now of only historical interest, is based on the following equation:

$$2NaCl + H_2SO_4 \Rightarrow Na_2SO_4 + 2HCl \quad (4)$$

$$Na_2SO_4 + 2C \Rightarrow Na_2S + 2CO_2 \quad (5)$$

$$Na_2S + CaCO_3 \Rightarrow Na_2CO_3 + CaS \quad (6)$$

2.7.2. Solvay Process

Solvay method is also the production method of synthetic soda ash. In the second half of the 1800s the Le Blanc soda ash process experienced serious competition from the Solvay process. In the first half of the 1800s, investigations were already being carried out into the industrial use of the double decomposition reaction of NaCl with NH_4HCO_3 , but without success. However, the Belgian Ernest Solvay (1838-1932) brought the development of the process to a successful conclusing during 1861-1865. The first plant was started up in 1865 in Guillet, Belgium with an initial production of 1.5 ton per day. The technically and economically superior Solvay process displaced the Le Blanc to such an extent that by the early 1900s only a few Le Blanc plants were in production. The last Le Blanc works ceased operation around 1923. Since then, the Solvay process has remained predominant.

Solvay soda ash is made by saturating purified NaCl brine with ammonia gas and then carbonating the solution with carbon dioxide gas to form a sodium bicarbonate precipitate. The sodium bicarbonate backs to the liquid phase. The liquid is reacted with milk of lime to recover the ammonia and to produce by-product calcium chloride. Limestone and coke are required to make the milk of lime. Disposition of effluent streams containing high concentrations of calcium chloride and sodium chloride is a major problem for all Solvay soda ash plants. The overall chemical reaction is given below.

$$2NaCl + CaCO_3 \Rightarrow Na_2CO_3 + CaCl_2 \qquad (7)$$

2.7.3. DUAL and NA Process

Many variants of the Solvay process exist. The DUAL process was developed and operated in Japan. This process combines soda ash production with ammonium chloride production. The importance of the process in Japan is due to the high cost of imported rock salt and use of the ammonium chloride as a fertilizer. In the dual process, ammonia is absorbed by the bicarbonate mother liquor, and solid sodium chloride is added. On cooling, ammonium chloride separates, is recovered in centrifuges, and is then dried in rotary dryers with air at 150 °C. The mother liquor is recycled to the carbonation towers where sodium bicarbonate is precipitated.

2.7.4. Monohydrate Process

Soda ash is generally produced from trona by monohydrate process that produces only dense soda ash. The first FMC Wyoming Corporation plant using this process went into operation in late 1972. In this process, the trona ore is first converted to crude soda ash by calcination and all subsequent operations are performed on the resulting carbonate solution, as given in following. Figure 3 outlines the main steps for that process.

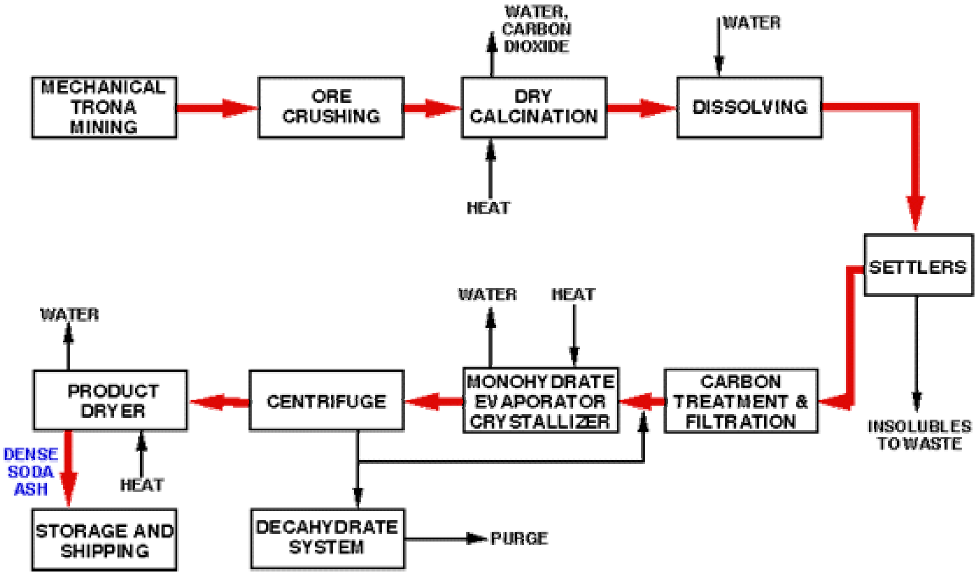

Figure 3. Flow diagram of monohydrate process

Crushed trona is calcined in a rotary kiln to dissociate the ore and drive off the carbon dioxide and water by the following reaction:

$$2\ (Na_2CO_3.NaHCO_3.2H_2O)_{\ (s)} \Rightarrow\ 3\ Na_2CO_{3\ (s)} + 5\ H_2O + CO_2 \qquad (8)$$

The calcined material is combined with water to dissolve the soda ash and to allow separating and discarding of the insoluble material such as shale or shortite by settling and/or filtration. The resulting clear liquid is concentrated as necessary by triple-effect evaporators, and the dissolved soda ash precipitates as crystals of sodium carbonate monohydrate, $Na_2CO_3.H_2O$. Other dissolved impurities, such as sodium chloride or sodium sulfate, remain in solution. The crystals and liquor are separated by centrifugation. The sodium carbonate monohydrate crystals are calcined a second time to remove water of crystallization. The resultant finished product is cooled, screened, and shipped by rail or truck.

2.7.5. Sesquicarbonate Process

An alternate method of soda ash production from trona is the sesquicarbonate process. This is the original process, developed by FMC Wyoming Corporation and put in operation in 1953, for producing pure soda ash from Wyoming trona.

Trona ore is leached in recycled mother liquor at as high a temperature as possible to maximize the amount dissolved. The solution is then clarified, filtered and sent to a series of evaporative cooling crystallizers where sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) is crystallized. Carbon is added to the filters to control any crystal modifying organics. The purified sesquicarbonate crystals may be calcined to produce a “light” soda ash product. Simplified flow diagram of sesquicarbonate process is shown in Figure 4.

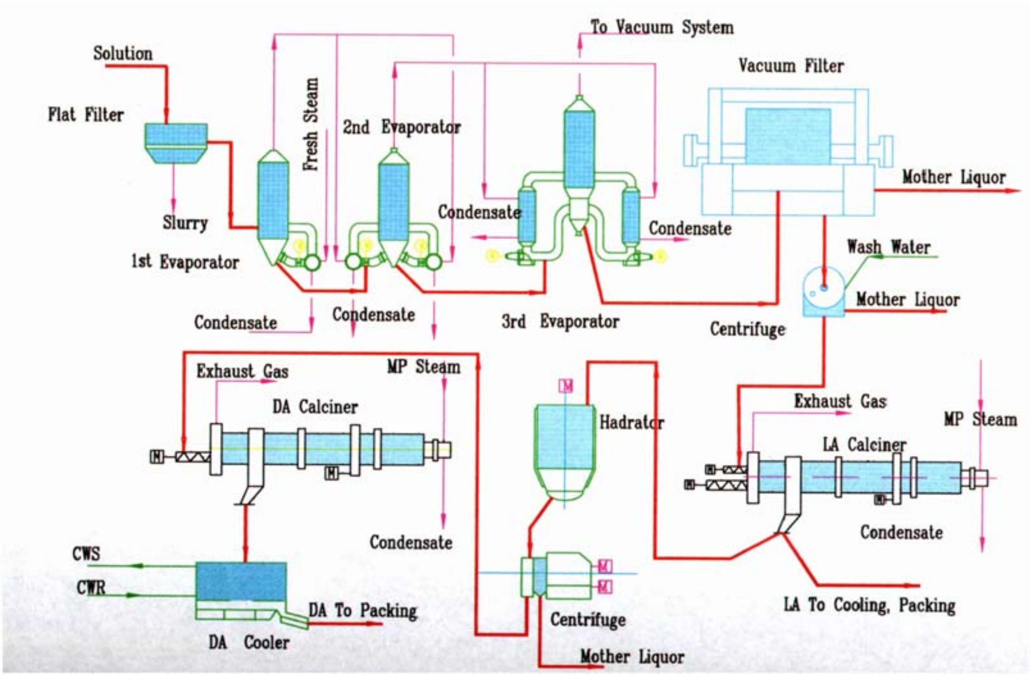

Figure 4. Flow diagram of sesquicarbonate process (Eggman, 2001)

The mother liquor is recycled to the dissolvers. In a variation of the process, trona ore is dissolved in hot water and the centrate is returned to the evaporator crystallizer (Haynes, 1997). This produced soda is the light soda ash. Densities similar to the monohydrate soda ash may be achieved by subsequently heating the material to about 350 °C. Alternatively, soda ash can be converted to the monohydrate and then calcined.

2.7.6. Alkali Extraction Process

Alkali extraction process is mainly to dissolve crude trona in an aqueous sodium hydroxide solution. In this process, trona is dissolved in an aqueous sodium hydroxide to obtain pregnant sodium carbonate solution. This method is generally used for bicarbonate content that dissolves to be an incongruent consisted in trona. The diluted solution has a composition of 2-7 % caustic soda. Dissolution reaction is given as follows:

$$Na_2CO_3.NaHCO_3.2H_2O + NaOH \Rightarrow 2\ Na_2CO_3 + 3\ H_2O \qquad (9)$$

The solution at 30 °C was filtered and the pregnant carbonate solution is heated, sufficient water is evaporated to form slurry of sodium carbonate monohydrate crystals and aqueous sodium carbonate. The slurry was filtered and the mother liquor was recycled to dissolve raw mineral. The regeneration was done by adding sodium hydroxide to the mother liquor. The monohydrate crystals were dried and calcined. The most important parameters in alkaline extraction process are; the dissolution temperature, concentration of sodium hydroxide and evaporative crystallization temperature. The appropriate temperatures for the dissolution and evaporative crystallization are 30 °C and 100 °C respectively. The flow diagram of alkali extraction process is shown in Figure 5 (Okutan et. al., 1986).

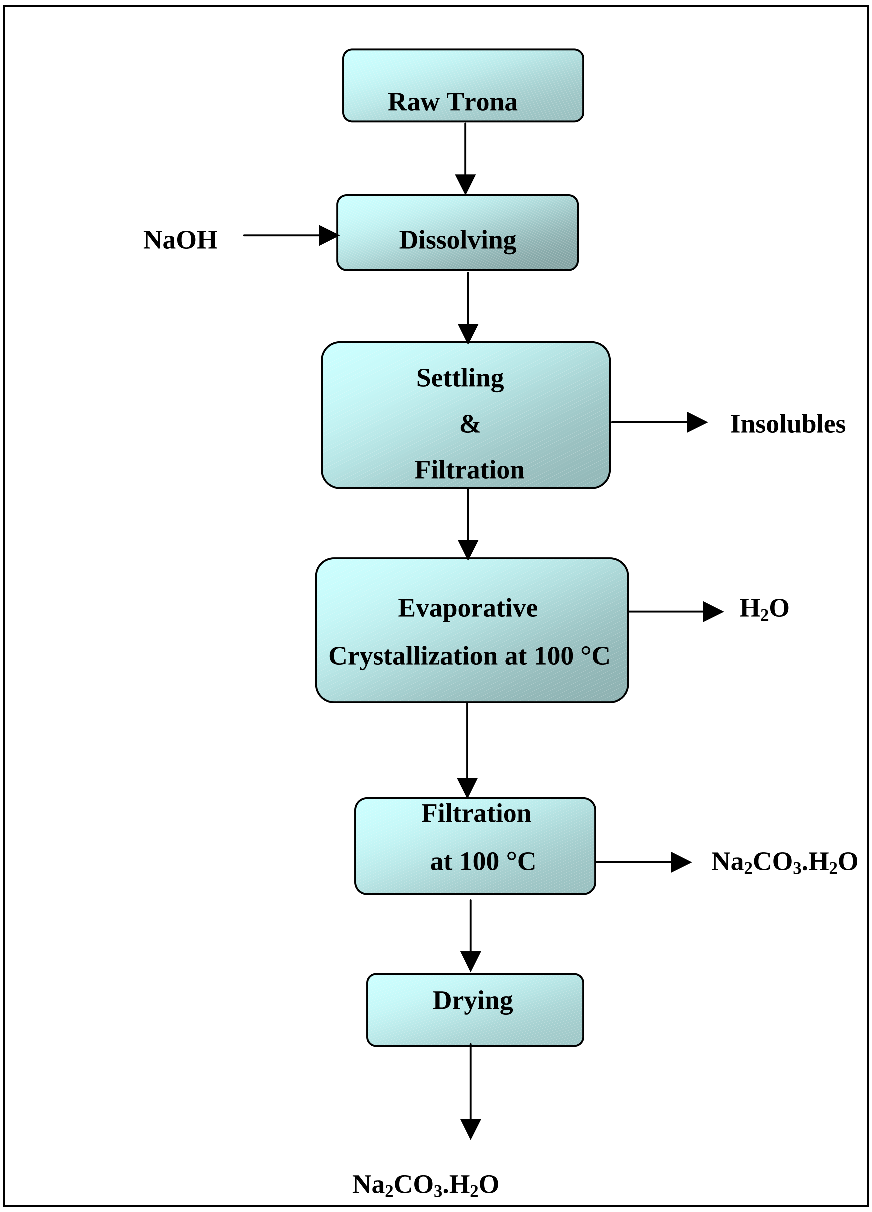

Figure 5. Flow diagram of alkali extraction process

In a trona bed, the effect of water on the solubility of sodium carbonate will decrease due to the precipitated bicarbonate. In the conventional mining technique, bicarbonate can be converted to carbonate with a pre-calcination stage. The problem associated with the presence of sodium bicarbonate in trona deposits can be solved by applying of sodium hydroxide solution. The required amount of sodium hydroxide is the stochiometric amount that is necessary to convert all of the bicarbonate to carbonate. The aqueous sodium hydroxide solvent preferably contains 1-15 wt% NaOH. Using an excess of sodium hydroxide causes unreacted NaOH to remain in the solution and this effect decreases the solubility of sodium carbonate.

2.7.7. Carbonation Process

Carbonation process is applied to convert the raw trona, multi-salt type mineral to basic salt sodium bicarbonate completely. By that type of process, incongruent trona in the beginning is dissolving easily. As in the case of monohydrate process that converts the trona to soda ash (sodium carbonate), in carbonation process it is converted to sodium bicarbonate.

Carbonation process is to extract trona mineral in hot water and then to add CO_2 to the brine solution to form sodium bicarbonate based on below reaction:

$$Na_2CO_3 + H_2O + CO_2 \Rightarrow NaHCO_3 \qquad (10)$$

Basic stages of the trona carbonation process are dissolution in hot water, removing of impurities, CO_2 adding and crystallization, filtration and drying. The most important parameter for every stage of carbonation process is the temperature. The problems may be encountered during carbonation process are the removal of impurities, filtration difficulties and the losses of saturated solution. The filtration difficulties were eliminated to a certain extent by maintaining sufficient vacuum and keeping the operation temperature constant. Figure 6 show the flow diagram of carbonation process.

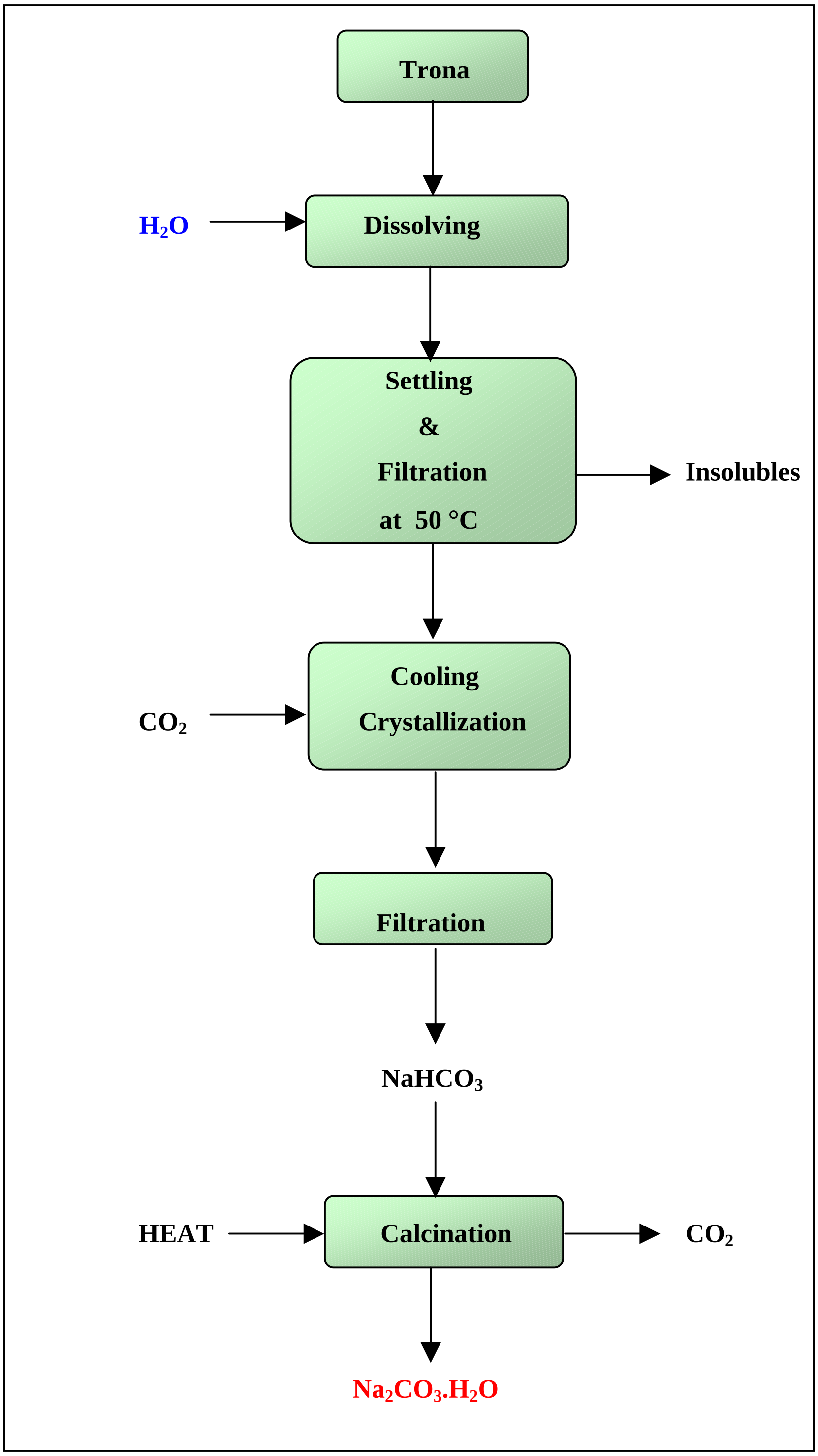

Figure 6. Flow diagram of carbonation process

Carbonation process has a narrower application then monohydrate and sesquicarbonate processes to trona mining in the world. Besides, carbonation process can be applied as an additional unit in settled plant either monohydrate or sesquicarbonate methods. The aim is the same by producing sodium bicarbonate as a product. However, the produced sodium bicarbonate can be converted to soda ash by calcining the crystals to obtain monohydrate product. CO_2 gases formed after calcination operation is regenerated in the carbonation unit.

CHAPTER 3

UNIT OPERATIONS OF SODA ASH PRODUCTION

The major parameters in process selection are: the characteristics of the trona deposit, available forms of energy and its costs and the geographical market under consideration for soda ash and suitable derivatives. The process selected must be considered in conjunction with the new developments. As mentioned above, monohydrate and sesquicarbonate processes, are preferably applied in conventional trona mining. Both approaches, however, involve the basic steps of dissolving the ore, filtering to remove insoluble impurities, crystallizing a sodium carbonate compound, and calcining the drive off excess carbon dioxide and water. According to the sesquicarbonate process, trona is crushed, ground and dissolved in water to remove the soluble organic compounds, and the solution is treated with activated carbon, filtered, and cooled so as to obtain crystals of sodium sesquicarbonate. Later on, sodium carbonate is produced by the calcination of sesquicarbonate. In the monohydrate process, trona is crushed, ground and calcined so as to transform into raw sodium carbonate. The raw soda is dissolved in water, treated with activated carbon in order to remove soluble organic compounds, filtered, and then crystallized evaporatively to obtain crystals of sodium carbonate monohydrate. Then, sodium carbonate monohydrate is dehydrated to produce anhydrous sodium carbonate. To remove soluble organic impurities, two conventional methods are generally used. One of them is the calcination of trona over a temperature of 675 K (402 °C). During this time, organic matters are burned and removed from trona ore. In the second method, trona is calcined below 650 K (377 °C) and the obtained raw soda is solvated in water. The solution is treated with activated carbon, and so organic compounds are adsorbed.

Monohydrate process incorporates the calcination of the trona near the beginning of the processing steps. This converts the trona into a crude soda ash, which still contains all of the insoluble materials. The crude soda ash is then dissolved in water, and the insolubles are removed from the solution in the same manner as in the sesquicarbonate process. Since soda ash has a nearly constant solubility in water (throughout the temperature range where monohydrate is the stable crystal form), the soda ash solution is evaporated, and the resulting sodium carbonate monohydrate crystals are heated to form dense soda ash. Most of the water vapor from the crystallization step is condensed and returned to the dissolvers. The final soda ash product from the monohydrate process is dense ash.

3.1. The Nature of Calcining Process

Solid-state pyrometallurgy consists of those high-temperature processes in which the primary metal-bearing species remain in the solid state throughout the process. Most operations in solid-state pyrometallurgy are preparation processes, which involve changes in the chemical or physical nature of a solid material. Physical preparation of material includes drying. Drying involves de-watering of the material by thermally assisted evaporation. Such preparation is needed prior to many processes in which the presence of significant quantities of water in the material would be detrimental in some way. The evaporation of water is an endothermic (heat-absorbing) process. This means that, in addition to the heat needed to bring the temperature of the substance up to the drying temperature, the heat of evaporation must also be supplied. Various types of dryers are available, the most important being rotary kilns and fixed-bed or fluidized-bed dryers. The rotary kiln consists of a long cylindrical drum inclined slightly to the horizontal and rotating about its long axis. The solids are introduced to the inside of the drum at the high end and migrate down the slope. As they migrate, they are turned over continually by the rotation of the drum. The fluidized-bed dryer is very similar in construction and operation to the fluidized-bed roaster (Hartman, 2001).

Calcination is preparation process in which chemically bound water and carbon dioxide or other gases are removed from a solid by thermal decomposition. The product of calcinations is always an oxide and is known as a *calcine*. When employed for the removal of water, calcining differs from drying in that it is not superficial water that is removed but water that is chemically bound. When calcinations compare with drying, it should be noted that there is often no sharply defined boundary between superficial and chemically bound water. With complex minerals some water is only loosely bound, while some is more strongly bound within the chemical structure of the mineral. In addition, superficial water may be present in the interstices between in mineral particles. If such a material is heated, the superficial water evaporates first. When the proportion of superficial water is low, some of the loosely bound water will begin to be removed. Thereafter, as heating continues, the more strongly bound water will begin to be removed.

As the process of calcination is more endothermic than drying, heat must be supplied at a relatively high temperature. A number of different types of furnaces are used. A shaft furnace is preferred when material is coarse. For materials of mixed particle size, or for materials that disintegrate during the process, a rotary kiln is used. When the materials are fine and of relatively uniform size, they can be calcined in a fluidized-bed furnace (Hu et.al., 1986). The rate at which calcination proceeds is determined by a number of factors. The major factor seems to be supply of heat from the environment to the particles. As with other solid-state processes, the reactions proceed from the outside of each particle so that concentric outer layers of the decomposition product are formed. Heat must be conducted through these layers if the inner core of unreacted material is to decompose. To promote the conduction of heat and so obtain reasonable calcinations rates, the operating temperatures must be significantly higher than is required for decomposition itself. Other parameters than these are calcination duration, and the particle size of the material. Calcination duration is directly related with the calcination rate and calcination temperature.

3.2. Trona Calcination

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

$$2(Na_2CO_3.NaHCO_3.2H_2O) \overset{90\text{-}150\ °C}{\Rightarrow} 3\ Na_2CO_3 + 5\ H_2O + CO_2 \qquad (11)$$

The mechanism is based on thermal treatment of the ore that affects its decomposition and the elimination of gangue minerals. The thermal decomposition of trona during calcining has been extensively studied. To produce the probable main product, dense soda ash, from trona requires the stoichiometry given in Eq. (11).

The calcining step is both a simple and an exceedingly demanding operation. Trona can be decomposed or calcined (Eq. 11) at any temperature over about 70 °C, but the rate does not become reasonable until the temperature are above about 120 °C. Above approximately 800 °C the entire ore fuses (Dogan, et.al., 1997).

This calcining reaction can be carried out on solid trona at about 150 °C or by steam stripping the carbon dioxide from a water solution at lower temperatures. Various sodium compounds can be produced in intermediate steps by manipulation of solution compositions, temperature and pressure. These are sesquicarbonate, anhydrous carbonate, monohydrate and bicarbonate. Calcining any of these compounds yields soda ash having various physical properties, crystal size, shape and bulk density (Saygılı and Okutan, 1996).

3.2.1. Dry Calcination

The dry calcination process is widely used one in which dry trona is subjected to calcination operation in industrial size rotary kilns.

Currently, the conversion of trona into soda is done industrially by calcining of the raw ore in rotary calciners at 120 °C or higher. It is postulated that the decomposition reaction according to Eq.(11) occurs only at temperatures beyond 160 °C. At lower temperatures wegscheiderite ($Na_2CO_3.3NaHCO_3$) and sodium carbonate monohydrate ($Na_2CO_3.H_2O$) form as intermediates (Ball et.al., 1991).

$$3(Na_2CO_3.NaHCO_3.2H_2O)_{(s)} \Rightarrow (Na_2CO_3.3NaHCO_3)_{(s)} + 2Na_2CO_{3\,(s)} + 6\,H_2O \quad (12)$$

$$2\,(Na_2CO_3.3NaHCO_3)_{(s)} \Rightarrow 5\,Na_2CO_{3\,(s)} + 3\,H_2O + 3\,CO_2 \quad (13)$$

In an aqueous solution of solubility equilibrium composition, trona is technically stable to the boiling point. Under dry conditions, trona is reported to be stable till ~ 55-57 °C (Ball, et.al., 1986). Above this temperature trona starts to decompose at a slow rate. Similar to the thermal decomposition of bicarbonate ($NaHCO_3$) this process is kinetically impeded and only reaches sufficiently high conversion rates for industrial applications at temperatures of 120 °C or higher (Demirbas, 2002). Besides, dry calcining of bicarbonate is employed in alternative process route for the production of soda.

$$2NaHCO_{3\,(s)} \Rightarrow Na_2CO_{3\,(s)} + H_2O + CO_2 \quad (14)$$

3.2.2. Wet Calcination

The other type of calcination, wet calcination has many advantages over dry calcination, except that the degree of decomposition is not as complete. This can be remedied by adding small amounts of lime, which will convert the bicarbonate to sodium carbonate.

Wet calcination process as taken from recent soda ash patent, is one of several possible configurations for this process. In both dry and wet types of calcination processes, the final product is obtained by precipitating sodium carbonate monohydrate crystals in evaporators, centrifuging the crystals, and dehydrating to the anhydrous dense soda ash in steam tube dryers or fluid bed dryers, as shown by the reaction:

$$Na_2CO_3.H_2O \Rightarrow Na_2CO_3 + H_2O \uparrow \qquad (15)$$

As is the case in all reactions in this field, they are reversible and driven in one direction or the other by concentrations, temperatures, and by removing components from the reaction medium (Chen, et.al.,2001).

Various patents addressed the possibility of wet-calcining slurry of sodium sesquicarbonate (or also trona ore or sodium bicarbonate) to produce anhydrous sodium carbonate or the monohydrate, which would perhaps be less expensive than dry calcining. The objective was also to form a more pure and higher- bulk-density soda ash product than can be obtained in a conventional dry calciners. Steam “stripping” of the excess carbon dioxide can be readily accomplished in either towers (such as the Solvay type tower) or crystallizers. Also the monohydrate or the anhydrous product can be crystallized directly from the decomposed solid, if desired, but the temperature needs to be over 109 °C and the pressure over one atmosphere for anhydrous soda ash. However, with either product, with practical time and equipment limitations the reaction does not go to completion. The concept has many virtues and it is quite new.

3.2.3. Microwave-induced Calcination of Trona

The objective in all methods of trona processing is to structure a trona-refining operation that will maximize economic returns for the long term that is consistent with safe and environmental safeguards. As solution mining becomes more popular, current methods, which are geared to accept dry trona, will need to be re-evaluated. It would be possible to alter existing systems to accept the slurry, but the added drying costs would make these options economically unattractive. An alternate possibility, called *wet calcination*, actually completes the decomposition with the trona remaining in solution. Whereas conventional processes require the soda ash to be crystallized out of a solution before calcinations to decompose the trona; microwave wet calcination process may decompose trona in solution by application of microwaves to soda ash without the need for drying.

The technical feasibility of a microwave-based trona process is investigated. Microwave-induced calcination of trona has the potential to re-evaluate many of the aspects currently necessary in the conventional processing of trona into soda ash. This includes high temperature calcinations, with the goal of improving economics and simplifying the process.

For microwave heating to be of benefit, it is concluded that the conversion of trona in solution to sodium carbonate (wet calcination) is imperative than dry trona. Since trona in solution absorbs microwaves better than dry alone. The amount of microwave energy that the trona absorbed is directly related with the operated power of microwave. The measurements of microwave are of input power (directly from the generator), reflected power (back to the generator from the load), and transmitted power (through the load). The power absorbed by the trona is then calculated by substracting the transmitted and reflected power from the input power. The studies in the literature showed that only the trona in solution was capable of absorbing most of the input power. The dry trona did not prove to be a very good absorbent alone. It is interesting to note that pure water only absorbed approximately a tenth of the power that the trona in solution absorbed, and the reactor's load was near zero in comparison. This is conclusive result that trona in solution is a very good microwave absorbent and an excellent candidate for decomposition in microwave field (Streuber and Cha, 1998).

3.2.4. Microwave Heating

Microwaves posses several characteristics that are not available in conventional processing (heating) of materials, including:

- Penetrating radiation
- Controllable electric-field distributions
- Rapid heating
- Selective heating of materials through differential absorption
- Self-limiting reactions
- Energy transfer, not heat transfer
- Heating starts from interior of the material body

Due to the strong absorption of microwaves by water, microwave drying of ceramics has been successful for both powders and bulk materials. While the cost of microwave energy makes microwave drying inefficient at high moisture contents, at low moisture contents the removal of water using conventional processes becomes inefficient, making microwave processes more competitive (National Academy Press, 1994).

The primary motivation for use of microwave heating has been time saving through rapid heating, rather than any non-thermal effects. Penetrating radiation (and reverse thermal gradients), the ability to superheat polar solvents, and the ability to selectively heat reactive or catalytic compounds were responsible for time savings realized in chemical processes. Finally, materials with permittivity or loss factors that change rapidly with temperature during processing can be susceptible to uneven heating and thermal runaway.

The chemical industry has long known of the ability of microwaves to provide quick and precise heating; however, the misconceptions about the benefits of microwave application to certain reactions have precluded common utilization aiding chemical reactions until very recently. Certain substances which contain charged particles (ions) or which contain molecules, such as silicon carbide, with a charged gradient (dipole moment) across the molecule can be preferentially heated.

3.2.5. Microwave Fundamentals

Development of new routes for the synthesis of solids is an integral aspect of materials chemistry. Some of the important reasons for this are the continuing need for fast and energy-efficient techniques, necessity to avoid competing reactions in known processes, and the challenge implied in the synthesis of metastable phases bypassing thermodynamically reversible routes.

Microwave synthesis is generally quite faster, simpler, and very energy efficient. The exact nature of microwave interaction with reactants during synthesis of materials is somewhat unclear and speculative. However, energy transfer from microwaves to the material is believed to occur either through resonance or relaxation, which results in rapid heating. This knowledge is widely used as the basis in the discussion of reaction mechanism (Rao et.al. 1999).

Microwaves are electromagnetic radiation, whose wavelengths lie in the range of 1 mm to 1 m (frequency range of 0.3 to 300 GHz. A large part of the microwave spectrum is used for communication purposes and only narrow frequency windows centered at 900 MHz and 2.45 GHz are allowed for microwave heating purposes. Very few microwave applications involving heating have been reported where frequencies of 28, 30, 60 and 83 GHz have been used.

As is well known, microwaves are produced by magnetrons, which are principally thermionic diodies with heated cathodes acting as sources of electrons. From the magnetrons the microwaves are generally directed toward a target (places in so-called microwave cavities) with the use of microwave guides. These guides are usually made of sheet metal, and the intensity distribution within waveguides is homogenized by the use of mode stirrers. In the microwave field, the electromagnetic flux of the microwaves as they pass through the sample causes a local distribution of charge along the sample. This charge causes dipolar molecules to try aligning with the field and causes ions to try to separate with the positive ions moving towards the negative part of the field and with the negative ions towards the positive area. However, as the field oscillates, it changes the charge distribution periodically so that the ions and dipoles can never quite line up and are continually readjusting to the field. This continuous readjustment causes the ions to essentially vibrate with the field, and the dipoles to rotate. Both of these movement cause friction among the ionic or dipolar particles resulting in rapid localized heating (Haque, 1999).

In general, materials fall into three categories, with respect to their interaction with microwaves; (i) microwave reflectors, typified by bulk metals and alloys, such as brass, which are therefore used in making microwave guides; (ii) microwave transmitters which are transparent to microwaves, typified by fused quartz, zircon, several glasses, and ceramics (not containing any transition element), Teflon etc.; they are employed for making cookware and containers for carrying out chemical reactions in microwaves; (iii) microwave absorbers which constitute the most important class of materials for microwave synthesis; they take up the energy from the microwave field and get heated up very rapidly (Rao et.al. 1999).

3.3. Leaching

Leaching is the primary extractive operation in hyrometallurgical processing. The ore is brought into contact with an active chemical solution known as lixiviant or leaching solution. Although one of the simpler steps in processing trona, the leaching of the calcined ore never-the-less generated a moderate patent literature. A patent by Hellmers et.al. concerns handling the solution temperature rise and steam generation, which could plug ducts and result in excessive leach tank turbulence as hot calcined ore contacts the leach liquor. The heat of solution is exothermic in addition to the high sensible heat of the hot calcined ore (Haynes, 1997).

Three important factors influence the viability of a leaching operation. These are as follows:

- the degree of dissolution that can be achieved
- the selectivity of the leaching reactions
- the cost of the lixiviants used.

Various other considerations enter into the leaching circuit design. The size to which the ore is ground helps determine both the completeness of calcining and the rate at which the calcine dissolves. The calcined ore dissolves very rapidly in fine particle size, especially compared to raw ore or coarser calcined ore. However, in order to obtain fairly complete leaching efficiency the soda ash solution is never quite saturated, typically containing about 28.5 to 30.0 % Na_2CO_3. Raw trona ore is ground to a fairly fine size to increase the solubility. The ore then is leached at as high temperature as possible to maximize the amount dissolved. This temperature is generally reported to be near the boiling point.

To optimize the extent of a leaching operation, both the thermodynamics and the kinetics of the process require attention. What becomes important is how long it takes for the leaching system to approach the equilibrium condition, and how much time the operation allows for it to do so. An understanding of kinetic factors is important in the implementation of trona leaching. Based on particle size, diffusion rates and rate of chemical reaction, kinetic decisions about the most suitable operating conditions can be made in a rational manner. Leaching kinetics can be assessed quite readily. For this, the solids are mixed in water and samples of leach liquor are taken over a period of time. The concentration of dissolved trona in the liquor can be plotted as a function of time. It is very important to remember that a leaching curve is very dependent on the conditions used in the test. The most important parameters taken in the tests are leaching time, leaching temperature, particle size and solid density of leach liquor (Muraoka, 1985).

In the implementation of a leaching system, an appropriate means of bringing the lixiviant and solid into intimate contact must be engineered. There are a variety of ways in which this can be done for trona. The method of contacting the solids and lixiviant does not influence the type of leaching reaction that can be used, but it can affect the rate at which it takes place (Clay, 1985). In trona processing, two types of leaching method can be mentioned. One of them is direct leaching of agitation used in the sesquicarbonate process, and the other is in situ leaching also known as solution mining. In agitated systems, trona are mixed with water in a vessel to form a slurry. To keep the solids in suspension, the slurry must be agitated in some way. Obviously, when the application of sesquicarbonate process, the raw trona solids first have been reduced to a fine particulate state. Whereas in situ leaching application, the water is pumped into the ore body through the drilling wells. The porosity of the trona has been supported this system. Both the extent and the rate of the leaching are directly related to that property.

3.3.1. In-situ Leaching (Solution Mining) of Trona

The solution mining of trona has long found an application as an attractive alternative to underground mechanical mining. However, numerous early efforts to solution mine virgin trona seem to meet with only limited success, and mechanical mining took the forefront, where it remains today.

A number of primary factors affect the commercial feasibility of a trona solution mining operation: design of stable solution mining cavities; trona bed thickness and quality; selection of the appropriate solvent in view of trona’s incongruent solubility; dissolving rate of trona and recovery of the sodium carbonate values from the solution remaining after solution mining has been terminated in a cavity.

The solution mining of trona has been improved with the first patent issued to Pike in 1945. Pike’s method employs a single well comprising an outer casing and inner casing. Hot solvent is injected through the inner casing to contact the trona bed, and the product is withdrawn through the annulus. This method proved unsuccessful, however, and currently there are two other approaches to solution mining that are actively being pursued. In one of these, which shall be designated a “Type I” solution mine, two or more wells are drilled into the trona bed and low-pressure connection is established by some means (hydraulic fracturing or directional drilling).

The practicing a “Type II” form of solution mining whereby a previously mined region is flooded, creating an underground lake. Dissolution of trona takes place and the brine is pumped to the surface for processing. The lake may also serve as a disposal for mine tailings.

It seems certain that solution mining will grow in importance in years to come. Thin beds are accessible only to solution mining as are deep beds. Mechanical mining is an expensive operation, and typically a third of the cost of producing a ton of trona is associated with the mining operation. Additional savings are to be realized in the processing of solution-mined product, since the need for solids handling is reduced. From the standpoint of economics, it is always advantageous that the product brine to be concentrated, but it appears that modern processes can economically handle brines as dilute as 8-wt% total alkali value (Haynes, 1997).

3.3.2. Direct Leaching (Sesquicarbonate Process)

The sesquicarbonate technology consisted of mining trona ore, leaching it, purifying the solution, recrystallizing trona, calcining it and selling the product directly. This process became known as the sesquicarbonate process because trona or sesquicarbonate is not only the ore but also the purified product prior to conversion into soda ash. The virtues of this process its simplicity and the easy cyclic nature of the dissolving, solution purification and crystallization sequence. The features of the sesquicarbonate process are given in Section 2.7.5.in Chapter 2. The basic principle in the that type of leaching of trona is based on the raw trona ore leaches more slowly than after being calcined, and the soda ash product that is directly produced is “light” soda ash.

There is a very large quantity of circulating leach liquor because of the comparatively small amount of ore dissolved, and the product crystallized, per pass. This liquor tends to change constantly in composition and is difficult to control because of carbon dioxide loss at the high leach and processing temperature.

The ore is mined from seams generally underlain by and sometimes containing small impurities, so some dissolved organics are always present –usually more in the sesquicarbonate liquor than with calcined trona. In addition, the treatment is needed to remove iron leached from the ore, as well as heavy metals dissolved by corrosion. The crystals produced are small and elongated, and upon calcining make a low bulk density product.

3.4. Crystallization

Sodium carbonate is an incongruently dissolving double salt; that is, when dissolved in water, the sodium sesquicarbonate is not in equilibrium with water and attempted crystallization results in the production of a different salt. Therefore, when crude trona is dissolved in hot water, sodium sesquicarbonate cannot be crystallized from solution by cooling or evaporation. The temperature and the composition of the solution are prepared by using phase diagrams. The detailed information of phase diagram is given in Section 3.4.1.

Crystallization of sesquicarbonate is generally more difficult than crystallization of sodium carbonate monohydrate as the to trona tends to form needle-shaped, elongated crystals or clusters of such crystals. It is hard to settle and dewater these crystals well enough to obtain a solid product of the desired bulk density and purity. Crystal modifying additives can be used to improve the crystallization, as noted, but their effect is not perfect, they are expensive, and often secondary problems arise, such as foaming, inconsistent operation, additional color o drying and so forth. Even with the additive, however, dewatering still is somewhat more complicated than it would be if a larger, better shaped crystal are produced. It is debatable whether filters or washing type centrifuges, but generally the latter are chosen. Some washing of the centrifuged cake is done to reduce the impurities with the product, and a moderate amount of sesquicarbonate brine is bled from the system both for CO_2 control and to remove impurities.

Above 109 °C, at slightly elevated pressure, the evaporation of soda ash solutions will crystallize anhydrous sodium carbonate as the stable phase. Thus the water of hydration of the otherwise produced monohydrate could be removed in the evaporators with multiple-effect economy, rather than in the less thermally efficient dryers. The capacity of either gas fired or steam-tube dryers would be greatly increased and the water would be reclaimed in the evaporator condensate. The crystallizers are of the multiple-effect evaporative cooling, external circulation Oslo type, in which a fairly thick crystal magma is always kept in the body to allow better crystal size and habit control, and to produce a more uniform product. The slurry density is maintained by withdrawing a partially settled solution from the crystallizers` settling chambers to advance primarily liquor to the next stage. Slurry is removed from the bottom of the circulating section as desired to maintain a slurry density of 15 to 30-wt %.

3.4.1. Phase Diagram (Equilibria)

An understanding of soda ash-water phase diagram that is shown in Figure 7 is critical to the trona solution mining and to the processing of the brines so produced. Phase diagrams are the main road maps guiding the process design. As for all road maps and ventures, it is crucial that they are for the right system with the relevant components. They show what solid sodium carbonate hydrates are in equilibrium with the liquid phase as a function of temperature and concentration of sodium carbonate. In this diagram, the curve traces the solubility, expressed as percent Na_2CO_3, for temperatures between –2.1 °C and 82 °C. A diagram of this kind is useful in tracing the effects of cooling, heating, or changing concentrations (Saygılı and Okutan, 1996).

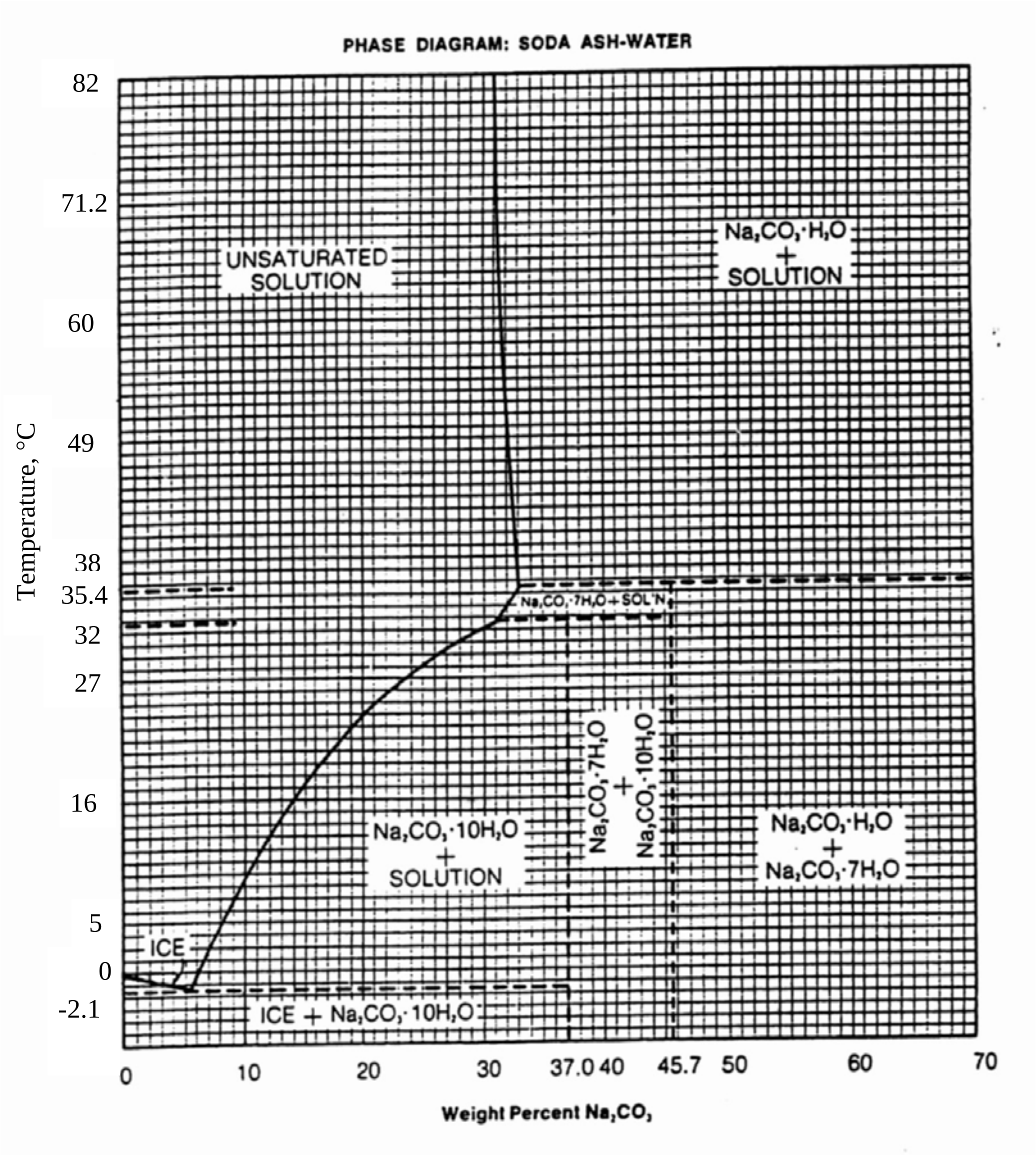

Figure 7. Phase diagram of soda ash-water system (Soda Ash, 1992)

In this diagram the curve traces the solubility, expressed as percent Na_2CO_3, for temperatures between -2.1 °C and 82 °C. The area above and to the left of this curve is the region of unsaturated solutions within which complete solubility is obtained. Below and to the right of the curve undissolved solids exist in contact with saturated solutions, or the liquid phase disappears entirely, and only solids exist.

The fundamental processes, which ultimately determine the success or failure of the operation, are those that occur at the liquid-solid interface. Thermodynamics (phase equilibria) plays an important role by providing the driving force for phase transitions, i.e., dissolution and crystallization. Dissolution rate phenomena are also of critical importance. In some systems chemical reactions must be considered. Chemical reactions can impose additional equilibria on the system and they can also affect dissolution rates. Much of the discussion to follow will focus on sodium salts and sodium salt hydrates that can be formed stoichiometrically from the ternary system H_2O-CO_2-Na_2O. The specific compounds of interest are located on a triangular diagram in Figure 8. Triangular diagrams are particularly convenient for developing mass-balance relationships. Note the regions corresponding to solid sodium bicarbonate or nahcolite ($NaHCO_3$), trona ($Na_2CO_3.NaHCO_3.2H_2O$), wegschederite ($Na_2CO_3.3NaHCO_3$), anhydrous sodiumcarbonate (Na_2CO_3), sodium carbonate decahydrate or natron ($Na_2CO_3.10H_2O$) and ice.

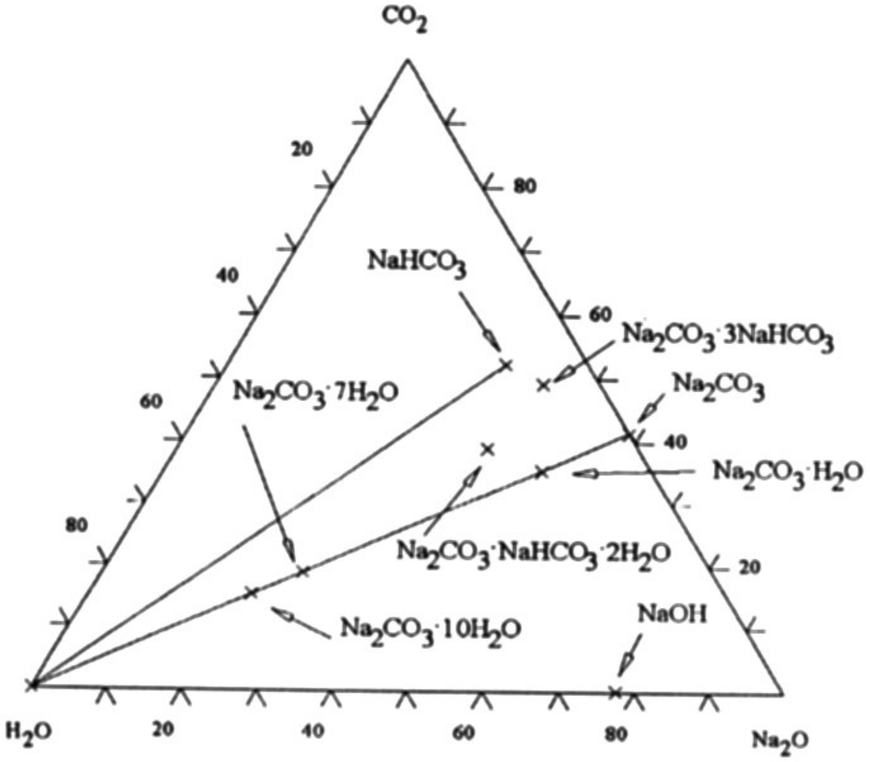

Figure 8. Location of various sodium salts on a H_2O-CO_2-Na_2O ternary system (Haynes, 1997)

CHAPTER 4

MATERIALS AND METHODOLOGY

4.1. Materials

The trona samples used in this study were taken from the trona deposit in Beypazarı located 100 kilometers northwest of Ankara. Beypazarı trona deposit consists of two lensoidal bodies named as the upper vein (seam) and the lower vein (seam). Due to limited development and preparation work in the mine, the samples named as U3, U4, U5 and U6 (Figure 2) taken from different layers in the upper vein and were mixed to prepare the “representative trona ore sample”. The amounts and the grades of the samples are tabulated in Table 6.

Table 6. Trona grade variations in Beypazarı Trona deposit

Layer Name	**Grade, % Trona**	**Taken Amount, kg**
U3	73.53	43.5
U4	91.82	22.5
U5	91.88	30.0
U6	92.63	20.2
Representative samples	85.12	Total : 116.2 kg

Characteristics of these layers are given in Table 7.

Table 7. Characteristics of different layers

	U3	U4	U5	U6
Na_2CO_3	34.48	43.06	43.09	43.44
$NaHCO_3$	27.84	37.76	35.45	35.25
Total Alkalinity, % Na_2CO_3	52.04	66.88	65.46	65.69
Trona, %	73.53	91.82	91.88	92.63

The blended sample (116.2 kg) was first crushed to the size of -19 mm by jaw crusher. Half of the -19 mm sample was divided into four parts. Then each part was reduced to different size fraction by crushing and screening. At the end, five samples of different size namely, -19 mm, - 12.7 mm, -9.53 mm, -6.35 mm and -3.35 mm, were prepared and kept in 0.5 kg lots nylon bags to prevent moisture or carbon dioxide contact. The -19 mm sample was kept in stock separately until the determination of the optimum particle size. After determined the optimum size, this fraction was ground to that particle size.

The hand-picked trona samples having a 99.5 % trona grade were also obtained from Beypazarı deposit. These were used in the analyses of XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope) for the determination of the structural changes during the thermal decomposition of trona.

4.2. Analysis of Trona Samples

The representative Beypazarı trona ore sample was analyzed to examine the mineralogical structure and chemical composition. The chemical analyses of representative sample are given in Table 8 and Table 9.

Table 8. Chemical composition of the representative Beypazarı trona sample

Component	**Weight, %**
$NaHCO_3$	33.00
Na_2CO_3	38.59
Excess $NaHCO_3$	2.43
Total Alkalinity, % Na_2CO_3	59.40
Insolubles	15.30
NaCl	0.025
Na_2SO_4	0.026
Loss of ignition	25.27
TRONA	**84.70**

Table 9. Chemical analysis of the Beypazarı representative trona ore sample by semi-quantitative optical spectrophotometer

Element	%
Na	(main element)
Mg	0.7
Ca	0.7
Fe	0.4
Al	0.7
Ti	0.01
Si	> 4

Undetected elements and detection limits as %

DL	%	DL	%	DL	%	DL	%	DL	%
Co	0.004	Cr	0.004	Cu	0.0004	Ga	0.01	Ge	0.01
Mn	0.01	Nb	0.004	Pb	0.004	Sn	0.004	V	0.004
Ag	0.0004	In	0.004	Bi	0.002	Mo	0.004	Sc	0.004
Zr	0.01	Y	0.004	Au	0.004	Cd	0.04	Ce	0.4
La	0.01	Ni	0.002	Ta	0.2	Tl	0.004	B	0.004
W	0.1	Zn	0.1	Sb	0.04	As	0.4	Ba	0.02
Sr	0.04	Li	0.1	P	1	Te	0.4		

a. Total alkalinity (Na_2CO_3 %) is determined by colorimeteric titration of soda ash. The details of the method are given in Appendix A.1.

b. Sodium bicarbonate ($NaHCO_3$ %) is determined by $BaCl_2$ titration. The details of the method are given in Appendix A.2.

c. Loss of ignition is determined by gravimetric and Thermogravimetry analysis.

Trona grade was calculated by the summation of trona mineral and nahcolite mineral contents. The details of grade determination calculations are given in Appendix A.3.

The total alkalinity and insoluble content of different size fractions of sample are given in Table 10.

Table 10. Chemical analysis of size fractions

Particle Size, mm	Weight, %	Total Alkalinity, % Na_2CO_3	Insolubles, %
-19 + 12.7	21.76	68.31	2.64
-12.7 + 9.53	10.45	64.83	7.60
-9.53 + 6.35	10.55	64.18	8.50
-6.35 + 3.35	11.95	62.08	10.91
-3.35	45.27	53.87	23.37
Total	100.00		

As seen from Table 10, total alkalinity is decreasing with particle size fineness. It means that insoluble gangue minerals are passing into fine size fractions more than trona mineral due to their friability. Analyses of Beypazarı trona samples were also conducted by TG-DTG analysis to determine the heating characteristics and XRD analysis to determine the crystallographic or mineralogical structure. TG-DTG and XRD analyses of representative Beypazarı trona ore sample are given in Figure 9 and Figure 10, respectively.

TG-DTG curves of sample coincide with the loss of ignition content of sample given in Table 8.

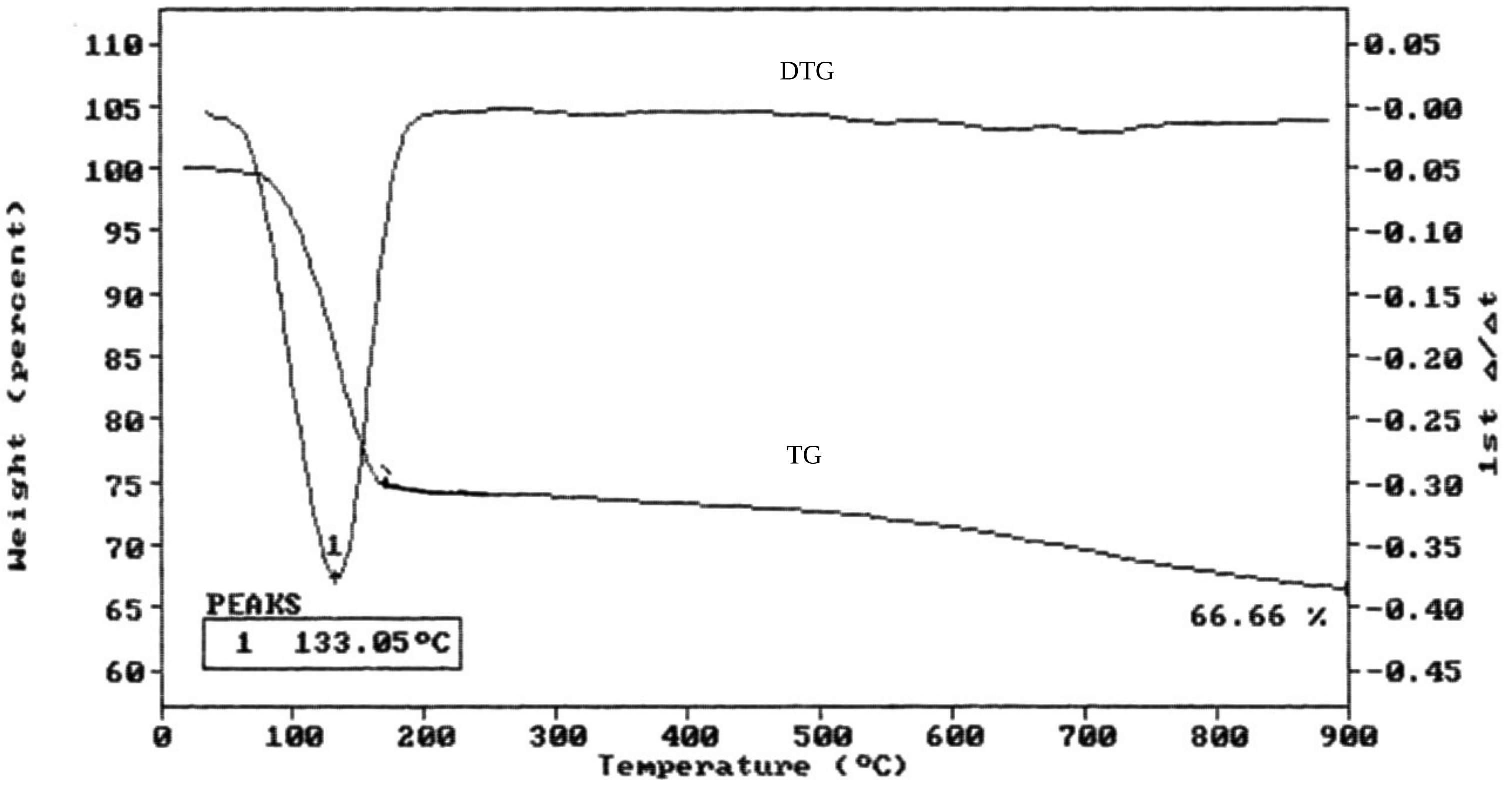

Figure 9. TG and DTG curves of representative trona ore samples

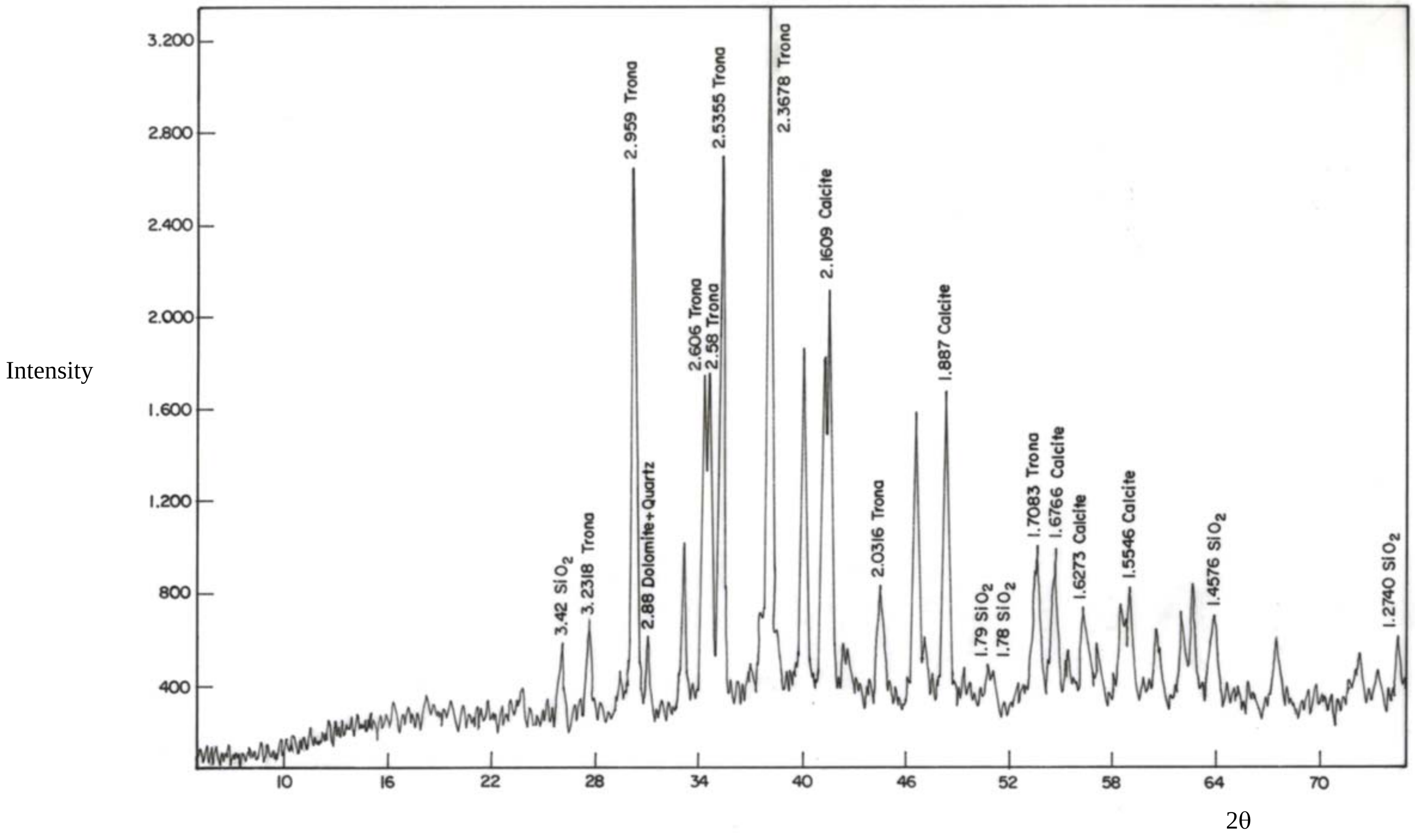

Figure 10. XRD analysis of representative Beypazarı trona ore sample

The X-ray diffraction pattern in Figure 10 confirms that the dominant mineral is trona along with some nahcolite, trace amounts of pirssonite and thermonatrite. Calcite, zeolites (analcime, klinopitolite), feldspar and clays were the most common gangue minerals within the associated rocks of the trona deposit. In the glycolated trona pattern, mixed layer smectite clay could be seen. The trona crystals, which are generally white and occasionally grayish due to the presence of impurities, formed in massive beds and disseminated crystals in claystone and shale. Zeolitization, dolomitization and chlorization are rather common within the associated rock units of the trona and probably occurred shortly after deposition, or during diagenesis.

4.3. Equipment and Methodology

The production parameters of soda ash from Beypazarı trona ore studies were focused on two points: calcination and leaching.

4.3.1. Calcination

The calcination of trona was extensively studied by three type of calcination:

a. Muffle furnace calcination
b. Up draught calcination
c. Microwave calcination

The calcination tests were first performed in the Memmert brand heavy-duty muffle furnace with 2000 watts power. Five different size fractions, namely -19 mm, -12.7 mm, -9.53 mm, -6.35 mm and -3.35 mm samples (sieve analysis of these feed are given in Appendix A.4.) were heated at three different calcination temperature of 150 °C, 175 °C and 200 °C, respectively. Since the thermal decomposition of trona is an endothermic reaction (Solvay Technical

Publication, 2001). The furnace temperature was set before the calcination and then the sample was put into the furnace with stainless steel container. The sample weight was 35-40 grams for each run. The calcination operation was terminated when weight loss reached around 25-26 %. This much weight loss is the theoretically maximum reachable weight loss for the trona sample.

The next set of calcination experiments were carried out with up draught furnace designed and built in workshop of Metallurgical Engineering Department of Middle East Technical University. Figure 11 illustrates the up draught furnace used in the experiments.

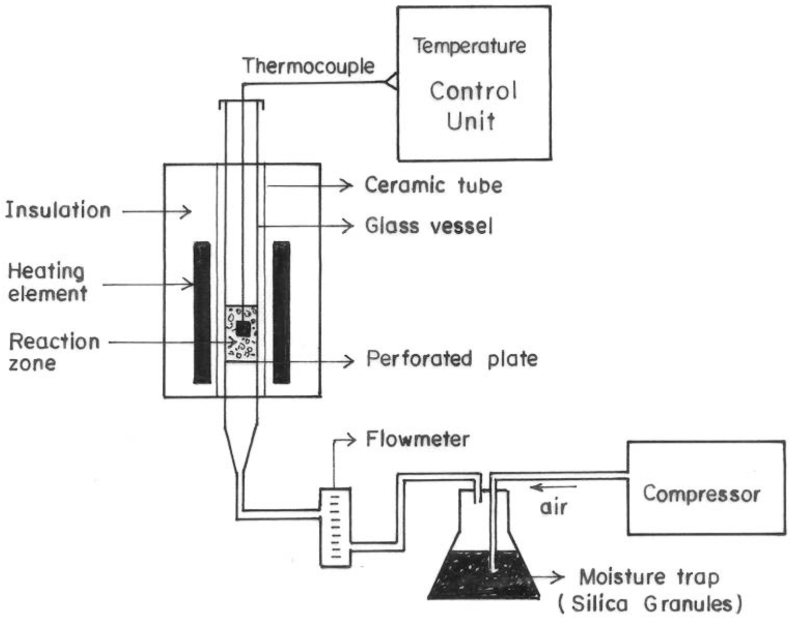

Figure 11. Up draught calcination furnace

This system is consisted of a 50 mm inner diameter glass tube with welded, 2 mm thick, 50 mm diameter porous silica plug (perforated plate) acting as the distributor plate. Glass tube was inserted into vertical tube furnace, which had its own temperature control device. Air for calcination was introduced from the bottom end of the glass tube by means of compressor. The experimental procedure involved heating of empty system to desired test temperature under air flow. Upon reaching a steady temperature inside the system, air flow was stopped and pre-weighed sample was introduced into the system from the top and air flow restarted. Upon completion of test, air flow was stopped and calcined sample was removed from the glass tube and weight losses were recorded. Experiments were performed in three different calcination temperatures of 150 °C, 175 °C and 200 °C.

Calcination operation was also performed with a kitchen type Moulinex brand name microwave oven with a 50 Hz frequency, 900-watt maximum power. The microwave oven has the inner dimensions of 33.5x21cmx33cm with a rotating circular glass plate. Experiments were conducted in microwave oven by using dry solid samples so the process is named as dry type microwave calcination. Samples having a particle size of -6.35 mm were used in dry microwave calcination in the power settings of 400 watts, 620 watts and 900 watts. The effect of the particle size in microwave calcination was studied by calcination experiments at the power settings of 620 watts. To examine the effect of calcination time, samples were heated in pre-determined times 1.50, 3.00, 5.00, 7.00 and 10.00 minutes. For each run approximately 30 grams of dry sample in a pyrex erlenmeyer flask was placed in microwave oven. Before and after each run, the sample weight was recorded as ± 0.01 g accuracy.

Another series of experiment was conducted in microwave oven by applying the principle of wet calcination. Before the wet calcination operation, trona solution samples having 10 grams of dry trona in 1000 cc water was prepared as a stock solution. Then, 50 cc solution samples were pipetted out from the stock, put in a 500 cc flat bottom glass flask to prevent the loss of solution by splashing out of solution during calcination. After heat treatment, samples were taken out from the oven and $NaHCO_3$ content of samples was determined by $BaCl_2$ titration method. Chemical analysis of $NaHCO_3$ determination is selected in wet microwave calcination instead of weight loss as in dry microwave calcination due to the form of the samples. Microwave oven used in calcination studies is shown in Figure 12.

Figure 12. The microwave oven used for calcination

4.3.2. Leaching Experiments

Agitated leach experiments of the trona samples were conducted in a 400 cc glass beaker. The leaching experiment of both calcined and uncalcined samples were carried out with 30 grams of –6.35 mm size samples at 25 % solids by weight (S/L ratio of 1:4). The temperature of the leaching was adjusted by setting the temperature of the water to be used in the experiments to that leaching temperature, immediately before the leaching experiments. The pregnant leach solution was analyzed for Na_2CO_3 % by colorimetric titration method to determine the leach recoveries. The simplified leaching and titration equipment is illustrated in Figure 13.

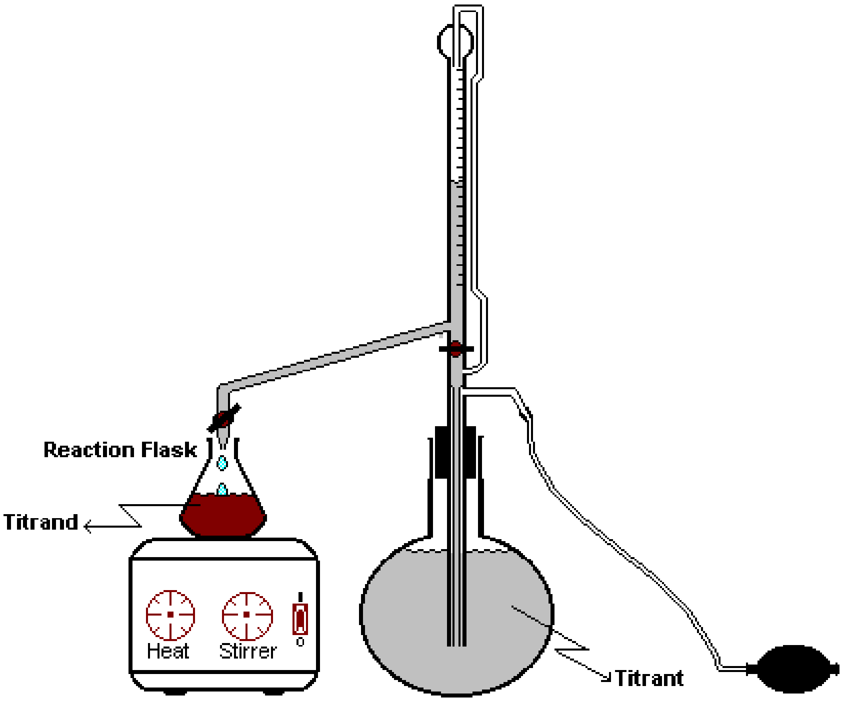

Figure 13. Leaching and titration equipment

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Calcination of Trona

Calcination is a necessary step in the production of soda ash from trona. It is accomplished by heating trona to an appropriate temperature to drive away CO_2 and H_2O. The calcination reaction may proceed in a sequence of steps according to the following reactions. Depending on the conditions, these may result in the formation of sodium carbonate monohydrate ($Na_2CO_3.H_2O$), sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$), or wegscheiderite ($Na_2CO_3.3NaHCO_3$). The rates of formation and subsequent decomposition of these compounds are vital in the overall efficiency of the calcination stage of the process (Ball, et.al. 1992):

- Decomposition of sesquicarbonate to produce wegscheiderite and sodium carbonate monohydrate:

$$3(Na_2CO_3.NaHCO_3.2H_2O) \Rightarrow 3NaHCO_3.Na_2CO_3 + 2Na_2CO_3.H_2O + 4H_2O \quad (16)$$

- Decomposition of monohydrate:

$$2\ Na_2CO_3.H_2O \Rightarrow 2\ Na_2CO_3 + 2\ H_2O \quad (17)$$

- Decomposition of wegscheiderite:

$$3NaHCO_3 . Na_2CO_3 \Rightarrow 2.5\ Na_2CO_3 + 1.5\ H_2O + 1.5CO_2 \qquad (18)$$

In this part of the study, calcinations of Beypazarı trona was investigated in order to optimize the process parameters, to determine the end products and their properties. Calcination was carried out employing three different methods using a muffle furnace, an up draught furnace and microwave oven.

5.1.1. Laboratory Type Muffle Furnace Calcination

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

$$2\ (Na_2CO_3.NaHCO_3.2H_2O)_{(s)} \Rightarrow 3\ Na_2CO_{3\ (s)} + 5\ H_2O + CO_2 \qquad (19)$$

Both chemical analysis and also TG analysis of representative trona ore samples showed that 25-26 % of weight loss would be realized at the end of the complete calcination. CO_2 gas and H_2O vapor removal are indicated in the weight loss of original uncalcined samples.

This first group of experiments was performed in a muffle furnace to get general idea about calcination of Beypazarı trona. The weight loss was in good agreement with that the expected (theoretical) weight loss value of 25.27 % for the formation of sodium carbonate. The percentage of weight loss was calculated by using Eq. (20).

Weight loss % values were calculated from the decrease in sample weight, W_0-W, at any time with the equation:

$$W_{loss}(\%) = \frac{W_0 - W}{W_0} * 100 \qquad (20)$$

W_{loss} = Weight loss %

W = sample weight at any time (g)

W_0 = weight of original sample before calcination (g)

During calcination process, 2 moles of trona, which is 452 grams, converted to 3 moles of sodium carbonate (318 g), 5 moles of water (90 g) and 1 mol of carbon dioxide (44 g). Beypazarı trona ore is having a grade of 84.70 %. After calcination excess water and carbon dioxide are driven off so the theoretical weight loss for that grade is 25.11 %.

The effects of various calcination parameters on weight loss of trona were investigated to better understand the calcination process. The calcination parameters studied were

- Calcination temperature
- Calcination duration
- Particle size

The particle size effect was studied with the samples of particle size -19 mm, -12.7 mm, -9.53 mm, -6.35 mm and -3.35 mm. Calcination temperature effect was studied in the ranges of 150 °C, 175 °C and 200 °C. Calcination operation was continued until the weight loss remained constant. The studied calcination parameters are tabulated Tables 11-13 in Appendix A.5. The graphical results of changes in weight loss are given in Figures 14-20.

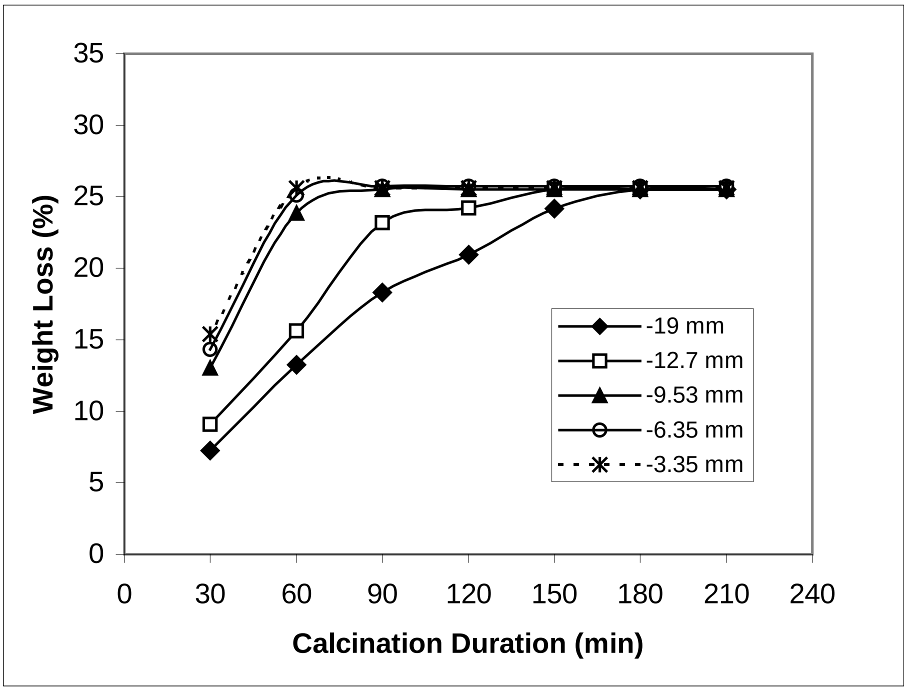

Figure 14. Effect of calcination duration on weight loss of trona in a muffle furnace at 150 °C calcination temperature

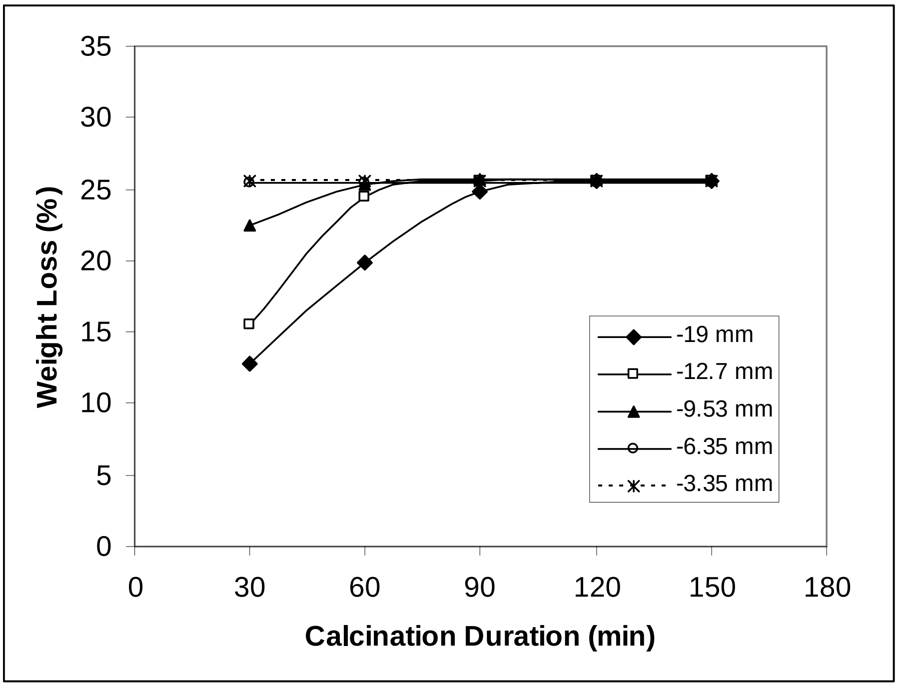

Figure 15. Effect of calcination duration on weight loss of trona in a muffle furnace at 175 °C calcination temperature

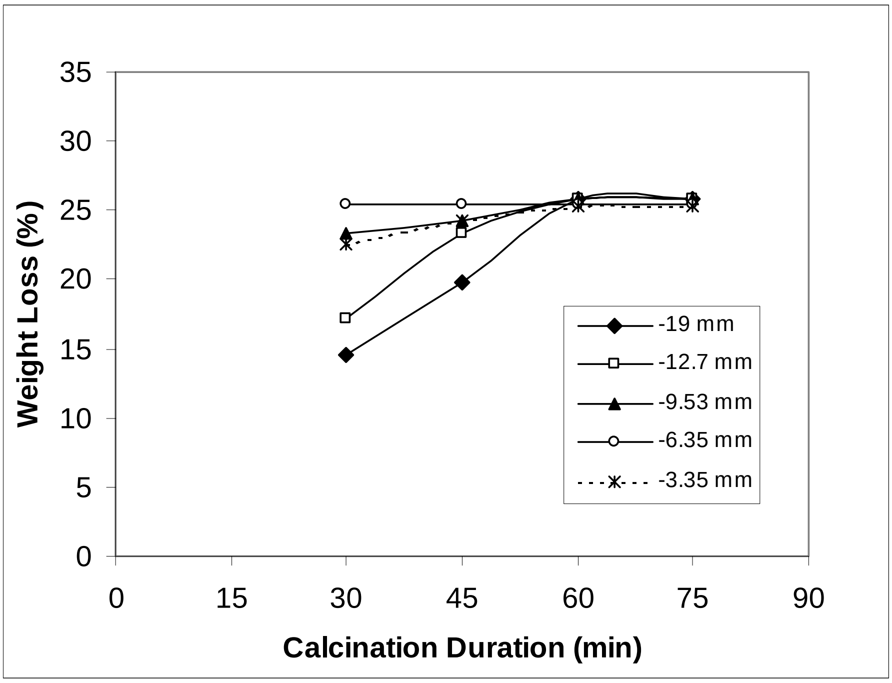

Figure 16. Effect of calcination duration on weight loss of trona in a muffle furnace at 200 °C calcination temperature

Experimental results showed that weight loss % is increasing with calcination temperature and decreasing with particle size. It was concluded that the coarser particles require longer calcination time for complete calcination because of the slow heat transfer to the inner part of the particle. Calcination is completed in a shorter time for fine size particles. The weight loss of –3.35 mm particles was lower than –6.35 mm particles. Lower weight loss might be explained by the low porosity of the compact bed.

In addition, the fusion on the surface of the particles and considerable sintering of fine sized particle samples were observed which causes the difficulty in exhausting of CO_2 and water vapor at high calcination temperatures of 200 °C. The retardation of calcination process beyond this point may be due to changes in the nature of the remaining Na_2CO_3, or the structure of the Na_2CO_3 product surrounding the unreacted $NaHCO_3$.

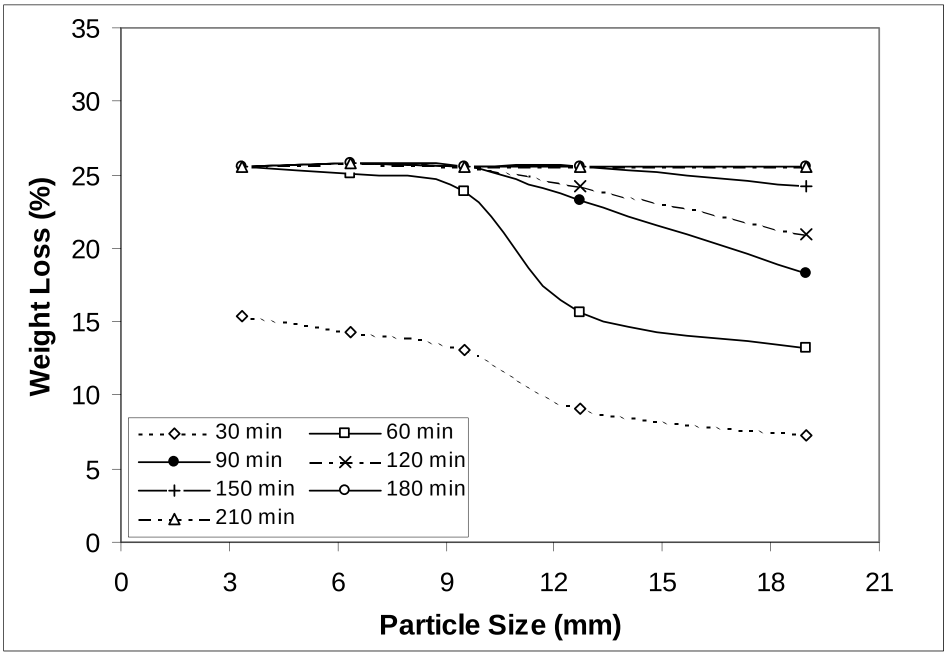

Figure 17. Effect of particle size on weight loss at 150 °C calcination temperature

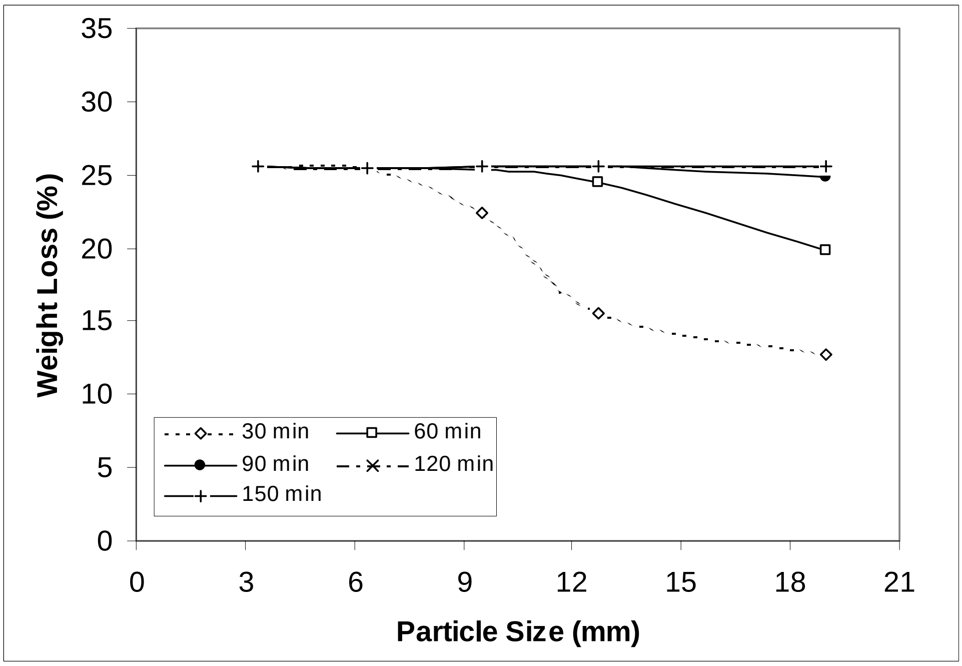

Figure 18. Effect of particle size on weight loss at 175 °C calcination temperature

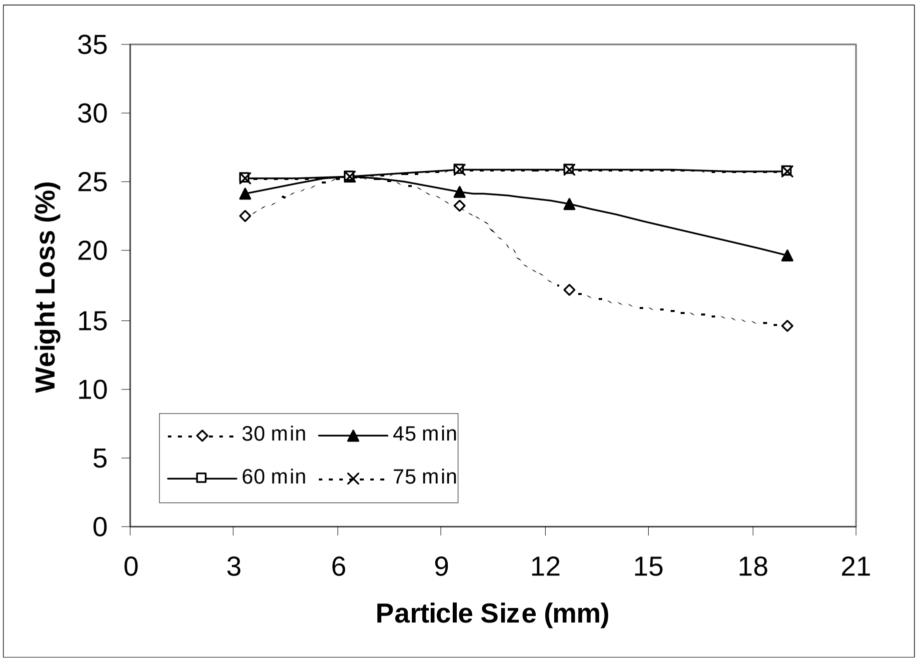

Figure 19. Effect of particle size on weight loss at 200 °C calcination temperature

As an economical view of calcination process, the optimum calcination conditions are evident with -6.35 mm trona samples at 175 °C calcination temperature.

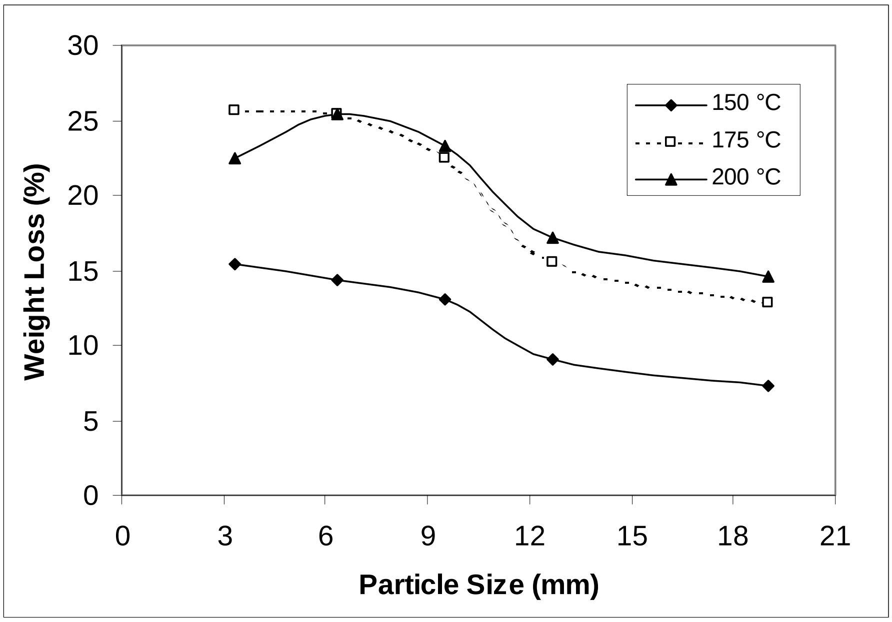

Figure 20. Effect of temperature for different particle size samples in 30 minutes of calcination

It was concluded from the repeated experiments that 30 minutes of calcination time was enough for the complete calcination of -6.35 mm trona material. The basis of calcination process said that calcination operation should be made with heat transfer through the particles in the furnace. The conversion of $NaHCO_3$ to Na_2CO_3 was occurring at high rate in the high temperatures of calcination e.g. 200 °C.

5.1.2. Up Draught Furnace Calcination

Calcination process was also investigated by using the previously described up draught furnace. The sample solids are contained in a glass vessel and air introduced into the system via a distributor.

Experiments are conducted at three different temperatures, 150 °C, 175 °C and 200 °C. The adjustment of the airflow creates some problems. At a low air velocity the solids are in a packed-bed or fixed-bed state while solids are thrown away from the heating zone at a high airflow rate. During the tests, attention was given to the adjustment of compressed air flow. At a low airflow rate, the solid samples are in a packed-bed or fixed bed state and adverse effect of insufficient air flowing was observed noticeably for the small particle size of -3.35 mm. As the gas velocity is increased, the lifting force eventually overcome the weight of the particles and eliminate the interparticle forces, and the air with exhausted gases of CO_2 and H_2O found a way to go through the interparticle void space. When the gas flow was too high the tap was thrown away from the top and then the possibility of solid leaking was increased obviously. However, under the conditions of good adjustment of air flowing and temperature, trona decomposition was carried out for up draught in shorter time than it was in the muffle furnace.

The calcination parameters; particle size, calcination duration and calcination temperature have been investigated using the up draught furnace. The results are tabulated in Tables 14-16 in Appendix A.6. and plotted in Figures 21-28.

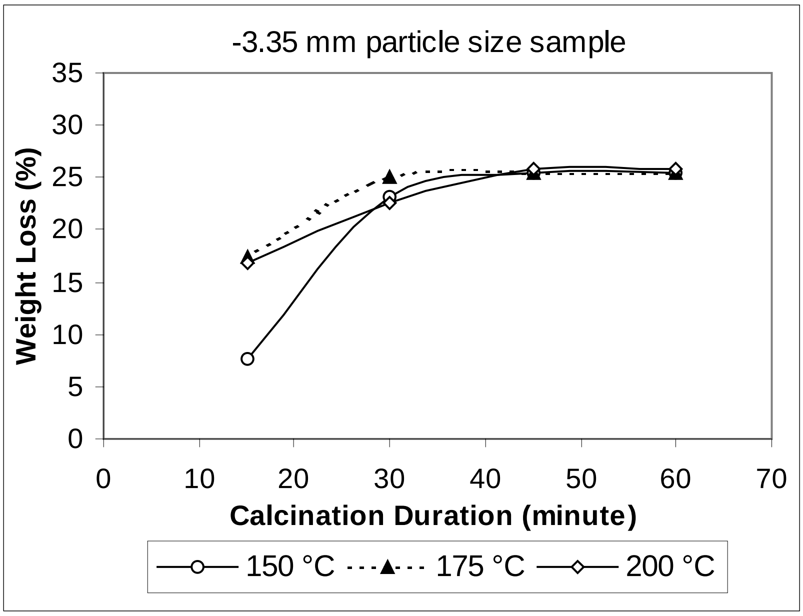

Figure 21. Effect of calcination duration on the weight loss of -3.35 mm trona sample calcined in an up draught furnace different temperatures

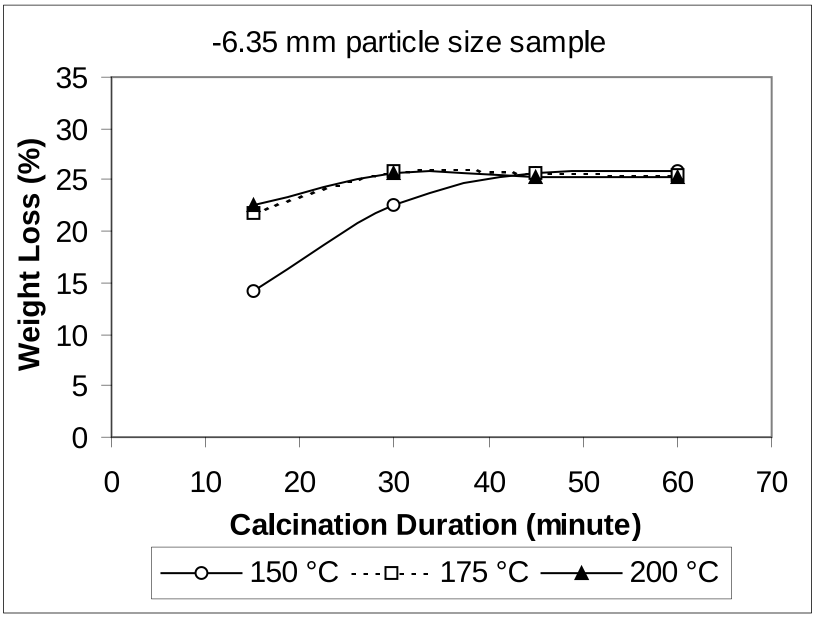

Figure 22. Effect of calcination duration on the weight loss of -6.35 mm trona sample calcined in an up draught furnace at different temperatures

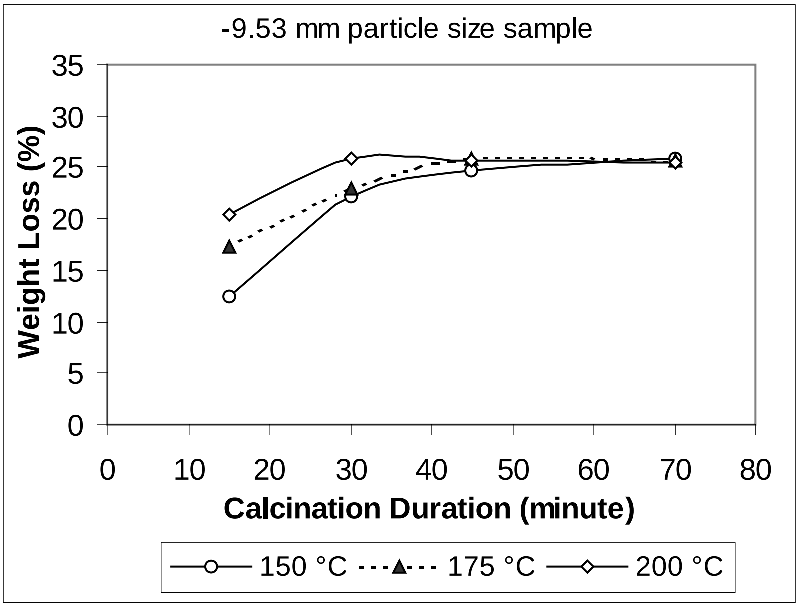

Figure 23. Effect of calcination duration on the weight loss of -9.53 mm trona sample calcined in an up draught furnace at different temperatures

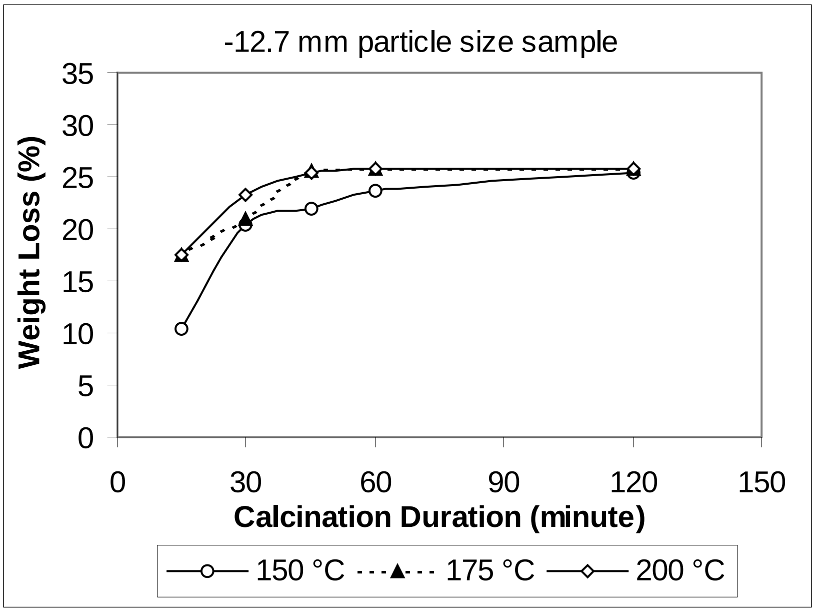

Figure 24. Effect of calcination duration on the weight loss of -12.7 mm trona sample calcined in an up draught furnace at different temperatures

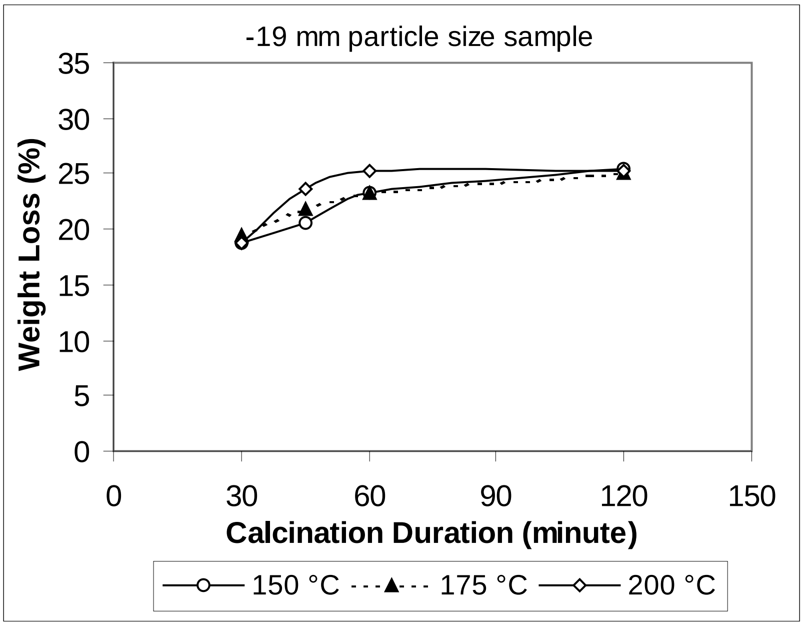

Figure 25. Effect of calcination duration on the weight loss of -19 mm trona sample calcined in an up draught furnace at different temperatures

The decomposition or trona appeared to be a single stage process across the temperature range studied (150-200 °C) and the complete weight loss was realized in a short time. It is possible to interpret that such short time decomposition might relate directly to the heating system and air flowing system through the particles. Sintering problem as observed in the muffle furnace for the particle size of -3.35 mm samples again occurred in somewhat lesser degree at high temperatures. However, the compaction of particles was prevented by flowing air. The effect of sample amount on the weight loss-time data was also researched by the initial experiments and it was found out that large amount of material increased fusion effect. So that sample amount was limited to 35 grams.

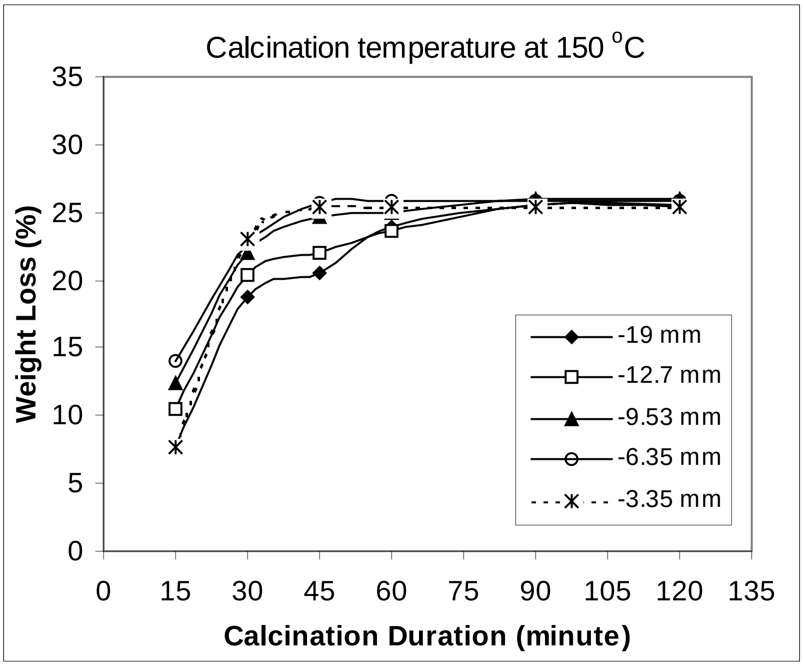

Figure 26. Up draught calcination of different size particles at 150 °C

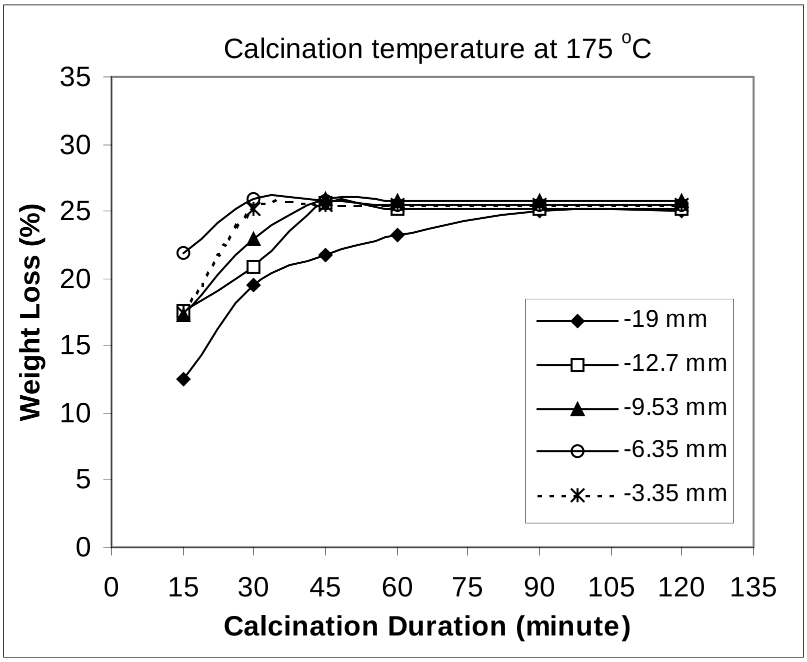

Figure 27. Up draught calcination of different size particles at 175 °C

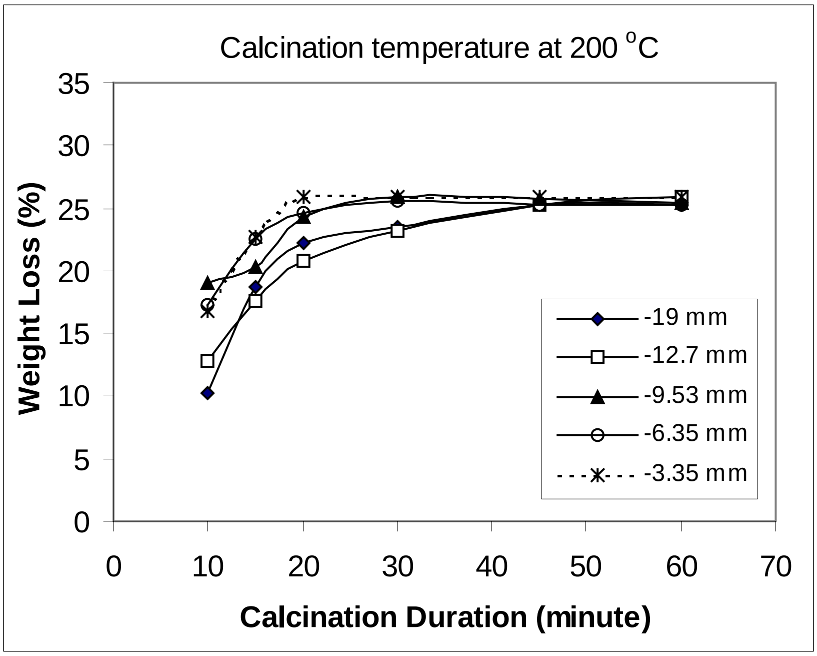

Figure 28. Up draught calcination of different size particles at 200 °C

Such rapid decomposition produced Na_2CO_3 product by constant temperature runs for up draught furnace in shorter time than that was in muffle furnace.

When analyzing the calcination duration, that was not continued to the longer times of 100-120 minutes. It was observed that complete calcination was realized in 80-90 minutes for coarsest particle size in the up draught calcination.

5.1.3. Dry Type Microwave-Induced Calcination

Microwave-induced calcination of trona has the potential to re-evaluate many of the aspects currently necessary in the conventional processing of trona into soda ash. This includes short time calcination, with the goal of improving economics and simplifying the process.

The goals of this part of the study are to explore the feasibility of producing soda ash from trona using a microwave process, to investigate the best possible process for converting all of sodium bicarbonate ($NaHCO_3$) content in trona to the required value into sodium carbonate or soda ash and to study the kinetics of the reaction. All of the comparing calcination experiments were examined by using samples having particles size of -6.35 mm. Since this particle size is the optimum particle size in the previously used heat treatment methods.

One series of experiment was conducted in microwave using dry samples so the process is named as dry type microwave calcination. For each run approximately 30 grams of dry sample was put in a glass beaker (microwave transparent) in three different microwave power settings as 400 watts, 620 watts and 900 watts.

In order to examine the effect of calcination time, the samples were heated for pre-determined times of 1.50, 3.00, 5.00, 7.00 and 10.00 minutes. Before and after each run, the sample weight is recorded ± 0.01gram accuracy. The weight loss values are calculated for each test and are tabulated in Tables 17-18 in Appendix A.7. and plotted in Figure 29.

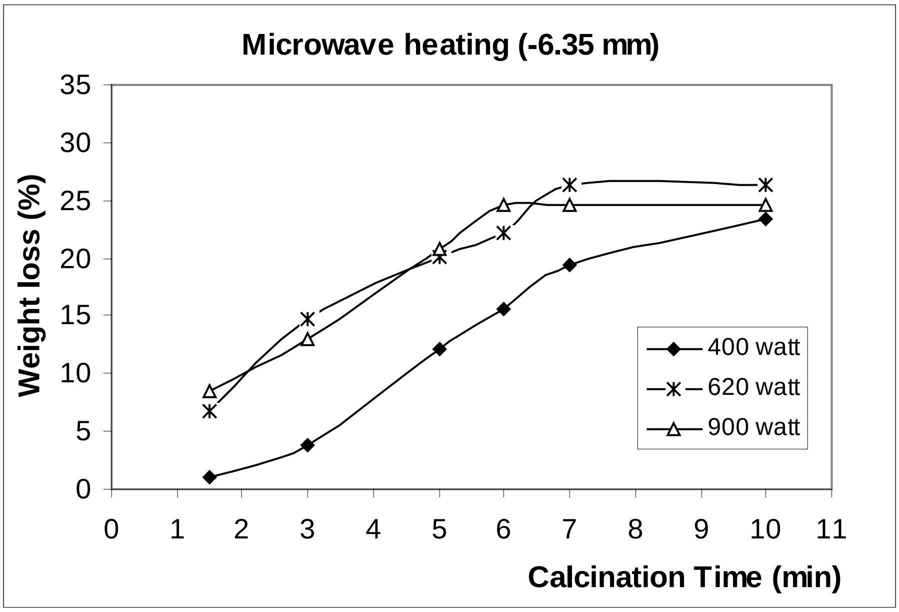

Figure 29. Effect of calcination time on the weight loss of -6.35 mm trona calcined in a microwave oven at different power settings

The first experiments were intended to compare effects of microwave heating versus conventional heating. Calcination is completed in at least 30 minutes in conventional heating whereas the same weight loss value was obtained in very short calcination time as 6-7 minutes depending on the applied power for the particle size of -6.35 mm. Dry microwave calcination of –6.35 mm particles showed that weight loss increased with increasing calcination duration and power setting. That means, the complete calcination occurs in the highest power setting (900 watt) in 6 minutes, whereas at 620 watt setting it takes 7 minutes and at 400 watt setting it takes longer than 10 minutes.

The effect of particle size on the calcinations behavior of trona was investigated by calcining one finer and one coarser fraction namely -3.35 mm and -9.53 mm in the microwave oven. The result is given in Figure 30. The results showed that which both –3.35 mm and –6.36 mm sample would be completely calcined in 10 minutes and that calcination time is not sufficient for complete calcination of –9.53 mm particle samples.

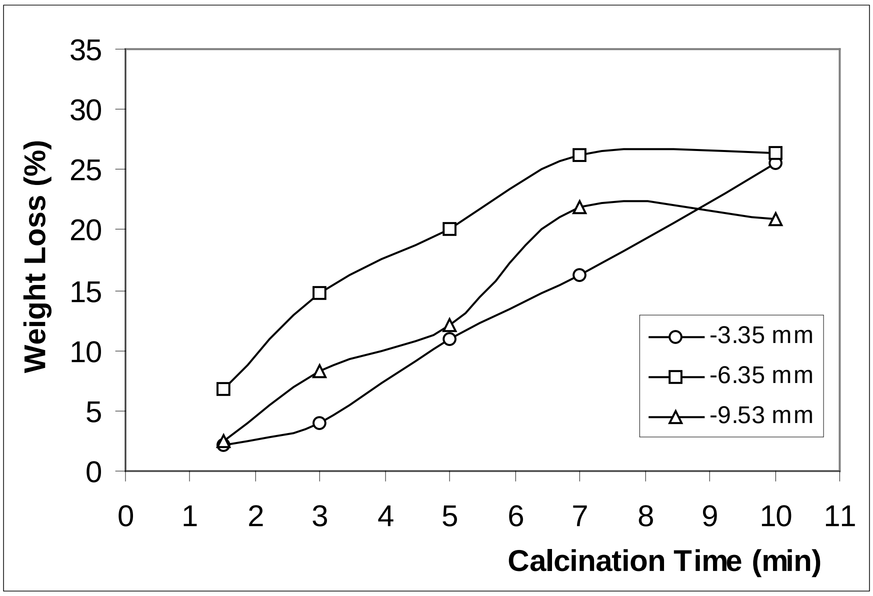

Figure 30. Microwave heating of different particle size sample

5.1.4. Wet Type Microwave-Induced Calcination

Microwave processing of materials is a technology that can provide the material processor with a new, powerful, and significantly different tool to process materials that may not be amenable to conventional means of processing or to improve the performance with existing materials.

The focus of this part is wet calcination performed by the application of microwave energy. Whereas conventional processes require the soda ash to be crystallized out of solution before calcination to decompose the trona, microwave wet calcination process converts trona to soda ash in solution by the application of microwaves without the need for pre-drying (Streuber and Cha, 1998).

Various patents addressed the possibility of wet-calcining a slurry of sodium sesquicarbonate (or also trona ore or sodium bicarbonate) to produce anhydrous sodium carbonate or the monohydrate, which would perhaps be less expensive than dry calcining. The objective was also to form a more pure and higher bulk density soda ash product than can be obtained in conventional dry calciner.

It is the first expected result that shorter calcination time is directly related higher calcination kinetic. The main handicap of dry type microwave heating is that the overheating of microwave oven in longer periods and consuming of the required input energy as a reflected power or transmitted power instead of absorbed power (Streuber and Cha, 1998). This effect is easily observed in high power setting, 900 watt. So it is necessary to determine whether a microwave process could be utilized for catalyzing the conversion of trona in solution to sodium carbonate (named wet microwave calcination). It is well known that the solution samples absorb microwaves better than the dry sample alone. Before wet calcination operation, trona solution samples having 10 grams dry representative trona ore sample in 1000 cc water was prepared as stock solution. Then, 50 cc solution samples were pipetted out from the stock, put in a 500 cc glass flask to prevent splashing of solution during calcination. After heating, samples were taken out from the oven and $NaHCO_3$ content of samples was determined by $BaCl_2$ titration method. Chemical analysis of $NaHCO_3$ determination is preferred in wet microwave calcination instead of weight loss as in dry microwave calcination due to the liquid state of sample. $NaHCO_3$ (%) of dissolved sample during the wet microwave calcination process is tabulated in Table 19 in Appendix A.8. and graphically presented in Figure 31.

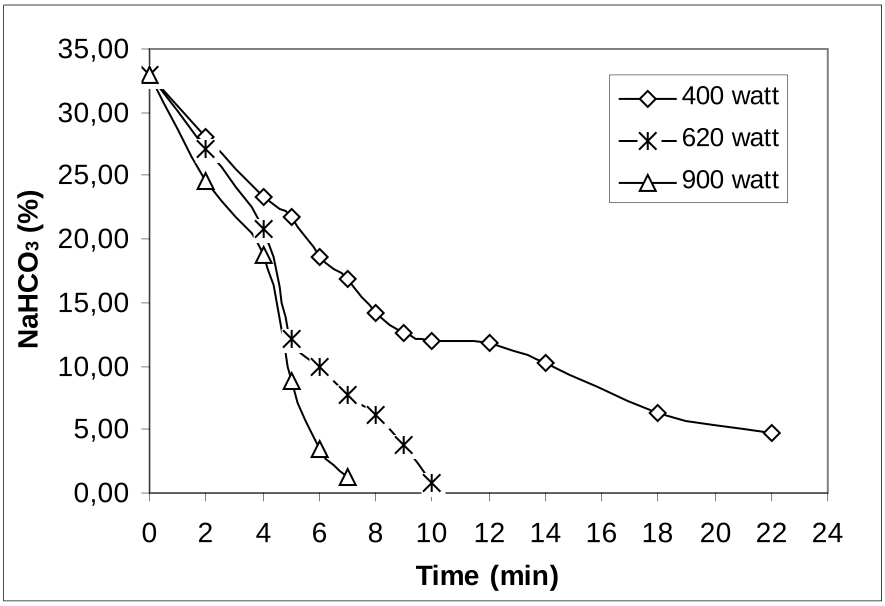

Figure 31. Effect of time and $NaHCO_3$ content of dissolved trona wet calcined in a microwave oven at different power settings

The results of the wet type microwave calcination experiments show that the decomposition of trona in a microwave field is possible. Furthermore, microwave energy is far superior in decomposition of sodium bicarbonate to sodium carbonate through microwave field even in low power settings being much faster than in conventional heating. The medium power setting of 620 watt brought up a very high impact on decomposition rate. It was further suggested that the decomposition reaction began to proceed rapidly as half of $NaHCO_3$ content in trona within 5 minutes of exposure to microwave.

The data were then plotted accordingly to $NaHCO_3$ conversion ratio, which is fraction of $NaHCO_3$ converted to Na_2CO_3 and calculated by the following equation.

$$X = (C_0 – C)/ C_0 \tag{21}$$

X = conversion ratio
C = $NaHCO_3$ percentage at any time (%)
C_0 = $NaHCO_3$ percentage of original sample (33 %)

The graphical presentation of conversion ratio is given in Figure 32. From the conversion graph, the conversion ratio values approach to 1.0 indicating complete conversion as a function of time. That means, all of the sodium bicarbonate is converting to sodium carbonate by microwave heating. The power of 900 watts experiments was not continued after 6 minutes due to the overheating and breaking down the microwave oven when operated in longer periods of that time.

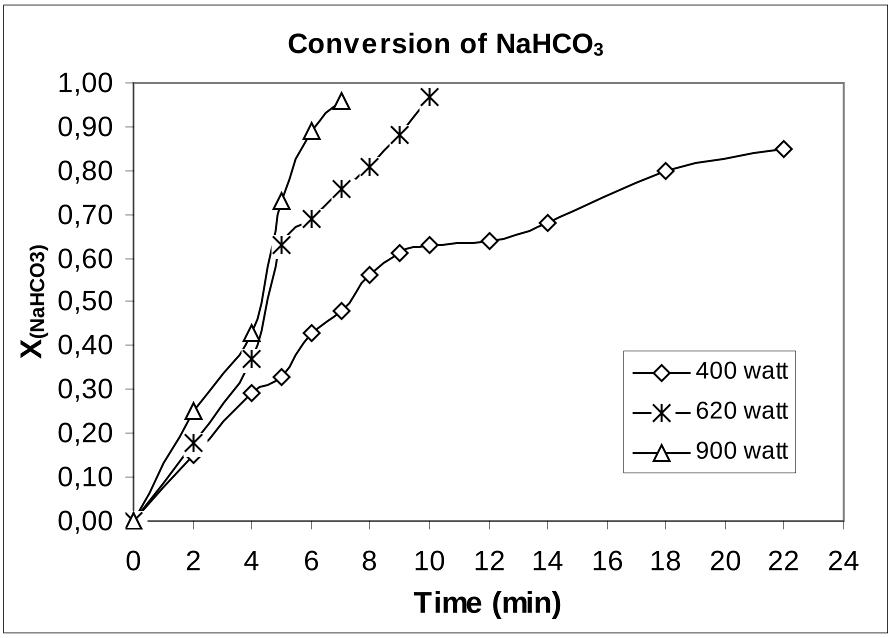

Figure 32. Conversion of $NaHCO_3$ with time

As seen clearly from the results, the microwave induced wet calcination of trona in solution is a feasible process with advantages over conventional methods of soda ash production as trona in solution absorbs microwave better than dry trona. This might be an added advantage in the production of soda ash from trona via solution mining- wet calcination combination.

5.2. Examination of Calcination Process

The thermal processes and the physical or chemical phenomena, which arise on heating a material determine all the aspects of the methods of instrumental techniques, which covers SEM, TG, DTG and XRD analyses. In order to classify these methods one must first of all start from the nature of the trona and compare that with the calcined products. The compounds in the system of Na_2CO_3 - $NaHCO_3$ - $2H_2O$ were investigated extensively. TG, XRD and SEM (Scanning Electron Microscopy) analyses were used to determine the nature and thermal reaction characteristics of materials.

5.2.1 SEM Examinations

The mode of calcination of trona affects its decomposition and dissolution. Therefore, (SEM) scanning electron microscope analysis of samples was performed to observe the changes in the chemical and crystal structure during calcination operation. Leitz brand AMR1000 model scanning electron microscope was used for the examinations.

Trona samples were heated to 50 °C, 100 °C, 150 °C and 200 °C for 1 hour of calcination to varying degrees of decomposition before examining in SEM. These temperatures were chosen to cover the high- and low- temperature regions identified in the kinetic studies. Seven different trona samples were identified by SEM analysis with EDX (Energy Dispersive X-ray Analysis) patterns of each related samples.

The crystal structure of trona is defined as monoclinic. Each sodium ion is coordinated by six oxygen atoms, 1 ion of Na by oxygens from carbonate ions, while 2 ions of Na has four oxygens from carbonate ions and two from water molecules. These water molecules lie in sheets between layers made up of pairs of hydrogen-bonded carbonate ions linked by sodium ions. SEM analysis of first group of samples is the hand-picked trona samples. The original material was well crystallized, with smooth faces (Figure 33a). The related EDX pattern of starting material is shown in Figure 33b. Sodium, carbon and oxygen elements were observed in the structure. The deviations of these elements would be compared with EDX patterns of other following samples.

There was no change in SEM image of the sample calcined at 50 °C (Figure 34a). Just the grain spaces were opened very little. Small increment was observed in Na element intensity of EDX pattern (Figure 34b).

At higher temperature (100 °C) decomposition caused a change in the image of sample (Figure 35a). The smoothness of surface started to change and the sample became porous. The porous structure can be easily seen with enlarging the scale five times (Figure 35b). These pores were extremely fine. The changes in the intensity of elements continued to increase. Carbon, oxygen and sodium element peaks had higher intensity in EDX (Figure 35c).

Small cracks were apparent in the SEM image of samples calcined at 150 °C (Figure 36a). There was some development of the porosity as the extent of decomposition increased. At high magnification, it was seen that the porosity increased compared to lower temperatures (Figure 36b). These pores appear as decomposition progressed in high temperatures giving rise to material, which was microporous with the wide deep pores extended into the material. EDX pattern of those temperature-calcined samples deviated from this point (Figure 36c).

Larger cracks along the one axis or wide cracks in different areas were sign of the completing decomposition at 200 °C (Figure 37a). The structure was transformed into spongy texture containing open pores. As the closer interest to this figure by five times increasing magnification, deep porosity image was observed (Figure 37b). Weak boundaries possibly to be broken on the surface were observed. A broken layer was generated very rapidly, which could be easily broken away from its place. As the extent of decomposition increased, the number and characterization of these pores increased, they are the most obvious feature in micrographs. Carbon, oxygen and sodium element peaks were clearly observed in EDX pattern (Figure 37c).

The other group of SEM analysis was made with the representative trona ore samples. The uncalcined experiment sample was non-porous, with uneven surfaces of outgrowths although this material very occasionally showed large internal pores (Figure 38a). These outgrowths while not uncommon were uniformly spread across the crystal surface. When examining EDX pattern of gangue minerals of experiment samples of trona; Mg, Al, K, Ca, Fe, Si small amounts of Na elements were observed (Figure 38b).

The product morphology of calcined experiment samples was very different from that of the original samples (Figure 39a). Cracks were observed longitudinally along the cleavage planes and porous structure was detected. High temperature decomposition revealed wide cracks. In fully calcined material, the stratified layers can be seen in porous surface. The intensity variations of elements in gangue minerals were seen in EDX pattern (Figure 39b). The differences of uncalcined (Figure 40) and calcined samples (Figure 41), in C, O, Na elements can be highlighted to compare the EDX patterns.

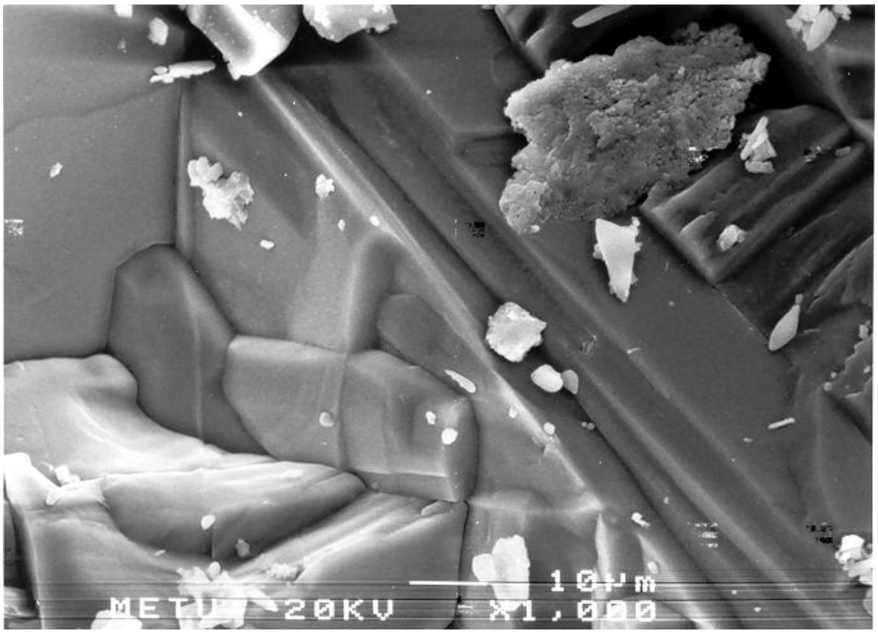

Figure 33a. SEM Image of hand-picked trona samples (bar = 10μm, magnification 1000x)

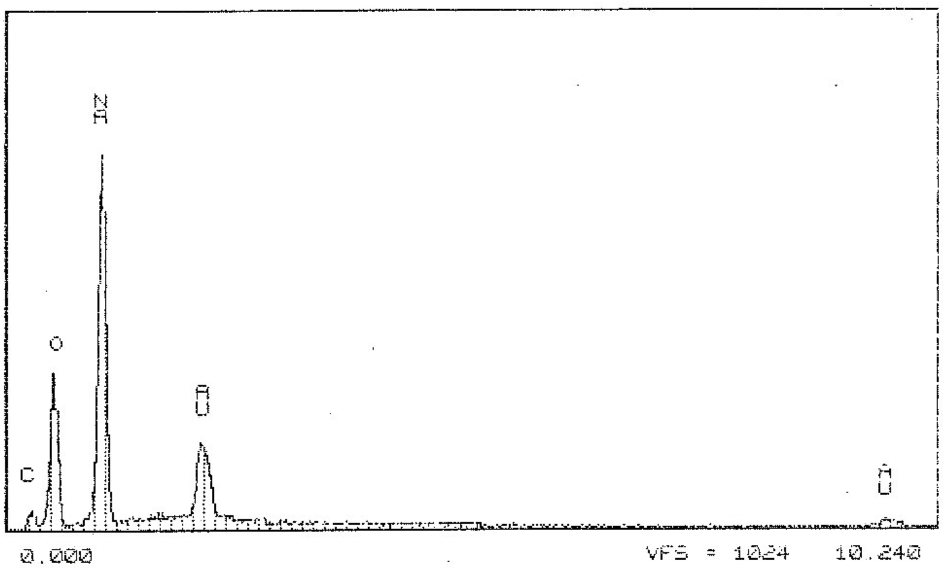

Figure 33b. EDX pattern of hand-picked trona samples

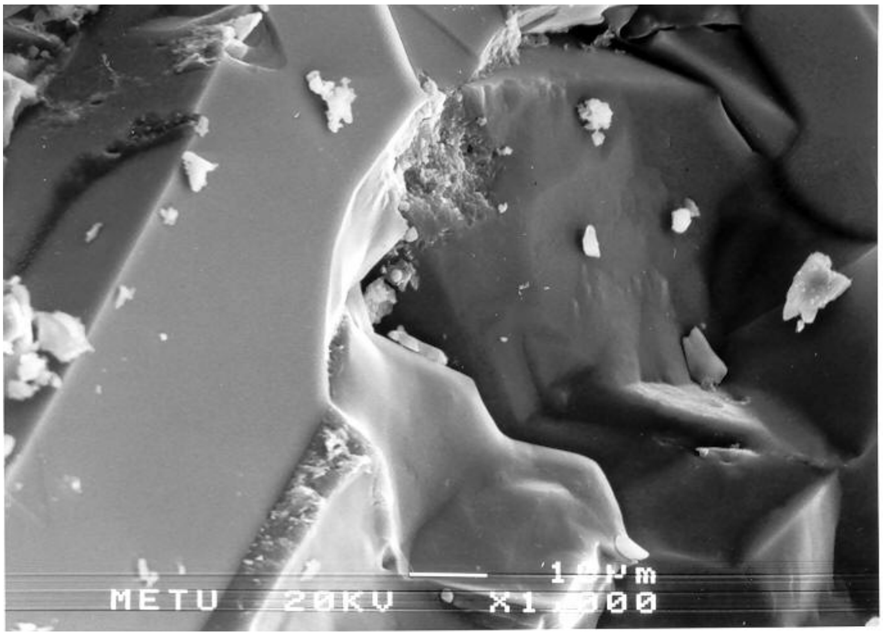

Figure 34a. SEM image of hand-picked trona samples calcined at 50 °C (bar = 10μm, magnification 1000x)

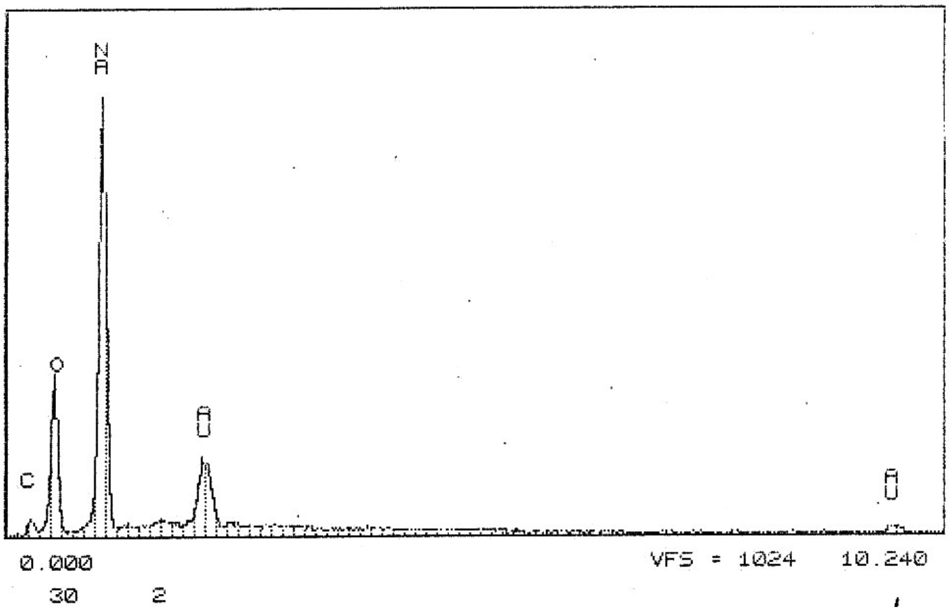

Figure 34b. EDX pattern of hand-picked trona samples calcined at 50 °C

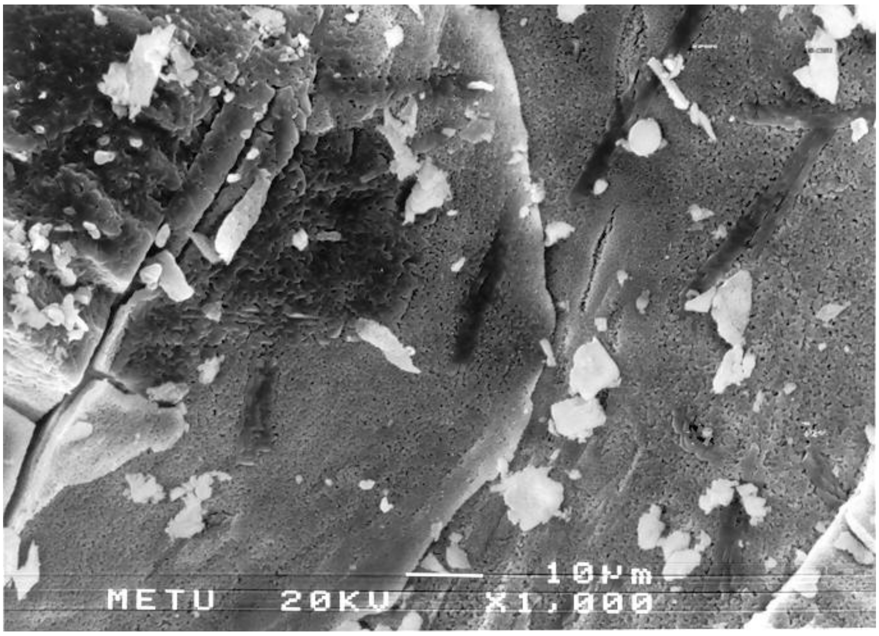

Figure 35a SEM image of hand-picked trona samples calcined at 100 °C (bar = 10μm, magnification 1000x)

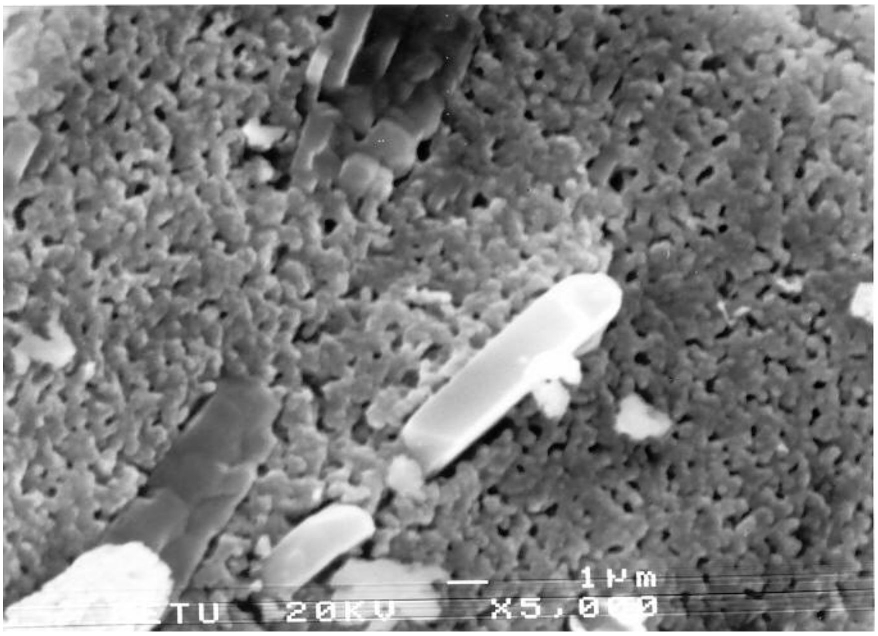

Figure 35b. SEM image of hand-picked trona samples calcined at 100 °C (bar = 1μm, magnification 5000x)

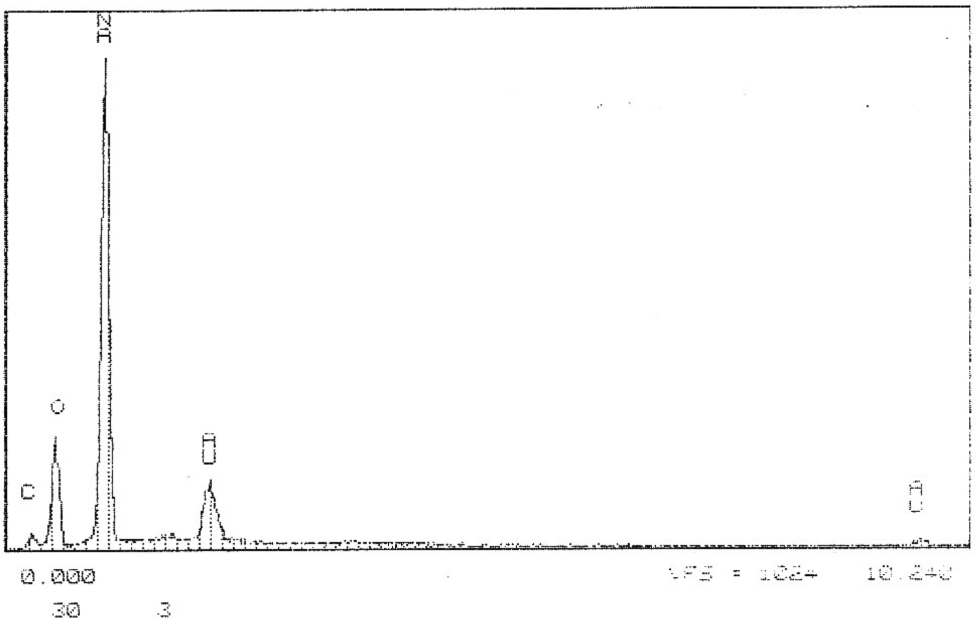

Figure 35c. EDX pattern of hand-picked trona samples calcined at 100 °C

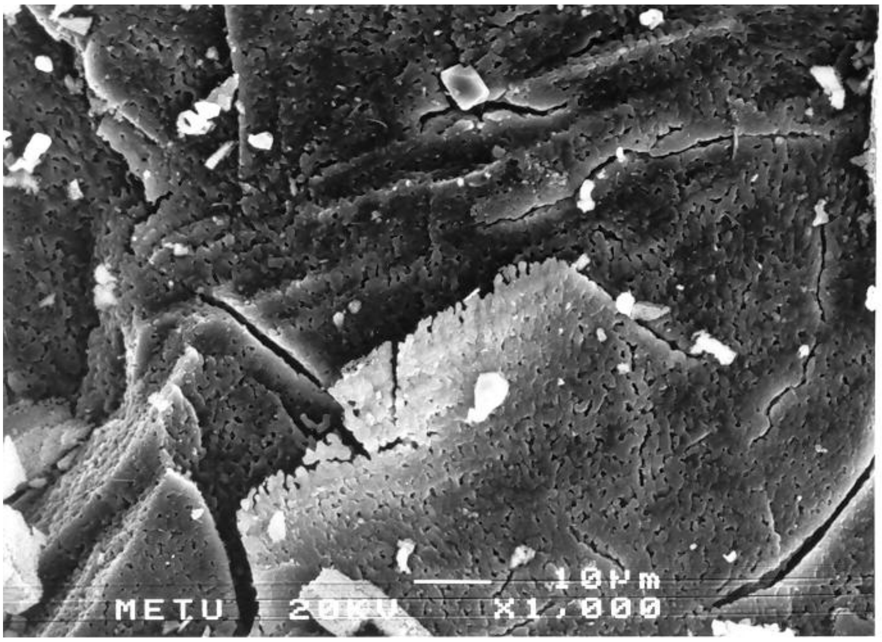

Figure 36a. SEM image of hand-picked trona samples calcined at 150 °C (bar = 10µm, magnification 1000x)

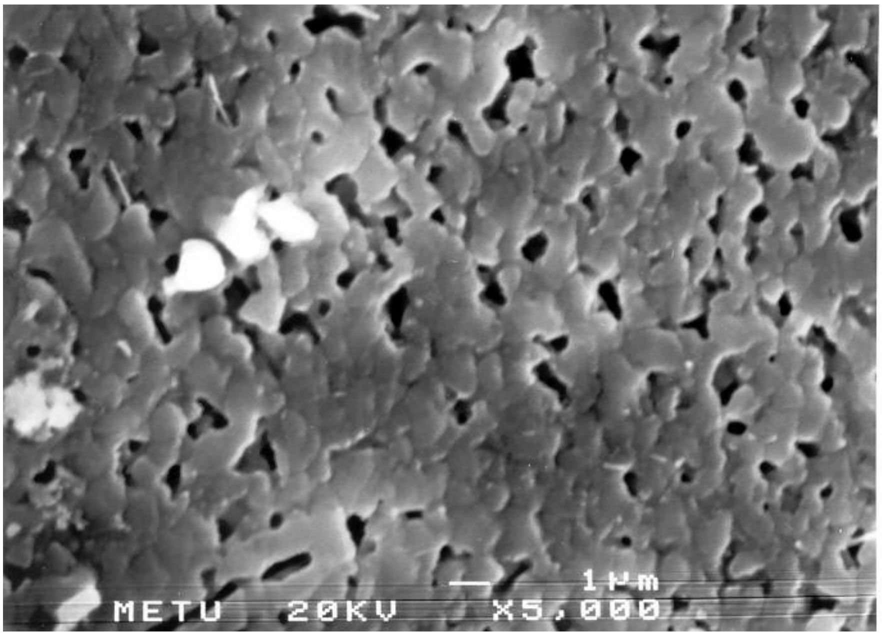

Figure 36b. SEM image of hand-picked trona samples calcined at 150 °C (bar = 1μm, magnification 5000x)

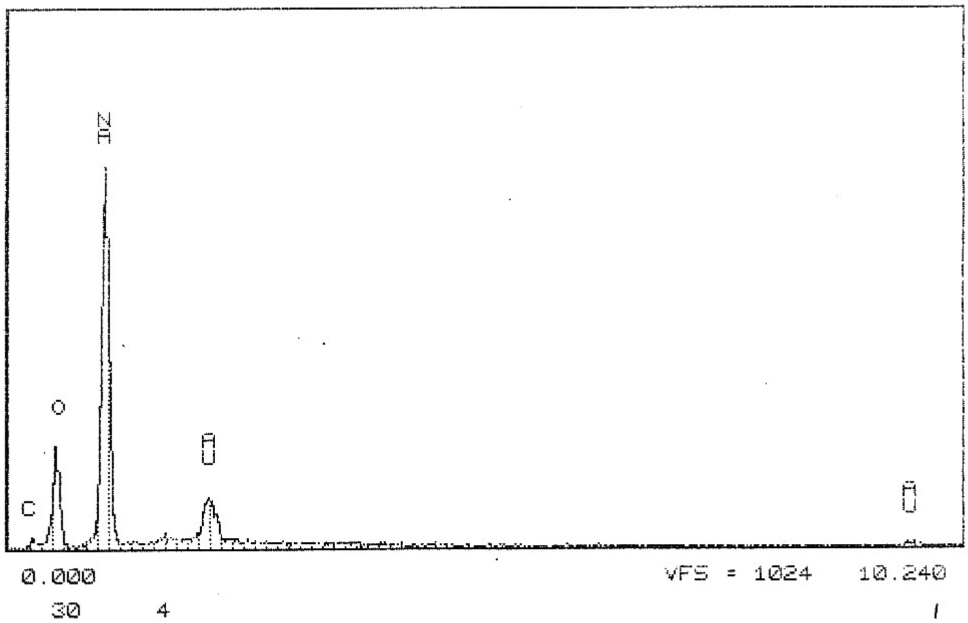

Figure 36c. EDX pattern of hand-picked trona samples calcined at 150 °C

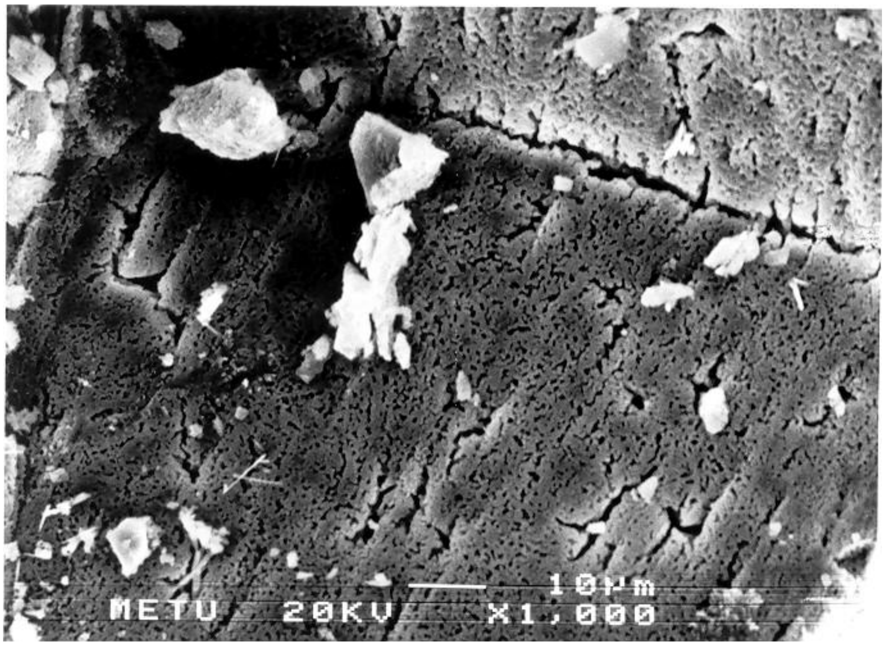

Figure 37a. SEM image of hand-picked trona samples calcined at 200 °C (bar = 10µm, magnification 1000x)

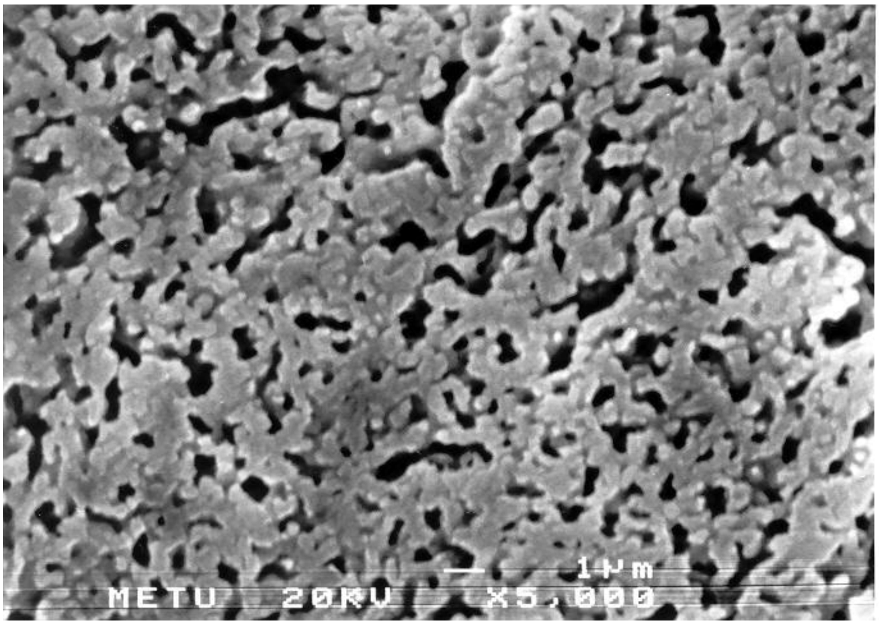

Figure 37b. SEM image of hand-picked trona samples calcined at 200 °C (bar = 1µm, magnification 5000x)

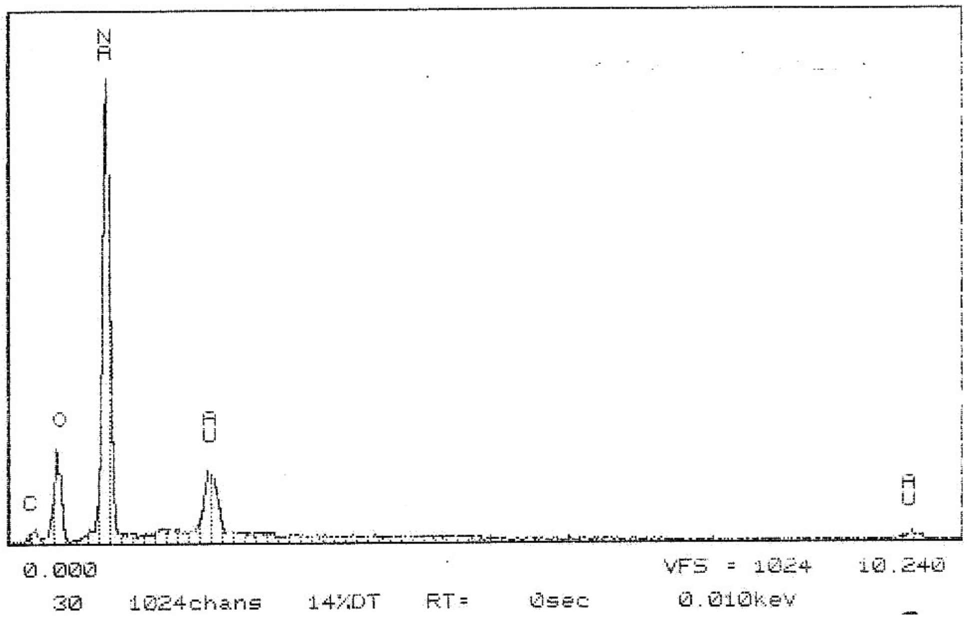

Figure 37c. EDX pattern of hand-picked trona samples calcined at 200 °C

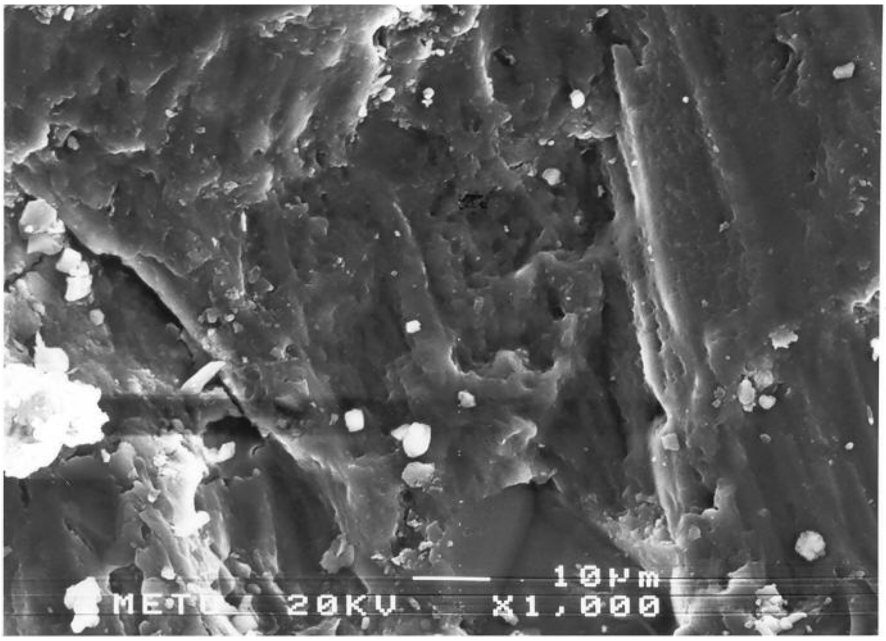

Figure 38a. SEM image of representative trona ore samples (bar = 10μm, magnification 1000x)

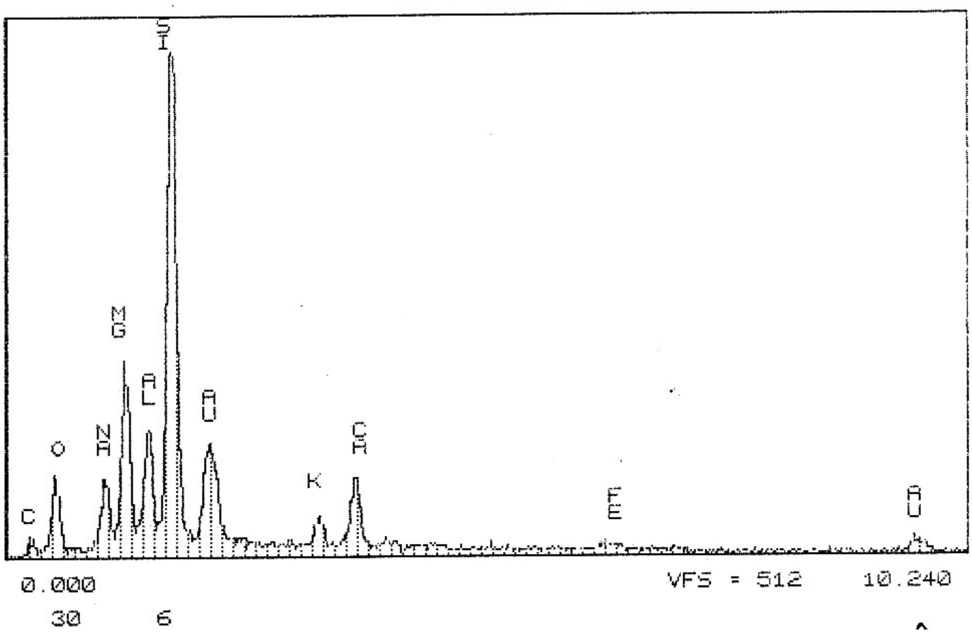

Figure 38b. EDX pattern of gangue minerals of representative trona ore samples

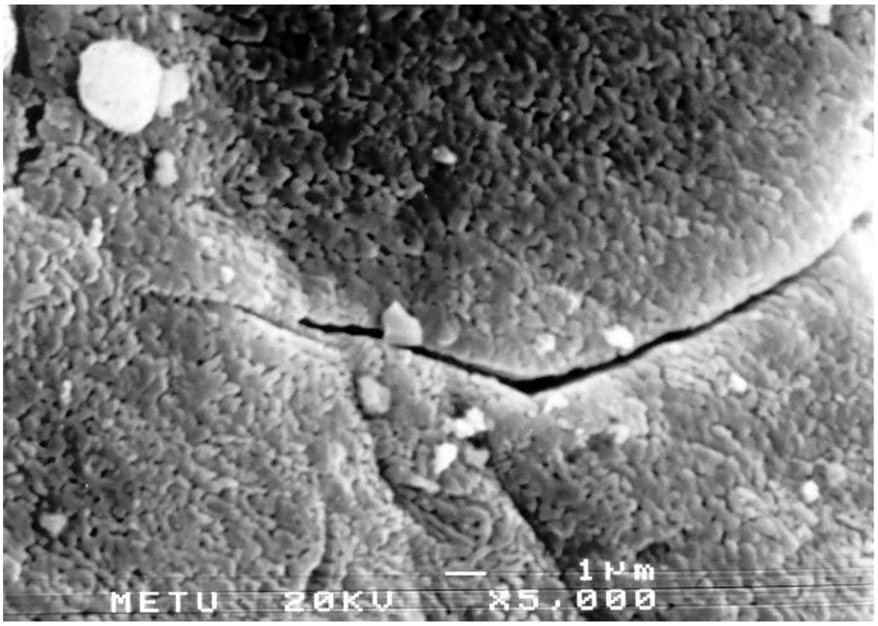

Figure 39a. SEM image of representative trona ore samples calcined at 200 °C (bar = 1µm, magnification 5000x)

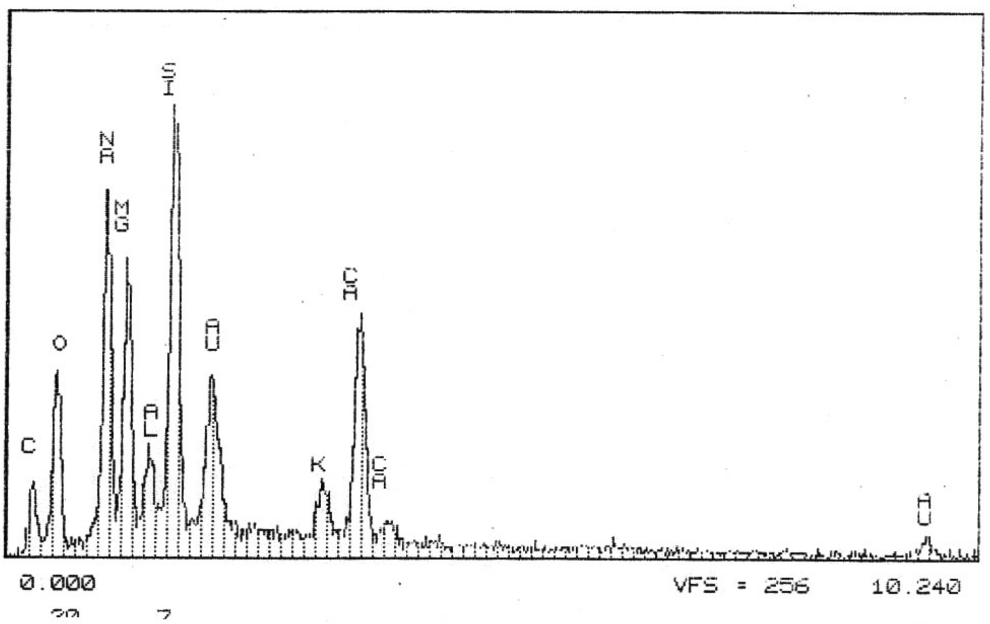

Figure 39b. EDX pattern of gangue minerals of representative trona ore samples calcined at 200 °C

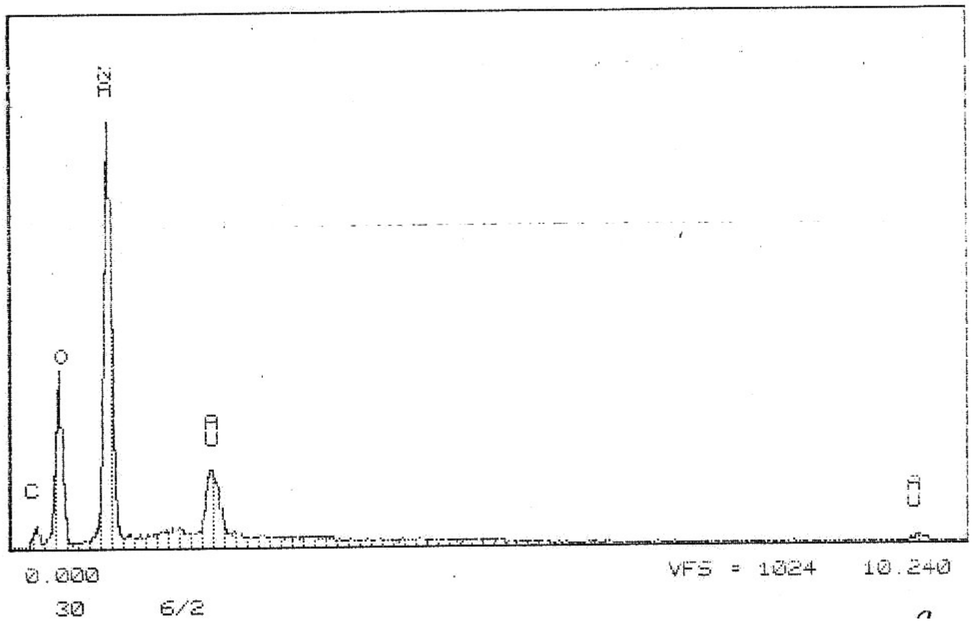

Figure 40. EDX pattern of representative trona ore samples

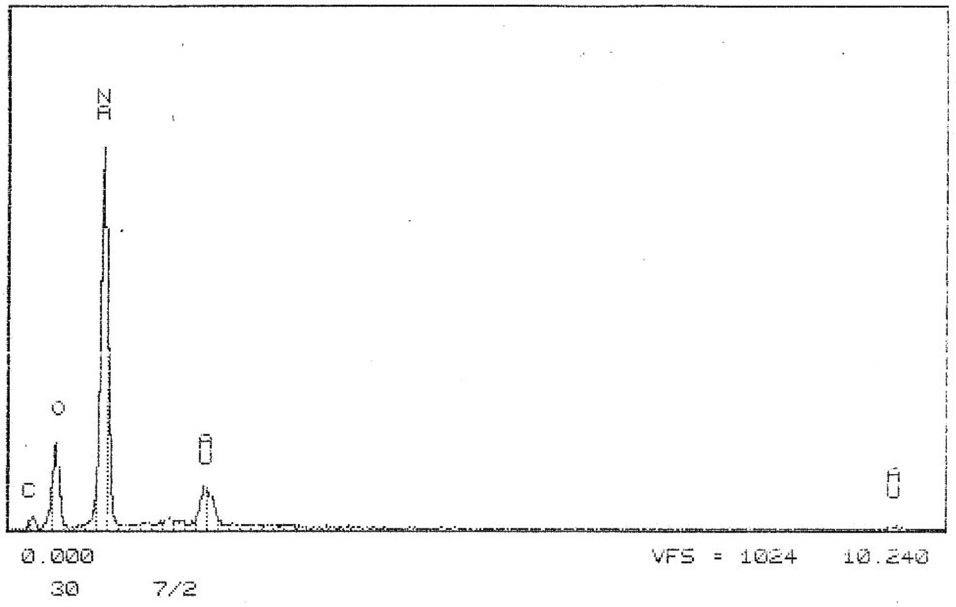

Figure 41. EDX pattern of representative trona ore samples calcined at 200 °C

5.2.2. TG and DTG Analyses

The control of thermal treatment process should be total in the sense that the determination of weight loss taken into account of understanding the thermal mechanism of trona decomposition. All the information is needed to strike an accurate, detailed and complete balance of thermal process shall be available.

TG (thermogravimetry) instrumental technique by means of which the mass of a substance in given surrounding, heated under controlled conditions at a constant rate, is recorded as a function of temperature. This mass is plotted as ordinate, with negative mass variations downward, vs. time or temperature as abscissa, increasing from left to right.

DTG (derivative thermogravimetry) instrumental technique indicates the first derivative of the experimentally determined thermogravimetric curve as a function of time or temperature. The derivative of mass variations is plotted as ordinate, with negative variation downward vs. temperature as abscissa, increasing from left to right. DTG measurements indicate exactly the temperatures of the beginning, the maximum rate and the end of the change.

TG and DTG analysis of the representative trona ore samples were investigated by thermogravimetric (TG) and differential thermal (DTG) analyses. The Polymer Laboratories Thermal Science brand TG 1500 model thermogravimetric analyzer equipped with a micro-balance system was used to obtain the TG and DTG data. The results are given in following figures.

TG plot indicates the weight loss percentage and DTG plot indicates the rate of the weight loss depending on temperature or the point derivative of TG at a heating rate of 10 °C/min in purged air atmosphere.

It was seen in Figure 42 that the weight of the material decreased smoothly from starting to the level of nearly 66.66 % when heated till to 900 °C. It made a peak at that point means that the maximum weight loss was obtained as 25.50 % in the temperature ranges 100 °C -200 °C. The reaction then gradually continued up to around 900 °C. The recording of the mass-loss curve for rapid reactions can have a pronounced effect on the shape of the curve with a long horizontal plateau. The TG curve in Figure 49 indicates the characteristics of a single-stage mass-loss of trona decomposition. The trend of the curve showed that thermal decomposition of trona is an endothermic reaction with a negative mass variation. From the same figure, the corresponding DTG curve, which is obtained, is the first derivative of the mass-loss change curve (TG).

The theoretical weight loss percent was 25.40 %. Being a higher weight loss presented thermal decomposition of trona ($Na_2CO_3.NaHCO_3.2H_2O$) completely. According to the composition reaction given below trona decomposes to anhydrous sodium carbonate at the low temperatures of below 150 °C. The peak at 133.05 °C was seen in DTG curve of Figure 42 verified this concept. If anhydrous sodium carbonate is heated, loss in weight due to dissociation and volatilization – begins at 400 °C carbon dioxide is evolved as indicated by the reaction equation.

$$Na_2CO_3 \Rightarrow Na_2O + CO_2 \tag{21}$$

The melting point of sodium carbonate is 854 °C. TG analyzing of pure sodium at the higher temperatures proved that phenomena. TG and DTG plot of pure analytical grade sodium carbonate is given in Figure 43. Weight percent of material was ended in 66.05 %. Weight loss was realized near 900 °C peak point.

Temperature ranges in which chemical reactions take place can be established much better and more exactly by means of the DTG curve than by means of the TG curve. TG curves can show the temperature intervals which indicate the beginning and the end of the reaction; but in conjunction with DTG curves, they indicate the development of thermal processes and the temperatures at which changes occur in them.

TG and DTG analyses were performed in the wider range of temperature to the ending temperature of 1200 °C in order to see whether there was a point or peak in higher temperatures. The results are shown in Figure 44. The question could be answered above 900 °C some changes or reactions may occur or not. The trends of curves in Figure 44 were similar to these in Figure 42. The maximum weight loss was obtained as approximately 25.25 % in the temperature range of 150 °C-200 °C in TG curve. The corresponding DTG curve of that figure gave the same results with the Figure 42. The peak point is 129.39 °C for the decomposition reaction. No appreciable variation was observed except for that peak.

The peak value of weight loss amounts is 25-26 % at the temperature of nearly 130 °C verified the theoretical value of weight loss and the complete decomposition reaction temperature, which were obtained from the experimental studies.

The heating rate of TG analyzer is important because the rate at which temperature is raised in the furnace affects determinations quantitatively. Three different heating rates namely 5 °C/min, 15 °C/min, 20 °C/ min of TG analyses are given in Figure 45-47. In the heating rate below 15 °C/min, the slower the heating rate, the larger the intervals at which the conversions appeared in the recording. When the heating rate was in the range of 15-20 °C/min, the recording of the thermal effects taking place was narrow. The influence of the heating rate on TG curves could be accounted for by the fact that with increasing heating rate the amount of H_2O and CO_2 products evolved within the sample also increased, giving rise to a temperature difference between the sample and the furnace. At a slow heating rate, thermal effects occurred at lower temperatures than that was at faster heating rates. As in the case of 5 °C/min heating rate, the peak temperature of decomposition was 111.81 °C, whereas in the heating rate of 15 °C/min it increased to 132.41 °C, finally in the heating rate of 20 °C it reached to 138.46 °C. The extent of decomposition of trona was greater at a slow rate of heating (5 °C/min) as 26.08 % than that was at a faster rate (20 °C/min) as 24.96 %. Moreover, the applied heating rate affects the height and width of thermal effects recorded by DTG curve. These effects could be seen in DTG curves of different heating rate TG-DTG plots.

The thermal behavior of calcined trona samples is given in Figure 48 showed that a little loss in the temperature range of 300 °C. This loss was re-gained from the moisture in surrounding atmosphere.

Thermal decomposition of trona gives information about the thermal treatment and mechanism during calcination operation. Therefore, TG and DTG analyses should be performed in a broader range of samples. The used representative experiment samples which were ranged according to the particle size analyzed with TGA. The particle sizes of samples were -19+12.7 mm, -12.7+9.53 mm, -9.53+6.35 mm, -6.35+3.35 mm and -3.35 mm The plots are given in the Figures 49-53.

TGA plots of different particle sized samples (screen analyzed) are confirmed the expected weight loss values which were nearly 26 %. Coarser sized samples represented higher weight loss than fine sized ones. Since the trona grade of coarser size fraction is more than the trona grade of finer size fraction. All of these plots have a peak temperature point around 120-130 °C. The peak temperature of decomposition decreased with a decrease in sample particle size. Decomposition temperature was 127.94 °C for coarsest size sample and it was 132.87 °C for the finest size sample.

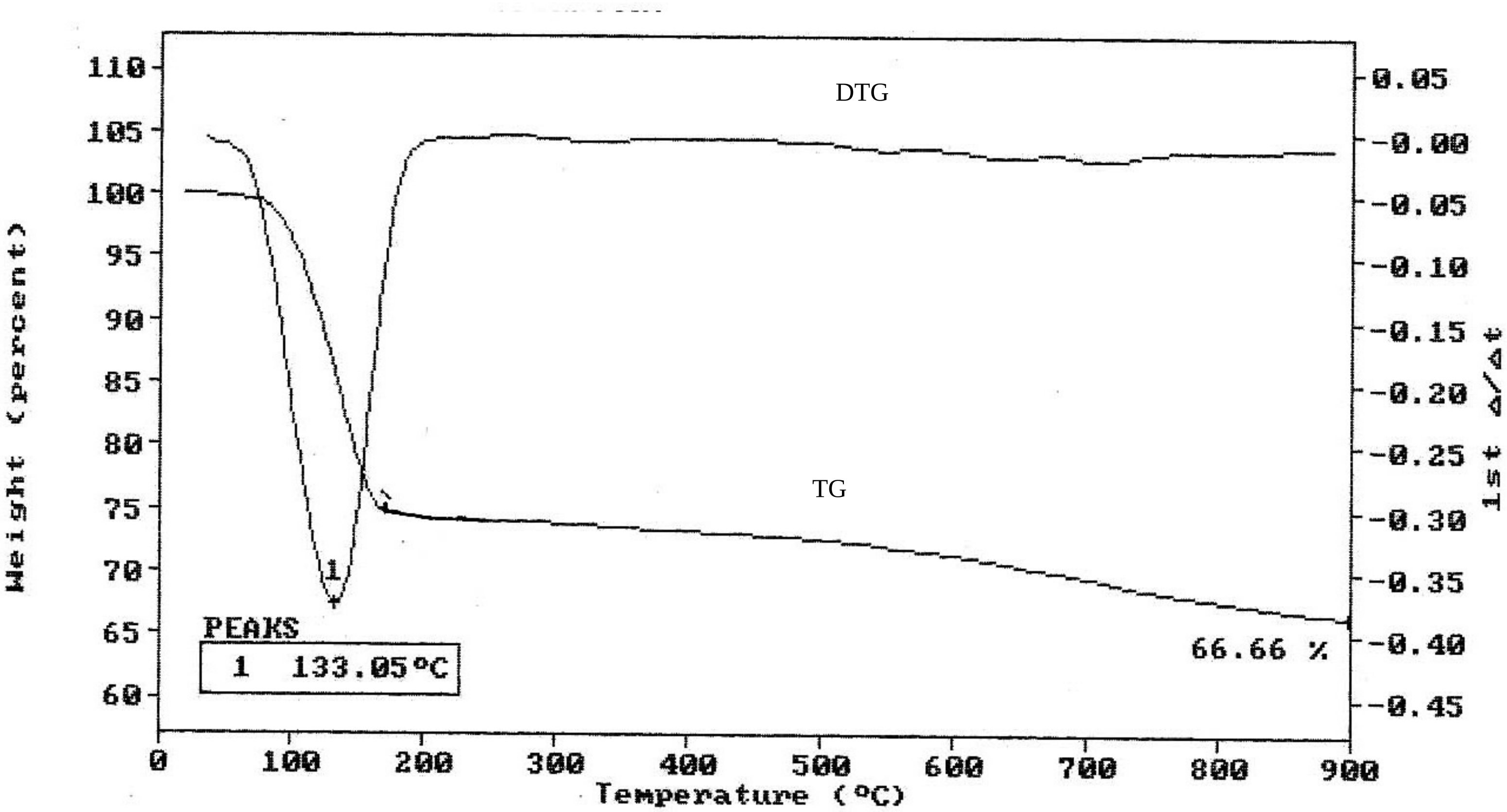

Figure 42. TG and DTG curves of representative trona samples up to 900 °C

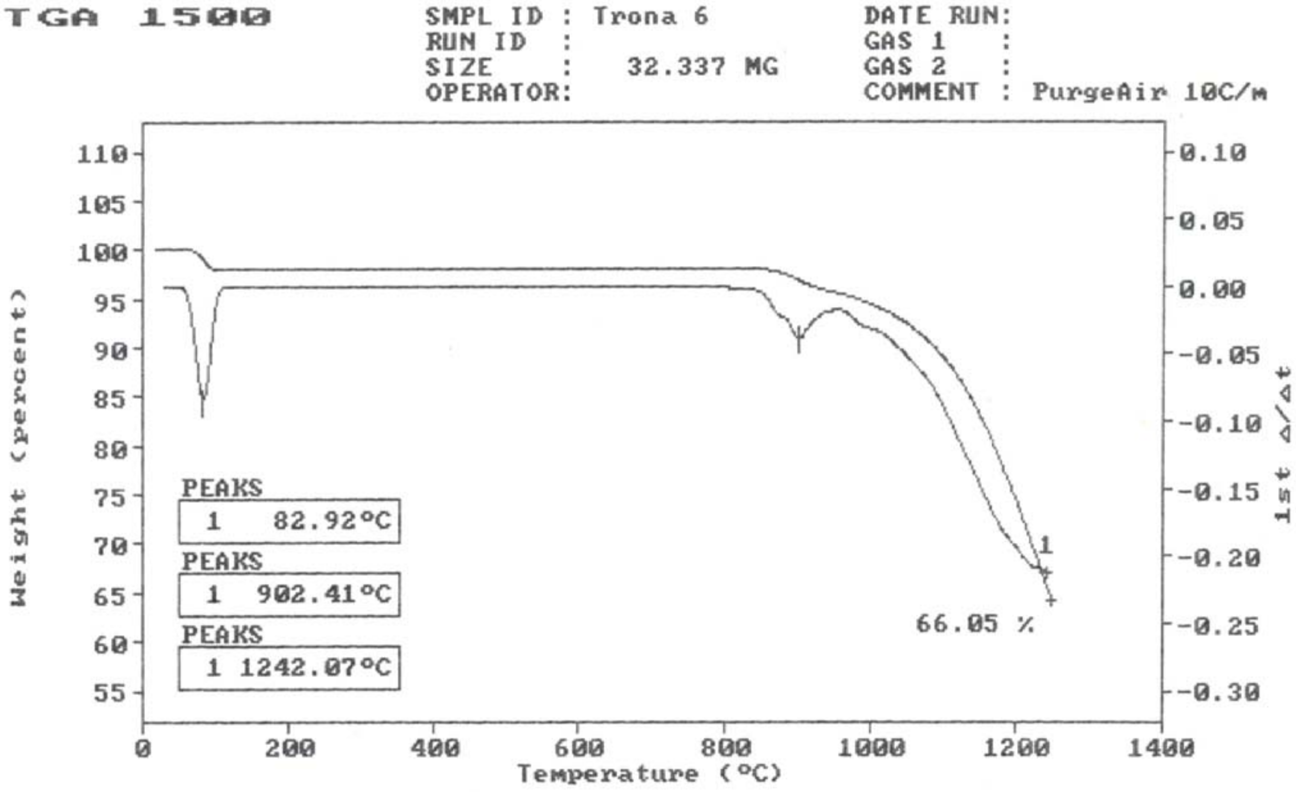

Figure 43. TG and DTG curves analytical grade Na_2CO_3

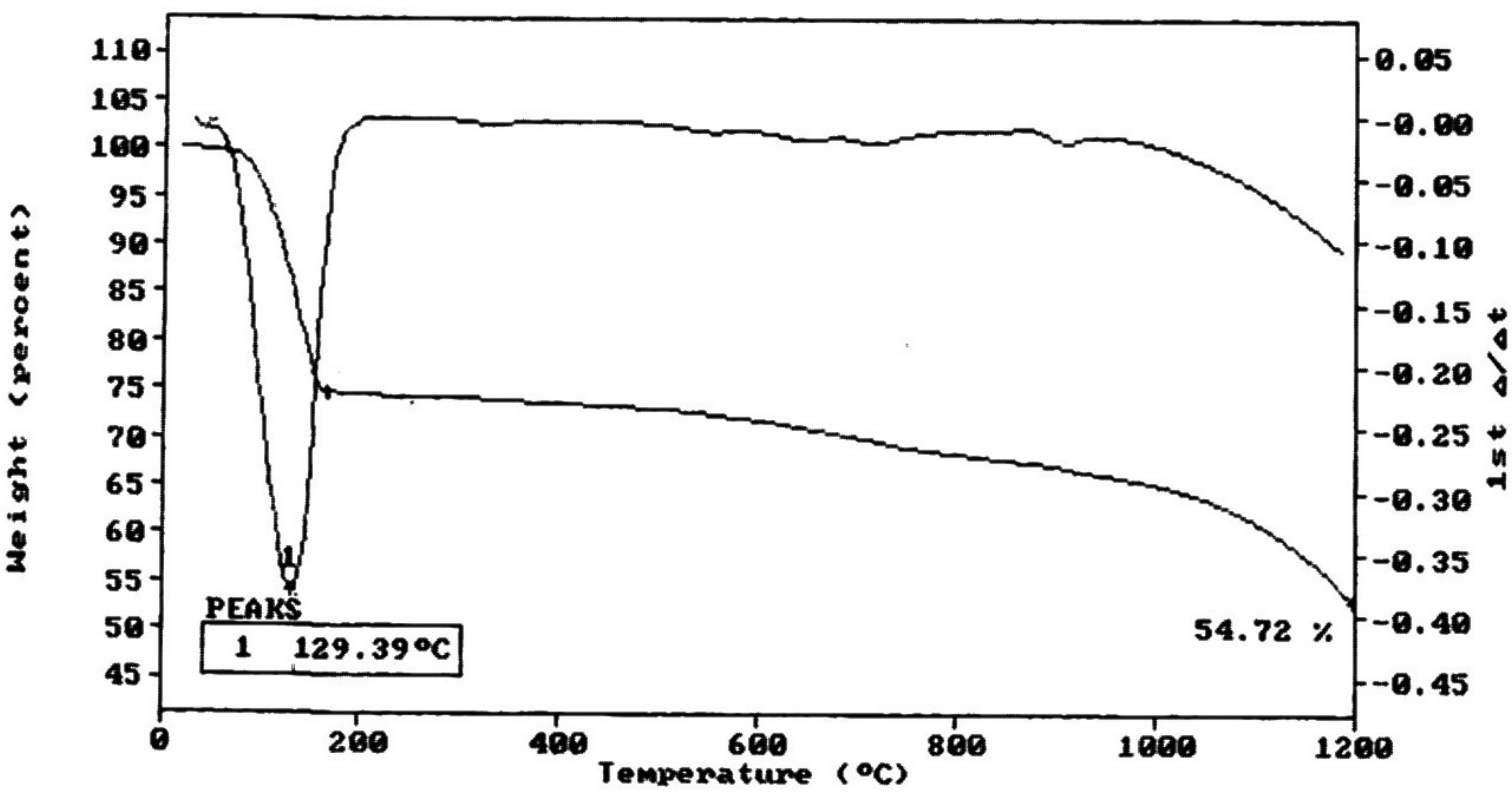

Figure 44. TG and DTG curves of representative trona samples up to 1200 °C

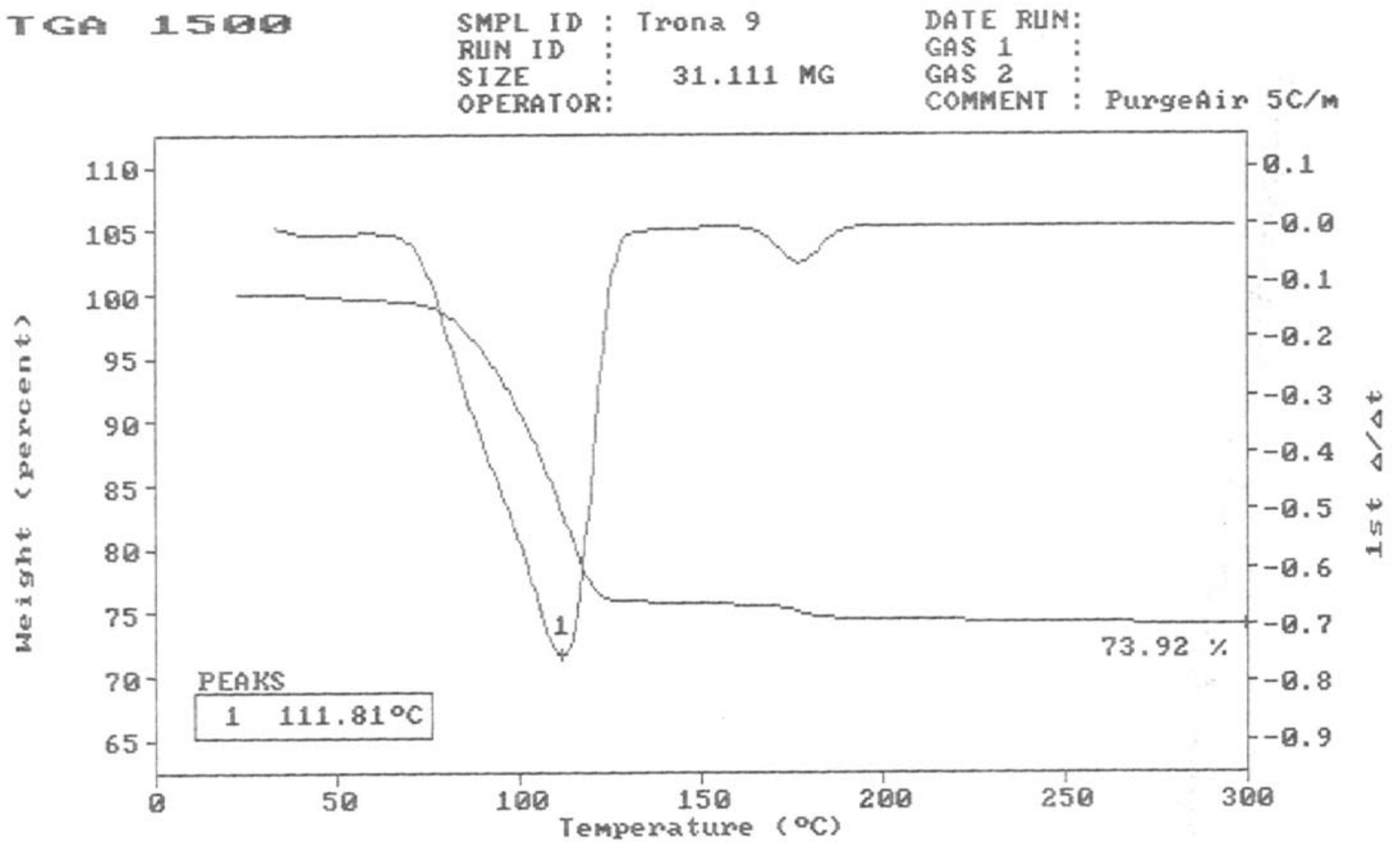

Figure 45. TG and DTG curves of representative trona samples at 5 °C/min heating rate

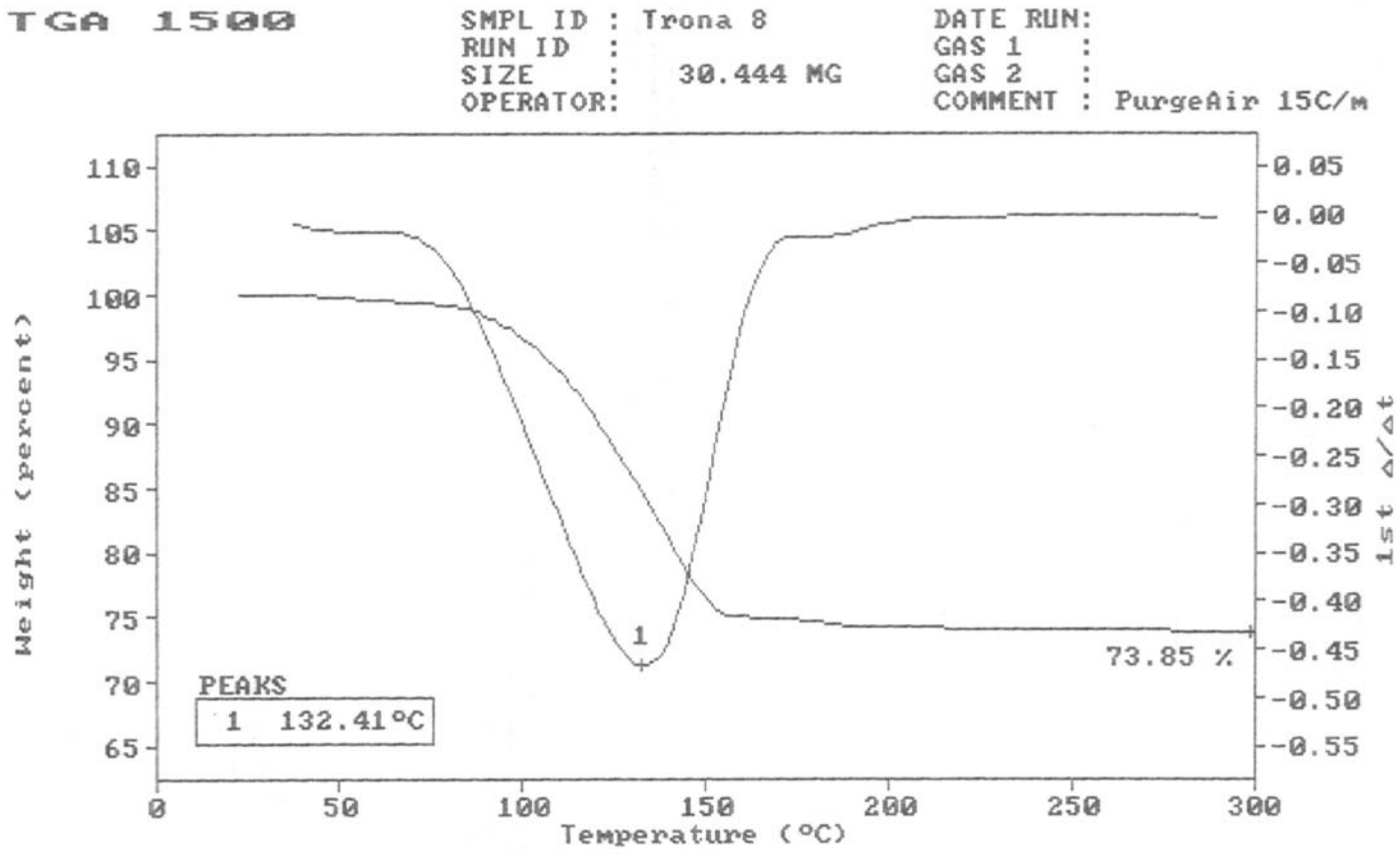

Figure 46. TG and DTG curves of representative trona samples at 15 °C/min heating rate

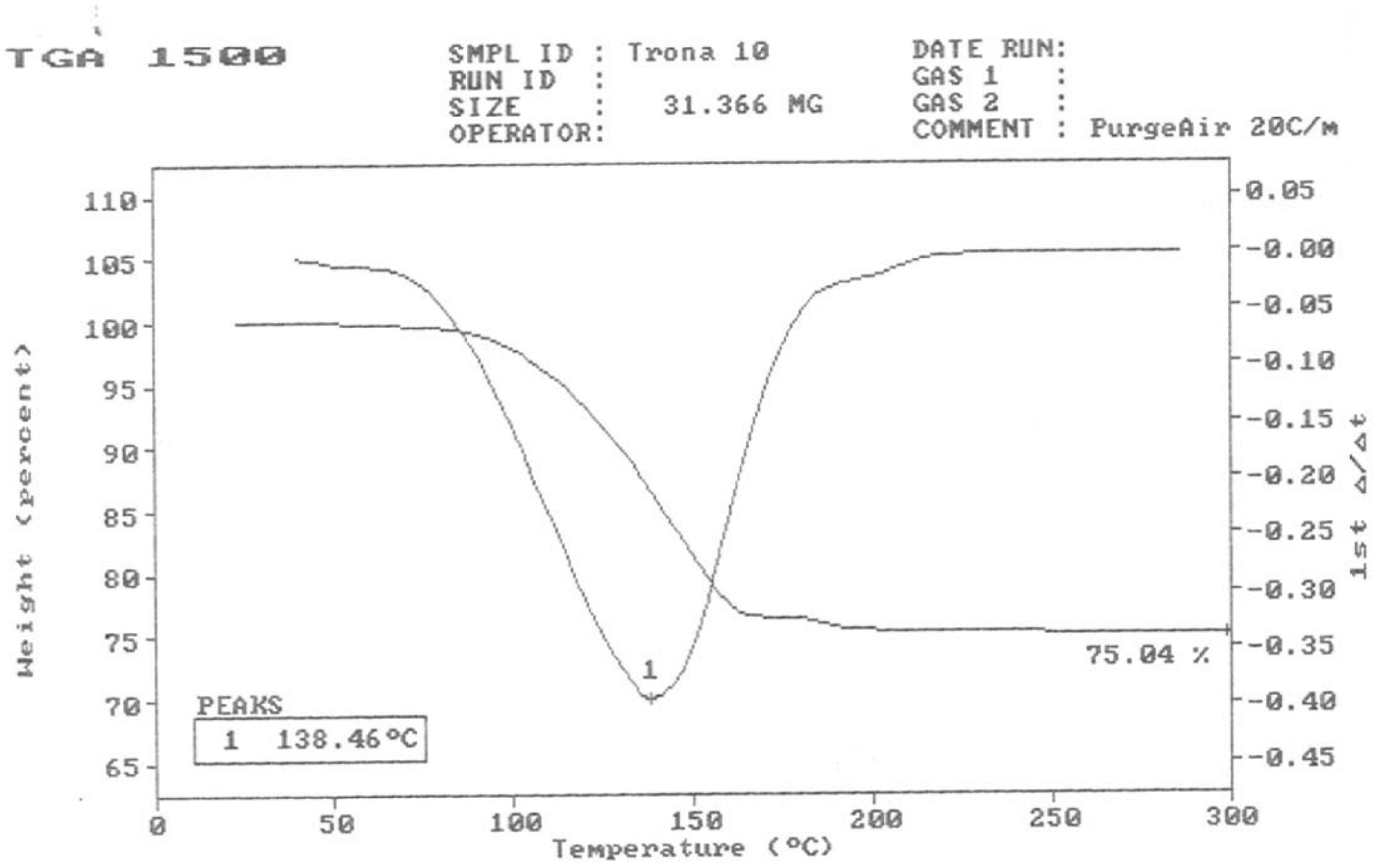

Figure 47. TG and DTG curves of representative trona samples at 20 °C/min heating rate

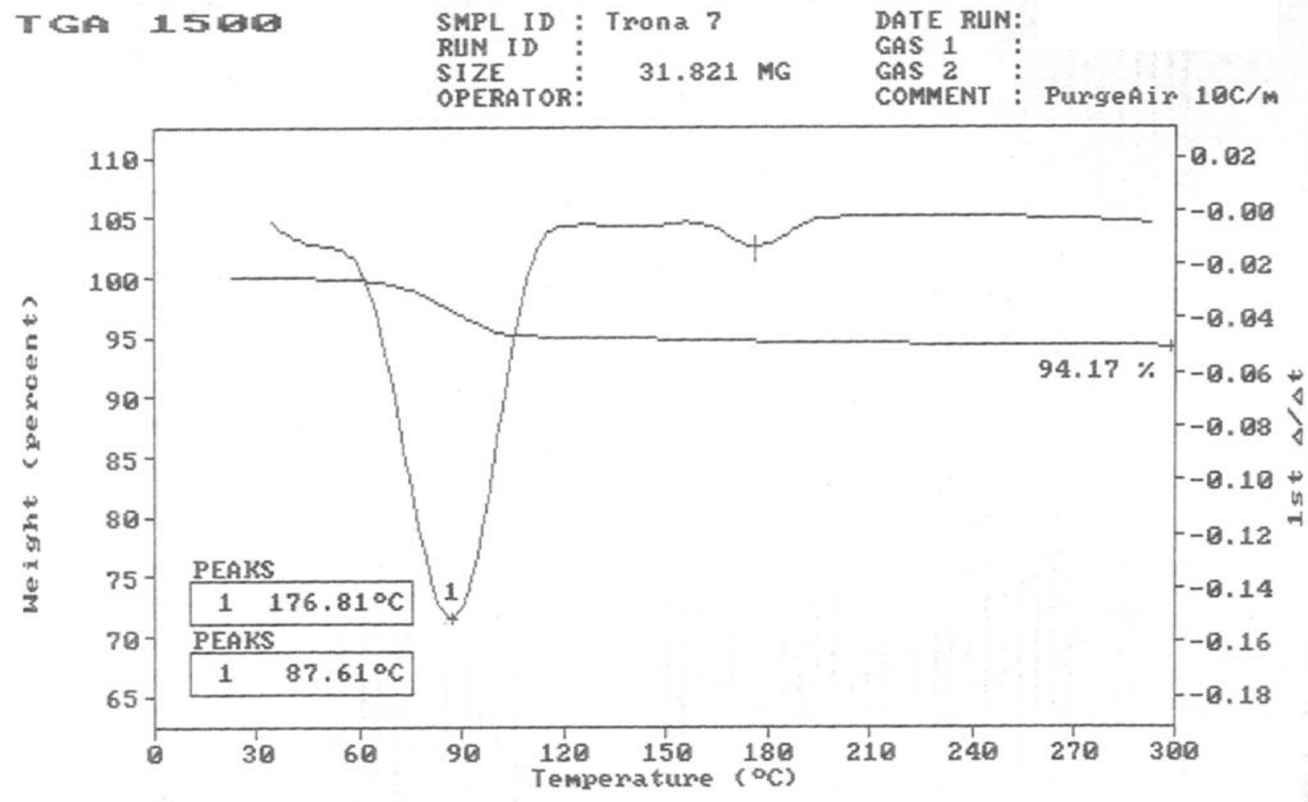

Figure 48. TG and DTG curves of calcined representative trona samples

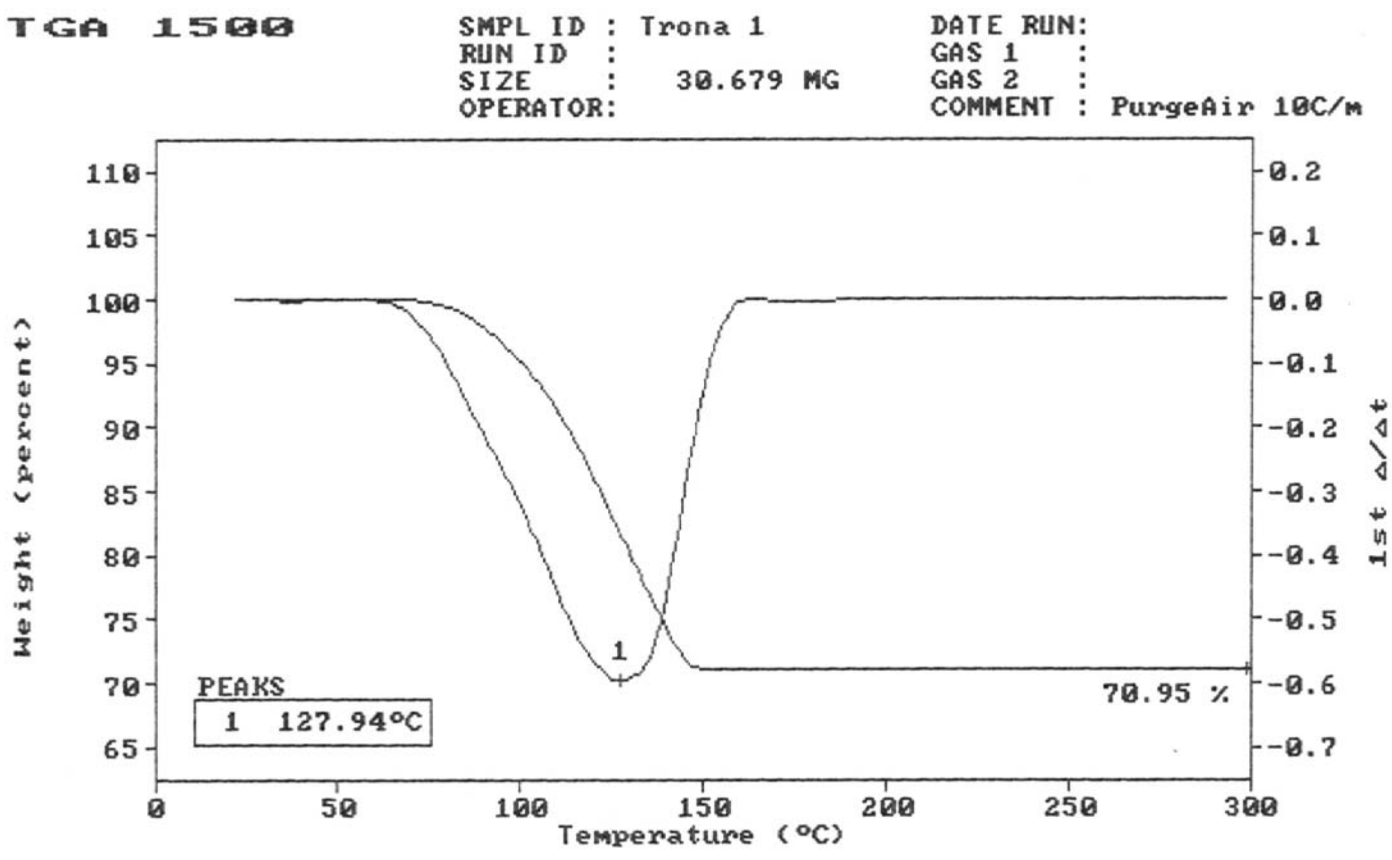

Figure 49. TG and DTG curves of representative trona samples of -19+12.7 mm particle size samples

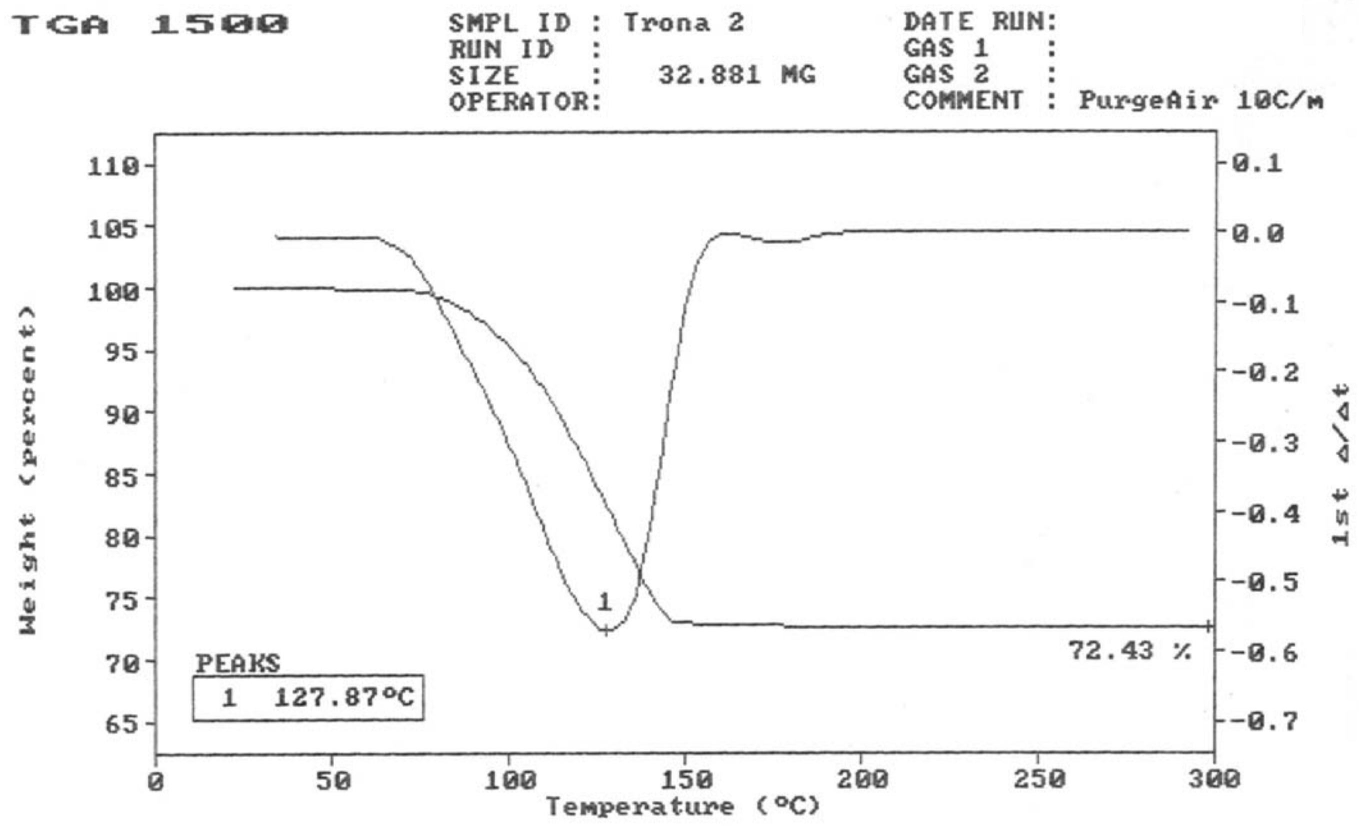

Figure 50. TG and DTG curves of representative trona samples of -12.7+9.53 mm particle size samples

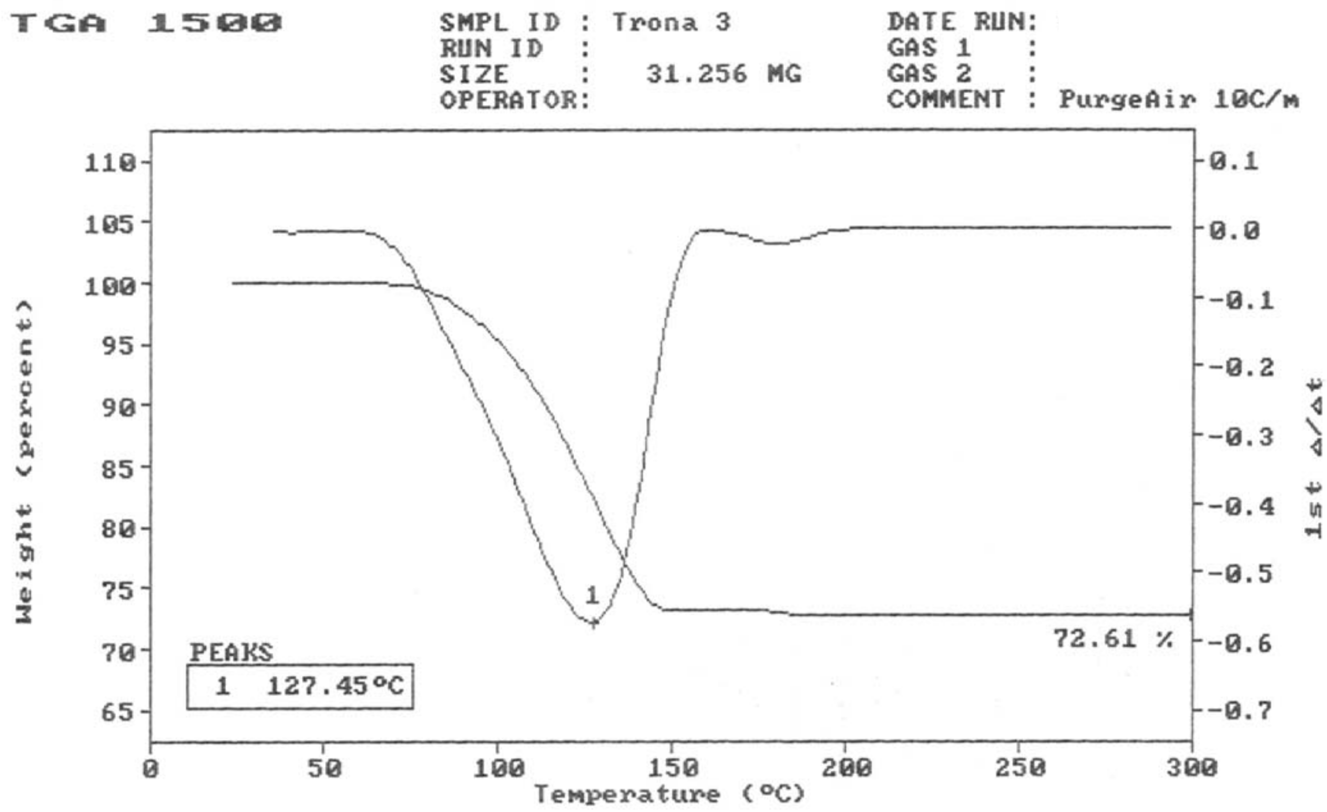

Figure 51. TG and DTG curves of representative trona samples of -9.53+6.35 mm particle size samples

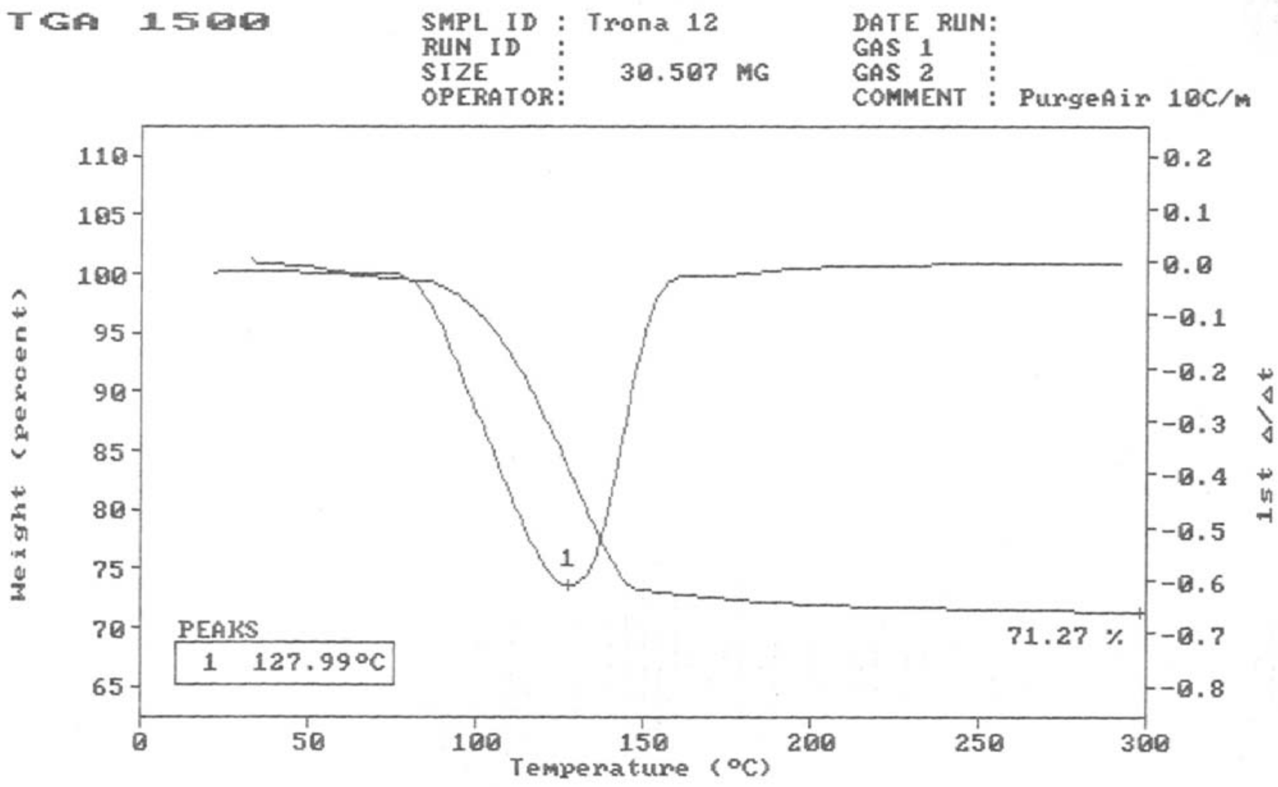

Figure 52. TG and DTG curves of representative trona samples of -6.35+3.35 mm particle size samples

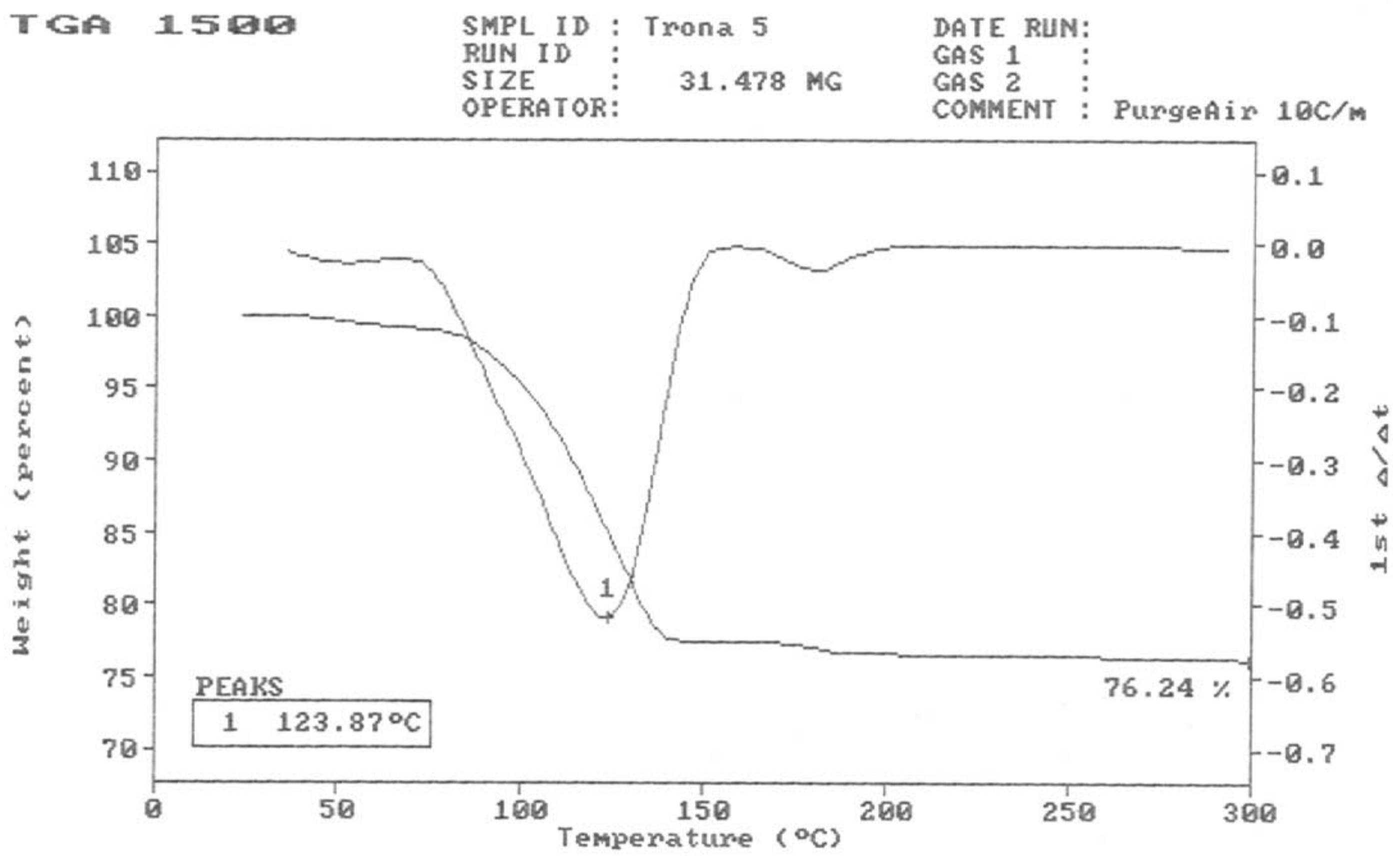

Figure 53. TG and DTG curves of representative trona samples of -3.35 mm particle size samples

5.2.3. XRD Analyses

Calcination products of trona samples were investigated by XRD analyses, which give crystal structure differences between the calcined products of various temperatures. For that purpose, the representative trona ore samples and hand-picked pure trona samples were calcined at the same temperatures. XRD analyses were performed on the uncalcined samples and the calcined products at the temperatures of 50, 100, 150, and 200 °C. In the identification of structures, XRD technique with Philips PW1840 brand X-ray powder diffractometer instrument was used.

Both representative Beypazarı trona ore sample and also hand-picked trona samples were examined in order to see the effect of calcination on the XRD pattern. ASTM data cards of XRD patterns are given in Appendix A.10. Figure 54 represents the XRD pattern of the representative trona ore sample. The peaks showed only the trona structure, $Na_3H(CO_3)_2.2H_2O$ sodium hydrogen and carbonate hydrate. Feldspar and analcime, smectite, amorphous silica minerals existed in the structure but not a quantitative amount. XRD pattern of calcined samples at 50 °C indicated the same pattern and showed the same stable structure with that in Figure 55. Being determination of the samples calcined at 100 °C and analyzed by XRD (Figure 56), there was an uncertainty in existency of wegschederite. This provides evidence that the product formed at this stage was microcrystalline (or amorphous). However, the dominant structure in XRD pattern of Figure 56 is that of sodium carbonate, Na_2CO_3. XRD patterns of calcined samples at 150 °C (Figure 57) and at 200 °C (Figure 58) indicated only one structure; sodium carbonate, Na_2CO_3.

The other group of XRD analyses was carried out with the hand-picked trona samples. The XRD pattern of the hand-picked trona samples is given in Figure 59. The only mineral in the sample was trona. The identifying peaks matched those of trona very well. XRD pattern of 50 °C calcined sample indicated the stable trona structure in Figure 60. The sample calcined at 100 °C (Figure 61) exhibits a similar behavior to that calcined at 50 °C. By increasing calcination temperature to 100 °C, it was observed that there was a decrease in main trona peak intensities. Somewhat trona peaks began to disappear and some peaks may be associated the intermediate product possibly wegschederite mineral peaks. The hand-picked trona samples calcined at higher temperatures of to 150 °C and to 200 °C demonstrated a different XRD pattern (Figure 62 and Figure 63). In one side amorphous structure preserved its continuity in other side different peak values were observed in both of the XRD patterns.

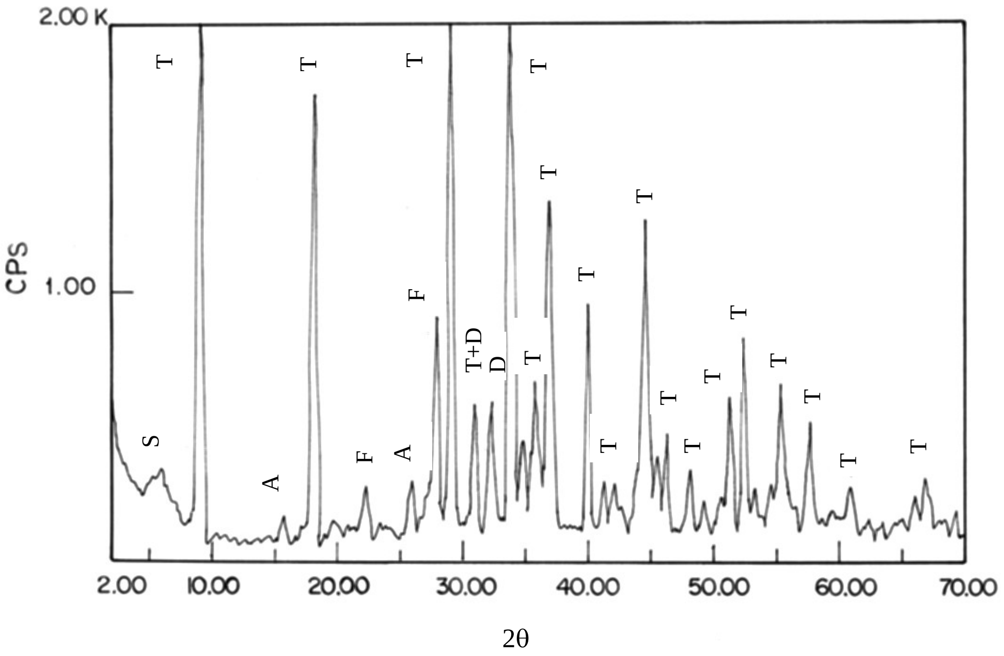

Figure 54. XRD pattern of the representative trona ore sample (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

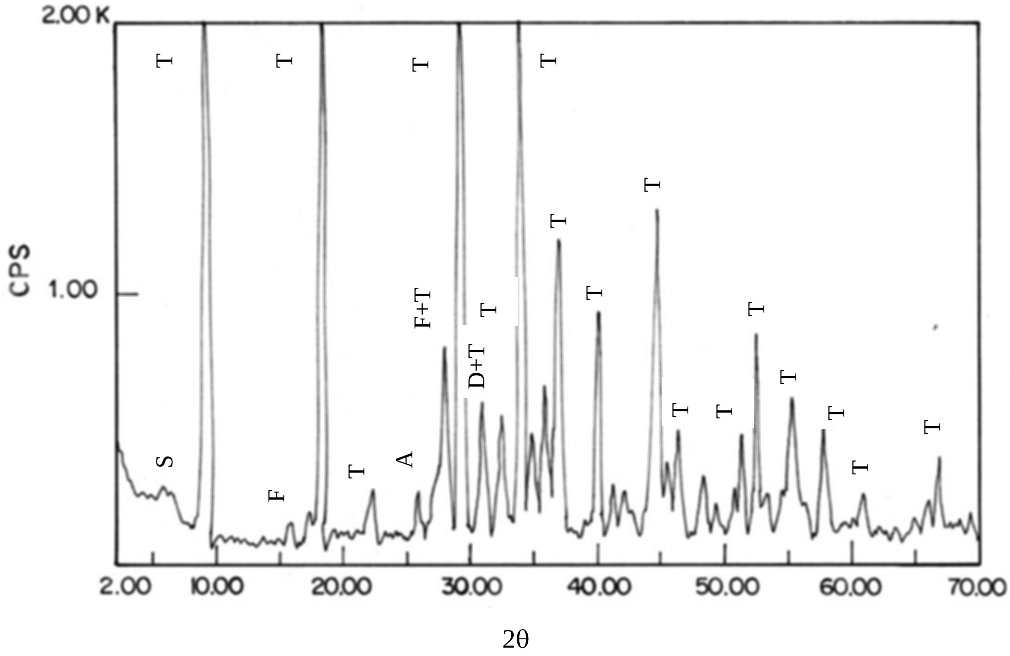

Figure 55. XRD pattern of representative trona ore sample calcined at 50 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

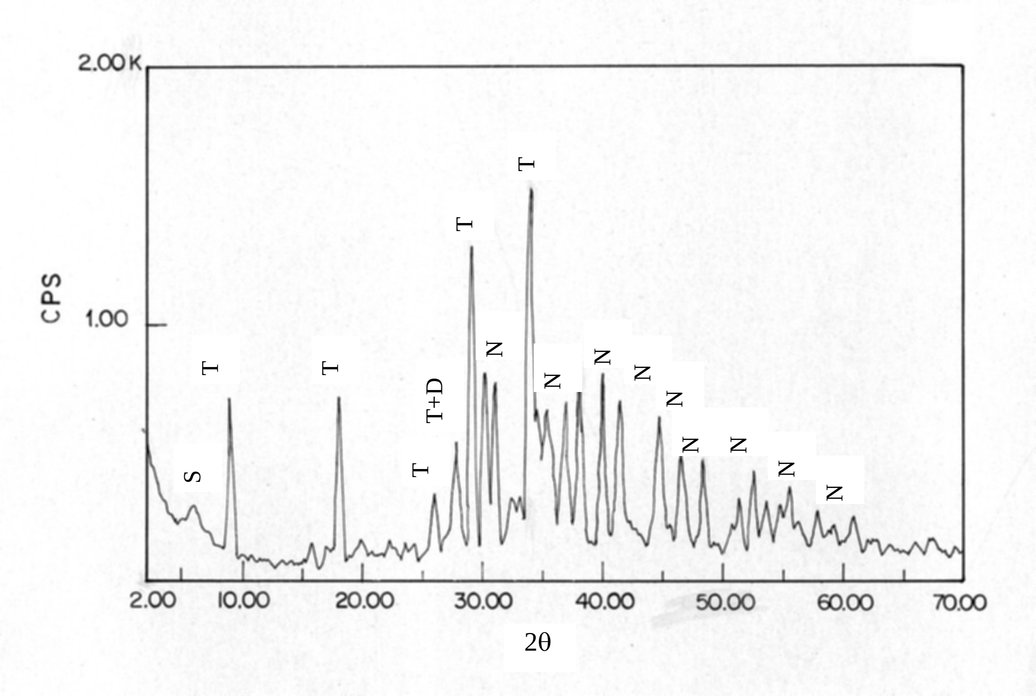

Figure 56. XRD pattern of representative trona ore sample calcined at 100 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

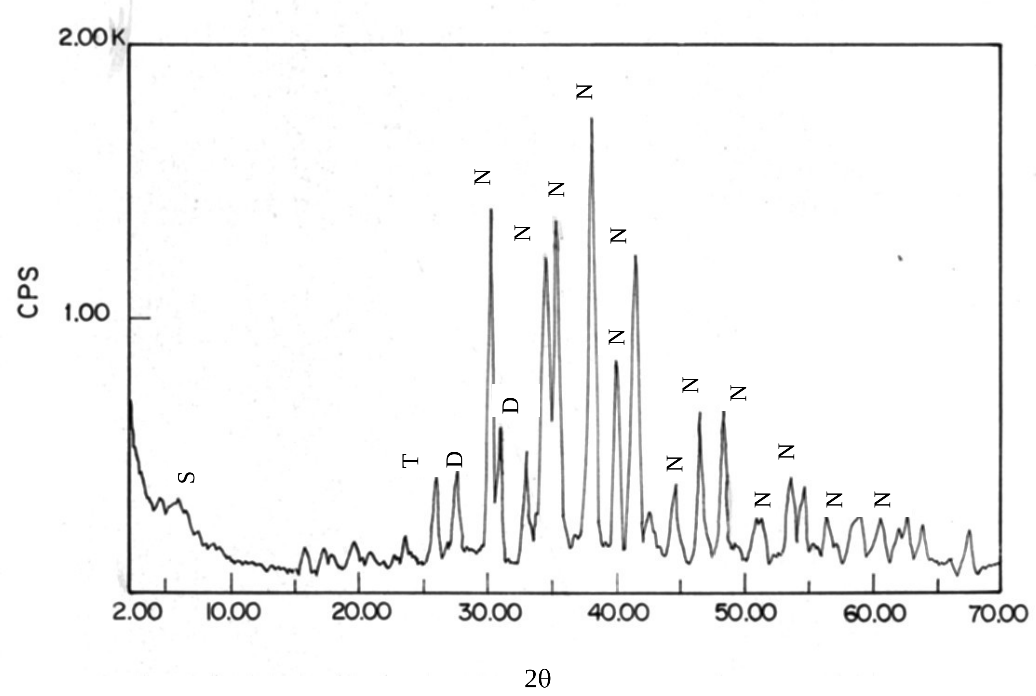

Figure 57. XRD pattern of representative trona ore sample calcined at 150 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

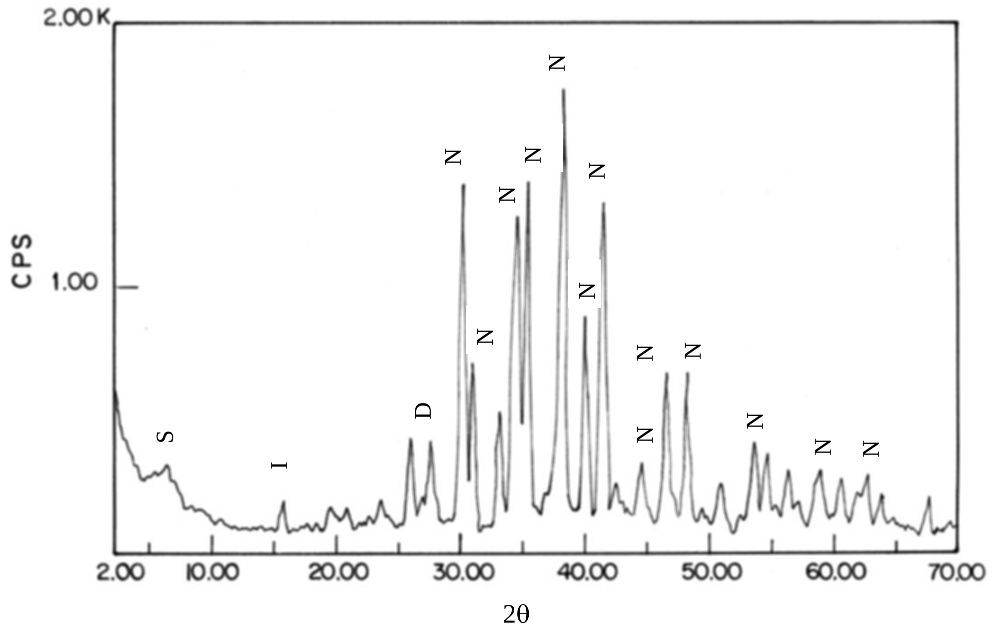

Figure 58. XRD pattern of representative trona ore sample calcined at 200 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite, I: Illite)

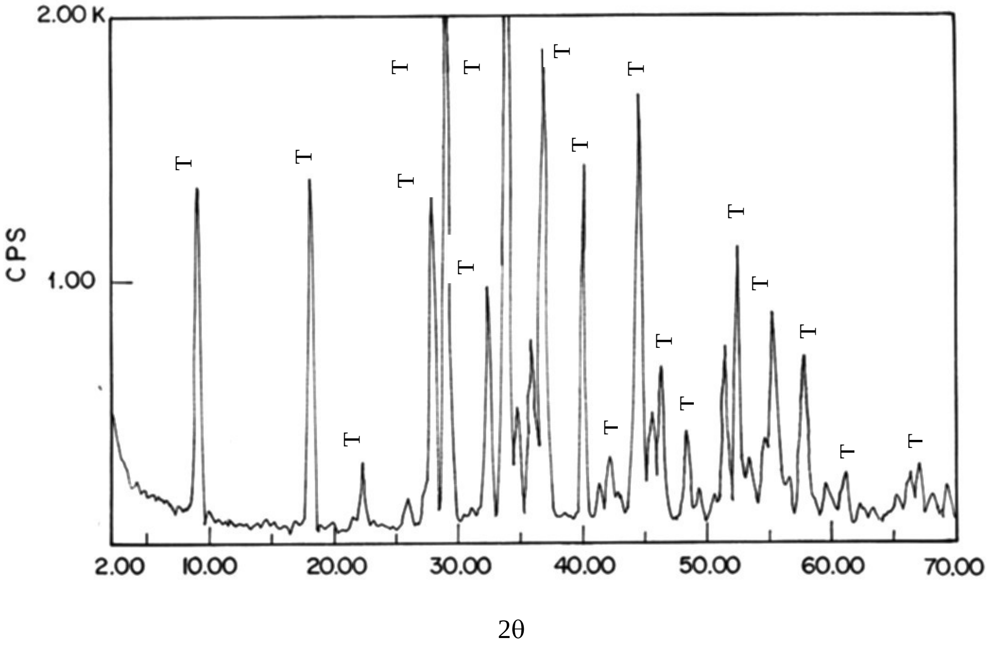

Figure 59. XRD pattern of the hand-picked trona sample (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

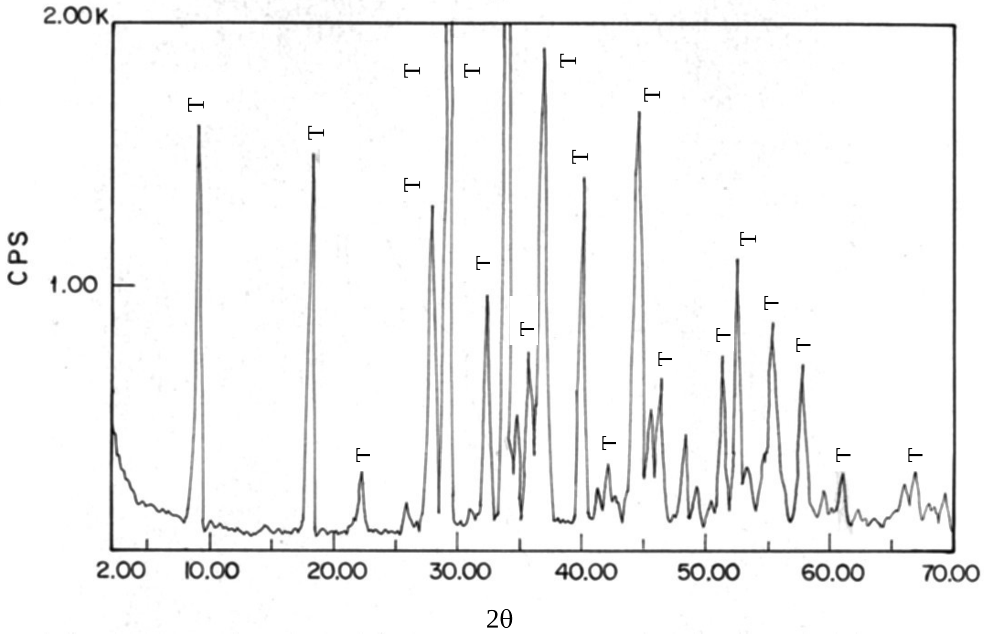

Figure 60. XRD pattern of the hand-picked trona sample calcined at 50 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

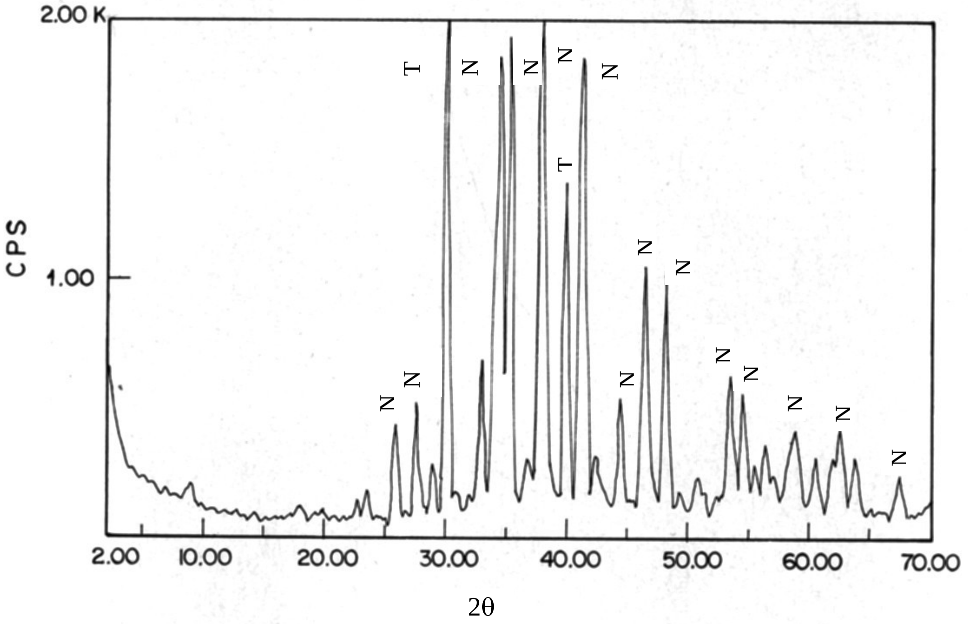

Figure 61. XRD pattern of the hand-picked trona sample calcined at 100 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

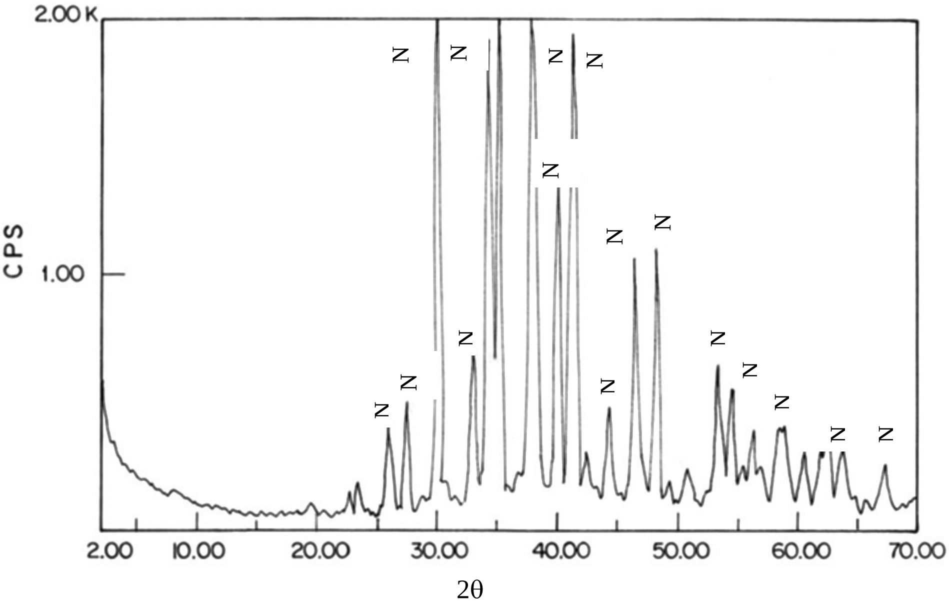

Figure 62. XRD pattern of the hand-picked trona sample calcined at 150 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

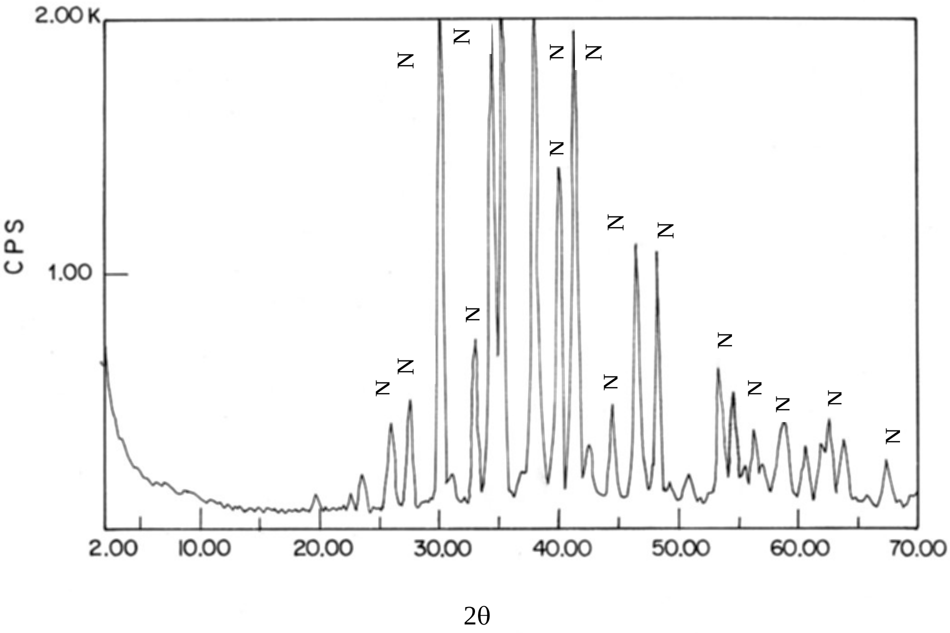

Figure 63. XRD pattern of the hand-picked trona sample calcined at 200 °C (T: Trona, N: Na_2CO_3, S: Smectite, A: Analcime, F: Feldspar, D: Dolomite)

5.3. Characteristics of Calcined Trona

5.3.1. Decrepitation

Thermal treatment of minerals also results in some structural modifications, due to formation of micropores and the resultant expansion of the crystal matrix upon development of uneven distribution of stresses. Such internal stresses subsequently induce fractures and in turn, fragmentation of the crystals.

Decrepitation of materials is a fairly well known phenomenon. The crackling or breaking up of certain crystals of materials when they are heated is named as decrepitation. Decrepitation occurs due to the phase and chemical changes in the materials and the resultant volume changes associated with these phase changes.

Whether decrepitation of materials due to thermal treatment during calcination operation happen or not was controlled by screen analysis of materials before and after calcination. -6.35 mm sized sample was calcined at 175 °C for 45 minutes of calcination duration. The screen analysis of -6.35 mm particle size samples is given in Table 21.

Table 21. Size distribution of -6.35 mm trona samples before and after calcination at 175 °C for 45 minutes

Particle Size (mm)	Before Calcination		After Calcination	
	Weight, %	Cum. Weight Retained, %	Weight, %	Cum. Weight Retained , %
-6.35+3.35	15.13	15.13	13.97	13.97
-3.35+2.0	19.06	34.19	18.48	32.45
-2.0+1.2	17.28	51.47	17.66	50.11
-1.2+0.417	22.37	73.84	23.53	73.64
-0.417+0.21	8.16	82.00	8.58	82.22
-0.21+0.105	6.61	88.61	6.68	88.90
-0.105+0.075	2.53	91.14	2.30	91.20
-0.075	8.86	-	8.80	-
TOTAL	100.00		100.00	

These data were evaluated in an effort to explain the decrepitation of trona. The graphical result of data is given in Figure 64.

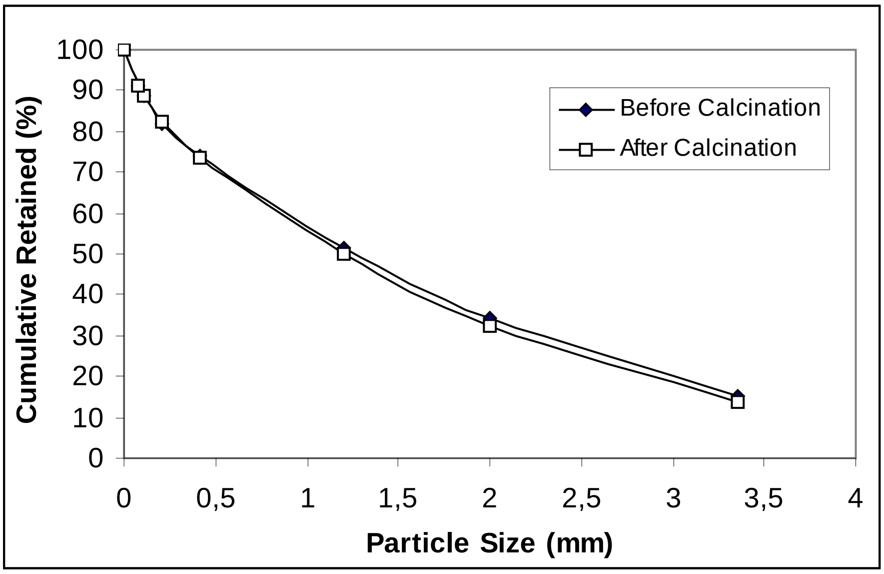

Figure 64. Size distribution of –6.35 mm trona samples before and after calcination of 175 °C for 45 minutes

As it is seen from Figure 64, there was no significant decrepitation on calcined samples. However, size reduction is expected in an industrial scale process due to the tumbling of ore particles in rotary kiln. The outlet (exhaust) gases of rotary kilns should be directed to cyclone and filters to prevent the loss of very fine valuable calcined particles.

5.3.2. Grindability

The determination of grindability of trona plays an important role to evaluate the material characteristics.

As it is convenient to express, understand and compare physical properties in terms of numbers known as indices, grindability is also similarly expressed by grindability index popularly known as Hardgrove Grindability Index (HGI).

Hardgrove Grindability Index and Work Index of Beypazarı trona ore were determined with calcined and uncalcined trona samples to compare the heat treatment effect on samples. The grindability (HGI) of the uncalcined samples and trona samples calcined at 175 °C in 45 minutes of calcination duration was determined with Grindability Index Machine. The standard Hardgrove grindability test was employed in weight basis with Neco brand Hardgrove machine in accordance of ASTM D 409-93a, 1971. The HGI values of both samples were converted to Work Index (kWh/ton) values by using the following equation.

$$\text{Work Index} = 435/\ (\text{HGI})^{0.91} * 0.91\ (\text{kWh/ton})$$

Table 22. Grindability values of trona before and after calcination

Grindability	Before calcination	After calcination
Hard Grove Index (HGI)	98.10	137.80
Work Index (kWh/ton) (calculated)	6.01	4.46

As shown in Table 22, there was an increase in the grindability of calcined materials. In accordance of grindability values, size reduction of calcined materials before leaching operation does not require high energy. Trona is easily ground due to the crystal structure changing (observed in SEM images given in Section 5.2.1.) after the heat treatment.

5.3.3. BET Analysis

Surface area variation plays an important role in the efficiency of the leaching operation. The BET Surface Area Analyzer estimates the specific surface of solid by determining the volume of a specific gas that is absorbed under controlled conditions. The specific surface areas of the trona samples were analyzed by single point BET nitrogen adsorption method (procedure is given in Appendix A.11.) in order to determine the surface area changes with respect to calcination temperature. The graphical result is given in Figure 65.

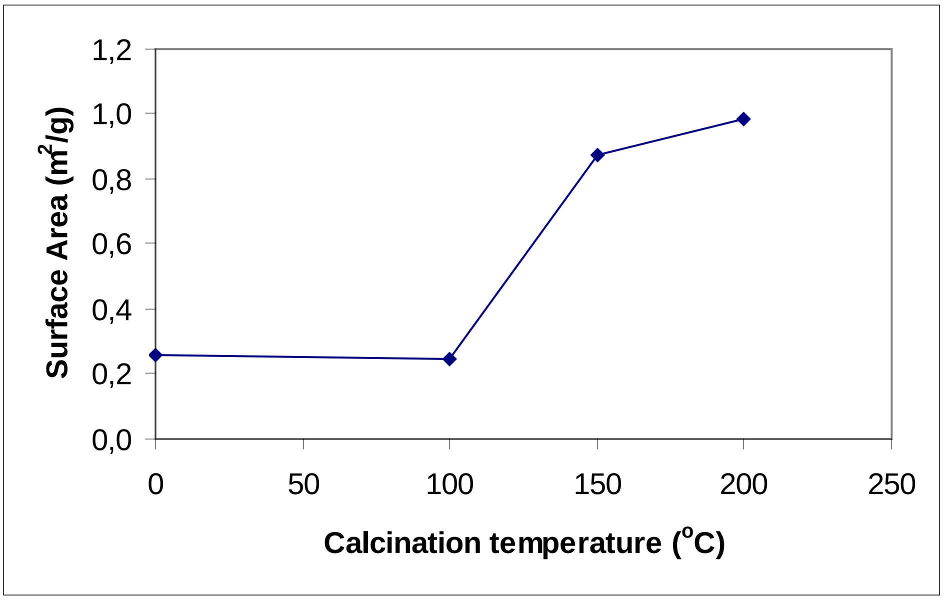

Figure 65. Effect of calcination at different temperatures on specific surface area of -200+270 mesh trona samples

The representative trona ore samples were heated to 100 °C, 150 °C and 200 °C for 1 hour of calcination to varying degrees of decomposition. Then trona samples were ground in the size of -200+270 mesh (-74+54 μm) before examining in BET analyzer.

As it is seen from Figure 65, BET surface area values of trona samples varied from 0.25 to nearly 1.00 m^2/g and there was no change in specific area of sample up to calcination temperature of 100 °C. It means there was no significant change below that temperature. At higher calcination temperatures trona samples had larger surface area which means that the surface area become more suitable for leaching operation. The larger surface area at higher calcination temperatures matched well with the porous structures verified by SEM images (Figure 36b and Figure 37b).

5.4. Leaching of Trona

Leaching is another vital process in production of soda ash from trona ore. During the leaching of trona, considerable amount of ore is in contact with relatively large volumes of water over a period of time. The effectiveness of contacting ore with solution and the recovery of leach solutions from the system without appreciable loss are two important physical factors.

The objective of the leaching experiments on Beypazarı trona ore was to evaluate the feasibility of leaching of trona from a technical viewpoint. Solubility and rate of dissolution are the two main factors. Since the soda ash production process most likely to involve evaporators, the higher the solubility the less water to be evaporated per ton of product and the lower the energy costs. The rate of dissolution is a function of time, temperature, concentration and surface area exposed for dissolution.

Dissolution characteristic of trona is directly related with its solubility affinity due to its chemical composition. Free H_2O molecules exist in the crystal lattice of trona make easier the interaction of molecules in water solution according to dissolution reaction.

$$2(Na_2CO_3.NaHCO_3.2H_2O)_{(s)} + H^+_{(aq)} \Rightarrow 2NaHCO_{3\,(s)} + Na^+_{(aq)} + 2H_2O_{(aq)} \qquad (21)$$

Because of its leaching characteristics the trona ore is ground to a fairly fine size. The ground ore then is leached at as high a temperature as possible to maximize the amount dissolved. This temperature generally is reported to be near the boiling point 97-98 °C.

The effect of three different leaching parameters; leaching time, pulp density and leaching temperature on the leaching rate were examined in agitating leaching. Uncalcined and calcined samples were used during leaching experiments. Firstly representative uncalcined sample having –6.35 mm particle size was leached. By determining the optimum leaching parameters with this sample, leaching of calcined samples was carried out in the pre-determined leaching conditions. The leaching results are tabulated in Tables 23-26 in Appendix A.9.

Leach recoveries of samples were evaluated in terms of dissolved trona percentage in leaching operation. Because the carbonate compounds which exist in chemical composition of trona are easily converting to each other. The best expressing of leaching recovery of sodium carbonate materials is total alkali determination in terms of Na_2CO_3 content (%). At the beginning of the leaching experiments, % Na_2CO_3 values of uncalcined and calcined samples were found as 58.06 % and 71.10 % respectively.

5.4.1. Effect of Leaching Time

The effect of leaching time was studied starting from 1 minute leaching and ending at 4 minutes at 25 % pulp density with the particle size of –6.35 mm. The leaching results are shown in Figure 66.

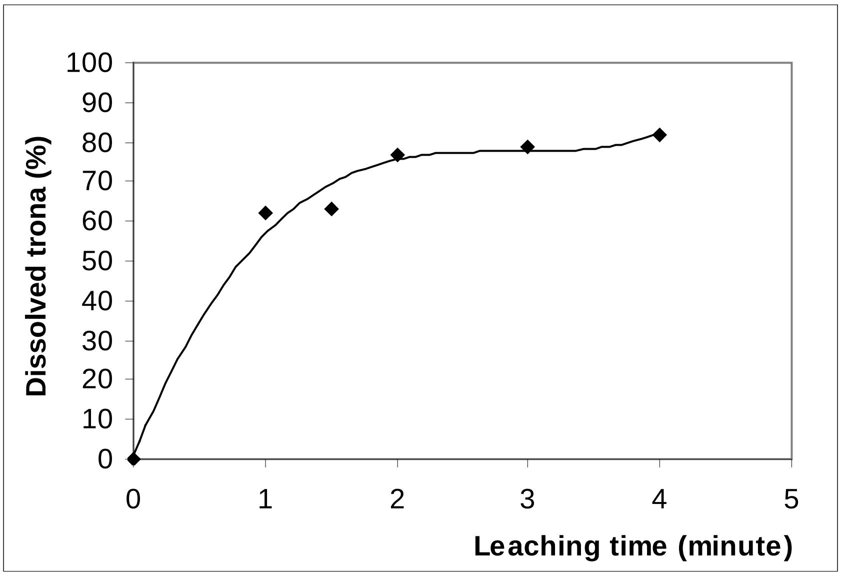

Figure 66. Effect of leaching time on dissolution of raw trona

As seen from this figure, leach recovery is increasing with increasing leaching time. The first 2 minutes of leaching was occurring very fast. The recovery reached to obtainable 80 % values in 4 minutes at room temperature. The leaching time of trona is very short which means that trona has a high solubility in water.

5.4.2. Effect of Pulp Density

In the pulp density studies, three different solid by weight pulp density values, namely 15 %, 25 % and 30 % that are generally used in leaching operation were examined. The effect of leaching time on dissolution of trona at different pulp densities is shown in Figure 67.

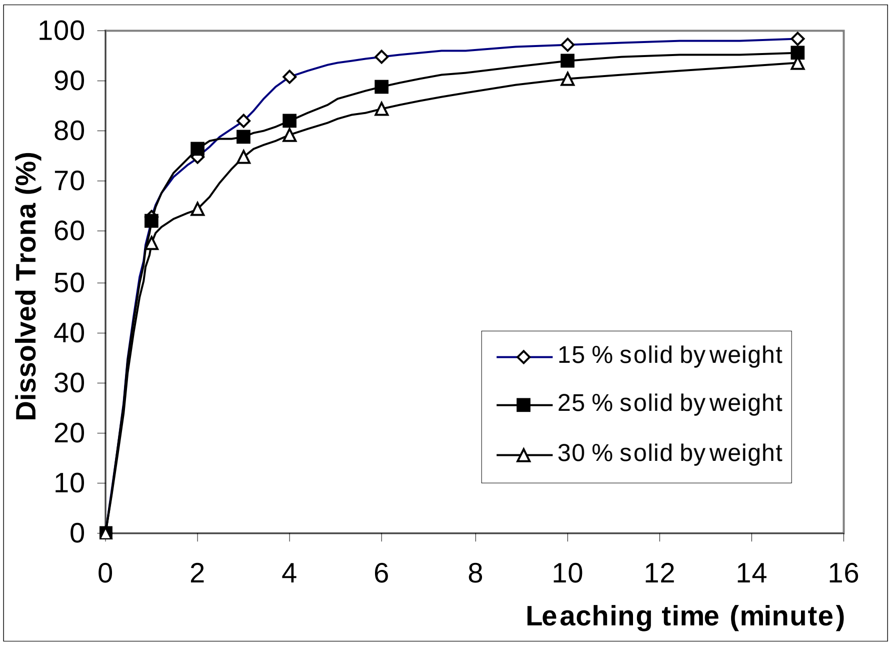

Figure 67. Effect of leaching time on dissolution of raw trona at different pulp densities

As shown in Figure 67, dissolved trona % is decreasing with increasing pulp density. The optimum pulp density was selected as 25 % since that would be economic in an industrial scale application. The rest of the leaching experiments were conducted at the 25 % pulp density. Leaching with high solid content above 30 % will have risk of re-crystallization of pregnant solution due to closing of saturation point.

5.4.3. Effect of Leaching Temperature

In order to see the effect of leaching temperature, experiments conducted at temperatures of 20 °C, 40 °C, 60 °C, and 80 °C. During these tests, leaching time of 3 minutes and pulp density of 25 % solid by weight was kept constant. The effect of leaching temperature on dissolution of raw trona is shown in Figure 68.

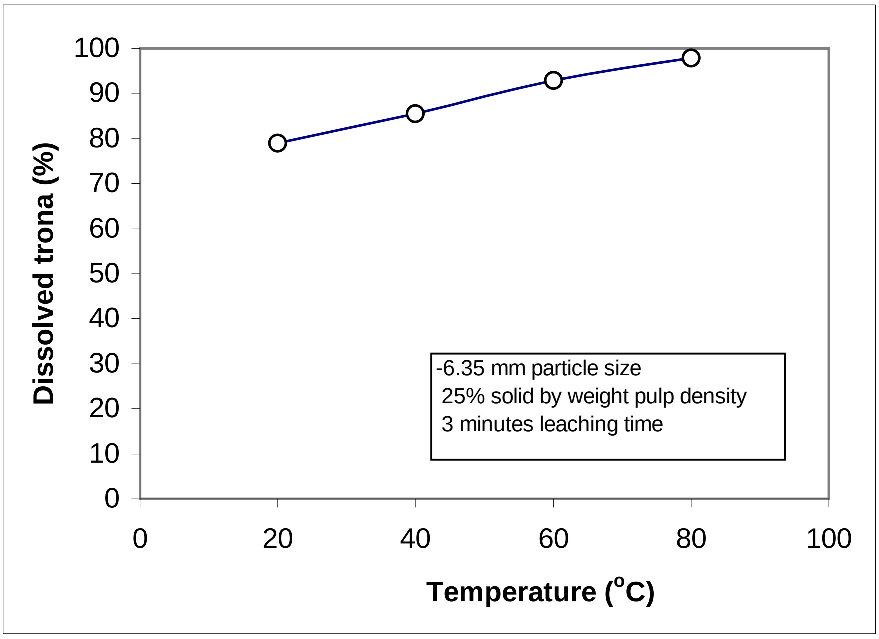

Figure 68. Effect of leaching temperature on dissolution of raw trona

In general, high temperature has a positive effect on leaching rate and kinetics. This effect is also observed in trona leaching experiments, dissolved trona is increasing with increasing leaching temperature. Although the rate of dissolution of trona is rather high at room temperature, some other higher temperature levels were examined and complete dissolution was obtained at 90 °C.

The effect of temperature on dissolution mechanism of trona could be vital for the solution mining of trona. While trona dissolves in water, adverse effect of crystallization would be seen if appropriate temperature and concentration were not taken into consideration carefully.

It is difficult to obtain on an industrial scale a saturated solution at a temperature around 90 °C. This temperature may lead to an undesirable crystallization in the production wells (Saygılı, 2003).

5.4.4. Leaching of Calcined Samples

Detailed studies of the leaching parameters such as particle size, temperature and solid-liquid ratio were carried out on calcined trona sample. Only, the effect of leaching time was investigated. Leaching experiments were carried out at ambient temperature (20 °C) with samples of –6.35 mm particle size and pulp density of 25 % solid by weight. Experimental results are presented in Figure 69.

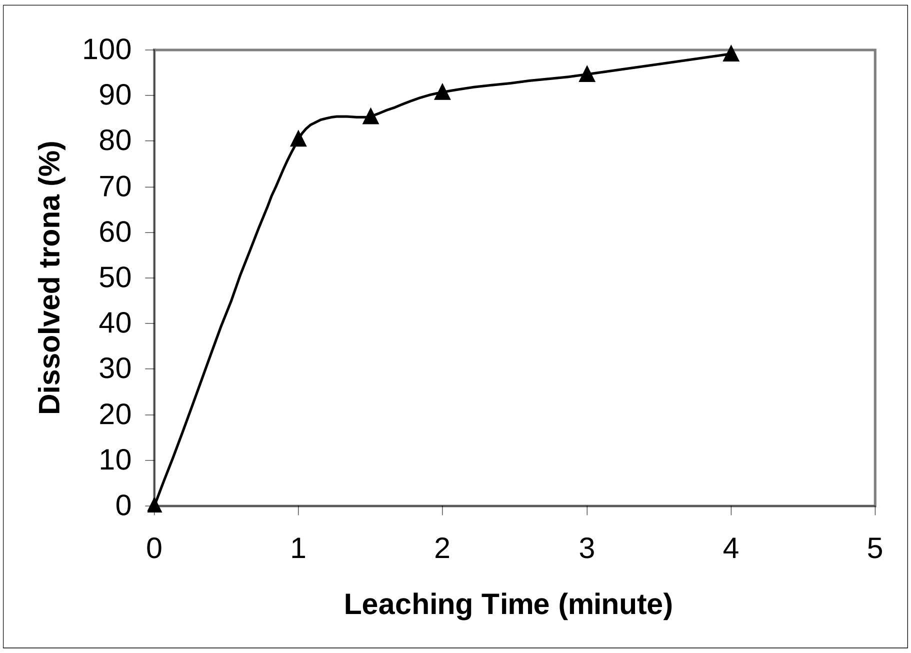

Figure 69. The dissolution of calcined samples with particle size of -6.35 mm

It is understood from the results that the increase in dissolved trona % increases with the leaching time and leaching operation is completed in a very short time. The rate of trona dissolution was very rapid in the first minute of leaching then it increased gradually with longer time and completed in 4 minutes.

Comparison of dissolution rate of calcined and uncalcined samples for the same operating conditions showed that there is a significant improvement in trona dissolution for calcined sample. From Figure 70, it is observed that leaching operation is completed for calcined trona sample in a very short time, 4 minute, whereas the uncalcined leach recovery was about only 80 % in the same leaching time.

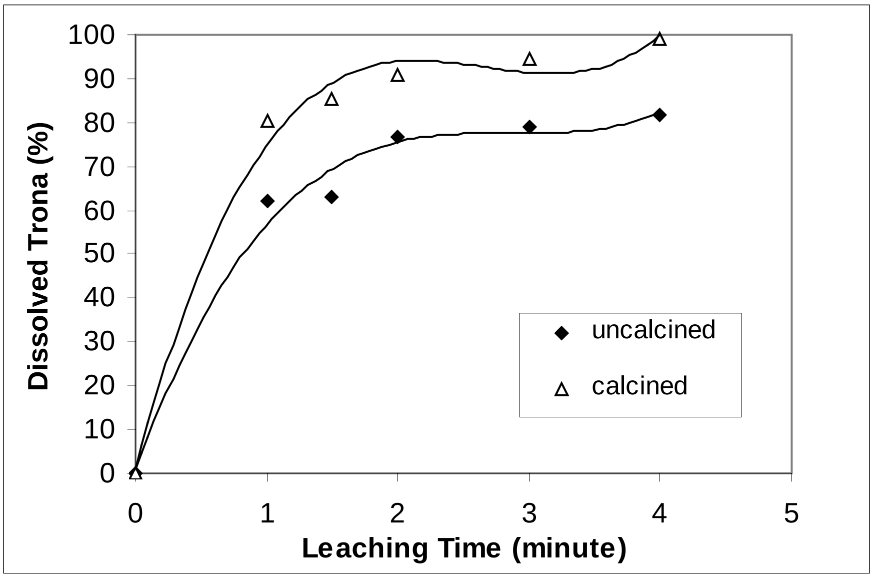

Figure 70. The comparison of calcined and uncalcined samples of leaching

As proved with SEM examination and BET analysis, the porosity and specific surface area of trona sample changes with thermal treatment. The increase in specific surface area and porosity has a positive effect on the dissolution of calcined trona sample. The increase in porosity and specific surface area of calcined particle will allow much more water, the leachant to contact and dissolve trona in the particle.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATION

Based on the experimental results, the following conclusions are drawn:

- Beypazarı trona are can easily be processed for soda ash production due to its low NaCl (0.025 %) and Na_2SO_4 (0.026 %) content.
- Trona can be decomposed at any temperature over about 70 °C, but the rate does not become reasonable below 120 °C.
- The thermal decomposition of trona at low calcination temperatures produces sodium carbonate monohydrate ($Na_2CO_3.H_2O$) and wegschederite ($Na_2CO_3.3NaHCO_3$) as intermediate products.
- 30 minutes of calcination time was sufficient for complete calcination – 6.35 mm feed at complete 175 °C in muffle furnace. For same feed calcination was performed in shorter time with up draught furnace.
- The weight loss 25.44 % after complete calcinations is explained by removal of crystal water and exposure of CO_2.
- Microwave-induced dry calcination of trona was possible and 5 minutes of calcination time at a power level of 900 watts was sufficient for complete calcination of -6.35 mm feed.
- All of the sodium bicarbonate is converted to sodium carbonate by microwave heat treatment in 5 minutes during wet calcination. Wet calcination of trona with microwave energy could be a cost effective process in the future due to applicability of process to trona produced by solution mining technique.

- No degradation or decrepitation was detected during the calcination, while significant increase in specific surface area and Hardgrove Index value of calcined sample were observed.
- Almost 100 % leach recovery was observed with calcined –6.35 mm trona sample at a pulp density of 25 % solid in 4 minutes, while leach recovery was only 80 % for the uncalcined sample at the same leaching conditions.
- Leaching experiments demonstrated that highest dissolution rate for trona was obtained at 80 °C.
- Further studies of dry or wet type microwave induced calcination of trona is recommended.

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APPENDIX A.1.

Total Alkali Determination

This test method covers the titrimetric determination of the total alkalinity of soda ash (ASTM E 359-90). This alkalinity is expressed in terms of sodium carbonate Na_2CO_3 content (%).

Total alkalinity is determined by titration with standard 1 M HCl (hydrochloric acid) using methyl orange indicator that is prepared by dissolving 0.5 grams of methyl orange in 1 liter distilled water (TS 755, TS 759).

The test sample of 10 ml solution is pipetted out from the agitated leached* solution, 100 ml of distilled water and 3 drops of methyl orange indicator are added to the beaker. The titration operation is starting by dropping of HCl acid slowly. This solution is titrated to the end point of orange color from the yellow color. The consumed volume of HCl acid is recorded and this value is used in the calculation of Na_2CO_3 (%) as given below.

$$\text{Total Alkalinity (\%)} = \frac{100*A*V*S}{m}$$

V: volume of titrated HCl acid (ml)

S: safety factor -calculated from titrated volume of HCl with equal weight of analytical Na_2CO_3 - (g) m: weight of sample

A: taken as 0.053- the equivalent weight of primary standard sodium carbonate to 1 ml of HCl acid solution

APPENDIX A.2.

Sodium Bicarbonate Determination

This test method describes the titrimetric determination of sodium bicarbonate ($NaHCO_3$, %) in soda ash (Natural Soda Ash, 1999). The lower limit of determination is 0.02 % sodium bicarbonate.

Sodium bicarbonate is determined titrimetically by adding a sample to an excess of standard sodium hydroxide (0.1 M NaOH) solution (thus converting sodium bicarbonate to sodium carbonate), precipitating the carbonate with barium chloride solution and back-titrating the excess sodium hydroxide with standard 1 M HCl acid solution using phenolphthalein indicator (TS 778).

A primary standard (analytical grade of Na_2CO_3) is run simultaneously to find the correction factor of titration of sodium hydroxide on the barium carbonate.

The test sample of 1 gram is dissolved in 100 ml of distilled water in a 750 ml volumetric flask by agitating magnetic stirrer. 50 ml of 0.1 M NaOH solution is added to the flask. After dissolving completely, 170 ml of $BaCl_2$ solution (100 g/liter) is added so slowly that minimizing excess CO_2 entrance to the flask. Then the flask is closely tightened with parafilm and the flask is shaken severely in 30 seconds. The flask is allowed to wait for 5 minutes and 4 drops of phenolphthalein is added. The solution will become deep red if sodium bicarbonate is present. Then, the solution is titrated slowly with 1 M HCl using 20 ml burette, stirring continuously. The titration is stopped when obtaining the end point of white color solution from deep red color. The volume of the titrant is recorded to the nearest 0.05 ml.

$$NaHCO_3\ (\%) = (at-b) * \frac{100}{m} * A$$

a: volume of the consumed NaOH solution in the titration (50 ml)

t: calculated equivalent volume of NaOH solution with the below equation ($t = C/50$)

C: volume of titrated HCl acid with analytical grade of Na_2CO_3 (ml)

b: volume of titrated HCl (ml)

m: weight of sample (g)

A: taken as 0.08402 - theoretical equivalent weight of sodium bicarbonate to 1 ml of 0.1 M NaOH

APPENDIX A.3.

Stoichiometric Calculations of Trona

To calculate, % trona, % total alkali, excess Na_2CO_3 (Thermonatrite) and Na_2HCO_3 (Nahcolite) (TS 779)

Given: % Na_2CO_3, %$NaHCO_3$

1-) % $NaHCO_3$ x 0.6309 + % Na_2CO_3= % total alkali

2-) $\frac{\% Na_2CO_3}{106}$ = Mol. % Na_2CO_3

3-) $\frac{\% NaHCO_3}{84}$ = Mol. % $NaHCO_3$

4-) If, Mol % $Na_2CO_3 \leq$ Mol. % $NaHCO_3$:

a) Mol. % Na_2CO_3 x 2,1324x106= % Trona . –In sample-

b) % TRONA x 0,37167= % Amount of Bicarbonate in TRONA

c) % $NaHCO_3$ – Result of 4 b= % Excess $NaHCO_3$ (Nahcolite)

5-)If, mol. % Na_2CO_3> Mol. % $NaHCO_3$:

a)Mol %$NaHCO_3$x2,6905+84= % TRONA IN SAMPLE

b)% TRONA x 0,46894=Amount of Na_2CO_3 in TRONA.

c) % Na_2CO_3- Result of 5 b = % Excess. % Na_2CO_3 (Thermonatrite)

6-) % Insolubles= 100- %TRONA- Results of 4 c or 5 c

EXAMPLE- 1:

Givens: (Results of analysis):

32 % $NaHCO_3$ And

40 % Na_2CO_3

1-) 40+32x 0, 6309= %60.2 {Amount of Total Alkali}

2-) $\frac{40}{106}$ = % 0,37736 % Mol. Na_2CO_3

3-) $\frac{32}{84}$ = % 0, 380 % Mol. $NaHCO_3$

4-) % Mol. Na_2CO_3 < % Mol. $NaHCO_3$

a) 0,37736 x 2,1324 x 106 = % 85,29 % TRONA
b) 85,29 x 0,37167 = %31,70 (Amount of $NaHCO_3$ inTRONA)
c) 32-31,70= % 0,3 Excess, $NaHCO_3$ (Nahcolıte)

5-) % Insolubles = 100 – (85,28+0,3) = % 14,41

To Check

85,28 x 0, 7034 = 59,99
0,3 x 0,6309 = $\underline{0,189}$
% 60,179 TOTAL ALKALI

EXAMPLE –2 :
Givens: (Results of Analysıs)

30 % $NaHCO_3$
50 % Na_2CO_3

1-) 30 x 0,6309 + 50 = 68,927 % TOTAL ALKALI
2-) $\frac{50}{106}$ = % 0, 471 Mol. Na_2CO_3
3-) $\frac{30}{84}$ = % 0,357 Mol. $NaHCO_3$
4-) % Mol. Na_2CO_3> % Mol. $NaHCO_3$

a) % Mol. $NaHCO_3$ x 2,6905 x 84 =

0,357 x 2,6905 x 84 = 80,715

b) 80,715 x 0, 46894 = % 37,851 Amount of Na_2CO_3 in TRONA

c) 50 – 37,851 = % 12,149 Exces, Na_2CO_3 (Thermonatrite)

To Check

80,715 x 0,7034 = 56, 775
12,149 x 0, 6309 = <u>12,149</u>
68,294 TOTAL ALKALI

Moleculer weights and equivalents

Formula	M.W
Na_2CO_3	105.993
$NaHCO_3$	84.010
$Na_2CO_3 . NaHCO_3 . 2H_2O$	226.035
Na_2O	61.982
NaCl	58.448
Na_2SO_4	142.048
H_2O	18.016
H_2S	34.082

Equivalents

Multiply	By	Gives
Na_2CO_3	0.58477	Na_2O
Na_2CO_3	2.1325	Trona
$NaHCO_3$	2.6905	Trona
$NaHCO_3$	0.63083	Na_2CO_3

APPENDIX A.4.

Sieve Analysis of The Different Size Fractions

Particle Size, mm	Weight, %	Cum. Weight Retained, %
-19+12.7	21.76	21.76
-12.7+9.53	10.45	32.21
-9.53+6.35	10.55	42.76
-6.35+3.35	11.95	54.71
-3.35	45.29	-
TOTAL		100.00

a. Feed Size: -19 mm

Particle Size, mm	Weight, %	Cum. Weight Retained, %
-12.7+9.53	13.84	13.84
-9.53+6.35	16.91	30.75
-6.35+3.35	19.33	50.08
-3.35+1.20	18.80	68.88
-1.20	31.20	-
TOTAL		100.00

b. Feed Size: -12.7 mm

Particle Size, mm	Weight, %	Cum. Weight Retained, %
-9.53+6.35	18.73	18.73
-6.35+3.35	24.23	42.96
-3.35+1.20	22.82	65.78
-1.20+0.417	15.15	80.93
-0.417	19.07	-
TOTAL		100.00

c. Feed Size: -9.53 mm

Particle Size, mm	Weight, %	Cum. Weight Retained, %
-6.35+3.35	15.13	15.13
-3.35+2.0	19.06	34.19
-2.0+1.2	17.28	51.47
-1.2+0.417	22.37	73.84
-0.417+0.21	8.16	82.00
-0.21+0.105	6.61	88.61
-0.105+0.075	2.53	91.14
-0.075	8.86	-
TOTAL		100.00

d. Feed Size: -6.35 mm

Particle Size, mm	Weight, %	Cum. Weight Retained, %
-3.35+2.0	16.64	16.64
-2.0+1.20	30.99	47.63
-1.20+0.417	25.60	73.23
-0.417+0.21	8.68	81.91
-0.21+0.105	7.36	89.27
-0.105+0.075	5.42	94.69
-0.075	5.31	-
TOTAL		100.00

e. Feed Size: -3.35 mm

APPENDIX A.5.

Results of Laboratory Muffle Furnace Calcination

Table 11. Calcination of Trona in a Muffle Furnace at 150 °C

Particle Size, mm	**Weight Loss, % Calcination Time, min**						
	30	60	90	120	150	180	210
-19	7.25	13.24	18.29	20.93	24.19	25.53	Same
-12.7	9.10	15.62	23.20	24.22	25.51	Same	-
-9.53	13.03	23.85	25.50	Same	-	-	-
-6.35	14.30	25.11	25.74	Same	-	-	-
-3.35	15.40	25.60	Same	-	-	-	-

Table 12. Calcination of Trona in a Muffle Furnace at 175 °C

Particle Size, mm	**Weight Loss, % Calcination Time, min**				
	30	60	90	120	150
-19	12.77	19.81	24.80	25.54	Same
-12.7	15.49	24.48	25.61	Same	-
-9.53	22.43	25.38	25.63	Same	-
-6.35	25.44	Same	-	-	-
-3.35	25.62	Same	-	-	-

Table 13. Calcination of Trona in a Muffle Furnace at 200 °C

Particle Size, mm	**Weight Loss, % Calcination Time, min**			
	30	45	60	75
-19	14.59	19.73	25.77	Same
-12.7	17.21	23.39	25.85	Same
-9.53	23.29	24.23	25.87	Same
-6.35	25.45	Same	Same	-
-3.35	22.51	24.21	25.31	-

APPENDIX A.6.

Results of Designed Up Draught Calcination

Table 14. Calcination of Trona in Up Draught Furnace at 150 °C

Calcination Time, min	**Weight Loss, %**				
	Particle Size, mm				
	-19	-12.7	-9.53	-6.35	-3.35
15	7.71	10.47	12.47	14.10	7.63
30	18.69	20.42	22.07	22.65	23.10
45	20.57	22.01	24.72	25.71	25.37
60	23.23	23.70	25.00	25.86	25.37
90	25.48	25.55	25.95	25.86	25.37
120	25.48	25.46	25.95	25.86	25.37

Table 15 Calcination of Trona in Up Draught Furnace at 175 °C

Calcination Time, min	**Weight Loss, %**				
	Particle Size, mm				
	-19	-12.7	-9.53	-6.35	-3.35
15	12.54	17.51	17.33	21.86	17.46
30	19.53	20.87	23.00	25.92	25.11
45	21.77	25.66	25.91	25.70	25.51
60	23.24	25.20	25.73	25.44	25.51
90	25.07	25.20	25.73	25.44	25.51
120	25.02	25.20	25.73	25.98	25.51

Table 16. Calcination of Trona in Up Draught Furnace at 200 °C

Calcination Time, min	**Weight Loss, %**				
	Particle Size, mm				
	-19	-12.7	-9.53	-6.35	-3.35
10	10.19	12.85	18.97	17.20	16.79
15	18.69	17.57	20.33	25.53	22.66
20	22.17	20.77	24.36	24.59	25.84
30	23.56	23.25	25.91	25.65	25.86
45	25.30	25.33	25.71	25.30	25.86
60	25.30	25.85	25.48	25.30	25.86

APPENDIX A.7.

Results of Dry Type Microwave Calcination

Table 17. Dry Type Microwave Calcination

Calcination Time, min	Weight Loss, %		
	Microwave Power, watt		
	400	620	900
1.50	0.99	6.73	8.48
3.00	3.74	14.81	13.05
5.00	12.13	20.14	20.77
6.00	15.60	22.12	24.63
7.00	19.40	26.26	24.63
10.00	23.31	26.35	24.63

Table 18. 620 watt Experiments with Dry Type Microwave Calcination

620 watt microwave experiments					
Calcination Time, min	Weight Loss, %				
	Particle Size, mm				
	-3.35	-6.35	-9.53	-12.7	-19
1.50	2.19	6.73	2.44	5.14	3.06
3.00	3.91	14.81	8.32	17.6	10.37
5.00	10.98	20.14	12.17	22.01	13.32
7.00	16.24	26.26	21.82	17.89	11.16
10.00	25.56	26.35	20.98	19.82	15.00

APPENDIX A.8.

Results of Wet Type Microwave Calcination

Table 19. $NaHCO_3$ (%) of Dissolved Sample in Wet Type Microwave Calcination

Calcination Time, min	**$NaHCO_3$,% Microwave Power, watt**		
	400	620	900
0	33.00	33.00	33.00
2	28.00	27.04	24.62
4	23.39	20.76	18.76
5	21.80	12.07	8.90
6	18.61	9.98	3.49
7	16.88	7.67	1.26
8	14.26	6.14	
9	12.68	3.83	
10	12.02	0.76	
12	11.88		
14	10.30		
18	6.34		
22	4.75		

Table 20. Conversion of $NaHCO_3$ with Time

Calcination Time, min	**Conversion Ratio**		
	Microwave Power, watt		
	400	620	900
0	0.00	0.00	0.00
2	0.15	0.18	0.25
4	0.29	0.37	0.43
5	0.33	0.63	0.73
6	0.43	0.69	0.89
7	0.48	0.76	0.96
8	0.56	0.81	
9	0.61	0.88	
10	0.63	0.97	
12	0.64		
14	0.68		
18	0.80		
22	0.85		

APPENDIX A.9.

Results of Leaching Experiments

Table 23. Leaching of Raw Trona in Different Leaching Time

Leaching Time, min	Dissolved trona, %
0	0
1.0	62.14
1.5	62.92
2.0	76.64
3.0	78.89
4.0	81.96

Table 24. Leaching of Raw Trona at Different Pulp Density

Leaching Time, min	Dissolved Trona, %		
	Pulp Density, %		
	15	25	30
0	0	0	0
1.0	62.94	62.14	57.82
2.0	74.78	76.64	64.54
3.0	82.15	78.89	74.78
4.0	90.92	81.96	79.34
6.0	94.69	88.90	84.65
10.0	97.37	94.13	90.32
15.0	98.45	95.78	93.54

Table 25. Leaching of Raw Trona at Different Leaching Temperature

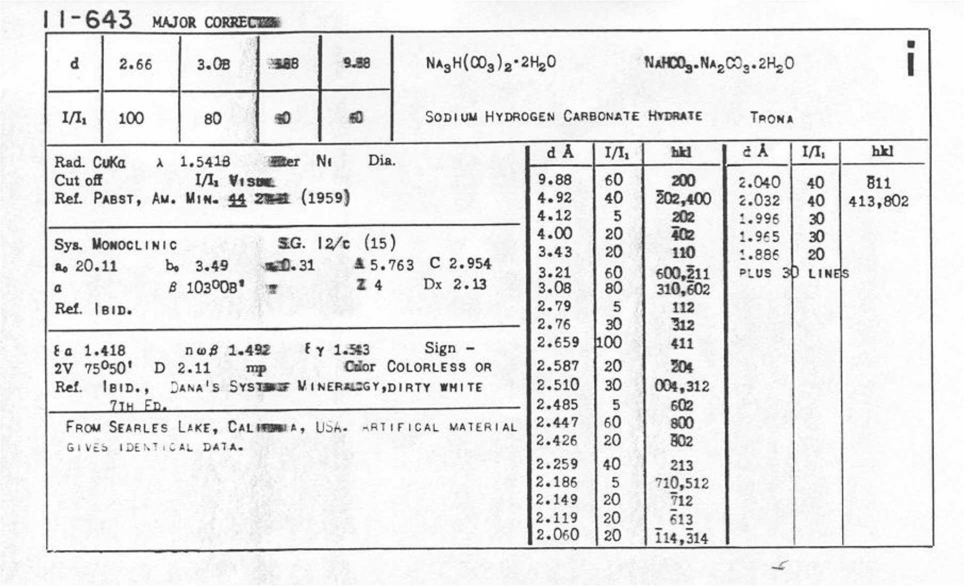
Temperature, °C	**Dissolved Trona, %**
20	78.92
40	85.53
60	92.96
80	97.81

Table 26. Leaching of Calcined and Raw Trona

Leaching Time, min	**Dissolved Trona, %**	
	Uncalcined Samples	**Calcined Samples**
0	0	0
1.0	62.14	80.43
1.5	62.92	85.34
2.0	76.64	90.78
3.0	78.89	94.66
4.0	81.96	99.10

APPENDIX A.10.

ASTM Data Cards



11-643 MAJOR CORRECTION

d	2.66	3.08	[illegible]	9.88	$NA_3H(CO_3)_2 \cdot 2H_2O$	$NaHCO_3 . Na_2CO_3 . 2H_2O$	i
I/I_1	100	80	60	60	SODIUM HYDROGEN CARBONATE HYDRATE	TRONA	

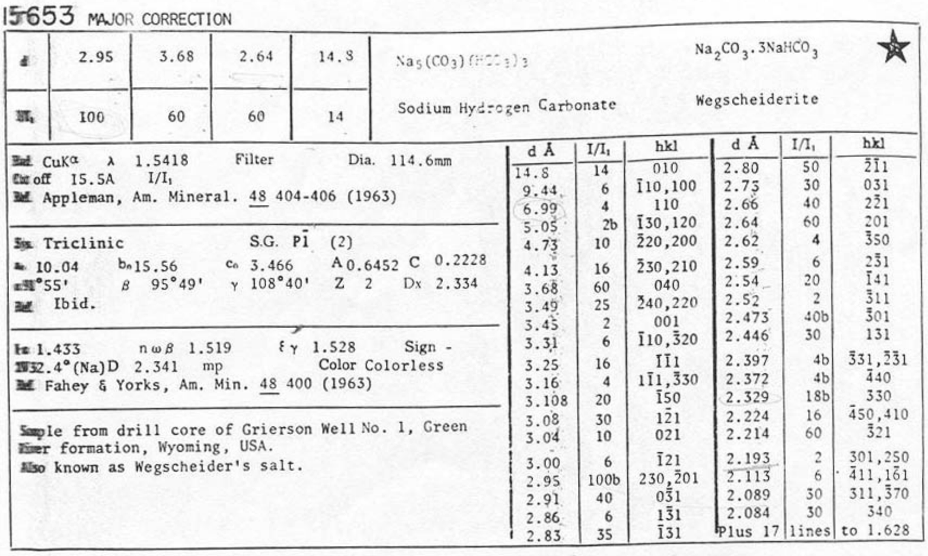
Rad. CuKα λ 1.5418 Filter Ni Dia.
Cut off I/I_1 VISUAL
Ref. PABST, AM. MIN. 44 [illegible] (1959)

Sys. MONOCLINIC S.G. I2/c (15)
a_0 20.11 b_0 3.49 c_0 10.31 A 5.763 C 2.954
α β 103°08' γ Z 4 Dx 2.13
Ref. IBID.

εα 1.418 nωβ 1.492 εγ 1.543 Sign −
2V 75°50' D 2.11 mp Color COLORLESS OR DIRTY WHITE
Ref. IBID., DANA'S SYSTEM OF MINERALOGY, 7TH ED.

FROM SEARLES LAKE, CALIFORNIA, USA. ARTIFICAL MATERIAL GIVES IDENTICAL DATA.

d Å	I/I_1	hkl	d Å	I/I_1	hkl
9.88	60	200	2.040	40	$\bar{8}11$
4.92	40	$\bar{2}02,400$	2.032	40	413,802
4.12	5	202	1.996	30	
4.00	20	$\bar{4}02$	1.965	30	
3.43	20	110	1.886	20	
3.21	60	$600,\bar{2}11$	PLUS 30 LINES		
3.08	80	$310,\bar{6}02$			
2.79	5	112			
2.76	30	$\bar{3}12$			
2.659	100	411			
2.587	20	$\bar{2}04$			
2.510	30	004,312			
2.485	5	602			
2.447	60	800			
2.426	20	$\bar{8}02$			
2.259	40	213			
2.186	5	710,512			
2.149	20	$\bar{7}12$			
2.119	20	$\bar{6}13$			
2.060	20	$\bar{1}14,\bar{3}14$			



15-653 MAJOR CORRECTION

d	2.95	3.68	2.64	14.8	$Na_5(CO_3)(HCO_3)_3$	$Na_2CO_3.3NaHCO_3$ ★
I/I₁	100	60	60	14	Sodium Hydrogen Carbonate	Wegscheiderite

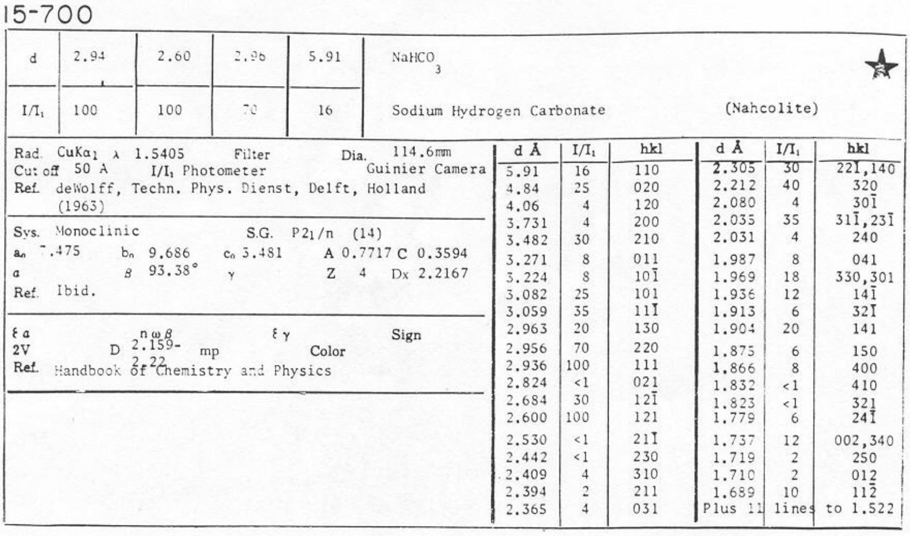
Rad. CuKα λ 1.5418 Filter Dia. 114.6mm
Cut off 15.5A I/I₁
Ref. Appleman, Am. Mineral. 48 404-406 (1963)

Sys. Triclinic S.G. P$\bar{1}$ (2)
a₀ 10.04 b₀ 15.56 c₀ 3.466 A 0.6452 C 0.2228
α [illegible]°55' β 95°49' γ 108°40' Z 2 Dx 2.334
Ref. Ibid.

εα 1.433 nωβ 1.519 εγ 1.528 Sign -
2V 32.4°(Na) D 2.341 mp Color Colorless
Ref. Fahey & Yorks, Am. Min. 48 400 (1963)

Sample from drill core of Grierson Well No. 1, Green River formation, Wyoming, USA.
Also known as Wegscheider's salt.

d Å	I/I₁	hkl	d Å	I/I₁	hkl
14.8	14	010	2.80	50	$\bar{2}\bar{1}1$
9.44	6	$\bar{1}10,100$	2.75	30	031
6.99	4	110	2.66	40	$2\bar{2}1$
5.05	2b	$\bar{1}30,120$	2.64	60	201
4.73	10	$\bar{2}20,200$	2.62	4	$\bar{3}50$
4.13	16	$\bar{2}30,210$	2.59	6	$2\bar{3}1$
3.68	60	040	2.54	20	$\bar{1}41$
3.49	25	$\bar{2}40,220$	2.52	2	$\bar{3}11$
3.45	2	001	2.473	40b	$\bar{3}01$
3.31	6	$\bar{1}10,\bar{3}20$	2.446	30	131
3.25	16	$\bar{1}\bar{1}1$	2.397	4b	$\bar{3}31,\bar{2}\bar{3}1$
3.16	4	$1\bar{1}1,\bar{3}30$	2.372	4b	$\bar{4}40$
3.108	20	$\bar{1}50$	2.329	18b	330
3.08	30	$1\bar{2}1$	2.224	16	$\bar{4}50,410$
3.04	10	021	2.214	60	$\bar{3}21$
3.00	6	$\bar{1}21$	2.193	2	$\bar{3}01,\bar{2}50$
2.95	100b	$230,\bar{2}01$	2.113	6	$\bar{4}11,1\bar{6}1$
2.91	40	$0\bar{3}1$	2.089	30	$311,\bar{3}70$
2.86	6	$1\bar{3}1$	2.084	30	340
2.83	35	$\bar{1}31$	Plus 17	lines	to 1.628



15-700

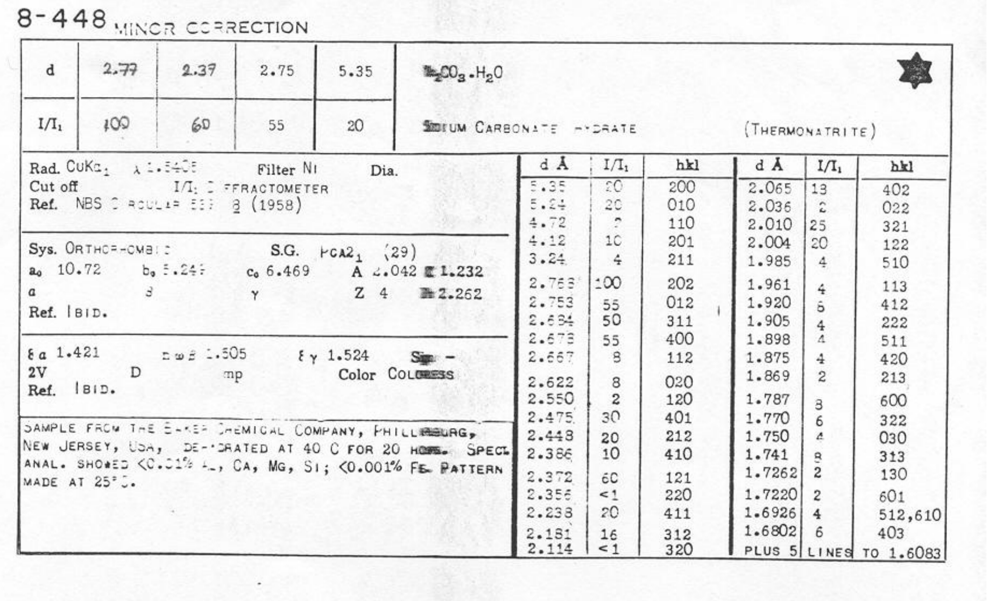
d	2.94	2.60	2.96	5.91	$NaHCO_3$	★
I/I₁	100	100	70	16	Sodium Hydrogen Carbonate	(Nahcolite)

Rad. CuKα₁ λ 1.5405 Filter Dia. 114.6mm
Cut off 50 A I/I₁ Photometer Guinier Camera
Ref. deWolff, Techn. Phys. Dienst, Delft, Holland (1963)

Sys. Monoclinic S.G. P2₁/n (14)
a₀ 7.475 b₀ 9.686 c₀ 3.481 A 0.7717 C 0.3594
α β 93.38° γ Z 4 Dx 2.2167
Ref. Ibid.

εα nωβ εγ Sign
2V D 2.159-2.22 mp Color
Ref. Handbook of Chemistry and Physics

d Å	I/I₁	hkl	d Å	I/I₁	hkl
5.91	16	110	2.305	30	$22\bar{1},140$
4.84	25	020	2.212	40	320
4.06	4	120	2.080	4	$30\bar{1}$
3.731	4	200	2.035	35	$31\bar{1},23\bar{1}$
3.482	30	210	2.031	4	240
3.271	8	011	1.987	8	041
3.224	8	$10\bar{1}$	1.969	18	330,301
3.082	25	101	1.936	12	$14\bar{1}$
3.059	35	$11\bar{1}$	1.913	6	$32\bar{1}$
2.963	20	130	1.904	20	141
2.956	70	220	1.875	6	150
2.936	100	111	1.866	8	400
2.824	<1	021	1.832	<1	410
2.684	30	$12\bar{1}$	1.823	<1	321
2.600	100	121	1.779	6	$24\bar{1}$
2.530	<1	$21\bar{1}$	1.737	12	002,340
2.442	<1	230	1.719	2	250
2.409	4	310	1.710	2	012
2.394	2	211	1.689	10	$11\bar{2}$
2.365	4	031	Plus 11	lines	to 1.522



8-448 MINOR CORRECTION

d	2.77	2.37	2.75	5.35	$Na_2CO_3 \cdot H_2O$
I/I_1	100	60	55	20	Sodium Carbonate Hydrate (Thermonatrite)

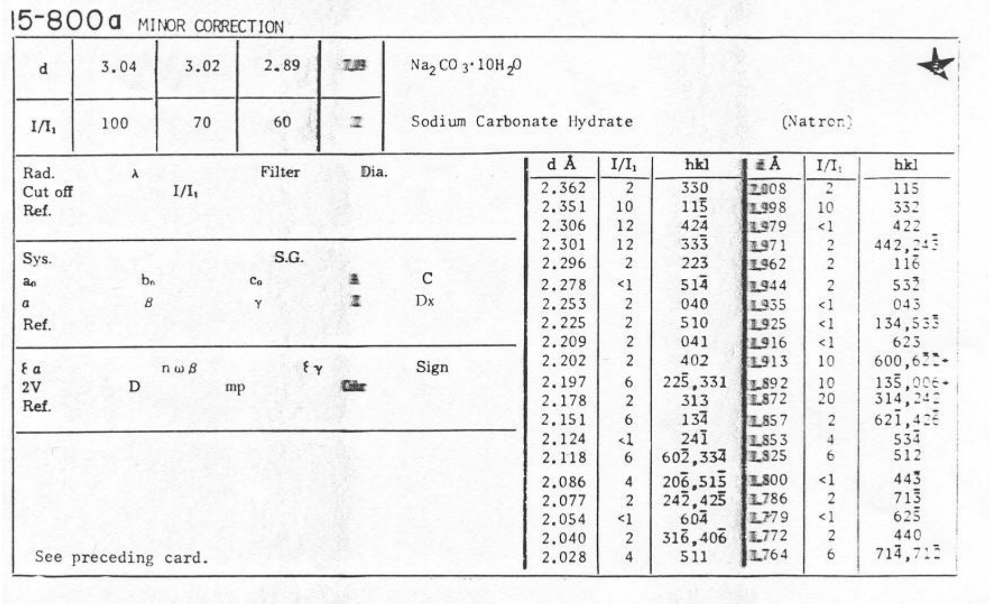
Rad. $CuK\alpha_1$ λ 1.5405 Filter Ni Dia.
Cut off I/I_1 Diffractometer
Ref. NBS Circular 539 8 (1958)

Sys. Orthorhombic S.G. $Pca2_1$ (29)
a_0 10.72 b_0 5.249 c_0 6.469 A 2.042 C 1.232
α β γ Z 4 Dx 2.262
Ref. Ibid.

εα 1.421 nωβ 1.505 εγ 1.524 Sign −
2V D mp Color Colorless
Ref. Ibid.

Sample from the Baker Chemical Company, Phillipsburg, New Jersey, USA, dehydrated at 40 C for 20 hours. Spect. anal. showed <0.01% Al, Ca, Mg, Si; <0.001% Fe. Pattern made at 25°C.

d Å	I/I_1	hkl	d Å	I/I_1	hkl
5.35	20	200	2.065	13	402
5.24	20	010	2.036	2	022
4.72	[illegible]	110	2.010	25	321
4.12	10	201	2.004	20	122
3.24	4	211	1.985	4	510
2.763	100	202	1.961	4	113
2.753	55	012	1.920	6	412
2.684	50	311	1.905	4	222
2.673	55	400	1.898	4	511
2.667	8	112	1.875	4	420
2.622	8	020	1.869	2	213
2.550	2	120	1.787	8	600
2.475	30	401	1.770	6	322
2.448	20	212	1.750	4	030
2.386	10	410	1.741	8	313
2.372	60	121	1.7262	2	130
2.356	<1	220	1.7220	2	601
2.238	20	411	1.6926	4	512,610
2.181	16	312	1.6802	6	403
2.114	<1	320	PLUS 5	LINES	TO 1.6083



15-800a MINOR CORRECTION

d	3.04	3.02	2.89	[illegible]	$Na_2CO_3 \cdot 10H_2O$
I/I_1	100	70	60	[illegible]	Sodium Carbonate Hydrate (Natron)

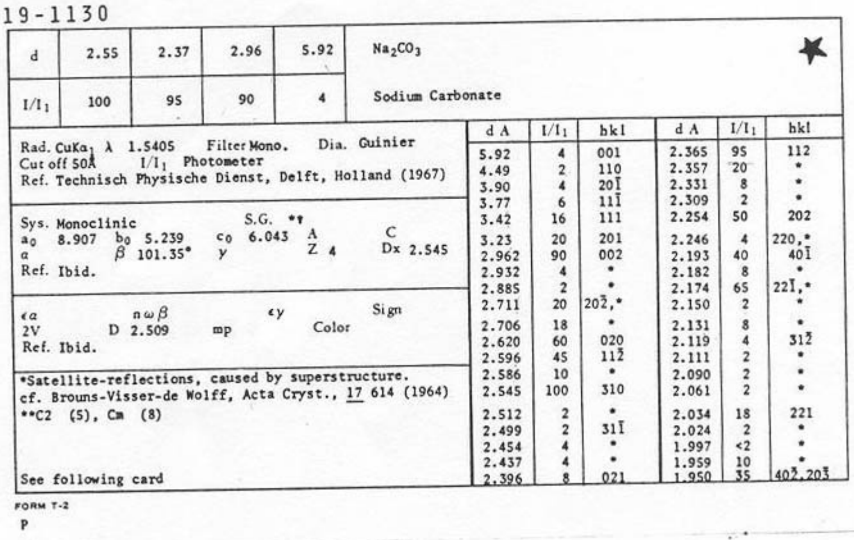
Rad. λ Filter Dia.
Cut off I/I_1
Ref.

Sys. S.G.
a_0 b_0 c_0 A C
α β γ Z Dx
Ref.

εα nωβ εγ Sign
2V D mp Color
Ref.

See preceding card.

d Å	I/I_1	hkl	d Å	I/I_1	hkl
2.362	2	330	2.008	2	115
2.351	10	$11\bar{5}$	1.998	10	332
2.306	12	$42\bar{4}$	1.979	<1	422
2.301	12	$33\bar{3}$	1.971	2	$442,24\bar{3}$
2.296	2	223	1.962	2	$11\bar{6}$
2.278	<1	$51\bar{4}$	1.944	2	$53\bar{2}$
2.253	2	040	1.935	<1	043
2.225	2	510	1.925	<1	$134,53\bar{3}$
2.209	2	041	1.916	<1	623
2.202	2	402	1.913	10	$600,6\bar{2}\bar{2}$+
2.197	6	$22\bar{5},331$	1.892	10	$13\bar{5},006$+
2.178	2	313	1.872	20	314,242
2.151	6	$13\bar{4}$	1.857	2	$62\bar{1},42\bar{5}$
2.124	<1	$24\bar{1}$	1.853	4	$53\bar{4}$
2.118	6	$60\bar{2},33\bar{4}$	1.825	6	512
2.086	4	$20\bar{6},51\bar{5}$	1.800	<1	$44\bar{3}$
2.077	2	$24\bar{2},42\bar{5}$	1.786	2	$71\bar{3}$
2.054	<1	$60\bar{4}$	1.779	<1	$62\bar{5}$
2.040	2	$31\bar{6},40\bar{6}$	1.772	2	440
2.028	4	511	1.764	6	$71\bar{4},71\bar{3}$



19-1130

d	2.55	2.37	2.96	5.92	Na_2CO_3
I/I_1	100	95	90	4	Sodium Carbonate

Rad. CuKα₁ λ 1.5405 Filter Mono. Dia. Guinier
Cut off 50Å I/I_1 Photometer
Ref. Technisch Physische Dienst, Delft, Holland (1967)

Sys. Monoclinic S.G. **
a_0 8.907 b_0 5.239 c_0 6.043 A C
α β 101.35° γ Z 4 Dx 2.545
Ref. Ibid.

εα nωβ εγ Sign
2V D 2.509 mp Color
Ref. Ibid.

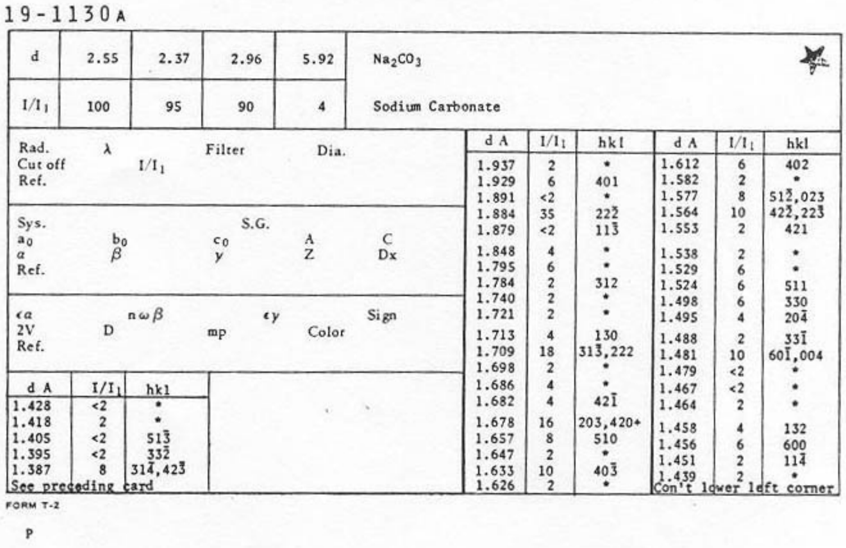
*Satellite-reflections, caused by superstructure.
cf. Brouns-Visser-de Wolff, Acta Cryst., 17 614 (1964)
**C2 (5), Cm (8)

See following card

d A	I/I_1	hkl	d A	I/I_1	hkl
5.92	4	001	2.365	95	112
4.49	2	110	2.357	20	*
3.90	4	20$\bar{1}$	2.331	8	*
3.77	6	11$\bar{1}$	2.309	2	*
3.42	16	111	2.254	50	202
3.23	20	201	2.246	4	220,*
2.962	90	002	2.193	40	40$\bar{1}$
2.932	4	*	2.182	8	*
2.885	2	*	2.174	65	22$\bar{1}$,*
2.711	20	20$\bar{2}$,*	2.150	2	*
2.706	18	*	2.131	8	*
2.620	60	020	2.119	4	31$\bar{2}$
2.596	45	11$\bar{2}$	2.111	2	*
2.586	10	*	2.090	2	*
2.545	100	310	2.061	2	*
2.512	2	*	2.034	18	221
2.499	2	31$\bar{1}$	2.024	2	*
2.454	4	*	1.997	<2	*
2.437	4	*	1.959	10	*
2.396	8	021	1.950	35	40$\bar{2}$,20$\bar{3}$

FORM T-2

P



19-1130A

d	2.55	2.37	2.96	5.92	Na_2CO_3
I/I_1	100	95	90	4	Sodium Carbonate

Rad. λ Filter Dia.
Cut off I/I_1
Ref.

Sys. S.G.
a_0 b_0 c_0 A C
α β γ Z Dx
Ref.

εα nωβ εγ Sign
2V D mp Color
Ref.

d A	I/I_1	hkl	d A	I/I_1	hkl
1.937	2	*	1.612	6	402
1.929	6	401	1.582	2	*
1.891	<2	*	1.577	8	51$\bar{2}$,023
1.884	35	22$\bar{2}$	1.564	10	42$\bar{2}$,22$\bar{3}$
1.879	<2	11$\bar{3}$	1.553	2	421
1.848	4	*	1.538	2	*
1.795	6	*	1.529	6	*
1.784	2	312	1.524	6	511
1.740	2	*	1.498	6	330
1.721	2	*	1.495	4	20$\bar{4}$
1.713	4	130	1.488	2	33$\bar{1}$
1.709	18	31$\bar{3}$,222	1.481	10	60$\bar{1}$,004
1.698	2	*	1.479	<2	*
1.686	4	*	1.467	<2	*
1.682	4	42$\bar{1}$	1.464	2	*
1.678	16	203,420+	1.458	4	132
1.657	8	510	1.456	6	600
1.647	2	*	1.451	2	11$\bar{4}$
1.633	10	40$\bar{3}$	1.439	2	*
1.626	2	*	Con't lower left corner		

d A	I/I_1	hkl
1.428	<2	*
1.418	2	*
1.405	<2	51$\bar{3}$
1.395	<2	33$\bar{2}$
1.387	8	31$\bar{4}$,42$\bar{3}$

See preceding card

FORM T-2

P

APPENDIX A.11.

Specific Surface Area Measurement Procedure

1. Sample Holder was installed at Degas and Test position and a U-tube was installed at Cold Trap position on the BET instrument.
2. Dewar was filled with liquid nitrogen and then set on Cold Trap position with U-tube inside.
3. Dual channel mass flow controller (call box) was brought to “on” position and was put on hold for 30 minutes.
4. He and N_2 gas tubes were turned on and the tube manometer was adjusted to 15 psi (atm).
5. Dual channel mass flow controller was set to choose channel buttons. Channel 1 was set at 3.0 for nitrogen and Channel 2 was set at 7.0 for helium.
6. Toggle valve on the lower rıght side of the flowsorb was opened to allow the flow through the instrument.
7. Flow at the left of the instrument control panel was adjusted by using the knob so that the flot is centred on or near the calibration mark of the flowmeter tube.
8. For Short and Long path purping the system was used for 5-10 minutes and 20-25 minutes respectively. Power swıtch of the anlalyzer was kept in “off” position while purging. Short and Long paths provided downstream of the sample Test position. The purpose of both was to delay the arrival at the detector of the nitrogen-rich gas created by the sample desorption upon the removal of liquid nitrogen long enough for the flow rate to return the to normal. The Short path was usually

sufficient for surface area testing, but greater surface area materials and samples tested pore volume gave up too much gas over too long a time for it, hence the Long path was used.

9. The power switch located at the lower right side of the instrument was turned “on” and put on hold for 30 minutes for complete temperature equilibration and attainment of full operational stability. During this period, DET and X1 or X10 pushbutton and the Short or Long path was selected when appropriate for the sample to be analyzed subsenquently. Materials with unknown characteristics were always best tested with the multiplier set on X1. Only samples having less than 3.5 m^2 of surface area were tested with a setting of X10. The Dewar tray left hanging down as an intial starting condition.
10. After equilibration, the display was brought zero using Coarse Zero and Fine Zero pushbuttons.
11. Calibration was accomplished by injecting a precise volume of gas mixture into the instrument through a septum using a syringe and needle. 1 ml syringe filled with 1 ml of nitrogen gas, was laid aside and put on hold for 1 minutes so that the gas can come to room temperature. The syringe was flushed a few times to be sure of obtaining a proper fill. Short path was set on, Dewar tray was put down, flowmeter float level was correct, Det and X1 or X10 buttons were depress and the display was zero.
12. Surface area and the Clear SA Display pushbuttons were depressed.
13. Syringe needle was inserted in the septum at inject, and pushed all the way in. Gas was injected at a modarate rate. The needle was withdrawn when the syringe was completely discharged. After the Threshold light started flashing, the indicator started accumulating surface area information after aproximately 1 minutes (5 minutes for Long path)
14. 1.0 cm^3 of nitrogen gas corresponded to 2.84 m^2 of sample surface. The result obtained for a 30 % N_2 70 % He mixture adsorbed at liquid nitrogen temperature when room temperature is 22 °C and atmospheric pressure was 760 mm Hg has the expression

$$S = V\left(\frac{273.2}{\text{Room Temp.}}\right)\left(\frac{\text{Atm. Press.}}{760}\right)\left(\frac{A \text{ x } N}{M}\right)\left(\frac{1\text{-}(\%N_2/100)\text{xAtm.Pres}}{\text{Sat. Press.}}\right)$$

$$= V \text{ x } \frac{273.2}{295.2} \text{ x } \frac{760}{760} \text{ x } \frac{6.023 \text{ x } 10^{23}\text{x}16.2\text{x}10^{-20}}{22.414 \text{ x}10^{3}} \text{ x } \frac{1\text{- }(0.3\text{x}760)}{775}$$

$$= 2.84V$$

where S is the surface area in square meters. For calibration, a syringe injection of V=1.00 cm^3 of nitrogen at 22 °C and 760 mmHg produced an indicated surface area of 2.84 m^2. However, the value of S can vary considerably for conditions different from the above.

15. The instrument was calibrated. Confirmation of calibration was established by making repeat injections. Reproducibility was within ±0.02 units on the display meter.
16. The sample was degassed for sample conditions.
17. When adequately degassed, the sample was transferred from Degas to Test Another sample installed at the Degas position for conditioning.
18. DET was pressed so the display increased and then returned to 0.02, the display was cleared by depressing the Surface Area and the Clear SA Display.
19. A Dewar of liquid nitrogen was placed about the sample to be analyzed. The level of liquid nitrogen was maintained as nearly constant as possible about 1 to 2 cm below the Dewar lip. The Cold Trap Dewar was maintained with an adequate level of liquid nitrogen.
20. The threshold light began blinking and the indicator started accumulating data approximately 1 minutes (5 minutes on Long Path) after the cold bath was placed about the sample. The float of the flowmeter returned to

its normal position before data accumulation began i.e., thresold light blinking.

21. When blinking subsided, adsorption of N_2 gas was complete. The value on the display was read as m^2 of surface area. At this moment DET indication returned to 0.02 or less. The display was cleared by depressing clear SA Display in preparation for registering the desorption information.
22. Desorption was obtained by removing the Dewar of liquid nitrogen and bringing the sample to room temperature. The sample tube was immersed in a beaker of room temperature water. Dewar platform was kept down in order to continue the warming procedure until the flowmeter float returned essentailly to its normal level. As with adsorption, the threshold light blinked and the display accumulated for several minutes.
23. The indicated numbers divided by the sample weight in grams was the sample specific surface in square meters per gram.

VITA

Sibel Örgül was born in Ankara on January 7, 1972. She received her B.S. degree in Mining Engineering from the Middle East Technical University in July 1995 and MSc. degree in Mining Engineering from the Middle East Technical University in January 1999. She worked as a research assistant in the Department of Mining Engineering from 1995 to 2003. Her main areas of interest are hydrometallurgical processing, trona and gold mining.