CHAPTER V

LABORATORY TESTING

TABLE V.1

CHARACTERISTICS IN RAW STATE

Properties	1C	1D	2A
a. Raw color	Light grey to dark at depth, medium hard lumps	Greyish black with layers of plant fossils.	Grey to dark grey hard lumps
Color of powder	Grey	Grey	Grey
b. Visual impurities.	Mica flakes, carbonaceous (coaly) matter	Mica flakes occasional, carbonaceous matter	Mica flakes quartz grains, little carbonaceous matter.
c. Slaking nature	Fair	Fair	Fair
d. pH	7.3	7.8	7.3
e. Residue on 150 B.S.S. Sieve			
Percent Residue	1.1	6.2	2.8
Nature of Residue	Fine quartz grains, carbonaceous matter, mica flakes	Fine quartz grains, carbonaceous matter, mica flakes	Fine quartz grains, carbonaceous matter, mica flakes, undispersed clay.
f. Percent loss on ignition	13.66	14.07	13.42
g. Sp. Gr.	2.32	2.35	2.37

CHARACTERISTICS IN RAW STATE..(Contd.)

Properties	3A	4C	5B
a. Raw color	Greyish white to dark grey hard flinty lumps	Dark grey lumps, Homogeneous color	Grey hard lumps
Color of Powder	Grey	Grey	Grey
b. Visual impurities	Fine quartz grains, mica flakes, carbonaceous matter is more	Mica flakes on fresh cut sample more, little organic matter	Fine quartz grains, carbonaceous matter, Ferruginous matter trapped in joints; mica flakes
c. Slaking Nature	Moderate	Moderate	Fair
d. pH	7.9	7.3	7.7
e. Residue on 150 B.S.S. Sieve			
Percent Residue	6.5	2.4	4.5
Nature of Residue	Little fine quartz grains, carbonaceous matter, mica flakes, undispersed clay	Fine quartz, grains, mica, carbonaceous and ferruginous matter, undispersed clay	Fine quartz sand mica, carbonaceous matter, little undispersed clay
f. Percent Loss on Ignition	14.31	13.59	14.18
g. Sp. Gr.	2.39	2.62	2.29

CHARACTERISTICS IN RAW STATE..(Contd.)

Properties	6	7B	8A
a. Raw Color	Grey hard lump	White and faint brown alternate layers with flinty fractures.	Greyish white hard lumps
Color of Powder	Grey	Pinkish white	Faint grey
b. Visual Impurities	Little fine quartz grains, mica flakes	Fine quartz sand, faint brown ferruginous matter, little mica	Fine quartz sand, brown specks, carbonaceous matter
c. Slaking Nature	Moderate to slow	Non-slaking	Moderate
d. pH	7.0	7.3	7.1
e. Residue on 150 B.S.S. Sieve			
Percent Residue	2.4	9.0	2.2
Nature of Residue	Carbonaceous matter, mica flakes, undispersed clay	Fine quartz sand, coarse ferruginous particles, buff undispersed clay	Fine quartz sand little brown ferruginous matter, carbonaceous matter, undispersed clay
f. Percent Loss on Ignition	12.56	11.86	13.13
g. Sp. Gr.	2.41	2.44	2.08

CHARACTERISTICS IN RAW STATE...(Contd.)

Properties	9	10A	11
a. Raw Color	Grey homogeneous	Brown with grey nodules	Grey hard lumps with occasional brown nodules
Color of Powder	Grey	Brown	Dirty grey
b. Visual Impurities	Little carbonaceous matter, mica flakes	Ferruginous coarse grained material	Mica flakes, ferruginous matter in the joints and little carbonaceous matter
c. Slaking Nature	Moderate	Non-slaking	Slow to non-slaking
d. pH	7.1	7.2	8.2
e. Residue on 150 B.S.S. Sieve			
Percent Residue	2.2	10.4	3.2
Nature of Residue	Fine quartz sand, carbonaceous matter mica flakes, little undispersed clay	Fine quartz, grains, ferruginous grity matter, undispersed clay	Fine quartz, grains, little gerruginous matter, carbonaceous matter, buff undispersed clay
f. Percent Loss on Ignition	11.19	11.2	12.84
g. Sp. Gr.	2.36	2.52	2.12

CHARACTERISTICS IN RAW STATE..(Contd.)

Properties	12	13	14
a. Raw Color	Brown red nodules	Reddish brown with grey nodules	Light grey with buff colored layers
Color of powder	Brown red	Brown	Greyish white
b. Visual Impurities	Fine quartz particles, dark red coarse matter	Fine quartz, particles, brown red coarse nodules	Fine quartz grain, mica flakes, buff and purple colored thin layers
c. Slaking Nature	Non-slaking	Non-slaking	Slow to non-slaking
d. pH	8.1	7.05	6.9
e. Residue on 150 B.S.S. Sieve			
Percent Residue	12.0	10.4	5.0
Nature of Residue	Fine quartz, sand, gritty brown, material -rial, more undispersed clay	Quartz sand, gritty brown material, buff undispersed clay	Quartz sand, brown coarse matter, brown undispersed clay
f. Percent Loss on Ignition	10.84	10.87	10.23
g. Sp. Gr.	2.16	2.61	2.32

GREEN AND DRYING PROPERTIES

Green properties are those, that prevail while the plasticizing water is still present in the clay bodies.

Methods of Testing

1. Water of Plasticity (Plastic Basis) :

Fireclay is ground till it passes through 200 mesh B.S. Sieve. 100 gm of minus 200 mesh fireclay is taken into a porcelain crucible. Water from 100 cc. burette is added drop by drop till clay in crucible becomes just plastic. Burette reading gives value of water of plasticity (Plastic Basis).

Solid bodies absorbing or holding liquid in their pores and forming a mass which can be pressed into any desired shape, which is retained even after the release of pressure, are said to have the property of plasticity. Removal of water by evaporation changes the plastic body into a hard mass.

Whitelaker, 1935 (Grim, R.G. 1962), observed that the plasticity is inversely related to particle size.

Plasticity is attributed to the finess and shape of the particles.

2. Green Strength

A small rectangular (about 7.5 cm x 1 cm x 1 cm) test piece of plastic mass of clay was moulded with the help of wooden mould. Green strength is measured as a transverse breaking strength (gm/cm^2) of a test bar suspended on two narrow supports. In ceramic ware, green strength should be adequate to permit the ware to be handled. Green strength is related to particle size and crystallinity.

3. Dry Strength

A test piece similar to that used for measuring green strength is prepared and dried in air for 24 hrs and then dried in oven at 105°C for 5 hrs. The test piece is suspended on two narrow supports and traverse breaking strength is measured in gm/cm^2.

The strength of dry clay is an important property and has a practical bearing on problem of handling. A high strength body withstands the shocks and strain of handling. The particle size of the clays showing high dry strength are well graded.

TABLE V.2

GREEN AND DRYING PROPERTIES

Properties	1C	1D	2A	3A	4C	5B	6	7B
1. Plasticity by hand feel	Fair	Moderate to fair	Moderate	Moderate	Fair	Moderate to fair	Fair	Moderate
2. Water of plasticity Plastic basis (%)	30	23	21	21	25.5	23	28	21
3. Green strength(gm/cm^2)	1120	710	405	-	1180	1400	980	-
4. Dry strength (gm/cm^2)	1550	1180	610	450	1750	2290	1450	450
5. Dry linear shrinkage on plastic length(%)	7	5	5	6	6	6	7	5

TABLE V.2..(Contd.)

Properties	8A	9	10A	11	12	13	14
1. Plasticity by hand feel	Fair	Moderate	Low	Moderate to fair	Moderate	Low	Low
2. Water of plasticity plastic basis (%)	24.5	22	17	22	20	18	17
3. Green strength(gm/cm^2)	410	520	-	460	-	-	-
4. Dry strength (gm/cm^2)	770	910	450	800	450	450	450
5. Dry linear shrinkage (%)	6	6	5	5	6	6	5

West and Veale, 1953, (Singer and Singer, 1971) have shown that great increase in dry strength of fireclay composed of kaolinite or illite is attained by the addition of small amount of sulfuric and phosphoric acids. The reaction product formed by the action of acids on clay minerals, cement or bind the clay particles together.

4. Dry Shrinkage

A test piece similar to that used for measuring dry strength is prepared. The test piece was marked with two parallel lines 1 cm apart. The test piece was kept overnight to dry at room temperature and then was dried in oven at 105°C for 5 hrs. Dry shrinkage is measured as percent reduction in the length of test piece between parallel lines. Dry shrinkage is directly related to the water of plasticity. It increases with increase of water of plasticity and decrease in the particle size.

FIRED PROPERTIES

In ceramics almost all the properties are interlinked and are dependant on heat treatment.

The present author has made a careful study of the chemical and pyrochemical changes taking place during dehydration, oxidation and vitrification stages in fireclay, and suggest the proper use of fireclay, and the rate of firing. The changes which are likely to take place during the vitrification of a clay can be predicted by measuring the increase in shrinkage, and transverse strength, by visual observation of change in color and impurities at successive intervals of temperature.

Fired color is the most significant property in the classification of fireclays for commercial purposes. If a clay burns to a white or near white color, it has a possible use in white ware; if it burns buff the clay could be tried for stoneware and refractories, while if it burns to dark red or brown color, its use is limited to the dark colored structural wares and some cheaper forms of pottery. Fired color depends on the following :

i) The quantity of iron oxide present in the clay.

ii) The presence of other colouring oxides like titanium oxide.

iii) The composition of the fire gases and the kiln atmosphere.

iv) The degree of vitrification. Clay is heated at successively higher temperatures, and it is observed that other things being equal, the color depends on rise of temperature.

Firing shrinkage mainly depends on the degree of vitrification. The amount of firing shrinkage and the progressive change in shrinkage during firing are important parameters in testing clays for commercial purposes. A high shrinkage usually indicates a strong dense body; low shrinkage indicates that there is a large quantity of non-plastics, or the clay has been carried beyond the temperature at which the shrinkage was minimum. Excessive shrinkage indicates the necessity to add non-plastic clay to maintain proper shape and size without warpage, cracking, etc.

The strength of fired clay is not generally used in determining the degree of vitrification. Strength deteriorations indicate overfiring, when it is caused by development of vesicular structure.

As vitrification progresses in a clay body, the true and apparent specific gravity increases with rise in temperature. Specific gravity serves as an index of the degree of vitrification. Belinger and Leonis, 1949, (Singer and Singer, 1971) observed that in general the larger

TABLE V.3

FIRED PROPERTIES

Properties	1C	1D	2A
A. Fired properties at 1100°C			
Fired color and visual examination	Dull white, upper surface is reacted and become yellow,no cracks, no specks.	Dull white reacted upper surface with yellow tinge, no cracks, no specks.	Yellowish White upper surface shows reaction with yellow tinge,no cracks no specks.
Linear shrinkage(%)	10	9	10
Water absorption(%)	12.72	13	12.8
Vitrification	None	None	None
B. Fired properties at 1250°C.			
Fired color and visual examination.	Dull white, no cracks, no specks	Dull white, no cracks, no specks	Dirty white yellow tinge turns to faint, no cracks or specks.
Linear shrinkage(%)	13	9	9
Water absorption (%)	12.15	12.35	12.1
Vitrification	Fair	None	None
C. Fired properties at 1350°C.			
Fired color and visual examination.	Near to white, bright white, specks visible no cracks.	Near to white, no cracks,some specks of faint yellow and white observed.	Dull white, specks with bright white color, no cracks.
Linear shrinkage (%)	15	11	11
Water absorption (%)	5.71	3.82	4.1
Vitrification	Fair	Fair	Fair

TABLE V.3 (Contd.)

Properties	3A	4C	5B
A. Fired Properties at 1100°C.			
Fired color and visual examination	Yellowish white, reacted upper surface with yellow tinge,No cracks, No specks.	Pale white, upper surface reacted,become light brown, no cracks, no specks.	Dull white no cracks, no specks,visible
Linear shrinkage(%)	10	11	9
Water absorption(%)	12.65	12.82	13.2
Vitrification	None	None	None
B. Fired properties at 1250°C.			
Fired color and visual examination	Yellow to white, surface shows more yellowish, no cracks, no specks.	Yellowish white surface melted and become dull, no cracks, no specks.	Yellowish white, no cracks or specks.
Linear shrinkage(%)	10	12	10
Water absorption(%)	11.92	12.14	12.61
C. Fired properties at 1350°C.			
Fired color and visual examination	Yellow surface melting is observed,white specks, no cracks	Yellowish white surface, grey patches are visible, no cracks are seen.	Faint yellow upper surface covered with grey patches, no cracks
Linear shrinkage(%)	12	14	12
Water absorption(%)	4.95	5.72	6.1
Vitrification	Fair	Fair	Fair

TABLE V.3 (Contd.)

Properties	6	7B	8A
A. Fired properties at 1100°C			
Fired color and visual examination	Dull white, no cracks, no specks	Pinkish white no cracks, no specks	Dull white no cracks, no specks developed.
Linear shrinkage (%)	10	9	12
Water absorption(%)	11.81	10.52	10.22
B. Fired properties at 1250°C			
Fired color and visual examination	Yellowish white color, no cracks, no specks, upper surface is reacted and become yellow	Faint brown to white, surface shows reaction, no specks, no cracks	Yellowish white with some cracks, surface shows melting
Linear shrinkage (%)	13	10	13
Water absorption(%)	10.54	9.23	9.63
Vitrification	Fair	None	Fair
C. Fired properties at 1350°C			
Fired color and visual examination	Yellowish white with grey and white patches some cracks are visible	Whitish with pink and brown tinge, upper surface, melted,white specks,little cracks	Yellowish white, with grey specks and cracks
Linear shrinkage (%)	15	12	15
Water absorption(%)	4.22	3.05	3.12
Vitrification	Fair	Fair	Fair

TABLE V.3 (contd.)

Properties	9	10A	11
A. Fired properties at 1100°C			
Fired color and visual examination	Dull white with brownish tinge, no cracks visible	Brown, no cracks and flakes.	Dull white surface becomes pale brown, no cracks and specks.
Linear shrinkage (%)	10	9	10
Water absorption(%)	10.75	10.21	11.25
Vitrification	none	None	None
B. Fired properties at 1250°C			
Fired color and visual examination	Yellowish white,borders become pale brown, no cracks	Homogeneous brown small cracks, no specks	Faint Yellowish brown, white specks,surface slightly melted, no cracks
Linear shrinkage (%)	11	10	10
Water absorption(%)	10.2	9.75	10.6
C. Fired color and visual examination	Pale yellow, multing and pale brown surface, no cracks,white specks	Dark brown with white specks, cracks observed	Yellowish surface covered with grey and white patches, small cracks
Linear shrinkage (%)	13	12	12
Water absorption(%)	3.35	4.12	5.85
Vitrification	Fair	Fair	Fair

TABLE V.3 (contd.)

Properties	12	13	14
A. Fired properties at 1100°C			
Fired color and visual examination	Dark brown, little cracks, no specks	Reddish brown, small cracks, no specks	Dull white no cracks or specks
Linear shrinkage (%)	10	10	10
Water absorption(%)	9.82	9.51	11.72
Vitrification	None	None	None
B. Fired properties at 1250°C			
Fired color and visual examination	Homogenous brown with reacted surface, cracks developed, specks absent	Brown with grey specks, some cracks are seen	Yellowish white upper surface is slightly melted, no cracks, no specks
Linear shrinkage (%)	10	11	11
Water absorption(%)	8.22	8.05	11.75
Vitrification	None	Moderate	Fair
C. Fired properties at 1350°C			
Fired color and visual examination	Dark brown, cracks observed, grey specks surface reacted and melted	Dark brownish with cracks and grey specks	Yellowish white surface slightly melted, no cracks, white specks visible
Linear shrinkage (%)	11	11	13
Water absorption(%)	4.82	5.76	5.71
Vitrification	Moderate	Moderate	Fair

TABLE V.4

PYROMETRIC CONE EQUIVALENTS

Fireclay Mines	P.C.E. Value IS:1528 Part -I - (1974)	Classification (ASTM C27 1958)
1B	30	Near to refractory
1C	30	Near to refractory
1D	28	Semi refractory
2A	24	Low refractory
3A	26	Low refractory
3C	31	Refractory
4C	30	Near to refractory
5B	30	Near to refractory
6	26	Low refractory
7B	29	Semi refractory
8A	28	Near to refractory
9	24	Low refractory
10	28	Semi refractory
11A	18	Non refractory
11B	22	Low refractory
12	19	Non refractory
13	18	Non refractory
14	26	Low refractory
Ranipat	31	Refractory

the temperature interval between the point of high density, lowest porosity and higher the temperature at which over-firing cause, the more useful should be the clay as a refractory material.

MECHANICAL PROPERTIES

The objective to study these properties was to consider relationship of clay mineral composition to the properties of clay minerals, and to consider how the clay mineral composition influences these properties. In addition to the clay minerals, other fractors such as particle size, distribution, non-clay mineral composition, organic material and geologic history, control the mechanical properties of clays.

Atterberg Limits

Liquid Limit - (WL) is the moisture content expressed as a percentage by weight of the oven dired clay at which it will just begin to flow when jarred slightly. The degree of crystallinity and particle size influences liquid limit.

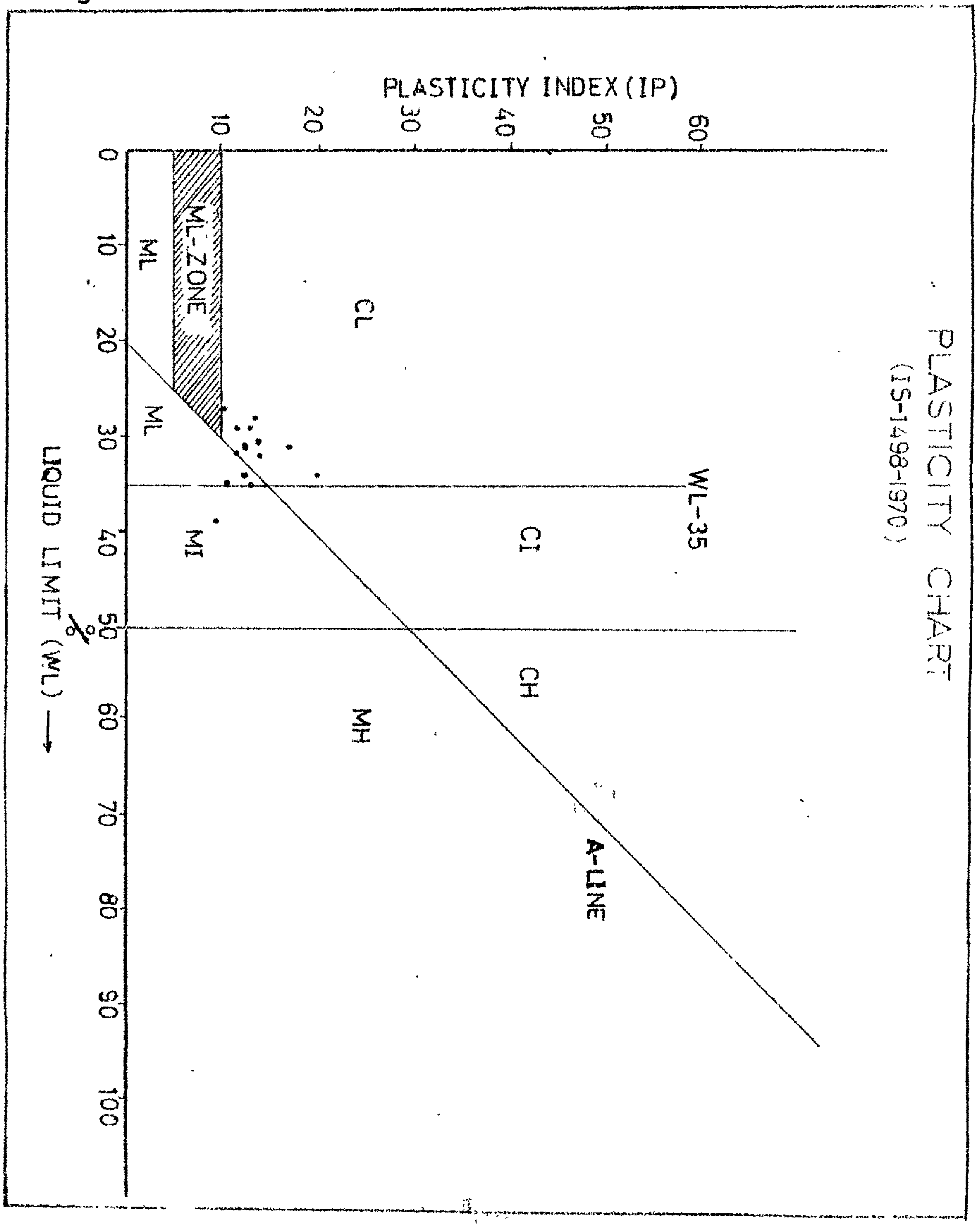
The liquid limit values for fireclays from Saurashtra vary from 25 to 34. Fireclay showing higher values consist

TABLE V.5

Atterberg Limits - IS : 2720 (Part V) 1970

	Locality	Liquid Limit. (WL)	Plastic Limit. (WP)	Plasticity Index. (IP)
1	Gadhada(6)	35	24	11
2	Songadh (1C)	38	28	10
3	Khanpar (2A)	28	16	12
4	Palasa (5B)	32	20	12
5	Thangadh (1D)	32	20	12
6	Sadala (4C)	34	21	13
7	Tarnetar (3A)	31	18	13
8	Makansar (14)	28	14	14
9	Vinaygadh (8A)	35	22	13
10	Ratidevali (7B)	27	17	10
11	Lunsar (9)	31	17	14
12	Jambudia (13)	34	14	20
13	Saltanpur (10A)	31	14	17
14	Paneli (12)	29	16	13
15	Matel (11)	32	18	14

Fig.V.1


PLASTICITY CHART
(IS-1498-1970)
PLASTICITY INDEX (IP)
0
10
20
30
40
50
60
LIQUID LIMIT (WL) % →
0
10
20
30
40
50
60
70
80
90
100
ML
ML-ZONE
CL
ML
MI
CI
CH
MH
WL-35
A-LINE

of poorly crystalline kaolinite.

Plastic limit (WP) influences liquid limit. It is the lowest moisture content expressed as a percentage by weight of the oven dried clay at which it can be rolled into threads 1/8 inch in diameter without breaking into pieces. Fireclays which cannot be rolled into threads at any moisture content are considered non-plastic. The degree of crystallinity and particle size influences plastic limit. Fireclays from study area shows variation in plastic limit from 14 to 28.

Plasticity index (IP) is the difference between the liquid limit and the plastic limit. It is the range of moisture content in which clay is plastic.

The plasticity indices for fireclay vary from 10 to 20 usual values about 25 (Fig. V.1).

Particle Size Analysis

The particle size analysis of fireclay is a very important characteristics, since it influences many other properties such as plasticity, dry strength, and base exchange capacity. The most feasible method of analysis is the sedimentation method, where the rate of settling of the particles in water is measured and then converted by stocks low into particle size. The assumption must be made that the particles are individual and that their settling rate is the same as that of equivalent spheres. This requires a dilute suspension and complete defloculation.

Pre-treatment	IS : 2720 Part I (1970)
Hydrometer Analysis	IS : 2720 Part IV (1970)

Particle size distribution shown by graph (Fig. V.2 to V.6).

Textural classes are computed from gravel, sand, silt and clay percentage obtained from above mentioned figures. Trangular diagram showing textural classes (Fig. V.7).

Hydrometer Analysis of Material Passing 63 Micron I.S.Sieve

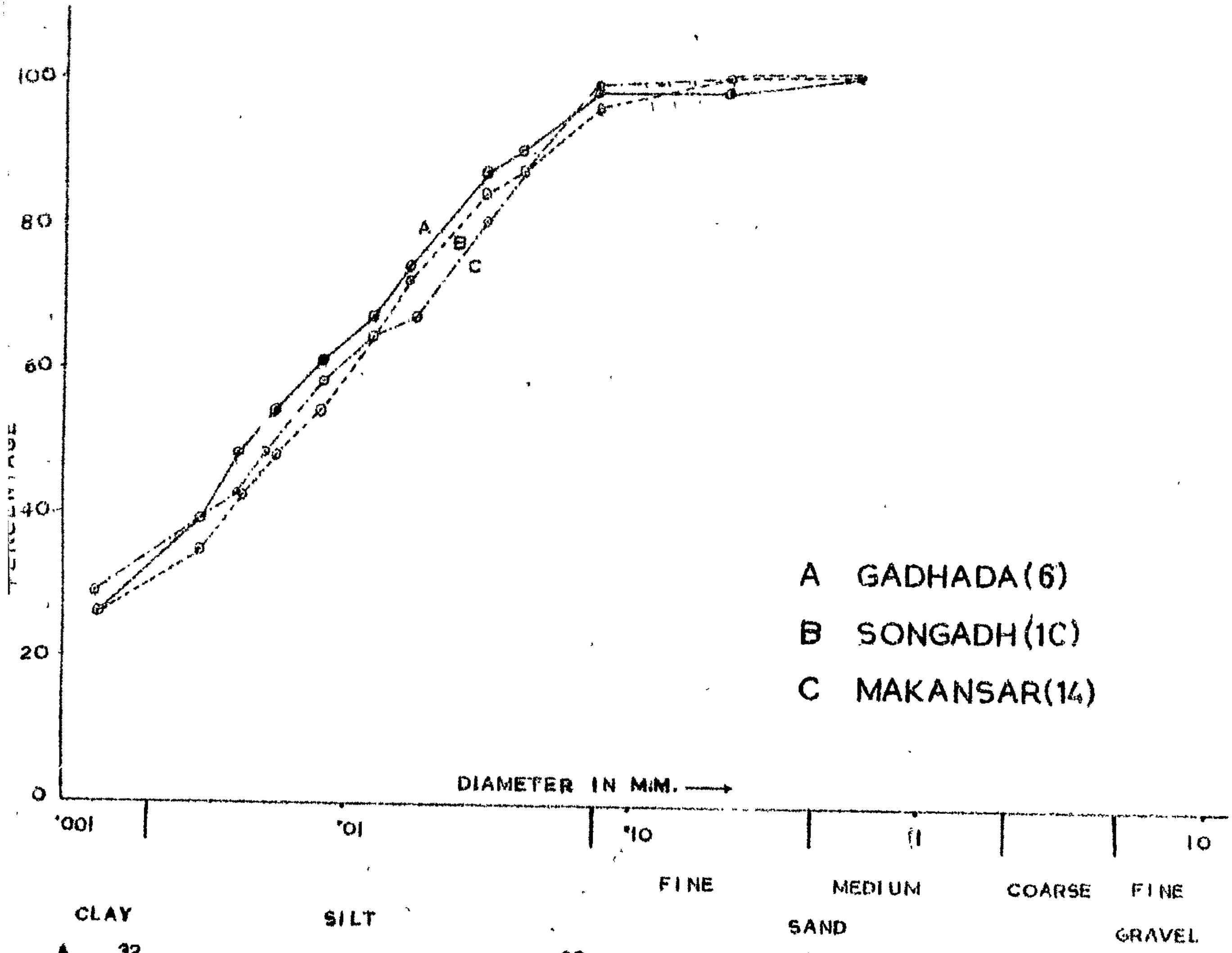
Weight of pre-treated oven dry fireclay	100 gm
Hydrometer reading observed at Temp.	26°C
Temperature correction	1
Miniscus correction	1.0
Dispersing agent (Sodium Hexa-Meta Phosphate)	
Strength	4%
Quantity used	100 ml
Correction	4

TABLE V. 6

HYDROMETER ANALYSIS

	Gadhada (6)		Songadh (10)		Makansar (14)	
	Diameter (mm)	Percentage Finer Than	Diameter (mm)	Percentage Finer Than	Diameter (mm)	Percentage Finer Than
Sieve Analysis	0.600	100	0.600	100	0.600	100
	0.212	98	0.212	100	0.212	100
	0.075	98	0.075	96	0.075	99
Hydrometer Analysis	0.040	90	0.042	87	0.042	87
	0.030	87	0.030	84	0.030	80
	0.016	74	0.016	71	0.017	67
	0.012	67	0.012	64	0.012	64
	0.0081	61	0.0081	54	0.0081	58
	0.0056	54	0.0056	48	0.0056	48
	0.0041	48	0.0042	42	0.0042	42
	0.0030	39	0.0030	35	0.0030	39
	0.00129	26	0.00129	26	0.00126	29

Fig. V.2



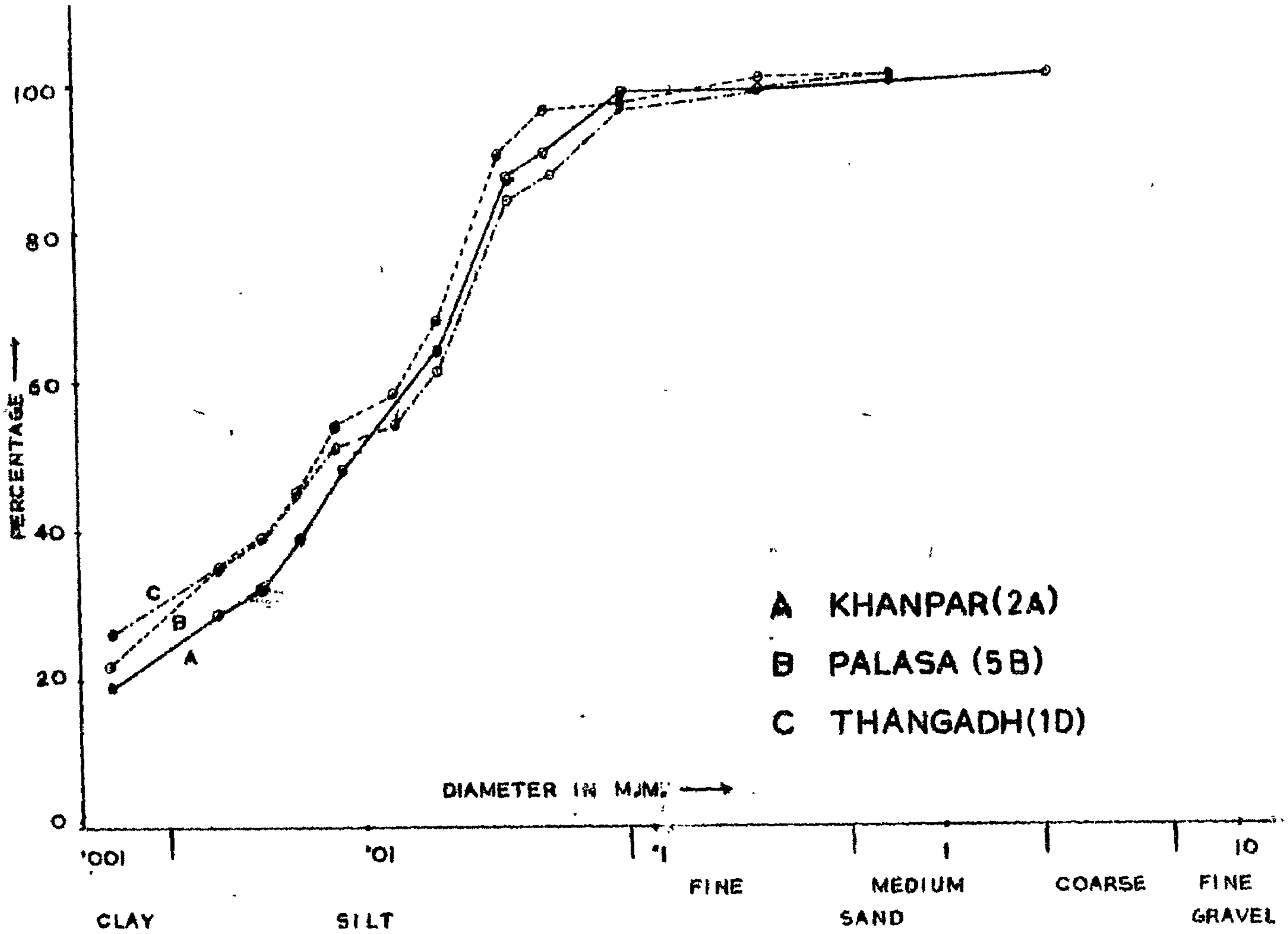
A	32	98	99	100
B	30	96	99	100
C	34	99	99	100

PARTICLE SIZE ANALYSIS BY HYDROMETER

TABLE V.6 (Contd.)

	Khanpar(2A)		Palasa (5B)		Thangadh(1D)	
	Diameter (mm)	Percentage Finer than	Diameter (mm)	Percentage Finer than	Diameter (mm)	Percentage Finer than
Sieve Analysis	0.60	99	0.6	100	0.6	100
	0.212	98	0.212	100	0.212	98
	0.075	98	0.075	97	0.075	96
Hydrometer Analysis	0.04	90	0.04	96	0.042	87
	0.03	87	0.028	90	0.03	84
	0.017	64	0.017	64	0.017	61
	0.012	58	0.012	58	0.012	54
	0.0081	48	0.0078	54	0.0078	51
	0.0058	39	0.0056	45	0.0056	45
	0.0042	32	0.0042	39	0.0042	39
	0.003	29	0.003	35	0.003	35
	0.00129	19	0.00129	22	0.00129	26

Fig. V·3



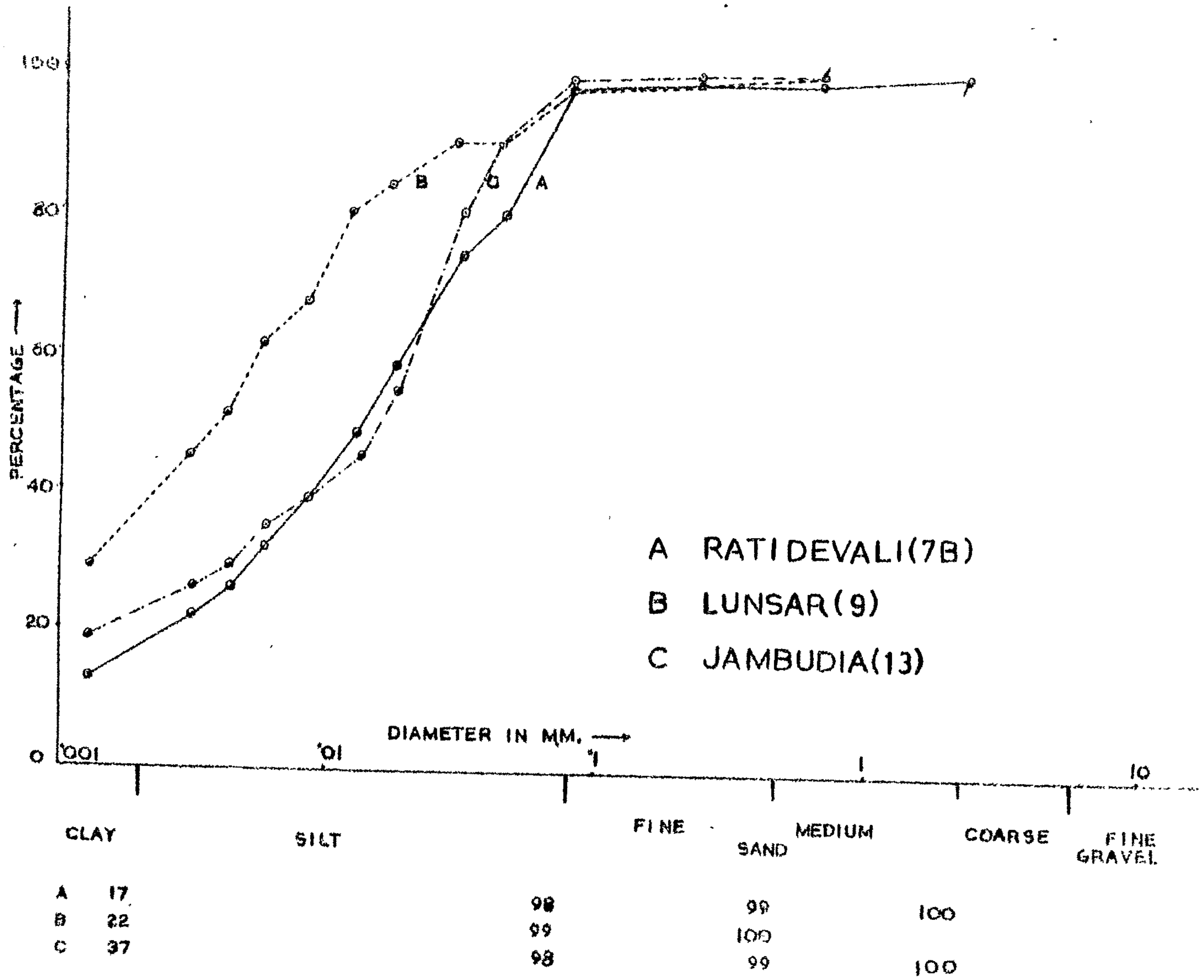
A	24	98	99	100
B	29	97	100	
C	31	96	99	100

PARTICLE SIZE ANALYSIS BY HYDROMETER

TABLE V.6 (contd.)

	Ratidevali(7B)		Lunsar (9)		Jambudia (13)	
	Diameter (mm)	Percentage Finer than	Diameter (mm)	Percentage Finer than	Diameter (mm)	Percentage Finer than
Sieve Analysis	0.6	99	0.6	100	0.6	100
	0.212	99	0.212	100	0.212	99
	0.075	98	0.075	99	0.075	98
Hydrometer Analysis	0.042	80	0.04	90	0.04	90
	0.03	74	0.03	80	0.028	90
	0.017	58	0.017	54	0.016	84
	0.121	48	0.0125	45	0.0115	80
	0.0083	39	0.0083	39	0.0081	67
	0.0058	32	0.0058	35	0.0056	61
	0.0043	26	0.0042	29	0.0041	51
	0.0031	22	0.0031	26	0.003	45
	0.00129	13	0.00129	19	0.00126	29

Fig. V.4

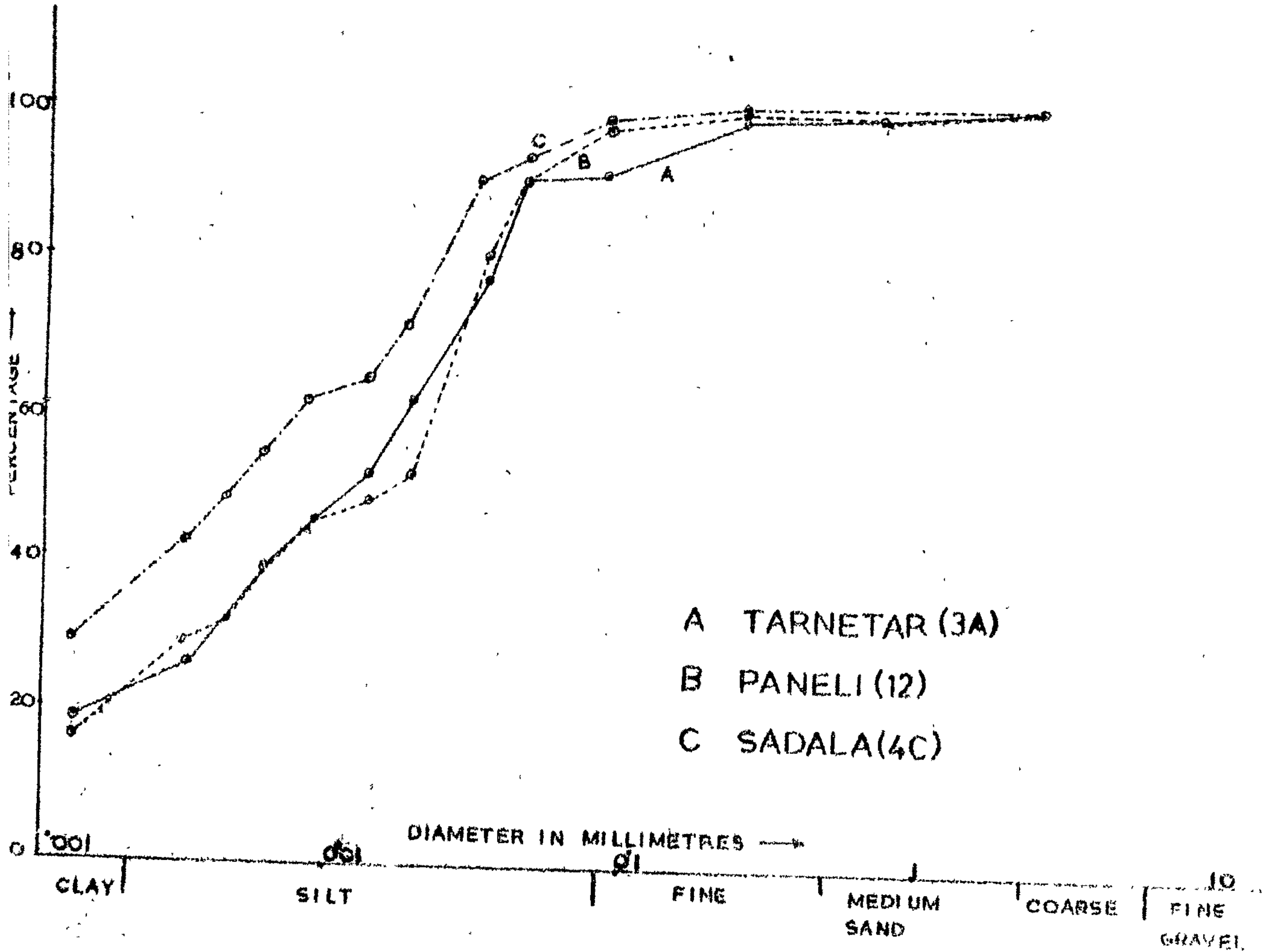


PARTICLE SIZE ANALYSIS BY HYDROMETER

TABLE V.6 (contd.)

	Tarnetar(3A)		Paneli (12)		Sadala (4C)	
	Diameter (mm)	Percentage Finer Than	Diameter (mm)	Percentage Finer Than	Diameter (mm)	Percentage Finer Than
Sieve Analysis	0.6	99	0.6	99	0.6	100
	0.212	98	0.212	99	0.212	100
	0.075	91	0.075	97	0.075	98
Hydrometer Analysis	0.04	90	0.04	90	0.04	93
	0.03	77	0.03	80	0.028	90
	0.017	61	0.017	51	0.016	71
	0.012	51	0.012	48	0.012	64
	0.0081	45	0.0081	45	0.0078	61
	0.0056	39	0.0056	39	0.0054	54
	0.0042	32	0.0042	32	0.0041	48
	0.0031	26	0.003	29	0.003	42
	0.00129	19	0.00129	16	0.00129	29

Fig. V.5



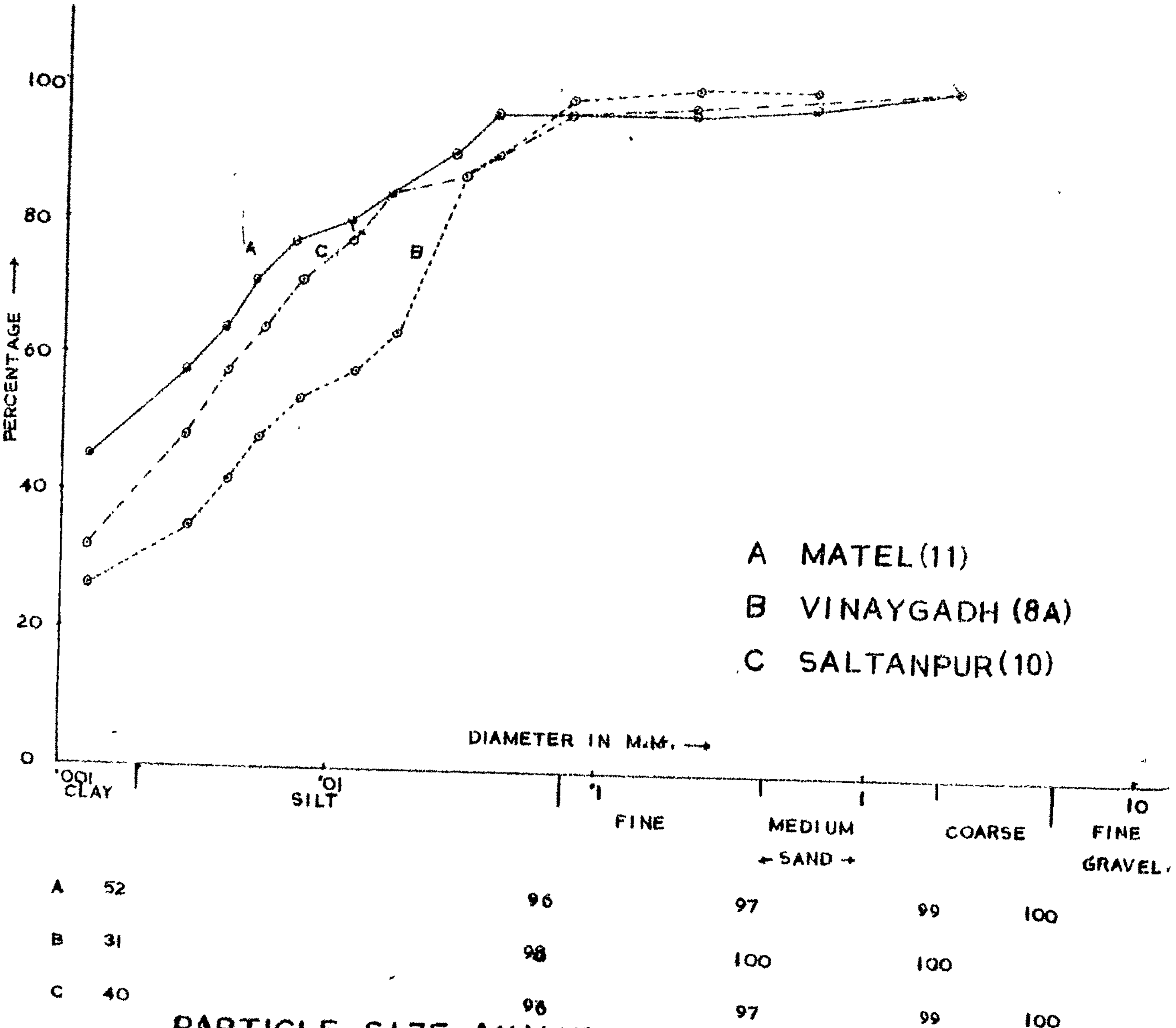
A	22	91	99	100
B	23	97	99	100
C	36	98	99	100

PARTICLE SIZE ANALYSIS BY HYDROMETER

TABLE V.6 (contd.)

	Vinaygadh (8A)		Saltanpur(10A)		Matel (11)	
	Diameter (mm)	Percentage Finer Than	Diameter (mm)	Percentage Finer Than	Diameter (mm)	Percentage Finer Than
Sieve Analysis	0.6	100	0.6	98	0.6	97
	0.212	100	0.212	97	0.212	96
	0.075	98	0.075	96	0.075	96
Hydrometer Analysis	0.04	90	0.04	90	0.04	96
	0.03	87	0.03	87	0.028	90
	0.017	64	0.016	84	0.016	84
	0.012	58	0.0115	77	0.0115	89
	0.0078	54	0.0078	71	0.0074	77
	0.0054	48	0.0056	64	0.0052	71
	0.0042	42	0.0041	58	0.0041	64
	0.003	35	0.0029	48	0.0029	58
	0.00129	26	0.00126	32	0.00126	45

Fig. V. 6



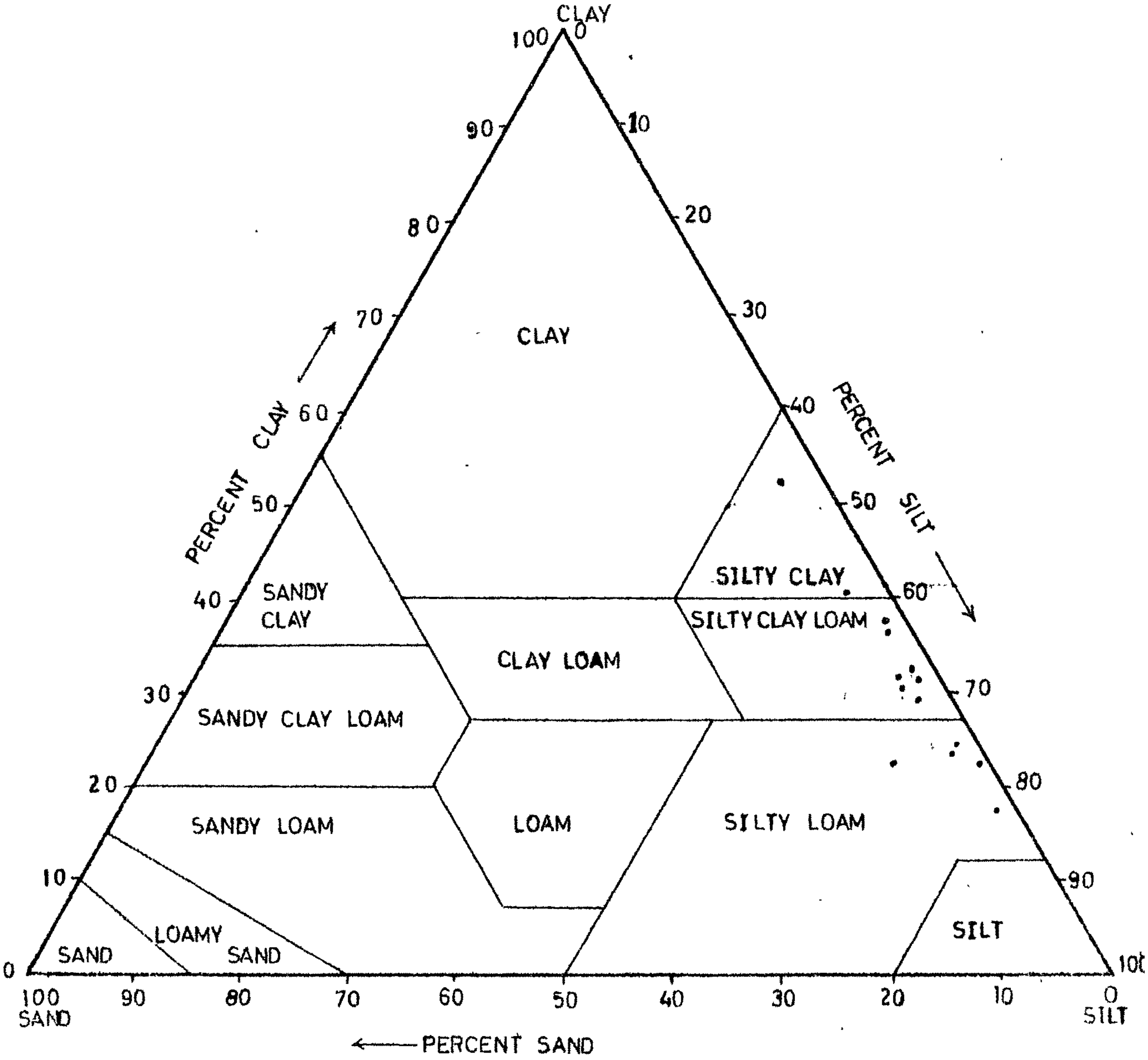
PARTICLE SIZE ANALYSIS BY HYDROMETER

TABLE V.7

MECHANICAL ANALYSIS

S No.	Locality	% Gravel (>2.0mm)	% Sand (2.00mm to 0.06mm)	% Silt (0.06mm to 0.002 mm)	% Clay (<0.002mm)
1	Gadhada (6)	Nil	2	66	32
2	Songadh (1C)	Nil	4	66	30
3	Makansar (14)	Nil	1	65	34
4	Khanpar (2A)	Nil	2	74	24
5	Palasa (5B)	Nil	3	68	29
6	Thangadh (1B)	Nil	4	65	31
7	Vinaygadh (8A)	Nil	2	57	31
8	Ratidevali (7B)	Nil	2	81	17
9	Lunsar (9)	Nil	1	77	22
10	Jambudia (13)	Nil	2	61	37
11	Saltanpur(10A)	Nil	4	56	40
12	Tarnetar (3A)	Nil	9	69	22
13	Paneli (12)	Nil	3	74	33
14	Sadala (4C)	Nil	2	62	36
15	Metel (11)	Nil	4	44	52

Fig. V.7



CLAY BELOW 0'002, SILT 0'002 TO 0'06, SAND 0'06 TO 2'0 mm.

TEXTURAL CLASSES OF FIRECLAY

TABLE V.8

ATTENBERG LIMIT VALUES IN RELATION TO PARTICLE SIZE

Locality	WP (%)	WL (%)	IP (%)
Thangadh (1D)			
1 u	36.6	62.4	25.8
0.5 u	39.2	68.8	29.6
Sadala (4C)			
1 u	37.2	65.2	28.0
0.5 u	39.9	72.6	42.7
Lunsar (9)			
1 u	36.8	64.2	27.4
0.5 u	39.6	71.4	31.2

Effect of Particle Size

The plastic limit and liquid limit values increases with decrease in particle size, and the liquid limit tends to increase somewhat more than the plastic limit. Therefore, most affecting factors are fineness of particles, degree to which the particles are cleaved or dispersed.

Another factor is that poorly ordered clay minerals break down into smaller particles more easily than well ordered minerals. So poorly ordered clay disperse with less effort; and it will show less difference in liquid and plastic limit values with variations in particle size.

Poorly crystalline fireclays consisting of finer particles show higher liquid and plastic limits.

Well crystalline fireclays consisting of coarser particles show lower liquid and plastic limits.

ION EXCHANGE CAPACITY

Physical properties of clay minerals are frequently dependent on exchangeable ions carried by a clay. Plastic properties of a clay depends on whether Na^+ or Ca^{++} is the exchangeable cation. The plastic characteristics of fireclays can be changed as per requirement by carrying out a base exchange reaction. In fireclay, common exchangeable cations are Ca^{++}, Mg^{++}. K^{+}, Na^{+}, H^{+} and common exchangeable cations are Cl^{-}, SO_4^{--}, NO_3^{--}, PO_4^{---}.

Method of Testing

1. Conversion of fireclay into H^{+} form

1 gm fireclay is kept on pre-prepared resion. 100 ml of 0.1 NaOH is continuously added to a column and washing is continued for 48 hours at room temperature with occasional shaking. The consumption of NaOH is determined by titration with 25 cc of 0.1 N HCl. Moisture content of raw clay is carried out before determining cation exchange.

$$\text{Cation Exchange} = \frac{(100 \text{ x N of NaOH}) - 4(\text{ml of HCl x N of HCl})}{\text{Wt of sample x } \frac{\%\text{ solid}}{100}}$$

2. Conversion of fireclay into OH^{-} form

This method is similar to conversion of fireclay into 'H' form, 0.1 N HCl is used instead of 0.1 N NaOH to convert clay into 'OH' form.

TABLE V.9

ION EXCHANGE CAPACITIES

Mine	Cation Exchange Capacity (miliequivalent/ 100 gm)	Anion Exchange Capacity (miliequivalent/ 100 gm)
1C	4.08	7.15
2A	6.47	7.25
4C	4.04	7.07
5B	5.20	7.49
6	6.44	7.52
7B	6.52	8.25
8A	6.06	8.15
9	4.58	8.53
10A	6.45	12.34
11	8.15	10.53
12	9.56	14.34

Anion Exchange Capacity

$$= \frac{(100 \times N \text{ of HCl}) - 4\ (\text{ml of NaOH} \times N \text{ of NaOH})}{\text{Wt of sample} \times \frac{\%\ \text{solid}}{100}}$$

Weiss and Russow (1963) concluded that for kaolinite, the exchangeable cations occur only on the basal oxygen surface of the silica tetradedral units, and therefore, cation-exchange capacity depends upon the thickness of kaolinite particles.

Cation exchange capacity of fireclays of Saurashtra shows low values from 4.04 to 9.15 indicating that the particle size of kaolinite is very small.

Kaolinite in fireclay shows absence of isomorphous substitution, so it has a small but definite ion exchange capacity. The sites of the exchange reactivity of kaolinite are generally agreed to be associated with the structural OH group on the exposed clay surfaces. Because of the differences in the balance of electrical charges of those hydroxyl ions along the lateral surfaces and those formed by the hydration of silica at the broken edges of the crystals, there may well be more than one class of exchange sites on kaolinite.

TABLE V.10

CHEMICAL ANALYSIS

Mine	Loss on Ignition %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	CaO %	MgO %	Na_2O %	K_2O %
1B	13.66	49.34	32.51	1.34	0.8	0.72	0.15	0.71	0.17
1C	13.49	53.45	30.65	0.67	0.8	0.74	0.18	0.25	0.15
1D	14.07	50.70	31.39	1.39	1.2	0.49	0.10	0.36	0.24
2A	13.42	51.02	31.42	1.34	0.9	0.48	0.98	0.22	0.27
2B	12.25	52.07	30.09	2.32	1.2	0.94	0.29	0.23	0.24
3B	14.31	50.36	32.15	0.57	0.8	0.93	0.08	0.29	0.22
3C	13.38	49.84	28.58	3.25	1.8	1.00	1.80	0.22	0.18
4C	13.59	52.04	30.41	1.36	1.1	0.60	0.24	0.33	0.26

Contd...

TABLE V.10 (contd.)

Mine	Loss on Ignition %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	CaO %	MgO %	Na_2O %	K_2O %
5B	14.18	53.6	30.14	0.55	0.7	0.36	0.08	0.23	0.10
6	12.56	53.07	29.49	1.58	0.9	0.60	0.24	0.34	0.28
7A	11.86	53.10	30.91	1.29	1.1	0.86	0.17	0.27	0.14
7B	11.25	53.84	31.55	1.21	1.4	0.75	0.03	0.28	0.15
8A	13.13	49.84	32.81	1.50	0.8	0.71	0.09	0.44	0.22
8B	12.40	53.09	31.40	0.94	0.8	0.73	0.28	0.29	0.25
9	11.19	53.51	31.25	1.51	0.8	0.72	0.15	0.23	0.27
10A	11.20	50.42	27.26	6.25	3.9	0.87	0.24	0.22	0.09
11	13.39	49.01	33.45	0.95	0.7	0.82	0.96	0.42	0.10
12	10.84	51.02	26.01	6.12	3.6	1.35	0.15	0.29	0.17
13	10.87	49.88	28.11	6.22	3.2	0.88	0.27	0.27	0.33
14	12.23	53.70	29.70	2.19	1.2	0.38	0.12	0.24	0.11

CHEMICAL ANALYSIS

Present author has combined normal methods of silicate analysis with methods given in IS : 1527-1971 for determining major elements of fireclays from Saurashtra. Na_2O and K_2O were determined by using flame photo-meter. The results are shown in Table V.10.

The Mineral Make-up from Chemical Analysis of Fireclay and the Calculations of Ionic Formula of Fireclay Minerals

The results of the work of Heindle (1932), Phelps (1950, 59), Weyl (1953), White (1959), Holdridge (1963), Norton (1970) are summarised below.

The mineral make-up of the fireclay fraction of a ceramic body has significant effect on the forming and firing properties of the ceramic mass. Presence of muscovite mica in primary fireclays greatly reduces the formation of high thermal expansion cristobalite. The superior fired color is obtained if TiO_2 content in fireclays is less. Presence of sub-sieve muscovite mica is responsible for the excellent casting and finishing properties of ceramic bodies. Fine muscovite has a much greater affinity for water than kaolinite of comparable particle size, which improves forming quality. Organic matter provides beneficial effects in white-ware forming. Free quartz in fireclays is important in thermal expansion and health hazard.

Holdridge (1963), devised a technique for calculating the major minerals in commercial fireclays from their ultimate chemical analysis. Present author has followed this technique to calculate mineral make-up of fireclays of Saurashtra. This technique can be illustrated by the following example.

Ultimate chemical analysis of fireclay from Mine 1B.

SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	CaO %	MgO %	K_2O %	Na_2O %	Ignition loss %
49.34	32.51	1.34	0.8	0.72	0.15	0.17	0.71	13.66

1. <u>Determination of Mica Content in Fireclay</u>

It is assumed that all K_2O is present as muscovite mica (K_2O, $3Al_2O_3$, $3SiO_3$, $2H_2O$) and all Na_2O is present as paragonite mica (Na_2O, $3Al_2O_3$, $2H_2O$).

Muscovite		Paragonite	
K_2O	11.81 %	Na_2O	8.12 %
Al_2O_3	38.44 %	Al_2O_3	40.05 %
SiO_2	45.23 %	SiO_2	47.12 %
H_2O	4.52 %	H_2O	4.71 %

(a) The muscovite content of the fireclay is

$$(0.17 + 11.81) \times 100 = 1.44\ \%$$

(b) The paragonite content is

$$(0.71 + 8.12) \times 100 = 8.74\ \%$$

Total mica = 10.18 %

2. Assignment of Al_2O_3, SiO_2, H_2O to Muscovite and Paragonite

(a) Assignment of Al_2O_3 to muscovite and paragonite :

Muscovite	Paragonite
1.44 x 0.3844 = 0.55	8.74 x 0.4005 = 3.496

Total Al_2O_3 in mica = (0.55 + 3.496) = 4.046%

(b) Assignment of SiO_2 to muscovite and paragonite

Muscovite	Paragonite
1.44 x 0.045 = 0.065	8.74 x 0.0471 = 0.412

Total H_2O in mica (0.065 + 0.412) = 0.48 %

(c) Assignment of H_2O to muscovite and paragonite

Muscovite	Paragonite
1.44 x 0.045 = 0.065	8.74 x 0.0471 = 0.412

3. Determination of Clay as Kaolinite

(Al_2O_3, $2SiO_2$, $2H_2O$)

Kaolinite	
Al_2O_3	39.53 %
SiO_2	46.51 %
H_2O	13.96 %

Total Al_2O_3 in fireclay		Al_2O_3 in mica		Al_2O_3 available for Kaolinite
(32.51	-	4.05)	=	28.46%

$$\frac{28.46}{39.53} \times 100 = \underline{71.99\% \text{ Kaolinite}}$$

4. Determination of free silica :

Total SiO_2 in fireclay		SiO_2 in mica		SiO_2 available for Kaolinite
(49.34	-	4.77)	=	44.57%

Silica Content in Kaolinite $= \frac{71.99 \times 46.51}{100} = \underline{33.48\%\ SiO_2}$

Free silica = Total silica - silica in kaolinite

$$44.57 - 33.48 = \underline{11.09\ \%}$$

5. Assignment of H_2O to Kaolinite :

$$\frac{71.99 \times 13.96}{100} = \underline{10.05\ \%\ H_2O}$$

6. Assignment of ignition loss to $CaCO_3$, $MgCO_3$

$$CaCO_3 = 56\ CaO + 44\ CO_2$$
$$MgCO_3 = 47.8\ MgO + 52.2\ CO_2$$

(a) $\frac{0.72}{56} \times 100 = 1.2g\ \%\ CaCO_3$

$1.29 - 0.72 = 0.57\%\ CO_2$

(b) $\frac{0.15}{47.8} \times 100 = 0.31\%\ MgCO_3$

$0.31 - 0.15 = 0.16\%\ CO_2$

Total CO_2 = 0.57 + 0.16 = 0.73%

Total Ignition loss %	H_2O in mica %	H_2O in Kaolinite%	Co_2 in $CaCO_3$ and $MgCO_3$ %
13.66	- 0.48	- 10.05	- 0.73

= 2.4 % ignition loss due to coaly matter.

7. (a) Assignment of Fe_2O_3 and TiO_2 to Ilmenite :

Ilmenite	Fe_2O_3	67.0 %
	TiO_2	33.0 %

$$\frac{1.34}{67} = \frac{X}{33}$$

X = % TiO_2 in ilmenite = 0.66%

∴ Total ilmenite = 1.34 + 0.66 = 2.0 %

(b) Assignment of TiO_2 to Rutile

TiO_2 as Rutile = Total TiO_2 - TiO_2 in ilmenite

= 0.8 - 0.66

= 0.14 % Rutile

8. The calculated mineral make-up of fireclay from mine 1B is given below in percentage :

Mica	10.18
Kaolinite	71.99
Free Silica	11.09
$CaCO_3$	1.29
$MgCO_3$	0.31
Ilmenite	2.00
Rutile	0.14
Coaly Matter	2.40

Calculation of Ionic Formula of Fireclay Mineral

Marshall (1949) devised a technique for calculation of ionic formula of fireclay mineral. Worrall (1959) has used this technique to calculate ionic formula of fireclay mineral for fireclays studied by him. Present author followed this method to calculate ionic formula for some of the fireclays from Saurashtra. Illustrated

TABLE V.11

RESULTS OF MINERAL MAKE-UP OF FIRECLAYS FROM SAURASHTRA

Mine	Mica %	Kaolinite %	Free Silica %	CaCO$_3$ %	MgCO$_3$ %	Ilmenite %	Rutile %	Coaly matter %
1B	10.18	71.99	11.09	1.29	0.31	2.00	0.14	2.40
IC	4.35	73.18	17.68	1.32	0.38	1.00	0.47	2.29
1D	6.46	72.96	13.77	0.88	0.21	2.07	0.52	3.08
2A	5.00	74.53	13.04	0.86	2.05	3.44	0.23	1.34
2B	4.86	71.29	16.66	1.68	0.61	3.46	-	1.01
3B	5.43	75.92	12.53	1.66	0.17	0.85	0.52	0.38
3C	4.23	68.84	15.90	1.77	3.77	4.85	0.2	1.32
4C	6.26	70.66	19.18	1.07	0.50	2.03	0.43	2.49
5B	3.68	72.55	18.15	0.64	0.17	0.82	0.43	3.46
6	6.56	68.05	18.38	1.07	0.50	2.36	0.12	2.02
7A	4.52	73.66	16.73	1.54	0.36	1.93	0.46	0.50
7B	4.72	75.08	16.72	1.34	0.06	1.18	0.80	-
8A	7.28	75.71	11.24	1.27	0.19	2.64	0.06	1.56
8B	5.69	73.76	16.14	1.30	0.58	1.40	0.34	0.98
9	5.12	73.97	16.74	1.29	0.31	2.25	0.06	0.50
10A	3.51	66.30	17.94	1.55	0.50	9.33	0.82	0.05
11	6.02	78.54	9.67	1.34	2.16	2.01	0.23	0.56
12	5.01	61.47	22.10	2.41	0.31	9.11	0.54	-
13	6.12	65.04	16.80	1.57	0.57	9.28	0.12	-
14	3.89	71.21	18,80	0.68	0.25	3.27	1.20	0.68

Example of fireclays from mine 1B is shown in Table V.12.

TABLE V. 12

Oxide	Weight Percen-tage	Equiva-lents per 100gm	Equiva-lents per Unit Cell	Number of Atoms per Unit Cell
SiO_2	53.75	3.5833	9.1530	2.288
Al_2O_3	30.65	1.8029	4.6050	1.535
Fe_2O_3	00.67	0.0250	0.0639	0.021
TiO_2	00.80	0.0400	0.1020	0.260
CaO	00.74	0.0260	0.0660	0.033
MgO	00.18	0.0038	0.0970	0.048
-	-	5.481	13.999	-

From chemical analysis it is expected that some of the alumina is replaced by other atoms. However, with this structure, the number of octahedral atoms must lie between two and three and number of tetrahedral atoms must be equal to two.

The equivalents per 100 gm was calculated by dividing weight percentage by equivalent weight.

In the ideal kaolinite formula $Al_2 Si_2O_5(OH)_4$ there are 18 ionic valencies (since the number of oxygen atom is exactly 9) so, the number of cation valancies must be equal to 18. Four of these are hydrogen, leaving 14 valancies to be filled by Al, Fe, Ti, Ca and Mg.

The total of equivalents per 100 gm was converted to 14 and each equivalent per unit cell was proportionately calculated from corresponding equivalent per 100 gm. The latter figures total 13.999 which is within the limits of error of calculation.

Each equivalent per unit cell was divided by appropriate valency giving number of atoms per unit cell.

The position of each atom now must be decided. In the 'ideal' formula the number of Si atoms must be equal to 2. Any deficiency must be made-up by Al^{+3}.

Since within the limits of experimental error, the number is 2, there can presumably be no substitute of Si^{4+} by Al^{3+}. The remainder of the atoms must be present as units of the octahedral layer (i.e. substituting for Al) or as exchangeable ions. Magnesium, ferric ion, and possibly titanium are all capable of entering the lattice, but calcium, on account of its considerable size, must be present as an exchangeable ion, external to the structure. Hence the formula is written as :

$$(Al^{+3}_{1.535}\ \underset{\underset{Ca^{2+}_{0.033}}{\downarrow}}{Fe^{+3}_{0.021}}\ Ti^{4+}_{0.26})\ (Si^{4+}_{2.288})\ (O_5(OH)_4)$$

The arrow indicates that Ca^{2+} is external to the main structure.

Fireclay Mine	Ionic Formula
2B	$(Al^{3+}_{1.519}\ \underset{\underset{Ca^{2+}_{0.043}}{\downarrow}}{Fe^{3+}_{0.075}}\ Ti^{4+}_{0.039})\ (Si^{4+}_{2.235})\ (O_5(OH)_4)$
3B	$(Al^{3+}_{1.65}\ \underset{\underset{Ca^{2+}_{0.044}}{\downarrow}}{Fe^{3+}_{0.019}}\ Ti^{4+}_{0.026})\ (Si^{4+}_{2.197})\ (O_5(OH)_4)$
4C	$(Al^{3+}_{1.516}\ \underset{\underset{Ca^{2+}_{0.027}}{\downarrow}}{Fe^{3+}_{0.043}}\ Ti^{4+}_{0.035})\ (Si^{4+}_{2.207})\ (O_5(OH)_4)$

5B $$(Al^{3+}_{1.527}\ \underset{\substack{\downarrow \\ Ca^{2+}_{0.017}}}{Fe^{4+}_{0.018}}\ Ti^{4+}_{0.228})\ (Si^{4+}_{2.208})\ (O_5(OH)_4)$$

6 $$(Al^{3+}_{1.496}\ \underset{\substack{\downarrow \\ Ca^{2+}_{0.027}}}{Fe^{3+}_{0.051}}\ Ti^{4+}_{0.029})\ (Si^{4+}_{2.288})\ (O_5(OH)_4)$$

DIFFERENTIAL THERMAL ANALYSIS

In the case of fireclay mineral (disordered kaolinite), differential thermal analysis shows characteristic endothermic reactions due to dehydration and loss of crystal structure, and exothermic reactions due to the formation of new phases at elevated temperatures.

The method of preparation of sample for DTA analysis influences the result. Spiel et al (1945) showed that for fireclays, the thermal curve varies with the particle size of the component minerals, particularly when the maximum size is about 2 micron. The intensity of the thermal reaction and the temperature of the peak decreases as the particle size decreases. The decrease in particle size is due to decrease in crystallinity, which is reflected in the differential thermal curve by lower intensity of reactions and a decrease in the temperature of the reaction peaks. Because of this reason the present author has kept the particle size between 0.6 to 2 micron for all the samples. Packing density is also kept nearly same for all samples because according to Evans and White (1958) though the thermal decomposition of loose powdered clay is chemically a first-order reaction, the decomposition rate decreases appreciably as the depth of the clay bed or packing density increases. Spiel et al (1945) presented a series of curves for kaolinite diluted by various quantities of an inert material, showing that the intensity of the reaction and the temperature of the peak decreases as the amount of material decreases; i.e. one can find out relative percentage of kaolinite in fireclays from different horizons. The present author has carried out differential thermal analysis of fireclays from different horizons of Tarnetar and Ratidevali mines and has concluded that kaolinite percentage in fireclays decreases from lower horizons to upper horizons.

The standard operating conditions for DTA instrument were as follows :

Model	DTA 02 Universal
Amount of sample material	100 mg fireclay mixed with 20 mg Al_2O_3
Reference Material	150 mg annealed Al_2O_3
Grain size (Ø) of sample material	0.6 - 2 micron
Location of sample material	Thermocouples located exactly in the centre of the sample, with direct contact to the heated substance
Furnace atmosphere	Air, without any current or turbulence
Sample holder	Platinum crucible Ø ~ 5 mm, ratio of length to diameter: 4 wall thickness 0.1 mm
Thermocouples	$pt\text{-}pt_{90}/Rh_{10}$, Ø 0.1-03 mm
Heating rate	10°C/min
Packing density	Loose packing without
Amplification	100
Paper speed	200 mm/hour

TABLE V.13

D.T.A. RESULTS OF FIRECLAYS FROM SAURASHTRA

Sample from Mine	Nature of the Reaction	Peak Temperature (°C)	Height of peak (ΔT)
Songadh (1C)	Exothermic	455	1.2
	Endothermic	535	0.5
	Endothermic	600	0.4
	Exothermic	960	0.6
Tarnetar (3A)	Exothermic	400	2.5
	Endothermic	540	2.8
	Exothermic	950	0.8
Sadala (4C)	Exothermic	420	2.3
	Endothermic	525	2.3
	Exothermic	950	0.3
Palasa (5B)	Exothermic	410	0.8
	Endothermic	530	2.9
	Exothermic	945	0.6
Ratidevali (7B)	Endothermic	540	2.8
	Exothermic	970	0.6
Vinaygadh (8A)	Endothermic	540	2.9
	Exothermic	950	0.6
Matel (11)	Exothermic	390	0.7
	Exothermic	450	0.4
	Endothermic	535	2.4
	Exothermic	950	0.4
Makansar (14)	Endothermic	530	2.9
	Exothermic	950	0.6

Characteristics of Peaks

All the samples have given broad endothermic peak of dehydration between the temperature range 70 to 115°C.

At the temperatures of the order of 200 to 300°C, the oxidation of any organic material begins. The rate of oxidation depends on the nature of the organic material, the amount of oxygen available, the ease of its access through the mass of clay to the organic material, and the temperature. This reaction is not shown by any fireclay though some organic remains are present in some of the fireclays. At 600°C peak is observed in the case of fireclay from Songadh (1C) because it contains more carbonaceous matter.

The oxidation, of sulfides, present in many fireclays, generally in the form of pyrite, begins between 400 and 500°C. Fine grained pyrite in the presence of abundant oxygen, loses its sulfur and oxidizes with an abrupt exothermic reaction in this temperature range. Fireclays from Songadh, Tarnetar, Sadala, Palasa and Matel show this characteristics peak as it contains some fine grained pyrite.

The sulfur liberated from the sulfides may react with alumina and/or iron, made available by the partial disruption of the lattice structures of some of the clay minerals at about the same temperature, to form compounds which are resistant to oxidation, the lattice disruption is that accompanying the loss of hydroxyl from the structure of the clay mineral. Their presence is often indicated by a black core showing up in the centre of fire bricks. In fact, black coring is a particular problem in the firing of refractory fireclay. The present author recommends removal of pyrite from these fireclays before they are used for refractory industries.

Characteristics of Kaolinite Peak

In all the fireclay samples the initial "moisture" peak is larger as compared to that for well crystallized kaolinite peak. The main endothermic peak is somewhat lower usually at about 540°C or less. The endothermic reaction corresponds only to the dehydration of the mineral. An exothermic reaction occurs when reconstruction of mineral occurs at high temperature. The exothermic peak is known to be very much affected by extraneous materials, e.g. it is suppressed by substances containing alkali metals. Wahl (1958) concluded that considerable primary mullite is formed on heating of well-organized kaolinite, whereas very little develops from poorly organized kaolinite.

Since the exothermic peak between 950 to 970°C range, shown by fireclays is small and broad, the present author feels that this peak may be due to the formation of very little primary mullite from poorly organized kaolinite.

The effects of impurities on the thermal reactions of kaolinite have been studied by Gruvey, Henry and Heystek (1949). Fluxing impurities, present in brick clays, tend to suppress the thermal reactions, whereas some oxide additions accelerate the formation of mullite.

The ordered structure of Kaolinite varies considerably from sample to sample. This peak does not appear to be of a consistent magnitude even for different samples of same material, but the presence of this peak (exothermic) may reflect a series of reactions.

DTA curves of the fireclay from study area show a strong endothermic deflection (upto 2.9ΔT) between 510 to 540°C due to the dehydration and the decomposition of the structure, and a middle-strong (small and broad) exothermic effect between 940 and 970°C; reflecting the crystallization of a spinel phase. (Orcel, Norton, 1939). The dehydration temperatures of kaolinites depend strongly on the degree of disorder of the structure. The DTA is suitable to determine the degree of this disorder (disordered after the crystallographic b-axis).

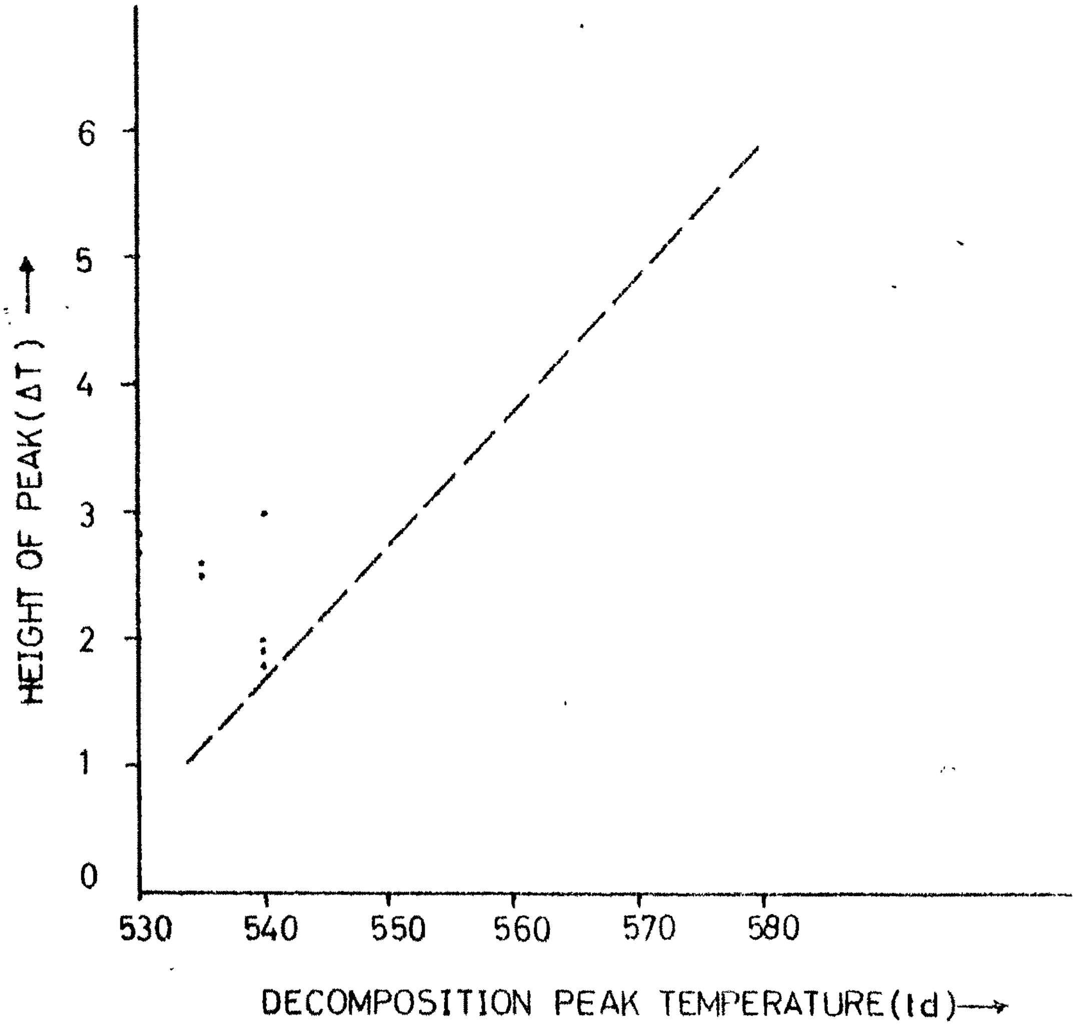
Determination of the Degree of Disorder in Fireclay-Kaolinites

Werner and Smykatz-Kloss (1974) devised a method of to find out degree of disorder in Kaolinites from fireclays.

Kaolinites from fireclays are frequently disordered. The different sheet packets are disordered in the direction of crystallographic b-axis by an amount n.bo/3. During diagenetic process the disorder of kaolinite - decreases. Sometimes during carbonization disorder is completely lost.

Endothermic peak temperature of kaolinites and Δ T values of this peak decrease with increasing disorder, as observed in the graph (Fig. V.8).

Fig. V. 8



FIRECLAY SHOWING PRESENCE OF DISORDERED KAOLINITE
FROM DTA DATA

Exothermic peak also reflects the degree of disorder. The exothermic peak appears between 980° and 1005°C in DTA curves of well ordered kaolinites and decreases down to 940° ± 1°C or still less with increasing disorder. All the samples decomposed below 555°C could be identified as being disordered.

The ΔT-values increase with increasing homogeneity of the samples, but generally decrease with decreasing grain size. The finer the sample, the more homogenous is its grain size. So the present author has kept the grain size (Ø) fraction as 0.6 - 2 micron for all samples.

The classification of disordered kaolinite into following sub-groups is based on the decomposition peak temperature alone.

Sub-groups	Decomposition peak Temperature (°C)
Extremely disordered	530
Strongly disordered	530-555
Little disordered	555-575
Well ordered	575

This classification is valid only if the determination is carried out under the standard operating conditions of DTA mentioned earlier.

According to this classification fireclay from Sadala (4C) is extremely disordered, and all other fireclays are strongly disordered.

The decomposition peak temperature (td) of 530°C seems to be very low according to all published DTA data of kaolinites. Therefore this value is taken as "Zero Value" for the exact determination of the degree of disorder.

1. The multiplication of the factor (td = 530) by the ΔT value delivers a first index for this degree of disorder (compare with Smykatz-Kloss, 1940).

2. The relation of all indices to the index of well-ordered reference material (with the relative order = 100) gives the degree of order of each studied sample in percent of the order of the reference kaolinite. The degree of disorder of all investigated kaolinites is more than Murfreesboro, has been chosen as a reference material because it is fine-grained homogenous and strongly disordered.

If the values of decomposition temperature are less than or equal to 530°C, the calculation of degree of disorder is almost impossible. In present studies out of 8 samples analysed for DTA, only 4 samples of fireclays showing value of td more than 530° were calculated for disorder in kaolinite.

	Endothermic Peak (ΔT)	Exothermic Peak (ΔT)
Kaolinite Murfreesbora	578 (6.1)	983 (2.1)
Fireclay Tarnetar (3A)	540 (2.8)	950 (0.8)

540-530 (value considered as zero) = 10, Tarnetar (3A).

10 x 2.8 (ΔT value) = 28

578 - 530 = 48 Murfreesbora (Standard)

48 x 6.1 = 232.8

232.8 is considered as 100.

So order of kaolinite for Tarnetar Fireclay

$$- \text{equal to} = \frac{28}{232.8} \times \frac{100}{1} = 12.03\ \%$$

$$100 - 12.03 = 87.97\ \%\ \text{disorder.}$$

Degree of disorder in kaolinite in some of the fireclays from Saurashtra is given below:

1. Tarnetar (3A) = 87.97%
2. Ratidevali (7B) = 87.97%
3. Vinaygadh (8A) = 87.54%
4. Matel (11) = 94.85%

Combination of Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) of Fireclays from

Wiedemann (1964), Tets and Wiedemann (1968) and F. Paulik et al (1966), are among the pioneer workers in the field of combined DTA and TGA studies.

Thermogravimetric Analysis

Reactions occurring in minerals during thermal treatment (heating), result in the weight and energy changes which can be identified and measured very precisely by thermogravimetric analysis.

The operating conditions for DTA and TGA instruments were as follows:

Crucible	... Platinum
Atmosphere	... Oxygen free, inert nitrogen
Furnace	... Kanthal Super

Fig. V. 9

Differential Thermal Analysis and Thermogravimetry of Fireclays of Saurashtra

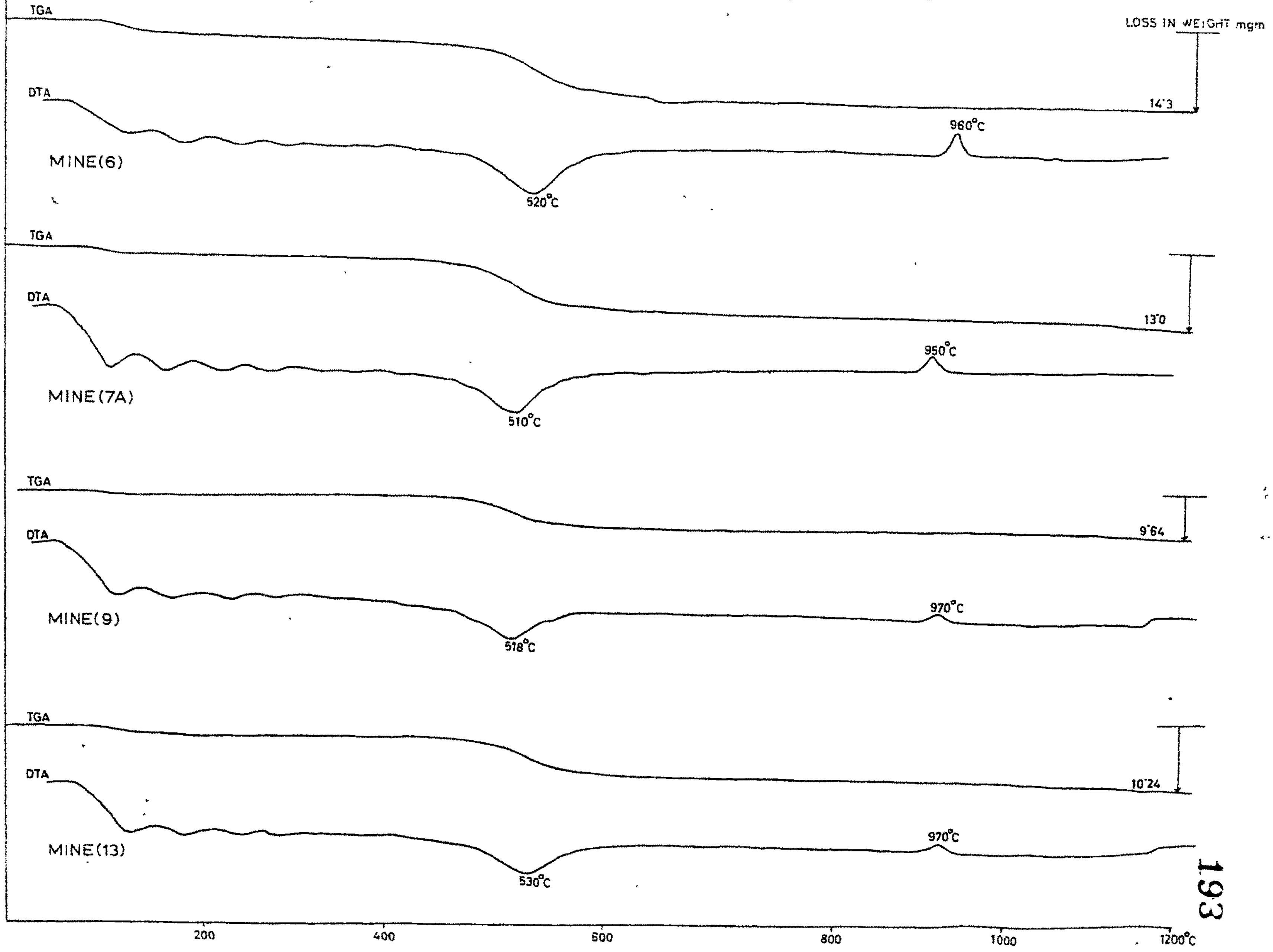
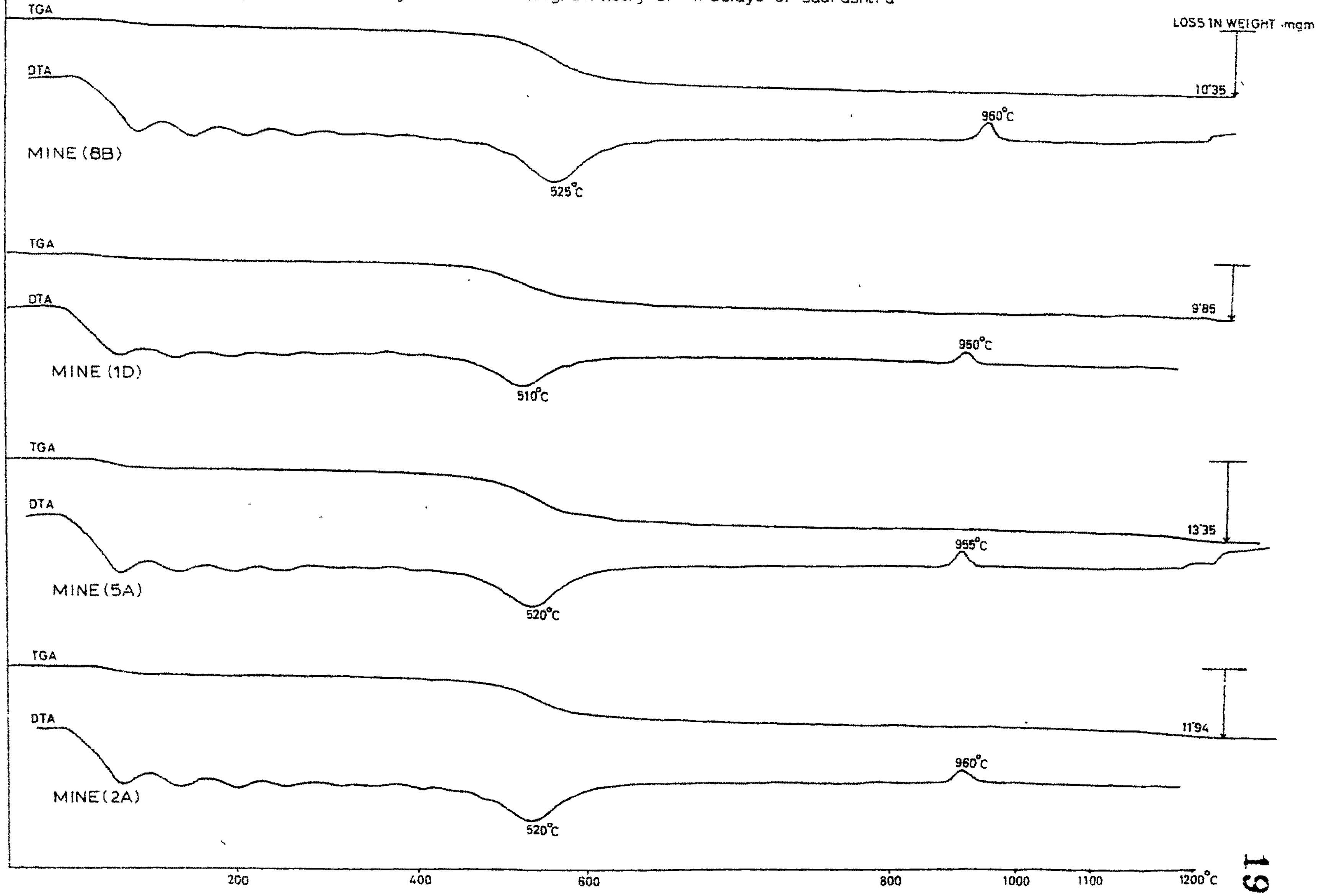


Fig.V.10

Differential Thermal Analysis and Thermogravimetry of Fireclays of Saurashtra



Heating Rate	... 6°C/min
Maximum temperature	... 1200°C
Temperature of cold junction	... 25°C
TG Range	... full scale of 100 division = 100 mgm
DTA Range	... 200 uv
Reference Substance	... AR Grade Al_2O_3
Chart Speed	... 6"/hour

DTA and TGA graphs are given as Fig. V.9 and V.10.

The results of TGA curves indicates quantitative weight loss due to loss of H_2O, CO_2 or SO_3 etc.

Results obtained from TGA are given below:

TABLE V.14

Sample	Wt of Sample before the run (mgm)	Wt loss Recorded/ Removed after the run (mgm)
Gadhada (6)	101.00	14.30
Khanpar (2A)	99.15	11.94
Vinaygadh (8B)	99.80	10.35
Palasa (5A)	100.00	13.35
Ratidevali (7A)	98.90	13.00
Songadh (1D)	99.60	9.85
Jambudia (13)	99.68	10.24
Lunsar (9)	97.26	9.64

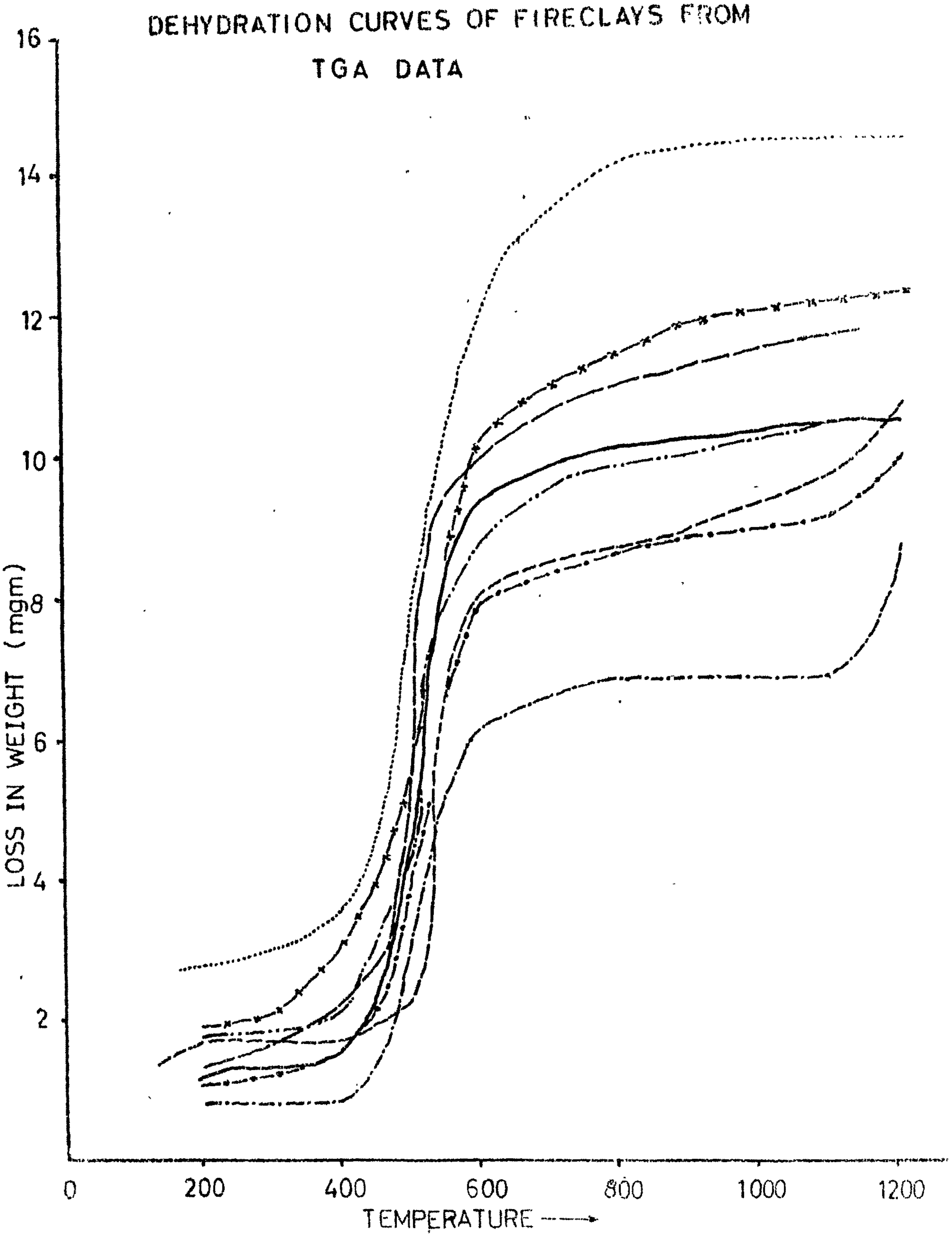
Dehydration curves obtained from the Thermal Gravimetric Analysis are given in Fig. V.11.

Dehydration and Phase Change on Heating of Fireclays

Dehydration curves for all fireclays are almost flat upto about 400°C, showing little loss of water at low temperatures. Thermal reactions are also absent in the low-temperature region of DTA curves. DTA curve for fireclay (poorly crystalline kaolinite) shows a small initial endothermic reaction indicating that, when there is irregularity in the arrangement of the kaolinite units, a small amount of water may be present between the layers. This is in accord with the slightly greater c-axis spacing of poorly crystalline kaolinite as compared with well-crystallized kaolinite.

A series of dehydration curves obtained by the present author shows that most of the dehydration has taken place between 400 and 600°C. Ross and Kerr (1931) show that precise temperature for the loss of this (OH) lattice water varies from kaolinite to kaolinite, and this variations may be explained by variations in particle size; since dehydration temperature is known to decrease with decreasing particle size. Poorly crystalline material

Fig. V-11


DEHYDRATION CURVES OF FIRECLAYS FROM
TGA DATA
LOSS IN WEIGHT (mgm)
16
14
12
10
8
6
4
2
0
200
400
600
800
1000
1200
TEMPERATURE ---→

loses its hydroxyl water more readily than well-crystallized kaolinite.

A small amount (2 to 3%) of water is retained at about 600°C, and this is lost gradually upto about 750 to 800°C, where dehydration is essentially complete. A reduction of particle size, particularly if it is accompanied by poorer crystallinity tends to reduce the temperature required for the loss of hydroxyls and causes them to be lost more gradually over a longer temperature interval. Brindley and Nakahira (1957) have deduced activation energies of 65 Kcal per mole for the dehydration of poorly crystalline kaolinite.

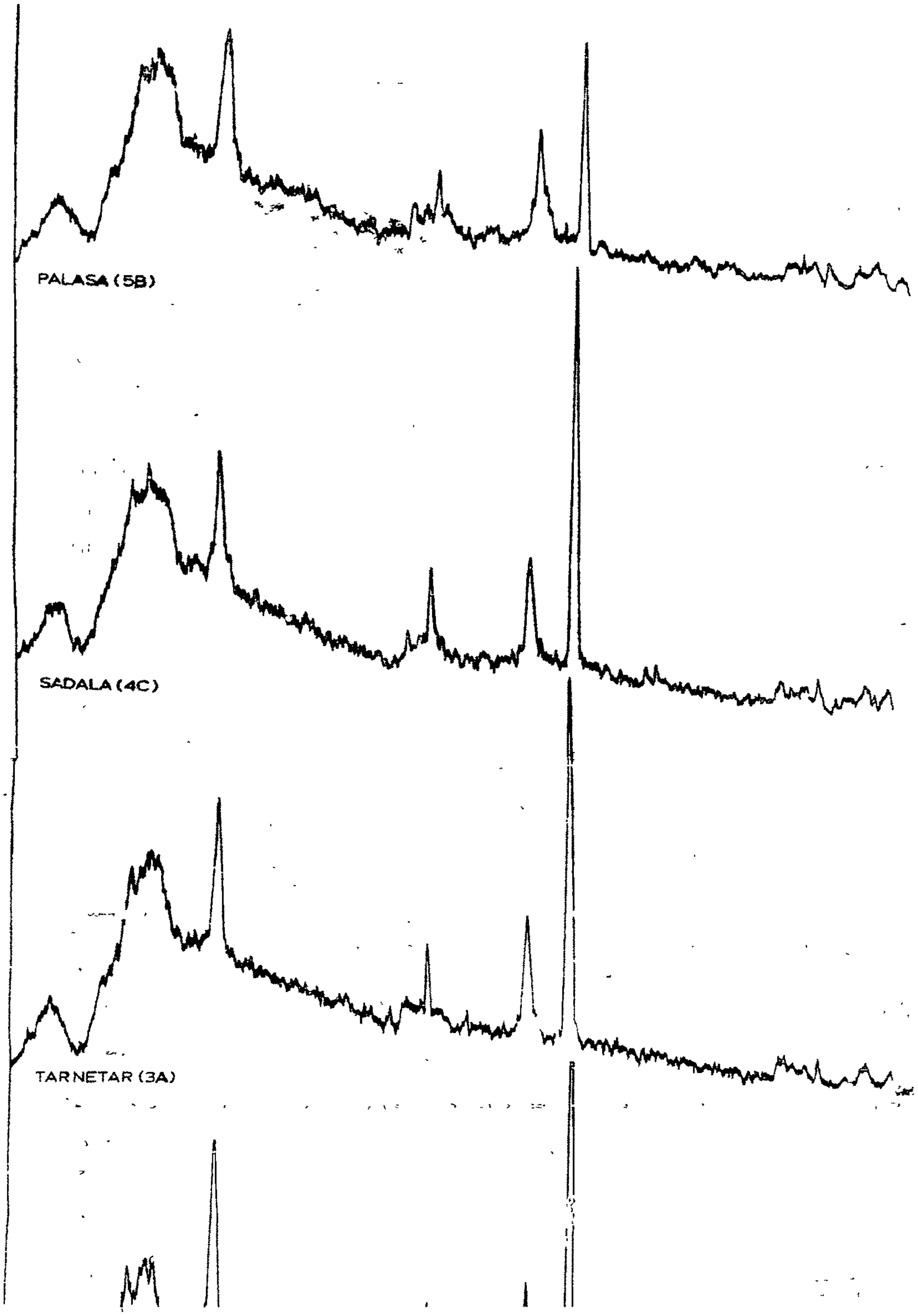
X-RAY DIFFRACTION

As X-ray diffraction patterns are directly related to crystal structures, they are better suited for the recognition of structural groups and structural varieties of clay minerals.

The majority of clay minerals have layer silicate structures with a marked basal cleavage and platy habit. The basal reflections generally designated as 001, are

Fig. V.12

X RAY DIFFRACTOGRAMS



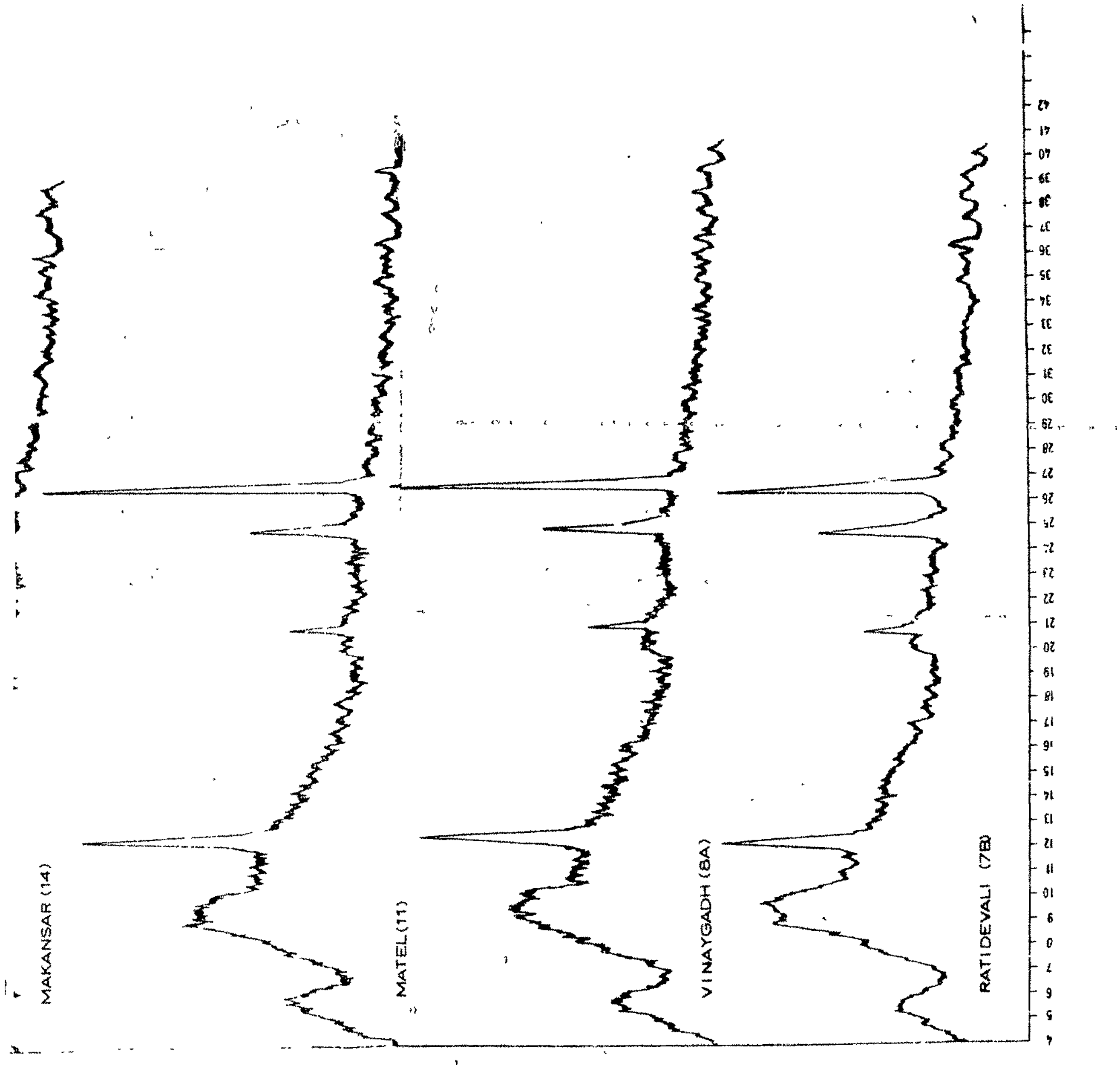

MAKANSAR (14)
MATEL (11)
VINAYGADH (8A)
RATIDEVALI (7B)
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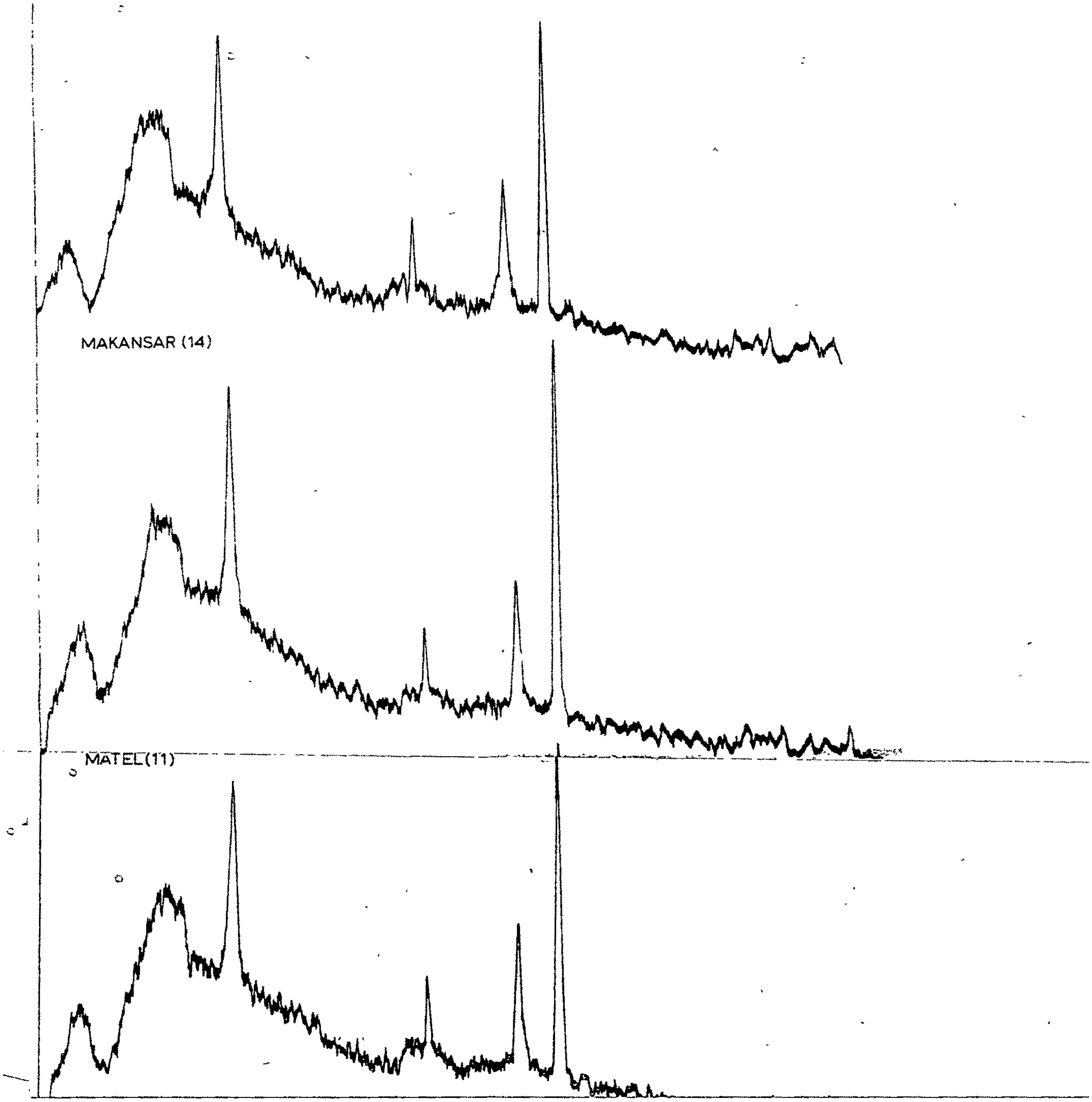
Fig. V.13

X RAY DIFFRACTOGRAMS



easily recognized more particularly when preferentially oriented aggregates are used. These reflections, if indexed 001, 002, 003 etc. give directly the thickness of the structural layers. The structure of the unit cell often contains more than one such layer depending on the manner in which the layers are stacked on each other. The stacking sequence determines the particular structural variety of the mineral and generally is less easily determined than the layer thickness.

Interpretation of 14A° Spacing

14A° Spacing indicates the presence of chlorite, vermiculite or montmorillonite.

The chlorite mineral is modified by partial dehydration at 600° to 700°C so that the 14A° reflection is of enhanced intensity. This effect is of particular interest in regards to iron-bearing chlorite which normally gives a very weak 14A° reflection.

The (001) reflection of chlorite falls at the same location (002) reflections of vermiculite and montomorillonite as observed in present studies. To confirm the presence of chlorite, heat treatment of the fireclay

Tarnetar (3A) and Ratidevali (8B) was carried out in air at 600°C. At this temperature heat treatment caused vermiculite and montmorillionite to collapse to a spacing of about 9.5 to 10.5A°, whereas chlorite was unaffected. In the present studies (Fig. V.14) chlorite remained unaffected but no enhanced intensity was observed in 9.5 to 10.5A° spacings. The presence of chlorite is clearly indicated by 14A° spacing. At 600°C chlorite is modified by partial dehydration so that the 14A° reflection is enhanced in intensity. This effect is of particular interest in regard to iron-bearing chlorite which normally gives a very weak 14A° reflection.

As chlorite is very fine grained, (< 1 micron) it becomes very difficult to determine the nature of chlorite. It appears to be closely intergrown with a kaolinite mineral. It has not been possible so far to separate these minerals hence the identity of chlorite remains unknown.

Interpretation of 10A° Spacing

10A° Spacing indicates unexpanded mica type layers or the presence of hydrated halloysite. Mica tends to be preferentially oriented parallel to the basal plane.

White (1950) treated illite with $MgCl_2$ to precipitate the exchanged potassium. The range of basal spacings extending from 10A° to 14A° or more, is connected primarily with hydration which is extremely variable in many of these minerals. Therefore, all these minerals are placed in mica type structural group. Barshad (1950) considers that the ionic radii, the valency, and the total charge of the interlayered cations, as well as the nature of the interlayered substances seems to determine the extent of the interlayer expansion of the mica type of crystal lattice.

Interpretation of 7A° Spacing

Spacing of 7A° indicates a kaolinite type mineral. In all fireclays studied by the present author 14A° chlorite reflection is not pronounced, so chlorite is confused with kaolinite because (002) reflection of chlorite coinsides with the (001) of kaolinite. In some cases if the amount of chlorite is small, the (004) reflection forms only a sholder on the high angle side of the (002) kaolinite peak. This was not observed in present samples. A weak 14A° line and a strong 7A° line does not mean a small amount of 14A° mineral (chlorite) and a predominance of a 7A° mineral (kaolinite). The interpretation requires a careful evaluation of the particular minerals which are present. Following treatments were made to confirm the presence of 7A° spacing minerals.

1. Fireclay samples were heated to 600°C to suppress kaolinite peak (Fig. V.14).

At this temperature kaolinite tends to lose its crystalline character, whereas chlorite is only partially dehydrated, causing increased intensity of the 14A° reflection.

2. Since chlorite is soluble in warm dil HCl, it can be removed from fireclay and easily recognized. (Fig. V.14). Fireclays from Tarnetar (3A) and Ratidevali (8B) were treated with hot HCl and observed that 14A° spacing disappears, while there is practically no change in the intensity of 7A° spacing.

It is, therefore, confirmed that fireclays contain little chlorite and predominant kaolinite mineral.

Structure of Kaolinite

Brindley and his colleagues (1946, 1951) explained

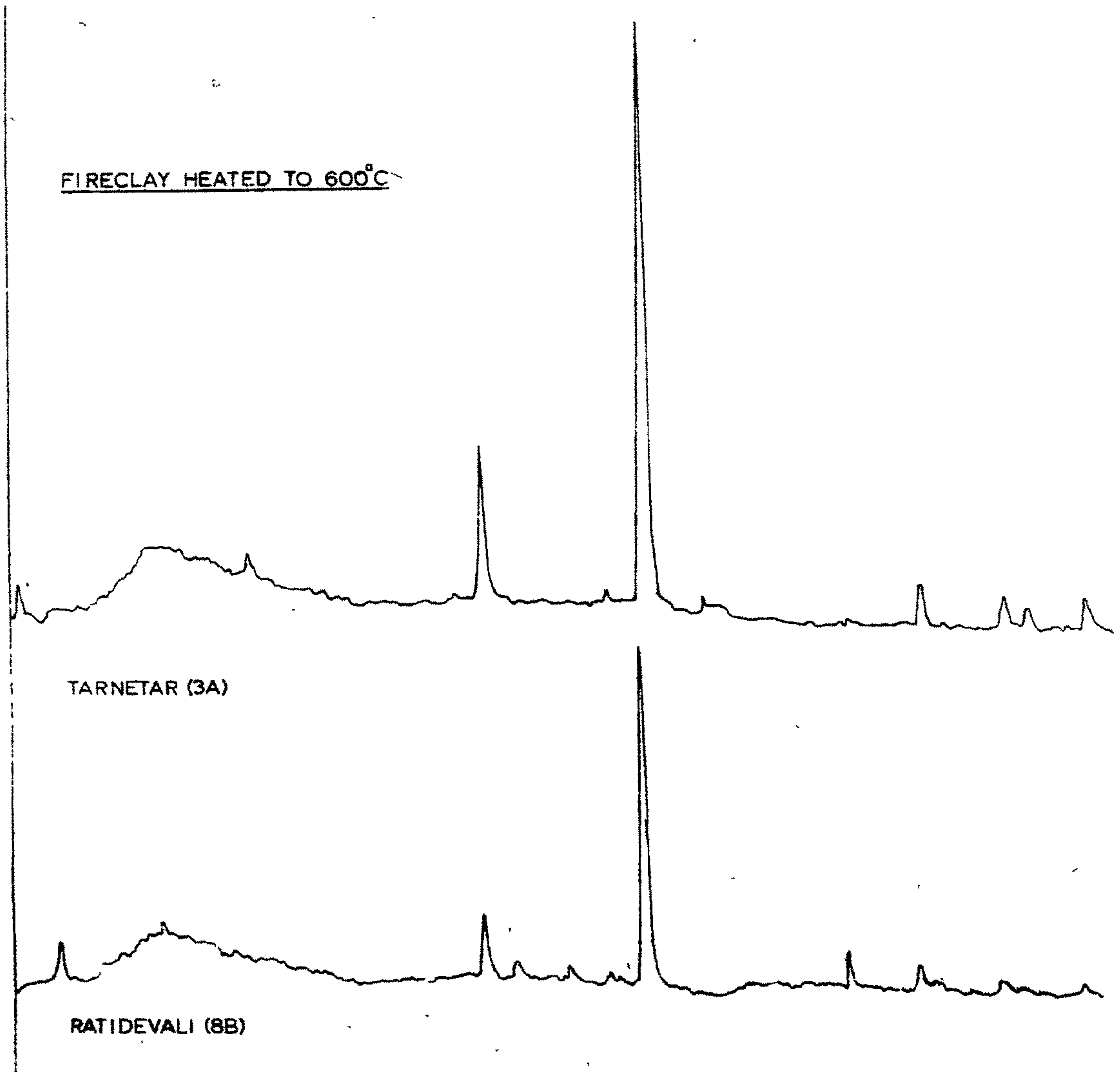


Fig. V.14

X RAY DIFFRACTOGRAMS

the structure of kaolinite more precisely. It is composed of a single tetrahedral sheet and a single alumina octahedral sheet so combined that the tips of the silica tetrahedron and one of the layers of the octahedral sheet form a common unit. All the tips of the silica tetrahedrons point in the same direction and towards the centre of the unit made of the silica and octahedral sheets. The dimension of the sheets of tetrahedral units and of the octahedral units are closely similar in their a and b dimensions, and consequently composite octahedral-tetrahedral layers are readily formed.

In the layer common to the octahedral and tetrahedral groups 2/3 of the atoms are shared by the silicon and aluminium, and then they become oxygen instead of hydroxyl. Only 2/3 of the possible positions for aluminium in the octahedral sheet are filled, and there are three possible planes of regular population of the octahedral layer with aluminium. The aluminium atoms are considered to be so placed that two aluminium atoms are separated by a hydroxyl above and below; thus, making a hexagonal distribution in a single plane in the centre of the octahedral sheet. The hydroxyl group is placed so that each hydroxyl is directly below the perforation of the hexagonal net of oxygen in tetrahedral sheet.

The changes within the structure are balanced i.e., there are no charges on the lattice due to substitutions within the lattice. The structural formula is (OH) and $Si_4Al_4O_{10}$ and the theoretical composition expressed in oxides is SiO_2 (46.54%), Al_2O_3 (39.50%) and H_2O (13.96%). In relatively poor crystalline variety such as kaolinite from fireclay, substitution of iron and titanium for aluminium is common.

Kaolinite group consists of sheet units continuous in the 'a' and 'b' directions and stacked one above the other in the 'c' direction. The thickness of these units is about 7A°.

The plane between the unit layer is a cleavage plane. In kaolinite the cleavage is not so pronounced as in other clay minerals. So the mineral is not readily dispersible in water into extremely small units.

Brindley (1951) has pointed out that distinction between well crystallized kaolinite and poorly crystalline "fireclay kaolinite" may be made by studying the two groups of three reflections at 2.55, 2.52, 2.49A° and 2.37, 2.33, 2.28A°. Fireclay kaolinite shows only two reflections at about 2.5 and 2.3A°. It is observed for all studied fireclay samples from Saurashtra that 2.5 and 2.3A° reflections are present in all samples while other reflections are seldom present.

The transition from well-crystallized to poorly crystallized kaolinite is shown by broadening and weakening of the reflections with the complete elimination of weaker ones. The basal reflection also increases from 7.14 to as much as 7.20A° and even more for Saurashtra fireclays. The group of lines from (020)/(d=4.46) to (002)/(d=3.57) particularly reflect the change to lower crystallinity. In this region the clearly resolved doublet ($11\bar{1}$) and ($1\bar{1}1$) of well crystallized material gives way to a single band, affording good evidence for the decrease in crystallinity.

Characteristics of Fireclay Kaolinite

The poorly crystallized kaolinite occurs in less distinct hexagonal flake shaped masses than the well crystallized variety and the particle size is generally smaller. The poorly organized material tend to be somewhat more dispersible in water so that there is more cleavage between units and reduction in particle size as compared to well crystallized kaolinite.

In the poorly organized kaolinite the structure is highly disordered along the b-axis with unit layers randomly displaced by multiples of one third of the 'b' dimension. There is some randomness in the distribution of aluminium atoms among octahedral positions. The first order spacings are slightly higher (7.15 to 7.20A°) and less sharply defined for the poorly crystalline than for well crystallized, suggesting some occasional interlayer water between the silicate units. Dehydration curves (Fig. V.11) tend to confirm the presence of such water.

The operating conditions for the X-ray diffraction instrument were as follows:

Instrument used	...	Phillips Holland
X-ray Generator	...	PW 1130/00
Goniometer	...	PW 1050/25
Recorder	...	PM 8000
Scanning speed	...	1°/min
Paper speed	...	10mm/min
Time constant	...	4 sec
H.V.	...	40 kv/15 MA

Receiving slit	...	0.2 mm
Divergent slit (Scattering slit)	...	1°
Target	...	Copper Kα radiation
Filter	...	Nickel

Results obtained from the graphs (Fig. V.12 and V.13) of the fireclays studied under X-ray diffraction are given in Tables (V.15 to V.22).

TABLE V.15

Locality : Songadh(1C) : X-ray Diffraction Results.

$(2\theta)^{\circ}$	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.65	15.62	13	16.66	Chlorite
8.9-10.00	9.52	16	20.51	Degraded illite with some expandable mineral [illegible] interlayer in it Poor crystallinity
12.20	7.25	40	51.28	Poorly crystalline Kaolinite (001)
20.90	4.25	25	32.05	Quartz
24.90	3.57	32	41.02	Kaolinite (002)
26.75	3.33	78	100.00	Quartz
36.50	2.46	6	7.66	Kaolinite (131,200)
37.60	2.39	4	5.12	Kaolinite (003)
38.40	2.34	5	6.17	Kaolinite (202, 131)
39.40	2.29	6	7.66	Kaolinite (132,201)
40.20	2.24	4	5.12	Kaolinite (040, 221)

TABLE V.16

Locality : Tarnetar (3C) : X-ray Diffraction Results.

(2 θ)°	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.68	15.55	12.0	17.14	Chlorite
8.8 - 9.90	9.50	20.0	28.57	Poorly crystalline degraded illite with some expandable mineral in it.
12.35	7.16	31.0	44.28	Poorly crystalline kaolinite (001)
20.94	4.24	14.0	20.00	Quartz
24.96	3.56	25.0	35.71	Kaolinite (002)
26.70	3.34	70.0	100.00	Quartz
35.20	2.55	3.5	5.00	Kaolinite ($20\bar{1}$, 130)
36.74	2.48	5.0	7.14	Kaolinite ($13\bar{1}$, 200)
38.62	2.33	5.0	7.14	Kaolinite ($20\bar{2}$, 131
39.60	2.27	3.5	5.00	Kaolinite ($13\bar{2}$, 201)

TABLE V.17

Locality : Sadala (4C) : X-ray Diffraction Results.

$(2\theta)^\circ$	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.62	15.71	10.5	13.13	Chlorite
8.78-10.00	9.87	23.0	28.75	Degraded illite with expandable mineral interlayer within it Poorly crystalline
12.28	7.20	26.0	32.50	Kaolinite (001)
19.82	4.48	5.0	6.25	Kaolinite (02 -)
20.78	4.27	15.0	18.75	Quartz
25.00	3.56	22.0	27.50	Kaolinite (002)
26.68	3.34	80.0	100.00	Quartz
34.90	2.57	4.0	5.00	Kaolinite ($20\bar{1}$, 130)
36.40	2.47	6.0	7.50	Kaolinite (131, 200)
38.30	2.35	6.5	8.13	Kaolinite ($20\bar{2}$, 131)
39.25	2.29	5.5	6.88	Kaolinite ($13\bar{2}$, 201)

TABLE V.18

Locality : Palasa (5B) : X-ray Diffraction Results.

(2 θ)°	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.72	15.44	10.0	24.39	Chlorite
9.00-10.20	9.67	23.0	56.09	Degraded illite with expandable mineral interlayer within it Poorly crystalline
12.38	7.19	26.5	64.63	Poorly crystalline kaolinite (001)
20.98	4.23	12.0	29.27	Quartz
25.00	3.56	23.0	56.09	Kaolinite (002)
26.75	3.33	41.0	100.00	Quartz
33.55	2.52	4.0	9.75	Kaolinite (13$\bar{1}$, 200)
36.55	2.46	5.0	12.19	Quartz
37.72	2.38	3.5	8.53	Kaolinite (003)
38.50	2.33	4.2	10.24	Kaolinite (20$\bar{2}$, 131)
39.50	2.27	3.5	8.53	Kaolinite (13$\bar{2}$, 201)

TABLE V.19

Locality : Vinaygadh (8A) : X-ray Diffraction Results.

$(2\theta)^{\circ}$	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified
5.72	15.43	12.0	20.00	Chlorite
8.8-10.20	9.65	16.5	27.30	Degraded Illite with some expandable mineral in it Poorly crystalline
12.39	7.13	35.0	58.33	Poorly crystalline Kaolinite (001)
20.90	4.25	14.0	23.33	Quartz
24.92	3.57	25.0	41.66	Kaolinite (002)
26.84	3.32	60.0	100.00	Quartz
36.00	2.49	5.0	8.33	Kaolinite ($13\bar{1}$, 200)
36.60	2.45	5.0	8.33	Quartz
37.75	2.38	4.0	6.66	Kaolinite (003)
38.50	2.33	4.0	6.66	Kaolinite ($20\bar{2}$, 131)
39.45	2.28	4.0	6.66	Kaolinite ($13\bar{2}$, 201)

TABLE V.20

Locality : Ratidevali (7B) : X-ray Diffraction Results.

(2Θ)°	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.60	15.77	11.0	23.40	Chlorite
8.8-9.90	9.45	21.0	44.68	Degraded illite with expandable mineral in it Poorly crystalline
12.30	7.19	28.0	59.57	Poorly crystalline kaolinite (001)
20.85	4.26	13.0	27.63	Quartz
24.90	3.57	26.0	55.32	Kaolinite (002)
26.60	3.34	47.0	100.00	Quartz
36.45	2.48	6.0	12.76	Kaolinite ($13\bar{1}$, 200)
36.45	2.34	3.5	7.44	Kaolinite (131, 200)
39.25	2.29	3.0	6.38	Kaolinite ($13\bar{2}$, 201)
40.10	2.25	3.0	6.38	Quartz

TABLE V. 21

Locality : Matel (11) : X-ray Diffraction Results.

$(2\ \theta)^{\circ}$	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.90	14.97	15.0	22.73	Chlorite
9.0- 9.80	9.48	18.0	27.27	Degraded illite with some expandable mineral in it poorly crystalline
12.38	7.19	39.0	59.09	Poorly crystalline Kaolinite (001)
20.98	4.23	12.0	18.18	Quartz
25.00	3.56	22.0	33.33	Kaolinite (002)
26.72	3.33	66.0	100.00	Quartz
35.10	2.55	4.0	6.06	Kaolinite (20$\bar{1}$, 130)
36.60	2.45	4.0	6.06	Quartz
37.82	2.38	4.5	6.82	Kaolinite (003)
39.52	2.28	5.5	8.33	Kaolinite (13$\bar{2}$, 201)

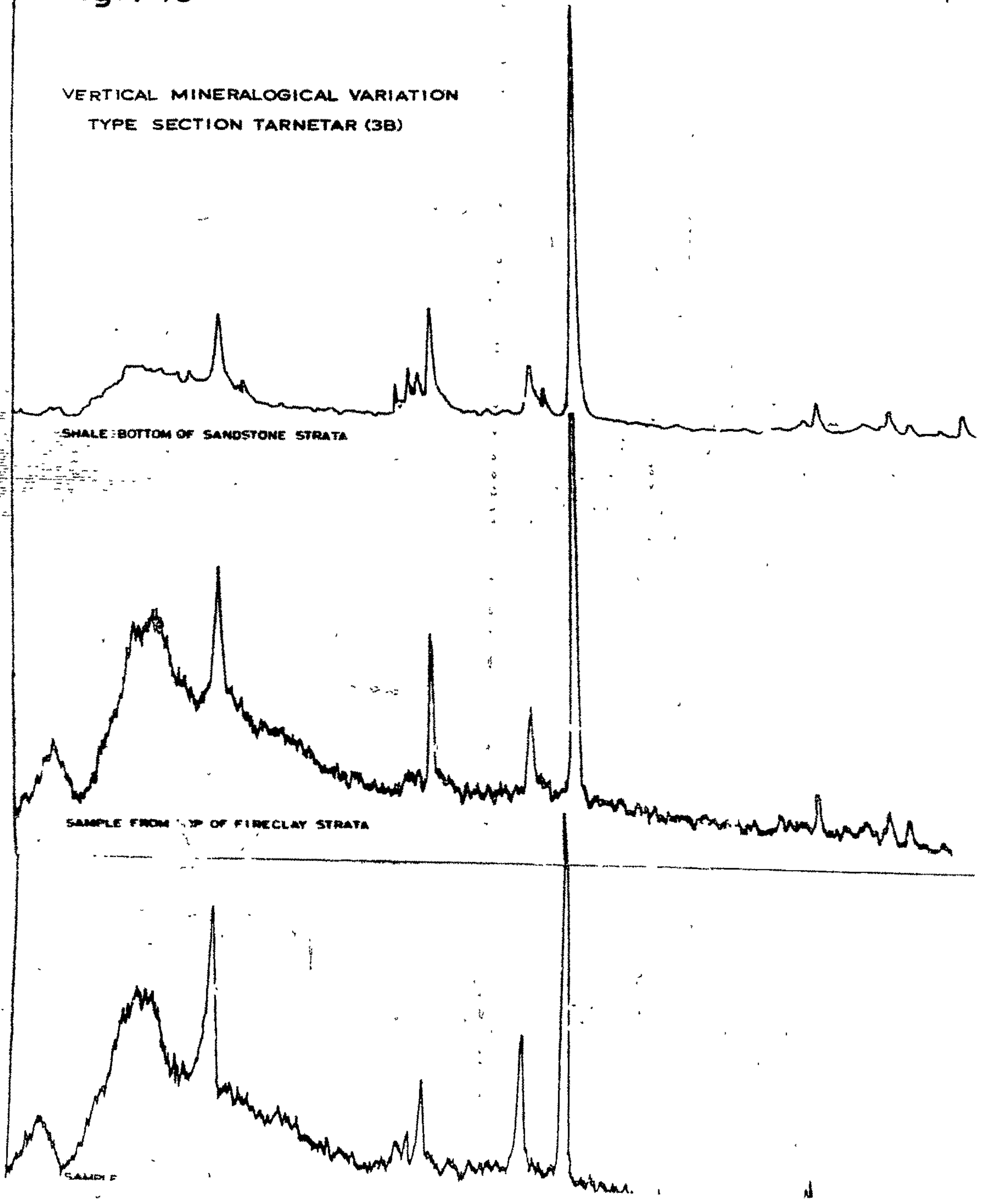
TABLE V.22

Locality : Makansar (14) : X-ray Diffraction Results.

(2)°	(d)A°	Observed Intensity (Io)	Calculated Intensity (Ic/I)	Mineral Identified (Indices)
5.45	16.20	13	25	Chlorite
8.5-10.00	9.65	19.5	37.5	Poorly crystalline degraded illite with some expandable mineral interlayer in it.
12.22	7.24	32	61.54	Poorly crystalline Kaolinite (001)
20.72	4.28	14	26.92	Quartz
24.72	3.59	22.5	43.27	Kaolinite (002)
26.42	3.77	52	100	Quartz
34.85	2.57	4	7.69	Kaolinite($20\bar{1}$,130)
35.75	2.51	3	5.77	Kaolinite($13\bar{1}$,200)
36.35	2.47	5	9.62	Quartz
38.15	2.38	3.5	6.73	Kaolinite (003)
39.15	2.29	4.5	8.66	Kaolinite ($13\bar{2}$, 201)

Fig.V.15

VERTICAL MINERALOGICAL VARIATION
TYPE SECTION TARNETAR (3B)



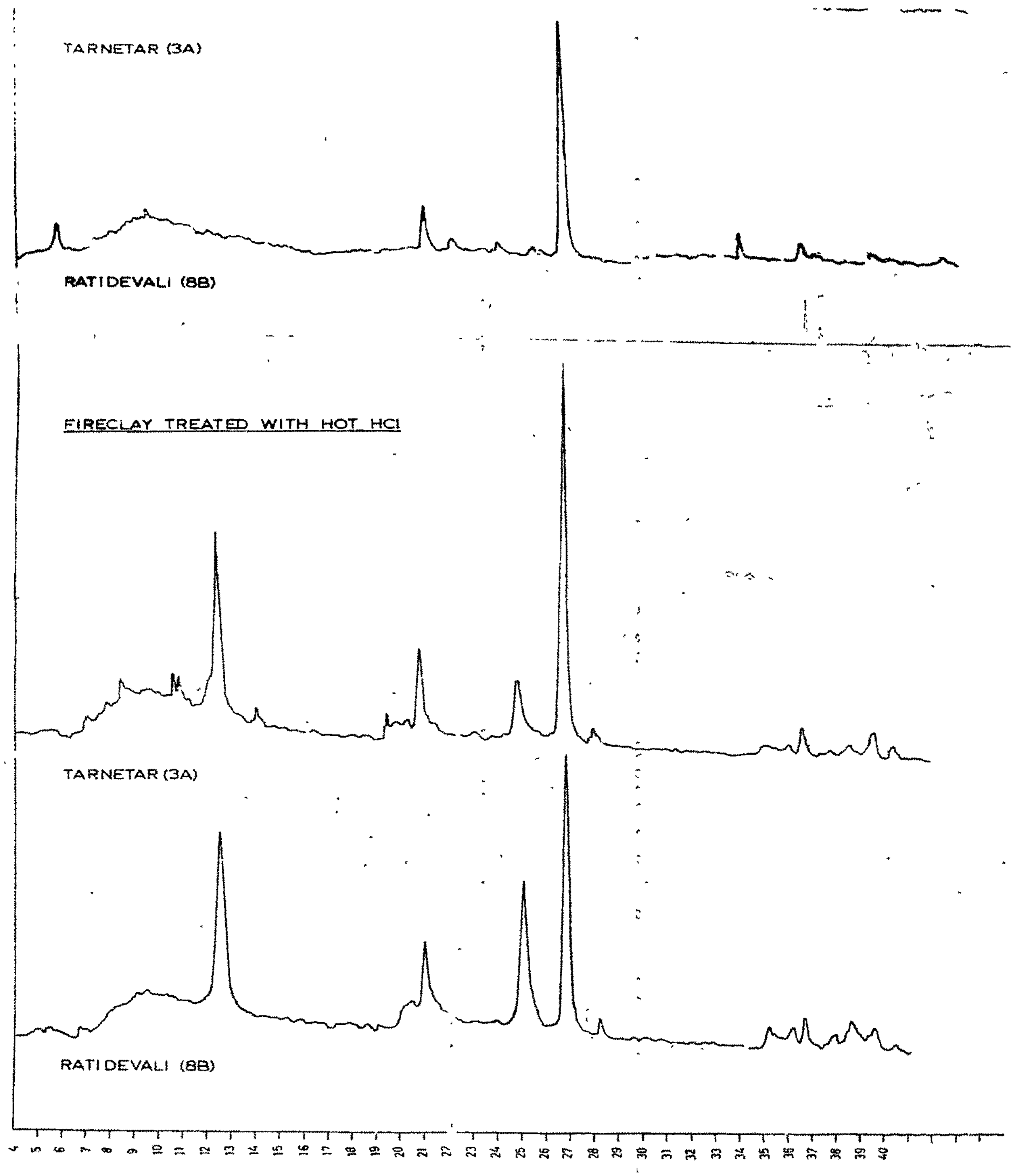

TARNETAR (3A)
RATIDEVALI (8B)
FIRECLAY TREATED WITH HOT HCl
TARNETAR (3A)
RATIDEVALI (8B)
4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

TABLE V.23

Tarnetar (3B) Vertical Mineralogical Variation

Horizons of Fireclay	2θ (Degree)	d (A°)	Observed Intensity	Mineral
Upper Fireclay	5.58	15.82	14	Clorite
	9.70	9.11	21	Illite
	12.35	7.16	30	Kaolinite
	20.75	4.28	32	Quartz
	24.75	3.59	18	Kaolinite
	26.65	3.33	80	Quartz
Middle Fireclay	5.68	15.55	12	Chlorite
	9.70	9.11	20	Illite
	12.38	7.14	31	Kaolinite
	20.94	4.24	14	Quartz
	24.96	3.57	25	Kaolinite
	26.70	3.33	70	Quartz
Lower Fireclay	5.76	15.33	12.5	Chlorite
	9.56	9.24	20	Illite
	12.38	7.14	36	Kaolinite
	20.96	4.23	17.5	Quartz
	25.05	3.56	27	Kaolinite
	26.76	3.33	66	Quartz

TABLE V.24

Songad (1A) Vertical Mineralogical Variation

Horizon of Fireclays	2θ (Degree)	d (A°)	Observed Intensity	Mineral
Upper Fireclay	5.62	15.71	12	Chlorite
	9.40	9.40	18	Illite
	12.50	7.08	40	Kaolinite
	20.75	4.28	29	Quarts
	24.88	3.57	28.5	Kaolinite
	26.82	3.32	80	Quartz
Middle Fireclay	5.65	15.63	13	Chlorite
	9.65	9.16	16	Illite
	12.40	7.13	40	Kaolinite
	20.90	4.25	25	Quartz
	24.90	3.57	32	Kaolinite
	26.75	3.33	78	Quartz
Lower Fireclay	5.60	15.77	11.5	Chlorite
	9.40	9.40	14.5	Illite
	12.20	7.25	45	Kaolinite
	20.98	4.23	16.5	Quartz
	24.98	3.56	35	Kaolinite
	26.70	3.33	64	Quartz

TABLE V.25

Ratidevali (7A) Vertical Mineralogical Variation

Horizons of Fireclays	2θ (Degree)	D (A°)	Observed Intensity	Mineral
Upper Fireclay	5.60	15.77	14	Chlorite
	9.50	9.30	21	Illite
	12.40	7.13	23	Kaolinite
	20.75	4.28	14	Quartz
	24.82	3.58	23	Kaolinite
	26.65	3.34	71	Quartz
Middle Fireclay	5.60	15.77	11	Chlorite
	9.55	9.25	21	Illite
	12.30	7.19	28	Kaolinite
	20.85	4.26	13	Quartz
	24.90	3.57	26	Kaolinite
	26.60	3.34	60	Quartz
Lower Fireclay	5.70	15.49	11	Chlorite
	9.65	9.16	20	Illite
	12.40	7.13	40	Kaolinite
	20.98	4.23	13	Quartz
	24.98	3.56	27	Kaolinite
	26.7	3.33	47	Quartz

TABLE V.26

Vinaygadh (8B) Vertical Mineralogical Variation

Horizons of Fireclay	2θ (Degree)	d (A°)	Observed Intensity	Mineral
Upper Fireclay	5.62	15.71	13	Chlorite
	9.65	9.16	21	Illite
	12.39	7.13	33	Kaolinite
	20.80	4.27	14	Quartz
	24.90	3.57	25	Kaolinite
	26.65	3.34	63	Quartz
Lower Fireclay	5.72	15.43	12	Chlorite
	9.55	9.25	16.5	Illite
	12.42	7.12	35	Kaolinite
	20.90	4.25	14	Quartz
	24.92	3.57	26	Kaolinite
	26.84	3.32	60	Quartz

To study the vertical mineralogical variation of fireclay samples from Songadh (1A), Ratidevali (7A), Vinaygadh (8B), and Tarnetar (3B), were examined by X-ray diffraction method. Samples of fireclays were collected from bottom to top horizons of fireclay at different vertical interval. X-ray diffractogram of fireclay samples from Tarnetar (3A) Mine are given in Fig. V.15.

Results obtained from the graphs of the above mentioned samples are given in table V.23 to V.26.

The relative observed intensities indicate that fireclays from upper horizon contain more percentage of quartz more illite and chlorite and less kaolinite as compared to fireclays of lower horizon.

This variation is probably due to upward movement of ground water during alteration of fireclay. Harmful constituents such as K^+, Na^+ (alkalies) were carried away by ground water from lower horizons and were concentrated in upper horizon of fireclay beds.

Scanning Electron Microscopy

Freshly cut fireclay samples mounted on stub and plated with Au-Pd alloy, were scanned under electron microscope.

Fireclays contain appreciable quantities of organic matter that has undergone various physical and chemical changes to form bituminous coal. Organic matter in fireclay is the result of direct contamination from adjacent coal seam, but some of it is intimately associated with fireclay and possibly adsorbed on to it - (Plate V.1 and V.2). Many coal partings are concentrated in the upper portion of fireclay (just below coal), where it occurs as underclay. Organic matter content varies from 0.5 to 2.5 percent.

Gibbsite in the form of nodule was found in Ratidevali (7A) fire clay (Plate V.3). Gibbsite is identified with the help of X-ray probe unit attached with scanning electron microscope. It indicates that beauxitic minerals were present in fireclay and might have been destroyed through silicification to form kaolinite. Gibbsite is an index of intense leaching above ground water table and upward movement of ground water. Bauxitic minerals might have been responsible for the compaction of fireclays.

Micaceous flakes (Plate V.4) are observed on fresh cut surface of upper portion of fireclays of Saurashtra. X-ray probe unit employed to identify these flakes from Sadala (4C) gave hydrous alluminium silicate with presence of potassium - probably illite. Presence of illite is

PLATE NO. V.1: Thin partings of coal in Songadh (1B) Fireclay

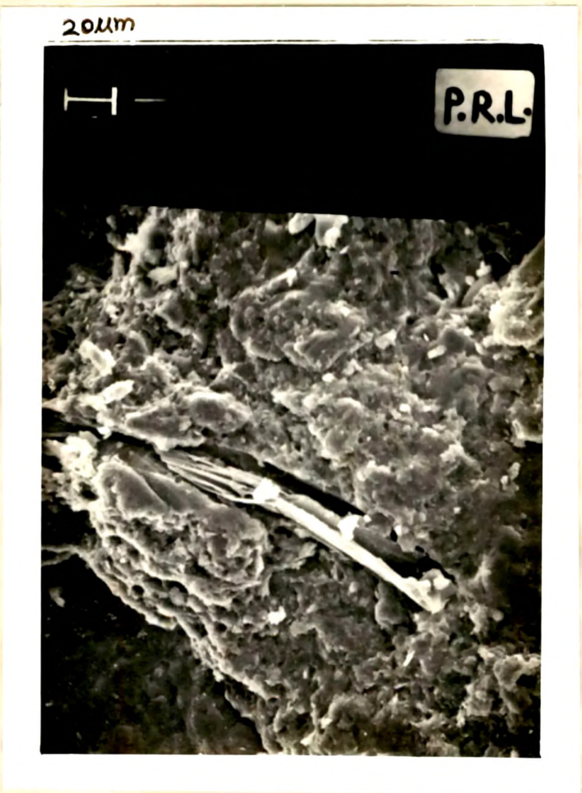


PLATE NO. V.2 : Contamination of Coaly matter in Tarnetar (3B) fireclay.

PLATE NO. V.3: Gibbsite nodule in Ratidevali (7A) fireclay.

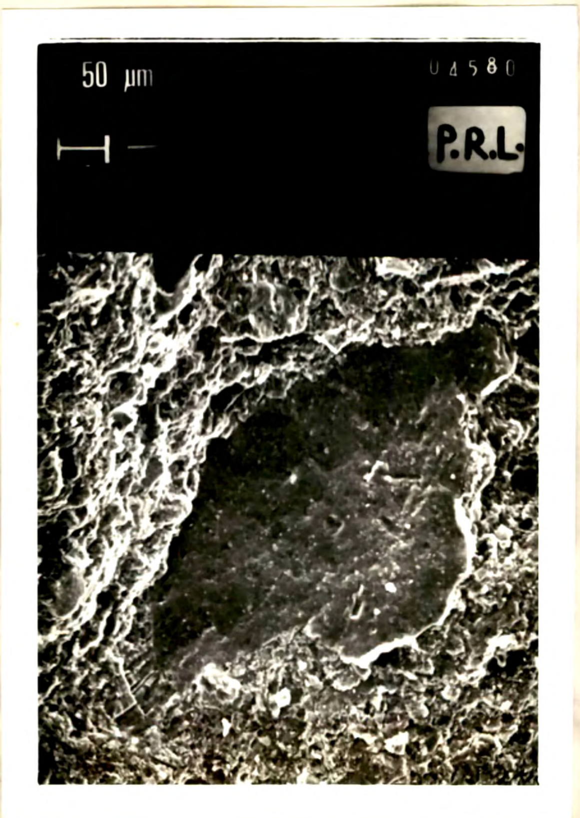


PLATE NO. V.4: Micaceous illite along the bedding planes in Sadala (4A) fireclay.

further supported by X-ray diffraction studies. Upward movement of ground water carried Na^+, K^+ ions with them and formed micaceous flakes on upper portion of fireclay. These flakes are concentrated along the bedding planes of fireclay.

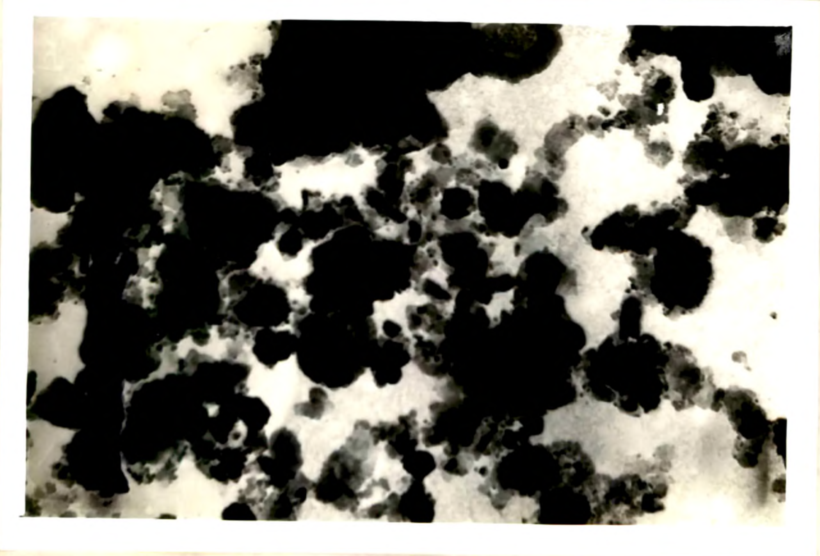
Transmission Electron Microscopy

A few milligram of -300 mesh (ASTM) fireclay sample was taken in a small test tube and diluted with double distilled water till just few particles of clay appear in water. With the help of micropipette a drop of water was taken on a pre-prepared thin film on a grid and was scanned under Transmission Electron Microscope after drying.

Fireclay samples from Songadh (1D), Khanpar(2A), Sadala (4C), Gadhada (6), Jambudia (10) and Saltanpur (13) show the presence of poorly crystalline to occassionally perfectly crystalline kaolinite. (Plate V.5 to V.16) Jambudia and Saltanpur fireclay (red) due to leaching of iron from overlying ferruginous sandstone: A border of kaolinite crystals from these clays appear corrosive. Tarnetar (3A) fireclay shows well crystalline kaolinite crystals (Plate V.11).

PLATE NO. V.5

T.E.M.

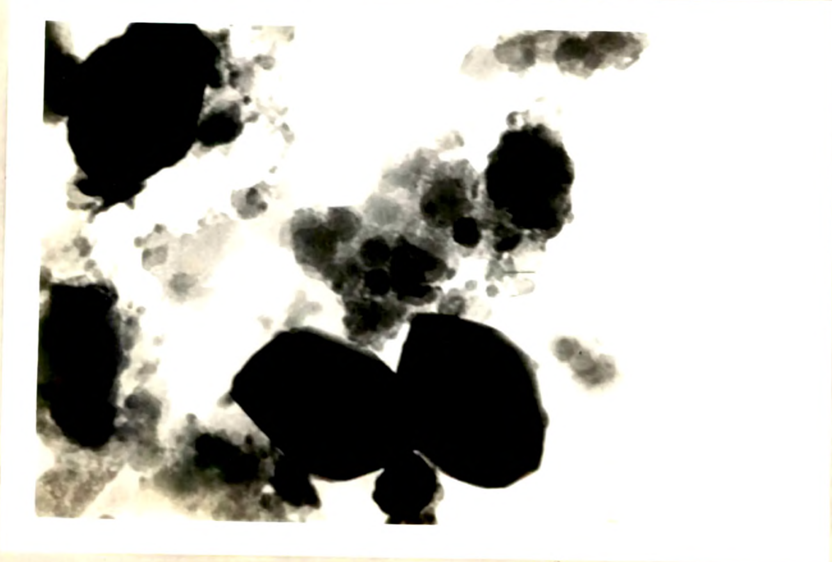


Poorly crystalline kaolinite in
Khanpar (2A) fireclay.

Mag. - 48,600

PLATE NO. V.6

T.E.M.

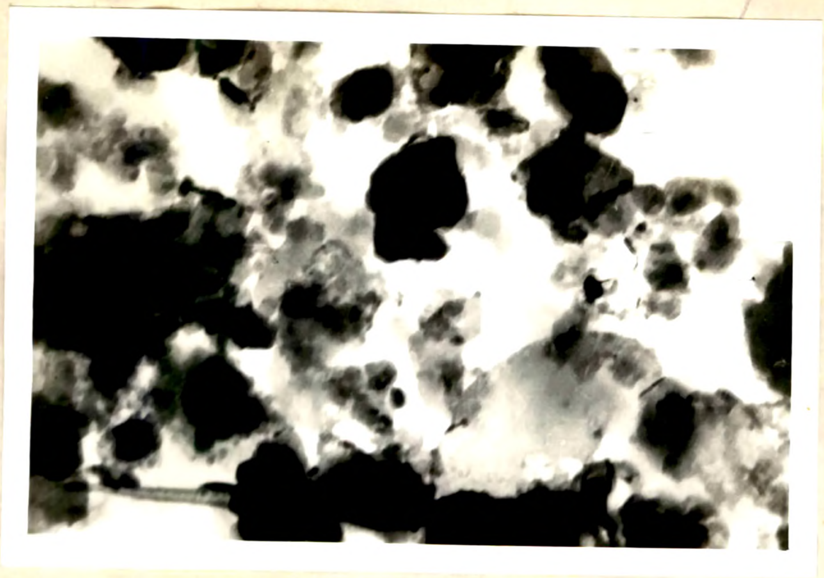


Poorly crystalline Kaolinite crystals
(Subhedral) in Songadh (1D) fireclay.

Mag. - 58,800

PLATE NO. V. 7

T.E.M.

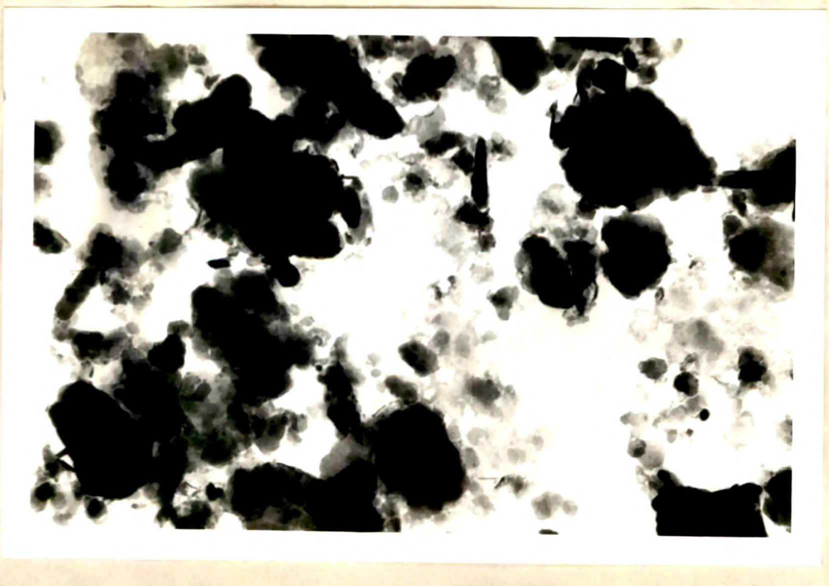


Poorly crystalline subhedral crystals of Kaolinite in Sadala (4C) fireclay

Mag. - 55,600

PLATE NO. V.8

T.E.M.

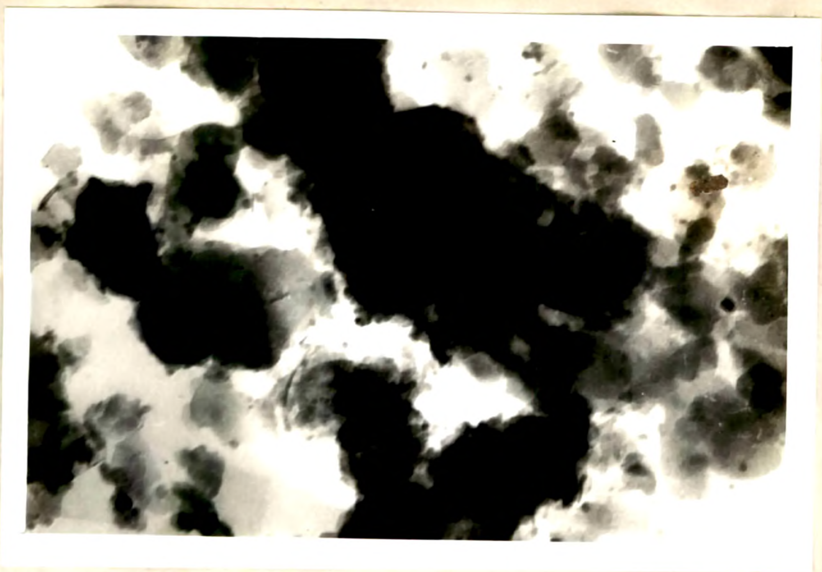


Poorly crystalline Kaolinite in Gadhada(6) - fireclay.

Mag.- 58,500

PLATE NO. V.9

T.E.M.

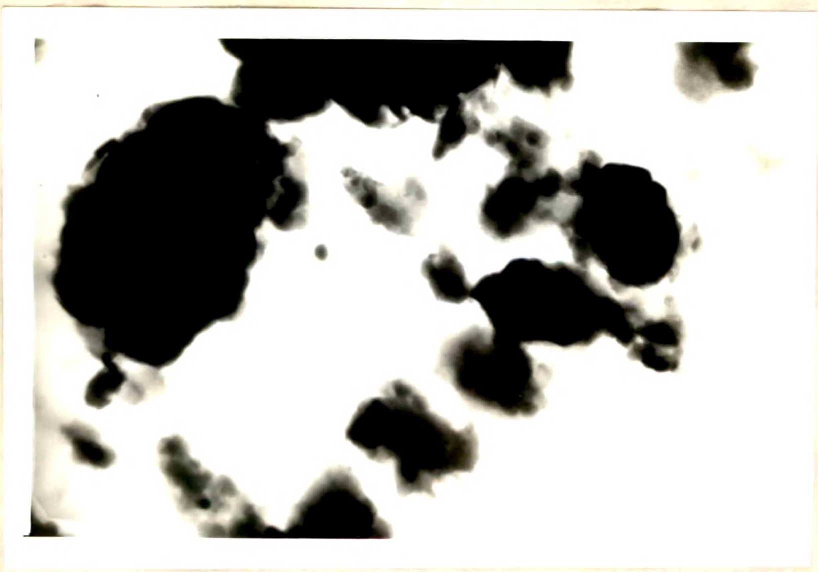


Corrosive border of Kaolinite crystal due to addition of iron oxide. Jambudia (13)

Mag. - 48,300

PLATE NO. V.10

T.E.M.

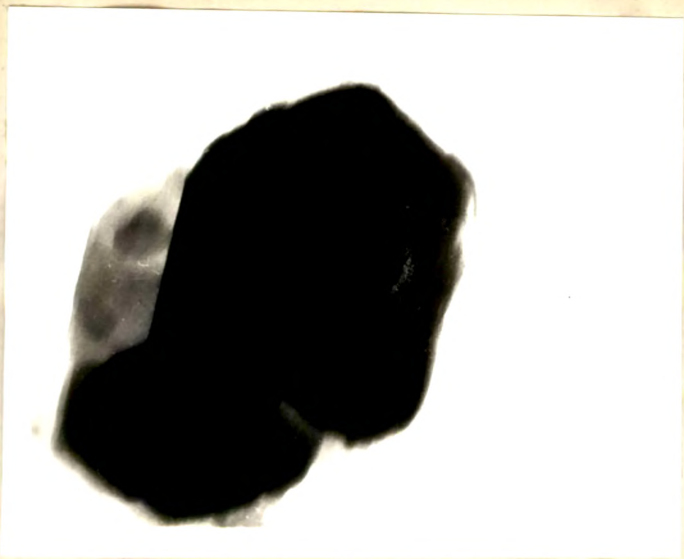


Corrosive border of Kaolinite crystal due to addition of iron oxide. Saltanpur (10A)

Mag. - 58,800

PLATE NO. V.11

T.E.M.



Perfectly crystalline Kaolinite in Tarnetar (3A) fireclay.

Mag. - 60,000

PLATE NO. V.12

T.E.M.

Perfectly crystalline Kaolinite in Ratidevali (7B) fireclay.

Mag. - 45,600

PLATE NO. V.13

T.E.M.

Poorly crystalline kaolinite crystals in Vinaygadh (8A) fireclay.

Mag. - 45,600

PLATE NO. V.14

T.E.M.

Poorly crystalline (Subhedral) Kaolinite in Songadh (1D) fireclay.

Mag. - 44,100

PLATE NO. V.15

T.E.M.

Corrosive border of Kaolinite crystal due to addition of iron oxide in Paneli (12) fireclay.

Mag. - 58,200

PLATE NO. V.16

T.E.M.

Corrosive border of Kaolinite in Saltanpur (10A) fireclay.

Mag. - 60,000