CHAPTER I

INTRODUCTION

Chromatography is a technique used for separation of substance.
It is based on partitioning of a sample between two phases: a mobile
phase, which can be gas or liquid, and a stationary phase, liquid or
solid. Chromatography was first employed by Ramsey (1) in 1905 to
separate mixtures of gases and vapors using gas-solid chromatography
and has been applied and developed so far. It is a rapid and comfort-
able method, especially gas-liquid chromatography, in the routine
analysis using a small amount of the sample. Analyses of drug (2),
pestcides (3-9), steroids (10), alcohols (10), hydrocarbons (10),
and other compounds (10-15) are carried out by using chromatography.
Inasmuch as the column is the heart of the chromatographic system, the
support has played a key role in the development of gas chromatography.
The basic function of the support is to hold the stationary phase on
its surface as a thin film. Although the ideal chromatographic support
has not been found, diatomite (16-17) in one form or another has
dominated the field of supports because it is the most inert porous
one among natural materials. A small percentage of supports consists
of fluorocarbon (16) resins and, even smaller extent, glass beads.

1.1 Diatomite

Diatomite is known by several names. This includes the term
diatomaceous earth, diatomaceous silica and the German word, kieselguhr.
Diatomite is a siliceous, sedimentary rock composed of the skeletal
remains of single-celled water plants, called diatoms. The skeletons

which have accumulated in huge beds in various parts of the world consist primarily of silica with some mineral impurities, mainly metal oxides. There are approximately ten thousand species of diatoms, some of which live in fresh water and others in salt water (marine form). The skeleton consists of two half cell walls joined by a connecting band or girdle. Examples of salt water diatoms are shown in Figure 1.1. Diatoms have been part of earth's ecology since prehistory time (for at least 15 million years). The diatom is basic to the ocean cycle. Appearing singly and in colonies as a benthonic or a planktonic, gelatineous growth, the diatom is food for minute animal life which, itself, serves as food for the higher forms of marine life. It reproduces by itself-division. Under ideal conditions, each diatom may divide every eight hours. In about a month's time, a single diatom could produce 10 billion offspring.

While living, the diatom extracts opaline (amorphous) silica from the water and converts it into a skeleton by a machanism which is still obscure. Diatoms exist in great variety of shapes, each of which has mesh-like or network structure. At the end of its life cycle, the diatom settles to the bottom of a body of water. The organic part disintegrates, leaving a skeleton as full of minute holes and passages as a sponge. Since the total thickness of the cell wall is only a few ten thousandths of an inch, it results in an internal structure that is highly porous on a microscopic scale. The submicrometre sized pores make diatomite the superior filtration medium, it is today, capable of passing liquid through its mesh-like structure while retaining particles that are micrometres in size.
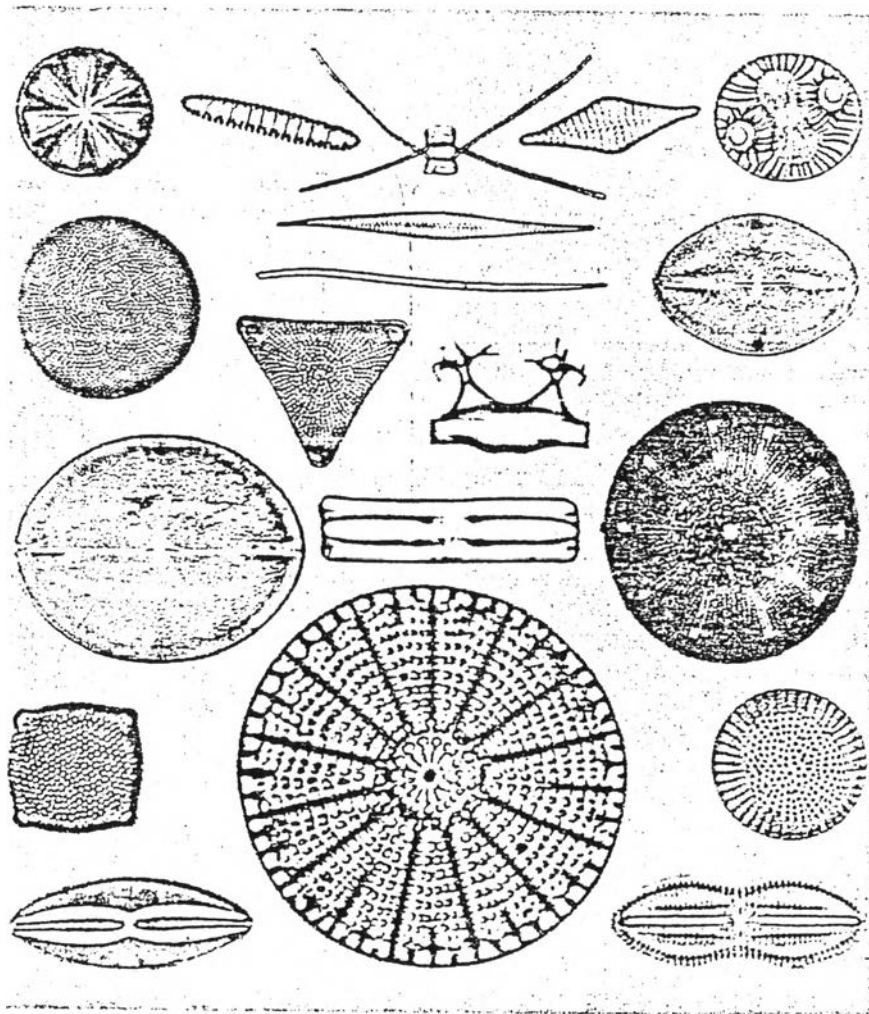
Figure 1.1 Photomicrograph of a number of typical diatom skeletons (16).

1.1.1 Properties of Diatomite

Generally, diatomite is composed of hydrous silica. Thus its surface is silanol groups (Si-OH) that can cause adsorption with polar molecules. The compositions of diatomite at some reserves such as Hollywood, California (18); the village of Dragowistiza near Sofia (19), Bulgaria; and the Gurmen deposit, Blagoevgrad, Bulgaria (20) are shown in Table 1.1. As mentioned above diatomite consists of the minuscule skeletons of diatoms whose cell-wall remains are almost-pure opaline silica. These holes or pores provide a relatively high surface area of approximately 20 m^2/g. Its hardness is about 1-1.5 in Mohs' scale, it is very fragile, easy to break down in handling. It has specific gravity of 2.30. Particle size of pure diatomite is about 2 to 40 μm. The color range of diatomite is light yellow to white.

1.1.2 Application of Diatomite

Diatomite is very useful in several industrial processes. It is used as filter media for sugar, syrup, vegetable oils, petroleum, etc.; thermal insulator; building bricks; filler in plaster of Paris, cement, pulp, rubber, asphalt and paint; abrasive material; explosive material; adsorbent and solid support for chromatographic columns.

1.1.3 Background of Diatomite Supports

Two types of supports are made from diatomite. One is a pink material derived from brick and the second is a white material derived from filter aid. These two differ considerably in physical properties as well as in performance as chromatographic supports.

The filter aid, or white material (16), is prepared by

Table 1.1 Chemical analyses of diatomite from some reserves.

    1. Hollywood, California (18)

    2. Dragowistiza near Sofia, Bulgaria (19)

    3. The Gurmen deposit, Blagoevgrad, Bulgaria (20)

composition in %	1	2	3
SiO_2	73.71	83.50	68.80
Al_2O_3	7.25	10.56	13.70
Fe_2O_3	2.63	2.04	5.30
MgO	1.47	0.67	0.90
CaO	1.72	1.18	1.10
Na_2O	1.19		
		2.05	1.80
K_2O	1.00		
loss on ignition	6.94	8.52	-

mixing diatomite with a small amount of flux, sodium carbonate, and calcining it at temperatures above 900°C. During calcination, a number of changes take place. The fluxing agent causes incipient fusion of the finer particles forming coarser aggregates. A portion of the microamorphous silica is converted to a crystalline form, cristobalite. The original light-gray diatomite becomes white because of the flux, which is believed to convert the iron originally present as an oxide to a colorless complex sodium iron silicate. A bed of the material has a density of roughly 0.2 g/cm^3 and about 90% void space. Its surface area is approximately 1 m^2/g.

The brick, or pink material (16), consists of diatomite that are crushed, blended and pressed into brick, then calcined or burned above 900°C to permit its use as a high temperature insulation. During calcination the diatomite particles fuse and a portion of the silica is converted to cristobalite. At the same time the mineral impurities form complex oxides or silicates. The oxide of iron is thought to impart the characteristic pink color. A bed of the crushed firebrick has a density of roughly 0.4 g/cm^3 and about 80% void space. Its surface area is approximately 4 m^2/g.

Most of the differences in the properties of the two materials stem from the differences in preparation. Because of the differences in preparation, the pink particle is a relatively dense mass of diatomite and contains a small amount of internal void space which consists of small pores producing a high surface area. Owing to the compactness of the diatomite and the fusion occurring during the calcination, the particle is relatively hard.

On the other hand, the white particle consists of a mass of diatomite fragments lightly fused together in a very open structure. Because of the open structure, the internal void space is large. Little of the very small pore character remains in the diatomite fragments, and due to the fact that the diatomite fragments are weakly fused together, the whole particle is weak or friable. Values for the typical physical properties of the pink and white supports are tabulates in Table 1.2 and a typical chemical analysis of the two is given in Table 1.3. Chemical analysis showed that the white and pink materials were very similar. The higher Na_2O and K_2O content of the white reflects the use of the flux in its preparation.

The surface of both the pink and white supports is very similar as it is covered with silanol groups (Si-OH). The principal difference lies in the density of the two and the resulting total surface area. The pink material, having a greater specific surface area, shows greater adsorption than the white material. For this reason, the white material is generally favored as the support in columns used to separate polar compounds. At the same time the white material has an inherent column efficiency less than that of the pink material. The white material is also very friable, easily breakable, as contrasted to the pink material and shows considerable breakdown in handling. Breakdown causes fines and increases column back pressure which results in a poorer column.

In the original work in gas-liquid chromatography Celite 545 (16), a filter aid, was used as a support for separation of fatty acids. To obtain a coarse fraction of Celite 545, James and Martin (16) repeatedly suspended the material in water, allowed the coase fraction to settle, and decanted the fines with the supernatant liquid. This was necessary since most of the Celite 545 is very fine with

Table 1.2 Typical physical properties of diatomite supports (16)

	Pink	White
pH	6-7	8-9
True density, g/cm^3	2.26	2.20
Free fall density, g/cm^3	0.41	0.21
Packed density, g/cm^3	0.47	0.24
Void space	0.80	0.90
Surface area, m^2/g	4.00	1.00

Table 1.3 Typical chemical analysis of diatomite supports (16)

	Pink		White	
	Non-acid washed Percent	Acid washed Percent	Non-acid washed Percent	Acid washed Percent
SiO_2	90.6	91.6	88.9	90.0
Al_2O_3	4.4	4.1	4.0	3.6
Fe_2O_3	1.6	1.4	1.6	1.4
TiO_2	0.2	0.2	0.2	0.2
CaO	0.6	0.4	0.6	0.4
MgO	0.6	0.5	0.6	0.5
$Na_2O + K_2O$	1.0	0.9	3.6	3.2
Moisture	0.3	0.3	0.3	0.3

approximately 90 per cent finer than 100 mesh. In 1955 A.I.M. Keule-
mans (16) reported the use of the sterchmol, a German diatomite fire-
brick calcined at $2012^{o}F$ and $2100^{o}F$. In 1956 M. Dimbat, P.E. Porter
and F.H. Stross (22) reported the use of Johns-Manville Sil-0-Cel C-22
brick, a diatomite brick calcined at $1350^{o}C$ ($2460^{o}F$). A coarse frac-
tion of the Sil-0-Cel C-22 brick was prepared by crushing the brick
and then size-grading the material with screens.

Considering the pink materials, the techniques had the
disadvantages of extended processing time and high operating temperature
conditions which were impractible in most cases and consequently econo-
mically undesirable. These persuaded D.M. Ottenstein (23) to prepare
a new support that exhibited low adsorptive effects but had good column
efficiency and good handling properties. On the other hand, the support
had the combined good properties of the white and pink materials. The
support was prepared in 1968 by flux calcining crushed diatomite fire-
brick, Sil-0-Cel C-22 which was previously calcined. Fluxs included
Na_2O, K_2O and Na_2F. The first calcination, without flux, was in a
standard manner of the firebrick preparation. The second calcination
involving 5.0 per cent flux except Na_2F which was 4.0 per cent was
carried out for 6 hours at $2100^{o}F$ ($1148^{o}C$) except in the case of Na_2F
which was calcined for 1 hour.

However, the double calcination is energical waste and
the temperature is also high. This is still impractical Additional
to the difficulty of surface area, the diatoms in some deposits are
associated with undesirably large amounts of impurities. These impuri-
ties comprise water, clay (generally aluminum compounds in the form of
minute particles of about 1-2 μm size or less), fractured diatoms, and
inorganic impurities such as iron oxide, calcium and magnesium sulphate.

Association with large quantities of clay naturally reduces the surface
area of diatoms because the clay portion not only fills the porous
diatom skeletons but also acts as a cementing agent between individual
diatoms. Inorganic materials cause adsorption on the diatom surface and
a large amount of iron oxide makes the flux-calcined product colred,
white, as required. Therefore, benefication of raw diatomite is needed.
J. Visman and J.L. Picard (24) patented their research of the benefica-
tion of diatomite in Canada in 1972. A number of benefication methods
were developed in the prior art, however they were not applicable to
diatomite of the Quesnel type in Canada. For example, air classifica-
tion was used to separate the diatoms from fragmented diatoms in the
high grade ore deposits of the United States of America. Selective
settling techniques were also known in the art, as were floatations
techniques, but they were too expensive or inefficient when applied to
ores of Quesnel type. The patented process comprised the following
steps: washing the raw material to completely leach out water soluble
salts such as gypsum and hydrous sulphate of sodium, potassium and
magnesium; separating the wash water from the residue; re-pulping the
residue with water in association with a dispersant; subjecting the
product slurry to centrifugal separation to separate the first and
second fractions from the intermediate fractions predominantly
comprising diatoms. The flow diagram of this process is shown in
figure 1.2. Washing of the ore before separation is necessary. It
was found that soluble salts presenting in ores of the Quesnel type
cause them consuming conventional dispersing agents. This can render
the precess uneconomically. Washing will remove the great bulk of
these salts. The particle size distribution of diatomite is illustrated
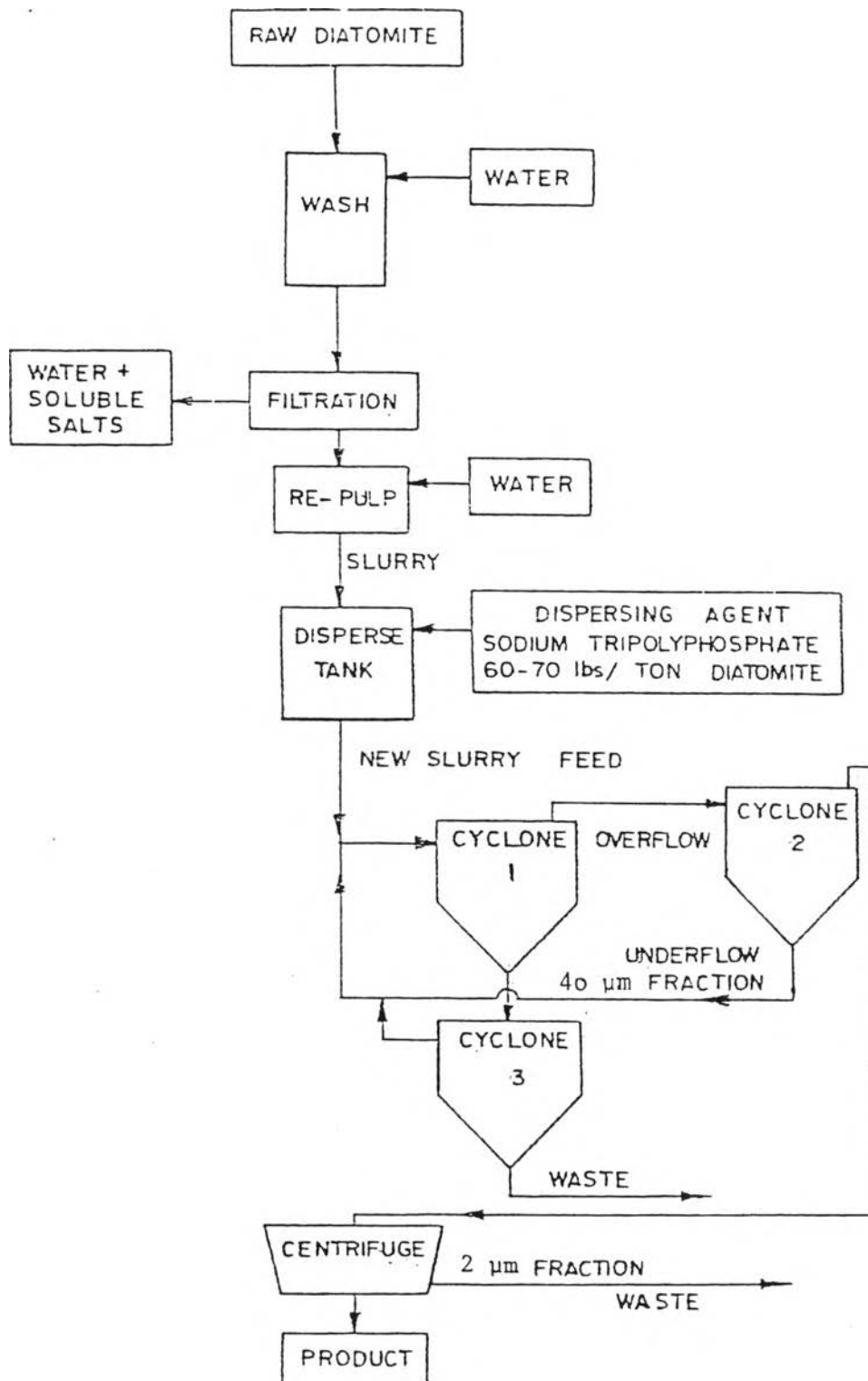in Figure 1.3 and the separated fractions are shown in Figure 1.4.

RAW DIATOMITE

WASH ← WATER

WATER + SOLUBLE SALTS ← FILTRATION

RE-PULP ← WATER

SLURRY

DISPERSE TANK ← DISPERSING AGENT
SODIUM TRIPOLYPHOSPHATE
60-70 lbs/ TON DIATOMITE

NEW SLURRY FEED

CYCLONE 1   OVERFLOW   CYCLONE 2

UNDERFLOW
4o μm FRACTION

CYCLONE 3

WASTE

CENTRIFUGE   2 μm FRACTION
WASTE

PRODUCT

Figure 1.2 Flow diagram of the benefication of diatomite.
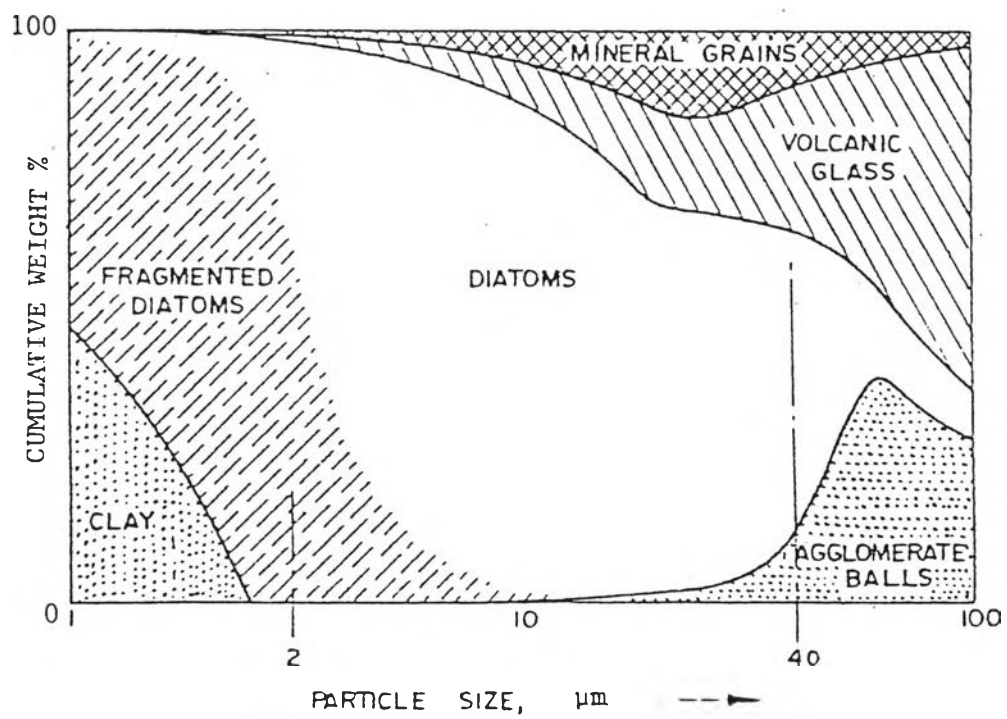
Figure 1.3 Illustration of particle distribution of diatomite.

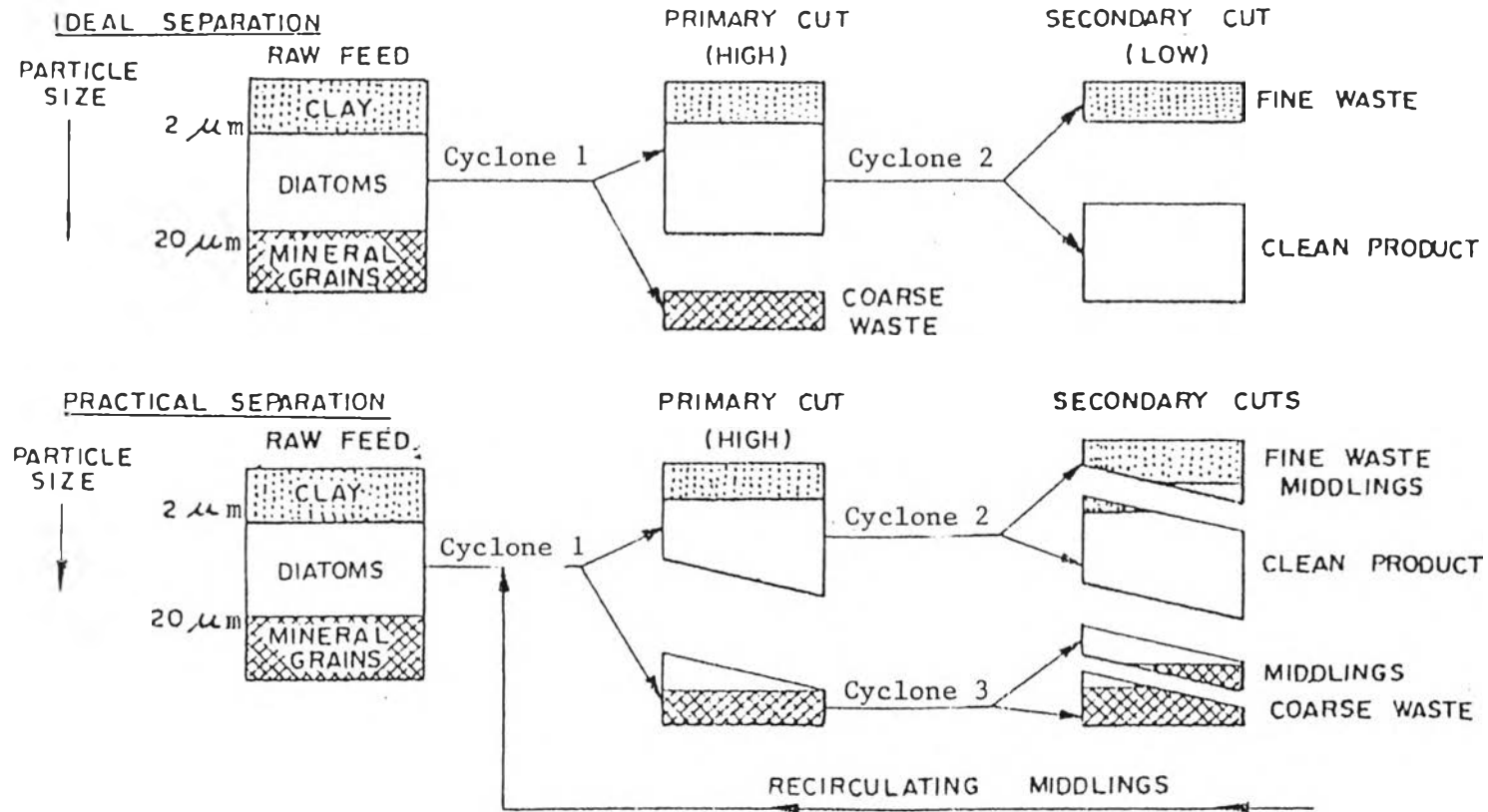IDEAL SEPARATION

PARTICLE SIZE

RAW FEED

2 μm CLAY

DIATOMS

20 μm MINERAL GRAINS

Cyclone 1

PRIMARY CUT (HIGH)

Cyclone 2

COARSE WASTE

SECONDARY CUT (LOW)

FINE WASTE

CLEAN PRODUCT

PRACTICAL SEPARATION

PARTICLE SIZE

RAW FEED

2 μm CLAY

DIATOMS

20 μm MINERAL GRAINS

Cyclone 1

PRIMARY CUT (HIGH)

Cyclone 2

Cyclone 3

SECONDARY CUTS

FINE WASTE
MIDDLINGS

CLEAN PRODUCT

MIDDLINGS
COARSE WASTE

RECIRCULATING MIDDLINGS

Figure 1.4   Results of the impurity separation from diatomite.

Considering Figure 1.2, coarse particles (more than 40 μm) were separated
in cyclone 1, diatoms and fine particles were transferred into cyclone
2 still comprised diatoms and clay particles which could be separated
by centrifugation or filtration. This indicated that the cyclones were
used for separation of coarse particles not clay particles from diatoms.
Clay particles (2 μm or less) were separated from diatoms by centri-
fugation.

Not only Canadian diatomite, but also Bulgarian diatomite
comprised a large amounts of impurities. In 1972 At. P. Atanasov (19)
used acid treatment for impurities removal, i.e., adding 200 g of
diatomite to 1000 cm^3 of 20% hydrochloric or sulfuric acids, heating
for 2 hours at 95-100°C, filtering and washing. The procedure was
made three times with 20% acid. The final washing was made until
neutrality was achieved. There was no difference in treatment with
hydrochloric or sulfuric acids. Then the support was produced by
calcining with 5% of an eutectic mixture of sodium and potassium carbo-
nate. In 1974 A. Atanasov (25) produced a new support from Bulgarian
kieselguhr by crushing to 0-3 mm, 4-stage benefication by mechanical
disintegration and sedimentation in solutions containing sodium carbo-
nate 250 g/ton and sodium silicate 125 g/ton (at a solid: liquid ratio
of 1:(30-40)), 3-stage washing with 10-20% hydrochloric acid at 90-95°C
with intermediate and final washing with water, drying at 150°C, mixing
with 5% by weight of a eutectic mixture of sodium and potassium carbo-
nate, calcining for 3 hours at 900-950°C and crushing to the required
particle size. In the same year A. Atanasov and G. Shterev (20) produced
another support for GC from Bulgarian kieselguhr by crushing to 0-3 mm,
enriching by 5-stage wet disintegration-sedimentation at a solid: liquid
ratio of 1:(30-40) in the presence of sodium carbonate 1250 g/ton and

sodium silicate 625 g/ton, washing 3 times with hydrochloric acid, flux
calcining as the former and crushing to the required particle size.
The three products from Bulgarian kieselguhr were similar to Chromosorb
W.

Although the surface area of support is 20-fold reduced,
its surface contains a number of different types of active sites such
as the silanol group and mineral impurities. The surface acts as if
it has at least three types of active sites:

1. Hydrogen bonding sites causing the tailing of neutral
compounds such as alcohols, aldehydes, ketones, esters, etc.

2. Basic sites causing the tailing of acidic compounds
such as aliphatic and aromatic carboxylic acids, phenols, barbiturates,
etc.

3. Acidic sites causing the tailing of basic compounds
such as amines.

There are three major methods of deactivating the support.
There are:

1. Removal of mineral impurities by acid or base washing
of the support.

2. Removal of surface silanol groups by reaction with a
silanizing agent to form a silyl ether.

3. Saturation of the active sites with an active agent.

Deactivation of support by acid and/or base washing and
silane treatment was compared and evaluated by D.M. Ottenstein (26).
It was discovered that acid washing or base washing of the support
was highly effective in removing mineral impurities from the support
surface. Comparing acid and base washing, the former was more effec-
tive than the latter in removing mineral impurities. A base washing

did little to improve the surface that had already been effectively acid washed.

The acid washing or base washing appeared to be ineffective in reducing tailing. It might be that the tailing caused by the removal of the mineral impurities was small compared to the tailing caused by the surface silanol group which was removed by silanization. It was shown that acid washing reduced the mineral impurity content of the support by about 10 per cent. When the acid washing was followed by silanization, the support surface was much more inert than a support which had been only silanized. The real benefits of acid washing were not seen until the support was silane treated. However, the effectiveness varied considerably among the various agents. Dimethyl dichlorosilane (DMCS) was the most effective, hexamethyl disilizane (HMDS) less so, and trimethyl chlorosilane (TMCS) even less.

As mentioned the diatomite supports can be divided into two main types. One is the firebrick-derived supports such as Chromosorb P and Gas Chrom R which are used for analysis of non polar compounds, hydrocarbons. Alcohols, amines, acids and other polar compounds are adsorbed on the surface of those support and this adsorption results in chromatographic-peak tailing severely. The other one is the white support derived from filter aid. The white supports are almost widely used such are Chromosorb W, Chromosorb G, Supelcoport , Gas Chrom Q and Anakrom ABS. The Universal support is Chromosorb W because its price is not so expensive. Although Gas Chrom Q is much more expensive than the other, it is the most inert support (27) and it has been widely used for separation of polar compounds such are steroids, drugs, pesticides, phosphate compounds, etc.

Gas Chrom Q (28-29) is a gas chromatographic support from diatomaceous earth which is carefully silanized to eliminate nearly all reactive sites. The particle sizes of the diatoms are usually too small for effective use as gas chromatography supports, since they cause excessive pressure drop when packed in a column. To increase the usable particle size range the material is calcined with a small amount (5 per cent) of sodium carbonate flux to produce a white porous solid which serves as the starting material for Gas Chrom S, A, P, Z and Q. The condition of calcination such as period and temperature was not unknown. After the Celatom (28) has been calcined, it is screened, then water-washed to remove the bulk of fines. After drying, the support is carefully screened to size (60/80, 80/100, and 100/120 mesh) and checked for screening efficiency. This product is Gas Chrom S. The support is soaked in concentrated hydrochloric acid for a minimum of 16 hours, this product is Gas Chrom A, and washed with 2% KOH solution for a minimum of 16 hours, this end product is Gas Chrom P.

In order to prepare Gas Chrom R, the Gas Chrom P is again thoroughly water washed. After the water washing, the support is thoroughly dried, then soaked in a solution of dimethyldichlorosilane (DMCS) in toluene. This brings about reaction of the surface hydroxyl groups with the silane to form silyl ethers. Finally, the support is washed with methanol to react with any remaining chloro groups. Moisture must be rigidly excluded during this process to prevent hydrolysis of the silyl group, which would destroy the effectiveness of the deactivation process. After drying, the support is Gas Chrom Q. Free fall density (in the 60/80 mesh size) as about 0.22 g/cm^3.

1.1.4 Diatomite in Thailand

In Thailand there are several reserves of diatomite.
Most of them are found in Lampang, a province of northern Thailand.
The diatomite deposits in the Lampang basin appears as low hills
having an average height about 10 to 20 meters from the ground level
and being covered with laterite, gravel and cobble beds. The main
deposits were found at Amphoe Ko Kha, Amphoe Muang and Amphoe Mae Tha.
P. Kumanchan and A. Traiyan (21) reported that the deposits at Ban Mon
Hin Kaew, Amphoe Ko Kha; Ban Kluai Phae, Amphoe Muang; and Ban Ouan,
Amphoe Mae Tha were the significant deposits. Other diatomite deposits
found at Ban Phichai, Amphoe Muang; Ban Huai Nam Khem, Amphoe Muang;
Ban Huai Nam Long, Amphoe Sop Phrap; and Ban Kui Lom, Amphoe Muang were
considered as small deposits. The areas of diatomite deposits are
shown in Figure 1.6. P. Kumanchan and his partner also reported the
diatomite reserves as tabulated in Table 1.4 which indicated that the
dry diatomite reserves were totally 242.9 million metric tons.

Diatomite in Lampang has a micro-structure of diatoms,
namely Melosira granulata which is a fresh-water diatom. By means of
electron microscope scanning a particle of the diatomite is 4-31 microns
wide and 8-35 microns long as shown in Figure 1.7. The chemical
analyses (21) of diatomite from some areas at the Lampang basin is
shown in Table 1.5. It indicated that the Mae Tha deposit has the
highest silica content which is used as a measure of diatom quantity.
However, the iron content and alumina content which is used as a measure
of the clay quantity are also high. Therefore, the diatomite is not
utilized as much as it should be. If these undesirable minerals are
removed, the diatomite in Thailand will be more useful, e.g., as
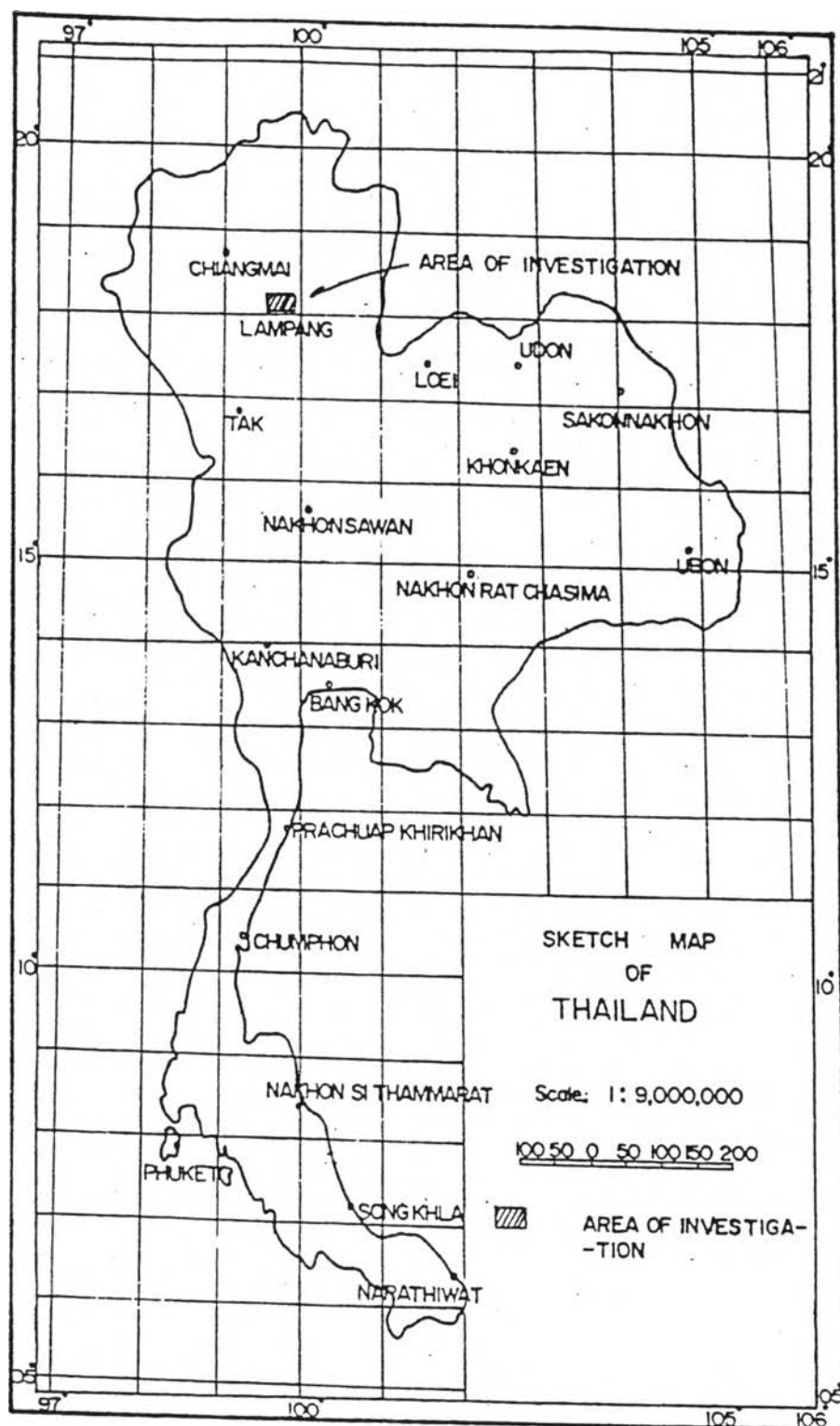filtering media, adsorbent and solid support for chromatography.

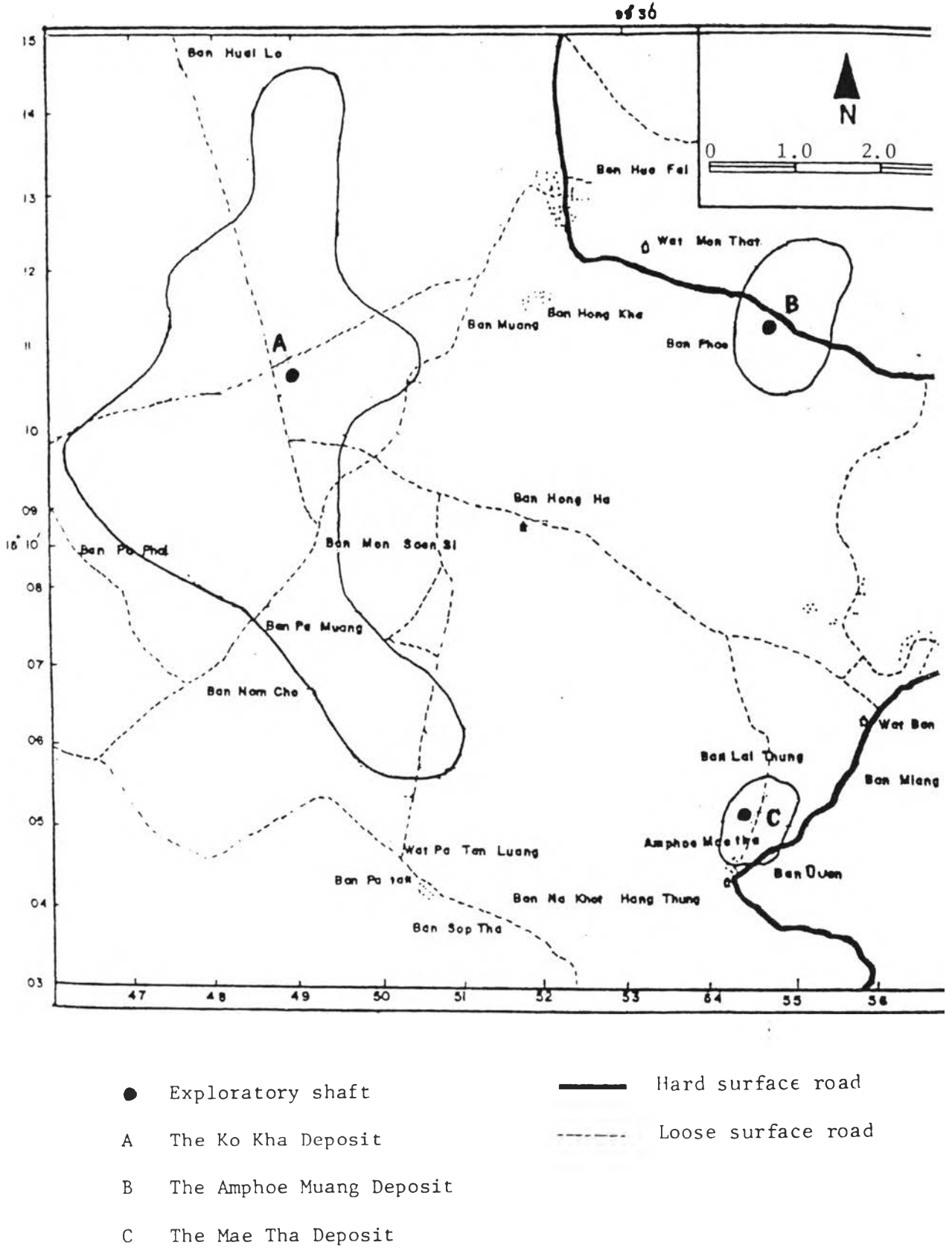Figure 1.5 Location map of diatomite deposits, Lampang, northern

Thailand.

- ● Exploratory shaft
- A The Ko Kha Deposit
- B The Amphoe Muang Deposit
- C The Mae Tha Deposit

——— Hard surface road

-·-·-·- Loose surface road

Figure 1.6 Showing areas of diatomite deposit (21).

Table 1.4 Showing diatomite reserves of the Lampang basin (21).

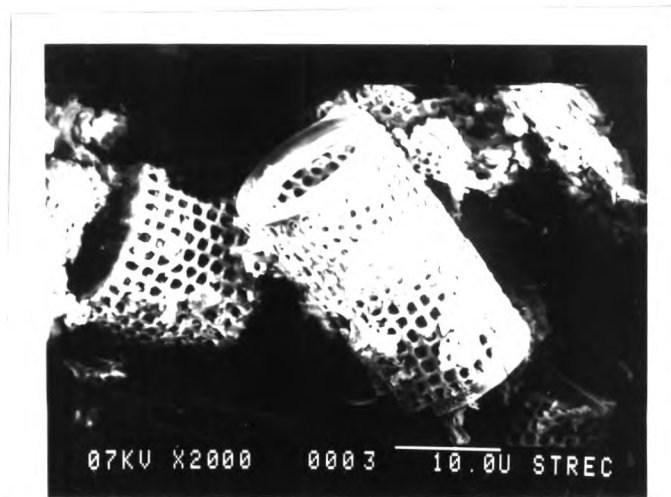| Area	Total Volume (m^3)	Reserve (metric tons)
Ban Mon Hin Kaew Amphoe Ko Kha	310.97×10^6	223.89×10^6
Ban Klaui Phae Amphoe Muang	15.20×10^6	12.16×10^6
Ban Ouan Amphoe Mae Tha	13.20×10^6	6.85×10^6
Total	339.37×10^6	242.90×10^6

Figure 1.7 Photomicrograph of diatomite in Lampang, Thailand.

Table 1.5 Chemical analyses of Lampang diatomite (21)

(The average contents from different depth)

1. From the Ko Kha deposit

2. From the Amphoe Muang deposit

3. From the Mae Tha deposit

composition (%)	1	2	3
SiO_2	63.95	62.39	69.50
Al_2O_3	15.68	11.88	12.09
Fe_2O_3	9.15	6.87	3.56
CaO	–	–	0.89

1.2 Objective and Scope of This Study

In the past, diatomite in Thailand was crushed and used as a filler in other products (30). Association with clay, sand and iron minerals made the diatomite not of interest even several large reserves of diatomite deposits were found in Lampang. To develop the diatomite as the most valuable product, a solid support for chromatography, many researches have to be done. From the primary study of the micro-structure of Lampang diatomite as shown in Figure 1.7, its structure is similar to Gas Chrom Q which is the most inert support now. Thus the preparation of Gas Chrom Q from Thai diatomite is quite possible and many studies has planned as the followings:

1. Chemical analysis and surface study of Lampang diatomite.

2. Benefication of Lampang diatomite for use as the starting material.

3. Preparing the solid support from step 2.

4. Physical and chromatographic studies of the prepared support using Gas Chrom Q as the reference support.

5. Application of the prepared support in chromatographic columns.