"ECONOMIC GEOLOGY OF THE REFRACTORY CLAYS IN THE UNION OF SOUTH AFRICA."

BY JOHN M WARDE.

SUMMARY.

ECONOMIC GEOLOGY OF THE REFRACTORY CLAYS IN THE UNION OF SOUTH AFRICA WITH PARTICULAR REFERENCE TO THE TRANSVAAL DEPOSITS.

By

John M. Warde.

(Submitted in partial fulfilment of the Requirements for the Degree of Doctor of Philosophy from the University of Cape Town, 1949).

S U M M A R Y.

The commercial refractory clays in the Union of South Africa occur in the coal measure rocks of the Middle Ecca stage of the Karroo system and deposits of economic importance are so far confined to the central and southern Transvaal.

The basal Karroo conglomerate, and the Dwyka "tillite" with which it is frequently confused, is a prominant horizon marker of the base of the refractory clay bearing strata. The refractory clays and associated strata are terrestrial sediments laid down under aqueous conditions and have been generally preserved from denudation by being sunk below the surrounding resistant rocks. The most conspicuous catchments are sink holes and collapse valleys formed by solution of the underlying dolomite, although differential erosion in pre-Karroo times also provided protective basins which served as refuges for these deposits. The refractory clay strata is generally horizontally disposed and shows extreme lateral and vertical variations in character and extent.

The types of clay found include flint, semi-flint and

2/...plastic.....

plastic clay and silicious refractory shale. Quartz, iron and manganese are the principal visible impurities. The flint clays in the Vereeniging area occur as a parting in the main coal seam, while the plastic clays are closely associated with the top coal seam and probably represent sapropelic deposits in ancient water courses. Elsewhere the relationships between the flint and plastic clays and the coal is not so apparent. The semi-flint clays generally overlie the workable coal seams when such coal is present. The silicious refractory shales occur above the semi-flint clays and frequently contain well preserved plant remains.

The formation of the clays is primarily dependent upon the environmental conditions and the principal sources of sediments are the residuum from weathered dolomite and the decomposition products of feldspathic igneous rocks, while to a lesser extent plant ash derived from oxidation of coaly matter also contributed.

The refractory clay reserves are difficult to estimate since prospecting so far has been confined to easily accessible areas and further because of the considerable variation of the clays within short distances. It is apparent however that the reserves of the high grade clays, though large, are by no means unlimited. Most of the clays are mined by open cast methods which facilitate selective mining. Transportation costs are important controlling factors in exploiting new deposits.

Differential thermal analysis supported by x-ray, chemical and optical data, carried out on representative samples, indicate that the principal mineral present in the

3/...South.....

African fireclays is kaolinite. Differential thermal analysis also indicate the occurrence of higher hydrocarbons in the carbonaceous flint and plastic clays. The presence of clay minerals, other than kaolinite, in the plastic clay and refractory shale was suggested by base exchange studies and during this work it was found that the electrodialysis method offered certain advantages over the replacement leaching method in control work. It is of interest to note that the clays tested all showed radio-activity, suggesting a fresh approach in the field of research on the genesis of the fireclays.

The ceramic properties of the selected clays were evaluated by empirical tests and it was considered that the results obtained were in good agreement with theoretical deductions. The plasticity of the plastic clay is much greater than for the other types studied owing to the fineness of particle size, presence of organic matter and the occurrence of clay minerals (illite?) other than the kaolinitic group. The flint and semi-flint clays represent good kaolinite types with quartz as a principal accessory and the dry strength and dry shrinkage of these clays is low compared with the plastic clay and silicious refractory shales. The drying shrinkage of the clays with low base exchange capacity represents a smaller proportion of the total shrinkage (drying and firing) than those of higher base exchange capacity. The plastic clay shows the most pronounced tendency to sinter of any of the clays examined which is to be expected from the high alkali content of this clay and the presence of non-clay minerals (illite) would account for this difference in behaviour from the kaolinite types. The

4/...silicious...

silicious refractory shales contain a large amount of quartz which expands on firing and counter-acts the shrinkage of the clay minerals present. The comparative coarseness of the particles causes the quartz to behave individually rather than to form a eutectic with the clay minerals which accounts for the relatively high refractoriness of this clay. The carbonaceous type of flint clay contains sufficient combustable matter to require pre-calcination before it can be used.

X-ray examination of the commercial high alumina clay shows kaolinite as the only mineral present and it is suggested that such clays represent a high alumina member of the isomorphous kaolinite - anauxite series.

An intensive study of the lithology and ceramic properties of typical Middle Ecca strata shows the pronounced variations in ceramic properties of the strata found within short distances and emphasizes the need for careful selection. Some of the poorly plastic types of refractory clays were found to respond satisfactorily to alkali treatment in a preliminary investigation of the improvement of workability by this means.

The Union is self-sufficient with regard to clay refractories and is in a position to export. The producing plants are located in Vereeniging, Olifantsfontein, Boksburg and Springs in the vicinity of the principal consumer centres. These South African products are comparable with American and British ware and the future of the industry is dependent upon the continued application of improved methods in research and development.

ECONOMIC GEOLOGY OF THE REFRACTORY CLAYS IN THE UNION OF SOUTH AFRICA WITH PARTICULAR REFERENCE TO THE TRANSVAAL DEPOSITS

By

John W. Warde

B.S. in Chemistry, Metallurgy and Ceramics,
University of Alabama, 1935

M.S. in Geological Engineering,
Montana School of Mines, 1937

Submitted in Partial Fulfillment of
the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

From the

University of Capetown

1949

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

PLATES

FIGURES

I - INTRODUCTION.

GENERAL STATEMENT.

The term "refractory clay" is applied herein to those clays which do not fuse below 1680°C. * and are principally used for the manufacture of fire-clay refractories, including fire-brick and fire-clay goods.

Firebrick are structural materials used at high temperatures in industrial furnaces and fire-clay goods embrace such allied materials as assay ware, crucibles, insulating firebrick, and various specialty products including mortars, ramming mixes, cements and wall coatings, all of which are intended for service at elevated temperatures.

Fire-clay refractories are required in large quantities for boiler settings where steam is raised for the generation of power and as a source of heat and for the commercial production of iron and steel and many non-ferrous metals. Other important consumers include the portland cement, lime, ceramic, glass, chemical, and food processing industries, railways and shipping. Indeed there are but few industries of more basic importance to the national economy than the manufacture of fire-clay refractories and the fortuitous occurrence of extensive deposits of refractory clay near the industrial centres of the Union has been a leading, though not generally appreciated, factor in the economic development of South Africa.

The domestic production of fire-clay refractories began before the Anglo-Boer War and has developed rapidly in recent years especially during World War II until today the Union is practically self-sufficient with respect to these essential commodities and is an active exporter of these products as well.

Refractory clays of economic importance to the Union of South Africa have so far been obtained only from deposits of

* Pyrometric cone equivalent (P.C.E.) -- 31. (A.S.T.M. C.24-42).

MAP OF THE UNION OF SOUTH AFRICA

LOCATIONS OF REFRACTORY CLAY PRODUCING AREAS SHOWN THUS ——

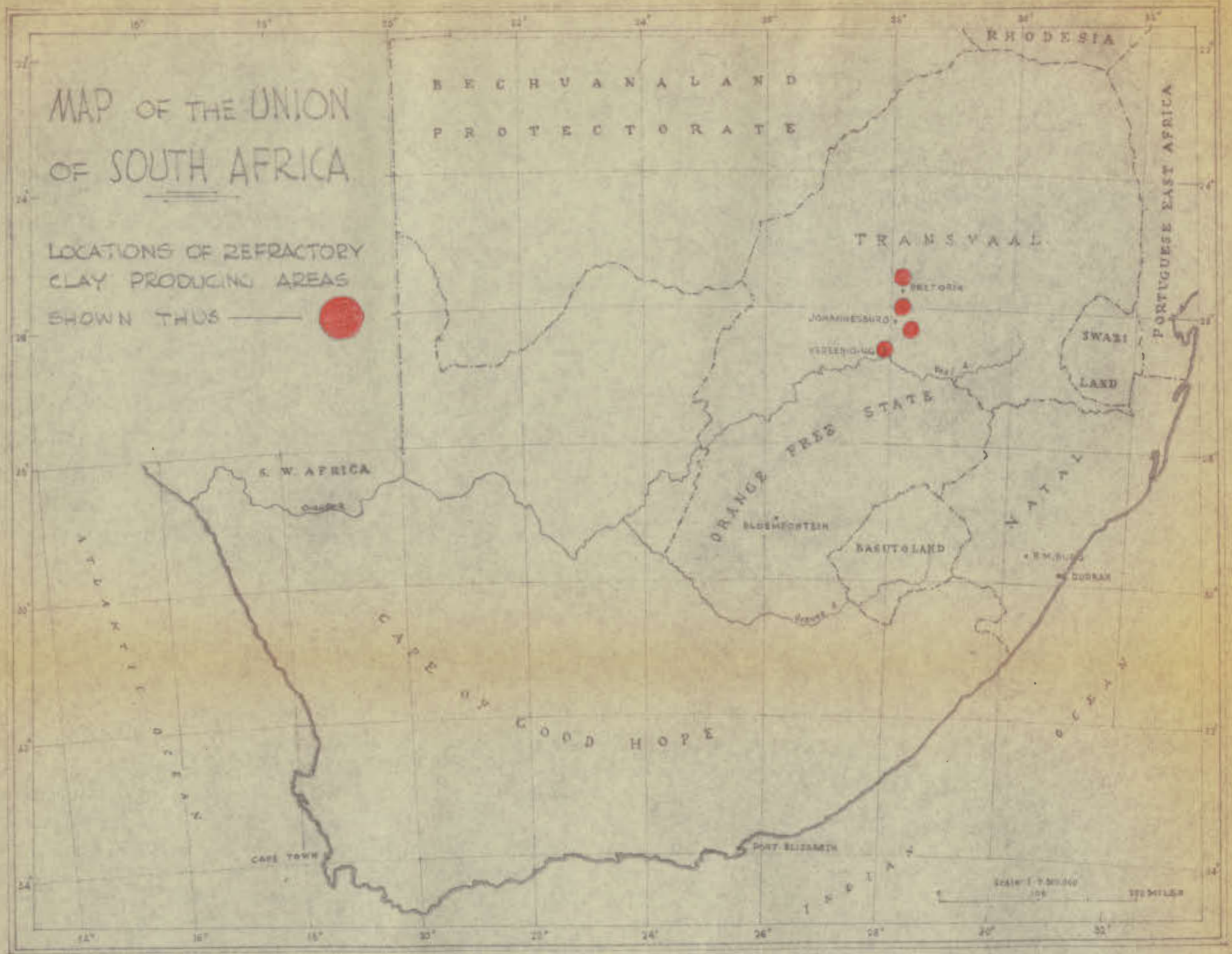


FIG. 1

Middle Ecca rocks of the Karroo System in the Transvaal. Locations of the producing fields are shown in the accompanying map, Fig. 1. Other occurrences have been reported from elsewhere in the Union but no deposits comparable commercially to those in the Transvaal are being worked at this time.

The purpose of this thesis is to describe the occurrence, nature, properties, and utilization of the refractory clays in South Africa with particular reference to the Transvaal deposits, focusing on those characteristics which may be of direct value in the future development of this important mineral resource.

Principal attention has been devoted to producing areas and generally confined to those materials used in the production of fire-clay refractories; however, in many cases these identical clays are employed in the manufacture of "golden brown" building brick, sewer pipe, earthenware, etc.

A fundamental study of the constitution of the commercial refractory clays was carried out on selected samples obtained from operating workings. The differential thermal method of analysis was featured in these studies, supplemented by X-ray examination and other recognized determinative procedures. The basic data so obtained were correlated, where possible, with the ceramic properties of the clays in order to lead to a better understanding of the relationship between the refractory clays and the ware made from them.

PREVIOUS WORK.

The number of workers publishing results on the refractory clays of the Union have been strikingly few. Except for occasional brief references in earlier literature, these materials were not the subject of an adequate report until 1916 when Wagner (1) discussed the occurrence of the

refractory clays at Cliftonstein, and Halford (2) described the deposits at Boksburg. Little further information appeared in print from 1916 to 1941 when Bosazza reported on the clays of the Witwatersrand in a publication of the Mineral Research Laboratory (3). This work includes the description of a number of deposits of Ecca fire-clay together with chemical and physical data. Bosazza also wrote a number of papers which included various aspects of the study of clays, and he further treated the subject in a published thesis in 1946. (4) Ahrens published data on the spectro-chemical analysis of South African clays, including Ecca fire-clays, in 1945 (5), and Gardé and Denysschen contributed an article on the differential thermal analysis of some South African refractory clays in 1949 (6).

Considerable information on the geology of the Middle Ecca rocks of the Transvaal have appeared in the literature, and excellent accounts are given by Molengraaf (1904) (7), Mellor (1906) (8), and Du Toit (1939) (9). The subject is treated in detail in many of the publications of the Union Geological Survey covering areas underlain by these rocks. The general geology of the Union is well summarized by Du Toit (9), Hamilton and Cooke (10), and the Mineral Resources of the Union (11). Courteous acknowledgement is made of the free use of this literature in presenting the geologic background of the refractory clays of the Union.

PRESENT INVESTIGATION

The present work was first begun in May, 1941. It was interrupted in October, 1942, because of the departure of the writer from the Union on active service with the United States Army and the interruption was further prolonged by the writer's services as Ceramics Specialist on the staff of the Military Governor of Germany (U.S. Zone). The work was resumed in 1947 after the writer's return to South Africa, and this thesis was submitted in July, 1949. All of the field work and laboratory

investigations took place within the periods mentioned.

ACKNOWLEDGEMENTS

This programme of investigation was suggested by Dr. H. Jacobs, supervisor, and approved by Prof. F. Walker of the Department of Geology, University of Capetown.

The writer is particularly indebted to Dr. Jacobs, who in his capacity of General Manager, of the Vereeniging Brick and Tile Co. Ltd., made this investigation possible by providing research facilities and granting permission for this work to be undertaken in addition to the writer's professional duties as Ceramic Engineer for the Company.

The valuable guidance of Dr. F.C. Truter of the Union Geological Survey in studying the occurrence and origin of the refractory clays is gratefully acknowledged. Thanks are especially extended to Dr. B. Wasserstein of the Union Geological Survey for the assistance and helpful criticisms given in the X-ray work and optical examinations and for carrying out the spectro-chemical investigations.

The kindness of Dr. P.C. Carmen of the National Chemical Laboratories and his staff members Messrs. H. Heystek and P. Theron in placing equipment and assistance at the writer's disposal greatly facilitated the fundamental studies.

Dr. N. Dobbins, Research Manager of the Vereeniging Brick and Tile C. Ltd., and his staff including Messrs. E. Mooi, E.R. Newbury, and L. van Vuuren are thanked for their general co-operation.

The assistance of Mr. J.H. Denysschen was of great benefit in the construction and operation of the differential thermal analysis equipment.

Grateful acknowledgement is due Dr. R.E. Grim, Illinois Geological Survey; Mr. O.C. Ralston, Chief Non-Metallics Division, Mr. Paul Ambrose, Chief College Park Branch, and Mr. H.F. Carl, Physicist, College Park Branch, all of the United States Bureau

of Mines: Prof. Harry Hess, Princeton University, and Dr. Armand Fredericksen, Washington University, for the kindly and active interest they displayed in carrying out confirming tests to prove the efficacy of the differential thermal analysis equipment built by the writer.

The kindly advice of Prof. Walt Keller, Department of Geology, University of Missouri, and the timely suggestions and assistance of Dr. R.F. Bradley, Director of Research, A.P. Green Firebrick Co., Mexico, Missouri, are acknowledged with thanks.

Thanks are extended to Mr. A.W. Charman, Sales Manager of the Vereeniging Brick and Tile Co. Ltd., for assistance in compiling the statistics on firebrick production and sales and to Mr. R.C.P. Jack of that Company's staff for his efforts on the illustrations appearing in this work.

The advice and encouragement of Mr. G.V. White, former geologist, African & European Investment Co. Ltd., are gratefully appreciated.

II - GENERAL GEOLOGY.

STRATIGRAPHY

General Statement

The refractory clay producing region in South Africa is restricted to areas in the Transvaal which are underlain by Middle Ecca rocks of the Karroo System.

The geologic formations exposed in the Transvaal range from the Archaean Archaeozoic to Recent Mesozoic in age. Recent deposits of sand, limestone, laterite, and occasional gravel patches cover much of the terrain and mask the underlying formations.

An outline of the principal geological formations found in the Transvaal is given in descending order in the following table:

Table I.

Geologic Formations in the Transvaal.

Stratified Formations:

System.	Series.	Lithology.
Recent		Gravel, sand, silt, mud.
		Surface limestone, ferricrete.
Karroo	Stormberg	Bushveld Amygdaloid
		Bushveld Sandstone
		Bushveld Marls
	Beaufort	Shales, sandstone, coal
	Ecca	Shales, sandstone, coal
	Dwyka	Shales, "tillite"
Waterberg		Sandstones, shales, conglomerates

Table I (cont'd).

System.	Series.	Lithology.
Transvaal	Rooiberg	Quartzites, shales, lavas
	Pretoria	Shales, lavas, quartzites
	Dolomite	Dolomite, chert, shale
	Black Reef	Quartzite, shale, conglomerates.
Ventersdorp		Lavas, quartzites, conglomerates.
Witwatersrand	Kimberley-Elsburg	Quartzites, slates, conglomerates
	Main-Bird	-do- -do-
	Jeppestown	Sandstone Shales
	Government Reef	Quartzites, shales, conglomerates
	Hospital Hill	Quartzites and shales.
	Dominion Reef	Lavas, arkose, quartzite, conglomerates.
Pongola	Upper	Quartzites, conglomerates, shales and lavas.
	Lower	-do- -do-
Swaziland	Moodies	Quartzites, lavas, cherts banded ironstones.
	Onverwacht	-do- -do-

Intrusives:

Dolerite (late Karroo)

Dolerite (pre-Karroo)

"Bushveld Igneous Complex"
- Red Granite
- Granite porphyry
- Porphyritic granite
- Norite
- Granophyre

"Jamestown Igneous Complex"
- Old Granite.

Pre-Karroo Rocks of the Transvaal.

The pre-Karroo rocks exposed in the Transvaal, many of which contributed sediments for the formation of the refractory clays and associated Middle Ecca strata, may be summarized as follows:-

Fundamental Complex.

The oldest known rocks in the Transvaal are the sedimentary and volcanic types grouped under the heading "Swaziland System", which are best developed in the Barberton area with occasional occurrences in the Murchison Range. Intrusive into the rocks of the Swaziland System is a widespread mass of granite and gneiss which is called the "Old Granite" to distinguish it from the later "Red Granite" of the Bushveld Complex. The old Granite crops out over an extensive area in the northern and eastern Transvaal and is represented by a large oval outcrop about 20 miles wide extending almost from Johannesburg to Pretoria.

Pongola System.

The Pongola System comprises a series of quartzites, phyllites, and amygdaloidal andesites with occasional shales, conglomerates, and ironstones. The system occupies an area in the south-eastern Transvaal.

Witwatersrand System.

This system includes alternations of argillaceous and arenaceous sediments probably derived from the denudation of a region of Swaziland rocks and Old Granite to the north-west of the present Witwatersrand where the system is best known. The rocks of this system rest on the Old Granite and are generally overlain by the Ventersdorp System. The Witwatersrand rocks occupy an elongated synclinal basin stretching from the Witwatersrand, south to Vredefort in the Free State, and from Wolmaransstad in the west to Springs in the east. The maximum thickness of strata assigned to

the Witwatersrand is about 24,000 ft. on the central Rand. The gold-bearing conglomerates of this system are the most important strata found in the Union from the point of view of national wealth.

Ventersdorp System.

This is chiefly a volcanic group composed of amygdaloidal andesitic lavas, which occupy large areas in the southwest Transvaal. Near Vredefort and Heidelberg the system is developed to about 5,000 feet made up for the most part of lavas. Near Kempton Park, strongly developed beds of agglomerates are found at the base of the series. In the Klerksdorp and Ventersdorp areas, the system includes quartzites and boulder beds as well as volcanic breccia and an upper zone of quartz porphyry.

Transvaal System.

The Transvaal System, including several well recognized series, is the most widespread of the pre-Karroo rocks found in the Union.

Black Reef Series: The Black Reef Series which includes quartzites and conglomerates with occasional shales or slates is the basal member of the Transvaal system.

Dolomite Series: The Black Reef is overlain by the Dolomite Series in which the predominating rock is massive dolomitic limestone more commonly called "dolomite". The top of the series is generally marked by a thick band of chert known, as the "Giant Chert", and numerous bands of chert and banded ironstone occur in the series. The dolomite is grey in colour, finely crystalline, and on weathering exhibits a peculiar surface resembling elephant hide which is responsible for its descriptive term "Olifantsklip". It varies in thickness from 120 feet near Carolina to 3,500 feet near Haenartzburg in the northern Transvaal.

Karroo System --General.

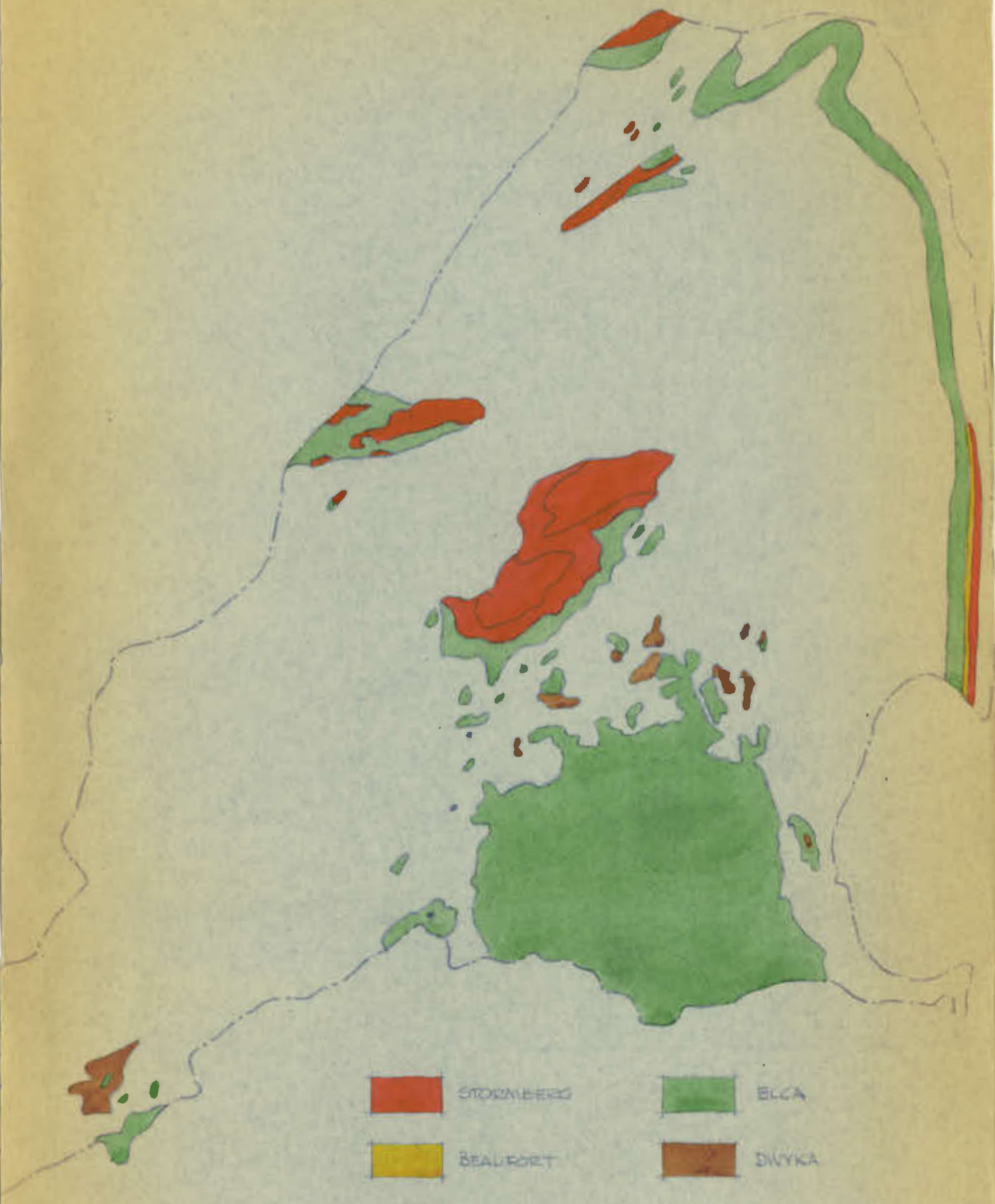
The Karroo System, of which the refractory clays and associated Middle Ecca strata form but a very small part, is the most widespread and dominant stratigraphic division in South Africa. The remnants of this great thickness of strata today cover more than half of the Union and have been recognised in South-West Africa, the Rhodesias, Nyasaland, the Belgian Congo, and even further north on the African continent.

Fossil evidence indicates that the Karroo System does not correspond exactly with any specific period in the Northern Hemisphere sequence but, ranging in age from the Upper Carboniferous to the Jurassic, it includes several recognised systems of that sequence. Du Toit (9) points out the close similarity in the lithology of the rocks and the characteristics of the fossils contained in them in the Karroo System of South Africa and corresponding systems in India, Australia and South America.

The Karroo rocks occur in a huge shallow trough which occupies the central portion of the Cape Province, the entire Orange Free State, the western part of Natal and large areas in the Transvaal. This enormous basin forms the most prominent structural feature in South Africa.

The System attains maximum development in the "Karroo Region" of the Cape Province where the type area is located. Here a succession of about 20,000 feet of strata is assigned to the Karroo System. The thickness of the System is considerably reduced in the Northern part of the Union, where the members are less well developed and some partly or entirely missing, and rarely exceed a few thousand feet.

The Karroo System in the Union consists principally of sandstones, shales, grits, and conglomerates laid down for the most part by fresh water agencies. The base of the Karroo is composed of a series of deposits which were products of widespread glaciation in contrast with the close of the



GEOLOGIC SKETCH MAP OF THE TRANSVAAL
SHOWING AREAL DISTRIBUTION OF THE KARROO

AFTER UNION GEOLOGICAL SURVEY

FIG. 2.

Karroo period which was marked by extensive volcanic activity. The constancy of character and widespread distribution of the Karroo System give rise to the development of some of the principal physical features of South Africa. The dry sandy uplands broken by occasional flat-topped buttes and mesas are characteristic of the "Karroo Region" of the interior plateau. The deeply dissected topography of the eastern part of the Union, including Basutoland, is also the result of weathering of the Karroo rocks. In the Transvaal the Karroo strata produce vast expanses of gently undulating terrain unmarred by sharp topographic features.

Karroo System -- Transvaal Facies.

The Karroo System in the Transvaal differs appreciably from the southern facies as found in the Cape Province. In the Transvaal the succession is much thinner and more imperfectly represented than farther south; further, the glacial deposits so consistent in the South are only developed sporadically in the North. The northern Ecca member is dissimilar in lithology to the southern equivalent, and carries coal. Finally, a hiatus exists in the northern strata representing the absence of the upper part of the Beaufort series, and the Stormberg rocks rest directly on the Ecca or older formations. (9)b.

The main divisions of the Karroo System in the Transvaal will be described below with special reference to the Dwyka series and Middle Ecca stage because of their particular association with the refractory clays. The basal Karroo Conglomerate is also mentioned since it is an important horizon marker along with the Dwyka Tillite. A map showing outcrops of the Karroo formation, in the Transvaal is given in Figure 2.

Dwyka Series.

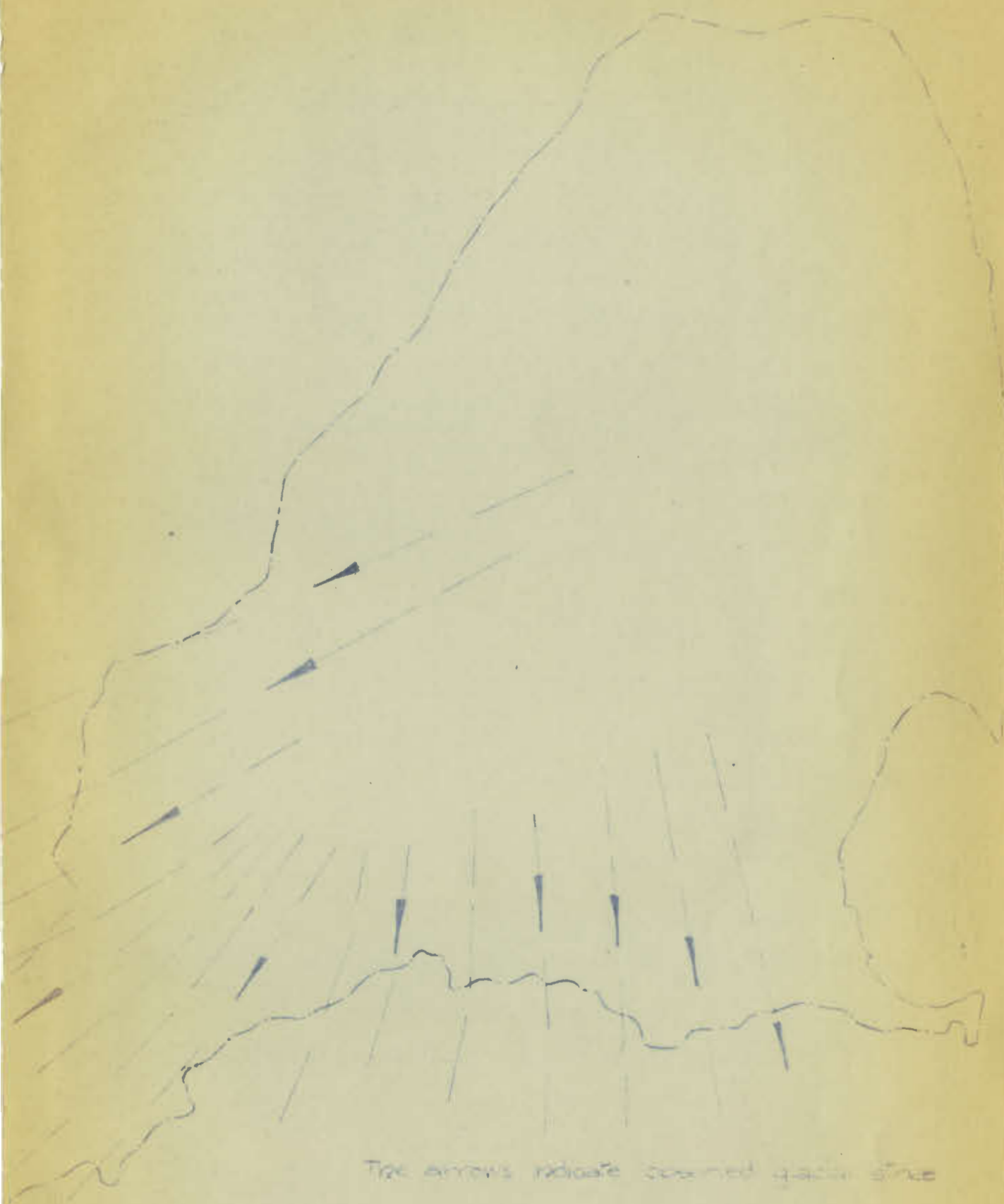
The Karroo sediments throughout the southern Transvaal, northern Free State, and Natal are generally underlain by a peculiar boulder-bearing rock which is probably the most generally recognised horizon in the whole of the geologic col-

umn in South Africa. This rock has long been recognised as a marker in prospecting for refractory clays and is used extensively as a guide in searching for coal.

As far back as 1868, geologic opinion was advanced that this boulder bed was of glacial origin. Dunn in 1873 proved that this boulder bed was continuous with the stratum in the Southern Karroo to which he gave the name "Dwyka Conglomerate" after an occurrence in the Dwyka river near Prince Albert, C.P. Penck introduced the more acceptable descriptive term "Tillite" for this rock from the soft "till" or glacial boulder clay from which it was formed. After a long stormy session which gave widespread publicity to this interesting portion of South African stratigraphy, the accumulated evidence has been accepted as confirming this opinion (12).

Du Toit (9) calls attention to the continental dimensions of the ice mass that acted as the agency of formation and refers to almost identical deposits in India, Australia and South America of similar geological age. The mechanical disintegration accompanying the movement of the glacier which transported rocks of various origin, and the subsequent deposition of this material on the land surface where it was exposed to a long period of sub-aerial weathering in the Transvaal had an important bearing on the formation of the refractory clays and other strata of the later Middle Ecca stage.

The Dwyka "Tillite" is composed of a generally argillaceous matrix containing pebbles and boulders of a large variety of pre-Karroo rocks ranging in size from huge blocks weighing several tons to mere grains. The distribution of the rocks and pebbles in the gound mass is independent of their size and shape. While the smaller fragments are commonly angular, the larger ones show a certain amount of rounding. Many of the boulders exhibit the scratch marks or "striae" found in glacial ground moraine and the striated old land mass over which the ice sheet moved is sometimes visible.



The arrows indicate [illegible]

It is generally considered that throughout most of the region underlain by the Dwyka, the "Tillite" was a morainal material associated with continental glaciation. After the melting of the glaciers this moraine became buried under later Karroo sediments. In the Transvaal, however, the elevated region covered by the moraine was apparently exposed to weathering agencies for a long period after the disappearance of the glacier. In consequence the "Tillite" of the Transvaal is thin and irregular and missing in places as a result of post-glacial erosion. Further, having been bleached by long exposure it is quite different in appearance and texture from the Dwyka tillite found in the southern extension of glacial activity. There the typical development of this stratum is a hard, bluish, sandy mudstone containing scattered boulders so well embedded in the matrix in many cases that the rock fractures across the inclusions. Bedding is frequent in the southern area although absent in the north and it is generally regarded that in the southern region the glacial material was deposited in fairly deep water, from the melting ice and over 2,000 feet of glacial sediments have thus accumulated. In the north the glacial sediments were deposited directly on the low lying land mass and owing to subsequent erosion seldom exceed 100 feet in thickness.

Du Toit has studied the movement of the glacial ice in detail and concludes that one of the three principal ice caps connected with the continental glaciation of this period in South Africa was located in the northeastern Transvaal and that the direction of the ice movement was generally south to southwest as shown in Figure 3, scouring over the vast expanse of rocks exposed on the old land surface and transporting this material elsewhere to contribute to the formation of the refractory clays and associated Middle Ecca Strata.

The "Tillite" often has a local character because of the preponderance of debris derived from rocks underlying the area.

It weathers very easily and consequently it is seldom found in outcrops, although its presence may be indicated on the surface by numerous scattered boulders embedded in sandy soil.

The Lower Dwyka Shales and Upper Dwyka, which together with the "Tillite" make up the three divisions of the series, are not recognised in the Transvaal.

Fossil evidence points to an age corresponding approximately to the Carboniferous of the Northern Hemisphere for the Dwyka Tillite.

Basal Karroo Conglomerate

In many areas in the Transvaal overlain by Karroo rocks, the characteristic Dwyka Tillite is not recognised and the base of the Karroo is composed of a secondary conglomerate which is frequently confused with the older "Tillite" from which it was derived. This conglomerate has been formed by the denudation of the "Tillite" and through "reworking" under fluvial conditions it has been transformed into succeeding sedimentary strata.

The existence of this derived conglomerate was well recognised by Mellor (8) and he offers the following distinguishing criteria:

"Tillite"	Derived Conglomerate
1. Absence of grading and arrangement of pebbles.	1. Rough grading apparent and general orientation of boulders and pebbles with larger axis parallel to bedding planes noticeable.
2. Matrix unstratified and frequently clayey in nature.	2. Matrix usually stratified and always sandy.
3. Stratification absent or local.	3. Stratification frequently persistent over long distance.
4. Shows great variation in thickness and level over short distances depending upon surface contours of underlying rocks.	4. Not so variable in thickness and maintaining same general level over large areas.
5. In most cases lies directly on rocks of older systems.	5. Frequently succeeds or interstratified with beds of Karroo sandstones or grits.

PLATE I.

SPECIMEN OF "DERIVED CONGLOMERATE" (BASAL KARROO CONGLOMERATE)
VEREENIGING AREA.

This derived conglomerate is generally confined to the portion of the strata between the "Tillite" and the Middle Ecca and may be the basal member of the Karroo in some regions, in which case it should be recorded as the Basal Karroo Conglomerate since no definite age has been assigned to this stratum.

The pebbles and boulders of the conglomerate include the same varieties found in the Dwyka "Tillite" from which it was derived. This conglomerate is usally associated with fine to coarse grained sandstone, frequently massive and generally lenticular.

The secondary conglomerate is difficult to distinuish from the Dwyka Tillite when seen in small weathered surface exposures or in bore-hole cores; however, if the rock can be examined in a sufficiently large exposure it can generally be told from the "Tillite" by Kellor's criteria. An excellent exposure of the secondary conglomerate is to be seen in the Vereeniging district on the Farm Klipplaatdrift 83, where in addition to the existence of the distinguishing criteria just mentioned, the conglomerate in this exposure contains large fragments of soft clay from the underlying Transvaal rocks which by their nature could not have withstood transport by glacial ice. A typical specimen from this deposit is shown in Plate I. Similar rock containing soft clay fragments was noticed from the base of the Karroo in a prospect pit on the Farm Rietfontein 14, near Springs.

The areal extent of this basal Karroo conglomerate is not accurately known and it is possible that strata at present assigned to the Dwyka "Tillite" in many areas should more properly be described as Basal Karroo Conglomerate. This rock offers an interesting subject for further regional study.

Ecca Series.

The Dwyka "Tillite" or the Basal Karroo Conglomerate is followed unconformably in the Transvaal by a succession of

sandstones, grits, shales, refractory clays, and coal seams, with occasional stratified conglomerates, which form the most conspicuous part of the Karroo System in the Province. Du Toit (9),[e] after a study of the phasal varieties of these rocks assigned them to the Middle Ecca. The Lower Ecca, well developed in Pondoland, is not important in the Transvaal, while the Upper Ecca, represented by a thin group of dark blue shales, overlies the Middle Ecca in only limited areas in the Transvaal.

A more detailed account of the Middle Ecca rocks which include the refractory clays will be given separately in view of their importance to this study.

Beaufort Series.

The Beaufort Series which follows the Ecca conformably is found in a very small area in the southeastern Transvaal where it is represented by sandstones, mudstones, and shales. The upper part of this series is missing in the Transvaal.

Stormberg Series.

The Stormberg Series in the Transvaal is represented by the Bushveld marls, Bushveld sandstone, and Bushveld amygdaloid which overlie the Ecca in several patches in the northern part of the Province.

Igneous Intrusives.

The Karroo sediments and older rocks were invaded by numerous sills and dykes of dolerite during the period of volcanic activity that marked the close of the Karroo System. The sills, frequently of great size, are generally confined to the flat lying sedimentary beds of the Karroo while the dykes occur in these as well as in the older rocks.

Middle Ecca Stage.

General Statement.

The Middle Ecca stage generally occupies depressions in the old land surface which have served to preserve these rocks from the subsequent erosion that has removed most of the Karroo strata from the Transvaal. The refractory clays are found interbedded with the coal seams or in overlying strata separat-

ed from the coals by a considerable thickness of intervening rocks. In some deposits it is extremely difficult to correlate the position of the clay beds with the coal seams since the coals are frequently poorly developed or missing in many areas where the clay occurs.

Physical Geology.

Regionally, the Middle Ecca Strata lie nearly horizontally and so give rise to flat or gently undulating terrain traversed by poorly defined marshy water courses. The surface of the terrain is conspicuously lacking in outcrops. Where the older rocks which do crop out are in contact with the Middle Ecca there is usually a marked difference in the topography of the land surface underlain by the two types of strata. The surface of areas underlain by the Middle Ecca is generally covered with yellow to red sandy soil which usually masks the character of the underlying strata and extends beyond the limits of the Middle Ecca, obscuring any contacts that may occur. Accurate mapping of the Middle Ecca is therefore exceedingly difficult. The Middle Ecca land surface is generally covered with grass and trees are scarce. The presence of "pans", shallow depressions resulting from surface erosion, is a common topographic feature of regions underlain by Middle Ecca rocks and sometimes indicates the existence of clay strata.

Distribution and Thickness.

The Middle Ecca stage occurring in the southeastern Transvaal represents a northern extension of the Karroo System which covers the Orange Free State. Besides this connected area, numerous patches of Karroo strata occur to the north and west lying conformably on rocks of the Swaziland, Witwatersrand, and Transvaal Systems. Thus patches of Middle Ecca occur on the South Rand and at Boksburg, overlying the Hospital Hill Series and the Kimberley-Ellsberg Series, while at Vereeniging they rest on the Dolomite Series. At Belfast they are underlain by the Pretoria Series and north of Pretoria at Waterval

Grits: The grits occur mainly in the lower portion and middle portion of the Middle Ecca and frequently form the only prominent outcrops of this stage. They are generally associated with secondary conglomerates and sometimes contain pebble washes and small boulder "erratics". The lower grits are usually more variable in texture than the upper grits. The upper grits are frequently very coarse and are characterised by a great uniformity of grain sizing, the particles averaging one eighth to one-quarter inch in diameter. The grains are irregular, angular and in general show little signs of attrition. The outer surface of the grits is usually much harder than the inner portion which according to Du Toit (9) is apparently due to secondary silicification. The differential effect of silicification gives rise to the peculiar type of weathering often seen where grits outcrop.

Sandstones: The sandstones show a wide variation in texture. In some areas they merge into grits, in others they pass into shales. The coarser sandstones are usually massive or thickly bedded while the finer varieties are often thinly laminated and micaceous. The upper sandstones are generally composed of quartz grains set in a matrix that is well kaolinized and sometimes these sandstones pass into arkose. The coarse-grained sandstones, which are frequently lenticular, are quarried in some localities for building stone.

Clays: The clays of the Middle Ecca include mudstones varying in texture from fine grained soft material to hard indurated rocks that break with a conchoidal fracture. Iron and manganese oxide penetrates along bedding planes or traverses these rocks in more or less irregular manner. Some of the clays show alternating dark and light banding resembling varved clays. (The refractory varieties of the Middle Ecca clays will be fully discussed later in this work.).

Shales: The shales are generally arenaceous in character and might be best described in some localities as finely laminated sandstones. They frequently contain carbonaceous matter

in the lower portion of the stage and are sometimes highly micaceous. Like the clays they show evidence of the penetration of iron and manganese. Red shales usually occur associated with the coarse grits and massive sandstones and are probably formed by the secondary infiltration of iron into thinly laminated clay shales. They are hard, thinly laminated rocks rich in iron oxides frequently resembling ironstones. Gypsum is sometimes found in the shale beds.

Coals: The Middle Ecca stage is the principal coal-bearing horizon in the Union. Seams of workable coal are generally confined to the lower portion of the succession and their most striking characteristic is the great thickness sometimes encountered, seams 10 to 20 feet thick not being unusual in the Transvaal. The coals are generally non-coking and high in ash. They are regarded for the most part to have been formed in situ in wide swampy flats under cold and humid conditions. The torbanites, oil bearing shales, of the Ermelo and Wakkerstroom districts are closely associated with the coals and sometimes form a compound seam of coal and shale.

Superficial Deposits.

Consideration of the superficial deposits overlying the Middle Ecca rocks is of importance in mining operations.

Areas underlain by the Middle Ecca strata are generally well covered by sandy soil or ferricrete. Sand is derived from the underlying sandstones or grits and forms a highly pervious mantle. Though not confined to the Middle Ecca, the formation of the "ferricretes" by iron-secreting bacteria has been active owing to the porous nature of these rocks. The formation of hydrated iron oxides from the decomposing underlying rocks has given rise to the typical slaggy-looking, yellow to red lateritic rocks, commonly called "ouklip", which possess the characteristic property of hardening on exposure.

Deposits of silica, resembling the "silicretes" of the

Cape, are also encountered in the superficial portion of the outcrops of Middle Ecca sandstones and represent the alteration of pre-existing rocks. Surface limestones or "calcretes" are more rarely encountered. Gravel beds are fairly common in areas underlain by the Middle Ecca and in some regions a considerable thickness of soft, plastic, "soapy" clay is encountered which is grey to yellow in colour and frequently associated with overlying "ouklip".

It is of economic interest to note that the deep red sandy soils overlying the Middle Ecca are frequently suitable for the manufacture of "stock bricks", or as an ingredient in clay mixtures for the manufacture of face bricks.

Fossils.

Although faunal forms are rare, an abundant flora of fern-like plants is present in the Middle Ecca stage, associated with sandstones and clays. The bulk of the Middle Ecca fossils described in the literature came from the Vereeniging district and are largely the result of the careful and persistent efforts of Dr. T.N. Leslie. According to Du Toit the Middle Ecca flora can be regarded as of Lower Permian age (9)g

The most common genus is glossopteris which flourished in India, Australia, South America, the Falkland Islands, and the Antarctic continent. Gangamopteris is also conspicuous. Plants of larger growth were also well represented, being distinguished by broad impressions in the sandstones and clays and sometimes noted in the bright bands of the coal seams.

In addition to the Vereeniging finds, Middle Ecca flora have also been described from Olifantsfontein (1) and Hammanskraal (13), occurring in the shales and sandstones associated with the refractory clays.

The following list of fossils associated with the Middle Ecca rocks in the Transvaal is given by Mellor (8).

PLATE II.
SPECIMEN OF SILICEOUS REFRACTORY SHALE SHOWING GLOSSOPTERIS FAUNA, VEREENIGING AREA.

Glossopteris browniana	Sigillaria bardi
Gangamopteris cyclopteroides	Bothrodendron leslii
Sphenopteris sp.	Psygomophyllum kidstoni
Neuropteris validum	Noeggerathiopsis hislopi
Phyllotheca	Cardiocarpus sp.
Schizoneura sp.	Conites

A specimen of silicious refractory shale with glossopteris flora from the Vereeniging district is shown in Plate II.

(It is noteworthy that Leslie discovered gangamopteris flora directly beneath a stratum identified by him as Dwyka Tillite in the Vereeniging district and this find has been used as evidence of the possibility that this flora appears earliest in South Africa, assuming that the principal phase of the great period of glaciation occurring at the time synchronized in regions throughout the southern hemisphere (9)[h]. The basal Karroo conglomerate, derived from the Dwyka Tillite and consequently of later age, usually forms the base of the Karroo in the Vereeniging district, according to the writer's investigations supported by the recent work of the Union Geological Survey, and the Tillite was not seen in natural exposure or recognized underground in the coal mines. It is suggested therefore that the conjectures based on Leslie's discovery may require revision pending further regional study of the Basal Karroo Conglomerate).

Weathering

The Middle Ecca rocks weather in a manner which is peculiarly different from the surrounding older formations. These characteristics are of special consideration in prospecting and mining of the refractory clays.

Surface Weathering: In general the only rocks in the stage which form surface outcrops are the massive grits and sandstones. As previously mentioned, the grits exhibit a characteristic mode of weathering which oftimes results in extremely fantastic sculpturing. This phenomenon is well seen in the Witbank area.

The sandstones which are generally lenticular in character sometimes show spheroidal or "flagstone" weathering.

/ In .....

the latter case the weathering is due to fissures regularly arranged to give a pavement-like appearance.

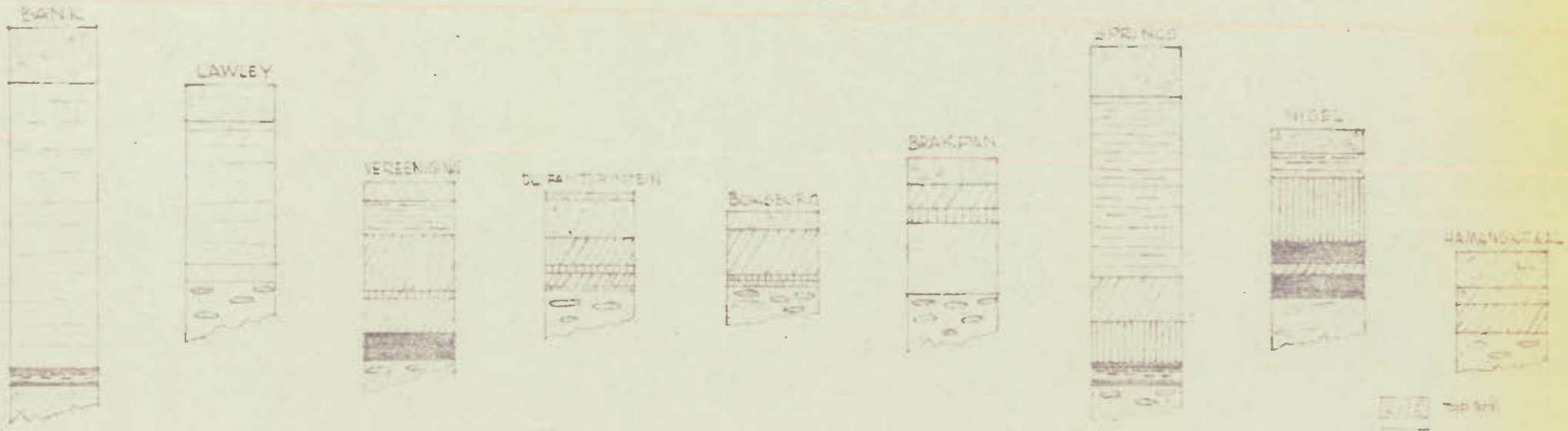
Very occasionally, the clays and shales and even coal seams are exposed to weathering in deep dongas in which case the surface is extremely crumbly and where the clays and shales are exposed oftimes the characteristic "onion peel" type of weathering is encountered. The colour of these strata is generally much lighter at the surface than that encountered at depth.

Underground weathering: The material overlying the Middle Ecca rocks is frequently a sandy covering which protects the underlying rocks from spalling due to temperature changes and from the action of winds. This cover is, however, very pervious to meteoric water and as a result run off is small. The generally horizontal lie and high water absorption properties of the Middle Ecca rocks give rise to active circulation in the stage. These effects are particularly marked on the carbonaceous rocks which decompose, accompanied by a loss in organic material and removal of pyrite to form soft laminated shales or clays. Such a cause is generally attributed to the occurrence of "wash-outs" as pointed out by Mellor (8).

Sometimes the carbonaceous material may be removed from considerable areas by underground streams through the action of decomposition, solution and denudation giving rise to a series of subsidences.

Stratigraphic Relationships.

The Middle Ecca stage is characterised by the extremely erratic occurrence of the included strata. The condition prevails to such an extent that it is not possible to present by detailed sections a clear cut picture of even a moderately sized area underlain by these rocks and the difficulty is increased by the fact that many of the existing borehole records and measured sections were prepared by different workers and in



COLUMNAR SECTIONS OF THE MIDDLE ECCA SERIES IN THE TRANSVAAL

VERTICAL SCALE 1" = 50 FEET

consequence there is no uniformity in description and nomenclature. Columnar sections of the Middle Ecca stage measured in various areas in the Transvaal are given in Figure 4., and they demonstrate the change in thickness and character of the formation in different localities. Borehole records and measured sections will be given in the description of specific clay producing areas later on, insofar as these data are available.

III-DEPOSITS OF REFRACTORY CLAY.

GENERAL STATEMENT..

The refractory clay deposits of commercial importance in the Union, as previously stated, are known to occur only in the Middle Ecca stage in the Transvaal. These clays are not uniformly distributed throughout the formation but are confined to certain horizons and to limited areas. Considered broadly there are four principal areas producing such clays for the manufacture of refractories: (a) in the Vereeniging district, which includes a patch of Karroo representing the northern extension of a large occurrence of these rocks in the Orange Free State; (b) an outlier of Karroo rocks at Olifantsfontein, 14 miles south of Pretoria; (c) the area between Boksburg and Springs, which includes a large patch of Karroo strata and (d) the area around Hammanskraal, 16 miles north of Pretoria, which is underlain by Karroo rocks.

Generally speaking, many other occurrences of Middle Ecca strata in the Transvaal and northern Natal are potential sources of refractory clays. Such clays are known to exist outside of the areas mentioned above and are used for the manufacture of golden brown building brick and other ware; however, owing to prevailing economic factors they are not of commercial importance for the manufacture of refractories at this time. The absence of refractory clays in many deposits of Middle Ecca is probably explained by the fact that they were either removed by denudation or conditions favourable for their formation never occurred.

The refractory clays in one area differ from those in other areas and there are even marked variations of the seams within the particular areas. The character of the associated rocks is also different in the different areas. In all cases, however, the refractory clays in the areas described are either

resting directly on the Dolomite or not far distant from these rocks and it is interesting to speculate on the relationship between the Dolomite and the refractory clays.

Kinds of Clay.

South African Refractory clays may be most simply defined for industrial purposes as non-plastic or plastic, depending upon their workability. There is no generally accepted terminology for a more elaborate description of South African refractory clays although some manufacturers do make use of certain industrial classifications, based on texture, which have been adopted by overseas workers. Such a classification is given as follows and will be adopted here to assist in descriptions of the local clays.

Flint Clay.

The flint clays are so called because of their textural and structural resemblance to "flint". They are homogeneous, fine grained, hard, smooth, poorly plastic, and break with a characteristic conchoidal fracture. The flint clays vary in colour and though generally found in various shades of white, grey and black, they may also be pink, red, or buff. The colour of the darker varieties is due to organic matter and sometimes the clay seam passes into a bed of poor grade coal. The pink, red, and buff varieties owe their colour to the presence of iron oxide. Generally speaking, raw colour is no indication of the colour of the burned ware, for quite frequently the coloured varieties burn white or buff.

Semi-flint Clay.

This is an arbitrary term applied to the bulk of the refractory clays in the Union because they approach the flint type in hardness. In this category are included the smooth, hard, dense clays which break with a sub-conchoidal to shaly fracture. The colour range of these clays is similar to the flint clays. Many of these clays show the peculiar "onion

peel" type of weathering on exposure which results in a complete breakdown of the clay, through a succession of spheroidal structures, until the material is reduced to fine particles. The plasticity of these clays is variable but it generally does not approach that of the plastic types. Many of these clays contain considerable amounts of quartz and sometimes are stained on the surface with manganite (MnOH) which may also be disseminated throughout the clay.

Plastic Clays.

The South African plastic clays are generally well recognised as extremely fine grained, soft, compact clays which possess highly developed plastic properties and are characteristically chocolate to black in colour, though both purple and pink varieties are known commercially. These clays generally exhibit a varved structure with extremely fine lamellae composed of light and dark coloured materials. They are usually less pure than the flint and semi-flint types in that they contain more alkalies, iron, and silica. These clays frequently show slickensides and they may be generally recognised by the polished surface that can readily be developed by scratching them with the fingernail.

Siliceous Refractory Shale.

This type is characterised by well developed parting parallel to the basal plane giving the material a thin bedded structure. Although properly classified as a shale in geolic terminology this type is herein considered a clay within the standard ceramic definition as given by the A.S.T.M. designation C.71-42. * This material is rich in quartz, often containing up to 50% of this mineral, and frequently passes into sandstone within short distances. The colour of this material is generally pink to reddish-brown.

---

* "Clay - an earthy or stoney mineral aggregate consisting essentially of hydrous silicates of alumina, plastic when sufficiently pulverised and wetted, rigid when dry and vitreous when fired at a sufficiently high temperature".

General Geologic Features of the Clay Deposits.

The productive horizons of refractory clay in the Middle Ecca are usually encountered at shallow depths which facilitate open-cast working; however, this advantage is somewhat offset by the thinness of the seams and the extensive variation and lenticular nature of the seams. Some geologic features characteristic of these clay deposits are:

(a) Faults: In general the faults encountered in the clay deposits are on a small scale. Dislocation seldom exceeds three feet and more often the movement is only a matter of inches. Slickensides are common in the plastic clays reflecting the slips that have occurred. There are notable exceptions to the usually small amount of displacement found, however, as seen in one case at Vereeniging where the faulting involved has a throw of up to 200 feet.

(b) Folding: Folding is not encountered in the Middle Ecca strata in the Transvaal and geologic evidence indicates that no structural changes of mountain building intensity occurred in this area since the beginning of Karroo times.

(c) Dip of Beds: The clay strata and associated rocks are generally flat-lying, dips seldom exceeding 3°. Gentle undulations are common as the beds respond more or less to the contours of the rocks upon which they were deposited. Pronounced "rolling", local in extent, is frequently developed in areas where the Middle Ecca strata are underlain by dolomite and slumping has occurred owing to the formation of underground sinks. In such cases the beds show abrupt variation in dip conforming to the irregularities of the dolomite floor.

(d) Igneous Intrusives: Intrusion of dolerite in the form of sills and dykes is fairly common in the Middle Ecca strata and they frequently alter to clayey products near the surface. An example of this is indicated in drill cores from the Springs area where decomposed dolerite, yellowish in colour, was encountered at a depth of 35 feet. Vertical intrusion of dolerite may be seen exposed in the workings on the Farm

GEOLOGIC SKETCH MAP
VEREENIGING AREA
SCALE 1 : 50 000

(After Union Coal)

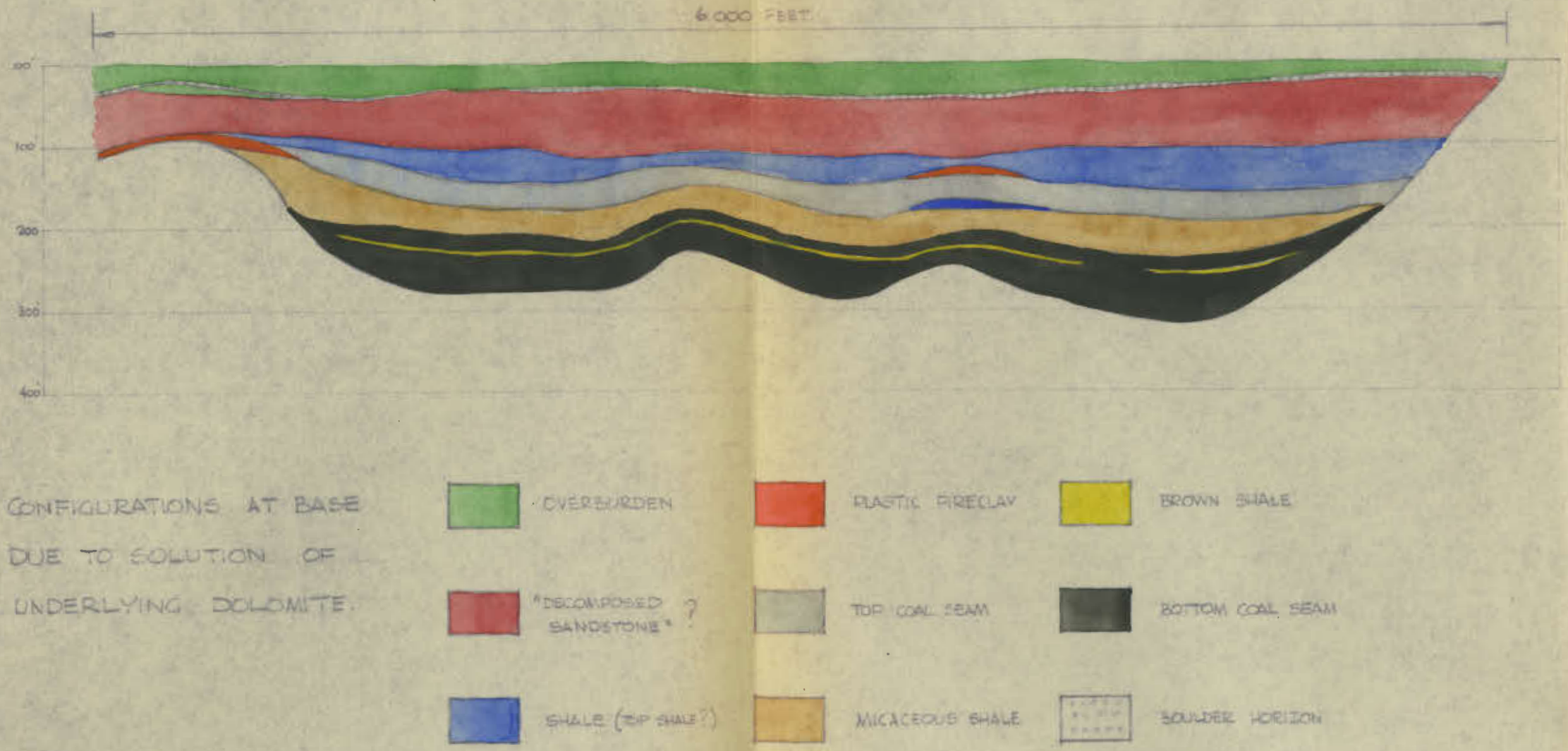
Rietfontein 14 in the Springs area where they have been left behind in the mining operations and remain in the form of "bosses" rising from the pit floor.

Description of Producing Areas.

Vereeniging.

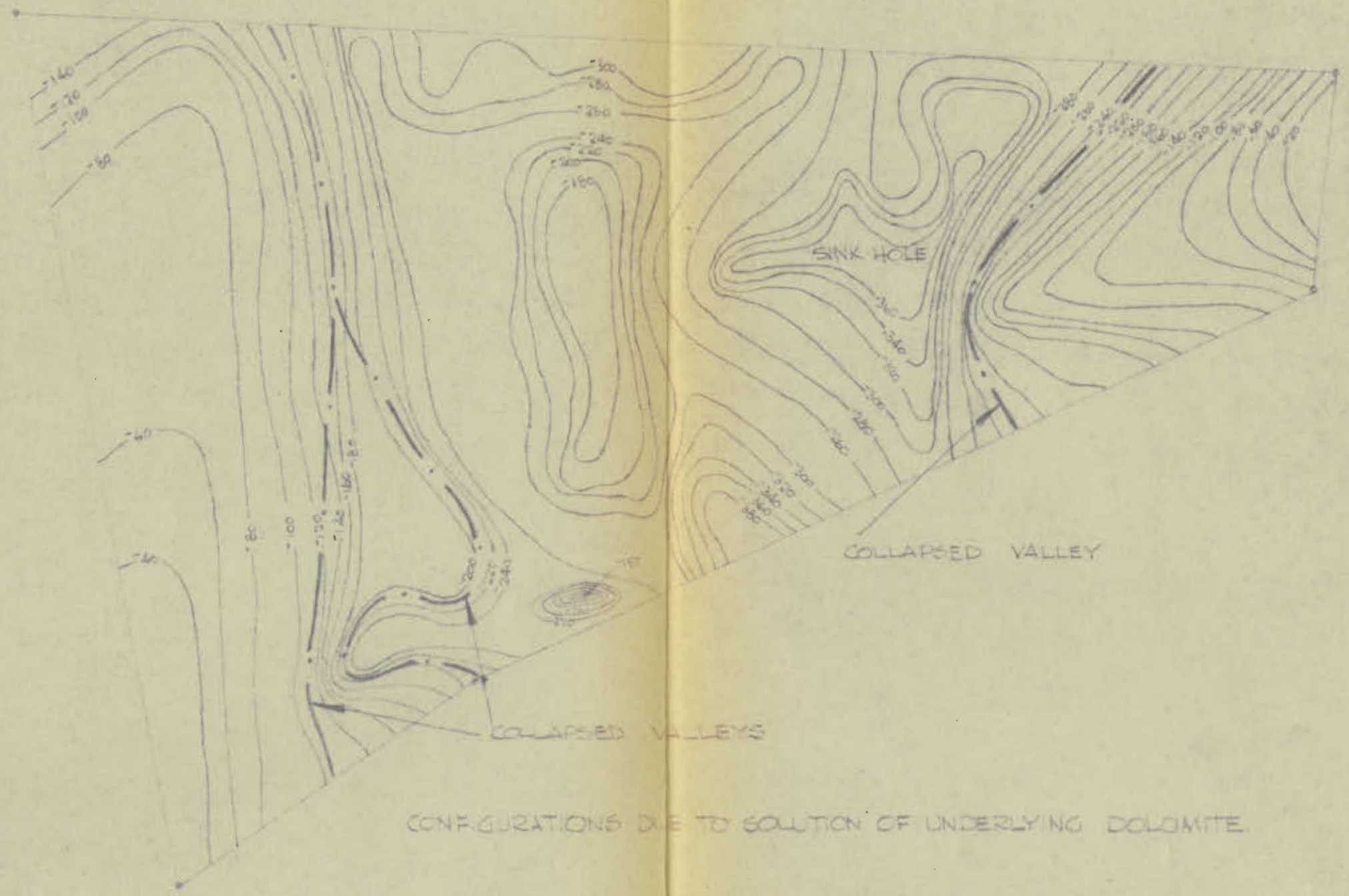
The patch of Middle Ecca strata containing workable seams of refractory clay in the Vereeniging district lies just to the north of an extensive occurrence of Karroo rocks in the Orange Free State. The area near Vereeniging underlain by these rocks covers about 150 square miles, but the deposits of refractory clay which have been worked by the Vereeniging Brick & Tile Company Ltd., since 1883, have so far been found in limited extent. A geologic sketch map showing the clay producing fields at Vereeniging is given in Figure 5. The most productive areas lie to the north of the Vaal River in the Transvaal since the Vaal in northward meanderings has denuded much of the upper portion of the Middle Ecca strata on the Free State side.

The Vereeniging district is underlain for the most part by the dolomite, which through sub-surface leaching has led to the formation of sinks into which the Middle Ecca strata have subsided. Field evidence suggests that these subsidences were generally contemporaneous with or followed the deposition of the refractory clays. It is also quite probable that they were formed in pre-Karroo times as well, in which case they served as depositional basins for the later Middle Ecca sediments. The refractory clays represent terrestrial sediments laid down in various environments. The immediate principal sources of the sediments were probably the Dwyka Tillite that once covered the area, and the underlying dolomite. The predominant rocks in the "tillite" were derived from the Dolomite Series, and vestiges of these rocks are still represented by huge blocks of "Giant Chert" overlain by the Basal Karroo Conglomerate seen on the Farm Klipplaatdrift 83. Fragments of Red Granite similar to the Bushveld rocks have also been found in the Basal Conglomerate exposed on Klipplaatdrift 83, along



GENERALIZED GEOLOGIC SECTION OF THE MIDDLE ECCA IN THE VEREENIGING AREA

FIG. 6

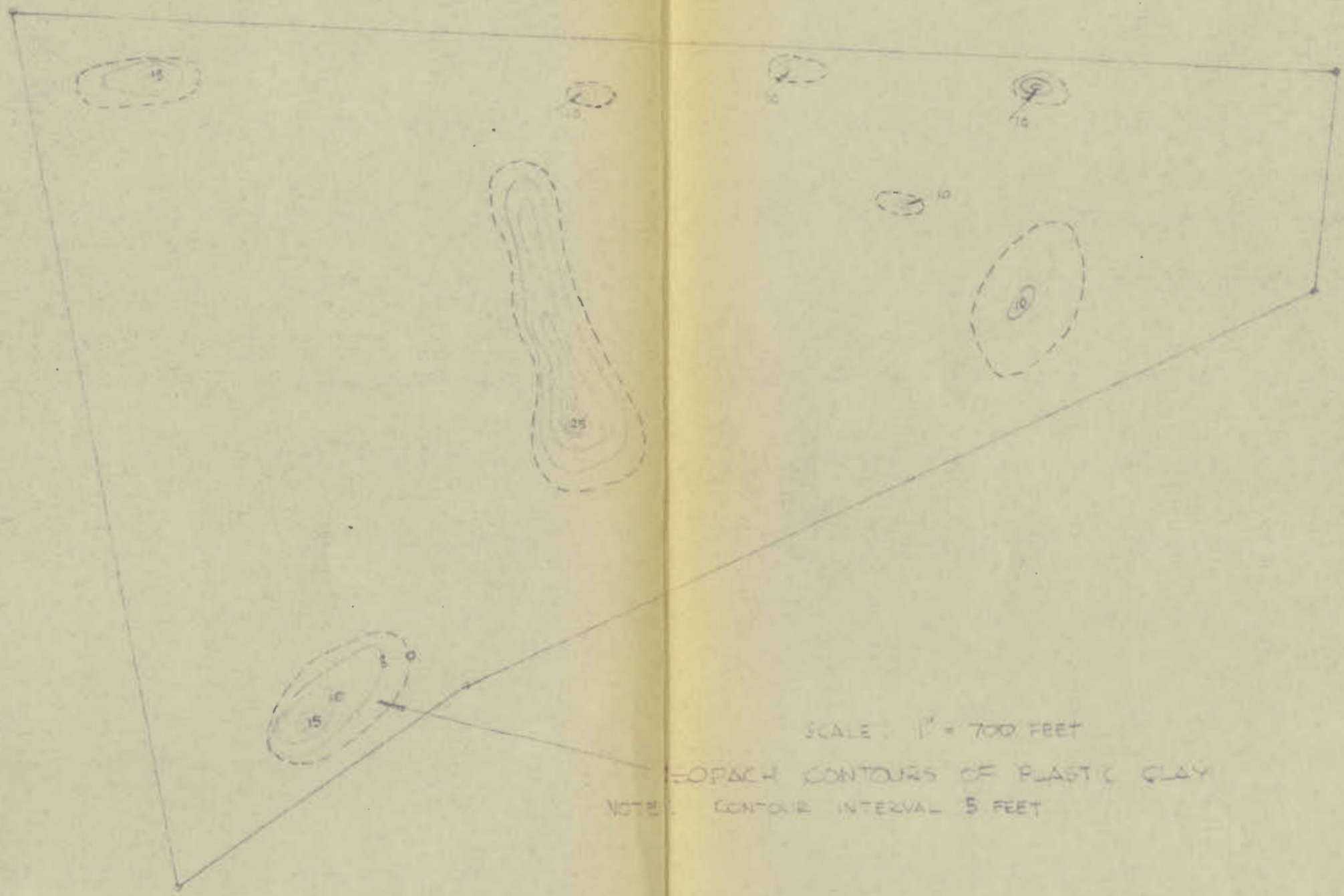


CONFIGURATIONS DUE TO SOLUTION OF UNDERLYING DOLOMITE

SUB-SURFACE CONTOUR PLAN OF THE BASE OF THE MIDDLE ECCA IN A PORTION OF THE VEREENIGING AREA

SCALE: 1" = 700 FEET DATUM 4780 FEET.

FIG 7



SCALE : 1" = 700 FEET

ISOPACH CONTOURS OF PLASTIC CLAY

NOTE : CONTOUR INTERVAL 5 FEET

PLAN SHOWING SUB-SURFACE OUTCROPS OF PLASTIC CLAY IN THE VEREENIGING AREA.

FIG 3

with boulders of quartzite from the Black Reef, Waterberg, and Pretoria strata, which indicates the varied source of the "Tillite".

As mentioned previously, the extreme variation of the Middle Ecca makes it difficult to portray by sections and borehole records; however, a generalised geologic section shown in Figure 6, prepared from borehole data, gives an indication of the strata encountered just north of Vereeniging. The unevenness of the underlying dolomite floor is shown by the sub-surface contour plan of the same area, given in Figure 7. Contemporaneous erosion took place in the lower portion of the strata in the Vereeniging areas, as shown by the fragments of flint clay that occur in the thin bands of conglomerate occurring above the main coal seam.

Four types of refractory clay are recognised in the area (a) flint, (b) semi-flint, (c) plastic, and (d) siliceous refractory shale.

The flint clay which is black, grey, or brown in colour occurs as a parting in the main coal seam in the district. This clay is remarkably continuous over the area and is found in the coal workings on both sides of the Vaal. In addition to the principal flint clay seam there are numerous bands of this material occurring above or below the main clay seam which are frequently intercalated with the coal seams. The flint clay breaks with the typical conchoidal fracture as exhibited by flint clays in Missouri and it is further similar in its lack of plasticity and smooth, hard texture. The Vereeniging flint clay generally contains a large amount of organic matter and some varieties will pass as low grade coal. The flint clay usually contains enough combustibles to render it self-calcining so that it may be stacked in heaps and set alight to remove the troublesome carbonaceous material before being processed.

The semi-flint clays of the Vereeniging district occur above the coal seams in the upper portion of the Middle Ecca found in the district. They are usually separated from the coal beds by intervening carbonaceous and micaceous shales. These clays vary in colour and include shades of purple, pink, buff and grey, with the latter predominating. Some of the beds contain numerous visible particles of manganite disseminated throughout. Manganite occurring along joint planes is also noted in some strata. These clays frequently show evidences of root markings which indicate that they were exposed to sub-aereal conditions at least for short periods during their formation.

The plastic clays have been found in irregular sporadic patches associated with the top coal seam in the district. They are generally purple to black in colour showing alternations of light and dark material, and frequently contain coaly matter. Some varieties of chocolate coloured plastic clay similar to the deposits near Springs have been found in the area.

The relationship of the plastic clays to the coal seams was examined from a study of borehole records. The outcrops of plastic clay, when drawn in plan, appear as irregular pockets occurring at the same horizon as the top coal seam, as seen in Figure 8. These pockets suggest "water holes" in ancient stream channels or "deeps" in old lake beds. The banded alterations in colour of the sediments suggest rhythmic fluctuations in their character and the extremely fine texture of the sediments would indicate that they were laid down in quiet waters. The plant remains associated with this clay, as well as its general character, suggests that it represents sapropelic sediments derived from weathered and denuded coal seams, drained by the water courses effecting the transport and laid down in the old channels and basins from which coal, previously present, was removed. Such types of depositions are frequently associated with bacterial

activity according to Twenhofel. (14)

Silicious refractory shales are found overlying the semi-flint clays. These shales vary from extremely fine grained argillaceous shales to proper sandstones and in all cases they contain visible quartz grains. They are generally pink in colour and well bedded. Some occurrences contain felted masses of leaf imprints, generally glossopteris. The perfect preservation of the delicate plant membranes indicates that these shales were laid down in extremely quiet waters.

The flint clay is at present being mined in the area, and open cast workings on the Farm Leeuwkuil 87, have exposed the semi-flints, plastics, and silicious refractory shales. Semi-flint clays are also being worked on the Farm Koekfontein 87. Geologic Sections prepared from borehole records in this area are given as follows:

Section**********

	Feet
Top Soil	½
Loose Sand	31
Fireclay, black, flint	2
Coal	5
Shale, black, micaceous	27
Fireclay, black, flint	2
Coal, with flint clay parting	23
Fireclay, black, flint	1
Conglomerate	1
Coal	1
Conglomerate	4
Coal	3
Fireclay, black, flint	3
Coal	2
Conglomerate	2
Coal	½
Fireclay, black, flint	1½
Coal	1
Basal Karroo Conglomerate	

Section**********

	Feet
Loose sand and gravel	5
Fireclay, grey, thin-bedded	4
Fireclay, grey, thick-bedded	5
Shale, refractory, silicious	3
Fireclay, grey, thick-bedded	3
Shale, varicoloured	6
Fireclay, black, plastic	½

0 1/4 1/2 3/4 1 Miles

GEOLOGICAL SKETCH MAP OF THE
OLIFANTSFONTEIN AREA

Section**********

	Feet.
Fireclay, grey, thick-bedded.....	1
Fireclay, black, plastic.....	2
Fireclay, grey, thick-bedded.....	1
Fireclay, black, thick-bedded.....	2½
Coal, with alternations of shale..	4
Shale, black, micaceous.....	6
Coal.....	1
Fireclay, black, flint.....	2
Coal.....	1
Fireclay, black, flint.....	1
Coal.....	4
Basal Karroo Conglomerate.....	

Section**********

	Feet.
Top Soil.....	1
Fireclay, buff, ironstone.....	3
Fireclay, buff.....	2
Sandstone.....	2
Fireclay.....	1
Sandstone.....	2
Basal Karroo Conglomerate.....	

These detailed sections well illustrate the character of the strata encountered in the area.

Olifantsfontein.

A deposit of Middle Ecca clays occurring on the Farm Olifantsfontein 559 has been worked since 1903 by the Consolidated Rand Brick, Pottery and Lime Co. Ltd., This deposit consists of an outlier of Karroo rocks which has been preserved from denudation by slumping into solution cavities formed in the underlying Dolomite. This patch of Karroo rocks entirely surrounded by Dolomite is roughly elliptical in ground plan, as shown in the geologic sketch map given in Figure 9, and covers approximately 3 square miles.

The character of the strata in the area is well shown by the detailed sections measured by Wagner (1) and even though the mining operations have long since exposed other combinations of rocks, these sections will be given to illustrate the general stratigraphic relationships that prevail.

"Description of sections on the North and East faces of the main pit, taken 120 feet apart, are given below:

North Face.

	Thickness.
Red Soil	28'6"
Alternations of pink and grey sandstone, shale, clayey sandstone and grit merging down into small pebble conglomerate enclosing fragments of underlying clay	12'0"
Pale brownish grey fire-clay traversed along joints and shrinkage cracks by seams of ferruginous material	3'0"
Ferruginous clay	0'1"
Laminated Pale Pink fire clay	1'6"
Coarse feldspathic grit	1'0"
White fire clay	0'6"
Gritty arkose	2'0"
Laminated pink-brown, chocolate weathering clay "Chocolate layer"	1'0"
Laminated grey-white clay	0'3"
Pale pink-brown clay	0'4"
Bluish grey clay	0'4"
Greyish white sandy clay becoming more arenaceous in lower portion of layer	1'6"
Grey sandy clay with scattered glacial erratics	1'0"
Grey sandstone with glacial erratics exposed in bottom of pit	

South Face

	Thickness.
Red Soil	2'0"
Alternations of sandstone, shale, ferruginous sandstone and grit	10'0"
Pale brownish pink, white weathering fire clay	6'0"
Coarse feldspathic grit	1'8"
Greyish white fire clay	2'0"
Feldspathic grit merging locally into small pebble conglomerate	1'6"
Chocolate Layer	1'0"

South Face (cont'd).

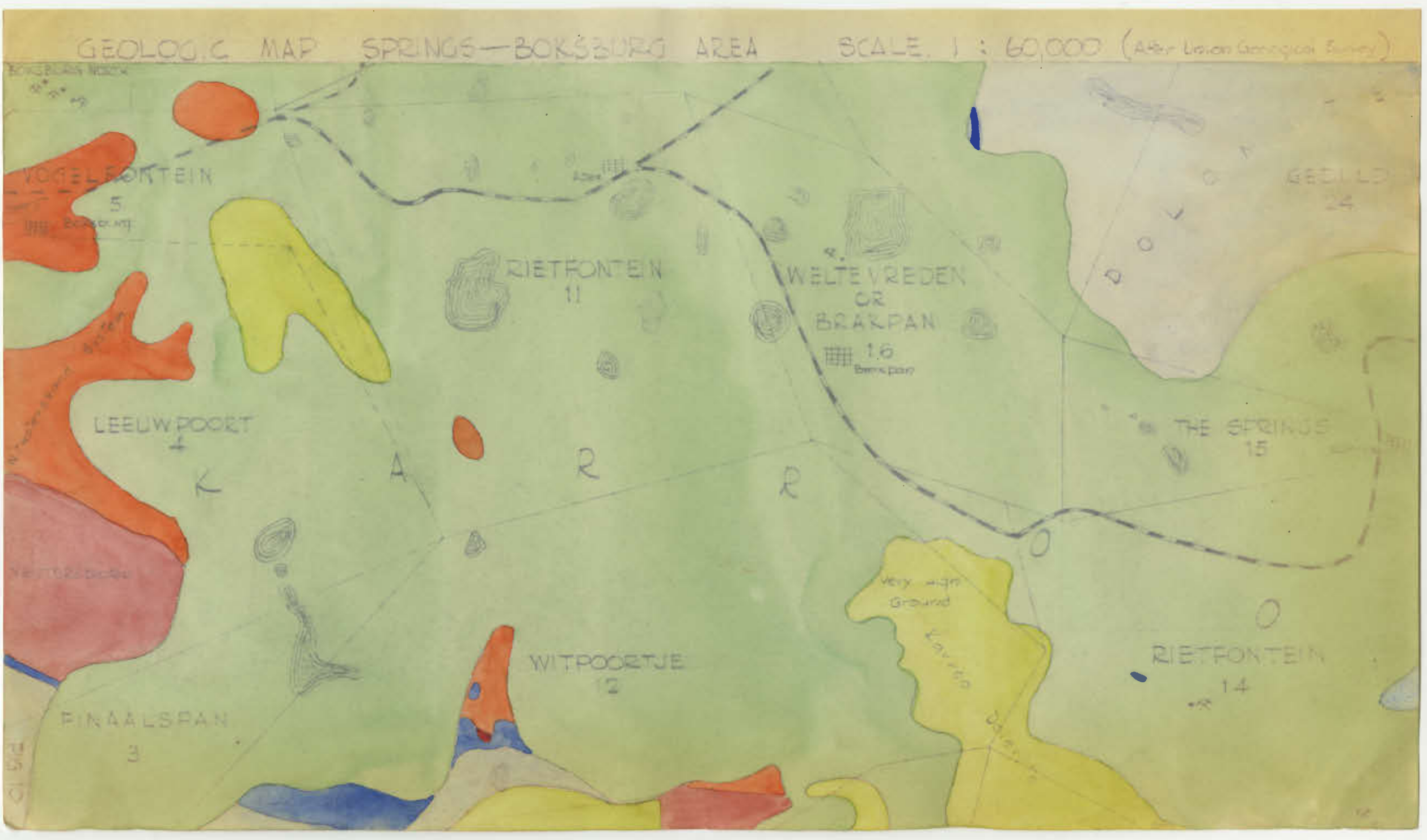
	Thickness.
Laminated greyish white clay	0'3"
Brownish pink layer	0'8"
Greyish white sandy clay becoming more arenaceous in lower portion	2'0"
Clayey sandstone with scattered glacial erratics exposed in bottom of pit	

The characteristic variations of the Middle Ecca strata are again demonstrated by the abrupt changes from extremely fine sediments to coarse materials that occur in the stage which suggests the frequent changes in depositional conditions that took place while these sediments were being laid down. The beds are also lenticular in character and grade into other materials over short distances. The deposit contains impure coal bands in the lower portion and a thin layer of brownish yellow feldspathic sandstone immediately overlying the main clay seam was reported by Wagner to contain abundant plant remains including glossopteris indicta, glossopteris angustifolia, gangamopteris, and cordiates. Both the nature of the enclosing rock and the fossil finds are similar to the Vereeniging occurrence.

The non-plastic clay seams are massive in character and vary in colour including shades of buff, pink, and grey. Occurrences of both the flint and semi-flint types are mined for refractory purposes from this deposit.

The plastic clays of the area are chocolate to pink in colour and resemble the plastic clays so well developed in the Springs area. They show light and dark coloured bands and are extremely fine textured.

Wagner (1) reports the occurrence of epidote, rutile, garnet and muscovite in the clays of this area, and he points out the unusually low silica to alumina ratio of some of the refractory clays. He also comments on the occurrence of coarse grits which form the only outcrops in the area. He states that

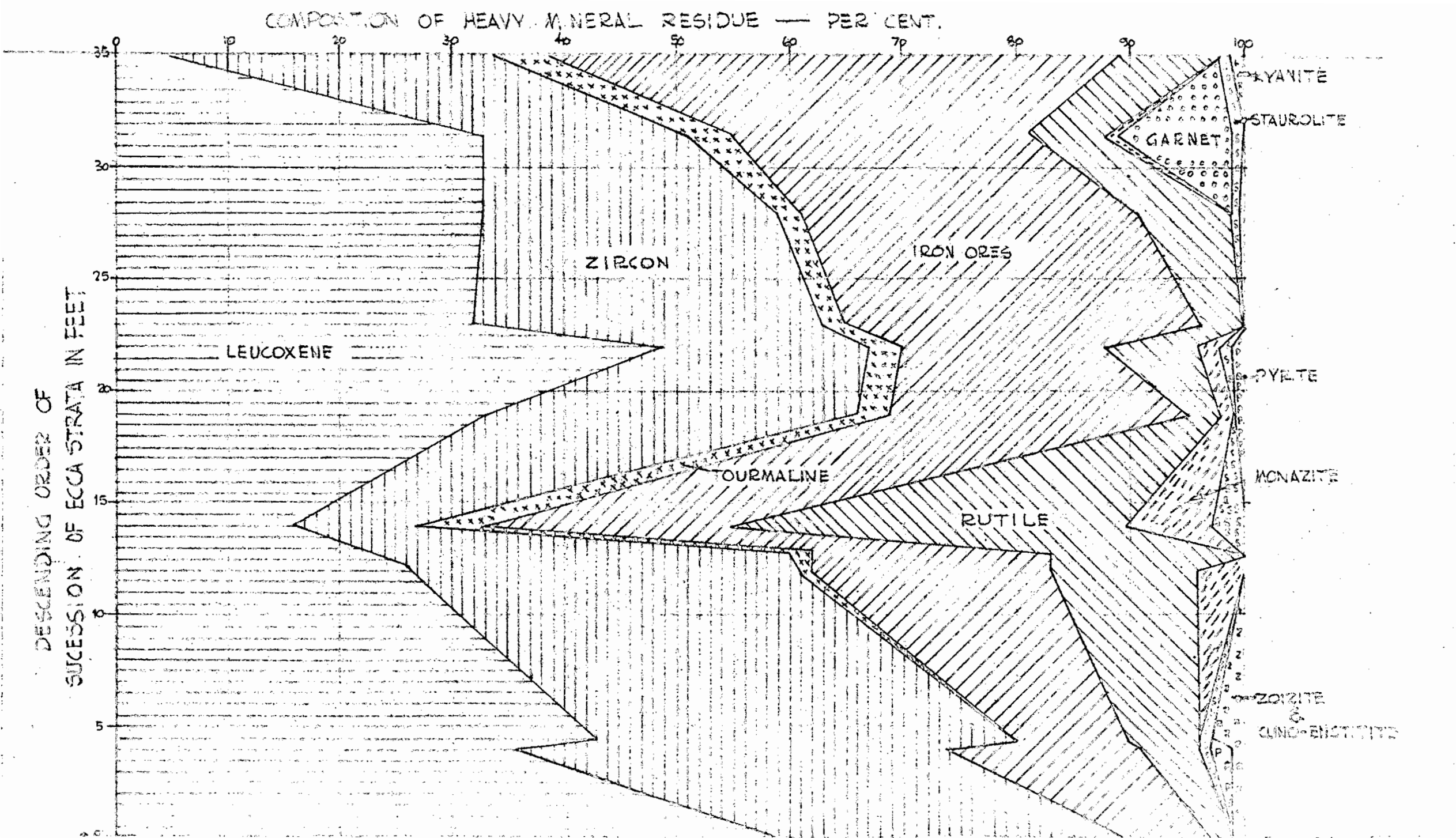

GEOLOGICAL MAP SPRINGS—BOKSBURG AREA SCALE 1 : 60,000 (After Union Geological Survey)
VOGELFONTEIN
5
RIETFONTEIN
11
WELTEVREDEN
OR
BRAKPAN
16
Brakpan
GEELLO
24
LEEUWPOORT
4
K
A
R
R
O
THE SPRINGS
15
Very High
Ground
WITPOORTJE
12
RIETFONTEIN
14
PINAALSPAN
3

these grits consist mainly of sub-angular fragments of quartz and also include a good deal of feldspar which is sometimes so abundant that the grit on weathered surface resembles decomposed granite. He also remarks that contemporaneous erosion must have taken place as evidenced by the occasional fragments of underlying clays found in the grits.

The clay-bearing strata are underlain by sandstones, conglomerate, [illegible], and chert. The character of the conglomerate, as described by Wagner (1), suggests that it is derived from the Tillite and represents the Basal Karroo Conglomerate seen at Vereeniging. The chert seams mentioned by Wagner (1) as occurring interstratified with the conglomerate band are unique.

Springs - Boksburg.

The occurrence of the Middle Ecca strata on the East Rand between Springs and Boksburg includes a number of deposits of refractory clay. The Middle Ecca in this area is part of a much larger body better developed still further east. A geologic sketch map of the area is given in Figure 10. The entire thickness of Karroo strata in this area does not generally exceed 200 feet, much having been removed by denudation which has been continuous up to the present. As elsewhere the area is characterised by featureless grass-covered bults and frequent marshy vleis. The Middle Ecca is generally horizontal disposed and outcrops are rare. The stage contains coal seams which were worked at Boksburg, Brakpan, and Springs. The base of the Middle Ecca in the area is generally marked by a conglomeratic horizon as deduced from borehole data and it is extremely difficult to distinguish from such records whether this bed represents the Dwyka Tillite or derived conglomerate. Where this rock has been exposed in prospect pits and mine shafts the extent of the exposure is generally not sufficient to afford conclusive evidence of the presence or absence of sorting, however, samples of this conglomerate obtained from a pit on the Farm Rietfontein 14 contained angular fragments


COMPOSITION OF HEAVY MINERAL RESIDUE — PER CENT.
0
10
20
30
40
50
60
70
80
90
100
35
30
25
20
15
10
5
DESCENDING ORDER OF SUCESSION OF ECCA STRATA IN FEET
ZIRCON
LEUCOXENE
IRON ORES
GARNET
KYANITE
STAUROLITE
PYRITE
TOURMALINE
RUTILE
MONAZITE
ZOISITE
&
CLINOENSTATITE

of clay which would suggest secondary origin at least for some of this material.

The general lens-like character of the Middle Ecca strata here or elsewhere, makes it difficult to compare sections and borehole records from localities even close together to depict the stratigraphic correlation of the strata.

The Middle Ecca strata either overlie the Dolomite or they occur in its vicinity. The influence of solution sinks in the underlying dolomite, causing slumping in the overlying strata, can be clearly seen in the clayworkings on the Farm Riotfontein 14. At Boksburg the Middle Ecca and associated Karroo rocks overlie the Witwatersrand strata but are not far from the Dolomite outcrops.

Figure 11 shows a profile chart of the heavy mineral distribution in the Middle Ecca stage near Springs, prepared from data kindly supplied by Mr. H.C.H. Whiteside*. Many of the species identified are common accessories of the granites though not necessarily derived directly from these rocks.

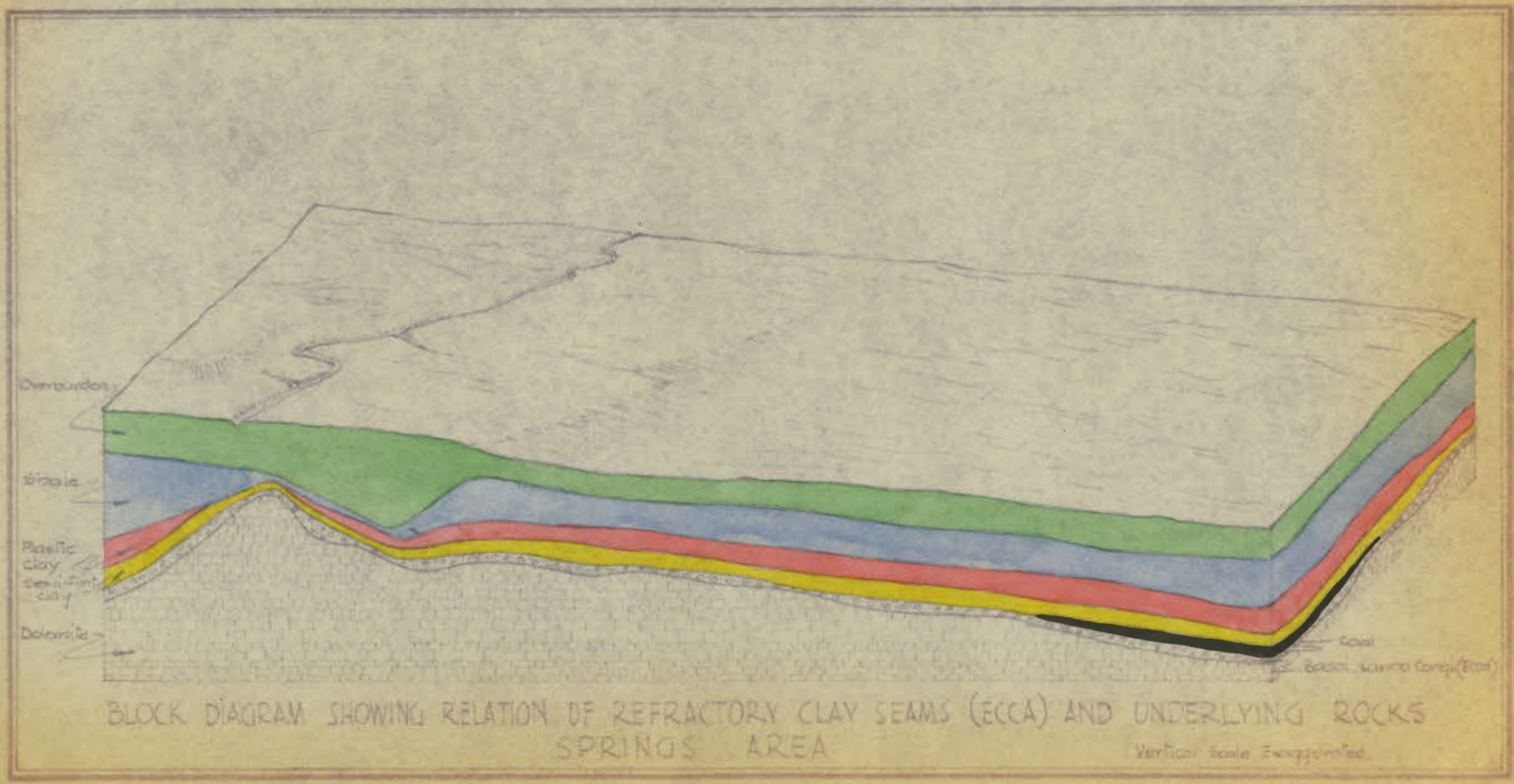
Middle Ecca clays are mined for refractory purposes in the vicinity of Springs by the Vereeniging Brick and Tile Co. Ltd., and the Elgin Fire Clay Co. These clays are also mined for the manufacture of building brick at the Jansen Brickyard a mile south of the Elgin Fire Clay Co. workings. A deep borehole shows coal seams underlying the refractory clays in this area.

The sections given below are typical of the character of the strata in this portion of the area.

Section **********

	Feet
Top Soil	3
Ouklip	9
Shale, buff, sandy	12
Fireclay, chocolate, plastic	8
Fireclay, grey, thick-bedded	9
Basal Karroo Conglomerate	

* H.C.H. Whiteside, Personal Communication



BLOCK DIAGRAM SHOWING RELATION OF REFRACTORY CLAY SEAMS (ECCA) AND UNDERLYING ROCKS
SPRINGS AREA

Vertical scale Exaggerated.

Section at Elgin Brickworks

	Feet.
Top Soil.....	2
Ouklip.....	12
Shale, buff, sandy.....	8
Fireclay, chocolate, plastic....	6
Fireclay, grey, thick-bedded....	10
Basal Karroo Conglomerate.....	

Section at Janzen Brick Co.

	Feet.
Top Soil.....	2
Ouklip.....	6
Fireclay, buff.....	4
Fireclays, buff and chocolate, plastic, mixed.....	4
Fireclay, chocolate, plastic.....	4
Basal Karroo Conglomerate.....	

The principal clay seams in the Springs area consist of flint, semi-flint, and plastic types. The flint and semi-flint clays are generally grey to black in colour. The plastic clays are well developed in this locality and are generally chocolate to pink in colour. Occasionally dykes and sills of dolerite, usually highly weathered, are encountered in mining operations. A block diagram illustrating the Middle Ecca strata in a portion of the Springs area is given in Figure 12. This diagram was prepared from borehole data obtained with a dry-drilling technique to ensure complete core recovery, on a controlled prospecting grid. The undulating character of the strata is well known and is due to slumping into the underlying dolomite. In this particular locality the overlying strata were let down gradually into the underlying cavity as evidenced by the lack of faults and slickensides seen on exposures in the quarry face.

Boksburg clays around Boksburg are principally of the flint and semi-flint types and the plastic clays, though present, are generally not as extensive as encountered in the Springs area. Clays are mined for the manufacture of refractories on the Farm Klipfontein 6 (Boksburg Fireclay Co. Ltd., and Union Fireclay Co.) and Volgelsfontein 5 (Economic Fireclay CO.).

A geologic section at Boksburg North given below is indicative of the clay bearing strata encountered in this area.

Section at Boksburg North

	Feet.
Top soil, reddish.....	5
Fireclay, buff, soft.....	4
Fireclay, buff, thick-bedded.....	10
Fireclay, brown, plastic.....	2
Sandstone	

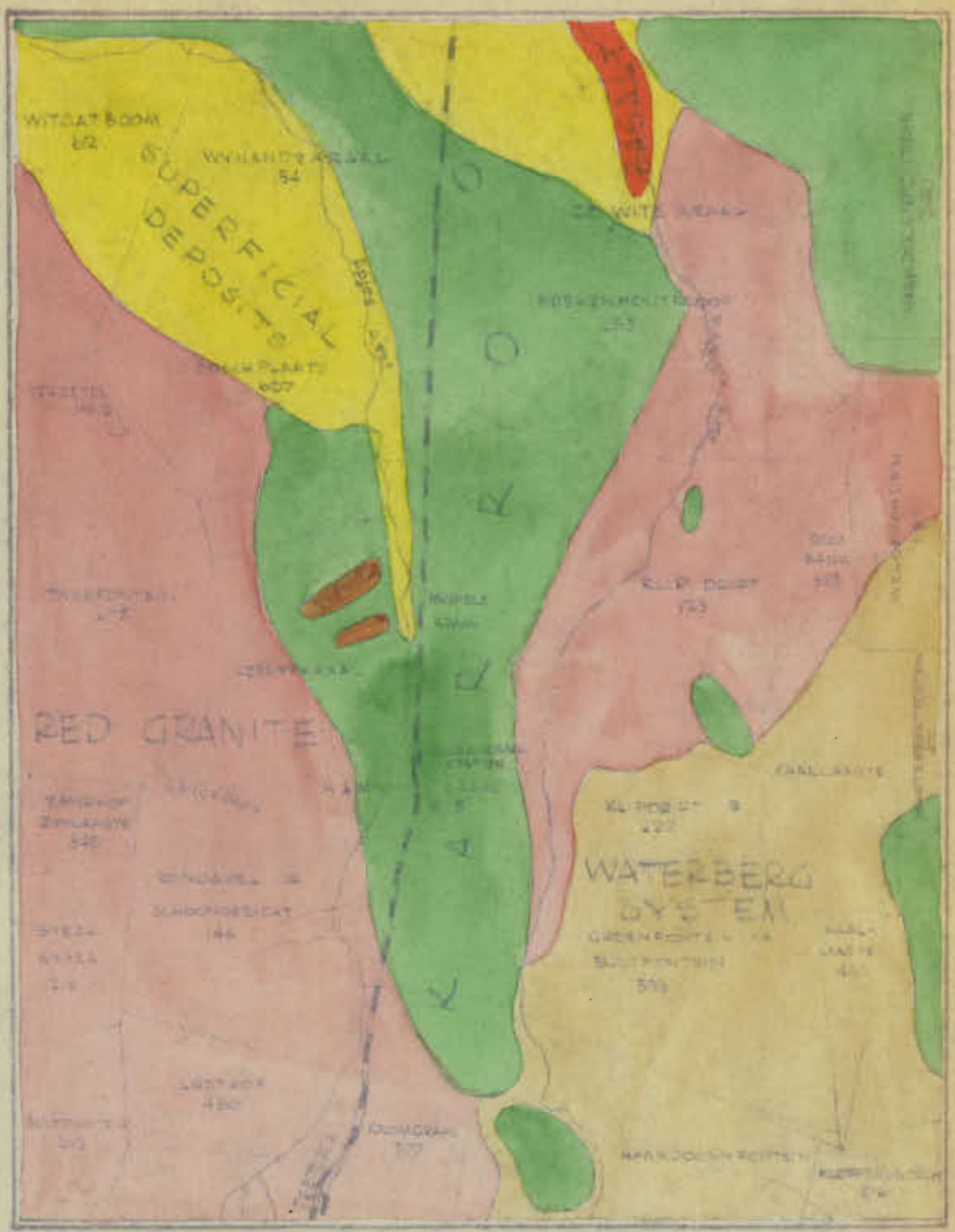
Brakpan clay workings adjacent to the pan from which the town of Brakpan gets its name, were opened in 1905. Sandstone was quarried from these workings and the clay was used for the manufacture of stock brick. In recent years the refractory clays were supplied for the manufacture of firebrick and fireclay goods. The workings were closed in 1944; a typical section of the quarry is shown below and gives a picture of the character of the Middle Ecca in this locality.

Section at Brakpan

	Feet.
Sand, yellow.....	2
Clay, greenish-ivory coloured.....	5
Fireclay, buff, thick-bedded.....	2
Fireclay, buff with intercalated purple clay.....	3
Fireclay, buff.....	2
Fireclay, chocolate, plastic.....	4
Fireclay, black, flint.....	1½
Sandstone, with pebbles.....	20
Basal Karroo Conglomerate.....	

Benoni: A geological section measured in a pit at Rangeview Station near Benoni shows the Middle Ecca strata to be as follows:

	Feet.
Top Soil.....	1
Ouklip.....	8
Fireclay, buff to white.....	8
Fireclay, buff to white, intercalated with purple clay.....	3½
Sandstone.....	6½
Basal Karroo Conglomerate.....	



GEOLOGIC SKETCH MAP OF THE HAMANSKRAAL AREA

SCALE : 1" = 2·34 MILES.

After Union Geological Survey.

Hammanskraal.

Flint clay deposits have been opened in recent years near Hammanskraal station and on the farms Kromdraai and Nabot. The Hammanskraal deposits are located on the Farm Hammanskraal 435, about half a mile from the station which is on the Pretoria-Warmbaths line, 24 miles north of Pretoria. A geologic sketch map of the area is given in Figure 13. Present workings include two small quarries and some prospect pits. The deposits south of Hammanskraal are located on Farms Kromdraai 577 and Nabot and are reached by motor road from Petronella Station.

The region lies just within the Bushveld region at an altitude of under 4,000 feet. The Aapies and Pienaars Rivers form the principal drainage channels and have cut through the underlying Karroo rocks exposing them in the river channels.

The whole area is underlain by the Red Granite of the Bushveld Complex, with the Ecca rocks forming a capping or occupying depressions. The Ecca series includes sandstone, grits and shales, and is generally horizontally disposed although local irregularities in the floor cause erratic dips. The general trend of the slight dip is towards the northwest.

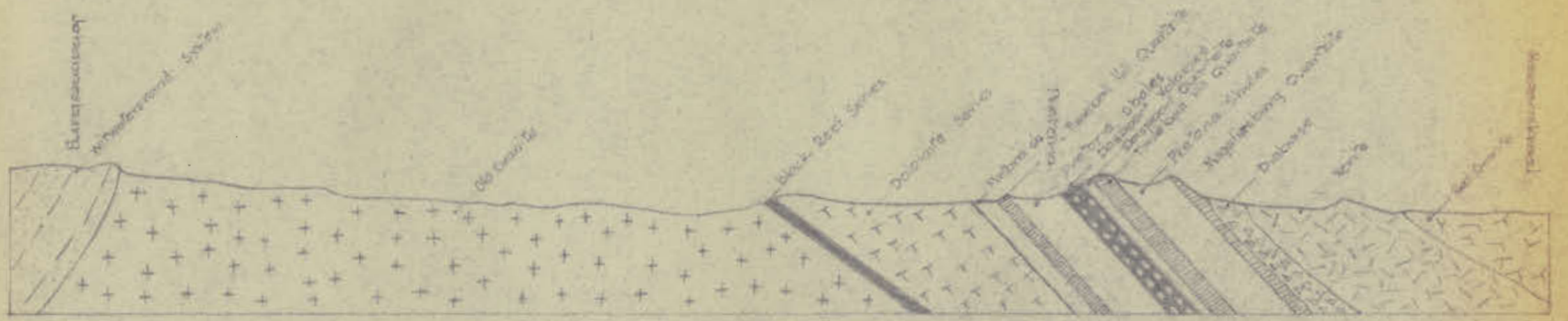
Geologic sections measured in a quarry on Hammanskraal 435 are given as follows:-

	Feet.
Top soil and sand.....	1
Sandstone, medium-grained.....	5
Shale, thick-bedded with fissile bedding at base.....	3
Flint clay, light grey.....	1½
Shale, thick-bedded, with fissile bedding at top with thin coal seam near base....	5

Geologic sections measured in a quarry on Kromdraai 577 are given as follows:

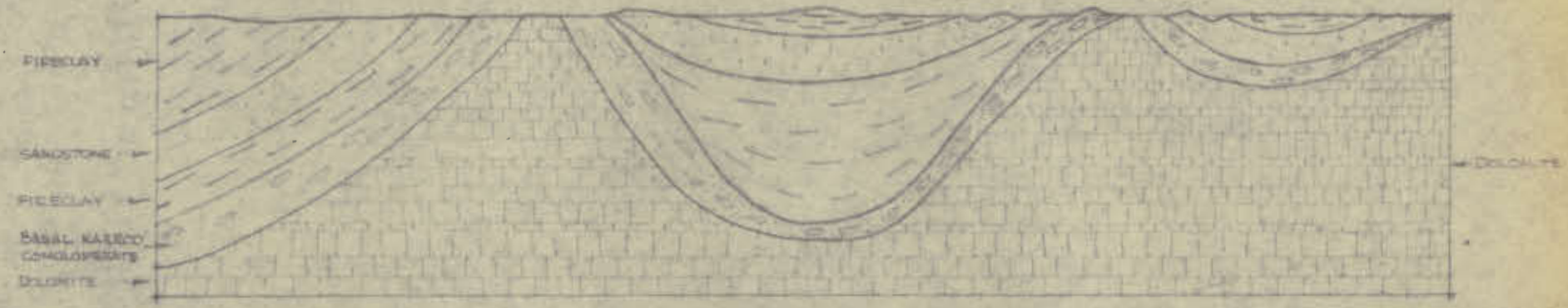
	Feet.
Loose sand, coarse.....	½"
Grit, hard, pink, coarse.....	1'0"
Fireclay, grey, "flint".....	1½
Grit, hard, pink, coarse.....	1½
Fireclay, grey, "flint".....	5
Grit, hard, pink, coarse.....	

Although overlying the Red Granite, the Middle Ecca



GENERALIZED GEOLOGIC SECTION OF THE AREA, JOHANNESBURG PRETORIA AND HAMANSKRAAL.

FIG. 4



GENERALIZED GEOLOGIC SECTION IN RAILWAY CUTTING NEAR VEREENIGING
SHOWING SINK HOLE DEPOSITES

FIG 15

sediments of the Hammanskraal area could have been contributed by Dolomites cropping out south of Pretoria since the northward drainage has persisted in this region from pre-Karroo times. This possibility is shown in the generalized geologic section of the country north of Pretoria as given in Figure 14.

Other Occurrences.

Refractory clays occurring in the Middle Ecca stage are known to occur in other localities in the Southern Transvaal and are being worked along with semi-refractory clays of the series for the manufacture of golden brown building brick and other non-refractory products at Heronmere, Driefontein, Marievale, Lawley, Kempton and Springs. A deposit of Middle Ecca clay is being opened up at Middelburg for the manufacture of building brick in the near future by the Middelburg Brick & Tile Co. Ltd.

Geomorphology.

Although the Middle Ecca strata are sometimes found overlying older rocks in elevated portions of the general land surface, these deposits most generally occur in patches which have been protected against denudation by being sunk into depressions in the surrounding more resistant formations. The most conspicuous cause of such preservation is the slumping of the overlying rocks into sinks formed by sub-surface leaching of the underlying dolomite. Depressions formed by extinct drainages and by pre-Karroo tectonics also serve to protect the sediments deposited in them from removal.

Influence of Dolomite Floor.

The Dolomite series as previously described, is composed predominantly of dolomitic limestone which is readily susceptible to solution giving rise to the formation of "collapse sinks" into which the overlying Middle Ecca sediments slumped. A Section exposed in a railway cutting near Vereeniging showing typical sink hole deposits is given in Figure 15. The existence of these solution features is a predominant characteristic of dolomite country and they

have been the principal means of retaining the refractory clay-bearing rocks and coal seams during the long erosional period to which the Middle Ecca rocks have been subjected. These collapse sinks are generally circular or irregular in ground plan and sometimes they become sufficiently extensive to merit the name "collapse valleys". In the first stages of their formation small solution sinks are formed along joint planes and pits are developed on the face of the joint blocks resulting from selective solubility. Drainage is diverted through these passages into underground cavities which increase in size until the collapse of the cave roof occurs.

In regions where the Dolomite includes a fair amount of chert near the top of the series, solution of the underlying dolomite leaves behind a relatively strong roof which does not collapse until a much larger area of dolomite has been acted upon. Solution by both surface and sub-surface waters has doubtless been in progress ever since the dolomite was in existence so that the subsidences could have been formed in either (a) pre-Karroo times, (b) contemporaneous with Karroo deposition, or (c) post-Karroo times. These conclusions are well supported by field evidence. The slumping into the sinks occurred abruptly or gradually depending upon the nature of the roof, the rate of solution, and the weight of overlying sediments.

Extinct Drainages.

Ancient drainage patterns and depressions formed in the pre-Karroo floor by the action of wind, water and ice have also played a major role in the preservation of the Middle Ecca strata. A good example of such features is found at Hammanskraal where the ancient pre-Karroo drainage pattern of the Aapies and Pienaars Rivers provided a deposition basin for the formation and retention of the Middle Ecca strata.

Post-Karroo Tectonics.

In more recent times post-Karroo tectonics have produced depressions in the land surface in which Middle Ecca rocks are protected from erosion. Such depressions

are the result of faulting and may be in the form of grabens or structural basins. A structure of this kind may be seen in the Zoutpansberg region.

Mode of Occurrence: Summary of Field Evidence.

1. The refractory clays are terrestrial sediments laid down in an aqueous environment. In all cases where the commercial refractory clays of the Middle Ecca are found they have been preserved from denudation by being below the surrounding resistant rock surface. The most conspicuous catchments are the sink holes and collapse valleys formed in pre-Karroo, Karroo and post-Karroo times, by sub-surface solution of the underlying Dolomite series. Differential erosion of the pre-Karroo land mass also provided hollows in which the deposited sediments were protected and to a lesser extent post-Karroo tectonics have provided refuge for these strata.

2. The refractory clay strata are generally horizontally disposed except where localised slumping has changed the attitude of the beds.

3. The clay strata show such extreme lateral and vertical variation that accurate correlation is not possible even over short distances.

4. Joint planes are frequently stained with limonite and manganite and these minerals sometimes occur as thin beds inter calated with the clays, suggesting leaching and infiltration.

5. The flint clays in the Vereeniging area are associated with the coal seams and the principal bed occurs as a parting in the main coal seam in the area. These clays are generally black, dark grey, or brown, depending on the amount of carbonaceous matter present. They are homogeneous, smooth, hard, and break with a conchoidal fracture and do not show "slickensides".

6. The plastic clays as investigated in the Vereeniging area are associated with the top coal seam and probably represent sapropellic deposits in ancient water courses. They occur as sporadic deposits and can be traced through altered zones to

beds of coal. These clays are extremely fine grained and exhibit varved structure with alternating light and dark bands. They frequently show "slickensides". Similar clays are found at Olifantsfontein and in the Springs-Boksburg area but their relationship with the coal seams is not so apparent in these localities.

7. The semi-flint clays, which usually comprise fairly thick bedded sediments, generally overlie the workable coal seams wherever these coals are present. These clays are generally hard and homogeneous, and frequently contain disseminated manganite. On exposure to the atmosphere, they usually exhibit a peculiar "onion peel" type of weathering. Slickensides are sometimes present but are not common.

8. The siliceous refractory shales, best developed in the Vereeniging area, occur above the semi-flint clays. These shales are well bedded, frequently showing a fissile structure, and are rich in quartz, which is usually visible to the naked eye. They contain abundant well preserved plant remains at Vereeniging.

9. A most striking observation with the occurrence of the refractory clays is that quite frequently all types exist together in the same deposit. Soft plastic clay may lie inter-bedded with strata of hard semi-flint clay.

Origin of the Refractory Clays.

In the Middle Ecca deposits of the Transvaal, the carbonaceous flint clays are overlain by the plastic semi-flint, and siliceous shales which were clearly deposited under different conditions at later times. No single origin can therefore be ascribed for these various types of refractory clays, since they were formed in different ways depending upon: (a) environment during deposition, (b) source of sediments and mode of transportation, and (c) geochemical and geo-physical conditions.

(a) Environment During Deposition.

The final character of the refractory clays was to a large extent influenced by the environmental conditions prevailing when these materials were deposited and changes of

environment are reflected by corresponding changes in the refractory clays and associated strata.

The Middle Ecca sediments are continental deposits laid down for the most part under aqueous conditions succeeding the glacial environment of Dwyka times.

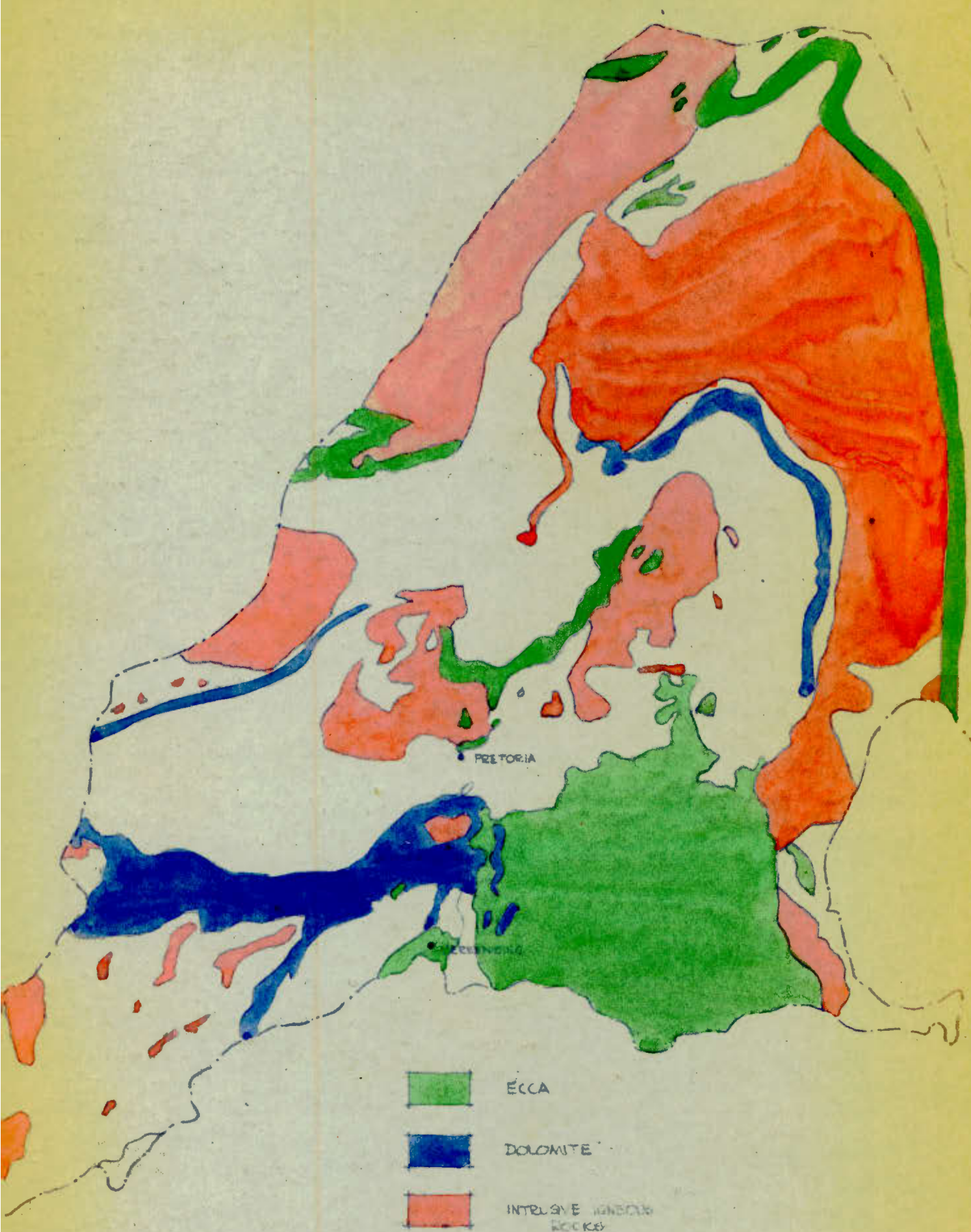
At the close of pre-Karroo times, the ancient land surface of the Transvaal, diversified by many ridges and valleys, several of which correspond to those of the present, was nearly base-levelled. With the onset of the great period of Dwyka refrigeration that prevailed over most of Southern Africa, one of the continental ice caps developed in the northeastern Transvaal and spread over most of the Province. As the glacial ice moved in a generally southern direction it slid and gouged its way over the old land mass plucking off and carrying with it pebbles and boulders in addition to the rock "flour" formed by the abrasion of the rocks which it traversed. These materials frequently had a local character depending on the extent and type of rocks cropping out in the path of the moving ice. It is probable that the glacial movement was not continuous but took place in a series of advancing and retreating stages with contemporaneous fluvio-glacial conditions prevailing. As the ice mass melted and receded, it left its load of rock debris strewn over the Transvaal landscape in the form of ground moraine, while further to the south, the glacier discharged its load into the sea. This morainal material was compacted in places to form "Tillite" and the thickness of this stratum in the Transvaal was extremely variable, owing to the irregularities of the ancient land surface and to the subsequent erosion of this material before further deposition took place. At the close of the glacial period, therefore, the Dwyka landscape was generally hilly and strewn with moraine and mountain ridges separated by broad intervening valleys were in evidence.

The glacial environment gave way to the fluvial and lacustrine environment of Ecca times which persisted over a long period while the moraine-covered Transvaal land mass under-

went denudation. The streams and currents prevailing during this period were sometimes exceptionally swift and the consolidated "Tillite" was broken up, resorted, and washed from the higher ground into the valleys and basins that existed. The effect of this "re-working" was to re-deposit these materials as sandstones, shales, clays, and conglomerates. The length of this period would appear to be considerable since the rocks forming these beds in many regions cannot be identified today.

A stratigraphic break occurs frequently between the "Tillite" or the conglomerates derived from it, and succeeding stratified beds so that every member of the present Middle Ecca stage, from the coals at the base to the grits at the top, are found to rest on these older rocks in various localities.

Marsh environment became prominent over most of the area about this time and fresh or brackish water swamps existed at or near base level. Under these conditions a comparatively small change in water level affected a considerable area. The occurrence of swamps was wide-spread; some were connected while others were divided by land barriers. Coals were formed from the vegetable matter growing in these swamps and in some areas the incursion of terrestrial sediments into the swamps gave rise to the formation of flint clay. The swamp environment alternated with and was finally succeeded by fluvial, lacustrine, and delta environments, and it was during this transition period that some of the plastic clays associated with the coals were formed. The prevailing environment following the disappearance of the swamp conditions was aqueous and included a network of lakes and rivers with constantly shifting channels of discharge. The semi-flint clays and probably some of the flint clays and later the siliceous shales, all found above the coal seams, were formed during the lacustrine phases of the aqueous environment. During this period of aqueous environment the sediments were subjected to repeated cycles of erosion and deposition and much of this activity was contemporaneous so that the present striking lack of continuity of the strata resulted. It is probable that



GEOLOGIC SKETCH MAP OF THE TRANSVAAL SHOWING AREAL DISTRIBUTION OF INTRUSIVE IGNEOUS ROCKS AND THE ECCA SERIES

AFTER UNION GEOLOGICAL SURVEY

F.G. 16

desert conditions alternating with periods of aqueous environment were prevalent at least over part of the Transvaal in these times as well.

The accurate reconstruction of the influence of the environmental factors is difficult since the bulk of the sediments laid down in Karroo times have been removed by denudation leaving only a small part of the complete stratigraphic record in the rocks remaining.

(b) Source of Sediments.

Two principal sources for the clastic sediments forming the refractory clays must be considered: (a) clay residue from the chemical disintegration of the dolomitic limestone of the Dolomite Series, and (b) weathering of pre-existing feldspathic igneous rocks. The areal distribution of these rocks in relation to the Ecca Series rocks and sediments is given in Figure 16. A further, though probably minor, contributory source is the mineral matter contained in the plant ash associated with the coal formation. The magnitude of the contributions from each of these sources is not known, but undoubtedly they all have been more or less involved in the erosional and depositional cycles resulting in the formation of the refractory clays.

The mode of transport of these sediments, of course, also played an important part in the clay forming process.

Dolomite Series: The dolomitic limestone of the Dolomite Series is found underlying or in the vicinity of all of the present commercial deposits of refractory clay in the Transvaal. The clay sediments could have been derived from the decomposition of the dolomite since it is known that residuals from dolomites are relatively high in iron and low in silica. Sediments derived from similar rocks have been regarded by Wheeler (15) and Thornberry (16) as the source of the refractory clays of Missouri, and Nel has suggested such a source rock for the formation of the highly aluminous shales of the Postmasburg district (17).

The residuum from the dolomite could have been trans-

ported in colloidal suspension by surface waters and flocculated in the depositional areas by the action of the water-borne electrolytes. The amount of dolomite required to be decomposed is admittedly considerable.

Analyses of typical Transvaal dolomite samples kindly supplied by Dr. F.C. Truter, Union Geological Survey are given in Table II, along with additional, partial analyses of these rocks contributed by Mr. E. Mooi, Works Chemist of the Vereeniging Brick and Tile Co. Ltd.

Considering the Al_2O_3 content of the refractory clays to average 36% and assuming the Al_2O_3 content of the dolomite to be 1.00%; the specific gravity of the refractory clays to be 2.65 and that of the dolomite to be 2.90; then following the method described by Nel (17), one cubic foot of refractory clay would require the destruction of 33 cubic feet of dolomite, a not unreasonable volume considering the amount of dolomite that must have been removed in the Transvaal by erosion and solution.

It is interesting to note that the manganese oxide found permeating the refractory clays along joints and bedding planes and oftimes disseminated throughout the clays is probably derived from the dolomite as well.

Pre-Existing Igneous Rock and Sediments: More than half of the pre-Karroo land surface in the Transvaal consisted of intrusive igneous rocks comprising the Old Granite and the rocks of the Bushveld Complex which include the Red Granite, norite, syenite, and other types. Typical analyses of these rocks are given in Table III (18). Other pre-existing rocks of sedimentary and extrusive origin contain a number of argillaceous and feldspathic members. Some analyses of such rocks are given in Table IV. (18).

It is quite probable that the refractory clays derived sediments from these pre-existing rocks as well, as suggested by the accessory minerals found in some of the clays.

Table II

Analyses of dolomites
from the Transvaal *

Oxides & Elements	Sample Numbers.						
	FT 434	T_2 1	T_2 2	T_2 3	T_2 4	T_2 5	T_2 6
SiO_2	0.27	5.43	5.08	17.97	7.96	20.61	38.84
Al_2O_3	nil	0.40	0.45	2.08	0.54	5.39	10.89
Fe_2O_3	0.96	1.29	1.12	1.47	0.32	1.12	3.35
FeO	0.72	0.57	1.01	2.44	1.87	4.45	5.46
MgO	21.07	18.03	18.61	17.45	19.77	15.57	10.36
CaO	30.28	32.08	31.96	28.32	28.60	21.31	10.09
Na_2O	0.05	nd.	nd	nd	nd	nd	nd
K_2O	nil	nd.	nd	nd	nd	nd	nd
H_2O+	0.31	1.30	1.22	1.51	0.64	1.61	3.01
H_2O	0.03						
CO_2	45.82	39.82	40.63	28.90	40.03	27.47	11.12
TiO_2	nil	nd.	nd	nd	nd	nd	nd
P_2O_5	0.01	0.06	0.06	0.07	0.05	0.07	0.14
S	0.02	nd.	nd	nd	nd	nd	nd
F	0.015	nd.	nd	nd	nd	nd	nd
V_2O_3	tr.	nd.	nd	nd	nd	nd	nd
V_2O_5	nd.	0.02	0.01	0.01	tr	0.05	0.01
MnO	0.75	0.38	0.40	0.30	0.70	1.20	2.10
BaO	nil	nd.	nd	nd	nd	nd	nd

FT. 434 from Lyttleton
T_2 1-3 " Kwaggashoek, near Thabazimbi.
T_2 4-6 " Buffelshoek, near Thabazimbi.

nd-- not determined.
tr-- trace.

Partial analyses of dolomite
from the Transvaal **

Loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO.
46.37	1.68	0.27	0.78	0.01	29.54	21.32	0.09
44.80	4.32	0.60	0.80	0.01	28.62	20.69	0.12
34.50	3.20	2.11	1.75	0.01	28.11	20.26	0.36
45.26	2.20	0.77	0.45	0.01	31.00	20.70	0.20

* Supplied by Dr. F.C. Truter, Union Geological Survey.

** Supplied by Mr. E. Mooi, Vereeniging Brick & Tile Co. Ltd.

Analyses of Pre-Karroo Igneous Rocks in the Transvaal.

	I	II	III	IV.
SiO_2	73.92	74.00	52.48	58.15
Al_2O_3	14.07	11.85	16.95	14.05
Fe_2O_3	0.52	nil	1.62	0.50
FeO	0.89	3.00	6.68	6.50
MgO	0.38	0.35	7.50	2.70
CaO	1.22	1.50	11.06	5.05
Na_2O	3.83	3.20	2.50	5.85
K_2O	4.35	5.25	0.30	3.25
H_2O +	0.44	0.70	0.30	0.35
H_2O -	0.01	0.25	0.07	1.10
TiO_2	0.21	0.10	0.56	2.05
ZrO_2	nil	nil	nil	nil
P_2O_5	0.09	0.20	0.10	0.65
S	0.01			
MnO	0.04	0.05	0.22	0.15
BaO	0.02			
TOTAL	100.00	100.25	100.34	100.35
SP. GR.	2.63	2.63	3.24	2.77

I--Old Granite, Halfway House; Anal. T. Kameda
II--Red Granite, Petronella; Anal. H.G. Weall
III---Norite, Bon Accord; Anal. F. de Quervain
IV-- Syenite, Petronella; Anal. H.G. Weall.

Table IV.

Analyses of Pre-Karroo Stratified Rocks in the Transvaal.

	I	II	III	IV*
SiO_2	54.48	53.00	61.42	51.14
TiO_2	0.51	nd	0.45	0.78
Al_2O_3	12.11	19.70	22.77	24.96
Fe_2O_3	25.38	10.93	1.24	5.38
FeO	nd	2.88	nd	nd
MnO	nd	tr	nd	nd
CaO	0.40	7.20	0.45	0.52
MgO	0.95	4.00	tr	1.48
K_2O)	1.36	0.79	(	nd
Na_2O)		0.82	(8.21	nd
FeS_2	nd	0.25	nd	nd
P_2O_5	nd	tr	nd	nd
CO_2	nd	tr	nd	nd
H_2O	5.00	nd	nd	nd
Ignition Loss	nd	nd	4.50	6.80
TOTAL	100.19	99.57	99.04	91.06
SP. GR.	nd	2.864	nd	nd

I--Witwatersrand System, Hospital Hill. Avg. of 10 analyses; Anal. George Renny.

II--Ventersdorp Lava, Heidelberg District; Anal. J. McCrae.

III---Transvaal System, Dolomite shale, Vereeniging District; Anal. E. Mooi.

IV-- Transvaal System, Pretoria Shale, Vereeniging District; Anal. E. Mooi.

* Partial analysis.

Plant Ash:

The mineral matter in the ash derived from the decay of the coal forming plants, though not regarded as a principal cause, has been shown to contribute to the formation of refractory clays by Mietzsch and Kratsmann (19). These workers have found that the kind of inorganic matter held in plants, depends largely on the kind of plant. Minute quantities of mineral matter are known to be incorporated with organic molecules in the cell walls of all plants and the studies of these investigators on the alumina content of genera from the whole vegetable kingdom indicated that while many genera contain no alumina, others contained up to 50%, as in the case of Lycopodium, a prominent coal forming plant in the Northern Hemisphere.

No work, however, has been recorded in this respect on the South African coal-forming plants.

A number of analyses of ash from South African coals kindly contributed by the Fuels Research Institute of South Africa are given in Table V. These analyses were carried out on ashes from finely ground coal samples (-20 Mesh B.S.S.), floated at 1.58 to 1.60 Sp.Gr. Such coals would be reasonably free from other mineral impurities.

The data given represent averages calculated from a variable number of ash analyses of different samples, in one case as many as sixteen of the same seam.

Table V.

Analyses of Ash from South Africa Coals.

Seam No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O / K_2O	SO_3
Witbank Area.								
No. 5 (7 analyses)	58.8	26.3	3.8	1.5	4.6	1.1	0.8	3.1
No. 4 (4 analyses)	49.2	34.4	3.1	2.3	6.7	1.1	0.5	2.7
No. 4A (1 analyses)	49.7	29.2	8.3	1.6	5.3	0.4	2.4	3.1
No. 3 (3 analyses)	49.4	37.6	6.0	2.0	2.1	0.3	1.7	0.9
No. 2 (bright & dull) (2 analyses)	47.8	42.4	1.6	2.7	2.1	0.7	0.9	1.8
No. 2 (smithy coal) (5 analyses)	43.3	39.4	5.3	1.6	5.7	0.7	1.6	2.4
No. 2 (gas coal) (5 analyses)	47.9	37.5	2.7	2.7	4.4	0.8	2.6	1.4
No. 2 (16 analyses)	45.2	39.9	3.0	2.1	5.6	0.5	1.2	2.5
No. 2A (2 analyses)	47.9	36.3	3.3	2.9	5.8	1.0	1.2	1.6
No. 1 (10 analyses)	49.9	39.0	2.9	2.1	3.0	0.5	0.7	1.9
Breyten Area.								
Seam A (lanalysis)	62.8	23.1	4.7	1.1	3.4	1.6	1.6	1.7
Seam B (1 analysis)	50.7	24.7	5.1	2.0	7.3	2.0	2.6	5.6
Seam C (1 analysis)	45.5	31.3	4.7	1.5	7.2	2.4	1.8	5.6
Seam D	54.2	26.8	4.3	2.0	4.3	2.1	3.0	3.3
Ermelo Area.								
Seam A (1 analysis)	54.0	23.0	9.8	1.4	4.4	1.1	2.2	4.1
Seam B (1 analysis)	52.8	23.8	6.0	1.4	6.8	2.4	1.7	5.1
Seam C	46.7	31.2	6.6	1.5	5.7	1.4	2.0	4.9
Vereeniging Area.								
Springfield Colliery, Working Seam (1 analysis)	43.9	36.4	3.5	2.7	6.5	1.2	2.1	3.7
Heidelberg Area.								
Bottom seam (4 analyses)	50.2	38.3	3.1	2.1	3.2	0.1	1.2	1.8

The following average analysis, on the burned basis, of 7 samples of commercial carbonaceous flint type refractory clay from the Vereeniging area is included for comparison. This clay occurs as a parting in the main coal seam in this area.

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O & K_2O
51.0	44.6	1.6	0.9	1.6	0.5	nil

While it is realized that there is a great variation in the composition of coal ash, there does seem to be a certain relationship existing between the composition of the ash and the clay, as in the case illustrated above. The mineral matter present in the ash would be expected to influence the quality of the clays associated with the coals, and the analysis data given suggests the selective concentration of certain elements by the plants; however, owing to the great variation of the amount and kind of mineral matter derived from plant ash, no definite conclusions are possible on the basis of such meager information to explain the exact relationship of the plant ash to the refractory clays.

Transporting Agencies.

The sediments giving rise to the refractory clays may have entered the process of formation, according to Hodson, as (a) the original soil of the depositional area, (b) as sediments carried in suspension, in solution, or in colloidal form, and laid down in the depositional basin by streams draining the area around the basin, (c) as mineral ash from decayed vegetation accumulated either in place or transported from areas in which vegetation was undergoing oxidation, and (d) as wind-blown dust. (20).

Geo-Chemical and Geo-Physical conditions.

Refractory clays represent products formed by geo-chemical-physical changes involving the source rocks. The exact mechanism of such changes is imperfectly understood but certain suggestions can be made on the basis of the evidence collected.

The pre-Karroo rocks were strewn over much of the Transvaal in the form of ground moraine left in the area deserted by the melting of the continental glacier that covered the region in Dwyka times, and the mechanical disintegration accompanying the glacial movement was very active in accelerating chemical destruction by exposing fresh surfaces to attack by water, carbon dioxide and oxygen. The breakdown of the igneous and sedimentary rocks was undoubtedly hastened by this process. Under the conditions of glacial transport the full effects of oxidation would be curtailed and it is probable that much of the rock flour carried by the ice resisted chemical attack until it was deposited as morainal material. The chemical decomposition of the dolomite that was left in the ground moraine was no doubt speeded up through ice abrasion; however, it seems more probable that the greatest contribution of clay sediments from the dolomite were derived from huge masses of the original rock which were acted upon by meteoric waters which dissolved the dolomite and carried off the calcium, magnesium and alkalies, leaving behind a residue of hydrous silicates, quartz, iron and manganese ores, etc. This clay residuum served as a source for the formation of the refractory clays, decomposition of the other rocks in the ground moraine also yielded clay residues and in the case of the feldspathic rocks, the principal products are regarded as members of the kaolinite group of minerals. (21). The probable contribution of additional sediments from the breakdown of pre-Karroo rocks in situ and from the re-working of all existing sediments is also recognised.

The flint and semi-flint clays and refractory shales appear to have been laid down as such in the form of fine sediments deposited in bodies of quiet water. These deposits were possibly subjected later to alteration by

leaching in the presence of carbon dioxide charged waters. Ross (22) points out that the removal of SiO_2 in the leaching process can result in aluminous enrichment.

The plastic clays which are associated with the coal seams represent fine sediments derived from the weathering of coaly material and deposited in contemporaneous water channels and lake beds.

The flint and semi-flint clays and siliceous refractory shales differ from the plastic clays in composition, plasticity, and hardness. The flint clays are generally nearly pure kaolinite with some free quartz; the semi-flint clays approximate the flint clays, although usually their free quartz content is higher and their alumina content is lower. The siliceous refractory shales are characterised by their high quartz content. The plastic clays contain non-kaolinite group clays in addition to the predominant kaolinite type suggesting that their alteration was much less than the flint and semi-flint types.

The plastic clays are soft and extremely plastic, while the flint types are non-plastic. The semi-flint clays have plasticity characteristics ranging from fair to poor.

The differences in degree of hardness between the different types of clay are quite pronounced. According to Stout (23) this property is not due to crystallization, for the material does not show the characteristics of this physical state to any marked extent; secondary alteration does not explain the differences in texture since they are sheet deposits and not concretionary masses as could be expected as a result of such changes; nor does pressure appear to play a major part since all types are found in the same deposit and the effect of pressure on one type would be expected to modify the others; the effectiveness of heat in producing the differences in texture is ruled out since the flint clays have normal amounts of water of crystallisation and further they are frequently found in contact with the

soft plastic clays which show no signs of heat effects.

The most adequate explanation of the differences in hardness of these clays, suggested by Stout's work on Ohio clays (23), seems to be the flocculation or colloidal particles of the sediments, owing either to the extreme fineness of the particles themselves or to the influence of water-borne electrolytes such as carbon dioxide charged water furnished by streams draining the dolomite or the organic acids formed in the coal swamps. The purity of the flint and semi-flint types indicate that the decomposition of the original sediments was very complete or that they were reduced to a state of fine division before settling. The settling of the colloidal particles or finely divided materials was not complete because even the most indurated types show plasticity on prolonged grinding, and in the case of the flint clays from Hammanskraal the restored bonding properties produced by water grinding this clay are nearly equal to that of the chocolate plastic clay from Springs. There were doubtless other complex changes that accompanied the formation of the clays in addition to the factor of partial settling which are not properly understood.

To summarize then, the plastic clays appear to represent "sapropelic" deposits associated with the coal measures and their formation may have been accompanied by bacterial action. It would seem that the flint and semi-flint clays and silicious refractory shales are best accounted for by the influx of very fine terruginous sediments into depositional areas, with or without the presence of coal-forming plants, after which partial settling influenced probably by the presence of existing water-borne electrolytes took place. The solvent action of these water-borne reagents doubtless affected the removal of iron, alkalies, and even silica, to leave behind a concentration of hydrous aluminium silicate.

Economic Aspects.

Practically all of the refractory clay mined in the Transvaal is used directly by the producers for the manufacture of clay products. Mining of refractory clay for sale is not an important consideration.

The successful exploitation of the refractory clay in the Union is dependent on the following factors:

1. Character and extent of reserves.
2. Method of Mining.
3. Transport.
4. Uses.

Character and Extent of Reserves

An accurate estimate of the total available reserves of refractory clay in the Union is not easily arrived at because:

(a) prospecting has so far been generally confined to easily accessible deposits in the proximity of the present manufacturing centres in the Transvaal.

(b) the Middle Ecca deposits from which the refractory clays are obtained at present vary considerably in character both vertically and laterally.

The results of exploration work in recent years bring out the significant fact that although the refractory clay reserves are large, they are by no means unlimited, especially in the vicinity of the present manufacturing centres. This condition is emphasized by the need of the larger firms to bring refractory clay from considerable distances, up to 60 miles, to their Works in order to maintain quality standards.

Careful prospecting operations with bore holes and pits laid out according to a pre-arranged plan, are essential in order to determine whether the refractory clays in specific areas are sufficiently accessible to be mined profitably. The data available from such controlled prospecting enable an estimate to be

made of the character and extent of overburden, waste rock, and inferior clay seams. In view of the extreme variation of the strata from place to place, such information is of great importance in opening up clay deposits.

Methods of Mining.

The output of the refractory clay deposits of the Transvaal ranges from 50 to 5,000 tons per month. The clay deposits are subjected to considerable lateral and vertical variation in quality and extent and the strata are generally horizontally disposed with local conditions of undulation and usually lie at shallow depths, which has resulted in the selection of open cast methods for the bulk of the refractory clay winning operations.

There is little regularity in the thickness and character of the overburden overlying the Ecca refractory clays, owing to the general undulating character of the basement rocks. This is particularly so in the case of the areas underlain by dolomite which, as previously pointed out, readily forms solution cavities into which the overlying strata have slumped. The proportion of overburden to refractory clay which can be mined depends on the value of the refractory clay and also whether the overburden can be used in the manufacture of building brick or other products. The depth of overburden seldom exceeds 20 feet in depth in present commercial workings and the overburden to clay ratio usually does not exceed 4 to 1. The overburden is removed either by hand, with power shovels, or with scrapers, depending upon the size of the operation.

In general, the thickness of the seams of refractory clay encountered in the Ecca Series is not great. In some workings, beds only 3 feet thick are mined, although a more usual average thickness would be 5 feet. The usable seams are frequently

interbedded with waste rock or inferior clay which imposes a sorting problem; however, open cast methods greatly facilitate selective mining.

The thinness of the seams and the need for sorting imposes considerable limitations on the types of mining equipment usable which lead to increased costs. In general, the softer clays are mined by hand or with pneumatic tools or power shovels; dragline scrapers are also used. The harder varieties are usually drilled and blasted. All of the refractory clays are generally hand sorted at the pit face before being loaded into coco pans, lorries, or dumpers for shipment to the Works.

Underground mining is resorted to at Vereeniging and Olifantsfontein for obtaining clays too deep for open cast operations. Such clays are taken out by drilling and blasting operations and they are transported to the surface by coco pans. This method of mining is only applicable to high grade clays since differences in mining costs can be up to 5 to 1 in favour of open cast methods.

Transport.

The distance and accessibility of the deposits from major industrial centres are important controlling factors for the economic development of the refractory clays. In general, most of the refractory clay is used for the manufacture of articles of low economic density (value per ton) so that they cannot be economically shipped any great distance. The current value of refractory clays in situ is 1/- per ton at most; the bulk of the deposit being valued at 6d. per ton or less. Where railway facilities are available on site, certain clays of exceptional quality can sometimes be profitably shipped. However, it is emphasised that such clays are restricted to the manufacture of ware having greater value than normal fire-clay goods.

In addition to the cost of mining and transport, there are the usual charges for royalty to property owners, overhead administration, and maintenance, which must be applied to the cost of the clay.

Uses.

The refractory clays of the Union are used by producers in a number of clay products as follows:

(a) Clay refractories: By far the largest consumer of refractory clay is the clay refractories industry and because of its importance in this field, it will be described in further detail in a later section.

(b) Building Brick: South Africa is perhaps unique in the world in utilising high grade refractory clay for the manufacture of building brick. In the Union, "Golden Brown" and similar shades of face brick are preferred over the more prosiac red brick and while semi-refractory clays form a portion of the mixture used for these bricks, quite frequently high-grade refractory clays are used as well because of the economic factors involved in the production and sales of these bricks.

(c) Salt Glazed Ware: Refractory clays are used in the manufacture of sewer pipe and allied salt glazed products in order to provide the mixture with sufficient refractoriness to enable the ware to be burned without distortion.

(d) Earthenware: Earthenware bodies for the manufacture of crockery, sanitary ware, and electrical insulators have varying amounts of refractory clays incorporated in them to produce the desired physical properties.

IV-NATURE AND PROPERTIES OF THE REFRACTORY CLAYS.

GENERAL STATEMENT.

A controlled investigation of the constitution of five selected South African refractory clays * together with their more important ceramic properties was undertaken with a view to bringing to light some of the underlying reasons for the various phenomena observed in industrial utilization of these clays.

A study of the changes in the ceramic properties of the clays and shales of a section of the Middle Ecca strata was carried out to determine the effect of the geological features of such deposits in relation to mining and manufacture.

A preliminary investigation of the beneficiation of some South African refractory clays through pH control is presented.

CONTROLLED INVESTIGATION

General Statement

Refractory clays, although classified by the ceramist into general groups, i.e.- flint, semi-flint, plastic, etc., show intense individualism when studied in detail. They possess inherent variable properties resulting from their geological background, which profoundly affects their behaviour in manufacture and service life. Rather than present random data on different varieties of refractory clays, a complete body of relating data has been accumulated on master samples of five commercial refractory clays selected as being representative of the types employed in the manufacture of fire-clay refractories in the Union. These data include investigations of the constitution and ceramic properties of the selected clays. Additional test data have been included to illustrate divergences in varieties of these clays.

---

* See ceramic definition for clay p.

The general points involved in the investigation of the constitution of the refractory clays include:

1. Nature of the predominating clay minerals present.
2. Composition and amount of accessory minerals.
3. Particle Size.
4. Base Exchange phenomena.

Methods of Investigation.

All of the methods used for the identification of the clay minerals and accessories are comparative and depend for their efficacy on the existence of relevant data for pure minerals, few of which are readily available. They are also limited by the effects of varying grain size, and mutual interference of the minerals in the mixture. In consequence no one method can be relied on to produce reliable results. It is the purpose of this investigation, therefore, to apply as many methods as possible to the determination of the clay minerals and accessories present. Differential thermal analysis seems to offer one of the most informative methods available for the study of clays and it has been features in this work. X-ray diffraction studies are included, supplemented by optical examination, quantitative chemical analyses, morin dye tests, and spectrochemical analyses. Particle size determinations and base exchange studies were made and the results of radioactivity measurements and observations with the electron microscope are given. Ceramic behaviour was determined by laboratory tests evaluating the plasticity , refractoriness, and drying and burning characteristics of the selected clays.

The full programme of study is summarized below:

1. Differential thermal anlysis
2. X-ray examination
   (a) Spectrometer method
   (b) Photographic method
3. Optical examination
   (a) Thin section study
   (b) Powder study.

4. Electron Microscope.
5. Quantitative chemical analysis.
6. Morin Dye test.
7. Spectro-chemical analysis.
8. Radio activity.
9. Particle size distribution.
10. Base exchange phenomena
    a. Leaching method.
    b. Electrodyalysis method
11. Ceramic behaviour.
    a. Plasticity
    b. Drying shrinkage
    c. Dry Strength
    d. Burning shrinkage
    e. Burned strength
    f. Refractoriness.

Clay Minerals: General Statement.

Refractory clays in general are composed essentially of the clay minerals together with various accessory minerals.

The clay minerals are broadly classified into three groups:

1. Kaolinite.
2. Montmorillonite
3. Illite.

The principal members of each group together with their salient ceramic properties are given in Table VI. (24) (25)

Table VI

Classification of the Principal Clay Minerals

Group	Kaolinite	Montmorillonite	Illite
Members	Kaolinite--$(OH)_8Al_4Si_{10}$ Dickite--similar to kaolinite, differs in way layer units are superimposed. Rare in sediments. Nacrite--similar to kaolinite, differs in way layer units are superimposed. Rare in sediments. Halloysite--similar to kaolinite, differs in way layer units are superimposed. Hydrated halloysite--similar to halloysite with 2 additional water molecules. Anauxite--higher in silicon, lower in aluminium than kaolinite.	Montmorillonite--$(OH)_4Al_4Si_8O_{20}\cdot xH_2O$ (usually contains Mg) Beidellite--lower silicon, higher aluminium. Nontronite--aluminium replaced by ferric iron. Saponite--aluminium completely replaced by magnesium.	Illite--$(OH)_4K_yAl_4(Si_{8-y}Al_y)O_{20}$ "y" varying from 1 to 1.5 "Hydro-micas". "Sericite-like" minerals.
Characteristic Ceramic Properties			
Slaking in water	Difficult	Easy	Intermediate between kaolinite and montmorillonite groups
Plasticity	Poor	Good	
Dry Bond Strength	Poor	Good	
Base Exchange Capacity	Low	High	
Fired Colour	White	Coloured	
Refractoriness	High	Low	

The wide differences among the properties of the three groups are fundamental and result from differences in their atomic structure.

Atomic Structure

The principal clay minerals are crystalline and with few exceptions occur in flat platelike particles. Bragg (26) states that, "Their structures are based on the hexagonal network of linked silicon-oxygen tetrahedrons." "Two main structural units are present in their atomic lattices: (1) The aluminium hydroxide (gibbsite) sheet consisting of two layers of closely packed oxygens or hydroxyls between which aluminium ions are embedded in such a position that they are equidistant from six oxygens or hydroxyls to form a network of the composition $(OH)_8Al_4O_4$; and (2) a sheet of tetrahedral silica (SiO_4) groups which when linked to form a continuous hexagonal network has the composition Si_4O_{10}."(2)

Kaolinite Group

This group has a crystal structure known as the 1 : 1 lattice type. "The unit cell consists of a gibbsite sheet and a single tetrahedral silica sheet which are held together by the valence bonds of four oxygens which occur commonly in both layers." (27) The group includes four polymorphic varieties; nacrite, dickite, kaolinite, and halloysite, which, according to Hendricks (28), differ in degree of disorder in stacking of the layer units as: nacrite, nil; dickite, slight; kaolinite, considerable; halloysite, great. Kaolinite, dickite, and nacrite have the formula $(OH)_8Al_4Si_4O_{10}$. Halloysite, according to Roberts (24), is thought to exist in two forms: one (hydrated halloysite) which contains two additional water molecules, and the other (halloysite) which is chemically s milar to kaolinite. A continuous series between the two forms can be expected since the hydrated halloysite loses the two water molecules when heated to 50°C. and forms halloysite. In addition to the greater degree of disorder of stacking already mentioned, halloysite

differs further from the other kaolinite group minerals in that the crystals are small, and lath or rod shaped, while those of kaolinite consist of hexagonal plates.

Anauxite, which has the formula $(OH)_8Al_4Si_4O_{10}.SiO_2$, is also included in the kaolinite group. The excess silica which characterises this mineral is suggested by Hendricks (28) to be present in the kaolinite structure as neutral silica layers with the constitution SiO_2, or possibly $4SiO_2.H_2O$ alternating with the kaolinite layers in irregular sequence, thus making possible a series between kaolinite and anauxite.

Hendricks (28) states that isomorphic replacements in the kaolinite group are largely restricted to mutual substitution of Al and Si in the (Si_2) positions with resulting variations, quoting from Ross and Kerr (29) in the SiO_2 : R_2O_3 ratio from 1.6 to 2.9 : 1. Hendricks and Alexander (30) point out that if iron oxide combined with silica exceeds 2% Fe_2O_3, or if more than 1% of non-exchangeable potassium or magnesium is determined, clay minerals other than the kaolinite group are present.

Illite Group

The name "illite" is generally used as a group classification for clay minerals of the "hydrated mica" or "sericite like" type. The general formula proposed for this group is $(OH)_4K_yAl_4(Si_{8-y}Al_y)O_{20}$ with "y" varying from 1 to 1.5. (27) The structure of these minerals is of the 2 : 1 lattice type, consisting of two silica sheets and one gibbsite sheet. (27) The Si^{++++} positions are replaced by Al^{+++} and the resulting excess charges satisfied by K^+ ions between the silica sheets of two successive units.

Replacement of Al^{+++} in the gibbsite sheet is considered possible. (27) Isomorphous substitutions of Fe^{+++} and of Fe^{++} and Mg^{++} for Al^{+++} lower the Al_2O_3 content by 25% according to Pask and Davies. (27) The illites therefore comprise a complex series of minerals, the structures of which are not completely known.

Montmorillonite Group

This group includes four minerals: montmorillonite, beidellite, nontronite, and saponite; all of which belong to the 2 : 1 lattice type, i. e., two sheets of silica to one of gibbsite (2). Water is loosely held between the silicate layers and varies with the humidity of the atmosphere causing corresponding expansion of the lattice which characterises this group (27).

The general formula for montmorillonite as suggested by Hoffman, Endell and Wilm (31) is $(OH)_4Al_4Si_8O_{20}.nH_2O$. Partial replacement of the Al in the gibbsite sheet by Mg and/or Fe is possible and if the substitution of magnesium is complete the mineral saponite is derived or if ferric iron, nontronite (27). Marshall (32) states that beidellite is structurally similar to montmorillonite but substitutions of Al for Si occur in the silica sheet. The validity of this species (beidellite) is open to question according to Pask and Davies (27). They cite Grim on the belief that beidellite may be a mixture of several clay minerals and state their conception that this mineral is an interlayer mixture.

Accessory Minerals

Allophanes (or allophanoids): All non-crystalline solid solutions of silica, alumina, and water are included under this term. Salmang (33) gives the range of compositions as $Al_2O_3.0.3$--$1,3SiO_2.1.8$-$8.5\ H_2O$. The allophanes are thought to be present in small amounts in practically all clays; however, Ries (34) points out that there is always some doubt as to whether these amorphous clay minerals are definite species or simply absorption compounds of colloidal silica and alumina with variable amounts of water.

Other non-clay minerals: The hydrous alumina minerals including gibbsite (alpha alumina trihydrate); boehmite (alpha

alumina mono-hydrate); and diaspore (beta alumina monohydrate) and clichite (an amorphous variety) have been found in certain overseas clays in varying amounts. Muscovite, quartz, calcite, pyrite, hematite, limonite, goethite, leucoxene, and manganite, as well as carbonaceous material of various types are known to occur as common impurities in clays.

Description of Selected Samples

Master samples of approximately 50 pounds each were collected from stock piles of five commercial refractory clays normally used in the manufacture of refractories.

The samples were inspected for hardness, colour, fracture, structure, texture, and visible impurities. Hardness was determined roughly by the ease with which the lump was broken. This property varies with the different types of clays and is useful in estimating the ease and manner in which it may be ground in preparation for manufacture. Hardness also controls the type of particles produced in the crushing, grinding, and screening of the clays. The soft clays break down readily, yielding small round particles, whereas the semi-flint and flint types which are reduced with difficulty produce sharp angular fragments. The fracture of the material also indicates the type of fragments obtained in grinding. The samples were also examined for colour. This property serves merely to identify the clay in the raw state, since original colour generally has little or no effect on burned colour.

The structure of the clays, including the extent of bedding; texture, whether coarse or fine; the texture, or degree of homogeneity, were also recorded; such data are particularly important in mining operations and also useful in manufacturing.

The visible impurities were noted. The principal ones are: quartz, in the form of sand grains or concretions; iron, in the form of colouring oxides along the joint planes or dispersed throughout the clay seam as a yellow, brown, or red stain; carbonaceous matter discolouring the clay black or brown; and manganese as staining along joint planes or disseminated throughout the clay.

This descriptive information on the selected clays is tabulated and photographs of lumps of the materials are given below.

Clay I

Type: flint
Origin: Hammanskraal area
Hardness: very hard
Colour: grey
Fracture: chonchoidal
Structure: thickly bedded
Texture: homogeneous
Visible impurities: nil

Clay II

Type: flint (carbonaceous)
Origin: Vereeniging area
Hardness: very hard
Colour: black
Fracture: chonchoidal
Structure: thickly bedded
Texture: homogeneous
Visible impurities: carbonaceous matter

Clay III

Type: semi-flint
Origin:: Springs area
Hardness: hard
Colour: grey
Fracture: Hackley
Structure: thickly bedded
Texture: homogeneous
Visible impurities: nil

Clay IV

Type: plastic
Origin: Springs area
Hardness: soft
Colour: chocolate
Fracture: earthy
Structure: varved
Texture: alternations of light and dark coloured material with included organic matter
Visible impurities: iron and manganese stains and carbonaceous matter

Clay V

Type: silicious refractory shale
Origin: Vereeniging area
Hardness: medium
Colour: reddish brown
Fracture: shaley
Structure: shaley
Texture: mixture of fine clay particles and coarser quartz grains
Visible impurities: abundance of quartz

Differential Thermal Analysis

General Statement

Differential thermal analysis is a recognised method of mineral determination which has proved particularly useful as a means of identifying and estimating the clay minerals, carbonates, hydrous oxides, and other substances which yield diagnostic curve patterns by this method.

The technique is based on a study of the thermal history of a substance revealed by the amount of energy required or released when that substance undergoes chemical or physical changes on heating or cooling. These thermal changes may be due to loss of mechanically or chemically combined water, oxidation, or decomposition, or changes in crystal structure.

In practice, differential thermal analysis is normally carried out by identically heating the sample together with a thermally inert material at a constant and fairly rapid rate to about 1000°C., or as near to fusion as possible, in an electric furnace. Temperature differences between the sample and the inert material are measured by means of a differential thermocouple and these data are recorded, together with the actual furnace temperatures measured with a normal thermocouple, to give a curve pattern. The usual method of illustrating these thermal effects is to plot the exothermic changes above and the endothermic changes below the zero or base line. The final curve pattern shows the magnitude of the thermal effects, the actual temperatures at which they occur, and whether they represent endothermic or exothermic changes. These curve patterns are diagnostic of particular minerals and can be used to investigate their presence, either alone or in admixtures. This is accomplished by comparing curves prepared from the sample with curves obtained from known pure minerals since, as in X-ray patterns, a mixture will give a superimposition of characteristic effects of individual components.

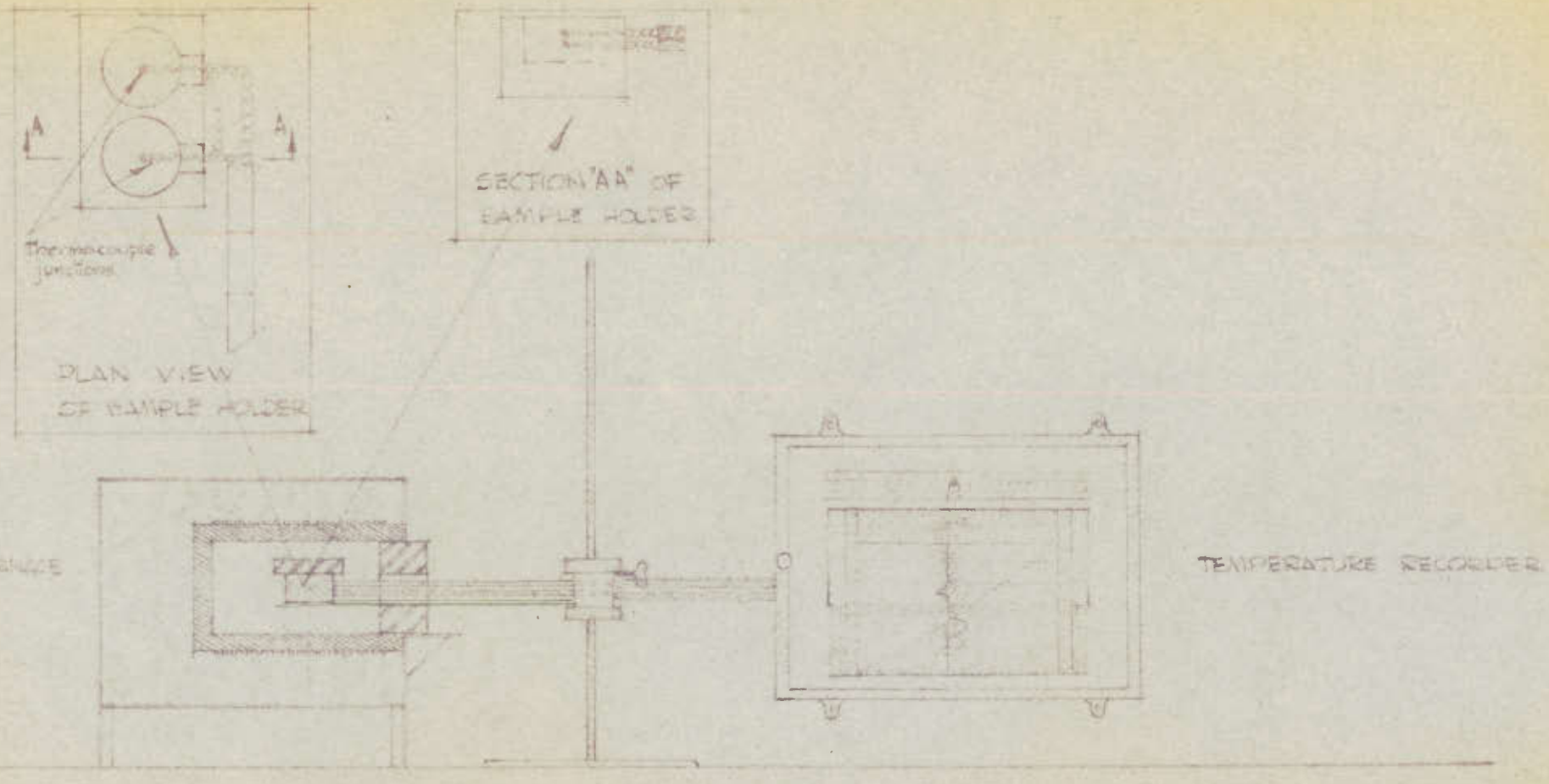


FIG 17

SCHEMATIC LAY-OUT OF APPARATUS FOR DIFFERENTIAL THERMAL ANALYSIS

Factors which require standardisation if results are to be reproducible are duplication of heating rate, size of particles, density of packing of sample and reference material, and positioning of the thermocouples. A common problem encountered in this method is the tendency of the zero or base line to deviate from the horizontal owing to the occurrence of temperature changes other than the differential thermal effects. This phenomenon is known as the "base line drift" and can be caused by uneven heating of the specimens or changes in shrinkage and specific heat of the sample upon dissociation. Uneven heating rates are usually due to faults in design or construction of the apparatus and can be rectified. The other causes are not easy to overcome since they are inherent properties of the materials being tested. No attempt has been made in this work to correct for base line drift and the results are presented as obtained. In general the reproducibility of the results is good with the apparatus described below.

Apparatus and Procedure

The apparatus constructed by the author was similar in principle to that designed by Norton (35) and Berkelhamer (36) with certain modifications adopted to permit available instruments to be used. In general the equipment consisted of an electric muffle furnace, sample holder, thermocouple, and temperature recorder. A diagram of the set-up is given in Figure 17.

The electric furnace was constructed by winding a "D" type andalusite muffle, 6" high x 6" long, with Nichrome wire, and insulating it with 6" of expanded vermiculite. One end of the muffle was closed and a plug made of insulating firebrick was provided to seal the other end. The furnace temperature was manually controlled by means of a slide wire resistance so as to maintain a heating rate of approximately 12°C. per minute.

The sample holder was prepared by drilling two circular cavities, ½" in diameter and 3/4" deep, 1/8" apart in a chrome

steel block, 1-3/8" x 3/4" x 7/8". Small holes were drilled in the wall of each cavity to admit the thermocouples.

The sample as received, undried and untreated, was ground to pass a 48 mesh Tyler screen and tamped in place in one cavity, and alundum, which is thermally inert in the temperature range of these tests, was placed in the other.

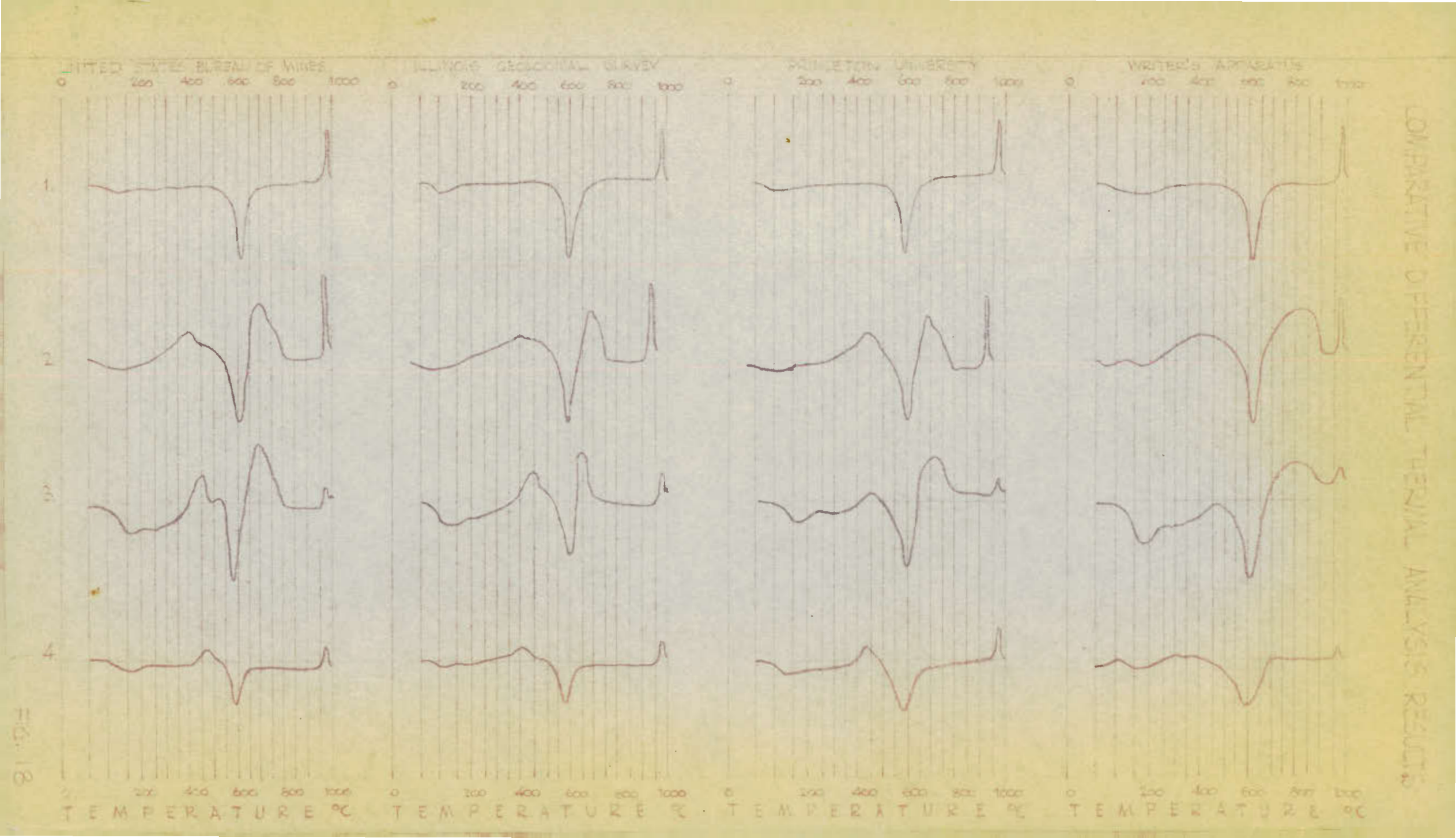
A two-junction, chromel-alumel differential thermocouple consisting of two leads of chromel, joined by a common lead of alumel, was prepared; one function was inserted into the sample and the other into the inert material. The chromel-alumel c couple was preferred over a platinum-platinum 13% Rhodium couple because of the larger e.m.f. developed for the same temperature, and because of its greater sensitivity. A normal platinum-platinum 13% Rhodium thermocouple was inserted in the inert material to record the furnace temperature.

The sample holder with thermocouples in place, was set on a monel metal stand, supported independently of the furnace and so arranged as to position the sample holder in the center of the muffle. The insulating firebrick plug, grooved to carry the thermocouple leads, was then put in place and sealing of the furnace was completed with asbestos wool.

A Brown multi-point recording instrument with built-in cold junction compensation was used to record both differential and actual temperatures. In order to obtain plus and minus deflections in the case of the differential temperatures, a battery box in series with the differential thermocouple was used to position these recordings conveniently on the chart. The noble metal couple measuring furnace temperature was directly connected to the recording instrument. The recorded results were replotted to present the data in conventional form for comparison with the work of other investigators.

Experimental Results

Since there was no other differential thermal analysis


UNITED STATES BUREAU OF MINES
ILLINOIS GEOLOGICAL SURVEY
PRINCETON UNIVERSITY
WRITER'S APPARATUS
0 200 400 600 800 1000
1.
2.
3.
4.
TEMPERATURE °C
COMPARATIVE DIFFERENTIAL THERMAL ANALYSIS RESULTS

equipment in the Union at the time, it was necessary to check the operation of the author's equipment against the work of overseas researchers. Accordingly, duplicate samples* were submitted to Dr. H. Hess of Princeton University, Mr. H.F. Carl of the United States Bureau of Mines, and Dr. R.E. Grim of the Illinois Geological Survey.

The results obtained by these observers using different apparatus and operating techniques were plotted to the same scale and are given in Figure 18 together with the results obtained by the writer on the apparatus described. In general, the agreement among the results was very good. Some variations in the position of the endothermic peaks are noted in the curves presented, which are very probably due to differences in heating rates by the different workers.

Reference samples illustrating each of the principal clay minerals were obtained from Grim, and thermal analysis curves of these specimens were prepared. Data on the chemical analyses and origin of these reference clays are given in Table VII.

Thermal Analysis of Kaolinite: The decomposition of the kaolinite specimen on heating to 1000°C. is shown in the following curve, given in Figure 19.

Two major reactions are noted (38, 39): (a) the dehydration of the kaolinite, which is represented by an endothermic change at about 620°C. under the conditions of the author's equipment; and (b) the formation of crystalline gamma alumina, which is here accompanied by a sharp exothermic reaction at 980°C.

The first reaction is due to the loss of structurally held water and is represented by the following chemical equation:

$$Al_2O_3.2SiO_2.2H_2O = Al_2O_3.2SiO_2 + 2H_2O$$

---

*See selected clays: 1-III; 2-II; 3-IV; 4-V; pp. 71, 72.

Table VII

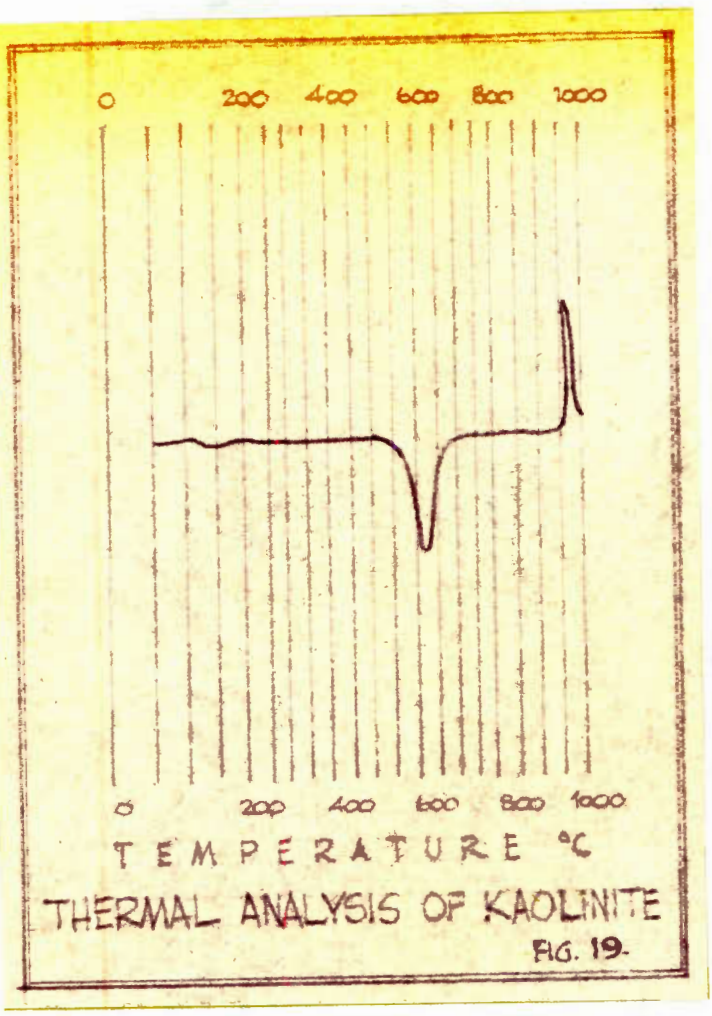
Chemical Composition of Reference Clays*
(In percent)

No.	Ignition loss	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Totals
1	13.87	45.18	38.80	2.15	0.31	0.00	0.03	0.24	0.01	100.59
2	6.29	58.48	20.27	1.20	7.74	0.52	2.00	1.28	3.33	101.11
3	4.86	64.41	20.80	0.19	3.65	0.83	2.33	2.86	0.39	100.32

Key to Table VII

No.	Type of Clay	Location	Mineral Composition
1	Soft kaolin	Dry Branch, Georgia	Kaolinite, medium grain size
2	Shale	Menard County, Illinois	Illite (high iron variety), quartz (15% ±) trace of pyrite, limonite, kaolinite.
3	Bentonite	Clay Spur, Wyoming	Montmorillonite, quartz (10% ±)

* Data after Grim and others, (37).



THERMAL ANALYSIS OF KAOLINITE
FIG. 19.

The second reaction coincides with the formation of crystalline gamma alumina according to Insley and Ewell (40) and is represented by the following chemical equation:

$Al_2O_3.2SiO_2$ = Al_2O_3 + mixture of SiO_2 and Al_2O_3.

These workers explain the sharp endothermic peak of the kaolinite minerals on the grounds that the SiO_2 present retards the crystallisation of the gamma Al_2O_3 so that when it occurs it does so very rapidly and the heat of crystallisation is liberated suddenly.

Studies by Eitel (41) show that there is no change in the electron microscope picture or diffraction diagram for kaolinite heated from room temperature to 500°C. Diffuse halos appear in the X-ray diffraction patterns and remain unchanged up to 900°C. in sharpness and position, but increase in intensity with rising temperature. All of the kaolinite lines in the X-ray diagram disappear at about 900°C. and mullite is detected above

1100°C. According to Hyslop (42), cristobalite lines also begin to make their appearance at this temperature.

Some factors influencing the size and position of the exothermic peak for kaolinite are given as follows:

(1) Amount of kaolinite present in sample.

(2) Particle size. Simultaneously flocculated silica and alumina gels give inflections at lower temperatures than naturally occurring kaolinite. (40)

(3) Crystallinity of the material. Calliere, Henin, and Pere (43) have shown that kaolinite specimens recrystallising through the 950°-1000°C. range give large exothermic peaks and that specimens showing poor crystallisation, by X-ray methods, give a small exothermic peak. Frederickson (44) suggests that the magnitude of the exothermic phenomenon seems to be the consequence of a quasi-explosive cause of the re-crystallisation process and anything affecting the rate of crystallisation also affects the exothermic peak.

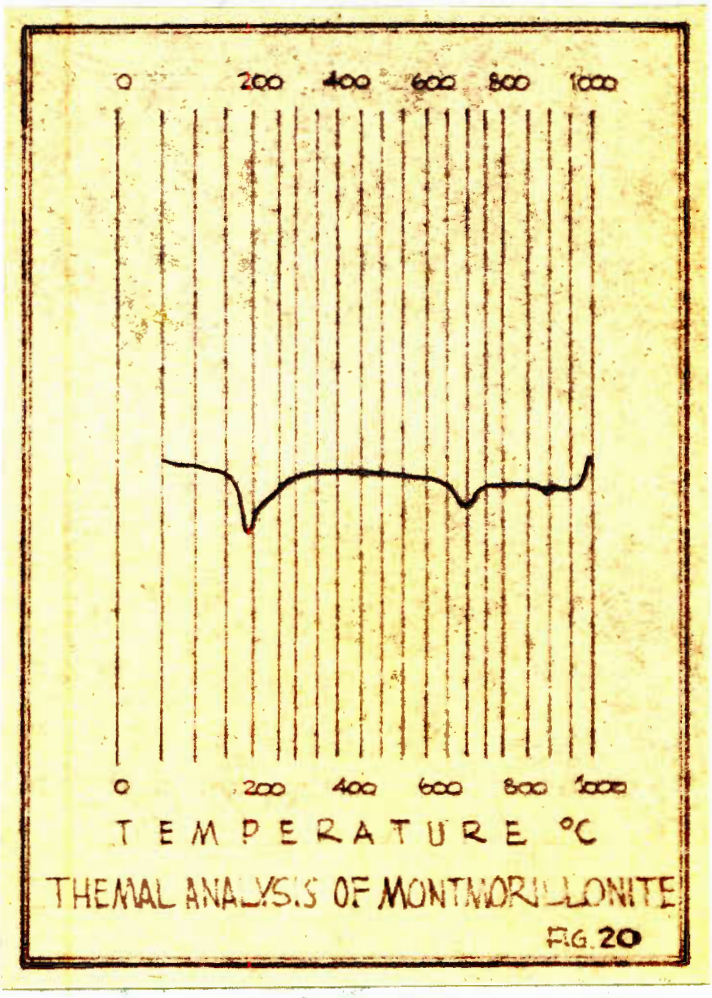
(4) Nature and amount of fixed ions. Calliere et al (47) found that the fixation of Al, H, or NH_4 increased the magnitude of the exothermic peak while Ca, Mg, Na, K, Fe, and alkaline earths decreased it. They point out that the exothermic reaction of some clays can be affected to such an extent that if the clay behaves as an H- or NH_4-clay, the inflection of the thermal curve does not imply necessarily the existence of kaolinite.

(5) Rate of heating.

All members of the kaolinite group are characterised by a sharp exothermic peak at about 980°C. Variation in the temperature at which the endothermic peak occurs is claimed to distinguish certain of the individual group members. Thus the dickite peak at 685°C. (27), and the nacrite peak above 685°C. (27) would differentiate these minerals from kaolinite peaks, (580°-625°C.) (27), and halloysite peaks (555 - 565°C.) (27)

According to Speil (45) it is not possible to distinguish anauxite from kaolinite on the basis of thermal analysis alone since their peak temperatures are similar.

Thermal Analysis of Montmorillonite: The thermal changes undergone in heating the montmorillonite sample to 1000°C. are shown on the curve below, in Figure 20.



Three endothermic reactions are noted, the last of which is followed by an exothermic change.

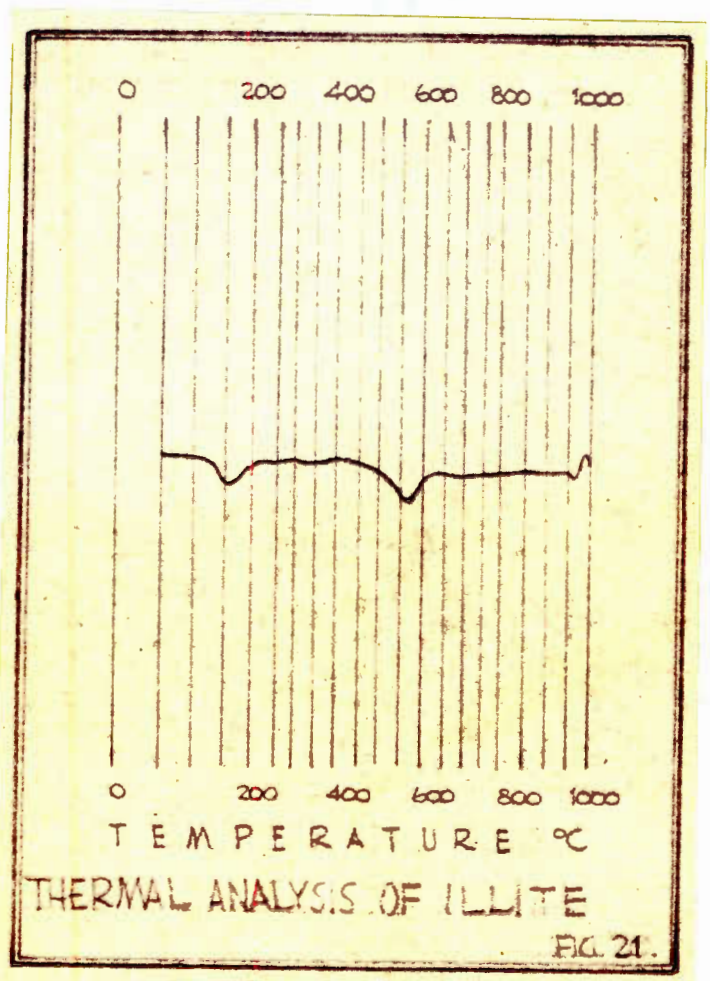
The first peak at about 130°C. represents the loss of mechanically held water. The second peak at about 700°C. represents a partial breakdown of the lattice structure which is presumed to be completely destroyed in this case at about 850°C. The final exothermic peak is observed to occur at 1000°C.

These results compare favourably with those of other workers (27) who report the first peak extending from 100°-300°C.,

the second slightly above 700°C. but variable, and the third peak, which is still more variable, between 840°C. and 930°C. The final exothermic peak according to Grim is dependent upon the iron content, i.e., the lower the iron content, the higher the temperature at which this peak occurs. Thus relatively iron free Texas montmorillonite does not show this peak until 1050°C.

The decomposition of the montmorillonites by heat has not been studied in as great detail as is possible in the case of kaolinite because of the greater variation in composition of these minerals.

Thermal Analysis of Illite: The thermal curve for the illite sample as shown below in Figure 21 depicts the thermal dissociation of this material.



Like the montmorillonite curve, the illite material

shows three endothermic peaks with a final exothermic change. The first peak occurs at about 150°C., the second at 580°C., and the third at 960°C. The exothermic peak occurs at about 980°C. These results are in fair agreement with some published data on illite; however, because of the complex nature of the illites, a variety of curve patterns is to be expected.

Summary of Results on Reference Specimens

Both the illite and montmorillonite samples gave much weaker thermal responses than the kaolinite. The amplified curves recommended for an intensive study of the non-kaolinite groups are outside the scope of this equipment; however, the general shape of the patterns obtained was sufficiently well defined to be compared with the work of other investigators. Considering that both the illites and montmorillonites include a complex series of minerals, a wide variation in the thermal effects may be expected, and under some circumstances the thermal method alone would not provide a method of distinction between them. Despite these limitations, the curves do illustrate the pronounced differences brought out by the thermal method between the kaolinite and the other clay minerals groups, and indicate the scope of usefulness of the method as a rapid means of evaluating the kaolin type clays.

Thermal Analysis of Other Minerals:

Quartz: Estimation of quartz is based on the measurement of the energy change which accompanies the alpha to beta inversion at 574°C. This change is small (2.5 calories per gram (46)) and under the best test conditions the temperature change is of the order of only 3°C. for a sample consisting entirely of quartz. For the estimation of quartz it is therefore necessary to employ a more sensitive technique than used in the other determinations. (36) The differential thermal thermocouple was therefore connected to a Brown potentiometer, and the differential temperature recorded manually and plotted by the point method against the furnace temperature which was automatically recorded;

in other respects the apparatus used is the same as described previously.

A thermal curve was prepared for a sample of quartzite (Black Reef) containing 98.5% SiO_2 and is shown below, in Figure 23.

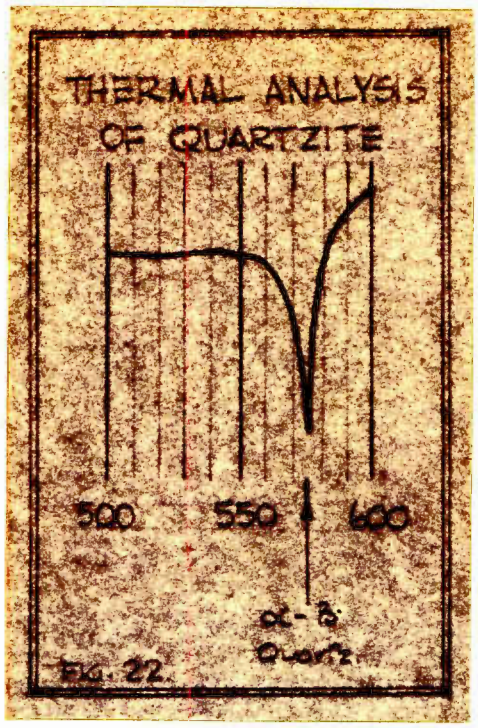
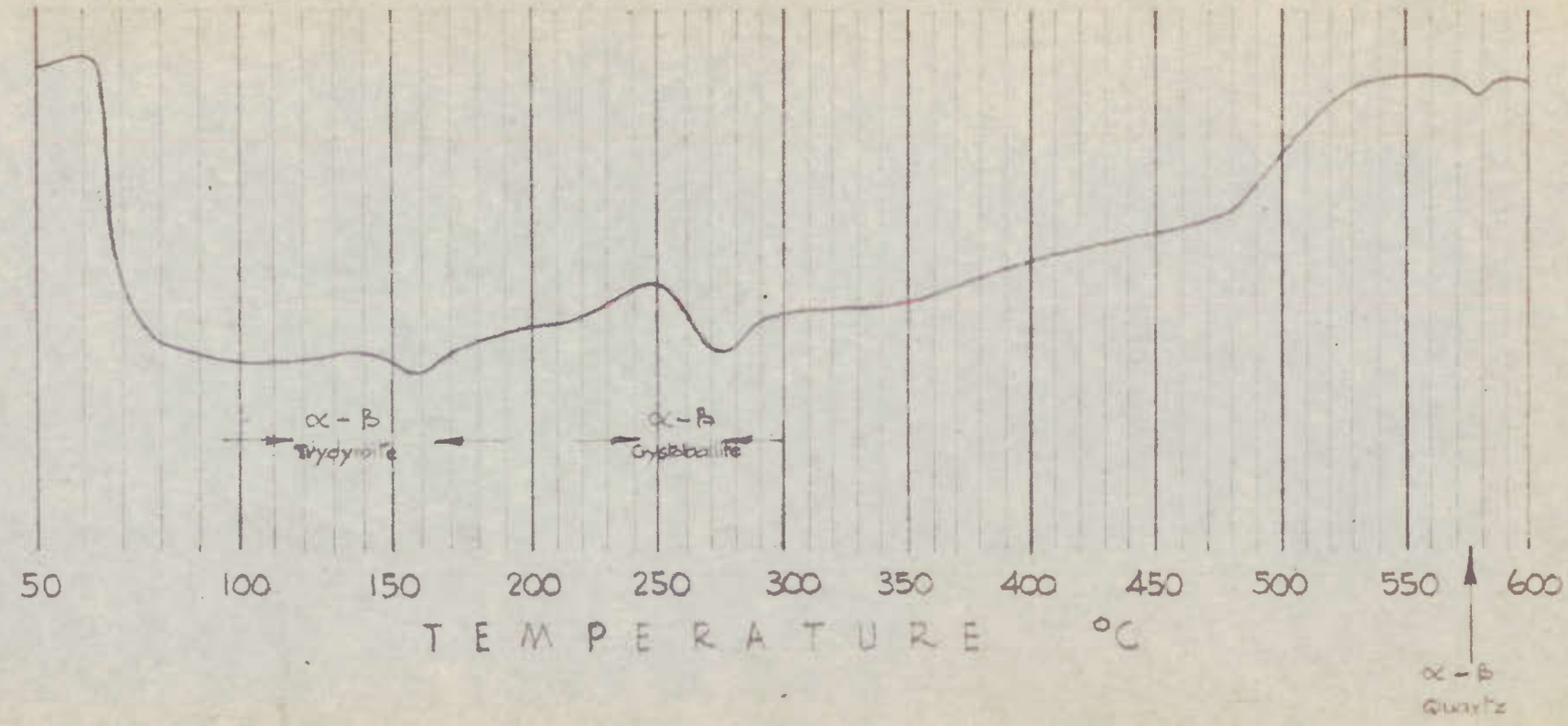


Fig. 22.

It will be seen that the major temperature effect is confined within a narrow range of temperature, the peak occurring just about at 574°C., the accepted temperature at which the alpha to beta inversion occurs. The amount of "base line drift" is large because of the pronounced increase of the specific heat of quartz with the rise in temperature.

Because of the very small thermal response of quartz occurring in a temperature range where the prohounced endothermic effects of kaolinite take place, it is understandable that the presence of this mineral is not detectable in the presence of kaolinite or any other mineral giving a large thermal reaction around 574°C. In order to examine the thermal effects of tridymite and cristobalite, a thermal curve was prepared on a sample of silica firebrick containing 96% silica, and shown by X-ray examination to contain these minerals with some quartz.



THERMAL CURVE SHOWING CRYSTOBALLITE, TRIDYMITE AND QUARTZ IN A SILICA BRICK

FIG 23.

The curve produced in accordance with the modified method just described is shown in Figure 24. The small peak at 158°C. is taken to represent the tridymite inversion; the peak at 250°C., the cristobalite inversion; and the sharp peak at or near 574°C., the alpha-beta inversion of quartz. All these changes take place very near the accepted temperatures. The very small thermal effects of tridymite and cristobalite would make them extremely difficult to detect in the presence of other minerals with greater responses.

Diaspore: A mineral specimen from the Postmasburg district, determined optically by Nel (17) as diaspore, was kindly contributed by the Union Geological Survey. This specimen was subjected to differential thermal analysis with a specimen of commercial diaspore used for refractory purposes, from Missouri, supplied by R.E. Grim. Thermal curves for these specimens are shown in Figure 24. Typical chemical analyses of the diaspore samples are given in Table VIII.

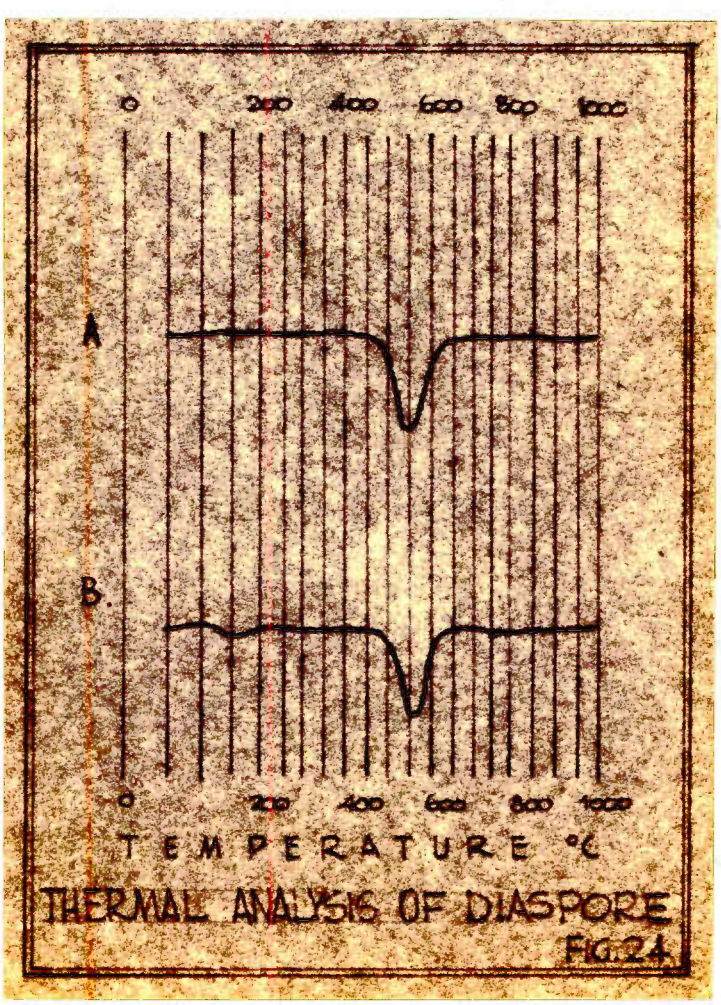


Table VIII

Chemical Composition of Diaspore Samples

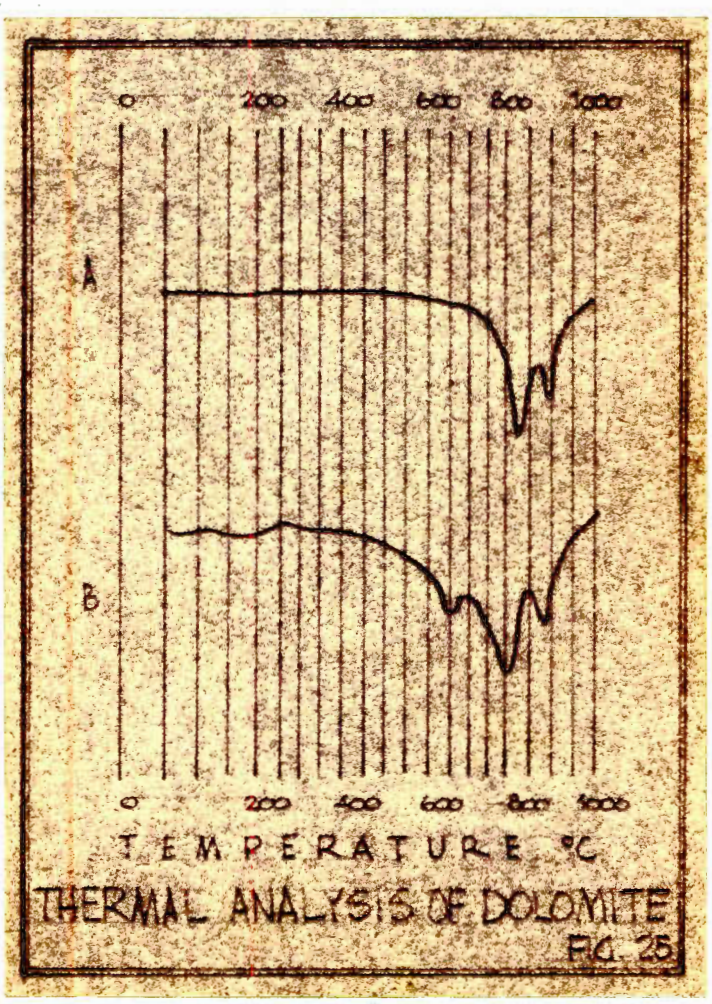
Location	Moisture	Ignition loss	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	Cr_2O_3	Totals
Postmasburg, C.P. 1/ (Doornfontein, No. M82)	0.2	14.9	1.0	82.80	0.3	0.15	0.35	nd	nd	nd	nd	0.4	100.10
Swiss, Missouri 2/	nd	13.10	10.97	68.45	4.29	1.70	nd	0.33	0.07	0.69	1.10	nd	100.72

1/ Chemical analysis after Nel (17).

2/ Chemical analysis after Grim and others (37).

Curve A , Figure 24, of the Postmasburg specimen, and Curve B, Figure 24, of the Missouri sample, both show a strong endothermic reaction between 500°C. and 600°C., corresponding to the loss of structurally held water, (OH), from the diaspore. No exothermic reactions were observed and these patterns are consistent with the characteristic patterns for diaspore given by other investigators (27, 35, 45, 47, 48). The weak thermal effects of the free quartz known to be present in the Missouri diaspore sample were apparently beyond the sensitivity of this equipment.

Dolomite: Samples of dolomite from deposits in the Transvaal and Southern Rhodesia were analysed by the differential thermal method and the curves are given in Figure 25.



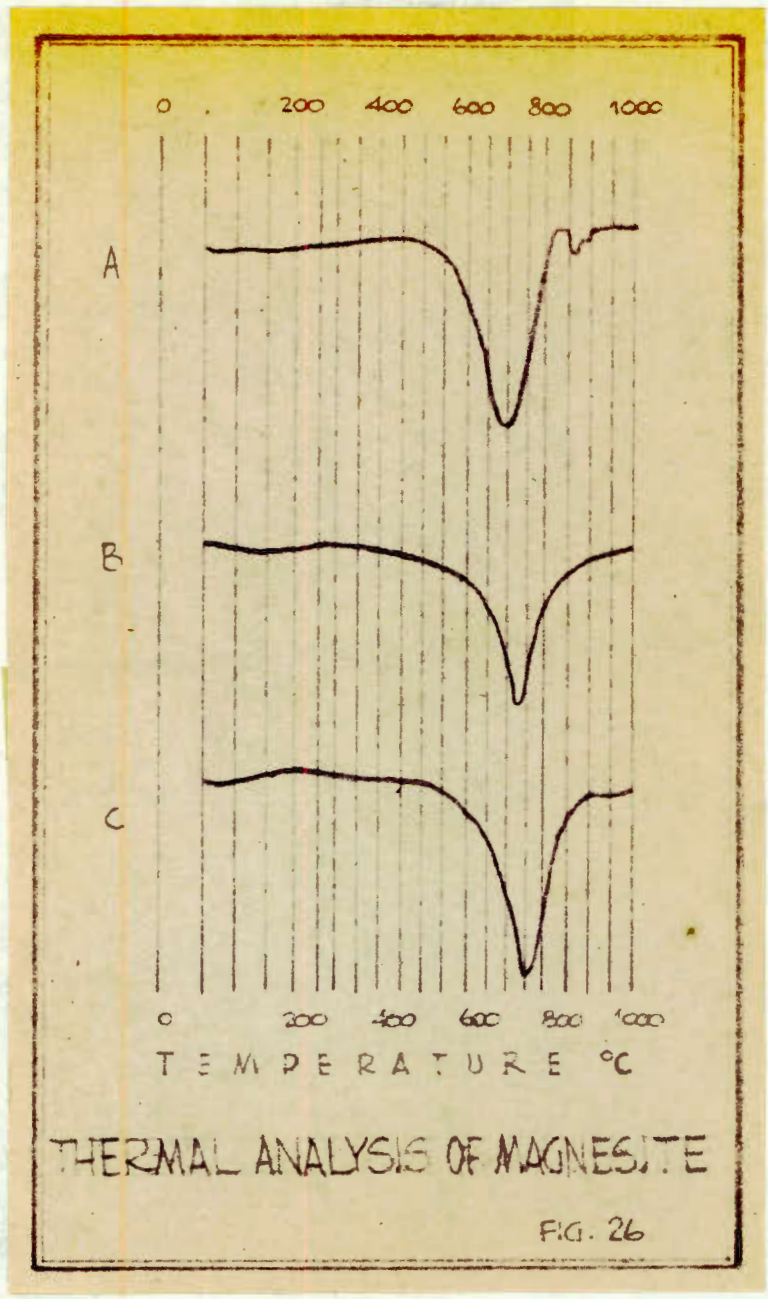
Curve A, Figure 25, for the Transvaal sample, is representative of the dolomite limestones occurring in the Dolomite Series. The thermal effect shown by this material is consistent with the double endothermic pattern obtained for dolomite by Kerr and Kulp (49), and Cuthbert and Rowland (50). The predominance of dolomite is confirmed by X-ray examination.

Curve B, Figure 25, for the specimen of dolomite from Southern Rhodesia, showed a well defined third endothermic peak at about 650°C., in addition to the usual double endothermic peaks indicative of dolomite. This peak is attributed to magnesite and the occurrence of this mineral was proved by X-ray examination by Wasserstein.

Magnesite: Magnesite samples from commercial sources in the Transvaal and Southern Rhodesia gave thermal curves shown in Figure 26. Curve A, Figure 26, of Rhodesian magnesite, shows evidence of the admixture of a small amount of dolomite as indicated by the endothermic doublet around 870°C. X-ray analysis by Wasserstein supports this conclusion. Curve B, Figure 26, was obtained for the crystalline variety of Rhodesian magnesite used for refractories manufacture. The thermal pattern indicates the predominance of the magnesite minerals and this was confirmed by Wasserstein's X-ray analysis.

Thermal results in Curve C, Figure 26, for the Transvaal sample, show the magnesite mineral but do not indicate the occurrence of quartz which is shwon to be present by Wasserstein in X-ray examination.

Thermal Analysis of Refractory Clays: Determination of the clay minerals (in naturally occurring clays) by differential thermal methods is made difficult because of the possible presence of more than one clay mineral, together with carbonates, hydroxides, and organic materials which undergo thermal reactions. Fluxes and other minerals may cause the thermal reactions of the clay minerals to occur at lower temperatures or may

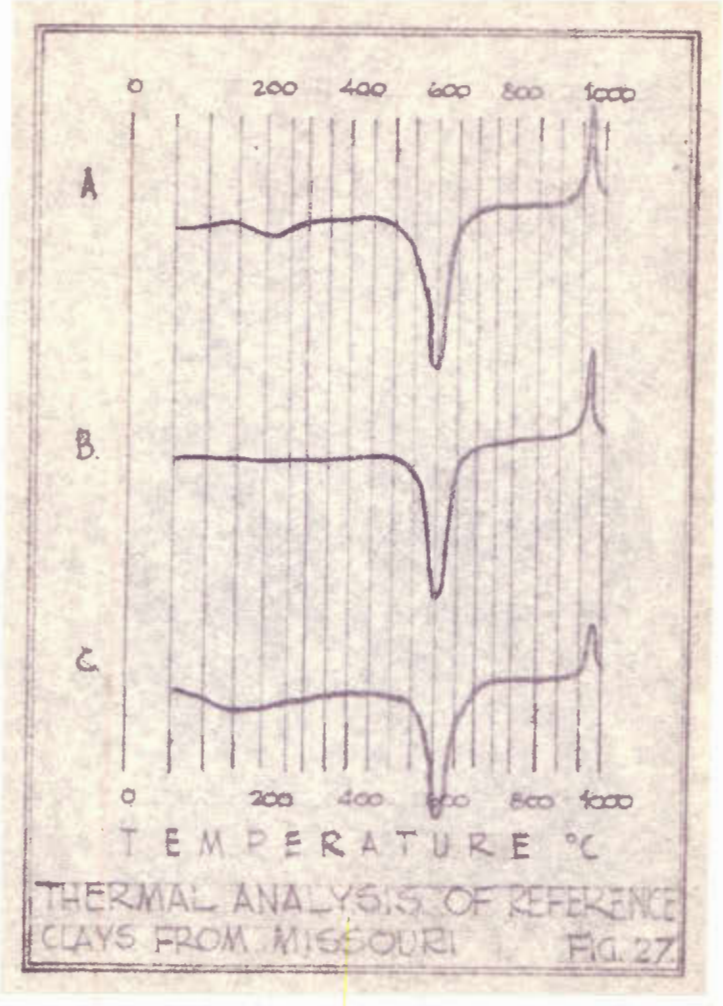


THERMAL ANALYSIS OF MAGNESITE

FIG. 26

diminish the intensity of the peaks.

Reference Clays from Missouri: Differential thermal curves were prepared representing flint, and plastic types of Missouri fire-clays supplied by Grim, and on Missouri semi-flint fire clay supplied by R.S. Bradley, Director of Research, A.P. Green Firebrick Co., Mexico, Missouri. These clays were intended as reference materials. Their curves are shown in Figure 27. The chemical analyses and origins of these clays are given in Table IX.



THERMAL ANALYSIS OF REFERENCE CLAYS FROM MISSOURI FIG. 27.

Curve A, Figure 27, is typical of the kaolinitic patterns obtained from Missouri flint clay by Keller and Westcott (47).

Curve B, Figure 27, representing Missouri semi-flint clay, also shows a good kaolinite pattern which is in accordance with Keller and Westcott's findings (47).

Curve C, Figure 27, of Missouri plastic clay, is of a kaolinite type as well, which is also confirmed by Keller and Westcott (47).

Table IX.

Chemical Analyses of Reference Clays from Missouri

Clay	1	2	3
Ig. loss	13.58	9.50	9.03
SiO_2	45.07	50.80	56.09
Al_2O_3	38.58	36.28	28.34
TiO_2	2.47	nil	1.95
Fe_2O_3	0.51	2.17	2.29
CaO	0.17	0.36	0.35
MgO	0.08	0.36	0.50
Na_2O	0.21	0.60	0.28
K_2O	0.08		1.79
TOTAL	100.75	100.07	100.62

Key:

Clay 1--Missouri flint clay*
Clay 2--Missouri semi-flint clay**
Clay 3--Missouri plastic clay*

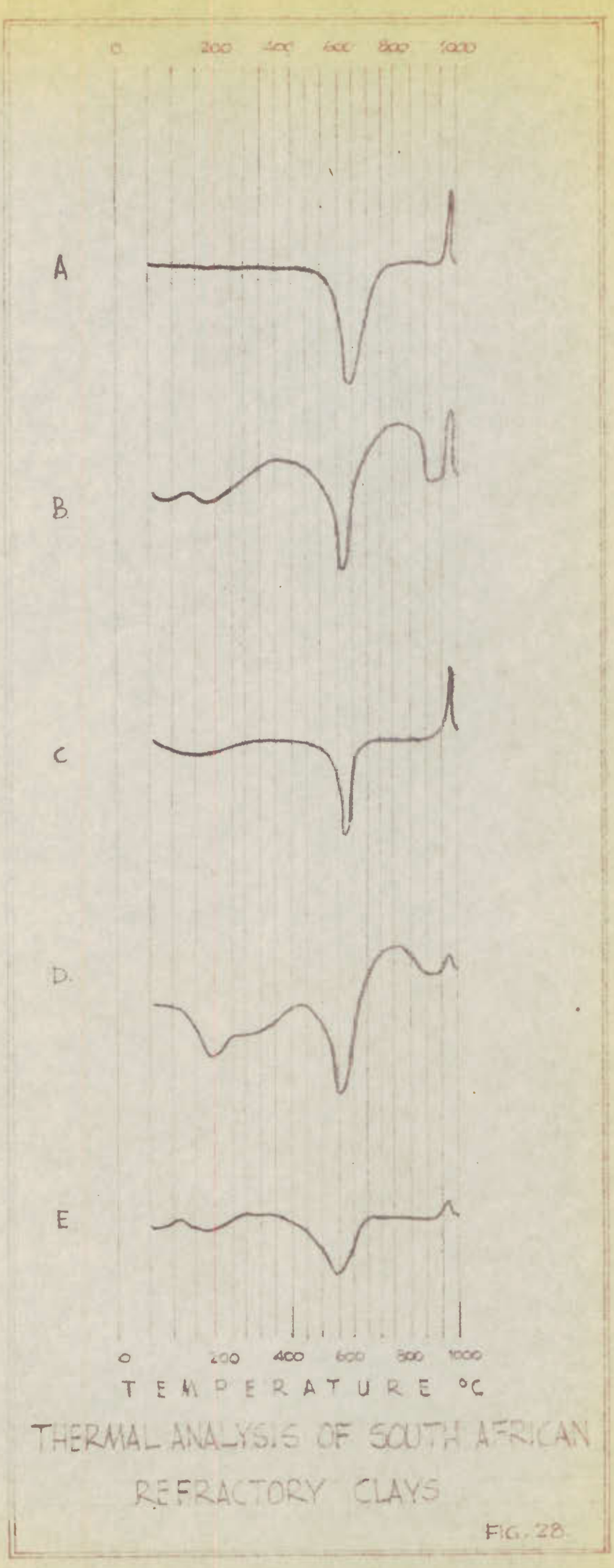
* Analyses supplied by R.E. Grim, Illinois Geological Survey.

**Analyses supplied by R.S. Bradley, A.P. Green Firebrick Co., Mexico, Missouri.

South African Refractory Clays: Qualitative thermal analyses of the five selected clays were made together with other specimens illustrating the behaviour of varieties of these types. The chemical analyses of these clays are given in Table XIII, and they are further described in the accompanying discussions.

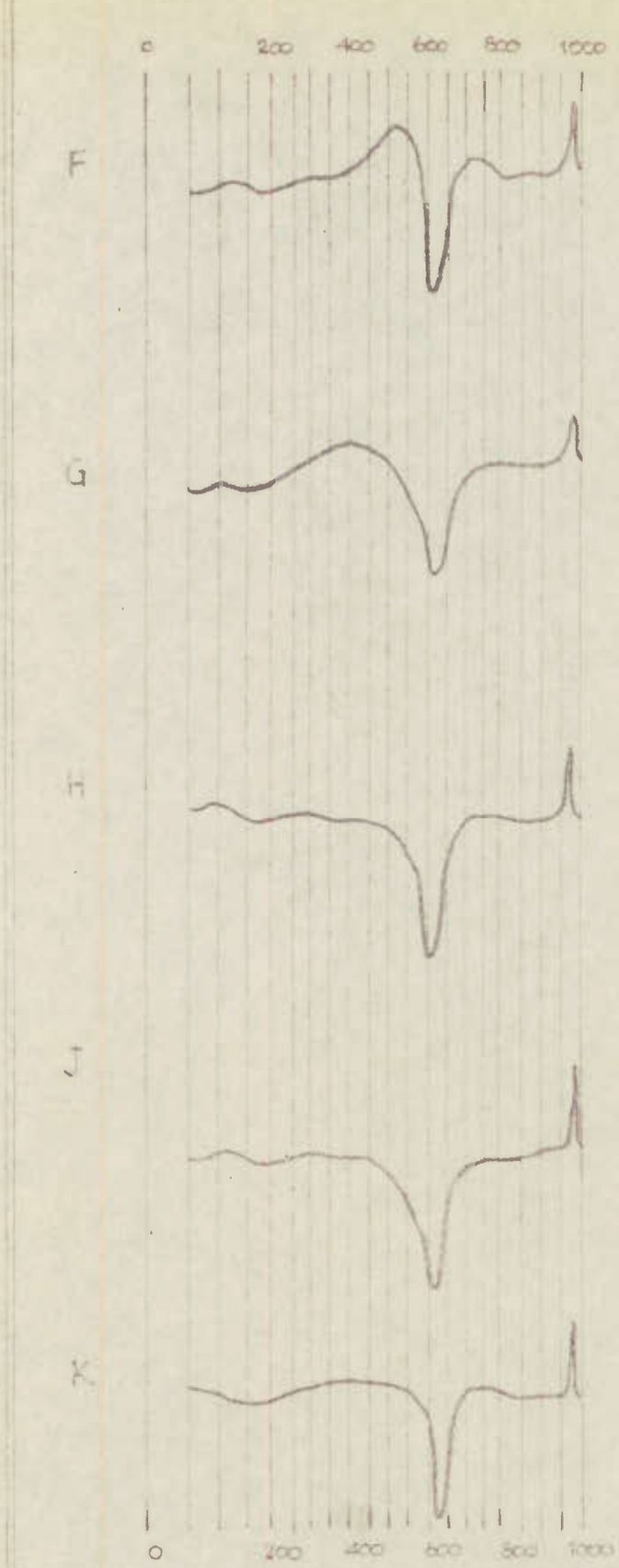
The complex nature of some of the South African refractory clays tested and the presence in some cases of considerable organic matter, make it extremely difficult to apply any single method for their identification; however, the differential thermal analysis of these samples did yield much useful information and offers a simple, quick, and inexpensive means for their general classification which could be used to advantage as a method of control in prospecting and mining.

Thermal curves (shown in Figure 28) confirmed the pre-



THERMAL ANALYSIS OF SOUTH AFRICAN REFRACTORY CLAYS

Fig. 28.



THERMAL ANALYSIS OF SOUTH AFRICAN REFRACTORY CLAYS

FIG 28 (continued)

dominance of the kaolinite group and suggest kaolinite as the principal mineral present in the refractory clay, but the accompanying quartz so well defined by X-ray patterns was not detected by these means. Quartz is known to produce a very weak endothermic response at about 570°C., which in view of the small amount present is beyond the sensitivity of this equipment, especially since this tiny effect occurs at about the same temperature range as the strong endothermic reaction of the kaolinite. (See Figure 19.) The pronounced endothermic reactions shown in the curves C, E, F, and J, Figure 28, taking place between 200°C. and 450°C., are due to organic matter. The significance of a second large exothermic reaction immediately after the major endothermic reaction, which is noted in curves C and J, Figure 28, is not definitely explained although it might possibly be the result of the presence of some organic matter having a relatively high combustion temperature. Grim*, after examining these particular specimens by thermal analysis (see Figure 18), suggests that this second exothermic effect may be due to siderite or organic matter; however, the presence of siderite could not be confirmed by X-ray or chemical analysis by the writer.

The intensity of the exothermic reaction around 980°C., exhibited by the kaolinite type minerals is known to be an indication of the amount of alumina present in the clay, although according to published information, strict proportionality does not apply. The height of this peak may be used as a criterion for selecting probable refractory clays.

For more complete study of the constitution of the carbonaceous clays, the organic matter could be destroyed by oxidation with hydrogen peroxide. This was not done, however, since the possible effects of this treatment on the other constituents have not been studied in detail insofar as they affect the differential thermal analysis.

*R.E. Grim, Illinois Geological Survey, Personal Communication

Clay I: Curve A, Figure 28, for Clay I, is that of a rich kaolinite type clay.

Clay II: Thermal results on Clay II, given in curve B, Figure 28, indicate free organic matter (carbon) mixed with a kaolinite type clay.

Clay III: Curve C, Figure 28, for Clay III, shows a good kaolinite pattern.

Clay IV: Curve D, Figure 28, obtained on Clay IV, shows a kaolinite type pattern, with organic matter, together with a quantity of another clay mineral which produced no well defined thermal pattern but suppressed the typical kaolinite exothermic peak. Carl*, who examined this clay, points out that the X-ray diffraction method is more sensitive to small amounts of the montmorillonite than thermal analysis and that none of these minerals were evident in the diffraction pattern he obtained for this specimen. He suggests that the non-kaolinite mineral present is probably illite.

Clay V: Curve E, Figure 28, for Clay V, shows the effect of dilution on the kaolinite curve pattern by the large amount of quartz present.

Curves F and G for Vereeniging and Springs carbonaceous semi-flint clays were distorted by the effect of oxidation of the organic matter present; however, the predominant kaolinite pattern was readily distinguishable.

Thermal curves H and J for semi-flint clays from Vereeniging and Brakpan also show good kaolinite type patterns.

The endothermic changes occurring in the low temperature range below 250°C., of the curves obtained for the flint and semi-flint clays, are not sufficiently well defined to diagnose the presence of other mineral groups and X-ray data do not support

---

*H.F. Carl, Physicist, U.S. Bureau of Mines, Personal Communication.

the occurrence of significant amounts of such admixtures in these clays. These endothermic reactions are most probably due to the presence of mechanically held water since the technique used did not include pre-drying the samples. The use of differential thermal analysis for distinguishing the types of plastic clays is well illustrated by curves D and K, and this method could be adopted for control work. (51, 52)

Summary and Conclusions of Thermal Analysis

1. Differential thermal analysis of the flint and semi-flint types of South African fire-clay tested gave characteristic thermal patterns of the kaolinite group type, the only group detected.

2. Owing to the complex nature of some of the plastic clays tested, as shown in curve D, Figure 28, differential thermal analysis alone is not sufficient to identify completely the constituents; however, this method was helpful in their general classification and could be used as a control procedure. The plastic clays are composed of the kaolinite group minerals and in some cases, as shown in curve K, Figure 28, organic matter and possibly illites are present.

3. Large amounts of quartz occurring in the silicious refractory shales tended to suppress the thermal curve pattern and make identification difficult.

4. Differential thermal analysis confirms that thermal reactions expressed by quartz are very feeble compared to the large thermal change accompanying the dissociation of kaolinite and the presence of this mineral is not detectable in the presence of large amounts of kaolinite group minerals.

5. The diaspore sample from Postmasburg gave a curve in close agreement with that of the Missouri sample, although the

latter contains accessorial quartz which does not visibly influence the thermal pattern.

6. The dolomite and magnesite samples examined gave characteristic curves for these minerals. The occurrence of small amounts of quartz detected in the sample of Transvaal magnesite by X-ray examination was not shown in the thermal analysis.

7. The possibility that small amounts of other minerals in all of the materials examined have escaped detection by the differential thermal analysis is recognised.

8. Differential thermal analysis applied to the fire-clay was useful in confirming the presence of the kaolinite group, although it is of lesser value for the identification of the montmorillonite and illite groups in the presence of kaolinite minerals.

9. The presence of organic matter did not obscure the kaolinite group pattern in the fire-clays tested.

10. Differential thermal analysis is a relatively simple, inexpensive, and rapid method of mineral determination and when properly supplemented by optical and X-ray analysis it frequently yields interpretations of identity not apparent from the other methods of examination.

X-Ray Examination

General Statement

X-ray diffraction studies are particularly valuable as a means of identification of the minerals present in clays, especially since the particle size of these minerals is, in general, too small to permit complete identification by petrographic methods. Results obtained by X-ray procedures are generally less affected by minor varieties than other methods, since they are directly dependent upon atomic structure.

The X-ray powder method is important for identification purposes. It consists of subjecting a small amount of powdered crystals, which give the desired random orientation, to a narrow beam of mono-chromatic X-rays. Diffraction of the X-rays takes place in accordance with Bragg's Equation:

$$n\lambda = 2 d \sin\theta$$

where:

n equals an integer (usually 1 in powder pictures)

λ equals wave length of X-rays used

d equals distance between atomic planes (lattice spacing)

θ equals diffraction angle.

The diffracted X-rays are recorded on a photographic film and since the spacings and intensities of the lines are dependent on atomic structure and composition, the resultant pattern photographed gives absolute identification since no two materials give identical patterns. Identification is accomplished by measuring the position and relative intensities of the more important lines, calculating the "d" values from the Bragg Equation, and referring to a catalogued index. In general the number of coincident "d" values is small and the method works like a fingerprint file, so that any material listed is rapidly identified. (53)

A useful variation of the powder method is accomplished by the use of the recording Geiger-counter X-ray diffraction

spectrometer, which completely eliminates the photographic record by substituting an automatically drawn curve representing intensity vs. angle of X-ray diffraction. This is done by recording the output of a special Geiger-counter tube on a standard strip chart recorder. The Geiger-counter tube is mechanically driven through a 90° arc, corresponding to 0° to 45°. Through a collimating and filter system the counter tube receives the diffracted rays from the sample which was radiated by the X-ray beam similarly collimated. (54)

Experimental Results

X-ray examination was made of each of the selected clays using the X-ray spectrometer. These results were confirmed by the photographic method in collaboration with Dr. Wasserstein. A detailed examination of the clay mineral present in these clays was made on a specially chosen, nearly mono-mineralic, sample, with the X-ray spectrometer.

Spectrometer Method*: The recording X-ray spectrometer, because of its greater ease of manipulation and speed in attaining results, affords many advantages over the photographic technique in making a detailed X-ray examination of the clay minerals. Spectrometer diagrams were prepared for the selected clays on a "Norelco" (N.A. Philips Co.) X-ray spectrometer using copper KL radiation. The instrument was calibrated against a sample of pure quartz before the clays were examined. The samples were ground to pass a 150-mesh Tyler Screen and placed in the sample holder. Attention was given to producing a uniformly smooth surface of the powdered sample, by tamping and smoothing with the aid of a small spatula. The quantity used was that sufficient to fill the holder cavity which was about 0.1 cc in volume. The prepared mount was positioned in the specimen holder and the spectrometer arm carrying the counter tube was set at the desired starting point. This point was marked on the

* Assisted by the National Chemical Laboratories.

Table X

X-ray Powder Data for Some Kaolinites (Spectrometer Method)
With Some Possible Quartz Reflection Interferences

Observed "d" values	Calculated "d" values*	Observed Intensity	A "d" value	B "d" value	C "d" value	D "d" value	E "d" value	Quartz "d" value
7.15	7.132	vvs	7.09	7.14	7.13	7.14	7.12	
4.35	4.361	m	4.43	4.35	4.36	4.34	4.36	4.22
4.17	4.164	m	4.15	4.16	4.17	4.18	4.19	
3.566	3.566	vvs	3.54	3.56	3.55	3.57	3.56	3.34
2.553	2.561 2.558 2.543	ms	2.550	2.560	2.550	2.560	2.548	
2.486	2.495 2.485	s	2.498	2.500	2.500	2.500	2.485	2.45
2.331	2.336	vs	2.329	2.340	2.380	2.340	2.340	
2.284	2.284	s	2.290	2.294	2.290	2.295	2.290	2.275
1.985	1.990 1.985	ms	1.990	1.995	1.995	1.990	1.980	1.974
1.778	1.783	m	1.785	1.791	1.790	1.790	1.785	1.813
1.659	1.663 1.659	s	1.664	1.663	1.665	1.670	1.670	1.667
1.616	1.614	ms	1.627	1.614	1.620	1.629	1.630	
1.539	1.539 1.534	m	1.540	1.539	1.540	1.535	1.530	1.536
1.486	1.487 1.484 1.483	vs	1.491	1.487	1.490	1.490	1.488	
1.449	1.455 to 1.439	wm	1.458	1.453	1.455	1.450	1.451	1.448

0%----------Increasing Percentage of Quartz----------100%
(according to H.F. Carl, U.S. Bureau of Mines)

* Brindley and Robinson, "The Structure of Kaolinite"; Mineral Mag., Vol. XXVII, p. 242, 1946.

Key to Table X.

A--Clay IV	(analysis see Table XIII)
B--Clay I	" " " "
C--Clay II	" " " "
D--Clay III	" " " "
E--Clay V	" " " "

recorder chart, which was then synchronized with the motor driven spectrometer arm. The scanning arm was driven at 1 r.p.m. and the recorder chart at 20 inches per hour. Lattice spacings ("d" values) were calculated from the Bragg Equation using θ values obtained by observing the position of the peaks recorded on the chart in relation to division lines representing diffraction angles. The "d" values and the principal reflections given by the selected clays are shown in Table X.. The results are arranged in ascending order of quartz content in accordance with estimates made on these particular samples by Carl who has developed a special X-ray technique for such analyses. (23) These estimates are as follows:

Quartz Contents of Selected Clays
(after Carl*)

Clay	Quartz
I	5%
II	5%-10%
III	10%-15%
IV	2%
V	35%-40%

The data given for kaolinite and other clay minerals in the Hanawalt Tables and other publications varies considerably. It was decided to take the recent data given by Brindley and Robinson (55) as a standard for comparison because of the detailed nature of their studies. The "d" values for quartz are also included.

Photographic Method: X-ray powder photographs were made by Dr. B. Wasserstein of the selected clays together with a sample of Missouri flint clay supplied by Grim and known to contain kaolinite as the principal mineral. A Picker X-ray unit was used on which was mounted a Debye-Scherer camera 114 mm in diameter, such as described by Buerger (56). Lattice spacings ("d" values) were determined in collaboration with Wasserstein

* H.F. Carl, Physicist, U.S. Bureau of Mines, Personal Communication

Table XI

X-Ray Powder Data for Some Kaolinites (Photographic Method)
With Some Possible Quartz Reflection Interferences

Observed "d" Value *	Calculated "d" Value*	Observed Intensity *	A "d" Value	B "d" Value	C "d" Value	D "d" Value	E "d" Value	F "d" Value	Quartz "d" Value
7.15	7.132	vvs	7.12	7.14	7.13	7.12	7.13	7.10	
4.35	4.361	m	4.37	4.38	4.36	4.35	4.34	(4.23)	4.22
4.17	4.164	m	4.15	4.16	4.17	4.14	4.18	nd	
3.566	3.566	vvs	3.560	3.552	3.560	3.543	3.535	3.521	3.34
2.553	(2.561 (2.558 (2.543	ms	2.551	2.551	2.548	2.547	2.542	2.533	
2.486	(2.495 (2.485	s	2.490	2.492	2.488	2.478	2.478	(2.439)	2.45
2.331	2.336	vs	2.329	2.330	2.332	2.328	2.333	2.341	
2.284	2.284	s	2.285	2.285	2.280	2.275	2.276	2.273	2.275
1.985	(1.990 (1.985	ms	1.977	1.982	1.981	1.977	1.977	1.970	1.974
1.778	1.783	m	1.783	1.779	1.782	1.782	1.778	(1.808)	1.813
1.659	(1.663 (1.659	s	1.651	1.654	1.655	1.653	1.656	(1.661)	1.667
1.616	1.614	ms	1.612	1.614	1.613	1.614	1.612	nd	
1.539	(1.539 (1.534	m	1.539	1.536	1.536	1.537	nd	1.535	1.536
1.486	(1.487 (1.484 (1.483	vs	1.484	1.484	1.484	1.483	1.482	1.482	
1.449	(1.455 (to (1.439	wm	1.448	1.450	1.447	1.451	1.447	1.445	1448

0%----------Increasing Percentage of Quartz----------100%

Table XI (cont'd.)

Observed "d" Value*	Calculated "d" Value*	Observed Intensity*	A "d" Value	B "d" Value	C "d" Value	D "d" Value	E "d" Value	F "d" Value	Quartz "d" Value
1.335	1.338	m	1.334	1.336	1.338	1.336	1.336	1.337	
1.302	(1.305 (1.300	ms	1.302	1.303	1.302	1.304	1.304	nd	
1.280	1.280	m	1.281	1.281	1.279	1.282	1.282	1.281	1.283

0%----------Increasing Percentage of Quartz----------100%
(according to H.F. Carl, U.S. Bureau of Mines)

* Brindley and Robinson, "The Structure of Kaolinite"; Mineral Mag. Vol. XXVII, p. 242, 1946.
( ) = quartz lines?

Key to Table XI

A -- Missouri flint clay (analysis see Table IX)
B -- Clay IV (analysis see Table XIII)
C -- Clay I " " " "
D -- Clay II " " " "
E -- Clay III " " " "
F -- Clay V " " " "

using the diffraction angles of the reflections, obtained from measurement of the photographic film. The results obtained are shown in Table XI, in comparison with Brindley and Robinson's data (55). The "d" values for quartz are also given.

A print of an X-ray film obtained with one of the selected clays is given in Plate XII to illustrate the photographic method of recording results.

Detailed Examination of a Quartz-Free High Alumina Clay: A specimen of nearly mono-mineralic, high alumina clay from a commercial source in the Transvaal was very kindly supplied by the National Chemical Laboratories. Differential thermal analysis of this clay by the N.C.L. indicated that the dominant mineral was kaolinite. Chemical analysis* shows this clay to have an Al_2O_3 : SiO_2 ratio of 1 : 1.69. A curve for this specimen was prepared on the recording X-ray spectrometer and is reproduced in Figure 29 to show the method of recording results in the spectrometer procedure. The "d" values were calculated for the higher order lines and these values are compared with data published by Brindley and Robinson, in Table XII. It is interesting to note the absence of quartz reflections in this sample, confirming the high degree of purity of the material.

The absence of aluminium hydroxide minerals from the diffraction pattern is particularly interesting in this high alumina clay inasmuch as Heystek**, examining flint fireclays from Missouri by X-ray spectrometer methods, found pronounced diaspore and gibbsite peaks in addition to the kaolinite minerals, in some of those materials.

Summary and Conclusions

1. The prominent clay mineral appears to be the same in all specimens of South African refractory clay examined. The reflections obtained are comparable with those observed for Missouri flint clay and with the data on kaolinite

---

* See Table XIII.

** H. Heystek, National Chemical Laboratories, Personal Communication.

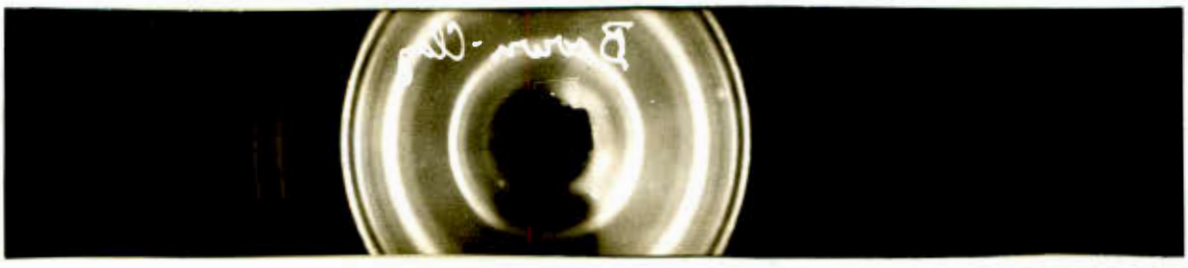


Plate III--X-ray powder photograph of a selected clay.

given by Brindley and Robinson.

2. Quartz was present in varying amounts in all of the selected clays examined. The reflections produced by the quartz in many cases were so nearly coincident with those of the clay mineral as to produce line broadening or a shift in intensity which made measurement by the photographic method difficult. Since the intensity of the quartz reflections increases according to the amount of that mineral present, the patterns for the clay mineral in the specimens gave increasingly divergent "d" values from that of kaolinite.

3. The presence of illite in clay IV, suspected from differential thermal analysis, could not be definitely proved by X-ray methods.

4. All of the reflections obtained with the South African refractory clays were checked for gibbsite, boehmite, and diaspore, and no diffraction effects from these minerals were noted.

5. The "d" values obtained with the sample of South African high alumina clay were in good agreement with the "d" values given by Brindley and Robinson for kaolinite.

6. Of the two methods employed, the recording X-ray spectrometer certainly affords the most rapid results with a minimum of manipulative skill. According to Frederickson (44), the tendency for the clay minerals to orient as a result of the treatment used in preparing samples for the X-ray spectrometer facilitates the identification of minerals that give similar X-ray patterns. He further remarks that this preferred orientation is, however, a disadvantage where difficulty is encountered in identifying the constituents of a sample when all the reflections are present, and recommends the photographic method in this case.

Table XII

"d" Values for the Higher Order Lines of
A South African High Alumina Clay

Observed Values Kaolinite (Brindley & Robinson)	Observed Values South African Clay (Experimental)
"d" Values	"d" Values
7.15	7.12
4.45	----
4.35	4.36
----	4.34
4.17	4.145
4.12	3.935
3.837	3.82
3.734	3.73
3.566	3.555
3.365	3.37
3.138	3.14
3.091	3.10
2.748	2.75
2.553	2.55
2.521	2.525
2.486	2.49
2.374	2.38
2.331	2.336
2.284	2.29
2.243	2.24
2.182	2.18
2.127	2.13
2.057	2.06
1.985	1.985
1.935	1.94
1.892	1.892
1.865	1.865
1.835	1.835
1.805	1.805
1.778	1.784
1.704	1.706
1.682	1.68
1.659	1.66
1.616	1.618
1.581	1.587
1.539	1.539
1.486	1.4875
1.464	1.453
1.449	1.449
1.426	1.426
-----	1.3385
----	1.305
----	1.245
----	1.241
----	1.237

OPTICAL EXAMINATION

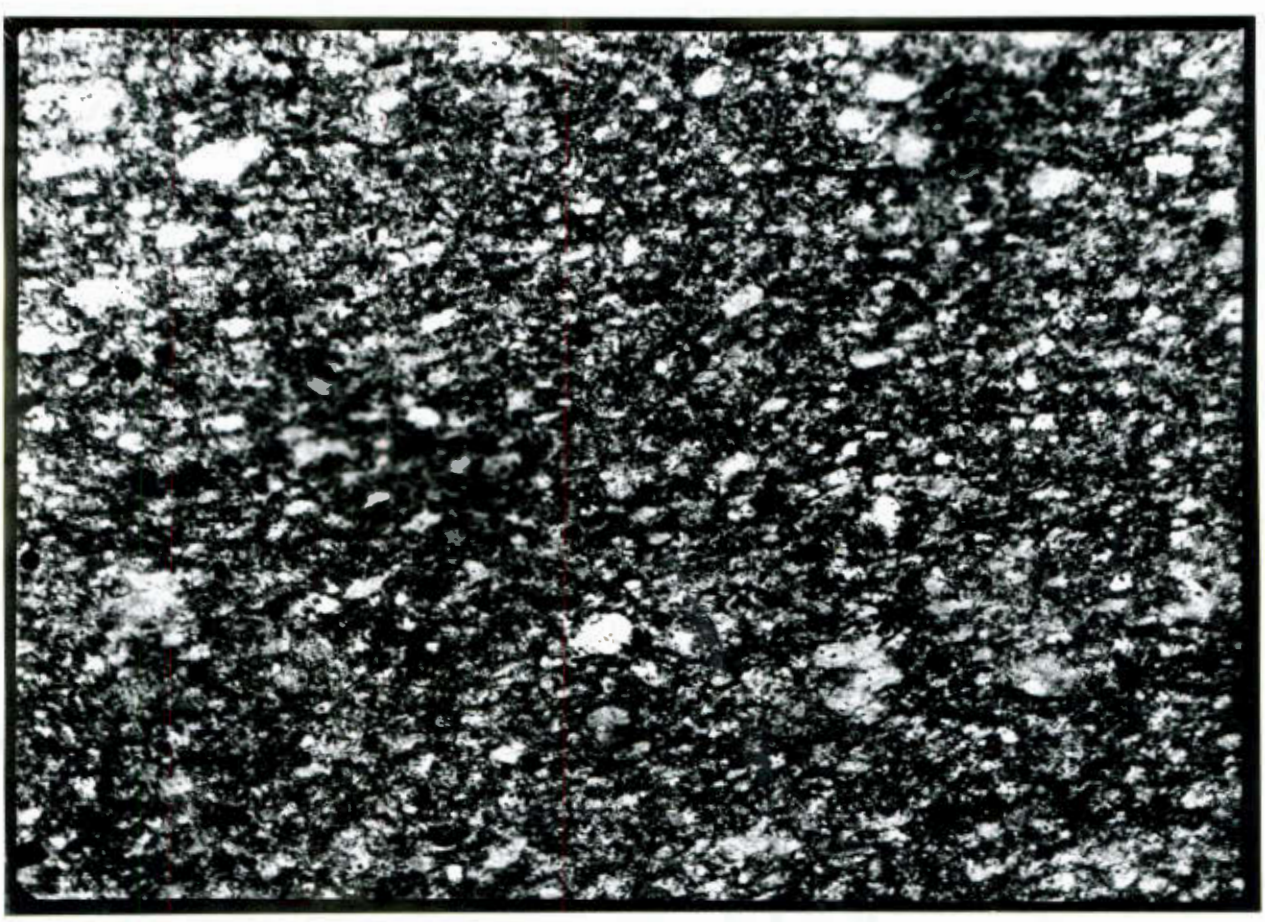
General Statement

An examination of the selected clays with the petrographic microscope was undertaken to supplement the other determinative procedures. Petrographic methods with thin sections were useful in studying texture and relation of constituents, and examination of the powdered samples was made to obtain additional data. Residues obtained in the particle size examination were also checked with the microscope. The heavy minerals were extracted by bromoform separation and investigated to complete the study.

Experimental Results

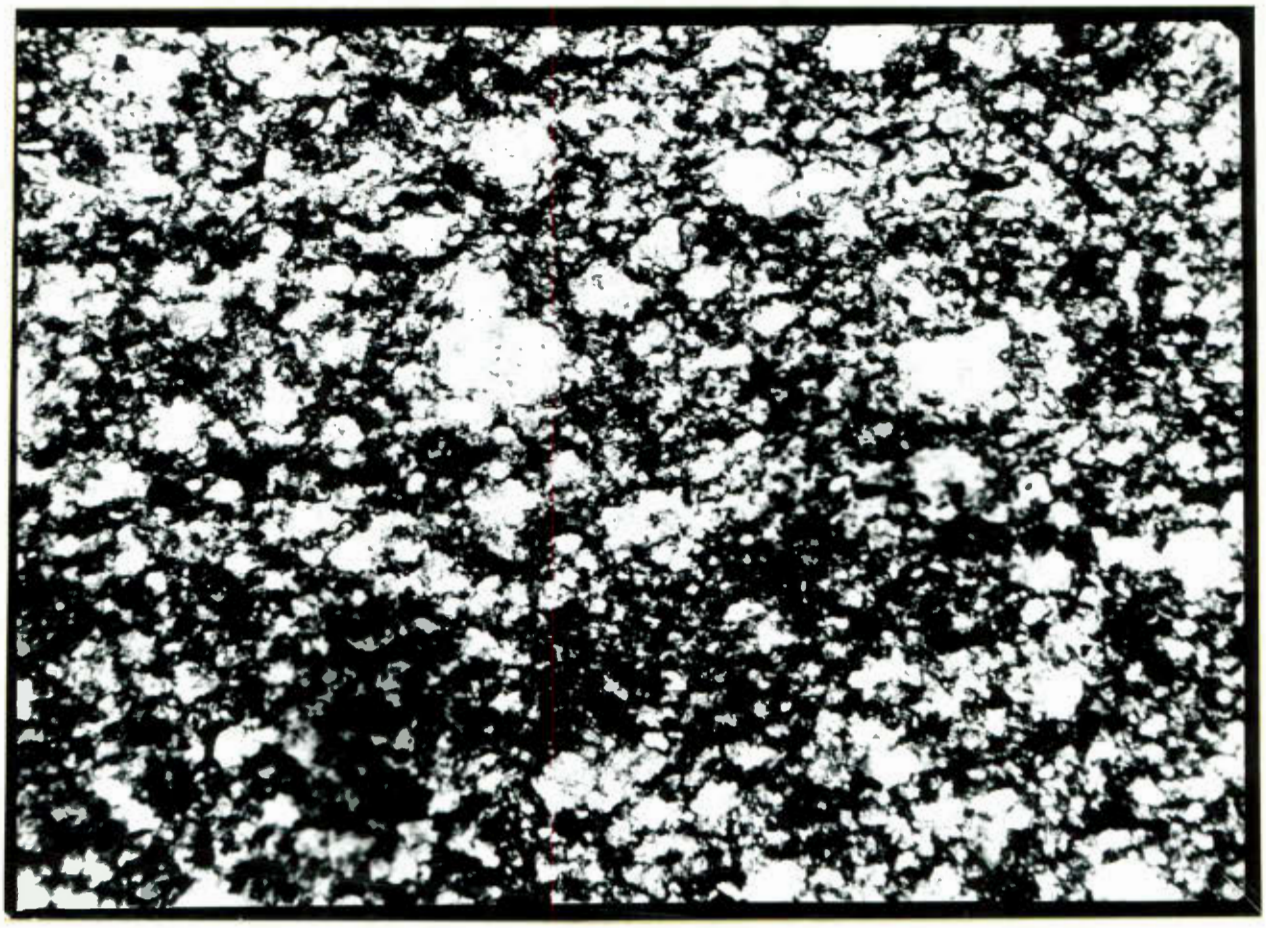
Thin Sections Study

Photomicrographs of the selected clays taken with white light, x87, are given below together with relevant comments.

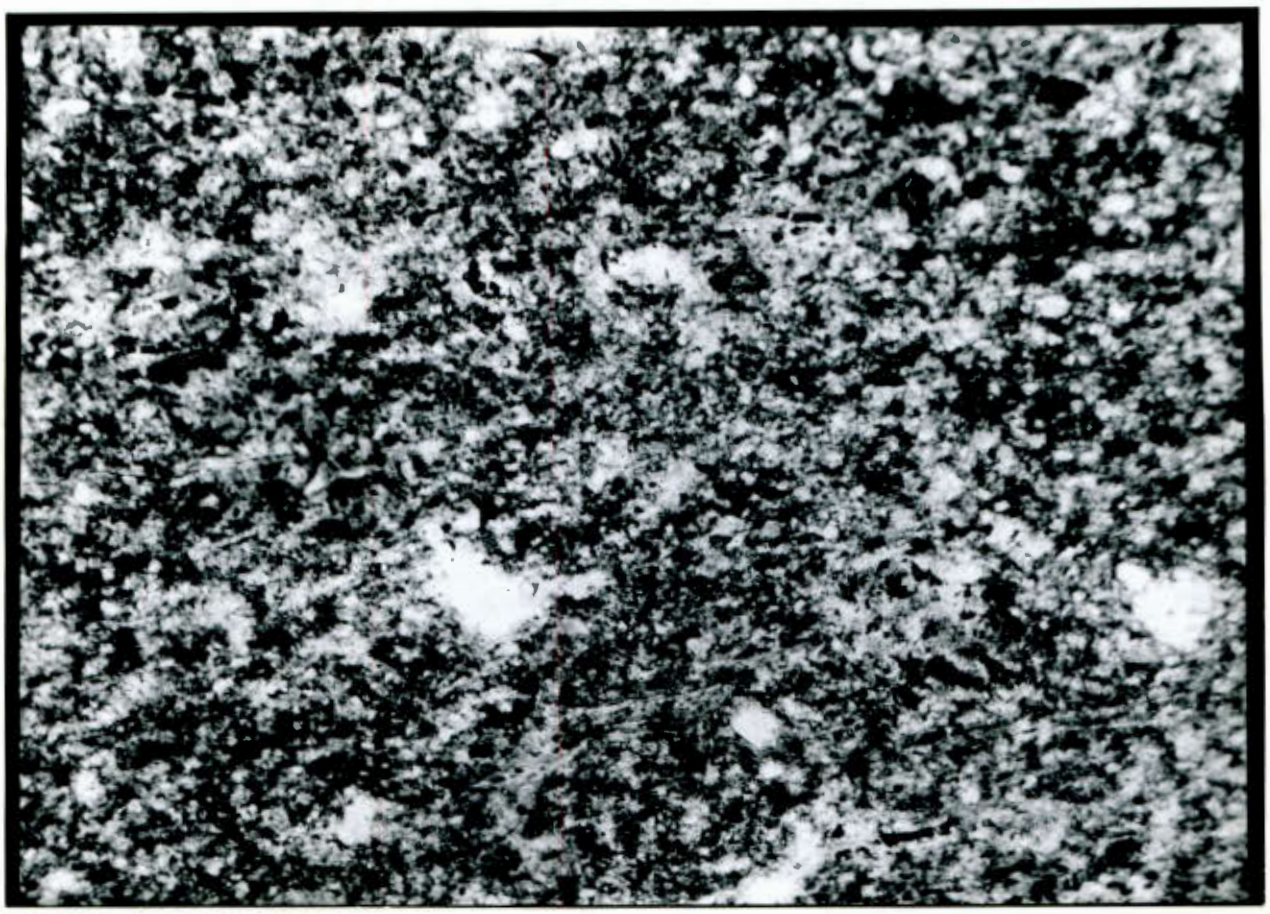


Clay I. This clay contains a good development of rather coarse kaolinite flakes. The thin section shows, under the microscope,

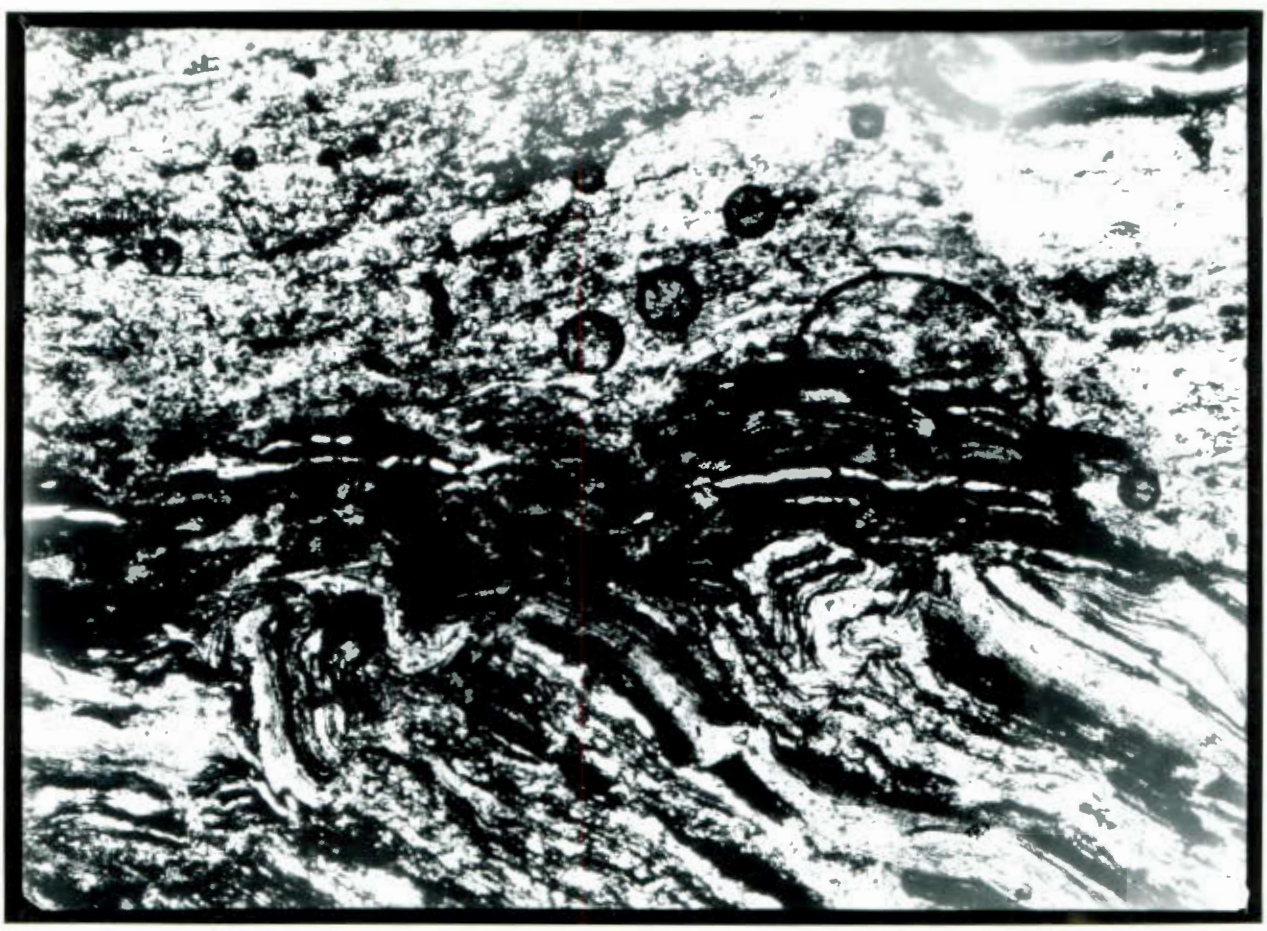
pseudo-schistose structure possibly caused by preferred orientation of the platey clay minerals. The particles range in size from 0.4 to 4.0 mm in length and from .01 to 1.0 mm in breadth. A very small amount of quartz was noted. No feldspars were seen.



Clay II. This specimen also shows large, well developed kaolinite particles. Pseudo-schistose structure was noted under the microscope though not so pronounced as in Clay I. A small amount of quartz was seen. Much of the material present is isotropic under crossed nicols owing to the occluded organic matter.



Clay III. The sample showed a predominance of kaolinite aggregates. Pseud-schistose structure was observed to some degree although less than seen in Clays I and II. Quartz is present, probably less than 15%.



Clay IV. The contorted banding resulting from local pressure adjustment was conspicuous. The alternating light and dark bands are clearly distinguishable in the section. A small amount of quartz is present, probably less than 5%.

Clay V. Quartz, ranging in size from coarse to fine particles, is very abundant, probably more than 30%. Kaolinite flakes are well developed. The pseudo-schistose structure was observed.

Powder Study

Specimens of the five selected clays were ground to pass a 100 mesh sieve and powder mounts were made in oils of various indices of refraction. The heavy mineral residue was extracted by bromoform separation from 100 gm. samples each of the prepared specimens and mounted in oils for microscopic study.

An examination was also made of the various fractions obtained in the mechanical analyses used in determining particle size.

Results: Clay I. In addition to the kaolinite particles which predominate, a very small amount of fine quartz, less than 5%, was observed. The refractive index of the clay varies from 1.56 to 1.57. The yield of heavy minerals was small. A few grains including zircon, tourmaline and rutile were observed.

Clay II. The highly carbonaceous nature of this clay made examination difficult and the clay mineral could not be clearly observed. Some quartz, probably less than 10%, was present. Heavy mineral extraction gave a small yield. The grains identified were tourmaline, rutile, and zircon.

Clay III. The clay mineral present had an index of refraction ranging from 1.56 to 1.57. Quartz was present, probably less than 15%. Heavy mineral study revealed the presence of zircon, rutile, tourmaline, garnet, iron ores, leucoxene.

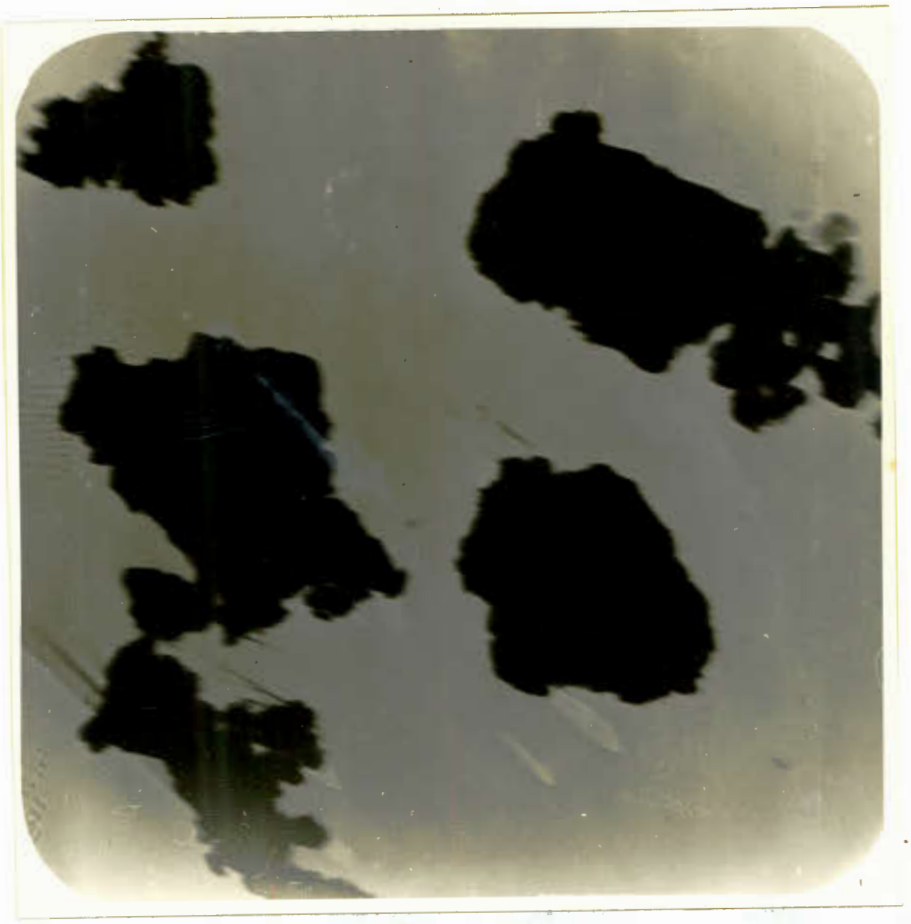
Clay IV. The clay particles were too fine to be distinguished and the organic matter present further obscured the field. A very small amount of quartz, probably less than 5% was present. Minerals identified in the heavy residue include garnet, rutile, tourmaline, zircon, iron ores, leucoxene.

Clay V. This clay contains an abundance of quartz, probably more than 30%. The clay particles could not be readily distinguished. Fragments of mica and feldspar were noted. The heavy mineral residue included garnet, zircon, tourmaline, and rutile.

Observations with the Electron Microscope

Electron micrographs were prepared by Dr. Poulsen, Veterinary Research Laboratory, Onderstepoort, of Clays I and IV. The equipment used was an R.C.A. Electron Microscope, Type EMU, magnifying 5,000 diameters. The micrographs are reproduced in Plate IV.

Apart from rough crystalline outline, nothing diagnostic was observed inthe examination with the electron microscope, but certainly no rod shaped crystals indicative of halloysite and used to distinguish halloysite from kaolinite (57) were seen.



Clay I, x 15,000

Clay IV, x 15,000

Plate IV - Electron Micrographs

Quantitative Chemical Analysis

The selected South African refractory clays were analysed and the results given in Table XIII along with some analyses illustrating variations in these types. An analysis of a South African high alumina clay, supplied by the National Chemical Laboratories, which was found to show no quartz in X-ray examination is also included.

Quartz is known to be present in all of the selected clays and estimates of the amounts present were made by Carl using X-ray methods. (See page 99.) Calculations of the SiO_2 : Al_2O_3 ratios and the SiO_2 : R_2O_3 ratios were made using Carl's estimates. Such data are of course only an approximation depending on the limits of accuracy of the quartz determination; however, the results so obtained tend to confirm deductions made by other determinative procedures. For instance Clays I, II, and III show SiO_2 : R_2O_3 ratios of 1.83, 1.75, and 1.84, respectively, which though low for kaolinite fall within the range given by Hendricks. (30) The lime, magnesia, and iron contents of these clays are all within the limits that the kaolinite lattice may conatin without distortion (30). The alkali content is also low as confirmed by spectro-chemical analysis (see page 110). The chemical analysis data indicate that these clays are essentially kaolinite types. It is of interest to note that Clay II shows the highest ignition loss of the selected clays owing to the carbonaceous material present. This clay also has the highest titania content which is probably explained in part by the presence of titanium bearing minerals such as rutile and titanite; however, it may be that the titania may exist as a surface ion or be combined in the lattice, according to Mitchell and Henry (58).

Clay IV shows the largest amounts of iron, lime, and magnesia present in the selected clays. Spector-chemical analysis indicates a relatively large amount of alkali as well. This information suggests the presence of a non-kaolinite mineral, possibly illite, in addition to kaolinite. The SiO_2 : R_2O_3 ratio is 1.97 which confirms that the clay is essentially kaolinite.

Clay C contains a large amount of quartz which is easily visible to the naked eye. The iron content is below 0.9% though the colour of the material is distinctly reddish brown. The SiO_2: R_2O_3 ratio is 2.32 which is high for kaolinite, however, it is quite probable that in this particular case the quartz estimate was low. The lime content is highest of any of the selected clays though no magnesia is reported.

The chemical analyses of the other typical clays show the generally low content of iron and fluxes, such as lime, magnesia, soda and potash, which characterize many of the commercial types of South African refractory clays.

The specimen of high alumina clay shows a SiO_2 : Al_2O_3 ratio of 1.72 which is near the lower limit of the range for kaolinite suggested by Hendricks (30).

Table XIII.

Chemical Analyses of South African Refractory Clays.

A. Selected Clays: *

Sample.	Clay I.	Clay II.	Clay III.	Clay IV.	Clay V.
Loss	13.59	16.90	13.96	14.40	7.21
SiO_2	46.86	44.46	50.14	43.20	67.70
Al_2O_3	38.22	35.04	34.50	33.80	21.78
TiO_2	0.41	2.12	0.88	1.76	0.87
Fe_2O_3	1.10	0.84	0.26	2.56	0.83
CaO	0.00	0.40	0.00	2.06	1.24
MgO	0.00	0.58	0.41	0.61	0.00
Total	100.18	100.34	100.42	98.39	99.63
Estimated Quartz [2]	5	7.5	12.5	2.0	37.5
SiO_2: Al_2O_3	1.85	1.78	1.85	2.06	2.49
SiO_2: R_2O_3	1.83	1.75	1.84	1.97	2.32

1. Analysist E.R. Newbury (Vereeniging Brick & Tile).

2. Estimates by X-ray methods according to H.F. Carl (Note: average values taken for clays II - III - IV, see p).

Table XIII, (Cont'd).

B. Typical Clays:

	A.	B.	C.	D.	E.
Ig. Loss	13.84	13.94	14.04	14.10	14.20
SiO_2	45.62	48.50	49.98	43.10	44.00
Al_2O_3	38.64	33.41	33.95	39.60	38.20
TiO_2	0.54	1.40	1.40	2.00	1.75
Fe_2O_3	0.44	1.51	0.21	1.50	1.20
CaO	0.52	0.66	0.52	0.00	0.00
MgO	0.66	0.92	0.40	0.00	0.42
TOTAL	100.26	100.34	100.50	100.30	99.77

	F.	G.
Ig. Loss	14.84	10.44
SiO_2	45.38	50.70
Al_2O_3	37.60	35.90
TiO_2	0.98	1.52
Fe_2O_3	0.98	1.80
CaO	0.10	0.16
MgO	0.35	0.52
Total	100.23	101.04

A. Flint Clay (carbonaceous), Vereeniging.
B. Semi-flint clay (Carbonaceous), Vereeniging.
C. Semi-flint clay (carbonaceous), Springs.
D. Semi-flint clay, Vereeniging.
E. Semi-flint clay, Brakpan.
F. Plastic clay, Springs.
G. Siliceous refractory shale, Vereeniging.

Analysts: E. Mooi, E.R. Newbury, L. van Vuuren, (Vereeniging Brick & Tile Co. Ltd).

C. Specimen of High Alumina Clay Showing no quartz in X-ray Examination. *

Ig. Loss	12.40
SiO_2	42.50
Al_2O_3	41.50
TiO_2	0.06
Fe_2O_3	1.00
CaO	0.30
MgO	0.30
Na_2O	0.60
K_2O	0.70
Sulphuric anhydride	1.60
	100.96
$SiO_2 : Al_2O_3$	1.74
$SiO_2 : R_2O_3$	1.72

* Analyst: F. Grey, (National Chemical Laboratories).

Note on Organic Matter in the Selected Clays.

Clays II and IV gave prominent indications of the presence of carbonaceous matter in the differential thermal analyses and these clays were subjected to further investigation to determine the amount of such material present.

The estimation of the total organic matter in clays is difficult since there is no simple method of separating it and making a direct determination. (59). For this work the method suggested by Waksman (60) was followed in which the total carbon was determined and the result multiplied by 1.724 a factor recommended by Van Bemmelen based on the assumption that the average carbon content of the soil organic matter is 58%.

Results are given below:

Organic Content of Selected Clays.

Sample	Total Carbon *	Total Organic Matter.
Clay II	2.61%	4.50%
Clay IV	1.70%	2.93%

* Analyses by Union Steel Co. Ltd.

"Morin Dye" Test -- Free Alumina.

General Statement.

Tetrahydroxy-Flavonol ("Morin" Dye) produces a green fluorescence with aluminium salts in solution and is used as a micro-chemical test for this metal. Tschrischwilli, Bussem, and Weyl (61) employed "Morin" Dye to detect the presence of free aluminium ions in clays. Mitchell (62), who also used this test to distinguish between clays containing combined and uncombined aluminium ions, suggests that clays which show the presence of free aluminium ions by this test have a less stable structure than others which do not. The test was further developed to yield quantitative results by Mitchell and Henry. (28). The general procedure adopted by all these workers was to leach out the soluble aluminium ions with standard HCl solution, by soaking overnight, and then examining the supernatent liquid. The liquid was neutralized with NaOH and then made slightly acid with HCl. A few drops of "Morin" Dye were added and fluorescence was observed with the ultra violet light.

Experimental Procedure.

The method just described was found to give erratic results when applied to South African refractory clays, possibly because of the presence of other ions, removed in the leaching process which affect fluorescence. Reproducible results more in keeping with chemical analysis data were obtained by using acetic acid and shortening the leaching period. The procedure finally adopted was to add 22.5 cc of cold distilled water to approximately 0.75 grams of the clay sample and then to add 2.5 cc of 5 N acetic acid to bring the final volume of liquid to 25 cc. The suspension was stirred well and to it was added 0.1 cc. of a 2% solution of "Morin" Dye in methyl alcohol. The test, carried out in a porcelain dish to afford a good background for observations, was allowed to stand for one half

hour and then observed under ultra-violet light.

The typical clays were examined, along with other minerals, by this test and the results are tabulated below:

Material	Fluorescence.
Clay I	Strong.
Clay II	Very weak.
Clay III	none.
Clay IV	"
Clay V.	"
Missouri flint clay	weak.
Missouri diaspore	very strong.
English China clay	none.

Summary and Conclusions.

The efficacy of this test cannot be absolutely relied upon to determine the stability of the structure of the clay minerals until further work has shown the effect of ions other than aluminium released during the leaching process. The test does, however, suggest the presence of small amounts of active aluminium compounds in Clays I and II and in the flint clay and diaspore from Missouri and these results seem to be substantiated by the low silica to alumina ratio of these materials as shown by chemical analysis. The amount of free alumina detected in Clays I and II was too small to be confirmed by X-ray and D.T.A. examination.

Spectro-Chemical Examination

A spectro-chemical examination of the selected clays, together with standard samples of Missouri semi-flint and plastic clays, was made by Dr. Wasserstein at the Union Geological Survey. The instrument used was a Littrow-type Hilger spectrograph employing copper electrodes. All of the samples were arced for 20 seconds using 5 amps; for the boron determinations additional samples were arced for 50 seconds with a different setting of the spectrograph.

Although other minor elements were noted*, only those that could best be determined under the test conditions are mentioned. The results of the examinations are given in Table XIV below:

Table XIV.

Selected Minor Constituents of Refractory Clays

Sample	Elements Present													
	Pb	K	Cs	Na	Li	Cr	V	Mn	Ni	Ga	B	Ba	Sr	Sn
Clay I	4	nil	tr	nil	nil	8	6	tr	3	2	1	1	tr	nil
Clay II	4	tr	2	1	1	7	4	1	3	6	nd	1	1	nd
Clay III	3	tr	2	tr	tr	8	6	1	6	7	3	nd	tr	tr
Clay IV	7	6	4	6	4	9	7	5	6	8	5	6	6	2
Clay V	1	tr	3	tr	tr	8	5	1	3	4	2	nd	1	nd
Missouri Semi-flint	3	1	1	tr	1	9	7	tr	7	6	6	tr	1	nd
Missouri Plastic	4	5	2	1	1	8	7	1	7	7	nd	tr	2	tr

1 is very weak, 10 is very strong.

The mode of occurrence of the elements present is discussed by Goldschmidt (63, 64).

The limits of detection of certain elements as determined experimentally by Wasserstein, using analysed samples, are given as follows:

Elements	Percent Present as Oxide
Na, Li	0.1
K	0.5
Ba	0.05
B	0.02

cont'd.

---

* For further information on the trace elements in clay see Ahrens (65).

Elements	Percent present as Oxide
Mn, Sn	0.001
Pb, Cr, V, Ni	0.00x
Sr	0.01

Note: Wasserstein states that while better sensitivity is obtainable with the equipment, under the conditions of the tests the above limits prevail.

Summary and Conclusions

1. This examination brings out the striking difference in the amount of K, Na, and Li present in the plastic clays, represented by Clay IV and Missouri plastic, compared to the poorly plastic types including Clays I, II, III, V, and Missouri semi-flint clay.

2. The elements K, Na, and Li are abundant metals of the alkaline group. They may be present as ionic replacements or exchangeable bases in the clay minerals or occurring in the associated minerals.

3. Caesium, a rare metal of the alkaline group, is allied to potassium and commonly found with that element.

4. The atomic radii of gallium (0.62A) and aluminium (0.57A) are similar and gallium is invariably found with aluminous materials.

5. Vanadium and chromium occur in all of the clays examined, probably as replacements for Fe.

6. Manganese is widely diffused in small quantities in most rocks.

7. Nickel is closely related to iron in chemical properties, further the ionic potentials of Fe^2 (1.56) and Ni^2 (1.60) are similar and in consequence these elements may be expected to be found together. Nickel also substitutes for magnesium.

8. The boron detected may be present in the accessory mineral tourmaline noted in the heavy mineral separations.

9. Barium, strontium, and tin were readily detected in Clay IV but were not noted in any of the other samples.

10. The spectro-chemical examination brings out the many problems in geochemistry and geophysics involved in a study of the clays. In this connection Frederickson(44) draws attention to the importance of the ionic potential in the interactions between the ions and water molecules. He states that ions with a low ionic potential

(large ions with a small charge) tend to concentrate in evaporates if they are not first absorbed by the hydrated oxides.

Radioactivity of the Selected Clays

The selected clays were examined for radioactivity in a beta counter by Dr. D.J. Simpson of the Union Geological Survey. The results are given as follows:

Clay	K_2O Equivalent
I	1.30%
II	1.23%
III	3.57%
IV	4.47%
V	1.03%

In obtaining these results it was assumed that all of the radioactivity measured was due to potassium. This assumption also holds for the analysed clay sample used as a standard.

The K_2O equivalents for all of the selected clays are higher than indicated by the spectro-chemical results, suggesting the presence of either thorium or uranium. Clay IV, which shows the highest K_2O equivalent is known to contain potassium; however, the spectro-chemical data suggest that the quantity present is not sufficient to account for all of the radioactivity noted. Clay III gives evidence of the largest amount of radioactivity from sources other than potassium. This condition may be at least partially explained by reference to the profile chart for heavy minerals of the Middle Ecca strata in the Springs area (Figure 11), which shows that monazite, a thorium bearing mineral, occurs in the area.

In addition to the occurrence of thorium and uranium as accessory minerals it is also possible that these ions are adsorbed ions on the clays. Frederickson (44) suggests a possible method for the concentration of uranium (and thorium) in the presence of carbonaceous matter which is summarized as follows: Uranium ions are released by weathering from parent sources. These ions are adsorbed by base exchange phenomena on the layer lattice minerals such as the clays. The uranium is later displaced

because of an increase in thermal environment, aging, or introduction of more chemically active ions, and is put into solution. The carbonaceous matter present would then serve as a filter and concentrate and fix the ions. The presence of alkaline solutions cause graphite layers to expand to such an extent that they may be converted into colloidal suspension leading to a final breakdown of the graphite structure. Colloids containing uranium would then be adsorbed on clays and similar minerals.

Differential thermal analysis has indicated the possible presence of hydrocarbons in some of the plastic and flint clays which are associated with the coal seams. From this very brief inspection of the radioactivity of these clays an interesting method of accounting for this occurrence suggests itself--could the breakdown of the coaly matter be part of a radioactive process possibly connected with the polymerization of some of the carbon into hydrocarbon. This point is worthy of further investigation, particularly as regards possible influence of radioactivity on the genesis of coal measure clays in general.

Particle Size Distribution.

General Statement.

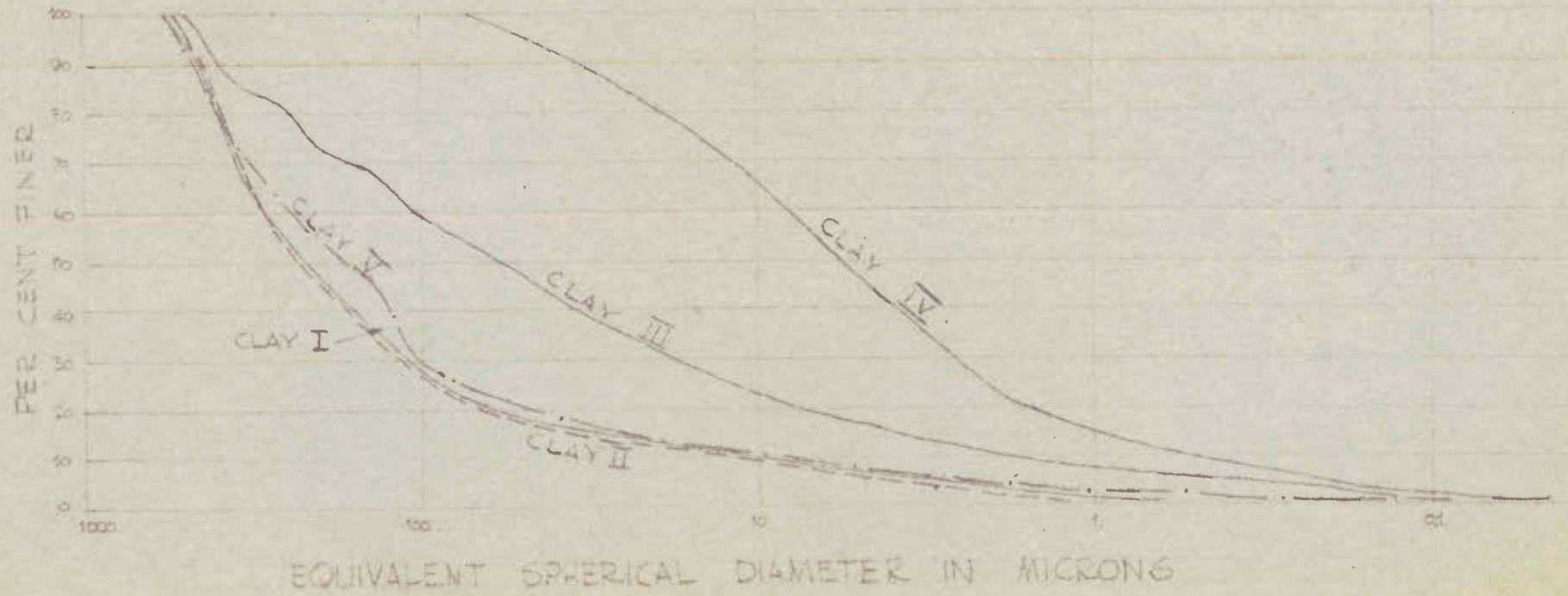
It is well known that many of the physical properties of a clay vary with the effective particle size, i.e.- the particle size of the clay as it is actually used.

Grim (54) points out that the correlation of particle size and properties depends upon the assumption that the breakdown of the clay particles is of the same order of magnitude in analysis and in working. Since grading analyses of clays are preceded by disaggregation to get the clay in suspension, Grim cautions that the dispersion of the clay in water will tend to break up the particles of the clay minerals by cleavage along the basal planes and by breakage across thin flakes. In making such analyses then, the measurements made clearly represent the degree of disaggregation and frequently nothing else. Further he states that there may be little or no relation between the particle size distribution determined and that of the natural clay. He mentions that some illites retain their size during dispersion and analysis while others are easily reduced. Mechanical analyses of kaolinite clays give a fair picture of the make-up of the natural clay whereas analyses of montmorillonite clays measure little more than the degree of dissociation.

Following Grim's contention that the objective in correlative work (such as this) should be to determine the effective particle size, the procedure recommended for wet screen analysis by the A.S.T.M. Designation C. 92--46 was employed. Such results while not an absolute measure of effective particle size, serve to illustrate the comparative differences between the selected clays.

Experimental Procedure.

The selected clays, after grinding to pass a 28 mesh screen for use in making up the test bars were sampled for particle size determination. The sample, weighing approximately 250 gms. was transferred to a litre container, and sufficient water was added to form a slurry. Slaking was allowed to proceed



PARTICLE SIZE DISTRIBUTION FOR VARIOUS CLAYS

FIG. 30

for one hour. The sample was then transferred to the finest screen used in the analysis and washed with a water jet. The washed residue was dried to constant weight, transferred to the coarsest screen in the series used, and screened. The screening test was carried out using Tyler Screens and the Ro-Tap apparatus. The washings were collected and subjected to sedimentary analysis in accordance with the usual technique involving the use of a 20 cc pipette to withdraw samples for a known distance from the surface at known time intervals.(66). The equivalent spherical diamater of the particles was calculated from Stokes Law which presumes that a particle of a given size and density settles in a liquid of lesser density with a velocity "V" which is equal to $2gr^2(d_1-d_2) \div 9K$ where

g is the gravity constant,

r is the equivalent radius of the particle if it were a sphere of some volume,

d_1 is the density of the sphere,

d_2 is the density of the suspending liquid,

K is the viscosity of the liquid.

The comparative particle sizes of the selected clays as determined by the above method are shown graphically in Figure 30.

Summary and Conclusions

1. Clays I and I[1] show relatively little breakdown under the conditions of the test. This is borne out in plant practise.
2. Clay III contains a fair amount of fine particles though it does not slake readily under the test conditions.
3. Clay IV contains a much finer range of particle sizes than is apparent in the other four samples. This clay slakes readily.
4. Clay V disaggregates fairly readily in the test and in practice. Under the microscope the coarse fraction is seen to be composed largely of quartz grains while the fine fraction is made up of clay.

Base Exchange Phenomena.

General Statement.

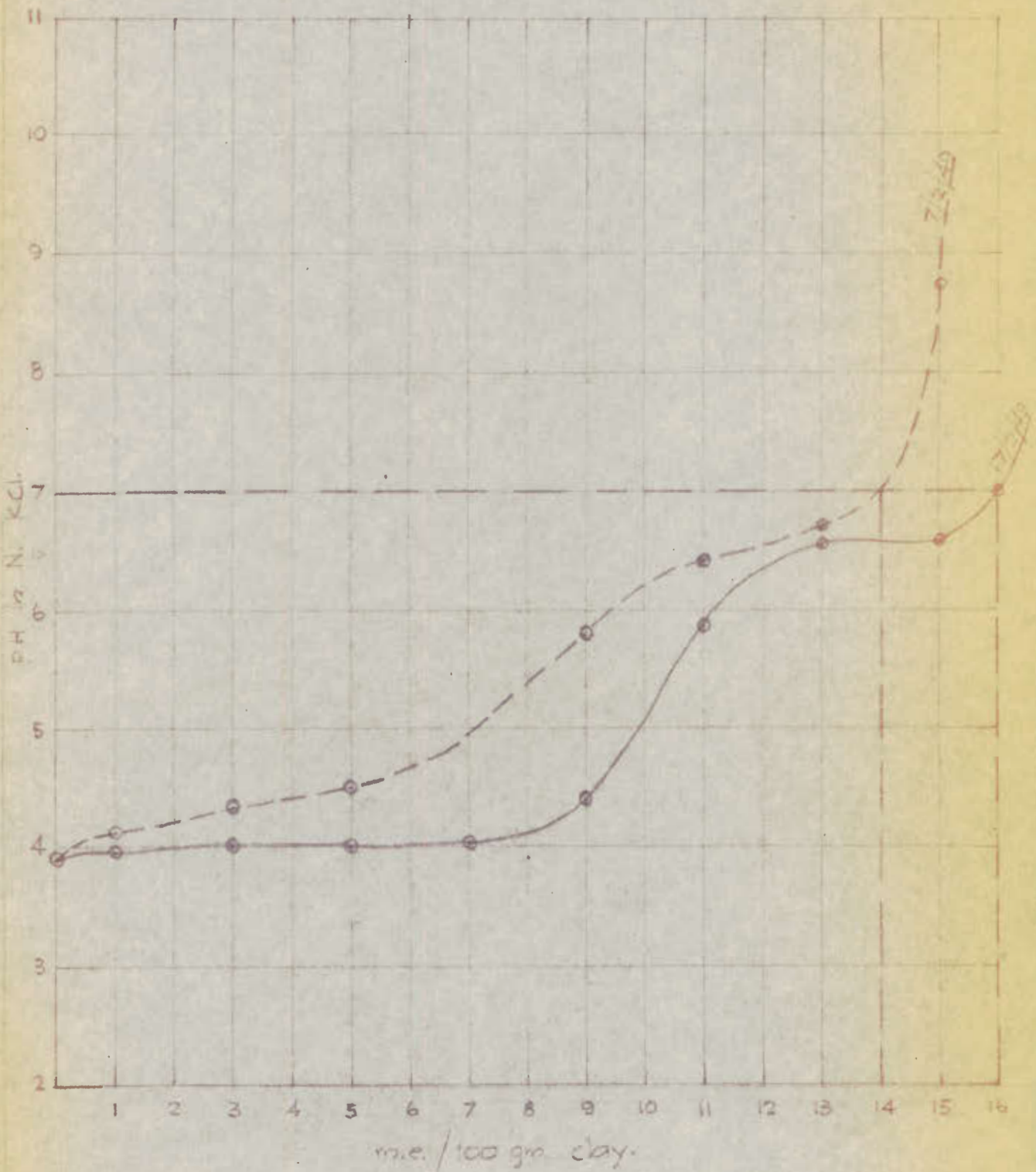
The clay minerals are generally regarded to contain ions attached to the broken corners and edges of their crystal structure, and some in the internal structures as well, which can readily be replaced with other ions. This replacement phenomena is known as "base-exchange" and for clays the base exchange capacity is expressed in milli-equivalents per 100 grams of dry clay.

The action of base exchange is most commonly illustrated by zeolite water softeners wherein the hard water is softened by percolating through the zeolite where the calcium, which gives the water its hardness, is exchanged for sodium from the zeolite. When the zeolite has lost its effectiveness it may be reactivated by passing a solution of sodium chloride through it thus reversing the base exchange process (22).

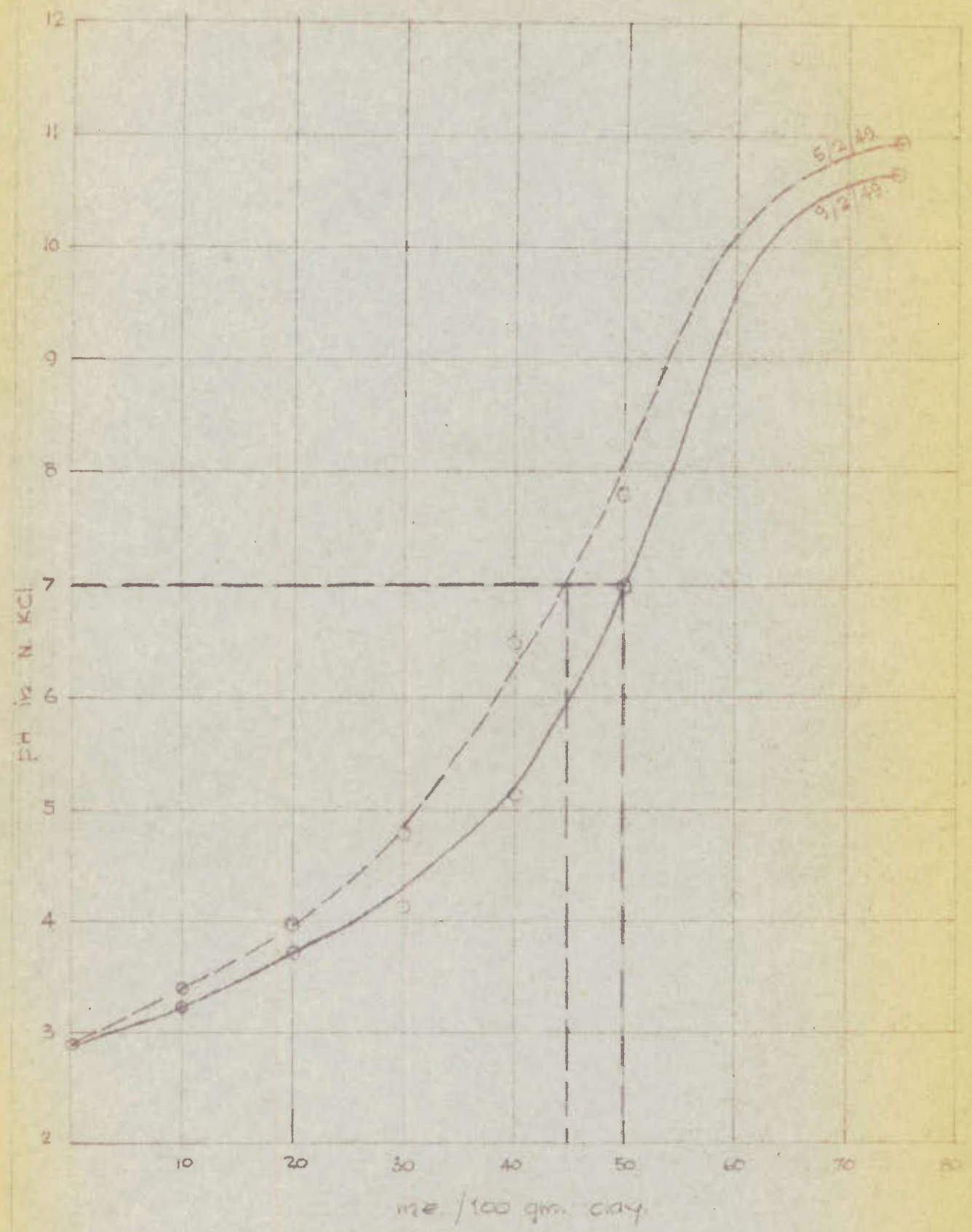
The total base exchange capacity is the sum of the metallic hydrogen and other cations. This property can be used broadly to classify the clay minerals. The magnitude of the total base exchange capacities of the principal clay mineral groups as given by Grim (32) are shown below:-

	Base-Exchange Capacity (me. / 100 g.)
Montmorillonite	60-100
Illite	20 -40
Kaolinite	3- 15

The total base exchange capacity is determined by (1) electrodialysis, or (2) replacement leaching (67) (68). In the electrodialysis method the material is converted to the hydrogen form which in turn is treated with varying amounts of standard alkali and the pH of the resulting slip or liquid is determined. Plotting these data yields



TITRATION CURVES FOR CLAY II



TITRATION CURVES FOR CLAY IV

FIG 31 (continued)

the titration curve from which the base exchange capacity is read off at pH 7. In the leaching method the clay is converted to the ammonium form by treatment with neutral ammonium acetate. The excess lixivant is removed by washing with alcohol and the ammonia from the ammonium clay is distilled by the Kjeldhal method. The ammonia distilled is equivalent to the base exchange capacity.

Experimental Results *

It was decided to examine the selected clays by both of the methods given for the determination of base exchange in order to compare the two procedures.

Clays I, III, IV and V were investigated first by the replacement leaching technique then clay IV was repeated, along with Clay II by electrodialysis methods.

Replacement Leaching Method:- The procedure consisted of leaching a 25 gm sample of the clay, ground to pass a 100 mesh Tyler screen, with 100 cc of 1 N ammonium acetate. The sample and leach reagent were placed in a stoppered bottle and agitated on a mechanical shaker for about 1 hour and then transferred to a centrifuge, operating at about 3,000 r.p.m., until the solution became clear. This operation took about 40 minutes. The clarified solution was decanted and another 100 cc. of leach reagent was added. The residue at the bottom of the centrifuge bottle was broken up with a glass stirring rod and the agitation and centrifuging operations were repeated. Five successive leachings were made. The residue was then treated with 5 successive washings in 80% neutral ethyl alcohol by the same agitation and centrifuging procedure. The washed residue was then analysed for NH_4 by the Kjeldhal method using NaOH as the alkali and HCl as the acid with brom-cresol green and methyl red as mixed indicator in accordance with standard procedure recommended by the American Organisation of Agricultural Chemists. Test results are given below:-

---

* Assisted by the National Chemical and Scientific Laboratories.

	Base Exchange Capacity (me/100gms)
Clay I	5
Clay III	14
Clay IV	46
Clay V	6

Electrodialysis Method: A sample of about 50 grams of clay, ground to pass a 100 mesh Tyler screen, was suspended in about 200 cc of water. The electrodialysis was carried out in a Mattson cell using an anode and cathode of sheet platinum. The cell consisted of three compartments made of hard rubber. The size of the compartments was 2½ x 6 inches and the compartments were separated with a special cellophane membrane. The submerged surface of the electrodes was 2 x 5 inches. At the beginning of the dialysis, distilled water was placed in the two outer compartments and the clay suspension in the center. D.C. current was applied at 250 volts and provision was made to control this voltage as required. The clay suspension was stirred at intervals with a glass rod and the water in the outside compartments was changed frequently. The dialysis was continued until titration with N/10 HCl indicated that no additional alkalis were removed from the material. The dialysed clays were dried and broken up to pass a 100 mesh Tyler screen. Two gram samples were transferred to a glass bottle and treated with varying amounts of standard NaOH in 50 cc solution. The bottle and contents were shaken by hand at intervals over a period of four days and the contents then filtered to separate liquids and solids. The pH of the liquid was measured with the glass electrode and the pH was plotted against the amount of base added. The point was taken at pH 7 to represent the neutralization of hydrogen clay, or the base exchange capacity. The pH curves for the two clays examined are given in Figure 31. The base exchange capacity of

the two clays is as follows:

Clay II	16 me/100gms
Clay IV	50 me/100gms

Clay IV showed a strong initial tendency to release ions as noted by the high readings of the milliameter. End point was reached in 38 hours. During the dialysis it was noted that the yellowish brown colouring matter migrated through the membrane along with some extremely fine clay particles.

Clay II was dialysed for 28 hours, when the end point was reached. The sample showed no signs of decomposition or of migration of the colouring matter. There was no migration of fine particles noted.

Summary and Conclusions

1. Clays I, II, III, and V gave results within the range of base exchange values as given by Grim for the kaolinite group minerals. Clay IV gave a relatively high base exchange value which may be due both to the organic matter present and to the occurrence of clay minerals other than the kaolinite group.
2. The presence of extremely fine particle sizes in Clay IV is indicated by the migration of the clay through the membrane during the dialysis.
3. The replacement leaching method was relatively rapid but careful attention to alcohol washings was necessary to remove all traces of ammonium acetate. Further, the Kjeldhal determination requires careful preparation and manipulation. On the other hand the electrodialysis method while admittedly slower requires lesspersonal attention and the actual determination of the base exchange capacity is made by simple titration.

Ceramic Properties

General Statement

The accepted methods for evaluating the ceramic behaviour of clays are essentially empirical because of the complex nature of these materials.

Tests were made in the laboratory from each of the five selected clays together with a sample of English china clay and from specimens of different varieties of South African refractory clay for comparative purposes.

The ceramic tests were carried out on small bars made in accordance with the standard methods for clay testing outlined in the Standards Report of the American Ceramic Society (1928), with some modifications as required by equipment available. The test bars were fired at Cones 6, 8, 10, and 12, in an electric "Glo-Bar" kiln.

In making up these test bars it was appreciated that (a) it would not be possible to duplicate the firing conditions of an industrial kiln in a laboratory kiln, (b) exact duplication of the physical structure of the test bars and that of factory made products could not be attained, and (c) the clays would rarely be used alone in the manufacture of refractories. It was believed, however, that making the test bars under controlled laboratory conditions would better facilitate reproducibility, and further that information of value would be obtained from this work not only to compare with test data from manufactured ware, but also to learn what effect variations in nature of the clays would have on certain physical properties.

This study included the determination of water of plasticity, dry strength, drying shrinkage, firing shrinkage, apparent porosity, bulk density, and refractoriness. (89)

Plastic and Dry Properties

Preparation of Samples: The clays were first crushed in a

TABLE XV - PLASTIC AND DRYING PROPERTIES OF CLAYS TESTED.

SAMPLE	TYPE	ORIGIN	EASE OF GRINDING	PLASTICITY	WATER OF PLASTICITY	DRY SHRINKAGE %	DRY STRENGTH P.S.I.	DISTORTION ON DRYING
A	Flint	Hammanskraal	Hard	Poor	12.1	1.3	3818	None
B	Flint	Vereeniging	Hard	Poor	12.2	2.4	177.9	None
C	Semi-flint	Springs	Hard	Poor	9.8	2.4	140.6	None
D	Plastic	Springs	Soft	Good	20.8	5.7	300 plus	None
E	Silicious Refractory Shale	Vereenigigg	Medium	Fair	15.2	3.1	80.9	slight warping and cracking
F	China Clay	Cornwall, England	Soft	Good	27.5	7.4	less than 10 badly cracked	None
G	Semi-flint	Brakpan	Hard	Poor	12.2	2.0	87.0	None
H	Semi-flint	Vereeniging	Hard	Poor	16.0	2.0	34.8	None
J	Semi-flint	Vereeniging	Hard	Poor	18.1	3.0	25.5	None
K	Semi-flint	Vereeniging	Hard	Fair	13.6	2.5	182.9	None
L	Semi-flint (carbonaceous)	Springs	Hard	Fair	14.2	2.8	23.1	None

laboratory size jaw crusher to approximately ½" in size and then fed to a disc mill which reduced the material to pass a 28 mesh Tyler screen. The ease of grinding was noted during the preparation stage.

Plasticity: The plasticity of a clay is an important property in the manufacture of ceramic ware. By plasticity is meant that property which a clay when wet possesses of permitting itself to be moulded into desired shapes and retaining that shape on drying. No completely satisfactory method for the evaluation of the plastic properties of clay has ever been devised, principally because the property has never been satisfactorily defined. Plasticity is generally determined by the feel and workability of the material in the hands of an experienced operator, the estimates thus obtained (although influenced by personal elements) being of general practical application.

Preparation of Tests: The ground clay was mixed with sufficient water to develop good plasticity, the quantity being indicated by feel and judgment of the operator. The sample was then thoroughly kneaded or wedged by repeated pounding on a smooth surface until it showed a homogeneous character free from air pockets when cut with a fine wire. Following the wedging process, the clay was formed by hand into test bars, 14 cm x 3½ cm x 3 cm, in a mould box; three trials were made up for each burn.

Drying Behaviour: The drying behaviour exhibited by the test bars was observed and any tendency for the ware to warp, crack, or otherwise show drying defects was noted.

Water of Plasticity: The amount of water added to a clay to give the best working conditions is designated "water of plasticity". This value is calculated by the standard formula using an average of four trials:

$$T = \frac{Wp - Wd}{Wd} \times 100$$

where T equals per cent water of plasticity,

W_p equals weight of plastic trial pieces,

W_d equals weight of dry trial pieces.

Drying Shrinkage: The drying shrinkage of a clay is extremely important in manufacturing processes since it generally controls the safe rate of drying. The drying shrinkage of a clay is directly dependent upon particle size, which in turn determines the number of water films present. Shrinkage may be measured either by length or volume change, the former being more generally applicable to plant practice. In this work each test bar was marked in the green state along with its longest dimensions with a tool which inscribed two indentations exactly 10 cms apart. After drying for approximately 24 hours at 110°C., the distance between the indentations was determined and the drying shrinkage was reported in Table XV on the basis of the original length.

Dry Strength: The dry strength of clay is a property that so far has not been completely explained. Studies indicate that dry strength is increased as the area of particles are increased and further that the character of absorbed ions play an important role in cohesion. In general it may be said that dry strength is dependent upon the phenomena of the attractive forces between the clay mineral crystals.

In this work dry strength was studied by determining the modulus of rupture on the dried test bars by means of a simple laboratory cross breaking machine. The modulus of runture value was calculated from the formula

$$M = \frac{3Pl}{2bd^2}$$

where M equals modulus of runture in kilograms per sq cm,

P equals breaking load in kilograms,

l equals length of span in centimeters,

b equals breadth of bar in centimeters,

d equals depth of bar in centimeters.

Test results are given in Table XV.

Firing Properties

Changes in Clay on Firing: The behaviour of a clay on firing involves successive steps which are particularly important for proper heat treatment to produce the most desirable product.

The changes accompanying the heating of a clay can be directly observed by a number of methods, one of the most satisfactory of which is differential thermal analysis. The thermal history of the selected clays, from room temperature to 1000°C., as determined by this method, has already been discussed; however, the salient points brought out by this study may be conveniently reviewed at this point. A small endothermic change at about 150°C. was evidenced in most of the samples, owing to the loss of moisture from the surface of the grains. The carbonaceous clays generally showed exothermic reactions at 450°C. and sometimes between 600°C. and 700°C. which accompanied the loss of organic matter. A large endothermic change was noted in the case of the kaolinite type clays at around 600°C., caused by the evolution of the structurally held water. A sharp exothermic change was again noted at about 980°C., in the kaolinite type clays, probably as a result of the formation of gamma alumina. The effect of non-kaolinitic clay minerals and large amounts of quartz was to suppress the kaolinite pattern and introduce some other thermal changes generally of a minor nature.

From thermal analysis data on montmorillonite and illite it would appear that the crystal breakdown begins, in the case of montmorillonite, around 600°C. and continues to 800°C. An endothermic change at around 970°C. occurs which according to Grim and Bradley (70) represents a spinel phase. The breakdown of illite below 1000°C. seems to be similar to that of montmorillonite. Mullite is said to appear at 1050°C. in the case of montmorillonite, and at 1100°C. in the case of illite, according to Grim and Bradley (70).

Quartz, the principal accessory mineral, is converted by

heat into a number of polymorphous stages wth varying stability ranges. The important crystalline varieties are quartz, tridymite, and cristobalite, each with a high and low temperature modification. Transformations are very slow, and quartz, tridymite, and cristobalite can exist at room temperature. A reversible conversion from quartz to tridymite takes place between 117°C. and 163°C. and a similar reversible conversion from quartz to cristobalite occurs between 200°C. and 275°C. Quartz is converted from the low to the high temperature modification at 574°C. The density change accompanying the inversions of quartz from low to high is -0.02, while that accompanying the change of cristobalite from low to high is -0.04. The tridymite change from low to high is -0.01. (53) These changes affect the firing shrinkage if large amounts of quartz are present.

At elevated temperatures the oxides remaining from the low temperature reactions, such as iron oxide, lime, and alkalis, react with the clay to form a glass which has a predominant influence on the mechanical strength of the finished article. (22) These oxides act to a certain extent as mineralizers in accelerating the rate of mullite formation and it is desirable to promote the maximum development of glass at the lowest temperature possible to attain good bond strength; on the other hand too much or too fluid glass is objectionable as a cause of deformation.

X-ray analysis was selected as the best method for studying the thermal effects above 1000°C., and X-ray photographs were made of the selected samples burned to Cone 12 (1335°C.). Mullite lines were apparent in all of the clays. Strong cristobalite lines were seen in all of the samples except Clay IV which showed relatively weak reflections. In the case of Clay IV the lack of strong cristobalite lines was probably due to the more abundant formation of the glassy phase.

Firing Shrinkage and Porosity

The most useful information on the burned behaviour of a clay is the determination of the shrinkage and porosity when fired at various temperatures. Standard pyrometric cones were used to measure the heat effects attained.

In this study the linear shrinkage of the selected samples was measured after separate sets of test bars were fired at Cones 6 (1230°C.), 8 (1260°C.), 10 (1305°C.), and 12 (1335°C.).

The "apparent porosity" which includes the open pores, was measured on these samples after firing by making three weighings: (a) dry, (b) immersed in water, (c) saturated in air. Using these data the apparent porosity was then calculated from the following formula:

$$P = \frac{W-D}{W-A}$$

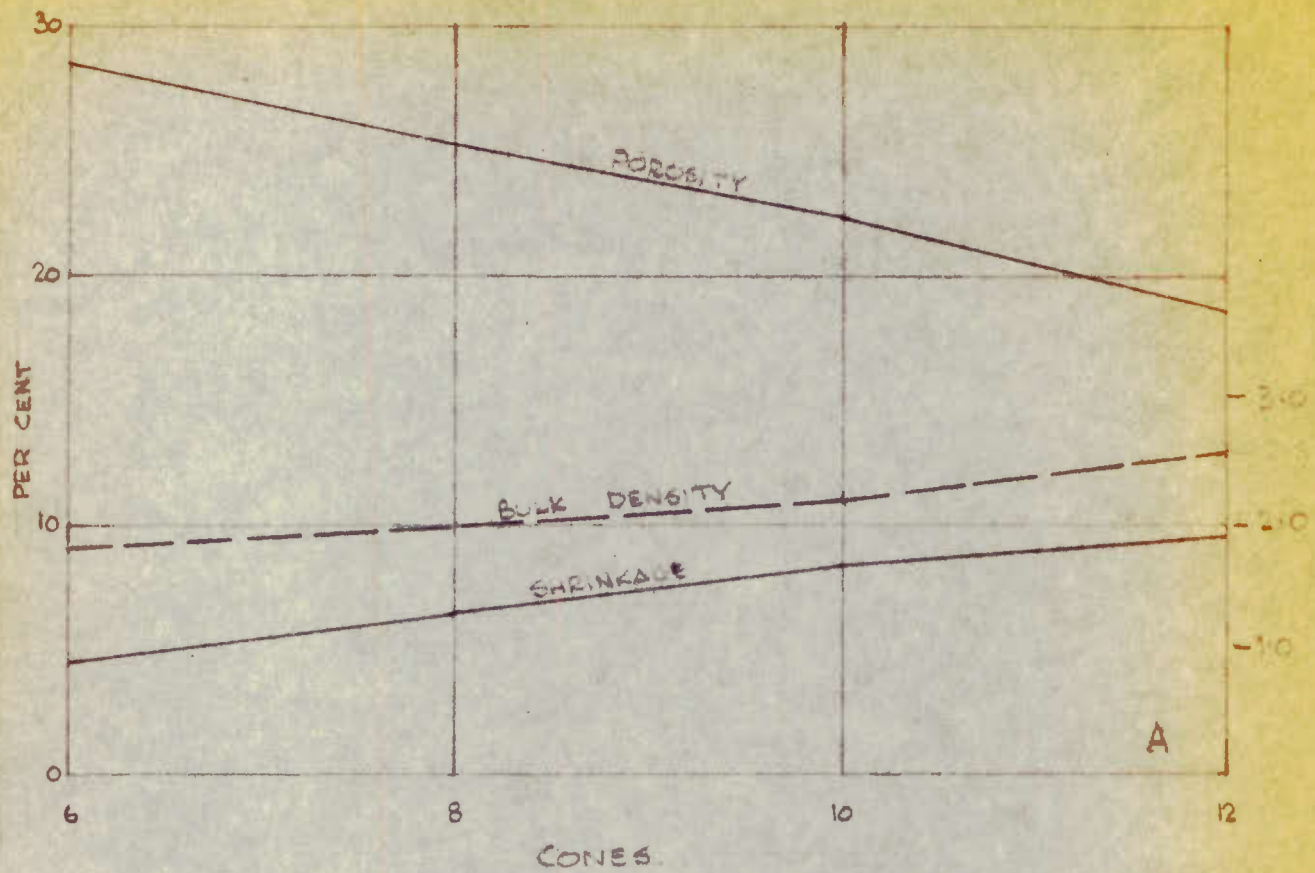
where P equals per cent porosity,

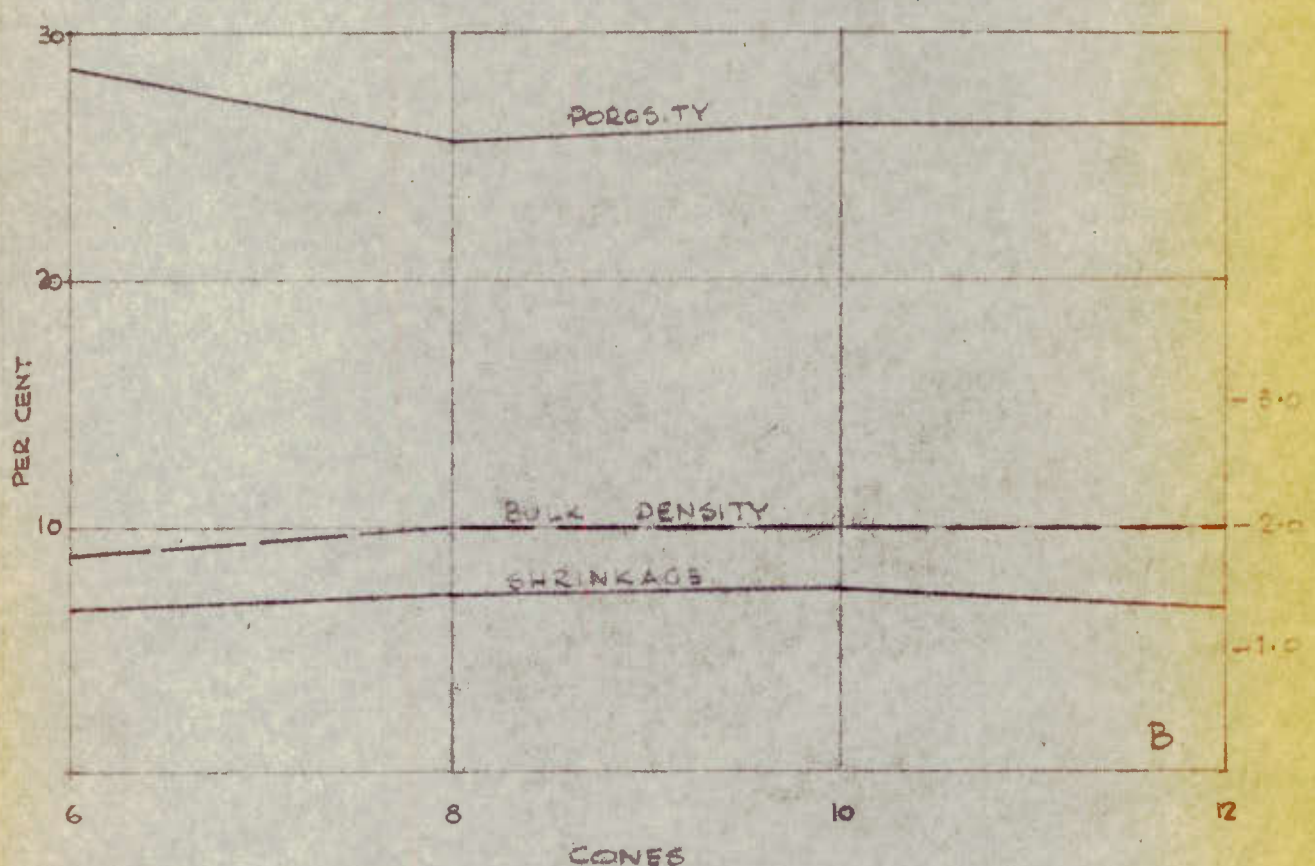
W equals weight in air, saturated,

D equals weight in air, dry,

A equals weight saturated in water.

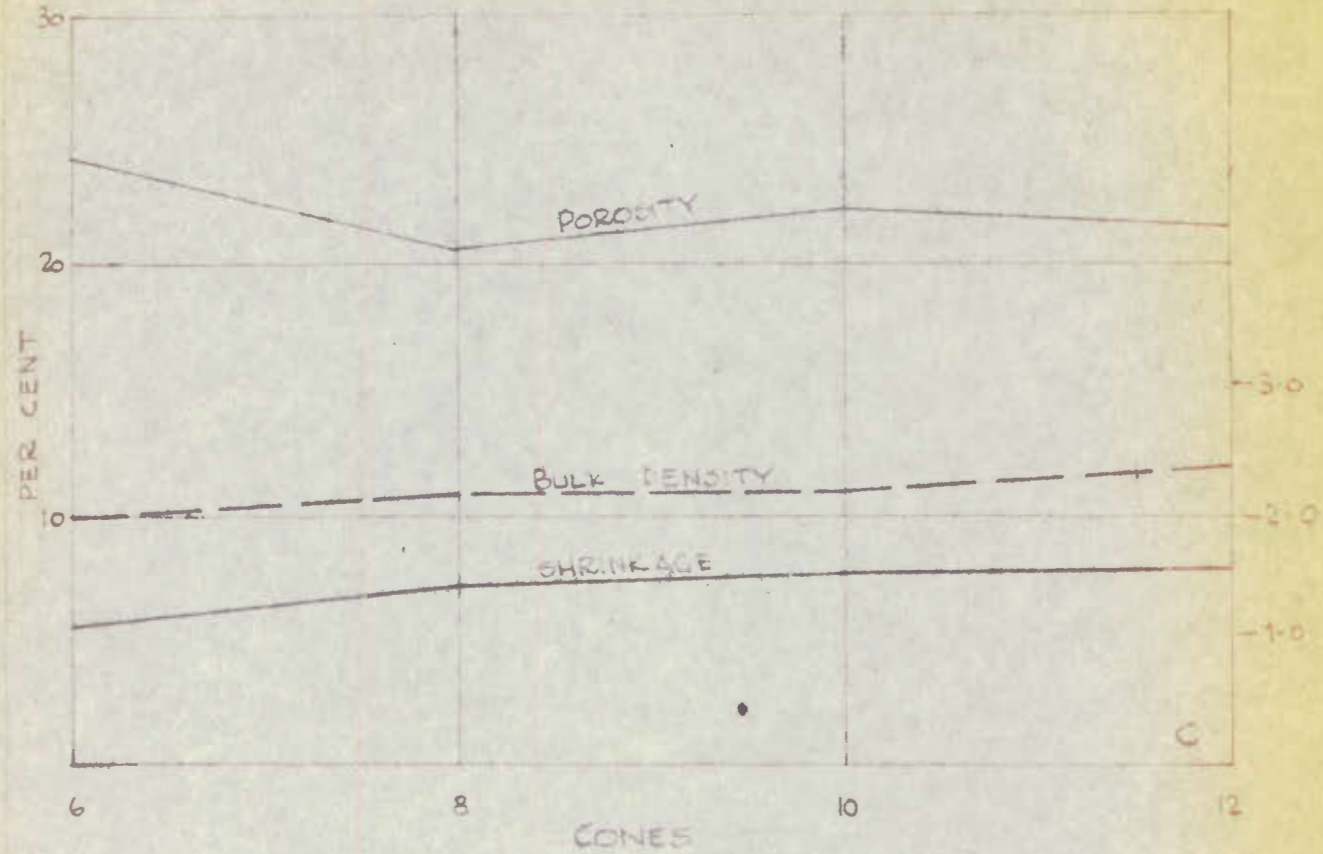
It is obvious that the fired shrinkage and porosity determination will be greatly influenced by the conditions under which the test bars are moulded; however, by attempting to maintain uniform treatment a general idea of the behaviour of

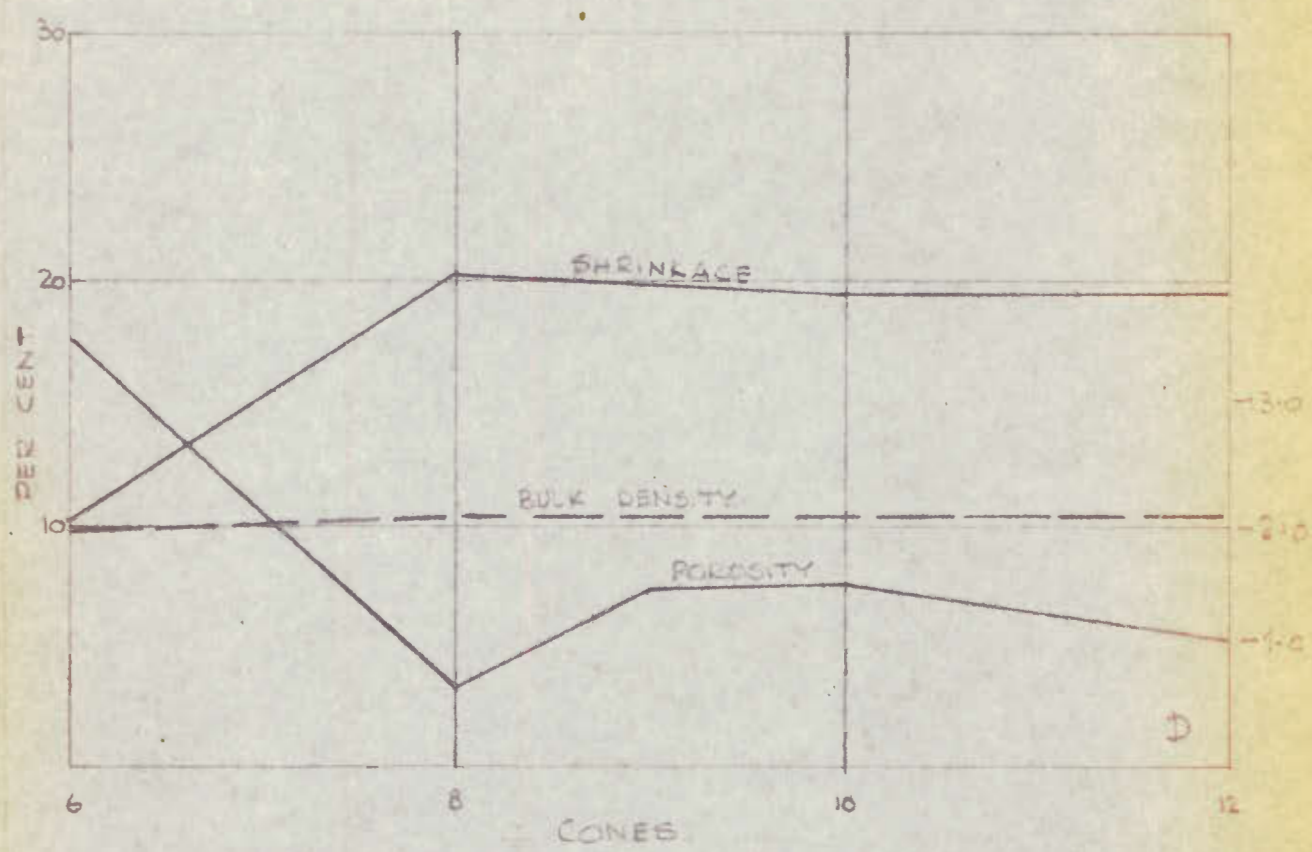




CURVES SHOWING BURNING RANGE OF SOUTH AFRICAN REFRACTORY CLAYS

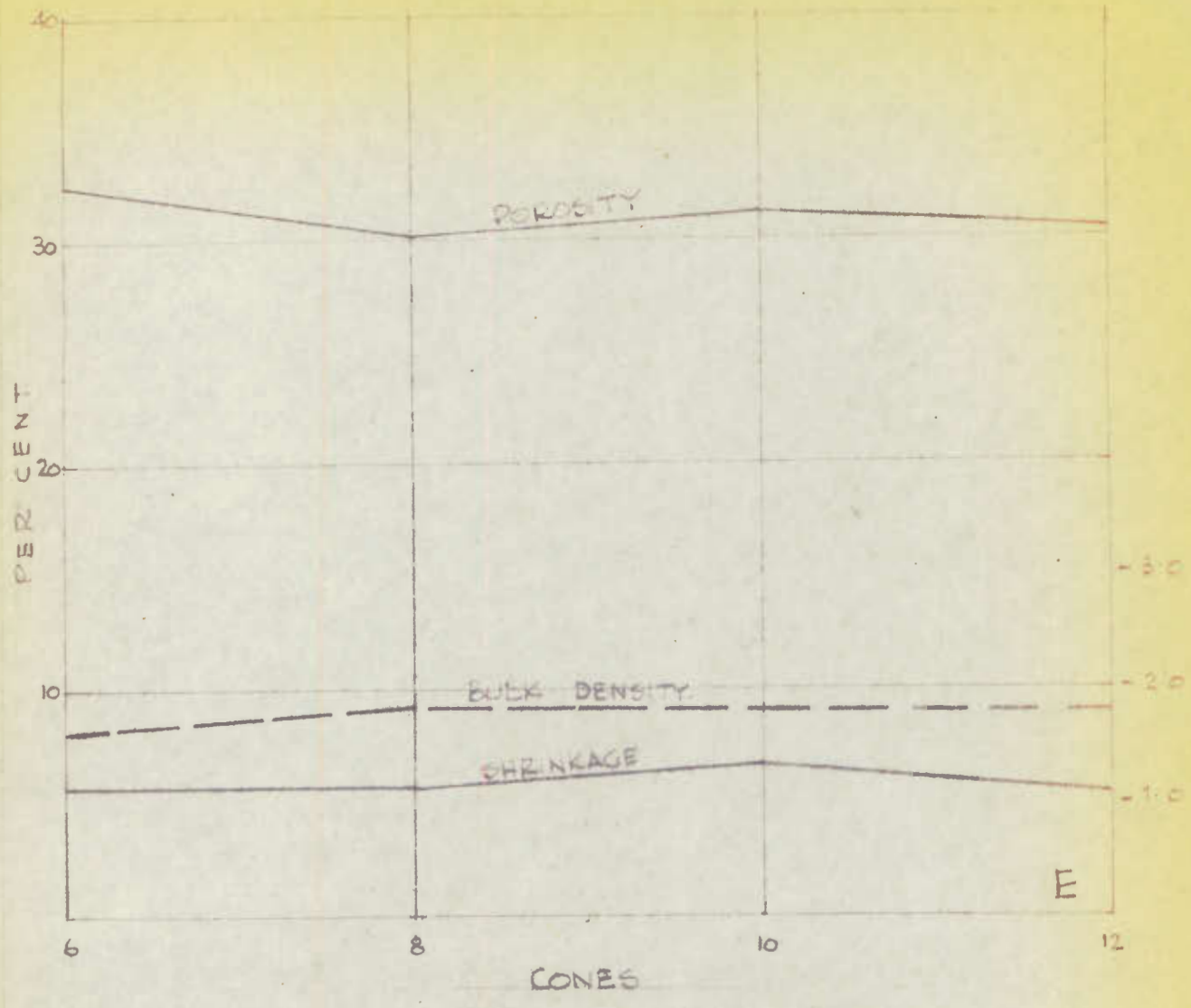
FIG 32

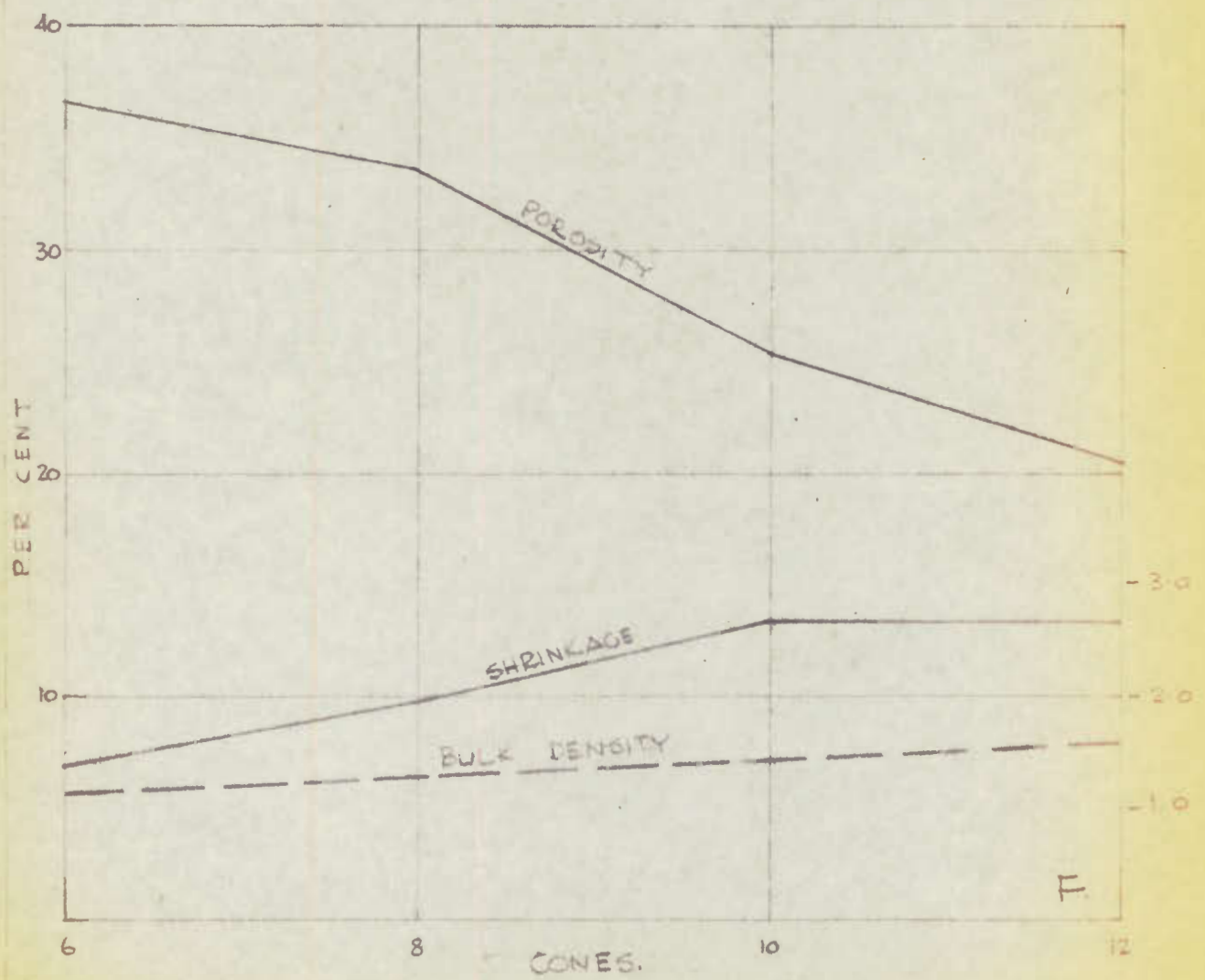




CURVES SHOWING BURNING RANGE OF SOUTH AFRICAN REFRACTORY CLAYS

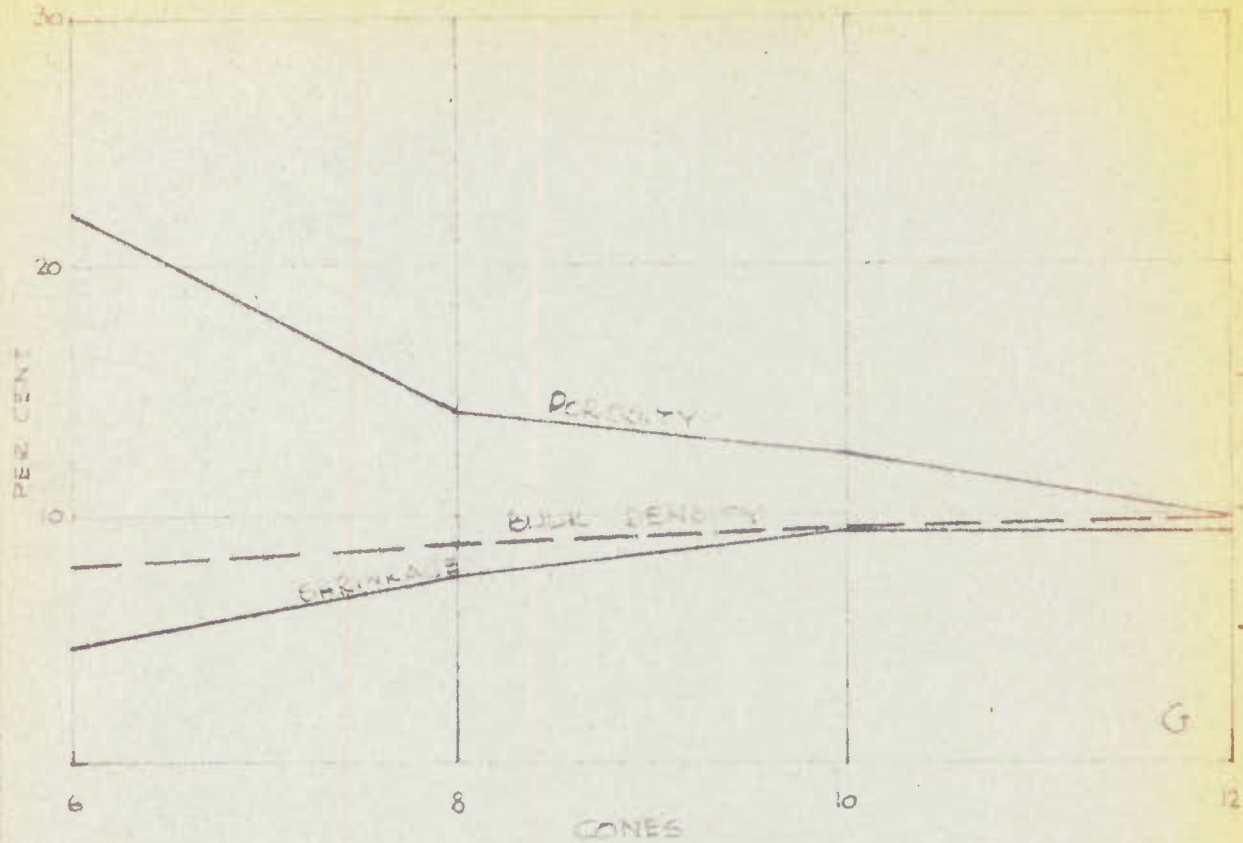
FIG. 32 (continued)

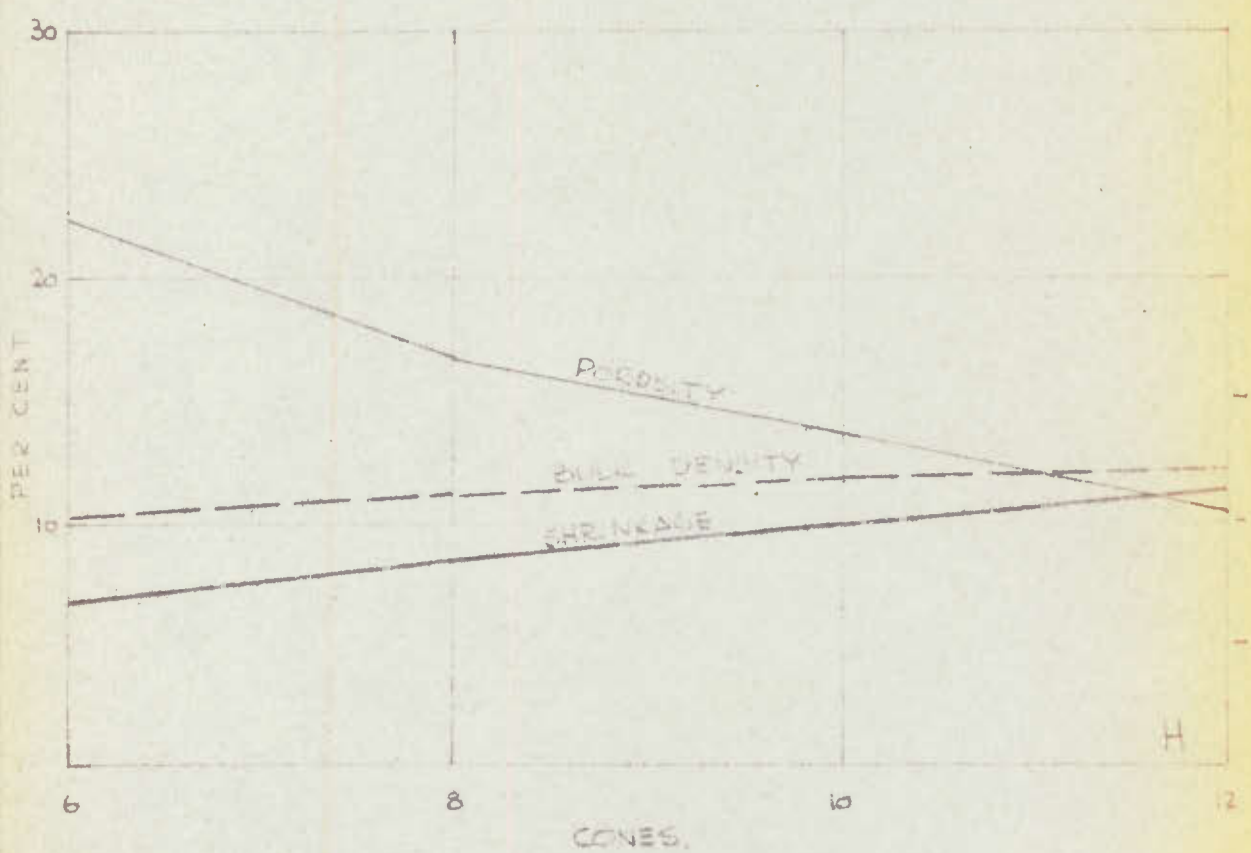




CURVES SHOWING BURNING RANGE OF SOUTH AFRICAN REFRACTORY CLAYS

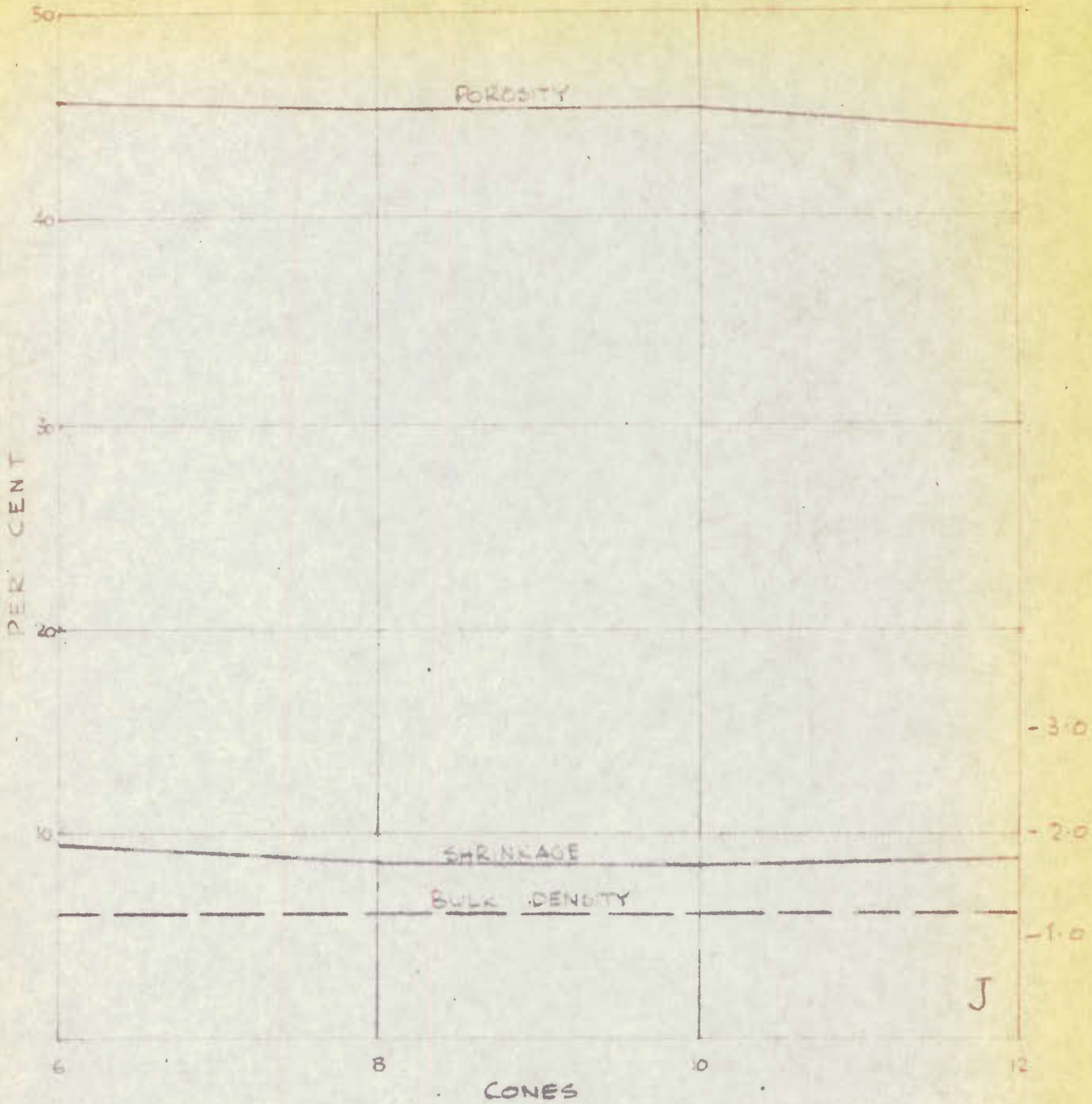
FIG. 32 (continued)

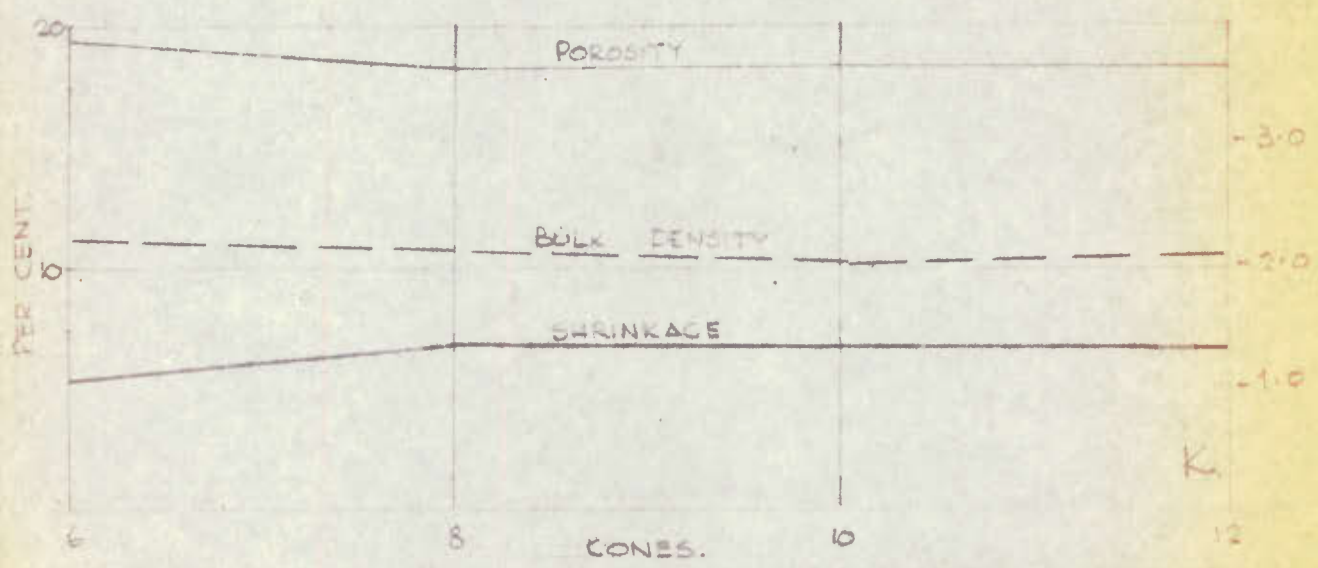




CURVES SHOWING BURNING RANGE OF SOUTH AFRICAN REFRACTORY CLAYS

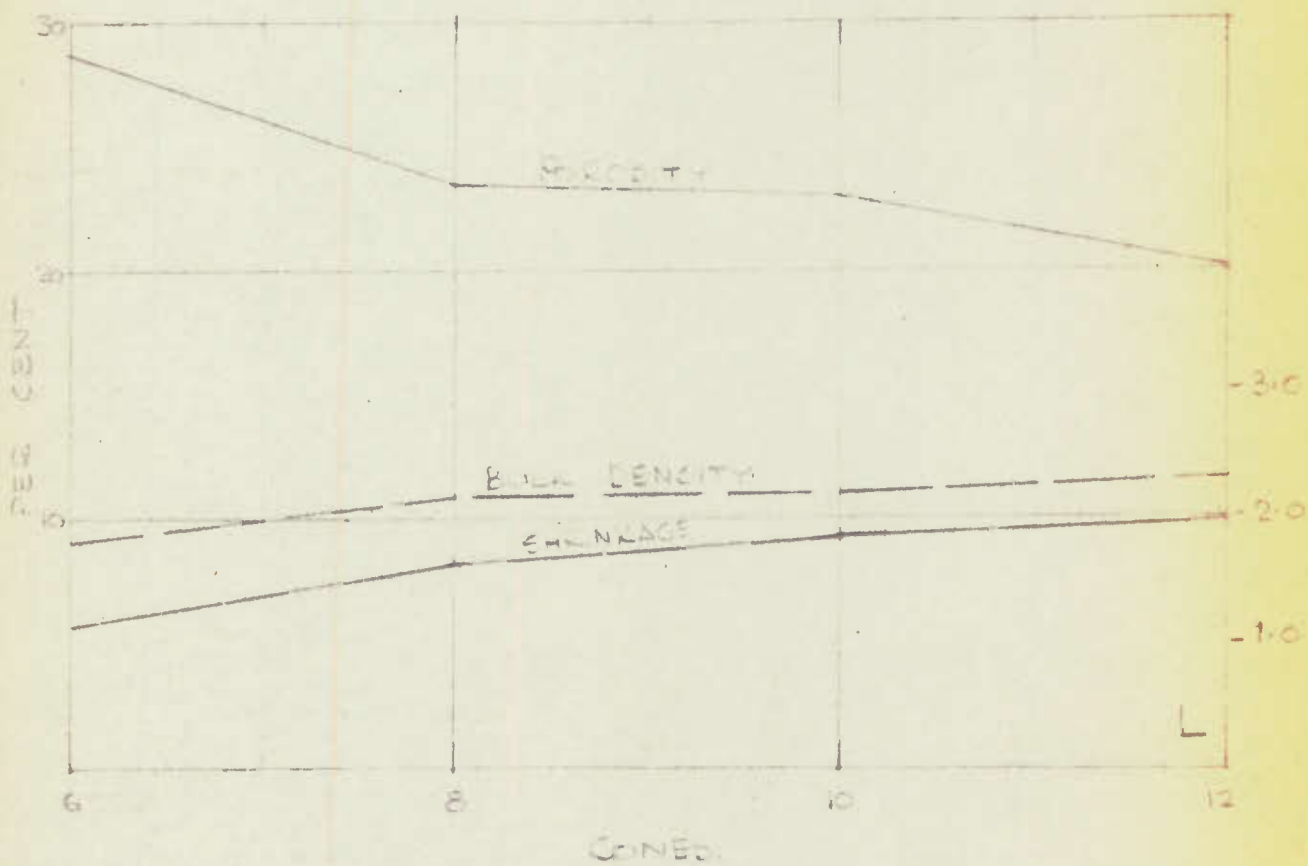
FIG 32 (continued)





CURVES SHOWING BURNING RANGE OF SOUTH AFRICAN REFRACTORY CLAYS

FIG 32 (continued)



CURVES SHOWING BURNING RANGE OF SOUTH AFRICAN REFRACTORY CLAYS

Fig. 32 (continued).

the clays may be obtained. For a specific plant development test the firing tests should of course be made under operating conditions.

A further property of interest in following the burned behaviour of clay is the determination of the bulk density of the sample fired at various temperatures. The bulk density is the density of the solid material plus sealed pores, cavities, and water-permeable pores. It is obtained by dividing the weight of the sample by the exterior volume. The exterior volume was obtained from the W-D relationship in the calculations for "apparent porosity" just described.

The burning range or temperature interval during which there is little change in the porosity and shrinkage of a clay may be obtained by plotting burning shrinkage, porosity, and bulk density of the test bars against the different temperatures at which the test bars were burned. A long burning range is a desirable property in clays since it is difficult to obtain uniform temperature throughout commercial kilns and it is important that the finished ware from different parts of the kiln do not vary materially in size, porosity, and other properties.

Curves showing burning ranges for the selected samples and other varieties of these types*, along with a specimen of English china clay for comparison, are given in Figure 32.

Description of Curves

1. Curve A.: Clay I shows progressive shrinkage and decrease in porosity over the range examined and will require a higher burning temperature to attain optimum results. The bulk specific gravity shows a continuous increase which would substantiate these conclusions. In actual practice it was found necessary to burn brick made from this clay to Cone

* See Table XIII.

18-19 to reach constant volume.

2. Curve B: Clay II gave inconsistent and high porosity values which result from bloating due to incomplete oxidation before vitrification commenced, as evidenced by the "black core" developed on firing. This condition suggests that the heating rate in the laboratory trials was too rapid for this material. Plant tests bear out this conclusion since trials burned in commercial kilns showed no signs of "black coring". The shrinkage and bulk specific gravity data of this sample are questionable in view of the "black coring" developed in the specimens.

3. Curve C: Clay III has a fair burning range since little change in shrinkage, porosity, and bulk specific gravity was noted between Cone 8 and Cone 12. This conclusion is borne out in practice in that ware made from this clay shows little volume change above Cone 12, the normal burning temperature.

4. Curve D: Clay IV sinters at comparatively low temperatures (Cone 8) and possesses a good burning range. The porosity of this clay is only 5.0% at Cone 12. No signs of over-fired bloating are indicated from the curves or from examination of the trial bricks. This clay is used successfully as a refractory bond clay in commercial practice.

5. Curve E: Clay V shows little change after Cone 6. The porosity values are exceptionally high throughout the range of burned trials. This phenomenon is attributed to the large amount of quartz present as fine sand which expands during the burn, counteracting the shrinkage of the clay minerals and "opening up" the body as the result of this "differential" shrinkage.

6. Curve F: English china clay shows progressive decrease in porosity and increase in shrinkage in the testing range. The porosity is high (20%) at Cone 12.

7. Curve G: A semi-flint clay from Brakpan shows progressive decrease in porosity and increase in shrinkage in the test range characteristic of the kaolinitic clays. This clay has a good burning range with a final porosity of 10% at Cone 12.

8. Curve H: A semi-flint clay from Vereeniging. This curve which also represents a kaolinite type clay is similar to the pattern given in Curve G above.

9. Curve J: A carbonaceous semi-flint clay from Vereeniging. The high porosity values are the result of burning out of coaly matter. The shrinkage remains constant over the entire range of Cone 8-12. A higher temperature is needed to mature this clay properly and pre-calcination is necessary to get rid of the troublesome carbon.

10. Curve K: A semi-flint clay from Vereeniging. This clay has a good burning range. The final (Cone 12) porosity value is still higher than desirable, indicating the "open burning" characteristics.

11. Curve L: A carbonaceous semi-flint clay from Springs. Porosity is high owing to burning out of carbon, but not so excessive as in the Vereeniging clay (Curve J). The shrinkage continues progressively throughout the range tested.

Refractoriness Test.

Like most of the other properties of clay at high temperatures comparatively little is known of the mechanism of their fusion. Norton (53) points out that in the case of the silicates, the bond strength holding the silicon in the centre of an oxygen tetrahedron is very strong, and probably does not break until sufficient temperature to rupture the weaker bonds has been reached. Further, he states that when a silicate fuses, the weaker bonds are first broken and a very viscous liquid develops which comprises aggregates of the

silicon oxygen groups and as the temperature increases these groups are further broken up by thermal agitation until the viscosity decreases. Attempts to correlate atomic structure with fusion have not been successful in the case of clays because of the complexity of the clay minerals.

The influence of a very small amount of impurities has very pronounced effect on the fusion point of clays and in particular the particle size of quartz which is usually the principal accessory.

Method of Testing: Clays have no sharp boundary between the liquid and solid state and in consequence the defining of a fusion point is difficult. The usual method of testing fusibility involves the determination of the temperature at which a specimen under a defined stress will flow at specified rate. This technique is subject to experimental difficulties in the case of clays and a more common method of determining the fusion characteristics of a clay is by comparing it with those of a series of standard pyrometric cones under similar conditions in the same furnace. The test was carried out in an oxy-acetylene fired furnace in accordance with A.S.T.M. procedure designation C.24-42 on the selected clays together with reference samples of Missouri flint, semi-flint and plastic clays. The results are reported in Segar Cones in Table XVI below:

Table XI.

Refractoriness of Clays.

Sample	P.C.E. *	Temperature degrees C.
Clay I	35	
Clay II	34 - 35	
Clay III	33 - 34	
Clay IV	31	
Clay V	32	
Missouri flint clay	34	
Missouri Semi-plastic	33	
Missouri Plastic	32	

Summary and Conclusions.

1. The P.C.E. values of Clay I, II and III compare well with that of Missouri flint clay, in fact Clay I shows one cone

---

* Pyrometric Cone Equivalent.

higher value.

2. Clay Iv has a P.C.E. value one cone less than the Missouri plastic. In practice, it has been found that considerable variation exists in the P.C.E. of the South African plastic clays, the range being from Cone 30-33.
3. Clay V possesses a good P.C.E. value for refractory clays. This relatively high value is interesting since this clay is known to contain a large amount of quartz. The explanation lies in the fact that the quartz is present in coarse particles which act independently in the fusion process and do not combine with the kaolinite to form a eutectic. If this clay was very finely ground it probably would show a reduced P.C.E.

Table XVII.

Analytical Data for Selected Clays.

Clay Mineral Composition.	I Kaolinite; Quartz ± 5.0%	II Kaolinite; Quartz 5.0 - 10%.	III Kaolinite Quartz 10-15%.	IV Kaolinite; Illite (?) Quartz ± 2%.	V. Kaolinite; Illite (?); Quartz 35-40%.
Base Exchange Capacity	5	50	15	36	6
Water of Plasticity (%)	12.1	12.2	9.8	20.8	15.2
Dry Strength (p.s.i.)	38.8	177.9	140.6	300.plus	80.9
Dry Shrinkage (%)	1.3	2.4	2.4	5.7	3.1
Total Shrinkage % (Cone 12)	9.7	6.9	7.7	14.6	5.3
Fired Colour	white	white	white	tan	buff
Fired Porosity % (Cone 12)	18.7	26.6	21.7	6.1	30.5
Fired Bulk Density (Cone 12)	2.3	2.0	2.2	2.3	1.9
P.C.E.	35	34-35	33-34	31	32

Analytical Data for Selected Clays.

A tabulated summary of the mineral composition and ceramic behaviour of the five selected clays is given in Table XVII.

Summary and Conclusions.

1. In general the ceramic properties of the selected clays were in good agreement with those deduced from theoretical considerations.

2. The plasticity of Clay IV was greater than for the other specimens owing to the fineness of the particle size, presence of organic matter, and the occurrence of clay minerals (illite?) other than the kaolinite group. This clay possesses a relatively high base exchange. Clays I, II, and III are poorly plastic and all represent good kaolinite types with quartz as the principal accessory mineral; clay II contains carbonaceous matter. These clays all possess low base exchange capacities. Clay V which is composed of kaolinite and a large amount of quartz and possibly non-kaolinite minerals had a higher base exchange capacity than Clays I, II, and III, but lower than Clay IV. This clay is fairly plastic.

3. The dry strength and drying shrinkages of Clays I, II, and III, the predominantly kaolinite types, are low compared to Clay IV and V. The drying shrinkage of the clays with low base exchange capacity represents a smaller proportion of the total shrinkage (both drying and firing) than those of higher base exchange capacity.

4. Clay Iv has lower refractoriness and shows the most pronounced tendency to sinter of any of the clays examined, which is to be expected from the higher alkali content for this clay, and further, this clay burns to a tan colour. The presence of non-clay minerals (illite?) which contain alkalis or alkali earths either within the lattice or as adsorbed ions together with iron, would account for the difference in behavior from Clays I, II and III which are

kaolinitic types and behave as such on burning, firing white, possessing high refractoriness, and showing a generally "open-burning" tendency at the temperature conditions of the test. Clay V contains a large amount of quartz which expands on firing and counteracts the shrinkage of the clay minerals present. The comparative coarseness of the quartz particles causes the quartz to behave separately from the clay minerals rather than to form a eutectic, which accounts for the high refractoriness of this clay.

5. The carbon content of Clay II is sufficiently high to leave a porous mass when burned out. This type of clay must be pre-calcined to remove the troublesome carbonaceous matter before it can be used in manufacture.

Problem of the High Alumina Content of Some South African Clays

The tendency of some South African refractory clays to have alumina contents greater than the proportions indicated by the formula $Al_2O_3.2SiO_2.2H_2O$ for kaolinite has long been recognised. Wagner (1) in 1916 called attention to this fact in his investigation of clays at Olifantsfontein and he suggested that the excess alumina probably existed in the clays in the form of the minerals bauxite or pholerite.

One of the difficulties in examining the composition of the clay minerals in commercial clays is to obtain a pure specimen free of quartz and other accessories. For the purpose of this investigation a sample of South African high alumina clay which showed no quartz or crystalline aluminium hydrates (I.E., diaspore, boehmite, and gibbsite) in X-ray examination was supplied by the National Chemical Laboratories. The X-ray pattern for this specimen agrees well with published data for kaolinite (see page 102.) Heystek* reports that differential thermal analysis of this clay gives a good kaolinite type curve. Calculation of the SiO_2 : Al_2O_3 ratio gives a value of 1.72 indicating a higher alumina content than required to satisfy the kaolinite formula.

It is possible that the extra alumina may be accounted for by the presence of a small amount of " amorphous bauxite" or allophane as suggested by Ross and Kerr in their investigations of kaolinites and they point out that such material may escape detection (presumably by optical and X-ray study) in extremely fine grained material especially if very thin films of colloidal substances formed coatings on the surfaces of the crystals. (29)

---

*Personal communication.

A more probable way of accounting for the excess alumina in this clay is by recognising the existence of a member of the kaolinite-anauxite series which is higher in alumina than the 1 : 2 ratio. Ross and Kerr (29) point out that there is no essential difference in the optical properties or X-ray patterns in the high and low silica members of the kaolinite series, although the members of the series are shown to differ recognizably from nacrite and dickite in such examinations. Further they found that the alumina - silica ratio of 1 : 2 prescribed for kaolinite is not constant but can vary from 1.7 to 2.9. Under these conditions the clay mineral represented by the specimen could be regarded as occurring in the high alumina range of the isomorphous series brought about by the substitution of Si for Al.

Examination of one specimen can hardly yield sufficient information to permit generalization however this investigation does suggest a valid premise for at least one way in which the high alumina clays in South Africa may be accounted for. Further work, preferably with quartz free specimens, is required to provide a complete answer to this problem.

Variations in Ceramic Properties of Middle Ecca Refractory Clays.

General Statement.

As previously stressed, the Middle Ecca refractory clays are terrestrial deposits and as such are subject to changes in lithology within short distances. Variations in ceramic properties corresponding to these changes in lithology have long been known to clay workers.

The purpose of this investigation was to determine the effect of the geologic features of these deposits on mining and manufacture.

The area selected for a detailed study is in the Vereening district, an important refractory clay producing field. While the results obtained apply specifically to the area studied they do offer a basis for some generalisations applying to the Middle Ecca Refractory Clays as a whole.

Procedure.

Geologic Sections.

Exposures of Middle Ecca refractory clay bearing strata in two adjacent pits near Vereeniging were carefully sampled. The sampling interval between sections was 200 feet and the distance between the pits was 400 feet. The samples taken were representative of the clay seams encountered on the vertical face. Geologic sections, prepared from the field data, are given in Figure 34. Lithological details for each section measured are shown in Table XVIII.

Ceramic Properties.

The samples, after visual inspection, were crushed in a laboratory jaw crusher and screened through a 4 mesh screen. The minus 4 mesh material was further screened through a 6 mesh and a 48 mesh screen. The resulting fractions were blended according to the following mixture which was selected from accumulated data on plant tests:

5% through 4 m. on 6 m.
75% on 48 mesh.
20% through 48 mesh.

This procedure gives constant grain sizing and minimizes the effect of this variable when comparing the test bars. After grain sizing the material was tempered with water to dry pressing consistency by feel and judgement of the operator, who adds water until the clay just clings together when squeezed by hand. About 8-10% water was required. After thorough mixing by hand the clays were allowed to age in closed containers for 24 hours to ensure complete distribution of moisture. It was found that this procedure greatly increased the workability of the dry press mix, a fact confirmed in plant tests. A small sample of the ground material was tested separately for plasticity which was determined by feel.

In forming the test bars, a constant weight of 1 pound, 1 ounce of clay was weighed out and pressed into bars 1¼" x 2½" x 4½" on a hand press. Four test bars were made up for each sample. The test bars were dried on the hot floor and placed in a down-draught kiln along with regular fire brick production and burned to Cone 12. The test bars were purposely fired under commercial conditions in this test. The following tests were carried out on the fired bars:

A. Physical Appearance.

A visual examination of the fired bars was made to note the impurities such as iron, manganese etc., present. The burned behaviour, including any tendency to warp, bloat, or soften was also noted.

B. Total Shrinkage.

This was obtained by carefully measuring the length of the fired bar and calculating the shrinkage based on the original green length.

Table.XVIII

Geologic Sections at Vereeniging.

East Pit. Section No. 1.

Thickness.	Lithology.	Sample No.
5 ft.	Overburden, loose sand and gravel.	1.
4 ft.	Semi-flint clay, thin bedded.	2.
5 ft.	Semi-flint clay, thick bedded.	3.
2½ ft.	Silicious refractory shale, thin bedded.	4.
3 ft.	Semi-flint clay, thick bedded.	5.
2 ft.	Varicoloured shales.	6.
½ft.	Plastic Clay, black.	7.
1 ft.	Semi-flint clay, thick bedded.	8.
2 ft.	Plastic clay, black.	9.
1 ft.	Semi-flint clay.	10.
2½ ft.	Semi-flint clay (carbonaceous).	11.
28½ ft.	TOTAL.	

East Pit. Section No. 2.

Thickness.	Lithology.	Sample No.
4½ ft.	Overburden, loose sand and gravel.	12.
3 ft.	Semi-flint clay, thin bedded.	13.
3/4 ft.	Semi-flint clay, thick bedded.	14.
¼ ft.	Silicious refractory shale, soft.	15.
3½ ft.	Semi-flint clay, thick bedded.	16.
2½ ft.	Silicious refractory shale, thick bedded.	17.
4 ft.	Semi-flint clay, thick bedded.	18.
½ ft.	Plastic clay, black.	19.
1 ft.	Semi-flint clay, thick bedded.	20.
2½ ft.	Plastic clay, black.	21.
1 ft.	Semi-flint clay.	22.
4 ft.	Semi-flint clay, (carbonaceous).	23.
27½ ft.	TOTAL.	

East Pit. Section No. 3.

Thickness.	Lithology.	Sample No.
4 ft.	Overburden, loose sand and gravel.	24.
4 ft.	Semi-flint clay, thin bedded.	25.
3/4 ft.	Semi-flint clay, thick bedded.	26.
4 ft.	Silicious refractory shale, thin bedded.	27.
3½ ft.	Semi-flint clay, thick bedded.	28.
2½ ft.	Silicious refractory shale, thin bedded.	29.
4 ft.	Semi-flint clay, thin bedded.	30.
2 ft.	Plastic clay, black.	31.
1 ft.	Semi-flint clay.	32.
4½ ft.	Semi-flint clay (carbonaceous)	33.
30¼ ft.	TOTAL.	

Table XVIII (cont'd).

West Pit. Section No. 1.

Thickness.	Lithology.	Sample No.
7½ ft.	Overburden, loose sand and gravel.	1.
1½ ft.	Semi-flint clay, thick bedded.	2.
1½ ft.	Yellow shale, thick bedded.	3.
3 ft.	Silicious refractory shale, thin. bedded.	4.
3 ft.	Silicious refractory shale, (red concretions), thin bedded.	5.
1 ft.	Yellow shale, (topped by 1" seam of limonite).	6.
5 ft.	Silicious refractory shale.	7.
2 ft.	Semi-flint clay.	8.
2 ft.	Semi-flint clay, (carbonaceous).	9.
26½ ft.	TOTAL	

West Pit. Section No. 2.

Thickness.	Lithology.	Sample No.
7½ ft.	Overburden, loose sand and gravel.	10.
1½ ft.	Semi-flint clay, thick bedded.	11.
1½ ft.	Yellow Shale, blockey.	12.
6 ft.	Silicious refractory shale, with some bands of yellow shale.	13.
1 ft.	Silicious refractory shale and yellow shale interbedded.	14.
5 ft.	Silicious refractory shale, thin bedded.	15.
2 ft.	Silicious refractory shale.	16.
3 ft.	Semi-flint clay, (carbonaceous)	17.
1 ft.	Semi-flint clay, carbonaceous, inter-bedded with limonite.	18.
1 ft.	Silicious refractory shale.	19.
1 ft.	Silicious refractory shale.	20.
1 ft.	semi-flint clay.	21.
31½ ft.	TOTAL.	

West Pit. Section No. 3.

Thickness.	Lithology.	Sample No.
7 ft.	Overburden, loose sand and gravel.	22
5 ft.	Buff shale, thick bedded.	23.
2 ft.	Semi-flint clay.	24.
1 ft.	Yellow sandy shale.	25.
2½ ft.	Silicious refractory shale, thin. bedded.	26.
2 ft.	Plastic clay, brown.	27.
1½ ft.	Silicious refractory shale.	28.
3½ ft.	Silicious refractory shale inter-bedded with plastic clay.	29.
2 ft.	Silicious refractory shale.	30.
6 ft.	Semi-flint clay, (carbonaceous).	31.
1 ft.	Flint clay.	32.
33½ ft.	TOTAL.	

Table XVIII (cont'd).

West Pit. Section No. 4.

Thickness.	Lithology.	Sample No.
7 ft.	Overburden, loose sand and gravel.	33.
3 ft.	Buff shale, thick bedded.	34.
6 ft.	Silicious refractory shale, thin bedded.	35.
4 ft.	Silicious refractory shale, interbedded with plastic clay.	36.
2 ft.	Silicious refractory shale.	37.
4 ft.	Semi-flint clay, (carbonaceous).	38.
26 ft.	TOTAL.	

Table XIX

DATA ON RAW CLAY SAMPLES FROM WEST PIT.

Geologic Location.	Photo No:	Hardness	Colours	Plasticity	Structure	Remarks.
Section 1, No: 2	1	S.F.	Tan and Grey	Poor	Thin Bedded Shale.	Small Black Specks (Gritty)
3	2	S.F.	Buff	Fair	Thin Bedded Shale.	Yellow iron stains (Grit.)
4	3	S.F.	Tan	Fair	Thin Bedded Shale.	Thin seams of Limonite (Grit.)
5	4	S.F.	Tan	Fair	Blocky	Small amount of Manganese, yellow iron stains (Grit.)
6	5	S.F.	Buff	Good	Blocky	Yellow tints of iron present. Some Grit.
7	6	S.F.	Red	Fair	Thin Bedded Shale.	Brown iron stains in joints (No Grit.)
8	7	S.F.	Red with dark purple seams.	Poor	Blocky Shale.	Purple banded.
9	8	F.	Black.	Poor	Thick Bedded Shale.	Bottom Black.
Section 2, No:11	9	S.F.	Grey	Poor	Thick Bedded Shale.	Some brown iron and manganese iron stains (Gritty.
12	10	S.F.	Grey	Fair	Thin Bedded Shale.	Pinkish tints, some yellow iron stains and manganese.
13	11	S.F.	Red and Yellow	Fair	Thin Bedded Shale.	Some Limonite stains (Gritty)
14	12	S.F.	Red	Poor	Thin Bedded Shale.	Sandy.
15	13	S.F.	Red and Buff	Fair	Thin Bedded Shale.	Some Manganese.
16	14	S.F.	Red with Black streaks.	Poor	Blocky	Purple Band.
17	15	F.	Black.	Poor	Blocky	Bottom Black.
18	16	S.F.	Black tinged with Red.	Poor	Thick Bedded.	Some Grit.
19	17	S.F.	Red.	Poor.	Thin Bedded.	Sandy.

Table XIX, cont'd.

DATA ON RAW CLAY SAMPLES FROM WEST PIT (2).

Geologic Location.	Photo No.	Hardness.	Colours.	Plasticity.	Structure.	Remarks.
Section 2 No. 20	18	S.F.	Red with iron stains.	Poor	Blocky.	Sandy clay.
21	19	F.	Black.	Poor	Thick Bedded	Bottom Black. Hard.
Section 3 No. 23	20	S.F.	Yellow	Good	Thin bedded.	Sandy soft material.
24	21	S.F.	Grey.	Fair.	Thin bedded.	Clay, some manganese.
25	22	S.F.	Buff.	Fair.	Thick bedded.	Some manganese.
26	23	S.F.	Red.	Fair	Thin bedded.	Some grit.
28	24	S.F.	Red.	Fair.	Thin bedded.	
29	25	S.F.	Reddish.	Fair.	Thin bedded.	Clay no grit, some grit.
30	26	S.F.	Red with purple streaks	Fair.	Thick bedded.	Purple banded.
Section 4, No.34	27	S.F.	Grey	Very good	Thick bedded	soft sandy material.
35	28	S.F.	Grey and red	Very good	Thick bedded	No grit.
36	29	S.F.	Red	Poor	Thin bedded	Reddish tint, yellow iron stains.
37	30	S.F.	Red	Poor	Thin bedded	No grit.
38	31	F.	Black with reddish tints	Poor	Thick bedded	Some grit.

S.F. - Semi-flint type of clay.
F. - Flint type of clay.

Table XIX, cont'd.

Photo No:	Mfg. Skg.	Reheat.	Cone 12 Burn Colour.	Cone 12 Burn Appearance.	Remarks.
1.	.48"/ft.C.	2.2% C.	White	Some iron spots.	High in free silica.
2.	.61"/ft.C.	3.2% C.	Tan	Even colour.	Abnormal after shrinkage.
3.	.44"/ft.C.	.43% E.	White	Some iron spots.	Good refractory clay.
4.	.50"/ft.C.	.58% C.	Buff	Some iron spots.	Poor bond at Cone 12.
5.	.78"/ft.C.	.24% E.	Brown.	High in iron.	Reheat expansion due to over-fired bloating.
6.	.48"/ft.C.	2.30% C	White.	Some iron spots.	After shrinkage high.
7.	1.70"/ft.C.	.82% E	Tan.	Some iron spots.	After expansion due to cracking.
8.	.48"/ft.C.	.58% C	White.	Free from iron spots.	Good refractory clay.
9.	.72"/ft.C.	.47% C	White.	Free from iron spots.	Good refractory clay.
10.	.48"/ft.C.	1.60% C	Buff	Free from iron spots.	Silicious clay, high after shrinkage.
11.	.48"/ft.C.	.35% C	White.	Free from iron spots.	Good refractory clay.
12.	.32"/ft.C.	1.10% C	Brown.	Very irony.	Too irony for use.
13.	.78"/ft.C.	2.3% C	Buff.	Some iron spots.	After shrinkage high.
14.	.94"/ft.C.	.36% C	Mottled Brown.	Some iron spots.	Good refractory clay.
15.	.61"/ft.C.	.15% E.	Brown.	Very irony.	Expansion due to overfired bloating.
16.	.24"/ft.C.	1.30% C.	Buff.	Free from iron spots.	Silicious clay, good pipe clay.
17.	.50"/ft.C.	.45% C.	White.	Free from iron.	Silicious clay, good refractory clay.

BURNED DATA - WEST PIT CLAYS (2).

Photo No.	Mfg. Skg.	Reheat.	Cone 12 Burn Colour.	Cone 12. Burn Appearance.	Remarks.
18	.30"/ft. E.	3.00% C	Mottled Brown	Very irony	Highly silicious.
19	1.00"/ft. C.	.79% C	Buff Mottled	Some iron	omewhat high after shrinkage
20	.78"/ft. C.	1.30% C.	Brown	Some iron spots	High after shrinkage.
21	.67"/ft. C.	.35% C.	Brown	Free from iron spots	Good refractory clay.
22	.32"/ft. C.	3.80% C.	Brown	Free from iron spots	Hig. after shrinkage.
23	.32"/ft. C.	1.20% C.	White	Free from iron spots	Silicious clay.
24	.78"/ft. C.	.48% C.	Brown discoloured	Some iron spots	Hair checked too discoloured.
25	1.00"/ft. C.	.00% C.	Buff	Some iron spots	Slight hair checking, good refractory clay.
26	1.00"/ft. C.	..36% C.	White		
27	1.00"/ft. C.	2.70% C.	Buff	Some iron spots	High after shrinkage.
28	.78"/ft. C.	.14% C.	Mottled buff	Some iron spots	Slight hair shrinkage, good refractory clay.
29	.94"/ft. C.	.09% C.	Brown	Free from iron	Good refractory clay.
30	.13"/ft. C.	.08% C.	White	Free from iron	Good refractory clay.
31	.67"/ft. C.	.00% C.	Buff	Iron spots	Good refractory clay.

Table XIX, cont'd.

Data on Raw Clay Samples from East Pit.

Geologic Location.	Photo No.	Hardness.	Colour.	Plasticity.	Structure.	Remarks.
Section 1 No. 2	1	S.F.	Grey	Fair	Blocky	Some grit.
4	2	S.F.	Red	Fair	Thin bedded	Some grit.
6	3	Soft	Brown	Good	Thin bedded	No grit.
7	4	Soft	Brown	Good	Clayey	Pot Clay.
8	5	S.F.	Grey	Fair	Blocky	No grit.
9	6	Soft	Black	Good	Clayey	Pot Clay.
10	7	S.F.	Buff	Poor	Thin bedded	Some grit.
11	8	F.	Grey	Poor	Blocky	No grit.
13	9	S.F.	Grey	Poor	Thin bedded	Some grit.
14	10	S.F.	Grey	Fair	Blocky	No grit.
15	11	Soft	Red	Poor	Thin bedded	Sandy.
16	12	S.F.	White	Fair	Thick bedded	No grit.
17	13	S.F.	Red	Fair	Thick bedded	No grit.
18	14	S.F.	Grey	Fair	Thick bedded	No grit.
19	15	Soft	Black	Good	Clayey	Pot clay.
20	16	S.F.	Grey	Fair	Thick bedded	No grit.
21	17	Soft	Black	Good	Clayey	Pot clay.

Table XIX, cont'd.

Data on Raw Clay Samples from East Pit.

Geologic Location.	Photo No.	Hardness.	Colour.	Plasticity.	Structure.	Remarks.
Section 1 NO. 22	18	S.F.	Grey	Poor	Thick bedded	No grit.
23	19	F.	Black	Poor	Blocky	No grit
25	20	S.F.	Grey	Fair	Blocky	No grit.
27	21	S.F.	Red	Fair	Thin bedded	No grit.
28	22	S.F.	Grey	Fair	Blocky	No grit.
29	23	S.F.	Red	Poor	Thin bedded	some grit.
30	24	S.F.	Grey	Fair	Blocky	No grit.

Table XIX, cont'd.

Burned Data - East Pit Clays

Photo No.	Cone 12 Mfg. Skg.	1400°C. Re-heat.	Cone 12. Burned Colour.	Cone 12. Burned Appearance.
1	.17"/ft. C.	.25% C.	White	Some manganese spots, hair checking.
2	.33"/ft. C.	3.00% C.	White	Some manganese spots, hair checking.
3	.68"/ft. C.	.14% E.	Tan	Some hair checking.
4	.69"/ft. C.	1.50% C.	Brown	Cracked badly.
5	.26"/ft. C.	4.00% C.	Buff	High re-heat shrinkage.
6	1.45"/ft. C.	1.60% C.	Tan	Cracked badly.
7	1.16"/ft. C.	.47% C.	White	Free from iron, hair checked.
8	1.04"/ft. C.	.35% C.	White	Free from iron, hair checked.
9	.45"/ft. C.	.26% C.	Buff.	Some iron spots, highly silicious.
10	.03"/ft.C.	4.0% C.	White	Manganese spots, hair checked.
11	.30"/ft. E.	2.8% C.	Mottled	Manganese and iron spots, hair checked.
12	.29"/ft. C.	1.0% C.	White	Manganese spots, hair checked.
13	.42"/ft. C.	.36% C.	Mottled Tan	Free from hair checking.
14	.63"/ft. C.	1.00% C.	White	Hair checked.
15	1.25"/ft. C.	.42% C.	Brown	Hair checked.
16	.60"/ft. C.	2.3% C.	Brown	Hair checked.

Table XIX, concl'd.

Photo No.	Cone 12 Mfg. Skg.	1400°C. Re-heat.	Cone 12 Burned Colour.	Cone 12. Burned Appearance.
17	1.44"/ft. C.	.25% C.	Brown	Hair Checked.
18	1.05"/ft. C.	.51% C.	Brown	Hair Checked.
19	.87"/ft. C.	1.3% C.	White	Poorly bonded.
20	.19"/ft. C.	2.1% E.	Buff.	Highly silicious.
21	.02"/ft. C.	1.80% C.	Buff	Manganese spots, hair checked.
22	.83"/ft. C.	1.20% C.	Brown	Iron spots, hair checked.
23	.49"/ft. C.	.96% C.	White	Iron spots, no hair checking.
24	1.57"/ft. C.	.69% C.	Dark brown	Some iron, no hair checking.

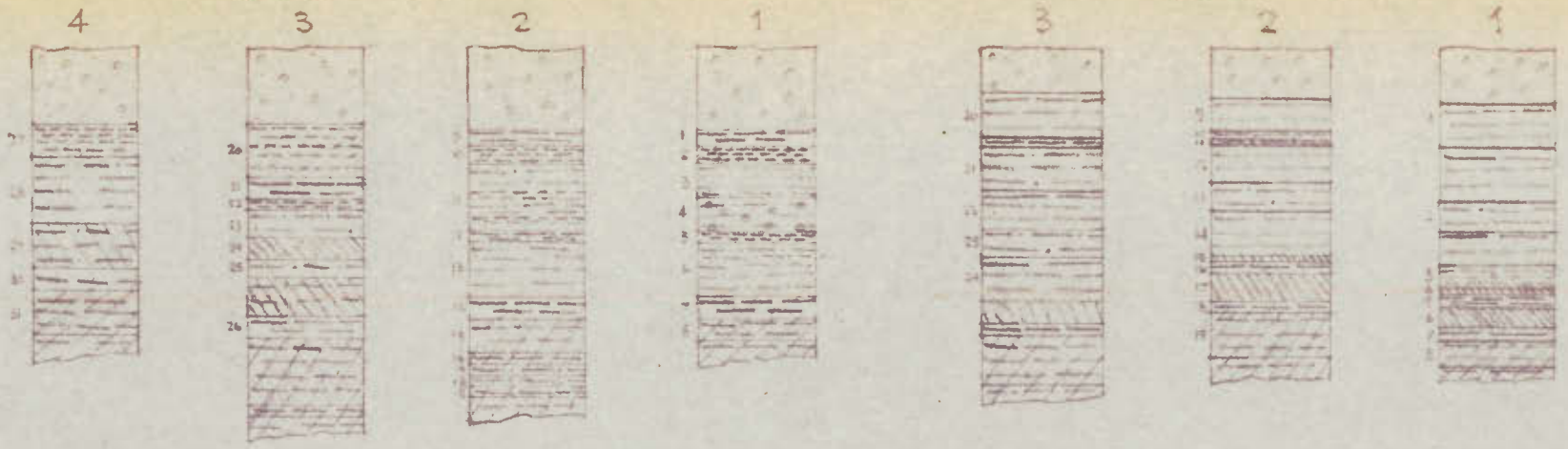
157

WEST PIT

4 3 2 1

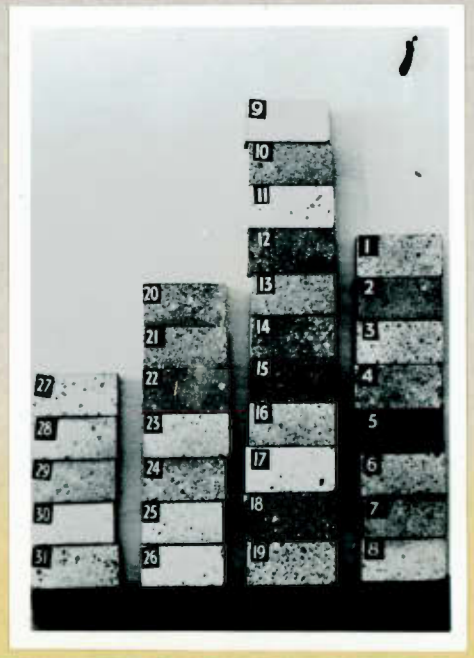
EAST PIT

3 2 1



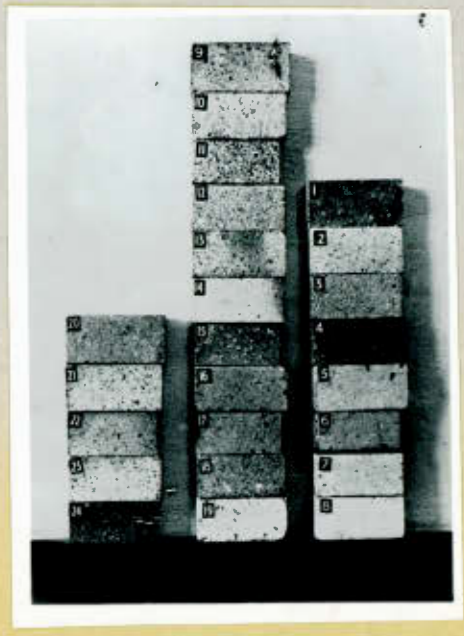
GEOLOGICAL SECTIONS

(Numbers indicate strata sampled and correspond to numbers of test bars given in photographs.)



BURNED TEST BARS

NOTE DIFFERENCES IN SPRINGAGES AND COLOUR.



WEST PIT

EAST PIT

C. Re-Heat Behaviour.

Two test bars of each lot were measured accurately in length with a vernier caliper and then placed in an oil fired laboratory furnace. The furnace was brought up to a temperature of 1400°C. in 3½ hours and held at that temperature for 5 hours. After the test pieces were cool they were remeasured and the linear changes noted. The physical appearance of the test pieces was also examined for signs of over firing or bloating. This simulative test is intended to evaluate the fitness of the particular clay under temperature conditions prevailing during their service life.

D. Refractoriness.

The P.C.E. test as described in Section IV was carried out on the more promising samples.

Photographs of the burned bars are included in Figure 34 along with the geologic sections.

Tests done on small bars yield results which bear a relative relationship to work on full-sized brick, and such data can be used effectively as a basis of comparison.

Results of the ceramic investigation are tabulated in Table XIX.

Summary and Conclusions.

1. The ceramic investigation brings out the pronounced variations in properties of the strata even when sampled within a relatively small area, a feature which is generally characteristic of the Middle Ecca Refractory clays.

2. The need for careful sorting is emphasized. In most cases an adequate classification can be made on the basis of visual inspection alone; however, differences sometimes exist which are not easily detected by this means which give rise to manufacturing troubles.

3. A programme of sampling and testing prior to mining is desirable to minimize production difficulties and maintain quality standards. This can be most effectively accomplished by arranging mining operations so as to enable samples of exposed strata to be made up into test bars and examined before

removal.

Note: One South African manufacturer arranges to have such test results in the hands of the mining foreman at least a week before the clay is mined and from them he plans selective mining operations.

Preliminary Investigation of the Improvement of South African Clays through pH Control

General Statement

Considerable overseas research has been done on the improvement of the workability and other qualities of clays, by proper alkali treatment, and the results of these investigations have been confirmed in plant test. (37, 38) It was found in many cases that if the acidity or alkalinity in the clay mass was controlled within rather narrow limits an appreciable improvement was made in the manufacturing behaviour of the clays. The hydrogen-ion concentration of pH offers a true measure of the active acidity or alkalinity, and the ease of measuring this property makes it an effective control for adjusting the clay mass to produce the optimum improvement in physical properties. Because of its cheapness and effectiveness, sodium carbonate is the usual chemical compound used to adjust the pH of clays.

It has been found that a curve showing pH vs. sodium carbonate addition will usually supply information on the clays that will indicate the probable results obtainable by adjustment of the pH. Accordingly, a series of such curves was prepared for various samples of commercial South African refractory clays in order to determine the effects of such treatment.

Experimental Procedure

The method outlined in Barker and Truog was followed in preparing the samples. A summary of the procedure is as follows: To a series of 20 gm samples of clay in beakers, 50 cc of distilled water were added to each with varying amounts of sodium carbonate ranging from 0.2% to 1.0% of the weight of the clay. After stirring occasionally the pH of the specimens was determined with the Beckman pH meter.

Description of Samples

Sample A -- silicious type refractory shale.
" B -- grey, semi-flint clay.
" C -- soft black plastic clay.
" D -- black semi-flint clay.
" E -- purple semi-flint clay.
" F -- black flint clay.
" G -- buff semi-flint clay.

The data accumulated are as follows:

Sample	pH of clays with varying percentages of Na_2CO_3 added					
	0.0%	0.2%	0.4%	0.6%	0.8%	0.1%
A	7.0	9.0	9.6	9.8	9.9	10.0
B	6.5	9.2	9.6	9.9	10.0	10.0
C	6.4	7.3	7.6	8.1	8.4	8.6
D	6.9	9.0	9.5	9.7	9.7	9.9
E	6.9	8.8	9.4	9.7	9.8	10.0
F	7.0	8.3	9.0	9.3	9.7	9.9
G	6.5	8.6	9.3	9.6	9.7	9.9

Note: pH of distilled water was 6.4

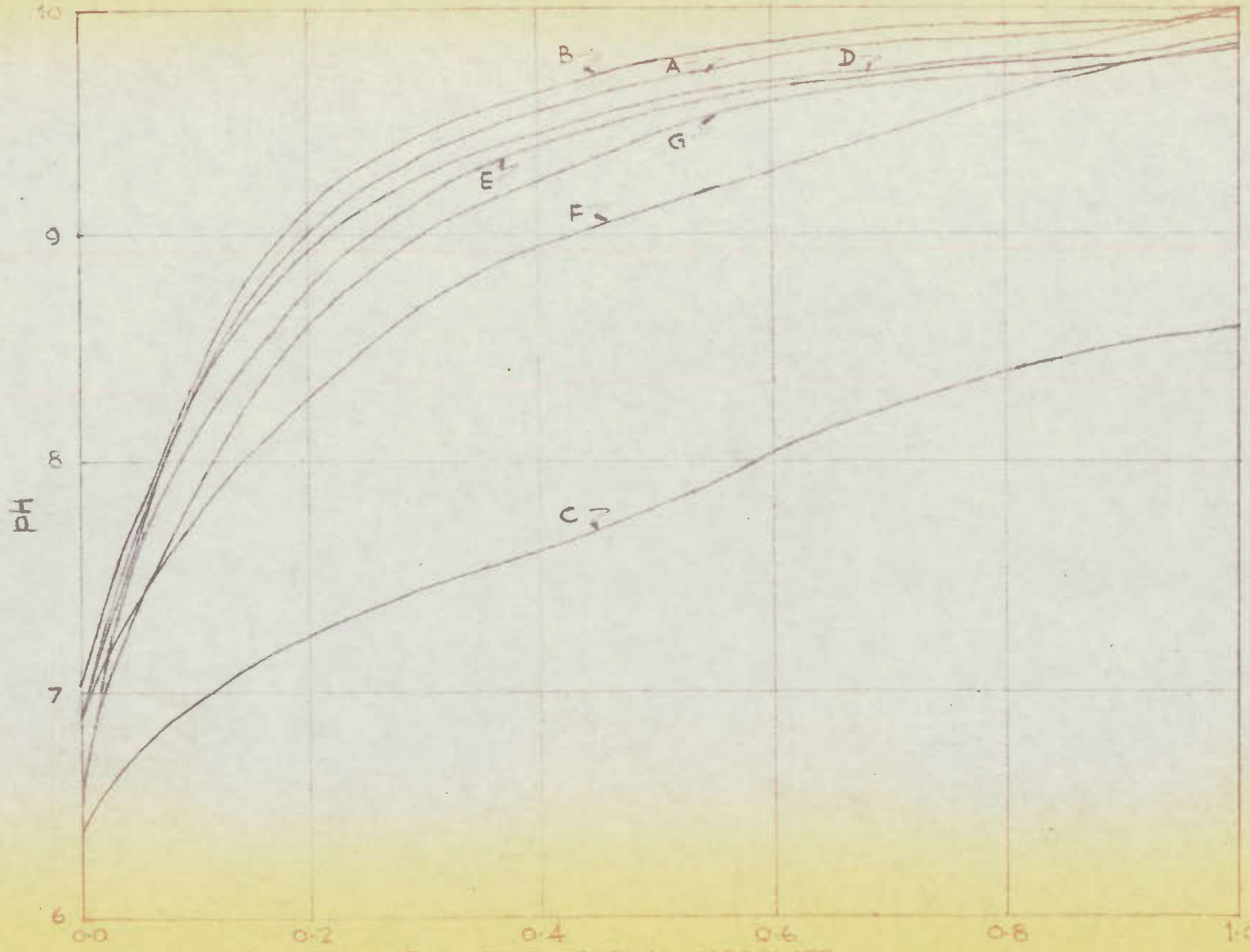
The results of this wpk are shown on accompanying curves in Figure 33.

Remarks

A noticeable characteristic of samples C and D was the relative length of time required for their pH readings to become constant. This phenomenon is known as "drift", and is characteristic of slightly buffered solutions which change in pH as a result of absorption or evolution of CO_2 or SO_2, etc. Drift is also observed when chemical reactions of any nature take place in the solution. Samples A and B showed little drift even without the addition of buffers. Some drift was noted in unbuffered samples of clays D, E, and G, but the tendency usually disappeared when the sodium carbonate was added, the first decreasing with the addition of the chemicals. In the case of clays G and F drift was not apparent after the addition of 0.2% of Na_2CO_3. The tendency disappeared in samples C, D, and E after a 0.4% addition of Na_2CO_3.

Summary and Conclusions

1. All of the clays examined were shown to be naturally non-acid.
2. From the curves given, it is interesting to note that samples A, B, D, E, and G all fall within the same narrow optimum pH range of 8 to 10.
3. Sample C, which was the only plastic clay examined, showed marked variation in pH behaviour from the other samples,



CURVES SHOWING THE ADDITIONS OF SODIUM CARBONATE TO VARIOUS SOUTH AFRICAN REFRACTORY CLAYS

FIG. 33.

with the addition of alkalis. Its curve showed no tendency to flatten out within the range of Na_2CO_3 additions made.

4. Sample F did not show as pronounced an effect in flattening in the presence of increased amounts of Na_2CO_3 as samples A, B, D, E, and G, but lies somewhere between these clays and clay C in effectiveness.

5. The curves indicate the possibilities of the poorly plastic clays being amenable to alkali treatment with about 0.6% Na_2CO_3, and this information offers an interesting basis for further investigation.

V - CLAY REFRACTORIES INDUSTRY OF SOUTH AFRICA

HISTORY

Fireclay bricks are known to have been manufactured at Vereeniging in 1891 when such bricks were produced at the old Works of the Vereeniging Brick and Tile Company, Limited, under the supervision of Mr.Buchanan, plant engineer. Vereeniging-made firebricks in those days were transported by ox-wagon as far afield as Kimberley.

Firebrick were also made at Olifantsfontein before the Anglo-Boer war, and a number of small plants on the Reef apparently produced some of this type of ware during that period; however, details on these earlier manufacturers are obscure. The output of the early producers was generally quite small, principally because the total demand for firebrick was not important in South Africa during these years. The firebrick requirements for early industrial activities on the Witwatersrand were generally met by overseas suppliers, particularly in the field of assay ware in which Great Britain became the principal shipper.

Industrial expansion on the Witwatersrand following the Anglo-Boer war, increased the demand for firebrick and more local producers began to enter the field. The first manufacturers of firebrick were those plants which had been producing building brick. Among the earliest contenders for the domestic market were the Vereeniging Brick and Tile Company, Limited, the Consolidated Rand Brick Pottery and Lime Company, and the Boksburg Brick & Tile Company. World War 1 brought about increased demands for firebrick, and soon after the war period the Union Fireclay Company, the Economic Fireclay Company, and the Elgin Fireclay Company came into production. The manufacture of assay ware was soon taken over by domestic producers and all manufacturers began to expand production of fireclay, brick, and tile during the twenties and thirties. The rise of the steel industry gave a great impetus to local

fireclay manufacturers, and close co-operation between the steel industry and the brick manufacturers resulted in further growth of the industry.

The advent of World War II caused the local firebrick industry to be faced with the production of all of the domestic requirements because of the difficulty in obtaining overseas materials. Fortunately plant expansion and modernization was under way before the war commenced and these programmes were increased to enable domestic suppliers to meet all local needs and to supply neighbouring countries as well. This period was one of great technical advance for the local industry, and following the war the domestic producers have retained their advantage over overseas suppliers.

PRODUCTION--EXPORT AND IMPORT

The manufacture of clay refractories is a very important secondary industry in South Africa. The trend of production of clay refractories from 1935 to 1944, the last year for which published statistics are available, is shown graphically in Figure , which was prepared from estimates based on existing data for production of all types of refractory products for these years*. Production increases during the war years reflected the expansion and technical advances, in particular the application of the tunnel kiln made by local manufacturers. The increased demands of expanding consumer industries, especially iron and steel, accelerated domestic output. The clay refractories industry received preferential attention during the war years because of its vital support of the war industries, and output was increased to meet the domestic requirements in the Union and all neighbouring countries as well, since South Africa was virtually cut off from overseas suppliers of these commodities as a result of lack of transportation.

---

* Census of Industrial Establishments, Government Printer, Pretoria

Prior to the war, substantial amounts of clay refractories were obtained from overseas sources. Considering that clay refractories generally have a low economic density (value per ton) the development of the domestic industry has affected a lasting economy and practically made the Union self-sufficient in the supply of these materials. The trend of imports and exports of clay refractories between 1935 and 1945 is illustrated by the graph given in Figure 35.* The principal pre-war suppliers of clay refractories included Great Britain, the United States, and Germany. After the war, the customers for Union made products included Southern Rhodesia, Northern Rhodesia, Belgian Congo, and Portuguese East Africa.

LOCATION

The clay refractories industry of South Africa is concentrated in the Southern Transvaal where favourable deposits of refractory clay are located. This concentration fortunately coincides with the major industrial districts and principal coal fields of the Union. These producing centres are located at Vereeniging, Olifantsfontein, Boksburg, and Springs.

The early plants were located primarily on a geographic basis in the proximity of the rapidly expanding consumer centres. The geological factors were secondary, owing to the fortunate occurrence of extensive deposits of good fire-clay in the proximity of these consumer centres. Until recently, the plants have been located at the site of the clay deposits, but recent trends indicate that as workable deposits are exhausted, the producers must search further afield. Transportation has always been a big factor in the evaluation of the commercial possibilities of refractory clay deposits, so that even today only a portion of the clay reserves can be worked economically. Coal, water, and electric power are relatively cheap and accessible at all of the producing centres, which has tended to keep

---

* Reports of the Department of Customs and Excises.

the producing centres close to the consumer centres.

STATUS

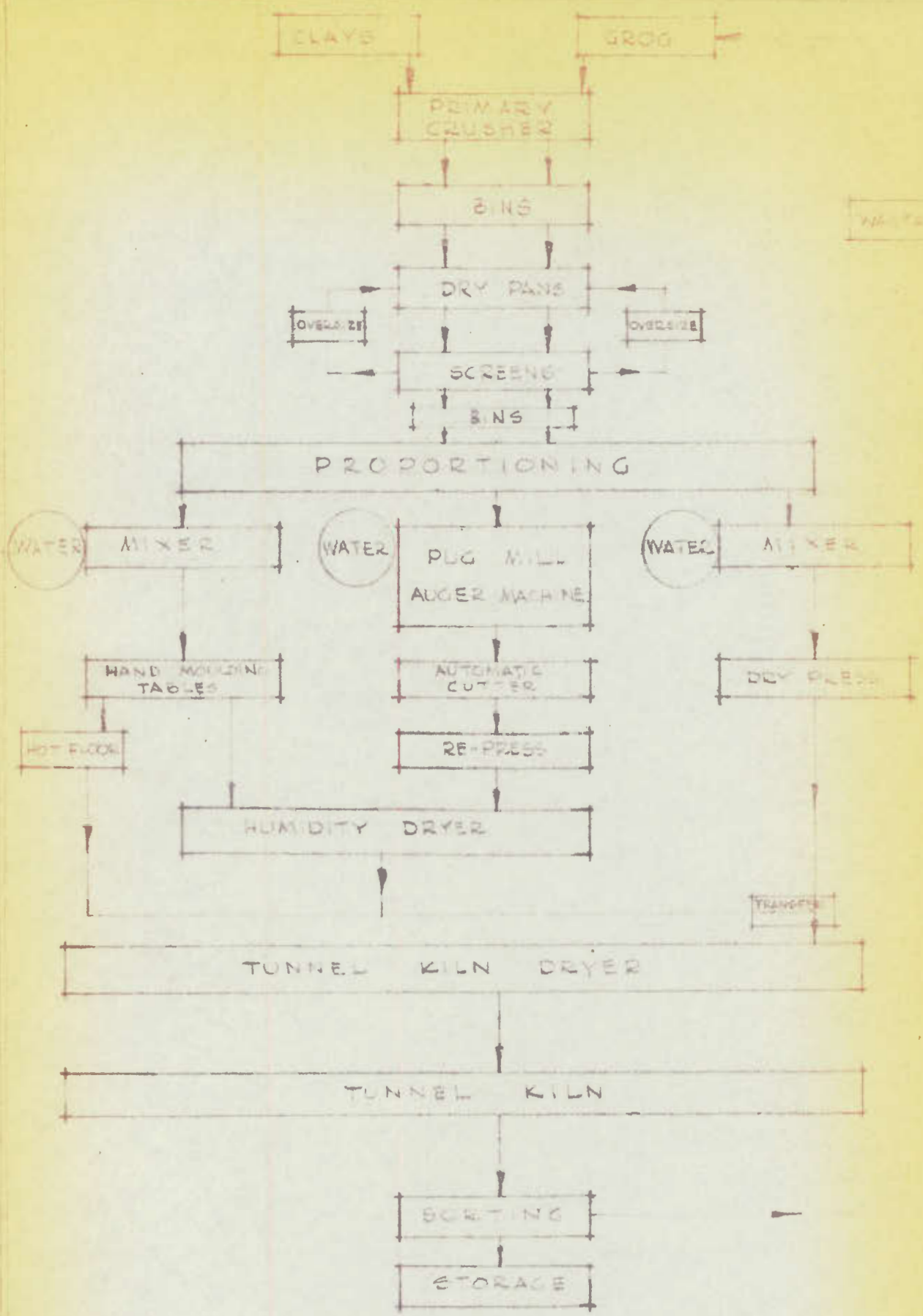
There are six plants in the Union producing clay refractories at present, as enumerated below:

1. Boksburg Brick and Tile Co., Ltd., Boksburg
2. Consolidated Rand Brick Pottery and Lime Co. Ltd., Olifantsfontein
3. Economic Fireclay Co., Boksburg
4. Elgin Fireclay Co., Ltd., Springs
5. Union Fireclay Co., Ltd., Boksburg
6. Vereeniging Brick and Tile Company,Ltd., Vereeniging

The Consolidated Rand Brick Pottery and Lime Co.Ltd. and the Vereeniging Brick and Tile Company, Ltd., are the two largest producers in the Union and manufacture a complete range of silica, magnesite, chrome, and other refractories and together supply practically all of the requirements of the domestic iron and steel industry. The Boksburg Brick and Tile Co.Ltd., the Elgin Fireclay Co., Ltd., the Economic Fireclay Co. and Union Fireclay Co., Ltd., produce clay refractories for boiler-work and non-ferrous metallurgy, in particular refractory ware for the gold mines.

A common characteristic of these plants is the wide diversity of products manufactured in addition to clay refractories, often under the same roof, a condition necessitated by the relatively small but great variety of clay products requirements to be met in the Union. This is in marked contrast to the overseas trend toward specialization.

The refractories manufacturers of the Union are all members of the Transvaal Clay Association, which is devoted to the advancement of the industry and the exchange of ideas.



FLOW SHEET FOR THE MANUFACTURE OF FIREBRICK IN A MODERN SOUTH AFRICAN TUNNEL KILN PLANT.

FIG. 3.

Research and development is a prominent consideration among the larger firms particularly, and the newer plants represent the latest in overseas design and equipment. A flow sheet for the manufacture of firebrick in a modern South African tunnel kiln plant is given in Figure 37.

MARKETING

Practically, up to 95% of the refractories produced in the Union are sold directly to industrial consumers, although Agents and stockists are used to handle these products in some of the coastal towns. Important marketing conditions existing in the Union are the manufacture of various products to specifications of industrial users or furnace designers and the development of products comparable with overseas materials.

The problem of overcoming the prejudice of local industries for imported materials has largely disappeared since the wartime expansion of the industry, but vestiges of the reluctance to discuss specifications in terms of physical performance in favour of chemical analysis still remains.

Foreign competition in the field of clay refractories has declined to a position of relative unimportance largely owing to the improvement in quality of local production and to the protection afforded in preferential rail tariffs and customs duties.

SPECIFICATIONS FOR FIREBRICK

The South African Bureau of Standards, in cooperation with domestic manufacturers and users of clay refractories has recently drawn up suggested specifications for firebrick. These specifications are as follows:

Normal Duty: Firebrick in this classification must possess a minimum P.C.E. of Cone 28. They must not show more than 1.0% linear change when subjected to a re-heat test of 1410°C. for 2 hours.

High Duty: In this classification firebrick must have a

The test data shown below are average results of control tests on 9" brick and are subject to normal variations on individual tests. These results cannot be taken as maximum or minimum requirements for specification purposes.

Table XX

Quality.	Normal Stiff-mud repress; hand made; dry pressed	Casting Pit Hollow Ware Stiffmud repress	High Heat Duty Stiff-mud repress; hand made	Super Duty Dry Pressed; hand made.
Pyrometric Cone Equivalent:				
Standard Cone (British Seger)	32-33	32-33	34	34-35
Temperature Equivalent	1710-1730°	1710-1730°	1750°	1750-1770°C.
Orton Cone	32⁺-33⁺	32⁺-33⁺	34⁻	34⁻-35⁻
Rehsat (Permanent Linear Change).				
Percent Contraction or Expansion				
at 1400°C. for 5 hours	0-.6% C.	0-.6% C	0-.5% C.	0-.2% C.
at 1600°C. for 5 hours	-	-	-	0-.8% C.
✱ Hot Load Test:				
A.S.T.M. C.16-41 (25/sq. in.)				
Percent Deformation at				
1350°F.	2-4	2-4	-	-
1450°F.	-	-	4-7	4-7
✱ Panel Spalling:				
A.S.T.M. C.107-42				
Percent Loss.				
Preheated 1600°C.	2-8	2-8	2-5	2-5
Apparent Porosity				
Percent	20-25	22-25	20-23	17-22
Chemical Analyses:				
SiO_2	60.5	59.8	55.4	53.8
Al_2O_3	35.3	35.4	41.4	43.0
TiO_2	1.2	1.3	1.2	1.2
Fe_2O_3	1.6	1.8	.8	.6
Other Constituents	1.4	1.7	1.5	1.0
Modulus of Rupture				
A.S.T.M. C.133-39				
Lb. per sq. in.	900-1200	800-1000	800-1100	1200-1500

✱ Note: The A.S.T.M. Hot - load and spalling tests were performed overseas because of the rather elaborate specialised equipment required.

Table XX, cont'd.

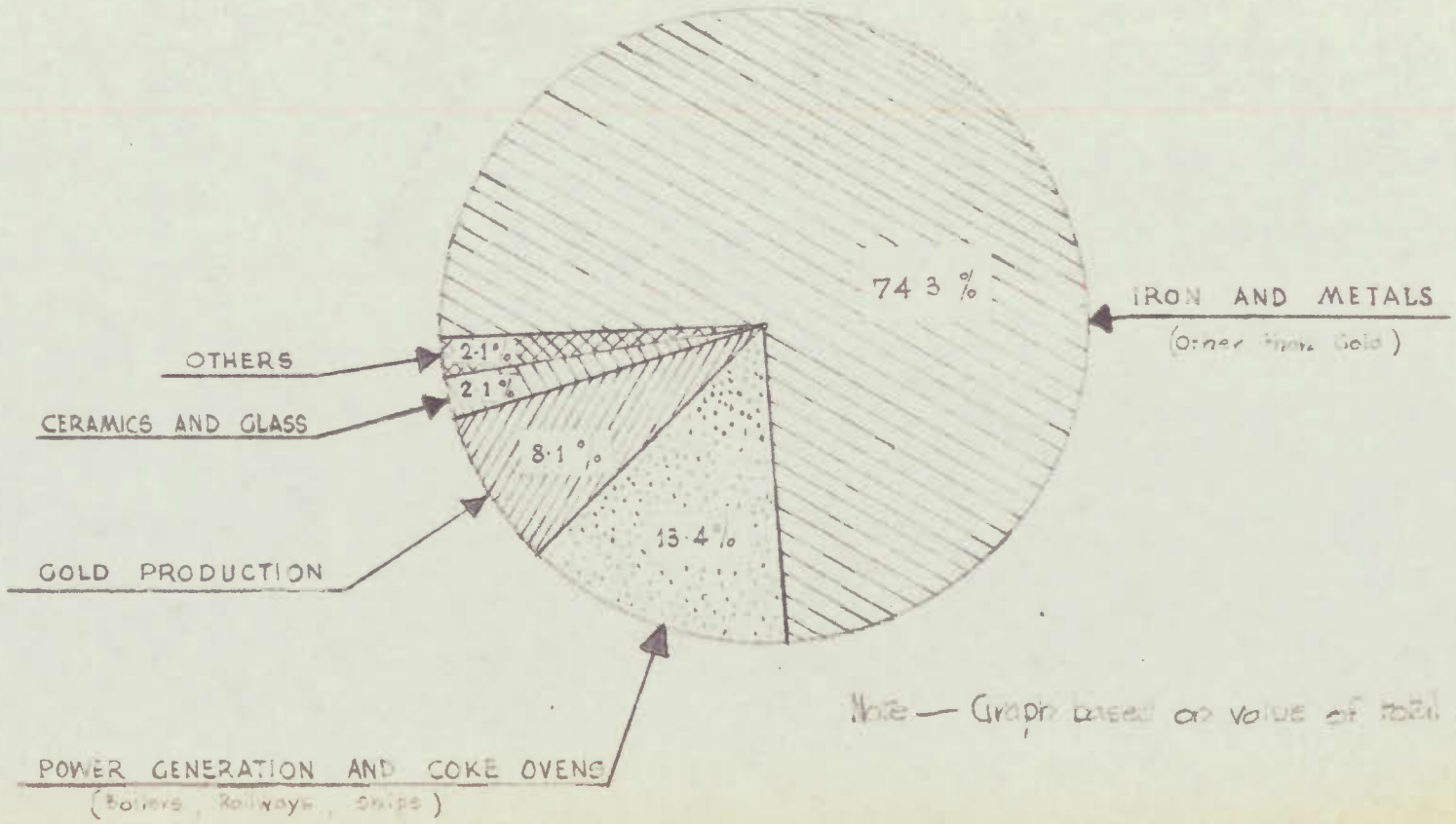
PROPERTIES OF SELECTED AMERICAN FIRECLAY REFRACTORIES*.

	Intermediate Heat Duty.	High Heat Duty.	Super Duty.
Silica content, per cent.	60	53	52
Alumina content, %	35	42	43
P.C.E.	30-31	32½	33-34
Approximately °C	1665	1723	1752
Density (Bulk) g.p.c.c.	2.114	2.082	2.323
Porosity.	18	18	14
% Spalling loss -			
High Duty Schedule	-	7.5	0
Low Duty Schedule	-	-	2.7
Reheat test-change-linear - %.			
5 Hours at 1400°C.	0.5	+0.5	-
" " 1600°C.	-	-	-0.2
Load test-25 lbs. per sq.in., 1½ hours, % subsidence-			
At 1300°C.	3.0	-	-
At 1350°C.	-	5.0	3.0
At 1450°C.	-	-	5.0

PROPERTIES OF SELECTED BRITISH FIRECLAY REFRACTORIES.* *

	Siliceous	Medium Alumina	42% Alumina.
Apparent porosity, %	30.6	19.4	16.4
Density, g.p.c.c.	1.85	2.08	2.00
Apparent specific gravity	2.67	2.59	2.48
Cold crushing strength	1940	2500.	6050
Permeability	0.011	0.028	0.071
Linear change on firing per cent.			
2 Hours at 1410°C.	+6.5	0.0	+0.3
Cone melting point, °C.	1580	1700	1750
Refractories-under-load-50 lb per.sq.in.rising temperature test.-			
Initial deformation	1150	1500	1300
Rapid deformation	1270	1550	1540
Shear or 10% collapse	1410,	1600	1610
Thermal shock resistance	4	30+	30+

* After Chesters-J.H. - SteelPlant Refractories, p.175-176, London, 1944.



Note — Graph based on value of total deliveries

UNION OF SOUTH AFRICA

FIREBRICK CONSUMERS

1947

FD 37

minimum P.C.E. of Cone 32. They may not show more than 0.75% linear change when subjected to the 1410°C. reheat test for two hours.

Super Duty: Such firebrick in this classification must not have a P.C.E. value less than Cone 32. In the reheat test conducted at 1600°C. for two hours they must not show more than 1.0% linear change.

PROPERTIES OF SOUTH AFRICAN CLAY REFRACTORIES

The properties of some South African clay refractories are tabulated in Table XX. These materials compare very favourably with the foreign products, also included in the table.

CONSUMER INDUSTRIES

The graph given in Fig. 37 shows the relative percentage of total deliveries of domestic production to principal clay refractory consumers in the Union in 1942, based on estimates from private data.

Iron and Steel

The iron and steel industry located at Pretoria and in the Vaal Basin at Vereeniging and Van der Bijl Park is the largest consumer of clay refractories. Requirements for these commodities are so important that both ISCOR and USCO maintain an active programme of co-operative research and development with domestic manufacturers. The iron blast furnace and accompanying stoves are large consumers of refractories, a modern installation consuming up to a million brick and strong efforts are being made to obtain all future requirements locally. Cupolas and heat treating furnaces are also important users of clay refractories. Casting pit refractories including lining for steel melting ladles and nozzles, stoppers, and sleeves which are used in the ladle assembly are important consumers of refractory goods. Clay refractories are also used in electric furnace roofs for the manufacture of special steels, in soaking pits, and billet heating furnaces.

Non-Ferrous Metallurgy

Gold industry: Clay refractories in the form of assay ware are used in large quantities in the gold industry. Clay refractories are also used in the refining process both in the form of crucibles and liners, and for the construction of refining furnaces.

Copper industry: Condensers and retorts used in zinc distilling furnaces are made of refractory clays and fireclay refractories are used in smelting furnace sidewalls.

Lead industry: The upper parts of lead refining furnaces are lined with fireclay brick.

Aluminium industry: Fireclay linings are employed in aluminium melting furnaces.

Power Generation

Boiler furnaces used in the production of power from coal are one of the major outlets for clay refractories in the Union. A popular type is the B. & W. cross drum boiler with chain grate stoker. In this case the boiler furnace is lined with high duty brick and the remainder of the setting is generally in normal quality fireclay brick. The sugar industry in Zululand employs various types of boilers designed to use bagasse(spent sugar cane)for fuel all of which are lined with fireclay refractories.

Other Uses

Ceramics industry: Clay refractories are used in large amounts for the construction of periodic and continuous kilns for the manufacture of clay products. They are also used for the production of saggers and kiln furniture.

Glass industry: The glass industry uses special types of clay refractories in the form of large blocks for lining the melter and refiner sections of the glass furnace. Clay refractories are also used in breast walls, port jambs and sills, port wall sides, port crown, port paving, mantle black, regeneration wall crown, checkers, tuckstoves, skimmers, plugs, and troughs.

Lime and cement industry: Clay refractories are used in the construction and lining of shaft and rotary lime kilns and portal and cement kilns.

Gas production: By-products coke ovens use clay refractories in the foundation mat, main flues, checkers, certain walls, oven chamber floors over roof ends, charging holes, jamb, blocks, and top mat.

Incinerators: Incinerators are constructed mainly from fire-clay refractories.

Enameling: Enamel furnaces and frit furnaces have clay refractories incorporated in their constituents.

Railways: Locomotive arch tiles are important installations of clay refractories.

Chemical industry: Various furnaces for use in the chemical industry use clay refractories in their constituents.

FUTURE OF THE CLAY REFRACTORIES INDUSTRY

Attention is constantly focused on the production of better quality materials and new types of refractories. Improved techniques and advances in research and development can be expected to keep the domestic industry up-to-date. New methods will effect improvements in making and burning. The emphasis is becoming more pronounced on the part of manufacturers in the desirability of producing refractories to suit the individual needs of consumers and this condition is expected to continue. The refractory specialty products--plastics, mortars, and castables--will increasingly displace burned refractories and with further advances in installation techniques will lead to a new era of technical development in the industry.

BIBLIOGRAPHY

1. Wagner, P.A.: An interesting outlier of Karroo rocks to the north of Olifantsfontein station, on the Germiston-Pretoria railway. Trans. geol. Soc. S. Afr., Vol. 19, pp. 36-45, July, 1916.

2. Holford, W.G.: Discussion on paper by Dr. P.A. Wagner, "An interesting outlier of Karroo beds to the north of Olifantsfontein". Proc. geol. Soc. S. Afr., Vol. 19, pp. XLVIII-L, Sept., 1916.

3. Rosazza, V.L.: Clays of the Witwatersrand and adjoining areas. Mem. Min. Res. Lab. S. Afr., No. 2, 109 p., 1941.

4. Rosazza, V.L.: The petrography and petrology of clays. Lund, Humphries, & Co., London. 313 p., 1946.

5. Ahrens, L.H.: Trace elements in clays. S. A fr. J. Sci., Vol. 41, pp. 152-160, 1945.

6. Warde, J.M., and Denysschen, J.H.: Differential thermal analysis of some South African refractory clays and other ceramic raw materials. Proc. geol. Soc. S. Afr. (Accepted for publication.)

7. Molengraaff, G.A.F.: Geology of the Transvaal. Johannesburg, 1904.

8. Mellor, E.T.: The Geology of the Transvaal Coal Measures with Special Reference to the Witbank Coal Field. Mem. 3, Geol. Sur. of the Transvaal. 60pp., 1906.
   a. p. 16, p. 48
   b. p. 53

9. Du Toit, A.L. The Geology of South Africa.: Oliver and Boyd, Edinburgh. 539 pp. 1939.
   a. p. 318-319
   b. p. 233
   c. p. 237
   d. p. 245
   e. p. 252
   f. p. 253
   g. p. 313
   h. p. 312-313

10. Hamilton, G.N.G., and Cooke, H.B.S.: Geology for South A frican Students. Central News Agency, Johannesburg. 240p., 1939.

11. Mineral Resources of the Union of South Africa: Dept. of Mines, Pretoria. 544pp. 1940.

12. Corstorphine, G.S.: --- S.A.A.A. S.C., p. 145, 1904.

13. Wynaston, H.: The geology of a portion of the Bushveld north of Pretoria, explanation of sheet no. 2, Pienaar's River. Transvaal Mines Dept., 28 pp., 1907.

31. Hofman, U., Endell, K., and Wilm, D.: Crystal structure and swelling of montmorillonite and halloysite. Ztschr. Kristal., Vol. 102, pp. 417-431, 1940. (German)

32. Marshall, C. E.: Soil science and mineralogy. Proc. Soil Science Soc. America, Vol. 1, pp. 23-31, 1937.

33. Salmang, Hermann: Physical and chemical principles of ceramics. Verlag Julius Springer, Berlin, 1932, pp. 8-10. (German)

34. Ries, H.: Clays, Occurrence, Properties, and Uses. p. 76, 1927.

35. Norton, F.H.: Critical study of the differential thermal method for the identification of the clay minerals. J. Amer. Ceram. Soc., Vol. 22, pp. 54-63, 1939.

36. Berkelhamer, L.H.: Differential thermal analysis of quartz. U.S. War. Mines. Rept. Inv., 3763, 1944., 18 p.

37. Grim, R.E., Machin, J.S., and Bradley, W.F.: Amenability of various types of clay minerals to alumina extraction by the lime sinter and lime soda sinter processes. Bull. 69, State Geological Survey, Urbana, Ill., 1945, pp. 11-12.

38. Caillere, S., and Henin, S.: New observations on the differential thermal analysis of kaolinite. Comp. rend., 209, pp. 694-699, 1939. (French)

39. Orcel, J.: Differential thermal analysis in the determination of the constituents of clays, laterites, and bauxites. Cong. Internat. Mines, Met. Geol. Appl. 7th Sess., Paris, 1935., pp. 273-293. (French)

40. Insley, H., and Ewell, R.H.: Thermal behavior of kaolin minerals. Nat. Bureau of Standards Jour. Research, Vol. 14, pp. 615-627, 1935.

41. Fitel, W.: Electron microscope and its application to problems in ceramics. Ber. deut. Keram. Ges., 24, 37-53, 1943. (German)

42. Hyslop, J.F.: The decomposition of clay by heat. British Ceram. Soc. Trans., Vol. 42, pp. 49-51, 1944.

43. Caillere, S., Henin, S., and Terc, M.: Research on the differential thermal analysis of clays. Comp. rend., Vol. 208, pp. 383-384, 1940. (French)

44. Frederickson, A.F.: Mineralogy of a drill core of Arkansas bauxite. Unpublished thesis for Ph. D., Massachusetts Institute of Technology, 1947, 101 p.

45. Speil, A.: Applications of thermal analysis to clays and aluminous minerals. U.S. Bureau of Mines Tech. Paper 664, 1945, pp. 33-55.

46. Sosman, R.B.: The properties of silica. Chemical Catalog Co., New York, 1927.

47. Keller, W.D., and Westcott, J.F.: Differential thermal

analysis of some Missouri fire clays. J. Amer. Ceram. Soc., Vol. 31, pp. 100-105, 1948.

48. Norton, F.H.: Analysis of high-alumina clays by the differential thermal method. J. Amer. Ceram. Soc., Vol. 23, pp. 261-282, 1940.

49. Kerr, P.F., and Kulp, J.L.: Multiple differential thermal analysis. Amer. Min., Vol. 33, pp. 387-419, 1948.

50. Cuthbert, F.L., and Rowland, R.A.: Differential thermal analysis of some carbonate minerals. Amer. Min., Vol. 32, pp. 111-116, 1947.

51. Grim, R.E., and Rowland, R.A.: Differential thermal analysis of clay minerals and other hydrous materials. Amer. Min., Vol. 27, pp. 54-63, 1939.

52. Grim, R.E.: Relation of the composition to the properties of clays. J. Amer. Ceram. Soc., Vol. 19, pp. 141-151, 1939.

53. Norton, F.H.: Refractories. McGraw-Hill, 1942, 798 p.

54. Card, F.J.: Quantitative mineral analysis with a recording X-ray diffraction spectrometer. Amer. Min., Vol. 32, pp. 508-517, 1947.

55. Brindley & Robinson: The structure of kaolinite. Mineral Mag., Vol. XXVII, p. 242, 1946.

56. Buerger, M.J.: An X-ray powder camera. Amer. Min., Vol. 21, pp. 11-17, 1936.

57. Humbert, R.P.: Particle shape and the behavior of clay as revealed by the electron microscope. Jour. Amer. Ceram. Soc., Vol. 21, pp. 260-263, 1942.

58. Mitchell, L., and Henry, F.C.: Nature of Georgia kaolins. J. Amer. Ceram. Soc., Vol. 26, pp. 105-109, 1943.

59. Sharpett, F., and Francis, W.: The organic matter of ball clay, part I. Trans. Brit. Ceram. Soc., Vol. 42, pp. 111-121, 1943.

60. Taksman, S.W.: --- Soil Science, Vol. 30, p. 97, 1930.

61. Tschotschwilli, T., Bussem, W., and Peyl, F.: Beta-kaolin. Ber. deut. Keram. Ger. 20 (6) 249-76, 1939. (German)

62. Mitchell, L.: Mineral and colloidal constitution of some Georgia kaolins. Thesis for Ph.D., Penn. State Coll., 1941.

63. Goldschmidt, V.M.: The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc., pp. 655-673, 1937.

64. Goldschmidt, V.M.: Geotherine and the cycle of sediments; ionic potential. Soil Science, Vol. 62, 1946.

65. Krumbein, W.C., and Pettijohn, F.J.: Manual of sedimentary petrography. 549 p. 1938.

66. Graham, R.P., and Sullivan, J.D.: Critical study of methods

of determining exchangeable bases in clays. J. Amer. Ceram. Soc., Vol. 21, 5, p. 176, 1939.

67. Holdridge, D.A., and Francis, W.: Studies on base exchange phenomena in clays and ceramic materials. Trans. Brit. Ceram. Soc., Vol. 47, pp. 131-154, 1948.

68. Verde, J.M.: Clays of the Eocene formation in Montana. Unpublished thesis for M.S. degree, Montana School of Mines, 1937.

69. Grim, R.E., and Bradley, W.F.: Investigation on the effect of heat on the clay minerals illite and montmorillonite. J. Amer. Ceram. Soc., Vol. 23, pp. 242-249, 1940.

70. Barker, G.J., and Truog, Emil: Improvement of stiff-mud clays through pH control. J. Amer. Ceram. Soc., Vol. 21, 9, pp. 324-330, 1938.

71. Barker, G.J., and Truog, Emil: Factors involved in improvement of clays through pH control. J. Amer. Ceram. Soc., Vol. 22, 9, pp. 309-312, 1939.