DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ALTERNATIVE DRYING METHODS FOR THE PRODUCTION OF Na_2CO_3 AND $NaHCO_3$ WITH MICROWAVE ENERGY IN THE SODA INDUSTRY

by
Barış ÖZALP

August, 2005
İZMİR

ALTERNATIVE DRYING METHODS FOR THE PRODUCTION OF Na_2CO_3 AND $NaHCO_3$ WITH MICROWAVE ENERGY IN THE SODA INDUSTRY

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of Science in
Mining Engineering, Mineral Processing Program

by

Barış ÖZALP

August, 2005
İZMİR

This thesis is dedicated to:
Prof. Dr. Hasan MORDOĞAN

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"ALTERNATIVE DRYING METHODS FOR THE PRODUCTION OF Na_2CO_3 AND $NaHCO_3$ WITH MICROWAVE ENERGY IN THE SODA INDUSTRY"** completed by **Barış ÖZALP** under supervision of **Assist. Prof. Abdullah SEYRANKAYA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ALTERNATIVE DRYING METHODS FOR THE PRODUCTION OF Na_2CO_3 AND $NaHCO_3$ WITH MICROWAVE ENERGY IN THE SODA INDUSTRY

ABSTRACT

In this study, dehydration of sodium carbonate monohydrate ($Na_2CO_3.H_2O$) (SCM) in microwave (MW) field with silicon carbide (SiC) as an indirect heating medium and drying of sodium bicarbonate ($NaHCO_3$) with microwave energy were investigated.

SCM samples containing up to 3% free moisture were placed in the microwave oven. The heating experiments showed that SCM is a poor microwave energy absorber for up to 6 minutes of irradiation at an 800 W of microwave power. The heat for SCM calcination is provided by SiC which absorbs microwave. The monohydrate is then converted to anhydrous sodium carbonate on the SiC plate by calcining, i.e. by removing the crystal water through heating of the monohydrate temperatures of over 120ºC. The calcination results in a solid phase recrystallization of the monohydrate into anhydrate.

Sodium bicarbonate samples containing 7-15% moisture were placed in the microwave oven to dry off the free moisture below 60 ºC selectively, without any loss of structural water.

In industrial applications, SCM and sodium bicarbonate are dried in steam tube rotary or fluidized bed dryers. However, drying in rotary dryers is slow due to limitations in mixing and low gas temperatures. Higher temperatures are not permitted due to possible dehydration of the product. Fluidized bed dryers cause dusting and powder formation as a result of attrition caused by collision of particles in the bed. In this investigation, microwave energy has been considered as an alternative approach to solve the problems with current drying processes. With this alternative drying process, sodium bicarbonate samples were dried successfully with no decomposition and disintegration of crystalline

molecules and dehydration of SCM in terms of indirect heating can be accelerated by increasing the microwave field power.

Keywords: sodium bicarbonate; sodium carbonate monohydrate; drying; microwaves

SODA ENDÜSTRİSİNDE Na_2CO_3 VE $NaHCO_3$ ÜRETİMİNDE MİKRODALGA ENERJİSİ İLE ALTERNATİF KURUTMA METODLARI

ÖZ

Bu çalışmada, sodyum karbonat monohidratın ($Na_2CO_3.H_2O$) mikrodalga alanında SiC ile indirekt olarak susuzlandırılması ve sodyum bikarbonatın mikrodalga enerjisi ile kurutulması araştırılmıştır.

Mikrodalga fırınına konulan sodyum karbonat monohidrat örnekleri maksimum %3 serbest nem içermektedirler. 800 W gücünde 6 dakika süreyle yapılan ısıtma deneyleri göstermiştir ki sodyum karbonat monohidrat zayıf bir mikrodalga absorblayıcısıdır. Sodyum karbonat monohidratın kalsinasyonu için gerekli olan ısı, mikrodalgaları absorblayan SiC tarafından sağlanmaktadır. Daha sonra monohidrat 120ºC'nin üzerinde kristal suyunu atmasıyla birlikte SiC plakanın üzerinde kalsine olarak susuz sodyum karbonat haline dönüşmüştür. Kalsinasyon işlemi, monohidratın anhidrata katı fazda kristalizasyonu şeklinde olmaktadır.

%7–15 nem içeren sodyum bikarbonat örnekleri mikrodalga fırınına konularak 60°C'nin altında kristal suyuna zarar vermeden, serbest nemi selektif olarak kurutulmuştur.

Endüstriyel uygulamalarda, sodyum karbonat monohidrat ve sodyum bikarbonat buhar tüplü döner kurutuculardа ve akışkan yataklı kurutuculardа kurutulmaktadır. Bununla birlikte, döner kurutuculardaki kurutma işlemi düşük gaz sıcaklıkları ve karıştırmadaki sınırlamalar nedeniyle yavaştır. Akışkan yataklı kuruculardа ise yataktaki partiküllerin birbirleriyle çarpışmalarından dolayı oluşan aşınmadan dolayı pudra formasyon oluşumlarına ve tozlanmalara yol açılmaktadır. Bu çalışmada şu andaki kurutma proseslerindeki bu gibi problemlerini çözmek için mikrodalga enerjisi bir alternatif düşünülmüştür. Bu mikrodalga ile kurutma prosesinde, sodyum bikarbonat

kristalleri hiç kristal yapılarına zarar verilmeden başarılı bir şekilde mikrodalga enerjisi ile kurutulmuştur ve sodyum karbonat monohidrat susuzlandırılması, mikrodalga enerjisin altında indirekt ısıtma ile sağlanmıştır.

Anahtar sözcükler: sodyum bikarbonat; sodyum karbonat monohidrat; kurutma; mikrodalga

CONTENTS

Page

THESIS EXAMINATION RESULT FORM.....iii
ACKNOWLEDGEMENTS.....iv
ABSTRACT..... vi
ÖZ..... viii

CHAPTER ONE – INTRODUCTION.....1

CHAPTER TWO – NATURAL SODA ASH.....3
2.1 Natural Sodium Carbonate Minerals..... 3
2.2 The Origin of Soda Ash Deposits..... 4
2.3 Deposits..... 5
2.3.1 Deposits in U.S.A..... 5
2.3.2 Deposits in Turkey.....8
2.3.3 Deposits in China.....11
2.3.4 Other Deposits in the World..... 12
2.4 Soda Ash Production Methods.....12
2.4.1 Conventional Operations..... 13
2.4.1.1 Monohydrate Process.....13
2.4.1.2 Sesquicarbonate Process.....15
2.4.2 Solution Mining..... 16
2.4.3 Processing of Solution Mined Product..... 17
2.5 Sodium Bicarbonate Production Method.....23
2.6 Soda Ash Utilization.....24
2.6.1 Glass Production.....25
2.6.2 Flue Gas Desulfurization..... 26
2.6.3 Soaps & Detergents.....26
2.6.4 Chemicals.....27

Page

2.6.5 Water Treatment..... 27
2.6.6 Pulp and Paper..... 28
2.6.7 Metallurgy.....28
2.7 Production, Consumption Statistics.....29
2.7.1 Production.....30
2.7.2 Consumption.....31

CHAPTER THREE – CRYSTALLIZATION.....33
3.1 Introduction.....33
3.2 Crystal Quality – Performance and Composition..... 34
3.2.1 Product Performance.....34
3.2.2 Product Composition..... 35
3.2.3 Product-Related Design Specifications.....36
3.3 Crystallization Mechanisms.....36
3.3.1 Nucleation.....38
3.3.2 Crystal Growth and Dissolution.....39
3.3.3 Agglomeration..... 41
3.3.4 Breakage..... 42
3.3.5 Segregation..... 43
3.4 Design Procedure of Crystallization Processes and Products.....43
3.4.1 A Design Hierarchy..... 44
3.4.1.1 Initial Design Specifications.....49
3.4.1.2 Design of the Crystalline Product.....51
3.4.1.3 Physical/Chemical Design of the Crystallisation Task.....52
3.4.1.3.1 Solvent, Additives and Impurities.....53
3.4.1.3.2 Crystallization Method.....55
3.4.1.3.3 Other Design Variables.....57
3.4.1.4 Flowsheet Design of the Crystallization Process.....57
3.4.1.4.1 Operation Mode..... 59

Page

3.4.1.4.2 Staged Operation.....60
3.4.1.5 Design of a Crystalliser Stage.....61
3.4.1.5.1 Crystalliser Type, Circulation Device, Heat Exchanger and Classification.....62
3.4.1.5.2 Dimensioning and operating conditions..... 66

CHAPTER FOUR – MICROWAVE DRYING.....68
4.1 Introduction.....68
4.2 Fundamentals of Microwave Heating..... 69
4.2.1 Electromagnetic Waves..... 69
4.2.2 Heating Mechanism..... 71
4.2.3 Ionic Conduction.....72
4.2.4 Dipolar Rotation.....73
4.2.5 Interaction of Electromagnetic Fields with Materials.....75
4.3 Basic heating system.....82
4.4 Drying Applications of Microwave..... 84
4.5 Temperature measurement.....85
4.6 Economics of Microwave Drying System..... 86
4.6.1 Capital Equipment Costs.....87
4.6.2 Tube Replacement Costs.....89
4.6.3 Energy Costs..... 89
4.6.4 Other Costs..... 89

CHAPTER FIVE – MODEL DEVELOPMENT.....91
5.1 Introduction.....91
5.1.1 Drying Applications in the Soda Industry..... 91
5.1.2 Problems of Current Drying Applications.....92
5.2 Approach.....94
5.3 Design of Experiments.....95

Page

5.3.1 A New Process Alternative: Drying Of Sodium Bicarbonate with Microwave..... 95
5.3.2 A New Process Alternative: Drying Of Sodium Carbonate Monohydrate with Microwave..... 96
5.4 The Drawbacks of Microwave Drying Process..... 98

CHAPTER SIX– EXPERIMENTAL..... 99
6.1 Sodium Carbonate Monohydrate Production from Trona Ore..... 99
6.1.1 Composition of Tested Trona Ore Sample..... 99
6.1.2 Dissolving the Trona Ore in Aqueous Solution..... 100
6.1.3 Wet Calcination and Causticization..... 102
6.1.4 Evaporative Crystallization..... 105
6.2 Dehydration of Sodium Carbonate Monohydrate with Indirect Microwave Heating..... 107
6.2.1 The Indirect Microwave Heating System..... 108
6.2.2 Solid phase analysis..... 109
6.2.3 Temperature Measurement..... 109
6.2.4 Absorption Characteristics of SiC and SCM..... 110
6.2.5 Penetration Depth..... 113
6.2.6 Results and Discussion..... 114
6.3 Alternative Drying of Sodium Bicarbonate ($NaHCO_3$) With Microwave Energy..... 119
6.3.1 Drying Equipment and Procedure..... 119
6.3.2 Determination of Moisture and the Weights of Sodium Bicarbonate and Sodium Carbonate..... 121
6.3.3 Results and Discussion..... 121
6.4 Economics of These Alternative Microwave Drying Systems..... 131

CHAPTER SEVEN – CONCLUSION..... 133

REFERENCES..... 135

CHAPTER ONE
INTRODUCTION

Sodium bicarbonate, $NaHCO_3$ or "baking soda", and sodium carbonate, soda ash, are widely used in glass industry, in chemical and pharmaceutical industries, in animal feeds, in human food and other industrial and manufactured products (Garrett, 1992; Haynes, 1997). Sodium bicarbonate and sodium carbonate are refined in three different ways: a) from the mineral nahcolite (referred to as natural sodium bicarbonate), b) from the mineral trona or naturally occurring sodium-carbonate-bearing brines (both referred to as natural soda ash), c) manufactured with Solvay process which requires common salt and limestone (referred to as synthetic sodium carbonate) (Kostick, 2002).

In industrial applications, sodium bicarbonate is dried in steam-tube rotary or fluidized bed dryers by heating with air at about 50 ºC. In addition to this, the drying and dehydration of the monohydrate is carried out more frequently in steam-tube rotary dryers where the crystals are dehydrated into anhydrous soda ash at 150 °C to 200 ºC; however, fluidized bed dryers are also used (Garrett, 1992; Chen et al., 1999). However, all such drying methods have common limitations, that is, the heat transfer from the surface to inside of the particle is principally by conduction and the process is slow. The maximum temperature of the heated surface to avoid product degradation is a limiting factor in the use of conductive heat transfer for drying. In addition, in rotary dryers; mixing is not good and gas temperatures are low. In fluidized bed dryers; the possibility of powder formation and dusting of the product is quite high as a result of attrition caused by collision of particles (Jones, 1992; Kocakusak et al., 1998). To overcome these problems, microwave energy use has been considered as an alternative process for drying the sodium bicarbonate and sodium carbonate monohydrate.

The mechanism for drying with microwave is quite different from that for ordinary drying. In contrast to the conventional dryers, microwave drying eliminates the need to use the surrounding air as a mode of heat transfer to the contained water in the material.

With internal heat generation, in microwave systems, mass transfer is primarily due to total pressure gradient established because of the rapid vapor generation within the material. The quick energy absorption by water molecules causes rapid evaporation of water (results in higher drying rates of powder), creating an outward flux of rapidly escaping vapor. Most of the liquid is vaporized before leaving the sample. Ideally, the heat would be transferred only to the water molecules (Maskan, 2000; Schiffmann, 1995).

In recent years, microwave energy has found increasing application to the drying of various kinds of materials and products such as agricultural, chemical, mineral processing and food product, textile, paper, lumber and many more (Jones, et al., 2002; Khraisheh et al., 1997; Kingman, et al., 2000;. Kingman, et al., 2004; Cha and Carlisle, 2000). The unique heating mechanisms of microwaves permit dramatic energy savings in many instances, as well as providing competitive benefits (McCrone, 1995; Kingman and Rowson, 1998; Haque, 1999; Maskan, 2000; Sanio and Schmidt, 1988).

Microwave drying offers many advantages over conventional heating such as non-contact heating, energy transfer (not heat transfer), rapid heating, material selective heating, volumetric heating, quick start-up and stopping, higher level of safety and automation. In addition, heating is quite fast, so dryer sizes and necessary plant areas are rather small (Schiffmann, 1995; Haque, 1999; Kocakusak et al., 1998).

In this paper, the results of the experimental work to dry off the free moisture from the sodium bicarbonate powder and the from the sodium carbonate monohydrate powder using microwave energy will be presented.

CHAPTER TWO
NATURAL SODA ASH

2.1 Natural Sodium Carbonate Minerals

Trona is a naturally occurring mineral that is chemically known as sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). Trona gets its name from a discarded Arabic word for native salt, "tron", which is derived from the word "natrun". Trona is the type mineral so-to-speak for several sodium carbonates that form in non-marine evaporite deposits. Other naturally occurring sodium carbonates are given in Table 2.1**.** Trona is probably the most common and well known of these minerals (Garrett, 1992).

Table 2.1 Naturally occurring sodium carbonate minerals (Garrett, 1992)

MINERAL	**Composition**	**Na_2CO_3%**
Thermonatrite (Monohydrate)	$Na_2CO_3.H_2O$	85.5
Wegscheiderite	$Na_2CO_3.NaHCO_3$	74.0
Trona (Sesquicarbonate)	$Na_2CO_3.NaHCO_3.2H_2O$	70.4
Nahcolite (Sodium bicarbonate)	$NaHCO_3$	63.1
Bradleyite	$Na_2PO_4.MgCO_3$	47.1
Pirssonite	$Na_2CO_3.CaCO_3.2H_2O$	43.8
Northupite	$Na_2CO_3.NaCl.MgCO_3$	40.6
Tychite	$2MgCO_3.2NaCO_3.Na_2SO_4$	42.6
Natron	$Na_2CO_3.10H_2O$	37.1
Dawsonite	$NaAl(CO_3)(OH)_2$	35.8
Gaylussite	$Na_2CO_3.CaCO_3.5H_2O$	35.8
Shortite	$Na_2CO_3.2CaCO_3$	34.6
Burkeite	$Na_2CO_3.2Na_2SO_4$	27.2
Hanksite	$2Na_2CO_3.9Na_2SO_4.KCl$	13.6

Table 2.2 Physical Characteristics of Trona (Garrett, 1992)

- **Color** is gray, colorless, white, pale brown or yellowish.
- **Luster** is vitreous.
- **Transparency:** Crystals are transparent to translucent.
- **Crystal System** is monoclinic; 2/m.
- **Crystal Habits** include prismatic to blocky crystals, but usually massive, fibrous or columnar.
- **Cleavage** is perfect in one direction and poor in two others.
- **Fracture** is subconchoidal to uneven.
- **Hardness** is 2.5 - 3.
- **Specific Gravity** is 2.1 (well below average)
- **Streak** is white.
- **Other Characteristics:** Has an alkaline taste.
- **Associated Minerals** include hanksite, gaylussite, halite, pirssonite, northupite, nahcolite, borax and calcite.

2.2. The Origin of Soda Ash Deposits

In general, fossil soda deposits and recent soda playa-lakes were formed or are presently forming by evaporation within intercontinental basins, in arid or semi-arid areas, fed partly by surface streams and partly by thermal springs, and surrounded by abundant Na-rich volcanic and magmatic rock. Soda deposits alternate generally with shale and bituminous shale beds. Trona beds are deposited in playa-lake environment in basins, which are restricted by the mud flats and fed by Na-rich solutions and springs. Bituminous shales, which are accumulated during the expansion periods of playa-lake, alternate with trona beds. Soda extraction from deeper lakes, such as Van Lake, is not presently economical, as soda concentration has not yet reached to sufficient level (Helvaci, 2001).

2.3 Deposits

Trona occurs as a natural ore at locations all over the world (Table 2.3). This abundant availability makes trona ore an attractive source of material for soda production. There are at least 62 identified natural sodium carbonate deposits in the world, some of which have been quantified.

Table 2.3 Reserves, and Reserve Base of Trona (Data in thousand metric tons) (Kostick, 2005)

	Reserves	**Reserve base**
Natural:		
United States	23,000,000	39,000,000
Botswana	400,000	NA
Kenya	7,000	NA
Mexico	200,000	450,000
Turkey	200,000	240,000
Uganda	20,000	NA
Other countries	260,000	220,000
World total, natural (rounded)	24,000,000	40,000,000

NA is not available

2.3.1 Deposits in U.S.A.

Marly lacustrine rocks of the Eocene Green River Formation, which occupy parts of several basins in Wyoming, Colorado, and Utah, contain world-class resources of oil shale and sodium carbonate minerals. The formation contains the world's largest known resource of natural sodium carbonate as bedded trona ($Na_2CO_3.NaHCO_3.2H_2O$) in southwest Wyoming as well as the second largest known resource of sodium carbonate as bedded and nodular nahcolite ($NaHCO_3$) in northwest Colorado.

The lacustrine Green River Formation of Eocene age, which occupies several sedimentary basins in Wyoming, Colorado, and Utah (Fig. 2.1), has long been known for its oil shale resources but less so for its enormous deposits of sodium carbonate minerals. Large deposits of sodium carbonate salts occur in the three-state area. These deposits include relatively pure beds of trona, nahcolite, and eitelite; nonbedded

aggregates, nodules, and crystals of nahcolite; microscopic crystals of dawsonite in oil shale; veinlets and crystals of shortite; and brines of which some are highly enriched in organic acids. Five sodium carbonate occurrences including two in Utah, one in Colorado, and two in Wyoming, are being mined or have potential economic value.

The occurrences include deposits of bedded trona in the Green River Basin in southwest Wyoming, deposits of nahcolite and dawsonite commingled with high-grade oil shale in the Piceance Creek Basin in northwest Colorado, and bedded sodium carbonate salts near the town of Duchesne in the Uinta Basin, northeast Utah. The formation also contains two sodium carbonate brines that may have potential economic value. One of these brines occurs in a confined aquifer, the Birds-nest zone, in the eastern Uinta Basin about 30 miles south and east of Vernal, Utah. The other sodium carbonate brine-noteworthy for its unusually high content of soluble organic matter-underlies several townships at shallow depths near the communities of Farson and Eden in the northeastern part of the Green River Basin, Wyoming (Fig. 2.1) (Dyni, 1996).

In Wyoming, large deposits of trona are found in the Green River formation. There are 42 beds of trona that cover about 1,300 square miles. Approximately eleven of these seams are at least 1.83 meters in thickness, and 25 of them exceed 0.91 meters thick. The most common bed for trona mining, bed 17, is 0.49 meters deep. Amazingly, the bed is 3.66 meters thick and is of very high quality soda ash derived from trona. 47 billion tons of identified soda ash resources could be recovered from the 56 billion tons of bedded trona and the 47 billion tons of interbedded or intermixed trona and halite that are in beds more than 1.2 meters thick. About 34 billion tons of reserve base soda ash could be obtained from the 36 billion tons of halite-free trona and the 25 billion tons of interbedded or intermixed trona and halite that are in beds more than 1.8 meters thick. In addition to this, it has been estimated to have reserves of 27 billion tons grading an average of 9% dawsonite ($NaAl(CO_3)(OH)_2$) and 29 billion tons grading an average of 40% nahcolite ($NaHCO_3$).

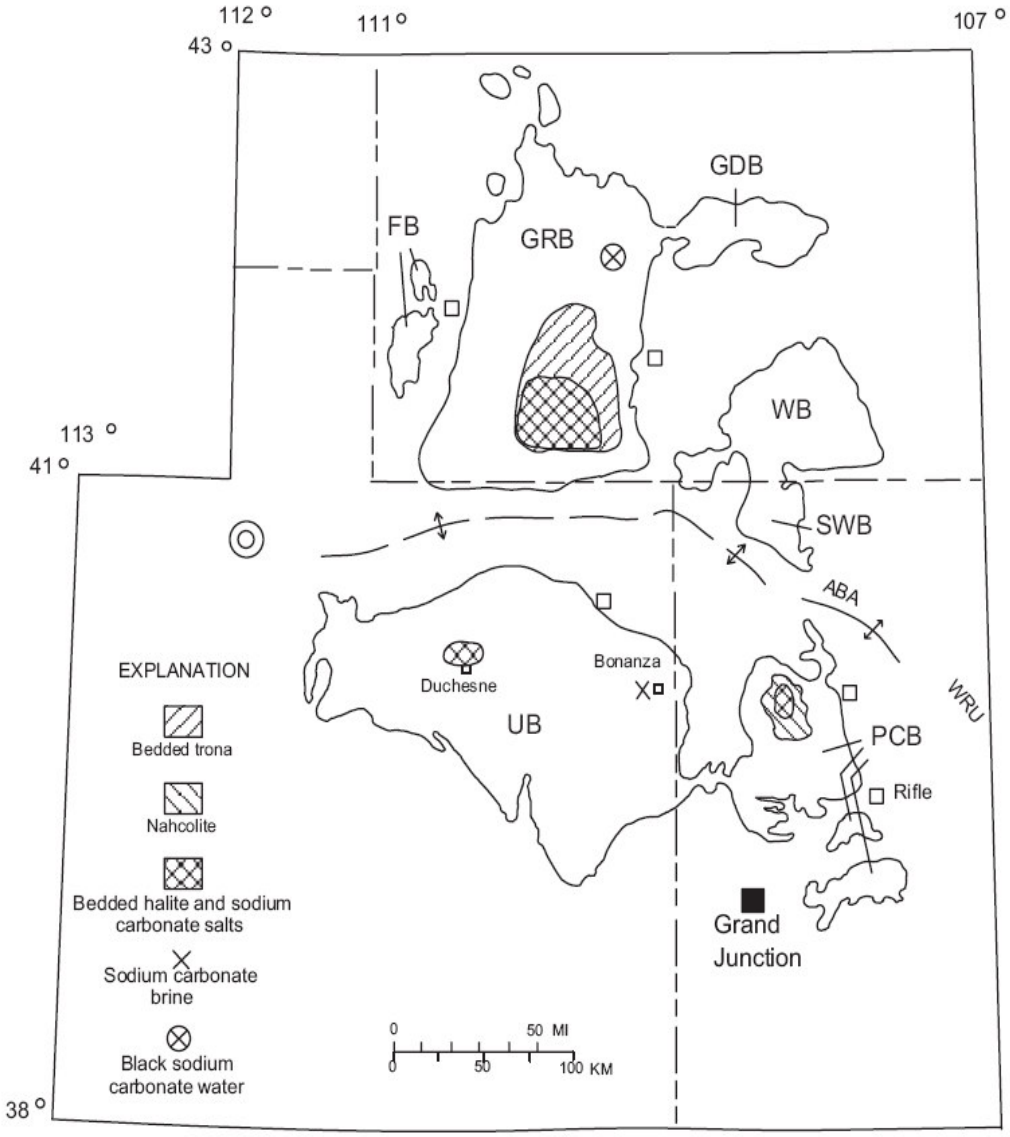


Figure 2.1 Map showing the areal distribution of the Green River Formation and the locations of five sodium carbonate deposits in Utah, Colorado, and Wyoming. ABA, Axial Basin Anticline; FB, Fossil Basin; GDB, Great Divide Basin; GRB, Green River Basin; PCB, Piceance Creek Basin; SWB, Sand Wash Basin; UB, Uinta Basin; UMU, Uinta Mountain Uplift; WB, Washakie Basin; WRU, White River Uplift (Dyni, 1996)

Another resource of natural soda ash is Searles and Owens Lakes in U.S.A. They are a huge resource of sodium and potassium minerals of the carbonate, sulfate, borate and halide classes of mineralogy. Searles Lake is one of a chain of Pleistocene lakes that

extends from Owens Lake to as far as ancient Lake Manly in Death Valley. The stratigraphic record at Searles Lake indicates that it once held brackish water as deep as 200 meters (650 feet). Fluctuations in lake levels correspond to the advances and retreats of glaciers in the Sierra Nevada Range. Thirty major lake levels occurred during the last 150,000 years, represented by a sequence of salt and mud beds. The precipitation of minerals occurred during long periods of lake evaporation. It has been estimated to have reserves of 2 billion tons grading an average of 25% trona in Searles Lake and 50 million tons grading an average of 82% trona.

2.3.2 Deposits in Turkey

Turkey has the distinction of being third country to discover large underground soda ash deposits (Green River, U.S.A.; two deposits in Henan, China; and two deposits in Ankara, Turkey).

One of this buried trona deposit occurs about 15 km northwest of Beypazari in central Turkey, and is about 30 km west of Ankara. The Beypazari trona deposit occurs within the lower levels of the Lacustrine and Mid-Upper Miocene Hirka Formation. The trona field is limited by the Cakiloba folding in the north and by the Zaviye faults in the south and it is a deposit N64E oriented, 4.7 km in length and 1.7 km in width, resulting in an area of 8 km^2 within a Neogene lacustrine basin (Fig. 2.2). The Neogene rock units are dominantly precipitated in shallow pond domain. The probable source of the Na ion required for the accumulation of trona deposit is the extended Neogene igneous rocks compacted with the sediments in the northeast of the basin.

Based on borehole data, the areal extent of the trona deposit is estimated to be approximately 8 square kilometers. The trona beds were deposited as two lensoidal bodies within a 70- to 100-meter-thickzone in the lower part of the shale unit (Onargan et al., 2004).

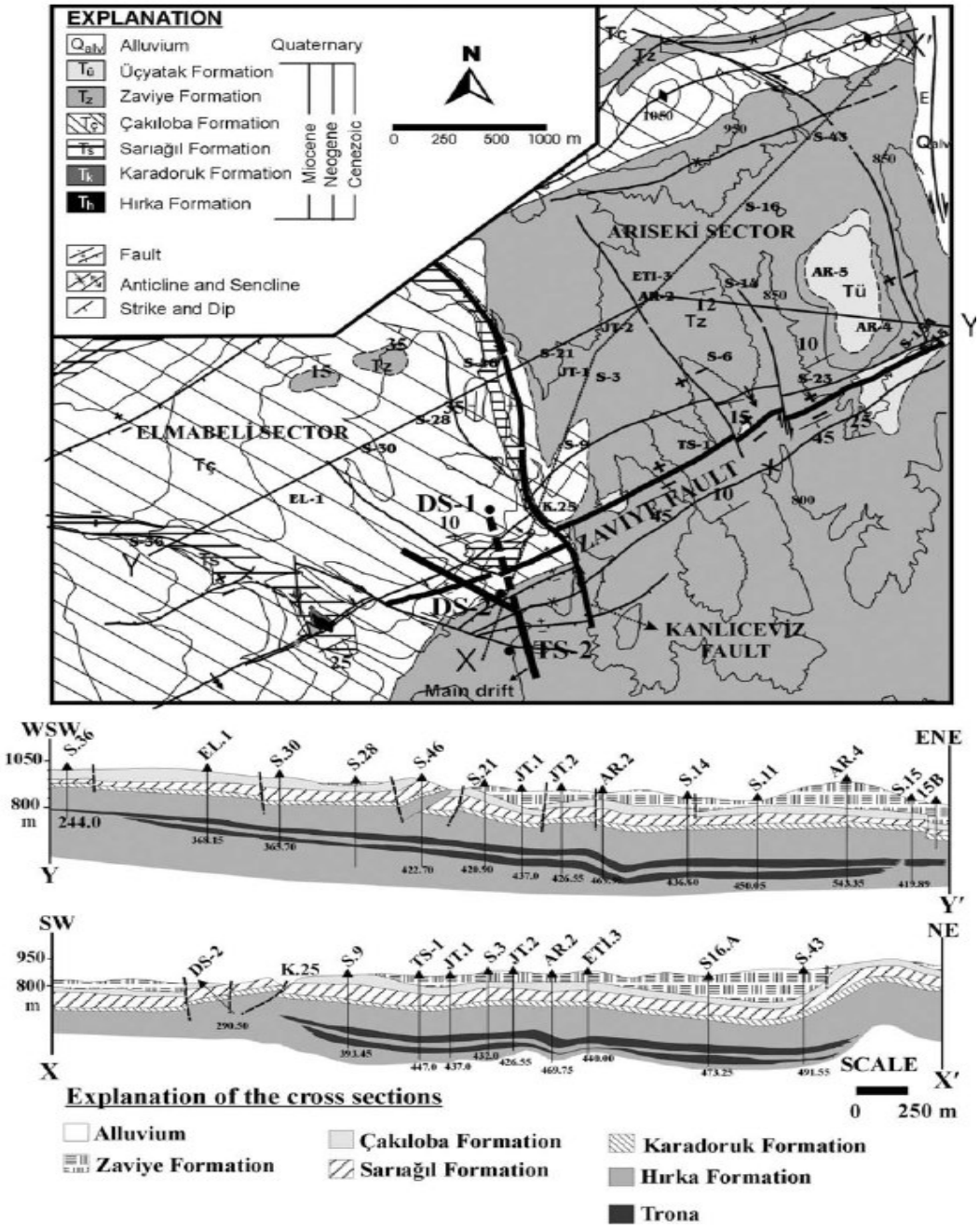


Figure 2.2 Geological map and cross-sections of the Beypazari natural soda field (Onargan et al., 2004)

A total of 33 trona beds are known: 16 in the lower trona lens and 17 in the upper lens. The total thickness of the lower trona sequence is about 40 meters. The interval between the lower and the upper trona sequence varies from 30 to 35 meters. The total

thickness of the trona beds in both lenses varies between 21 and 34 meters in the central parts, and between 2.5 and 12 meters in the marginal parts of the ore bodies. The thickness of the individual trona beds in both trona horizons ranges from 0.4 to 2 meters. Trona in the central parts and nahcolite in the marginal parts of the soda deposit are abundantly found (Helvaci, 2001).

The Kazan Trona deposit is located in central Turkey, approximately 35 km north-west of Ankara. The deposit is beneath low-lying hills and adjacent to a large valley. The project area contains both state and privately owned lands. The private land is generally farmed and part of the state land is being forested to contain land erosion. The geologic studies of Kazan natural soda field have revealed that the trona was deposited in a lake environment approximately 46 million years ago. A total of 12 trona beds have been discovered, collectively called the trona zone, with varying thicknesses and grades (Fig. 2.3). The trona zone is encountered at 420 m depth in the north-west and reaches a depth exceeding 850 m in the south-east with a dip angle varying from 5 to 16 degrees. The thickness of the trona zone reaches a maximum of 109 m with an average thickness of about 54 m. Resource evaluation studies revealed 607 million tones of economical ore body grading an average of 31% trona (Kostick, 2005).

Another soda ash occurrence is Lake Van in Turkey. It is a large freshwater lake that covers 3,730 km^2 with an average depth of 55 m. It is located on a 1,700-m-high plateau, and contains only a small concentration of sodium carbonate. Usually it averages from one to a few tenths of a percent Na_2CO_3, but with its great size the total mass of sodium carbonate is fairly large (perhaps 338 million tons). However, as so often is the case, Lake Van has other uses and is in a mountainous, high-altitude location. The solar evaporation rate is not great, and there is not a suitable shoreline for extensive solar evaporation. Various groups have considered producing soda ash from Lake Van, but it is quite unlikely that it will be utilized in the near future (Garrett, 1992).

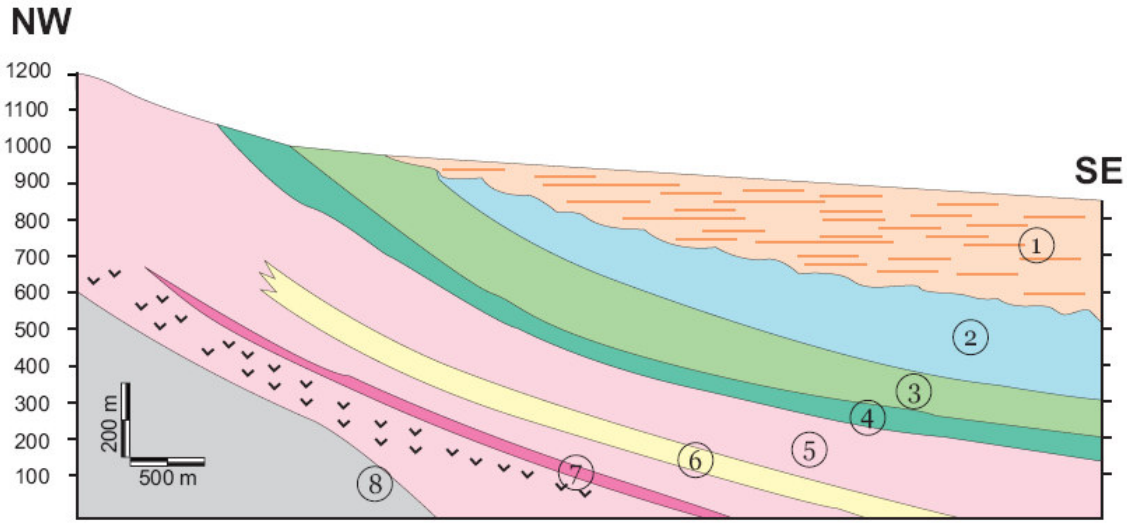


Figure 2.3 The cross-sections of the Kazan natural soda field; 1, Clastic Sediments; 2, Limestone; 3, Marlstone; 4, Dolomitic Sediments; 5, Oil Shale & Mudstone; 6, Bedded Trona; 7, Dolomitic Mudstone; 8, Volcaniclastics & oilshale (Kazan Trona Project Social & Environmental Report, 2003)

2.3.3 Deposits in China

Natural sodium carbonate-bearing minerals occur widely in China. Appraximately thirty alkali lakes and natural soda mines have been exploited. Some of the larger natural soda deposits are concentrated in the Nanyang basin on the Inner Mongolia plateau. Proven total sodium carbonate reserves are 154 Mt. about 83.5% of these reserves is contained in the Henan Province, and 15.5% of the reserves is contained in the Inner Mongolia Autonomous Region. The Wucheng trona deposit was discovered in 1971 during petroleum exploration. It is located in southern Henan Province, 18 km west of Tongbai County at latitude 32.4°N, longitude 113.5°E. The deposit occurs in the central part of the Paleogene faulted Wucheng basin and was formed in the Eocene Epoch. The trona beds occupy an area of 4.66 km^2 at depths 643 to 974 m. resources of the Wucheng trona deposit total 36.8 Mt of equivalent soda ash and 17.8 Mt of sodium chloride. The sodium carbonate-bearing minerals include mainly trona and nahcolite associated with shortite, northupite, and NaCl, $Na_2CO_3 \cdot (MgFe)CO_3$ (Helvaci, 2001).

2.3.4 Other Deposits in the World

The largest deposit of trona in the East Africa is found in the Lake Magadi, Kenya. Thickness of the trona bed varies from 20 to 40 meters that cover about 75 square kilometers in the Magadi and Natron Lakes. In these lakes; it has been estimated to have reserves of 4 billion tons grading an average of 94% trona in Searles Lake and 50 million tons black trona water grading an average of 82% trona. But, these lakes contain significant concentrations of sodium fluoride, sodium chloride and sodium sulfate).

Besides soda ash production from trona, soda ash produces from natural soda carbonate bearing lakes. One of these lakes is Texcoco Lake in San Cristobal, Mexico and the other one is Sua Pan Playa in Bostwana. It has been estimated to have reserves of 80 million tons concentrating an average of 3.7% sodium carbonate in Texcoco Lake with an average depth of 45 m (Garrett, 1992).

The Sua Pan Playa is located in central Makgadikgadi, north-east of Ankara. Alkali black water contains 128 g/l NaCl, 23.05 g/l Na_2CO_3, 9.64 g/l $NaHCO_3$ and 13.76 g/l Na_2SO_4. Aquifers have 233 million tones of sodium carbonate, 1.026 million tones of sodium chloride, and 110 million tones of sodium sulfate reserves.

Besides these deposits, existence of some deposits is also known in Cad, Ethiopia, Niger, Republic of South Africa, Tanzania, Uganda, Bolivia, Canada, India, Pakistan, Russia and Venezuela (Garrett, 1992).

2.4 Soda Ash Production Methods

For more than a century sodium carbonate, or soda ash, was produced in the world by the ammonia-soda process, which uses salt and limestone as raw materials. More recently, the production soda ash from trona is economically more attractive than the production of synthetic soda ash, and environmental problems associated with the ammonia-soda process, principally the disposal of byproduct $CaCl_2$, are avoided.

2.4.1 Conventional Operations

Mechanical mining at depths from about 250 m to 500 m is currently the primary means of extracting trona from the Green River deposits. All operators employ conventional room-and-pillar mining methods. The FMC Corporation also operates a longwall mining machine. Because run of mine trona contains shale and other insoluble impurities, organics, and small amounts of soluble impurities, above-ground processing is extensive. At present, the Green River operators produce soda ash by two processes, the "Monohydrate Process" and the "Sesquicarbonate Process". Only a very brief description of these processes will be presented in this chapter. Gärtner (2005), Garrett (1992), Haynes (1997) and Aitala (1997) give excellent reviews of the current state-of-the-art processes and feasible process alternatives.

2.4.1.1 Monohydrate Process

All five companies in the Green River Basin operate large sodium carbonate monohydrate plants. Briefly, the trona after crushing and screening is fed to a calciner where a crude soda ash is produced, i.e., the bicarbonate component is converted to carbonate by the reaction

$$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \rightarrow 3Na_2CO_3 + 5H_2O_{(g)} \uparrow + CO_{2(g)} \uparrow \qquad (2.1)$$

The crude soda ash then goes through a series of purification steps involving dissolution, classification, clarification, filtration, activated carbon treatment (if needed, to remove organics) and ultimately evaporite crystallization as sodium carbonate monohydrate. Monohydrate crystals form exclusively in the temperature range 35.4 to 109°C as is evident from the phase diagram of Figure 10. The crystals are separated from the mother liqour by centrifuge and dried to remove the water of hydration. The

centrate is recycled to the crystallizers. The soda ash produced by the monohydrate process is a dense, high-purity product (Haynes, 1997).

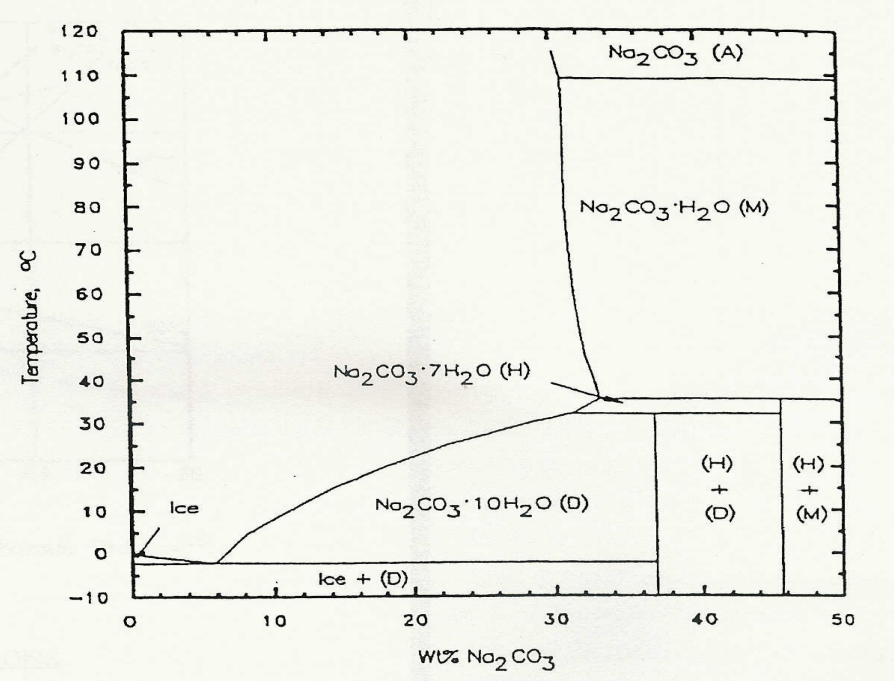


Figure 2.4 Solubility of sodium carbonate as a function of temperature (Haynes, 1997)

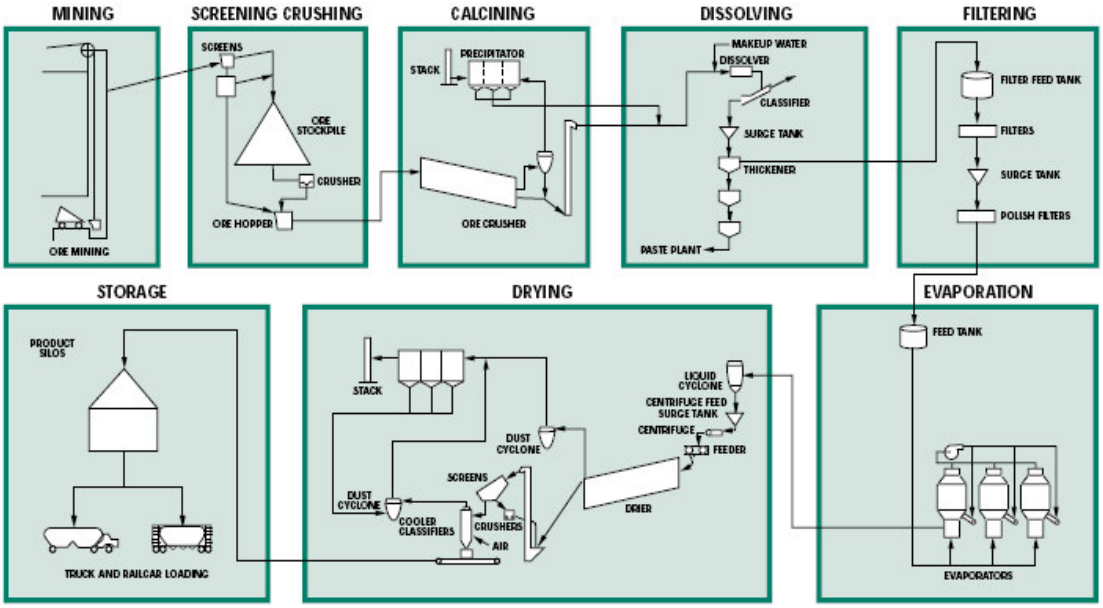


Figure 2.5 Simplified flowsheet of the Monohydrate Process at Wyoming, USA (Oci Chemicals)

2.4.1.2 Sesquicarbonate Process

One company in the Green River area also processes trona by the Sesquicarbonate Process. Trona ore is leached in recycled mother liquor at as high a temperature as possible to maximize the amount dissolved. The solution is then clarified, filtered and sent to a series of evaporite cooling crystallizers where sodium sesquicarbonate is crystallized. The purified sesquicarbonate crystals may be calcined to produce a "light" soda ash product. The mother liquor is recycled to the dissolvers. In a variation of the process, trona ore is dissolved in hot water and the centrate is returned to the evaporator crystallizers (Haynes, 1997).

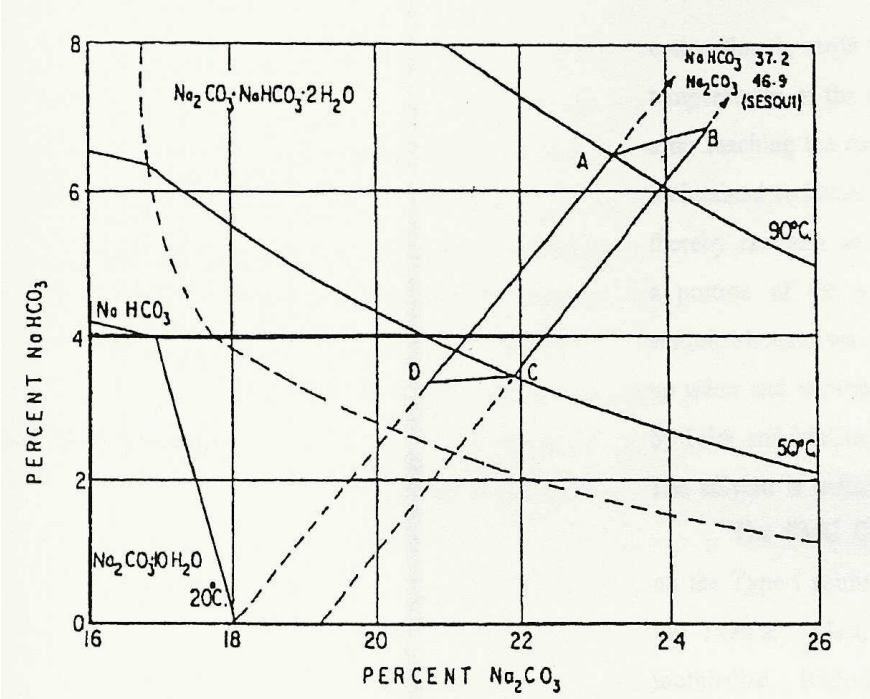


Figure 2.6 Phase diagram with path for the Sesquicarbonate Process (Haynes, 1997)

It is interesting to follow the Sesquicarbonate Process on the ternary phase equilibrium diagram of Figure 2.6. Only the trona region is of interest to this discussion. Point D on the figure represents this composition of the leach solution. Trona dissolves along a line connecting this point to the coordinates corresponding to pure trona (46.9

wt% Na_2CO_3, 37.2 wt% $NaHCO_3$). This line intersects the 90°C isotherm at Point A in the figure. The hot aqueous solution is sent to vacuum crystallizer where the solution is concentrated and cooled to approximately 50°C by evaporation of water. Line A-B, which extends through the origin (pure water), represents water loss from evaporation. The composition corresponding to Point B is unstable at 50°C, and the system separates into two phases, crystalline sodium sesquicarbonate and mother liquor of composition corresponding to Point C. The line B-C, which once again extends through the trona coordinates, represents the crystallization, i.e., removal of sesquicarbonate from solution. Make-up water is added to the mother liquor recycle line C-D, which passes through the origin, to complete the cycle (Haynes, 1997).

2.4.2 Solution Mining

The solution mining of trona has long been touted as an attractive alternative to underground mechanical mining, with the first patent issued to Pike in 1945. Pike's method employs a single well comprising an outer casing and an inner casing. Hot solvent is injected through the inner casing to contact the trona bed, and the product is withdrawn through the annulus. This method proved unsuccessful, however, and currently there are some approaches to solution mining that are actively being pursued. Two or more wells are drilled into the trona bed and a low-pressure connection is established by some means (hydraulic fracturing or directional drilling). Solution under high temperature and pressure is injected into the cavern from the injection well and pregnant solution is collected from the production well as illustrated in Figure 2.7.

It seems certain that solution mining will grow in importance in the years to come. Thin beds are accessible only to solution mining as are deep beds. Mechanical mining is an expensive operation, and typically a third of the cost of producing a ton of trona is associated with the mining operation. Additional savings are to be realized in the processing of solution-mined product, since the need for solids handling is reduced. From the standpoint of economics, it is always advantageous that the product brine is

concentrated, but it appears that modern processes can economically handle brines as dilute as 8 wt% total alkali value (Haynes, 1997).

$$\text{Total Alkalinity} = (\text{wt\% } Na_2CO_3) + 0.631 \times (\text{wt\% } NaHCO_3) \quad (2.2)$$

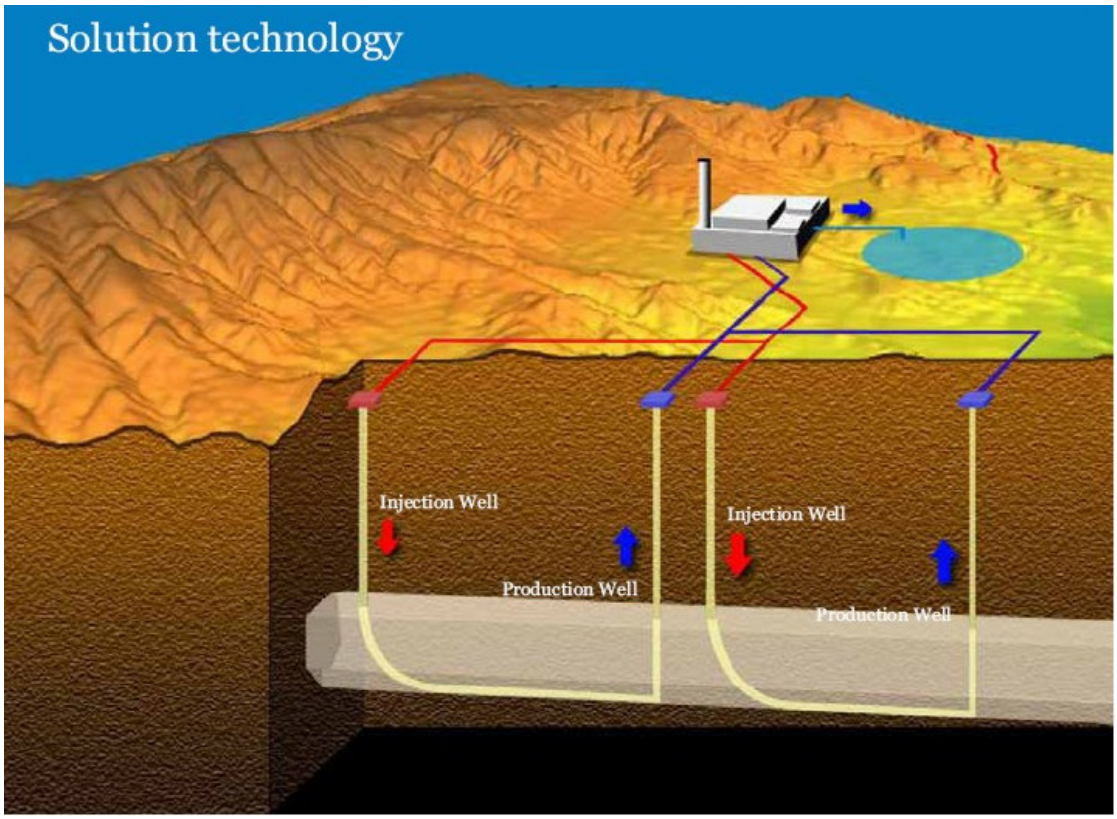


Figure 2.7 Solution mining of trona with directional drilling at Kazan, Turkey (Kazan Trona Project Social & Environmental Report, 2003)

2.4.3 Processing of Solution Mined Product

The processing of trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) in soda ash ($Na_2CO_3$) requires the following 3 process steps:

1. The break-up of the trona crystal lattice and the discharge of the crystal water
2. The conversion of bicarbonate to carbonate and the discharge of CO_2
3. The formation of the soda crystals (nucleation and growth)

$$2HCO_{3(aq)}^{-} \leftrightarrow CO_{3(aq)}^{2-} + H_2O_{(l)} + CO_{2(g)} \uparrow \quad (2.3)$$

The equilibrium between carbonate and bicarbonate ions in aqueous solution determines the stable solid phase in saturated solutions and the corresponding solubility concentrations of carbonate and bicarbonate. This equilibrium is strongly affected by the CO_2 partial pressure. At T < 90°C and ambient CO_2 partial pressure, solid bicarbonate (nahcolite) is the thermodynamically stable solid. At T > 90°C the equilibrium is sufficiently shifted towards carbonate to make trona the stable phase. The equilibrium can theoretically be shifted further towards carbonate by reducing the ambient carbon dioxide partial pressure. Intense carbon dioxide stripping could then allow crystallizing sodium carbonate monohydrate and achieving complete conversion into a bicarbonate-free solid phase (Gärtner, 2005).

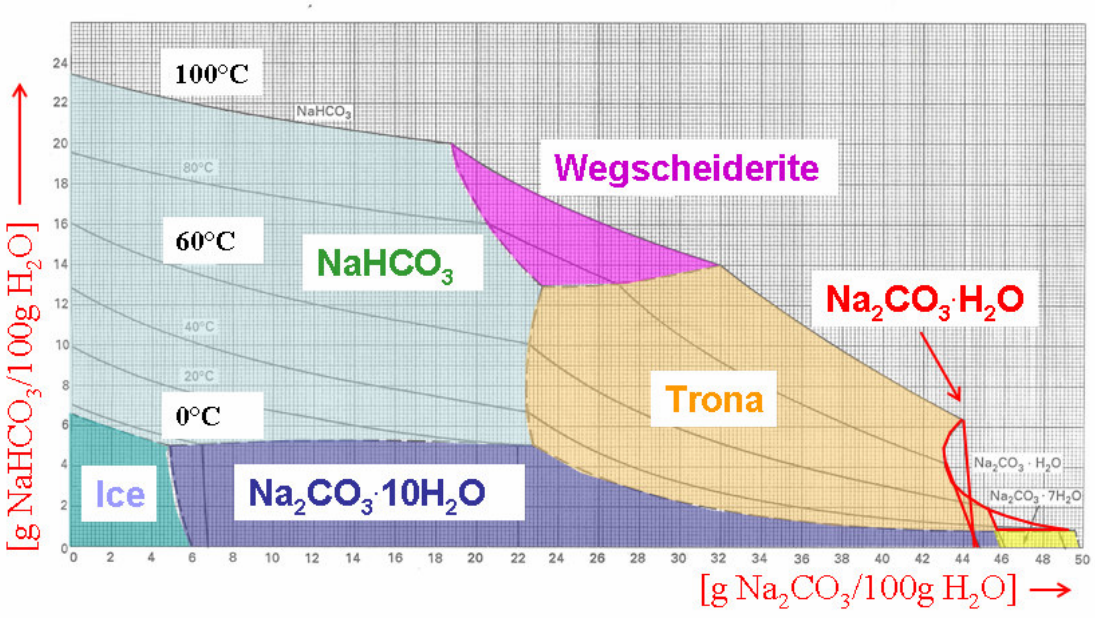


Figure 2.8 System Na_2CO_3-$NaHCO_3$; g/100 g water (Gärtner, 2005)

In aqueous solution only the recrystallization of solid bicarbonate to trona can be achieved at ambient CO_2 partial pressure, and an operating temperature T > 90°C and

intense CO_2-stripping have to be applied. For the complete conversion of bicarbonate to carbonate in solution, CO_2 has to be removed completely from the ambient gas phase and higher temperatures need to be applied. The highest available operating temperature at atmospheric pressure in aqueous solution is the boiling point of the saturated bicarbonate/carbonate solution which lies in the range between 101.4°C, (for a saturated $NaHCO_3$ solution), and 104.8°C, (for a saturated Na_2CO_3 solution) (Gärtner, 2005).



Figure 2.9 Views from Beypazari natural soda ash pilot plant; a) Steam stripper, b) Forced circulated evaporator

Steam stripping is preferably accomplished in a countercurrent flow column containing random or structural packing or in a tray type column. Heated feed brine enters the top of the column and stripped brine leaves the bottom of the column. Steam in introduced into the bottom of the column, and water vapor and carbon dioxide from the solution results from decomposing the sodium bicarbonate to sodium carbonate (Eq. 2.3).

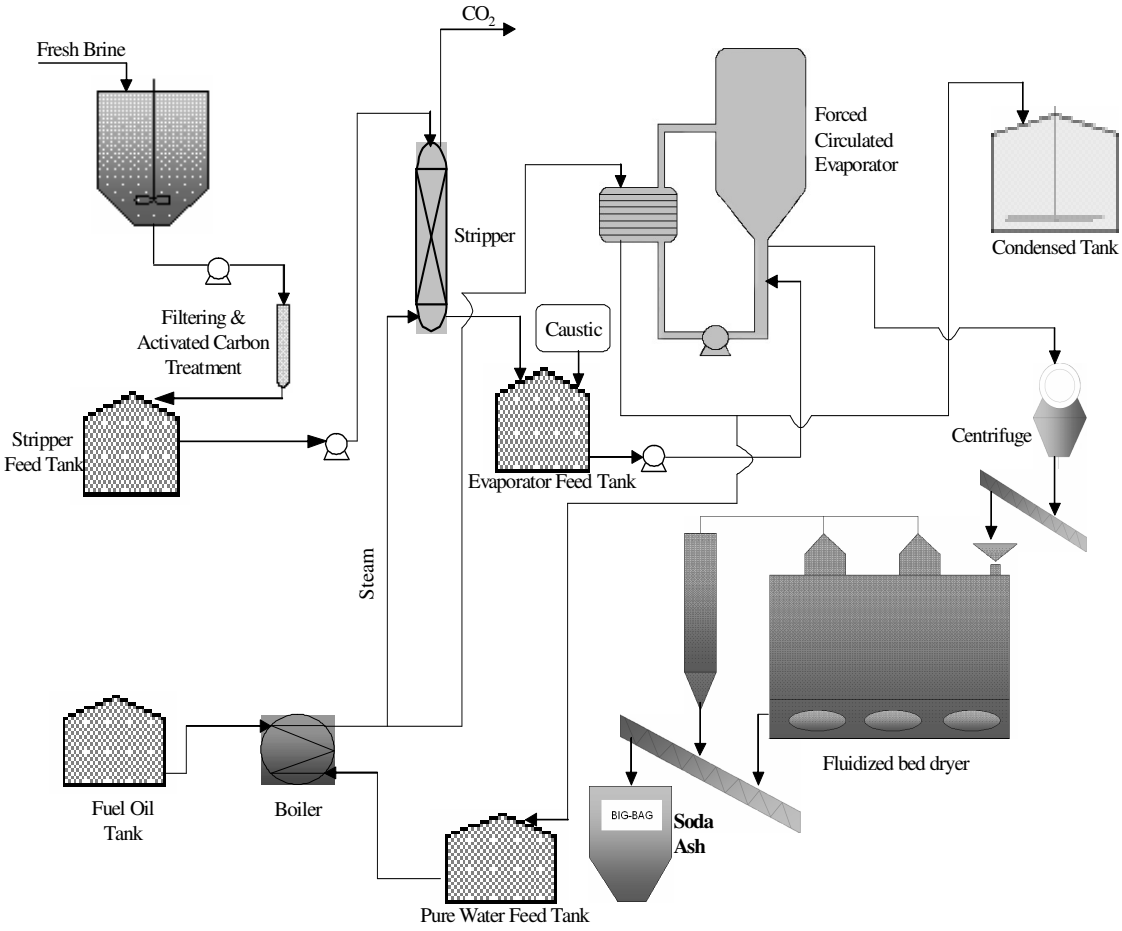


Figure 2.10 Flowsheet of the Beypazari natural soda ash pilot plant

Following steam stripping, the brine is neutralized to convert additional sodium bicarbonate to sodium carbonate (2.4). The term "neutralization" or "neutralization stage" represents the conversion of sodium bicarbonate to sodium carbonate by reaction with lime and/or sodium hydroxide. Sufficient caustic soda or lime is added to the brine to produce a final brine which will contain either about 0% to %2 by weight sodium bicarbonate or about 0% to %1 by weight sodium hydroxide, and more preferably either about 0% to 0.5% by weight sodium bicarbonate or about 0% to 0.5% by weight sodium hydroxide in the feed solution. Hence, the final brine passed along to a monohydrate evaporator circuit may contain a slight excess of sodium hydroxide.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad (2.4)$$

Following neutralization, the brine may be filtered or clarified to remove unreacted lime and other insoluble materials from the brine, if neutralization takes place with lime. The overall, simplified reactions taking place with lime in the causticizing unit are as follows:

I) $CaO+2NaHCO_3 \rightarrow CaCO_3 + Na_2CO_3 + H_2O$ (2.5)

II) $CaO+Na_2CO_3 + H_2O \rightarrow CaCO_3 + 2NaOH$ (2.6)

As is clear from reaction II above, one mole of lime (CaO) will react with each mole sodium carbonate in the brine stream fed to the causticizing unit to produce two moles of sodium hydroxide. However, since sodium bicarbonate also requires lime to convert it into sodium carbonate, as shown in reaction I, above before it can be reacted to form sodium hydroxide via reaction II, lower bicarbonate concentrations in the brine fed to the causticization unit means less lime usage in converting the total alkali into sodium hydroxide. Since the stripped brine from the stripper contains lower bicarbonate values than the brine feed, it becomes the preferred causticizer feed because it requires less lime to convert it into sodium hydroxide than the original brine feed. Causticization is carried out at elevated temperatures of about 70°C to about 100°C. This allows better utilization of lime since the causticization reaction is more efficiently carried out at such elevated temperatures and promotes better settling of the muds. Additionally, the reaction is exothermic and facilitates maintaining the solutions at elevated temperatures (Smith et al., 2002).

In the next step of the process, the 22-30 wt% sodium carbonate filtered solution is evaporated at temperatures above about 35.4°C and below about 109°C to form sodium carbonate monohydrate crystals (Fig. 2.4). This operation is carried out by means of suitable multiple-effect evaporators or more preferably by a vapor recompression evaporator which allows evaporation of the solution and crystallization of the sodium carbonate monohydrate. In a multiple-effect evaporator, the liquor temperature varies from effect to effect with much of the evaporation taking place at temperatures below

100°C. Although some thermal decomposition of sodium bicarbonate levels in the feed above about 0.5% can result in co-crystallization of sodium sesquicarbonate along with sodium carbonate monohydrate depending on operating conditions. By contrast, all of the liquor in a mechanical vapor recompression monohydrate evaporator is generally subjected to temperatures above 100°C, and more decomposition of sodium carbonate occurs. When the feed to the evaporator contains more than about 1% sodium bicarbonate, provisions should be made in the evaporator equipment design to allow venting of carbon dioxide gas resulting from decomposition of sodium bicarbonate.

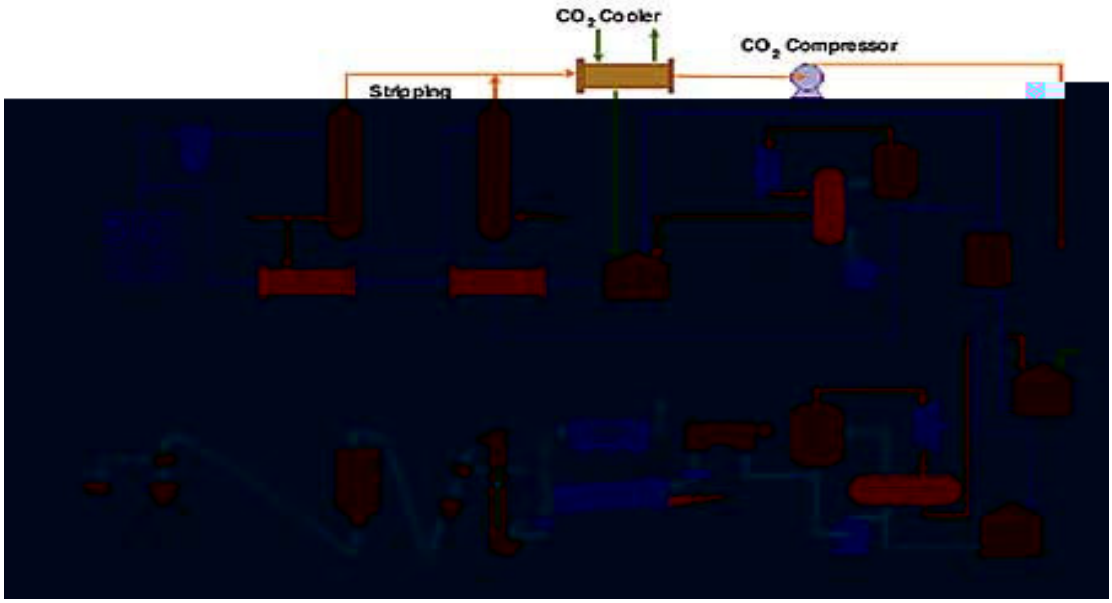


Figure 2.11 Flowsheet of the sodium carbonate production process from nahcolite at Colorado, USA (American Soda Corp.)

The monohydrate crystal slurry is removed from the monohydrate evaporator crystallizer and sent to a centrifuge where the crystals are separated from their mother liqour. The mother liqour is returned to the monohydrate evaporator crystallizer while the crystals are sent to a dryer and heated until converted into soda ash. Some of the mother liqour being returned from the centrifuge to the monohydrate evaporator crystallizer may be subject to purge from the process to control impurity levels.

Optionally, the monohydrate mother liqour purge can be sent to a sodium decahydrate crystallizer where the solution is cooled down to about 0°C to abut 30°C, with about 5°C to about 20°C being preferred. This permits recovery of some of the sodium carbonate values in the monohydrate mother liqour purge stream of mother liqour from the sodium decahydrate crystallizer is more concentrated in impurities, less sodium carbonate values are purged from the process. The sodium carbonate decahydrate crystals so recovered can be melted by adding a small amount of water and heating above 30°C to yield a relatively pure solution of about 30% by weight sodium carbonate which can be recycled back to the monohydrate evaporator feed. Alternately, the deca crystals can be melted in the fresh evaporator feed stream if the feed is not saturated. As another alternative, the solution formed by melting the crystals can be carbonated to form sodium bicarbonate to sodium sesquicarbonate crystals which can be separated and recovered as a product.

2.5 Sodium Bicarbonate Production Method

The purification step can be accomplished by crystallization of sodium bicarbonate. This route is particularly attractive for processing complex brines such as those produced at Searles Lake, California, and its success is due to the fact that among the various alkali salts present, sodium bicarbonate tends to be the least soluble. Since some solution-mined product brines from the Green River Basin deposits purification via bicarbonate crystallization may be worthy consideration. In some cases; the carbon dioxide gas leaving the steam stripping column may be recovered and used to make sodium bicarbonate (Fig. 2.9).

The brine is carbonated to convert sodium carbonate to sodium bicarbonate, i.e.:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \qquad (2.7)$$

The CO_2 Source is normally calciner gas. However, the Argus plant at Searles Lake employs a monoethanolamine scrubber to recover CO_2 from the power-plant flue gas.

The carbonation towers are designed for efficient gas-liquid contacting, and they operate at temperatures from about 30 to 70°C. It is claimed that the warmer temperatures produce better crystals. Calcination of the bicarbonate crystal produces a light soda ash (Haynes, 1997).

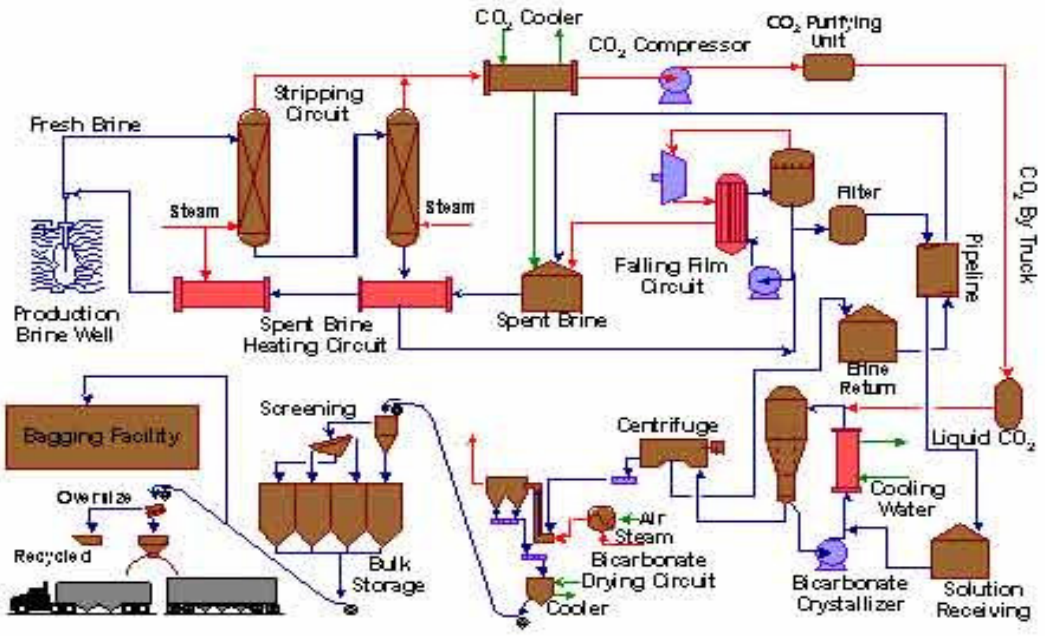


Figure 2.12 Flowsheet of the sodium bicarbonate production process from nahcolite at Colorado, USA (American Soda Corp.)

2.6 Soda Ash Utilization

Soda Ash, known chemically as sodium carbonate (Na_2CO_3), has been used since the earliest recorded times. More than 5000 years ago, the Egyptians made glass ornaments from sodium carbonate recovered from dried desert-basin lakes. Over the years the production techniques have evolved from the method employed by the Egyptians to the Solvay process (also known as the ammonia-soda process) and finally to the most efficient and environmentally friendly process- the refining of soda ash from rich, pure trona deposits. Today soda ash consistently ranks as one of the top 10 inorganic

chemicals produced in the world and is an essential raw material to a variety of industries.

2.6.1 Glass Production

In constant use since ancient Egyptian times, glass is still a highly valued material. Nowadays glass is a sophisticated product requiring state-of-the-art technologies to ensure ever faster and cheaper production.

The largest single use of soda ash throughout history has been the production of glass. Soda ash commonly contributes about 12% - 15% of the weight of raw materials making up glass. Soda ash, with its low melting point and reactivity, acts as a flux for other ingredients, primarily silica and other oxides, allowing them to be melted at reasonable temperatures and to have a low enough viscosity to be easily handled and formed.

New grades of glass have been developed to suit the requirements of customers and the many functions this material is called on to fulfill. Depending on their composition, distinctions can be made among around a dozen types of glass, which fall into the categories of hollow glass, flat glass and specialty glass.

Glass is produced by the fusion of 3 types of raw material:

- The glass formers are the network-forming oxides; the most widely used is silica, which is found in sand.
- The fluxes are the network-modifying oxides, which lower the melting point of the silica; the most frequently used is sodium oxide, derived from sodium carbonate.
- The network stabilizers (calcium and magnesium oxides) give glass its stability.

2.6.2 Flue Gas Desulfurization

Driven by the US Environmental Protection Agency's requirements governing removal of Sulfur Dioxide (SO_2) from utility stack (flue) gas even when burning low sulfur coal, soda ash has found application in this market segment either as a dry sorbent or as a feedstock in the conversion to sodium bicarbonate.

Sodium carbonate or its derivative sodium bicarbonate is used for the deacidification of combustion gases (energy generators). Flue gas cleaning using sodium carbonate can be carried out using a wet process or a dry process.

For the deacidification of incinerator fumes (domestic waste or special or hospital waste), sodium bicarbonate is injected using a dry process. This technology also allows the residues of the gas treatment to be recycled after treatment.

2.6.3 Soaps & Detergents

Sodium carbonate is being used increasingly in the production of high performance compact powders for laundry and dish washing. Soda Ash is used primarily as a builder or filler in formulations of soaps, detergents and other cleaning compounds. In addition to these roles soda ash may also add benefit as an agglomerating aid, a carrier for surfactants and as a source of alkalinity for pH adjustment.

The combined use of Zeolite and sodium carbonate may replace the sodium phosphates and is approved by a large number of detergent powder producers.

Sodium carbonate may also be used for the direct soaking of clothes, dishwashing, floor washing and for degreasing operations.

For these same applications, a large number of formulated domestic products, soaps, scouring powders, soaking and washing powders etc. contain a varying content of sodium carbonate.

2.6.4 Chemicals

Sodium carbonate is used in a large number of chemical reactions. A very large number of organic or inorganic substances can, when they combine with one or more sodium atoms , be made soluble or more soluble in water in a very economical way. In this way Soda Ash is acting as a major raw material for the production of sodium bicarbonate ($NaHCO_3$), sodium silicates (Na_2OxSiO_2), sodium tripolyphosphates ($Na_5P_3O_{10}$), sodium orthophosphate (NaH_2PO_4-Na_2HPO_4-Na_3PO_4), sodium metaphosphate ($NaPO_3$), sodium percarbonate ($2NaCO_3 3H_2O_2$), sodium bichromate ($Na_2Cr_2O_7 2H_2O$), sodium sulphite (Na_2SO_3), sodium metabisulphite ($Na_2S_2O_5$) and many others.

Soda Ash is also used as raw material for

- Production of various chemical fertilizers, such as synthetic sodium nitrates and fragmented phosphates;
- Production of artificial sodium bentonites or activated bentonites;
- Manufacture of synthetic detergents;
- Organic and inorganic colouring industry;
- Enamelling industry;
- Petroleum industry;
- Fats, glues and gelatine industry, etc.

2.6.5 Water Treatment

Soda Ash is a base and therefore finds application in the water treatment segment by adjusting the pH of water when it is in acidic condition. Because soda ash is safer to

handle than other alkalis and it's pricing is more stable over time, more and more companies are choosing soda ash to assist in their water treatment needs.

A large number of lakes and rivers in the Northern hemisphere are suffering from the effects of acid rain. Additionally, if the ground is of poor quality (consisting of limestone or rocks which are not easily liable to deterioration), this acidification of the water may lead to the disappearance of all aquatic, animal and plant life.

Based on a new invention, the sodium ions may be locked into the sediment in a lake using sodium carbonate added to the lake and acting as an ionic exchanger. Several Swedish lakes have been treated very successfully and this process is now under development.

2.6.6 Pulp and Paper

Soda Ash has a variety of uses in this market segment ranging from pulp digestion to water treatment. The primary opportunity for soda ash in the segment is in the replacement of caustic soda, which has historically demonstrated more dramatic price fluctuations.

2.6.7 Metallurgy

Sodium carbonate is also used in the metallurgy of a large number of non-ferrous metals:

- Oxidizing calcination of chrome ore;
- Precipitation of cobalt carbonate;
- Obtaining the solubility of sodium tungstate and sodium vanadate in water;
- Desulfurization of nickel cast irons;
- Recycling of the lead from discarded batteries and industrial dusts;
- Formation of a protective slag on baths of metal infusion during refining;

- Recycling of aluminium;
- Recycling of zinc.

Sodium carbonate is used in certain steelworks to improve the dephosphorization and desulfurization of steel.

Very high quality steels can be obtained by injecting soda ash into the cast iron after the removal of its silica by iron oxide.

The Soda Ash will reduce simultaneously the phosphorous and sulfur contents of the cast iron. The obtained slag can be recycled using a sodium carbonate recovery installation. This process allows specifications for very high quality steels to be achieved with great accuracy.

2.7 Production, Consumption Statistics

Soda ash is a mature commodity in which consumption tends to grow proportional to population and gross domestic product growth rates. For this reason, the largest customers of soda ash were, for the most part, developed nations that have lower growth rates compared with developing countries. The less developed nations tend to have higher soda ash demands and higher growth rates. Although the production and consumption quantities varied among the countries, the end-use patterns were basically the same, and glass, chemicals, and detergents were the major sectors.

Nine countries had the capacity to produce more than 1 million metric tons per year (Mt/yr). They were, in descending order, China, the United States, Russia, India, Germany, France, Italy, Poland, and the United Kingdom. Bulgaria, Romania, and Ukraine had production installations that were rated at about 1 Mt/yr; adverse economic conditions, however, caused these nations to produce below their design capacities. Recent acquisitions or joint ventures with major European soda ash producers that have

soda ash manufacturing expertise should reverse this situation in the next few years. In 2003, world soda ash production was estimated to be 37.8 Mt, which was a 2% increase compared with that of 2002 (Kostick, 2005).

Table 2.4 World Production (Data in thousand metric tons) (Kostick, 2005)

	Production	
Natural:	**2003**	**2004**
United States	10,600	10,800
Botswana	285	280
Kenya	350	350
Mexico	-	-
Turkey	-	-
Uganda	NA	NA
Other countries	-	-
World total, natural (rounded)	11,200	11,400
World total, synthetic (rounded)	26,800	27,600
World total	38,000	39,000

NA is not available

2.7.1 Production

U.S. production of natural soda ash from California, Colorado, and Wyoming in 2003 was 10.6 million metric tons (Mt), which was slightly higher than that of 2002. On the basis of about 14.5 Mt (16 million short tons) of total nameplate capacity, the U.S. soda ash industry operated at 73% of total capacity. The U.S. soda ash industry consisted of six companies in 2003—four in Wyoming operated four plants that produced soda ash from underground trona ore, one in California produced soda ash from sodium carbonate-rich brines, and one in Colorado produced soda ash and sodium bicarbonate from solution mining underground nahcolite; nahcolite is a mineral that is naturally occurring sodium bicarbonate; its name is derived from the chemical elements contained in sodium bicarbonate—Na (sodium), H (hydrogen), C (carbon), O (oxygen), and “lite” (stone).

Eti Soda, a public/private sector partnership, signed an agreement in April to proceed with the development of the Beypazari underground trona mine near Ankara. Although

about $7.1 million has been spent since 1998 on developing entry tunnels, drainage systems, and infrastructure, the trona will be solution mined by using directional horizontal drilling technology to establish communication between the injection well and the production well. The deposit, which has an estimated 250 Mt of reserves, was discovered in 1979 while exploring for coal. In 1983, the trona resources were held by the state-owned nonfuel mining group Etibank, which was later renamed Eti Holding. Eti Holding sought a private sector partner in 1998. Although several companies bid on the opportunity, Park Group was awarded a 76% majority partnership with Eti Holding a 22% share, and the state-owned bank Vakifbank was awarded a 2% stake of Eti Soda. Eti Soda was attempting to locate credit financing for 70% of the total investment cost of $300 million. The operation is scheduled to produce 500,000 t/yr when in full production in late 2005 or early 2006. A second trona deposit was discovered in 1998 at Kazan by Rio Tur Madencilik (a subsidiary of Rio Tinto Minerals Development Company). There is an estimated 600 Mt in reserves at this location. In 2003, Rio Tinto Industrial Minerals Group acquired a 40-year operating license for the Kazan trona project. The deposit contains about 607 Mt of identified resources with an average grade of 31% trona. The trona will be solution mined by using directional horizontal drilling technology to establish communication between the injection well and the production well. Beginning in 2004, Rio Tinto will start a 3-year pilot project to prove the viability of solution mining. Small-scale production will begin in 2007 with startup of a 900,000-t/yr soda ash plant scheduled for 2011 (Kostick, 2003).

2.7.2 Consumption

In the domestic market, large-volume buyers of soda ash were primarily the major glass container manufacturers whose purchases were seasonal; more beverage containers made in the second and third quarters for summertime beverage consumption. Soda ash sales to the flat glass sector were usually dependent on the state of the economy because the largest uses of flat glass were in automobile manufacture and in residential housing and commercial building construction. These two major industrial sectors were

especially sensitive to changing economic conditions, and soda ash sales followed the trends in the two sectors. The distribution of soda ash, by end use, in 2003 was glass, 49%; chemicals, 28%; soap and detergents, 11%; distributors, 4%; miscellaneous uses, 3%; flue gas desulfurization and pulp and paper, 2% each; and water treatment, 1% (Kostick, 2003).

CHAPTER THREE
CRYSTALLIZATION

3.1 Introduction

Crystallisation involves the formation of one or more structured solid phases from a fluid phase or an amorphous solid phase. It is one of the older unit operations in the chemical industry. Crystallisation stands out from most unit operations due to the presence of a solid product. Besides chemical composition, the quality of such a product is also determined by its crystal size distribution (CSD), morphology, habit, polymorphism, etc. Within the chemical industry crystallisation is applied extensively for both separation and production purposes.

Vast quantities of crystalline substances are manufactured commercially: inorganic materials such as sodium chloride ($>10^8$ t/a), potassium chloride (fertiliser, $>10^6$ t/a), ammonium sulphate (fertiliser), and urea ($>10^6$ t/a) and organic materials such as sucrose ($>10^8$ t/a), adipic acid (raw material for nylon), paraxylene (raw material for polyester), and pentaerythritol (used for coatings).

An enormous number of and diversity in crystallisation processes are found in the pharmaceutical, organic fine chemical, and dye industries: L-ascorbine (vitamin C), L-serine (amino acid), and aspartame (sweetener). Although the production in these industries is relatively low as regards tonnages, it constitutes a substantial part of crystallisation processes from an economic point of view. Overall, it is estimated that about 70% of the products sold by the process industry and pharmaceutical industry are solids. The main advantages of crystallisation are:

- *A high purity in one process step*. The rigid structure of the crystalline material results in a low tendency to incorporate foreign substances or solvent molecules. Therefore, high purity substances can be relatively easily produced in crystallisation.

However, a lot of time is needed to grow such a rigid structure, and crystallisation is thus a rather slow process. As a result, large vessels are generally needed to reach an acceptable yield.

• *Low level of energy consumption*. For instance, if cooling crystallisation can be used instead of distillation, a significant cost reduction is achieved.

• *Relatively mild process conditions*. This makes crystallisation a favourable unit operation for temperature sensitive or even temperature labile substances. A well-known example of an industry frequently dealing with such substances is the food sector.

3.2 Crystal Quality – Performance and Composition

Crystal quality can be defined in terms of product performance characteristics and product composition characteristics.

3.2.1 Product Performance

In practice, the quality of a crystalline solid is usually expressed in terms of performance characteristics. Most crystal quality requirements are imposed by the customers and the downstream solids processing. For instance, end-consumers usually define product performance in terms of aesthetic appearance, taste, smell, feel and handling properties. Of interest for downstream solids processing are first of all the filtration, washing and drying behaviour of the crystals. Secondly, caking behaviour and flowability are important characteristics for storage and transport. Caking is usually the result of mother liquor inclusions. During transportation or storage, mother liquor may seep from broken crystals. Subsequent re-crystallisation may cement the crystals together; a process referred to as the caking of crystals.

The main problem with performance characteristics is that they are often ambiguously defined. This is clearly the case for quality assessments such as taste and feel, which are largely subjective impressions. For other characteristics, such as crystal filterability, the ambiguous nature is not so obvious. The filtration rate using a specific piece of equipment is an objective definition of crystal filterability, but it is not universally applicable as it is equipment dependent.

3.2.2 Product Composition

For design purposes, translation of the often ill-defined performance characteristics to well-defined physical parameters is essential. Well-defined physical quantities to describe the quality of a crystalline product include size, purity, lattice structure, morphology and habit.

Usually the individual crystals in a crystalline product do not possess the same history as regards their formation processes. Consequently, their properties will not necessarily be the same. A product that consists of crystals with different sizes, morphologies, etc. is said to have distributed properties. As one usually considers volumes of crystalline material which are substantially larger than the volume of an individual crystal, the number of crystals is sufficiently large to justify the use of a statistical description to account for the distributed nature of the product properties. The first distributed property that jumps to mind in conjunction with industrial crystallisation is crystal size. As crystallisation usually takes place in vessels with a residence time distribution, the individual crystals will obviously have varying histories. The most noticeable result of this difference in history is usually a distribution of crystal sizes.

3.2.3 Product-Related Design Specifications

Defining product specifications in terms of composition instead of performance is clearly more suitable for modelling and design purposes. However, its use still raises a number of problems:

- Although product composition characteristics are well-defined, some are extremely difficult to measure, e.g. morphology and habit.

- Theoretically speaking all product composition characteristics can be uniquely defined in physical terms; however, in practice a reasonably accurate description of some characteristics would require a very substantial number of parameters.

- The lack of adequate product performance models, i.e. models predicting the performance on the basis of composition; without these models interpretation of product specifications imposed by downstream solids processing and customers remains a serious bottleneck. These three problems are all largely related to the distributed nature of crystalline products. In addition to a size distribution, a collection of crystals will usually also possess distributions with respect to morphology, purity, etc. A comprehensive description of the product composition therefore involves a multivariate distribution of the crystal population over the various product composition variables.

3.3 Crystallization Mechanisms

The product composition characteristics detailed in the before constitute the internal states of a crystalline product. The external state of a crystal is its geometric position, and the change in this external state is given by the external velocity of the crystal, which is a function of both the hydrodynamics of the solid/liquid system and the internal states of the crystal. This section focuses on the main crystallisation events or

mechanisms that can change (and hence determine) the internal states of a crystalline product, viz. nucleation, growth, dissolution, attrition, agglomeration and breakage. Besides influencing the internal crystal states, some of these events also change the states of the liquid phase. An overview of the states that are typically influenced by the various crystallisation events is given in Table 3.1

Table 3.1 States typically influenced by the various crystallisation events (Bermingham, 2003)

	internal crystal states					**slurry states**	
crystallisation event or mechanism	lattice structure	morphology	size	purity	lattice strain	crystal concentration	solute concentration (supersaturation)
nucleation; crystal formation	++	+	-	-/+	+	++	+
growth; continuous size enlargement of a crystal	+/-	+	++	+	+	++	++
dissolution; continuous size reduction of a crystal	-	+	++	+	+/-	++	++
agglomeration; discontinuous size enlargement of a crystal	-	++	++	+	-	-	+
breakage; discontinuous size reduction of a crystal; involves the fracture of a particle into two or more smaller pieces	-	++	++	-	++	-	-
attrition; discontinuous size reduction of a crystal; involves the fracture of the particle into one slightly smaller particle and many much smaller fragments	-	+	+	++	++	+/-	+/-

The rates of these crystallisation events are largely determined by the same states they affect, i.e. the internal crystal states and slurry states. More specifically, they are a function of rate coefficients and driving forces, which are in their turn determined by slurry states or local process conditions such as supersaturation, energy dissipation, solids concentration, pressure and temperature, as well as internal crystal states, such as size, strain and shape.

3.3.1 Nucleation

Nucleation, the formation of new crystalline particles, is classified as being primary or secondary according to the mechanism through which it occurs.

• *Primary nucleation*: Primary nucleation is the formation of a new solid phase from a clear liquid. This type of nucleation can be further subdivided into homogeneous and heterogeneous nucleation. In heterogeneous nucleation, nucleation starts on foreign substrates of mostly microscopic particles, e.g. dust or dirt particles. If such substrates are absent, new phase formation takes place by statistical fluctuations of solute entities clustering together, a mechanism referred to as homogeneous primary nucleation. Homogeneous nucleation rarely occurs in practice, as the presence of small quantities of microscopic particles is usually unavoidable.

The driving force for primary nucleation is the supersaturation of the crystallising substance, which is defined as the difference in chemical potential of that substance in the liquid and in the solid phase. The rate coefficient or resistance for primary nucleation is (among others) a function of the cluster-liquid interfacial tension and the diffusion coefficient. The internal states at the time of formation of the nuclei, such as size, lattice structure and purity, are also a function of supersaturation. For instance, the critical nucleus size, the size at which a nucleus is considered thermodynamically stable, is inversely proportional to the supersaturation.

• *Secondary nucleation*: Secondary nucleation refers to the birth of new crystals at the interface of parent crystals. Contrary to the relatively high supersaturations required for primary nucleation, secondary nucleation already occurs at low to moderate values of the supersaturation. There are various types of secondary nucleation, but the most important source of secondary nuclei in crystallisation is attrition. Attrition, also referred to as contact nucleation, occurs as a result of crystal-pump, crystal-vessel wall or crystal-crystal collisions.

The driving force for attrition is determined by the concentration of the various sized crystals and their relative motion with respect to the pump blades, vessel walls or other crystals. The relative kinetic energy of a collision is determined by the size and relative velocity of the particle, which in its turn is a function of the slurry motion, viscosity and particle inertia (thus particle size). The rate coefficient or resistance for attrition is a function of the shape, surface roughness and mechanical properties of the colliding crystal. The rate coefficient is also indirectly influenced by the supersaturation, which determines factors such as surface roughness and healing of corners and surfaces damaged due to previous collisions. The supersaturation also determines the effective secondary nucleation rate as a result of attrition: it determines the fraction of attrition fragments that actually grow out and thus 'survive'.

3.3.2 Crystal Growth and Dissolution

Crystal growth is the addition of solute molecules from a supersaturated solution to the crystal lattice. Besides being a mechanism responsible for increasing crystal size, crystal growth, or more specifically the relative growth rates of the crystal faces, also largely determines crystal morphology. Finally, the crystal face growth rates together with the growth mechanism determine the surface structure and purity of the crystal (van Rosmalen et al., 1997).

The growth rate of a particular crystal face is mostly described by its linear growth rate, which refers to the growth rate of that face in the direction normal to the face. Since the growth rates of the various crystal faces are usually not equal, an overall linear growth rate is often used.

Crystal growth is a three-step process consisting of mass transfer, surface integration and heat transfer. Mass transfer and surface integration occur sequentially and in parallel with heat transfer. Mass transfer involves the diffusion of growth units, i.e. molecules, atoms or ions, to the crystal surface. Surface integration consists of surface diffusion, orientation and the actual incorporation into the lattice. Various mechanisms exist for surface integration, the most important being spiral growth, 'birth and spread' growth and rough growth. Spiral growth is the most encountered growth mechanism under normal operating conditions (van Rosmalen et al., 1997). Heat transfer is often a rate-limiting step in melt crystallisation, but this is practically never the case in solution crystallisation. Supersaturation is the driving force for both mass transfer and surface integration. The rate of mass transfer has a first order supersaturation dependency. The supersaturation dependency of the surface integration step is determined by the mechanism: a second, exponential and first order dependency for respectively spiral growth, 'birth and spread' growth and rough growth. It is important to note that the supersaturation, i.e. the difference in chemical potential of the crystallising substance in the liquid and solid phase, need not be the same for each crystal. While the chemical potential in the liquid phase may be the same, the chemical potential of two neighbouring crystals may differ due to differences in lattice structure and/or lattice strain. As a result, similarly sized crystals exposed to identical growth conditions can exhibit different growth rates. This phenomenon is called growth rate dispersion and has been experimentally observed by among others Ristic et al. (1990). The mass transfer rate coefficient is a function of the diffusion coefficient, crystal size and local hydrodynamics. Besides on the surface integration mechanism, the rate coefficient for surface integration also depends on the size of the growth units (because of surface diffusion and steric orientation) and the lattice structure.

Crystal dissolution is not the exact opposite of crystal growth: dissolution does not require surface diffusion and orientation of atoms, ions or molecules, and is therefore in general limited by mass transfer. Crystal dissolution thus has a first order dependency on the supersaturation, its driving force. The rate coefficient for dissolution is a function of the diffusion coefficient, crystal size and local hydrodynamics. Because dissolution is usually mass transfer limited, dissolution at crystal edges and corners is faster due to steric favouring. For this reason, crystals are easily rounded off once dissolution starts.

3.3.3 Agglomeration

Agglomerate is defined as the mass formed by the cementation of individual particles, probably by chemical forces (Randolph and Larson, 1988). A mass formed by a group of particles held together by only interparticle forces is called an aggregate.

Agglomerates are usually undesirable because they contain mother liquor between the primary crystals that form the agglomerate. This liquor is hard to remove during drying, and promotes caking of the product during storage. Furthermore, agglomerates also tend to break more easily than solid crystals, during which they also release solvent. There are however also cases where agglomeration is stimulated, namely when the primary particles are too small for acceptable downstream solids handling.

Agglomeration first of all requires the collision of two or more crystals. The collision mechanism depends on the sizes of the crystals involved: perikinetic (due to Brownian motion; small particles), orthokinetic (due to fluid shear) or inertia (due to differences in relaxation time; differently sized particles). Next, these crystals must form an aggregate as a result of interparticle forces, such as Van der Waals (attractive), electrostatic (repulsive) and steric (repulsive) forces. Finally, cementation of these crystals as a result of growth, before the aggregate is disrupted, is required to create agglomerate.

The driving force for agglomeration is the supersaturation. Without supersaturation, aggregates can be formed but agglomerates cannot. The rate coefficient or kernel for agglomeration is a function of the number of particles (collision chance), the sizes of the particles involved (agglomeration mechanism), and in the case of orthokinetic agglomeration the fluid shear or energy dissipation (collision chance, time between collision and disruption).

The collision frequency increases with increasing shear rate, but if the shear rate becomes too high, aggregates are disrupted before sufficient cementation has taken place. As a result, the rate constant for orthokinetic agglomeration first increases and subsequently decreases with shear rate.

3.3.4 Breakage

Similar to attrition, breakage can occur as a result of crystal-pump, crystal-vessel wall or crystal-crystal collisions. The difference between breakage and attrition is not a distinct one. The fracture of a particle into one slightly smaller particle and many much smaller fragments is defined as attrition. Breakage involves the fracture of a particle into two or more pieces. To accomplish the total fracture of a particle requires considerably more energy than that needed for attrition. If the impact energy of a single collision is not sufficient, repeated collisions, which result in accumulation of crystal stress, are required for breakage.

The driving force and rate coefficient for breakage are mainly a function of the same process conditions and particle properties as discussed for attrition. In addition, the rate coefficient or resistance for breakage is also influenced by the collision history of the particles involved.

3.3.5 Segregation

Segregation is not a crystallisation mechanism in the sense that it forms a particle, increases its size or reduces its size. However, as it can have a significant effect on the final product quality it is discussed here. Particle segregation is a result of slip with respect to the liquid motion. An important effect that can only be described if segregation is taken into account is the non-uniform distribution of solids in a crystalliser. For instance, if the circulation intensity is lowered in a crystalliser, the relative amount of solids in the lower part of the crystalliser will increase.

Particle segregation is a function of particle size, liquid velocity, solids concentration, and the difference in material density between the liquid and solid phase.

3.4 Design Procedure of Crystallization Processes and Products

Typical benefits to arise from the use of a systematic design procedure are:

• The ability to deliver crystallisation process designs of a consistently high quality (*design effectivity*).

• A reduction in the duration of the overall design process, e.g. by removing the need for pilot scale experiments for scale-up purposes (*design efficiency*). This helps meet one of the increasingly more important design requirements, viz the available time-to-market, which is decreasing continuously.

• Reproducibility of the design process (*traceability of design decisions and rationales*). This is essential to improve on existing designs and identify any remaining errors in the applied domain knowledge and/or design procedure.

• A mutual awareness in a design team of the tasks that the various members have in the various stages of the design process.

The systematic design procedure presented in the remainder of this chapter contains many elements from both the field of systematic design procedures for chemical engineering processes in general as well as the field of crystallisation. Models used within this procedure are of both a rigorous and empirical nature. Heuristics are considered useful because their application is usually rapid and relatively simple. Furthermore, heuristics are often the only alternative for domains where fundamental knowledge is not available or applicable (Bermingham, 2003).

3.4.1 A Design Hierarchy

The design of crystallisation products and processes encompasses too many design specifications and degrees of freedom to be considered simultaneously. This is illustrated by Figure 3.1, which shows a large number of degrees of freedom or design variables that can affect the filterability, which is merely one of the many possible design specifications for crystallisation.

The first step in the development of a systematic design procedure for crystallisation processes and products, aimed at delivering the benefits, is to decompose the design process into sub problems concerned with fewer design specifications and degrees of freedom. Here a hierarchical decomposition is chosen that largely resembles the causal chain ‘equipment geometry and operating conditions; process conditions; crystallisation kinetics; product composition; product performance’. The proposed design hierarchy consists of one level at which the initial design specifications are formulated and four design levels (see Table 3.2) (Bermingham, 2003).

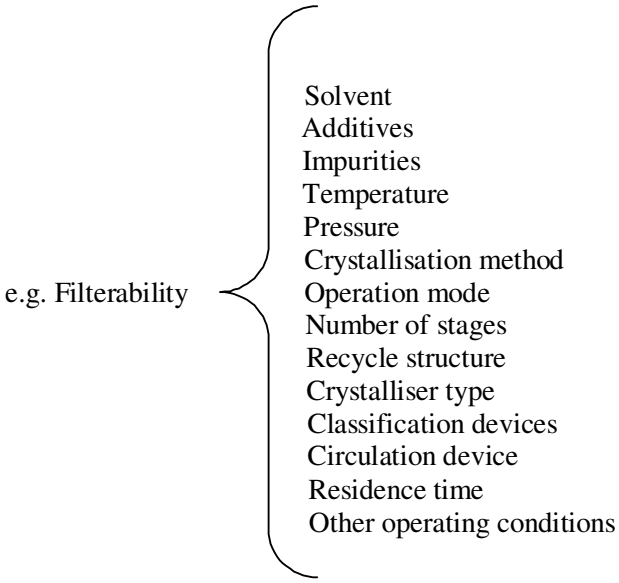


Figure 3.1 Design complexity illustrated (Bermingham, 2003)

Table 3.2 Proposed level decomposition (Bermingham, 2003)

0	Initial design specifications
I	Design of the crystalline *product*
II	Physical/chemical design of the crystallisation *task*
III	Flowsheet design of the crystallisation *process*
IV	Design of a crystallisation *stage*

Returning to the filterability example, Figure 3.4 shows how the hierarchical decomposition of the design process limits the number of design variables under consideration by focusing on one design level at a time. Later it will also become clear how this hierarchical decomposition reduces the number of design specifications and the amount of knowledge that needs to be considered simultaneously.

Design levels I through IV are aimed at finding design alternatives that meet the initial design specifications. As the designer progresses from one level to the next the emphasis shifts from product design (levels I and II) to process design (levels II and III)

and ultimately to crystalliser design (level IV). In contrast with methodologies as proposed by Douglas (1985), the degree of detail does not automatically increase with each level. For product related issues it actually decreases, and for process and equipment related topics it increases when progressing to the next design level.

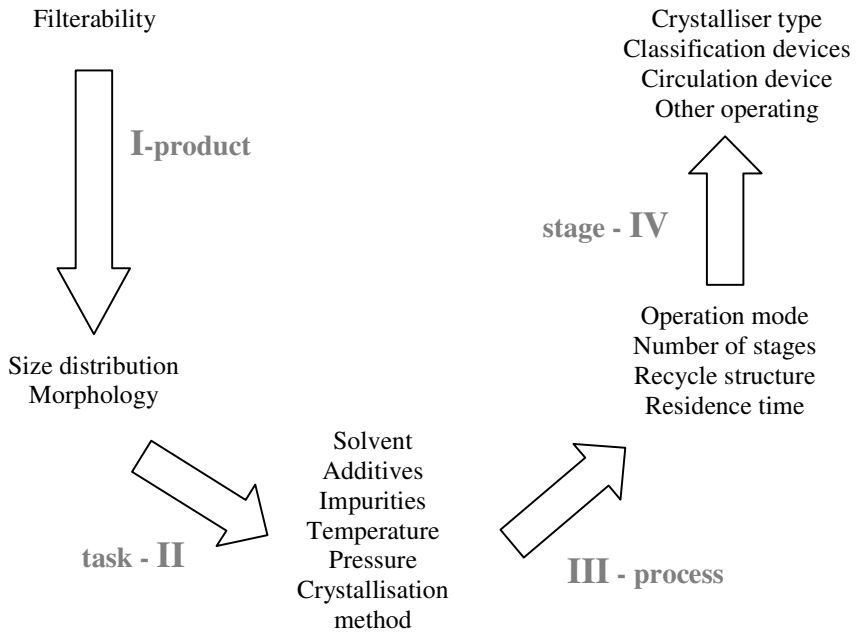


Figure 3.2 Illustration of hierarchical decomposition (Bermingham, 2003)

At all four design levels the same tasks are performed, i.e. definition of design space and specifications, assessing domain knowledge, synthesis, analysis, evaluation and optimisation. (see Figure 3.4). These tasks will be discussed briefly below and further on they will be exemplified at each level.

The first step at each level is to make an inventory of applicable design specifications and to identify the design space. The specifications consist of relevant initial design specifications from level 0 and design specifications propagated from a previous level. Propagated design specifications are in fact design variables, which are fixed after completion of a previous level. The design space is defined by the available design variables and operational variables.

The second step is to gather domain knowledge that relates the design variables and operational variables to the behaviour of a design alternative. This knowledge may consist of heuristics, experimental data and behavioural models. If parts of the domain knowledge are considered inadequate, additional experimental and modelling efforts may be required.

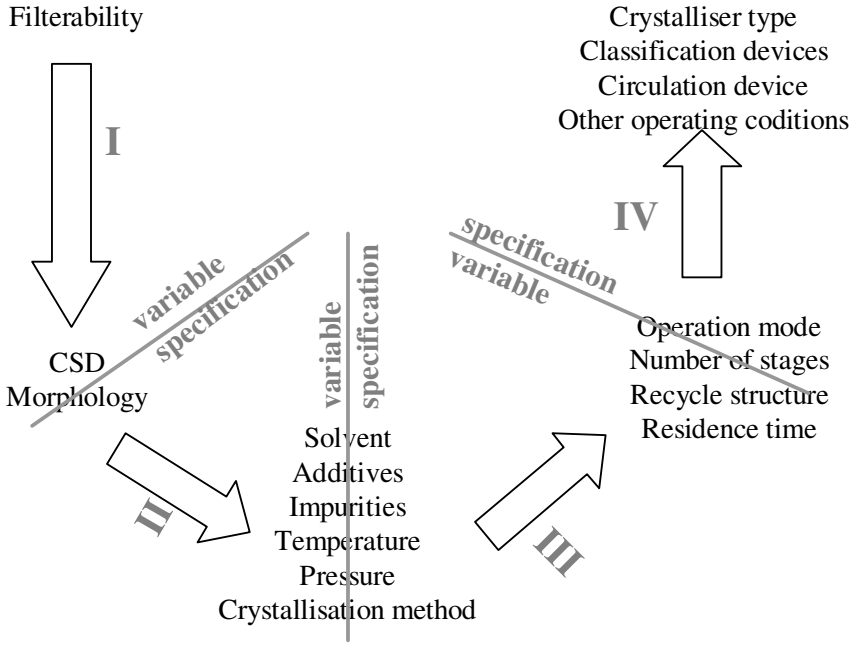


Figure 3.3 Illustration of interactions between levels, i.e. propagation of design variables from a previous level to a next level where they are treated as a design specification (Bermingham, 2003)

The third step, the synthesis task, involves the creation of design alternatives. A design alternative is characterised by its structure and its scale. In this design procedure, we will classify design and operational variables that determine the structure as discrete, and those that define the scale as continuous design and operational variables.

The fourth step is the analysis of the physical behaviour of the design alternatives. Subsequently, the set of behavioural results is evaluated (step five).

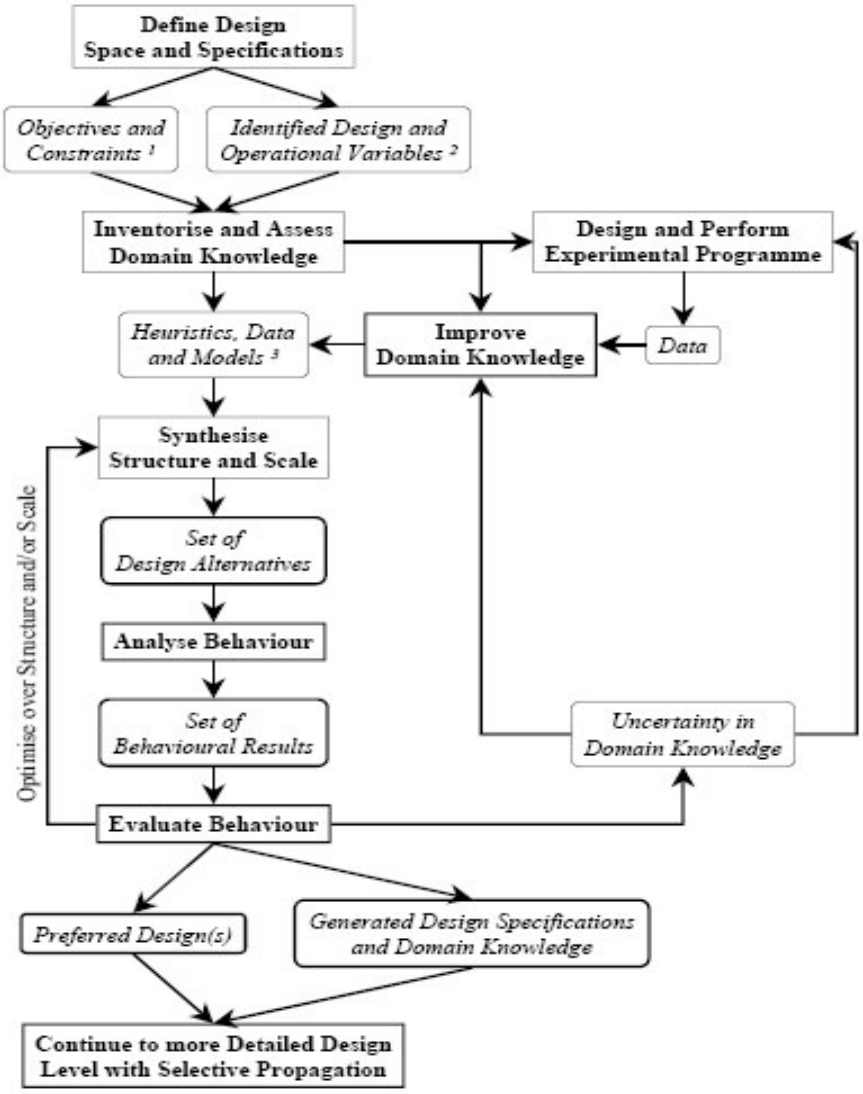


Figure 3.4 Typical sequences of design tasks and the outcome of these tasks. The superscripts refer to the column numbers of Table 3.4 through Table 3.8 (Bermingham, 2003)

The evaluation first of all concerns the compliance of the design alternatives' behaviour with the design specifications. If this evaluation is positive, the design alternative is propagated to a next design level, accompanied by new design specifications. These propagated specifications are in fact design variables and operational variables set at a previous level. This interaction between subsequent levels of the design hierarchy is again illustrated for the filterability example (see Figure 3.3).

If the design alternatives fail the evaluation step, their performance is optimised by modifying their structure and scale, i.e. by returning to the synthesis step. Normally, a screening of the economic potential will be part of any evaluation step. However, such screening is not covered in this chapter. Secondly, the evaluation phase may be used to judge the quality of the applied domain knowledge. If a part of the knowledge is considered inadequate, additional experimental and modelling efforts may again be called for.

Table 3.3 Level 0 - Initial design specifications (Bermingham, 2003)

Product performance requirements *In the crystalliser*: no flotation, suspendability *Downstream handling*: filterability, washability, dryability, dissolution rate, pneumatic handling, freedom from dust, flowability, mechanical strength *Customer application*: no caking in storage, dissolution rate, mechanical strength, freedom from dust, bulk density or porosity, aesthetic appearance
Process requirements feed composition, battery limits and conditions, production capacity, yield, energy consumption, controllability, reproducibility, resiliency, availability, SHE considerations
Design process requirements design budget, time to market, in-house or licensed technology, available skilled design staff, traceability, explicitness of design decisions

A comprehensive execution of all the above-mentioned tasks at all four design levels, while considering all the design specifications listed in Table 3.3, will obviously lead to very lengthy design trajectories. Assigning importance to the various initial design specifications is thus crucial, as the specifications taken into consideration largely determine the amount of effort put into each design level.

3.4.1.1 Initial Design Specifications

Table 3.3 shows the types of requirements considered at level 0. Depending on the nature of the crystalline product (main product, by-product or waste product) and the

role of the crystallisation process (conversion, separation or purification) some design specifications will be deemed necessary, desirable or irrelevant.

The product performance requirements listed in the table above are examples of criteria used in practice to specify the required quality of a crystalline product.

Most of the process related requirements are self-explanatory, but there is a few that merit elaborating on. First of all, the yield of a crystallisation process; for cooling crystallisation processes, the yield is calculated from the initial or feed solution composition and the solute solubility at the final or product temperature for respectively batch or continuous operation. For evaporative crystallisation, the amount of solvent removed also has to be taken into account in the yield calculation. If the crystalline product is a hydrate, account must be taken of the water incorporated in the crystal lattice, since this water is not available for retaining the solute in solution (Bennett, 1993). The yield is also influenced in most processes by the removal of some mother liquor as a result of adherence to the crystal surface during solid/liquid separation. The adhering mother liquor is typically in the range of two to 10 percent of the crystal weight (Bennett, 1984). Secondly, the availability or reliability of the crystallisation process; the main phenomena to determine a crystallisation process' availability are fouling and blockage. For many processes, controlling the fouling is the determining factor in improving their economic performance (see for instance Bermingham et al, 1999). Whether fouling or encrustation will occur depends firstly on the solubility characteristics of the fouling component. The location in the crystalliser where fouling occurs, depends on the method of supersaturation generation, e.g. on heat exchange surfaces in cooling crystallisers and on the walls and agitator shaft at the vapour release surface in evaporative crystallisers.

As regards the design process requirements, these are also largely self-explanatory and are mainly taken into account implicitly in the remainder of this chapter.

3.4.1.2 Design of the Crystalline Product

At this design level (see Table 3.4), the aim is to determine which product composition is required to meet the product performance criteria, and i.e. the product related initial design specifications. Some examples of the relationship between product performance and product composition criteria are:

Table 3.4 Design Level I - Design of the crystalline product (Bermingham, 2003)

Design specifications Objectives and Constraints		**Design Variables**	**Domain knowledge**
Product: • Filterability • No caking in storage • No flotation • Suspendability • Washability • Dryability • Dissolution rate	• SHE considerations • Pneumatic handling • Freedom from dust • Flowability • Mechanical strength • Abrasion resistance • Bulk density or porosity • Aesthetic appearance	*Discrete:* • Polymorphism *Continuous:* • Morphology • Crystal size distribution • Purity • Maximum inclusion content	• Filterability tests and models: permeability and compressibility • Shear tests • Indentation tests • Caking tests • Flowability tests • Safety aspects

• Filterability and freedom of dust are strongly related to the content of fine particles. Reduction of the fines content is a common requirement in practice, in order to increase the throughput and availability of downstream solids handling.

• Aesthetic appearance is usually related to particle size uniformity.

• The colour of certain inorganic pigments obtained by precipitation depends on the product's crystal size distribution.

• Although large crystals are preferred for many applications, there are also cases where small crystals are favoured, e.g. for fast dissolution.

• The liquor inclusion content is in its turn related to crystal size or more specifically to the surface area per unit crystal mass. As small crystals have a relatively large surface area, they will typically contain more adhering mother liquor after filtration than larger crystals.

• The bulk density is determined by the polymorphism and morphology of the crystals.

• The caking tendency in storage is related to the liquor inclusion content.

Most of the relevant domain knowledge for this design level belongs to the field of particle technology, and has a strong empirical character. This is mainly due to the fact that product performance criteria are often equipment specific and hence cannot be defined generically. The development of fundamental knowledge in this field is further complicated by the need to account for distributed properties, seeing as a collection of particles can rarely be described by one size, one morphology, one purity, etc. Depending on the importance of the product performance criteria, much experimental work may be needed for this design level. The design alternatives, i.e. sets of design variables, are propagated to design level II, where they are treated as design specifications.

3.4.1.3 Physical/Chemical Design of the Crystallisation Task

The design specifications of level II, the physical/chemical design of the crystallisation task, are composed of process requirements from level 0 and propagated product composition characteristics from level I. Consult Table 3.5 for a list of specifications.

Table 3.5 Design Level II - Physical/chemical design of the crystallisation task (Bermingham, 2003)

Design specifications Objectives and Constraints	**Design and Operational Variables**	**Domain knowledge**
Process: • Production capacity • Feed composition • Yield • Energy consumption • Availability • SHE considerations *Product:* • Polymorphism • Morphology • Crystal size distribution • Purity • Maximum inclusion content	*Discrete:* • Crystallisation method • Feed purification • Recrystallisation step • Solvent(s) • Additive(s) • Material of construction *Continuous:* • Pressure range • Temperature range • Concentration solvent(s) • Concentration additive(s)	• Thermodynamic activity of species/components in solid, liquid and vapour phase • Adsorption (energy) of components/species on the various crystal faces • Scaling or encrustation tendency of components/species • Metastable zone with respect to homogeneous and heterogeneous primary nucleation • Physical properties, e.g. material densities and specific heats • Safety aspects

3.4.1.3.1 Solvent, Additives and Impurities. The polymorphism and morphology of the crystalline product are influenced by the choice of solvent and additives, crystallisation temperature and crystal growth rates. The domain knowledge required for this selection issue was traditionally obtained from experimental work, but the latter is increasingly being replaced by molecular modelling. This modelling technique involves first principles calculations for the adsorption energy of a component on a specific crystal face.

The same knowledge is also essential to determine the sensitivity of the crystal purity, morphology and polymorphism for impurities in the feed, and hence determine the need for feed purification. Another possible source of impurities is the construction material

used for the crystalliser, auxiliary equipment and piping. Some examples of changes in morphology due to the presence of an additive or impurity are listed in Table 3.6.

Solvent selection also has a significant influence on the attainable size range of a crystalline product. Selecting a solvent that results in a high solubility for a given solute typically leads to low relative supersaturations, low primary nucleation rates, high crystal growth rates and hence to large crystal sizes (Mersmann et al., 1988). These relations are depicted in Figure 3.5.

Table 3.6 Examples of changes in morphology due to the presence of an additive or impurity (after Bennett, 1984)

Material crystallised	**Additive / Impurity**	**Effect**	**Concentration**
NaCl	urea	formation of octahedral	Small
$NaClO_3$	Na_2SO4, $NaClO_4$	formation of tetrahedrons	……
$Na_2CO_3.H_2O$	SO_4^{2-}	reduces L/D ratio	0.1-1.0%
$Na_2B_4O_7$	casein, gelatine	forms flat crystals	……
$(NH_4)_2HPO_4$	H_2SO_4	reduces L/D ratio	7%
$(NH4)_2SO_4$	Cr^{+3}, Fe^{+3}, Al^{+3}	formation of needles	50 ppm
	H_2SO_4	formation of needles	2-6%
	oxalic acid, citric acid	formation of chunky crystals	1000 ppm
	H_3PO_4, SO_2	formation of chunky crystals	1000 ppm
pentaerythritol	acetone solvent	forms plates	……
urea	biuret	reduces L/D ratio	2-7%
	NH_4Cl	reduces L/D ratio	5-10%
naphthalene	from cyclohexane	formation of needles	……
	from methanol	formation of plates	……

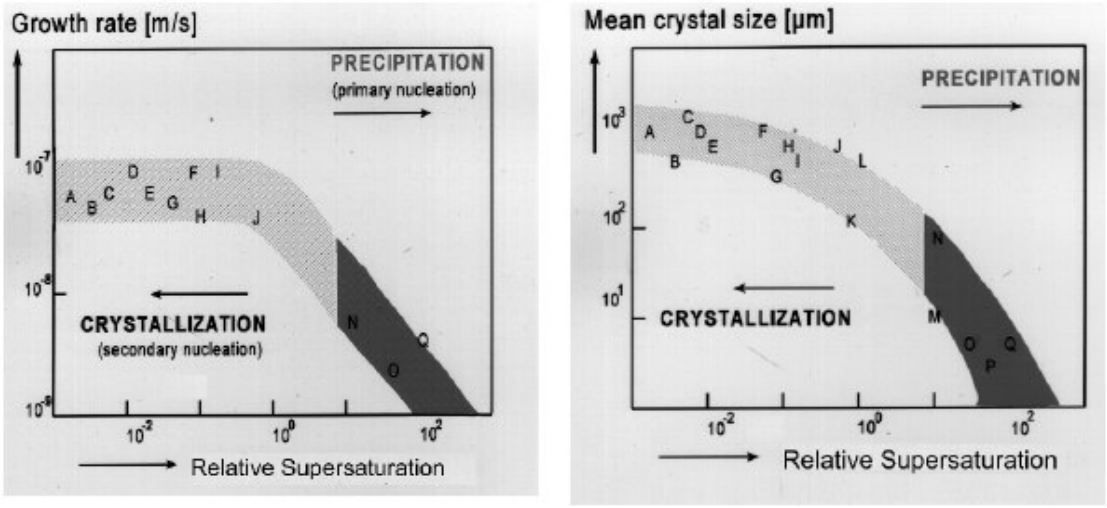


Figure 3.5 Growth rate and mean crystal size versus relative supersaturation for a number of salts (Mersmann et al., 1988). A: KCl, B: NaCl, C: $(NH_2)_2CS$, D: $(NH_4)_2SO_4$, F: Na_2SO_4, G: K_2SO_4, H: $(NH_4)Al(SO_4)_2$, I: $K_2Cr_2O_7$, N: $CaCO_3$, O: TiO_2, P: CaF_2, Q: $BaSO_4$

3.4.1.3.2 Crystallization Method. The crystallisation method is mainly selected on the basis of the thermodynamics of the solid/liquid equilibrium. For many systems, e.g. those involving electrolytes, these equilibria still need to be determined experimentally. A heuristic scheme for this selection process, based upon melt temperatures, *Tmelt*, and equilibrium concentrations, *Ceq*, is given in Figure 3.6.

Other factors influencing this selection are the scaling tendencies of components present in the solution and the production capacity. For instance, the availability of a direct cooling crystallisation process can be reduced significantly by scaling on the cooling surface. Depending on the added value of the product, this loss in availability may or may not be considered a problem. Another example, a crystallisation method requiring a vacuum system is very inconvenient for low capacity processes.

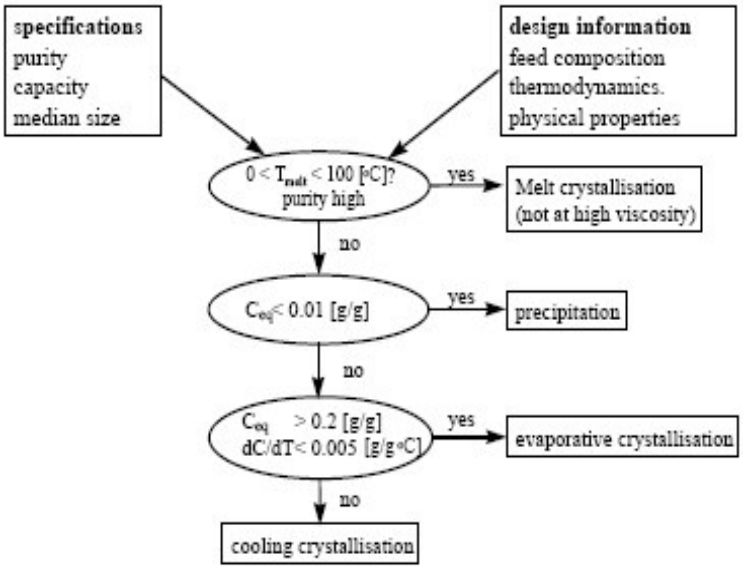


Figure 3.6 Crystallisation method selection (after Kramer et al., 1999)

• *Melt crystallisation:* Crystallisation from a melt is chosen when high product purity is required and the use of a solvent poses problems due to safety or environmental problems. This crystallisation method may pose problems at high melting temperatures or when the melt possesses a high viscosity.

• *Precipitation:* When the solubility of a component in a solvent is lower than approximately one weight %, precipitation is the appropriate crystallisation method. Because of the low solubility, high relative supersaturation values are required to obtain a reasonable production rate. These high supersaturations are obtained by adding two streams containing separate reactants that form a product with a very low solubility.

• *Evaporative crystallization:* Evaporative crystallization is economically more favourable than cooling crystallization if the solute's solubility has very small temperature dependence. However, the operation of such a process is usually more demanding as it typically takes place at sub atmospheric pressures and hence requires a vacuum system.

• *Cooling crystallization:* This crystallization method is energetically favourable and simple to operate. However, the prevention of fouling on the cooling surfaces and at the feed point may require major attention.

• *Flash cooling crystallization:* As an alternative for direct cooling using a heat exchanger, evaporative flash cooling can be used, which solves most of the fouling problems at the expense of a more complicated installation.

3.4.1.3.3 Other Design Variables. Operating conditions such as pressure and temperature are chosen such to obtain the highest possible yield, while obeying SHE constraints. Purity considerations determine the necessity for recrystallization steps and the maximum crystal growth rate. With increasing growth rates the tendency of components to cocrystallise and entrapment of mother liquor increase. This introduces an upper limit for the supersaturation. The maximum allowable supersaturation also depends on the metastable zone. When the concentration significantly exceeds this zone, excessive primary nucleation may occur, which is usually undesirable as it decreases the average crystal size.

3.4.1.4 Flowsheet Design of the Crystallization Process

The realisations of the design and operational variables from design level II are propagated to design level III, the flowsheet design of the crystallization process. Together with relevant initial design specifications from level 0, they constitute the objectives and constraints for level III. An overview of the design specifications, design and operational variables and domain knowledge for this level is given in Table 3.6. Note that at this level all products related specifications except the CSD have disappeared. If relevant, they are now present as operating windows for pressure, temperature and supersaturation. These operating windows are used, because it is currently unfeasible to incorporate calculations of product properties, such as

morphology and polymorphism, into dynamic process models including population balances.

To analyse the consequences of the choices at this design level on the CSD, a predictive process model consisting of thermodynamics, kinetics, mass, energy and population balances is required. As mentioned before, kinetic models cannot yet be derived from first principles only. Experimental design, experimentation and parameter estimation are hence an intrinsic step in crystallization design. The next chapter of this thesis is concerned with the development of a general crystallization process model for analysis and optimisation with respect to the CSD as well as domain knowledge acquisition concerning the kinetics.

Table 3.7 Design Level III - Flowsheet design of the crystallization process (Bermingham, 2003)

Design specifications Objectives and Constraints	**Design and Operational Variables**	**Domain knowledge**
Process: • Production capacity • Feed composition • Crystallization method • Yield • Pressure range • Temperature range • Supersaturation range • Energy consumption • Availability, controllability and Resiliency • SHE considerations *Product:* • Crystal size distribution	*Discrete:* • Operation mode • Number of stages • Feed configuration • Recycle structure • Location purge stream(s) *Continuous:* • Residence time in each stage or batch time • Recycle flow rates • Purge flow rate • Pressure and/or temperature in each stage • Heating/cooling duty or trajectory • Heat exchange rates	• Thermodynamic activity of species/components in solid, liquid and vapour phase • Physical properties, e.g. material densities, specific heats and viscosities • Crystallization kinetics, i.e. rate expressions for the nucleation, growth, attrition, agglomeration and breakage of crystals • Fouling kinetics • Shape factors of the crystalline components • Fire and explosion index

If a predictive crystallization process model is not available or a quick calculation is required, a first estimate for the residence time of a continuous process, τ, can be obtained from the following simple function involving the desired median crystal size, L_{50}, and an estimate for the crystal growth rate, G, (for instance taken from Figure 3.5):

$$\tau = \frac{L_{50}}{3.67 \times G} \qquad [3.1]$$

Another analysis, especially important for multiple stage evaporative crystallization processes, involves the energy consumption and heat Exchange surface area for the required heat exchange rates. The steam consumption and the total heat exchange surface area of an evaporative process consisting of N stages are proportional to respectively $1/N$ and N. Large deviations of the relationship for the surface area occur when a system exhibits significant boiling point elevations (BPE). When components with a high fouling tendency are present, time variant heat transfer coefficients need to be taken into account when sizing heat exchangers. For this purpose, another predictive model has been developed (Bermingham et al., 1999), which is not discussed any further in this thesis.

The resulting flowsheet design alternatives are propagated to level IV. If the suggested flowsheets contain multiple crystallization stages, the relevant information for each stage is propagated to different instances of design level IV.

3.4.1.4.1 Operation Mode. Criteria to select batch or semi-batch operation include a low production capacity, a short time-to-market, a short product lifetime, high value products, severe encrustation problems and a narrow CSD. According to Bennett (1993), continuous operation is typically only economically viable for relatively large production rates, viz from approximately 50 tonnes of product per day and upward. Nevertheless, a bulk product such as sugar is still produced batch wise because it leads to much narrower crystal size distributions than can be obtained from continuous

processes. Another reason for producing bulk crystalline materials via batch operation is the presence of materials that have a very strong fouling tendency and consequently lead to frequent interruption of an otherwise continuous operation. Batch crystallization is also employed when temperature or product characteristics require unusual precautions, or where very expensive materials are being handled and losses must be minimised, or when the cooling range is very wide. Finally, batch operated processes provide more flexibility with respect to feedstock and product requirements as they can be more easily adapted.

3.4.1.4.2 Staged Operation. A continuous crystallization process can be employed in a single or multiple stage configurations. Multiple stage or multi-effect operation can be attractive when evaporative requirements exceed the capabilities of a single vessel and/or energy costs dictate staging of the operation. Theoretically, the energy consumption and heat transfer area required for a multiple stage process are respectively inversely proportional and proportional to the number of stages. However, boiling point elevation decreases the temperature difference between the stages thus requiring an increased heat transfer area to maintain the same production capacity.

Multiple stage operation can also be economically interesting for cooling crystallization processes. A typical case is when a large flow at a high temperature and concentration is cooled and the mother liquor is returned from the final stage to a dissolving or leaching station for reconcentration. In such systems, multiple stages cooling are used to allow the mother liquor from the final crystalliser to be heated by the upstream crystallisers (Bennett, 1993).

Another possible reason to opt for a multiple stage configuration is the requirement to produce a narrow CSD. By operating a multiple stage process in series, the residence time distribution and hence the crystal size distribution will be narrower than the CSD produced in the same volume of crystallisers in parallel or in a single crystalliser of the same volume. The feed configuration of a multiple stage process is not only governed by

the required CSD but also by the feed temperature. A description of the various feed modes, viz forward, mixed, parallel and backward, is given by Mullin (1993).

Another potential advantage of multiple stage operation is the fact that crystal growth kinetics are usually favoured at higher temperatures. Because all stages except the last can be operated at a higher temperature than the corresponding single stage process, multiple stage operation can result in an enhanced overall crystal size distribution (Moyers and Rousseau, 1987).

3.4.1.5 Design of a Crystalliser Stage

Practically all the design specifications from the previous level are present at this design level. The set is extended with equipment related specifications and with design and operational variables propagated from the previous level (see Table 3.8). All products related specifications except the CSD appear implicitly in the form of operating windows for pressure, temperature and supersaturation.

At this level, hydrodynamics is added to the fields of domain knowledge. Applications of this knowledge include the sizing and operation of classification devices, determination of minimum circulation rates for adequate particle suspension and optimisation of the product removal location. The use of computational fluid dynamics (CFD) packages to obtain hydrodynamic information is on the increase for crystallization processes. However, it is not yet possible to combine CFD techniques with population balance modelling. To analyse the influence of kinetic-hydrodynamic interactions on the product CSD, the general crystallization model mentioned at the previous design level can be used in a compartmental manner to account for spatially distributed process conditions. The final design alternative can be propagated to a next level, design of instrumentation and control. This design level is not considered in this thesis. However, Westhoff (2002) has extended the hierarchical design procedure

presented here with two new levels, viz design of instrumentation and control and design of soft sensors.

Table 3.8 Design Level IV - Design of a crystallization stage (Bermingham, 2003)

Design specifications Objectives and Constraints	**Design and Operational Variables**	**Domain knowledge**
Process: • Production capacity • Feed composition • Crystallization method • Yield • Operation mode • Pressure and temperature range • Supersaturation range • Residence time (distribution) • Heat exchange rates • No boiling in heat exchanger • No entrainment of droplets by vapour • Suspension criterion • Availability, controllability and resiliency • SHE considerations *Product:* • Crystal size distribution	*Discrete:* • Crystalliser type • Fines classification and dissolution/clear liquor advance • Product classification • Heat exchanger type • Circulation device *Continuous:* • Equipment dimensions • Feed location • Product removal location • Solids concentration • Circulation flow rate • Operating conditions of classification devices • Flow rate through heat exchanger	• Equipment characteristics • Hydrodynamics • Thermodynamic activity of species/components in solid, liquid and vapour phase • Physical properties, e.g. material densities, specific heats and viscosities • Crystallization kinetics, i.e. rate expressions for the nucleation, growth, attrition, agglomeration and breakage of crystals • Fouling kinetics • Shape factors of the crystalline components

3.4.1.5.1 Crystalliser Type, Circulation Device, Heat Exchanger and Classification. The first selection at this level involves the crystalliser type, e.g. fluidised bed crystalliser, draft tube baffle crystalliser, draft tube crystalliser, forced circulation crystalliser or simply a mixed tank. The order, in which these crystallisers are mentioned here, usually coincides with decreasing crystal size for a certain crystallization system. This trend is also depicted in Figure 3.7.

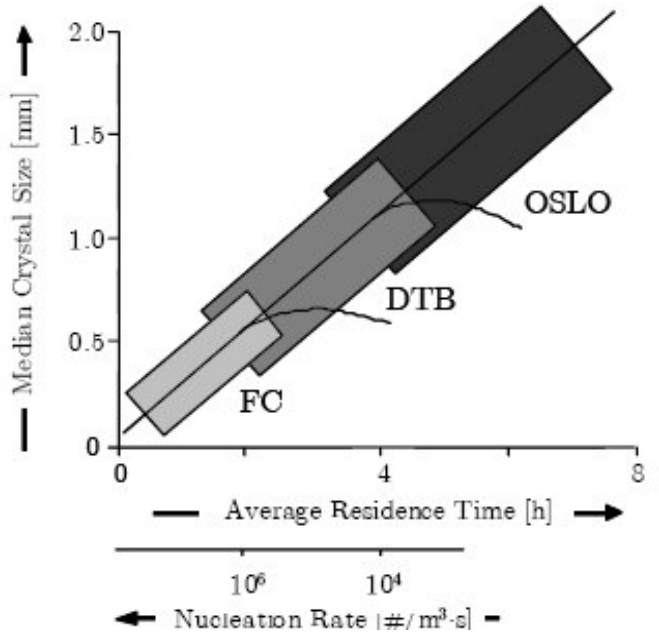


Figure 3.7 Expected median crystal size range for three basic crystalliser types as a function of residence time and nucleation rate (after Wöhlk et al., 1991)

The type of circulation device, impeller or pump, is determined by the crystalliser type and the mechanical properties of the crystals. For brittle materials, a device with a high pumping number must be selected to prevent excessive attrition.

Criteria for heat exchanger selection are low-pressure drops, to avoid flashing in heat exchanger, and fouling. If severe fouling is to be expected, a scraped surface heat exchanger should be considered. Alternatively, the heat exchanger will need to be cleaned regularly, in which case an external heat exchanger is preferable to an internal heat exchanger.

Fines or product classification can be employed to increase the average crystal size and/or stabilise the crystalliser with respect to the CSD. Fines classification with subsequent fines destruction is used to control the number of nuclei in a crystallization process. Fines classification can only be achieved in certain crystalliser types, as it

requires a settling zone, e.g. the annular zone of a draft tube baffle crystalliser and the upper part of the suspension chamber in a fluidised bed crystalliser. Product classification may be performed internally or externally. Internal product classification is induced by the use of an elutration leg, in which the product flow is withdrawn counter currently from the crystalliser with respect to the feed/circulation stream. Devices that can be used for external product classification include vibrating screens, hydrocyclones and hydrosizers (Gerla, 1995).

The different characteristics of the main crystalliser types with respect to the hydrodynamics, feed and product withdrawal configuration, mass and heat transfer are discussed below (after Neumann, 2001).

• *Agitated draft tube crystalliser:* After the agitated vessel, the draft tube (DT) crystalliser is the most commonly employed design in industry. This is mainly due to its simple design and good mixing characteristics. It is operated predominantly in batch or fed-batch mode, as vacuum or cooling crystalliser. An overview of practical and theoretical knowledge with respect to draft tube design and impeller selection is given by EKATO (1991). A more detailed analysis of the relationship between process and product performance on the one hand and crystalliser scale, impeller design and operating conditions on the other is given by Jancic and Grootscholten (1984) and Mersmann and Rennie (1995).

• *Forced circulation crystalliser:* The Forced Circulation (FC) crystalliser is the most common crystalliser type for continuous crystallization processes in industry. Distinguishing feature of this equipment type is an external circulation circuit. Typically, FC crystallisers are designed to operate at residence times of up to two hours and solid and densities within the range of 15 to 25 weight percent. Under these circumstances, the attainable median crystal size is in the range of 0.2 to 0.6 mm, which is comparable to that of the DT crystalliser. Generally speaking, the product obtained from commercial FC crystallisers is smaller and less uniform than that

produced in DTB or fluidised bed crystallisers. The FC crystalliser is therefore used for simple crystallization operation, where large crystal size is not a requirement. For further reading concerning design and operation of forced circulation crystallisers, the reader is referred to Bamforth (1965), Jancic and Grootscholten (1984), and Bennett (1993).

• *Draft tube baffle* crystalliser: The Draft Tube Baffle (DTB) crystalliser is employed to obtain larger average crystal sizes and narrower size distributions than can be produced in a DT or FC crystalliser. The main characteristics of this crystalliser are the removal and subsequent destruction of fine crystals in combination with relatively low volume specific attrition rates. Note that a prerequisite for operating a fines destruction system is an appreciably large density difference between solids and mother liquor. DTB units are designed to operate at residence times in the range of three to four hours and solid densities up to 25 weight percent. Under these circumstances the attainable median crystal sizes is in the range of 0.5 to 1.5 mm. More detailed information on this crystalliser type can be found in Bamforth (1965) and Bennett (1993).

• *Fluidised bed crystalliser:* A coarser crystalline product can be obtained by using a fluidised bed (FB) or Oslo crystalliser. This is a result of the fact that an FB crystalliser does not have a pump displacing the crystal suspension, such as the circulation pump in an FC crystalliser or the agitating device in a DT/DTB crystalliser. Instead, the crystals are kept in suspension in a fluidised bed, which is maintained by a large circulation flow of clear mother liquor. FB crystallisers typically operate at residence times of up to eight hours and solid densities of up to 40 weight percent. The resulting median crystal size is usually within the range of 0.6 to 2.5 mm. Note that successful operation of this crystalliser type also requires an appreciably large density difference between solids and mother liquor.

3.4.1.5.2 Dimensioning and operating conditions. Before using a comprehensive predictive crystallization process and product model to find the optimal crystalliser geometry and operating conditions, a number of empirical (shortcut) calculations can be performed to obtain initial guesses for these degrees of freedom. These calculations lead to a so-called basic crystalliser design (van Rosmalen et al., 1997).

• *Crystalliser volume:* The crystalliser volume is simply calculated from the desired production capacity, the maximum solids concentration that the equipment can handle and the residence time.

• *Area for heat Exchange:* The area required for heat exchange is a function of the production capacity, the selected crystallization method, the selected heat transfer mechanism and the system's thermodynamics. The selected crystallization method determines the maximum allowable temperature difference between the process and utility side. In cooling crystallization very small temperature differences, in the order of one to three Kelvin, have to be used to avoid fouling on the heat exchange surface. For evaporative crystallization the temperature difference is much less restricted provided the solubility curve of the crystallising component has a positive derivative with respect to temperature. However, care must be taken to avoid flashing in the heat exchanger, which requires the heat exchanger to be placed well below the liquid level in the crystalliser. In practice this poses few problems and as a result temperature differences of up to 25 to 30 Kelvin are possible.

• *Cross-sectional area for evaporation:* The diameter of an evaporative crystalliser has to be chosen such that entrainment of liquid droplets into the condenser zone is prevented. Formulas to calculate the maximum superficial velocity of the vapour and subsequently the minimum diameter that satisfies this criterion can be found in van Rosmalen et al. (1997) and Mersmann and Rennie (1995).

• *Circulation flow rate:* Initial estimates for circulation flow rates in crystallisers are typically obtained using empirical correlations for criteria such as a suspension criterion. To meet this criterion, the flow rate generated by a pump or impeller must be sufficient to keep most crystals in a suspended state. This implies that the local superficial velocity of the solution must exceed the settling velocity of a swarm of particles. A wide variety of relations are available in the literature to calculate this settling velocity, see for instance Mersmann (1988). A second criterion for the minimum required circulation flow rate or degree of macro mixing is related to liquid phase mixing. In order to prevent steep supersaturation gradients within the crystalliser, which may lead to excessive primary nucleation in certain areas and low crystal growth rate than others, the characteristic time for macro mixing must be less than the characteristic time for supersaturation depletion. Relationships for the calculation of these characteristic times are given by Garside (1985), Ploß (1985) and Mersmann (1988).

• *Flow through heat exchanger:* There are two aspects to the flow rate through a crystalliser's heat exchanger, viz the flow rate and superficial velocity. The flow rate is a function of the required heat duty and hence the process' production capacity as well as the temperature increases of the process stream per pass. As regards superficial fluid velocities, values in the range of 1.5 to 3.0 ms^{-1} are recommended to minimise fouling of heat exchanger surfaces and plugging of heat exchanger tubes (Moyers, 1987; Mersmann and Rennie, 1995).

CHAPTER FOUR
MICROWAVE DRYING

4.1 Introduction

The term dielectric heating can be applied logically to all electromagnetic frequencies up to and including at least the infrared spectrum. The lower frequency systems operate at frequencies through at least two bands: HF (3-30 MHz) and VHF (30-300 MHz). Thus the names high frequency (HF), dielectric, radiofrequency, and RF heating can often used interchangeably. However, it is generally accepted that dielectric heating is done at frequencies between 1 and 100 MHz, whereas microwave heating occurs between 300 MHz and 300 GHz. This makes the wavelengths in dielectric heating extend too many meters. Microwave wavelengths range from 1 mm to 1m. Practical heating applications, including those for drying, are done at 13.56, 27.12, 40.68, 896, 915, and 2450 MHz (Schiffmann, 1995).

Microwave energy is a nonionizing electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz. Microwave frequencies include three bands: the ultra high frequency (UHF: 300 MHz to 3 GHz), the superhigh frequency (SHF: 3 GHz to 30 GHz) and the extremely high frequency (EHF: 30 GHz to 300 GHz). Microwaves have extensive application in the field of communication; however, the Federal Communication Commission (FCC) has allocated certain frequencies for Industrial, Scientific, Medical and Instrumentations (ISMI) applications (Metaxas and Meredith, 1983; Cook, 1986; Roussy and Pearce, 1995). Currently, 2450 MHz is the most commonly utilized frequency for the home microwave oven which was invented by Percy L. Spencer almost 50 years ago (Spencer, 1949, 1952; Microwave Power in Industry, 1984; Schiffmann, 1995). It is reported that annual sales of home microwave ovens in the USA is $1.5 to $2.0 billion (Schiffmann, 1992, 1995). Although the basic principles of heating and drying at dielectric and microwave frequencies are the same,

the methods of generation and equipment are different (Schiffmann, 1995). These will be described separately later in this chapter.

4.2 Fundamentals of Microwave Heating

4.2.1 Electromagnetic Waves

We are surrounded by electromagnetic waves at all times. Light, x-irradiation, TV, AM and FM radio waves, ultraviolet, infrared, and microwaves are some of the common manifestations of these waves. All bodies in the universe, above absolute zero temperature, emit electromagnetic waves. The relationship of these waves is found in the electromagnetic spectrum (see Fig. 4.1). All electromagnetic waves are characterized by their wavelength and frequency, and illustration of a plane monochromatic electromagnetic wave is seen in Figure 4.2. It is seen that an electromagnetic wave is a blend of an electric component E and a magnetic component H. Note that E and H are perpendicular to each other and both are perpendicular to the direction of travel. This is what makes this a “plane” wave. Note further that the field strength at any point may be represented by a sine or cosine function, which is what makes it “monochromatic”. Further, it is “linearly polarized” since the electric and magnetic field vectors E and H lie in one direction only. The plane of polarization is YX for the E vector and ZX for the H vector.

Figure 1 also indicates that the wave is traveling in the X direction at the velocity C, which is equivalent to the speed of light in air or vacuum but slows as it passes through another medium, as indicated in Eg. (4.1):

$$V_p = \frac{C}{\sqrt{\varepsilon'}} \tag{4.1}$$

where

V_p= the velocity of propagation

C = the speed of light in air

ε' = the dielectric constant of the material through which the wave is propagated

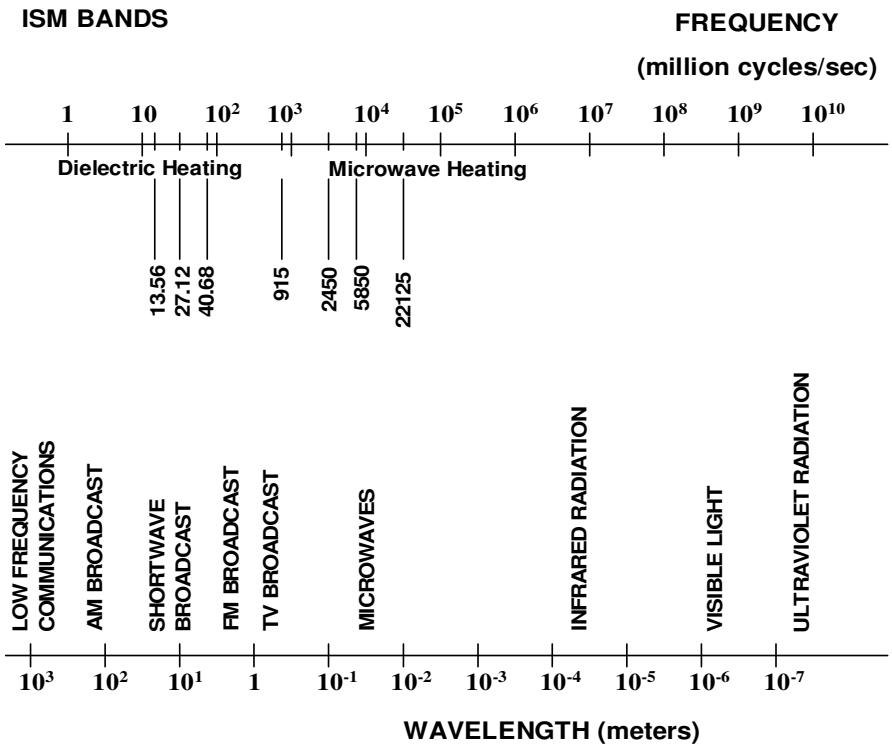


Figure 4.1 The electromagnetic spectrum (Schiffmann, 1995)

We further note the distance λ, which is the wavelength. Equation (4.2) shows the relationship between the frequency of the wave f, that is, how many times it goes through a full cycle per second, and the wavelength.

$$f = \frac{V_p}{\lambda} \tag{4.2}$$

Note that as an electromagnetic wave passes through a material its frequency remains the same; therefore, its wavelength changes, and this affects the depth of penetration, as will be seen later.

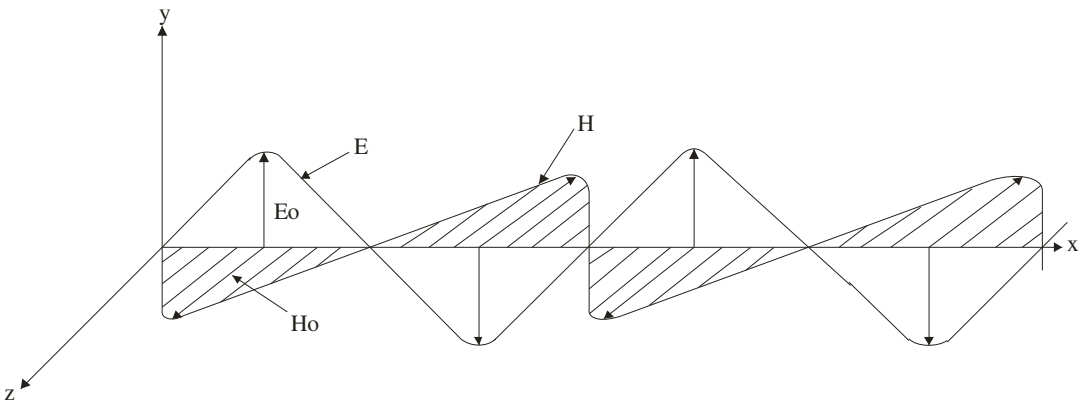


Figure 4.2 Diagrammatic illustration of a plane electromagnetic wave. E and H represent the electrical and magnetic components of the wave; E_0 and H_0 are their respective amplitudes (Schiffmann, 1995)

A further examination of Figure 4.1 indicates that an electromagnetic wave is an energy wave that changes its energy content and amplitude as its travels through a medium, as seen by a change in the amplitude of the wave. For example, if we trace the E component we see that at some point it is zero; then it builds up to a maximum value, decays to zero, and again builds up to a maximum value with the opposite polarity before again decaying to zero. The same thing happens to the H component. The amplitude of the wave any point along the X axis represents the electrical (E) or magnetic (H) field strength, which are measured as volts or amperes per unit distance, respectively. It is this periodic flip-flopping of the wave's polarity and its decay through zero that causes the stress upon ions, atoms, and molecules, which is converted to heat, and the greater the field strength, the greater will be the whole effect (Schiffmann, 1995).

4.2.2 Heating Mechanism

A crucial fact to keep in mind at the all times is that microwaves and dielectrics are not forms of heat but rather forms of energy that are manifested as heat through their interaction with materials. It is as if they cause materials to heat themselves

(Schiffmann, 1995). There are many mechanisms for this energy conversion, as can be seen in only a partial listing in Table 4.1.

Table 4.1 Partial list of energy conversion mechanisms (Schiffmann, 1995)

Ionic conduction
Dipole rotation
Entire molecule quantized
Twist
Bend
Interface polarization
Dipole stretching
Ferroelectric hysteresis
Electric domain wall resonance
Electrostriction
Piezoelectricity
Nuclear magnetic resonance
Ferromagnetic resonance
Ferrimagnetic resonance

4.2.3 Ionic Conduction

Since ions are charged units they are accelerated by electric fields. In a solution of salt in water, for example, there are sodium, chloride, hydronium, and hydroxyl ions, all of which will be caused to move in the direction opposite to their own polarity by the electric field. In so doing they collide with un-ionized water molecules, giving up kinetic energy and causing them to accelerate and collide with other molecules in billiard ball fashion, and when polarity changes the ions accelerate in opposite fashion. Since this occurs many millions of times per second, large numbers of collisions and transfers of energy occur. Therefore, there is a two-step energy conversion: electric field energy is converted to induced ordered kinetic energy, which in turn is converted to disordered kinetic energy, at which point it may be regarded as heat. This type of heating is not dependent to any great extent upon either temperature or frequency (Schiffmann, 1995). This power developed per unit volume (P_v) through is shown as

$$P_V = E^2 q n \mu \quad (4.3)$$

where

q = amount of electrical charge on each of the ions

n = ion density, the number of ions per unit volume

μ = level of mobility of the ions

4.2.4 Dipolar Rotation

Many molecules, such as water, are dipolar in nature; that is, they possess an asymmetric charge center. Water is typical of such a molecule. Other molecules may become "induced dipoles" because of the stresses caused by the electric field. Dipoles are influenced by the rapidly changing polarity of the electric field. Although they are normally randomly oriented, the electric field attempts to pull them into alignment. However, as the field decays to zero (relaxes); the dipoles return their random orientation only to be pulled toward alignment again as the electric field builds up to its opposite polarity. This build up and decay of the field, occurring at a frequency of many millions of times per second, causes the dipoles similarly to align and relax many millions of times per second. This causes an energy conversion from electric field energy to stored potential energy in the material and then to stored random kinetic to thermal energy in the material. This temperature-dependent, molecular size-dependent time for build up and decay defines a frequency known as the *relaxation frequency*. For small molecules, such as water and monomers, the relaxation frequency is already higher than the microwave frequency and rises further as the temperature increases, causing a slowing of energy conversion. On the other hand, large molecules, such as polymers, have a relaxation frequency at room temperature that is much lower than the microwave frequency but that increases and approaches it as the temperature rises, resulting in better energy conversion into heat. This may lead to runaway heating in materials that at room temperature are very transparent to the microwave field. This must be superimposed upon the fact such liquids as water and monomers are better

absorbers of microwave energy than polymers. Since in drying or curing applications it is the liquids and monomers that require heating, not the existing polymeric substrate, it is possible to execute the process well, often at a lower temperature. In fact, it is even possible to dry such materials as foods and medicinals at cold or subfreezing temperatures (Schiffmann, 1995).

The power formula for dipolar rotation is

$$P_V = kE^2 f\varepsilon' \tan\delta$$

or

$$P_V = kE^2 f\varepsilon'' \tag{4.4}$$

where

k = constant dependent upon the units of measurement used

E = electric field strength, in volts per unit distance

f = frequency

ε' = relative dielectric constant, or relative permittivity

tan δ = loss tangent or dissipation factor

ε" = loss factor

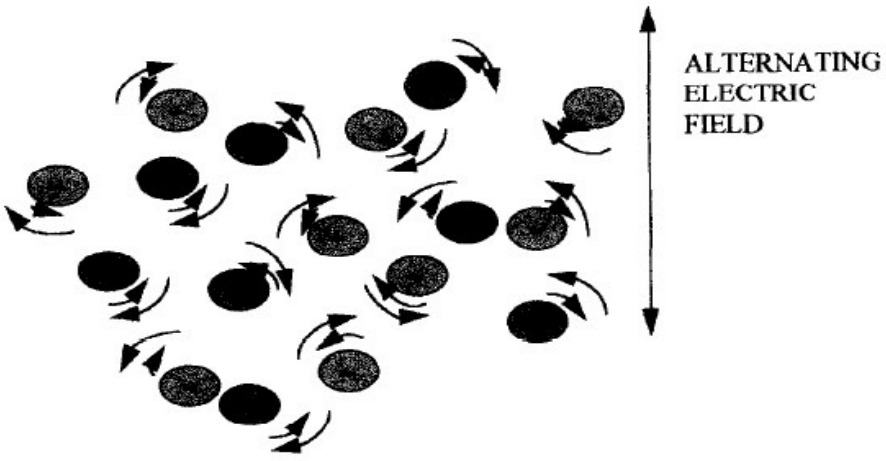


Figure 4.3 Dipole rotations (Haque, 1999)

The relative dielectric constant expresses the degree to which an electric field may build up within a material when a dielectric field is applied to the material. The loss tangent is a measure of how much of that electric field will be converted into heat.

A further examination of Eq. (4.4) reveals that E and f are functions of the equipment, whereas ε', ε", and tan δ are factors related to the material being heated. Another important point is that as frequency f is changed it is necessary to increase the electric field strength E in order to maintain a particular power level P_v. Since dielectric heating frequencies are much lower than microwave frequencies; this requires that the field strengths be much higher for comparable power output in a dielectric system. This may lead to voltage breakdown of air (arcing) or in the process material. The sparking threshold for air is about 30,000 V/cm (Schiffmann, 1995).

4.2.5 Interaction of Electromagnetic Fields with Materials

We may divide materials and the way they interact with electromagnetic fields into four categories:

- *Conductors*: Materials with free electrons, such as metals, are materials that reflect electromagnetic waves just as light is reflected by a mirror. These materials are used to contain and direct electromagnetic waves in the form of applicators and waveguides.

- *Insulators*: Electrically nonconductive materials, such as glass, ceramics, and air, act as insulators which reflect and absorb electromagnetic waves to a negligible extent and primarily transmit them (that is, they are transparent to the waves). They are field and may take the form of conveyor belts, support trays, dishes, or others. These materials may also be considered “nonlossy dielectrics”.

➢ *Dielectrics*: These are materials with properties that range from conductors to insulators. There is within this broad class of materials a group referred to as "lossy dielectrics", and it is this group that absorbs electromagnetic energy and converts it to heat. Examples of lossy dielectrics are water, oils, wood, food, and other materials containing moisture, and the like.

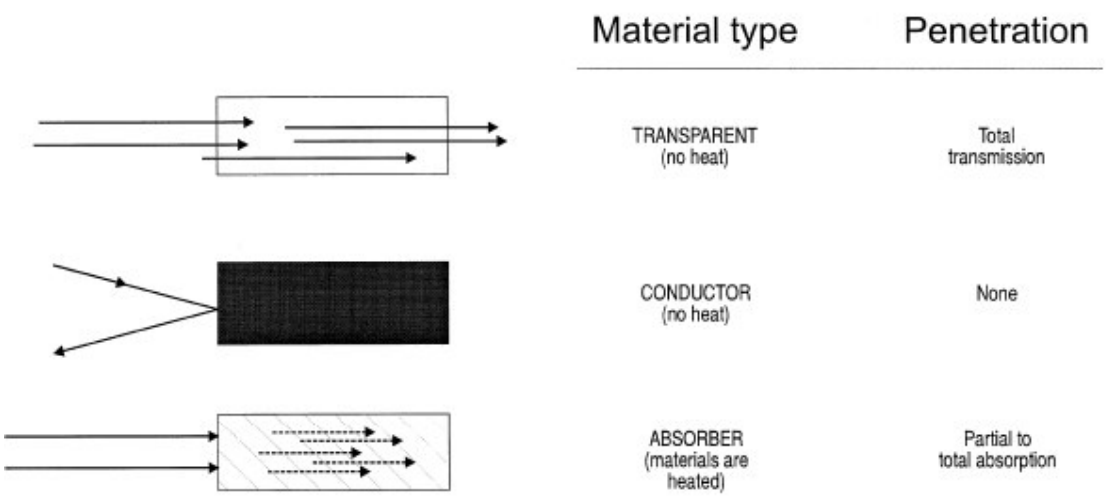


Figure 4.4 Interaction of microwave with materials (Haque, 1999)

➢ *Magnetic compounds*: These are materials, such as ferrites, that interact with the magnetic component of the electromagnetic wave and as such will heat. They are often used as shielding or choking devices that prevent leakage of electromagnetic energy. They may also be used for heating in special devices. As indicated earlier, those properties that govern whether a material may be successfully heated by a dielectric or microwave field are the dielectric properties: relative dielectric constant ε', loss tangent or dissipation factor (tan δ), and the loss factor ε".

Note that the complex dielectric constant ε may be expresses as

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (4.5)$$

where j = $\sqrt{-1}$, which indicates a 90° phase shift between the real (ε') and imaginary (ε") parts of the complex dielectric constant. The loss tangent is defined as the ratio of dielectric loss to dielectric constant:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{4.6}$$

These various factors are affected by several parameters:

Table 4.2 Heating properties of various materials (Schiffmann, 1995)

Heat Well	**Heat Poorly**
Water Acid anhydries Alcohols Aldehydes Ketones Amides Amines Nitrates Cyanides Proteins Halogenated hydrocarbons (unsymmetrical) Ferrites Ionic solutions	Hydrocarbons Halogenated hydrocarbons (symmetrical) Alkali halides (e.g., salt) Inorganic oxides (e.g., alumina) Some elements (e.g., sulfur) Boron nitride Mica

✓ *Moisture Content*: The amount of free moisture in a substance greatly affects its dielectric constant since water has a high dielectric constant, approximately 78 at room temperature; that of base materials is of the order 2. Thus, with a larger percentage of water the dielectric constant generally increases, usually proportionally. It should be emphasized that very complex phenomena occur when different dielectrics are mixed. However, a few rules of thumb may be applied.

a. The higher the moisture content, usually the higher is the dielectric constant.

b. The dielectric loss usually increases moisture content but levels off at values in the range of 20% to 30% and may decrease at still higher moisture.

c. The dielectric constant of a mixture usually lies between that its components.

Various materials, including alcohols and some organic solvents, also exhibit dielectric properties that make them suitable for heating with microwave and dielectric energy and, so, behave similarly to water. Table 4.2 indicates the heating properties of various classes of materials. Since drying is concerned with removal of water or a solvent, it is interesting to note that as these liquids are removed the dielectric loss decreases and hence, the material heats less well. In many cases this leads to self-limitation of the heating as the material becomes relatively transparent at low moisture content. This has great value in obtaining moisture leveling, especially in sheet materials, in which the electromagnetic energy is likely to preferentially dry the wetter areas. Figure 4.5 shows a general graph of the variation in loss factor with moisture content. Water exists in materials in different states, for example, bound or free, and these states may be ascribed to different regions on the graph, as indicated by the change of slope (dε"/dm). Thus at low moisture contents, below the critical moisture content, we are dealing primarily with bound water; above it we encounter primarily free water. (Note that the dielectric loss of bound water is very low since it is not free to rotate under the influence of the electromagnetic field. This is seen in an analogous situation with ice, which has a dielectric loss factor of approximately 0.003; that water is approximately 12.) The change in the slope may be quite gradual for some materials, making positive identification fairly difficult. The critical moisture content for highly hygroscopic materials occurs between 10% and 40% (dry basis); for nonhygroscopic materials it is in the region of about 1%. It is obvious that moisture leveling will be quite effective above the critical moisture content but not so effective below it. Although some materials become quite transparent below the critical moisture content, there are others, such as wood and textiles, that will continue to heat and may scorch or burn.

✓ *Density*: The dielectric constant of air is 1.0, and it is, for all practical purposes, transparent to electromagnetic waves at industrial frequencies. Therefore, its inclusion in materials reduces the dielectric constants, and as density decreases so do the dielectric properties, and heating is reduced.

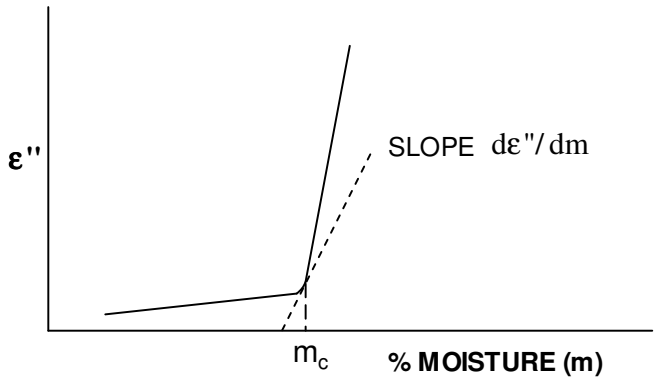


Figure 4.5 The critical moisture content is m_c. The dielectric loss factor is ε". The region below m_c is indicative of bound water, whereas above free water is more easily removed (Schiffmann, 1995)

✓ *Temperature*: The temperature dependence of a dielectric constant is quite complex, and it may increase of decrease with temperature depending upon the material. In general, however, a material below its freezing point exhibits lowered dielectric constant and dielectric loss. Above freezing the situation is not clear-cut, and since moisture and temperature are important to both drying and dielectric properties, it is important to understand the functional relationships in materials to be dried. Wood, for example, has a positive temperature coefficient at low moisture content; that is, its dielectric loss increases with temperature. This may lead to runaway heating, which in turn will cause the wood to burn internally if heating continues once the wood is dried.

✓ *Frequency*: Dielectric properties are affected by the frequency of applied electromagnetic field. However, since industrial heating is restricted to the ISM

frequencies, the engineer is limited in making use of this phenomenon. It may, however, be useful in measuring moisture content.

✓ *Conductivity*: Conductivity refers to the ability of a material to conduct electric currents by the displacement of electrons and ions; this effect is described in detail in Section 4.2.3. Suffice it to say that these charged units can have a major effect in heating, and in a drying situation in which the ion concentration increases as the water is removed, this effect can be very complex.

✓ *Thermal Conductivity*: Thermal conductivity often plays a lesser role in microwave and dielectric heating than in conventional heating because of the great speed with which the former heat thus reducing the time in which thermal conductivity can be effective. There are cases, however, in which it has a major role. For example, when penetration depth of the electromagnetic energy is small in comparison with the volume being heated, thermal conductivity may be dependent upon to transfer the heat to the interior. Another important case is to even out the nonuniformities of heating that may occur with electromagnetic fields. Sometimes the microwave or dielectric power is pulsed on and of to allow for this evening out of temperature, as in microwave thawing.

✓ *Specific Heat*: The specific heat parameter is often neglected by the researcher or engineer dealing with electromagnetic heating who focuses attention only the dielectric properties. However, specific heat can be have profound effects and may, in fact, be the overriding parameter, causing materials to heat much faster than one would predict by looking only at their dielectric prosperities.

✓ *Penetration Depth*: Although not a property of a material but rather a result of its various properties, penetration depth is of utmost importance. Since electromagnetic heating is, in effect, bulk heating, it is important that the energy penetrate as deeply as

possible. If it does not, field into the material are wavelength, the dielectric constant, and loss factor, as shown in Eq. (4.7)

$$D = \frac{\lambda_0 \sqrt{2}}{2\pi}\left[\varepsilon'\left(\sqrt{1+(\varepsilon''/\varepsilon')^2}-1\right)\right]^{-1/2} \tag{4.7}$$

where D is the penetration depth at which the available power in the material has dropped to about 37% (1/e) of its value at the surface and λ_0 is the free space wavelength. If ε" is low, Eq. (7) may be simplified:

$$D = \frac{\lambda_0 \sqrt{\varepsilon'}}{2\pi\varepsilon''} \tag{4.8}$$

This equation is reasonably accurate for most foods even though many have relatively high ε" values.

From these equations it is obvious that materials with high dielectric constants and loss factors will have smaller depths of penetration than those with lower values. It is also apparent that the depth of penetration is greatly affected by the wavelength (and hence the frequency) of the applied field.

A peculiarity of this type of heating is the unusual temperature gradients that may be generated. This is due to a number of factors. First, unless an auxiliary heat form is applied, the air in the system remains cold. Hence, the surface will be cooler than a zone somewhat below the surface. This is especially true in a drying system in which evaporative cooling the surface will occur.

Another circumstance concerns the depth of penetration as it relates to the size of the piece being heated. If the piece is several times larger than the depth of penetration, then the temperature gradient will resemble conventional gradients, with a cooler

interior and a warmer exterior. However if the piece is small in comparison with the penetration depth, for example only one or two times greater, then there may be a focused accumulation of the electromagnetic field in the center of the piece due to the multiple passes of the waves and internal reflections. In this case, the center may be the hottest place, and in fact, if it is overheated, the center may burn while the surface remains cool.

4.3 Basic heating system

The microwave heating system is made up of four basic components: power supply, magnetron, applicator (i.e., oven) for the heating of the target material and waveguide for transporting microwaves from the generator to the applicator. Fig. 4.6a shows a simplistic diagram of the microwave heating system. Fig. 4.6b and c represent industrial size batch and continuous operations microwave heating systems (Microwave Power in Industry, 1984). The batch-type microwave heating system is similar to a home microwave oven in that the work material is placed in a metal applicator (i.e., oven) for heating and removed when heating is complete. The microwave power is supplied from a self-contained microwave power supply unit that contains a magnetron tube, transformer, relay, choke and controls. The microwave energy is directed to the applicator by a waveguide. The continuous-type microwave heating system is equipped with a conveyor belt to move the material through the oven for heating. Generally, the conveyor belt is made from an insulator. Commonly, an industrial size microwave heating system employs 915 MHz frequency with a magnetron as high as 75 kW power and an average working life of 6000 h (Microwave Power in Industry, 1984; Smith, 1993). Applicator design for an industrial application is very much dependent on process specificity. It is usually not an off-the-shelf item. In fact, it is an engineering-intensive part of a microwave heating system. The critical issues in applicator performance are power efficiency, uniform power distribution, and consistent and reliable performance over the expected range of process conditions (Reid et al., 1993).

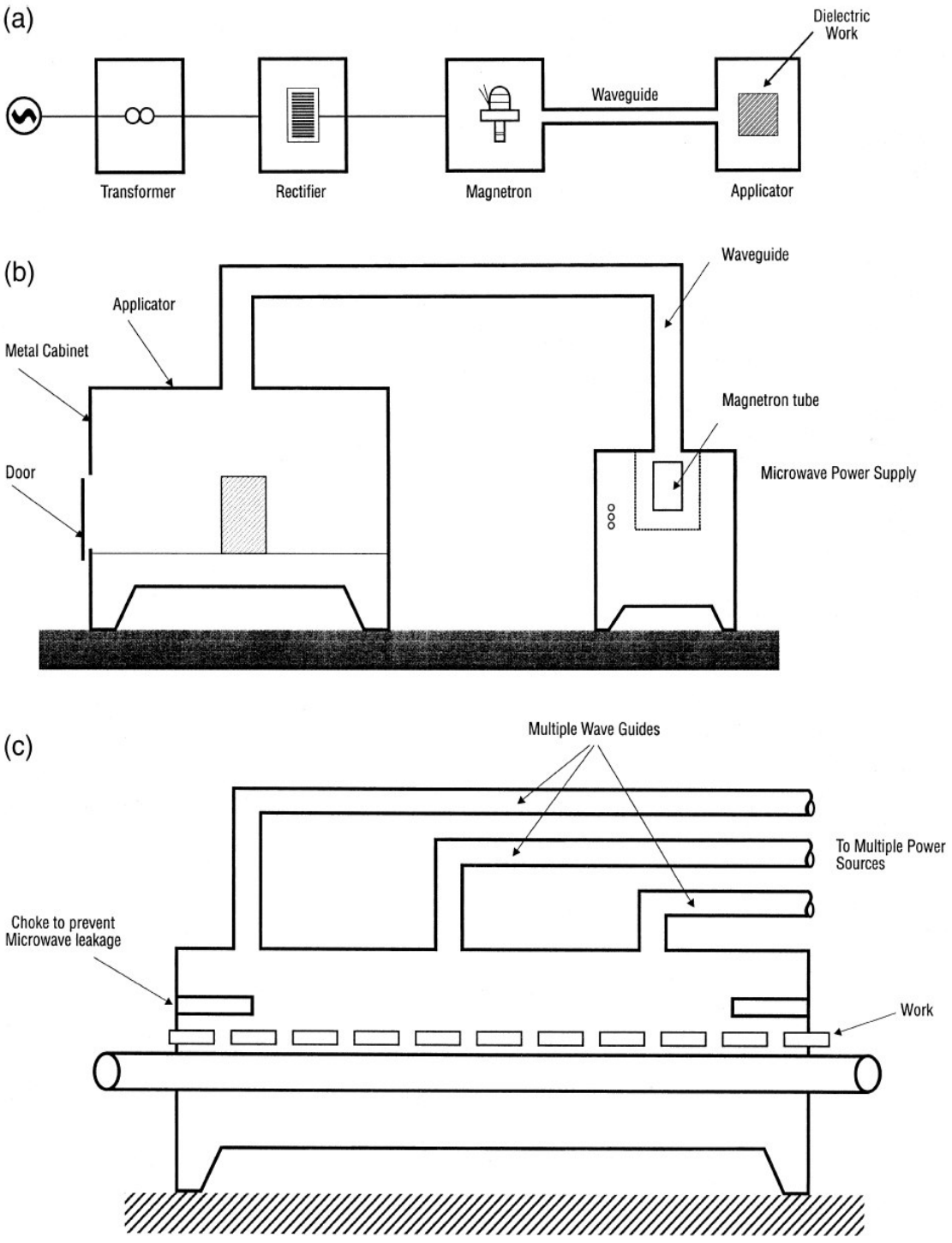


Figure 4.6 (a) Microwave Heating System. (b) Batch-type equipment. (c) Continuous-type equipment (Haque, 1999)

4.4 Drying Applications of Microwave

Microwave energy is finding increasing application to the drying of various kinds of materials and products such as agricultural, chemical and food product, textile, paper, lumber and many more (Cook, 1986; Schiffmann, 1995; Doelling et al., 1992). Generally, drying refers to the removal of physically adsorbed solvent such as water, acid or high vapour pressure organic substance (e.g., alcohol, acetone, ether, halogenated hydrocarbons, aromatics, etc.).

The major field of interest for microwave heating has been food processing, typical of which is the very successful applications to meat and butter tempering in which the product can be taken in 25 kg blocks from a cold store and brought to a condition suitable for mechanical processing such as grinding of beef for burger production or blending and portioning of butter into 250 gram retail packs. In the example of meat the microwave, normally based on the 900 MHz band, raises the temperature from -18°C to -4°C at which it is easily ground but has not reached a stage where bacterial growth can occur. In butter tempering the ingoing temperature in the order of -14°C and is conditioned to +2°C, in 5 minutes which allows continuous process and better production control.

There is little evidence of microwaves in common use for drying at normal atmospheric pressures in any one industry. There are many examples both of current installations and in the literature of microwaves used for drying but they tend to be for special applications. The exception to this general observation is in the drying of pasta where significant number of microwave units has been installed. There made use of the volumetric heating effect of microwave and of heated high humidity air to ensure that case hardening and subsequent cracking did not take place. The result was a reduction in drying time from 8 hours to one hour.

The advantages of boiling point reduction at low pressure are realized in treating materials which are damaged or decompose at temperatures above 40°C, or sometimes even 15°C. The technique has been used with conventional heating for many years bur is exceptionally slow because convection is virtually absent in a vacuum oven and the only effective and controllable heat transfer mechanism is conduction from heated platens. Using microwave energy the rate of heat transfer is increased greatly and the uniformity of drying is excellent. Drying times of a few minutes to low moisture content (<4%) are possible.

Anhydration refers to the removal of water chemically bound to a substance present intermolecularly as well as to the intermolecular elimination of water from hydroxyl or carboxylic compounds. Generally, the vast majority of solvents are easily heated by microwave energy. It was observed that the dielectric loss factor of a material to be dried often decreases with the loss of solvent (Schiffmann, 1995). The author's unpublished results indicate that microwave heating can remove water from hydrated magnesium chloride ($MgCl_2.7H_2O$) and convert goethite (O=Fe–OH) into hematite (Fe_2O_3) (Haque, 1999).

If both the solvent and the substance to be dried are transparent to microwaves (i.e., no heating by microwave energy), then a suitable microwave heat accelerator, such as carbon, magnetite or silicon carbide must be added to the system to heat the added material to volatilize the solvent. This heating concept may be applied in the removal of volatile contaminants from soil, or even ore material (George et al., 1994).

4.5 Temperature measurement

Continuous temperature measurement during microwave irradiation is a major problem. Luxtron fluoroptic or accufibre can be employed to measure temperature up to 400°C but are too fragile for most industrial applications. An optical pyrometer and thermocouple can be employed to measure higher temperatures. Optical pyrometers,

such as the thermovision infrared camera, only records surface temperature, which is invariably much lower than the interior sample temperature. When a thermocouple (metallic probe) is employed for temperature measurements, arcing between the sample and thermocouple can occur leading to failure in thermocouple performance (Chen et al., 1984; Kingston and Jassie, 1985; Wickeraheim et al., 1991). A recent development is the ultrasonic temperature probe, which covers temperatures up to 1500°C (Reid et al., 1993).

The US Bureau of Mines employed a Type K thermocouple with an unground tip sheathed in Inconel 702, and stainless steel 440 for temperature measurement of oxide and sulphide materials. The accuracy of thermocouple data was within ±2%; however, an error of greater than ±2% was expected for samples transparent to microwaves (Walkiewicz et al., 1988). The temperature of a microwave irradiated sample can be also measured by inserting a thermocouple into the hot material immediately after turning off microwave power. In addition to all these measuring devices, a temperature estimate can be made from phase changes of an easily identifiable mineral or compound present in the sample. However, the last method is not always reliable.

4.6 Economics of Microwave Drying System

In analyzing the economics of a microwave drying system, the cost can be divided into capital and operating costs, and this latter may be further broken down to tube replacement, general maintenance, energy, and floor space costs. We could also add costs for cooling water for the tubes or for materials specific to a system; however, we will concentrate on only the following: capital equipment cost, tube replacement cost, and energy costs (Schiffmann, 1995).

4.6.1 Capital Equipment Costs

Capital equipment costs refer to the cost of the equipment and are sometimes a bit difficult to define. For example, a microwave drying system may increase the throughput of a product dramatically and thereby necessitate the purchase of additional packaging equipment, conveyors, feed systems, and the like. In that case, the overall capital outlay would be much higher than for dryer alone.

Another problem in trying to compare the costs of microwave dryers is that the latter often include hydraulic or pneumatic presses, materials-handling devices, and the like, built into the system, whereas this is unusual for a microwave system. Also, suppliers express their costs in many different ways.

In general, though, we can limit ourselves to looking only at the basic drying system, consisting of the generator, tube, applicator, control system, and the conveyor, if there is one. In that case, some rough figures are available. Dielectric systems are usually the less costly of the two, especially at high power output, and recent estimates given by Schiffmann (1995) of $2500-$5000 per kilowatt, with the higher cost associated with lower power equipment. Microwave systems vary between $4000 and $7000 per kilowatt, again with the lower cost associated with higher power equipment. Higher costs are also related to higher degrees of sophistication and automation of these systems. Therefore, for drying systems, by estimating that 1kW of microwave or dielectric energy will remove 3.0 Ib of water per hour, we begin to get a feeling for the economic feasibility of applying these energy systems to a specific drying process. If it appears that over 100 kW is required to remove the water, then the capital cost may be prohibitive, particularly for the microwave system. However, it is imperative to remember that it is unlikely that all the water will be removed by microwaves, but they should be employed discretely along with a conventional form of heat energy. In that case, they may only be required to remove the last few percentages of moisture from a material, at a much reduced capital cost (Schiffmann, 1995).

Table 4.3 Tubes of approximate replacement costs (Schiffmann, 1995)

Size (kW)	Type	Frequency (MHz)	Life (h)[a]	Actual Cost ($)	($) per hour of operation per kW
2.5	Magnetron	2450	4,000	1,500	0.15
6.0	Magnetron	2450	6,000	3,300	0.09
50	Klystron	2450	25,000	69,000	0.06
30	Magnetron	915	8-10,000	5,300	0.02
50	Magnetron	915	6-8,000	6,000	0.02

[a]Approximate

As an example, consider the drying of bread crumbs from 27% to 5% moisture, at a rate of 1000 Ib of wet bread crumbs per hour. In such a system, it would be necessary to evaporate 231.6 Ib of water per hour (1000 Ib of bread crumbs contain 270 Ib of water, but when dried to 5% contain only 38.4 Ib of water). This would require about 77 kW to dry (231.6/3.0), plus an additional 20 kW to heat to the drying temperature, for a total of 97 kW, neglecting all heat losses. If we assume this system to have coupling efficiency of 75% (that is, the efficiency of coupling microwaves into the product), then a system of 130 kW is required, which would cost in excess of $650,000. On the other hand, if a conventional hot air is used to reduce the moisture from 27% to 12% and the microwave dryer to finish drying it to 5%, then the amount of water to be evaporated by the microwave system is only 61.6 Ibs, which requires 20.4 kW (61.1/3.0). Since the product is already hot, we need only increase the output to 27 kW to account for the 75% coupling efficiency (20.4/0.75). Such a system would cost of the order of $160,000 plus the cost of the less expensive conventional dryer (Schiffmann, 1995).

Note, however, that there are times when such a microwave dryer can be less costly than the conventional, especially when drastic improvements are made in the drying rate such that 25% or less time is required to dry a product (Schiffmann, 1995).

4.6.2 Tube Replacement Costs

The cost of tubes varies greatly, depending upon the output power. The least expensive tubes by far are the microwave oven tubes, the output power of which is of the order of 750 W and may be purchased, in quantity, for under $15 each. However, higher power tubes are far more expensive. The approximate replacement costs and the approximate tube lives are shown in Table 4.3.

4.6.3 Energy Costs

There was a time when electrically powered systems were considered too costly to operate for high-power applications. However, today, with the rising costs of oil and gas, this is no longer necessarily true, especially when far greater heating and drying efficiencies are possible with these systems. It is not practical to try to compare gas, oil, and electricity prices at this point since these are so variable. However, we can look at the conversion efficiencies of the various systems. In general, the conversion efficiency of electricity to microwave energy is estimated to be of the order of 45-50%, which includes losses in guide and applicator losses (about 10%). For dielectrics there is an approximately 60% overall efficiency, based on a combined filament, control, and dc supply efficiency of 92%, times a tube efficiency of 73%, times a circuit efficiency of 90% (Schiffmann, 1995). Thus the energy cost per hour may be calculated as

Energy cost/hour = (utility rate/kWh) (kW of system) (efficiency)

4.6.4 Other Costs

Other costs may be considered, such as the cost for floor space for the system and the cost of maintenance. These may vary for individual situations and cannot be considered here. We may, however, consider the cooling water cost. Many of the tubes are water cooled, and the cost for the cooling water should be considered. The water requirements

are directly proportional to the output power of the tube; for example, a 6-kW magnetron at 2450 MHz requires 1.5 gal/min; a 30-kW magnetron at 915 MHz requires 5 gal/min (Schiffmann, 1995).

CHAPTER FIVE
MODEL DEVELOPMENT

5.1 Introduction

5.1.1 Drying Applications in the Soda Industry

Sodium carbonate and sodium bicarbonate are the main products in the soda industry. The production methods of them were presented in Chapter 2. Sodium carbonate, soda ash is used as a source of Na_2O in the glass manufacture, in the production of various sodium chemicals for water treatment, paper production, iron desulphurization, and many other uses. Sodium bicarbonate, $NaHCO_3$ or "baking soda", is widely used in chemical and pharmaceutical industries, in animal feeds, in human food and other industrial and manufactured products (Garrett, 1992; Haynes, 1997).

In industrial applications, sodium bicarbonate and sodium carbonate monohydrate are dried after the crystallization operation. Drying operation carried out for the following reasons:

- To reduce cost of transport
- To make these products more suitable for handling
- To provide definite properties.

Sodium bicarbonate is dried in steam tube rotary or fluidized bed dryers by heating with air below 60 ºC (Thieme, 1992). In industry, the suspension of bicarbonate in the mother liquor (see Fig. 5.1) leaves the carbonation stage at 30 ºC and the centrifuged products may contain about 7% water (Thieme, 1992). In the case of using vacuum filters, the product may contain up to 18% water (Koksal, 2002). The free moisture removed by vaporization is generally carried away by air or hot gases.

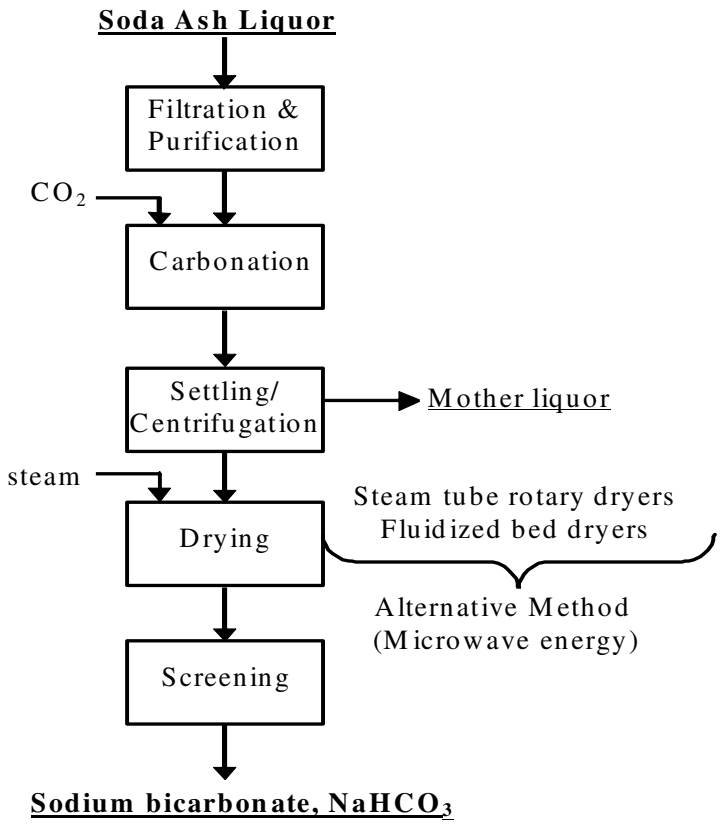


Fig. 5.1 Simplified flowsheet of the $NaHCO_3$ production process.

The drying and dehydration of the sodium carbonate monohydrate is carried out more frequently in steam-tube rotary dryers where the crystals are dehydrated into anhydrous soda ash at 150 °C to 200 ºC; however, fluidized bed dryers are also used (Garrett, 1992; Chen et al., 1999). The final product made by the monohydrate process is dense soda ash (Fig. 5.2).

$$Na_2CO_3 \cdot H_2O_{(s)} \rightarrow Na_2CO_{3(s)} + H_2O_{(g)} \qquad \Delta H_{298} = 58.770 \text{ kJ/mol } H_2O \qquad (5.1)$$

5.1.2 Problems of Current Drying Applications

With these products, it is essential that the crystals are not damaged during the drying process, and care must be taken to avoid contamination. In assessing the efficiency of

the drying process, the effective utilization of the heat supplied is the major consideration.

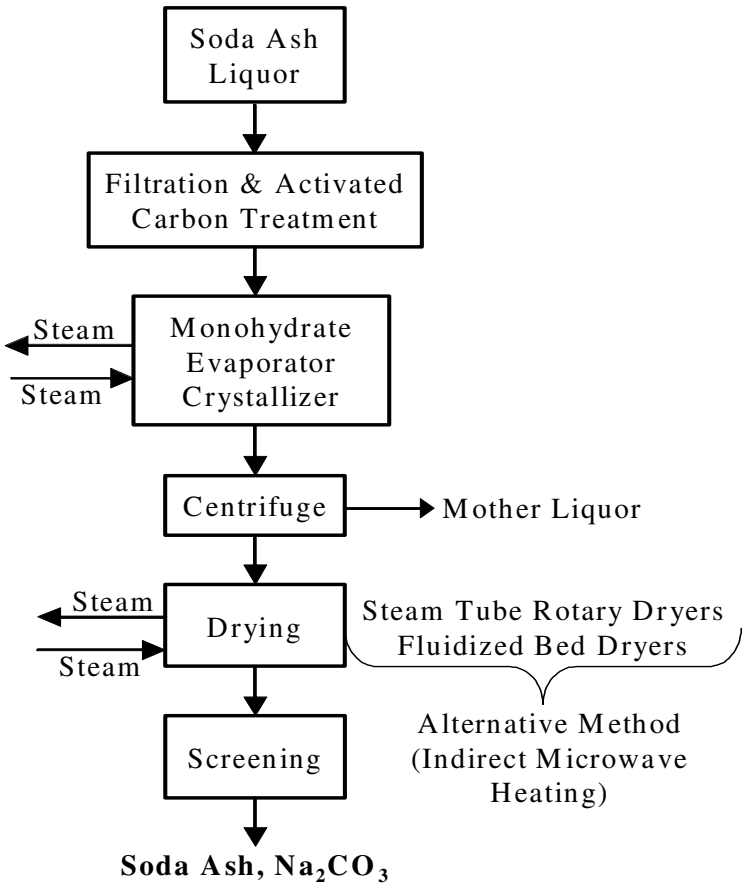


Fig. 5.2 Simplified flowsheet of the Na_2CO_3 production process

All such drying methods have common limitations, that is, the heat transfer from the surface to inside of the particle is principally by conduction and the process is slow. The maximum temperature of the heated surface to avoid product degradation is a limiting factor in the use of conductive heat transfer for drying. In addition, in rotary dryers; mixing is not good and gas temperatures are low. In fluidized bed dryers; the possibility of powder formation and dusting of the product is quite high as a result of attrition caused by collision of particles (Jones, 1992; Kocakusak et al., 1998).

5.2 Approach

In this investigation, microwave energy has been considered as an alternative approach to solve the problems with current drying processes.

Although drying techniques are cornerstones of many industrial applications and also almost universally understood these techniques have undergone dramatic developments over the last 30 years.

In recent years, microwave energy, was presented in Chapter 4, has found increasing application to the thermal processing of various kinds of materials and products such as agricultural, chemical, mineral processing and food product, textile, paper, lumber and many more (Jones, 1992; Khraisheh et al., 1997; Kingman and Rowson, 1998; Cha and Carlisle, 2000). MWs propagate through the materials and the accompanying transport processes result in dissipation of electric energy into heat, which lead to the term 'volumetric heat generation' due to MW radiations (Jones, 1992). MWs are widely preferred over conventional heating mainly for shorter processing times. During conventional heating the heat is radiated from the burner to the surface of the material and the material is heated due to surface heat flux whereas during MW heating, the material dielectric loss is responsible to convert electric energy into heat within the entire volume (Basak and Priya, 2005). The unique heating mechanisms of microwaves permit dramatic energy savings in many instances, as well as providing competitive benefits (Kingman and Rowson, 1998; Haque, 1999).

With this study a new drying technique is exposed that the sodium bicarbonate ($NaHCO_3$) powder can successfully be dried using alternative microwave energy with the evaporation of moisture only replacing the steam tube rotary or fluidized bed driers that are currently used in the industry to remove the excess moisture from the sodium bicarbonate powder (Fig. 5.1).

Energy transfer as heat from the surrounding environment to the wet solid can occur as a result of convection, conduction, or radiation and some cases as a result of combination of these effects (Haque, 1999). With this study a new drying technique is exposed as indirect drying with MW to dry sodium carbonate monohydrate, heat is transferred by conduction to the material, through a susceptor (Fig. 5.2). Silicon carbide was chosen as a susceptor due to its absorption characteristics of microwaves (MWs). Earlier studies on MW heating of ceramic materials show that SiC absorbs MWs considerably so that SiC resulting in greater heating in SiC (Basak and Priya, 2005; Chatterjee et al., 1998). One of the reasons to use ceramic in this study is that the ceramics can withstand high temperature. In addition, the temperature profile within the ceramic materials is uniform due to higher thermal conductivity and these materials may be the perfect choices to be used as supports.

5.3 Design of Experiments

The aim of this work was to develop novel, alternative process routes based on the principle of Drying with Microwave Energy to replace the entire, energy-consumptive, current production routes.

With the aim to fundamentally understand and to control this new process, not only the process routes were developed and tested experimentally, but also the fundamental conversion mechanisms were investigated.

5.3.1 A New Process Alternative: Drying Of Sodium Bicarbonate with Microwave

In this work, currently available process routes for the production sodium bicarbonate are compared, based on product qualities as after and before the drying operation. In industry, the suspension of bicarbonate in the mother liquor (see Fig. 5.1) leaves the carbonation stage at 30 ºC and the centrifuged products may contain about 7% water (Thieme, 1992). In the case of using vacuum filters, the product may contain up to 18%

water (Koksal, 2002). In this study, sodium bicarbonate, produced by Merck, was wetted with aqueous saturated sodium bicarbonate solution at 30 ºC to obtain samples containing 7% to 15% water respectively. A saturated solution was used to avoid dissolution of fine particles.

5.3.2 A New Process Alternative: Drying Of Sodium Carbonate Monohydrate with Microwave

In this work, currently available process routes for the production sodium carbonate are compared, based on product qualities as after and before the drying operation. Trona ore was used to produce the sodium carbonate monohydrate crystals. Trona ore was obtained from Eti Soda Production Marketing Transportation & Electric Production Industry & Trade Inc., Beypazari.

The Beypazari pilot soda ash plant was simulated in a laboratory scale to produce sodium carbonate monohydrate crystals (Fig. 5.3). First trona was dissolved in hot water to produce the feed brine that has at least about 15 wt% total alkali value. Then insoluble impurities were removed by settling and filtration and treatment of the resulting soda brine by activated carbon to remove organic impurities before the calcination step of sodium bicarbonate in the brine. The conversion of bicarbonate to carbonate and the discharge of CO_2 were achieved by wet calcination and causticization steps. Next the soda ash liqour feed through a batch crystallization step. Sodium carbonate was recovered from its aqueous solution as sodium carbonate monohydrate by atmospheric crystallization.

The monohydrate was then converted to anhydrous sodium carbonate by calcining, i.e by removing the crystal water through heating of the monohydrate to temperatures 120°C or higher, with air and indirect microwave heating to compare them.

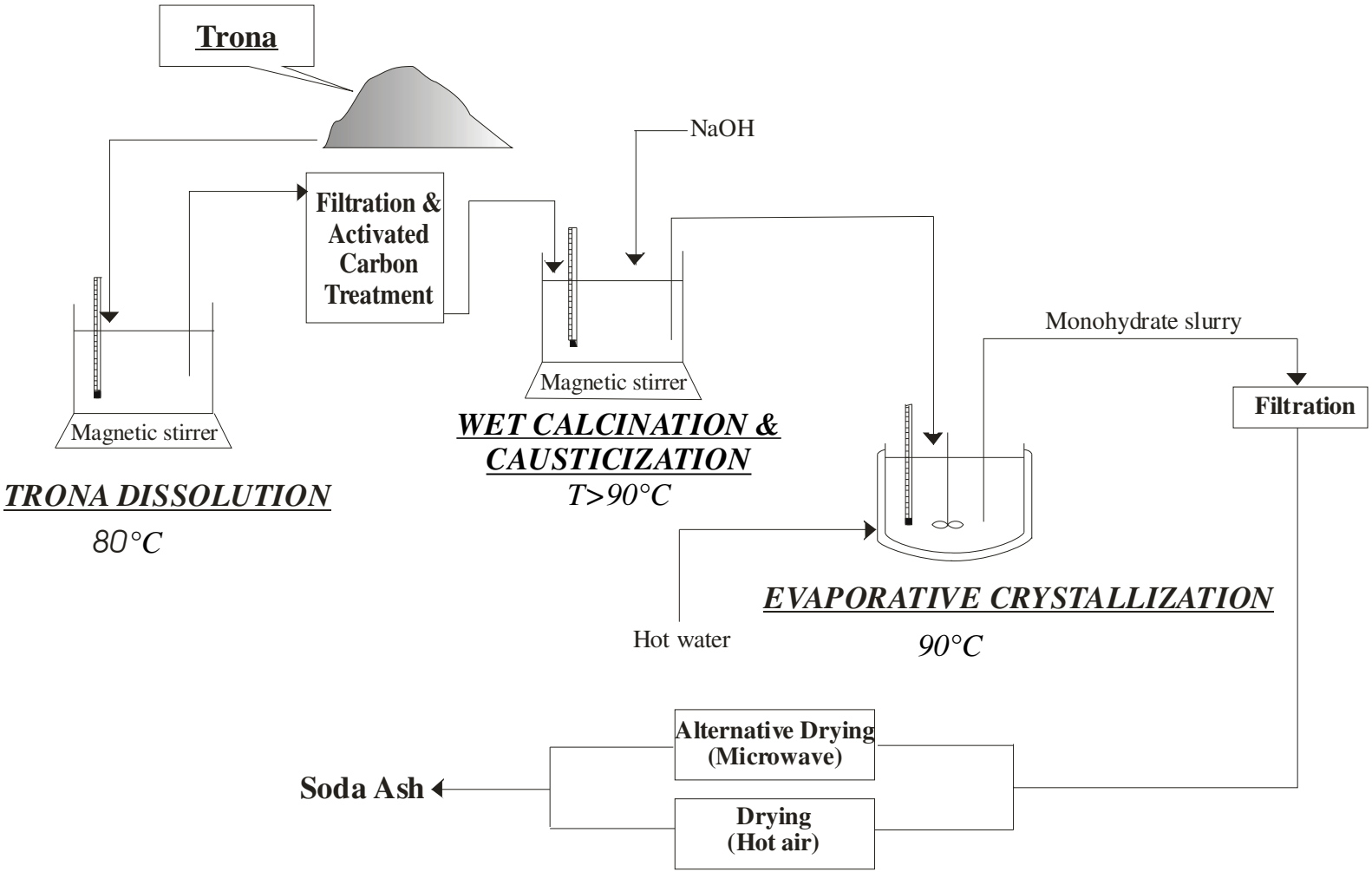


Figure 5.3 Experimental flowsheet of sodium carbonate production in laboratory scale

5.4 The Drawbacks of Microwave Drying Process

The application of microwave heating to industrial drying systems is of increasing interest, particularly because of the increased energy and operational efficiencies they afford. Their unique heating means provide benefits not obtainable from other, more conventional methods. However, their high capital costs generally require that they be used judiciously in conjunction with more conventional heat forms. Their unique properties also require the systems be designed by engineers thoroughly familiar with the art and science of microwave heating applications.

CHAPTER SIX
EXPERIMENTAL

6.1 Sodium Carbonate Monohydrate Production from Trona Ore

6.1.1 Composition of Tested Trona Ore Sample

Before beginning to characterize the trona sample obtained from the field, (1) a representative sample of the trona ore was obtained, (2) the sample for analysis was prepared, and (3) the most appropriate analytical procedure was selected.

Table 6.1 Composition of tested trona ore sample

Origin	Beypazari, Ankara, Turkey
Supplier	Eti Soda Production Marketing Transportation & Electric Production Industry & Trade Inc.
Trona Content	
Na_2CO_3	46,38 %-wt
$NaHCO_3$	35,93 %-wt
Insoluble impurities	1,05 %-wt
Soluble impurities	
Cl	230 ppm
SO_4	1250 ppm
Si	1240 ppm
Fe	210 ppm
Al	280 ppm
Ca	880 ppm
Mg	1160 ppm
K	200 ppm

The identification of trona sample was, of course, not only based on the instrumental analysis (Table 6.1), but also verified either from Scanning Electron Microscopy (SEM) images and powder X-ray diffraction (XRD) (Figs. 6.1, 6.2).

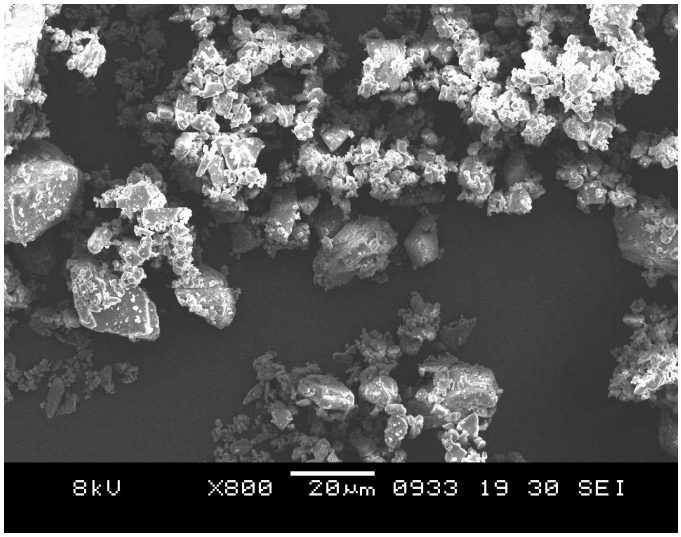


Figure 6.1 SEM image of trona ore sample

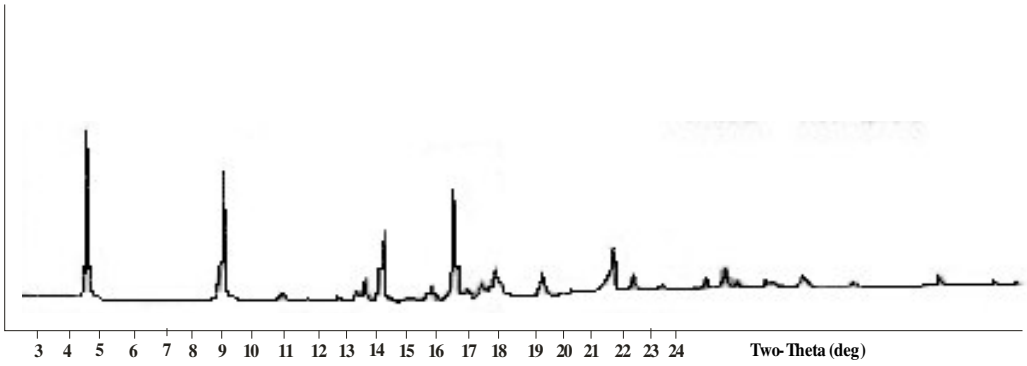


Figure 6.2 XRD pattern of trona ore sample

6.1.2 Dissolving the Trona Ore in Aqueous Solution

When trona dissolves in water, the situation is more complex. There is no simple dynamic equilibrium between trona and its dissolution products. As a matter of fact, the equilibrium solid phase is nahcolite or sodium bicarbonate. Under mass-transfer control, the solution at the interface is either supersaturated with respect to bicarbonate or bicarbonate will precipitate on the surface as trona dissolves and the composition moves to Point E on the phase diagram. In either case the mass-transfer model must take into account the separate identity of Na_2CO_3 and $NaHCO_3$. The resistance imposed by the

bicarbonate layer must also be included in the analysis if precipitation occurs on the trona surface (Haynes, 1997).

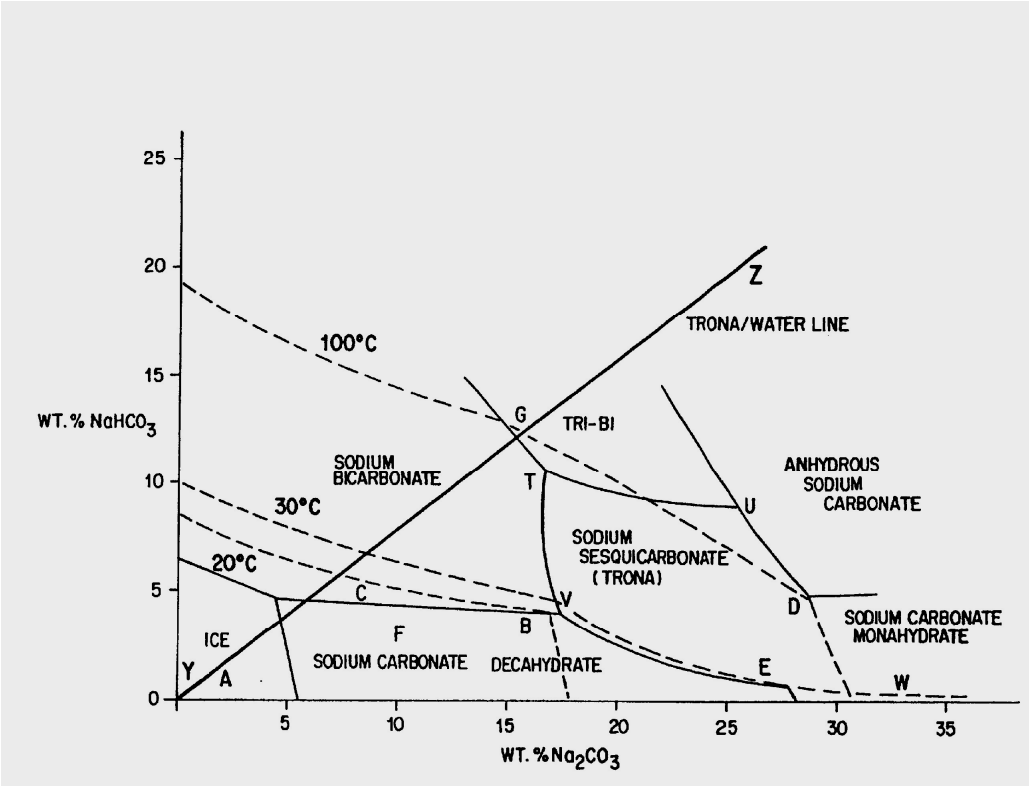


Figure 6.3 Ternary phase diagram for the system Na_2CO_3-$NaHCO_3$-H_2O

An understanding of this $NaHCO_3$-Na_2CO_3-H_2O equilibrium phase diagram (Fig. 6.3) is critical to the understanding of trona solution mining and to the processing of the brines so produced. Note the regions corresponding to solid sodium bicarbonate or nahcolite ($NaHCO_3$), trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), wegscheiderite ($Na_2CO_3 \cdot 3NaHCO_3$), anhydrous sodium carbonate (Na_2CO_3), sodium carbonate decahydrate or natron ($Na_2CO_3 \cdot 10H_2O$) and ice. Now consider the dissolution path A-A' when trona dissolves in water, and suppose that the system is being maintained at 40°C. Following the dissolution path from the origin, we see that the 40°C isotherm is encountered in the bicarbonate region. At this point the solution is saturated with respect to the bicarbonate but not with respect to the carbonate. With further trona dissolution,

the solution becomes supersaturated with bicarbonate. At some point thereafter, bicarbonate precipitates and the solution is enriched in carbonate until Point E reached. Here solid bicarbonate, solid trona and liquid of composition corresponding to point E (17.0 wt% Na_2CO_3 and 5.6 wt% $NaHCO_3$) are all in equilibrium. If the some case exercise is performed at other temperatures in the range 25°<T<87°C, it becomes evident that the carbonate solubility does not change greatly over this temperature range. In contrast, the bicarbonate solubility increases substantially as temperature is increased. Above 87°C the formation of solid wegscheiderite can occur (Haynes, 1997).

In all the dissolving experiments, preferably a recovered brine having a total alkali value of at least about 15 wt% by weight. Trona was dissolved in CO_2 free double distilled and deionized hot water to produce the feed brine. Such brine is normally about 4 wt% by weight sodium bicarbonate and about 13 wt% to about 16 wt% by weight sodium carbonate, the exact concentration and the residence time of the solvent against the trona ore. Sodium carbonate and sodium bicarbonate contents in the brine were always controlled by acid titration method.

Following dissolving operation, the brine was filtered to remove insoluble materials and treated with activated carbon to remove soluble organics from the brine.

6.1.3 Wet Calcination and Causticization

The thermal decomposition of sodium bicarbonate, $NaHCO_3$, to sodium carbonate, Na_2CO_3, is a key step in soda production. The decomposition of dissolved sodium bicarbonate in aqueous solution is commonly described by the following sum equation:

$$2NaHCO_{(aq)} \xrightleftharpoons{\Delta H_R} Na_2CO_{3(aq)} + H_2O_{(aq)} + CO_{2(g)} \uparrow \qquad (6.1)$$

$$\Delta H_{R,298.15K} = 19.75 \text{ kJ/mol}$$

The overall reaction mechanism is described by the following reaction scheme for pH>8.

1. Thermal decomposition of the bicarbonate ion:

$$HCO_{3(aq)}^{-} \xrightleftharpoons{\Delta H_R} OH_{(aq)}^{-} + CO_{2(aq)} \quad \Delta H_{R,298.15K} = 48.74 \text{ kJ/mol} \tag{6.2}$$

2. Neutralization of the excess bicarbonate by hydroxide:

$$HCO_{3(aq)}^{-} + OH_{(aq)}^{-} \xrightleftharpoons{\Delta H_R} CO_{3(aq)}^{2-} + H_2O_{(aq)} \tag{6.3}$$

$$\Delta H_{R,298.15K} = -40.99 \text{ kJ/mol}$$

3. Desorption of the excess carbon dioxide:

$$CO_{2(aq)} \xrightleftharpoons{\Delta H_R} CO_{2(g)} \uparrow \quad \Delta H_{R,298.15K} = 19.75 \text{ kJ/mol} \tag{6.4}$$

The predictive calculations indicate, that solid sodium bicarbonate is stable in contact with aqueous solution till about 70°C, i.e. carbon dioxide absorption / desorption will shift the composition of any saturated carbonate-bicarbonate slurry to form solid bicarbonate. Above 70°C, trona is predicted as the stable phase at atmospheric conditions.

The uncertainty in the calculated concentrations is about 10 wt%, which implies that the true transition temperature could lie between 60 and 90°C. Experimental data for dilute aqueous solutions from Splittgerber (1934) indicate that at 40, 60 and 80°C, the decomposition remains incomplete, reaching an equilibrium state between carbonate and bicarbonate, see Figure 6.4. This equilibrium is shifted towards almost complete

bicarbonate decomposition with increasing temperature and at 100°C complete conversion was achieved in two hours.

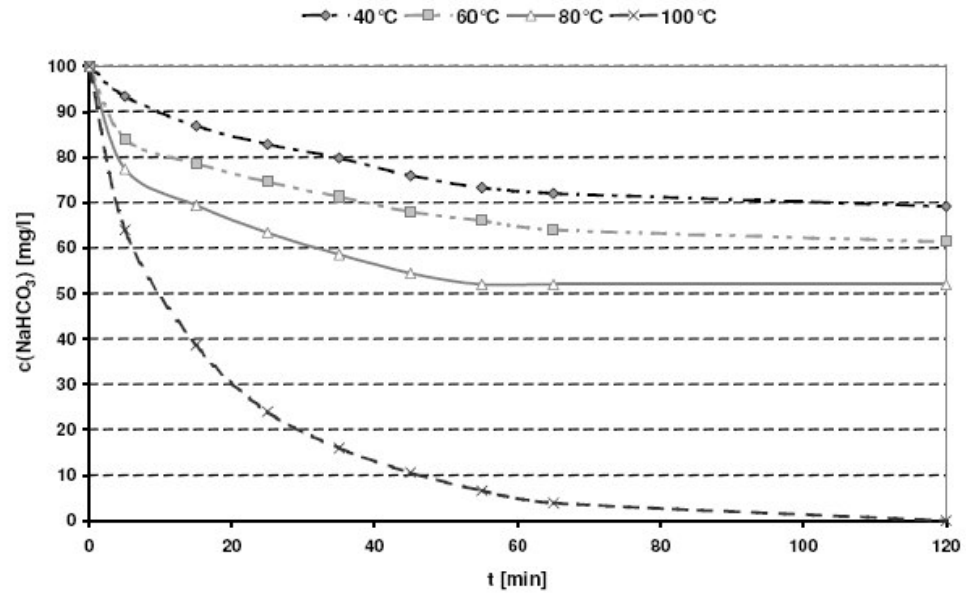


Figure 6.4 Thermal decomposition of aqueous $NaHCO_3$ (Splittgerber, 1934)



Figure 6.5 Experimental setup used for the fed-batch crystallization experiments

It can be concluded that the transition temperature for the recrystallization of solid sodium bicarbonate lies between 70 and 100°C, most probably around 90°C.

Following filtration, the first step involves the heating of the feed brine. The feed brine was heated to a temperature between about 90°C to about 100°C for 30 minutes (Eq. 6.2). Then its sodium bicarbonate content in the brine was calculated by acid titration method. According to its sodium bicarbonate content some sodium hydroxide, NaOH, was added the brine to neutralize of the excess bicarbonate by hydroxide (Eq. 6.3).

6.1.4 Evaporative Crystallization

It was the aim of the fed-batch experiments to grow crystals from a boiling solution. Figure 6.5 is a picture of the setup that was used for the experiments. From left to right the thermostat, crystallizer (with stirrer at the top) can be distinguished.



Figure 6.6 1.5 L jacketed stainless steel vessel (with 2 baffles)

All evaporative crystallization experiments were carried out in a jacketed 1.5 L stainless vessel (Fig. 6.6) that was heated with a water thermostat type U-15, MLW, Medingen. Stirring was provided with an Ika turbine stirrer (1000 rpm, which was sufficient to keep the particles suspended). At least 15 wt% soda brine was added to compensate for the evaporated water, thus ensuring a continuous addition of soda for growth of the monohydrate crystals. CO_2 free double distilled and deionized water was used in all experiments.

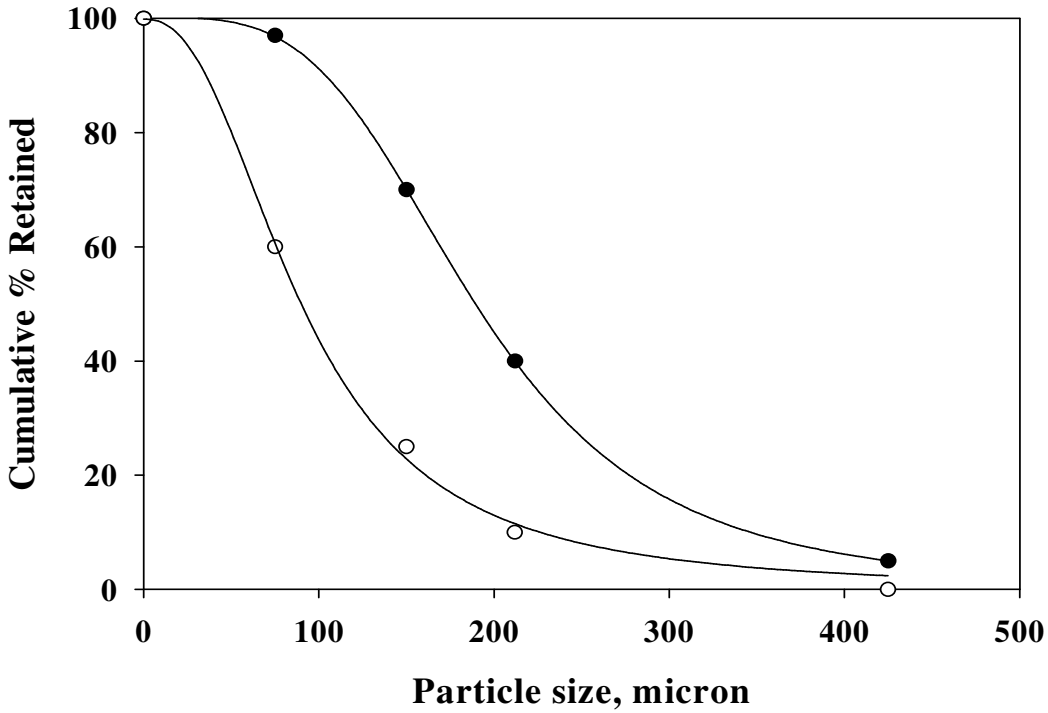


Figure 6.7 Particle-size distribution of monohydrate crystals for two different residence times; ●, 5 hours; ○, 2.5 hours

At the start of each experiment, the thermostating water was heated to 100°C. When this temperature was reached, the crystallizer was charged with 1500 grams of solution in which an amount of soda was dissolved to reach saturation the boiling temperature. This amount was based on the solubility concentration in the specified mixture at 90°C (see Fig. 2.4). When crystallizer content had reached the boiling temperature water was

added to compensate for the evaporated water. Then the experiment was started: 15 wt% brine was added from the storage vessel to crystallizer to replace the evaporated water.

During the experiment, the actual crystallizer temperature was measured with a calibrated thermometer to establish the exact boiling point of the solution. Slurry samples were taken from the crystallizer with 150-minute intervals. After filtering the monohydrate was dried in an oven (10 hours at 80°C).

Then the dried monohydrate crystals were screening to determine the particle sizes. The screens used were Tyler standard screens (Retsch, Germany). The monohydrous samples were taken with 150-minute intervals are depicted in figure 6.7. The product has an average particle diameter of over 75μm for a residence time of roughly 2.5 hours. However, the product has an average particle diameter of over 180μm for a residence time of roughly 5 hours. Residence time of 2.5 hours was resulted in a smaller average crystal size than the residence time of 5 hours.

6.2 Dehydration of Sodium Carbonate Monohydrate with Indirect Microwave Heating

The monohydrate crystals was then converted to anhydrous sodium carbonate by calcining, i.e by removing the crystal water through heating of the monohydrate to temperatures 120°C or higher, with air and indirect microwave heating to compare them.

Dehydration of sodium carbonate monohydrate ($Na_2CO_3.H_2O$) (SCM) in microwave (MW) field with silicon carbide (SiC) as an indirect heating medium was investigated. SCM samples containing up to 3% free moisture were placed in the microwave oven.

6.2.1 The Indirect Microwave Heating System

The present system was designed to generate a moderate thermal gradient, providing uniform and sufficient heating of the sample. In this study a Premier, PMO-20 microwave oven was modified as an indirect microwave heating system (see Fig. 6.8). It has a frequency of 2450 MHz with an output power of maximum 800 W and six different microwave output powers of 136, 168, 264, 440, 616 and 800 W. The heating profile of the oven conducted with water only shows an almost uniform magnetic field. The test was conducted by heating 100 ml water in a beaker and reading its temperature with about 5 seconds' delays, i.e., interrupting the power and reading the temperature.

A β-SiC plate (15 cm diameter) used as the susceptor material, containing the sample forming a layer of 1-2 mm thickness, was placed inside microwave cavity during treatment for absorption of microwave energy (see Fig. 6.8). Dehydration experiments were performed with 50 g samples.

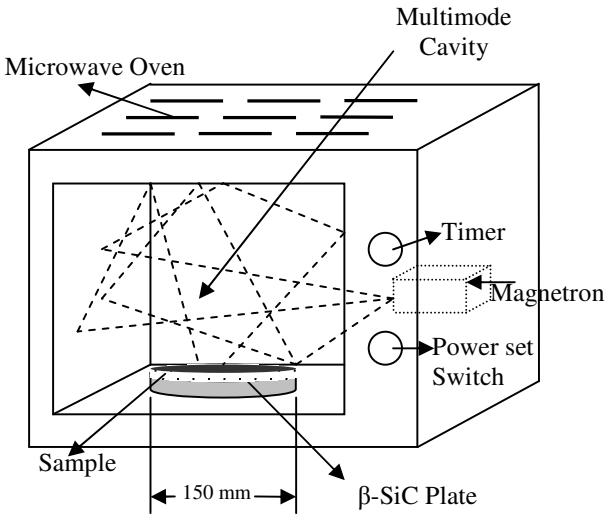


Figure 6.8 Schematic diagram of experimental apparatus

6.2.2 Solid phase analysis

As the crystal water of the monohydrate becomes unstable upon heating above ca.120 ºC, it desorbs to the surrounding air and monohydrate recrystallizes to anhydrate. The accompanying weigh loss of the sample due to desorption of the water can be used to determine the amount of monohydrate in the sample. The weigh loss for pure sodium carbonate monohydrate is:

$$X_{Na_2CO_3.H_2O} = \frac{M_{H_2O}}{M_{Na_2CO_3.H_2O}} = 0.1453 \qquad (6.5)$$

The weigh loss for pure sodium carbonate anhydrate is:

$$X_{Na_2CO_3} = 0 \qquad (6.6)$$

Whether the dehydration is complete or not is determined by placing the sample in an oven at 150 °C for 24 hours. The amount of crystal water in the samples was calculated from the decrease in weight. The identification of a crystal phase was, of course, not only based on the weigh loss of a sample, but also verified either from light microscopy, Scanning Electron Microscopy (SEM) images and powder X-ray diffraction (XRD).

6.2.3 Temperature Measurement

Continuous temperature measurement during microwave irradiation is a major problem (Haque, 1999). Owing to the thermocouple–field interaction leads to gross errors, temperature measurement in a continuous electromagnetic field using a thermocouple is usually impossible. Some researches used a very thin metal sheath surrounding the thermocouple could be used to overcome this problem, but contact between the thermocouple tip and the metal sheath must be avoided, while, shielding

reduces the response of the thermocouple (Ramesh et al., 1998). In this study, temperature of the irradiated sample was measured by DT-8819 non-contact infrared thermometer immediately after turning of the microwave power to overcome such these problems.

6.2.4 Absorption Characteristics of SiC and SCM

The rate of MW energy absorption by a material is determined by its dipole rotation and ionic conductance characteristics (Schiffmann, 1995). Here SiC is absorbed MW energy that provides heating by dipole rotation (Ramesh et al., 1998). The amount of thermal energy deposited into a material due to microwave heating (power absorption density) is dependent on the internal electric field strength within the minerals, the frequency of the microwave radiation, and on the dielectric properties of the material (Jones, 2004). If the electric field strength is known the power absorption density per unit volume for dipolar rotation of the mineral can be approximated from Eq. 6.7 and 6.8.

$$P_V = kE^2 f\varepsilon' \tan\delta \qquad (6.7)$$

or

$$P_V = kE^2 f\varepsilon'' \qquad (6.8)$$

where P_v is the power density (W/m^3), f is the frequency of the microwave radiation (MHz) current research is on 2.45 GHz, ε' is the relative dielectric constant or relative permittivity, ε" is the dielectric loss factor of the mineral, tan δ loss tangent or dissipation factor, and E is the electric field strength (V/m).

If a material does not have significant magnetic properties, only complex permittivity can be considered and defined by the following equations,

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (6.9)$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (6.10)$$

The complex permittivity, ε*, is related to the ability of material to couple electrical energy from a microwave field. The dielectric constant, ε', is a measure of the ability to store electrical energy in the material, and the loss factor, ε'', is related to the amount of energy a dielectric material can dissipate in the form of heat, and $j = (-1)^{1/2}$. The loss tangent, tan δ, is the ratio of dielectric loss to dielectric constant.

Table 6.2 The thermal and dielectric properties of SiC, Al_2O_3, and sodium carbonate, as collected from Basak and Priya (2005); Chatterje et al., (1998); Zhao et al., (2000)

Material Propety	Water*	SiC	Al_2O_3	Na_2CO_3
Density, ρ, (kgm^{-3})	1000	3100	3750	2533*
Thermal conductivity, *k*, ($Wm^{-1}K^{-1}$)	0.609	40	26	0.0418
Heat capacity, *Cp*, ($Jkg^{-1}K^{-1}$)	4190	3300	1046	1042
Dielectric costant, ε', (@2450 MHz)	78.1	26.66	10.8	5.3 - 8.4
Dielectric loss, ε'', (@2450 MHz)	10.44	27.99	0.1566	-

*Absolute density @25 ^oC

To explain the influence of microwave heating, the specific heat, thermal conductivity and dielectric properties of materials have to be considered. From Table 6.2, it is clear seen that SiC is the most suitable susceptor due to its high thermal conductivity and dielectric loss.

At a fixed microwave frequency, only the material properties ε* and $\tan\delta$ determine the total power dissipated within the sample. Both these parameters depend strongly on

temperature. Experimental time versus temperature curves for SiC and SCM are given in Fig. 6.9 and Fig. 6.10 for increasing power loadings.

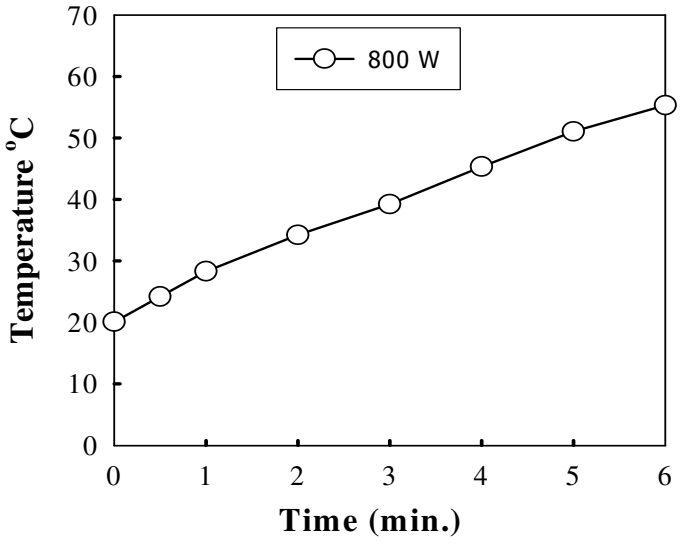


Figure 6.9 Heating behaviour of SCM in the microwave oven at 800 W for 6 minutes

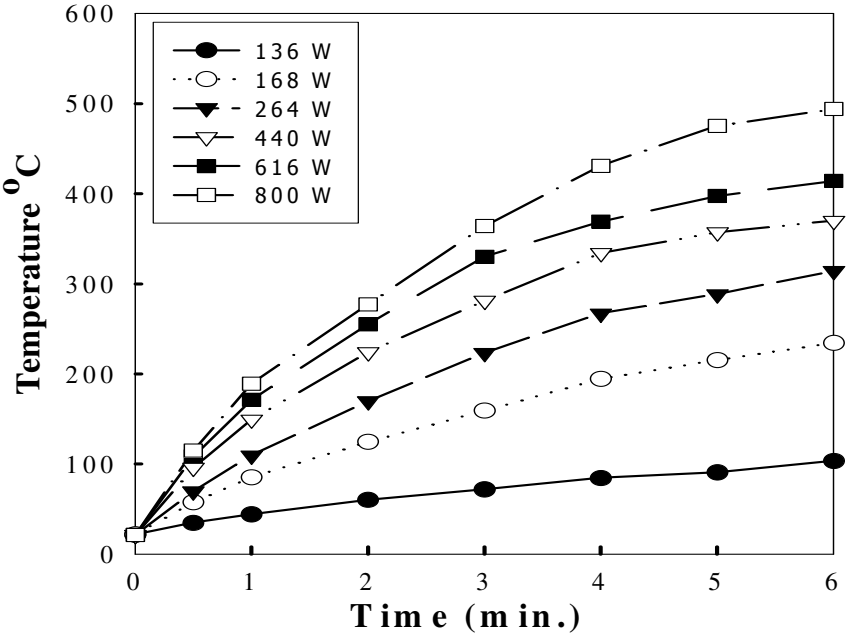


Figure 6.10 Effect of power-dependent microwave absorption on the heating of SiC plate

In order to understand interaction characteristics of SCM with MW, SCM powder, was spread on the teflon line sheet, placed into microwave oven and then irradiated at the highest power level (800 W). The results of irradiation tests, presented in Fig. 3, showed that the SCM was a poor absorber of the microwave energy for up to 6 minutes of irradiation. Experimental time versus temperature curves for SiC plate is given in Fig. 4 for increasing power loadings. A few minutes exposure, even at low power levels (136 W), the temperature of SiC plate increased rapidly. The figure clearly indicates the strong absorption of the SiC plate.

6.2.5 Penetration Depth

The dielectric constant and dielectric loss determine the depth of effective energy penetration into material. The penetration depth is defined as

$$D_p = \frac{\lambda_o \sqrt{2}}{2\pi}\left[\varepsilon'\left(\sqrt{1+\left(\varepsilon''/\varepsilon'\right)^2}-1\right)\right]^{-1/2} \tag{6.11}$$

where, D_P is the penetration depth, λ_o is the free space wavelength defined by $\lambda_o=c/f$, c being the velocity of light and f being the frequency.

In general, if the penetration depth exceeds sample thickness, the material behaves transparent. Volumetric heating results, if the penetration depth is comparable with the sample thickness. Otherwise, if the sample is too thick, absorption limits to the surface.

The results of irradiation tests, presented in Figure 6.9 and Figure 6.10, showed that while penetration depth exceeds the SCM thickness, it is comparable with the SiC plate. Due to the small penetration depth (~0.8 cm, estimated from Eq. 6.11) in SiC, the power decays rapidly from the faces. The property of SiC to rapidly heat in the presence of MWs is exploited to indirectly heat low loss materials like SCM, with SiC being used as a susceptor causing heat to be transferred by radiation to low loss sample. The

microwave penetration depth into the SiC plate also decreases as the temperature rises. Similar findings were reported in previous studies (Ramesh et al., 1998).

6.2.6 Results and Discussion

The SCM is a relatively poor microwave absorber (Fig. 6.9) then the SiC. Since, SiC is an excellent microwave absorber (Fig. 6.10), it was used to provide the quick warm-up of the SCM and the results are shown in Figure 6.11. The samples are processed for 6 min at 136, 168, 264, 440, 616 and 800 W. It can be seen that using SiC plate provided a significant increase in the sample temperature. Thus, a maximum temperature of 385 °C was achieved at 800 W. This strategy may be advantageous for achieving a greater heating rate.

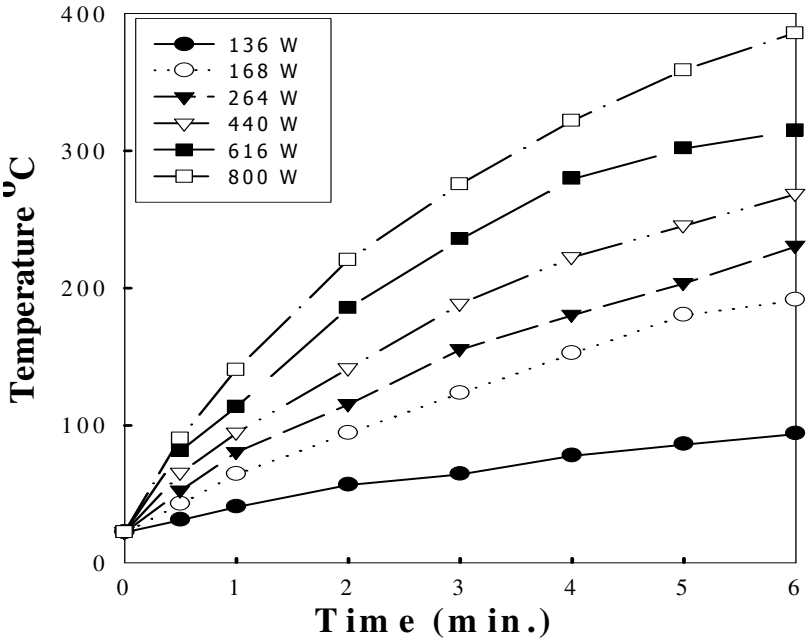


Figure 6.11 Effect of power-dependent microwave absorption on the heating of SCM on SiC plate

Besides the heat is transferred by conduction to the sample, the greater increase in the sample temperature is also explained by thermal runaway phenomenon. This type of

behaviour has been reported by a number of authors (Johnson et al., 1993; Barmatz and Jackson, 1992; Pickles, 2004). Though thermal conduction occurs to some extent, the dielectric loss tangent increases rapidly with temperature and thus steep temperature increases can occur. The area of the sample which interacts with SiC will heat faster than the rest of the sample. Then they will transfer their own temperature to the other parts of the sample and this phenomenon will occur again. Thermal runaway is a complicated phenomenon and depends on sample size, geometry and the relationship between the relative dielectric constant (ε') and temperature (Pickles, 2004).

It has been seen that the complete drying or conversion occur at 440 W and upper power levels as shown in the Fig. 6.12 from the heating weight loss analysis with heating in an oven at 150 °C for 24 hours. It was shown that the dehydration began almost immediately under microwave energy at a bulk temperature of 140 ^{o}C. Eighteen percent of SCM was converted within only two minutes at 440 W. At 136 W there is no dehydration was observed because the temperature did not increase significantly.

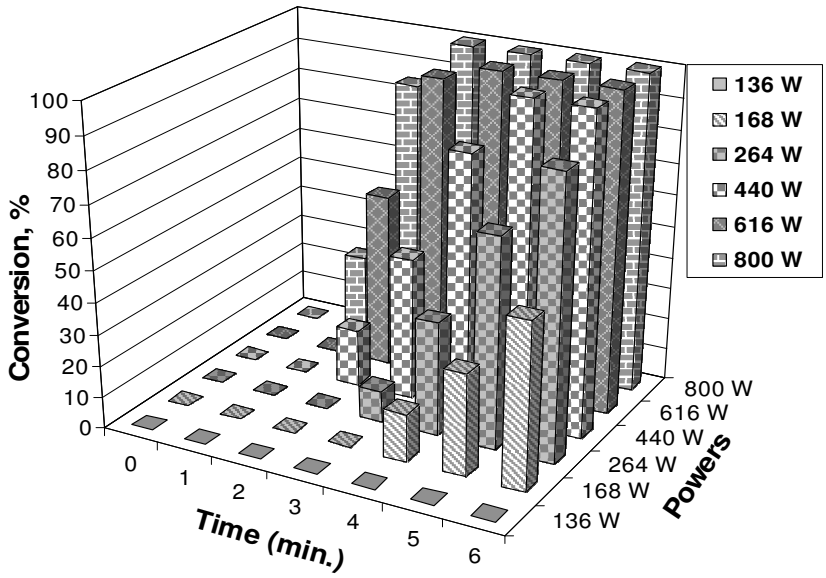


Figure 6.12 Sodium carbonate ratios after MW irradiation of SCM at different microwave energy levels

In an attempt to understand the effect of the different drying techniques on the quality of the produced sodium carbonate anhydrate, a comparison was made between dehydration and drying in a fluidized-bed versus indirect microwave heating using with the excellent study of Chen et al. (1999). According to this study monohydrate conversion begins approximately 100 s after the operation commences, a steady-state conversion of about 0.33 is reached after about 10^4 s. As seen from the Fig. 6 in MW heating complete conversion of SCM was achieved within only two minutes at 800 W. In addition to this the results of the microwave versus conventional heating experiments are clearly shown in Fig.7 as conversion of the SCM versus time. Moreover, microwave heating provides great time savings, compared with conventional drying.

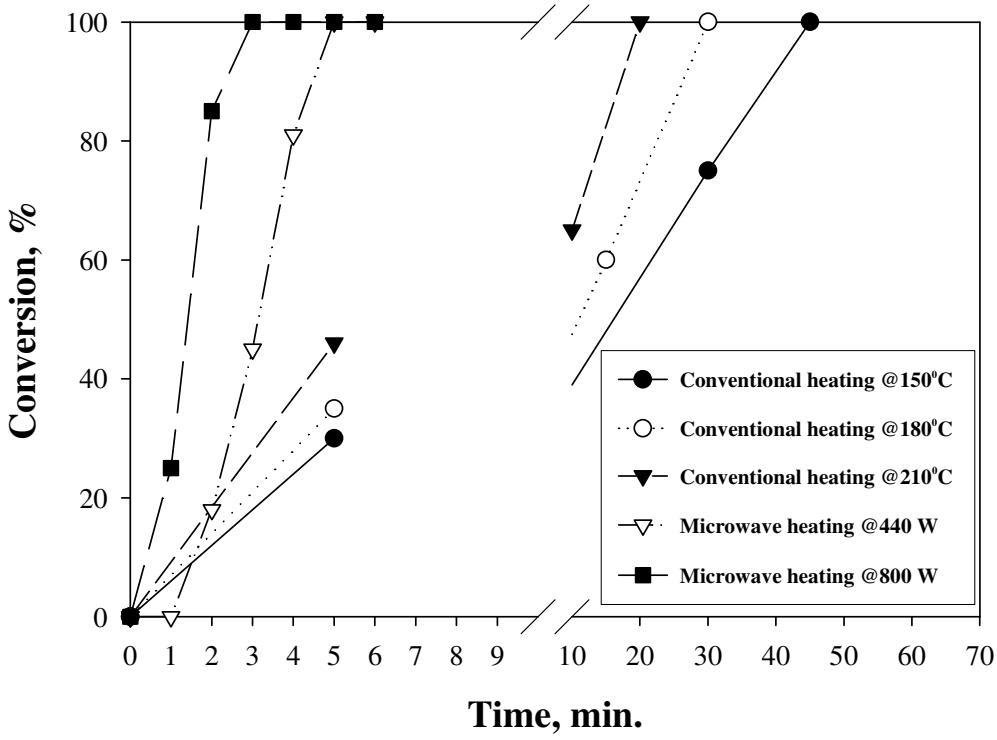


Figure 6.13 Comparison of conventional and microwave heating

This observation was confirmed by the analysis of the XRD-patterns of the samples. While powder X-ray diffraction of sample essentially showed peaks corresponding to

SCM in Fig. 6.14, in Fig. 6.15 powder X-ray diffraction of the microwave-irradiated product essentially showed peaks corresponding to anhydrous sodium carbonate.

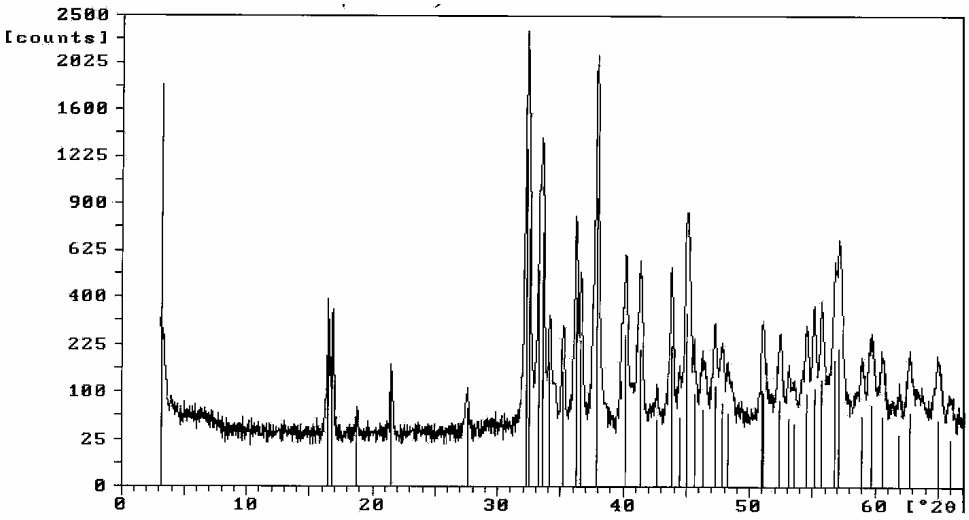


Figure 6.14 XRD pattern of $Na_2CO_3 \cdot H_2O$ before MW irradiation

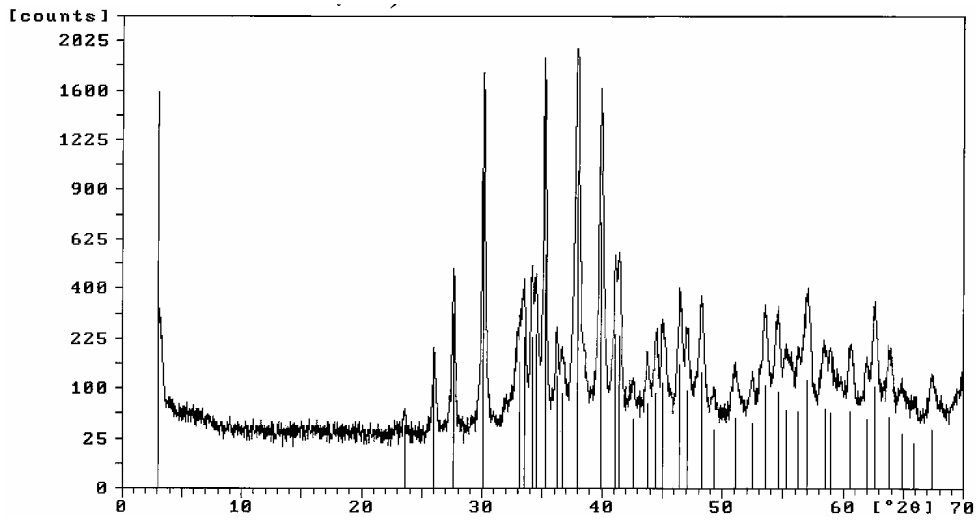


Figure 6.15 XRD pattern of Na_2CO_3 after MW irradiation of SCM

Two SEM photographs are depicted in Fig. 6.16 and 6.17. While in the first picture, monohydrate crystals, orthorombic, long needle-shaped crystals are visible, monoclinic

structure of the anhydrate crystals can be seen very clear in the second picture. Also it can be seen that there is no caking formation occurred from the Fig. 6.17.

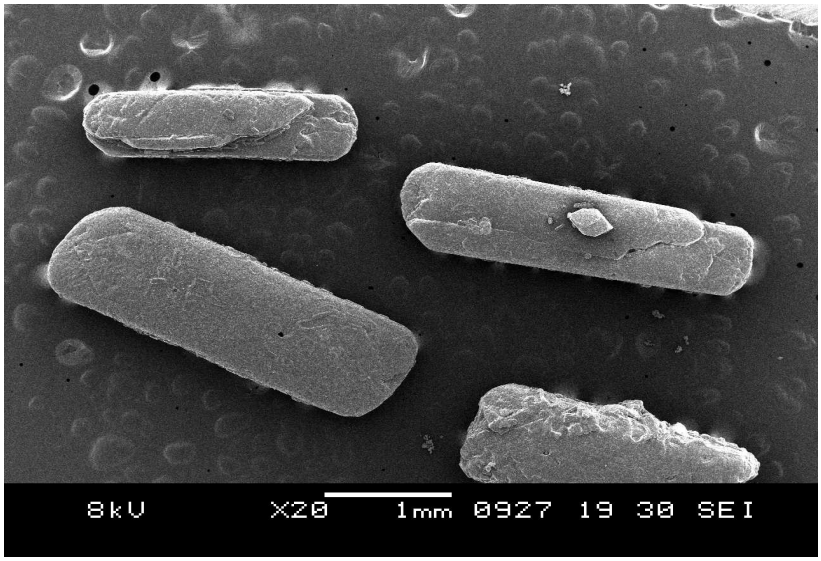


Figure 6.16 SEM image of $Na_2CO_3 \cdot H_2O$ before MW irradiation



Figure 6.17 SEM image of Na_2CO_3 after MW irradiation of SCM

There is also no distinct influence of the operating conditions in this hybrid system on the bulk density of the product. It was found that approximately 1000 kg/m^3 after complete dehydration was achieved which is the same value of the product that produced with the conventional drying methods.

6.3 Alternative Drying of Sodium Bicarbonate ($NaHCO_3$) With Microwave Energy

In this study, the results of the experimental work to dry off the free moisture from the sodium bicarbonate powder using microwave energy were investigated.

6.3.1 Drying Equipment and Procedure

In this study a Premier, PMO-20 microwave oven was used. It has a frequency of 2450 MHz with an output power of maximum 800 W. Drying experiments were conducted at six different microwave output powers of 136, 168, 264, 440, 616 and 800 W.

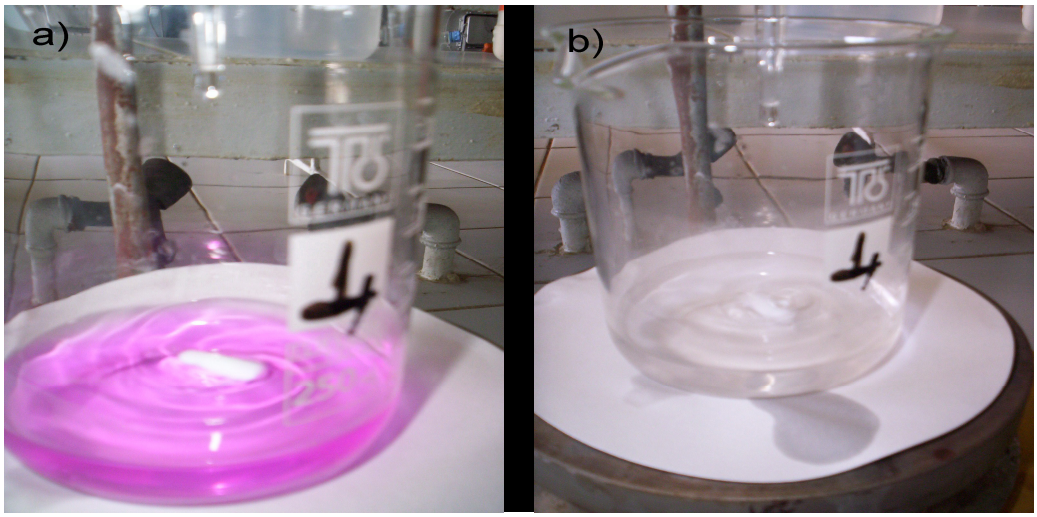


Figure 6.18 The phenolphthalein test; a) The solution has Na_2CO_3 content; b) The solution has not Na_2CO_3 content

In industry, the suspension of bicarbonate in the mother liquor leaves the carbonation stage at 30 ºC and the centrifuged products may contain about 7% water (Thieme, 1992). In the case of using vacuum filters, the product may contain up to 18% water (Koksal, 2002). In this study, sodium bicarbonate was wetted with aqueous saturated sodium bicarbonate solution at 30 ºC to obtain samples containing 7% to 15% water respectively. Preliminary heating of the wet $NaHCO_3$ to 30 ºC was carried out in closed containers to simulate heating under a saturated atmosphere.

Drying experiments were performed with 50 g samples. A teflon line sheet (15 cm diameter), containing the sample forming a layer of 1-2 mm thickness, was placed on the centre of the turntable inside microwave cavity during treatment for even absorption of microwave energy. The drying was performed according to a preset temperature and power.

Temperature of the irradiated sample was measured by inserting the K-thermocouple (Hanna instruments, model HI 93551) into the sample immediately after turning of the microwave power.

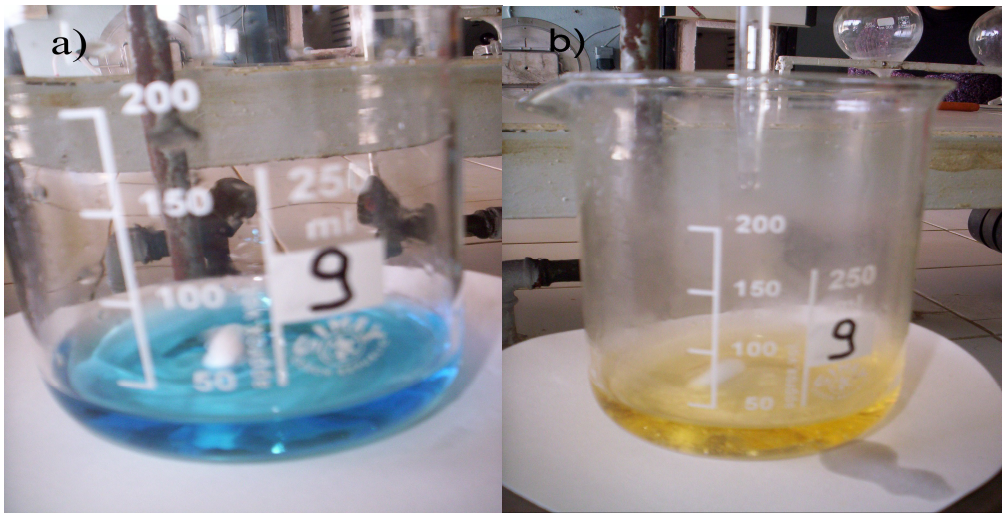


Figure 6.19 The bromocresol green test; a) Before titrating of hydrochloric acid solution; b) After titrating of hydrochloric acid solution

The thermocouple was calibrated using a thermometer at different water temperatures while heating it. Whether the drying is complete or not is determined by chemical analysis of the product via determination of $NaHCO_3$ and Na_2CO_3 content.

The heating profile of the oven conducted with water only shows an almost uniform magnetic field. The test was conducted by heating 100 ml water in a beaker and reading its temperature with about 5 seconds delay, i.e., interrupting the power and reading the temperature.

6.3.2 Determination of Moisture and the Weights of Sodium Bicarbonate and Sodium Carbonate

The amounts of moisture content and decomposition products were determined by acid titration method. After irradiation of the sodium bicarbonate samples in the microwave oven, about 2 grams of sodium bicarbonate powder was taken and dissolved in CO_2 free double distilled and deionized water. The sample, then, was transferred into a 100 ml volumetric flask bringing to volume. An amount of 10 ml of this solution was placed into a 100 ml beaker along with 10 ml water. Three drops of phenolphthalein indicator were added to this solution with stirring. If the color of this solution turns into pink, the amount of decomposition is considered significant. If the test appears to be negative, the sodium bicarbonate solution is titrated with a standardized hydrochloric acid solution (0.1 N) using bromocresol green indicator. Titration continues until its color turns into a yellow color. Finally, the amount of sodium bicarbonate in each sample was then calculated. The amounts of moisture content, sodium bicarbonate, and sodium carbonate were derived using mass balance before and after titration.

6.3.3 Results and Discussion

Wetted sodium bicarbonate powder was dried in the microwave oven at different energy levels. Drying of the sodium bicarbonate powder is dictated by the rate of

moisture removal and the rate of sodium bicarbonate decomposition to sodium carbonate.

First, drying behavior of the dry sodium bicarbonate powder was investigated in the microwave oven at 440 W to show that the sodium bicarbonate was a poor absorber of the microwave energy. The results of irradiation tests, presented in Fig. 6.20, showed that the sodium bicarbonate was a poor absorber of the microwave energy for up to 5 minutes of irradiation.

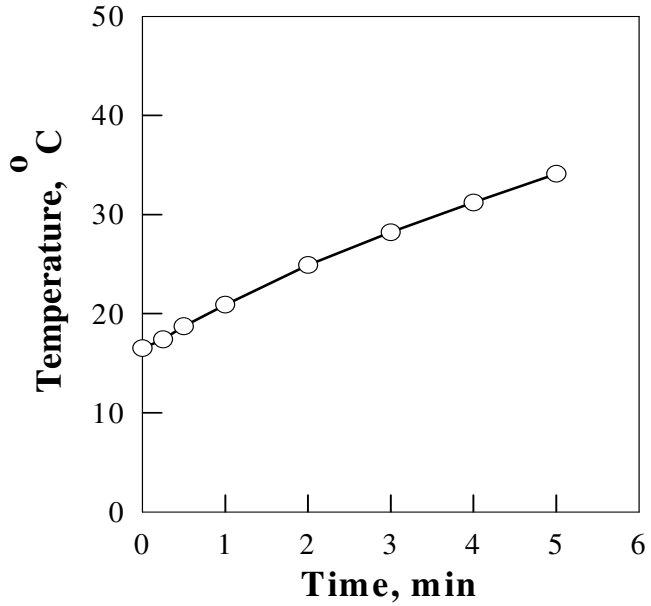


Figure 6.20 Heating behavior of dry sodium bicarbonate in the microwave oven at 440 W for 5 minutes

Particle size distributions of the original crystalline sodium bicarbonate ($NaHCO_3$) samples and the microwave dried $NaHCO_3$ were determined to examine the decomposition behavior. Dry screening test results of the sodium bicarbonate samples before and after microwave heating are presented in Table 6.3 which indicated that the size distributions after microwave irradiation remained the same.

Table 6.3 Size distributions of the sodium bicarbonate powder before and after microwave irradiation (30 minutes of screening)

Size (μm)	**Weight % [before]**	**Weight % [after]**
+150	1.44	1.95
-150+75	70.32	71.31
-75+45	21.61	21.00
-45	6.63	5.74

The results of drying experiments with the sodium bicarbonate samples, containing 7% and 15% moisture, at different microwave energy levels are presented in Fig. 6.21 to 6.24 and Table 6.4. The sample temperatures increased to a maximum and then their temperatures dropped indicating the removal of the moisture. This phenomenon can be used for easy control of the drying operation. In the last experiment at a microwave power level of 136 W, the temperature did not rise excessively, because microwave energy was not sufficient. As seen from the Figures 6.21 to 6.24, at high power levels, drying times were reduced substantially.

The tests were repeated at a different moisture level of 15% to see the effect of moisture content on the decomposition of the sodium bicarbonate powder. As seen from the Table 6.4 that the sodium bicarbonate decomposes at all three microwave power levels indicating that the water temperatures rose above the decomposition temperatures of the CO_2.

Complete drying of $NaHCO_3$, containing 7% moisture, was achieved, without any loss of structural water, i.e., no decomposition, as seen from the Fig. 6.21 and 6.22 and Table 6.4. Mass balance determinations after the titration showed a good correlation between the amount of evaporated water and the chemical composition of the dried mass.

Table 6.4 Decomposition of $NaHCO_3$ containing different moisture contents during microwave irradiation

Microwave power	% Na_2CO_3	
	@ 7% moisture	@ 15% moisture
136 W	0.0	3.81
440 W	0.0	2.54
800 W	0.0	2.23

Almost complete drying of $NaHCO_3$ was also achieved in the case of 15% moisture as seen from the Fig. 6.23 and 6.24, but structural water was lost as shown in Table 6.3. The amount of dissociation has decreased with increasing microwave power output indicating that the matter dried rapidly at high energy levels than the low energy levels as shown in Table 6.4.

$$2NaHCO_3 \leftrightarrow Na_2CO_3 + CO_2 + H_2O \qquad (6.12)$$

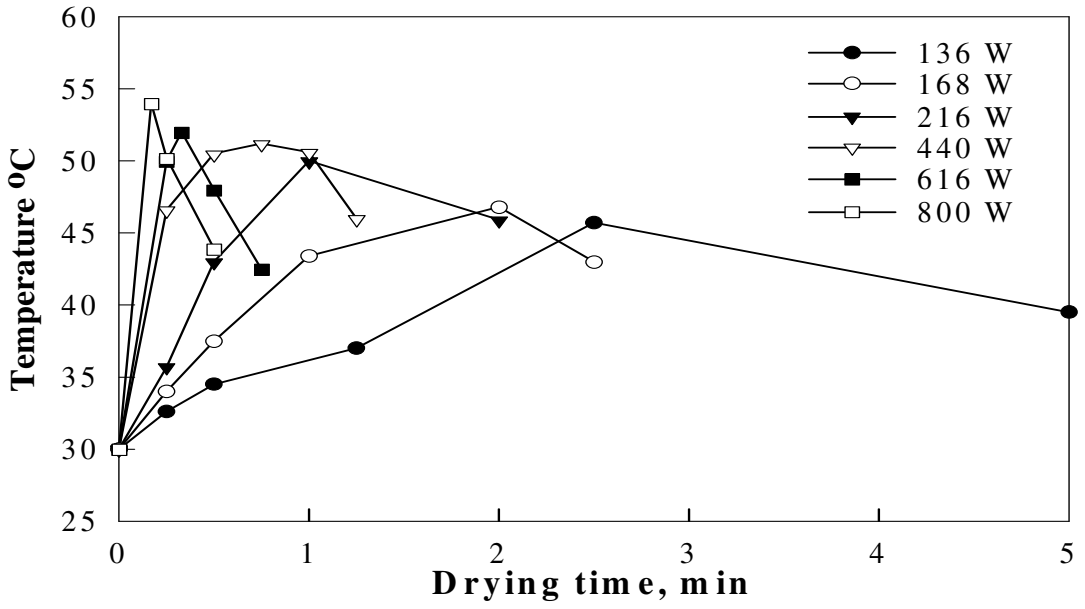


Figure 6.21 Drying results of sodium bicarbonate, containing 7% moisture, at different microwave energy levels.

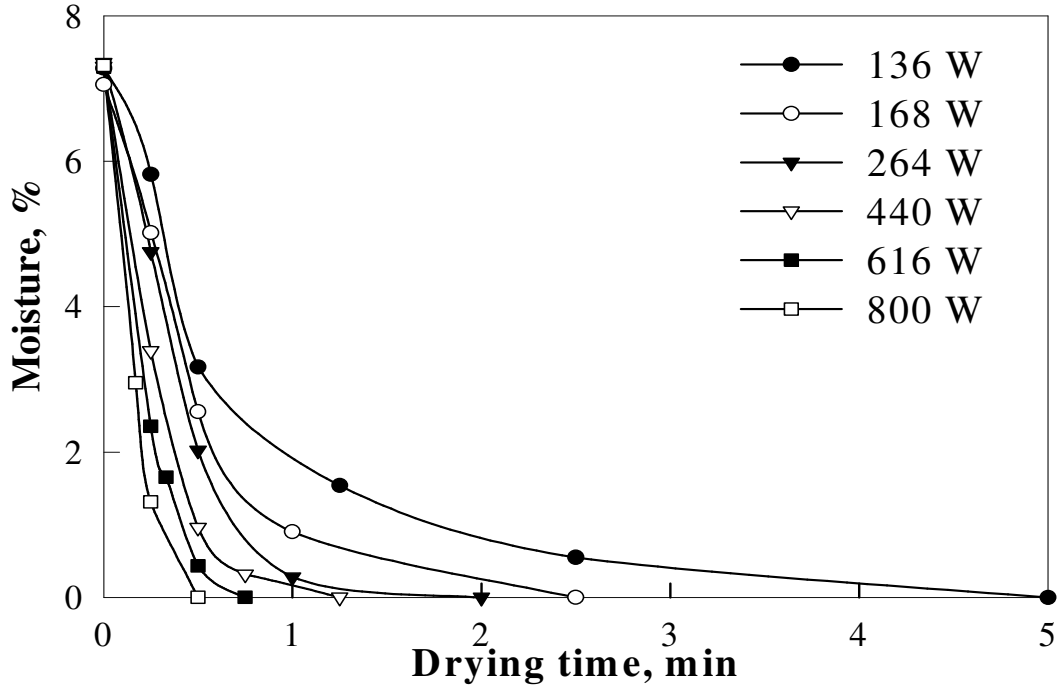


Figure 6.22 Reduction of moisture in sodium bicarbonate containing 7% moisture at different microwave energy levels

This is because (as explained by Kuu et al., 1998) at higher temperature, the solubility of CO_2 in the aqueous moisture layer is lower. Thus, the mass transfer rate of CO_2 increases; resulting in higher hydrolysis and decomposition rates of bicarbonate powder. The decomposition schemes can be postulated as

$$NaHCO_{3(s)} \xleftrightarrow{+H_2O,k_s} NaHCO_{3(aq)} \tag{6.13}$$

$$2NaHCO_{3(aq)} \leftrightarrow 2Na^+ + 2HCO_3^- \tag{6.14}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{-2} \tag{6.15}$$

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \tag{6.16}$$

$$H_2CO_3 \leftrightarrow H_2O_{(aq)} + CO_{2(aq)} \quad (6.17)$$

$$CO_{2(aq)} \leftrightarrow CO_{2(g)} \quad (6.18)$$

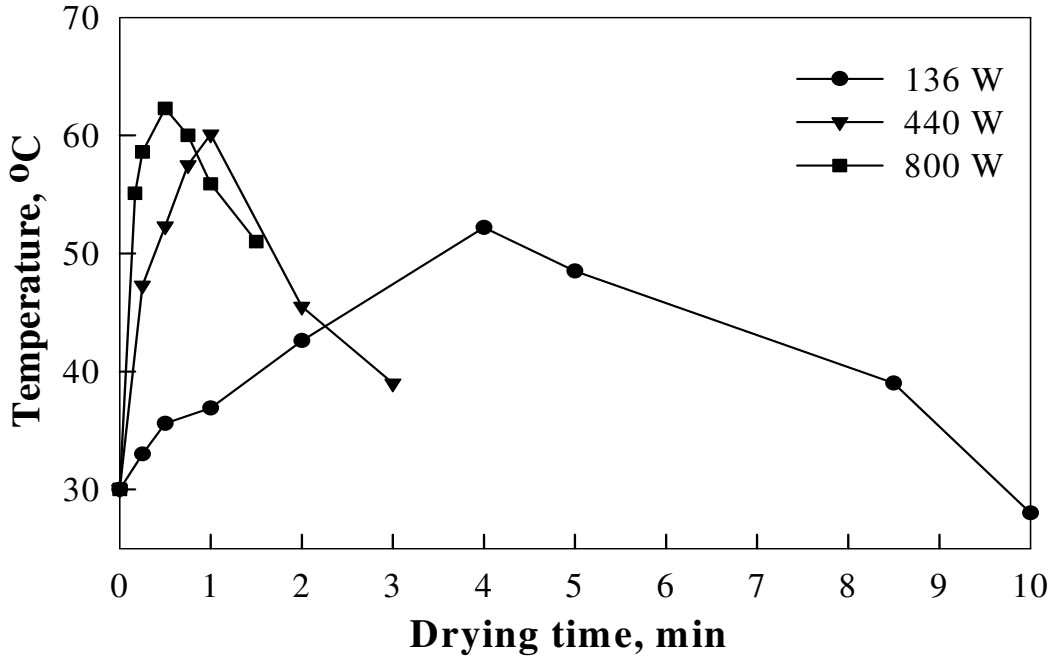


Figure 6.23 Drying results of sodium bicarbonate, containing 15% moisture, at different microwave energy levels.

Eq. (6.13) indicates that the bicarbonate powder in the solid phase, denoted as $NaHCO_{3(s)}$, after absorbing moisture from the ambient (with a sorption rate constant k_s), is dissolved into the sorbed moisture layer, denoted as $NaHCO_{3(aq)}$. The equilibrium reactions Eqs. (6.14)–(6.17) are subsequently established in the aqueous phase. Eq. (6.18) shows that the CO_2 molecules produced in the aqueous phase migrate to the ambient through a mass transfer process. This process will continue until the concentration of CO_2 in the gas phase increases to a sufficient level (for the case of placing samples in the desiccator) to establish an equilibrium with the dissolved CO_2. At

higher temperature, the solubility of CO_2 in the aqueous moisture layer is lower. Thus, the mass transfer rate of CO_2 increases; resulting in higher hydrolysis and decomposition rates of bicarbonate powder. It is noted that Eqs. (6.13) and (6.18) are physical processes, whereas Eqs. (6.14)–(6.17) are chemical equilibrium equations. The overall chemical reaction, from Eqs. (6.14)–(6.17), becomes

$$2NaHCO_3\,(aq) \leftrightarrow 2Na^+ + CO_3^{-2} + CO_2 + H_2O \qquad (6.19)$$

which is similar to Eqn. (6.12). It can be concluded that the rate of weight change of the bicarbonate powder depends on the rate of moisture sorption rate and the rate of losing carbon dioxide and water molecules.

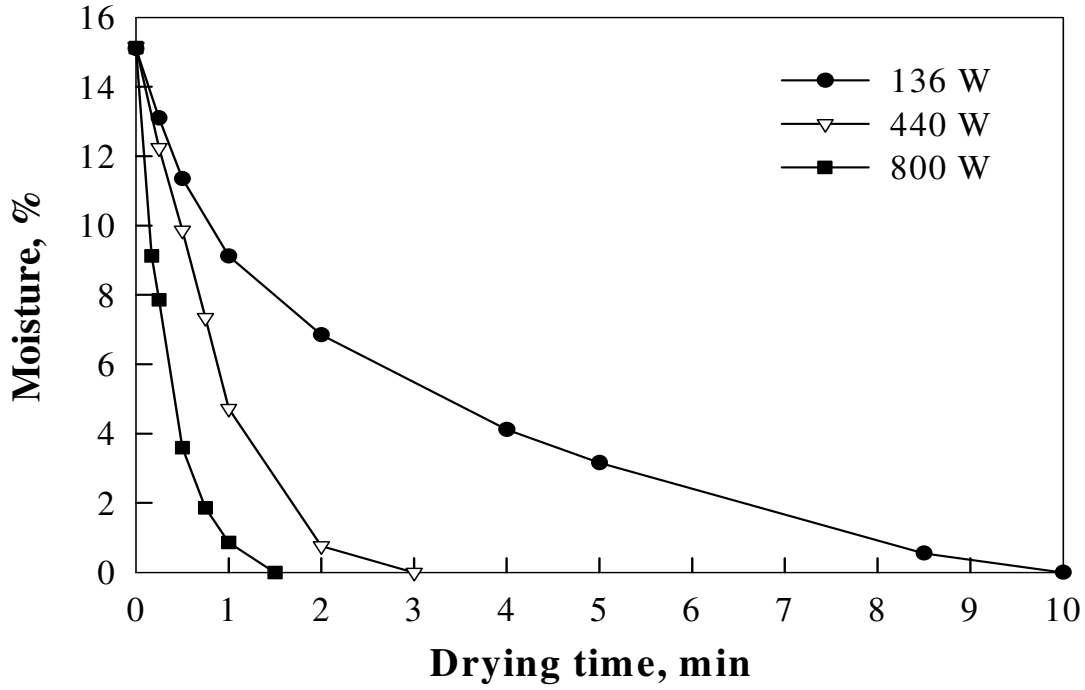


Figure 6.24 Reduction of moisture in sodium bicarbonate containing 15% moisture at different microwave energy levels

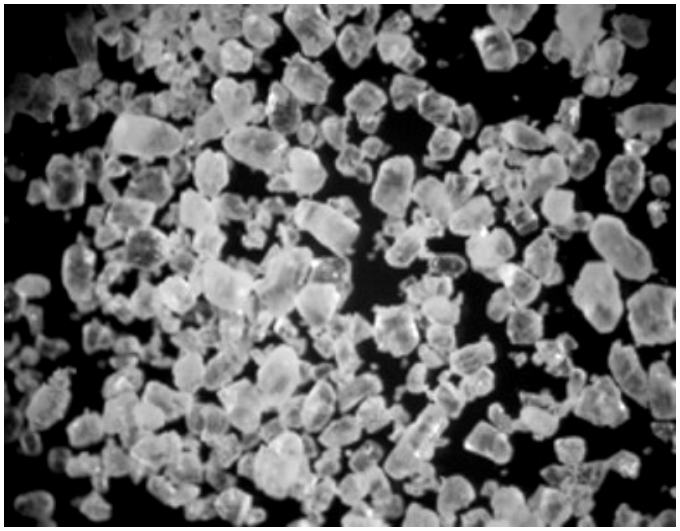


Figure 6.25a Optical micrographs of the original sodium bicarbonate, $NaHCO_3$

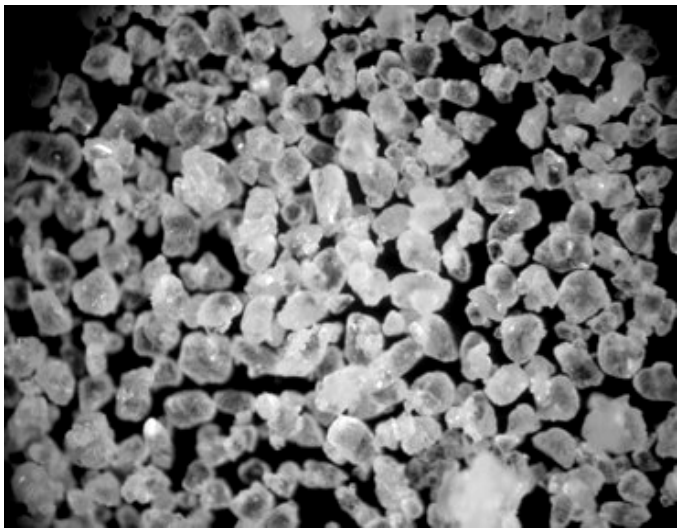


Figure 6.25b Optical micrographs of the sodium bicarbonate, $NaHCO_3$, after 70 sec. microwave irradiation. (Initial moisture: 7%, bed thickness: 2 mm, microwave power: 440 W)

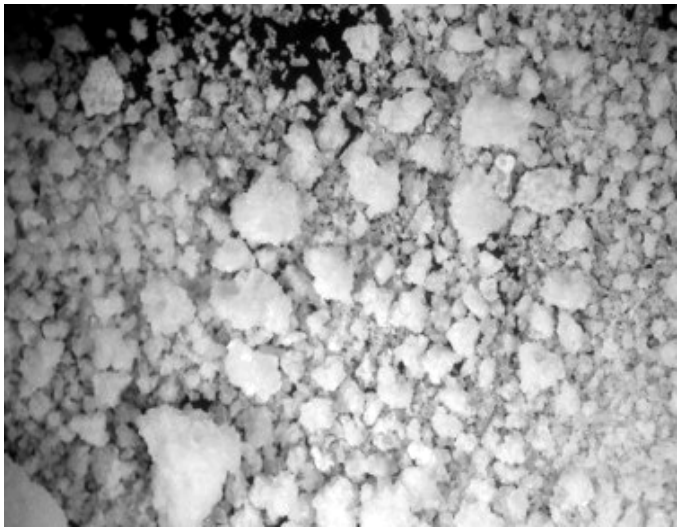


Figure 6.25c Optical micrographs of the sodium bicarbonate, NaHCO3, after 70 sec. microwave irradiation (Initial moisture: 7%, bed thickness: 5 mm, microwave power: 440 W)

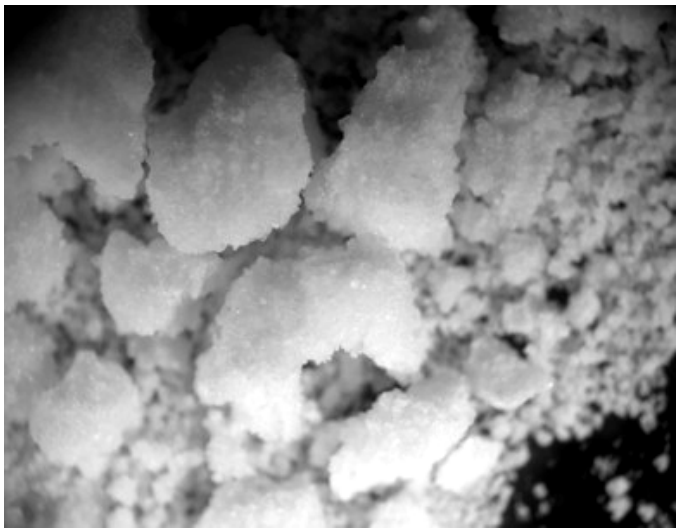


Figure 6.25d Optical micrographs of the sodium bicarbonate, $NaHCO_3$, showing caking after 70 sec. microwave irradiation. (Initial moisture: 7%, bed thickness: 10 mm, microwave power: 440 W)



Figure 6.25e Optical micrographs of the sodium bicarbonate, $NaHCO_3$, showing caking after 70 sec. microwave irradiation. (Initial moisture: 7%, bed thickness: 15 mm, microwave power: 440 W)

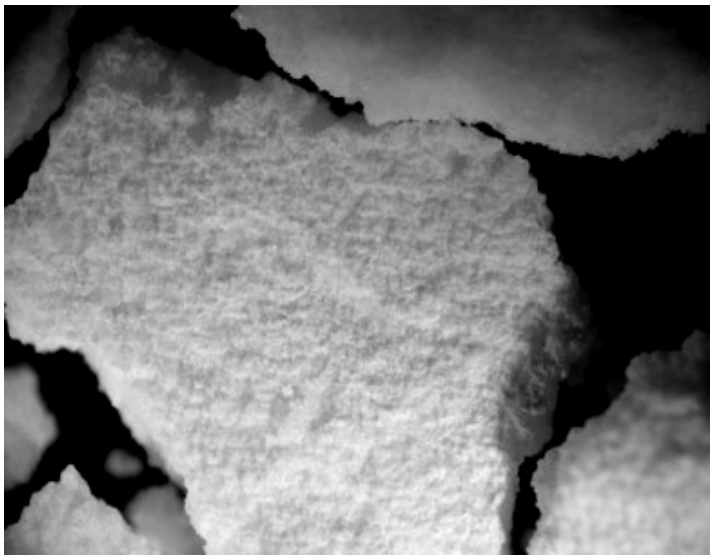


Figure 6.25f Optical micrographs of the sodium bicarbonate, $NaHCO_3$, showing caking after 70 sec. microwave irradiation. (Initial moisture: 15%, bed thickness: 2 mm, microwave power: 440 W)

Optical microscopy studies were carried out to investigate the visual changes at the surfaces of the sodium bicarbonate powder. The pictures taken were presented in Fig. 25a-b. There are no visual changes with the samples tested at 7% moisture and about 2 mm sample thickness. When the sample thickness has increased from 2 mm to 5 and 10 mm, caking of the particles occurred, i.e. adhering between the crystals. Caking was also seen with the sodium bicarbonate samples containing 15% moisture and a smaller sample thickness as low as 2 mm.

6.4 Economics of These Alternative Microwave Drying Systems

The dimensions of the equipment are calculated for a 100,000 t/year sodium bicarbonate plant. The basic equipment costs are taken from the DACE cost tables of 2004. The investment associated with the calciner was calculated using cost data from Perry (1997).

Table 6.5 Cost analysis of $NaHCO_3$ drying with steam tube dryer

Steam Tube Rotary Dryer		
Equipment Costs	Total $	Surface Area
Dryer	690,783	404 m^2
Lang Factors Design& Engineering Installation& Instrumentation	 1.4 3.15	
Capital Investment Total	3,046,353	
Annual Costs	$ / year	
Taxes, Royalties	91,390	3%
Maintenance	152,317	5%
Capital Cost	413,999	13.59%
Heating	925,000	
Electricty	96,600	
Operation Cost Total	1,679,306	

The drying of sodium bicarbonate is usually carried out in a calciner. In industrial applications, sodium bicarbonate is dried in steam tube rotary by heating with air below

60ºC. When 50ºC is used for a flow of 100,000 t/year of a solid is to be dried from 7 per cent to 0.1 percent moisture on a dry basis an internal surface area of 404 m^2 is needed.

Microwave will remove 0.42 kg of water per hour at 800 W for the drying of sodium bicarbonate from 7 per cent to 0.1 percent moisture on a dry basis. It means 7,000 t/year water will evaporate for a flow of 100,000 t/year capacity. This would require about 1,522 kW. The investment associated with the microwave system was calculated using cost data from Kaya and Flinn (1997).

Table 6.6 Cost analysis of $NaHCO_3$ drying with microwave system

Microwave System		
Equipment Costs	$/kW	Total $ million
Genarator (including waveguides and controls)	1,200	1.82
Cooling system, using plant water		0.50
Applicator		1.00
Power transmission	5%	0.091
Engineering	5%	0.091
Instrumentation	2%	0.0364
Installation	2%	0.0364
Commissioning and training	1%	0.0182
Subtotal		3.593
Contingency	%30	0.546
Capital Investment Total		4.139
Annual Costs		$ / year
Energy (electric at 75% eff.)		1,666,590
Tube replacement		1,076,140
General maintenance (% of capital)	2%	82,780
Subtotal		2,825,510
Contingency	30%	1,346,799
Operation Cost Total		4,172,309

While this technology is well established in the food, pharmaceutical and chemical industry, it might have only now have reached a stage, where its application to low-added-value bulk products might have any hope of being economically feasible. But the cost of microwave drying equipment is high, but microwave drying technology will have greater application in coming years.

CHAPTER SEVEN
CONCLUSION

In this investigation, first the influence of microwave heating on the modification of dehydration properties SCM was experimentally confirmed and the expressive shortening of the exposing time observed in comparison to the conventional heating. With the susceptor, SCM was converted to sodium carbonate with indirect microwave heating. The increase in microwave power and air temperature significantly reduced the drying time of the SCM crystals.

The results of this investigation show that the SCM crystals can successfully be dried using alternative microwave energy with the evaporation of moisture and crystal water replacing the steam tube rotary or fluidized bed driers that are currently used in the industry to remove the excess moisture and crystal water from the SCM.

In this investigation, second sodium bicarbonate powder containing 7-15% moisture has been dried using 136-800 W and 2450 MHz microwave energy under 60 °C selectively without any loss of structural water.

The results of this investigation show that the sodium bicarbonate ($NaHCO_3$) powder can successfully be dried using alternative microwave energy with the evaporation of moisture only replacing the steam tube rotary or fluidized bed driers that are currently used in the industry to remove the excess moisture from the sodium bicarbonate powder. Microwave energy does not cause any loss of structure water in the sample making it contingent on dewatering. Results of particle size analysis showed that the average particle size and distribution remain the same and dusting does not occur.

At higher moisture contents precautions need to be taken to dry the samples to prevent them from decomposition and caking, for example, using shorter intervals of heating and decreased sample layer. In addition, drying can be accelerated at low

temperatures if the process is conducted at reduced pressures, i.e., the lower the atmospheric pressure, the lower the boiling point of the water. A fluidized bed microwave system can also be utilized to prevent caking from occurring.

The cost of microwave drying equipment is high, but microwave drying technology will have greater application in coming years. The disadvantage of capital investment cost and the advantages of product quality and processing must be investigated.

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