

**EGE UNIVERSITY GRADUATE SCHOOL OF NATURAL AND
APPLIED SCIENCE**

(MASTER THESIS)

**PRODUCTION OF PURE CAUSTIC FROM
TRONA AND LIME WITHOUT RESIDUE**

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III

Arzu YÜKSEL tarafından YÜKSEK LİSANS TEZİ tezi olarak sunulan **“PRODUCTION OF PURE CAUSTIC FROM TRONA AND LIME WITHOUT RESIDUE”** başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 27.01.2009 tarihinde yapılan tez savunma sınavında aday oybirliği / oyçokluğu ile başarılı bulunmuştur.

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ÖZET**TRONA VE KİREÇ KULLANARAK
ATIK OLUŞTURMADAN YÜKSEK SAFLIKTA KOSTİK
ÜRETİMİ**

Yüksel, Arzu

Yüksek Lisans Tezi, Kimya Anabilim Dalı
Tez Yöneticisi: Prof. Dr. Berrin YENİGÜL
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Bu tezde, ülkemizde bolca bulunan trona ve kireç ile atık oluşturmada kostik üretimi gerçekleştirilebileceği kanıtlanmıştır. Trona ve kireç oda sıcaklığında 5 saat tepkimeye sokularak kostik üretimi kondüktometrik olarak izlenmiştir.

Tepkime sonunda, kalsiyum karbonat çökelir ve kostik ayrılır. Bu çökelek, fırınlarda yakılarak kalsiyum oksit (CaO) ve karbondioksit (CO₂) elde edilir. Karbondioksit istenirse bir yerde depolanıp tekrar kullanılabilir. Oluşan kalsiyum oksit sonraki partilerde kireç olarak kullanılır. Böylece bir önceki denemede çökelekte kalan sodyum hidroksit (NaOH) kazanılmış olur ve çevreye atık bırakılmadan üretim yapılmış olur.

Anahtar sözcükler: kondüktometri, trona, kostik

ABSTRACT

**PRODUCTION OF PURE CAUSTIC
FROM TRONA AND LIME WITHOUT RESIDUE**

Yüksel, Arzu

MSc Thesis in Chemistry
Supervisor: Prof. Dr. Berrin YENİGÜL
February 2009, 17 Pages

In this thesis, it has been proved that pure caustic can be obtained with trona and lime without waste. Trona and lime have been reacted during 5 hours at room temperature by monitoring with conductometry.

At the end of reaction, calcium carbonate has been precipitated and caustic has been separated. The precipitate has been burned in an oven and calcium oxide and carbon dioxide have been obtained. Carbon dioxide can be stored for use. Calcium oxide has been used for production of caustic so remainder of caustic in the precipitate has been recovered. Thus, there were no residue.

Keywords: conductometry, trona, caustic

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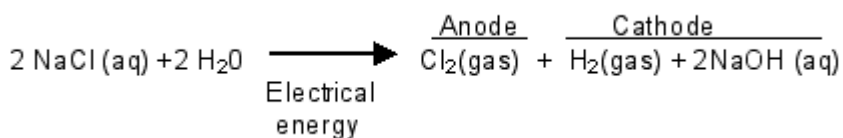
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1. INTRODUCTION

Caustic which is the important data of industry is manufactured approximately 45 million ton and has 30 billion\$ market per year in the world.

Industrial methods of caustic-soda production developed in the 18th century (the LeBlanc process) and 19th century (the Solvay, or ammonia-soda, process) have been largely displaced by electrolysis.

The principal method for its manufacture is electrolytic dissociation of sodium chloride; chlorine gas is a coproduct (chloralkali process). This involves the electrolysis of an aqueous solution of sodium chloride. The sodium hydroxide builds up at the cathode, where water is reduced to hydrogen gas and hydroxide ion:



To produce NaOH it is necessary to prevent the reaction of NaOH with the chlorine. This is typically done in one of three ways, of among them membran cell process is economically the most viable.

Mercury cell process (also called the Castner-Kellner process) – Sodium metal forms an amalgam at a mercury cathode; this sodium is then reacted with water to produce NaOH. There have been concerns about mercury releases, although modern plants claim to be safe in this regard.

Diaphragm cell process – uses a steel cathode, and the reaction of NaOH with Cl_2 is prevented using a porous diaphragm, often made of asbestos fibers. In the diaphragm cell process the anode area is separated from the cathode area by a permeable diaphragm. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment. A diluted caustic brine leaves the cell. The caustic soda must usually be concentrated to 50% and the salt removed. This is done using an evaporative process with about three ton of steam per ton of caustic soda. The salt separated from the caustic brine can be used to saturate diluted brine. The chlorine contains oxygen and is purified by liquefaction and evaporation.

Membrane cell process – similar to the diaphragm cell process, with a Nafion membrane to separate the cathode and anode reactions. Only sodium ions and a little water pass through the membrane. It produces a higher quality of NaOH. Of the three processes, the membrane cell process requires the lowest consumption of electric energy and the amount of steam needed for concentration of the caustic is relatively small (less than one ton per ton of caustic soda).

An older method for sodium hydroxide production was the LeBlanc process, which produced sodium carbonate, followed by roasting to create carbon dioxide and sodium oxide. This method is still occasionally used. It helped to establish sodium hydroxide as an important commodity chemical.

Small amounts of sodium hydroxide are produced by the soda-lime process in which a concentrated solution of sodium carbonate (soda) is reacted with calcium hydroxide (slaked lime); calcium carbonate precipitates, leaving a sodium hydroxide solution.

But, as is also understood from manufacture methods; caustic can has impurities from raw materials. Though trona (Etibank Trona Facilities Beypazarı) is used as raw material, there are no impurities. Also the main goal to use trona is produce caustic without leaving any residue.

1.1. The Aim of Thesis

The aim of this thesis is the production of caustic (NaOH) solution from the reaction of trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and slaked lime ($\text{Ca}(\text{OH})_2$) without leaving any residue.

For the determination of the optimum conditions in the production of caustic, limiting lime, stirring time and temperature were investigated.

2. EXPERIMENTAL

2.1. Materials

In this work; trona and slaked lime were obtained from Trona Etibank Facilities, Beypazarı, Ankara. Trona was grinded by ball mill and powdered before use.

Lime was heated at 300 °C in the oven during 8 hours.

Distilled water was used for the reaction mixtures.

2.2. Apparatus

Conductometer (CMD750) was used.

Magnetic stirrer (Agitateur Type AM2 N° 6092) and Chilten Hot Plate were used for stirring and heating.

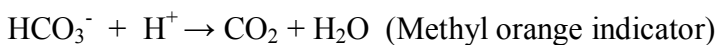
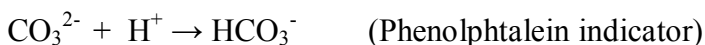
Distilled water was used throughout the experiments was supplied by distilled water machine (SS200).

Lime was heated in an oven called Ehret.

2.3. Analysis of trona by two indicators

For the determination of sodium carbonate and sodium bicarbonate percentages in trona, 0.200 g of dried trona sample was weighted and titrated with standardized HCl solution (0.0938M) using phenolphthalein and methyl orange indicators.

Titration reactions are shown below;



The experiments were carried out twice and the mean of the data was calculated.

<u>Experiment no</u>	<u>The Weight of Trona</u>		
1	0.200 g	V ₁ (P.P)=9.5 mL	V ₁ (M.O)=30.0 mL
2	0.200 g	V ₂ (P.P)=9.5 mL	V ₂ (M.O)=30.1 mL

$$\text{Na}_2\text{CO}_3 \% = 0.0938 \cdot 9.5 \cdot 10^{-3} \cdot 106.100 \cdot \frac{1}{0.200} = 47.23 \%$$

$$\text{NaHCO}_3 \% = (30.05 - 2 \cdot 9.5) \cdot 10^{-3} \cdot 0.0938 \cdot 84 \cdot 100 \cdot \frac{1}{0.200} = 43.37 \%$$

2.4. Analysis of trona by ICP and Flame Photometer

Raw material trona (Etibank Trona Facilities Beypazarı) used in experiments was prepared in the size of 40-50 μ . Full analyses of trona were carried out and their results were shown at Table 1. (Öğüt, S. İ. , 2003)

Table 1. : Full analysis of trona by ICP

Element	%
Na	37.8
B	0.93
Ca	0.75
Fe	0.97
Mg	0.80
Al	0.88
K	0.66

Flame Photometer was used for the determination of sodium content of trona. Calibration graph of sodium was shown in Figure 1.

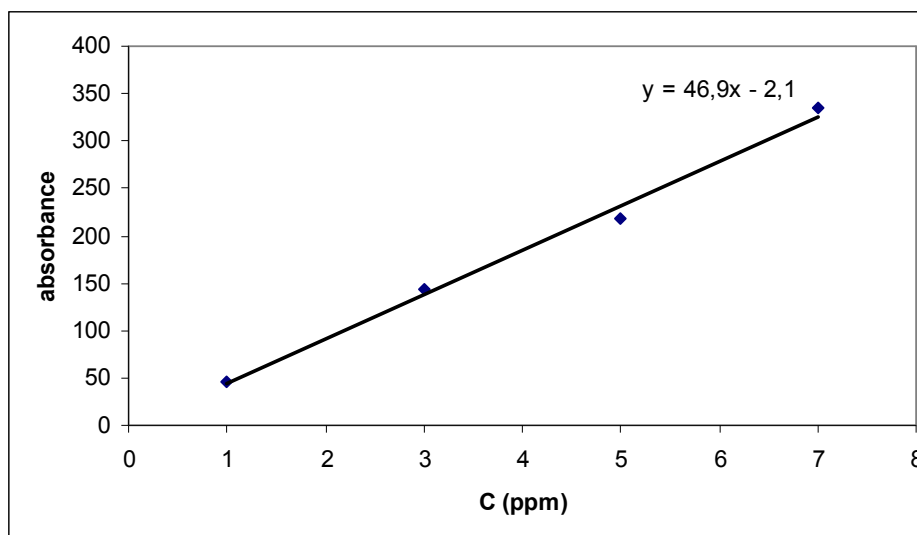


Figure 1. Analysis of trona by Flame Photometer

0.500 g of trona was weight and solved in 1 L of water. From this solution 1 mL was taken and diluted to 100 mL. The absorbance of this solution was read as 87. From the calibration graph (Figure 1.) sodium content of this solution was obtained at 1.9 ppm.

$$\text{Percentage of sodium} = \text{Na \%} = 1.9 \cdot 10^{-6} \cdot 10^5 \cdot 100 \cdot \frac{1}{0.500} = 37.8 \% \text{ Na}$$

2.5. Procedure for production of caustic from trona and lime

Suitable amount of trona and lime were solved in distilled water and stirred. The reaction was shown below,



The optimum conditions of the reaction and production caustic, stirring time, temperature and the ratio of lime to trona were investigated. The reaction was monitored by conductometer and compared to conductance of 1 M NaOH.

Calcium carbonate (CaCO_3) obtained from the reaction was filtered and by igniting in an oven at 1000°C calcium oxide (CaO) was obtained can be used for another experiments.

From the reaction, it can be seen that 1 mol trona gives 3 mol NaOH.

$$\text{MW}_{\text{trona}} = 225 \text{ g/mol}$$

$$\text{MW}_{\text{lime}} = 74 \text{ g/mol}$$

For the preparation of 400 mL 1M NaOH;

$$\frac{225}{3} \cdot 0.4 = 30 \text{ g trona}$$

$$\frac{74 \cdot 2}{3} \cdot 0.4 \cong 20 \text{ g lime are needed.}$$

Approximately, 1% excess of lime (22g lime) was decided to begin the experiments.

3. RESULTS AND DISCUSSION

3.1. Effect of excess lime on the efficiency of NaOH

400 mL of distilled water was boiled and then 30.0 g of trona and 22.0 g of lime were added. The mixture was stirred without continuing heating. Experiments were repeated by increasing the amount of lime. Each of the experiments were repeated 5 times. The change of conductance was monitored.

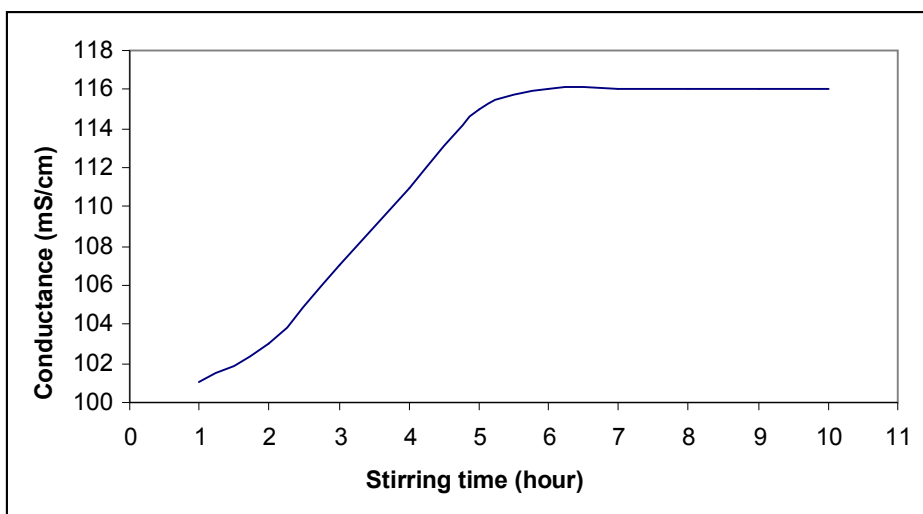


Figure 2. History of conductance in reaction for 30.0 g of trona and 22.0 g of lime

The conductance was increased through 5 hours and it was stabled after 5 hours. It was seen at Figure 2.

For the different ratio of trona to lime, measurements of conductivities and comparison to standard 1M NaOH conductivities were shown in Tables 2–6.

Table 2. Conductivity values of NaOH solutions which were produced from 30.0 g of trona and 36.0 g of lime

Stirring time	Experiment No	Conductivity of NaOH (mS/cm)	Conductivity of standard 1 M NaOH (mS/cm)	Average efficiency %
5 hours	1	113.7	196.4	57.60
	2	113.6	196.3	
	3	113.8	196.6	
	4	113.9	196.4	
	5	113.5	196.2	
24 hours	1	125.8	196.4	64.07
	2	125.9	196.3	
	3	126.0	196.6	
	4	125.8	196.5	
	5	125.6	196.2	

Table 3. Conductivity values of NaOH solutions which were produced from 30.0 g of trona and 32.0 g of lime

Stirring time	Experiment No	Conductivity of NaOH (mS/cm)	Conductivity of standard 1 M NaOH (mS/cm)	Average efficiency %
5 hours	1	176.5	196.4	89.90
	2	176.6	196.4	
	3	176.6	196.3	
	4	176.5	196.5	
	5	176.6	196.3	
24 hours	1	177.0	196.4	90.15
	2	177.1	196.2	
	3	177.0	196.3	
	4	177.2	196.4	
	5	176.9	196.5	

Table 4. Conductivity values of NaOH solutions which were produced from 30.0 g of trona and 36.0 g of lime

Stirring time	Experiment No	Conductivity of NaOH (mS/cm)	Conductivity of standard 1 M NaOH (mS/cm)	Average efficiency %
5 hours	1	170.0	184.2	92.30
	2	170.1	184.3	
	3	170.1	184.2	
	4	169.9	184.1	
	5	170.2	184.3	
24 hours	1	172.6	184.2	93.50
	2	172.4	184.2	
	3	172.5	184.3	
	4	172.6	184.2	
	5	172.7	184.2	

Table 5. Conductivity values of NaOH solutions which were produced from 30.0 g of trona and 40.0 g of lime

Experiment No	Conductivity of NaOH (mS/cm)	Conductivity of standard 1 M NaOH (mS/cm)	Average efficiency %
1	170.3	184.5	92.32
2	170.2	184.4	
3	170.3	184.4	
4	170.1	184.5	
5	170.2	184.3	

Table 6. Summary of % Efficiency of NaOH

Ratio of trona to lime (w/w)	Efficiency of NaOH % for 5 hours stirring	Efficiency of NaOH % for 24 hours stirring
30/22	57.60	64.00
30/32	89.90	90.15
30/36	92.30	93.50
30/40	92.32	-

The summary of results were shown in Table(6.). From the tables above, as is also understood that 36.0 g of lime was enough for stirring 5 hours. The reason of using excess lime was passivation of lime.

3.2. Production of NaOH at room temperature

From the Table 6. ,the optimum ratio of trona to lime was chosen as 30/36 (w/w) and the experiment was repeated at room temperature without boiling in the beginning and continued without heating. Results were shown at Table 7.

Table 7. Conductivity values of NaOH solutions which were produced from 30.0 g of trona and 36.0-40.0 g of lime by stirring 5 hours.

Amount of lime	Experiment No	Conductivity of NaOH (mS/cm)	Conductivity of standard 1 M NaOH (mS/cm)	Average efficiency %
36 g	1	169.6	184.1	92.25
	2	169.5	184.0	
	3	169.7	183.8	
	4	170.0	183.9	
	5	169.9	184.2	
40 g	1	170.0	184.1	92.30
	2	170.2	184.0	
	3	169.8	183.8	
	4	170.1	183.9	
	5	170.0	184.2	

It was seen that the same efficiency was obtained at room temperature without boiling water at the beginning.

3.3. Effect of temperature on the efficiency of NaOH

The experiment was started with boiling water of 400 mL. Then, 30.0 g of trona and 36.0 g of lime was added into the boiled water. The solution was heated on Chiltern Hot Plate for 5 hours at 80 °C also the solution was mixed. The solution was precipitated and caustic's conductivity was measured.

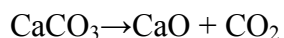
Table 8. Conductivity values of NaOH solutions which were produced from 30.0 g of trona and 36.0 g of lime by heating

Experiment No	Conductivity of NaOH (mS/cm)	Conductivity of standard 1 M NaOH (mS/cm)	Average efficiency %
1	180.3	196.0	91.97
2	180.2	195.9	
3	180.4	196.1	
4	180.1	195.8	
5	180.2	196.0	

4. CONCLUSION

A new method was described for producing caustic from trona and lime without any residue. So, the optimum conditions were determined. For the caustic production, 30.0 g of trona and 36.0 g of lime were reacted during 5 hours at room temperature.

Also calcium carbonate which was precipitated at the end of experiment was heated in an oven at 1000 °C and the reaction was happened below.



According to the reaction calcium oxide and carbon dioxide were obtained. Carbon dioxide can be stored for use. Calcium oxide was used for another production of caustic as lime, so remainder of caustic in the precipitate was recovered. Thus, the production of caustic from trona and lime was carried out without leaving residue.

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