MANUFACTURING OF SYNTHETIC SODA ASH

BY

TAKALANI MADIMA

Thesis presented in fulfillment of the requirements for the degree of Master of Sciences at the University of the Western Cape.

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Supervisor: Prof. D. Knoesen
Department of Physics
University of the Western Cape

Co-supervisor: Dr. S. Jongens
Nampak Research and Development

February 2009

DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature: ……………………………………………………………

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KEYWORDS

MANUFACTURING OF SYNTHETIC SODA ASH

Soda ash
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Elemental composition

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ABSTRACT

“Manufacturing of synthetic soda ash”

Takalani Madima

MSc. Thesis, Department of Physics, University of the Western Cape

The aim of the project was to study the manufacturing of synthetic soda ash (sodium carbonate, Na_2CO_3) on an industrial scale. Currently all Soda ash that is used in South Africa for manufacturing glass is imported at a high cost, and the company Nampak Wiegand Glass (South Africa) is investigating the possibility to locally manufacture synthetic soda ash.

About 75% of soda ash is synthetically produced from either the Leblanc process, Solvay process, Modified Solvay (Dual) process or dry lime process. This study concentrated on the Solvay process on a laboratory scale for eventual input into a larger pilot plant.

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The produced material was analyzed using analytical techniques such as FTIR (Fourier Transform Infrared spectroscopy), Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES). There are certain standard requirements for impurities in the soda ash, and this needed to be measured and determined what changes to the process will bring the impurities to the required minimum standard. Environmental issues around the manufacturing process were also studied.

After completing of the laboratory experiments and the extraction of required data from the results, Nampak will use the information to decide on a follow-up to the building of a small pilot plant to further test and develop the engineering and economical aspects of a full plant. If successful a full scale manufacturing plant can be developed in South Africa for producing soda ash.

This study thus will not only help Nampak Wiegand Glass in finalizing the decision to go ahead, but its result will also benefit other companies that use the soda ash in oil refining, water treatment, pulp and paper, chemical industry etc. Some parts of the work done will be proprietary to Nampak and subject to confidentiality agreement.

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To my family: Rachel, Shumani, Adivhaho,
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my father Aifheli Donald Madima

LIST OF ABBREVIATIONS

IR	Infrared
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray analysis
EDS	Energy Dispersive spectrum
MCA	Multichannel analyzer
ZAF	Atomic number, absorption and secondary fluorescence
FWHM	Full Width at half Maximum
ICP – MS	Inductively Coupled Plasma Mass Spectrometry
ICP – AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP – OES	Inductively Coupled Plasma Optical Emission Spectrometry

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CHAPTER 1

1.1 Introduction

Soda ash, also known as sodium carbonate is one of the chemicals that are produced in large amounts in the world. In 1998, in the USA, in terms of production, soda ash was the 11th largest inorganic chemical of all domestic inorganic and organic chemicals excluding petrochemical feedstocks.

Currently, an increasing percentage of the soda ash production in the world is obtained from the process of mineral trona (natural soda ash) $Na_2CO_3.NaHCO_3.2H_2O$. Mineral trona or carbonate-bearing brines is mainly found in United States.

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Soda ash is an important raw material in the manufacturing process of glass, chemicals, detergents and soaps, paper, ceramic materials, medicine, textiles, steel manufacture, petroleum and metal refining, water treatment and other important industrial products. Glass production uses half of global soda ash produced [Örg03], [Glo08]. In the USA Soda ash is also used in flat glass for automobile manufacturing and building construction.

Natural soda ash is found in the USA and other parts of Africa such as Lake Magadi in Kenya and Botash in Botswana. In other locations (Asia, Europe, Middle East and South America) that lack natural soda ash sources, soda ash is manufactured synthetically by means of the Solvay process (ammonia process). The Solvay process uses salt, limestone and ammonia. The other synthetic processes include the modified Solvay process and dry liming process. The Solvay process is widely used in other countries.

This study was motivated by the lack of suppliers of synthetic soda ash in Africa.

There is a growing demand for Soda Ash in South Africa, particularly in the glass manufacturing industry. The South African market is expected to double from 420,000 metric tons in 2007 to about 868,000 metric tons by 2010 [Lal08].

A major glass manufacturer, Nampak Wiegand Glass suggested an investigation into the development of a local South African manufacturing plant for the synthetic process. Nampak Wiegand Glass currently uses soda ash derived from natural deposits found in Botswana (Botash) and the USA. Botash cannot supply to all industries in South Africa and the quality of the soda ash is deteriorating due to increasing levels of Total Organic Carbon. The quality of soda ash coming from the USA is good but the cost is double of that originating from Botswana.

This project will focus on the study of synthetic processes (Solvay process and Dual process (Modified Solvay process)). Experimental work will be done to simulate the Solvay process in the laboratory. The experimental product from the experiment will be compared with the reference samples (natural soda ash from Botswana and synthetic soda ash from Germany) supplied by Nampak Wiegand Glass.

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CHAPTER 2

SODA ASH

2.1 Soda Ash (Sodium Carbonate)

Soda ash is a white crystalline powder or granular material which is readily soluble in water. Soda ash contains 99.3 % of Na_2CO_3 and is graded according to its bulk density [Wag92]. The commercial standard that is accepted is expressed in terms of the total equivalent sodium oxide (Na_2O) that it contains, meaning that commercial 58 % soda ash contains an equivalent of 58 % Na_2O. The equation to convert is % Na_2O x 1.71 = Na_2CO_3 %; 58 % of Na_2O is equivalent to 99.2 % Na_2CO_3 [Örg03]. In 1991 soda ash was said to be the eleventh largest world commodity chemical [Cur91].

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About 25% of the world soda ash production is from natural deposits and 75% from synthetic processes. About 90% of the natural deposits of sodium carbonate is found in the USA [Dsi95].

2.1.1 Definitions, grades and specifications of Soda ash

Soda ash is a common name for the industrial chemical sodium carbonate (Na_2CO_3); it is strongly alkaline [Cur91].

This chemical is manufactured in four types: light, medium, granular and dense soda ash according to the shape, size of the particles and bulk density to suit various industrial requirements [Dsi95].

The main manufacturing types that are used are the dense and light. Dense soda ash has a bulk density varying from 0.95 t/ m^3 to 1.1t/ m^3.

The dense soda ash is preferred in the glass industry because of its particle size that have the same size as the silica sand and this results in a homogeneous mixing of raw materials and produce a high quality product [Bac07]. The price of dense soda ash is slightly higher than that of the light soda ash [Örg03]. Light soda ash has a bulk density ranging from 0.52 t/ m^3 to 0.60 t/ m^3 [Wag92].

Light soda ash is mostly preferred for chemical, soaps and detergents applications. The advantage of using light soda ash in detergents and chemicals is that its smaller size of the particle provides a free flowing nature and it increases the reactivity [Bac07].

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Table 2-1: Soda ash specifications [Örg03], [Wag92]

	Light soda ash	Dense soda ash
Sodium carbonate (Na_2CO_3)	99.100%	99.100%
Sodium Chloride (NaCl)	0.500%	0.500%
Sodium Sulphate (Na_2SO_4)	0.040%	0.040%
Sodium oxide (Na_2O)	58.000%	58.000%
Fe_2O_3	0.004%	0.004%
H_2O	0.020%	0.020%
Bulk density	0.52 – 0.60 t/m^3	0.96 - 1.04 t/m^3

2.1.2 Physical properties and hydrates of sodium carbonate

In addition to the anhydrous sodium carbonate, Na_2CO_3, there are three known hydrates that exist; sodium carbonate monohydrate, $Na_2CO_3.H_2O$; sodium carbonate heptahydrate, $Na_2CO_3.7H_2O$ and sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.

Sodium carbonate monohydrate has a molecular mass of 124.00 g/mol. This hydrate contains 85.48 % of Na_2CO_3 and 14.52 % crystallized water. It can be formed by making soda ash to be wet using a calculated quantity of water at or above the temperature of 35.4°C. Sodium carbonate monohydrate loses water on heating and its solubility decreases a little with increasing temperature. If it is in contact with its saturated solution it changes to Na_2CO_3 at the temperature of 109°C [Örg03].

Sodium carbonate heptahydrate contains 45.7 % of Na_2CO_3 and 54.3 % of water of crystallization. This hydrate is of no commercial interest because of its narrow range of stability, which extends from 32°C to 35.4°C [Örg03].

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Sodium carbonate decahydrate is well known as “washing soda” or “sal soda”. It contains 37.06 % of Na_2CO_3 and 62.94 % of water of crystallization. This hydrate can be formed by making soda ash wet with the calculated quantity of water at the temperature below 32.0°C and above -2.1°C. The crystals effloresce in dry air to form monohydrate [Örg03].

The physical properties of the three known hydrates are listed in Table 2-2 and Table 2-3.

Table 2-2: Physical properties of sodium carbonate compounds [Thi03]

	Anhydrous	Monohydrate	Heptahydrate	Decahydrate
Chemical formula	Na_2CO_3	$Na_2CO_3.H_2O$	$Na_2CO_3.7H_2O$	$Na_2CO_3. 10H_2O$
Molecular mass	105.99	124.00	232.10	286.14
Density at 20°C (g/cm^3)	2.533	2.25	1.51	1.469
Melting point (°C)	851	105	35.37	32.0
Heat of fusion (J/g)	316			
Specific heat capacity at 25°C ($J\ g^{-1}\ K^{-1}$)	1.043	1.265	1.864	1.877
Heat of formation (J/g)	10.676			
Heat of hydration (J/g)		133.14	646.02	858.30
Crystal structure	Monoclinic	rhombic	rhombic - Bipyramidal	monoclinic - pseudohexagonal
heat of solution (J/g)	-222	-79.6	197	243

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Table 2-3: Solubility of the hydrates of sodium carbonate [Örg03].

Solid phase	T (°C)	Solubility (g Na_2CO_3/ 100g 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	105.0	31.15

2.1.3 Chemical properties of soda ash

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Sodium carbonate is hygroscopic and its weight increases by approximately 1.5 % within thirty minutes when it is in air at 96 % relative humidity. Sodium carbonate is alkaline and its alkalinity is reduced if it is stored under moist conditions because it absorbs carbon dioxide and moisture from the atmosphere. At a temperature greater than 400 °C, sodium carbonate reacts with water vapour to form sodium hydroxide and carbon dioxide [Örg03].

2.2 Uses of Soda ash

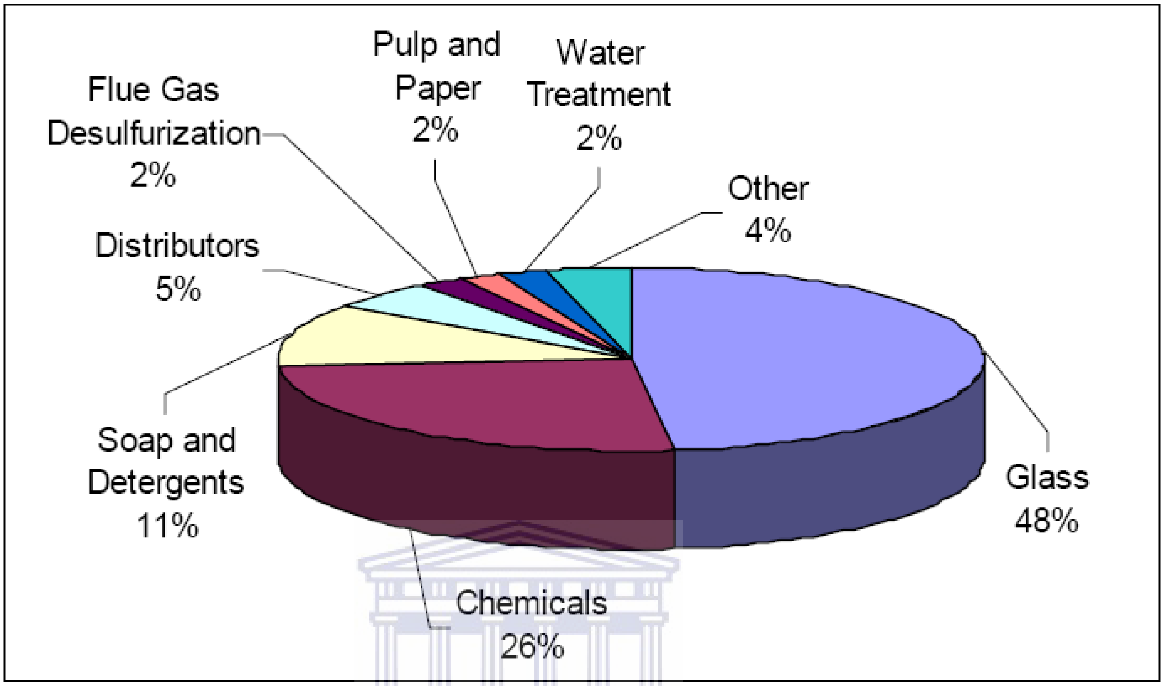

Figure 2-1: Distribution of soda ash by end use in 2001- USGS minerals information, 2002 [Örg03].

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1. Glass industry – About 48% of soda ash is used in the glass manufacturing, including flat glass and mirrors, bottles for beverages, jars for food, insulation, televisions, lighting, glassware, and labware. The soda ash acts as a fluxing agent, it lowers the melting temperature of the silica sand and also reduces the energy consumption.

2. Chemical industry - about 26 % of soda ash is used in the chemical industry processing.

   Soda ash is used in chemical reactions to produce organic and inorganic compounds that are used in several applications, including sodium phosphates, sodium silicates, sodium sulfites, sodium bichromate, Sodium sesquicarbonate (bath salts and water softener), Sodium percarbonate (it is a bleaching agent and is also used in cosmetology), chemically pure sodium carbonate (pharmaceuticals industry, fine chemicals, cosmetics and food industry), sodium bicarbonates in water ,flue and leather treatment, detergent and cleaning products, plastic foaming, paper industry, fire extinguisher powder, food products and animal feeds, pharmaceutical applications, domestic uses and drilling mud to improve fluidity .

3. Soaps and detergents - Soda ash acts as a builder or water softener in the formulation of soaps, detergents and other cleaning products. Soda ash also acts as a source of alkalinity for adjusting the pH.

4. Steel industry - Soda ash is used in steel industry as a flux, desulfurizer, dephosphorizer and denitrider.

5. Non-ferrous metallurgy industry – Soda ash is used in treatment of uranium ores, oxidizing calcination of chrome ore, lead recycling from discarded batteries, recycling of aluminium and zinc.

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6. Other applications – production of various chemical fertilizers, production of synthetic detergents, production of artificial sodium bentonites, organic and inorganic colouring industry, petroleum industry and natural gas refining, enamelling industry and fats, glue and gelatine industry, etc. [Örg03], [Bac07], [Eur03], [Glo08].

Table 2-4: Percentage breakdown of volume sales of soda ash in different countries for year 2005 [Glo08]

Country	Container glass	Chemicals	Soaps and Detergents	Pulp and Paper	Fluegas Desulfurization	Water Treatment
US	15.44	19.22	17.22	11.75	21.88	17.18
Canada	1.56	1.68	1.82	1.80	1.23	2.48
Japan	2.90	2.76	2.73	2.62	2.09	3.41
Europe	30.52	23.63	27.30	30.17	40.42	35.98
Asia Pacific	37.36	40.18	37.23	37.06	24.56	26.27
Latin America	6.94	6.83	7.61	10.17	4.30	8.58
Rest of World	5.28	5.70	6.09	6.43	5.52	6.10
Total	100.00	100.00	100.00	100.00	100.00	100.00

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2.3 Manufacturing methods

Historically, soda ash was produced by extracting the ashes of certain plants, such as Spanish Barilla [Cur91]. The land plants and the seaweed were harvested, dried and burned, the ashes were then washed with water to form an alkali solution. The solution was boiled dry to produce the final product, soda ash. The concentration of sodium carbonate in soda ash varied very widely, from 2-3 % for the seaweed (kelp) to 30% for the barilla from land plants in Spain [Sod08].

2.3.1 Synthetic processes

2.3.1.1 Leblanc process

The Leblanc or black ash process was discovered in the period around between 1825 and 1890 by the French physician Nicolas Leblanc [Eur03]. This synthetic process was named after its inventor [Kie02]. In this process, soda ash was produced from common salt, sulfuric acid, coal and limestone. Sodium chloride reacts with sulfuric acid to produce sodium sulfate and hydrochloric acid. The sodium sulfate is then roasted with limestone and coal and results into sodium carbonate and calcium sulfide mixture. The sodium carbonate and calcium sulfide mixture is also known as black ash. Black ash is then leached with water to extract the sodium carbonate [Örg03]. The Leblanc process which is now of only historical interest, is based on the following chemical reactions:

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl \qquad (1)$$

$$Na_2SO_4 + 2C \longrightarrow Na_2S + 2CO_2 \qquad (2)$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS \qquad (3)$$

The letter that was published in the Liverpool Mercury in October 1827 stated that the Muspratt's works poured out volumes of sulphurous smoke which made the whole atmosphere dark, and also changed the stone colour to dark [Hea96].

The smoke also affected the health of the people staying nearby [Hea96]. The other environmental impact was the emission of the large quantities of hydrochloric acid gas and the production of calcium sulfide which emit poisonous gas. This process was rediscovered and perfected by Ernest Solvay in 1861 [Eur03]. The last Leblanc plant was closed down in 1923 [Örg03].

2.3.1.2 Solvay process

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The Solvay process is also known as the ammonia soda process. The Solvay process was developed by the Belgian Ernest Solvay (1838 – 1932) in 1861. This process reduced the operating cost and environmental impact [Eur03].
The Solvay process is the most accepted technology for producing synthetic soda ash because the investment and maintenance costs are low compared to other processes [Dsi95]. The Solvay process is still the dominant production route for soda ash [Cur91]. The basic raw materials that are used in this process include salt, limestone and coke or natural gas and also ammonia as a cyclic reagent [Wag92].

In this process the ammonia reacts with carbon dioxide and water to form ammonium bicarbonate. The ammonium bicarbonate is then reacted with salt to form sodium bicarbonate, which is calcinated to form sodium carbonate. Chloride is formed as a byproduct and is neutralized with lime to produce calcium chloride. Almost all the ammonia used in the reactions is recovered and recycled. The Solvay process can be summarized by the following theoretical global chemical reaction, which involves two main components which are sodium chloride and calcium carbonate [Eur03] [Wag92].

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \qquad (4)$$

The above reaction can not be applied directly in practice, the Solvay process needs the use of other substances and also many different process steps before getting to the final product which is soda ash [Eur03].

The Solvay process includes the following stages:

1. Production of a saturated salt solution

   $NaCl + H_2O$ (5)

2. Burning of limestone and the CO_2 recovered which is used in stage 4 while CaO is used in stage 7.

   $CaCO_3 \longrightarrow CaO + CO_2$ (6)

3. Saturation of the salt solution with ammonia

   $NaCl + H_2O + NH_3 + CO_2$ (7)

4. Precipitation of bicarbonate by adding carbon dioxide (from stage 2 and 6)

   $NaCl + H_2O + NH_3 + CO_2 \longrightarrow NH_4Cl + NaHCO_3$ (8)

5. Filtration and washing of sodium bicarbonate

6. Thermal decomposition of sodium bicarbonate to sodium carbonate (the carbon dioxide that is given off is recycled to stage 4)

   $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$ (9)

7. Production of milk of lime

   $CaO + H_2O \longrightarrow Ca(OH)_2$ (10)

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8. Recovery of ammonia by distillation of the mother liquor from stage 4 with milk of lime (the ammonia that is released is recycled to stage 3)

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O \tag{11}$$

Process description

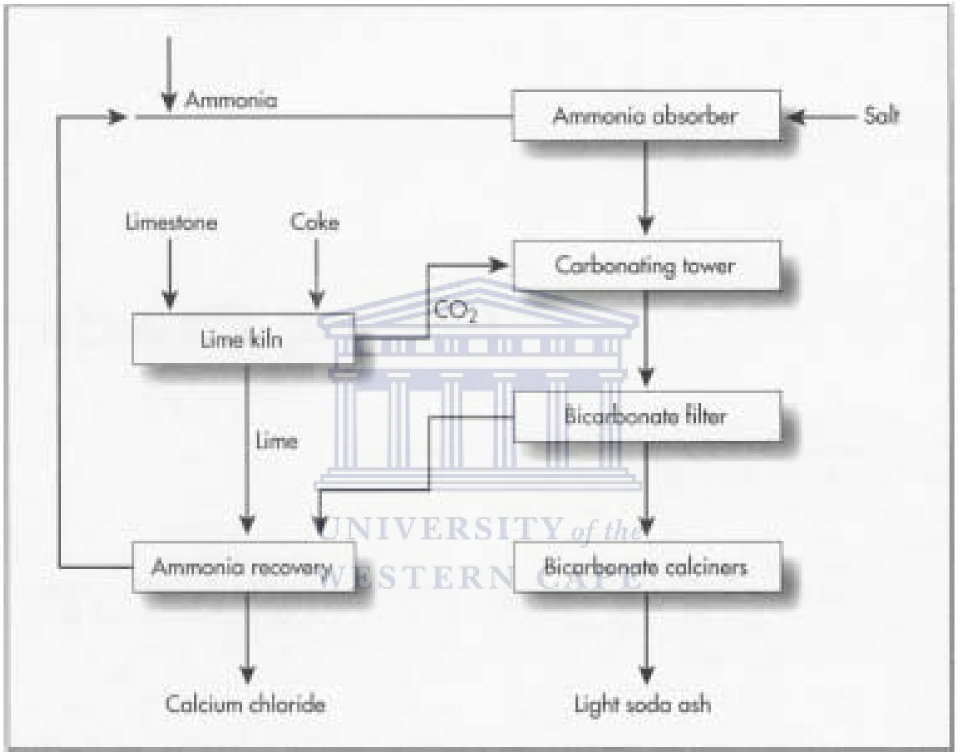

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Figure 2-2: The Solvay process flow diagram [How07]

1. Brine purification

The first step is brine purification, this step is done in order to get a pure sodium chloride solution. Sodium chloride used as a raw material in glass is available naturally, it is frequently obtained by solution mining of salt deposits. Brine always contains inorganic impurities such as magnesium and calcium salts and some brines also contain sulfates [Cur91].

If the impurities are not removed they cause production problems: they react with alkali and carbon dioxide to produce insoluble salts, and also affect the quality of the finally produced soda ash [Thi03], [Eur03].

The purification of the brine is carried out by the lime - soda treatment or lime – soda process. In the lime – soda process, magnesium ions are precipitated as hydroxide with milk of lime ($Ca(OH)_2$ concentration: 170 – 185 kg/m^3) and calcium ions are precipitated as carbonate with soda ash (Na_2CO_3 concentration: 65 – 80 kg/m^3). The lime – soda process is given by the chemical reactions:

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+} \quad (12)$$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^{+} \quad (13)$$

The brine is transferred to the ammonia absorbers after the separation form the precipitated impurities.

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2. Limestone burning and lime slaking

The acceptable limestone must be of very high purity (SiO_2: < 3% ; Fe_3O_3 – Al_2O_3: < 1.5%) or contain low concentration of impurities. The limestone must be hard and strong with the same coarse size. The limestone is frequently mixed with about 7 % of metallurgical – grade coke or coal and burned in vertical shaft kilns. The limestone is calcinated with coke to produce carbon dioxide which is used in the carbonation stage and it also produces calcium oxide which is used for the distillative recovery of ammonia. The burning of the limestone ($CaCO_3$) is carried out at a temperature between 950^{o}C and 1100^{o}C.

Carbon dioxide is produced by decomposition of limestone and also by combustion of carbon in the fuel:

$$CaCO_3 \longrightarrow CaO + CO_2 \text{ (burning of limestone in lime kilns)} \quad (14)$$

The kiln gases are diluted with nitrogen from the combustion air.

The gas contains 37 – 42% CO_2, stone dust, ash particles and other gaseous impurities. The hot gas is cooled and cleaned by direct contact with water. The gas is then transferred to the Carbon dioxide compressors and then passed through to the carbonating columns. The lime from the kiln is cooled by the air which is entering the lower parts of the shaft kiln. After the cooling, the lime is discharged from the kiln and reacted with used cooling water (50 – 65°C) to produce a thick suspension of calcium hydroxide ($Ca(OH)_2$) in water (concentrated milk of lime at temperature range of 90 – 100°C):

$$CaO + H_2O \longrightarrow Ca(OH)_2 \text{ (Lime slaking)} \quad (15)$$

The calcium oxide (CaO) content of the milk of lime can get to 5.5 mol/L in favourable conditions. The milk of lime is added to the distillation step in the recovery of ammonia. Before milk of lime is added to the distillation step, coarse sand and unburnt limestone are removed by sieves, mixed with new limestone and recycled to the kiln.

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3. Ammonia absorption

The gas from the distillation step contains ammonia (NH_3) and carbon dioxide (CO_2) and is saturated with water vapour in an absorption tower. At this stage of ammonia absorption, the gas is absorbed by purified brine. The obtained ammoniacal brine consists of 85 – 90 kg/m^3 ammonia and 40 – 50 kg/m^3 carbon dioxide.

The sodium chloride content is decreased from 300 g/L to 260 g/L because of the increase in the specific volume of the liquor caused by the addition of ammonia and by dilution with water. The reactions occurring in the absorption stage are strongly exothermic and given by the chemical equations:

$$NH_3 + H_2O \longrightarrow NH_4OH + \text{amount of heat} = -34\ 900\text{kJ} \quad (16)$$

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O + \text{amount of heat} = -\ 90\ 850\text{kJ} \quad (17)$$

The reaction requires cooling of the liquid. The brine needs cooling (394 kcal/kg) of the product soda ash during ammoniation. This process is done at slightly less than atmospheric pressure.

4. Precipitation of bicarbonate

The precipitation of sodium carbonate is an exothermic process.

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl + \text{energy} \tag{18}$$

This reaction involves the reaction of ammoniated brine and carbon dioxide. The ammoniated brine comes from the absorption stage whereas carbon dioxide comes from the lime kiln or from the calcination stage. The ammoniated brine is pumped to the top of one of the columns that is used to precipitate bicarbonate ($NaHCO_3$). Lime kiln gas is compressed to about 414 kPa, enters the bottom of the column and bubbles up through the solution and also absorbs a large amount of carbon dioxide. The concentration of carbon dioxide that is in the liquid leaving the column is kept below the bicarbonate precipitation level .The liquid is then placed in parallel to the top of the other columns. One of the columns is a cleaning column. The temperature in the columns is 50 – 60 ^oC. The precipitation of sodium bicarbonate happens after making the columns to receive the mixture of kiln gas and bicarbonate calciner gas that bubbles up through the solution. The suspension of bicarbonate in mother liquor leaves the carbonation stage at a temperature of 30^{o}C.

Nitrogen gas and some carbon dioxide and ammonia are vented from the crystallizing tower columns and collected before they are recycled to the absorption stage ([Cur91], [Thi03].)

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5. Filtration of Bicarbonate

Bicarbonate crystals are normally separated from the mother liquor by the use of vacuum filters, band filters and centrifuges.

When filters are used vacuum pumps pull the air through the cake and after that, the gas that is carrying ammonia and some carbon dioxide gas is cleaned and released to the atmosphere.

The filter cake is washed carefully with water and the remaining mother liquor chloride is eliminated. The mother liquor chloride is sent to a calcination stage and the mother liquor in liquid phase is sent to the distillation stage for the recovery of ammonia [Eur03], [Thi03], [Cur91].

6. Calcination of Bicarbonate to soda ash

Calcination of bicarbonate is usually performed in rotary calciners. The rotary calciners are heated externally with coal, oil or gas or internally with steam.

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Thermal decomposition of crude bicarbonate to carbonate gives out carbon dioxide, ammonia and water vapour. The carbonate product is technical-grade soda ash that contains sodium chloride. The main reaction is

$$2NaHCO_3 \longrightarrow CO_2 + H_2O + Na_2CO_3 \qquad (19)$$

and other reactions are

$$NH_4HCO_3 \longrightarrow NH_3 + CO_2 + H_2O \qquad (20)$$

$$NaHCO_3 + NH_4Cl \longrightarrow NH_3 + CO_2 + H_2O + NaCl \qquad (21)$$

Heat is required for the calcinations of bicarbonate. The amount of heat that is needed is 0.92 GJ/t of soda ash but the stated value does not include the amount of heat required for drying the product. The total heat required for calcinations of bicarbonate in rotary calciners is 3.7 GJ/t of soda ash.

The heat is provided at a temperature of 180°C. The temperature for the decomposition of sodium bicarbonate ($NaHCO_3$) is 87.7°C.

Gases removed from the rotary calciners contain carbon dioxide, ammonia, water, some leakage air and large amounts of sodium carbonate and bicarbonate dust.

The gas is cooled and also washed with brine and water to remove ammonia to condense water before it is used in the carbonation stage. The condensates that are formed are sent to the distillation stage for the recovery of ammonia [Thi03].

7. Recovery of Ammonia

The filtered liquor contains unreacted sodium chloride, hydrogencarbonate and ammonia as ammonium carbonate, they are recovered by distillation followed by absorption. $(NH_4)_2CO_3$ and NH_4HCO_3 are decomposed completely at the temperature between 85°C and 90°C and also gives out all the carbon dioxide and small part of ammonia from the solution. NH_4Cl react with milk of lime to release ammonia.

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$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2 \qquad (22)$$

The above reaction comes after the thermal decomposition of $(NH4)_2CO_3$ and NH_4HCO_3 to avoid precipitation of calcium carbonate and taking in of additional milk of lime. Ammonia can be fixed or free. Fixed ammonia corresponds stoichiometrically to the precipitated sodium carbonate. Distillation gas which contains ammonia and carbon dioxide is cooled to a temperature between 55°C and 60°C in the still condenser and still preheater.

2.3.1.3 DUAL (Modified Solvay process)

DUAL process is also known as modified Solvay process because the producers made several modifications to the original Solvay process. DUAL process was developed and operated in Japan. The modified Solvay process came in commercial use in 1980 [Wag92]. This synthetic process combines the production of soda ash with the production of ammonium chloride. The ammonium chloride produced is crystallized by cooling and through the addition of solid sodium chloride unlike in the Solvay process. The importance of the DUAL process in Japan is due to the high cost of imported rock salt and the use of the ammonium chloride as a fertilizer especially in rice cultivation [Örg03]. There are several plants that are using the DUAL process in other parts of the world, most of the plants are situated in China.

DUAL process uses mainly salt (sodium chloride), carbon dioxide and ammonia as raw materials. This process does not require limestone, an important raw material that is used in the Solvay process [Wag92]. The ammonium chloride is formed through the following chemical reaction:

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$$NaCl + NH_4 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl \qquad (23)$$

Ammonia is recovered in the Solvay process. In the modified Solvay process ammonium chloride is retained and crystallized out and separated by adding sodium chloride.

Sodium bicarbonate is calcined to form soda ash in both processes:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O \qquad (24)$$

Process description

1. Ammonia absorption

$$NH_3 + H_2O \longrightarrow NH_4OH \qquad (25)$$

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O \qquad (26)$$

2. Carbonation of the ammonia brine and production of sodium bicarbonate and ammonium chloride

$$(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow 2NH_4HCO_3 \; (NH_4)HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl \qquad (27)$$

3. Filtration of sodium bicarbonate
4. Crystallization and separation of ammonium chloride
5. Decomposition of bicarbonate into soda ash and recovery of carbon dioxide [Wag92], [Wip07]

$$2NaHCO_3 + \text{Heat} \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad (28)$$

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2.3.1.4 Environmental impacts of synthetic processes

The Solvay process results in the production of liquid, gas and solid wastes. The liquid and solid wastes are usually discharged into rivers, lakes and sea.

Gaseous effluents

Particulate dust

During the production of soda ash dust is released in limited quantities. The dust is emitted from handling process of the raw materials (carbon from coke; CaO from burnt lime; $CaCO_3$, Al_2O_3 and SiO_2 from limestone and sand), handling of soda ash and the production of dense soda ash from light soda ash and also limestone conversion in kilns.

Carbon monoxide and carbon dioxide

During the burning of limestone ($CaCO_3$) to produce CaO inside the limekilns, carbon dioxide (CO_2) and carbon monoxide (CO) are produced from the combustion of coke and from the burning of limestone.

Nitrogen oxides

During the combustion, nitrogen oxides are produced by oxidation of nitrogen inside the kiln.

Sulphur oxides

Sulphur oxides are produced by the oxidation of compounds that contain sulphur in the limestone and coke.

Ammonia

Atmospheric emissions containing ammonia is released from the filtration of sodium bicarbonate, the precipitation of sodium bicarbonate, from filters and handling and processing of distillation effluent.

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Liquid effluent

Liquid effluents in soda ash production are normally from wastewater from distillation, wastewater from brine purification, cooling water from lime kiln gas washer, cooling of CO_2, cooling in absorption and distillation towers and also calcilnation.

Solid effluent

Solid effluents produced in soda ash production are normally from fines of raw limestone from screening and also non recycled stone grits at slaker [Eur03], [Ste07].

2.3.2 Natural processes

Apart from synthetic processes, soda ash can also be produced from natural soda reserves and production from lake waters [Örg03]. Natural soda ash-containing brines and deposits were found in the United States at Searles Lake, Carlifonia and Green River, Wyoming in the late 1800s. During the first half of the 1900s the Searles Lake deposit was commercialized and the production facilities improved and expanded.

In 1938 large deposits of trona, $Na_2CO_3.NaHCO_3.2H_2O$ were found in the Green River basin [Cur91]. Deposits of sodium carbonate are found in large quantities in Botswana, China, Egypt, India, Kenya, Mexico, Peru, Turkey, and the USA.

The major natural sodium carbonate deposits include trona from Green River, Wyoming, USA (operated by FMC Industrial Chemicals, General Chemical Industrial Products Inc., OCI Chemical Corp. and Solvay Chemicals Inc.) (check Table 2-4 and 2-5 for the soda ash production in U.S.), brine from Searles lake, California, USA (Searles Valley Minerals Inc.), brines from Lake Magadi, Kenya (Magadi Soda Co., a wholly owned subsidiary of Brunner Mond, which has been bought by Tata Chemicals Ltd, India) and brines from Sua pan in Botswana (Botswana Ash or Botash) [Bac07].

Table 2-5: USA natural soda ash production [Kos08]

SALIENT SODA ASH STATISTICS (Thousand metric tons)			
Period	Production	Ending stocks	Wyoming trona production
2007			
January-March	2,710	xx	4,420
March	962	238	1,590
April	880	208	1,450
May	950	242	1,460
June	926	198	1,310
July	985	207	1,500
August	971	213	1,490
September	890	251	1,110
October	920	203	1,450
November	903	158	1,450
December	936	206	1,510
January-December	11,100	xx	17,200
2008			
January	922	221	1,510
February	878	190	1,370
March	955	194	1,510
January-March	2,760	xx	4,390

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xx – not applicable

Table 2-6: USA Exports of soda ash [Kos08]

USA EXPORTS OF SODA ASH BY COUNTRY, IN FEBRUARY 2008			
Country	Quantity (metric tons)	Value (thousands)	Unit value
Mexico	71,500	$11,800	$165
Brazil	61,800	10,100	164
Canada	38,600	5,420	140
Indonesia	36,100	6,080	168
Taiwan	34,300	7,000	204
Chile	32,400	5,390	167
Korea, Republic of	27,600	5,620	204
Japan	24,700	3,850	156
South Africa	21,400	3,290	154
Thailand	19,000	2,620	138
Malaysia	18,200	3,880	213
Venezuela	17,900	3,440	192
Lithuania	17,000	1,900	111
Other	92,700	16,000	173
Total or average	513,000	86,400	168

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Trona is a relatively rare, non-metallic mineral. The pure trona material contains 70.39% of sodium carbonate. Because trona is an impure sodium sesquicarbonate mineral ($Na_2CO_3.NaHCO_3.2H_2O$), it has to be processed by calcinations of the excess carbon dioxide and removing water to produce soda ash [Örg03] [Sci08].

2.3.2.1 Trona purification processes

The raw trona can be processed by the use of different methods: sesquicarbonate process, monohydrate process, alkali extraction process and carbonation process.

The two processes (monohydrate process and sesquicarbonate process) are mainly used to produce refined soda ash (sodium carbonate (Na_2CO_3)) from trona. Both processes entail the same unit operations only in different sequences.

Most soda ash is made using the monohydrate process. Figure 2-3 shows a simplified flow diagram for monohydrate process and sesquicarbonate process [Örg03], [Cur91].

Monohydrate Process

This process involves crushing and screening of trona ore. Trona ore contains sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) and also some impurities such as silicates and organic matter. After the screening of the trona ore, it is calcined (heated) at the temperature between 150^{o}C and 300^{o}C using rotary gas-fired and coal grate-fired calciners to convert sodium bicarbonate to sodium carbonate.

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The crude soda ash is then dissolved in hot, clear recycled liquor which is then clarified and filtered to separate the solution from the insoluble solids. Sometimes the liquor is sent through activated carbon beds before crystallization to remove dissolved organic matter which may affect the crystallizer performance by foaming and colour problems in the final product [Neu98].

Sodium carbonate monohydrate is precipitated by evaporative crystallization [Örg03]. The monohydrate slurry is centrifuged and the monohydrate crystals are then sent to dryers to produce soda ash.

Sesquicarbonate process

In this process trona ore is dissolved in hot liquor, clarified, filtered to remove insolubles and then sent to be crystallized by cooling to form sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$ [Cur91]. The sesquicarbonate crystals are then separated from the mother liquor, centrifuged and calcined to produce soda ash (anhydrous sodium carbonate) ([Örg03], [Cur91]).

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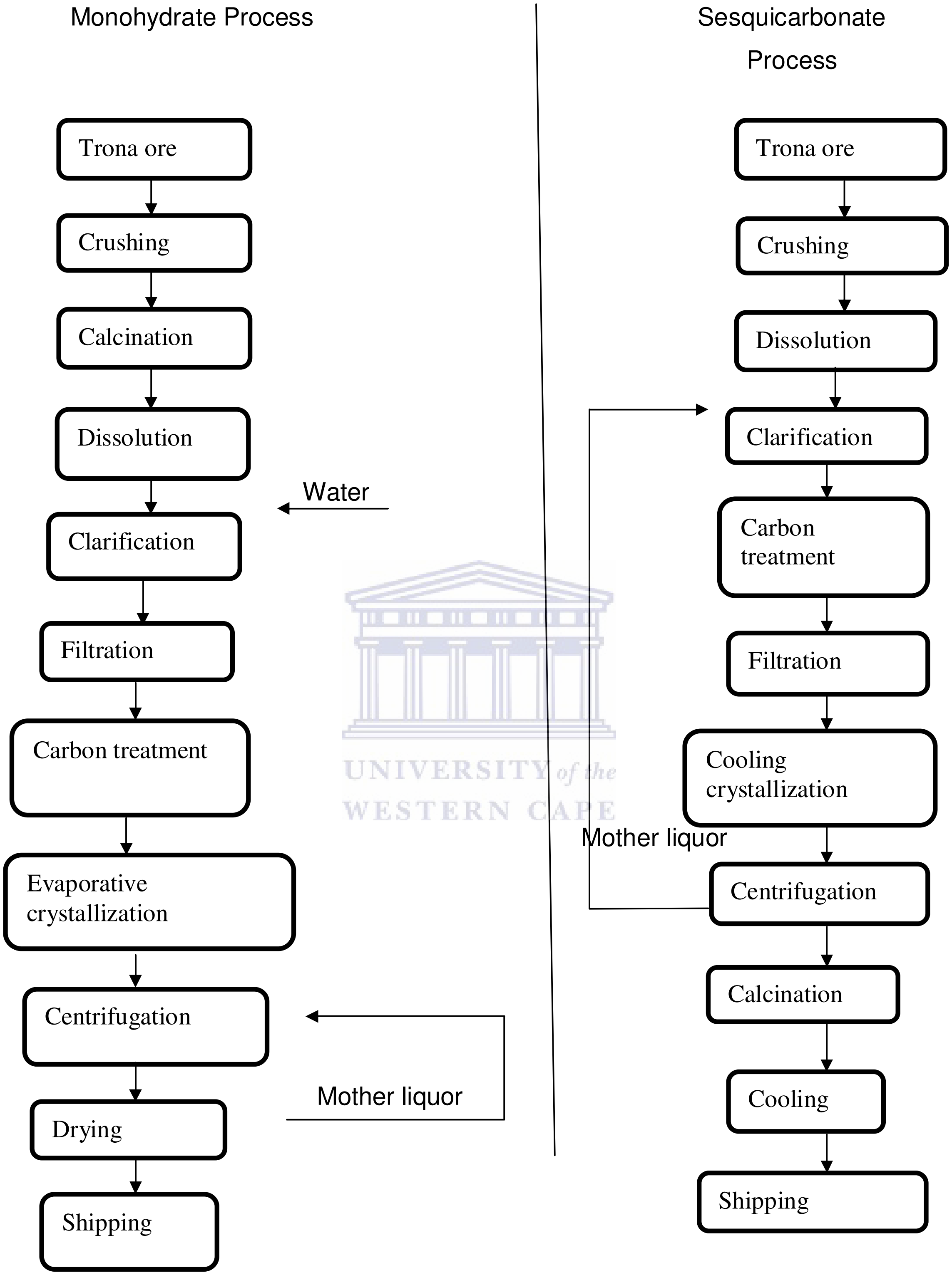

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Figure 2-3: Simplified flow diagram for production of soda ash from trona

CHAPTER 3

EXPERIMENTS

3.1 Introduction

The Solvay process involves the saturation of brine solution by ammonia and carbon dioxide gas and also shows the difference in solubility between ammonium and sodium bicarbonate that is produced in the reaction. The final products produced in the Solvay process are sodium carbonate and calcium chloride (figure 3-1).

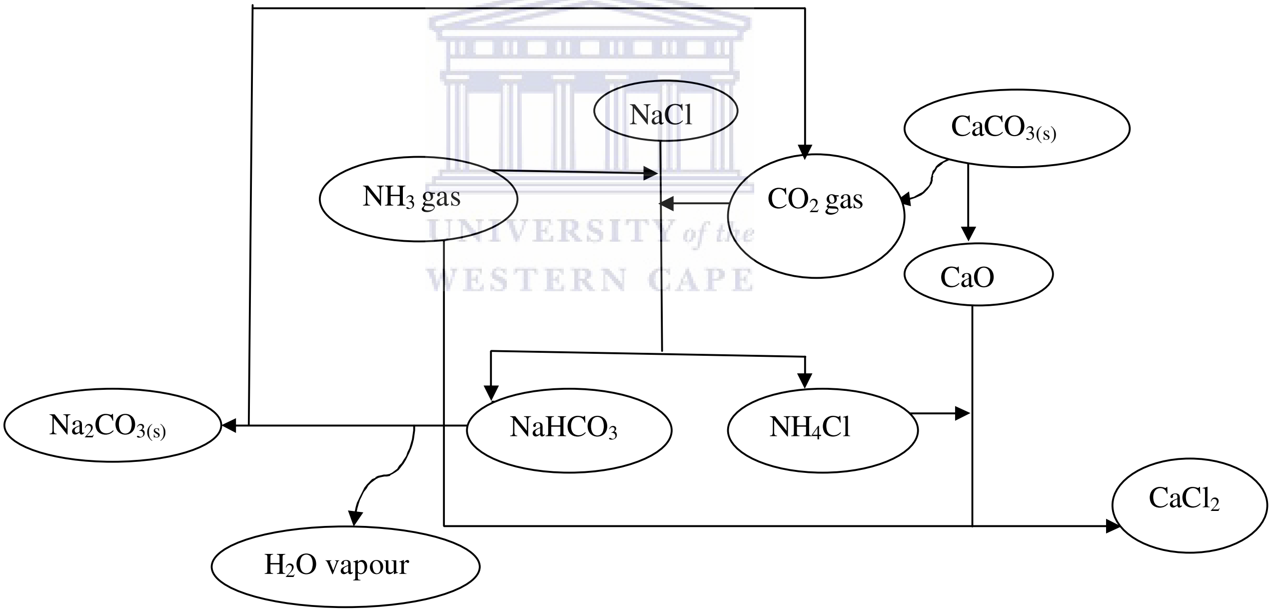

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Figure 3-1: Simplified flow diagram of the Solvay process

All the reactions involved in the Solvay process are important and simple. Examples of the experiments that investigate the synthesis of sodium carbonate by the Solvay process in the laboratory are rare to find.

The known experiments have little similarity to the unitary operations that occur in the industrial continuous process.

One of those experiments was done in the laboratory and it is explained below. The other experiment which was also done in the laboratory explained the new arrangement from those mentioned above, this experiment allows the accurate reproduction and it uses simple laboratory apparatus. The experiment involves the brine ammonization and carbonation process followed by the precipitation of sodium bicarbonate.

The apparatus used in this experiment allows the relative flow of ammonia and carbon dioxide gas in relation to brine flow against the current (see figure 3-2) .

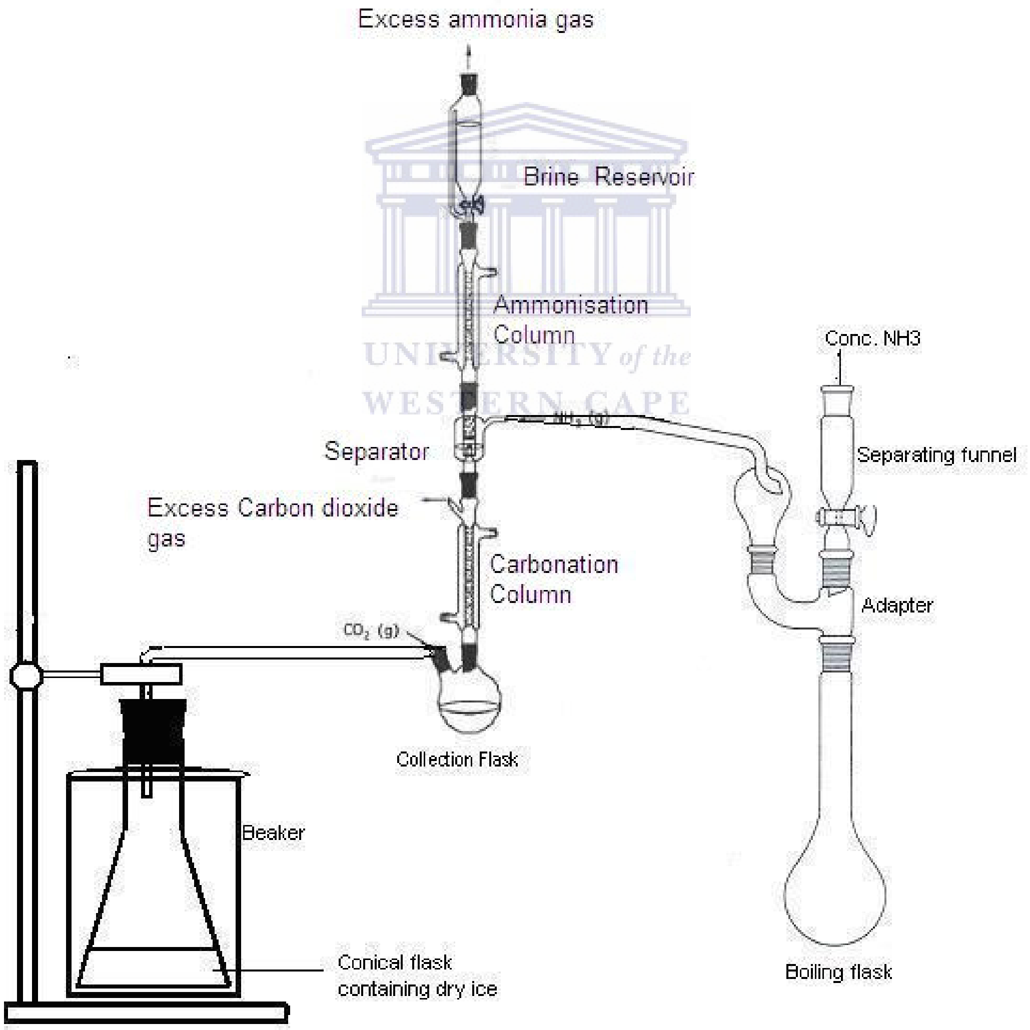

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Figure 3-2: Diagram of the complete apparatus used to simulate the Solvay process [Ara98]

3.2 SOLVAY PROCESS EXPERIMENT

3.2.1 Experimental procedure

3.2.1.1 Preparation of sodium bicarbonate

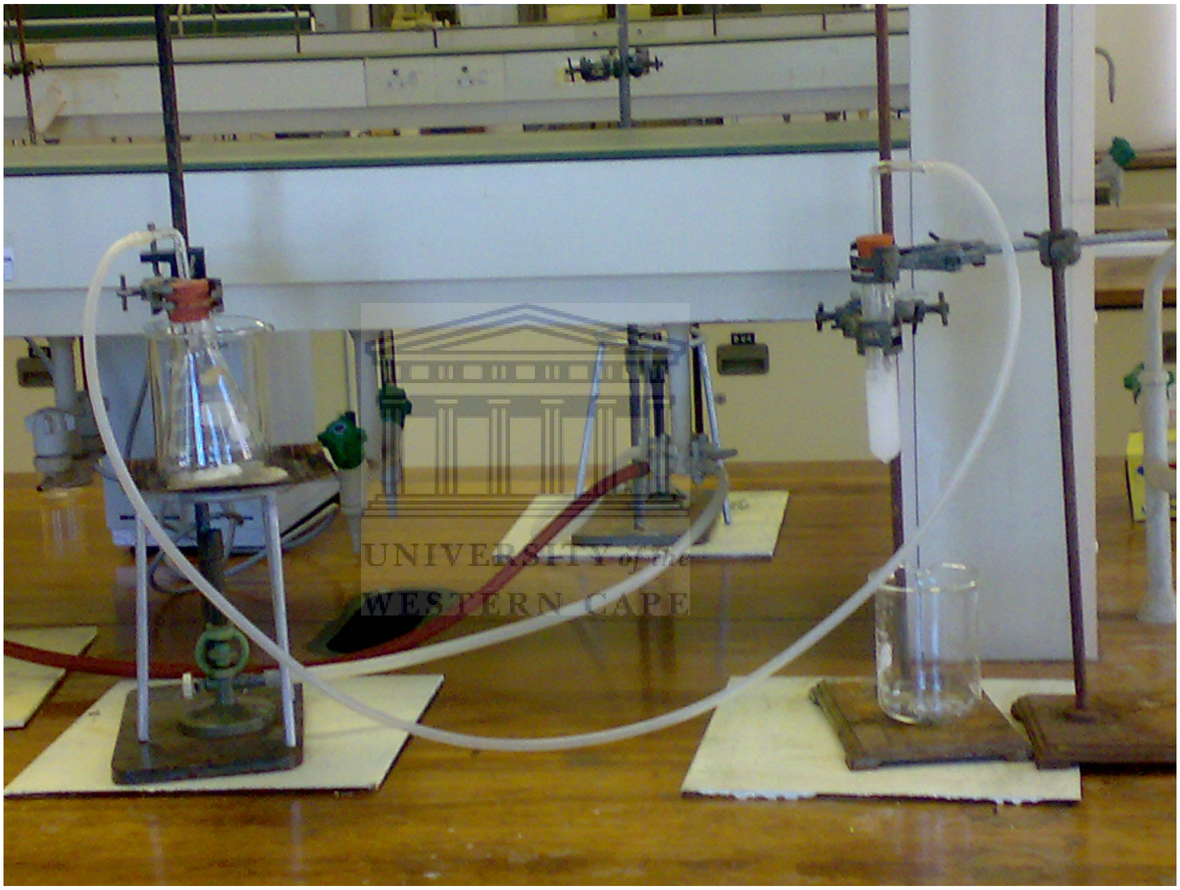

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Figure 3-3: The photographic representation of the experiment

The 40 ml of 4 M ammonia solution was measured with the measuring cylinder and transferred to a 250 ml conical flask.

A 20.0467 g of Sodium chloride, weighed using an analytical balance, was added to the ammonia solution. The mixture was swirled for a few minutes until all NaCl dissolved.

The filter paper was folded and fitted in the funnel. When the solution was saturated the excess solid was filtered out and the clear solution drained in the reaction test tube.
A 100 ml of powdered dry ice was added in the conical flask. The 600 ml beaker was used to hold a 250 ml conical flask containing dry ice. A gas delivering tube and a stopper were used. The gas delivery tube was extended from the conical flask to the bottom of the test tube.

Bubbles started to appear when carbon dioxide gas was transferred to react with the ammonia solution. The clamp was put above the gas generating conical flask surrounding the rubber tube. Another clamp was also put above the reaction test tube.
The reaction proceeded for 30 minutes until the significant amount of the precipitate started to form. The reaction proceeded for another 15 minutes at room temperature and a fairly heavy precipitate of sodium bicarbonate formed. After the 15 minutes period was over a 400 ml beaker was put under the reaction tube and the reaction was cooled to 0^oC by adding ice and water to the beaker. About 7 ml of distilled water was put in a large test tube and cooled in a 250 ml beaker containing ice and some water.

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The carbon dioxide continued bubbling into the cooled reaction test tube for an additional 15 minutes, more sodium bicarbonate formed as more carbon dioxide reacted with ammonia and more of the already formed sodium bicarbonate precipitated out (see figure 3-2). After 15 minutes the stopper at the top of the reaction test tube was carefully disconnected.
The cold precipitated sodium bicarbonate was collected in a clean Buchner funnel, filter flask and filter paper using a suction filtration. Some of the filtered mother liquor was used to rinse out sodium bicarbonate in the test tube. The suction ran for 1 minute and the vacuum was shut off.

A 3 ml volume of ice cold distilled water prepared in the test tube was added and distributed around the filter cake. After 10 seconds the vacuum was turned on.

The washing procedure was repeated to complete the removal of the mother liquor which contains impurities such as sodium chloride and ammonia chloride.

The filter paper was used to press the crystals with the suction on to dry them. The crystals of sodium bicarbonate were left for five minutes with the suction on and then the crystals were placed on a clean watch glass and allowed to dry in the laboratory locker.

3.2.1.2 Converting the sodium bicarbonate to sodium carbonate

The dry sodium bicarbonate on the watch glass was put in the mortar and ground in the clean and dry mortar with a pestle. The 0.7012 g of sodium bicarbonate was weighed in a dry clean test tube using an analytical balance. With the sodium carbonate at the bottom of the test tube, the test tube was held with the test tube holder.

The test tube and its contents were heated with the Bunsen burner. The test tube was heated gently until all the carbon dioxide and water were driven off. The test tube was heated below red heat for a few minutes continuously moving the tube in the flame.

After a few minutes of heating the test tube and its contents were left to cool to room temperature and the sodium carbonate was weighed using an analytical balance to be 0.3954 g.

3.3 SIMULATION OF SOLVAY PROCESS IN THE LABORATORY

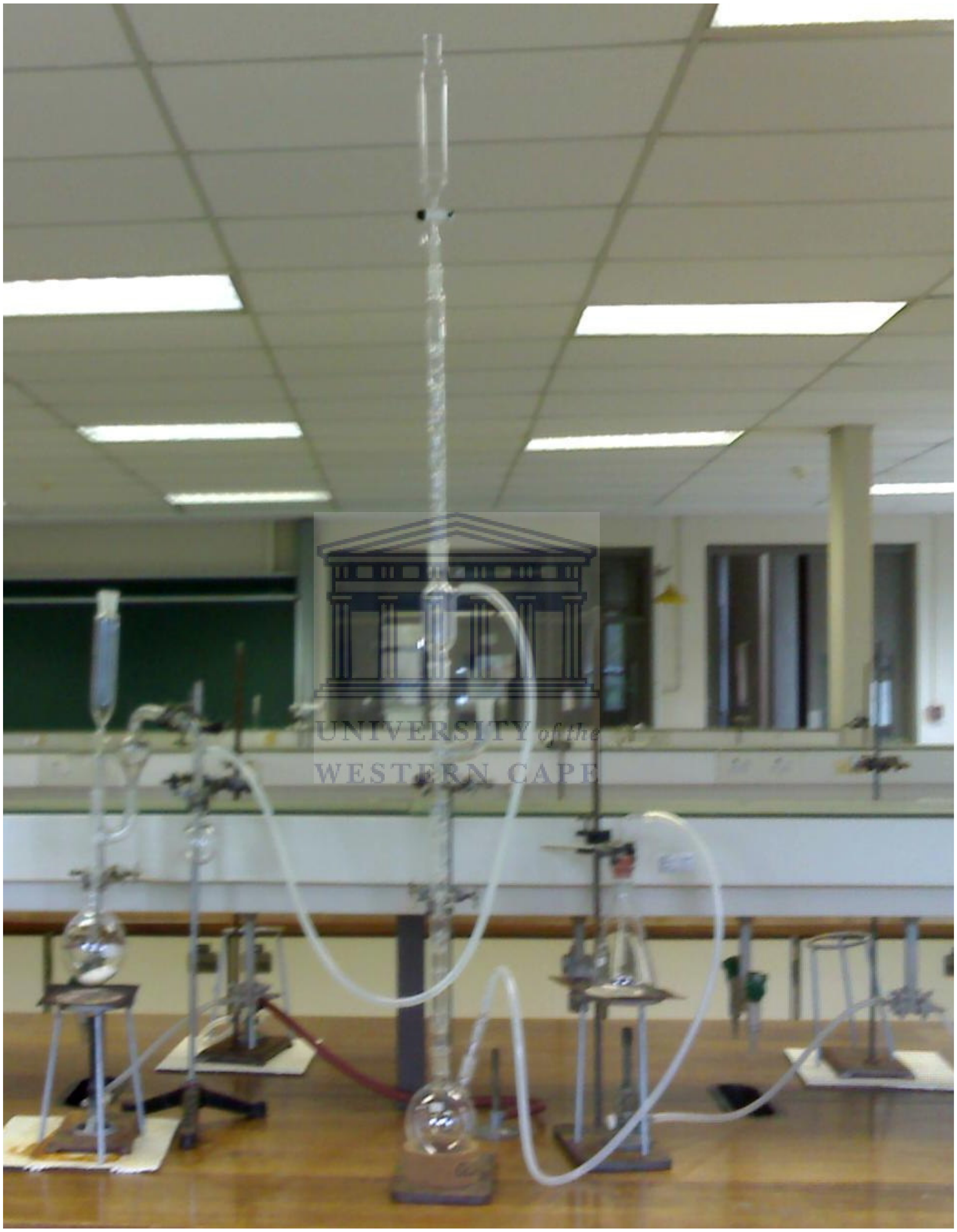
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Figure 3-4: The photographic representation of the Solvay process experiment

Method

The ammonization and carbonation processes are carried out using the flow against current method, similar to the industrial process. The apparatus includes two columns. The columns are connected by means of a bell-glass type separator which allows the drainage of the column above to the lower column due to gravity, and prevents the rise of CO_2 to the ammonization column (see figure 3-4.).

50g of Sodium chloride was weighed and 100ml of water was added to the NaCl salt. The solution was stirred with the magnetic stirrer until almost all sodium chloride dissolved. The experimental set-up was done as shown in the diagram (see figure 3-2). The ammonia gas was also generated by adding concentrated ammonia in drops over sodium hydroxide pellets. The carbon dioxide gas was generated by heating dry ice. The brine solution was added in drops to the top column. The experiment was left to run for five hours.

The sodium bicarbonate was filtered under suction, the crystals were washed by cold distilled water. The final product was weighed to be 0.2 g.

3.4 Second simulation of Solvay process in the laboratory

The experiment was conducted as the one in section 3.3, a carbon dioxide gas cylinder was used instead of generating carbon dioxide gas from dry ice and ammonia gas cylinder was also used instead of generating ammonia gas from concentrated ammonia solution. The gases were difficult to control as they were not flowing at the same rate.

CHAPTER 4

ANALYTICAL TECHNIQUES

4.1. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy (EDS) was performed on the samples using the Scanning electron microscope (SEM) (Figure 4-1). Analysis of the x-ray energy may be accomplished by energy dispersion which is the separation of x-rays according to their energy. This energy dispersion is done with a semiconductor detector.

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Figure 4-1: The Hitachi X650 Scanning Electron Microscope at the UWC EM Unit

When an x-ray strikes the semiconductor crystal, electrons are excited to the conduction band, the number of electrons excited is also greater.

An electric count pulse is generated closer to a high voltage applied over the semiconductor. The electric pulse is proportional to the energy of the x-ray. The amplified electrical pulses from the semiconductor are converted to digital form and fed into a multichannel analyzer (MCA) which sorts the signals by pulse energy and thus counts the number of x-rays at each energy level which strike the crystal. This information is then represented in the form of a spectrum.

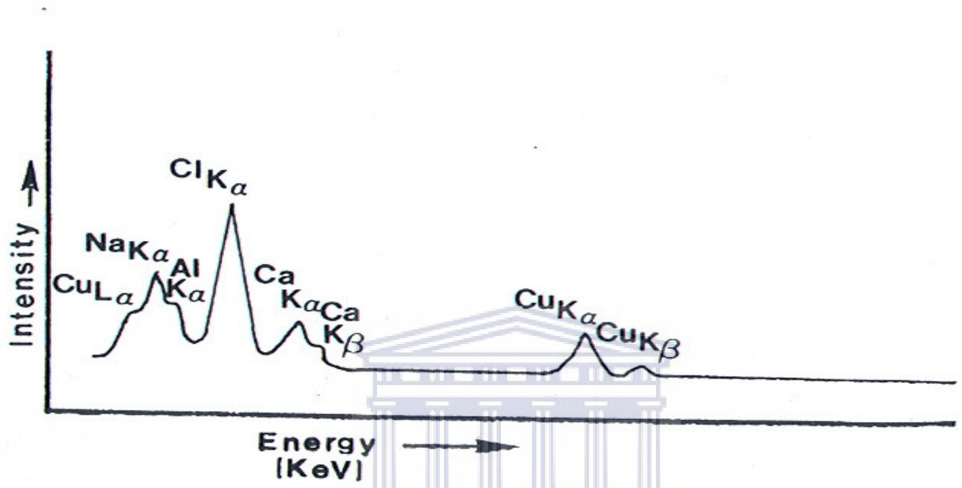

Figure 4-2: An analysis spectrum obtained through the use of an energy dispersive spectrometer, specimen is composed of copper, sodium, aluminum, chlorine and calcium [Pos80]

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4.1.1 EDS analysis

Energy Dispersive X-ray analysis (EDS or EDX) is a technique that is used to identify the elemental composition of the specimen.

During EDX analysis, the specimen is bombarded with an electron beam inside the Scanning Electron Microscope. The bombarding electrons collide with the electrons of the atoms and knock out some of the electrons.

The removal of an electron from a low energy inner shell will result in the immediate replacement by an electron from a higher energy outer shell. The second electron looses energy in this electron jump process and this energy is emitted as an x-ray whose energy is equal to the difference in energy between the two shells.

The atom of every element emits x-rays with unique amounts of energy depending on the energy levels of the atom. The identity of the atom from which the x-ray was emitted is found by measuring the energy of the x-rays being released by a specimen during electron beam bombardment. The output of an EDX analysis is the EDX spectrum. The EDX spectrum normally displays peaks corresponding to the energy levels for which the most x-rays had been received. Each of the peaks is unique to an atom and corresponds to the specific element. The higher the peak is in the spectrum, the more the concentration of the element in the specimen.

The EDX software does not only identify the element corresponding to the peak, it also shows the energy level to which it corresponds. A peak corresponds to the amount of energy possessed by x-ray emitted by an electron in the L-shell moving down to the K-shell is identified as a K-Alpha peak. The peak that corresponds to x-rays emitted by M-shell electrons moving down to the K-shell is identified as a K-Beta peak (Figure 4-3).

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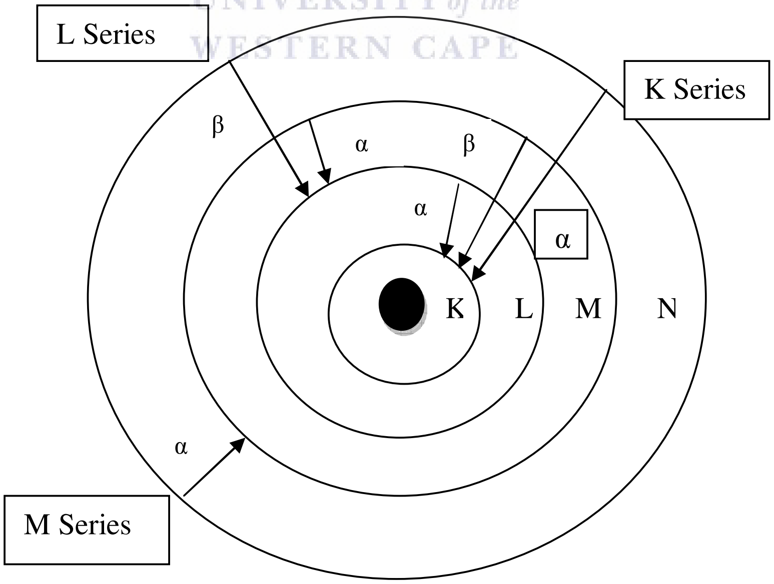

Figure 4-3: The spectrum of x-rays that may be generated from a single element

Quantitative energy dispersive analysis is the determination of the elemental composition of a sample as a percentage of the total detectable sample composition. The elemental analysis would be simple if the relative intensities of the spectral peaks shown on the multichannel analyzer (MCA) were equal to the relative abundance of atoms of the corresponding elements in the specimen. In that condition, peak's intensity's ratio to the sum of intensities of all peaks would be equal to the composition of the element as a percentage of the whole specimen. However peak intensity is not a direct measure of the specimen composition.

Elemental abundance is one of the many factors that affect the relative peak intensity. There are other several factors that affect relative peak intensity:

1. The rate of x-ray production varies with atomic number (Z) and accelerating potential e.g. heavy elements produce more x-rays than light elements.

2. An X-ray yield varies from one element to another because of differences in absorption (A) (see fig 4-4 for x-ray absorption graph) and secondary fluorescence (F).

   The absorption is given by Beer's law (Bar00)

$$\frac{I}{I_o} \alpha e^{-\mu_m \rho x} \qquad (1)$$

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Where μ_m is the mass absorption coefficient, ρ is the density of the material, x is the depth of the material and (I/I_o) is the fractional transmitted intensity.

The mass absorption coefficient, μ_m, is a function of the atomic number of the absorber (z) and the incident x-ray energy (E): $\left(\mu_m = \frac{kz^3}{E^3}\right)$ (2)

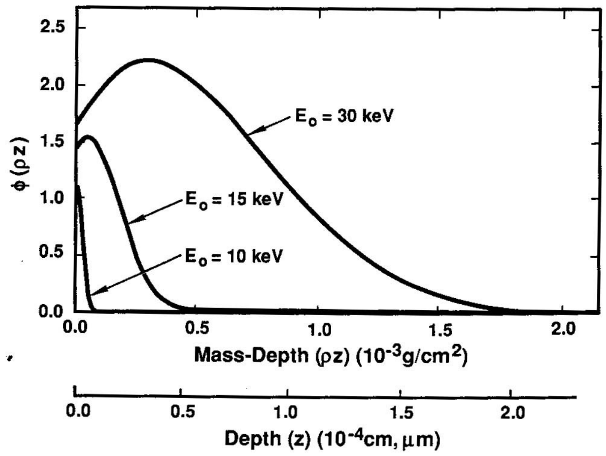

Figure 4-4: Calculated Φ(ρz) curves for Cu kα in cu at 10, 15, and 30 keV [Gol03]

3. The beryllium window of the detector absorbs lower energy x-rays to a greater extent than high energy x-rays.
4. The amount of background radiation varies across the energy spectrum leading to problems of intensity measurement.

The first three correction factors are together known as the "ZAF" correction [Pos80].

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To perform quantitative X-ray microanalysis using the conventional techniques, the sample must be flat, homogenous on the scale of the analyzed volume. The sample must also be thick enough with respect to electron beam penetration. If the above mentioned conditions are satisfied, quantitative analysis can be performed if attention is paid to detail in the data collection process.

Accuracy of analysis depends on the concentration level and the energy of the analyzed line. For a medium Z element of concentration greater than 10%, relative accuracies of 1 – 5 % are achievable (see table for ZAF results of soda ash. As the concentration drops towards 1%, accuracies will degrade from the 5 to 50 % relative level.

Below 1 %, results are often considered semi quantitative only. A general rule of thumb, to be used for rough estimations is that accuracies of ± 1 % absolute are achievable for concentrations in excess of 1% [Bar00].

Table 4-1: Detailed values of ZAF correction factor of natural soda ash

Element	Wt %	At %	K-Ratio	z	A	F
C K	6.90	10.71	0.0139	1.0493	0.1915	1.0008
O K	38.73	45.17	0.1703	1.0334	0.4249	1.0016
Na K	54.37	44.12	0.2377	0.9693	0.4510	1.0000
Total	100.00	100.00				

The ZAF technique is the most commonly used method of data correction in quantitative analysis.

There are several approaches that may be used to compensate for the ZAF effects. The most usual approach used is the comparison of unknown specimens with standards and computed corrections.

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Measurement of peak intensity is important in any quantitative energy dispersive spectrum analysis. Any of the following three approaches may be used viz. peak method, integral method and partial integral method.

- *Peak method* – This method measures the peak as the intensity of the channel with the highest intensity above background.

  The advantage of this method is the rapid evaluation of peak intensity with minimum interference from peak overlap relative to the other methods. The disadvantage of this method is the error resulting from differences in peak shape (small and large peaks).

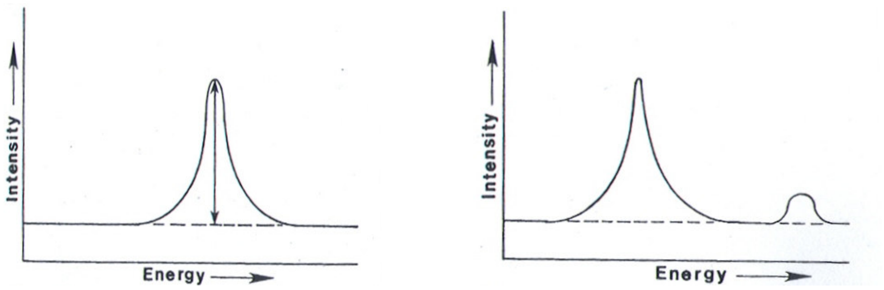

Figure 4-5: Measurement of the largest single channel above background and narrow peak measured than the low, broad peak [Pos80]

- *Integral method* – The errors due to peak shape may be minimized by calculating the integral of the peak. The integral is the sum of the counts above background in all channels in a peak. The disadvantages of this method are:
    - ➢ That it may be difficult to correctly subtract background counts from the counts due to the peak.
    - ➢ The peak-to background ratio for the peak integral is far less than for the single channel at the peak and it is caused by the inclusion of low intensity wings of the peak.
    - ➢ The combination of two peaks in some channels (spectral overlap); this can be a serious problem. The overlapping peaks can be analyzed by deconvolution.

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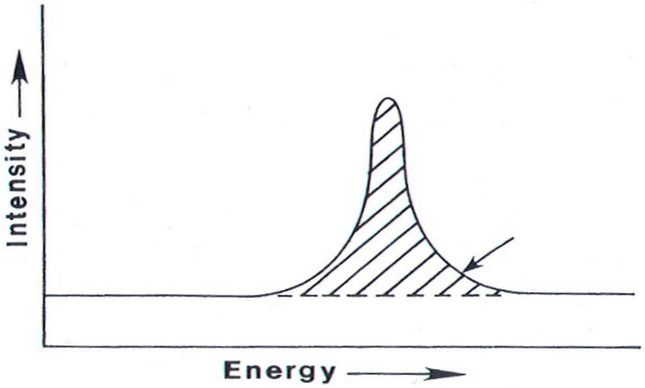

Figure 4-6: Measurement of all channels above background [Pos80]

- *Partial Integral method* – This method is commonly used as a compromise between the *peak* and integral methods of peak measurement. Partial integral is the area of a specified portion of a peak. The background ratio is better than with the full integral while counting errors are less than for the peak method. A most commonly used partial integral is "Full Width half Maximum" (FWHM).

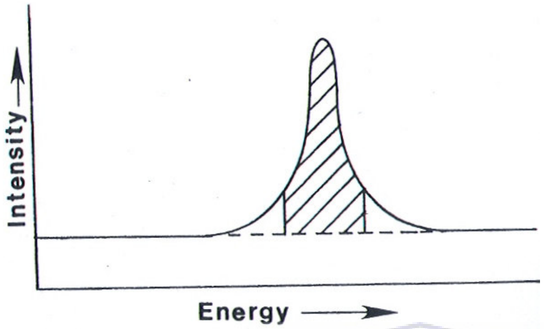

Figure 4-7: measurement of the most intense portions of a peak [Pos80]

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The ZAF Factors – There are a number of factors that affect the size of peaks and prevent the direct conversion of peak size ratios to elemental composition. ZAF is the most common corrections factors amongst other factors.

Atomic number (Z)

Z is used to designate the effects of atomic number on initial x-ray generation. The most important two Z effects are backscattering and energy loss. These two effects vary for different elements.

Backscattering effect

When primary electrons impinge upon a specimen, some of the electrons enter the specimen and loose energy by ionizing specimen atoms. Other electrons are backscattered and do not produce x-rays. Light elements (the elements that have low Z) are less effective at backscattering primary electrons than the heavier elements.

The proportion of electrons that penetrate a specimen and ionize specimen atoms is higher for light elements.

Energy-loss effect

While atoms of light elements are easily ionized by collisions with primary electrons, light elements are less likely to have these collisions than the heavier elements. An electron that is not backscattered is more likely to generate x-rays in a heavier element than in a light element.
A backscattering and energy loss correction may be determined theoretically for each element using Monte Carlo theory. Overall Z correction is small, it is often ignored in empirical techniques using standards.

Absorption (A)

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A is used to designate absorption effects. X-rays are generated throughout the volume of primary excitation. A significant fraction of these x-rays are reabsorbed by the specimen atoms. Absorption is minor for light elements and low accelerating voltages. Absorption is large for heavy elements and high accelerating voltages. Absorption is one of the most important factors affecting Energy Dispersive spectrum (EDS) quantification.

Absorption correction may be determined using a computer, the following must be considered: the size and shape of the volume of primary excitation, the take-off angle (figure 4-8) and angle of the specimen surface relative to the primary electron beam.

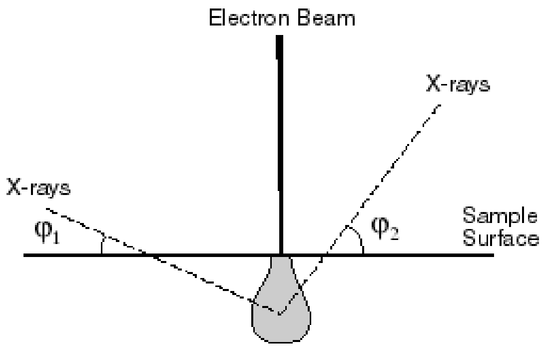

Figure 4-8: Schematic illustration of the take-off angle. For a given angle of electron incidence, the length of the absorption path is directly proportional to the cosecant of the take-off angle, Φ.

Fluorescence (F)

F is used to designate fluorescence effects. The atom is ionized when a specimen atom absorbs a generated x-ray. A new x-ray is generated if the energy of the incident x-ray exceeds the critical energy of one of the atom's electron shell.

This secondary x-ray is called "secondary fluorescence". X-rays of a given element may cause fluorescence in an element lighter than itself but not in heavier ones. Secondary fluorescence may also be caused by the continuum x-rays produced in the specimen by the primary beam.

ZAF effects are of great importance for most quantitative EDS analyses. Determination of theoretical ZAF corrections generally requires computer reduction of data because of the difficulty of the interactions within the specimen [Pos80].

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4.2 Fourier Transform Infrared Spectroscopy (FTIR)

4.2.1 Introduction

Fourier transform infrared spectroscopy is one of the most common spectroscopic techniques used for identifying chemicals that are either organic or inorganic. This technique can be applied to solid, liquid and gas sample. The sample is positioned in the path of an IR beam for the absorption measurement of different IR frequencies. This technique identifies chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation.

4.2.2 Sample Preparation

Liquid sample

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The easier way to prepare a liquid sample is to place one drop of a sample between two sodium chloride salt plates to produce a thin capillary film.

Solid sample

Solid sample is prepared by grounding a powder using agate mortar and pestle, a small amount of powder is mixed with Nujol to give a paste and it is then applied between two sodium chloride plates. Solid sample can also be prepared by dissolving powder in a solvent such as methylene chloride and the solution is placed onto a single salt plate.

Gas sample

Gas sample is prepared by using a cylindrical gas cell with windows at each end composed of an Infrared inactive material such as KBr or NaCl.

The gas cell generally has an inlet and outlet part with a tap to enable the cell to be easily filled with the gas to be analyzed [Eva08]; [Smi96].

4.2.3 Method

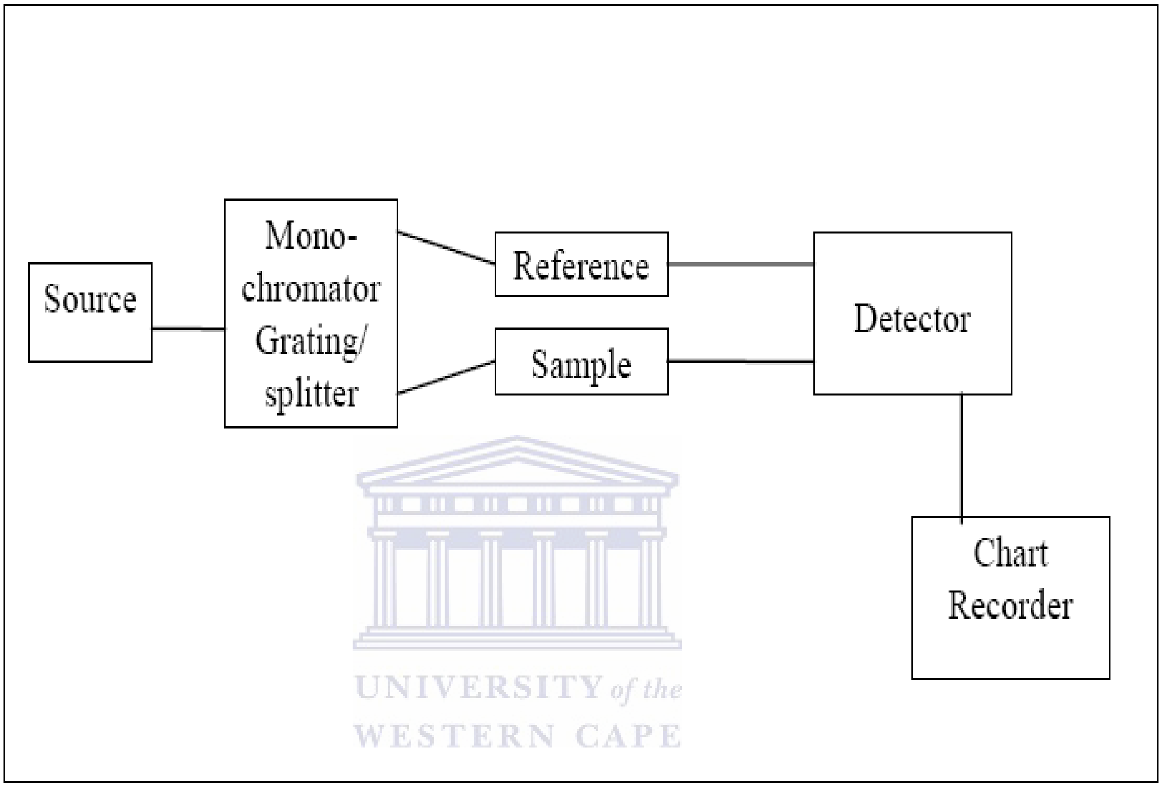

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Figure 4-9: Schematic diagram of an Infrared Spectrometer [Eva08]

A beam of light is produced and split into two beams, one is passed through the sample and the other through a reference. The beams are reflected back towards a detector. The two signals are then compared and a printout is obtained.

4.2.4 Interpretation

The tables of infrared data are used to interpret the spectra, stretching vibrations are most useful when assigning peaks. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds.

For any given bond there are several specific frequencies at which it can vibrate [Eva08].

Table 4-2: Tables of infrared spectra interpretation [Eva08]

Single Bonds to Hydrogen

Bond	Wavenumber/cm^{-1}	Notes
C–H	3000 – 2850	Saturated alkanes, limited value as most organic compounds contain C–H
=C–H	3100 – 3000	Unsaturated alkene or aromatic
≡C–H	3300	Terminal Alkyne
O=C–H	2800 and 2700	Aldehyde, two weak peaks
O–H O–H (free)	3400 – 3000 ~3600	Alcohols and Phenols. If hydrogen bonding present peak will be broad 3000–2500 (*e.g.* carboxylic acids)
N–H	3450 – 3100	Amines: Primary - several peaks, Secondary - one peak, tertiary - no peaks

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Double Bonds

Bond	Wavenumber/cm^{-1}	Notes
C=O	1840 – 1800 & 1780 – 1740	Anhydrides
C=O	1815 – 1760	Acyl halides
C=O	1750 – 1715	Esters
C=O	1740 – 1680	Aldehydes
C=O	1725 – 1665	Ketones
C=O	1720 – 1670	Carboxylic acids
C=O	1690 – 1630	Amides
C=C	1675 – 1600	Often weak
C=N	1690 – 1630	Often difficult to assign
N=O	1560 – 1510 & 1370 – 1330	Nitro compounds

Triple Bonds

Bond	Wavenumber/cm^{-1}	Notes
C≡C	2260 – 2120	Alkynes, bands are weak
C≡N	2260 - 2220	Nitriles

Single Bonds (not to Hydrogen)

Bond	Wavenumber/cm^{-1}	Notes
C–C	Variable	No diagnostic value
C–O, C–N	1400 – 1000	Difficult to assign
C–Cl	800 – 700	Difficult to interpret
C–Br, C–I	Below 650	Often out of range of instrumentation

4.2.5 Applications of FTIR

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- Identification of functional groups in unknown substances
- Identification of compounds by matching spectrum of unknown compound with reference spectrum
- Identification of reaction components and kinetic studies of reactions
- Identification of molecular orientation in polymer films
- Identification of polymers, plastics and resins
- Analysis of formulations such as insecticides and copolymers
- Detection of molecular impurities present in amounts of 1% and in some cases as low as 0.01%

4.3 Inductively coupled plasma mass spectrometry (ICP - MS)

ICP-MS has been in existence for more than 20 years as an important technique used daily for elemental analysis in many laboratories. ICP-MS is preferred for its low detection limits for most elements, its high degree of selectivity and also its reasonably good precision and accuracy.

This instrument can measure most of the elements in the periodic table. The samples that ICP – MS analyze are mostly liquid samples. Gas samples can also be analyzed by direct introduction into the instrument.

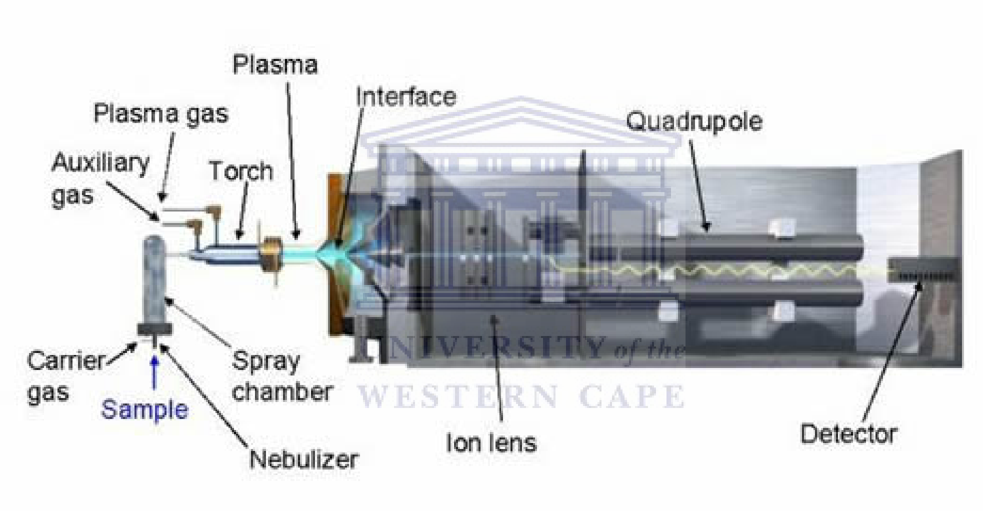

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Figure 4-10: ICP-MS diagram [Ess00]

4.3.1 Components of ICP-MS (figure 4-10)

- Sample introduction system – it allows the sample to get into the instrument. It consists of nebulizer and spray chamber.
- ICP torch – this torch serves as an atomizer and ionizer
- Interface – connects atmospheric pressure ICP ion source and the high vacuum mass spectrometer

- Vacuum system - this system supplies a high vacuum for ion optics, quadrupole and detectors.
- Lens - the lens focuses ions into a beam to be transmitted to the quadrupole
- Quadrupole - it acts as a mass filter, to sort ions by their mass-to – charge ratio (m/z)
- Detector – it counts individual ions passing through the quadrupole.
- Data system and system controller – this controls all parts of instrument control and data handling to get final concentration results [Hol07].

4.4 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

ICP-AES is also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES). This analytical technique is used for the detection of trace metals. ICP-AES uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

4.4.1 Components of ICP-AES (figure 4-10)

The ICP-AES consist of the following three main components:

- Sample introduction system – it allows the sample to get into the instrument and it consists of a peristaltic pump, a nebulizer and a spray chamber.

- ICP torch – it uses argon gas to create the plasma and it consists of three concentric quartz glass tubes that are water cooled and a coil of the radio frequency generator which surrounds part of the torch.

- Spectrometer – it analyzes a number of chemical elements and the two types that are used in ICP-AES analysis are the sequential (monochromator) and simultaneous (polychromator).

4.4.2 Differences between ICP-MS and ICP-AES

ICP-MS detection limits are in the 1 – 10 parts per trillion (ppt) range for solutions. ICP-MS has a better detection limit than ICP-AES which has detection limits in the range of 1 – 10 parts per billion (ppb) for most elements. ICP-MS analyzes all the elements whereas ICP-AES analyze only 5 – 30 elements.

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CHAPTER 5

RESULTS AND DISCUSSION

5.1 Scanning electron microscope results

SEM (Scanning Electron Microscope) analysis of the synthetic and natural soda ash samples was performed to examine the changes in the chemical composition. The Hitach X650 scanning electron microanalyzer was used for the examinations. Several different soda ash (natural and synthetic) samples were identified by SEM analysis with EDX (Energy Dispersive X-ray Analysis) spectra of each related samples.

Table 5-1: Elemental composition of the different prepared material

	Natural soda ash		Experiment 1		Experiment 2		Synthetic soda ash	
Element	Wt %	At %	Wt %	At %	Wt %	At %	Wt %	At %
C	10.52	15.99	14.28	21.37	14.88	21.24	7.70	12.01
O	37.30	42.57	38.07	42.75	46.92	50.28	35.79	41.92
Na	52.18	41.44	42.74	33.40	38.19	28.48	56.51	46.06
Cl			4.91	2.49				
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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The above table shows the different soda ash samples that were analyzed in EDX with their elemental composition and the percentage weight of the elements in the sample. The soda ash synthesized in experiment 1 was found to have chlorine impurities from NaCl. The spectra of soda ash samples are shown below with their images. The SEM images shows the different particle sizes and the most planar regions were used to do the spot analysis for EDS.

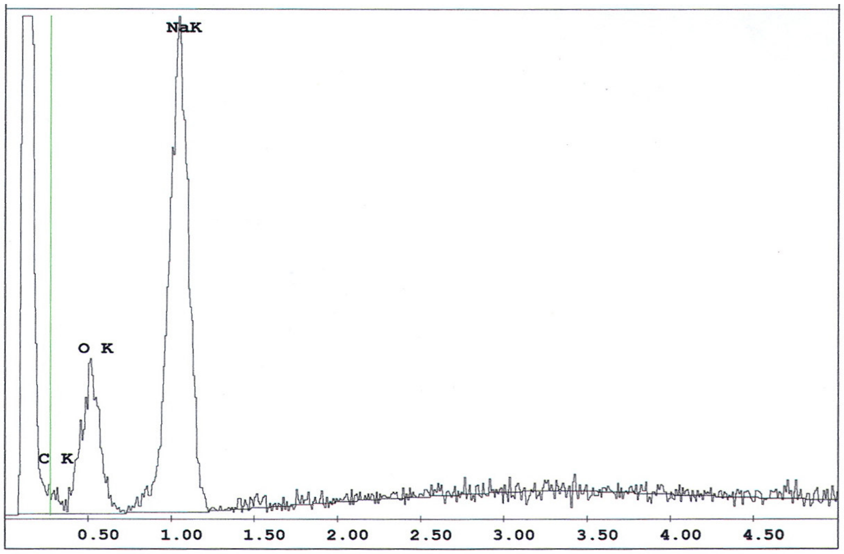

Figure 5-1: EDX spectrum of natural soda ash at the top of the large particle(Botash)

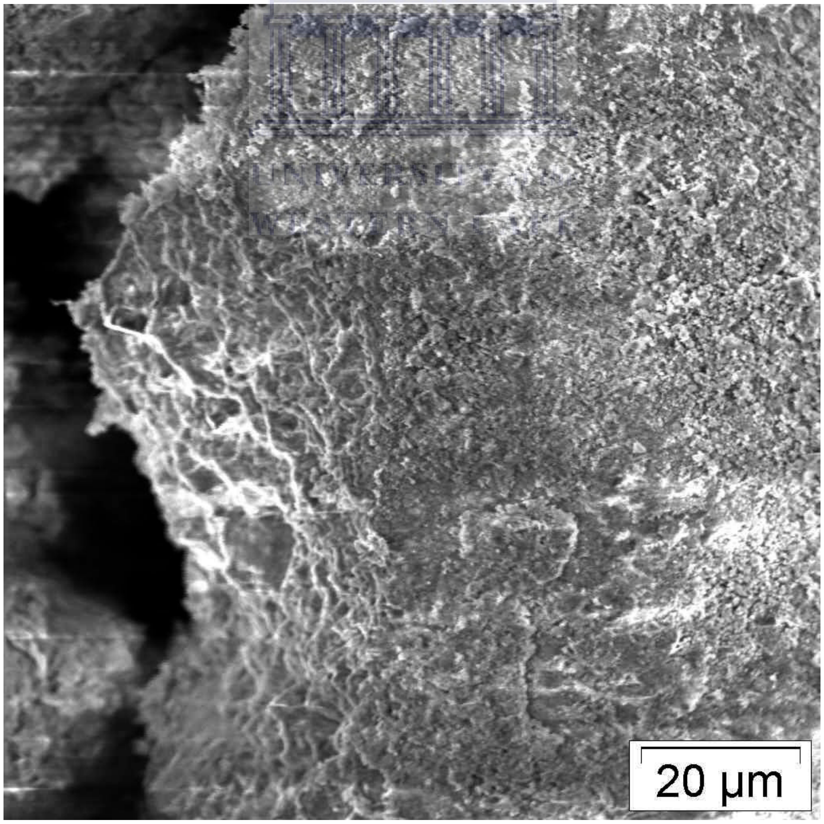

Figure 5-2: SEM image of natural soda ash large grain (magnification 1000x)

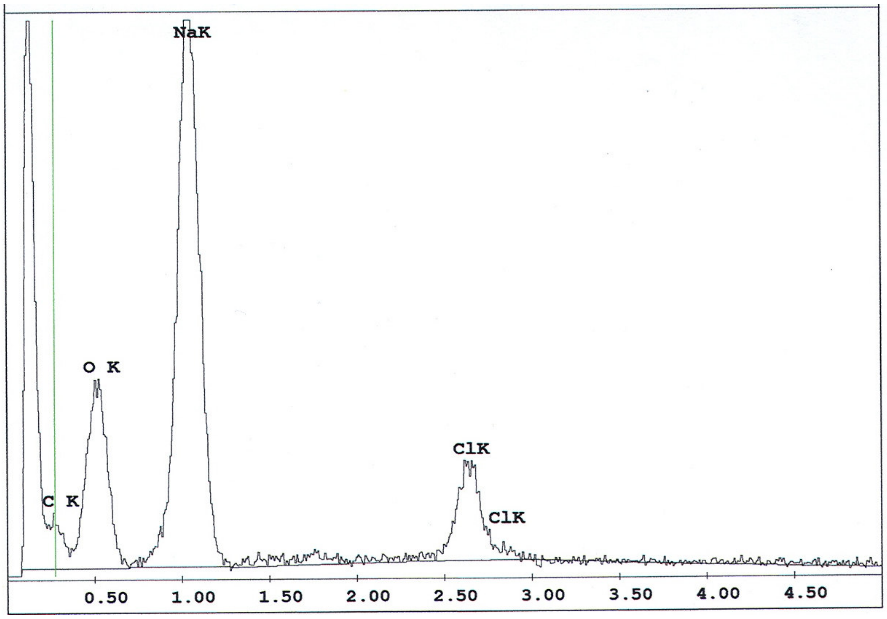

Figure 5-3: EDX spectrum of synthetic soda ash flat area of large grain (experiment 1)

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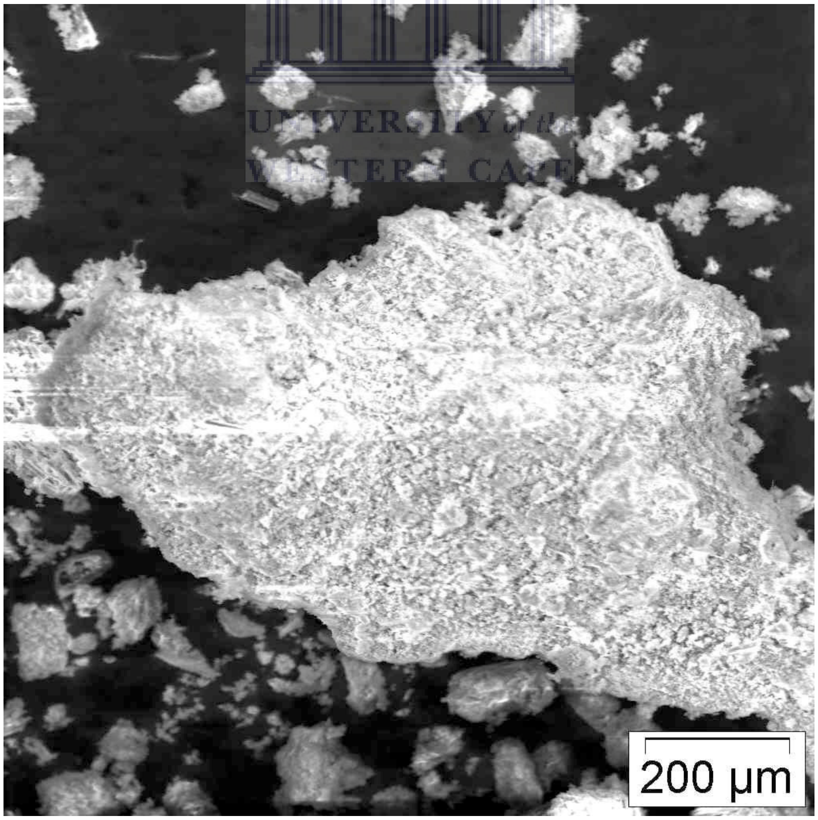

Figure 5-4: SEM image of synthetic soda ash large particle (magnification 95x)

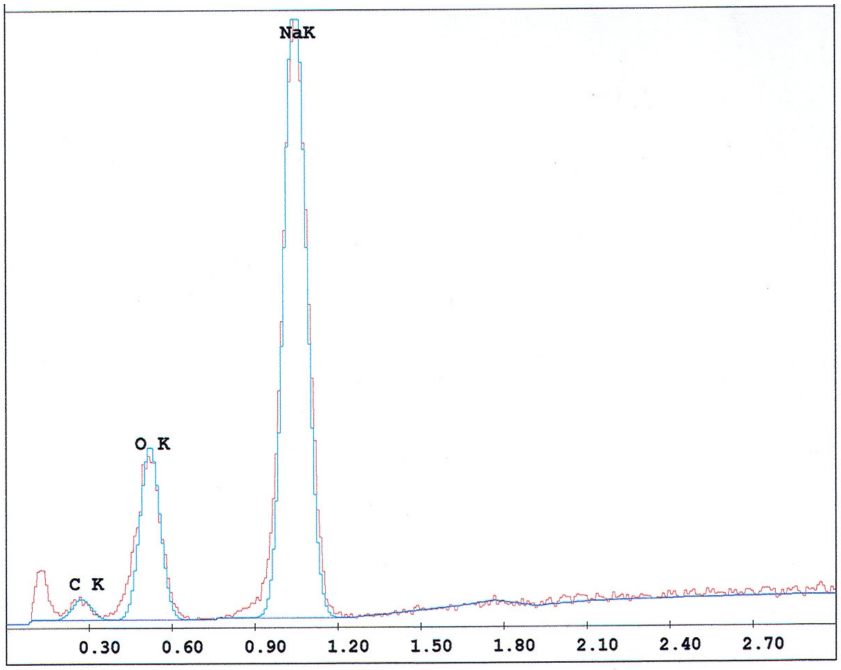

Figure 5-5: EDX spectrum of grain of synthetic soda ash (Solvay, Germany)

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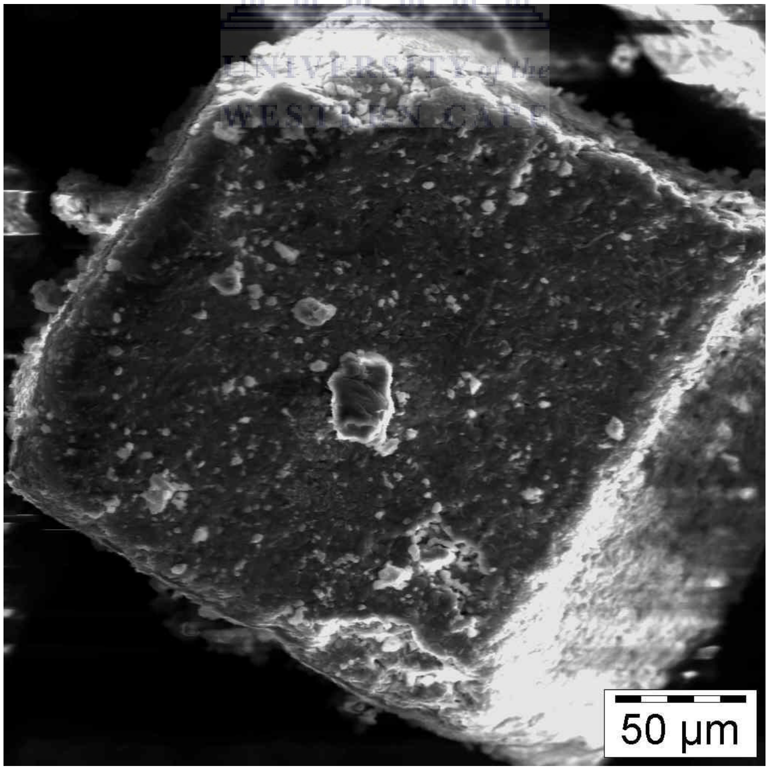

Figure 5-6: SEM image of a synthetic soda ash (Solvay, Germany)

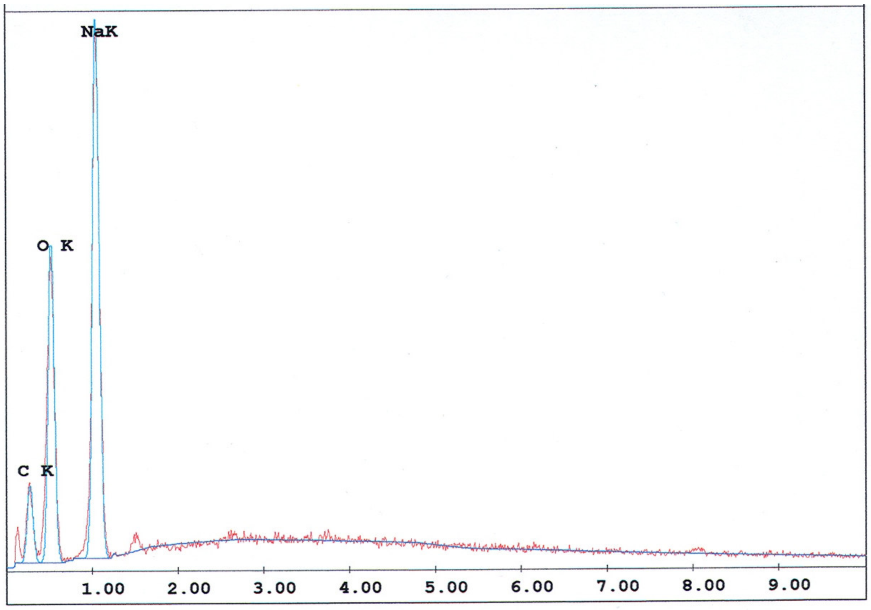

Figure 5-7: EDX spectrum of grain of synthetic soda ash (experiment 2)

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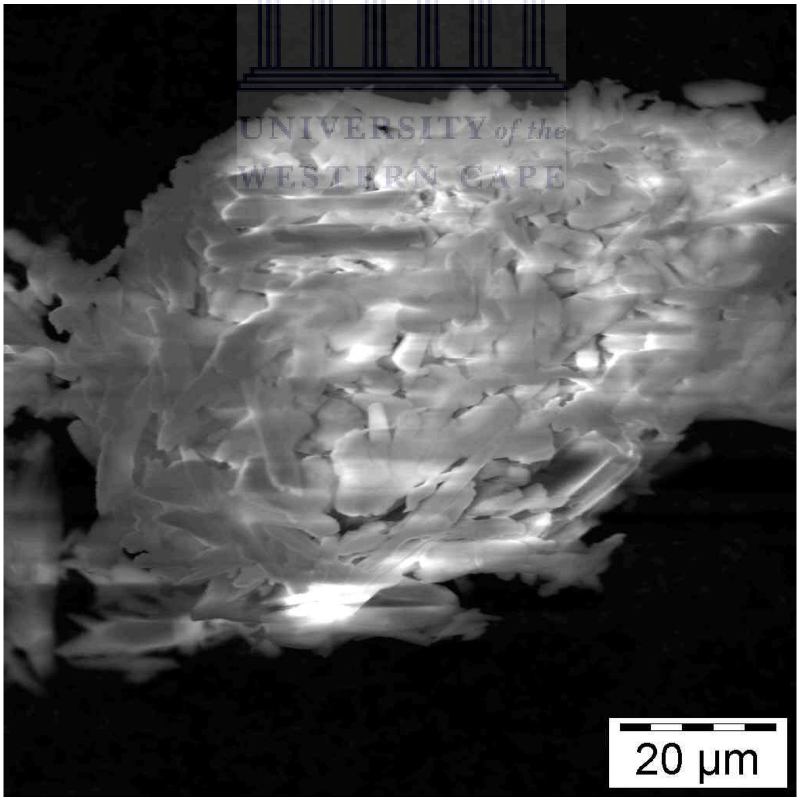

Figure 5-8: SEM image of a synthetic soda ash (experiment 2)

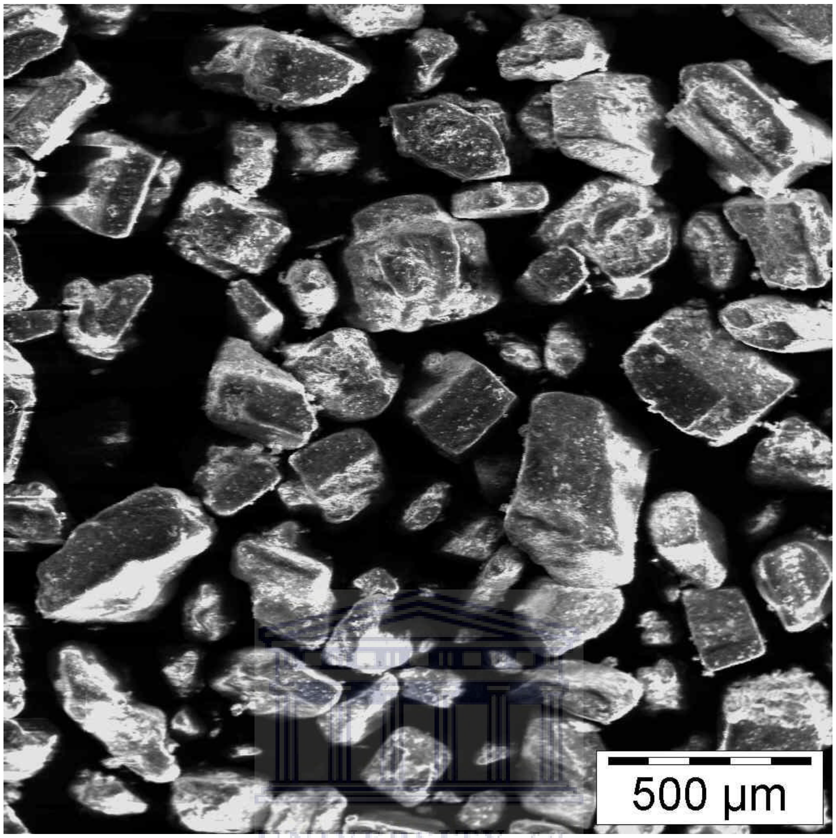

Figure 5-9: SEM image of synthetic soda ash area (Germany)

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5.2 The Fourier Transform Infrared Spectroscopy results

The spectra of natural and synthetic soda ash were analyzed by a FT-IR Spectrometer, PerkinElmer Precisely with Universal ATR Sampling Accessory. The spectra were recorded in the frequency range 650–4000cm $^{-1}$. The spectra were baseline corrected at zero level.

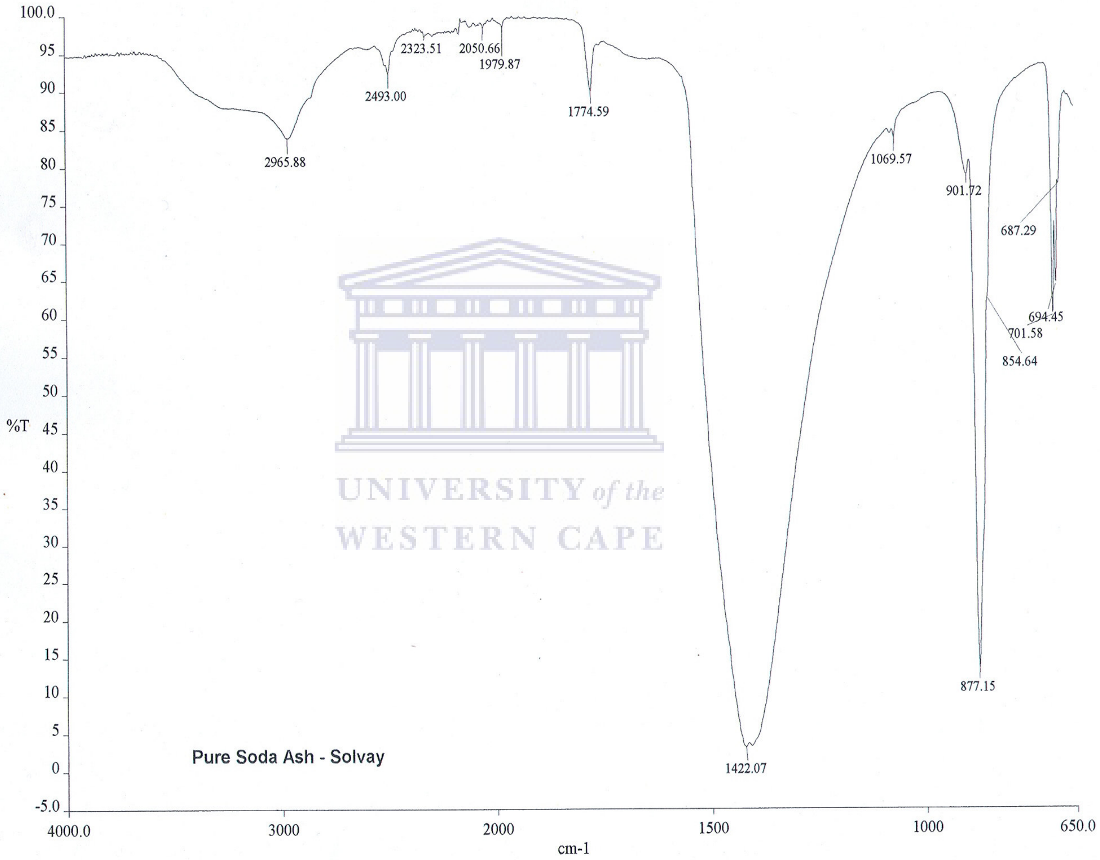

Figure 5-10: The Infrared spectrum of the synthetic soda ash from Solvay

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Table 5-2: Different soda ash samples with their absorbance from Infrared spectroscopy

SAMPLE	Wavenumber(cm^{-1})	Bond	% Transmittance	Absorbance
Pure soda ash (Solvay)	2965.88	O - H	85	0.071
	1422.07	C - O	2.5	1.602
	877.15	C-Cl	14	0.854
Natural soda ash	2852.14	O - H	97	0.013
	1421.00	C - O	4	1.398
	878.38	C-I	14	0.854
Anhydrous sodium carbonate	2965.90	O - H	74	0.131
	1427.26	C - O	3	1.523
	877.23	C-Cl	12	0.921
Synthetic soda ash (experimental)	2959.63	O - H	92.5	0.034
	1421.05	C - O	4	1.398
	878.46	C-Cl	17	0.770

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Only one spectrum of pure soda ash from Solvay is shown in figure 5.11 and the results for the other spectra (natural, anhydrous sodium carbonate and soda ash prepared in the laboratory) are shown in the table above with their wavenumber, stretching bonds, transmittance and absorbance. The Absorbance is calculated from Beer's law given by [Hol07]:

$$A = -\log T \qquad (3)$$

Where T is the Transmittance and A is the Absorbance

5.3 Inductively coupled plasma mass spectrometry (ICP - MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) results

The Agilent 7500ce ICP-MS and the Varian Liberty Radial ICP-AES located in Stellenbosch University were used for elemental analysis. The ICP-MS was used to determine the trace elements in the soda ash samples. The ICP-AES was also used for the detection of sodium (Na) which could not be detected by ICP-MS because the concentration was too high to be detected by ICP-MS. The results are shown in table 5-3 and table 5-4.

Table 5-3: ICP-MS results of different soda ash samples

ICP-MS semi-quantitative results (values in ppb)					
Element	**Solvay**	**Natural**	**EXPT 1**	**EXPT 2**	**Lab Na_2CO_3**
Be	4.06	6.79	4.8	4.2	ND
Mg	32784.63	ND	4,112	19,108	ND
Al	8.94	3144.17	6,666	28,031	10000
Si	62910.12	ND	48,382	67,310	ND
K	8278.04	164050.00	31,962	7,039	100000
Ca	65124.74	ND	83,355	370,938	ND
V	4.62	21.96	27.9	14.5	ND
Cr	107.73	55.02	925.4	3,682	ND
Mn	27.30	328.07	264.1	436.7	ND
Fe	337.60	2509.67	13,359	8,369	5000
Co	4.99	5.74	276.9	171.0	ND
Ni	98.75	49.63	3,044	502.3	ND
Cu	36.00	96.39	1,333	564.1	ND
Zn	25.45	192.15	37,904	3,701	ND
As	11.93	81.22	63.6	30.9	<5000
Se	206.04	219.85	163.2	176.9	ND
Mo	20.69	45.95	31.0	9.8	ND
Cd	0.40	-1.52*	347.8	7.2	<5000
Ba	16.95	1889.50	76,466	446.6	ND
Pb	3.80	0.23	22,481	1,177	<5000
B	ND	18075.00	ND	ND	ND
Sr	ND	5010.33	ND	ND	ND

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ND - not detected

*Negative results – below detection limit

Table 5-4: ICP-AES results of different soda ash samples

ICP - AES quantitative results (ppm)				
Element	**Solvay**	**Natural**	**EXPT 1**	**EXPT 2**
Na	626,656	642,688	590,424	424,372

5.4 Discussion of results

Natural soda ash samples were obtained from Botswana ash (Botash) which is a supplier of Nampak Wiegand Glas. Synthetic soda ash samples were sent from Solvay Chemicals in Germany which is a supplier of Wiegand glass. The other synthetic soda ash samples were synthesized in the chemistry department at UWC. Three separate experiments were done. The first experiment was of a Solvay process but did not replicate the industrial process.

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The second experiment which was performed was the simulation of the Solvay process in the laboratory, it contained two important processes that take place in the industrial plant which are the carbonation process and ammonization process. The ammonia gas was generated by heating a concentrated ammonia solution which was poured over the potassium hydroxide pellets, while the carbon dioxide was generated by heating dry ice.

The arrangement of apparatus described in the simulation of the Solvay process in the laboratory accurately reproduces the industrial process. The two Vigreux columns were used to simulate the ammonization and carbonation towers with gas flow against the current which is used in the industry. The Vigreux columns have the highest possible number of indentations which maximize the surface contact (see figure 3-2). The carbonate deposit started forming within an hour in a collecting flask.

There was a problem in maintaining the high flow of the ammonia gas and also utilizing high amount of sodium hydroxide in pellets and ammonium concentrated solution, because of the high solubility of ammonia gas in water. The ammonia gas was controlled so that it would not bubble in the solution because reflux can occur. There were no serious problems during the utilizing of solid dry ice as a source of carbon dioxide gas. The Solvay experiment was simulated in four hours and the results were excellent.

The actual yield was found to be lower than the theoretical yield. The percentage yield was found to be 0.28%. This is the good yield when working with gases.

The third experiment was performed like the second one but an ammonia gas cylinder and a carbon dioxide cylinder were used instead of generating ammonia and carbon dioxide gases because it was hard to control the flow of the gases. In the third experiment there was a problem with the control of the gases, the ammonia gas and carbon dioxide gas were not flowing at the same flow rate. It was difficult to control the gas ratios because of those variations in the gas flow. Another problem was because the gases from the cylinders were dry whereas in the second experiment the gases generated from ice and solution contained moisture which assisted the product (carbonate solution) to form well. It is proposed that the gas cylinders are good for the large scale (industry scale) where certain parameters will be taken into account, reaction stages monitored, expensive pure chemicals will be used and some of the chemicals will be recycled.

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The natural and synthetic soda ash samples were analyzed using the scanning electron microscope to get EDX spectra. The EDX analysis shows the elemental composition of soda ash samples. All the soda ash samples which were analyzed show that they contain a certain amount of carbon, oxygen and sodium. Soda ash that was produced in the first experiment shows that it contains some impurities such as chlorine.

The chlorine impurity is from Sodium chloride (the starting chemical); this is due to the fact that the product was not washed properly to remove all impurities during filtration.

This can be improved by washing the product with water and also with ethanol. All the soda ash samples contain almost the same amount of carbon, oxygen and sodium content (see table 5-1).
The EDX spectra show that the sample is sodium carbonate.

The soda ash samples were also analyzed using the Fourier Transform Infrared spectroscopy. The laboratory sodium carbonate was also analyzed in order to compare with the soda ash samples.
The Infrared spectra of soda ash samples have the same stretching bonds at similar frequencies (approximately 1427, 877 and 702 cm^{-1}) as the laboratory sodium carbonate. The stretching bonds in soda ash samples were found to be O-H at approximately 3000 cm-1, C-O bond at approximately 1427 cm-1 and the other stretching bond at approximately 877 cm^{-1} is difficult to interpret but it might be C-Cl bond due to the impurities in the sample.

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The strongest IR active vibration of the CO_3^{2-} ion is its asymmetrical inplane stretch at approximately 1427 cm^{-1} [Nic03]. The O-H stretching bonds at the frequency of approximately 3000 cm^{-1} may be due to the moisture in the sample. The less the transmittance the more the material is absorbed, the more the % transmittance the less the material is absorbed in infrared spectroscopy. CO_3^{2-} was absorbed more than the other elements in the sample.

The Infrared spectra were also compared with the typical sodium carbonate spectra (figure 5-11) to confirm the stretching bonds' frequencies.

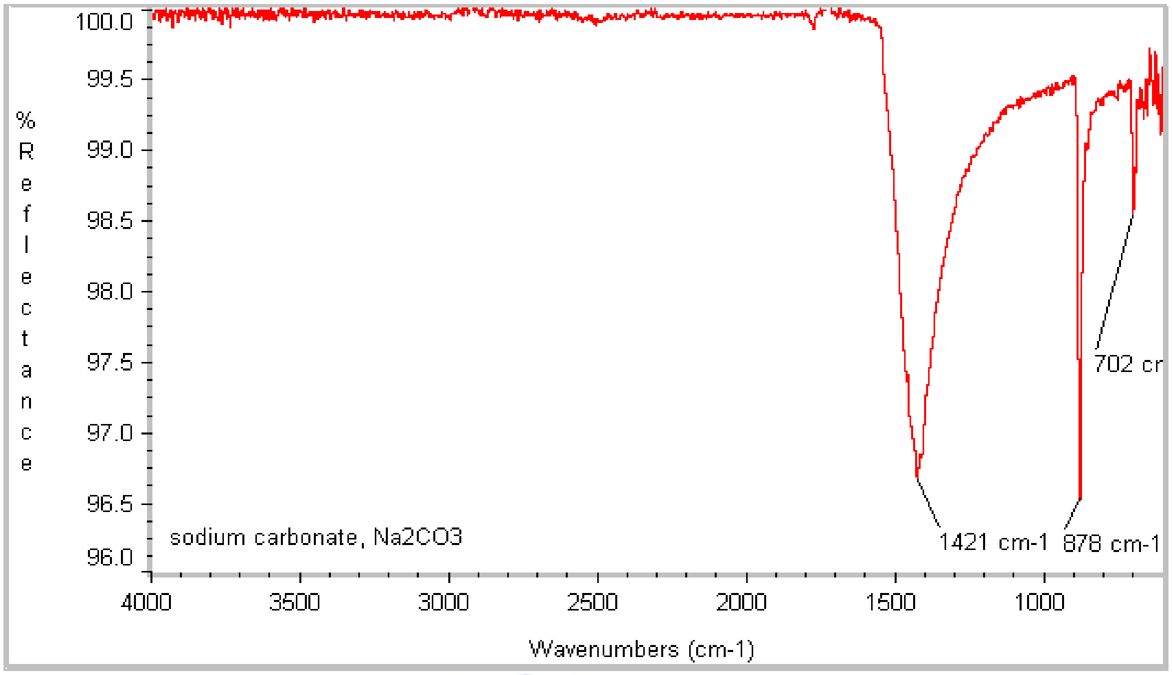

Figure 5-11: The infrared spectrum of sodium carbonate [low00]

The ICP-MS and ICP-AES were also used for the detection of trace elements in soda ash samples. The results were put in a table (table 5-3 and table 5-4).

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Mg, Si and Ca were not detected in natural soda ash but were detected in the Solvay and experimental soda ash samples. Natural soda ash was found to contain B and Sr which were not detected in the Solvay and experimental soda ash samples. The heavy metals were also detected in the soda ash samples. The heavy metals include Pb which was found to be too high in the experiment 1 soda ash sample. Al was found to be too high (>10000 ppb) in experiment 2 soda ash sample compared to the laboratory sodium carbonate. K was found to be high (>100000 ppb) than expected in natural soda ash and Fe was also found to be too high (>5000ppb) in experiment 1 and 2 soda ash samples.

We suggest that the reason for the high quantity of heavy metals in some soda ash samples is because of the apparatus that were used to manufacture the soda ash.

The heavy elements can also be from the raw materials that were used in the experiment for producing soda ash.

The Na could not be detected by ICP-MS, so ICP-AES was used to detect Na (table 5-4), which was found to be high in all the soda ash samples. This is because Na is one of the main elements found in sodium carbonate.

Table 5-5: Chemical specification of soda ash

Element	Typical analytical values	Specification (minimum)	Experiment 1	Experiment 2	Natural
Cl	0.05%	≤ 0.15%	ND	ND	ND
S	0.01%	≤ 0.02%	ND	ND	ND
Ca	70 ppm	≤ 150 ppm	83.4 ppm	371 ppm	ND
Mg	70 ppm	≤ 120 ppm	4 ppm	19 ppm	ND
Fe	3 ppm	≤ 20 ppm	13.4 ppm	8.4 ppm	2.5 ppm

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The ICP-MS results were also compared with the results in the specification sheet (Addendum II) provided by Solvay Chemicals company in Germany. The comparison of different soda ash results is shown in table 5-5. The concentration of Ca in the Solvay soda ash is less than 150 ppm, the results are comparable because the experimental results shows Ca concentration results that is below 150 ppm. These also apply to Mg, assuming it is less than 120 ppm; and also Fe which is less than 20 ppm. The trace elements in the experimental soda ash are less compared to the trace elements in the Solvay soda ash. The natural, Solvay and experimental soda ash have the trace elements with the concentration which is comparable. This shows that the soda ash produced in experiment 1 and 2 is acceptable in the industry.

5.5 STOICHIOMETRIC CALCULATIONS OF SODA ASH

Sodium bicarbonate is obtained by dissolving sodium chloride in distilled water, and that salt solution is mixed with ammonia solution or bubbled in ammonia gas. The mixture is then bubbled with carbon dioxide gas to form carbonate. The sodium carbonate is formed by heating sodium bicarbonate to remove water and carbon dioxide.

The % yield of sodium bicarbonate is calculated from the amount of Sodium chloride used in the experiment because Sodium chloride is the reactant that is consumed completely in the experiment and other reactants remain unused. Sodium chloride is therefore the limiting reagent with its amount determining the amount of product formed [Kot06]. Number of moles of sodium chloride is calculated from its molar mass and the mass used in experiment. The number of moles helps in determining number of moles of sodium bicarbonate, this is calculated from the stoichiometric ratio of the reactants and product in the balanced equation:

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Balanced equations: $NaCl + H_2O + NH_3 + CO_2 \rightarrow NaHCO_3 + NH_4Cl$

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

EXPERIMENT 1

Mass of NaCl = 20.0467 g

Molar mass of NaCl = 22.990 + 35.453 = 57.443 g/mol

Number of moles of NaCl = $\frac{mass}{molarmass} = \frac{20.0467g}{58.5g/mol}$ = 0.343 mol

From the balanced equations: 1 mol NaCl ≡ 1 mol $NaHCO_3$

Molar mass of $NaHCO_3$ = 22.990 + 1.008 + 12.011 + 15.999×3 = 84.006 g/mol

Therefore from the ratio: number of moles of $NaHCO_3$ = 0.343 ×1 = 0.343 mol

Mass ($NaHCO_3$) = number of moles × Molar mass
= 0.343 mol × 84.006 g/mol
= 28.814 g (theoretical yield)

Molar mass of Na_2CO_3 = 2×22.990 + 12.011 + 3×15.999 = 105.988 g/mol

Mass (Na_2CO_3) = number of moles × Molar mass
= 0.343 mol × 105.988 g/mol
= 36.354 g (theoretical yield)

Final mass of $NaHCO_3$ = 0.7012 g

Percentage yield ($NaHCO_3$) $= \frac{Actual yield}{theoretical yield} = \frac{0.7012 g}{28.814 g}$ × 100 = 2.43 %

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Final mass of Na_2CO_3 = 0.3954 g

Percentage yield (Na_2CO_3) $= \frac{Actual yield}{theoretical yield} = \frac{0.3954 g}{36.354 g}$ × 100 = 1.09 %

EXPERIMENT 2

Mass of NaCl = 50.00 g

Molar mass of NaCl = 22.990 + 35.453 = 57.443 g/mol

Number of moles of NaCl = $\frac{mass}{molar mass} = \frac{50.00 g}{58.5 g/mol}$ = 0.855 mol

From the balanced equations: 1 mol NaCl ≡ 1 mol $NaHCO_3$

Molar mass of $NaHCO_3$ = 22.990 + 1.008 + 12.011 + 15.999×3 = 84.006 g/mol

Therefore from the ratio number of moles of $NaHCO_3$ = 0.855 ×1 = 0.855 mol

Mass ($NaHCO_3$) = number of moles × Molar mass
= 0.855 × 84.006 g/mol
= 71.825 g (theoretical yield)

Molar mass of Na_2CO_3 = 2×22.990 + 12.011 + 3×15.999 = 105.988 g/mol

Mass (Na_2CO_3) = number of moles × Molar mass
= 0.855 mol × 105.988 g/mol
= 90.620 g (theoretical yield)

Final mass of $NaHCO_3$ = 0.2 g

Percentage yield ($NaHCO_3$) = $\frac{Actualyield}{theoreticalyield} = \frac{0.2g}{71.825g}$ × 100 = 0.28 %

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CHAPTER 6 CONCLUSIONS AND RECOMMENDATION

Based on the experimental results, we have demonstrated that it is possible to simulate the Solvay process in the laboratory using simple apparatus. The four hour experiment simulates the two main processes that take place on the industrial scale, the ammonization process and the carbonation process. The EDX, FTIR, ICP-MS and ICP-AES analyses confirmed the elemental composition of soda ash samples. From the experimental results of the small scale synthesis, the study will be taken to another scale which is a pilot plant.

There are certain parameters that need to be taken into account when setting up a pilot plant, the parameters includes reaction stages being monitored, expensive pure chemicals should be used and some of the chemicals will be recycled. The small scale synthesis in the laboratory demonstrated the process of synthetic manufacture of soda ash from readily available raw materials. Certain raw materials can be recovered and recycled (such as ammonia). However there are downstream impacts of the manufacture process, such as effluents and other waste materials. The requirements of South African environmental legislation and Environmental Impact Assessments (EIAs) will need to be taken into consideration when setting up a pilot plant. This will prepare for setting up a full manufacturing plant.

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After successfully setting up of a pilot plant, a manufacturing plant will be constructed. The other industries that use soda ash will also benefit. These industries include Consol, Sasol, Unilever, PG Group and Arcelor Mittal Steel and others. The country will also benefit because the establishment of a soda ash manufacturing plant will create jobs and the soda ash can also be supplied to other countries in Africa, leading to economic growth.

Although the pilot plant does not directly form part of the scope of this thesis, we have gathered much information about the manufacturing process which will be used in the decision to set-up the pilot plant.

A proposal has been submitted to the Industrial Development Corporation (IDC) for financial support to establish a pilot plant to model the synthesis of soda ash. The setting up of a pilot plant is the logical next step in preparation of an industry model. Nampak Wiegand Glass intends to take the project further with other industry partners and with the support of the IDC.

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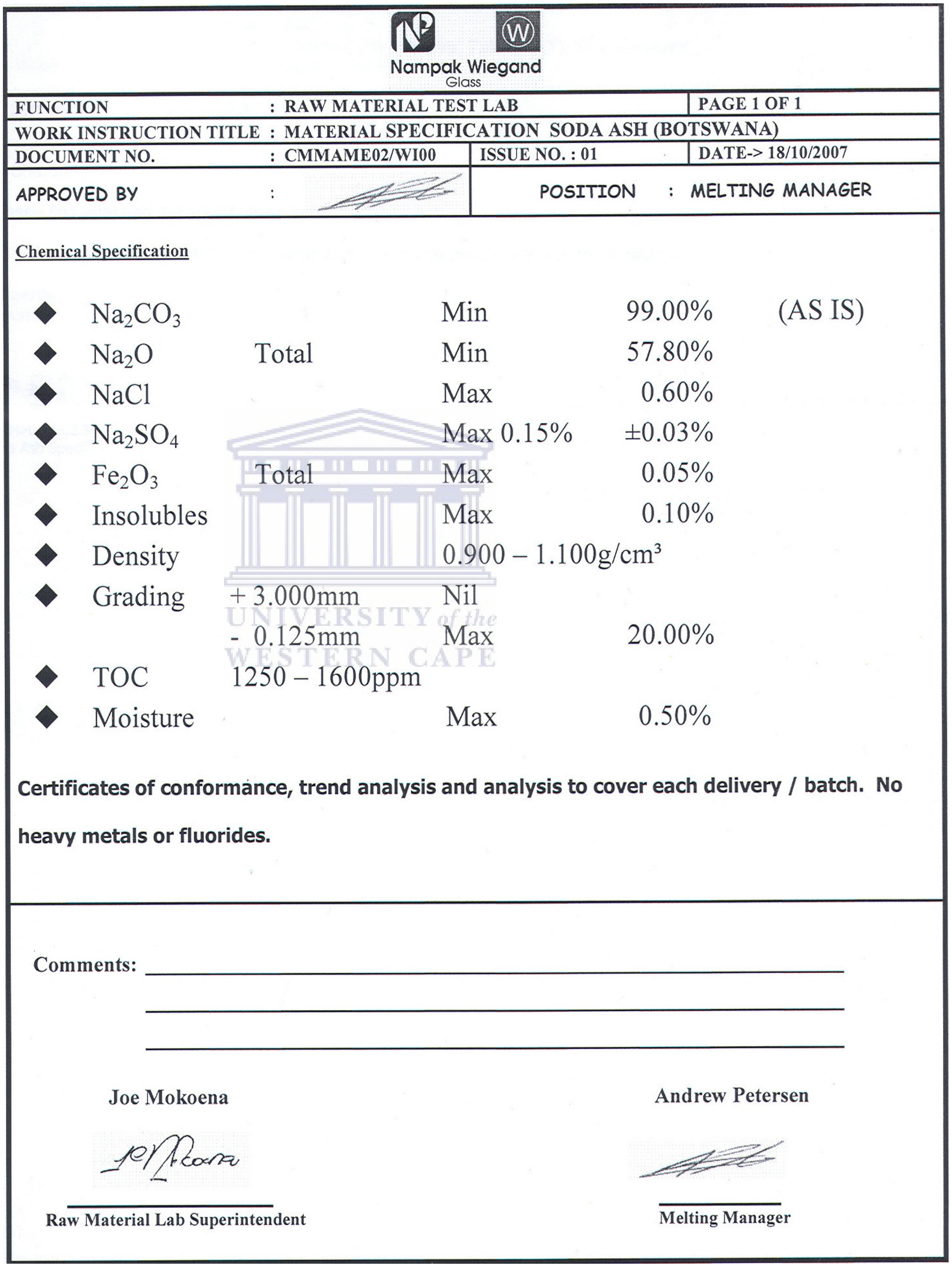
ADDENDUM I

The material specification of Botash soda ash samples



Nampak Wiegand
Glass

FUNCTION	: RAW MATERIAL TEST LAB		PAGE 1 OF 1
WORK INSTRUCTION TITLE	: MATERIAL SPECIFICATION SODA ASH (BOTSWANA)		
DOCUMENT NO.	: CMMAME02/WI00	ISSUE NO. : 01	DATE-> 18/10/2007
APPROVED BY	:	POSITION : MELTING MANAGER	

Chemical Specification

◆	Na_2CO_3		Min	99.00%	(AS IS)
◆	Na_2O	Total	Min	57.80%	
◆	NaCl		Max	0.60%	
◆	Na_2SO_4		Max 0.15%	±0.03%	
◆	Fe_2O_3	Total	Max	0.05%	
◆	Insolubles		Max	0.10%	
◆	Density		0.900 – 1.100g/cm³		
◆	Grading	+ 3.000mm	Nil		
		- 0.125mm	Max	20.00%	
◆	TOC	1250 – 1600ppm			
◆	Moisture		Max	0.50%	

Certificates of conformance, trend analysis and analysis to cover each delivery / batch. No heavy metals or fluorides.

Comments: ______________________________

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Joe Mokoena	Andrew Petersen
Raw Material Lab Superintendent	Melting Manager

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ADDENDUM II

Specification sheet of soda ash from Solvay (Germany)

SODASOLVAY®

SODASOLVAY **Schwere Soda**		***SODASOLVAY*** ***Dense Soda Ash***
Lieferwerk	**Bernburg**	*Factory*
Chemische Bezeichnung: Natriumcarbonat		*Chemical name:* *Sodium carbonate / Soda ash*
CAS Nr.	497-19-8	*CAS – N°*
EINECS Nr.	207-838-8	*EINECS – N°*
EG Nr.	011-005-00-2	*EC – N°*
EG Einstufung: Reizend		*EC Classification: Irritant*
Chemische Formel	Na_2CO_3	*Chemical formula*
Molare Masse	106	*Molecular weight*
Physikalische Eigenschaften		***Physical properties***
Aussehen: Weiβes Pulver		*Appearance:* *White powder*
Dichte in kg/dm³	2,533	*Density in kg/dm³*
Schmelzpunkt °C	851	*Melting point °C*
Löslichkeit in Wasser bei 20°C in g/1000g	214	*Solubility in water at 20°C in g/1000g*
pH (1% in Wasser)	11,26	*pH (1% in water)*

➢ **Anwendungen**	➢ ***Applications***
Glasindustrie – Rohstoff für die Schmelze	*Glass Industry – Raw material for melting*
Chemische Industrie – Herstellung von Na-Verbindungen	*Chemical Industry – Production of sodium derivatives*
Wasch – und Reinigungsmittel - Alkaliträger	*Detergents – Alkaline support*
Metallurgische Prozesse – z.B. Roheisenentschwefelung	*Metallurgical processes – e.g. Desulfurisation of pig iron*
Rauchgasreinigung – Entfernung saurer Schadstoffe	*Flue gas treatment – Removal of acidic components*
➢ **Transport / Verpackung**	➢ ***Transport / Packaging***
Lose: Waggon, LKW	*Bulk: Wagon, truck*
Verpackung: Kunststoffsäcke 25 kg PE-Säcke Schüttgutbehälter	*Packaging: Plastic bags* *25 kg PE-bags* *Bulk bags*

SOLVAY CHEMICALS INTERNATIONAL
Rue du Prince Albert, 44
B-1050 Brussels

Internet: http://www.solvay.com

Spezifikation *Specification*	SPE – C 05.04.20		
Date *Date*	10/2004	Ed./ Issue	05
Ersatz für *Replaces*	08/2003	Ed./ Issue	04

SOLVAY

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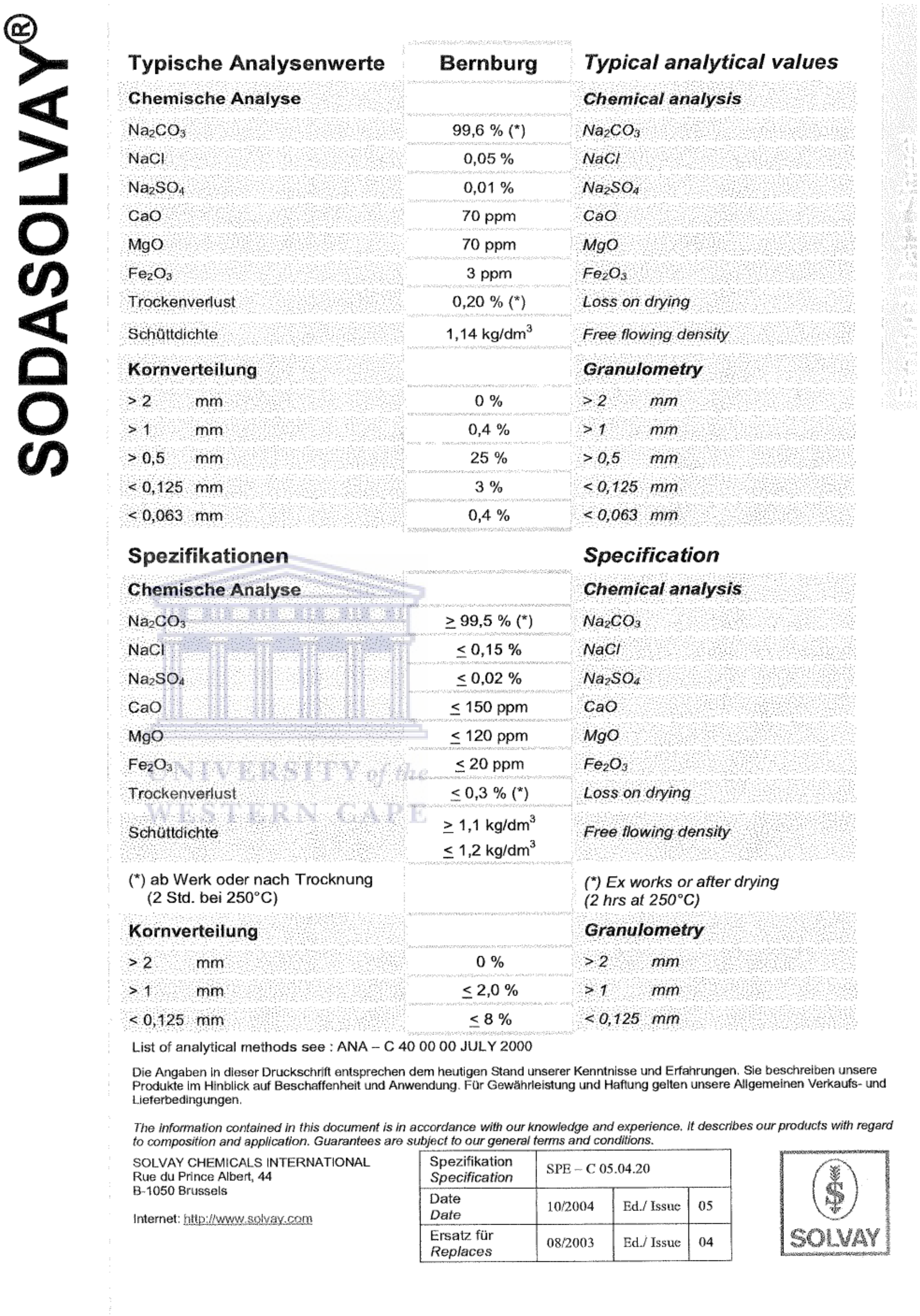

SODASOLVAY®

Typische Analysenwerte	Bernburg	Typical analytical values
Chemische Analyse		***Chemical analysis***
Na_2CO_3	99,6 % (*)	Na_2CO_3
NaCl	0,05 %	*NaCl*
Na_2SO_4	0,01 %	Na_2SO_4
CaO	70 ppm	*CaO*
MgO	70 ppm	*MgO*
Fe_2O_3	3 ppm	Fe_2O_3
Trockenverlust	0,20 % (*)	*Loss on drying*
Schüttdichte	1,14 kg/dm^3	*Free flowing density*
Kornverteilung		***Granulometry***
> 2 mm	0 %	*> 2 mm*
> 1 mm	0,4 %	*> 1 mm*
> 0,5 mm	25 %	*> 0,5 mm*
< 0,125 mm	3 %	*< 0,125 mm*
< 0,063 mm	0,4 %	*< 0,063 mm*

Spezifikationen		Specification
Chemische Analyse		***Chemical analysis***
Na_2CO_3	≥ 99,5 % (*)	Na_2CO_3
NaCl	≤ 0,15 %	*NaCl*
Na_2SO_4	≤ 0,02 %	Na_2SO_4
CaO	≤ 150 ppm	*CaO*
MgO	≤ 120 ppm	*MgO*
Fe_2O_3	≤ 20 ppm	Fe_2O_3
Trockenverlust	≤ 0,3 % (*)	*Loss on drying*
Schüttdichte	≥ 1,1 kg/dm^3 ≤ 1,2 kg/dm^3	*Free flowing density*
(*) ab Werk oder nach Trocknung (2 Std. bei 250°C)		*(*) Ex works or after drying (2 hrs at 250°C)*
Kornverteilung		***Granulometry***
> 2 mm	0 %	*> 2 mm*
> 1 mm	≤ 2,0 %	*> 1 mm*
< 0,125 mm	≤ 8 %	*< 0,125 mm*

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List of analytical methods see : ANA – C 40 00 00 JULY 2000

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SOLVAY