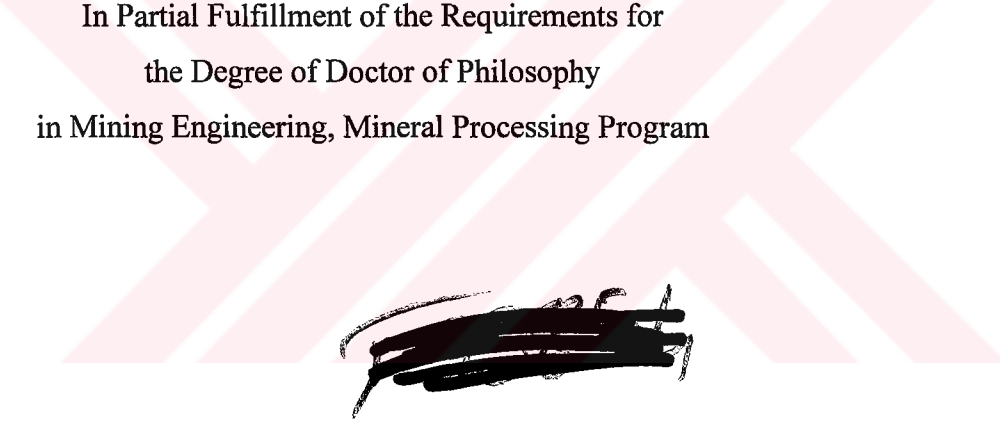


A NEW APPROACH TO BORAX PENTAHYDRATE PRODUCTION

95854

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 Doctor of Philosophy
in Mining Engineering, Mineral Processing Program



By
Hasan ÇEBİ

February, 2000
İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.



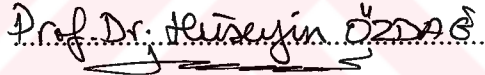
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In memory of my girlfriend
Akiko YAMASHITA

This study is dedicated with
deepest love and affection
to Yamashita Family.

Their love, vulnerability, wisdom, and strength
have inspired me to the best I can be
and to share what we have learned together.

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ABSTRACT

After the USA, Turkey is the largest producer of borates, and is the world's principal source of natural borate minerals. Etibank dominates the mining and processing of boron minerals and boron compounds in Turkey. Etibank's mining operations are centered upon four borate deposits, Bigadiç, Emet, Kestelek and Kırka. In this work, laboratory and pilot plant tests have been carried out on the run of mine tincal ore ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$) for direct production of borax pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5 \text{H}_2\text{O}$) by a combination of a leaching unit and a decanter centrifuge and these are compared to the process presently employed at Etibank's borax production plant in Kırka, Eskişehir, Turkey.

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CHAPTER ONE

INTRODUCTION

Year by year demands for borax pentahydrate products are increasing, therefore Eti Holding A.Ş. is planning to construct a new Borax Derivative Plant to make capacity 480.000 tpa. However, the capacity for Concentrator Unit won't be enough to feed three Borax Derivative Plants at the same time. Increasing capacity on Concentrator Unit means more liquid waste to tailing pounds.

In this study, a laboratory, 1 t/h and 10 t/h capacity tests were conducted to come up different processing techniques replacing Concentrator Unit and wiping out liquid wastes. Proposed processing techniques should have;

- ◆ Higher recovery than present process.
- ◆ Both processes should have at least same energy consumption.
- ◆ Present Borax Plant in Kırka has two tailing sites, one in Concentrator Unit, flow rate approximately 400 m³/h and the other one goes from Boron Derivative Plant, 25 t/h. Both wastes are liquid so it goes to tailing ponds. Increasing environmental impact pushes Eti Holding to come up with more friendly technology to environment. Proposed technology will focus on wastes that will be solid.
- ◆ Proposed process should be at least as easy as present process.
- ◆ Soda is being used to control some of the impurities at present, and should not be increased at proposed system.

CHAPTER TWO

GENERAL INFORMATION

2.1. Properties of Boron

(Ar. Buraq, Pers. Burah) Boron compounds have been known for thousands of years, but the element was not discovered until 1808 by Sir Humphry Davy and by Gay-Lussac and Thenard. The element is not found free in nature, but occurs as orthoboric acid usually in certain volcanic spring waters and as borates in boron and colemanite. Ulexite, another boron mineral, is interesting as it is nature's own version of "fiber optics." Important sources of boron are the ore rasorite (kernite) and tincal (borax ore). Both of these ores are found in the Mohave Desert. Tincal is the most important source of boron from the Mohave. Extensive borax deposits are also found in Turkey. Boron exists naturally as 19.78% ^{10}B isotope and 80.22% ^{11}B isotope. High-purity crystalline boron may be prepared by the vapor phase reduction of boron trichloride or tribromide with hydrogen on electrically heated filaments. The impure or amorphous, boron, a brownish-black powder, can be obtained by heating the trioxide with magnesium powder. Boron of 99.9999% purity has been produced and is available commercially (Lide, David R., & Hammond, C.R., 1913-1995).

General

Name	Boron	Symbol	B
Atomic number	5	Atomic weight	10.81
Density @ 293 K	2.34 g/cm ³	Atomic volume	4.6 cm ³ /mol
Group	Non-Metal	Discovered	1808

States

	State (s, l, g)	s	
Melting point	2352.2 K	Boiling point	3923.2 K
Heat of fusion	50.20 kJ/mol	Heat of vaporization	489.70 kJ/mol

Energies

1st ionization energy	800.6 kJ/mole	Electronegativity	2.04
2nd ionization energy	2427 kJ/mole	Electron affinity	26.7 kJ/mole
3rd ionization energy	3659.7 kJ/mole	Specific heat	1.02 J/gK
Heat atomization	573 kJ/mole atoms		

Oxidation & Electrons

Shells	2,3	Electron configuration	[He] 2s ² 2p ¹
Minimum oxidation number	0	Maximum oxidation number	3
Minimum common oxidation number	0	Maximum common oxidation number	3

Appearance & Characteristics

Structure	special: B ₁₂ icosahedra	Color	black
Uses	borax, glass making(B ₂ O ₃)	Toxicity	
Hardness	9.5 mohs	Characteristics	B ₁₂ icosahedra; 3 forms

Reactions

Reaction with air	mild, w/ht =>B ₂ O ₃	Reaction with 6M HCl	None
Reaction with 6M HCl	None	Reaction with 15M HNO₃	None
Reaction with 6M NaOH	None		

Other Forms

Number of isotopes	2	Hydride(s)	B ₂ H ₆ and many B _x H _y
Oxide(s)	B ₂ O ₃	Chloride(s)	BCl ₃ and many B _x Cl _y

Radius

Ionic radius (2- ion)	Pm	Ionic radius (1- ion)	pm
Atomic radius	85 pm	Ionic radius (1+ ion)	pm
Ionic radius (2+ ion)	Pm	Ionic radius (3+ ion)	41 pm

The world's principal borate deposits occur as evaporites inter-bedded with sequences of clays and limestones that have been deposited in non-marine (lacustrine) basins. The source of boron is invariably local volcanic activity: volcanic springs introduce boron- rich fluids into the basin of deposition, where boron is initially soluble: subsequent evaporation concentrates boron in the fluids to the point where precipitation occurs. Numerous such active geological settings are known throughout the world, particularly in South America, where volcanic springs can contain more than 50 ppm boron.

After precipitation, the borates are preserved in the geological record only as a result of burial under protective layers of clay or limestone sediments. The highly soluble borates would be easily leached by surface water if not protected. However, the absence of non-marine borates of pre-Tertiary age suggests that even burial is not adequate for prolonged preservation. The non-marine borates are mainly sodium- and calcium borates, such as tincal and colemanite, which are the most widely exploited borate minerals.

Marine evaporite borates deposits attain commercial importance where other minerals are extracted. Potash beds of Permian age are sometimes found to be borate-rich. It is thought that submarine volcanic vents introduced additional boron into the local marine environment where such beds were formed. Magnesium borates is the common constituent of marine borate deposits, and szaibelyite is of some commercial importance.

Due to the high solubility of borates, boron is also a constituent of some subsurface brines. Although these are not exploited specifically for their boron content, they are a source of by-product borates from other solution mining operations.



Table 2.1. Chemical Compositions of Commercial Borate Minerals

Mineral/ Composition	Weight % B₂O₃	Remarks
Sassolite B(OH) ₃	56.4	Natural boric acid. Once extracted in Italy: of historic interest only
Sodium borates		
Tincal(borax) Na ₂ O.2B ₂ O ₃ .10H ₂ O	36.5	The major ore mineral: produced in the USA, Turkey and Argentina
Tincalconite Na ₂ O.2B ₂ O ₃ .5H ₂ O	48.8	Intermediate or accessory mineral only
Kernite (rasorite) Na ₂ O.2B ₂ O ₃ .4H ₂ O	51.0	Major ore mineral: often converted to borax by weathering
Sodium-calcium borates		
Ulexite (boronatocalcite) Na ₂ O.2CaO.5B ₂ O ₃ .16H ₂ O	43.0	Major ore mineral: particularly in South America
Probertite (kramerite) Na ₂ O.2CaO.5B ₂ O ₃ .10H ₂ O	49.6	Secondary/accessory mineral
Calcium borates		
Inyoite 2CaO.3B ₂ O ₃ .13H ₂ O	37.6	Minor ore mineral
Meyerhoffite 2CaO.3B ₂ O ₃ .7H ₂ O	46.7	Intermediate mineral, rarely survives in quantity
Colemanite 2CaO.3B ₂ O ₃ .5H ₂ O	50.8	Major ore mineral, particularly in Turkey; Often secondary after inyoite
Priceite (pandermite) 5CaO.6B ₂ O ₃ .9H ₂ O	49.8	Ore mineral at Bigadiç, Turkey; minor Elsewhere
Calcium borosilicates		
Howlite 4CaO.5B ₂ O ₃ .2SiO ₂ .5H ₂ O	44.5	Accessory mineral
Datolite 2CaO.B ₂ O ₃ .Si ₂ O ₅ .H ₂ O	21.8	
Danburite CaO.B ₂ O ₃ .2SiO ₂	28.3	

Table 2.1. Chemical Compositions of Commercial Borate Minerals (Continued)

Mineral/ Composition	Weight % B₂O₃	Remarks
Magnesium borates		
Haydrotboracite CaO.MgO.3B ₂ O ₃ .6H ₂ O	50.5	
Inderite 2MgO.3B ₂ O ₃ .15H ₂ O	37.3	
Szaibelyite (ascharite) 2MgO.B ₂ O ₃ .H ₂ O	41.4	Major ore mineral in Kazakhstan
Kurnakovite 2MgO.3B ₂ O ₃ .15H ₂ O	37.3	Accessory mineral
Boracite Mg ₃ B ₇ O ₁₃ Cl	62.2	Accessory with potash deposits
Suanite Mg ₂ B ₂ O ₅	46.3	
Kotoite Mg ₂ B ₂ O ₆	36.5	
Pinnoite MgO.B ₂ O ₃ .3H ₂ O	42.5	
Other Borates		
Cahnite Ca ₂ AsBO ₆ .2H ₂ O	11.7	
Tunellite SrB ₆ O ₁₀ .4H ₂ O	52.9	

Source: Encyclopedia of Chemical Technology, Kirk-Othmer
Industrial Minerals and Rocks, Society for Mining, Metallurgy, and Exploration, Inc

2.2. Use of Boron

Borates are used in hundreds of products and processes in ways that touch the lives of almost everyone. Once employed almost exclusively by goldsmiths, who used borax as a flux, borates today play important roles in everything from cookware and medicine to nuclear waste storage and space exploration. Major uses include glass production, detergent preparations, agricultural applications and enamel and ceramic glazes. Amorphous boron is used in pyrotechnic flares to provide a distinctive green color, and in rockets as an igniter.

This diversity of uses is the result of the multiple properties of borates which include buffering, neutron absorption, ester formation, and enzyme stabilization.

Because of these diverse properties, new applications for borates continue to be discovered, indicating that their untapped potential remains vast.

The modern history of borate use in glass dates to the late 19th century when scientists discovered that adding boric acid to their glass formulations resulted in a borosilicate that had good resistance to acids and thermal shock. By controlling the coefficient of expansion in glass, boric oxide (anhydrous boric acid) keeps oven-to-table cookware, vacuum flasks, and innumerable pharmaceutical, laboratory and industrial containers from breaking when exposed to extreme and rapidly changing temperatures.

Boric oxide is also a critical component in glass wool (insulation fiberglass), widely used in construction, and in textile fiberglass, where it is employed chiefly to reinforce plastics that are used in construction and automobile parts. Small quantities of borates also serve to improve the resistance of crystal glassware to dishwashing liquids and to enhance the quality of art and optical glasses.

Sodium perborate (obtained by reacting borax with sodium hydroxide and hydrogen peroxide) has been the principal bleach in European laundry powders for most of the 20th century. Studies have shown that perborate is a gentler bleaching agent than chlorine. Recently, this substance has been introduced into "all-in-one" detergents in North America as an alternative to the tradition of using a chlorine bleach after the washing cycle. Perborate also acts as a stain-removing agent in advanced dishwashing powders. Other borates are used to stabilize enzymes in liquid laundry detergents. The detergents of the future are likely to be multifunctional products that combine the bleaching, water conditioning, stain-removing, and detergent-building properties of borates.

Boron is a micronutrient essential to plants. Where the boron content of soil is insufficient, crop yields and quality suffer. For the past 70 years, borate fertilizers have been used by farmers worldwide to rectify boron deficiencies. Because too much boron can be as bad for plants as too little, borate fertilizers are produced in

both granular and powdered forms to facilitate application of the appropriate amounts, whether used alone or mixed into compounds or solutions with other fertilizers.

In "fritted" or nonsoluble form, borates are added to glazes and enamel coatings in order to increase their durability, improve their appearance, and prevent cracking and crazing (by matching the coefficient of expansion of the glaze to that of the substrate).

Borate-containing glazes and enamels are applied to ceramics and metals that serve many purposes from the everyday (pots and pans, bone china, porcelain fixtures, floor tiles, home appliances, and signage) to the high-tech (insulators for electronics, and protective tiles that prevent the Space Shuttle from overheating during re-entry into the earth's atmosphere).

The isotope boron-10 is used as a control for nuclear reactors, as a shield for nuclear radiation, and in instruments used for detecting neutrons. Boron nitride has remarkable properties and can be used to make a material as hard as diamond. The nitride also behaves like an electrical insulator but conducts heat like a metal.

It also has lubricating properties similar to graphite. The hydrides are easily oxidized with considerable energy liberation, and been studied for use as rocket fuels.

Demand is increasing for boron filaments, a high-strength, light weight material chiefly employed for advanced aerospace structures.

Boron is similar to carbon that it has a capacity to form stable covalently bonded molecular networks. Carbonates, metalloboranes, and other families comprise thousands of compounds. In instruments used for detecting neutrons deoxidizer in non ferrous metallurgy, grain refiner in aluminum; in delayed action fuses; igniter in radio tubes; coating material in solar batteries cementation of iron; oxygen scavenger for copper and other metals; in semi conductors, boron-coated

tungsten wires ; for fibers and filaments in composites with metals or ceramics; in high - temperature brazing alloys amorphous: in pyrotechnic flares to provide distinctive green color. As a catalyst for olefin polymerization and dehydration of alcohols. As an abrasive imports superior durability to cut-off wheels , effective as the major component of an ultra-high-pressure gasketing composition. Used in composite structural materials, in high temperature abrasives in special purpose alloys, and in steel making.

Table 2.2. World Consumption of Boron Minerals by Region and Application, 1993
(000 t B₂O₃)

	USA	UK	Other EC	Japan	Others	Total	% Total
Glass products	212	14	76	17	99	418	37,49
Ceramics	11	11	60	9	53	144	12,92
Agriculture	16	4	22	5	30	77	6,90
Detergents	15	24	122	1	3	165	14,80
Other	101	7	35	23	145	311	27,89
Total	355	60	315	55	330	1115	100

Source: Annual Report-Boron, US Bureau of Mines, 1994

The estimates shown in Table 2.2 show how the use of sodium borate in the production of detergents is much more important in Europe than in the USA and elsewhere in the world. The proportion of boron minerals consumed in ceramics is also much greater in Europe. Glass, particularly insulation grade glass fibres, is the principal application in the USA. Accounting for almost 50% of all demand for boron minerals.

2.3. World Reserves, and Reserve Base

The global distribution of borate deposits depends upon the appropriate combination of volcanic activity and a climate that has been fairly arid from the time of formation of the deposit to the present. For this reason, commercial borate deposits are largely confined to three areas of the world:

- i) the Mojave Desert of the southwestern USA
- ii) the Alpine orogenic belt in south-central Asia (including Turkey)
- iii) the Andean belt of South America

Table 2.3. Reserves and Resources of Boron ¹, 1996

(000 t B₂O₃)

Countries	Reserves	Reserve base ²
United States	40.000	80.000
Argentina	2.000	9.000
Bolivia	4.000	19.000
Chile	8.000	41.000
China	27.000	36.000
Iran	1.000	1.000
Kazakstan	14.000	15.000
Peru	4.000	22.000
Russia	40.000	100.000
Turkey	30.000	150.000
TOTAL	170.000	473.000

Source: Mineral Commodity Summaries, 1996, US Bureau of Mines

Note: (1) B₂O₃ contained

(2) Reserves, plus sub-economic reserves and other resources

2.4. World Production

Table 2.4. Boron Minerals: World Production, by Country 1/2/

(000 t)

Country	1993	1994	1995	1996	1997 e/
Argentina	146	215	245	342 r/	270
Bolivia (ulexite)	12	10	7	4 r/	5
Chile (ulexite)	117	86	211 r/	149 r/	150
China e/ 3/	155	188	140	157 r/	140
Germany (borax) e/	2	2	2	2	2
Iran (borax) e/ 4/	1	1	1	1	1
Kazakstan	8 r/	7 r/	7 r/ e/	7 r/ e/	7
Peru	37	30	41 r/	39 r/	40
Turkey 5/	1.079	1.140	1.144 r/	1.300 r/ e/	1.250
United States 6/	1.060	1.110	1.190	1.150	1.190 7/
Total	2.640 r/	2.800 r/	3.000 r/	3.160 r/	3.070

Source: U.S. Geological Survey-Minerals Information, "Boron", 1997.

e/ Estimated. r/ Revised.

1/ World totals, U.S. data, and estimated data are rounded to three significant digits; may not add to totals shown.

2/ Table includes data available through May 20, 1998.

3/ B₂O₃ equivalent.

4/ Data are years beginning March 21 of that stated.

5/ Concentrates from ore.

6/ Minerals and compounds sold or used by producers, including both actual mine production and marketable products.

7/ Reported figure.

U.S.A.—The majority of boron production continued to be from Kern County, CA, with the representing 100% of the total boron produced. American Borate Co. mined small amounts of colemanite and ulexite/probertite from the Billie Mine. Colemanite was processed at Lathrop Well, NV. Storage and grinding facilities were at Dunn, CA. Fort Cady Minerals Corp. produced a salable product named CADYCAL 100. The product was 43% boron oxide that screens 81% less than 325 mesh. Because CADYCAL is a chemically precipitated product, it has advantages in consistency of

the chemical composition; i.e., high boron oxide content, low impurities, and consistent physical size. The production process involves injecting a dilute acid 427 meters (1,400 feet) into the borate ore and then precipitating the borate rich ore to obtain a pure calcium borate product.

Argentina.—Mineral resources, including several active borate mines, are one of Argentina's great assets. The Argentine The Infrastructure Development Trust has been conceived to develop the natural resource base with technology that allows for the efficient, profitable, and environmentally safe extraction of minerals resources.

Borax Argentina S.A., a subsidiary of Rio Tinto Borax, was the country's leading producer of borates. Borax mines tincal at Tincalayu, hydroboracite at Sijes, and ulexite from two dry lake beds, Salar Cauchari and Salar Diablillos, all in the Salta Province at elevations more than 4,000 meters.

Sucursal Argentina division of S.R. Minerals (Barbados) Ltd. developed the Loma Blance mine in Jujuy Province in 1996. The mines has tincal, ulexite, and inyoite with average ore grades around 16% boron oxide.

The third producer in Argentina is Ulex S.A. Ulex produces colemanite and hydroboracite from its mine in the Postos Grandes area of Salta Province.

Bolivia.—Borate production is from small companies mining ulexite from government concessions around Salar de Uyuni in the Bolivian Altiplano. Some of the crude mineral production is sold to Corban SA, La Paz. Corban produces dried and calcined ulexite at its Oruro plant and small volumes of borate decahydrate.

Canada.—Kobitex Inc. distributes Etibank's refined boron minerals in North America. Included is granular and powdered boric acid, borax penta and decahydrate from Bandirma, and Etibor-48 and anhydrous borax from Kirka. The products are shipped from Bandirma and Izmir.

Chile.—Boron Chemicals International Ltd. continued plans to develop the Aguas Blancas boron project in Northern Chile.

Quimica e Industrial del Borax Ltda. (Quiborax) mined from Salar de Surire, the largest ulexite deposit in the world.

There are other small mines such as Sdad Boroquimica Ltda., that mine ulexite from salars in regions I and II in the north.

China.—There are numerous producers of borates in the Liaodong peninsula in Liaoning province. The ores are primarily magnesium borates such as szaibelyite. Other production is from the playa lakes in Qinghai, where borate minerals such as ulexite, pinnoite, hydroboracite, and borax have been produced from brines. Total Chinese production is estimated around 100,000 tons per year, with an additional 20,000 tons per year of boric acid (Kendall, 1997).

Europe.—The industrial minerals market in Europe is characterized by high volumes of imported materials, mostly forwarded to the industrialized areas of Belgium, France, Germany, or the Netherlands for destinations in central Europe such as Austria, and (Chernyshov, 1997). the Czech Republic, or Slovenia.

India.—Submarginal borax reserves occur in the Puga Valley Districts of Jammu and Kashmir. In Rajasthan, the bitterns from Lake Sambhar are reported to contain about 0.5% borax.

Kazakstan.—More than 100 boron deposits have been discovered in northern Prekaspiy. Boron deposits of the Inder groups are concentrated in the gypsum of salt domes and salt rock masses. Borates associated with the gypsum include asharite, hydroboracite, inyoite, and ulexite. At two sites, dredging takes place at a depth of 15 to 20 meters below the water level using drag lines. Borate ore reserves do not exceed 2 million tons, but the potential could reach 120 million tons of 9% boron oxide (Alexeev and Chernyshov, 1997).

Mexico.—Vitro SA de CV sold its raw material subsidiary, Materias Primas y Minería to Unimin Corp., the U.S. silica sand giant. The \$131 million cash deal is subject to the signing of a definitive agreement and government-regulatory approval.

Materias Primas's primary customer is the Vitro Group, and this relationship will be maintained under a 10-year feldspar and silica sand supply arrangement (Industrial Minerals, 1997c). Materias Primas was formerly in a joint venture with Borax for the development of the Magdalena colemanite property, until 1993, when the venture was dissolved.

Peru.—Cia Minera Ubinas SA and Quimica Oquendo SA, linked under the Inkabor name and owned by the Italian Colorobbia Group, mined ulexite. Ubinas mines at Laguna Salinas, 80 kilometers east of Arequipa. The open pit operation produces some 150,000 to 180,000 tons per year of ulexite ore during 6 or 7 months of mining. Large stocks are maintained for sales during the winter season. The crude ulexite is washed to produce an ulexite concentrate or supplied to Oquendo for boric acid production. Oquendo's plant near Lima produces around 12,000 tons per year of boric acid and 15,000 tons per year of concentrated ulexite. Small volumes of calcined ulexite is sold for fertilizer and the rest of the Inkabor's output is exported (Kendall, 1997).

Russia.—Boron ore reserves are concentrated in deposits of magnesias-karn and lime-karn formations found in Southern Yakutiya (Tayozhnoye), in Buryatiya (Solongo) and in the northeast (Titovskoye and Nalyodnoye). The boron-iron deposit at Tayozhnoye is of Archean age. Here karn ore bodies lie among dolomite, marble, shale, and gneiss. The ore bodies are formed from magnetite and sometimes from ludwigite and ashanite. The reserves exceed 100 million tons of 34% boron. Presently there are no known processing technologies to make the production profitable (Alexeev and Chernyshov, 1997).

Serbia.—A joint-venture company Ras-Borati Ltd., began drilling the Piskanja boron deposit in the Jarandol basin, located near Baljevac in southern Serbia. Ras-Borati Ltd., established February 1997, is a 50-50 joint venture between Erin Ventures Inc. of Kelowna, British Columbia, Canada, and Elektroprivreda, the national power company of Serbia. The drilling program is planned to raise the status of a 7-million-ton block of reserves grading 35% to 39% from indicated to proven. The minerals are

primarily colemanite and ulexite. Ras-Borati also holds rights to a borate deposit in the Jarandol basin named the Pobrđjski Potok deposit. Proven and probable reserves of 140,000 tons ore averaging 37% boron oxide were identified (Industrial Minerals, 1997b).

Tajikistan.—A skarn borosilicate deposit at Ak-Arkhar, situated at an elevation of 4,400 to 5,000 meters, has measured and indicated reserves of danburite ore that exceed 80 million tons (Alexeev and Chernyshov, 1997).

Turkey.—Turkey's boron operations are under the control of the Government corporation, Etibank. Ulexite is mined at Bigadic; colemanite at Bigadic, Emet, and Kestelek; and tincal at Kirka. Bigadic Colemanite Works, in Bigadic District of Balıkesir Province, has a production capacity of 500,000 tons of run-of-mine colemanite and ulexite ores from three open pits and two underground mines. The concentrator has a capacity of 400,000 tons per year. The Bigadic borate district was reported to be the world's largest colemanite and ulexite deposits. All products at Bigadic are for export. Emet Colemanite Works, located in Emet District of Kütahya Province, had a production capacity of 700,000 tons per year of run-of-mine ores, both open pit and underground mines. Colemanite ores are processed in a 500,000-ton-per-year concentrator and supplied to domestic and international markets. Most of the colemanite concentrates are exported. The remaining production is used in the boric acid plant in Bandırma. Kestelek Boron Mine is located in Mustafakemalpaşa, a district of Bursa Province. The underground mine was closed at the end of 1994 because of high cost and low sales. Production is now from the open pit. The Kirka Borax Works is near Seyitgazi District of Eskişehir produces tincal concentrate, borax pentahydrate. The concentrator has a capacity of 600,000 tons per year of tincal concentrates. A derivatives facility was begun in 1984 for the production of 160,000 tons per year of borax decahydrate and 60,000 tons per year of anhydrous borax. Technical problems regarding the anhydrous production are being studied. An expansion project was under way to increase pentahydrate production capacity to 320,000 tons per year.

Uzbekistan.—An oil and gas condensate deposit at Dzhartchi, has the potential to produce 377 tons per year of boron oxide at a pumping rate of 4,000 cubic meters per day for over 20 years (Alexeev and Chernyshov, 1997).



CHAPTER THREE

BORAX PROCESSING AT KIRKA PLANT

3.1 Geology of the Kirka Orebody

The principal ore mineral is tincal, a sodium borate with the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. The ore has an average content of 25.4% B_2O_3 , although some parts of the ore body have values up to 26-27% B_2O_3 . Ulexite, inyoite, colemanite, and tincalconite, and alteration products of tincal also found in the deposit, but in lesser quantities, and only in the upper part of the orebody.

There are three types of ore. The most common is layered material, which makes up by far the greatest bulk of the ore, but there is also a breccia type of ore and a secondary material, which is a crystalline glassy ore. The glassy material is relatively rare, which is unfortunate, because it is the highest purity ore found in the mine. With such a high percentage of the B_2O_3 in the glassy phase it could almost be utilized without any concentration.

The majority impurity in the ore is clay, which makes up an average 10% of the ore. Within the main ore type of layered material, thin layers of clay interlayered with tincal. The deposit as a whole consists of layers of conglomerate, tuff, dolomite, marl, and a clay with borax. Ore in the dipping orebody is found at depths of 2-150 meters. The average overburden thickness is about 70 meters (Ted Dickson, 1985).

3.2 Mining and Processing

3.2.1 Mining the Kirka Deposit

From information developed in the geological study, large tonnage's of ore can be mined economically by open pit techniques. .The pit is worked in benches 8 meters high and 25 meters wide, and the angle of the pit slope is 20-22°. Eventually the step width will be reduced to 145 meters and the pit slope angle will be 45°. There is a total of 500 m. tones of reserves (combined proven, probable, and possible), which will last 500 years at current rates of production.

After removal of overburden, the ore is blasted and loaded into trucks with a front end loader for the short trip to concentration plant, 13-14 minute round trip.

Good mining control is an absolute necessity for efficient beneficiation and profitable milling operations. It is necessary to maintain constant surveillance of ore faces being mined so as to reject undesirable calcium borates from mill ore feed.

Figure 3.2.1.1 and 3.2.1.2 shows topographic view of Kirka Open Pit Mine.



Figure 3.2.1.1 Topographic View of Kirka Open Pit Mine



Figure 3.2.1.2 Top View of Open Pit Mine in Kirka3.2.2 Processing Kirka Ore

3.2.2.1 The Concentrator Unit

After the short trip from the mine, the ore trucks tip their loads into bin from which the primary crushers are fed. Ore is passed through a screen before entering the crushers. Primary crushers reduce to minus 100 mm and hammer crushers reduce it further to minus 25 mm. Stocks of about 10,000 tones of this 25 mm material are held at the plant as surge feed for later processing. From the stocks, vibrator feeders are used to move the material onto screens that separate the minus 6 mm fraction. Oversize is crushed to minus 6 mm in roller crushers. From here the crushed borax ore is fed to scrubbers, where much of the clay, which is the major impurity, is removed. Clay is removed from the minus 1 mm fraction by passing it through cyclones, then through a classifier, and finally through a centrifuge drier. The final product from the plant is a minus 6 mm concentrate with about 6-8% moisture and 32% B_2O_3 . Figure 3.2.2.1 shows flow sheets of Concentrator Unit in Kırka.

3.2.2.2 The Derivatives Plant

Feedstock for the plant comes either direct from the concentrator or from stockpiles of concentrate. The concentrate is initially dissolved in live steam (98°C), and the resultant solution is saturated to 26% $\text{Na}_2\text{B}_4\text{O}_7$. The concentrated solution is then filtered through a series of 8 filters before going into a 1,000 tone liquid storage tank. From the storage tank, solution is fed to the crystallizer circuits. If the solution is cooled from its storage temperature of 98°C to 66°C in a vacuum with absolute pressure of 0.23 atmospheres, pentahydrate crystals form. Fine crystals are put through hydrocyclones to reduce the water content and coarser crystals that fall to the bottom of the tank are separated from the water using centrifugal dryers. The pentahydrate crystals has 4-5% moisture is fed to rotary dryer and after that sent to storage tank for shipment. After 1997, the capacity of borax pentahydrate is doubled to 320,000 tpa. Figure 3.2.2.2.1 shows Borax Derivative Plant 1 and Figure 3.2.2.2.2 shows Borax Derivative Plant 2.

FLOW SHEET OF BORON DERIVATIVE PLANT 2

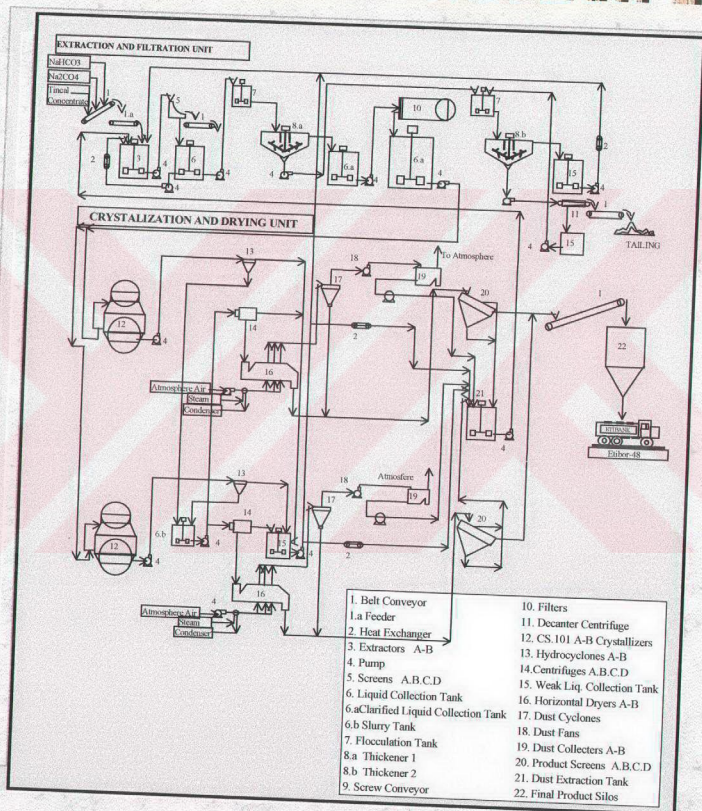


Figure 3.2.2.2.2 Borax Derivative Plant 2 in Kırka

3.3 Direct Production of Borax Pentahydrate Using Crushed Borax Ore

Since two companies are controlling entire boron market, most of the industrial applications or technologies are kept secret or publicly not known. As far as our knowledge, this study will be first to apply borax, therefore there is no report to summarize here.

Tincal ore in Kirka-Eskişehir is the largest borax deposit of the world. The main constituent being water-soluble borax decahydrate, tincal ore containing 20-45% of water insoluble materials which consists mainly of dolomite and montmorillonite in varying proportions. In conventional beneficiation process, a large part of these impurities are removed from the ore by washing it at ambient temperature with dilute solution. Tincal concentrate thus produced is dissolved in dilute borax solution at high temperature and rest of the water insoluble materials are separated from the concentrated borax solution by flocculation in order to obtain a clear solution for the crystallization of borax pentahydrates.

Proposed system starts directly extraction of crushed ore in extraction unit. These type of extractors called "Screw-Conveyor Extractors", employing the screw-conveyor principle, is neither a percolator nor a dispersed-solids extractor. Although it is often classed with percolators, there can be sufficient agitation of the solids during their conveyance by the screw. Concurrent extraction takes place in Extractor 1 and the solids to be leached are fed together with live steam and partially enriched borax solution. Until reaching the density of 1250 g/l, the borax rich(saturated) solution is returned to Extractor 1 and then fed to thickener 1 and 2 for removal of suspended clay particles. Overflow of Thickener 1 is fed to filter and then crystallizer for production of pentahydrate. The underflow of Thickener 1 goes to Thickener 2 for flocculation of fine suspended particles. The overflow of Thickener 2 returns to Extractor 1 and underflow of Thickener 2 goes to decanter centrifuge for further processing.

The flocculation operation is the most important step of the whole process, because inefficient flocculation can cause problems such as contamination of the product with impurities, a loss of yield and environmental pollution. In the production of tincal concentrate, borax pentahydrate, flocculation conditions such as temperature, solid and borax concentration of the suspensions to be flocculated may vary in a wide range. The chemical compositions of the water insoluble materials to be flocculated is also determined to be different.

In this study, effects of process conditions such as temperature, solid and borax concentration of the suspension, composition of the suspension, composition of the insoluble materials, the time required to dissolve the ore, and the type of synthetic polymeric flocculants were investigated in order to determine optimal flocculation conditions of tincal slimes.

In this study, a laboratory, 1 t/h and 10 t/h capacity tests were conducted to come up different processing techniques replacing Concentrator Unit and wiping out liquid wastes. Proposed processing techniques should have;

- ◆ Higher recovery than present process.
- ◆ Both processes should have at least same energy consumption.
- ◆ Present Borax Plant in Kirka has two tailing sites, one in Concentrator Unit, flow rate approximately $400 \text{ m}^3/\text{h}$ and the other one goes from Boron Derivative Plant, 25 t/h. Both wastes are liquid so it goes to tailing ponds. Increasing environmental impact pushes Eti Holding to come up with more friendly technology to environment. Proposed technology will focus on wastes that will be solid.
- ◆ Proposed process should be at least as easy as present process.
- ◆ Soda is being used to control some of the impurities at present, and should not be increased at proposed system.

CHAPTER FOUR

EXPERIMENTAL STUDIES

4.1. Materials Used in Experimental Studies

4.1.1 Sample Preparation

Ore samples from the Kirka deposit were used to develop processing flow sheets. For the three different orebody, approximately 1000 kg of each, total 3000 kg sample was collected, mixed and blended to form representative samples. In order to prepare the samples for analysis and leach tests, the samples were subjected to comminution. Siebtechnik Laboratory Type Single-Toggle Crusher EB for primary crushing, Siebtechnik Laboratory Type Hammer Impact-Mill for secondary crushing and Siebtechnik Laboratory Type Disc Mill for fine grinding were used for the preparation of sample for physical, mineralogical and chemical studies. Sample preparation and material characterization and experimental studies flowsheet is shown in Figure 4.1.1.1

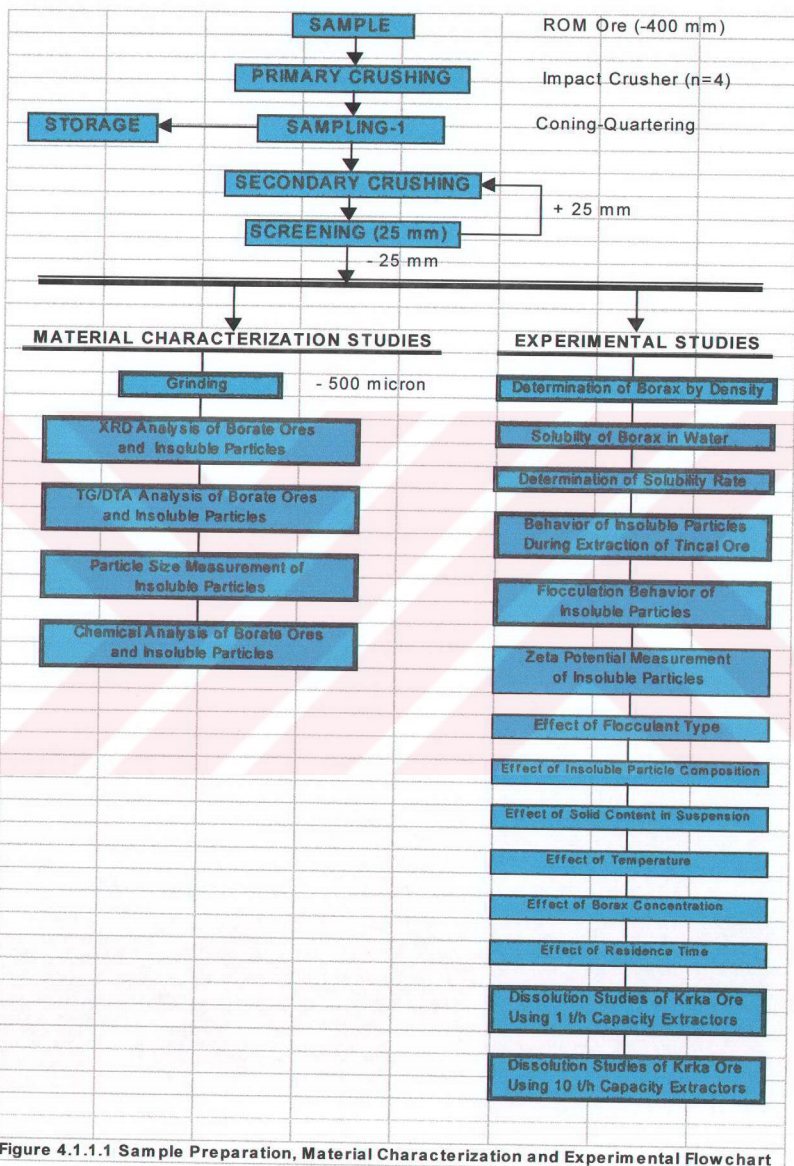


Figure 4.1.1.1 Sample Preparation, Material Characterization and Experimental Flowchart

4.1.2 Flocculants

Various polymeric flocculants used in this study are listed in Table 4.1.2.1

Table 4.1.2.1 Flocculants used for test

Commercial Name	Producer Name	Physical State	Chemical Structure	Charge	Molecular Weight	Acrylic Acid Content
FO4190	SNF Floerger	Solid	PAM+ ADAMMECl	Cationic (10% Cationic)	$(1-1.5)10^7$	-
Cat Flocc TL	Calgon	Liquid	DADMAC	Cationic (100% Cationic)	$(3-4)10^5$	-
SUPERFLOC N100	Cyanamid	Solid	PAM	Non-ionic	$(3-4)10^6$	4,27
SUPERFLOC A100	Cyanamid	Solid	PAM	Anionic (10% Anionic)	$(3-15)10^6$	10,68
SUPERFLOC A110	Cyanamid	Solid	PAM	Anionic (15% Anionic)	-	14,91
PEO	Union Carbide	Solid	PEO	Non-ionic	5×10^6	-

4.2 Methods

4.2.1 Mineralogy of Kırka Borate Ores

With the development of X-ray diffraction (XRD) it became possible to rapidly and precisely characterize the crystal structures of crystalline materials. Since each mineral has its own characteristics crystal structure, it is possible to identify unknown minerals by comparison of their XRD spectra with the spectra of standard minerals whose identities are known (N.L Weiss, 1985).

Kırka deposit were investigated in detail by Eti Aluminum A. Ş, Seydişehir, KONYA, Materials Laboratory, December, 1999 using x-ray diffraction methods. For the x-ray diffraction studies, Siemens D 5000 instrument were used.

4.2.2 Differential Thermal Studies of Kirka Borate Ores

Differential thermal analysis (DTA) was one of the first instrument to be used in the study of minerals. Most early DTA instrument were individually hand built and the quality of the instrument varied widely. It was found that the results obtained by DTA of a single sample were not reproducible by other workers using other instruments. It was determined that different results were obtained depending on the design of the instrument used for the analysis, sample preparation (particle size), atmosphere in contact with samples, and many other variables. Because of the numerous problems with DTA, the technique fell into relative disuse until about 1960, when carefully designed instruments capable of controlling the variables became commercially available. By this time, many other thermal analytical techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and evolved gas analysis (EGA) had been developed. The thermal analysis methods are quite versatile and can analyze a wide range of sample sizes and purities, depending upon the information desired.

Thermal Analysis covers a series of techniques which determine the physical and chemical properties of a substance or a mixture as a function of temperature and/or time. The sample is subject to a controlled temperature program, which can have preselected heating, cooling or isothermal stages. Seteram/France origin TG/DTA instrument were used for differential thermal studies.

4.2.3 Particle Size Measurements

Recently, the application of laser has been introduced to the particle size measurement of powdered products. The principle used is based on the diffraction of a coherent light beam by the grains of powder to be analyzed, which results in the presence of light outside the geometrical limits of the beam. The powder to be examined is dispersed in a liquid which is then circulated through a glass cell. A parallel beam from a low-power laser lights up to the cell, and the beam which leaves is focused by means of a convergent optical system. The values of

illumination with and without sample are read by an electronic detector and fed to into a programmed processor, which then displays the results as cumulative percentage undersize.

This method has many attractive advantages for routine analysis, such as simplicity of use, extremely quick results, and reproducibility.

For the particle size measurements of insoluble particles at Kirka ore body, Malvern System 2600 Particle Sizer were used.

4.2.4 Chemical Composition of Clay Materials been with Kirka Borate Ores

Four different samples were selected from Kirka open pit tincal mine, cleaned from tincal mineral to obtain water insoluble part of the ore and labeled according to their native color as blue, green, gray and white.

Selected insoluble particles first ground to minus 0,074 mm by pulverised disc mill. It was placed in a laboratory oven at 60 °C for 24 hours, main constituents were determined by Varian 300A Atomic Absorption Spectrophotometer analytical instrument and wet-chemical methods.

Chemical composition also were determined using X-ray fluorescence (XRF) analysis. XRF analysis is a physical method which directly analyses almost all chemical elements of the periodic system in solids, powders or liquids. Elemental analysis using XRF provides a non-destructive and environmentally friendly analysis method without having to bring solid samples into solution and without having to dispose of solution residues, as is the case with all wet-chemical process. Basic prerequisite for an exact and reproducible analysis is a plane, homogenous and clean analysis surface. For analysis of very light elements, e.g. beryllium, boron and carbon, the fluorescence radiation to be analyzed originates from a layer, whose thickness is of only a few atom layers up to a few tenths of micrometer and which strongly depends on the sample material (Bruker Axs, 1995). XRF studies using

Shimadzu, Japan origin XRF-1700 model instrument on insoluble clay materials were used for analysis.

4.2.5 Relationship between Concentration of Borax and Density

The easiest and fastest way of measuring $\text{Na}_2\text{B}_4\text{O}_7$ % would be determining the density of liquor. Hydrometers are used for this purpose. During laboratory and pilot scale studies, hydrometers are used for measuring densities.

Because of big difference between Garret Company and Eti Bor A.Ş., Kırka Plant, Laboratory on the values of density-borax content, these values were measured again at Eti Holding A.Ş., Research Laboratory.

4.2.6 Solubility of Borax in Water

For the solubility studies Laboratory type jacketed glass vessel reactor, maintaining desired temperature laboratory type cryostat and measuring density calibrated hydrometer were used. Figure 4.2.6.1 shows laboratory experimental apparatus being setup for running test on solubility and flocculation studies

4.2.7 Determination of Solubility Rate for Borax Decahydrate at 95 °C

Solubility tests were done by Garret Company using borax decahydrate crystal. For 98 °C, and 1000 rpm. It was also done in Eti Holding A.Ş., Research Center, using 500-1000 µm borax decahydrate crystals.

To see how close we are for the solubility rate equation found using borax decahydrate crystals, we had also run solubility tests using run of mine ore brought from Kırka deposit. Kırka crystalline glassy ore were used to determine solubility rate at 95 °C. Known amount of water first put into jacketed glass reactor at 95 °C, and 25 rpm. After that, weighted Kırka crystalline glassy ore pieces were put into

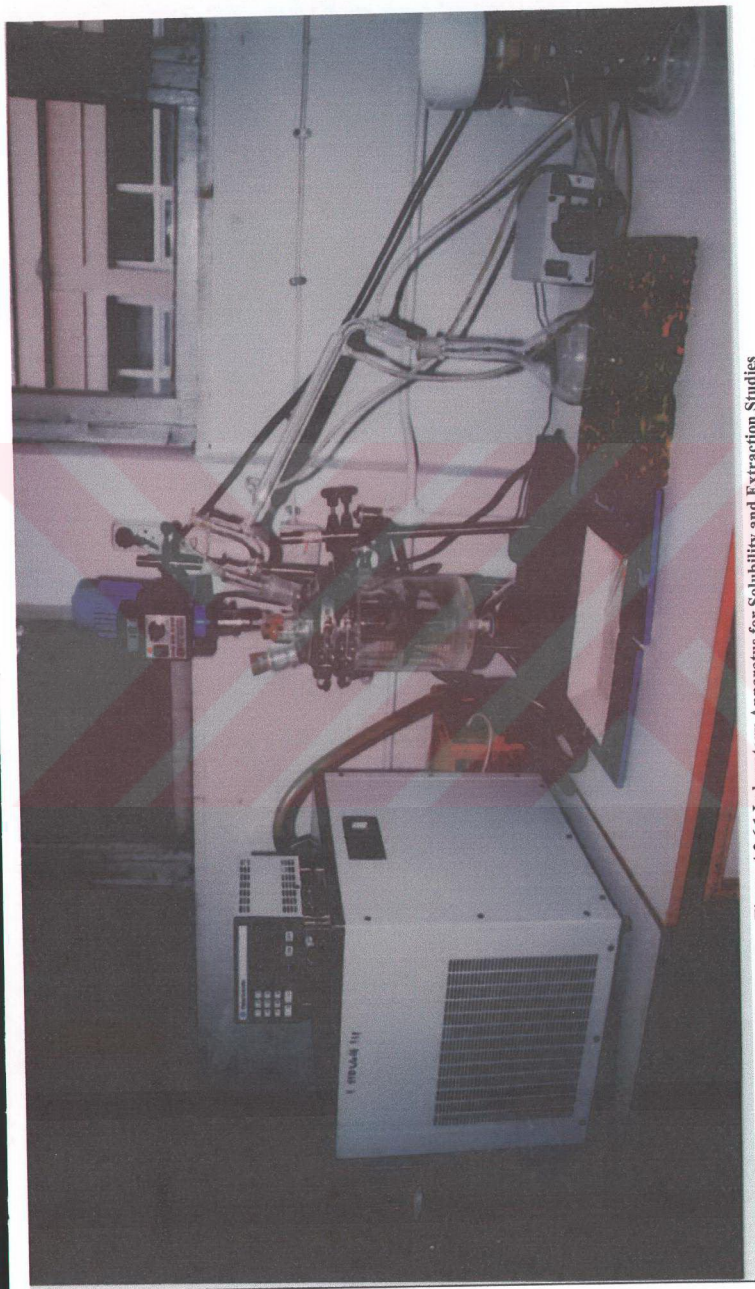


Figure 4.2.6.1 Laboratory Apparatus for Solubility and Extraction Studies

reactor and waited until totally dissolve, and dissolution time were recorded. Dissolution step followed one piece to other until saturation point were reached. During the experiment 20 grams and 70 grams crystalline glassy ores were used. After each experiment, the density of liquor were measured.

To have better understanding, the solubility rate tests were done using laboratory size extractor which will be similar to industrial design. The extractor was first filled with borax saturated solution, and to keep the temperature about 95°C , hot steam and heat exchanger were used. Travelling time on screw type extractor were set to 10 minutes by frequency control device, and after 10 minutes passed, the solid was checked for undissolve borax.

4.2.8 Behavior of Insoluble Particles During Extraction of Tincal Ore

Insoluble particles comes into weak mother liquor with borax stays suspended in solution but minor amount of insoluble particles or some other borax minerals beside tincal dissolve and get into borax solution.

4.2.9 Flocculation Behavior of Insoluble Particles

Flocculation involves the information of much more open agglomerates than those resulting from coagulation and relies upon molecules of reagent acting as bridges between separate suspended particles. The reagents used to form the "bridges" are long-chain organic polymers, which were formerly natural materials, such as starch, glue, gelatine, and guar gum, but which are now increasingly synthetic materials, loosely termed polyelectrolytes. The majority of these are anionic in character but some of them are non-ionic, and some cationic, but these form a minor proportion of the commercially available products of today's flocculant market. Inorganic salts are not able to perform this bridging function, but they are sometimes used in conjunction with an organic reagents as a cheaper means of charge neutralization, although an ionic polyelectrolyte can and often does perform both function.

The polyacrylamides, which vary widely in molecular weight and charge density, are extensively used as flocculants. The charge density refers to the percentage of the acrylic monomer segments which carry a charge.

Charge density may be controlled in manufacture between the limits 0-100%, to produce a polyacrylamide of anionic character, weak or strong, depending on the degree of hydrolysis.

By similar chemical reactions, polymers of cationic character can be produced. It would be expected, since most suspension encountered in the minerals industry contain negatively charged particles, cationic polyelectrolytes, where the cation adsorbs to the particles, would be suitable. Although this is true for charge neutralization purposes, and attraction of the polymer to the particle surface, it is not necessarily true for the for the "bridging" role of the flocculant. For bridging, the polymer must be strongly adsorbed, and this is promoted by chemical groups having good adsorption characteristics, such as amide groups. The majority of commercially available polyelectrolytes are anionic, since these tend to be of higher molecular weight than the cationics, and less expensive.

The mode of action of the anionic polacrylamide depends on a segment of the very long molecule being adsorbed on the surface of a particle, leaving a large proportion of the molecule free to be adsorbed on another particle, so forming an actual molecular linkage, or bridge, between particles (B.A. Wills, 1988).

All flocculation experiments were performed using a Jar test apparatus modified by a thermostated jacketed to carry out the flocculation at different temperatures. Suspension of the required solid density were prepared in borax solutions of known concentrations and the mixtures were agitated at 130 rpm for 30 minutes. 0.05 % solutions of flocculants were added and the suspension were further agitated for floc formation for 1 minute. After being allowed to settle for 10 minutes, the turbidities of supernatants were determined with Orbeco Hellige, USA origin 965 model turbidity instrument.

4.2.10 Zeta Potential Measurement of Insoluble Particles

Zeta potential measurement are made using a technique called microelectrophoresis. A high quality stereoscopic microscope is used to comfortably observe colloidal particles inside a chamber called an electrophoresis cell. Electrodes placed in each end of the chamber are connected to a power supply which creates an electric field across the chamber. Charged colloids move in the field and their velocity and direction are related to their zeta potential. The instrument first measures the electrophoretic mobility of the particles, which is expressed as "micron/second per volt/centimeter". The first term, micron per second, is simply velocity measurement, while the second is an expression of the electrical field strength. Zeta potential (in millivolts) is calculated from the measured electrophoretic mobility.

Surface forces are much more important than gravity effects in controlling the behavior of colloidal systems. Therefore, zeta potential measurement on insoluble particles were carried out using Zeta-Meter, Inc., USA origin, Zeta-Meter System 3.0+ instrument. These particles were characterized based on their color as blue, green, gray and white. Concentration of insoluble particles were 0,2 g/l.

4.2.11 Effect of Flocculant Type

For this purpose, suspension of the four different samples in borax solution containing 3% $\text{Na}_2\text{B}_4\text{O}_7$ were flocculated at 35 °C and optimal flocculant dosages were determined. The solid concentration of the suspension were kept at 30g/l.

4.2.12 Determination of Effect of Insoluble Particles Composition

Turbidity of the solutions at optimal polymer dosage increased from the blue, green, gray and white samples, respectively. This tendency was also observed for all other flocculants.

4.2.13 Effect of Solid Content in Suspension

A100 and PEO type flocculants were used for flocculation studies where the solution containing 3% borax and 30, 50, 75 and 100 g/l impurities in suspension were tested for half an hour. Targeted turbidity values derived from flocculation results done before solution containing 3% borax and 30 g/l impurities. For example, the suspension containing 30 g/l impurities had 47 NTU turbidity value for blue particles were taken as targeted value, therefore flocculant dosage kept feeding until targeted values reached for 50, 75 and 100 g/l suspension.

4.2.14 Effect of Temperature

To be able to determine temperature effect on flocculation of different insoluble particles, flocculation tests were carried out at 35 °C, and 65 °C using non-ionic (N100), light ionic (A100) and PEO.

4.2.15 Effect of Borax Concentration on Flocculation

Previous studies indicated that increase on borax concentration has positive effect for flocculation. Therefore, flocculation studies for different insoluble particles were carried out at different borax concentration.

Flocculation studies of insoluble particles on 3%, %8 and %15 borax concentration were carried at 65 °C using A100 and PEO flocculants.

4.2.16 Effect of Suspension's Residence Time

During the extraction of tincal concentrate, the insoluble particles remains at least 30 minutes in suspension before borax concentration of solution reaches 30% borax. Therefore, to determine the effect of residence time on flocculation, the insoluble particles kept in solution for 30 minutes before carried out any test.

4.2.17 Dissolution Studies of Kirka Ore Using Pilot Scale Extractor

Pilot Scale Extractors were made in Eti Bor A.Ş., Bandırma Plant with the capacity of 1 t/h. These type of extractors called "Screw-Conveyor Extractors", employing the screw-conveyor principle, is neither a percolator nor a dispersed-solids extractor. Although it is often classed with percolators, there can be sufficient agitation of the solids during their conveyance by the screw. Concurrent extraction takes place in Extractor 1 and the solids to be leached are fed together with live steam and partially enriched borax solution. Until reaching the density of 1250 g/l, the borax rich(saturated) solution is returned to Extractor 1 and then fed to thickener for removal of suspended clay particles. Overflow of thickener is fed to filter and then crystallizer for production of pentahydrate, the underflow of thickener goes to decanter centrifuge for further processing. Figure 4.2.17.1 shows schematic view of leaching unit.

Leaching mainly takes place in Extractor 1 which uses a horizontal screw section. In Extractor 2, the axis of the extractor is tilted to about 20 °C from the horizontal and a screw in an inclined section for washing, draining, and discharging the extracted solids.

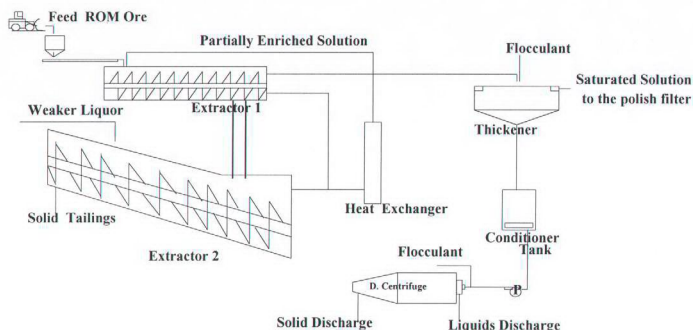


Figure 4.2.17.1 Leaching Unit

4.2.18 Decanting

The pilot scale decanter centrifuge which was tested at Etibank Kirka Borax Works was made of Flottweg (Germany), model Z-23-4/401, with capacity of $1 \text{ m}^3/\text{h}$. During the experiments the temperature of the slurry was 92°C , feed rate $0.7\text{--}1.0 \text{ m}^3/\text{h}$ and decanter speed was between $2600\text{--}3000 \text{ min}^{-1}$.

Separation of solid particles in underflow of thickener was succeeded by using decanter centrifuge with flocculant dosage.

A decanter centrifuge separates liquids from solids fast and efficiently by sedimentation. Solid particles settle out of liquids, because they are heavier. Normally this process takes time, but it can be speeded up by spinning the solid/liquid mixture, so that centrifugal forces cause solid particles to separate out faster (Flottweg 1993).

The decanter can be set for optimum separation of any mixture by simple adjustment to;

- ◆ The bowl revolutions per minute
- ◆ The differential speed of the scroll
- ◆ The scroll geometry
- ◆ The weir setting
- ◆ The impeller setting

A cutaway drawing of a two-phase decanter centrifuge is given in Figure 4.2.18.1.

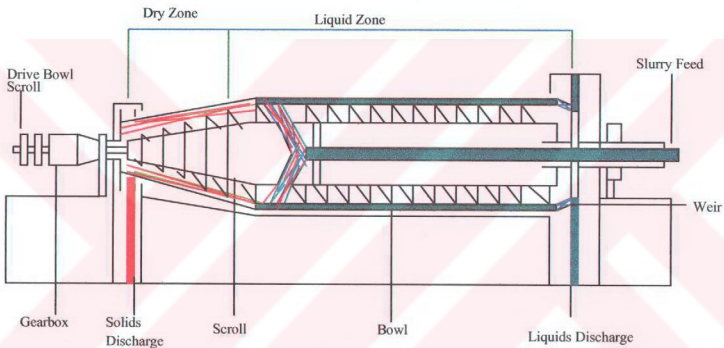


Figure 4.2.18.1 Two-Phase Decanter Centrifuge

4.2.19 Semi-Industrial Experimental Studies Using 10 t/h Capacity Extractors

Before deciding whether proposed system should applied to Kirka or not, first a 50 kg/h capacity laboratory extractor used and after successful results moved on building 1 t/h capacity two step extractor. In both studies, some mechanical and technical problems encounter, lots of confidence gained.

With the 10 t/h capacity extractors, proposed system will be controlled mechanically, technically, key parameters watch carefully, and final touch and look will be delivered.



4.3 Results and Discussion

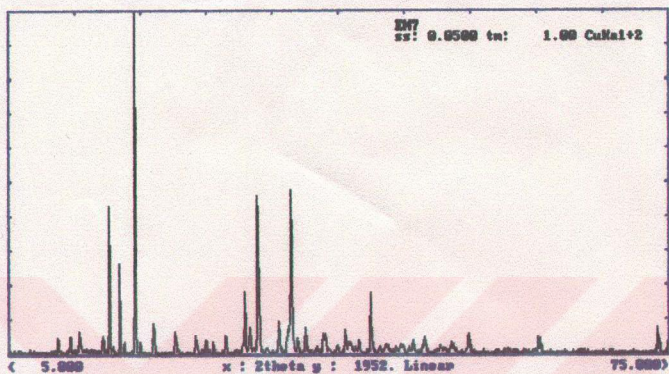
4.3.1 Mineralogy of Kirka Borate Ores

Kirka deposit were investigated in detail by Eti Holding, Research and Development Center, December, 1999 using x-ray diffraction methods. For the x-ray diffraction studies, Siemens D 5000 instrument were used. Figure 4.3.1.1 shows X-ray diffraction spectra for tincal ore and Appendix 4.3.1.1, 4.3.1.2, 4.3.1.3, 4.3.1.4, 4.3.1.5 and 4.3.1.6 shows X-ray diffraction spectra for insoluble particles.

Material is essentially massive borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), the gangue consists of montmorillonite clay, dolomite [$(\text{Ca}, \text{Mg}) \text{CO}_3$], and magnesite ($\text{Mg} \text{CO}_3$). Minor amounts of inderite ($\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$) and ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$) also is present.

Relative to the borax crystals, which range up to several centimeters in length, the gangue minerals are very small. The clay minerals are typically two microns or less and the carbonate minerals are generally less than 30 microns.

TINCAL ORE, KIRKA DISTRICT



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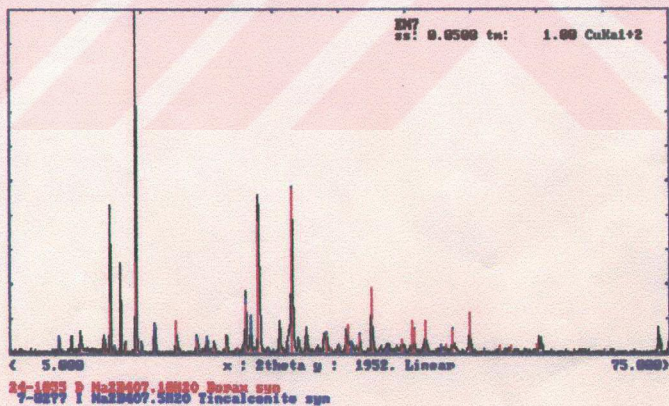


Figure 4.3.1.1 X-Ray Diffraction Spectra for Tincal Ore

4.3.2 Differential Thermal Studies of Kirka Borate Ores

Seteram/France origin TG/DTA instrument were used for differential thermal studies. TG/DTA studies indicated that three different clay minerals are present. The dominant clay is a buff-colored montmorillonite that shows the water of hydration is released over two distinct intervals. The first loss occurs at room temperature if the humidity is low, and continues up to approximately 250 °C. Clay that had been previously dried at room temperature (22 °C) lost 15% of its original weight at 300 °C. The second water loss begins at approximately 470 °C and is completed at 570 °C. Weight loss at the higher temperature amounts to 19.36% of the original weight, making the total weight loss due to dehydration 34.40%. Figure 4.3.2.1 and Appendix 4.3.2.1 shows TG/DTA Differential Thermal Analysis of buff-colored montmorillonite. The second clay, observed only in minor amounts and believed to be a contaminant, is a gray-colored montmorillonite-illite layer material. This gray clay has not been observed "in situ" as the buff-colored clay, but rather found only occasionally as lumps and concretions. Similar to the buff clay, the gray clay also releases water over two intervals. However, the water loss occurs at slightly higher temperatures and the weight loss is not as great. Appendix 4.3.2.2, 4.3.2.3, and 4.3.2.4 shows TG/DTA Differential Thermal Analysis of gray-colored montmorillonite-illite material. Appendix 4.3.2.5 shows TG/DTA Differential Thermal Analysis of white-colored dolomite. Appendix 4.3.2.6 shows TG/DTA Differential Thermal Analysis of tincal ore.

Figure 5.10

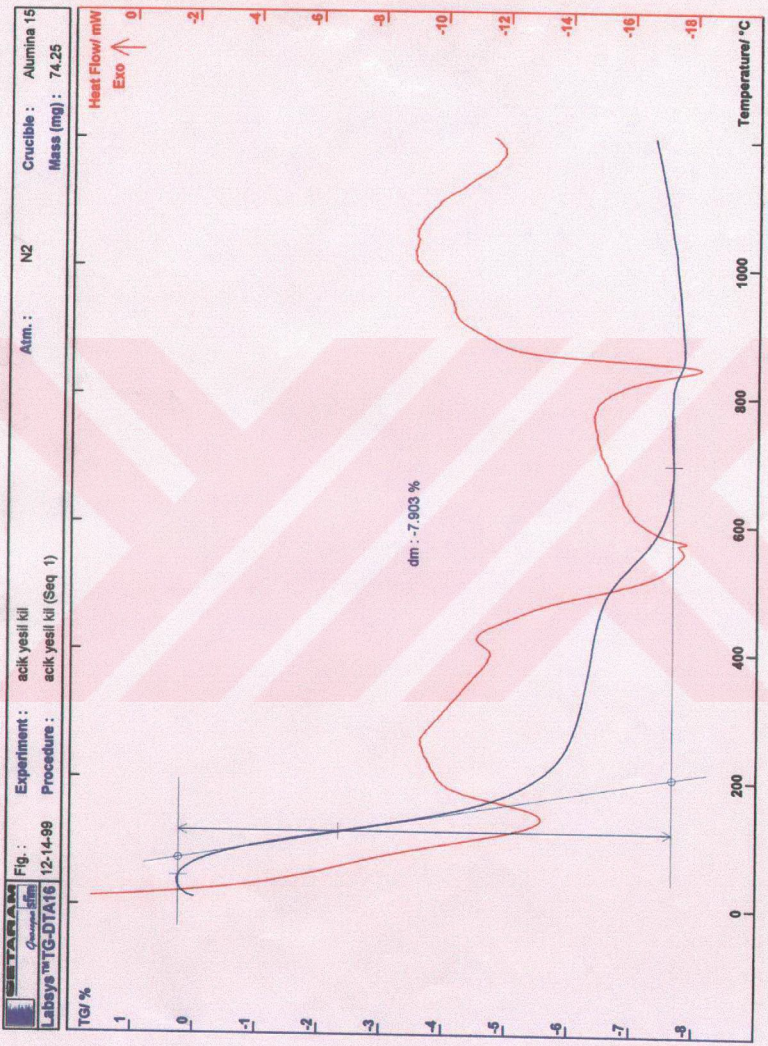
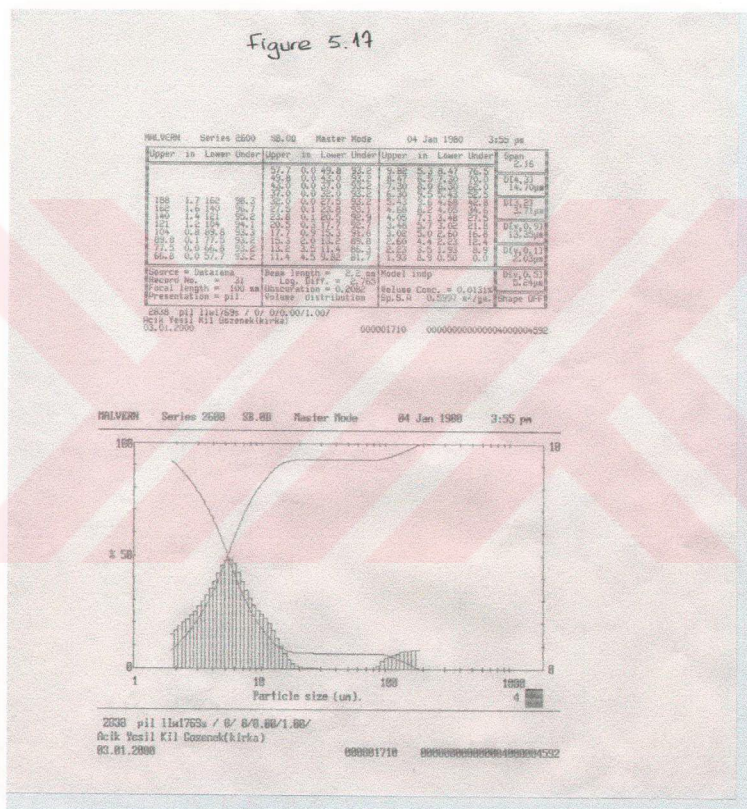


Figure 4.3.2.1 TG/DTA Graphics of Light Green Clay Particles

4.3.3 Particle Size Measurements

For the particle size measurements of insoluble particles at Kirka ore body, Malvern System 2600 Particle Sizer were used. Figure 4.3.3.1 and Appendix 4.3.3.1, 4.3.3.2, 4.3.3.3, and 4.3.3.4 shows particle size analysis of insoluble particles.



4.3.4 Chemical Composition of Clay Materials been with Kırka Borate Ores

Four different samples were selected from Kırka open pit tincal mine, cleaned from tincal mineral to obtain water insoluble part of the ore and labeled according to their native color as blue, green, gray and white. Wet chemical analysis of insoluble were given at Table 4.3.4.1.

Table 4.3.4.1 Chemical Composition of water insoluble materials in Kırka tincal deposits

Sample	SiO ₂ %	R ₂ O ₃ %	CaO %	MgO %	Moisture %	Loss of Ignition, %	Acid Insoluble, %
Blue	42,3	11,6	8,5	10,1	7,4	11,5	79,1
Green	29,0	8,0	15,1	16,3	5,1	22,6	53,8
Gray	25,3	6,1	16,7	17,8	4,7	25,3	45,7
White	12,1	0,8	24,0	22,8	3,7	37,0	22,5

The difference in the chemical compositions of the water insoluble materials indicate a decreasing amount of montmorillonite and an increasing amount of dolomite in the blue, green, gray, and white samples respectively. This can be visualized from loss of ignition and acid insoluble matter. Loss of ignition determined at 1000 °C results mainly from decomposition of dolomite. Insoluble material in acetic acid gives approximately montmorillonite content in the sample.

XRF studies using Shimadzu, Japan origin XRF-1700 model instrument on insoluble clay materials were shown on Table 4.3.4.2.

Analytical-Object	Light Green Clay Results (%)	Dark Green Clay Results (%)	Light Gray Clay Results (%)	Medium Gray Clay Results (%)	Dark Gray Clay Results (%)	White Clay Results (%)
SiO ₂	65,9515	64,5261	22,0863	35,9691	29,6275	17,7093
Al ₂ O ₃	15,9024	18,4264	2,0150	7,1634	4,1596	1,3907
B ₂ O ₃	4,0447	4,0206	3,0548	3,5106	5,0032	2,4957
BaO	0,0209	-	0,0004	-	-	0,0025
CaO	0,9327	0,6182	21,7166	8,4439	13,9215	26,0227
F	0,0852	0,1038	0,3753	0,3688	0,3802	0,2980
Fe ₂ O ₃	2,8234	2,9181	0,5563	1,8614	1,1335	0,3941
K ₂ O	3,0781	3,7148	0,4601	1,5800	0,7668	0,2579
MgO	5,9099	4,6230	20,2378	19,4650	19,6866	20,1037
MnO	0,0581	0,0542	0,0265	0,0545	0,0406	0,0142
Na ₂ O	0,3744	0,3005	0,1773	0,3110	0,8330	0,1443
SO ₃	0,3597	0,3027	0,5819	1,5351	0,9353	0,2216
SrO	0,1504	0,0717	1,0486	0,3649	0,6487	1,2807
TiO ₂	0,2987	0,3098	0,0562	0,1662	0,1166	0,0296
Others	0,0100	0,0100	27,6068	19,2063	22,7470	29,6348

Table 4.3.4.2 XRF studies on water insoluble materials in Kirka tincal deposits

4.3.5 Relationship between Concentration of Borax and Density

The easiest and fastest way of measuring $\text{Na}_2\text{B}_4\text{O}_7$,% would be determining the density of liquor. Hydrometers are used for this purpose. During laboratory and pilot scale studies, hydrometers are used for measuring densities.

Because of big difference between Garret Company and Eti Bor A.Ş., Kırka Plant, Laboratory on the values of density-borax content, these values were measured again at Eti Holding A.Ş, Research Laboratory. Experimental data are given at Table 4.3.5.1.

Figure 4.3.5.1 shows comparison of Kırka, Garret and Research Center for density-borax content values. Differences on density-borax content values for these three Institute could be result of differ calibration of hydrometers.

Table 4.3.5.1 Measurement of Liquor Density by Changing the Borax Content (t = 95 °C)

Experiment Number	$\text{Na}_2\text{B}_4\text{O}_7$, %	Density, g/cm ³
1	33,303	1,296
2	28,728	1,252
3	27,358	1,237
4	25,119	1,210
5	22,876	1,186
6	21,143	1,167
7	18,698	1,145
8	17,137	1,128
9	14,580	1,095
10	12,536	1,082
11	10,638	1,067
12	8,792	1,043

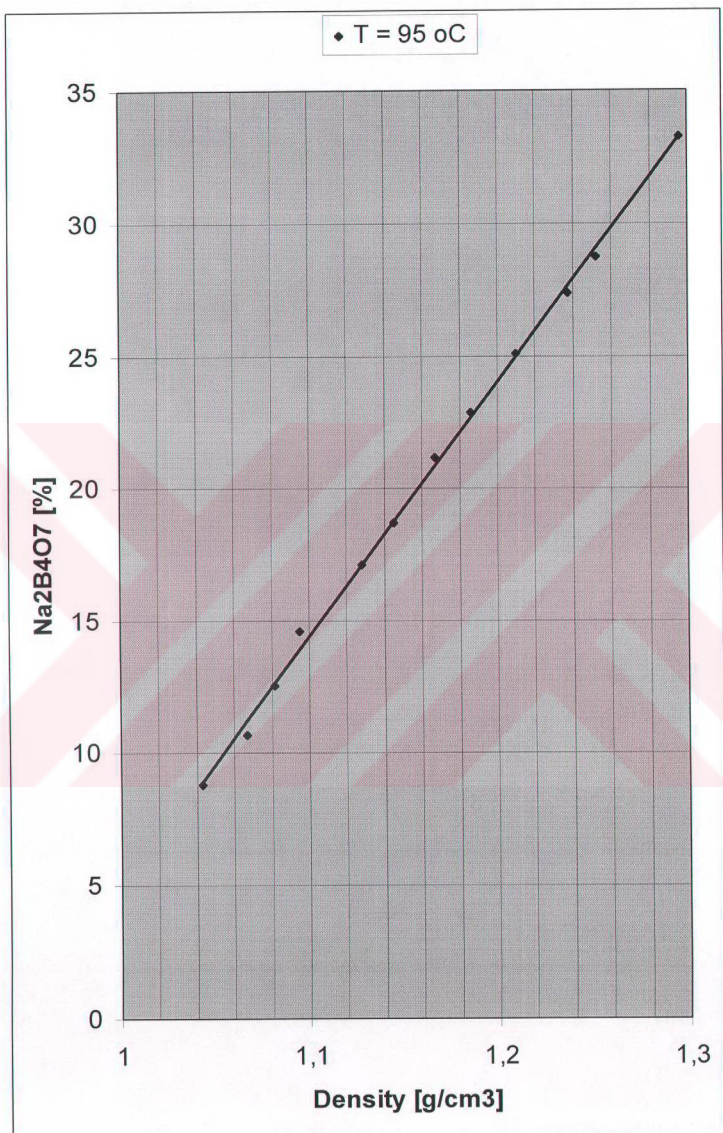


Figure 4.3.5.1 Measurement of Liquor Density by Changing the Borax Content (t = 95 °C)

4.3.6 Solubility of Borax in Water

For the solubility studies Laboratory type jacketed glass vessel reactor, maintaining desired temperature laboratory type cryostat and measuring density calibrated hydrometer were used.

Table 4.3.6.1 Solubility of Various Borax in Water

Temperature, °C	g Na ₂ B ₄ O ₇ /100 g Saturated Solution	Solid State
0	1,18	Na ₂ B ₄ O ₇ ·10H ₂ O
5	1,44	“
10	1,76	“
15	2,12	“
20	2,58	“
25	3,13	“
30	3,85	“
35	4,76	“
40	6,00	“
45	7,58	“
50	9,55	“
55	12,25	“
58,5	14,52	Na ₂ B ₄ O ₇ ·10H ₂ O + Na ₂ B ₄ O ₇ ·4H ₂ O
60	14,82	Na ₂ B ₄ O ₇ ·4H ₂ O
65	15,88	“
70	17,12	“
75	18,41	“
80	19,88	“
85	21,48	“
90	23,31	“
95	25,55	“
100	28,22	“
60,8 (m)	16,65	Na ₂ B ₄ O ₇ ·10H ₂ O + Na ₂ B ₄ O ₇ ·5H ₂ O
65 (m)	17,88	Na ₂ B ₄ O ₇ ·5H ₂ O
70 (m)	19,49	“
75 (m)	21,30	“
80 (m)	23,38	“
85 (m)	25,73	“
90 (m)	28,37	“
95 (m)	31,28	“
100 (m)	34,63	“
102,8 (boiling point)	36,73	“

m (metastable point)

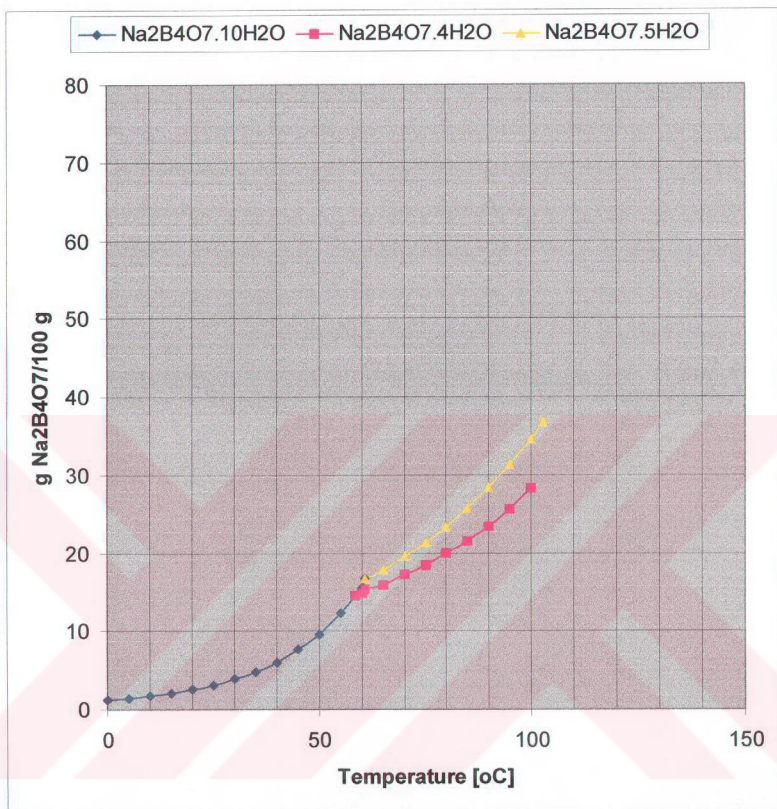


Figure 4.3.6.1 Solubility of Various Borax in Water

Figure 4.3.6.1 proves that solubility curves for borax pentahydrates and decahydrates intercept around temperature 60,6 and 60,8 °C. Therefore, if the saturated borax solution cools down to 60 °C, or lower, pentahydrate and decahydrate crystals can be produced.

4.3.7 Determination of Solubility Rate for Borax Decahydrate at 95 °C

Solubility tests were done by Garret Company using borax decahydrate crystal. For 98 °C, and 1000 rpm, the equation for solubility rate was calculated as follows;

$$R_D = (8857,952 - 89,04 * S) / 2204,6626 \quad (1)$$

R_D = Solubility rate (t/h*ft³ water)

S = Saturation, %

Solubility tests were also done by previous researchers using 500-1000 µm borax decahydrate crystals. For 96 °C, and 400 rpm, the equation for solubility rate was calculated as follows;

$$R_D = 0,11 + 18,1 * \Delta C \quad (2)$$

R_D = Solubility rate (kg decahydrate / kg liquor * h)

$\Delta C = C - C_0$

C = Final concentration (kg Na₂B₄O₇/kg liquor)

C₀ = Initial concentration (kg Na₂B₄O₇/kg liquor)

To see how close we are for the solubility rate equation found using borax decahydrate crystals, we had also run solubility tests using run of mine ore brought from Kirka deposit. Kirka crystalline glassy ore were used to determine solubility rate at 95 °C. Known amount of water first put into jacketed glass reactor at 95 °C, and 25 rpm. After that, weighted Kirka crystalline glassy ore pieces were put into reactor and waited until totally dissolve, and dissolution time were recorded. Dissolution step followed one piece to other until saturation point were reached. During the experiment 20 grams and 70 grams crystalline glassy ores were used. After each experiment, the density of liquor were measured.

During the experiment, it was observed that when different size crystalline glassy ore pieces were drop to hot liquor, it broke into pieces therefore the solubility rate were not depend on particle size. However, there were some pieces continued extraction without break into pieces.

Laboratory tests were showed that dissolution time were 3-5,5 minutes for 20 grams borax crystals, and 6-8,5 minutes for 70 grams borax crystals using hot liquor containing 0-30 $\text{Na}_2\text{B}_4\text{O}_7$ %. The results of dissolution tests were given at Table 4.3.7.1 and Table 4.3.7.2.

Table 4.3.7.1 Determination of Solubility Rate Using 70 Grams Crystalline Borax Pieces at 95 °C. C_o : Initial Concentration ($\text{Na}_2\text{B}_4\text{O}_7, \%$) C , Final Concentration ($\text{Na}_2\text{B}_4\text{O}_7, \%$) : 30,5 t : Dissolution time, (s)

Amount of Initial Liquid : 1000 grams

 R_D : (kg borax / kg solution * h)

Solution+Borax, gr	Time, s	Mass, gr	C_o	$C - C_o$	R_D
1071,04	425	71,04	10,57	0,20	0,56
1143,46	450	72,42	13,25	0,17	0,51
1213,95	360	70,49	15,54	0,15	0,58
1285,53	410	71,58	17,61	0,13	0,49
1356,29	395	70,77	19,45	0,11	0,48
1425,77	440	69,48	21,07	0,09	0,40
1497,37	495	71,60	22,59	0,08	0,35
1567,08	400	69,71	23,93	0,07	0,40
1636,48	445	69,41	25,15	0,05	0,34
1708,10	464	71,62	26,31	0,04	0,33
1779,23	435	71,13	27,37	0,03	0,33

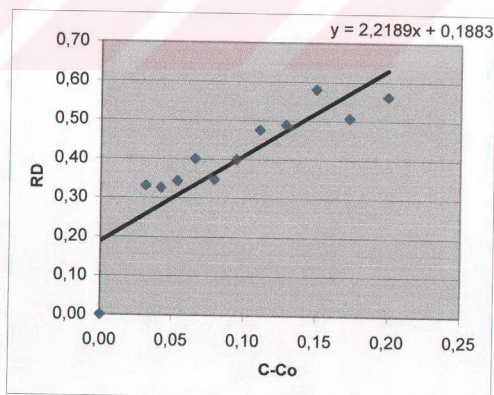
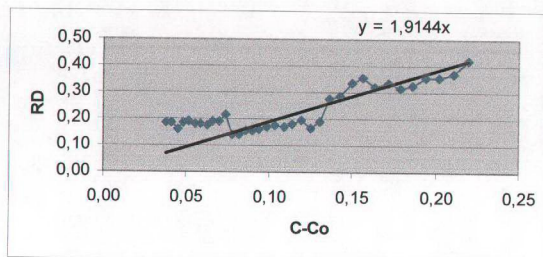


Table 4.3.7.2 Determination of Solubility Rate Using 20 Grams Crystalline Borax Pieces at 95 °C.

Solution+Borax,gr	Time, s	Mass, gr	Co	C - Co	RD
1022,38	188	22,38	8,56	0,22	0,42
1043,12	194	20,74	9,44	0,21	0,37
1063,85	197	20,74	10,29	0,20	0,36
1084,67	195	20,82	11,11	0,19	0,35
1105,26	205	20,59	11,88	0,19	0,33
1125,43	205	20,16	12,61	0,18	0,31
1147,70	210	22,27	13,39	0,17	0,33
1170,17	215	22,48	14,15	0,16	0,32
1192,56	190	22,39	14,88	0,16	0,36
1214,03	190	21,48	15,55	0,15	0,34
1235,87	225	21,84	16,20	0,14	0,28
1258,10	230	22,22	16,85	0,14	0,28
1278,75	305	20,65	17,43	0,13	0,19
1298,68	335	19,93	17,97	0,13	0,16
1320,31	305	21,63	18,54	0,12	0,19
1342,01	325	21,70	19,09	0,11	0,18
1363,51	335	21,49	19,63	0,11	0,17
1384,67	315	21,17	20,13	0,10	0,17
1406,91	338	22,23	20,65	0,10	0,17
1426,46	305	19,55	21,09	0,09	0,16
1445,60	308	19,13	21,51	0,09	0,15
1464,86	310	19,26	21,92	0,09	0,15
1483,89	325	19,03	22,31	0,08	0,14
1503,77	335	19,88	22,72	0,08	0,14
1525,54	240	21,77	23,15	0,07	0,21
1545,75	245	20,21	23,53	0,07	0,19
1567,79	265	22,04	23,95	0,07	0,19
1587,05	250	19,26	24,29	0,06	0,17
1606,98	250	19,93	24,65	0,06	0,18
1627,45	255	20,48	25,00	0,06	0,18
1649,23	247	21,78	25,37	0,05	0,19
1671,36	260	22,12	25,73	0,05	0,18
1691,03	265	19,68	26,05	0,04	0,16
1713,55	255	22,52	26,40	0,04	0,19
1735,14	245	21,59	26,73	0,04	0,18



For the 70 grams of particles, the solubility rate equation:

$$R_D = 2,2189 \cdot \Delta C + 0,1883 \quad (3)$$

For the 20 grams of particles, the solubility rate equation:

$$R_D = 1,9144 \cdot \Delta C \quad (4)$$

To have better understanding, the solubility rate tests were done using laboratory size extractor which will be similar to industrial design. The extractor was first filled with borax saturated solution, and to keep the temperature about 95 °C, hot steam and heat exchanger were used. Travelling time on screw type extractor were set to 10 minutes by frequency control device, and after 10 minutes passed, the solid was checked for undissolve borax. Figure 4.3.7.1 shows a schematic view of laboratory scale extraction tests apparatus and Figure 4.3.7.2 shows pilot scale extraction unit used in Kırka.

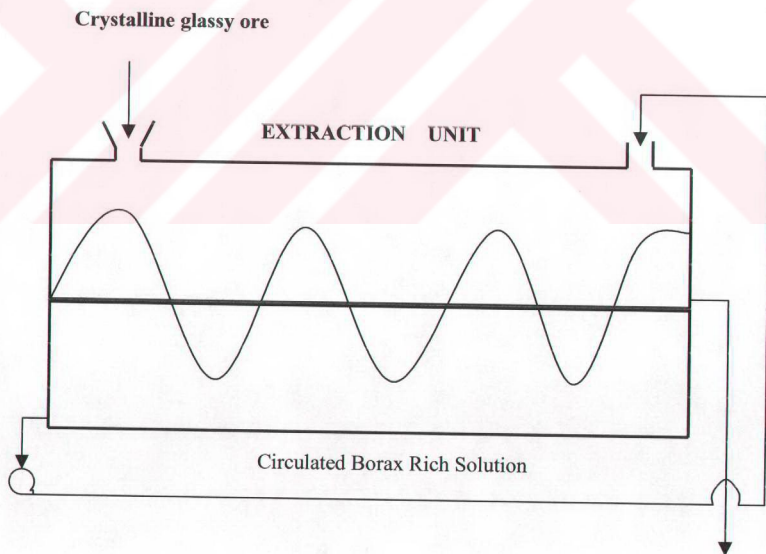


Figure 4.3.7.1 A Schematic View of Laboratory Scale Extraction Tests Apparatus.



Figure 4.3.7.2 Pilot Scale Extraction Unit

Table 4.3.7.3 The Test Results of Laboratory Extraction Unit

Extracting Liquid, Na ₂ B ₄ O ₇ , (%)		Crystalline Glassy Ore		Extraction Time (minutes)	1 Cycle Extraction	
Initial Concentration	Final Concentration	Mass (kg)	Size (mm)		Residence Time (minutes)	Undissolved Borax (kg)
7,5	17,26	10	- 50	< 15	15	-
27,7	30,2	5	- 50	< 16	10	0,1

Table 4.3.7.4 Dissolution Time Measurement for Same Size Crystalline Glassy Ore

Concentration of Extracting Liquid, Na ₂ B ₄ O ₇ , (%)	Crystalline Glassy Ore Size, (mm)	Dissolution Time (minutes)
17,7	~ 100	< 8
17,7	~ 50	< 7
30,2	~ 50	< 14

4.3.8 Behavior of Insoluble Particles During Extraction of Tincal Ore

Insoluble particles comes into weak mother liquor with borax stays suspended in solution but minor amount of insoluble particles or some other borax minerals beside tincal dissolve and get into borax solution. Table 4.3.8.1 shows typical analysis of borax pentahydrate product produced at Kırka Boron Derivative Plant. It can be seen from Table 4.3.8.1 that there are some impurities beside borax crystals remain in product.

Table 4.3.8.1 Chemical Analysis of Borax Pentahydrate

Analytical-Object	Borax Pentahydrate (Etibor-48)	
	Results (%)	Results (%)
	Minimum	Maximum
B₂O₃	47,80	49
Na₂O	21,28	21,81
SiO₂	0,0050	0,0600
Fe₂O₃	0,0020	0,0070
Al₂O₃	0,0020	0,0600
CaO	0,0200	0,0300
MgO	0,0040	0,0095
NaCl	0,0020	0,0060
Na₂SO₄	0,0060	0,0200
As	-	0,0001

(Source, Eti Bor A.Ş., Kırka Plant Laboratory, September 1999)

After the extraction of tincal concentrate, the solution is containing 28-30% Na₂B₄O₇ and 300-700 ppm calcium ion and calcium gradually settle as a probertite (Na₂O.2CaO.5B₂O₃.10H₂O) which cause blockage in piping line (Gür, G., September 1995). Laboratory results taken from Kırka laboratory shows that borax solution often reach to 1000 ppm Ca and the 50-60 ppm Si.

In this study, the insoluble particles were characterized with their color and appearance as blue, green, gray, and white. Insoluble particles were pour into borax solution in which temperature and the borax content were key parameter while recording change of calcium, magnesium and Si ions in system. Results of the studies supported that increase on temperature and borax content in solution cause increase on calcium, magnesium and Si ion. Figure 4.3.8.1 and 4.3.8.2 shows change on calcium and magnesium ions with time while solution containing 30 % $\text{Na}_2\text{B}_4\text{O}_7$ at 92 °C.

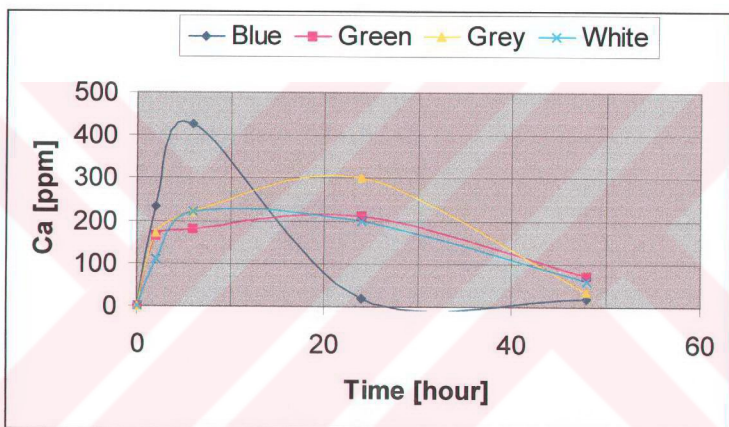


Figure 4.3.8.1 variations on calcium ion with time

Temperature : 92 °C

$\text{Na}_2\text{B}_4\text{O}_7$, % : 30

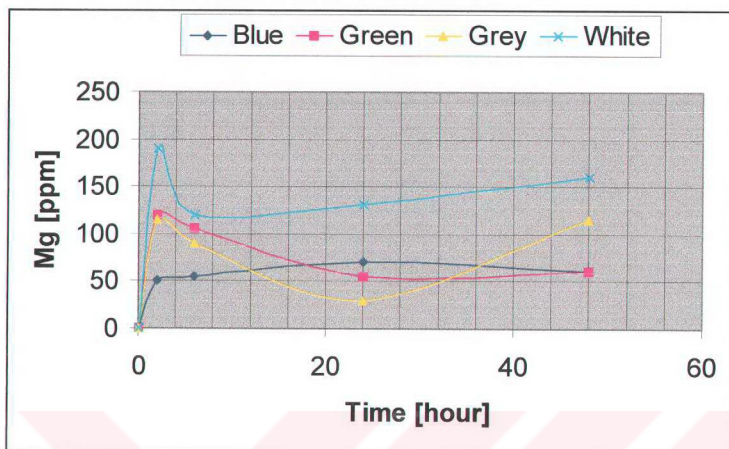


Figure 4.3.8.2 Variations on magnesium ion with time

Temperature : 92 °C

$\text{Na}_2\text{B}_4\text{O}_7$, % : 30

Figure 4.3.8.1 shows that there was an increase on calcium ion goes into borax solution in the beginning but after 10 hours it started decreasing. This was explained by probertite existing in the system. At figure 4.3.8.2, magnesium ions first increased for a while, start decreasing and again start increasing in the system. This was explained by ion exchange between montmorillonite and system.

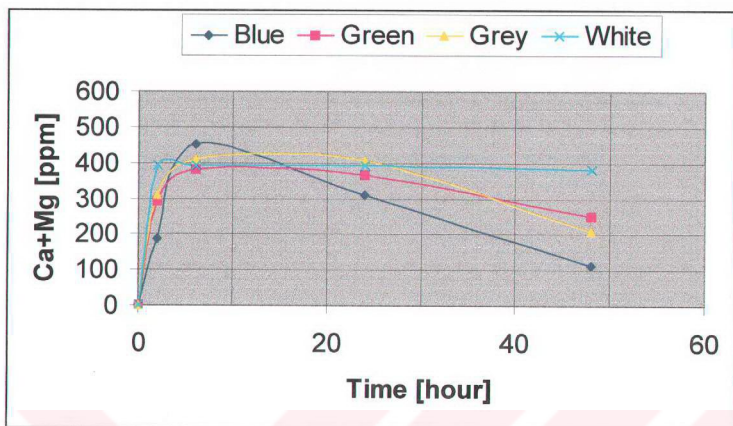


Figure 4.3.8.3 variations on Ca+Mg ions with time
Temperature : 92 °C

$\text{Na}_2\text{B}_4\text{O}_7$, % : 30

Figure 4.3.8.3 shows calcium and magnesium ions together in the system. It can be seen that in 10 hours change keeps constant, but after that when calcium increase magnesium start decreasing or if magnesium start increasing calcium drop down.

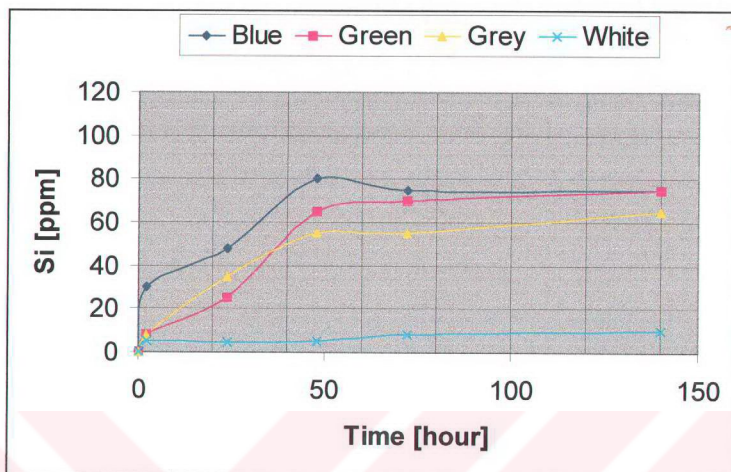


Figure 4.3.8.4 variations on Si ion with time

Temperature : 92 °C

$\text{Na}_2\text{B}_4\text{O}_7$, % : 30

Another indication of montmorillonite is being dissolved in borax solution comes from Figure 4.3.8.4 where when the blue insoluble particles which has highest montmorillonite content is being in system, Si content increase.

This study shows that during extraction of tincal ore, some insoluble particles also dissolve in less amount and dissolution rate changes with temperature and borax content. Therefore some changes on surface properties of insoluble particles is predicted.

4.3.9 Flocculation Behavior of Insoluble Particles

Flocculants used for test were made up to stock solutions of about 0,2%, which were diluted to about 0,05% before adding to slurry.

4.3.10 Zeta Potential Measurement of Insoluble Particles

Table 4.3.10 is based on experience with many flocculated and dispersed systems. It gives a “rule of thumb” (particularly for hydrophobic colloids) describing the relation between zeta potential determination and the probable response of the suspension being tested (Zeta-Meter, Inc., 1991).

Table 4.3.10.1 Relation between zeta potential and suspension

Stability Characteristics	Average zeta potential (millivolts)
Maximum agglomeration and precipitation	+3 to 0
Excellent agglomeration and precipitation	-1 to -4
Fair agglomeration and precipitation	-5 to -10
Threshold of agglomeration (agglomerates of 2 to 10 colloids)	-11 to -20
Plateau of slight stability (few agglomerates)	-21 to -30
Moderate stability (no agglomerates)	-31 to -40
Good stability	-41 to -50
Very good stability	-51 to -60
Excellent stability	-61 to -80
Maximum stability	-81 to -125

Surface forces are much more important than gravity effects in controlling the behavior of colloidal systems. Therefore, zeta potential measurement on insoluble particles were carried out using Zeta-Meter, Inc., USA origin, Zeta-Meter System 3.0+ instrument. These particles were characterized based on their color as blue, green, gray and white. Table 4.3.10.2 shows zeta potential values of insoluble

particles which are isolated from borax into distilled water. Concentration of insoluble particles were 0,2 g/l.

Table 4.3.10.2 Zeta potential values of borax free insoluble particles in distilled water

Time (hour)	Blue	Green	Gray	White
0	-21,4	-18,7	-22,2	-16,5
24	-18,9	-21,5	-15,9	-16,9
48	-15,4	-22,0	-17,1	-13,9
52	-17,4	-16,8	-17,6	-13,7

As it was predicted, different insoluble particles had different zeta potential values. Furthermore, time changes had little effect on zeta potential fluctuation. Figure 4.3.10.3 shows zeta potential values of insoluble particles into different borax concentration. Figure 4.3.10.4 shows zeta potential values of white color insoluble particles into different borax concentration.

Table 4.3.10.3 Zeta potential values of insoluble particles in borax solution

Borax Concentration (M)	Blue	Green	Gray	White
0	-21,4	-18,7	-22,2	-16,5
10^{-6}	-16,6	-17,5	-16,4	-15,2
10^{-5}	-18,0	-27,7	-21,0	-16,8
10^{-4}	-27,1	-26,3	-26,3	-21,7
10^{-3}	-49,6	-51,2	-51,1	-47,1
10^{-2}	-45,5	-51,0	-43,0	-40,1

Table 4.3.10.4 Zeta potential values of white color insoluble particles in borax solution

Borax Concentration (M)	0 hour	24 hour	48 hour
0	-16,5	-16,9	-13,9
10^{-6}	-15,2	-13,3	-16,0
10^{-5}	-16,8	-16,2	-15,3
10^{-4}	-21,7	-16,7	-13,1
10^{-3}	-47,1	-36,8	-27,0
10^{-2}	-40,1	-40,8	-33,7

Zeta potential studies explained that increase on borax content of solution dramatically changed the zeta potential of insoluble particles but changes on residence time didn't have any effect on zeta potential.

Although pH is a key parameter for flocculation studies, because of borax, did not take into consideration. Parameters which could be effective in flocculation studies;

- ◆ Flocculant type,
- ◆ Composition of insoluble particle,S
- ◆ Solid content of suspension,
- ◆ Flocculation temperature,
- ◆ Borax content of suspension,
- ◆ Residence time of suspension.

4.3.11 Effect of Flocculant Type

Four different insoluble particles (blue, green, gray and white) were flocculated at 3% borax content and 35 °C of suspension using different flocculant which diluted to about 0,05% before adding to slurry. For the testing of flocculant performance, turbidity measurement were performed.

Orbeco Hellige, USA origin 965 model turbidity instrument were used during test. Figure 4.3.11.1 shows variations of turbidity values on blue insoluble particles using different flocculant and changing the flocculant dosage.

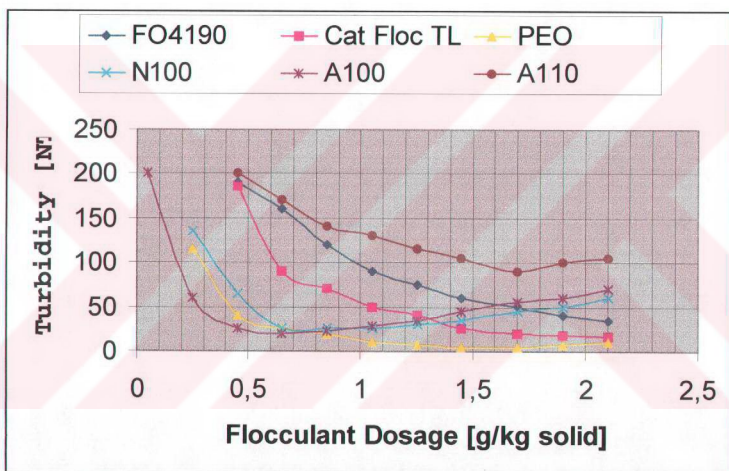


Figure 4.3.11.1 variations of turbidity values on blue particles using different flocculant

Sample : Blue Solid Content : 30 g/l

Temperature : 35 °C

Na2B4O7, % : 3

Residence time, hour : 0,5

It can be seen from Figure 4.3.11.1 that even the particles had negative surface charge, the cationic flocculants (Cat Flocc TL and FO4190) were not as good as non-ionic, or light ionic flocculant.

Comparing turbidity results of 10% anionic and 15% anionic PAM (N100, A100, A110), it can be seen that with minimum flocculant dosage and the most clear solution were achieved by using A100.

Figure 4.3.11.2 shows variations of turbidity values on green insoluble particles using different flocculant and changing the flocculant dosage.

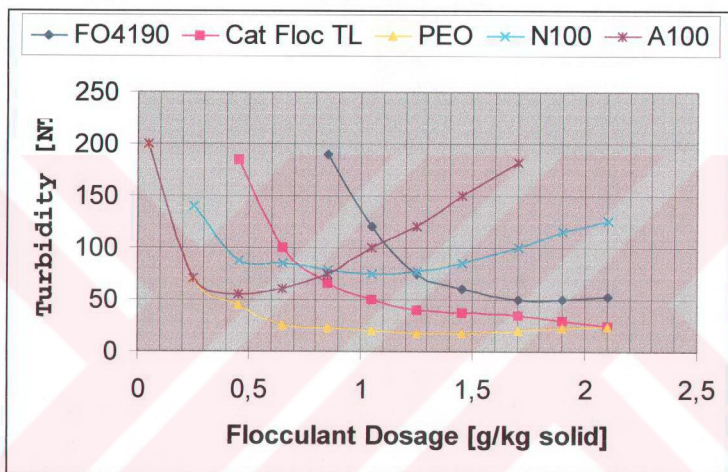


Figure 4.3.11.2 Variations of turbidity values on green particles using different flocculants

Sample : Green

Solid Content : 30 g/l

Temperature : 35 °C

Na2B4O7, % : 3

Residence time, hour : 0,5

Examining Figure 4.2.5.2.2, it can be seen that cationic flocculants were not as effective as non-ionic and 10% anionic flocculants.

When Figure 4.3.11.1 compared with 4.3.11.2, it is understood that because of increase on dolomite content, the turbidity results were not as good as blue particles. PEO was the only one less effected from dolomite. Flocculation studies were moved to gray and white particles which has high dolomite content. Figure

4.3.11.3 shows test results on gray particles which has 45% montmorillonite and 55% dolomite and Figure 4.3.11.4 shows test results on white particle which has 20% montmorillonite and 80% dolomite. Both insoluble particle were not able to flocculate using A110 and FO4190.

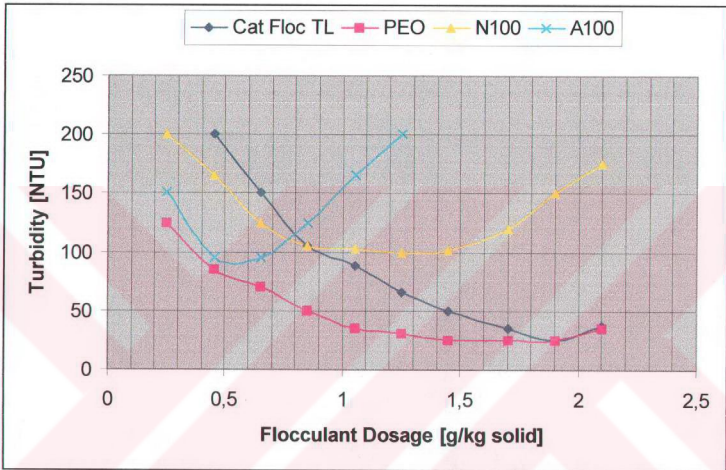


Figure 4.3.11.3 variations of turbidity values on gray particles using different flocculants

Sample : Gray Solid Content : 30 g/l

Temperature : 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

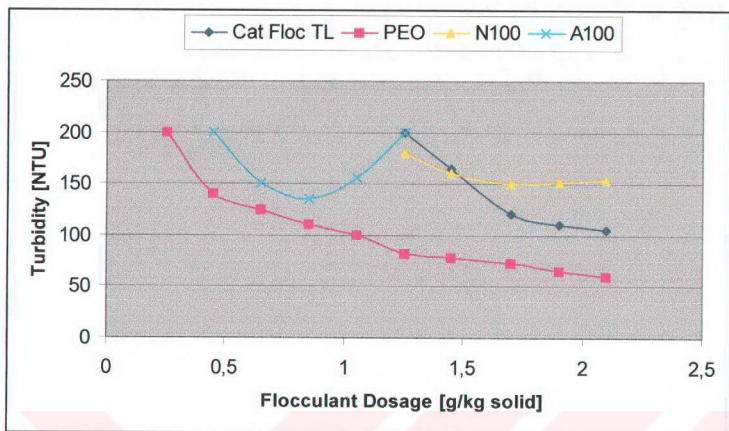


Figure 4.3.11.4 Variations of turbidity values on white particles using different flocculants

Sample : White

Solid Content : 30 g/l

Temperature : 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

It can be concluded that flocculation studies on solution containing 3 % borax and temperature approximately 35 °C succeeded successfully using PEO and A100.

4.3.12 Determination of Effect of Insoluble Particles Composition

Flocculation studies were carried and evaluated for each flocculant and given at Figure 4.3.12.1, 4.3.12.2, 4.3.12.3, 4.3.12.4 and 4.3.12.5 for different insoluble particles. From these figures;

Whichever flocculant had been used, the best results were always achieved on montmorillonite type blue clay and followed by green, gray and white clays. From this evidence we can postulate that there is a direct connection between all flocculants and montmorillonite. In other words, montmorillonite content is one of the most important factors effecting flocculation for all impurities.

PEO is the least effected flocculant on flocculation of dolomite type insoluble. Figure 4.3.12.6 shows how the different flocculant reacts if the insoluble particles dolomite content increase.

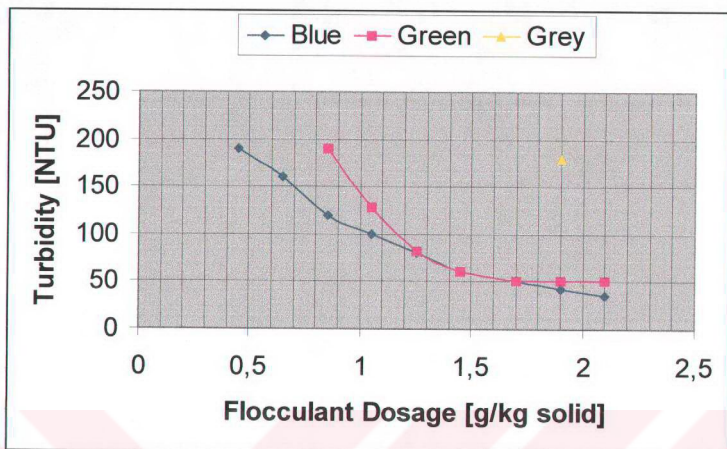


Figure 4.3.12.1 Flocculant Dosage versus Turbidity

Flocculant type : FO4190

Solid Content : 30 g/l

Temperature : 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

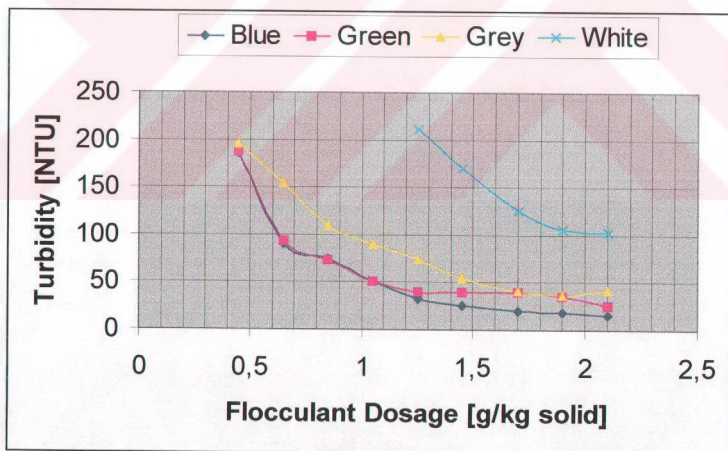


Figure 4.3.12.2 Flocculant Dosage versus Turbidity

Flocculant type : Cat Flocc TL

Solid Content : 30 g/l

Temperature: 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

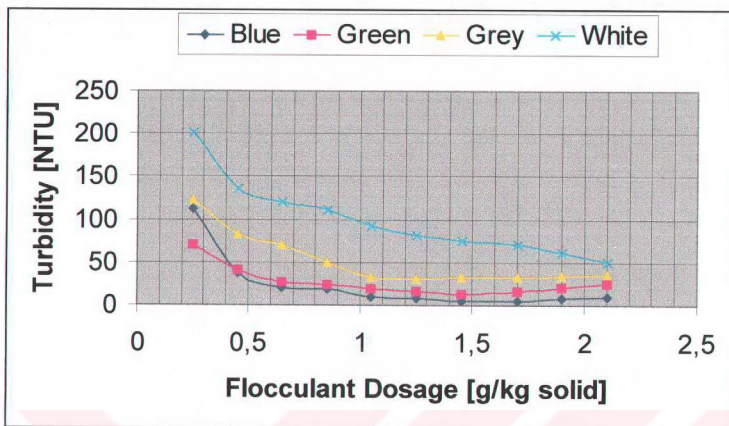


Figure 4.3.12.3 Flocculant Dosage versus Turbidity

Flocculant type : PEO

Solid Content : 30 g/l

Temperature : 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

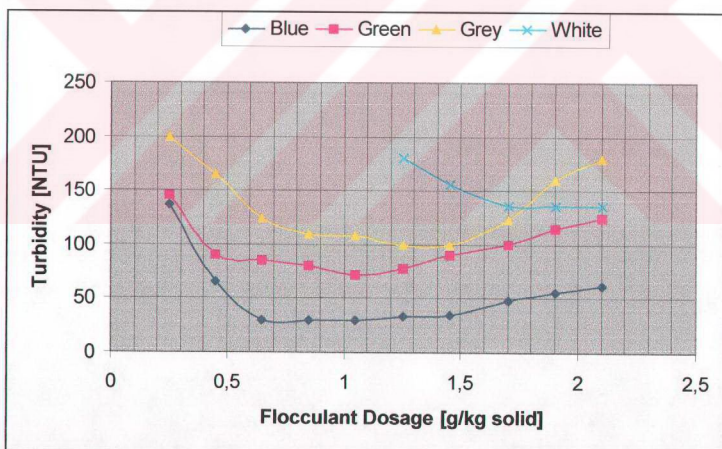


Figure 4.3.12.4 Flocculant Dosage versus Turbidity

Flocculant type : N100

Solid Content : 30 g/l

Temperature : 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

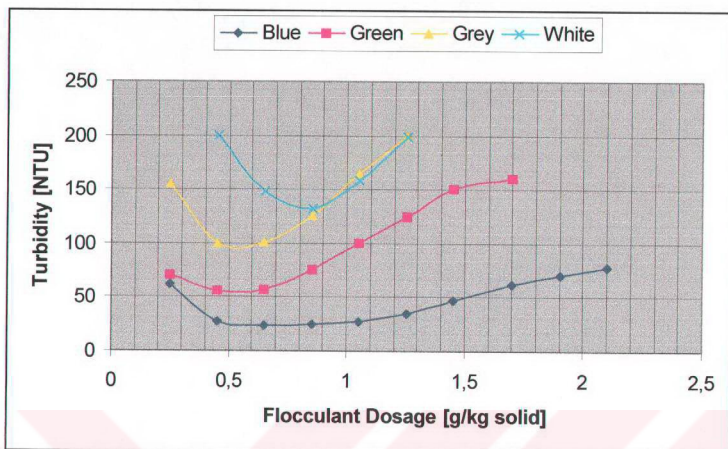


Figure 4.3.12.5 Flocculant Dosage versus Turbidity

Flocculant type : A100

Solid Content : 30 g/l

Temperature : 35 °C

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

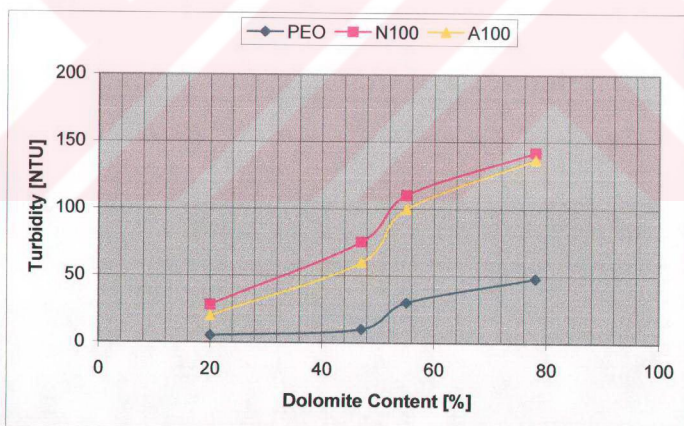


Figure 4.3.12.6 Dolomite Content versus Turbidity

Temperature : 35 °C

Solid Content : 30 g/l

Residence time, hour : 0,5

Na₂B₄O₇, % : 3

4.3.13 Effect of Solid Content in Suspension

A100 and PEO type flocculants were used for flocculation studies where the solution containing 3% borax and 30, 50, 75 and 100 g/l impurities in suspension were tested for half an hour. Targeted turbidity values derived from flocculation results done before solution containing 3% borax and 30 g/l impurities. For example, the suspension containing 30 g/l impurities had 47 NTU turbidity value for blue particles were taken as targeted value, therefore flocculant dosage kept feeding until targeted values reached for 50, 75 and 100 g/l suspension.

Figure 4.3.13.1 and 4.3.13.2 shows optimum flocculant dosage for suspension containing 30,50,75 and 100 g/l impurities.

It can be seen from Figure 4.3.13.1 that if 10% anionic flocculant (A100) is used, increase on solid content will cause increase on flocculant dosage. However, Figure 4.3.13.2 shows that if PEO type flocculant is used, increase on solid content won't cause any increase on flocculant consumption.

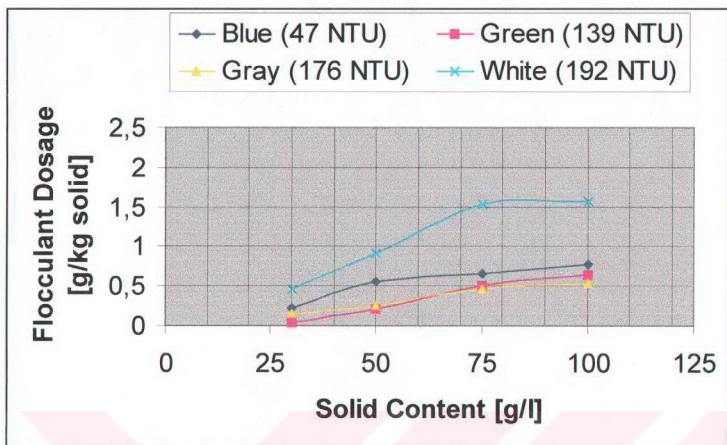


Figure 4.3.13.1 Solid Content versus Flocculant Dosage

Flocculant type : A100

Residence time, hour : 0,5

Temperature : 35 °C

Na₂B₄O₇, % : 3

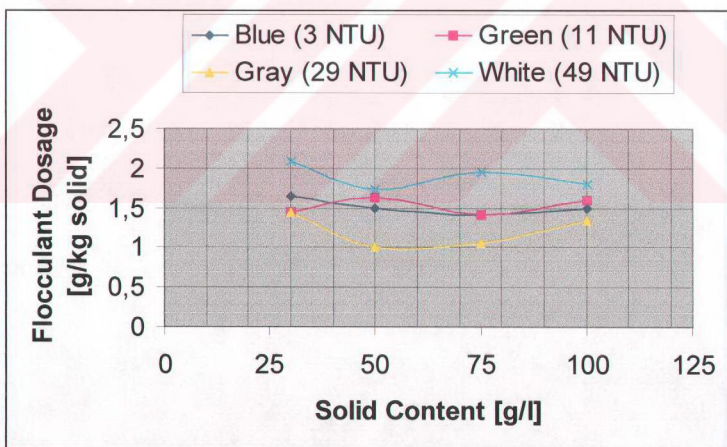


Figure 4.3.13.2 Solid Content versus Flocculant Dosage

Flocculant type : PEO

Residence time, hour : 0,5

Temperature : 35 °C

Na₂B₄O₇, % : 3

4.3.14 Effect of Temperature

To be able to determine temperature effect on flocculation of different insoluble particles, flocculation tests were carried out at 35 °C, and 65 °C using non-ionic (N100), light ionic (A100) and PEO.

Figure 4.3.14.1 shows test results for blue insoluble particles using N100 flocculant at the temperature of 35 °C, and 65 °C. With this flocculant, particles which were having higher dolomite content were not able to flocculate, therefore it were not shown graphically.

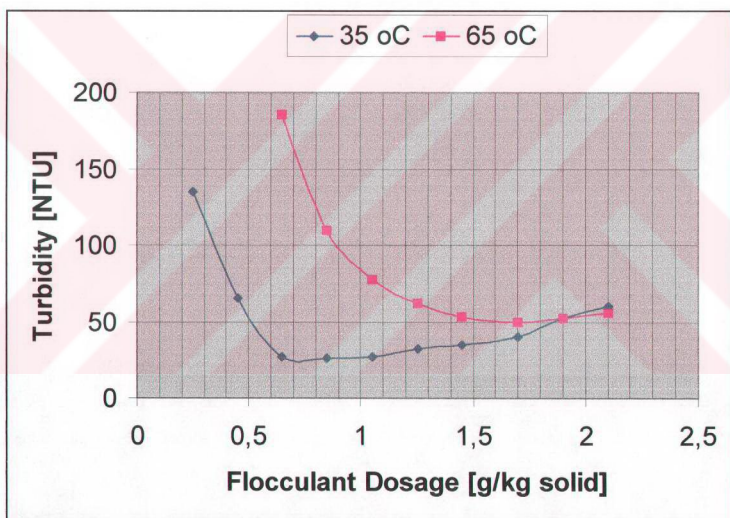


Figure 4.3.14.1 Temperature Effect on Flocculation of Blue Particles

Flocculant type : N100

Solid Content : 30 g/l

Sample : Blue

Na₂B₄O₇, % : 3

Residence time, hour : 0,5

It can be seen from Figure 4.3.14.1 that there is a negative effect of temperature increase on flocculation.

Figure 4.3.14.2 shows test results for insoluble particles categorized blue, green and gray using A100 focculant at the temperature of 35 °C, and 65 °C. With this flocculant, white particles which were having higher dolomite content were not able to flocculate, therefore it were not shown graphically.



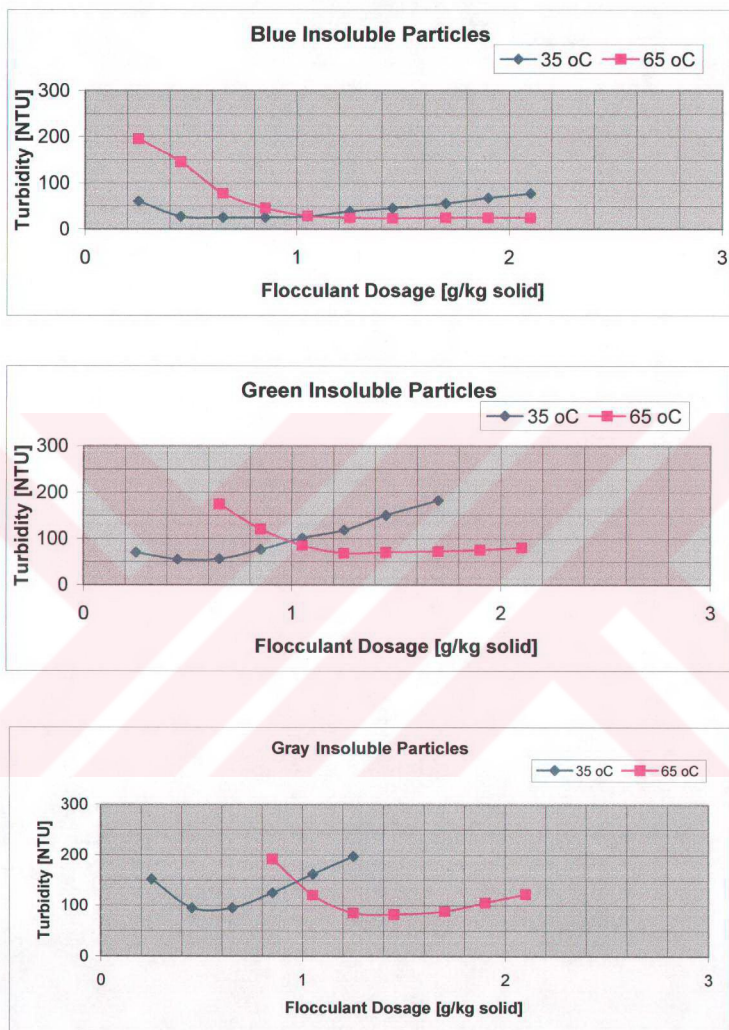


Figure 4.3.14.2 Turbidity Variations of Different Insoluble Particles versus Temperature

Flocculant type : A100

Solid Content : 30 g/l

Residence time, hour : 0,5

Na₂B₄O₇, % : 3

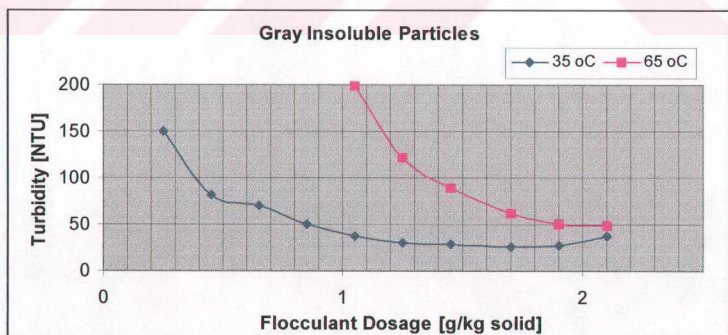
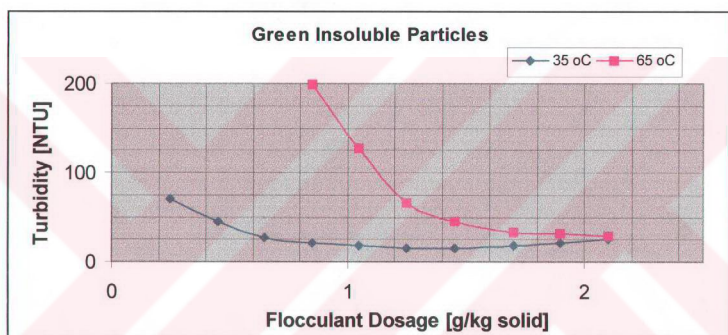
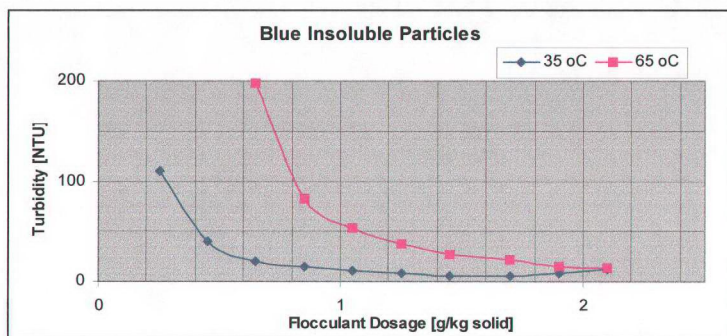


Figure 4.3.14.3 Turbidity Variation of Different Insoluble Particles versus Temperature

Flocculant type : PEO

Solid Content : 30 g/l

Residence time, hour : 0,5

Na₂B₄O₇, % : 3

Flocculation studies on blue, green and gray insoluble particles were carried using PEO flocculant at the temperature of 35 °C, and 65 °C shown at Figure 4.3.14.3. With this flocculant, white particles which were having higher dolomite content were not able to flocculate, therefore it were not shown graphically.

Since the production of borax pentahydrate in Kırka takes place at 95-98 °C, flocculation studies were also carried at 95 °C. However, white particles which were having higher dolomite content were not able to flocculate at 3% borax concentration, therefore flocculation studies taken place at 15% borax concentration using A100 and PEO flocculants. Figure 4.3.14.4 and 4.3.14.5 shows test results for insoluble particles using A100 and PEO flocculant at the temperature of 65 °C, and 95 °C respectfully. Examining these figures;

There were no difference on flocculation studies carried out solution containing 15% borax, and 65 °C, and 95 °C using A100 and PEO flocculants. Although white particles which were having higher dolomite content were not able to flocculate at solution containing 3% borax and 65 °C using A100 and PEO flocculants, it was possible to flocculate this substance with same flocculants solution containing 15% borax at the temperature of 65 °C, and 95 °C.

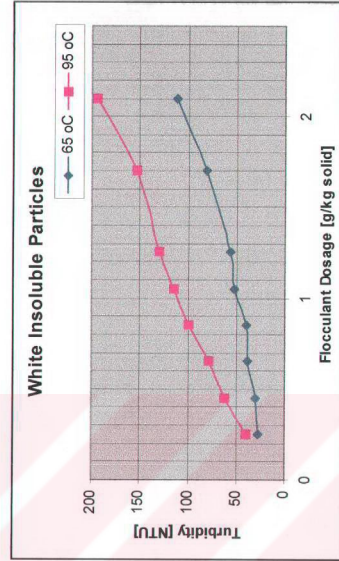
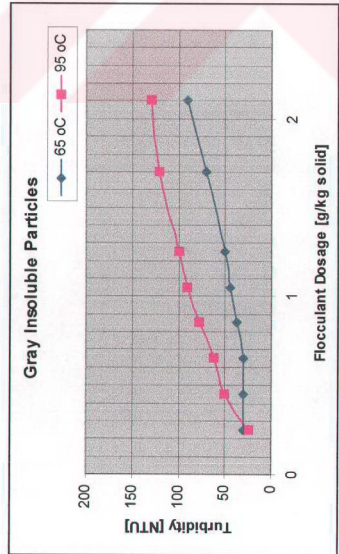
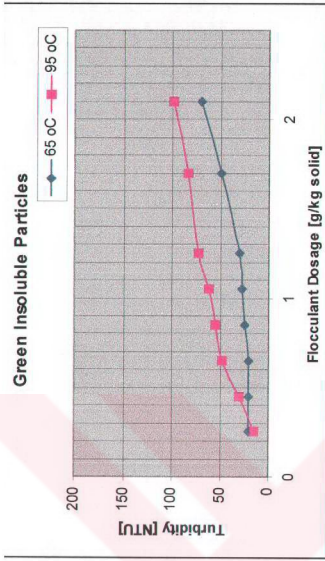
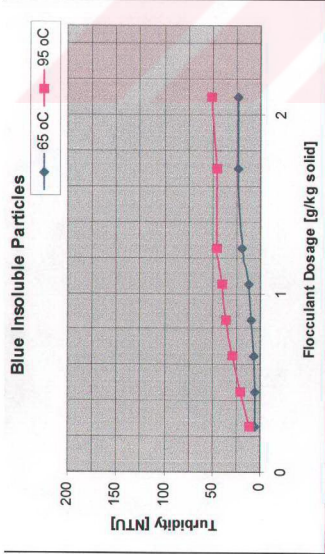


Figure 4.3.14.4 Turbidity Variation versus Different Temperature

Flocculant type : A100

Solid Content : 30 g/l

Residence time, hour : 0,5

Na2B4O7, % : 15

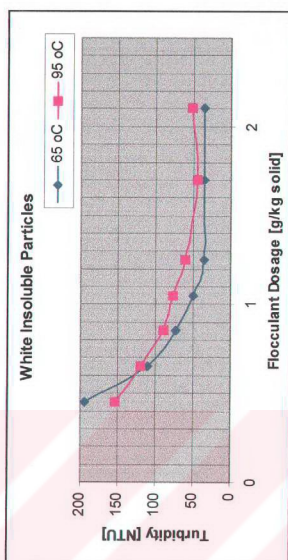
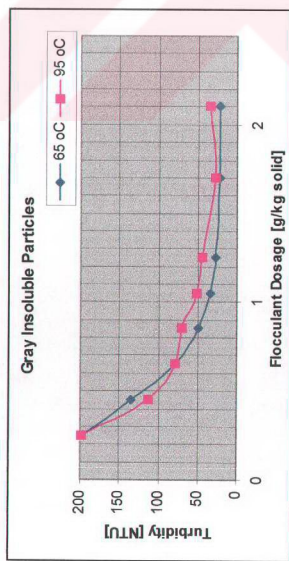
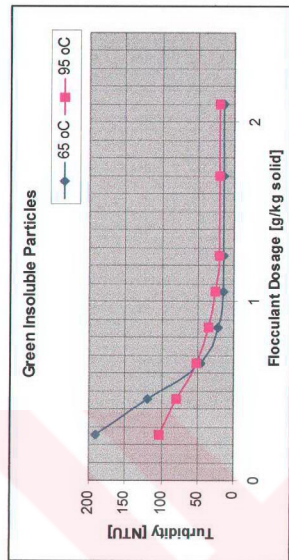
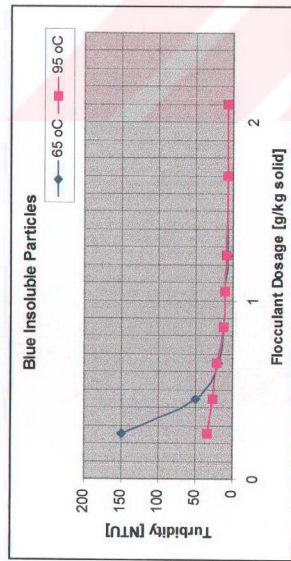


Figure 4.3.14.5 Turbidity Variation versus Different Temperature
 Flocculant type : PEO Solid Content : 30 g/l

Residence time, hour : 0,5

Na2B4O7, % : 15

4.3.15 Effect of Borax Concentration on Flocculation

Previous studies indicated that increase on borax concentration has positive effect for flocculation. Therefore, flocculation studies for different insoluble particles were carried out at different borax concentration.

Flocculation studies on different insoluble particles at 0 % borax concentration were carried out using PEO, N100 and A100 flocculants, but were not able to flocculate. 3% borax concentration studied before, and results and graphics were given previous section.

Flocculation studies of insoluble particles on 3%, 8% and 15% borax concentration were carried at 65 °C using A100 and PEO flocculants and results were given at Figure 4.3.15.1 and 4.3.15.2.

Increase on borax concentration from 3% to 8% had significant effect on flocculation and consumption for both flocculant were decreased. Even it was possible to flocculate white insoluble particles at 65 °C and 8% borax concentration. Increasing borax concentration from 8% to 15% didn't have any changes on flocculation of blue, green or gray particles, but did have positive effect on white particles.

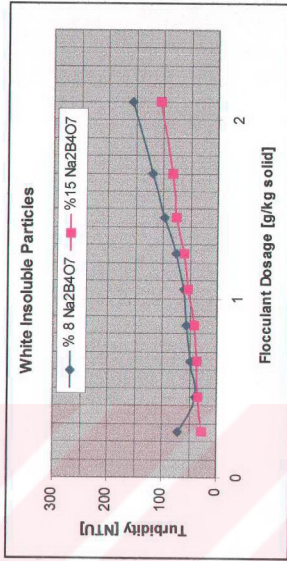
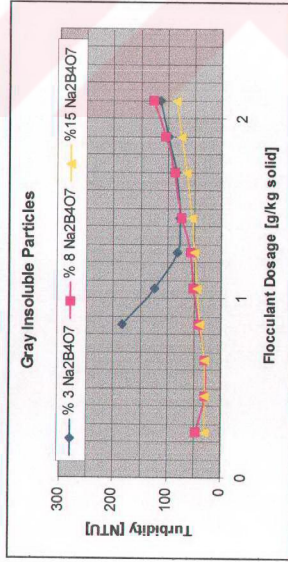
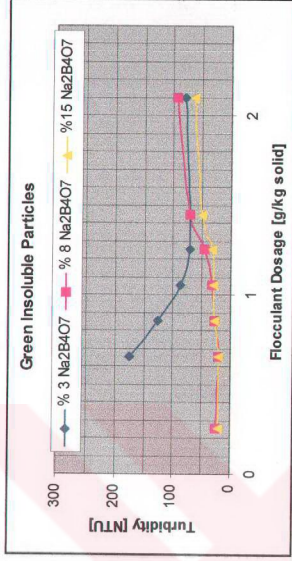
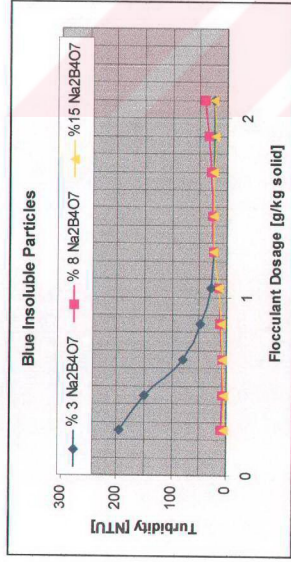


Figure 4.3.15.1 Turbidity Variation versus Different Borax Concentration

Flocculant type : A100

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature, °C : 65

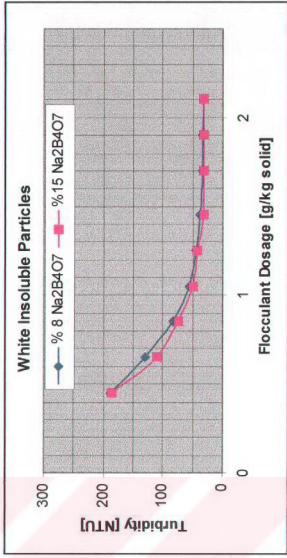
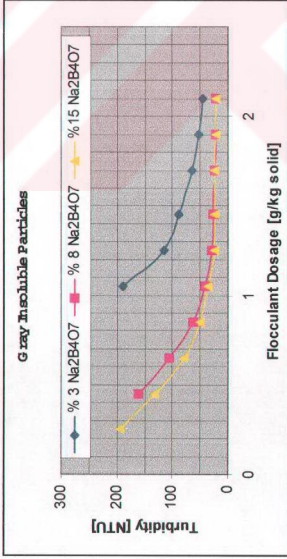
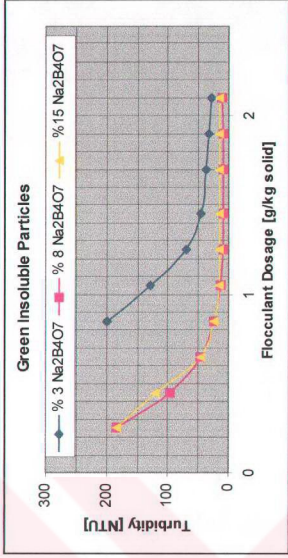
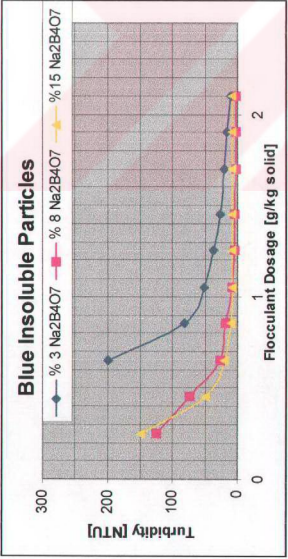


Figure 4.3.15.2 Turbidity Variations versus Different Borax Concentration

Flocculant type : PEO

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature, °C : 65

The effect of borax concentration were also investigated at 95 °C. Figure 4.3.15.3 shows flocculation studies of blue and white insoluble particles using N100 flocculant at 95 °C. Figure 4.3.15.4 and 4.3.15.5 shows flocculation studies of all insoluble particles using A100 and PEO flocculants at 95 °C.

Evaluation of these graphics, we can conclude that;

While there were no significant effect on increasing borax concentration from 8% to 15% for flocculation of insoluble particles at 65 °C, it turned out that there is a difference on consumption of flocculant using A100, N100, and PEO at 95 °C.

During the use of N100 flocculant for flocculation of blue and white insoluble particles, increasing borax concentration from 15% to 30% caused increase on consumption of flocculant.

Using A100 flocculants for flocculation of insoluble particles did cause increase on minimum consumption of flocculant but it was not as much as N100 flocculant, while the borax concentration were increased from 15% to 30% at 95 °C.

Using PEO flocculants for flocculation of insoluble particles did cause increase on minimum consumption of flocculant while the borax concentration were increased from 15% to 30% at 95 °C.

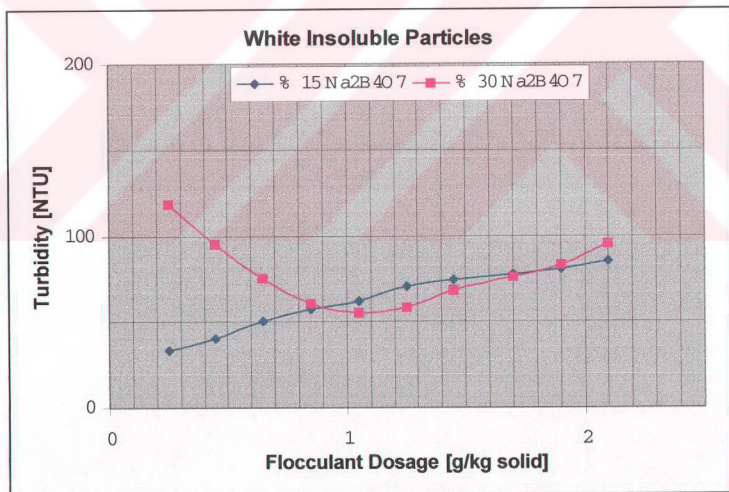
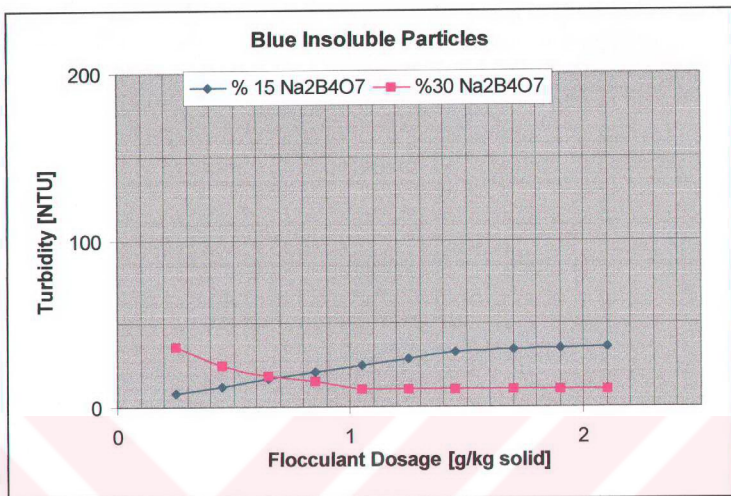


Figure 4.3.15.3 Turbidity Variations versus Different Borax Concentration

Flocculant type : N100

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature : 95 °C

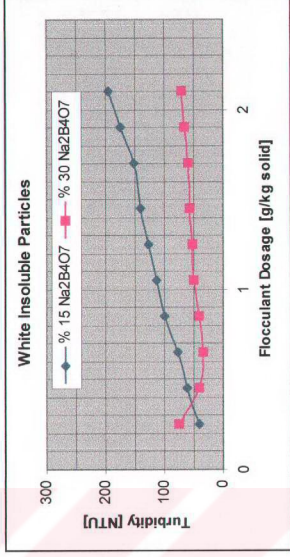
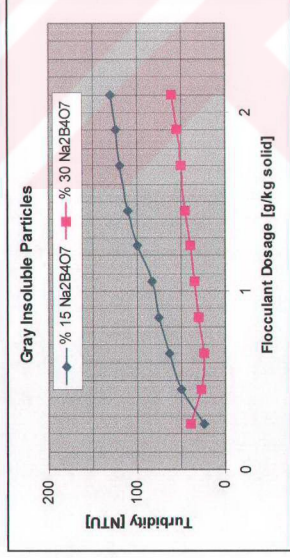
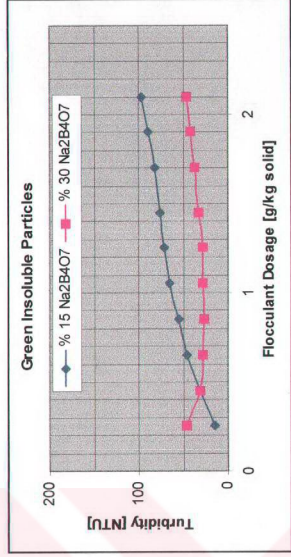
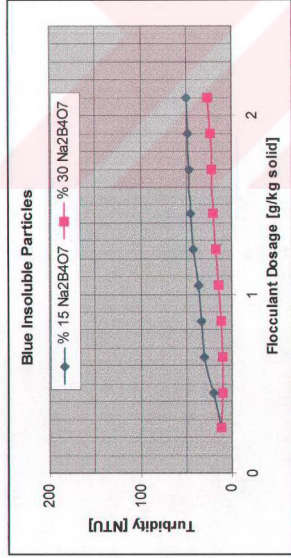


Figure 4.3.15.4 Turbidity Variations versus Different Borax Concentration

Flocculant type : A100

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature, °C : 95

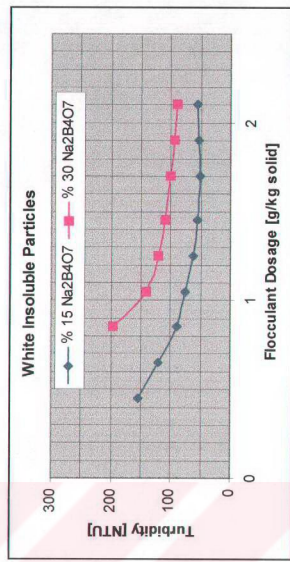
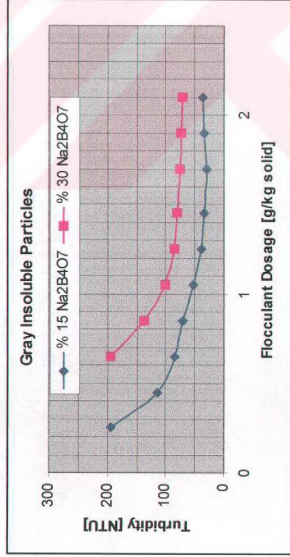
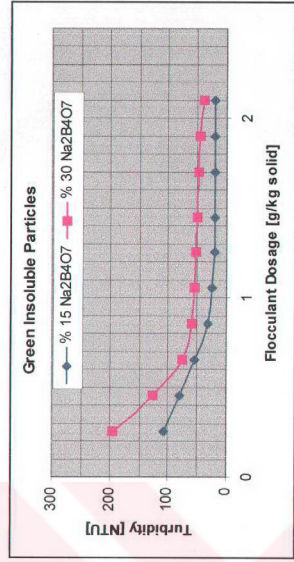
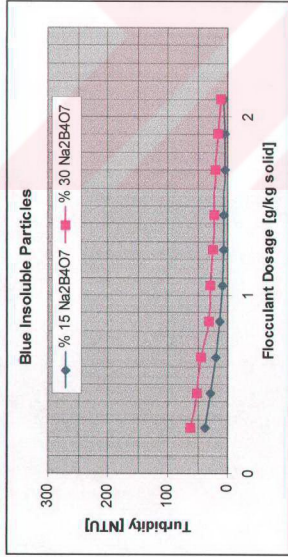


Figure 4.3.15.5 Turbidity Variations versus Different Borax Concentration

Flocculant type : PEO

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature, °C : 95

Figure 4.3.15.6 shows flocculation studies were carried during borax pentahydrate production using suspension containing %30 borax at 95 °C. Evaluating Figure 4.3.15.6, we can conclude that A100 is optimum flocculant during borax pentahydrate production and PEO won't be alternative in any matter. Optimum flocculant dosage would be 0,4 to 0,6 g/kg solid.

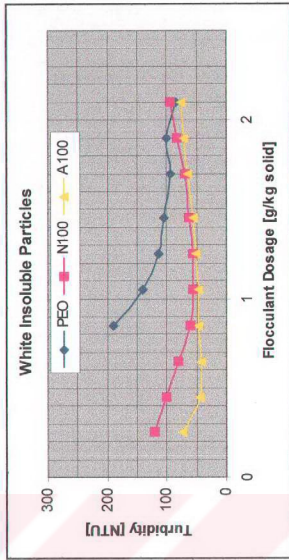
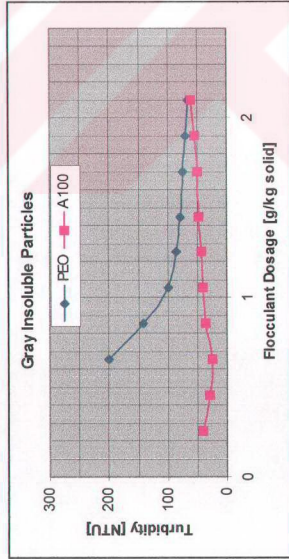
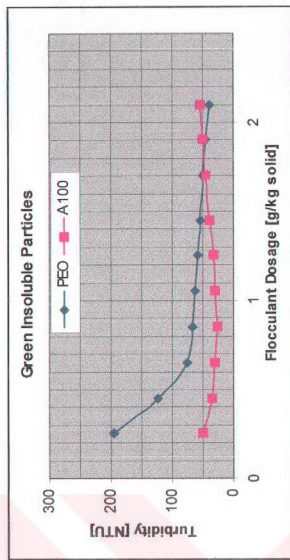
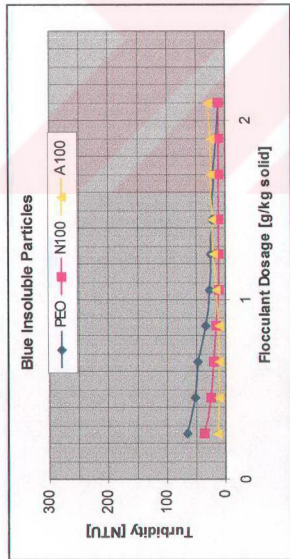


Figure 4.3.15.6 Optimum Flocculant Selection During Borax Pentahydrate Production

Na₂B₄O₇, % : 30

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature, °C : 95

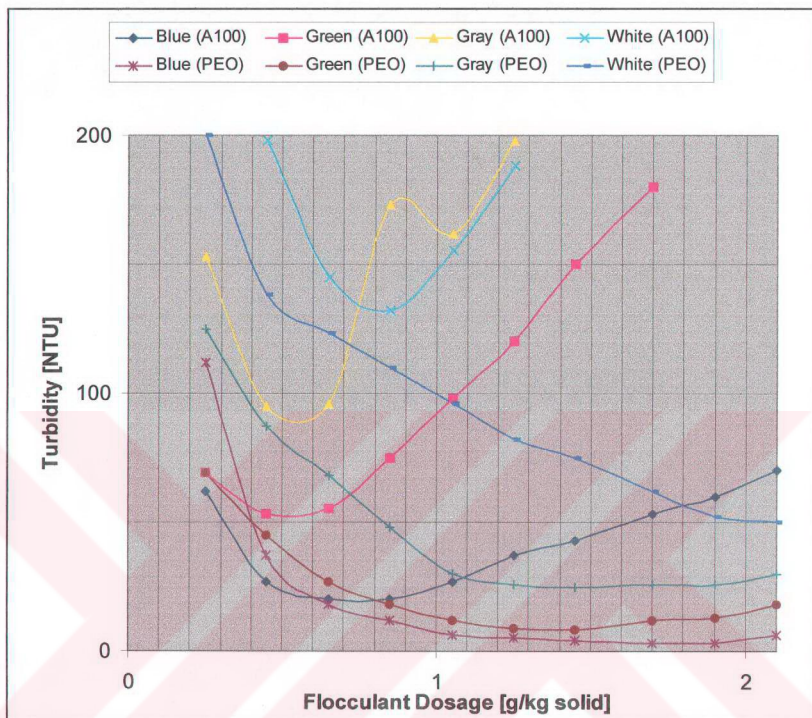


Figure 4.3.15.7 Optimum Flocculant Selection on Flocculation of Concentrator Tailing

Na₂B₄O₇, % : 3

Solid Content : 30 g/l

Residence time, hour : 0,5

Temperature : 35 °C

Flocculation tests on concentrator tailings were studied before and results were graphically shown at previous section. Figure 4.3.15.7 shows comparison between A100 and PEO flocculants for optimum flocculant selection at Kirka Concentrator Unit. From Figure 4.3.15.7, it can be concluded that PEO would be proper to use for flocculation of concentrator tailings. Since the hardness of montmorillonite type insoluble particles lower than that of dolomite, Kirka concentrator tailings mostly composed of montmorillonite type particles. Therefore, it is possible to flocculate tailings where flocculant dosage could be 0,5 g/kg solid.

4.3.16 Effect of Suspension's Residence Time

During the extraction of tincal concentrate, the insoluble particles remains at least 30 minutes in suspension before borax concentration of solution reaches 30% borax. Therefore, to determine the effect of residence time on flocculation, the insoluble particles kept in solution for 30 minutes before carried out any test.

Figure 4.3.16.1 shows the effect of residence time for the flocculation of concentrator unit tailings at 30 g/l solid, 35 °C, and 3% borax concentration. PEO consumption were selected 1 g/kg solid.

It can be seen from Figure 4.3.16.1 that the residence time did not have any negative effect on flocculation, even had some positive effect in 16 hours.

Figure 4.3.16.2 shows the effect of residence time for the flocculation of concentrator unit tailings at 30 g/l solid, 35 °C, and 3% borax concentration using A100.

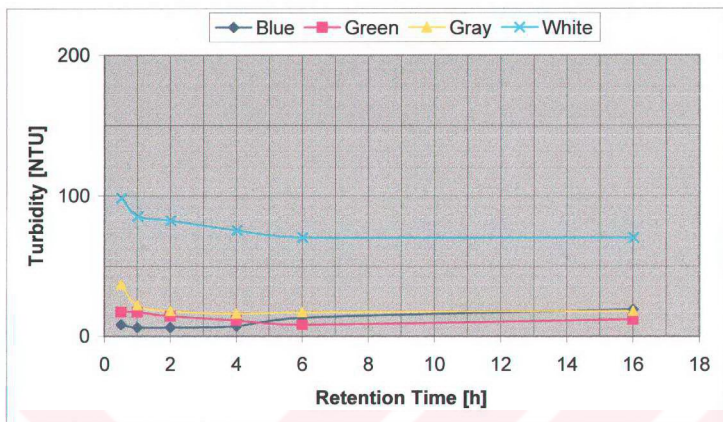


Figure 4.3.16.1 Turbidity Variations versus Retention Time

Na₂B₄O₇, % : 3

Solid Content : 30 g/l

Flocculant type : PEO

Temperature : 35 °C

Flocculant Dosage : 1,042 g/kg solid

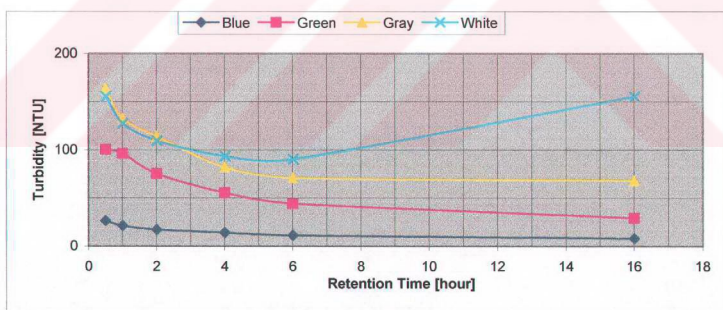


Figure 4.3.16.2 Turbidity Variations versus Retention Time

Na₂B₄O₇, % : 3

Solid Content : 30 g/l

Flocculant type : A100

Temperature : 35 °C

Flocculant Dosage : 1,042 g/kg solid

Figure 4.3.16.3 shows the effect of retention time for the flocculation of blue and white particles at 30 g/l solid, 95 °C, and 30% borax concentration using A100.

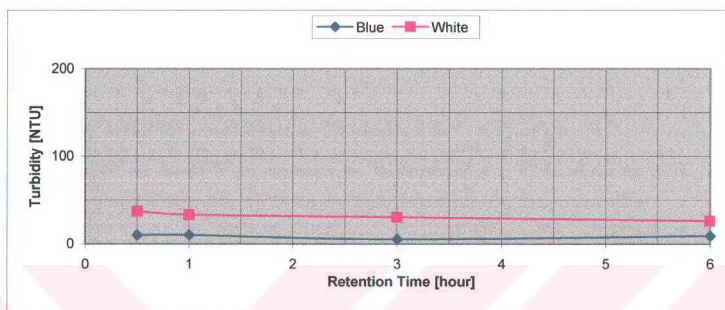


Figure 4.3.16.3 Turbidity Variations versus Retention Time

Na₂B₄O₇, % : 30

Solid Content : 30 g/l

Flocculant type : A100

Temperature : 95 °C

Flocculant Dosage : 0,625 g/kg solid

It can be seen from Figure 4.3.16.3 that there is no negative effect of retention time on flocculation of blue and white particles.

4.3.17 Dissolution Studies of Kirka Ore Using Pilot Scale Extractor

Minus 25 mm crushed ore was used during pilot plant tests. Particle size distribution was given at Table 4.3.17.1.

Table 4.3.17.1 Results of Sieve Test

Date : 20.04.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25,0	2,38	97,62	2,38
+ 15,0	7,53	90,09	9,91
+ 10,0	5,56	84,53	15,47
+ 8,0	5,07	79,46	20,54
+ 6,0	3,77	75,69	24,31
+ 4,0	11,11	64,58	35,42
+ 2,0	18,80	45,78	54,22
+ 1,0	18,11	27,67	72,33
- 1,0	27,67		
TOTAL	100,00		100,00

From the Table 4.3.17.1 , it can be seen that most of the crushed ore minus 4 mm and mainly powder.

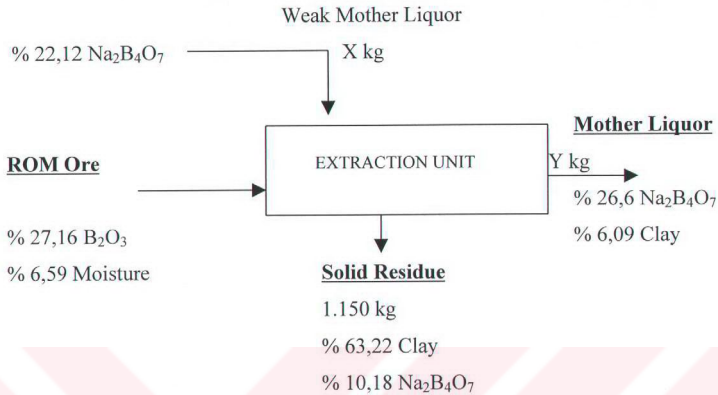
It can be seen from the overflow of Extractor 1 that the amount of weak mother liquor was not able to keep constant because of various ore feed. Table 4.3.17.2 shows pilot plant test results.

Time	Temperatures			ROM Ore			Weak Mother Liquor		Extractor 1				Solid Residue		
	Part 1	Part 2	Part 3	Feed, t/h	% B ₂ O ₃	% Moisture	Density g/l	% Na ₂ B ₄ O ₇	Flow, m ³ /h	Density g/l	% Na ₂ B ₄ O ₇	% Clay	% Na ₂ B ₄ O ₇	% Clay	% Moisture
13:00				1,3					1,90	1045					
13:30				"					2,06	1165					
14:00				"					2,36	1196					
14:30	98	98	98	"			1180		1,90	1215					
15:00				"	26,92	6,40	"	21,40	2,42	1235	23,27	4,25	7,90	68,22	16,81
15:30	99	99	99	"			"		3,29	1247					
16:00				"			"		2,42	1265					
16:30	99	99	98	"			"		2,23	1280					
17:00	99	99	98	"	27,30	8,23	"	22,26		1270	26,56		8,36	64,42	19,74
17:30	99	99	98	"			"			1270					
18:00				1,117			"		3,05	1262					
19:00	99	98	98	"	27,40	6,58	"	22,58	3,05	1275	27,67	7,28	11,34	61,43	17,08
20:00	99	98	98	"			"		4,12	1285					
20:30				"			"			1285					
21:00	99	99	98	"	27,05	7,32	"	23,49	4,85	1282	27,90	6,90	11,66	60,17	17,74
21:30	99	98	98	"			"			1282					
22:00	99	98	98	"			"		4,85	1285					
22:30	99	98	98	"	27,51	7,46	"	20,87		1282	27,16	6,90	11,66	61,86	16,05
23:00	99	98	98	"			"	20,87		1262					
23:40	99	98	98	"	26,77	3,60	"				27,03	5,18			

Table 4.3.17.2 Pilot Plant Test Results Using minus 25 mm ROM Ore

Ore type	:	Layered material	Solid residue, kg	:	1.150
Particle size, mm	:	minus 25	Total Test Time, hour	:	10,5
ROM ore, kg	:	11.100	Average pulp density, g/l	:	1.300
Date	:	20.04.1998	Dissolution time, minutes	:	20

Calculation was made based on average values derived from pilot test results.



From the clay mass balance equation:

Clay in Feed : $[100 - (27,16 / 0,3651) * (1-0,0659) - 6,59] * (11.100/100) = 2.655 \text{ kg}$

Clay in Solid Residue : $0,6322 * 1.150 = 727 \text{ kg}$

Clays Isolated in Extraction Process : $(727/2.655)*100 = \% 27,38$

From the borax mass equation:

$\text{Na}_2\text{B}_4\text{O}_7$ in ROM Ore : $[(27,16/36,51)*0,5278*(1-0,0659)*11.100 = 4.071 \text{ kg}$

$\text{Na}_2\text{B}_4\text{O}_7$ in Solid Residue : $1.150 * 0,1018 = 117,1$

$\text{Na}_2\text{B}_4\text{O}_7$ Loss in Solid Residue : $(117,1/4.071)*100 = \% 2,88$

Calculation of unknown X and Y values on flow chart :

Total mass balance equation : $11.100 + X = 1.150 + Y$ (1)

Total $\text{Na}_2\text{B}_4\text{O}_7$ balance equation : $4.071 + 0,2212*X = 117,1 + 0,266*Y$ (2)

Total clay balance equation : $2.655 = 0,0609*Y + 727$ (3)

Using the equation 1 and 2, $X = 29.179 \text{ kg}$ and $Y = 39.129 \text{ kg}$ found.

From the equation 3 itself $Y = 31.658 \text{ kg}$ found.

Using average values of flow;

$$Y = 2,96 \text{ (m}^3\text{/h)} * 10,5 \text{ (h)} * 1300 \text{ (kg/m}^3\text{)} = 40.404 \text{ kg calculated.}$$

Last Y value derived from flow pattern close the Y value derived from equation 1 and 2 but far from equation 3.

We can conclude that the average clay content in mother liquor was mismeasured and should recalculate;

$$\text{Clay content in mother liquor} = [(2.655 - 0,6322 * 1.150) / 39.129] * 100 = \% 4,93$$

Evaluation of test results shows that 1285 g/l (kg/m^3) density of mother liquor was easily attained using low mixing rate of extraction unit compare to existing borax derivative plant in Kırka. Liquid was saturated under these circumstances. While the density of borax saturated solution was 1270 g/l, the borax loss in solid residue was 8 % $\text{Na}_2\text{B}_4\text{O}_7$ and when it became 1285 g/l, the borax loss residue reached to 11,5 % $\text{Na}_2\text{B}_4\text{O}_7$. This means, because of already saturated liquid in the system, some of the borax pieces was not able to be dissolved. The problem were here short coming of weak mother liquor returning to extraction unit.

Considering existing process parameters, the density of mother liquor will be 1250-1260 g/l, therefore the borax loss in solid residue is approximately 8 % $\text{Na}_2\text{B}_4\text{O}_7$ expected.

To be able to sure whether all the ore dissolved or not, it is better to check the formation of solid residue. Since the solid consists of average 63,22 % clay, rest of the 36,78 % should be either contacting weak mother liquor or together with undissolved tincal. If the weak mother liquor contains 22,12 % $\text{Na}_2\text{B}_4\text{O}_7$, the borax loss in solid residue would be; $(36,78 * 22,12) / 100 = \% 8,14 \text{ Na}_2\text{B}_4\text{O}_7$. This proves that extraction for tincal is completed.

Next pilot test was run using 20 minutes for dissolution time and ROM ore crushed to minus 100 mm. Results of test given at Table 4.3.17.3.

Calculation was made using average value at Table 4.3.17.2. It was conclude that 65,6 % of clay in feed isolated during extraction process and borax loss was 5,84 % $\text{Na}_2\text{B}_4\text{O}_7$.

However, controlling of solid residue with open eyes showed that there were some tincal particles which were undissolved. Therefore using minus 100 mm crushed ore for extraction would be too risky.

Examining minus 100 mm crushed ore, it was observed that there were some pieces even more than 250 mm particle size, were very difficult to dissolve.

Date of 21.4.1998, another test were carried out using low B_2O_3 content homogenous minus 25 mm crushed ore by eliminating fine particles. Dissolution time were also extended to 30 minutes by slowing down of rotation speed in Extractor 1. Tests results shown at Table 4.3.17.4.

Calculation was made using average value at Table 4.3.17.4. It was conclude that 68,7 % of clay in feed isolated during extraction process and borax loss was 7,57 % $\text{Na}_2\text{B}_4\text{O}_7$.

Table 4.3.17.5 shows test results were carried out on date of 23.4.1998 using minus 25 mm crushed ore containing 23,40 B_2O_3 . Results concluded that 62,9 % of clay in feed isolated during extraction process and borax loss was 5,0 % $\text{Na}_2\text{B}_4\text{O}_7$. Beginning of the test, water was used in Extractor 1 as a liquid therefore couldn't reach targeted mother liquor density during working hours.

Table 4.3.17.6 shows test results were carried out on date of 23.4.1998 using minus 25 mm crushed ore containing 25,84 B_2O_3 . Results concluded that 58,5 % of clay in feed isolated during extraction process and borax loss was 5,43 % $\text{Na}_2\text{B}_4\text{O}_7$.

Table 4.3.17.7 shows test results were carried out on date of 24.4.1998 using minus 25 mm crushed ore containing 26,03 B_2O_3 . Results concluded that 47,7 % of clay in feed isolated during extraction process and borax loss was 4,12 % $\text{Na}_2\text{B}_4\text{O}_7$.

Table 4.3.17.8 shows summarized test results carried out on date between 20.4.1998 to 24.4.1998. Figure 4.3.17.1 shows feed grade versus clay % in solid residue at Extractor 2.

Figure 4.3.17.2 shows feed grade versus borax loss in solid residue at Extractor 2.



ROM Ore				Solid Residue					Mother Liquor					
Size, mm	Appearance	% B ₂ O ₃	% Moisture	Extraction Time, minutes	% Clay	% Na ₂ B ₄ O ₇	% Isolated Clay	% Borax Loss	% Na ₂ B ₄ O ₇ Average	% Na ₂ B ₄ O ₇ Max.	Density g/l Average	Density g/l Max.	% Clay Average	% Clay Max.
- 25	Mostly Fine Particle	27,16	6,59	20	63,22	10,18	27,38	2,88	26,60	27,90	1247	1285	6,09	7,28
- 100	Normal	26,56	5,23	20	67,74	8,50	65,60	5,84	28,53	30,23	1258	1282	3,61	4,56
- 25	Normal	21,81	8,24	30	69,60	7,57	68,70	7,47	28,25	28,25	1243	1245	4,02	5,49
- 25	Normal	23,40	6,52	30	75,20	5,63	62,90	5,00	23,20	25,94	1189	1232	2,55	4,31
- 25	Normal	25,84	5,93	30	68,09	8,07	58,50	5,43	27,93	28,93	1243	1265	4,85	5,39
- 25	Normal	26,03	5,60	30	66,30	7,51	47,7	4,12	28,30	30,04	1247	1268	5,50	5,80

Table 4.3.17.8 1 t/h Capacity Pilot Plant Test Results

4.3.17.1 Comparison of Laboratory and Pilot Scale Results

Results derived from a 50 kg/h capacity laboratory scale extractor compared with 1 t/h and capacity pilot scale extraction unit concerning on following parameters;

4.3.17.1.1 $\text{Na}_2\text{B}_4\text{O}_7$ Content in Mother Liquor

Both laboratory and pilot plant test results proved that the density of clarified mother liquor up to 1290 g/l was easily attained even some mechanical problems occurred during operation. 1290 g/l density means more than 30 % $\text{Na}_2\text{B}_4\text{O}_7$ content. The density requirement of clarified mother liquor on present Borax Derivative Plant is 1258 g/l, therefore it can be concluded that dissolution time were accurate in both laboratory and pilot plant tests.

4.3.17.1.2 Clay Content in Mother Liquor

Although during laboratory test the clay content in mother liquor was 2-4 %, that off reach to 5-6 % in pilot plant.

4.3.17.1.3 Dissolution Time

30 minutes of dissolution time for tincal ore were secure enough in laboratory. The extraction results in Kırka were even better and 20 minutes of dissolution time for minus 25 mm crushed ore were sufficient but there were some undissolved tincal particles if the ore size kept minus 100 mm.

4.3.17.1.4 Particle Size

In laboratory, minus 6 and 25 mm ore were used for extraction studies and minus 25 mm ore were found better fit. At Kırka plant, minus 25 and 100 mm ore used for extraction studies and it was noticed that there were some undissolved tincal particles when minus 100 mm ore were in line. In addition to these, it was also figured out that if there were too many fine particles in feed, it would cause increase on clay content of mother liquor.

4.3.17.1.5 Clay Content in Solid Residue

While the clay content in residue was found between 50-60 % at laboratory, it turned out 65-75 % during pilot plant studies in Kırka. Increase on clay content will simply increase recovery of borax, so better results achieved in Kırka.

4.3.17.1.6 $\text{Na}_2\text{B}_4\text{O}_7$ Content in Solid Residue

Before the pilot plant tests, all the assumptions were made based on $\text{Na}_2\text{B}_4\text{O}_7$ content in solid residue was 8-12 %, but it came out 6-8 %.

4.3.17.1.7 Recovery

50-60 % clay content in solid residue and 2-4 % clay content in mother liquor were used for mass balance calculation, but recalculation should be done because of new data derived in Kırka pilot plant.

4.3.18 Semi-Industrial Experimental Studies Using 10 t/h Capacity Extractors

Before deciding whether proposed system should applied to Kırka or not, first a 50 kg/h capacity laboratory extractor used and after successful results moved on building 1 t/h capacity two step extractor. In both studies, some mechanical and technical problems encounter, lots of confidence gained.

With the 10 t/h capacity extractors, proposed system will be controlled mechanically, technically, key parameters watch carefully, and final touch and look will be delivered.

4.3.18.1 Design Parameters

Working Hours	:	24 h/day
Ore Grade	:	Average 24 % B_2O_3 , varies 20-28 % B_2O_3
Moisture	:	Average 6 %, varies 4-10 %
Weak Mother Liquor	:	21 % $Na_2B_4O_7$, varies 19-23 % $Na_2B_4O_7$
Mother Liquor	:	Average 28,4 % $Na_2B_4O_7$ and 3.0 % clay, varies 27,5-28,7 % $Na_2B_4O_7$ and 2-5 % clay
Solid Residue	:	Average 65 % clay and 8 % $Na_2B_4O_7$, varies 55-75 % clay and 5,5-10,0 % $Na_2B_4O_7$
Capacity	:	10 t/h, 24 % B_2O_3 and 6 % moisture

4.3.18.2 Mass Balance

4.3.18.2.1 Mass Balance Calculations Based on Average Values

Feed Ore	:	24 % B_2O_3 and 6 % moisture
Capacity	:	10 t/h
Weak Mother Liquor	:	X t/h
Mother Liquor	:	y t/h
Solid Residue	:	$10 + X - y$ t/h

Total $\text{Na}_2\text{B}_4\text{O}_7$ Balance Equation : $0,24 \cdot (52,78/36,51) \cdot 10 + 0,21 \cdot X = 0,284 \cdot y + (10+X-y) \cdot 0,08$

Clay content of the ROM ore : $100 - [(100/36,51) \cdot 24 + 6] = \% 28,26$

Clay Balance Equation : $0,2826 \cdot 10 = 0,03 \cdot y + 0,65 \cdot (10+X-y)$

Solving these three equations;

X (weak mother liquor) = 17,42 t/h

Y (Mother liquor) = 24,18 t/h

Solid residue = 3.24 t/h

4.3.18.2.2 Mass Balance Calculations Based on Various Ore Feed

Constant Parameters

Ore, % moisture	: 6	Ore Feed, t/h	: 10
Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 28,40	Mother liquor, % clay	: 3
Weak Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 21,00		

	Ore Grade, % B_2O_3		
	20	24	28
Weak mother liquor, t/h	14,82	17,42	20,01
Mother liquor, t/h	19,70	24,18	28,68
Solid residue, t/h (% 65 clay + % 8 $\text{Na}_2\text{B}_4\text{O}_7$)	5,12	3,24	1,33

Table 4.3.18.1 Mass Balance Calculations Based on Various Ore Feed

Screws bring borax from opening to end at a constant time, therefore residence time for solid will be constant. However, keeping flow rate constant will cause mother liquor recirculate in a longer period of time in system because of changes on ore grade. Therefore, for the unvarying production, it is necessary to change flow rate.

4.3.18.2.3 Mass Balance Calculations for Fixed Production

Constant Parameters

Ore, moisture	: 6	Mother liquor flow rate, t/h	: 24,18
Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 28,40	Mother liquor, % clay	: 3

	Ore Grade, % B_2O_3		
	20	24	28
Ore Feed, t/h	12,28	10,0	8,43
Weak Mother Liquor, t/h (% 21 $\text{Na}_2\text{B}_4\text{O}_7$)	18,19	17,42	16,88
Solid Residue, t/h (% 65 clay + % 8 $\text{Na}_2\text{B}_4\text{O}_7$)	6,29	3,24	1,13

Table 4.3.18.2 Mass Balance Calculations for Fixed Production

Table 4.3.18.3 Effect of moisture content on flow rates

Constant Parameters

Mother liquor flow rate, t/h	: 24,18	Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 28,40
Mother liquor, % clay	: 3	Weak Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 21,00

	Ore Grade, % B_2O_3								
	20			24			28		
	Ore Moisture, %			Ore Moisture, %			Ore Moisture, %		
	4	6	10	4	6	10	4	6	10
Ore Feed, t/h	11,97	12,28	12,94	9,79	10,0	10,43	8,29	8,43	8,74
Weak Mother Liquor, t/h	18,68	18,19	17,14	17,83	17,42	16,53	17,24	16,88	16,12
Solid Residue, t/h (% 65 clay + % 8 $\text{Na}_2\text{B}_4\text{O}_7$)	6,47	6,29	5,90	3,44	3,24	2,78	1,35	1,13	0,68

Table 4.3.18.3 Effect of moisture content on flow rates

Table 4.3.18.4 Effect of clay ratio in solid residue on flow rates**Constant Parameters**

Mother liquor flow rate, t/h	: 24,18	Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 28,40
Mother liquor, % clay	: 3	Ore, moisture	: 6
Weak Mother liquor, % $\text{Na}_2\text{B}_4\text{O}_7$	: 21,00	Solid Residue, % $\text{Na}_2\text{B}_4\text{O}_7$	: 8

	Ore Grade, % B_2O_3								
	20			24			28		
	Clay Ratio, % in Solid Residue			Clay Ratio, % in Solid Residue			Clay Ratio, % in Solid Residue		
	55	65	75	55	65	75	55	65	75
Ore Feed, t/h	11,41	12,28	13,02	9,62	10,0	10,30	8,32	8,43	8,52
Weak Mother Liquor, t/h	19,59	18,19	17,00	18,18	17,42	16,80	17,16	16,88	16,66
Solid Residue, t/h	6,82	6,29	5,84	3,62	3,24	2,92	1,30	1,13	1,00

Table 4.3.18.4 Effect of clay ratio in solid residue on flow rates

Table 4.3.18.5 Effect of weak mother liquor on flow rates**Constant Parameters**

Mother liquor flow rate, t/h : 24,18 Mother liquor, % Na₂B₄O₇ : 28,40
 Mother liquor, % clay : 3 Ore, moisture : 6

	Ore Grade, % B₂O₃								
	20			24			28		
	Weak Mother Liquor % Na₂B₄O₇			Weak Mother Liquor % Na₂B₄O₇			Weak Mother Liquor % Na₂B₄O₇		
	19	21	23	19	21	23	19	21	23
Ore Feed, t/h	14,48	12,28	9,85	11,70	10,0	8,08	9,82	8,43	6,86
Weak Mother Liquor, t/h	17,32	18,19	19,16	16,45	17,42	18,50	15,86	16,88	18,03
Solid Residue, t/h (% 65 clay + % 8 Na₂B₄O₇)	7,62	6,29	4,83	3,97	3,24	2,40	1,50	1,13	0,71

Table 4.3.18..5 Effect of weak mother liquor on flow rates

4.3.18.3 Experimental Results for 10 t/h Capacity Extractors at Kirka Plant

4.3.18.3.1 Particle Size Distribution of Feed Ore

Minus 25 mm crushed ore was used during pilot plant tests. Particle size distribution was given at Table 4.3.18.3.1 and Appendix 4.3.18.3.1, 4.3.18.3.2, 4.3.18.3.3, 4.3.18.3.4 and 4.3.18.3.5.

Date : 25.03.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25	6,38	93,62	6,38
+ 18	7,35	86,27	13,73
+ 15	2,92	83,35	16,65
+ 12	7,12	76,23	23,77
+ 10	7,43	68,80	31,20
+ 8	7,95	60,85	39,15
+ 6	5,77	55,08	44,92
+ 3	19,70	35,38	64,62
+ 1	22,69	12,69	87,31
- 1	12,69		
TOTAL	100,00		

Table 4.3.18.3.1 Results of Sieve Test

4.3.18.4 Operating Parameters in Extraction Unit

10 t/h capacity extraction unit was designed by TÜSTAŞ, A.Ş., Ankara and manufactured by Türkiye Şeker A.Ş, Eskişehir facilities based on derived parameters resulted from 1 t/h capacity pilot scale extraction unit studies. The first test were carried on June 19th, 1997 and kept running until present. During test running some mechanical and technical problems encountered and fixed in Kırka. Even some problems still occur, we think the system mechanically and technically works fine and industrial results even will be better. Table 4.3.18.4.1 and Appendix 4.3.18.4.1, 4.3.18.4.2, 4.3.18.4.3, 4.3.18.4.4, 4.3.18.4.5, and 4.3.18.4.6 shows results of analysis were taking during test at 10 t/h capacity extraction unit. Figure 4.3.18.4.1 shows industrial application of similar design used in different industry.



Date	-25 mm Crushed Ore			Mother Liquor		Weak Liquor Density: g/cm ³	Solid Waste 1		
	% B ₂ O ₃	% Moisture	Density: g/cm ³	% Clay	Density: g/cm ³		% B ₂ O ₃	% Moisture	% Clay
19.06.1997	21,65	8,01	-	5,86	1,180		6,10	15,04	68,25
20.06.1997	26,13	5,22	-	6,04	1,180		8,73	13,15	62,94
21.06.1997	22,69	7,38	-	6,44	1,180		7,91	12,91	65,42
23.06.1997	25,25	6,24	-	2,87	1,180		9,20	16,01	58,79
24.06.1997	24,47	6,93	-	0,50	1,180		6,22	14,13	68,83
25.06.1997	23,27	7,33	-	5,01	1,180		6,71	13,69	67,93
25.06.1997	21,90	7,69	-	3,16	1,180		6,16	14,65	68,48
28.06.1997	19,50	6,02	-	1,40	1,180		7,65	15,00	64,05
30.06.1997	24,63	7,34	-	4,89	1,180		5,93	18,05	65,71
30.06.1997	24,70	5,51	-	2,75	1,180		5,64	15,73	68,82
01.07.1997	26,73	5,41	-	3,18	1,180		4,62	13,91	73,44
02.07.1997	26,11	5,57	-	1,94	1,180		11,01	15,98	53,86
05.07.1997	27,21	5,66	-	3,79	1,180		7,51	17,28	62,15
08.07.1997	25,74	5,54	-	3,26	1,180		4,53	12,40	75,19
08.07.1997	25,58	4,92	-	3,95	1,180		5,05	11,16	75,01
09.07.1997	23,41	5,81	-	2,85	1,180		10,94	16,45	53,59
10.07.1997	26,04	5,51	-	4,39	1,180		5,16	11,98	73,89
11.07.1997	24,93	7,29	-	4,92	1,180		10,8	15,23	55,19
12.07.1997	29,27	3,26	-	3,35	1,180		16,11	13,95	41,93
AVERAGE	24,70	6,14		3,71	1,18		7,68	14,56	64,39

Table 4.3.18.4.1 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 19.06.1997 to 12.07.1997

4.3.19 Isolating Fine Particles Comes From Mother Liquor Using Decanter Centrifuge

Feed			Clarified Liquid		Solids Discharge		
Time	Temperature, °C	% B ₂ O ₃	% Clay	% Na ₂ B ₄ O ₇	% Clay	% Na ₂ B ₄ O ₇	% Moisture % Clay
14:15	92	17,13	7,45	23,57	0,11	16,83	20,00 48,06
15:00	92	17,68	3,37	21,65	0,00	25,53	16,67 34,96
15:30	92	17,40	3,15	20,81	0,00	29,39	13,67 30,69
18:00	92	16,28	11,48	27,44	0,00	14,97	25,00 46,62
19:00	92	16,47	8,04	29,75	0,35	15,65	25,00 45,36
22:00	92	15,03	12,32	25,66	0,19	17,22	23,33 44,02
01:00	92	15,84	10,95	22,50	1,02	13,42	28,04 46,51
02:00	92	18,03	3,86	29,34	0,10	16,92	25,00 42,92
03:00	92	14,21	5,21	28,63	0,00	14,31	27,00 45,88
04:00	92	18,57	6,86	25,62	0,00	16,47	23,67 45,08
Average	92	16,66	7,27	25,50	0,18	18,07	22,74 43,01

Table 4.3.19.1 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 18.12.1998 to 20.04.1999.

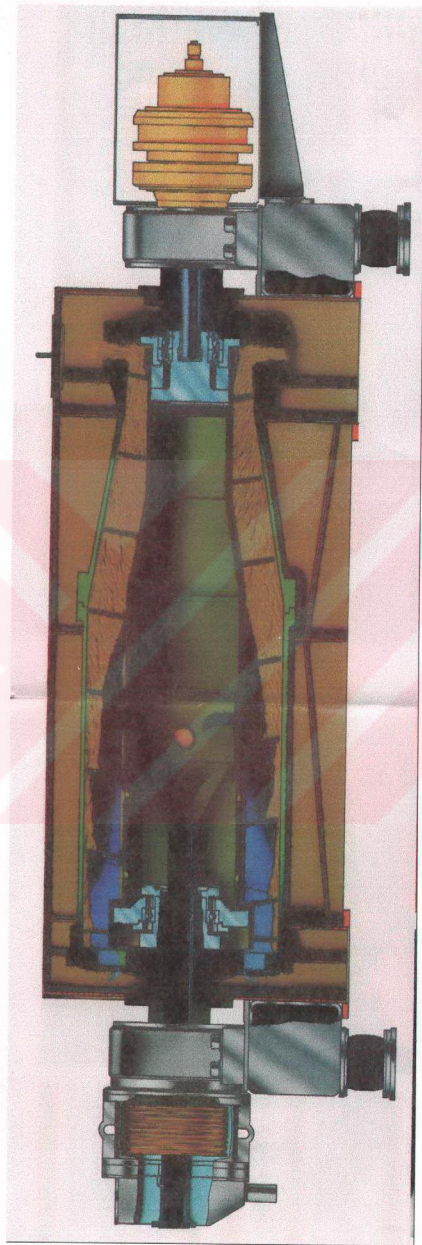


Figure 4.3.19.1 Industrial Type Continuous Solid Bowl Scroll Centrifuge

CHAPTER 5

PLANT DESIGN AND OPERATING PRACTICE

5.1 Design Parameters

Design parameters for Kırka Borax Plant is variable. The parameters that will be used during mass balance calculation and process design are derived from laboratory, 1 t/h capacity pilot plant, and 10 t/h capacity semi-industrial pilot plant test results and existing operations parameter in Concentrator1, Borax Derivative Plant 1 and Borax Derivative Plant 2 at Kırka.

- ◆ Plant Capacity : 160.000 t/y (borax pentahydrate)
- ◆ Final product: 48,5 % B_2O_3
- ◆ Working period : 330 day/year and 24 hour/day
- ◆ ROM ore grade : Varies between 20-27 % B_2O_3 , usually runs 25 % B_2O_3 .
- ◆ ROM ore moisture : It was assumed between 0-10 % but existing plant usually runs at 6 % moisture.
- ◆ Clay ratio of Tailing 1 isolated at extraction unit: Laboratory and pilot plant test results supported that clay ratio of tailing was between 50-75 %.
- ◆ $Na_2B_4O_7$ ratio of Tailing 1 isolated at extraction unit : Laboratory and pilot plant test results supported that $Na_2B_4O_7$ ratio of tailing was between 8-14 %. Most common value was 10 %.
- ◆ Clay ratio of mother liquor : 2-6 % clay. Most common value was 2 %.
- ◆ $Na_2B_4O_7$ ratio of mother liquor : Varies between 28,0 to 28,7 %.

- ◆ Flocculant consumption at Thickener 1 : Laboratory and pilot plant test results supported that anionic type flocculant consumption at Thickener 1 could be selected 0.2 kg flocculant / ton clay. Flocculants were made up to stock solutions of about 0,2 %, which were diluted to 0,05 %.
- ◆ Clay ratio of underflow at Thickener 1: 15 % clay was selected.
- ◆ Flocculant consumption at Thickener 2 : Laboratory and pilot plant test results supported that non-ionic type and PEO flocculant consumption at Thickener 2 could be selected 0.1 kg flocculant / ton clay and 0,2 kg flocculant / ton clay.
- ◆ Clay ratio of underflow at Thickener 2 : 15 % clay was selected.
- ◆ Clay ratio of final tailings at Decanter centrifuge : 40 % was assumed.
- ◆ Clarified liquid comes from overflow of Thickener 1 : 29,23 % $\text{Na}_2\text{B}_4\text{O}_7$ and 1,258 g/l density.
- ◆ Borax pentahydrate product from centrifuge : 5 % mother liquor was selected for product.

5.2 Mass Balance Calculations

5.2.1 Pentahydrate Dryer

Inputs;

Moist Borax Pentahydrate: X t/h, 5 % mother liquor (18 % $\text{Na}_2\text{B}_4\text{O}_7$)

Outputs;

Dry Borax Pentahydrate : 20,2 t/h and 48,5 B_2O_3

Water : y t/h

$$\text{Mass Balance : } X = 20,2 + y$$

$$\text{B}_2\text{O}_3 \text{ Equilibrium : } (0,4780) \cdot (0,95) \cdot X + (0,05) \cdot (0,18) \cdot (69,6/100,6) \cdot X = (20,2) \cdot (0,485)$$

$$\text{Solving two equations; } X = 21,28 \text{ t/h} \quad y = 1,08 \text{ t/h}$$

calculated.

5.2.2 Preparation of 0,05 % (v/v) flocculant

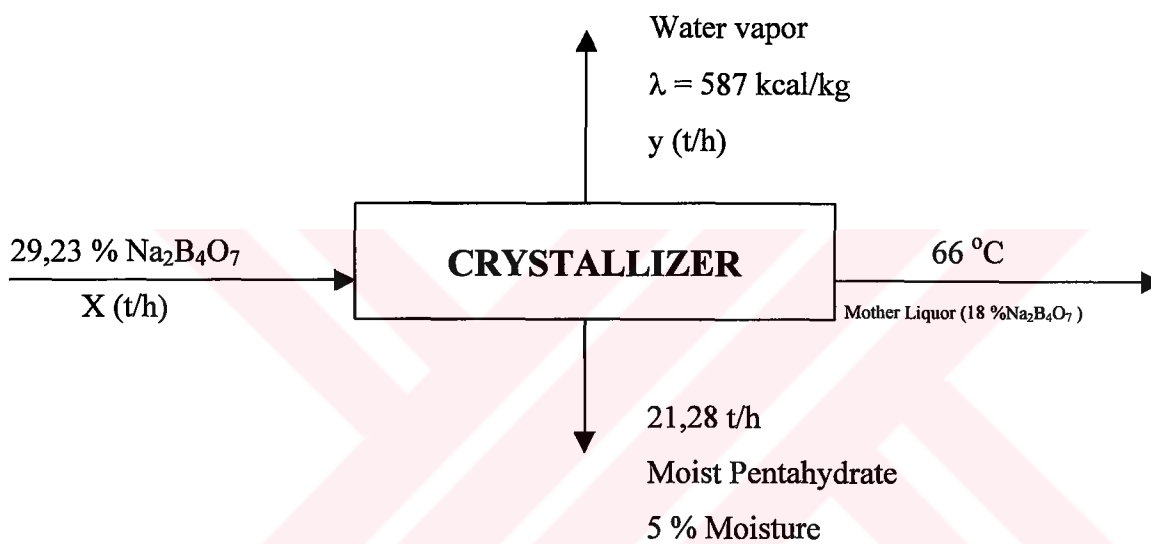
Inputs:

1 liter 0,2 % flocculant + 3 liter 18 % $\text{Na}_2\text{B}_4\text{O}_7$ ($d = 1,135$)

Outputs:

4 liter (4,405) 13,91 % $\text{Na}_2\text{B}_4\text{O}_7$ and 0,0454 % (w/w) flocculant.

5.2.3 Pentahydrate crystallization



Energy Balance:

$$(X-y) \cdot (96-66) = (0,71 + 0,82) / 2 = 587 \cdot y$$

$C_p(\text{mother liquor}) : 0,71 \text{ kcal/kg } ^\circ\text{C}$

$C_p(\text{weak liquor}) : 0,82 \text{ kcal/kg } ^\circ\text{C}$

$\lambda(\text{water vapor}) : 587 \text{ kcal/kg}$

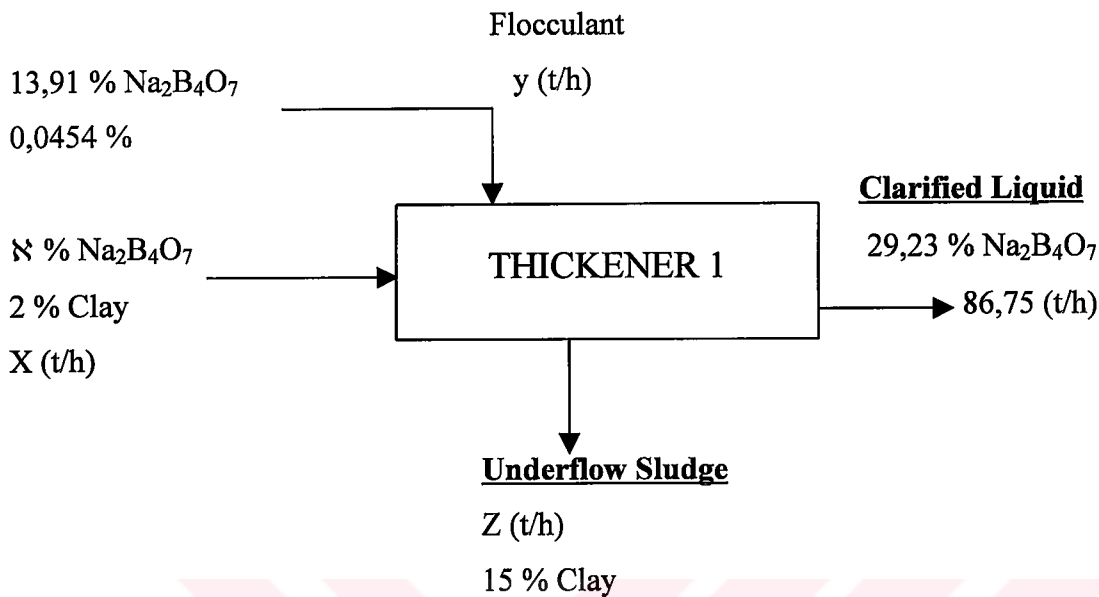
Mass Balance Equation:

$$[0,2923 \cdot X - (0,6909) \cdot (0,95) \cdot (21,28) - (0,18) \cdot (0,05) \cdot (21,28)] / (X - y - 21,28) = 0,18$$

$$X = 86,75 \text{ t/h}$$

$$y = 3,26 \text{ t/h}$$

5.2.4 Flocculation at Thickener 1



Clay Balance: $0,02 \cdot X = 0,15 \cdot Z$

Ratio of flocculant/clay : $[0,0454 \cdot 10^{-2} \cdot y] / (0,02 \cdot X) = 0,2/1000$

Total Mass Balance : $X + y = Z + 86,75$

$X = 99,09 \text{ t/h} \quad y = 0,87 \text{ t/h} \quad Z = 13,21 \text{ t/h}$

Na₂B₄O₇ concentration of suspension :

$$99,09 \cdot \aleph + (0,87) \cdot (0,1391) = (86,75) \cdot (0,2923) + (13,21) \cdot (0,85) \cdot \aleph$$

$$\aleph = 0,2872 \quad (28,72 \% \text{ Na}_2\text{B}_4\text{O}_7)$$

5.2.5 Flocculation at Thickener 2

Amount of clay entering to Thickener : $13,21 \cdot 0,15 = 1,982 \text{ t/h}$

Flocculant Consumption, 0,1 kg/ton non-ionic and 0,2 kg/ton PEO

Amount of flocculant, non-ionic : $0,2 \text{ kg} \Rightarrow 0,44 \text{ t/h}$

Amount of flocculant, PEO : $0,395 \text{ kg} \Rightarrow 0,20 \text{ t/h}$

Amount of sludge : 13,15 (15% clay)

Na₂B₄O₇ concentration of overflow (clarified liquid) :

$$(61,10)*(0,18)+(0,44)*(0,1420)+(13,21)*(0,2441) = (61,10+13,21*0,85)*\aleph$$

$$\aleph = 0,1958 \quad (19,58 \% \text{ Na}_2\text{B}_4\text{O}_7)$$

Na₂B₄O₇ concentration of underflow ;

$$[61,10*0,18+13,21*0,2441+0,44*0,1420-0,1958*61,10]/13,21 = 0,1664$$

$$(16,64 \% \text{ Na}_2\text{B}_4\text{O}_7)$$

5.2.6 Decanting

Amount of sludge : $[13,21*0,15]/0,4 = 4,95 \text{ t/h}$

Liquid discharge : $8,57 \text{ t/h}$

Na₂B₄O₇ concentration of liquid discharge ;

$$13,21*0,1664+0,12*0,1420 = 8,57*\aleph+4,95*0,6*\aleph$$

$$\aleph = 0,1919 \quad (19,19 \% \text{ Na}_2\text{B}_4\text{O}_7)$$

Na₂B₄O₇ concentration of solid discharge ;

$$[(13,21*0,1664+0,12*0,1420)-(8,57*0,1919)]/4,95 = 0,1151$$

All the flow parameters we have gathered until this point has been used for the calculations of ROM feed ore.

Assumptions:

Weak Mother Liquor : $19,53 \% \text{ Na}_2\text{B}_4\text{O}_7$ and $70,31 \text{ t/h}$ flow rate

ROM Ore : $24 \% \text{ B}_2\text{O}_3$ and $6 \% \text{ moisture}$

Weak Mother Liquor

19,53 % $\text{Na}_2\text{B}_4\text{O}_7$
70,31 t/h

Water
y t/h

ROM Ore

24,00 % B_2O_3
6,00 % Moisture
X t/h

EXTRACTION UNIT

Solid Residue

10 % $\text{Na}_2\text{B}_4\text{O}_7$
50 % Clay
Z (t/h)

Mother Liquor

99,09 (t/h)
28,72 % $\text{Na}_2\text{B}_4\text{O}_7$
2 % Clay

Tincal, B_2O_3 (%) : 36,51 Tincal, $\text{Na}_2\text{B}_4\text{O}_7$ (%) : 52,78

Total mass balance : $X + 70,31 + y = 99,09 + Z$

Clay balance : $0,2826 * X = 99,09 * 0,02 + 0,5 * Z$

$\text{Na}_2\text{B}_4\text{O}_7$ Equilibrium :

$(24/36,51) * 0,5278 * X + 70,31 * 0,1953 = 99,09 * 0,2872 + 0,1 * Z$

Solving these three equations;

X = 49,36 t/h

y = 3,37 t/h

Z = 23,94 t/h

found.

5.3 Mass Flow Diagram for Proposed Borax Derivative Plant in Kirka

Mass flow calculation were made based on design parameters which covers all possible alternatives in systems where ROM ore grade, moisture, clay ratio of Tailings 1, borax loss at Tailings 1, moisture content of Tailings 1, clay ratio of mother liquor, clay ratio of Tailings 2 play very important role on mass flow of system.

5.3.1 Mass Flow Diagram Calculations Based on Assumed Parameters

- ◆ ROM ore grade : 20-27 % B_2O_3
- ◆ Moisture : 6 %
- ◆ Clay ratio of Tailing 1 : 50-75 %.
- ◆ $Na_2B_4O_7$ ratio of Tailing 1 : 8-14 %
- ◆ Clay ratio of mother liquor : 2-6 %
- ◆ $Na_2B_4O_7$ ratio of mother liquor : 28,0-28,7 %
- ◆ Clay ratio of underflow at Thickener 2 : 15 %
- ◆ Clay ratio of final tailings at Decanter centrifuge : 40 %
- ◆ Clarified liquid comes from overflow of Thickener 1 : 29,23 %
 $Na_2B_4O_7$

Mass balance calculations were calculated for different case like variations on ore feed, borax loss in residue 1, clay content in residue 1, moisture content of solid residue, clay content of mother liquor, etc. Based on laboratory results recovery of system and flocculant consumption were calculated, Figure 5.3.1.1 and Appendix 5.3.1.1, 5.3.1.2, 5.3.1.3 and 5.3.1.4 shows mass balance of proposed system.

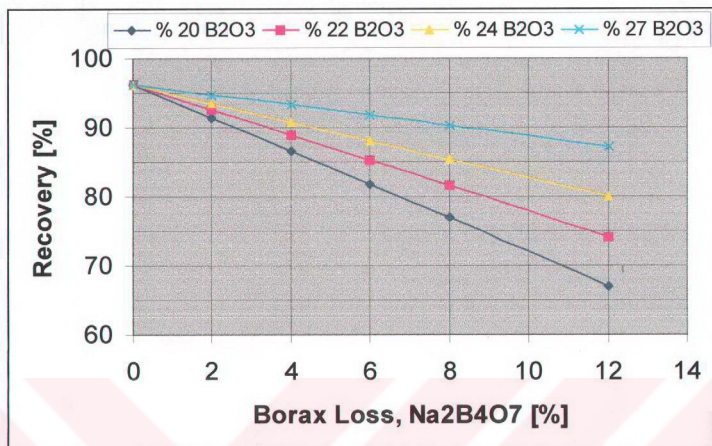


Figure 5.3.1.2 The Effect of Borax Loss in Talings1 to overall Recovery

Clay Ratio in Mother Liquor, % : 2

Feed Moisture, % : 6

Clay Content in Tailings 1, % : 50

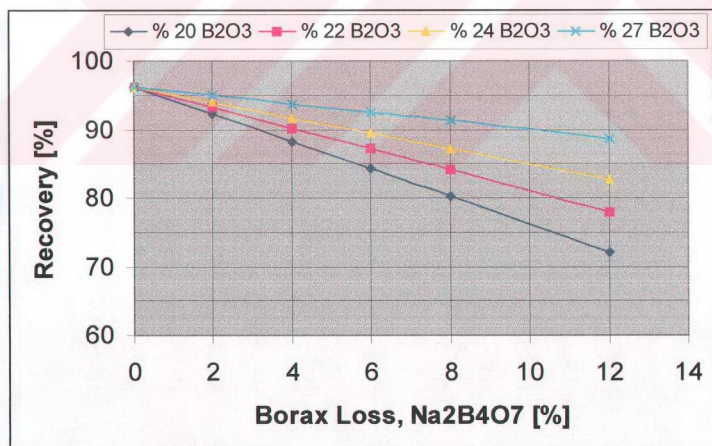


Figure 5.3.1.3 The Effect of Borax Loss in Tailings 1 to overall Recovery

Clay Ratio in Mother Liquor, % : 2

Feed Moisture, % : 6

Clay Content in Tailings 1, % : 60

Figure 5.3.1.2 and 5.3.1.3 shows how the borax loss in residue will effect the overall recovery. From the Figures we can conclude that backwash is playing very important step on recovery, therefore countercurrent washing of cake would be sufficient enough for better recover.

It can also be seen from the Figures that if crushed ROM ore has 25 % $\text{Na}_2\text{B}_4\text{O}_7$ or more, it is possible to attain 80 % recovery or higher.

Moisture of the ore is not effecting the recovery directly, but it does effect how much fresh water needs in system to dissolve borax. Figure 5.3.1.4 and 5.3.1.5 shows how much fresh water the system can tolerate while the moisture changes from 0-12 %, clay ratio 50-60 % and ore grade 20-27 % $\text{Na}_2\text{B}_4\text{O}_7$. From the Kirka practice, most common value of moisture is 6 %, for this particular moisture, the fresh water may vary between 1-10 t/h, and can be used for washing the residue.

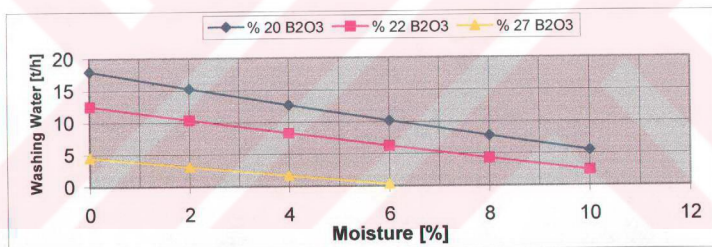


Figure 5.3.1.4 The Effect of Moisture on Amount of Washing Water

Clay Ratio in Mother Liquor, % : 2 Clay Content in Tailings 1, % : 50

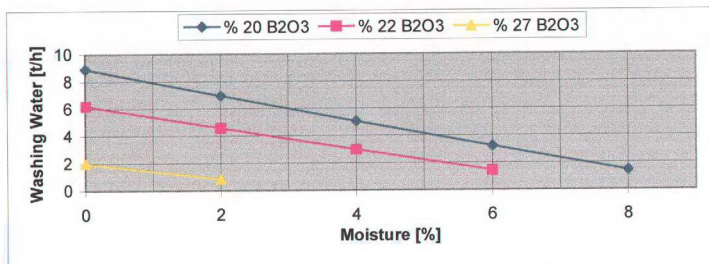


Figure 5.3.1.5 The Effect of Moisture on Amount of Washing Water

Clay Ratio in Mother Liquor, % : 2 Clay Content in Tailings 1, % : 60

The amount of ore needs to dissolved is a function of ore grade, borax loss in residue, clay content of residue, and clay goes to mother liquor. Figure 5.3.1.6 shows the feed rate versus ore grade changes. Figure 5.3.1.7 shows feed rate versus borax loss in residue changes.

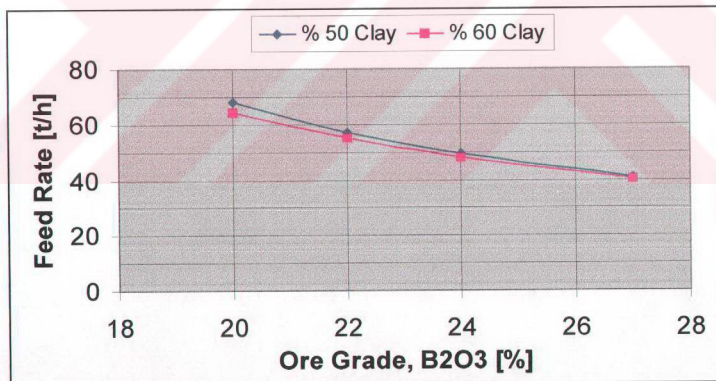


Figure 5.3.1.6 The Effect of Ore Grade on Feed Rate

Clay Ratio in Mother Liquor, % : 2

Moisture, % : 6

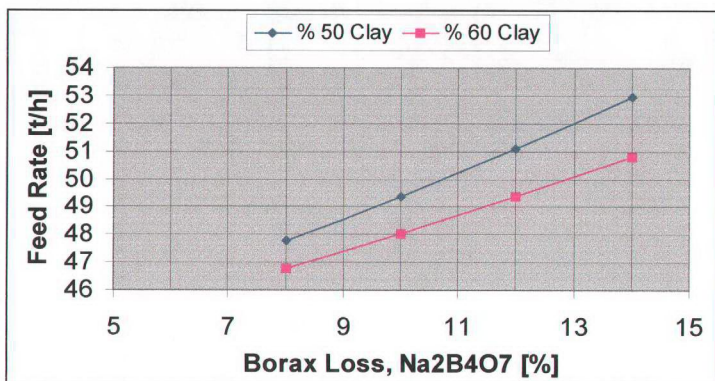


Figure 5.3.1.7 The Effect of Borax Loss in Residue on Feed Rate

Clay Ratio in Mother Liquor, % : 2

Feed Moisture, % : 6

Ore Grade, B₂O₃ : 24%

The amount of tailings comes from extraction is a function of ore grade, borax loss in residue, clay content of residue, and clay goes to mother liquor. Figure 5.3.1.8 shows ore grade versus rate of borax loss in residue changes.

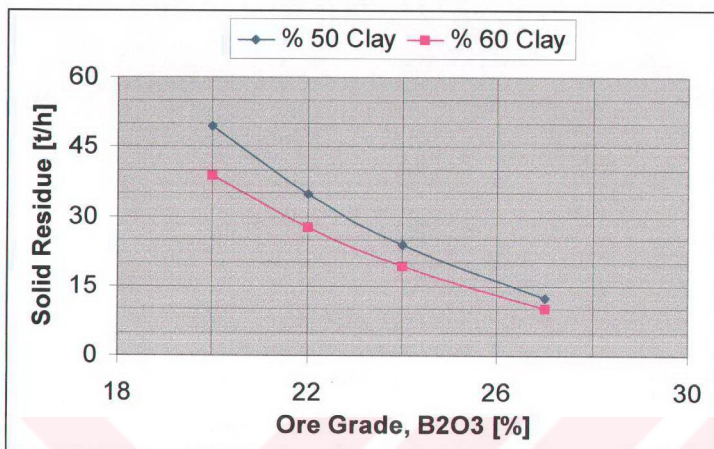


Figure 5.3.1.8 The Effect of Ore Grade on Residue Rate

Clay Ratio in Mother Liquor, % : 2

Feed Moisture, % : 6

Borax Loss, Na₂B₄O₇ : 10%

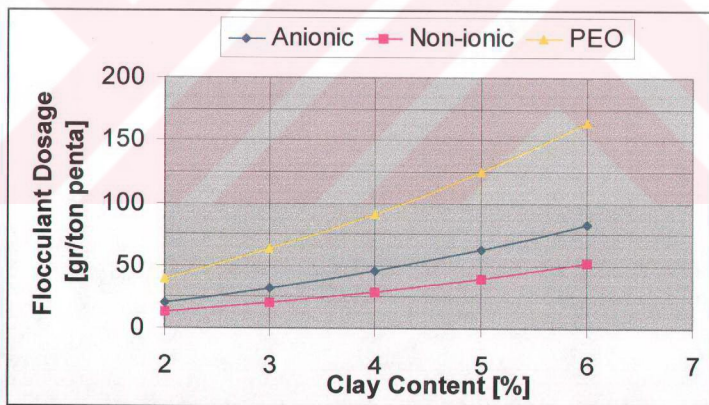


Figure 5.3.1.9 The Effect of Clay Ratio on Flocculant Consumption

Borax Loss, Na₂B₄O₇ : 10%

Feed Moisture, % : 6

Figure 5.3.1.14 shows the effect of B₂O₃ content of ore on overall recovery while keeping moisture content of the ore and borax loss in residue constant. Clay content of the mother liquor was also taken into consideration on calculation of recovery.

But, it can be seen from the Figure that clay content doesn't have major impact on recovery.

It can be seen from the Figure 5.3.1.10 that even with 20 % B₂O₃ ore, it is possible to reach more than 72 % recovery which is the overall recovery when concentrator and Borax Derivative Plant recovery taken 85% separately. Washing of cake was not put into recovery calculation.

However, with the high content borax ore, the difference on recovery for existing plant and proposed process becomes 20 % or more.

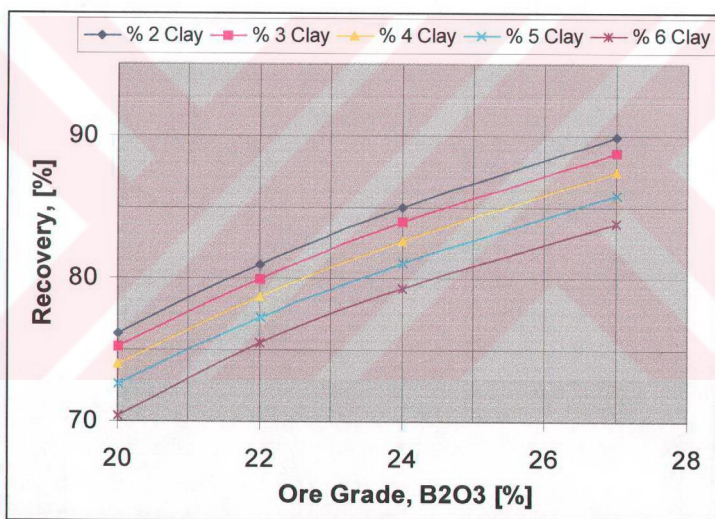


Figure 5.3.1.10 Overall Recovery of Proposed System on Various Ore Grade

Clay Ratio in Tailings 1, %

: 50

Feed Moisture, %

: 6

Borax Loss, Na₂B₄O₇

: 10%

5.3.2 Mass Flow Diagram Calculations Based on Semi-Industrial Plant Tests

10 t/h capacity semi-industrial plant Extraction Unit was put into operation on June 1997 and first experimental data was gathered after 19.06.1997. The first group of test were run between 19.06.1997 to 12.07.1997 and results were given at Chapter 4. Those data were put into mass flow diagram and calculated flow values were given at Figure 5.3.2.1.

Studies between 14.07.1997 to 20.04.1999 were also put into calculation and results were given at Appendix 5.3.2.1, 5.3.2.2, 5.3.2.3, 5.3.2.4, and 5.3.2.5.

Table 5.3.2.1 is summarized all the results derived from semi-industrial studies.

Table 5.3.2.1 Mass Balance Calculations Results of Test Studies

WORKING PERIOD	B2O3 %	Clay %	Recovery %	Flocculant Consumption		
				Anionic, gr/ton	Non-ionic, gr/ton	PEO, gr/ton
19.6.97 to 12.7.97	24,70	3,71	82,75	60,6	38,4	121,2
14.7.97 to 21.8.97	25,47	5,62	80,02	108,6	68,8	217,2
22.8.97 to 24.12.97	25,65	3,42	83,34	54,6	34,6	109,2
25.12.97 to 22.1.98	26,18	2,38	87,75	35,1	22,2	70,2
16.10.98 to 23.11.98	26,22	3,14	85,31	49,01	31,1	98,1
18.12.98 to 20.4.99	26,37	3,35	85,78	53,2	33,7	106,4

BORAX PENTAHYDRATE MASS BALANCE CALCULATIONS

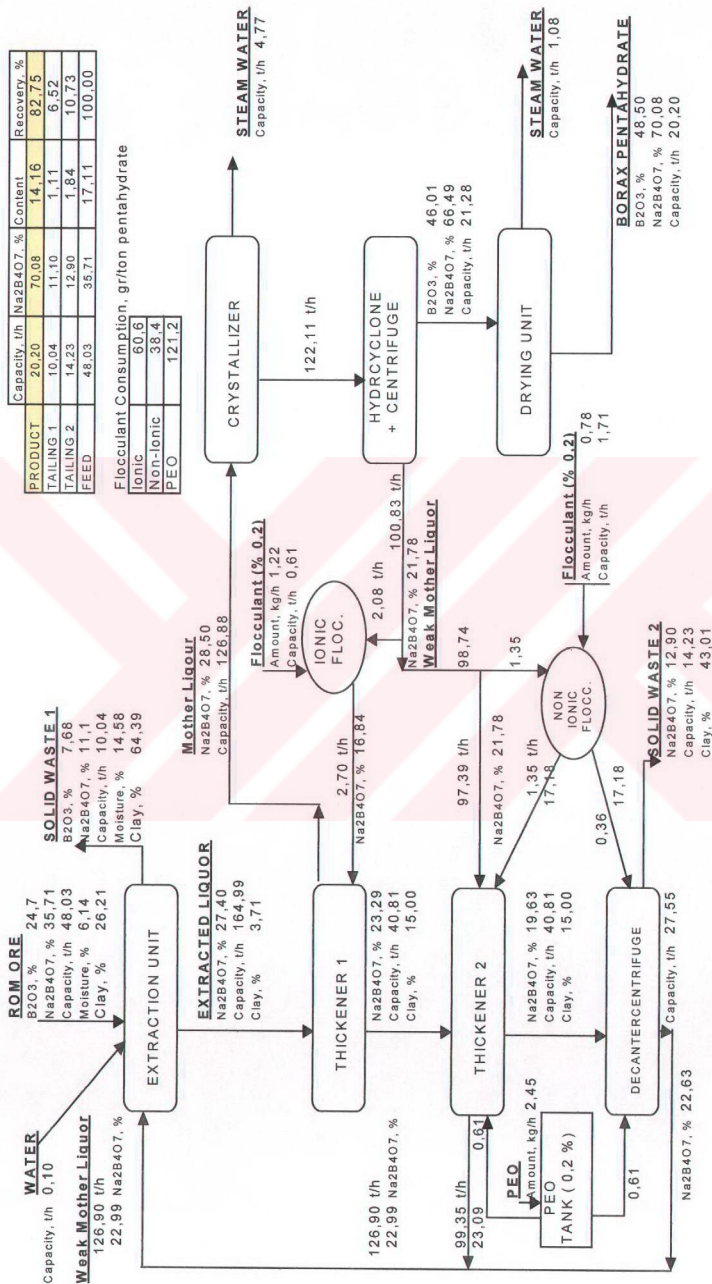


Figure 5.3.2.1 Mass Balance Calculations Based on Data Gathered Date Between 19.06.1997 to 12.07.1997

CONCLUSION

Most particles in water are charged and the electrical repulsion between them depends on the ionic strength of the solution. If the particles and polymer have opposite charges, then electrostatic attraction will give very strong adsorption. For nonionic polymers, or where particles and polymers have the same sign of charge, there must be some specific interaction responsible for adsorption, such as hydrogen bonding or hydrophobic bonding. These interactions are all of very short range and could not be effective if there were strong electrical repulsion between particles and polymer chains. In virtually all such cases, no adsorption occurs in the absence of added salt and a critical electrolyte concentration is required to promote adsorption. There is good reason to believe that this is not simply an ionic strength effect, but that ions such as Ca^{+2} promote adsorption by binding anionic groups on the polymer chain to negative sites on the particle surface. At low electrolyte concentrations the electrical double layer around a charged particle can be quite extensive and particles could not approach very close to each other. For bridging flocculation to occur, the adsorbed polymer must span the gap over which double layer repulsion operates.

Both non-ionic and anionic polyacrylamides are widely used in mining applications. They can be manufactured with very high molecular weights ($5-15 \times 10^6$), and thus are capable of forming large, rapid-settling, good-compacting flocs. Cationic polyacrylamides rarely used in the mining are. They are usually much less cost-effective than their non-ionic and anionic counterparts, because of higher cost and lower molecular weight ($2-6 \times 10^6$).

The flocs formed by anionic flocculants and negatively-charged suspended particles are fragile, and rupture if mixing is too vigorous.

By similar chemical reactions, polymers of cationic character can be produced. It would be expected that, since most suspensions encountered in the minerals industry contain negatively charged particles, cationic polyelectrolytes, where the cation adsorbs to the particles, would be most suitable. Although this is true for charge neutralization purposes, and attraction of the polymer to the particle surface, it is not necessarily true for the "bridging" role of the flocculant. For bridging, the polymer must be strongly adsorbed, and this is promoted by chemical groups having good adsorption characteristics, such as amide groups. The majority of commercially available polyelectrolytes are anionic, since these tend to be of higher molecular weight than the cationics, and are less expensive.

The mode of action of the anionic polyacrylamide depend on a segment of the very long molecule being adsorbed on the surface of a particle, leaving a large proportion of the molecule free to adsorb on another particle, so forming an actual molecular linkage, or bridge, between particles.

The effect of surface potential is also important highly charged surfaces will hinder good flocculation by nonionic polymers and will inhibit adsorption of similarly charged flocculants.

As a conclusion, charge neutralization may be accomplished by either double layer compression or adsorption of the flocculant onto the particle surface. Charge is neutralized by double-layer compression when flocculation is effected through an increase in solution strength. That means an increase in the borax concentration of the suspension caused double-layer compression, and optimal borax concentration is dependent on the temperature and the charge density of the flocculant.

During the production of borax pentahydrate or borax concentrate, there are some insoluble particles that create problem. Flocculation behavior of these particles has been examined and some interesting point has been achieved, these are;

Even though the particles had a negative surface charge, the cationic polymers didn't give good results as slightly anionic and nonionic flocculants. Comparing the results obtained with 10% anionic and nonionic polyacrylamides (A100 and N100) it was found that 10% anionic PAM was better. It is known that when the particle surface and the polymer molecules have suitable H-bonding sites, this may cause adsorption of an appreciable fraction of polymer segments. Furthermore, although most particles carry an overall negative charge in solution, the particles may contain areas of opposite ionic charges on their surface and edges. Thus, in addition to hydrogen bonding between the amide, hydrogen and particle, anionic polymers may attach to particle via ionic bonds, thereby increasing the stability of the formed flocs.

When the results obtained with nonionic PAM and nonionic PEO were compared, it was observed that PEO worked better under these conditions, because PEO has additional interaction with clay material when compared with polyacrylamides. PEO is a polymer with $-\text{CH}_2-\text{CH}_2-\text{O}-$ groups and the oxygen on the chain forms a strong water bridge with the exchange ion on the clays such as montmorillonite. Evidence also suggests that the alkyl group of PEO is directly adsorbed onto the surface of the clay by Van der Waals interaction. Thus PEO gives good results for mineral slurries containing large quantities of clays or claylike material.

Turbidity of the solution at optimal polymer dosage increased from the blue, green, gray and white samples respectively. This means that the montmorillonitic parts were more easily flocculated with respect to the dolomitic parts of samples.

It is generally thought that increase in temperature improves flocculation, although this is not always the case, since a change in temperature will exert different effects in different system. The rate of diffusion of flocculant and the rate of collision of particles must increase with rise in temperature but the adsorption step, which exothermic, must unfavorably be affected by higher temperature.

The effect of borax concentration was determined by flocculating the samples in 3, 8 and 15% borax solutions with A100 and PEO at °C. The increase in the borax concentration from 3 to 8% had a great effect on both the optimal dosages and the turbidities of the solution.

The effect of higher borax concentration at 95 °C was also investigated. At this temperature, increasing of the borax concentration from 15 to 30% had a negative effect on flocculation with PEO, N100 and A100. Conversely, by increasing the borax concentration from 15% to 30 % at 95°C, optimal flocculant dosage and turbidity of the solution decreased with A100.

It is known that since clay and coal particles have a negative charge, it is necessary that a adequate amount of calcium ions be present in order for the anionic flocculants to work properly. The addition of a small amount of cationic flocculant in combination with the anionic flocculant can provide improved performance over anionic alone.

In any circumstances, whichever flocculant, temperature or borax concentration used, the best results on flocculation were achieved if blue insoluble particles exists. At this point, we can postulate that all flocculant are easily adsorbed to montmorillonite surface. In other words, montmorillonite content of insoluble particles is very important parameter on flocculation.

PEO is less effected flocculant among others on flocculation of dolomite type insoluble particles. Therefore we can tell that PEO is much effective than PAM and better adsorbed to dolomite surface.

Flocculation studies also indicated that if solid content of suspension increased from 30 to 100 g/l, the consumption of A100 increased while PEO stayed constant. Therefore, for the suspension having high solid content, it is better to use PEO flocculant. Since PEO is not electrically charged, increase on solid content

won't effect its performance but for anionic flocculants, increase on solid content will cause more flocculant to put in system.

There were no negative effect of residence time on flocculant before pouring to suspension.

From the laboratory results we can postulate that, the best flocculation performance for each particle could be;

◆For the production of borax concentrate , the appropriate flocculant would be PEO. 10 % anionic (A100) is providing best performance on the flocculation of insoluble particles during production of borax pentahydrate.

Because of easy flocculation of montmorillonite type particles, it is better to mine borax ore which has high montmorillonite content. But, since montmorillonite type particles easily break into pieces during the production of borax concentrate, the particles comes with borax concentrate mainly dolomite type. Therefore, using proposed system will bring advantage of dolomite clay isolated as a solid in Tailings1 and take care fine insoluble particles which are expected montmorillonite type at flocculation step.

When we compare proposed system with existing Boron Derivative Plant in Kirka, we can put to comparison in several sub categories;

◆Assuming that existing both Concentrator Unit and Boron Derivative Plant in Kirka has the recovery 85 % separately, and all together overall recovery becomes 72 %. If we take average values of ROM borax ore, 24-29 % B_2O_3 content goes to Concentrator Unit, the recovery of proposed system would be at least 10 % higher than existing process.

◆We are expecting these values even higher when proposed system industrially available. Because, since ROM ore will be used directly without any

physical enrichment, we are expecting less break into pieces and carry less borax solution in tailing.

◆ It is possible to reduce borax loss in extraction unit. Especially feeding low grade ore into system require fresh water to be added.

◆ Borax Derivative plant in both system almost identical, therefore energy consumption will be close. However, steam consumption of the system will be much higher because of more clay going into system.

◆ All the tailings in proposed system can be transported and easily piled up as a solid material.

◆ In Existing plant, especially tailings comes from concentrator unit has liquid character, and has to be pumped into tailing pond. Existing method is not only becoming environmentally handicap for company also cause borax loss irrecoverable.

◆ Except extraction unit, the other equipment are same in both system. The only handicap for proposed system is, the variation of ore grade goes into system. This handicap could be solved by controlling density of mother liquor.

◆ Impurity will be same in both system, but procedure for isolating impurities would be different. Some more study should be done before coming any better solution.

◆ Particle size requirements for proposed system will be minus 25 mm. However, this requirement for existing system is minus 6 mm.

◆ We are expecting overall cost will be much less. As a result, proposed system not only has much higher recovery, it also has advantage of put away tailing pond and concentrator cost.

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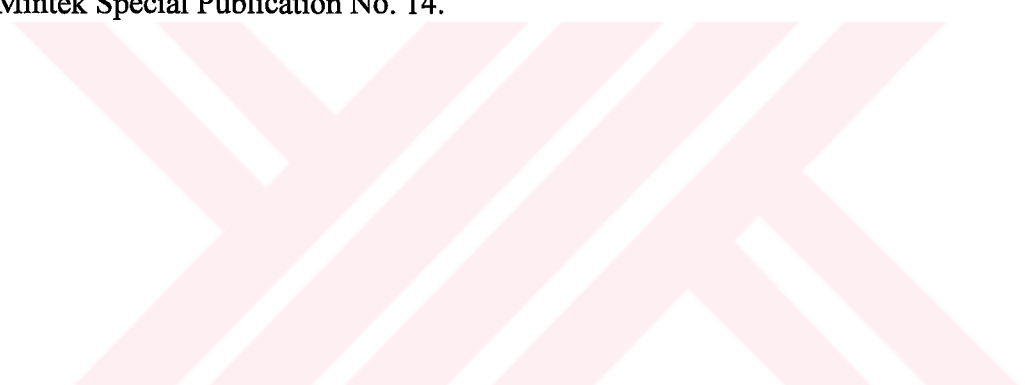
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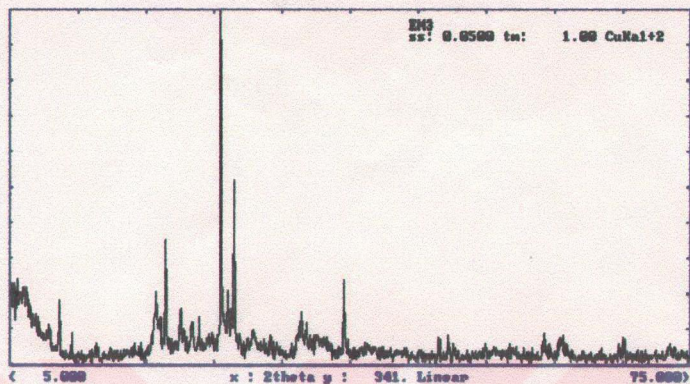
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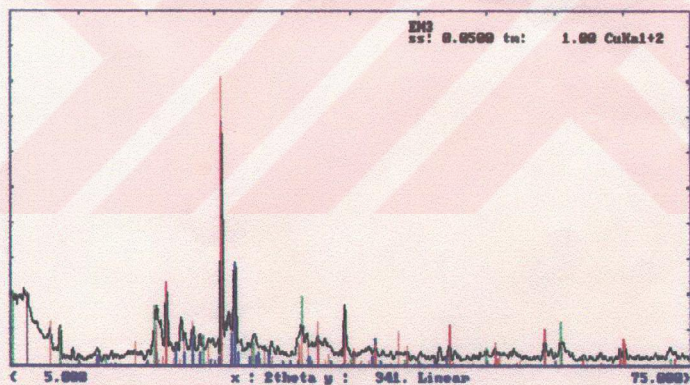
APPENDIX



Figure 5.4
Açık Yeşil kil



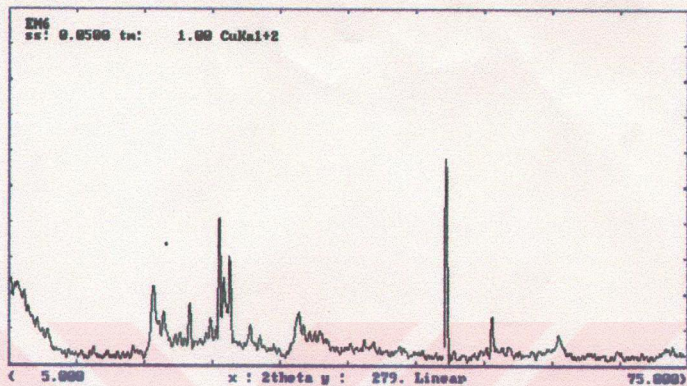
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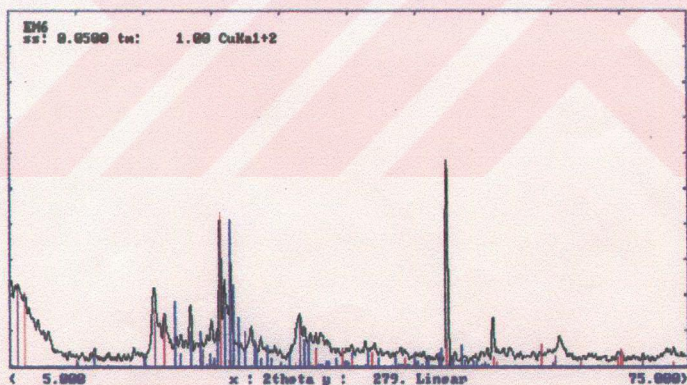
3-0470 d 2102 Quartz low
10-0393 d NaAl9(Si6)O38H2O Albite ordered
13-0259 d Na0.3(Al, Mg)2Si4O10(OH)2.xH2O Montmorillonite A
7-0832 d Na12Si10O38(OH)2 Muscovite M syn
12-0219 Na0.3(Al,Mg)2Si4O10(OH)2.xH2O Montmorillonite A

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Figure 5.5
Koyu Yesil Kil



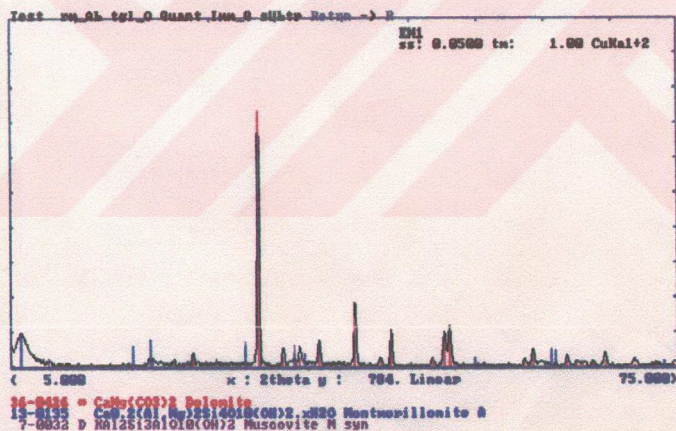
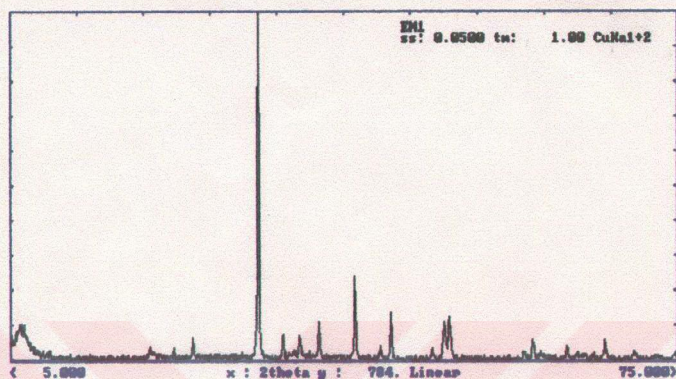
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3-0400 D SiO2 Quartz low
12-0301 I CaAl2Si2O8 Anorthite ordered
23-1497 Na0.3Fe25.14O19OH2.xH2O Montmorillonite A
13-0259 Q Na0.3(Al,Mg)2Si4O10(OH)2.xH2O Montmorillonite A

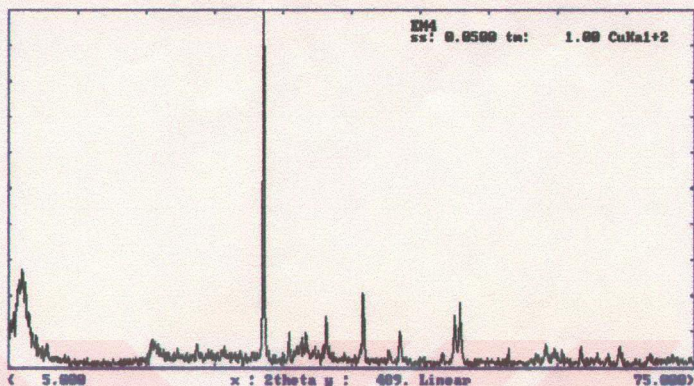
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Figure 5.6
Açık Gri kil

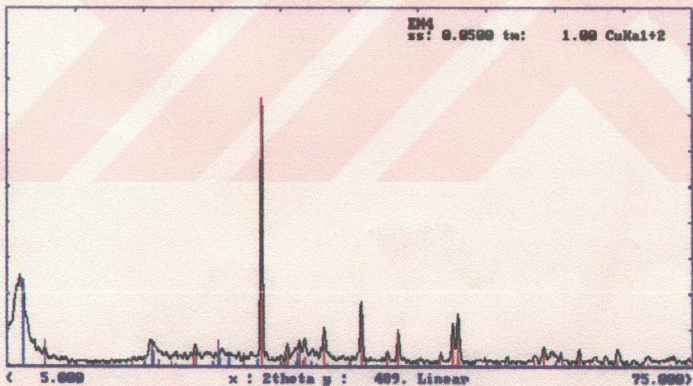


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Figure 5.4
Orta Akik Gri Kil



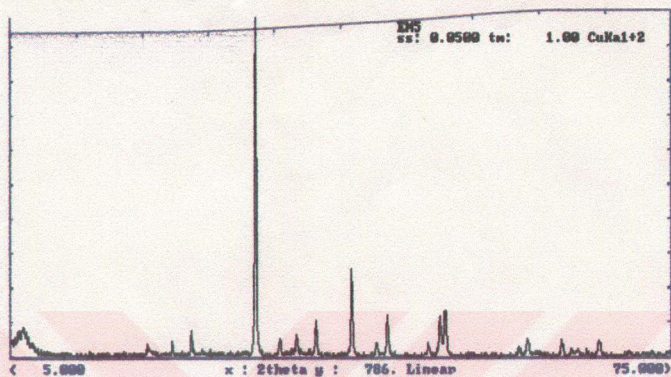
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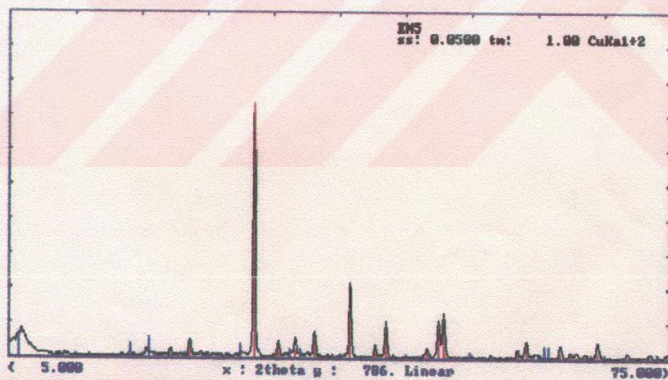
24-0434 • $\text{CaMg}(\text{CO}_3)_2$ Dolomite
13-0452 • $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ Montmorillonite A
7-0025 I $\text{Na}(\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ Muscovite II N RG syn

?help Zoom Match File Clear Back. Null K a2 Peaks Snoo. Comp. Wfile -> M

Figure 5-8
Beyaz Kil



?help Zoom Match File Clear Back. Null K a2 Peaks Smoo. Comp. Wfile -> F

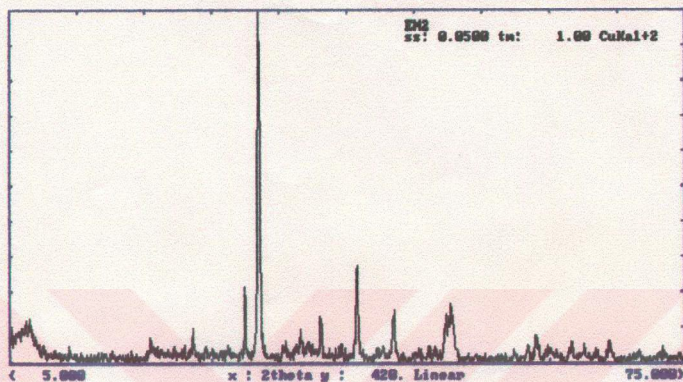


36-0426 = $\text{Ca}_2\text{Mg}(\text{CO}_3)_2$ Dolomite
19-0135 $\text{Ca}_2\text{Mg}(\text{Al},\text{Fe})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ Montmorillonite A

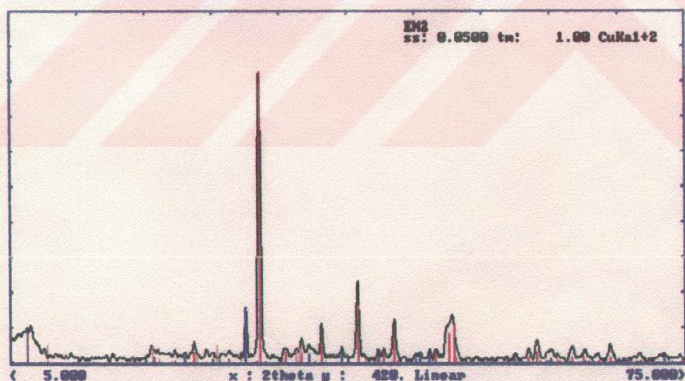
?help Zoom Match File Clear Back. Null K a2 Peaks Smoo. Comp. Wfile -> Z

Appendix 4.3.1.5 X-Ray Diffraction Spectra for White Insoluble Particles

Figure 5.9
Seçilmiş Beyaz Kil



?help Zoom Match File Clear Back. Null K a2 Peaks Smoo. Comp. Wfile -> ?

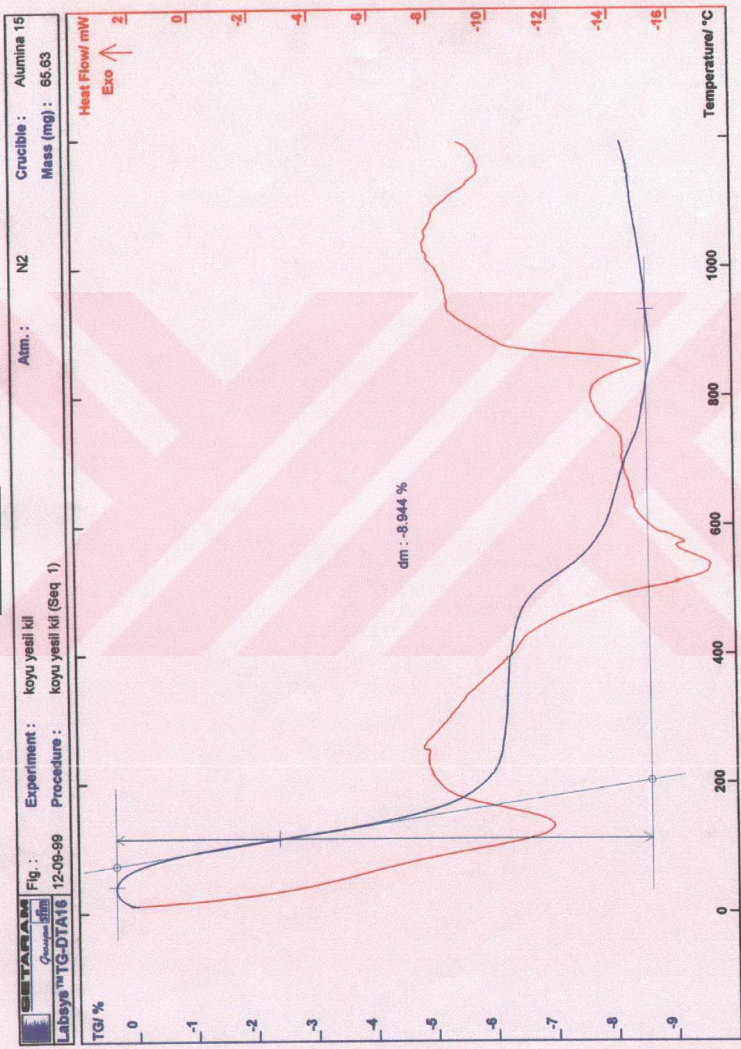


36-0426 • $\text{CaMg}(\text{CO}_3)_2$ Dolomite
 5-0584 • CaCO_3 Calcite syn
 13-0639 • $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ Montmorillonite A
 7-0023 • $\text{KAl}_2(\text{Si}_2\text{Al}_2\text{O}_{10})(\text{OH})_2$ Muscovite IT M RG syn

?help Zoom Match File Clear Back. Null K a2 Peaks Smoo. Comp. Wfile -> ?

Appendix 4.3.1.6 X-Ray Diffraction Spectra for Selected White Insoluble Particles

Blank box for identification



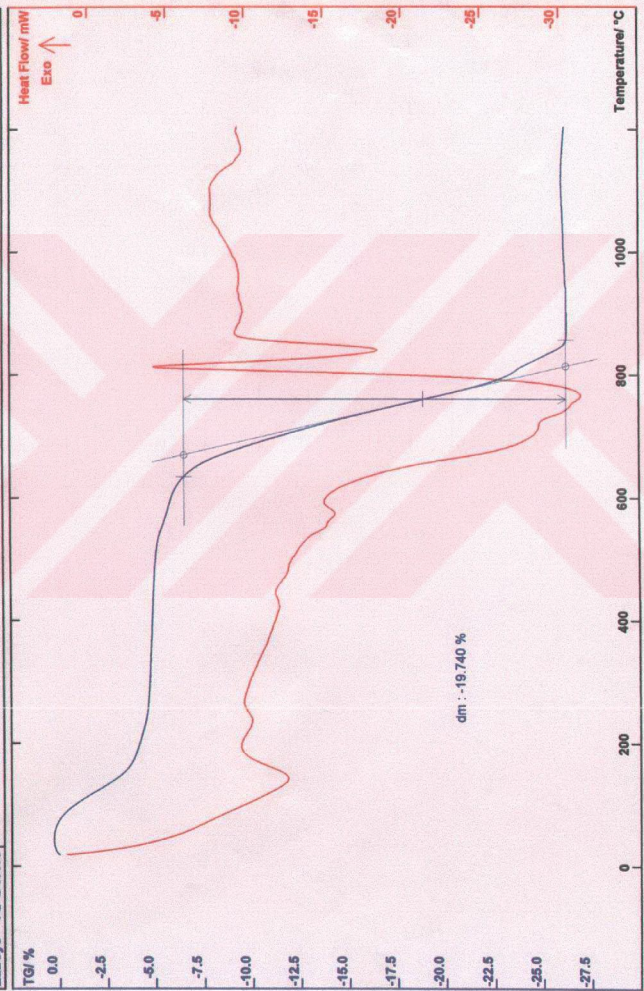
Appendix 4.3.2.1 TG/DTA Graphics of Dark Green Clay Particles

 LabSys TG-DTA16 Operating 50m	Fig :	Experiment :	ackl grl kil	Atm. :	N2	Crucible :	Alumina 15
	12-15-99	Procedure :	ackl grl kil (Seq 1)			Mass (mg) :	80.3



Appendix 4.3.2.2 TG/DTA Graphics of Light Gray Clay Particles

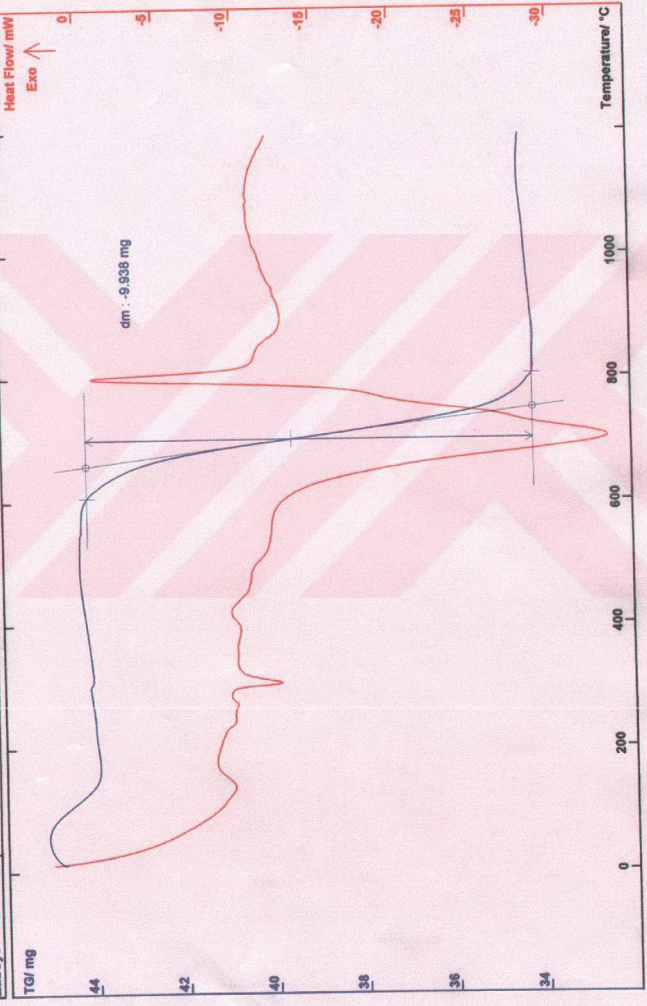
 Labays TG-DTA16	Fig. :	Experiment :	Crucible :	Alumina 15
	12-14-99	Procedure :	Atm. :	N2
		orta acik grl kil	Mass (mg) :	74.74
		orta acik grl kil (Seq 1)		



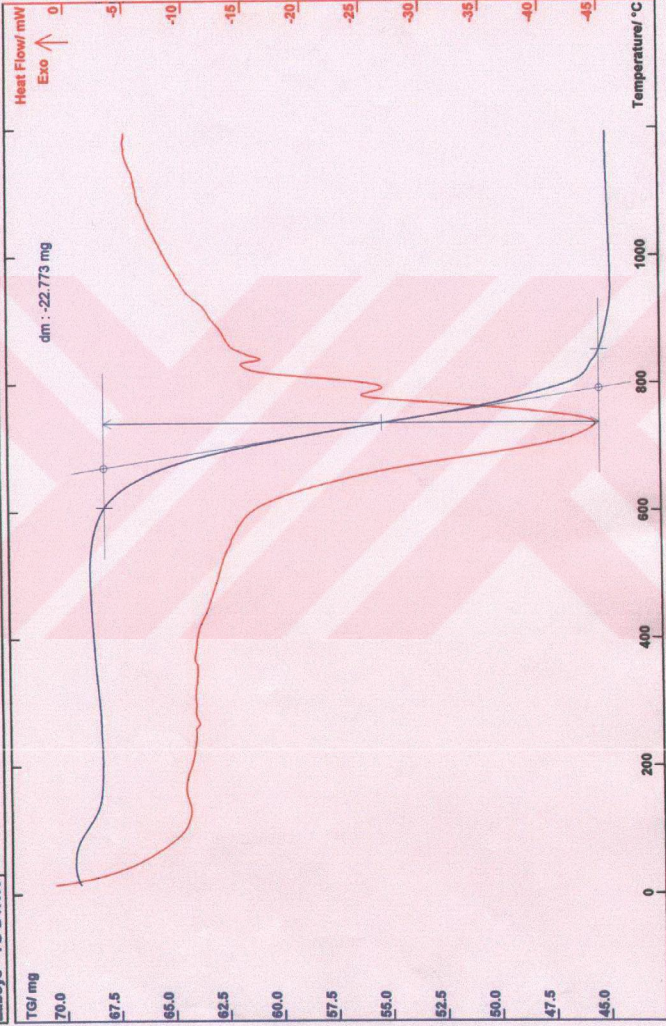
Appendix 4.3.2.3 TG/DTA Graphics of Medium Light Gray Clay Particles



Fig. :	Experiment :	koyugrt kil 1	Atm. :	N2	Crucible :	Alumina 15
Labsys TG-DTA16	Procedure :	koyugrt kil 1 (Seq 1)			Mass (mg) :	44.7

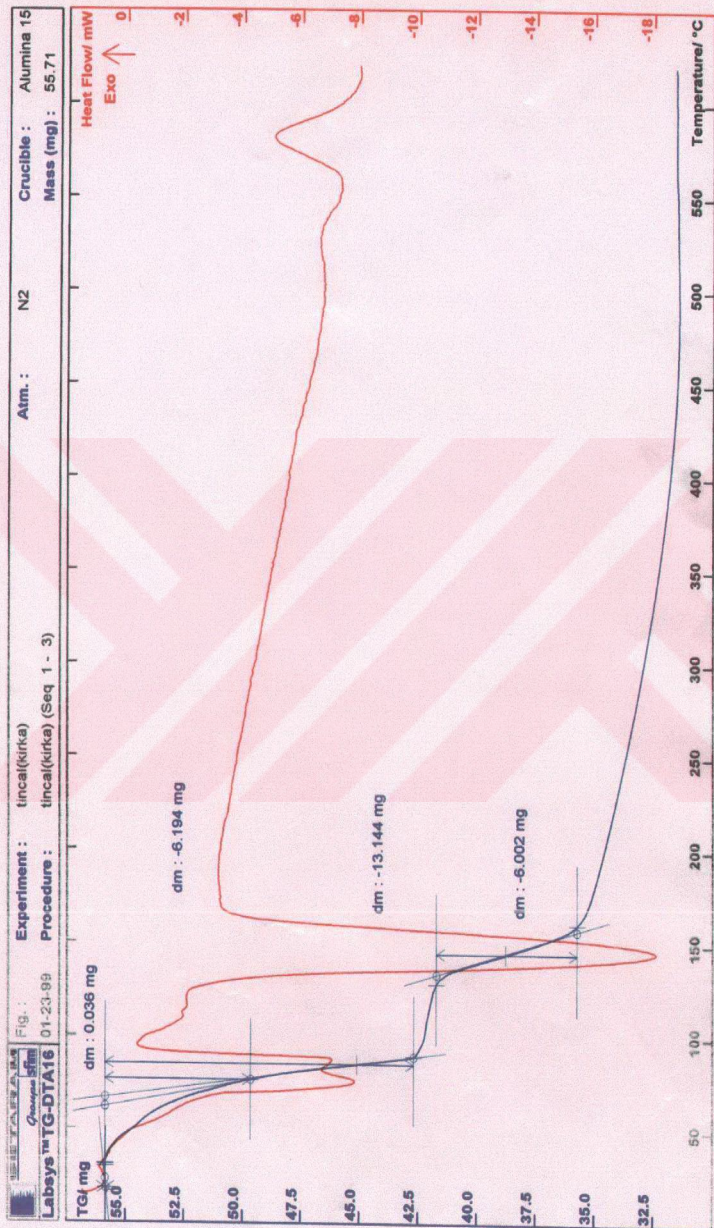


Appendix 4.3.2.4 TG/DTA Graphics of Dark Gray Clay Particles



Appendix 4.3.2.5 TG/DTA Graphics of White Clay Particles

Figure 5.1b

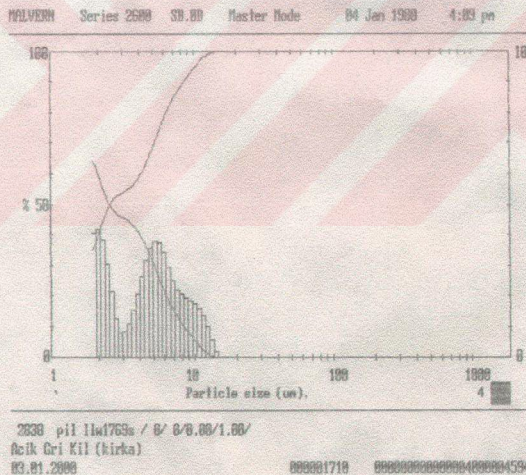


MALVERN Series 2500 SB.00 Master Mode 04 Jan 1980 4:05 pm

Upper in Lower Under			Upper in Lower Under			Upper in Lower Under			Span		
			51.7	0.0	43.8	100	9.82	3.8	8.47	90.3	
			49.8	0.0	43.0	100	8.47	4.3	7.30	86.0	
			43.0	0.0	37.0	100	7.30	5.3	6.20	80.7	
180	0.0	162	100	32.0	0.0	32.0	100	8.30	7.2	3.43	73.5
162	0.0	140	100	27.5	0.0	27.5	100	3.43	1.5	4.68	65.9
140	0.0	121	100	23.8	0.0	20.5	100	4.68	6.0	4.05	59.8
121	0.0	104	100	20.5	0.0	17.7	100	4.05	3.2	3.48	55.9
104	0.0	89.8	100	17.7	0.0	15.3	100	3.48	2.0	3.02	51.3
89.8	0.0	77.5	100	15.3	0.0	13.2	99.5	3.02	3.4	2.23	46.5
77.5	0.0	66.8	100	13.2	2.1	11.4	97.4	2.23	8.0	1.93	38.4
66.8	0.0	57.7	100	11.4	3.3	9.82	94.1	1.93	30.4	0.50	0.0

Source = :Sample Beam length = 2.2 mm Model indep Div, 0.51
 Log. diff. = 3.239
 Focal length = 100 mm Obscuration = 0.1886 Volume Conc. = 0.00225
 Presentation = pil Volume distribution Sp. S.R. = 1.1997 g/gg. Shape Diff. 2.43ga

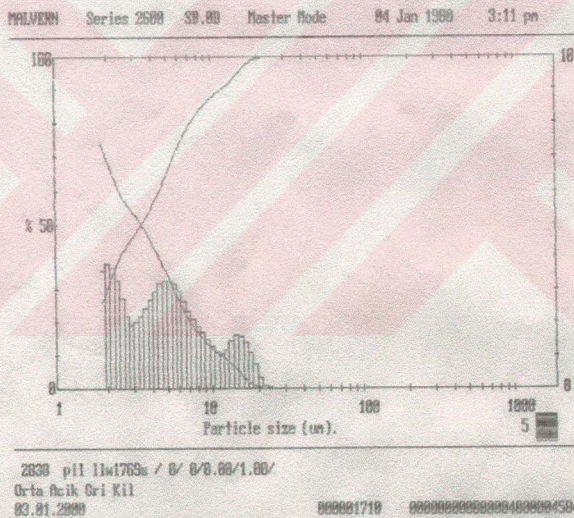
2838 pil llw1763s / 0/ 0/0.00/1.00/
 Acik Gri Kil (kirka)
 03.01.2000 000001710 00000000000004000004594



Appendix 4.3.3.2 Particle Size Measurement of Light Gray Clay Particles

MALVERN Series 2600 SB.00 Master Mode 04 Jan 1980 3:11 pm													
Upper in Lower Under				Upper in Lower Under				Upper in Lower Under				Span	
												3.07	
57.7 0.0 49.6 100				9.62 3.1 8.97 84.2									
29.8 0.0 43.0 100				8.47 9.0 7.30 90.2				D(4,3)					
43.0 0.0 37.0 100				7.30 4.9 6.30 73.3				4.77µm					
27.0 0.0 26.0 100				8.30 6.2 2.81 69.5				D(3,2)					
36.0 0.0 27.3 100				3.43 5.7 4.88 55.3				2.18µm					
180	0.0	162	100	27.3 0.0 23.8 100	4.68 5.2 4.05 56.2								
162	0.0	140	100	23.8 0.3 20.5 99.7	4.05 5.4 3.48 50.8								
140	0.0	121	100	20.5 1.5 17.7 98.2	3.43 4.3 3.02 46.6				D(4,0.9)				
121	0.0	104	100	17.7 2.6 15.3 95.4	3.02 4.2 2.60 42.3				11.6µm				
104	0.0	89.8	100	15.3 3.3 13.2 92.1	2.60 6.2 2.23 36.1								
89.8	0.0	77.5	100	13.2 2.4 11.4 89.7	2.23 7.4 1.93 28.6				D(4,0.1)				
77.5	0.0	66.8	100	11.4 2.3 9.62 87.4	1.93 28.6 0.50 0.0				1.13µm				
66.8	0.0	57.7	100										
Source = rSample				Beam length = 2.2 mm				Model indep				D(4,0.5)	
Focal length = 100 mm				Log. Diff. = 2.661								3.40µm	
Presentation = pil				Obscuration = 0.2038				Volume Conc. = 0.0075%					
				Volume distribution				Sp. S.H. 1.0194 #4/gm.				Shape OFF	
2838 pil 11w1769s / 0/ 0/0.00/1.00/													
Orta Acik Gri Kil													
03.01.2000													
0000001710												000000000000000400000450	

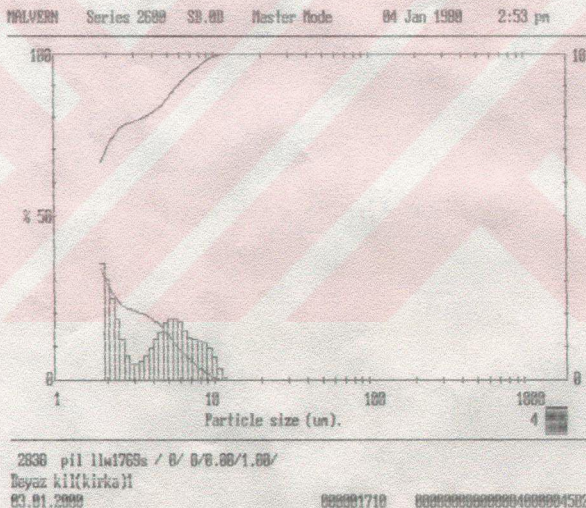
000001710 000000000000004000004584



Appendix 4.3.3.3 Particle Size Measurement of Medium Light Gray Clay Particles

Figure 5.21

MHLVERN Series 2500 SB.00 Master Mode 04 Jan 1980 2:53 pm												
Upper in Lower Under				Upper in Lower Under				Upper in Lower Under				Span
				57.7 0.0 49.8 100				9.82 2.0 8.47 97.1				3.64
				49.8 0.0 43.0 100				8.47 2.4 7.30 94.7				D(3,1)
				43.0 0.0 37.0 100				7.30 2.7 6.30 92.0				2.18µm
				37.0 0.0 32.0 100				6.30 3.6 5.43 88.3				
188	0.0	162	100	32.0 0.0 27.5 100				5.43 3.7 4.68 84.6				D(3,2)
162	0.0	140	100	27.5 0.0 23.8 100				4.68 2.8 4.05 81.8				1.28µm
140	0.0	121	100	23.8 0.0 20.5 100				4.05 1.2 3.48 80.0				
121	0.0	104	100	20.5 0.0 17.7 100				3.48 1.1 3.02 78.9				D(4,0.9)
104	0.0	89.8	100	17.7 0.0 15.3 100				3.02 1.2 2.60 77.6				5.80µm
89.8	0.0	77.5	100	15.3 0.0 13.2 100				2.60 3.2 2.23 74.4				
77.5	0.0	66.8	100	13.2 0.0 11.4 100				2.23 3.3 1.93 68.9				D(4,0.12)
66.8	0.0	57.7	100	11.4 0.8 9.82 99.2				1.93 68.9 0.50 0.0				0.74µm
Source = :Sample				Beam length = 2.2 mm				Model indp				D(4,0.5)
				Leg. Diff. = 3.100								1.33µm
Focal length = 100 mm				Obscuration = 0.1670				Volume Conc. = 0.00353				
Presentation = pil				Volume distribution				Sp.S.R 1.7411 #/g.				Shape OFF
2830 pil llw1769s / 0/ 0/0.00/1.00/												
Beyaz kil(kirkali)												
03.01.2000												
				000001710				000000000000000000004582				



Appendix 4.3.3.4 Particle Size Measurement of White Clay Particles

Date : 26.03.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25	4,41	95,59	4,41
+ 18	9,41	86,18	13,82
+ 15	2,2	83,98	16,02
+ 12	4,46	79,52	20,48
+ 10	5,49	74,03	25,97
+ 8	6,92	67,11	32,89
+ 6	4,75	62,36	37,64
+ 3	18,9	43,46	56,54
+ 1	25,53	17,93	82,07
- 1	17,93		
TOTAL	100		

Appendix 4.3.18.3.1 Results of Sieve Test

Date : 05.05.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25	10,01	89,99	10,01
+ 18	16,89	73,1	26,9
+ 15	5,51	67,59	32,41
+ 12	9,1	58,49	41,51
+ 10	9,07	49,42	50,58
+ 8	8,27	41,15	58,85
+ 6	8,62	32,53	67,47
+ 3	11,61	20,92	79,08
+ 1	13,73	7,19	92,81
- 1	7,19		
TOTAL	100		

Appendix 4.3.18.3.2 Results of Sieve Test

Date : 06.05.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25	6,76	93,24	6,76
+ 18	10,62	82,62	17,38
+ 15	2,94	79,68	20,32
+ 12	8,08	71,6	28,4
+ 10	8,28	63,32	36,68
+ 8	8,31	55,01	44,99
+ 6	6,36	48,65	51,35
+ 3	17,59	31,06	68,94
+ 1	18	13,06	86,94
- 1	13,06		
TOTAL	100		

Appendix 4.3.18.3.3 Results of Sieve Test

Date : 07.05.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25	10,47	89,53	10,47
+ 18	14,19	75,34	24,66
+ 15	1,96	73,38	26,62
+ 12	6,4	66,98	33,02
+ 10	6,25	60,73	39,27
+ 8	6,46	54,27	45,73
+ 6	5,2	49,07	50,93
+ 3	16,58	32,49	67,51
+ 1	19,97	12,52	87,48
- 1	12,52		
TOTAL	100		

Appendix 4.3.18.3.4 Results of Sieve Test

Date : 08.05.1998

Sieve Size Range (mm)	Sieve Fractions % wt	Cumulative % Undersize	Cumulative % Oversize
+ 25	6,21	93,79	6,21
+ 18	8,03	85,76	14,24
+ 15	2,65	83,11	16,89
+ 12	6,68	76,43	23,57
+ 10	6,36	70,07	29,93
+ 8	8,11	61,96	38,04
+ 6	5,94	56,02	43,98
+ 3	17,45	38,57	61,43
+ 1	21,2	17,37	82,63
- 1	17,37		17,37
TOTAL	100		

Appendix 18.3.5 Results of Sieve Test

Date	-25 mm Crushed Ore		Mother Liquor		Weak Liquor		Solid Waste 1	
	% B ₂ O ₃	% Moisture	Density, g/cm ³	% Clay	Density, g/cm ³	% B ₂ O ₃	% Moisture	% Clay
14.07.1997	25,10	4,41	-	3,55	1,180	7,72	12,12	66,74
16.07.1997	25,12	5,28	-	2,97	1,180	7,64	12,84	66,23
17.07.1997	26,27	1,98	-	4,33	1,180	6,46	14,83	67,48
18.07.1997	24,01	6,51	-	2,21	1,180	6,39	13,72	68,78
19.07.1997	28,54	5,86	-	3,21	1,180	5,76	14,54	69,68
21.07.1997	27,03	4,43	-	2,52	1,180	5,92	13,43	70,36
24.07.1997	23,43	5,62	-	5,25	1,180	11,72	10,11	57,79
25.07.1997	26,00	5,73	-	4,51	1,180	8,82	14,62	61,22
28.07.1997	24,67	5,53	-	3,31	1,180	8,04	13,20	64,78
29.07.1997	24,66	7,28	-	16,22	1,180	12,07	21,32	45,62
30.07.1997	27,69	5,28	-	6,76	1,180	8,98	13,92	61,48
31.07.1997	25,24	6,21	-	8,99	1,180	16,17	11,25	44,46
02.08.1997	25,32	5,50	-	9,50	1,180	12,24	16,41	50,06
05.08.1997	26,80	6,92	-	2,99	1,180	8,85	16,38	59,38
06.08.1997	23,87	7,76	-	15,00	1,180	14,63	16,70	43,23
08.08.1997	26,13	5,98	-	6,67	1,180	16,43	16,70	38,30
18.08.1997	24,8	4,19	-	6,13	1,180	6,03	14,2	69,28
19.08.1997	24,27	6,75	-	2,33	1,180	7,29	11,39	68,64
20.08.1997	25,9	6,19	-	3,32	1,180	7,8	10,65	67,99
21.08.1997	24,55	6,5	-	2,64	1,180	12,75	13,04	52,04
AVERAGE	25,47	5,70		5,62	1,18	9,59	14,07	59,68

Appendix 4.3.18.4.1 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 14.07.1997 to 21.08.1997

Date	-25 mm Crushed Ore			Mother Liquor		Weak Liquor Density, g/cm ³	Solid Waste 1		
	% B ₂ O ₃	% Moisture	Density, g/cm ³	% Clay	% B ₂ O ₃		% B ₂ O ₃	% Moisture	% Clay
22.08.1997	25,19	6,10	-	3,86	8,32	1,180	8,32	13,81	63,40
27.08.1997	27,29	5,23	-	3,39	8,57	1,180	8,57	14,21	62,32
28.08.1997	25,63	6,12	-	2,33	6,62	1,180	6,62	13,99	67,88
29.08.1997	27,88	4,93	-	2,59	4,57	1,180	4,57	10,17	77,31
11.09.1997	26,91	6,54	-	3,13	8,96	1,180	8,96	15,77	59,69
12.09.1997	23,64	6,61	-	3,73	9,61	1,180	9,61	15,04	58,64
13.09.1997	22,95	8,20	-	3,17	12,26	1,180	12,26	15,20	51,22
19.09.1997	21,51	7,97	-	5,47	11,48	1,180	11,48	17,85	50,71
20.09.1997	23,35	7,66	-	5,27	8,40	1,180	8,40	17,98	59,01
22.09.1997	24,04	7,32	-	3,96	14,45	1,180	14,45	16,21	44,21
04.12.1997	26,17	5,54	-	1,81	8,02	1,180	8,02	13,18	64,85
06.12.1997	26,65	5,76	-	3,62	7,51	1,180	7,51	14,37	65,06
08.12.1997	27,52	5,70	-	3,15	15,86	1,180	15,86	15,96	40,60
09.12.1997	28,55	5,10	-	3,66	7,08	1,180	7,08	13,44	67,17
10.12.1997	25,49	5,79	-	4,44	9,22	1,180	9,22	14,62	60,13
11.12.1997	27,36	5,00	-	3,24	15,61	1,180	15,61	11,79	45,45
12.12.1997	26	5,16	-	2,89	11,2	1,180	11,2	12,95	56,37
19.12.1997	27,11	4,97	-	1,92	5,52	1,180	5,52	14,69	70,19
23.12.1997	27,32	5,54	-	2,74	5,32	1,180	5,32	14,69	70,74
24.12.1997	22,47	7,31	-	3,94	6,02	1,180	6,02	15,15	68,36
AVERAGE	25,65	6,13		3,42	9,23	1,18	9,23	14,55	60,17

Appendix 4.3.18.4.2 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 22.08.1997 to 24.12.1997

Date	-25 mm Crushed Ore		Mother Liquor		Weak Liquor		Solid Waste 1	
	% B ₂ O ₃	% Moisture	Density, g/cm ³	% Clay	Density, g/cm ³	% B ₂ O ₃	% Moisture	% Clay
25.12.1997	25,80	6,56	-	2,90	1,180	12,93	13,32	51,27
02.01.1998	27,30	5,77	-	2,16	1,180	6,26	15,71	67,14
03.01.1998	28,11	6,25	-	1,89	1,180	16,48	15,80	39,06
06.01.1998	27,48	5,36	-	2,10	1,180	5,53	13,07	71,78
07.01.1998	27,59	5,74	-	1,86	1,180	4,36	11,25	76,81
08.01.1998	24,68	8,02	-	1,64	1,180	4,08	13,22	75,60
10.01.1998	26,87	6,27	-	2,83	1,180	3,94	13,90	75,31
13.01.1998	24,28	7,37	-	3,84	1,180	4,56	11,89	75,62
14.01.1998	25,55	4,87	-	2,50	1,180	9,88	13,73	59,21
22.01.1998	24,15	6,10	-	2,06	1,180	4,81	13,41	73,42
AVERAGE	26,18	6,23		2,38	1,18	7,28	13,53	66,52

Appendix 4.3.18.4.3 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 25.12.1997 to 22.01.1998

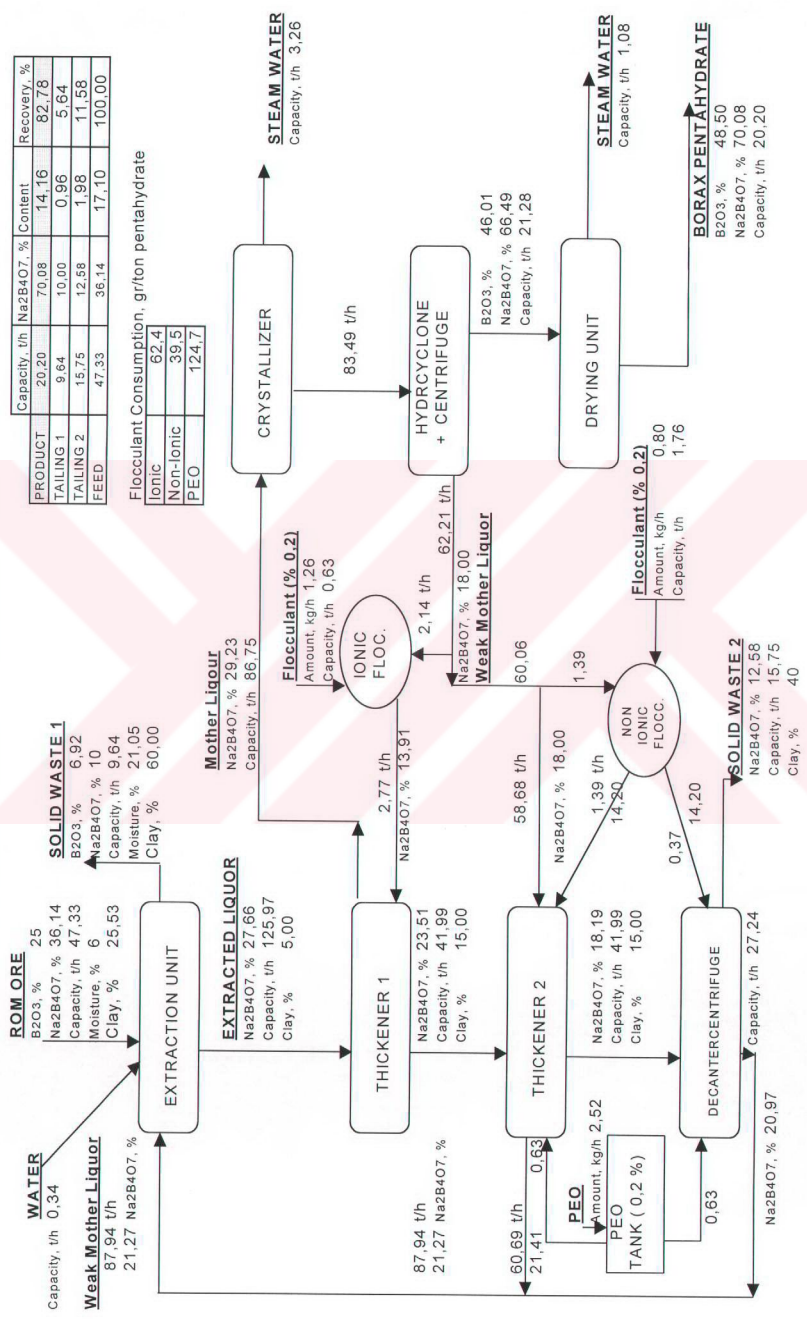
Date	-25 mm Crushed Ore		Mother Liquor		Weak Liquor		Solid Waste 1	
	% B ₂ O ₃	% Moisture	Density, g/cm ³	% Clay	Density, g/cm ³	% B ₂ O ₃	% Moisture	% Clay
16.10.1998	25,01	6,61	1,250	2,68	1,185	4,87	12,47	74,19
19.10.1998	23,14	6,61	1,190	2,13	1,168	5,14	13,16	72,76
20.10.1998	26,41	5,67	1,240	1,86	1,182	4,19	13,08	75,44
21.10.1998	25,69	6,40	1,190	1,09	1,165	4,54	14,70	72,87
23.10.1998	27,19	5,15	1,200	1,33	1,175	4,57	14,11	73,37
27.10.1998	24,73	3,92	1,225	2,27	1,180	4,14	13,30	75,36
05.11.1998	26,26	5,17	1,190	1,66	1,170	11,52	14,34	54,11
09.11.1998	27,75	2,93	1,220	1,55	1,172	5,07	12,65	73,46
10.11.1998	25,91	4,25	1,220	1,54	1,170	6,90	14,03	67,07
11.11.1998	24,47	6,22	1,220	3,91	1,170	4,30	13,36	74,86
12.11.1998	26,77	6,79	1,220	1,14	1,175	6,51	16,50	65,67
17.11.1998	26,62	5,36	1,225	4,71	1,170	12,78	13,91	51,09
18.11.1998	26,79	5,97	1,240	10,30	1,170	15,03	14,42	44,41
19.11.1998	26,73	5,36	1,220	3,99	1,170	17,39	13,41	38,96
20.11.1998	27,79	5,61	1,220	4,98	1,168	21,34	12,78	28,77
23.11.1998	28,21	4,39	1,220	5,02	1,223	5,25	15,33	70,29
AVERAGE	26,22	5,40	1,22	3,14	1,18	8,35	13,85	63,29

Appendix 4.3.18.4.4 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 16.10.1998 to 23.11.1998

Date	-25 mm Crushed Ore		Mother Liquor		Weak Liquor	Solid Waste 1		
	% B ₂ O ₃	% Moisture	Density, g/cm ³	% Clay	Density, g/cm ³	% B ₂ O ₃	% Moisture	% Clay
18.12.1998	26,88	4,92	1,230	2,86	1,170	12,96	14,13	50,37
21.12.1998	26,33	5,63	1,245	2,79	1,170	5,15	11,94	73,95
22.12.1998	27,96	2,83	1,220	2,48	1,170	13,72	15,08	47,34
24.12.1998	28,27	5,15	1,225	4,79	1,170	11,12	16,55	52,99
30.12.1998	23,12	7,69	1,235	4,31	1,170	5,77	15,05	69,15
31.12.1998	25,79	6,56	1,240	5,23	1,170	9,68	15,48	58,01
05.01.1999	27,55	5,70	1,230	3,66	1,170	6,59	17,33	64,62
06.01.1999	27,32	5,60	1,220	1,77	1,170	13,72	16,31	46,11
07.01.1999	27,56	5,71	1,215	1,92	1,170	4,60	14,45	72,95
14.01.1999	23,97	7,85	1,210	1,37	1,170	5,74	15,25	69,03
22.03.1999	27,70	5,38	1,230	3,02	1,170	5,90	16,44	67,40
24.03.1999	25,19	4,48	1,225	3,07	1,170	5,18	15,50	70,31
25.03.1999	25,56	7,47	1,224	2,88	1,170	10,60	5,69	65,28
06.04.1999	26,35	5,56	1,225	2,10	1,170	7,05	16,18	64,51
08.04.1999	25,65	6,77	1,225	4,68	1,170	5,47	14,35	70,67
13.04.1999	26,62	6,46	1,218	3,81	1,170	7,73	16,45	62,38
14.04.1999	27,53	5,85	1,204	1,44	1,170	6,75	14,14	67,37
16.04.1999	25,88	5,94	1,216	3,52	1,170	6,33	12,83	69,83
19.04.1999	24,41	5,67	1,223	8,52	1,170	8,12	16,48	61,28
20.04.1999	27,77	5,56	1,225	2,86	1,170	5,64	13,72	70,83
AVERAGE	26,37	5,84	1,22	3,35	1,17	7,89	14,67	63,72

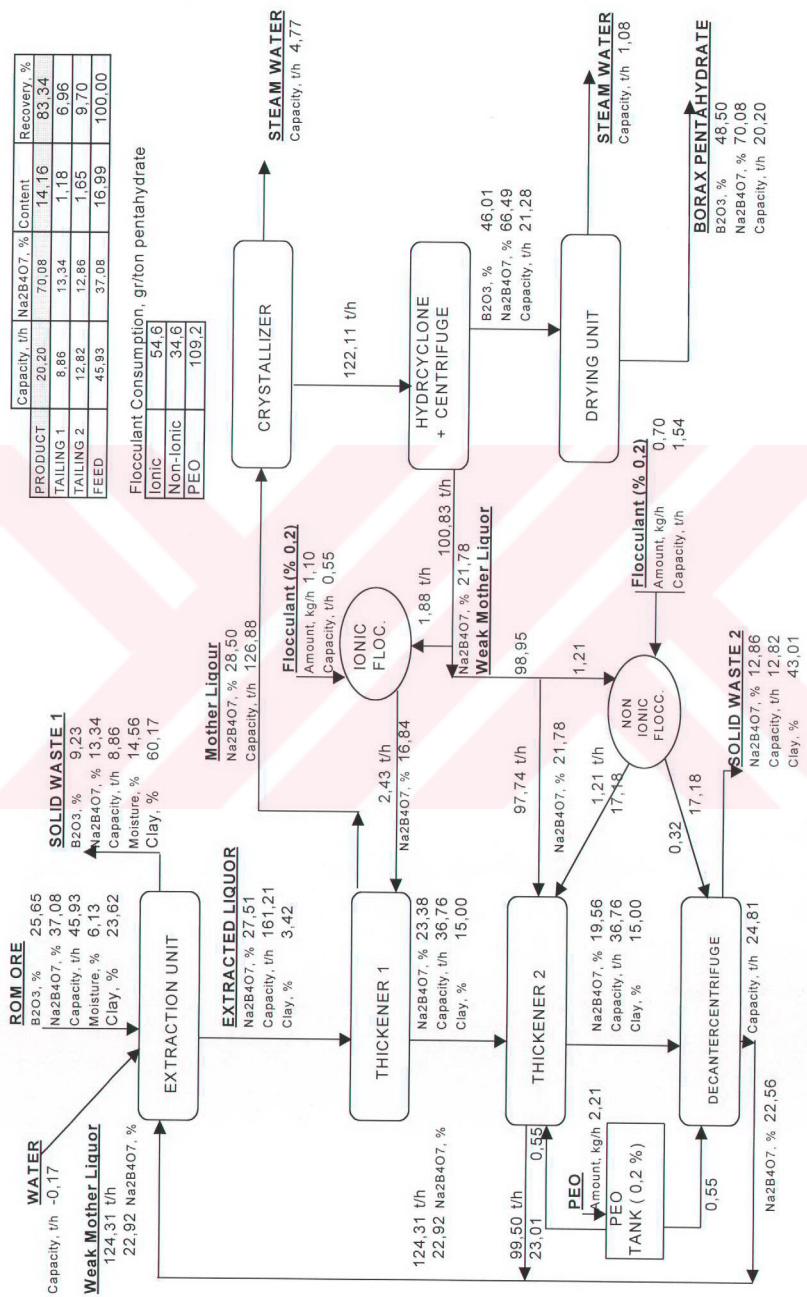
Appendix 4.3.18.4.5 10 t/h Capacity Pilot Plant Extraction Unit Operating Parameters Dated Between 18.12.1998 to 20.04.1999

DUKAA PENTAHYDRATE MASS BALANCE CALCULATIONS

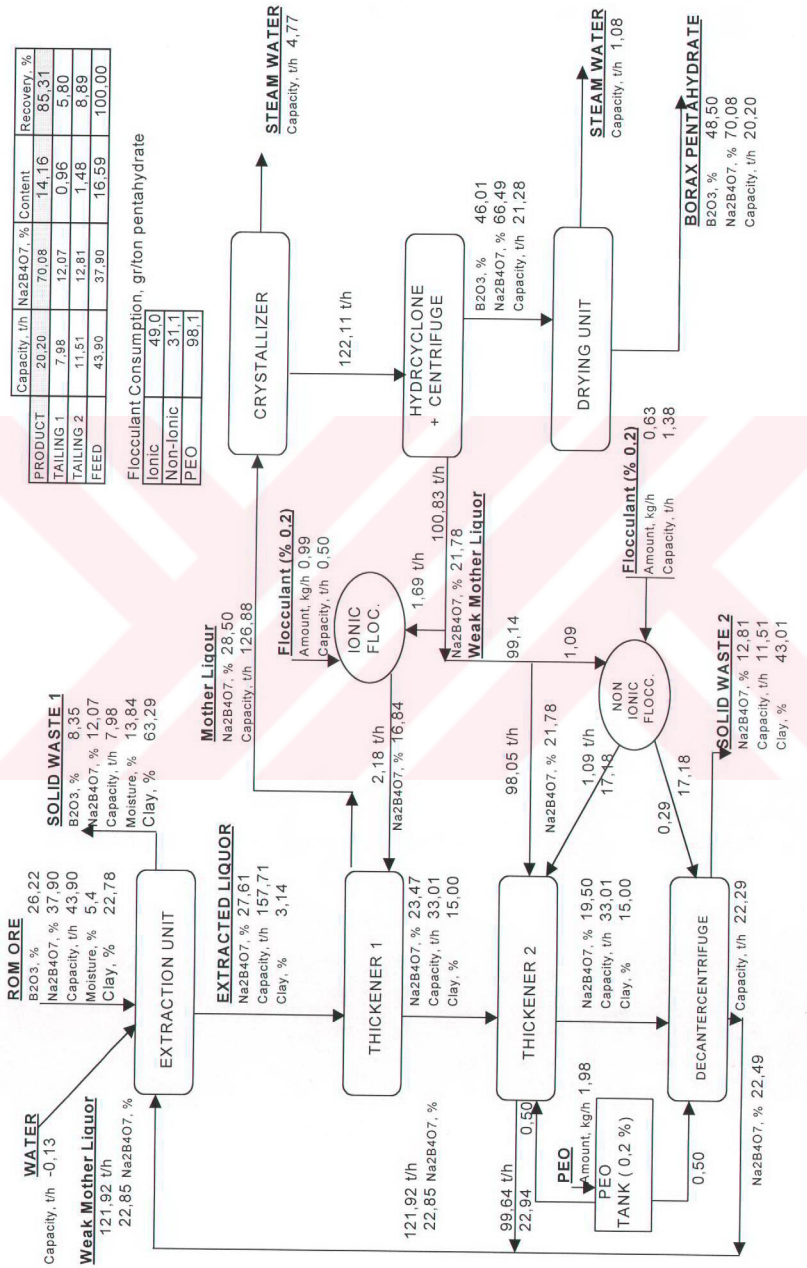


Appendix 5.3.1.3 Mass Balance Calculations of Borax Pentahydrate Plant in Kirka (Mother Liquor contains 5 % Clay)

DURAA PENIANTYKAIE MASS BALANCE CALCULATIONS



DURAK PENIAHYUKAIE MASS BALANCE CALCULATIONS



BORAX PENTAHYDRATE MASS BALANCE CALCULATIONS

