

**LINKS BETWEEN GEOCHEMICAL AND
ENGINEERING PROPERTIES IN WEATHERED
PYRITIC SHALES**

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properties in weathered pyritic shales

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SUMMARY

Natural weathering systems and resultant changes in the engineering properties of weathered rocks cannot be analysed in detail due to their inherent complexity. However, laboratory simulation of natural reactions under controlled conditions facilitates identification of specific factors which may contribute to changes in the physical behaviour of weathered rocks.

Experiments in which the Carboniferous Edale Shale was reacted with sulphuric acid of a concentration commensurate with that generated under natural conditions showed that the acid composition was markedly altered. Furthermore, the acid composition became qualitatively similar to that observed in a natural shale weathering system by Vear & Curtis (1981). Natural reactions may thus be reproduced in the laboratory.

The influence of pore solution composition on the residual shear strength and plasticity properties of Edale Shale were investigated using KNO_3 , NaNO_3 , acid and groundwater from a major landslip at Mam Tor, Derbyshire. These engineering properties were found to be sensitive to porewater composition and concentration.

The effects of physical breakdown on rock properties are less easy to assess because standard techniques for measuring grain size distributions, particularly the $< 2 \mu\text{m}$ size fraction are unreliable for indurated rocks. A statistical correlation between the $< 2 \mu\text{m}$ fraction and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was found to give a better estimate of the amount of fine material present in a sample. Using this method it was determined that rapid physical weathering does not reduce consolidated material to its fundamental grain size. In addition, residual shear strength and plasticity were found to be independent of the state of physical breakdown and are apparently influenced more strongly by mineralogy.

The implications of these investigations to slope stability are considered for the case of a major rotational landslip at Mam Tor, Derbyshire. Finally, a model is proposed in which weathering is divided into distinct components, each capable of separate investigation.



Approach to Mam Tor, June 1983

"Landslide refers to the statistical fact of a vote count; landslip has to do with the movement of mountains."

The Times - pre-Election period, June 1983

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CHAPTER I

INTRODUCTION

Together with other varieties of mudrock, shales are among the most commonly encountered rock types in engineering operations. Kuenen (1941) estimates that these rocks occupy about one half of the stratigraphical column. Shales frequently form the foundation materials for buildings, bridges, tunnels, dams and in embankments and cuttings. They are also a common source of backfill material in construction work and are a significant component of colliery spoil due to their close association with coal seams.

The engineering behaviour of shales varies widely and each formation presents its own challenge. The types of problems encountered with shales are summarised by Bell (1980). They include slaking, which is the tendency of shales to break up in water, rapid physical disintegration and low strength, particularly in the presence of high moisture contents. Shales are characterised by anisotropy with regard to strength, deformation and permeability due to their property of fissility. Swelling is also a common occurrence and is caused in a number of ways, for example, by rebound after unloading, or due to water uptake by certain minerals. The growth of secondary minerals within the rock structure also induces swelling as a result of pyrite oxidation and the subsequent formation of sulphate minerals including gypsum and jarosite.

1.1 Examples of engineering problems

There are many examples of ways in which the problems presented by shales have created major difficulties in engineering.

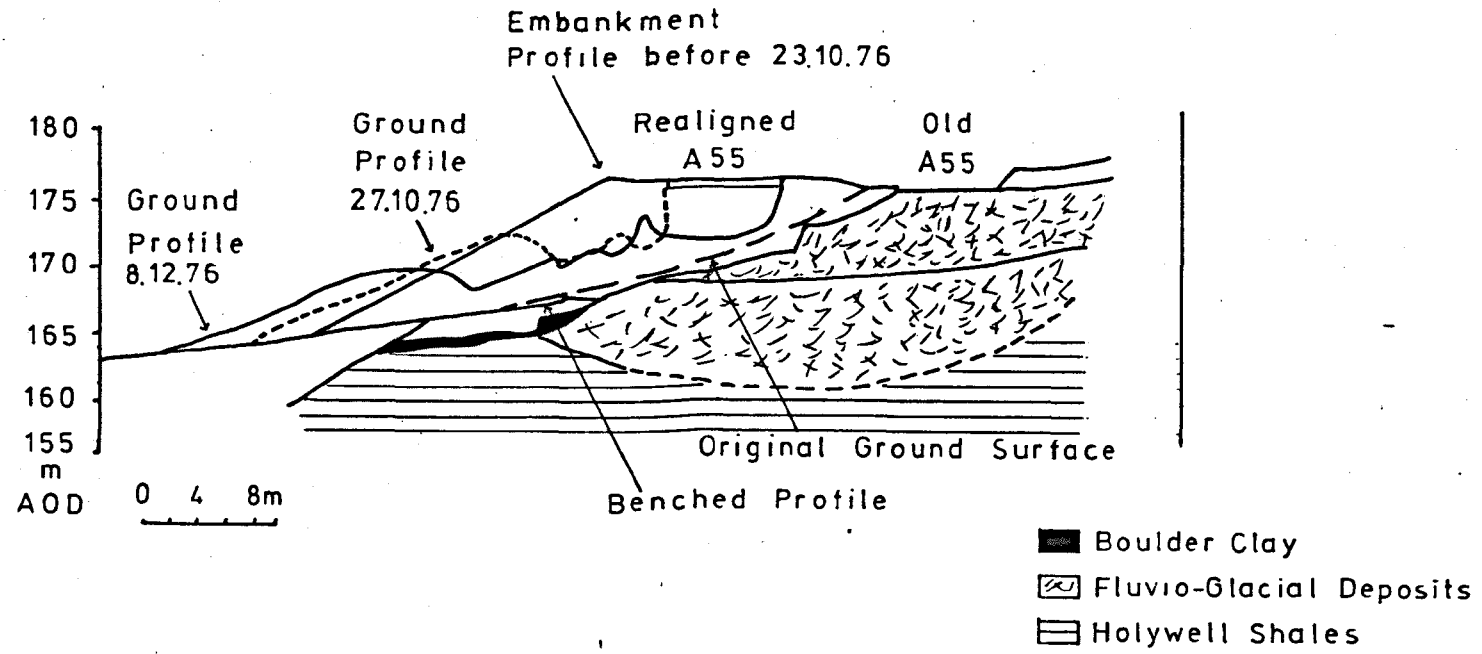
1.1.1 Physical disintegration

The tendency of certain shales to disintegrate physically on exposure to air and water has created difficult conditions for a number of building projects. Twort (1964) reported on the behaviour of shale during construction of the Tittesworth Dam in Yorkshire with particular regard to frequent collapse during tunnel driving. The soft, blue, finely laminated and thinly bedded material rapidly reverted to 'clay' in the presence of moisture and significant disintegration was experienced over periods of only one week, continuing as moist air penetrated bedding and newly exposed joints. Instant support and covering of exposed shale by concrete was required as tunnelling proceeded.

Nakano (1967) discovered that landsliding in Tertiary mudstones of Japan was related to their slaking properties and that mudstones easily deteriorated within the zone of fluctuating water vapour or groundwater levels, particularly within fracture zones. Hepworth (1965) considered that the capacity of shales to swell and slake was enhanced by the chemical and mechanical effects of gypsum formation within the material.

The physical degradation of shales may have extended effects. Fleming et al. (1970) described movements at the Point Lookout Landslide in Mesa Verde National Park, Wyoming, where about 613 m of thinly bedded, silty Mancos Shale with sandstone layers and limey concretion zones is overlain by sandstone in a flat topped spur. The shale disintegrates rapidly in the presence of water to the extent that about 18 m of colluvium now covers the slope. Slides occur at the contact between colluvial material and intact shale. Continuous weathering and disintegration steepen the slope until the angle of shearing resistance of the weathered material is reached and slides are then triggered when water levels are high. Eventually, the overlying sandstone is undermined and block failures are initiated as support is removed.

FIG. 1.1 Cross-section through slip - Subramaniam & Carr (1983)



1.1.2 Low strength

Low shale strength and evidence of strength reduction by weathering are frequently blamed as a cause of slope failure. Subramaniam & Carr (1983) give an account of a road embankment on the A55 Chester to Bangor trunk road at Pwll Melyn, 2 km S.E. of Holywell, Clwyd. The embankment failed seven years after construction for realignment work. A shear surface was identified comprising very soft light grey and yellow-brown clay between 5 and 25 mm thick at the top of the Holywell Shales and immediately below boulder clay (Fig. 1.1). The failure involved slipping at the interface between the glacial deposits and the completely weathered top of the shales with the failure surface extending up through glacial material and embankment fill.

The stability of the embankment was judged to be controlled by the weak weathered shale at the interface together with the porewater pressures on the failure surface. The process of progressive failure may have occurred, initiated by earlier movements which resulted in cracking. It is perhaps worth noting here that Pwll Melyn may be so called as a result of iron oxides deposited in the pool derived from weathering solutions which have passed through the Holywell shales. Similar deposits occur in streams and ponds where mudrocks or iron-rich deposits are weathered, for example, in Namurian shales at Mam Tor (Vear 1981) and Parys Mountain, Anglesey.

Prior & Graham (1974) made a study of shallow rotational slides in Carboniferous 'Calp' shales in the Magho district of County Fermanagh, Northern Ireland. In this area, the slides are responsible for considerable road damage for a distance of 3 km on the Enniskillen to Belleek road and they occur in strata comprising limestone underlain by Lower Carboniferous shales. The rate of movement of the slides are not cer-

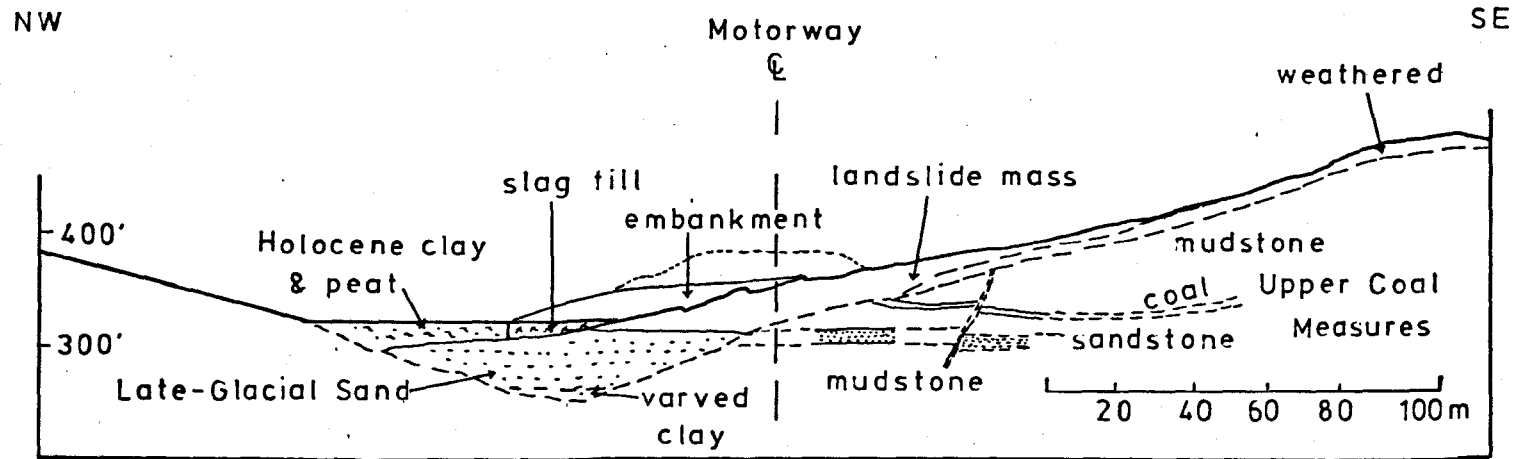


FIG. 1.2 Geology of the landslide mass - Walton's Wood, Staffordshire (from Early & Skempton 1972).

tain but they are known to occur sporadically. They are typically less than 2 m in depth and the base of each scar is defined by slickensided plane surfaces at inclinations between 23° and 29° . One particular slide was investigated in detail where soft fissured clay overlay hard stratified Calp shale with a single pronounced shear plane at a depth of 80 cm. The failure surface was confined to a relatively thin layer of clay about 1 cm thick and coloured grey/blue in contrast to the grey/brown of material above and immediately below the slip plane. Intact clay shale was encountered only a few centimetres below the shear zone. The shales weather to a clay-rich soil and it was considered that slope stability in this material was dependent on a reduction in strength as a result of weathering.

1.1.3 Strength reduction along ancient slip planes

In their classic paper on the landslide at Walton's Wood, Staffordshire, Early & Skempton (1972) described how slopes in mudstones of the Upper Coal Measures had suffered landslipping and rapid weathering. The slopes had been oversteepened by erosion of an ice marginal drainage channel during the retreat stage of the last (Weichselian) glaciation. Over steepening occurred to such an extent that final equilibrium was not attained by 1961 when construction of a motorway embankment was started. Failure of the partially built embankment occurred with maximum rates of movement of about 5 cm per month.

The landslide had a width of 300 m and extended about 200 m up the hillside from its toe to the highest scarp. The geology of the site is shown in Fig. 1.2. The landslide mass, or colluvium, attained a maximum thickness of 10 m and consisted of fragments of mudstone, sandstone and coal. At the top of the hillside weathering of the rocks was visible to a depth of roughly 3 m. In borings and trial pits, slip surfaces were

identified by their polished and striated appearance. It was inferred that movements had occurred on an old slide surface.

The clay in the immediate vicinity of these zones had a light grey colour in contrast to the adjacent yellow-brown clay with orange mottling. This colour change was attributed to secondary chemical development due to reducing waters percolating along the slip zone. Chemical analyses revealed a marked reduction in Fe_2O_3 content along the shear zone compared to that in the ambient clay; the values obtained as weight percent oxides were 2.5% and 11.9% respectively. No changes in clay mineralogy across the slip surface were observed although a higher percentage of clay-size material ($< 2 \mu\text{m}$) was recorded. The last property probably indicates that clay aggregates had been broken down during displacement of the landslide. However, Taylor (1973), in a further consideration of possible secondary chemical reduction along the slip plane, suggested that under such conditions, clay mineral changes towards kaolinite could be occurring. Such changes are unlikely to be detected by X-ray diffraction even if kaolinite increased by about 10% at the expense of illite and mixed layer clay. The possibility of clay mineral alteration was supported by a decrease in the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio from 0.092 in ambient clay to 0.068 in the shear zone (Early & Skempton 1972, Table 1, p.105) which was said to be symptomatic of K^+ leaching from illite and mixed layer clays.

The problems reviewed in sections 1.2 and 1.3 were remedied by excavation of the softened, weathered material and founding the new structure on sound bedrock.

1.1.4 Rebound and weathering

Swelling and rebound have been found to cause problems during construction work. Bjerrum (1967) studied the Culebra slides which occurred during excavation of the Panama Canal in 1907-15. The most dramatic problems

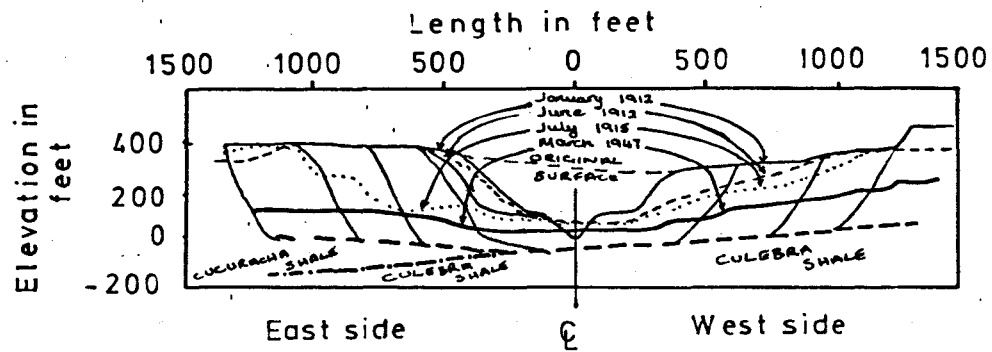


FIG. 1.3 Gradual development of East and West Culebra slides, from Bjerrum (1967) after Binger (1948)

apparently arose in excavations 92.3-123.1 m deep in the Gaillard cut which involved disturbances to the montmorillonitic Cucaracha Shale (Fig. 1.3). The most massive slides were termed breaks and continued to move for about 19 years. These were characterised by heaving of the cut bed and coincided in time with nearly vertical subsidence of the area at the upper boundary of the slide. Simultaneous movement of material between the cut and upper boundary was nearly horizontal. Sliding was thought to be initiated by a local massive failure in unweathered clay below the excavation due to a horizontal expansion of the clay and progressive development of a horizontal slip plane.¹

Fleming *et al.* (1970) have made extensive studies on a number of major engineering projects in shale materials which have involved failure at some time during construction work. In their account of the Oake Dam project on the Missouri River, they described two slides, both in Cretaceous Pierre Shale which is a thinly bedded, dark-grey to black, over-consolidated clay shale with thin layers of bentonite. It is covered with about 30.8 m of valley fill above the floor of the river trench. Upon weathering, the bentonite swells and the shale is reduced to a 'gumbo clay'. These processes occur rapidly and the volume increases result in generally weaker zones. Fault gouge and slickensided areas are affected similarly. It was anticipated that slope stability is controlled mainly by the strength of the weak zones, particularly along the randomly distributed, closely spaced faults. Other factors were thought to contribute to instability including long term reservoir seepage, an irregular distribution of weak zones and the activity of certain component clay minerals when exposed to water. In both instances, weathered shale was removed in order to found the structure in firm unweathered material.

¹ It is also possible that slip plane development was structurally controlled.

Fleming et al. (1970) also reported slides which interrupted the building of the Gardiner Dam on the south Saskatchewan River. These took place in Bearpaw Shale, an Upper Cretaceous formation which had been heavily compressed under 769 m of overburden prior to the Pleistocene Glaciation. The overburden was removed during glacial activity and rapid vertical elastic rebound was instigated accompanied by swelling due to water uptake. The latter process is still occurring. The river banks are scarred by slumping from the post-glacial period, but gradual creep in the soft zone still takes place. This progressive reduction in strength was attributed to softening due to successive wetting, drying, freezing and thawing activity, particularly when combined with expansion of shale within weathered 'chunks'. Creep movements in the soft near-surface material were thought to remould soft shale and to open additional joints. Major movements were probably initiated by radical imbalances in stresses created by toe erosion, loading and unloading during construction operations and high water contents. Smaller, localised failures were also triggered during embankment building and excavation activity. The planes of movement were invariably in the soft shale zone and at some localities within a bentonite layer. Many of the affected areas were removed immediately by excavation.

1.1.5 Salt precipitation

Rock swelling due to secondary mineral precipitation has been commonly observed in shales that have been recently exposed. The types of problems experienced involve uplifting of floors beneath buildings founded in shales or on shale fill. Nixon (1978) described a series of failures of the ground floor slabs of new houses in the Teesside area which were founded on local sources of shale fill. Lifting of the floors, interior walls and pushing out of external walls was reported; in some

cases movements of several centimetres were found. The timescale on which the problems became serious were short, of order 5 years. The shale associated with the failures was found to be extensively weathered, soft and laminar with gypsum crystals abundant on the shale surface and along laminae; jarosite was also identified. Detailed examination of the shales revealed that floor heave resulted from the oxidation of pyrites and the subsequent formation of secondary minerals. The volume increases which accompanied the transformation of pyrite into other minerals, namely gypsum and jarosite, accounted for the swelling experienced in the bedrock.

Grattan-Bellew & Eden (1975) gave a detailed account of the causes of extensive heaving in the basement floor of a church founded on the black, carbonaceous Eastview Shale in Canada. The church was built in 1913 and had to be repaired 15-20 years later. Investigations of the foundation material discovered that the concrete in the basement had been reduced to a mushy consistency and the top 4 cm of shale were badly weathered with abundant gypsum. Although material about 1 m below the floor was competent, gypsum and a little jarosite were seen along joints and bedding planes. Calcite veins were also present within the unweathered shale. Pyrite in the affected mass was very fine grained which was felt to be conducive to bacterial acceleration of pyrite oxidation. The production of sulphuric acid from pyrite oxidation was important and, furthermore, self-perpetuating since the residual acid after gypsum generation reduced the pH of the shale to a value of 3 which encouraged bacterial growth and continued oxidation reactions. An important observation at this particular site was that the conversion of calcite to gypsum did not necessarily occur at the location of gypsum crystallisation since calcium sulphate may be transported in solution by capillary action.

Migration of gypsum to sites of crystallisation was considered to be restricted initially to areas of maximum heave where the pressure gradient, opposing crystal growth, was lower. The deterioration of under-floor concrete was thought to result from acid dissolution of the cement from between aggregate particles leading to void creation. Disintegration in this manner is apparently caused in most cases if a slab is immersed in sulphate solution or when solutions are drawn through a slab due to evaporation on one side. In the example quoted here, however, disturbance took place well above the water table, thus it demonstrated a need to minimise contact between bedrock and concrete in buildings on shales where sulphates are likely to be hazardous. Alternatively, sulphur resistant concrete should be used.

Bell (1978) also discussed reactions which occur where calcium sulphate forms in the vicinity of Portland cement. Tricalcium aluminate in the cement can react with calcium sulphate to produce ettringite which has a greater volume than the aluminate and therefore causes breakdown of the cement.

Heave phenomenon attributable to gypsum formation in shales beneath buildings have also been reported by Quigley & Vogan (1970) and Penner *et al.* (1966). Thiobacillus and Ferrobacillus bacteria were found to aid pyrite oxidation. Remedial proposals recommended submerging the bedrock during building operations in order to exclude oxygen or to maintain a water-tight coating with asphalt to prevent access of oxygenated waters (Bérard, 1970).

1.2 Links between engineering problems and geochemical properties

The nature of these diverse problems suggests that there is a link between the geochemical properties of shales and their engineering behaviour. This is particularly true for shear strength, swelling and

	Yaalon (1961)	Shaw & Weaver (1965)	Spears & Amin (1981)
Shale	Average for a number of analyses	Average of 400 samples	Carboniferous Mam Tor Beds
Quartz	20%	30.8%	22.1%
Feldspar	8%	4.5%	3.5%
Clay minerals	59%	60.9%	35.7%
Carbonates	7%	3.6%	9.8%
Fe oxides	32%	< 0.5%	-
Organic matter	1%	1.0%	5.3%
Other minerals	2%	< 2.0%	3.6%

TABLE 1.1 The average mineral composition of shale

salt precipitation. If this is the case then an understanding of the geochemical properties will assist in predicting the likely behaviour of a formation under particular physical and chemical conditions. Implementation of preventive measures rather than remedial action after failure would appear to present a more practicable and economical approach where disturbance to natural systems is incurred.

Unfortunately, natural shale-water systems are difficult to analyse owing to the inherent complexity of this rock type in terms of chemical composition, structure and reactivity in the weathering environment. However, controlled investigations in the laboratory may provide valuable information on the rates and nature of chemical reactions which occur in the field. Even if complete natural systems cannot be simulated it is still helpful to take components and individual problems for separate investigation. The effects of chemical activity on specific physical properties of materials can also be studied under laboratory conditions.

1.3 Shale properties

1.3.1 Definition of shale

The term shale does not appear to hold a universally accepted meaning within engineering practice and the discrepancy between geological and engineering terminology is even more confusing. The lack of agreement probably arises from the complex composition, appearance and behaviour of shales resulting from their geological history.

Table 1.1 gives some average mineralogical compositions for various shales. Briefly, the main components are clay minerals, including illite, smectites, kaolinite and some chlorite, with large quantities of quartz. Other, less abundant constituents include feldspars, carbonates, organic matter and varying quantities of iron oxides.

These minerals are laid down in low energy, aquatic conditions in deep or shallow water. They are mainly related to deltaic and turbidite deposition on and near continents and to deep ocean environments where they are deposited from suspension. Shales are therefore nearly always marine and of fine grain size, typically with 50% of the components less than 62 μm in size (Potter et al. 1980). These authors give four major settings of ancient shales, shelf-to-basin transitions, rifts, island arcs and deep oceans and consider that these account for 80-90% of ancient shale occurrences. Other suitable conditions are found in lakes, alluvial valley fills formed by meandering river systems and in low energy deltas.

Small changes in sedimentation conditions, such as fluctuations in sediment supply, water chemistry or resuspension and settling during storms or floods, produce a laminated sediment. Post-deposition diagenesis within the muds then results in the formation of other minerals, such as pyrite and siderite, depending on the chemical environment. The importance of lamination and diagenetic processes are discussed in Chapter 2.

During subsequent burial, often to considerable depths of thousands of metres (Powers 1967), mineralogical and physical changes occur in response to the increased temperatures and pressures. Under intense compaction, components of platy habit, such as clay minerals and organic matter, become oriented. The sediment thus obtains anisotropic characteristics with regard to strength and permeability.

During erosion of the overburden, the large stresses imposed on the underlying shales are gradually released. As a result of burial and uplift, most shales are overconsolidated which is defined by Fleming et al. (1970) as a condition in which the existing overburden or load is less than the load at which the material was consolidated. Shales which have not experienced overburden pressures greater than present-day pressures are normally-consolidated. Underconsolidated (overpressured) shales occur

	Composition	Fissile	Non-fissile
After Blatt et al. (1972)	> $\frac{2}{3}$ silt	Silt shale	Siltstone
	> $\frac{1}{3}$ < $\frac{2}{3}$ clay	Mud shale	Mudstone
	> $\frac{2}{3}$ clay	Clay shale	Claystone
After Spears (1980)	> 40% quartz	Flaggy siltstone*	Massive siltstone
	30-40% quartz	Very coarse shale	Very coarse mudstone
	20-30% quartz	Coarse shale	Coarse mudstone
	10-20% quartz	Fine shale	Fine mudstone
	< 10% quartz	Very fine shale	Very fine mudstone

*following McKee & Weir (1953)

TABLE 1.2 Classification of shales

where high porewater pressures are developed during deep burial due to compaction dewatering in the presence of a permeability barrier, which inhibits upward fluid migration (Weaver and Beck, 1971).

When exposed at the surface, shales are subjected to weathering and develop their characteristic fissility, which is defined by Spears (1980) as the property of splitting or separating along approximately parallel surfaces in the plane of bedding.

Geologically speaking, shales are fine grained sediments containing silt and clay-sized material ($< 63 \mu\text{m}$) in varying proportions. In a number of classifications they are included under the general heading of mudrocks, e.g. Pettijohn (1975), Blatt *et al.* (1972) and McKee & Weir (1953). The term mudrock was described by Spears (1980) as embracing all fine-grained, lithified sediments. Shales are mudrocks which are distinguished from other members of the group by their fissility. Non-fissile mudrocks are called mudstone, siltstone or claystone depending on their silt-clay proportions (Table 1.2).

For ancient, well-lithified rocks in which grain size distributions are difficult to measure reliably, other classification parameters may be more useful. Stow (1981) considered that the classification based on quartz percentages which was proposed by Spears (1981) for Coal Measures rocks (Table 1.2) is particularly appropriate for such instances. The fissile/non-fissile division is still incorporated.

Geological definitions, however, in requiring that shales possess the characteristic of fissility do not convey any meaning to the engineer who classifies materials in terms of appearance and mechanical properties (Geological Society Engineering Group, 1970). Peterson, quoted in Johnson (1969) described shale as: "uncemented bedrock containing a high proportion of illite and montmorillonite, which has been overconsolidated and breaks down on weathering to form a clay". Bjerrum, also in Johnson

(1969), concurred that a high degree of overconsolidation is a characteristic feature of clay shales. If this condition is satisfied he proposed that:

- (a) clay without cementation should be termed overconsolidated clay;
- (b) weakly cemented material should be referred to as clay shale;
- (c) strongly cemented material should be called shale.

To the latter recommendation, Taylor, in the same discussion of Johnson (1969), concluded that the characteristic of high overconsolidation was common to all engineering definitions of shales. Cripps & Taylor (1981) noted, however, that on a strictly geological basis no distinction is drawn between mudrocks and overconsolidated clays. The current British Standard code of practice for site investigations¹ recommends that the term mudstone should obtain to lithified, homogeneous argillaceous rocks and that shale should be used if the constituents of the mudrock are laminated or fissile on the bedding planes.

The nomenclature problem is indeed complex and clearly in need of clarification. A recent paper by Stow (1981) has attempted to define mudrocks in terms acceptable to both geologists and engineers. This is a timely contribution which hopefully reflects improved interdisciplinary communication. He advised that the terms should be simple and readily applied in the field, using the results of more detailed laboratory or field analyses to provide descriptive modifiers. His classification incorporates basic terms based on a siliciclastic composition and still maintains the fissile/non-fissile division. Additional classes using metamorphic terms, textural descriptors and composition descriptors, such as carbonate mudrocks are included. The terminology is shown in Table 1.3.

In this work the classification of Stow (1981) is adopted and the term shale is intended to describe a lithified, fissile mudrock.

¹ British Standards Institution. Site Investigations. CP 2001 : 1957

Mudrock (> 50% siliciclastic, > 50% less than 63 μm)

Basic terms

Unlithified	Lithified/non-fissile	Lithified/fissile	Approximate proportions/ grain size
<i>Silt</i>	<i>Siltstone</i>	<i>Siltshale</i>	$> \frac{2}{3}$ 4-63 μm (<i>silt</i>)
<i>Mud</i>	<i>Mudstone</i>	<i>Mudshale</i>	< 63 μm (<i>mixture</i>)
<i>Clay</i>	<i>Claystone</i>	<i>Clayshale</i>	$> \frac{2}{3}$ < 4 μm (<i>clay</i>)

Metamorphic terms

<i>Argillite</i>	<i>Slightly metamorphosed/non-fissile</i>	<i>Silt & clay mixture</i>
<i>Slate</i>	<i>Metamorphosed/fissile</i>	<i>Silt & clay mixture</i>

Textural descriptors

	Approximate proportions
<i>Silty</i>	$> 10\%$ <i>silt size</i>
<i>Muddy</i>	$> 10\%$ <i>silt or clay size (applied to non-mudrock sediments)</i>
<i>Clayey</i>	$> 10\%$ <i>clay size</i>
<i>Sandy, pebbly etc.</i>	$> 10\%$ <i>sand size, pebble size etc.</i>

Compositional descriptors

	Approximate proportions
<i>Calcareous</i>	$> 10\%$ CaCO_3 (<i>foraminiferal, nannofossil etc.</i>)
<i>Siliceous</i>	$> 10\%$ SiO_2 (<i>diatomeaceous, radiolarian etc.</i>)
<i>Carbonaceous</i>	$> 1\%$ <i>organic carbon</i>
<i>Pyritiferous</i>] <i>commonly used for contents greater than about 1-5%</i>
<i>Ferruginous</i>	
<i>Micaceous & others</i>	

TABLE 1.3 Mudrock terminology - from Stow (1981)

1.3.2 General engineering properties of shales

Attewell and Farmer (1976) regard shales as intermediate between rocks and soils in geotechnical terms. The distinction between a rock and soil appears simple in that rocks are recognised as hard, competent materials and soils are merely deposits of rock particles. Shales, however, have an intactness, continuity and strength superior to that of soils yet their overall strength is lower than rocks generally because they comprise large quantities of clay minerals. In addition, their mass strength is lowered by the presence of fissures and partings including the property of fissility. Morganstern & Eigenbrod (1974) devised a rock-to-soil classification for mudrocks and clays based on the relative stability of a sample immersed in water; a soil disintegrates and loses most of its strength when exposed in an unconfined manner to water and a rock does not.

Terzaghi & Peck (1967) considered that the behaviour of shales is controlled to a large extent by their degree of compaction and cementation which governs the number of permanent interparticle bonds per unit volume of shale. The classification of Mead (1936) divides shales into compaction and cemented types (Fig. 1.4). Cemented shales are usually stronger and more durable, particularly with respect to disintegration when subjected to cycles of wetting and drying; de Graft-Johnson *et al.* (1975), for example, found that the cemented variety of Accra shale from Ghana could be distinguished from the uncemented variety on the basis of wetting and drying cycles.

Heavily overconsolidated clays possess low compressibility (compression occurs if the normal stress is increased and the pore fluid free to drain such that particles are forced closer together), low sensitivity (defined as the ratio between natural and remoulded strength) and low permeability (a measure of the resistance to movement of water through the voids).

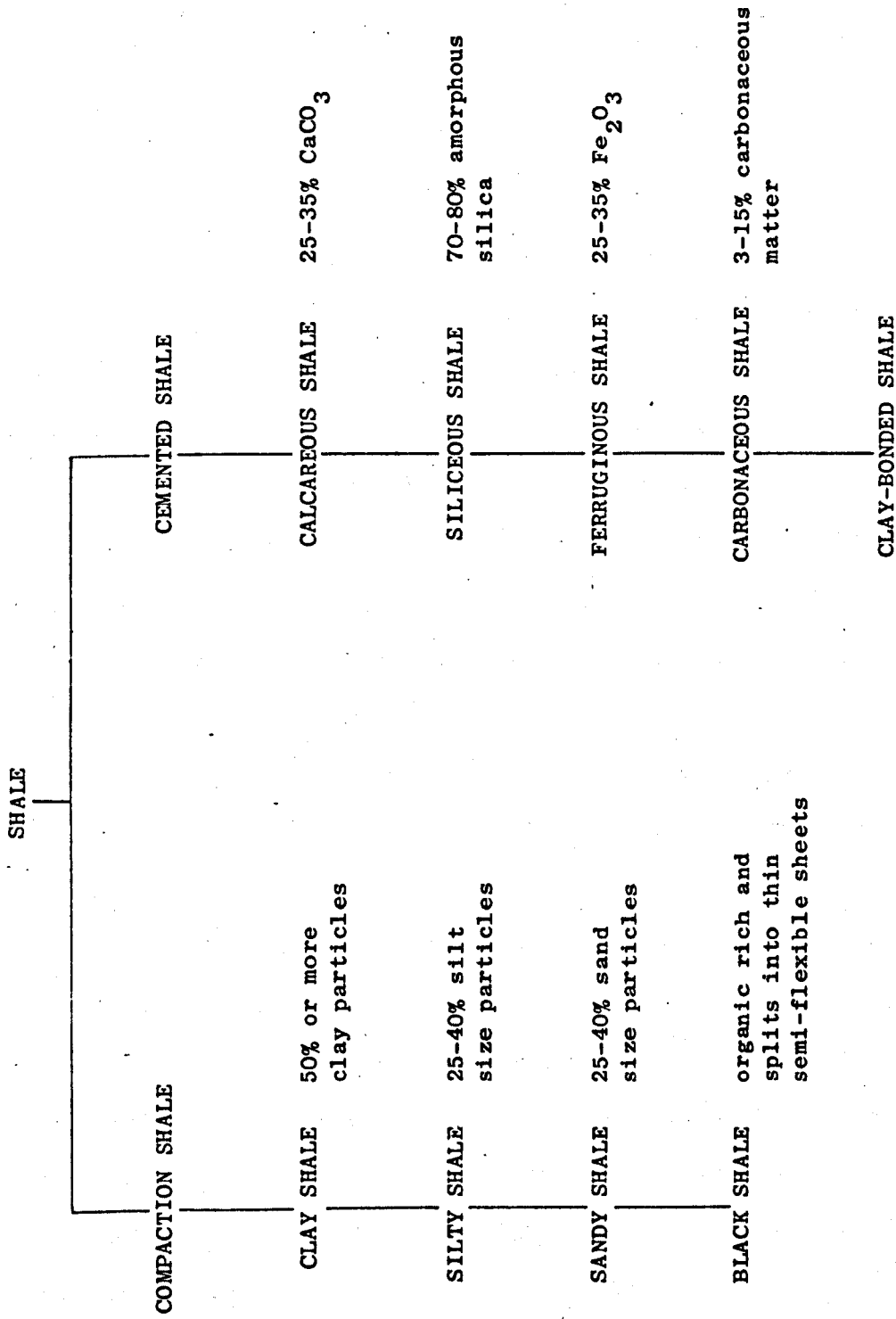


FIG. 1.4 Shale classification of Mead (1936) from Bell (1978)

These properties are related to the near-horizontal orientation of platy constituents adopted during sediment compaction. However, the overall properties of a shale are controlled more strongly by fissure development due to subsequent erosion and weathering by the micro-structure of the particles.

1.3.3 Shear strength

One property of particular interest is shear strength. This is essentially the resistance offered by a soil to an applied shear stress. The concepts of shear strength are given in Appendix B1. Briefly, shear strength is considered in terms of two parameters, cohesion (c) and angle of friction (ϕ). The magnitude of these values depends on the physical and mineralogical properties of the soil, principally the void ratio (defined as the ratio of voids to solids in a soil), particle friction characteristics, particle size, shape and sorting, degree of overconsolidation and soil-water content.

Cohesion is a property characteristic of clay minerals due to the electrical forces developed between clay particles. This is distinct from the apparent cohesion developed in soils of low clay mineral content in the presence of small water contents. Overconsolidated sediments containing clay minerals possess cohesion through the development of diagenetic bonds. Rocks and soils which are not overconsolidated do not have significant cohesion. One major effect of weathering on overconsolidated materials is the reduction of cohesion due to bond destruction, hence in shear strength tests on highly weathered clay or shale specimens a zero value for residual cohesion ($c_r' = 0$) is commonly recorded (Bishop *et al.*, 1965; Spears & Taylor, 1972).

In dry cohesionless soils, the peak angle of friction (ϕ_p') depends partly on particle interlocking, which is a function of the initial void

ratio and particle size, shape, sorting and on the sliding friction between surfaces. Whilst the residual angle of friction (ϕ_r') is also dependent on particle interlocking and on interparticle friction, it is not related to the initial void ratio or water content of the soil since considerable structural adjustment and particle comminution takes place during development of the residual condition. A parallel orientation of platy minerals occurs in the direction of shearing. The residual shear mechanism is governed by particle shape. Angular particles tend to roll (turbulent shear) rather than slide like platy ones (sliding shear). This is discussed in detail in Chapter 6.

The amount of clay size material present has a strong influence on ϕ_r' . Clay particles reduce the effects of interlocking due to their readiness to adopt parallel orientations during shearing. Surface friction is also lower compared to other important constituents like quartz. In addition, in wet soils clay mineral behaviour is influenced by porewater composition and concentration.

Attainment of ϕ_r' requires large displacements along a shear surface. Skempton (1964) stated that post-failure stability on natural shear surfaces is governed by residual shear strength since these have experienced large displacements. La Gatta (1970) emphasised the importance of shearing for large distances in laboratory shear strength tests in order to obtain the true residual condition for a sample. There is a real danger of stopping a test prematurely at an apparent residual shear strength which may in fact only represent an intermediate 'minimum shear resistance'. This is particularly important in highly indurated shale aggregates which may not be completely disaggregated either in preparation or during subsequent shearing. To account for this risk, all experimentally obtained values of ϕ_r' in this work are assumed to be apparent and are designated ϕ_{ra}' .

1.3.4 Index properties

The plasticity characteristics of shales are another important engineering property. Briefly, the water content of a sample determines its consistency. The water contents which represent the upper and lower limits of plastic behaviour are known as the liquid limit (L.L.) and plastic limit (P.L.) respectively. The difference between these limits is the plasticity index (P.I.). The mineralogy of a soil strongly influences its plastic properties. The liquid limit increases as the ratio of clay minerals to quartz increases. Porewater composition and particle aggregation also affect plasticity. The liquid limit has been found to provide a good indication of the slaking tendency of a shale (Morganstern & Eigenbrod, 1974).

1.3.5 Swelling and physical breakdown

Swelling due to water uptake in shales presents problems not just as a physical disintegration mechanism, but also where it causes heave in structural foundations. The magnitude of swelling depends on a number of factors including the nature and quantity of clay minerals present, presence and type of matrix cement, cation composition of the clay minerals and porewater, particle size and void distribution, soil structure, moisture content and applied pressure (Attewell and Farmer, 1976).

Swelling may be interparticle (water adsorption between individual clay minerals) or intraparticle (swelling of the crystal lattice). The latter is important in smectite, vermiculite and mixed layer clays.

Swelling is also caused by salt precipitation within shales. This process, together with water uptake and physical disintegration, are considered in Chapter 2.

1.4 Research objectives

The occurrence of shales in engineering projects does not imply that problems are inevitable.

Kennard et al. (1967) studied the behaviour of a Carboniferous shale with the intention of using the material as a fill in an embankment at Balderhead Dam, North Yorkshire. They were especially concerned about fragmentation, surface breakdown and hardness with a view to long-term changes in fill condition. Physical disaggregation was observed on exposure of fresh shales but this was found to be prevented by rapid excavation and placing of the shale in the embankment, hence further disintegration was not anticipated. Loss of cementation through leaching was not expected to occur significantly after compaction in the dam, particularly as the fill permeability was predicted to be reduced by rapid fragmentation of the surface shale, in the presence of water. This would provide an impermeable skin while still allowing free drainage and dissipation of porewater pressures. It was concluded that the shale available for construction would be suitable as a fill in the dam embankment, especially in view of the capabilities of modern plant to achieve rapid placement.

In an investigation on the geotechnical characteristics of colliery spoil at Yorkshire Main Colliery, Taylor & Spears (1972) found no evidence to show that unburnt spoil once buried after initial rapid breakdown is likely to suffer long-term degradation effects which would create ground engineering problems. This is encouraging in the context of coal-tip stability and to users of this material elsewhere, as in foundations or embankment fill. Burwell (1950) considered the behaviour of shales when subjected to large loads and concluded that well-cemented shales under structurally sound conditions presented few problems for large constructions such as dams, although he did state that their strength limitations and elastic properties may be of importance in the design of concrete dams of appreciable height.

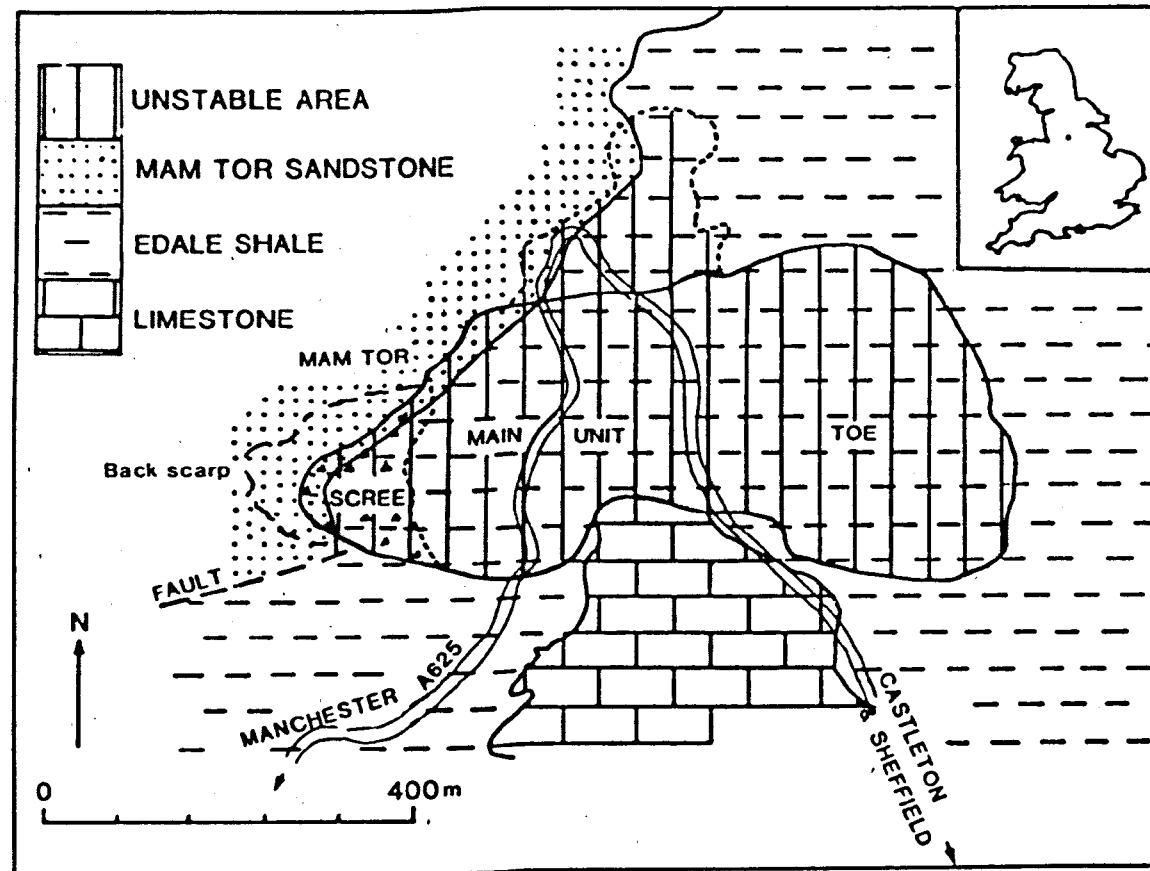


FIG. 1.5 Outcrop of Edale Shale at Mam Tor, Derbyshire

Knowledge of possible difficulties and appropriate preventive measures have, of course, been advanced through experiences of failure elsewhere. While some shales behave satisfactorily others present massive problems to engineering. The types of problems created are diverse and in nearly all cases weathered material and/or weathering processes seem to make a large contribution to the circumstances. The susceptibility of shales to weathering is a function of their physical structure and geochemical properties.

This project aims to look at the nature of some of the links between geochemical and engineering properties in pyritic shales. The work follows directly from an investigation by Vear (1981) on the chemical weathering system at a major active rotational landslide seated in pyrite-bearing shales. In a study of groundwaters at Mam Tor, 2 km. N.W. of Castleton, Derbyshire (Fig. 1.5), chemical weathering was concluded to be aggressive due to the production of sulphuric acid through pyrite oxidation. Mineral reactions such as carbonate dissolution, clay degradation and dissolution were considered to be occurring at rates comparable to acid generation.

Since some of the analysed groundwaters are derived from depth within the slide it is probable that weathering reactions involving sulphuric acid are concentrated along discontinuities where oxygenated waters have access to fresh rock. The slip plane of the slide is an important major discontinuity where chemical activity is probably taking place. Hence, the engineering properties of material on and adjacent to the shear zone are likely to be affected by chemical reactions. It is speculated that landslide activity is related to modification of engineering properties by aggressive chemical weathering.

Studies on the links between chemical activity and engineering properties in weathered pyritic shales focus on aspects which are applicable to

continued landslide instability. The research comprises investigations into the rates and nature of chemical reactions involving shales and sulphuric acid and changes in ϕ_{ra}' due to pore fluid composition effects. The influence of physical breakdown on ϕ_{ra}' and plasticity is also considered together with a method for estimating particle size distribution in indurated mudrocks and clays.

The project is essentially concerned with the residual shear strength properties of materials and centres on Carboniferous Edale Shale which outcrops in the Hope and Edale valleys, Derbyshire, and at Mam Tor. A detailed description of this material is given in Chapter 3. The studies undertaken were laboratory based. However, the appearance of Edale Shale at Mam Tor provided an opportunity to consider the results of laboratory tests in the context of slope stability.

CHAPTER II

GEOCHEMISTRY, STRUCTURE AND WEATHERING OF SHALES

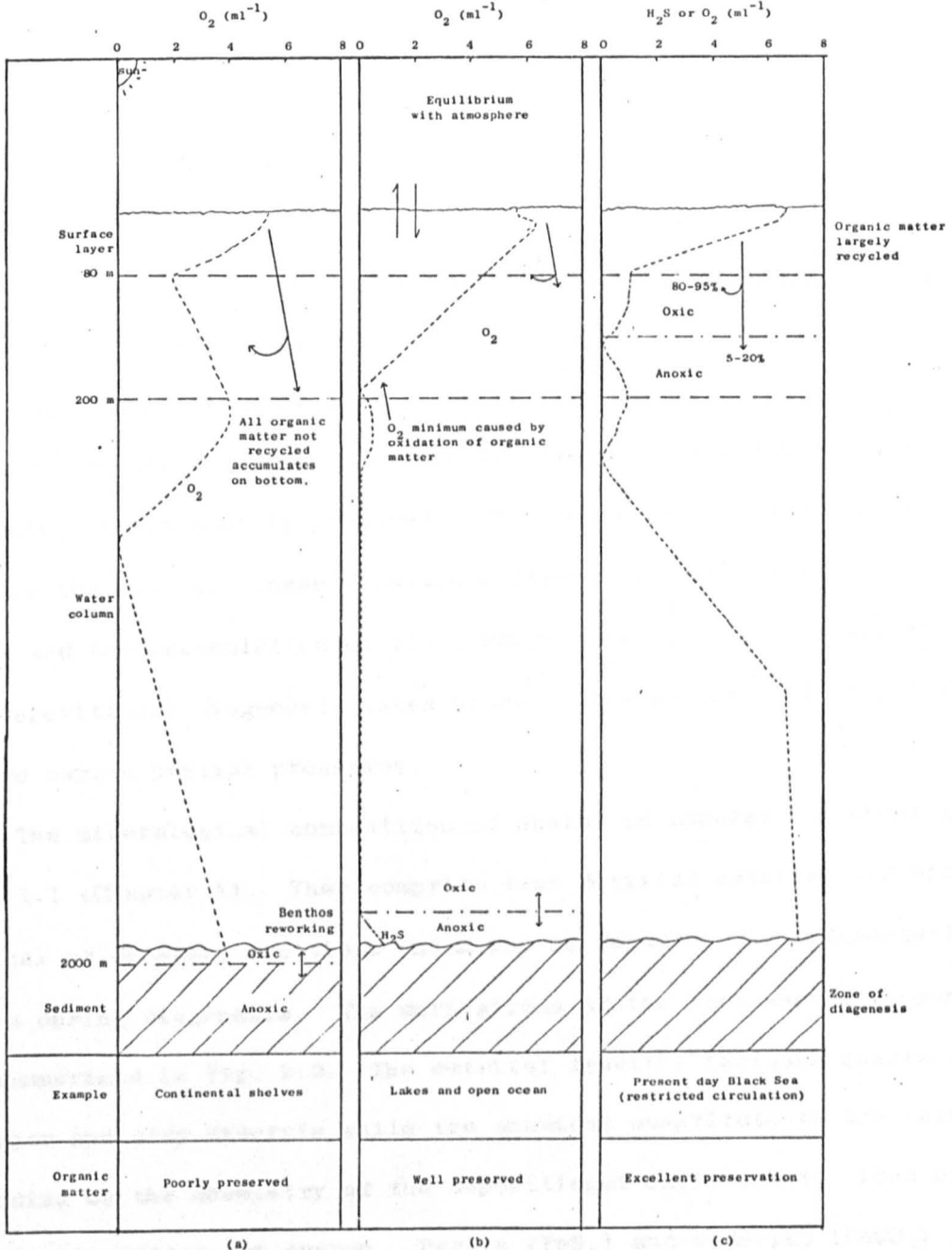
2.1 Introduction

The diversity of engineering problems which are frequently encountered with shales has been outlined in Chapter I. The type of difficulties which arise centre on the tendency for these materials to be both physically and chemically unstable when exposed to wet oxygenated conditions, hence it is often vital to reduce the exposure of shales during construction activities to prevent rapid disintegration and collapse.

The inherent instability of shales in weathering situations is fundamentally related to their environment of formation and subsequent geological history. Briefly, shales are deposited in low energy conditions which exist in a variety of geographical environments such as ocean basins, shelf seas and in water bodies with restricted connection to the oceans, as for example, the present day Black Sea. Suitable conditions are also thought to occur in basins which have experienced intermittent marine invasion, an environment in which Carboniferous Coal Measures rocks probably formed. Shales have developed throughout Earth history and in all parts of the world which, according to Tourtelot (1979), suggests that geological processes rather than geological settings control their accumulation. Didyk et al. (1978) proposed three types of environment in which these sediments are deposited. The models, which are based on the degree of oxygen deprivation experienced within the whole sediment-water system, are illustrated in Fig. 2.1 and are distinguished as follows:

(a) Oxidic waters and sediments - organic matter settling through the water column consumes most of the oxygen and only a little remains for further oxidation reactions in the top levels of sediment. This type of

FIG. 2.1 Schematic representation of typical sedimentary environments - after Didyk et al. (1978) and Tourtelot (1979).



system was applied by Tourtelot (1979) to continental shelf situations.

(b) Partially anoxic waters and anoxic sediments - oxygen availability is controlled by water circulation but on a larger scale, as in open oceans.

(c) Totally anoxic waters - atmospheric exchange of oxygen is limited. Such systems are typified by water bodies with restricted circulation.

There are certain characteristics which are apparently common in all shale depositional environments. First, slow settling rates in low energy conditions allow precipitation of clay and silt-size material. Secondly, the availability of oxygen is severely restricted, hence a reducing environment is produced within the sediments and also at depth in the waters. These conditions favour the preservation of organic matter and the accumulation of fine, muddy deposits. It follows that post-depositional diagenesis takes place in the presence of very low or zero oxygen partial pressures.

The mineralogical composition of shales is complex, as shown in Table 1.1 (Chapter I). They comprise fine detrital material and biochemical or chemical additions which may be deposited by sedimentation or formed during diagenesis. The derivations of the most common components are summarised in Fig. 2.2. The detrital fraction includes quartz, feldspar and clay minerals while the chemical constituents are varied, depending on the chemistry of the depositional environment. Iron oxides and organic matter are common. Pyrite (FeS_2) and siderite (FeCO_3) are also frequent but because different chemical factors probably govern their respective occurrences, as shown by Ashby & Pearson (1978) and Spears, in Curtis & Spears (1968), they rarely coexist in the same horizons. Pyrite is normally restricted to marine shales while siderite is characteristic of non-marine mudrocks.

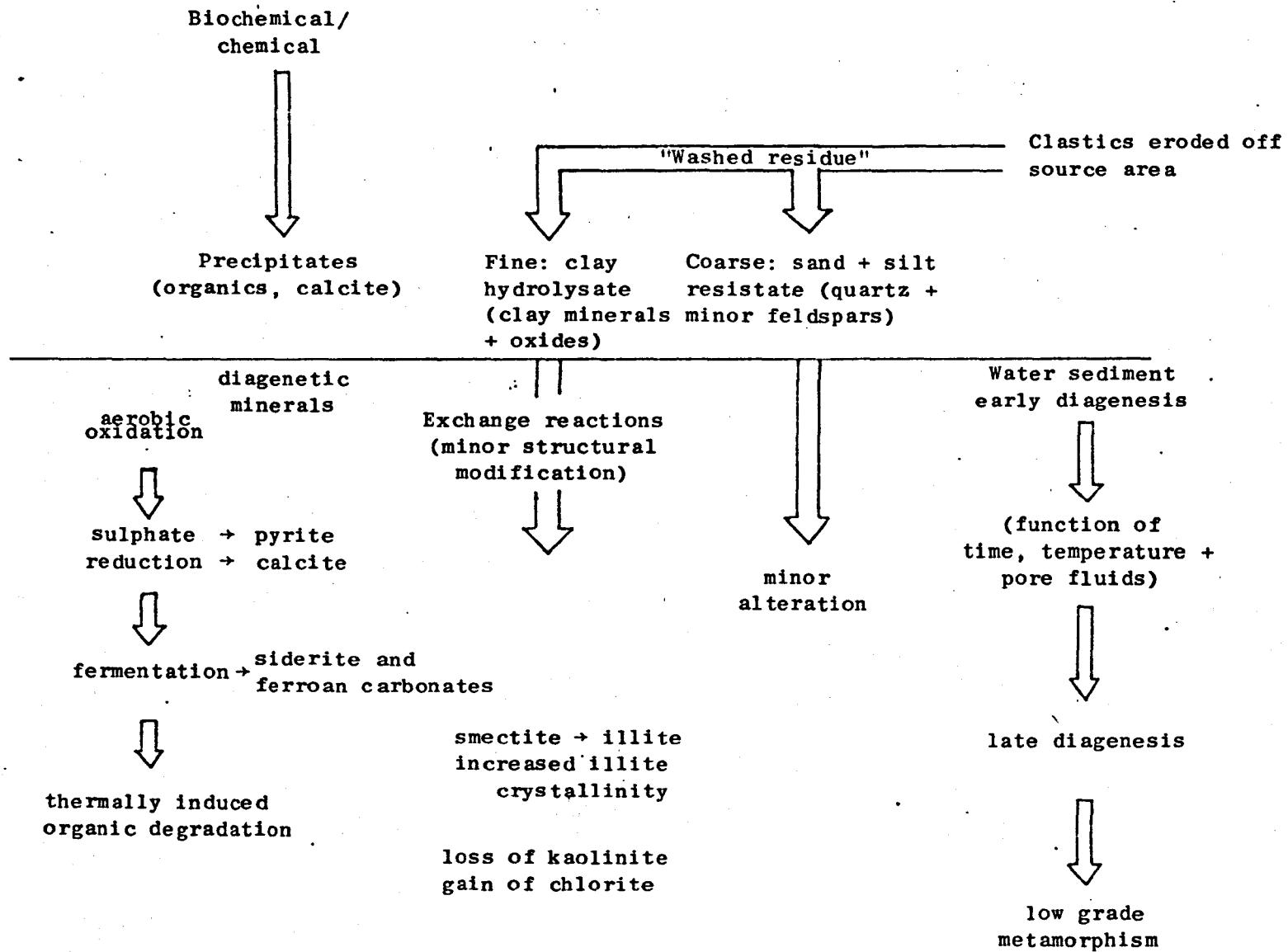


FIG. 2.2 Post-deposition processes and composition of mudrocks (from Taylor & Spears 1981)

During subsequent deep burial, increased temperatures and high ionic activities in the porewaters lead to structural modifications in the clay minerals (Curtis 1977). Interparticle forces are increased (Taylor & Spears 1981) and shales adjust physically to the imposed overburden stress. Later removal of overburden by erosion processes generally entails exposure to an oxygen rich atmosphere and to groundwaters of low ionic activities. Inevitably, shales formed in strongly reducing conditions and in the presence of high ionic activities in solution will be out of equilibrium with the new environment. Physical changes also occur as a consequence of the reduced overburden pressure.

Reiche (1950) defined weathering as: "the response of materials which were in equilibrium within the lithosphere to conditions at or near its contact with the atmosphere, the hydrosphere . . ."; although Ollier (1969) and Keller (1957) criticised the assumption of equilibrium existing between a rock and its formation environment, Since shales form under conditions far removed from those which exist at the earth's surface, according to Reiche's definition, their potential for weathering is obviously considerable. Chemically, however, the various components react in different ways and at different rates depending on their origins. The detrital minerals, including some clays such as kaolinite, have already passed through at least one cycle of erosion and transport and therefore are relatively stable compared with those constituents which were formed in the reducing diagenetic environments. Pyrite is of prime concern in this latter respect. Reactions involving clay minerals such as illite and smectite also take place and are complex owing to the nature of their structure. The structures and properties of the common clay minerals are discussed in section 2.3.

This chapter reviews the geochemical and physical properties of shales which render them peculiarly reactive in the weathering environment. The post-depositional processes which occur in muddy sediments during their accumulation are considered together with the recent concepts of chemical weathering and physical processes of adjustment to new stress conditions.

2.2 Chemical diagenesis in shales: pyrite and siderite formation

According to Curtis & Spears (1968), pyrite formation proceeds in diagenetic environments characterised by slow detrital addition, abundant organic matter and readily available sulphate. Under these conditions, high sulphide activities are maintained so that all iron compounds will tend to transform to pyrite. Clearly, the low energy, oxygen depleted marine conditions described by Didyk et al. (1978) potentially satisfy the requirements for pyrite development.

Sulphide is derived partly from structurally bound sulphur in organic matter and from waters in which the activity of the sulphate ion is high, as it is in seawater. Under conditions of slow settling rates, sulphate (SO_4^{--}) is able to diffuse into the sediment where intensive reduction occurs by microbial action (Lein 1978).

Iron is available mainly in the ferric form as hematite or adsorbed on clay minerals and newly deposited organic matter. After precipitation from normal depositional waters, ferric compounds are transferred to the ferrous form. Ferrous iron may also be derived from within clay minerals.

Sulphide and ferrous iron elements are subsequently concentrated into pyrite via a less stable iron monosulphide phase, as shown in Fig. 2.3. Pyrite is finely disseminated within the sediment or may occur as distinct bodies, as described by Love (1965).

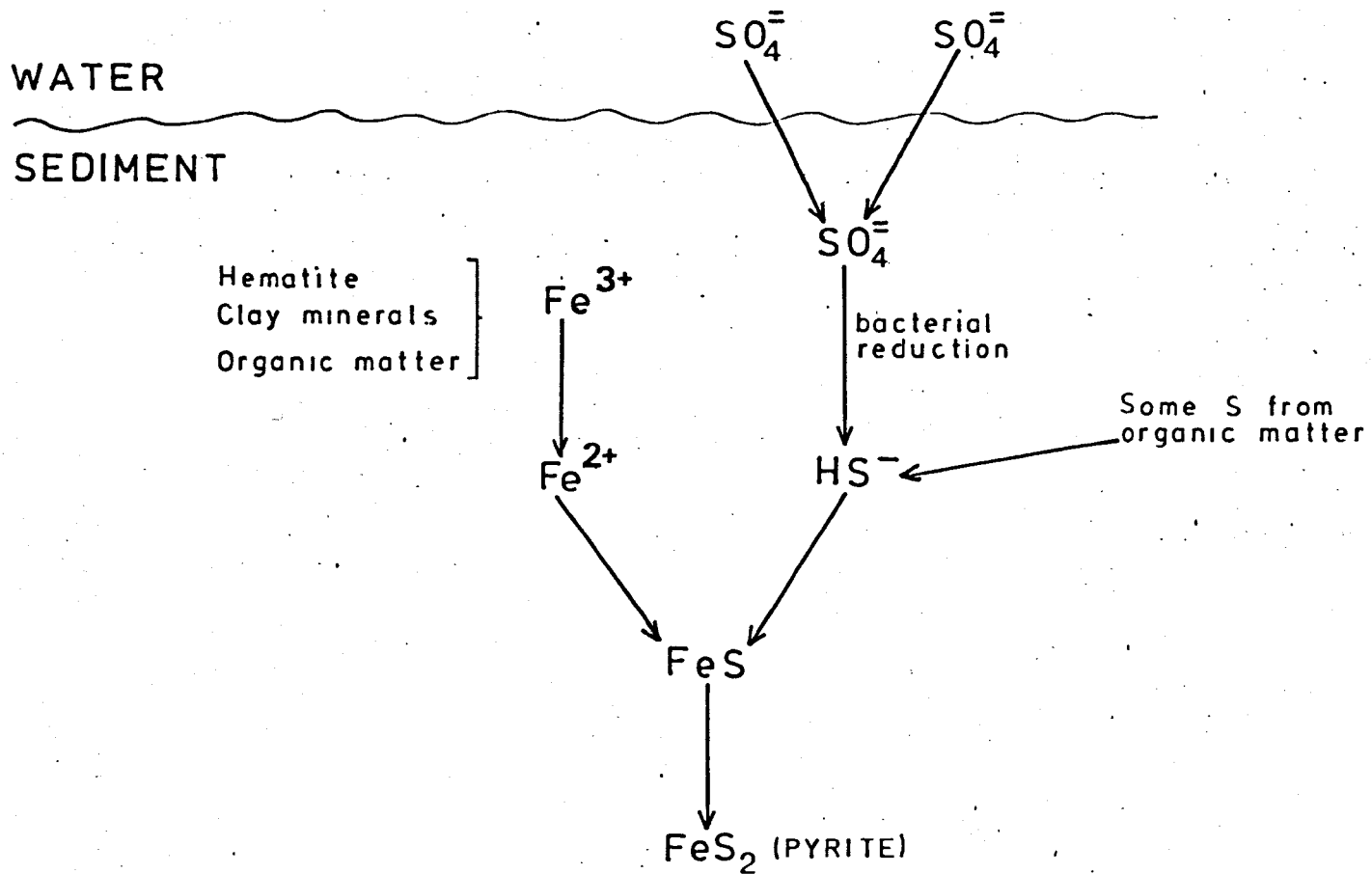


FIG. 2.3 Stages of pyrite formation within muddy sediment

In view of the preference for pyrite formation, even at very low sulphide activities, it is highly unlikely that pyrite will form simultaneously with other ferrous minerals. In the Coal Measures mudrocks, for example, Spears (1968) observed that pyrite beds were distinctly separate from overlying siderite-bearing material in the rock sequence. Curtis (1977) noted that sulphide producing processes could only occur at shallow depths where effective diffusive contact with overlying depositional waters is maintained. When the pyrite body becomes isolated from a sulphate source, for example after a large build-up of sediment or a freshwater incursion, or in the absence of sulphate reducing bacteria, other iron minerals may form of which siderite is particularly common. Spears, in Curtis & Spears (1968), describes its occurrence as nodules in Coal Measures rocks and as oolites and matrix material in Jurassic ironstones.

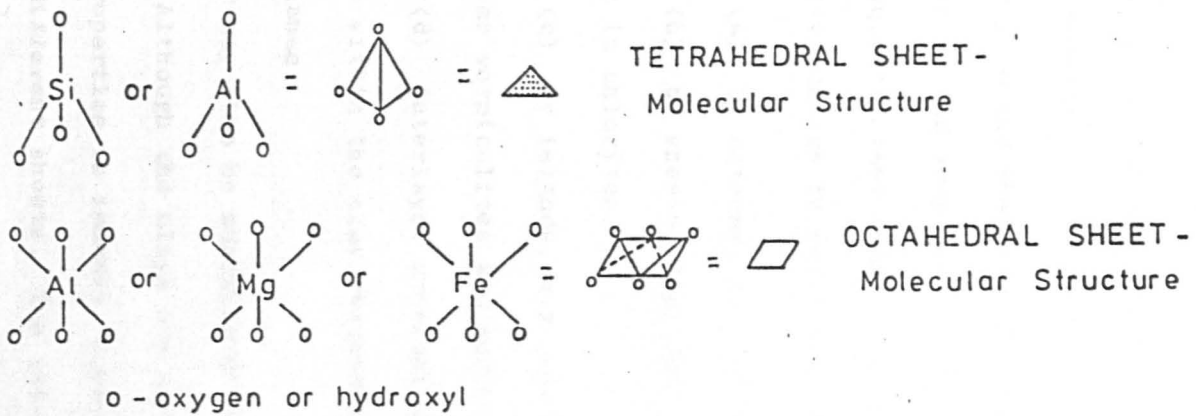
The optimum conditions for siderite formation appear to involve zero sulphide activity and severely restricted porewater circulation. Here, abiotic reaction between organic matter and precipitated ferric compounds are likely to result in the high dissolved ferrous iron and carbonate activities favourable for siderite formation.

Other ferrous compounds (pyrite not formed in the presence of appropriate bacteria, pyrrhotite, magnetite and chamosite) may also form where suitable conditions exist but only within sediment porewaters (Curtis & Spears 1968).

2.3 Clay mineral diagenesis

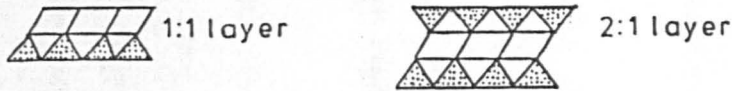
Table 2.1 summarises the structures and properties of the different clay minerals. They are all built from the same basic units, called sheets, which consist of silicon atoms in tetrahedral coordination with oxygen atoms (tetrahedral sheet) or aluminium in octahedral coordination

TABLE 2.1 Structures and properties of the common clay minerals.

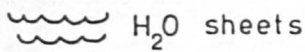
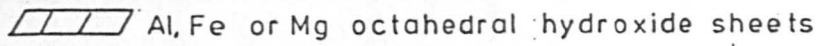


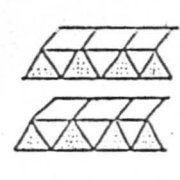
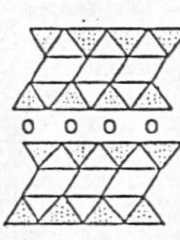
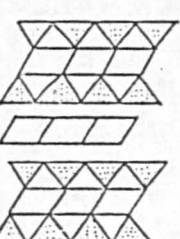
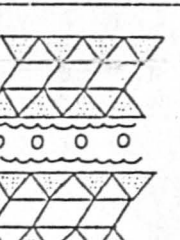
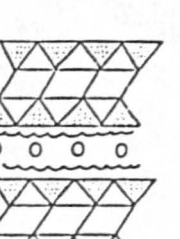
o - oxygen or hydroxyl

The fundamental aluminosilicate layers:



Different clays also include sheets of three other types:



CLAY	FORMULA	STRUCTURE	PROPERTIES
KAOLINITE	$Al_2 Si_4 O_{10} (OH)_2$ Grim (1968)	 7.1 Å	<ol style="list-style-type: none"> 1. Little isomorphous substitution - low negative charge. 2. Low surface area. 3. Low cation exchange capacity. 4. Non-swelling. 5. 1:1 layer structure.
ILLITE	$K_{1.5} Al_4 Si_{6.5} Al_{1.5} O_{10} $ $(OH)_4 \cdot nH_2O$ Prof. C.D. Curtis (pers. comm.)	 10 Å	<ol style="list-style-type: none"> 1. Small degree of substitution, mainly Al³⁺ for Si⁴⁺ in tetrahedral sheet with some Mg/Fe²⁺ for Al³⁺ in octahedral sheet. Charge - 1.3 per unit cell. 2. K⁺ and sometimes Na⁺ in interlayer. 3. Cation exchange capacity 10-40 meq/100 g. 4. Non-swelling. 5. 2:1 layer structure.
CHLORITE	$(Mg, Fe, Al)_{12}$ $ Si, Al)_8 O_{20} $ $(OH)_{16}$ Grim (1962)	 14.2 Å	<ol style="list-style-type: none"> 1. Substitution is usually Al³⁺ for Si⁴⁺ in tetrahedral sheet. Fe³⁺ in octahedral sheet. Charge -1.5 to -0.5 per unit cell. 2. Octahedral interlayer sheet with Al, Mg, Fe²⁺, Fe³⁺. 3. Low cation exchange capacity. 4. Non-swelling. 5. 2:1 layer structure.
SMECTITE	Trioctahedral: $Na_{0.7} Mg_{2.3} Al_{0.7} O_{20}$ $(OH)_4 \cdot nH_2O$ Dioctahedral: $Na_{0.7} (Al_{3.3} Mg_{0.7}) (Si_8 O_{20})$ $(OH)_4 \cdot nH_2O$ Grim (1968)	 15.0 Å	<ol style="list-style-type: none"> 1. Substitution varies; in trioctahedral minerals, Al³⁺ for Si⁴⁺ in tetrahedral sheet, in dioctahedral minerals, Mg²⁺ for Al³⁺ in octahedral sheet. Charge -0.66 per unit cell. 2. High surface area. 3. High cation exchange capacity 80-100 meq/100 g. 4. Swells, depending on relative humidity. 5. 2:1 layer structure.
VERMICULITE	$(Mg_3) (Si_3 Al) O_{10} (OH)_2 \cdot$ $Mg_{0.5} (H_2O)_4$ Brindley & Brown (1981)	 14.2 Å	<ol style="list-style-type: none"> 1. Substitution chiefly Al³⁺ for Si⁴⁺. Charge -1.0 to -1.4 per unit cell. 2. High cation exchange capacity. 3. Swells, depending on relative humidity. 4. 2:1 layer structure.

with oxygen atoms and hydroxyls (octahedral sheet). The sheets are bonded together in 2:1 or 1:1 layers, as shown in Table 2.1, and these are separated by an interlayer.

Ionic substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} or Fe^{2+} for Al^{3+} in the octahedral sheet bring about imbalances in charge on a clay structure and, less importantly, changes in the physical arrangements of the layers. Since substitution introduces ions of lower valency to the sheets a net negative charge is imparted to the minerals. The level and location of substitution varies between the types of clays, consequently they each carry different layer charges (Table 2.1). The negative charge is satisfied in the interlayer in a number of ways:

- (a) by cations, e.g. K^+ in illite, Na^+ or Ca^{2+} in smectites
- (b) by sheets, e.g. the positively charged octahedral hydroxyl sheet in chlorites.
- (c) by islands, e.g. the brucite ($\text{Mg}(\text{OH})_2$) or gibbsite ($\text{Al}(\text{OH})_3$) in some vermiculites and montmorillonites (Jackson 1963).
- (d) interlayer unoccupied, e.g. in kaolinite where ionic substitutions within the clay structures are insufficient to create a large charge imbalance.

Water may also be adsorbed within the layers, particularly in smectites.

Although the clays are made up from the same basic units, their range of properties is immense, depending almost exclusively on bonding types in the different sheets. The tetrahedral sheet is held together by covalent bonds while the interlayer is dominated by ionic bonds. The octahedral sheet is intermediate, possessing both types. From their widespread occurrence, the tetrahedral and octahedral sheets appear to be very stable in spite of the fact that, theoretically, they are thermodynamically unstable (Prof. C.D. Curtis, pers. comm.). However, Powers (1967) found

that almost perfect octahedral substitution occurs during diagenesis where displaced Al^{3+} is taken into the tetrahedral sheet to give the Al-rich composition frequently present in surface specimens; this is presumably a more stable arrangement.

Two very important chemical properties of clays which are of special relevance to this work are ion exchange capacity and swelling potential. Exchange processes and changes in basal spacing of the structure due to swelling or contraction dominate in the interlayers. The two reactions are linked since minerals with a high cation exchange capacity, notably the smectites, expand most and the energy for expansion is thought to be derived from the hydration, or solvation, energy of ions entering the clay structure.

Cations also occupy other exchange sites on the edges of silica-alumina layers to satisfy charges arising from broken bonds. This source of ion exchange capacity is important in kaolinites and, also, in highly crystalline illites and chlorites but in smectites and vermiculites, the contribution of broken bonds to total exchange capacity is very small. A third source of the exchange property involves the replacement of hydrogen ions on exposed hydroxyls but again, this is minor and only significant in kaolinite.

A detailed account of clay properties is given by Grim (1968, Chapters 7 & 8). It is sufficient here to appreciate that:

(a) The properties of ion exchange capacity and swelling are related to charge density in the mineral structure. The reactivity of the clays thus decreases in the order smectite > illite > chlorite > kaolinite.

(b) Interlayer reactions involve changes in energy. The energy is probably derived from the dehydration of cations entering the clay and associated changes in bonding between cations, water and clay structure.

(c) The exchange mechanism relies on activity ratios (effective concentrations) between clay interlayers and solution. In rock diagenesis and in weathering, clays react in order to attain equilibrium with the porewater composition.

(d) In very aggressive chemical conditions, or after prolonged weathering, the octahedral sheets, or more rarely the tetrahedral sheets, may be altered.

Post-depositional modifications of the clay minerals in buried shales are both physical and chemical, as noted by Pettijohn (1975).

As temperatures and pressures increase due to burial, clays show progressive mineralogical changes which Pettijohn (1975) considers to be largely isochemical in that during reaction the system bulk chemistry remains essentially unchanged. There is general agreement (Keller 1963; Potter *et al.* 1980; Yaalon 1969) on the fact that smectites gradually disappear at depth with a concomitant increase in illite so that the latter becomes the dominant clay mineral in deeply buried sediments. This transformation may be related to the onset of decomposition of detrital mica and K-feldspar which was estimated by Curtis (1977) to commence at burial depths of 3 to 4 km. Powers (1959) introduced the concept of an "equivalence level" below which K^+ is adsorbed into clay interlayers in preference to Mg^{2+} and Fe^{2+} . These ions are presumed to move into the octahedral layer while in turn, the displaced Al^{3+} substitutes for Si^{4+} in the tetrahedral layer. The whole conversion results in illite formation.

Kaolinite and chlorite are relatively stable at high temperatures and pressures. Curtis (1977) considers that neither of these clays appears to react under the deep burial conditions which impose changes in other clay minerals, although Blatt *et al.* (1972) report two instances

of a reduction in kaolinite accompanied by an apparent increase in illite and chlorite with depth.

Accompanying clay mineral alteration is the exclusion of porewaters under the physical influence of compaction pressures. Clays may also be dehydrated if temperatures are raised sufficiently for interlayer waters to be driven off.

Quartz and feldspar undergo very little change, except perhaps for minor sericitisation of some feldspars observed by Blatt et al. (1972) and the reaction of K-feldspar at depth as postulated by Curtis (1977).

2.4 Physical response of shales to burial and unloading

In addition to the chemical changes which occur during deep burial muddy sediments are also subjected to increased tectonic and thermal stresses. Important structural modifications are imposed under the influence of increasing overburden stresses. Void volumes are reduced which consequently increases sediment density and in saturated materials water is simultaneously expelled from the voids. This is the process of consolidation as described by Fleming et al. (1970). When the maximum consolidation pressure is reached, the sediment remains for a considerable length of time with very little change in load. During this period of burial Bjerrum (1967) postulates that physical and chemical processes take place which result in bond formation between constituent particles. At particle contacts, stresses are sufficiently high for recrystallisation to occur and for adhesion to develop from molecular bonds. Cementation may also result from the precipitation of certain minerals between particles. The combined effect of the bonding processes creates diagenetic bonds (Bjerrum 1967). The sediment structure, therefore, becomes stronger with no further volume change occurring. Bond strengths depend on consolidation pressure, on the minerals involved, on pore fluids, temperature and time. Clearly shales which formed early

in geological history can be expected to possess stronger diagenetic bonds than shales of a younger age because they have probably been buried at deeper levels for longer periods of time.

The porosity and permeability of buried sediments are reduced substantially during compaction under the pressure of overlying beds. Hedberg (1936), for example, quoted a value of 9-10% for a shale under an overburden of 1800 m compared with 70-90% for a freshly deposited mud. Compaction begins immediately after deposition and continues for a long period of time. Structural changes are also induced, including a progressive reorientation of clay platelets into a more parallel alignment, as reported by Oertel & Curtis (1972). The growth of diagenetic carbonate concretions is also affected as shown by their lensoid appearance (Raiswell 1971).

Later in geological time, erosion of the overburden causes the buried sediment to be unloaded and thus to experience lower overburden stresses. The sediment is then in an overconsolidated state; materials which have not been subjected to greater overburden stresses than at present are said to be normally consolidated.

The response of overconsolidated materials to a new stress environment depends on diagenetic bond strength and on the recoverable strain energy stored in those bonds. Sediments will tend to expand and increase their water contents as a result of possessing recoverable strain energy. According to Fleming et al. (1970), a system will tend toward equilibrium with the existing stress state and moisture environment. However, expansion is restricted by the strength of the bonds, consequently the final water content will be much lower than the original pre-consolidation water content. Expansion and water uptake is also time-dependent since the mechanism relies on the breakdown of bonds; Bjerrum mentions that

many shales may not yet have achieved their equilibrium water content owing to the time-dependent effect. Skempton (1964) also noted an increased water content in unloaded clays and considered that overconsolidated clays possess higher shear strengths than those which are normally consolidated because of their denser packing. Changes in water content and shear strength as proposed by Skempton (1964) are shown in Fig. 2.4.

Effective horizontal stresses due to continental compression, are also influenced by unloading. Bjerrum (1967) explains that during deposition, the effective horizontal stress increases as well as the effective vertical stress, depending on the shear resistance properties of the material. For weak sediments, the horizontal stress is larger than for strong ones. On unloading, the material expands but is only free to do so vertically, hence changes of vertical stress are larger than changes in horizontal stress. In stronger bonded sediments, expansion is inhibited and horizontal stresses are thus reduced because the diagenetic bonds retain a larger amount of lateral-strain energy. Terzaghi (1962), quoted by Bjerrum (1967), noted that at each depth there is an upper limit to the possible horizontal stress. When the difference between horizontal and vertical stresses reaches a certain level, shear stresses become larger than shear strength and failure ensues. In brittle, overconsolidated material, small movements may result after the development of incipient shear planes which would reduce horizontal stress to a limiting value. In strongly bonded materials the movements required to reduce the stresses are small while in those with weak or no bonds, the movements need to be greater. The effect of unloading on horizontal stresses is included in Fig. 2.4.

The consolidation history of many shales, especially very old formations, is often extremely complex because they have suffered several

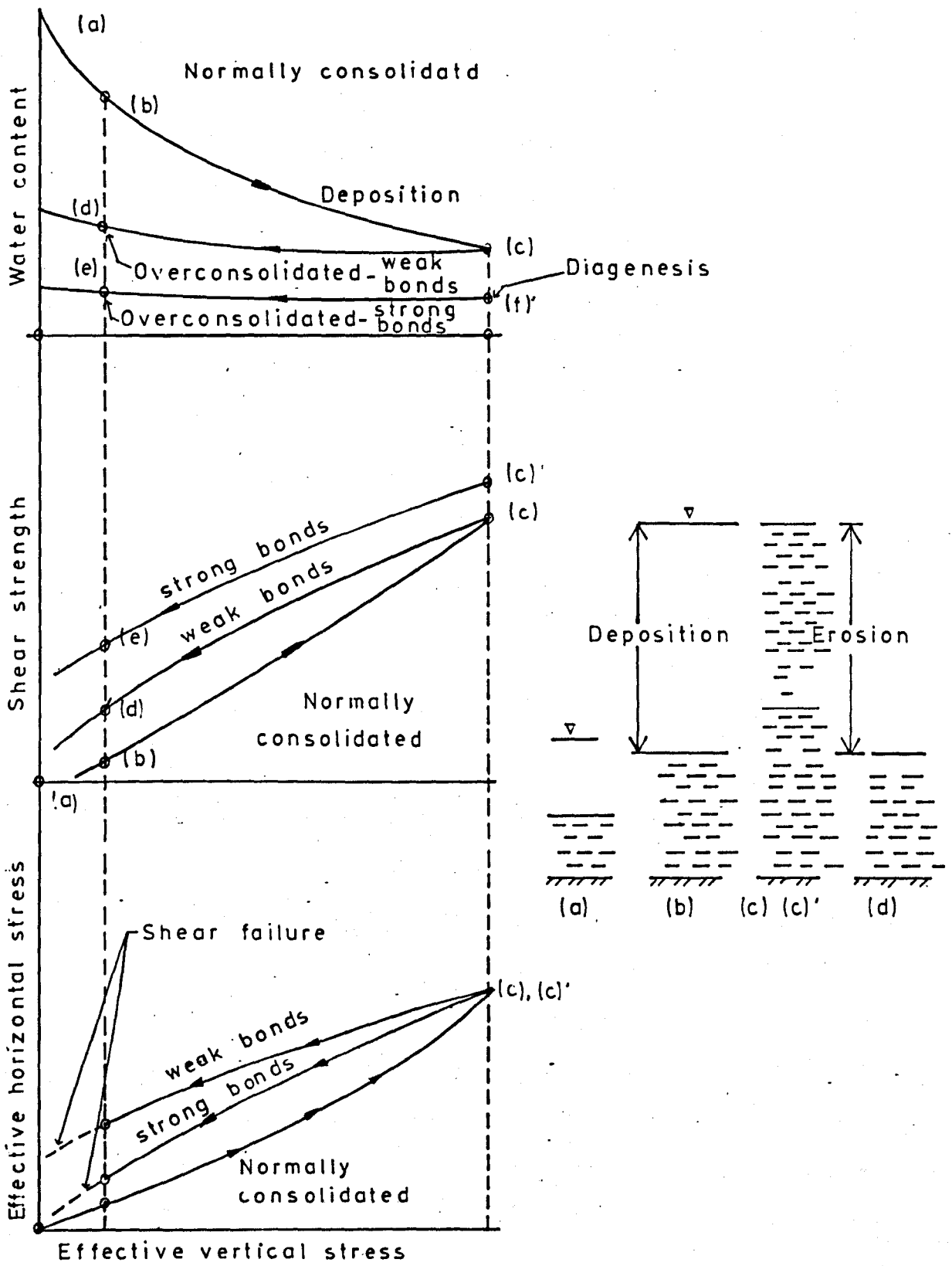


FIG. 2.4 Changes in water content, shear strength and horizontal and vertical stress during deposition and unloading of over-consolidated clay

cycles of deposition and erosion, glaciation and surface weathering. This was noted, for example, by Scott & Brooker (1968) for the development of the Bearpaw Sediments in Canada where a relatively recent glaciation event probably increased overburden stresses considerably. Changes in the stress environment imposed by processes such as glaciation and river valley erosion may exert a significant influence on the behaviour of shales because the rock-water system will tend to equilibrium with each new set of stress conditions.

2.5 Physical weathering in shales

Once uplifted and stripped of a large portion of overburden, shales are subjected to surface weathering processes. Bjerrum (1967) identified two distinct phases in weathering. The first phase is one of disintegration involving bond breakdown and results in disturbance to the soil or rock structure. During the second phase chemical changes and mineral decomposition occur.

The disintegration phase can be considered as a continuation of the unloading process, although Chandler (1972) emphasised that weathering is a distinctly separate stage. Its major effects are further bond destruction and liberation of the strain energy imparted to the rock during burial. Consequent upon these effects are material expansion and water uptake which in turn reduce shear strength. The total amount of expansion which occurs will depend on the stored energy; if the bonds are weak most of the strain energy will have been released during unloading and therefore the effects of disintegration will be small but in the case of strong bonds, little strain energy is lost on unloading, thus expansion in the disintegration zone is large.

Bjerrum (1967) found that the effect of disintegration reduced with depth and that it is possible to distinguish zones in which disintegration has proceeded to different degrees. He defined three zones:

(a) Zone of complete disintegration in which material has been subjected to freezing and thawing, repeated wetting and drying and temperature changes. Some chemical alteration has also occurred. The water content and strength in this zone are primarily dependent on climatic conditions rather than the state of the present material.

(b) Zone of advanced disintegration probably affected by the cyclic variation of effective stresses caused by pore pressure changes and seasonal freezing in the overlying soil. There is usually a system of open cracks which permit the circulation of water; this aids breakdown through slaking. There is possibly some chemical alteration. The material will generally be softer and have a higher water content than the underlying zone.

(c) Zone of medium disintegration where the effects of near-surface conditions are not felt. Non-uniform swelling resulting from a mixed clay mineral assemblage and consequent variation in water content within the zone is thought to be an important source of differential straining necessary for disintegration.

The existence of zones has been frequently observed in other studies of weathered materials. Herstus (1971) investigated weathering in a Miocene clay in north-west Bohemia and found four zones which were distinguishable on the basis of fissure frequency and hardness of the material. Similarly, Chandler (1969) subdivided weathered Keuper Marl into four zones by looking at the variation in particle size distributions while in Lias Clay, Chandler (1972) identified weathering classes by their different degrees of oxidation.

The effects of physical weathering apparently extend to considerable depths. Gould (1960) observed weathered zones to depths of 7 m to 13.7 m in some Tertiary shales of California. Skempton (1964) found weathering

at 9.9 to 12.1 m in London Clay and Spears & Taylor (1972) recorded visual weathering in Coal Measures rocks down to 6.6 m. Chandler (1972) described typical depths of oxidation in London Clay as large as 10 m.

2.5.1 Nature and causes of physical breakdown

Shales break down very rapidly on exposure to the weathering environment. Taylor & Spears (1970) recorded that medium- and fine-grained Coal Measures rocks were reduced to a gravel size aggregate in only two years while Kennard et al. (1967) observed that disintegration features developed within a few minutes of fresh shale being exposed.

From accounts of physical weathering, disruption to the rock fabric appears to take place in three ways:

- parting along bedding planes
- polygonal cracking on bedding surfaces
- expansion of joints

The observed modes of shale disintegration appear to be strongly controlled by pre-weathering structures. Perhaps the most obvious effect is that bedding or stratification act as zones of preferential parting giving shales their characteristic fissility. This property is often attributed to mineral segregation into fine laminae and is not simply related to clay orientation as commonly believed, as for example, by Pettijohn (1975, p.263). Spears (1980) defined a lamina as a stratum less than 1 cm in thickness. A stratum is a single layer of homogeneous or gradational lithology, separated from adjacent strata by surfaces of erosion, non-deposition or abrupt change in character (McKee & Weir 1953). Spears (1981) considered that lamination in Coal Measures sediments is an important genetic feature and that fissility is secondary, a surface manifestation of the lamination. The existence of lamination in shales has been attributed to a number of factors. Potter et al. (1980) noted that

lamination may be defined by differences of grain size, composition and/or fabric arrangement and perfection of orientation by particles.

Curtis et al. (1980) observed a laminar segregation of silicates from organic matter and detrital minerals in a highly fissile "paper shale" in the Hepworth sequence, Yorkshire. Spears (1969) described alternating lighter and darker bands in mudrocks due to differences in clay structure; darker layers tended to control breakdown because of their open fabric and propensity for water uptake and swelling. Spears (1976) demonstrated that the sizes of shale flakes was strongly controlled by the thickness of laminations; where these were widely separated or absent, shale flakes were thick and more equant compared to the disc-shaped fragments which were derived from more thinly laminated shales.

The disintegration mechanism for parting parallel to bedding planes has been explained by Taylor & Spears (1970) as a capillary phenomenon termed "air breakage". During dry periods, air may occupy pore spaces within a rock. On immersion in water, capillary pressures in the outer pores pressurise the air and the rock breaks along the weakest planes, thereby increasing the surface area exposed to subsequent drying and wetting. Capillary pressures are related to pore radius, therefore small pores will suffer greater pressurisation of air. Swelling from water uptake in layers with flocculated clay fabrics may reduce pore sizes and make these laminae more susceptible to air breakage. The above authors also pointed out the probability of air-filled cul-de-sacs occurring in flocculated fabrics which would enhance the likelihood of high capillary pressures.

In rocks, or layers within rocks, containing a high proportion of smectites, clay mineral expansion may be a significant factor in breakdown. Smectites are not necessarily present as a separate phase and

frequently occur as a swelling component in mixed-layer clay minerals. Work by Badger et al. (1956) on the disintegration of shales in water found that clay dispersion was a general cause of rock breakdown and was most effective with sodium as the interlayer cation. Although dispersion was attributed to dissociation of ions from clay colloids, it is also possible that intraparticle swelling may be responsible due to the uptake of water into the interlayers of smectites, particularly in the presence of sodium which has a high hydration energy and therefore produces higher swelling pressures.

Once bedding surfaces are exposed, desiccation causes polygonal cracking perpendicular to the bedding. Breakdown in this style is controlled by rock isotropy on these surfaces and results from the development of negative pore pressures with pore pressure gradients emanating radially from discrete centres in the material. The stress distribution is ultimately manifested in a hexagonal pattern of fracture which, according to Christensen (1970), suits the optimum shape of deformation required for maximum conservation of energy. Taylor & Spears (1970) observed that the development of a polygonal fracture pattern depended on the degree of interaction with jointing.

Joint frequency is a function of rock strength with the highest frequencies occurring in coals and mudrocks. Attewell & Taylor (1976) considered that joints preconditioned material for breakdown on exposure to a weathering environment. Initially, they will open up in response to wetting and drying while their subsequent role is to focus percolating solutions, not just at surface levels but often at depths below the zone of effective weathering. Percolating waters carry dissolved ions and if they become saturated with respect to particular minerals, these will be precipitated. Spears & Taylor (1972) noted that ironstaining in

joints at depths down to 6.6 m in Coal Measures rocks was indicative of water movement through the rock.

Physical disintegration is a rapid process. However, the complete breakdown of a rock into its constituent particles is relatively slower and is rarely seen below surface levels in weathering profiles. Kennard *et al.* (1967) concluded that mechanical effort or chemical decay were required to reduce particles below coarse sand/fine gravel size. This is not always the case and again, the presence of smectite clays provides an example. In many instances, however, the mechanisms by which physical disintegration takes place are insufficient on their own to produce material of fundamental grain size. Berkovitch *et al.* (1956) drew similar conclusions in their investigations of shale breakdown in water. It was found that physical abrasion was not enough to produce particles smaller than 10 μm in diameter but clays possessing swelling properties, particularly in the presence of Na^+ , broke down to sizes less than 5 μm .

Longer term breakdown involves the removal of cements and non-detrital minerals such as pyrite, accompanied by the degradation of unstable clay minerals such as smectites and illites. These slower chemical processes form the second, mineral decomposition, phase of weathering in Bjerrum's (1967) two-fold weathering scheme. They act most effectively after physical disintegration has increased the surface area of rock available for attack.

2.6 Chemical weathering in a thermodynamic context

Powers (1967) stated that "the direction of diagenesis is reversed during weathering" which is a fundamental maxim, in the case of shales. Krauskopf (1967) subdivided chemical weathering into ionisation, hydration, carbonation, hydrolysis and oxidation processes, commenting that

the reactions themselves are basically simple but weathering is complicated by the simultaneous operation of several reactions and by the complex nature of minerals and mineral mixtures. Curtis (1976a) considers that the concept of stability is essential to the comprehension of chemical reaction. A precise definition of stability is difficult to achieve but in qualitative terms it can be described as the property of resistance to change. This implies that a stable state has no spontaneous tendency to change with time (Curtis 1976b).

Several theories have been advanced to explain why some minerals are more resistant to breakdown than others. Krauskopf (1967) noticed similarities between the Goldich Stability Series and the number of silicon-oxygen-silicon bonds in minerals. The series lists minerals in descending order of apparent resistance and is the reverse of Bowen's crystallisation sequence from a rock melt. With the exception of muscovite and plagioclase, as bond number increases so does stability. Keller (1954) calculated bonding energies for some common oxides and the energies of formation for common silicate linkages. He found a positive correlation between stability and formation energy but agreement with the Goldich Series collapsed when other bond types were taken into account. Loughnan (1973) considered that mineral structures control the access of percolating waters to soluble cations.

A more modern approach involving chemical thermodynamics was proposed by Curtis (1976a). Thermodynamics deals with stability through the analysis of energy changes. All substances possess energy bound in their structures so that in a chemical system comprising several different substances, the total energy is equal to the sum of its individual parts. In any spontaneous chemical reactions there is a net release of free energy, denoted ΔG_r . The standard free energy change of a reaction

(ΔG°_r) is the sum of the free energies of formation of all the reaction products in their standard states (1 atm. pressure, 25°C temperature, concentration of solutions 1 molar or 1 molal) minus the sum of the free energies of formation of the reactants in their standard states thus

$$\Delta G^{\circ}_r = \sum \Delta G^{\circ}_f \quad - \quad \sum \Delta G^{\circ}_f$$

(products) reactants

where ΔG°_f is the standard free energy of formation of a substance, usually expressed in Kcal mol⁻¹.

If ΔG°_f of the products is less than the ΔG°_f of the reactants, energy must be liberated and the products are then stable relative to the reactants because of their lower potential energy. The maximum stability of a system occurs when the potential energy of a particular state is zero or at a minimum value. If the calculated energy change of reaction, ΔG_r , is zero, products and reactants are in equilibrium, that is, they coexist. If ΔG_r is positive, the reverse reaction is spontaneous. Almost without exception, free energy changes for realistic natural decomposition reactions are negative and thus they occur spontaneously in the natural environment. It is logical that the greater the magnitude of $-\Delta G_r$, the greater is the tendency for reaction to occur. Curtis (1976a) found a fair degree of correlation between ΔG°_r for particular minerals and their persistence in weathering, for example, ΔG°_r for dissolution of albite is $-0.75 \text{ Kcal g atom}^{-1}$ which is two orders of magnitude smaller than $\Delta G^{\circ}_r = -17.6 \text{ Kcal g atom}^{-1}$ for pyrite oxidation. A net energy change associated with chemical reaction is due to the breaking of molecular bonds and their reformation in a new, more stable configuration under the prevailing temperature, pressure and compositional conditions.

These principles may be applied to any chemical weathering processes.¹ Examples are given in Curtis (1976a). This author also notes that the standard states of temperature and pressure for expressing formational free energies closely approximate to average weathering conditions. Solution concentration and gas partial pressures vary in the natural environment but assumption of the standard states is sufficient to facilitate comparison of different mineral stabilities under particular conditions.

Although for most chemical reactions the net energy liberated during a reaction is a measure of the stability of reactants relative to the decomposition products, the rate at which they proceed is generally not linked to the magnitude of the energy change. Rates and mechanisms of reaction are dealt with in the subject of chemical kinetics. Briefly, rates are connected with the activation energy of a reaction. This is the energy that must be supplied to a system before reaction can begin; a high activation energy implies that a given system will change slowly relative to one with a low activation energy. Reaction rates also depend on the concentration of reactants, that is, the surface area of solids in a mixed solid/solution system and the partial pressures of individual gases within a gaseous phase. Furthermore, rates are very sensitive to temperature and to the addition of catalysts or inhibitors which alter the reaction mechanism.

Unlike most traditional explanations for the differential susceptibility of various minerals in the weathering environment, the thermodynamic approach considers the chemical environment in addition to the solid material involved in reaction. The value of this concept lies in the ability to predict the potential instability of a particular rock/mineral assemblage. It also allows for different weathering environments.

¹Thermodynamic calculations for clay mineral alterations are not straightforward, however, since equilibrium end-products of reactions under given weathering conditions are difficult to predict.

to be compared and contrasted in terms of their reactivity with respect to mineral breakdown, simply by writing realistic, balanced equations involving both reactants and products and by calculating the free energy changes of reactions.

2.7 Chemical weathering in shales

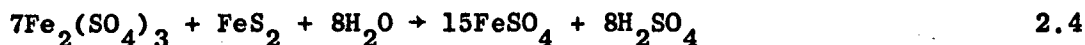
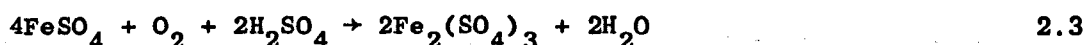
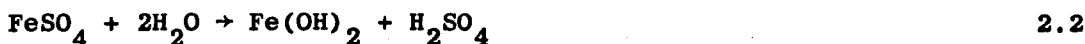
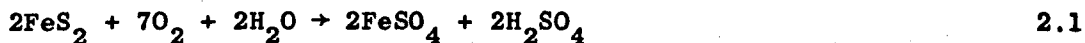
Three levels of reaction can be distinguished in the chemical weathering of shales:

(a) Rapid breakdown of minerals which participate in redox reactions, for example, pyrite.

(b) Very slow degradation, for example, quartz dissolution.

(c) Intermediate reaction times, usually involving clay minerals which commonly experience more than one rate of alteration, depending on mineral structure. Interlayer cation exchange is immediate but the more stable tetrahedral and octahedral sheets change much more slowly.

Taylor & Cripps (in press) express pyrite oxidation in humid conditions in terms of a series of chemical reactions:



Penner et al. (1972) have established that reactions 2.1 and 2.3 are dependent on the activities of autotrophic bacteria. *Ferrobacillus* and *Thiobacillus* species have been identified as participants in oxidation reactions in a number of investigations, e.g. Quigley & Vogan (1970), Penner et al. (1966), Ollier (1969). The bacteria require certain conditions for continued activity. An acid environment in the pH range 2 to 4.5 is necessary and optimum temperatures for reaction are between 30° and 35°C. Oxygen is also essential.

According to Bérard (1970), however, bacteria are not always essential for pyrite oxidation since reaction still proceeds under suitable redox and temperature conditions. Complete reduction of ferric iron to the ferrous form is achieved by reaction 2.4 given by Penner et al. (1972), where ferric sulphate formed in 2.3 reacts with remaining pyrite to reduce the ferric iron.

Pyrite breakdown occurs rapidly due to its thermodynamic instability, particularly when catalysed by moisture. Experiments reported by Kuznetsov et al. (1963) indicate that pyrite oxidation is most rapid for fine-grained, amorphous and impure forms but the process is apparently retarded by organic matter and cool temperatures.

The oxidation reaction is exothermic and since the energies liberated ($-17.68 \text{ Kcal g atom}^{-1}$) are of the same order as the oxidation of methane ($-20.54 \text{ Kcal g atom}^{-1}$ - Curtis 1976b), spontaneous combustion in pyrite-bearing material may occur, particularly in loose colliery spoil or in mine dust, as reported by Bérard (1970).

Sulphuric acid production is ubiquitous and according to Krauskopf (1967) it is particularly strong due to the concomitant production and precipitation of a very insoluble ferric oxide (or hydrated oxide). H^+ and SO_4^{--} are thus left in solution and when added to the pre-existing H^+ concentration of natural waters derived from the equilibration of atmospheric CO_2 in H_2O , the potential for aggressive weathering of fresh rock is greatly enhanced.

The production of sulphuric acid clearly results in a dramatic change of chemical environment of the shale-porewater system. Again, certain minerals will be affected more than others and of concern in this respect are carbonates, including siderite and calcite, phosphates if present (e.g. apatite) and, most importantly, the clay minerals.

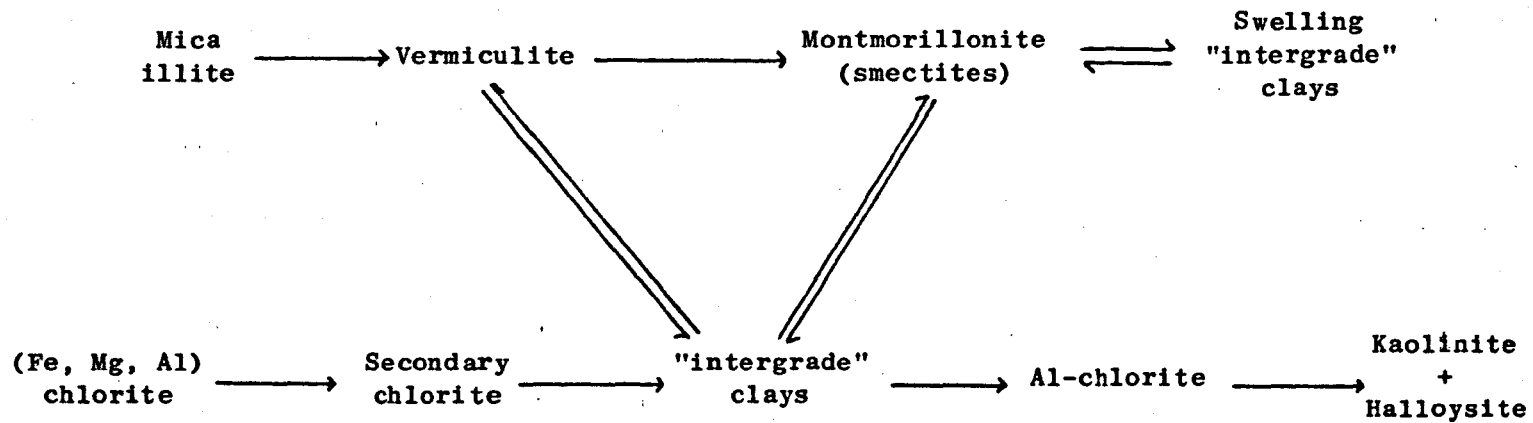


FIG. 2.5 Changes in clay mineralogy during chemical weathering (after Jackson (1963))

The structure and properties of the common clay minerals were discussed in section 2.3. During weathering, leaching of interlayer cations and attack on the alumino-silicate layers are important processes. The transitions between clay types which occur during degradation of the structures are summarised by Jackson (1963) in Fig. 2.5. Feigenbaum & Shainberg (1975) found that decomposition of montmorillonite clays appears to take place through the consecutive action of two mechanisms. Initially, H^+ in solution is rapidly exchanged with the adsorbed cations to form H^+ -clays. Fe, Mg and Al are then released from the octahedral and tetrahedral sheets into the interlayers to transform H^+ -clays into Fe, Mg and Al-clays. These cations are then ready to participate in further exchange reactions with H^+ from solution. The second reaction is slow and determines the rate of clay decomposition. In acid environments, Cook & Rich (1963) also found that hydrolysis of Al was promoted to form Al-hydroxy compounds within the interlayer which satisfied the negative charge in the clay structures; this corresponds with the "intergrade" stage suggested by Jackson (1963).

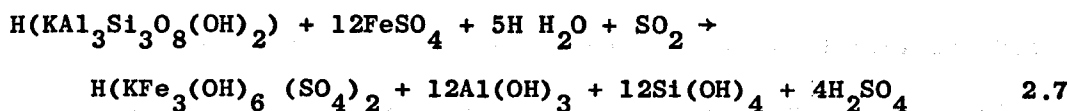
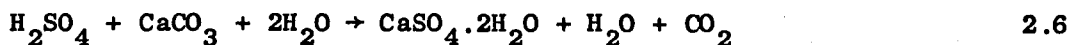
Rapid leaching of illite and smectite interlayer cations followed by decomposition of their lattice layers tends to bring about degradation into iron oxides, Al-hydroxides (gibbsite) and kaolinite (Norrish 1972) which, according to Paces (1978), are the thermodynamically stable, or metastable, products of aluminosilicate transformations at low temperatures. Chlorites are also thought to degrade to these secondary minerals through an aluminous interlayer "intergrade" phase (Jackson 1963) and are especially susceptible when Fe rich (Evans & Adams 1975). Vear (1981) and Attewell & Taylor (1971), however, observed in cores from boreholes, that chlorite can in fact increase on weathering. The reason for this unexpected behaviour is unclear, although in experiments to equilibrate

a soft clay fraction with sewage effluent in the laboratory, Wall et al. (1974) produced an increase in chlorite relative to mica; expandable clays and vermiculite. This suggests that microbial activity may possibly play a part in similar clay mineral alterations under natural conditions.

Apart from clay degradation, free gibbsite can appear as a weathering product where Al^{3+} is released into solution by rapid leaching. Goethite (FeO.OH) and hematite (Fe_2O_3) are also formed in weathered shales, partly from the release of Fe^{2+} or Fe^{3+} from clays and, more importantly, after pyrite oxidation. Chukrov et al (1972) observed that these minerals form where weathering processes are slow. In situations where Fe^{2+} is oxidised rapidly due to bacterial action and in the presence of high iron concentrations, an amorphous iron oxide termed ferrihydrite can be precipitated. This compound is unstable at low temperatures and depending on climate and availability of organic matter, spontaneously transforms into goethite or hematite (Schwertmann 1971). Chukrov encountered ferrihydrite precipitated from waters percolating through sulphide ores in mines and although its occurrence is not well documented, the observed conditions for its formation are not far removed from those associated with pyrite oxidation.

Leaching of cations from clays alters the composition of porewaters resident in the weathered material. Acid attack on other minerals also results in soluble cations being released into porewaters. Carbonate minerals such as siderite or ferroan dolomite were identified by Vear & Curtis (1981) as an important source of Ca, Mg and Fe. Although diagenetic, like pyrite, these minerals degrade at a slower rate because they generally occur in a more massive, nodular form. Acid consumption of calcite also occurs.

Release of certain cations frequently leads to the production of secondary minerals, notably gypsum, jarosite and limonite. Taylor & Cripps (in press) gave equations 2.6 and 2.7 for the formation of gypsum and jarosite after calcite dissolution and the release of K^+ from illites respectively:



Taylor & Cripps also reported that various other iron minerals may form including coquimbite, hematite and amorphous gels and base exchange reactions may give rise to sulphate minerals such as sodium jarosite, alunite and a variety of intermediate forms.

Gypsum precipitates within discontinuities which allow the passage of solutions under conditions facilitating evaporation of water. The requirements are met in fissures and along bedding planes where shale fissility is exploited, particularly in material where dry air can penetrate. This includes foundations beneath buildings where air gains access to unweathered rock through crushed rock fill or drainage systems and central heating ducts (see Penner et al. (1966) and Quigley & Vogan (1970)). In natural situations, fissures play an important role in the presence of air at depth. Surface evaporation also creates conditions conducive to gypsum precipitation. Jarosite is generally observed at greater depths than gypsum although in theory the two salts may occur together (Penner et al. 1966; Vear & Curtis 1981).

The heave problems associated with secondary mineral precipitation are well-known and arise from the volume increases which accompany the transformation of pyrite sulphide into the sulphate ion. Fasiska et al.

(1974) discussed this in terms of packing densities of ions and gave a volume increase of about 350% for the oxidation of the closely packed hexagonal sheets of the sulphide structure into the tetrahedrally coordinated sulphate structure. Greater expansions are induced on hydration of these compounds. Volume increases of 115% for pyrite to jarosite and 103% for calcite into gypsum are reported by Penner et al. (1966). Although the former reaction gives a greater volume increase, Nixon (1978) considers that gypsum formation is a more serious factor in shale swelling. He also mentions that the formation of calcium sulphate solutions creates the possibility of sulphate attack on concrete in contact with shale. Penner et al. (1966) determined that very small amounts of pyrite can support the processes of sulphate formation, particularly in the presence of bacteria. Significant alteration was attained after one month in a shale containing only 0.1 % pyrite inoculated with *Ferrobacillus-Thiobacillus* bacteria. The alteration zones contained jarosite which implies that in a very short time, pyrite oxidation and subsequent reactions such as clay mineral leaching and carbonate dissolution had taken place. The experiment, which was carried out under high temperatures (30°C) in humid but not wet conditions, illustrates the rapidity with which significant chemical weathering can occur on exposure of pyritic shales to humid, oxidising conditions.

2.8 The effects of weathering on engineering properties

Weathering processes have a great influence on the engineering properties of mudrocks. The processes involved, namely bond destruction, fissure development, water uptake and possibly chemical degradation, progressively return indurated rocks to a normally consolidated condition.

Table 2.2 presents physical data on a selection of rock types in their weathered and unweathered states. Generally, it appears that weathering results in higher plasticity and water content and lower shear strength. Apted (1977) also reported higher void ratios in weathered material.

Explanations for the reduced strengths, higher plasticity and water content values usually concern changes in the microstructure of the weathered materials. Herstus (1971) described how weathering of Miocene clay apparently produced individual clay aggregates, resulted in their mutual separation and formed a structure with large and numerous pores. Chandler (1969) observed that in the unweathered state, Keuper Marl is composed of silt-size aggregations of clay minerals and that a gradual degradation of this structure is responsible for changes in the mechanical properties of the soil. In Lias Clay, Chandler (1972) noted that for a given water content, relatively weathered soils show higher strengths than less weathered material and attributed this to restructuring of the originally anisotropic fabric by weathering. He did, however, report generally higher water contents and correspondingly lower shear strengths in weathered material. In London Clay, Apted (1977) and Russell & Parker (1979) described how weathering results in a more randomly orientated microstructure as a consequence of bond breaking. These changes are manifested as increased plasticity.

Chandler (1972) pointed out that weathering may not be totally responsible for the remoulding of soil fabrics, especially in British soils. Clays and clay-shales may be considerably disturbed as a consequence of Pleistocene permafrost processes. Weathering, however, still contributes considerably to structural changes in soils.

Secondary mineral precipitation was also noted. Apted (1977) considered that the volume increase and resultant distortion of material

Rock Type	Water Content %		Plasticity Index %		Clay Fraction < 2 μm %		Effective Cohesion c' kN m^{-2} (1)		Residual Shear Strength ϕ_r ' (2)	
	Weathered	Unweathered	Weathered	Unweathered	Weathered	Unweathered	Weathered	Unweathered	Weathered	Unweathered
Keuper Marl	12-40	5-15	17-35	10	30-50	10-35	<15	>30	24-18 ^o	23-32
Miocene Clay	39.2	25.6	50	30-40	-	-	-	-	-	-
London Clay	23-49	19-28 ^a	65	to 40 ^a	72	to 40 ^a	10 ^b	80 ^b	10.5	to 22 ^a
Barton Clay	21-32	-	55	to 21	70	to 25	7-11	8-24	15	-
Upper Lias	30 ^d	16 ^c	39	to 20 ^d	65	to 55 ^d	10-17	- ^d	9	to 13.5 ^d
Lower Oxford Clay	20-33	15-25	50	to 28	70	to 30	0-20	10-216	17	to 13

Reference: Keuper Marl - Chandler (1969)
 Miocene Clay - Herstus (1971)
 London Clay - a. Cripps & Taylor (1981)
 b. Apted (1977)
 Barton Clay - Cripps & Taylor (1981)
 Upper Lias - c. Chandler (1972)
 d. Cripps & Taylor (1981)
 Lower Oxford
 Clay - Cripps & Taylor (1981)

(1) and (2) These strength parameters are defined in Appendix 3.

Table 2.2 Comparison of some engineering properties in weathered and unweathered material

produced by selenite crystallisation in weathered London Clay creates significant strains within the clay, particularly as crystal growth, is unlikely to be uniformly distributed. Herstus (1971), having observed the formation of iron hydroxides in weathered Miocene clays, found that this imparts a brittle, metastable structure to the material. Russell & Parker (1979) found gypsum and jarosite in weathered Oxford Clay. They also noted a close association between illite degradation and reduction in strength on weathering of this material.

In section 2.5 the tendency for weathering processes to be concentrated along discontinuities was discussed. By exploiting discontinuities, weathering solutions gain access to fresh intact material. Apted (1977) considered that silt horizons in clays are also significant in this context because they are more permeable than the surrounding mass. Weathering reactions thus start in joints, fissures, bedding planes and faults which become expanded as fresh rock on exposed surfaces is attacked. The products of weathering, including physically disintegrated material, precipitated minerals, e.g. iron oxides and sulphate salts, and chemically degraded minerals accumulate in the discontinuities where they may eventually determine the physical behaviour of the whole rock. The influence of discontinuities on rock mass strength was reviewed by Leussink & Müller-Kirchenbauer (1967) who consider them to represent regions of weakness because they possess smaller shear strengths than the surrounding rock. Such weak zones are favourable for slide displacements and frequently form pre-determined planes for larger movements. Cancelli (1977) measured the shear strength of two samples of a highly overconsolidated Pliocene clay. One specimen was sheared along a joint and the strength was found to be substantially lower than in the second, unjointed sample. X-ray diffraction analysis of the joint surface

material showed that its mineralogy was markedly different from that of the ambient clay. The proportion of minerals such as quartz, calcite and dolomite was reduced by half, illite had a reduced crystallinity, vermiculite replaced chlorite and gypsum had been deposited along with amorphous minerals. Clearly, such alteration may contribute significantly to the development of slip surfaces by providing ready-weakened zones. This is supported by the observations of Bjerrum (1967) and Henkel & Skempton (1954) that sliding planes tend to be located in the lower part of active weathering zones or at the junction between weathered and unweathered material.

Skempton & Petley (1967) also found that the shear strengths along discontinuities in stiff clays were much lower than in intact clay. They proposed that initial opening of the joints destroys cohesion. In London Clay it was found that even small displacements of about 5 mm along joints were sufficient to reduce shear strength to levels which might facilitate slip plane development.

Material weakening and opening of fissures by weathering affects the shear strength of a rock or soil mass over a period of time. Brief mention should be made of two time-dependent processes affecting soils which can be significantly influenced by weathering. These are progressive failure and creep. Haefeli (1965) defined them as follows:

Creep is a process related to stress changes. It may either improve or lessen the stability of a system.

Progressive failure involves a gradual concentration of stresses, initiated and intensified by the formation of sliding surfaces leading to local loss of cohesion and reduction in shear strength. It may finally lead to catastrophe.

Bishop (1967) considered weathering to be particularly important in progressive failure because of its effect on the strength and permeability

of a soil. A reduction in strength gives rise to a non-uniform stress distribution and to local failures which vary with time. The zone of failure extends progressively along the potential slip surface and a state of limiting equilibrium is reached when failure has occurred over the whole surface. Major movement takes place when stresses exceed the shear strength of the affected mass.

Weathering accelerates progressive failure indirectly by opening discontinuities and creating stress concentrations which may stress material locally beyond its limiting strength value (Skempton 1964). In Bjerrum's (1967) model of progressive failure, which does not require a fissure structure, weathering aids failure surface development by relieving stored strain energy. This provokes displacements large enough to fail material along a slip plane.

The combined effects of physical and chemical weathering are obviously extremely important in an engineering context. In shales, where physical disintegration is very rapid and chemical weathering is potentially aggressive, engineering properties are almost certainly subject to considerable modification.

Even after the first phase of physical disintegration has occurred, chemical degradation still proceeds to alter the physical properties of weathered materials. Chemical activity may even occur at depth before significant surface alteration has taken place. Taylor & Spears (1973), for example, pointed out that secondary gypsum precipitation as a result of pyrite oxidation and reaction of sulphuric acid with available carbonates can be in advance of any near-surface oxidation.

Alteration of the physical properties of rock or soil masses due to the passage of modifying solutions is considered in studies by Early & Skempton (1975) and Prior & Graham (1974). Percolation of reducing solu-

tions along slip planes was thought to account for the blue-grey colour of disturbed areas in contrast with the brown-orange ambient weathered clay. Apter (1977) pointed out that during weathering the cation composition of porewaters would increase and possibly influence the geotechnical properties of clays while Vear & Curtis (1981), in their geochemical investigation of groundwaters at a major rotational landslide at Mam Tor, Derbyshire, speculated that the contribution of chemical weathering to maintaining and accentuating planes of weakness may have been underestimated in the past. Indeed, Taylor (1973) concluded that clay mineral changes across ancient slip planes may be important in that ionic bond strengths could be changing over protracted time intervals.

Bjerrum (1967) considered that the first, disintegration phase of weathering was by far the most significant in terms of mechanical properties. This should not, however, discount the probability that the post-failure or "post-disintegration" behaviour of weathered material will be influenced significantly by continued chemical activity, regardless of its apparently slower pace.

In Chapter I, accounts were given of soil heaving in shales due to secondary mineral precipitation. The possible influence of weathering solution composition on the physical properties of shales was also mentioned, particularly with regard to chemical reactions along existing slip planes. Acid weathering solutions which are produced initially by pyrite oxidation are very potent and are, therefore, likely to be capable of altering the physical properties of shales severely. In engineering, sustained chemical activity in certain situations, such as within landslides, may be just as significant as the initial rapid breakdown observed in shale exposures.

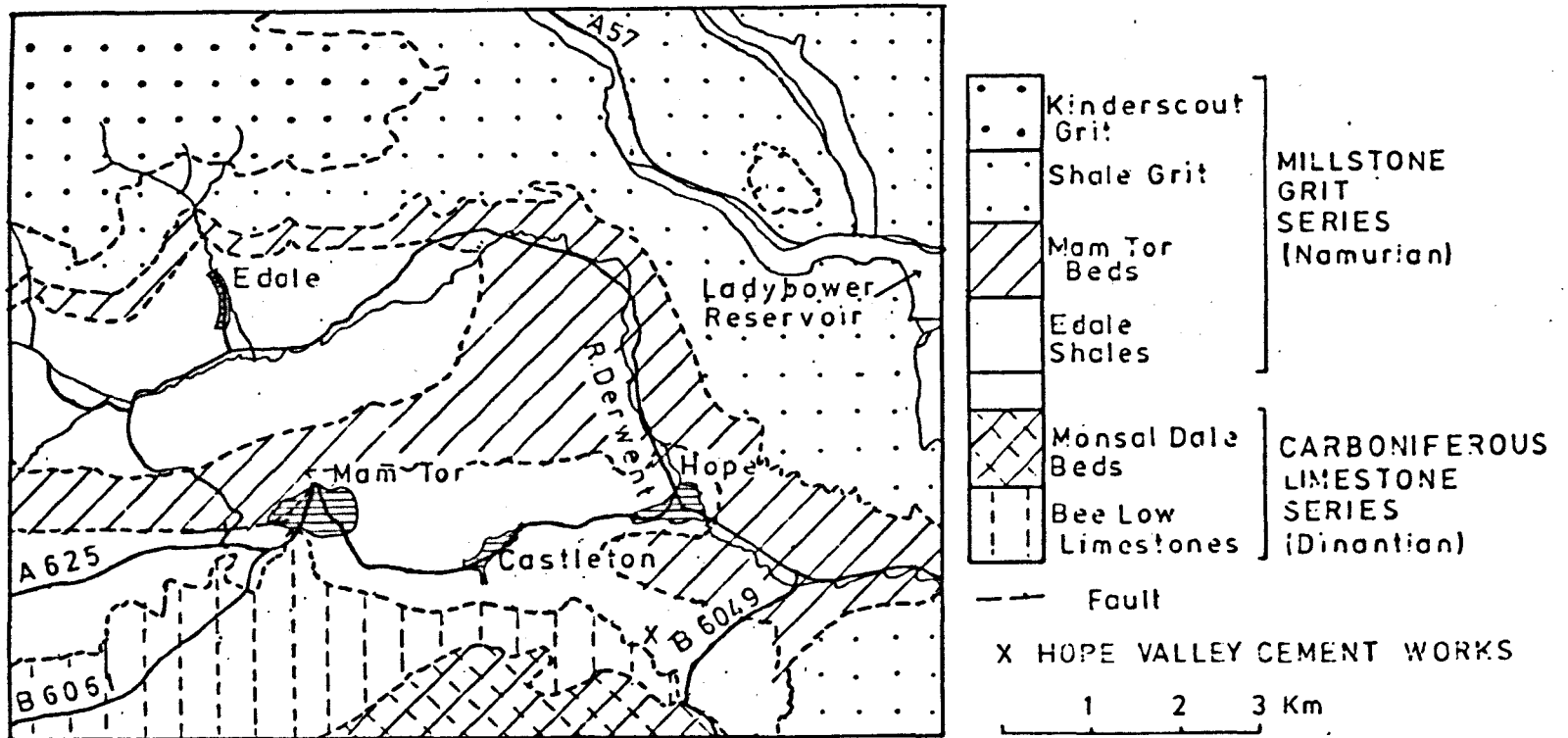


FIG. 3.1 Location and outcrop of Edale Shale.

CHAPTER III

EDALE SHALE AND ITS OCCURRENCE

AT MAM TOR

The effects of weathering on the engineering properties of shales were investigated using Edale Shale. This outcrops in the Peak District, Derbyshire, as part of the Namurian of the Central Pennines. The formation floors the Edale Valley and also outcrops at the major rotational landslide at Mam Tor (Fig. 3.1). It is quarried extensively at Hope Valley Cement Works (Fig. 3.1).

Edale Shale provided a useful material for weathering studies both in the laboratory and in the field due to its availability in a variety of weathered states. A large quantity of recently quarried shale was obtained from Hope Valley Cement Works and used in the experimental work described in Chapters V and VI. Material from various sites at Mam Tor was also taken for comparative studies, particularly the work outlined in section 4.5.

3.1 Stratigraphy and description of Edale Shales

Edale Shales were described by Collinson & Walker (1967) as deep basinal mudstones about 230 m in thickness at the base of the Namurian in Derbyshire. They are overlain by the repetitive sandstone/shale sequence of the Mam Tor Beds which are described by Allen (1960) as distal turbidites. These are exhibited in the backscarp of the landslide at Mam Tor (Plate 3.1). The sequence continues with more proximal turbidites, the Shale Grits, followed by the delta-slope deposits of the Grindslow Shales and finally, delta-top, fluvial Kinderscout Grit. The association of the Edale Shales with a turbidite/delta-slope/delta-top stratigraphy is indicative that the sequence represents infilling of a Lower Carboniferous

Edale Shale

Mam Tor Beds



PLATE 3.1 Back scarp and retrogressive scarps of Mam Tor.

cratonic basin, namely the central Pennine Basin, first by mudrocks and then by a southward advancing deltaic complex (Allen, 1960). A basin origin for the shales is supported by the proximity of limestones (Fig. 3.1) which accumulated on the Derbyshire Massif. The basin is now part of the Pennine Anticline with Edale Shale at the core (Ramsbottom et al., 1967).

The shales are black or dark-grey, finely bedded mudrocks which develop fissility in surface exposures. In the mudrock classification of Stow (1981) they are typical shales. Occasional bands of nodules, considered by Professor C.D. Curtis to be of ferroan dolomite, occur within the sequence.

A borehole was drilled in November (1981) by the University of Sheffield to obtain information about Edale Shales at depth within the landslide. Fig. 3.2 gives a description of the core extracted from successive depths to 27.7 m. Drilling procedures are also included in the log. Fresh rock was encountered at a depth of 26 m and become progressively more weathered towards the surface. At this depth, a change in bedding dip from 5° , commensurate with the regional dip, to $30-45^{\circ}$ was recorded suggesting that the slip surface is located here. Fresh shale thus occurs below the slip zone at Mam Tor.

In hand specimen, the fresh shale can be described as uniformly fine-grained, finely laminated black mudrock. It parts readily along laminae and vertical joints when exposed to the warm, dry conditions experienced in the laboratory. A white mineral can be seen deposited along some horizontal laminae and in vertical joints. This was observed under the microscope as clear to brown, tabular hexagonal crystals accompanied by a black flaky mineral which was identified as hematite. A brown mineral with a translucent appearance was also noticed on the edges of the crystal assemblages and this was thought to be limonite. X-ray diffraction analysis suggested that the white crystals were probably

SYMBOLIC LOG.



SHALE

CLAY

SANDSTONE

SILTSTONE

LAMINATED SILTSTONE

MATERIAL BROKEN UP

FIG. 3.2 Log description for the borehole at Mam Tor.

SHEET 2.1 CONTINUATION

Site		Survey Ref:		Borehole No. 1					
MAM TOR - MAIN UNIT									
Machine		Core Barrel Design & Bit		Orientation					
ENGLISH DRILLING				VERTICAL					
Instrumentation	Drilling & Casing Progress	Water Level Recovery	Solid Core Recovery %	R.Q.D. %	Fracture per m	Fracture Orientation	Description of Strata	Barrel Level m	Symbolic Log
								60'	
	9TH RUN						HW micaceous sandstone - graded bedding - 45°-horiz. Fracture staining on fracture	62'	
	CASING DEPTH FOR 11TH RUN SIZE 8X CORE SIZE 1 1/2"						HW shale/sandstone fragments. Laminar nod in both ~30°-horiz. staining on fracture surface.		
	11TH RUN						Sandstone with graded bedding ~45°-horiz. Fracture along oxidized weak planes. shale laminae 50°-horiz. slightly coarser than mudrock above. Competent.	69'	
	12TH RUN						CW competent shale fragments micaceous + oxidized on edges of laminae		
	13TH RUN						One piece siltstone - shows oxidized fracture surface with carbonaceous material. Possible is telenoides or helic plant stem. Graded beds ~30°	76'	
	14TH RUN						HW rounded fragments with oxidation on partings. Mudstone.		
					Series of small partings		Laminated micaceous siltstone with laminations ~45°-horiz. graded bedding 45°, grading into fine grained faintly laminated mudstone. Oxidation on bedding plane. Passed into non-oxidized laminated micaceous siltstone.	84'	
	13TH RUN				10		FW Uniformly fine grained, finely laminated black shale. Laminae ~5°-horiz. Partly readily along laminae + along vertical joints. Oxidation + gypsum crystallization along some laminae + calcite veins in vertical joints. Turb. present.	90'	
	14TH RUN				3				

SHEET 1.1

Site		Survey Ref:		Borehole No. 1					
MAM TOR - MAIN UNIT									
Machine		Core Barrel Design & Bit		Orientation					
ENGLISH DRILLING		DOUBLE TUBE NWX BIT - BORT DIAMOND JKS		VERTICAL					
Instrumentation	Drilling & Casing Progress	Water Level Recovery	Solid Core Recovery %	R.Q.D. %	Fracture per m	Fracture Orientation	Description of Strata	Barrel Level m	Symbolic Log
								60'	
	9TH RUN							62'	
	CASING DEPTH FOR 11TH RUN SIZE 8X CORE SIZE 1 1/2"								
	11TH RUN							69'	
	12TH RUN								
	13TH RUN							76'	
	14TH RUN								
								84'	
	13TH RUN							90'	
	14TH RUN								

1ST RUN - Borehole Depth
 - 1ST RUN - Casing Depth
 R.Q.D. - Rock Quality Designation
 ⊥ 80-90° } Attitude of Prominent Fractures
 √ 60-80° }
 < 30-60° }
 < 0-30° }
 F Fast } Relative Rate of Descent of Barrel
 S Slow }

+ Gain } Water Recovery Level
 - Loss }
 Constant Flow }

F Fresh } Weathered State
 FW Faintly Weathered }
 MW Medium Weathered }
 HW Highly Weathered }
 CW Completely Weathered }
 RS Residual Soil }

1ST RUN - Borehole Depth
 - 1ST RUN - Casing Depth
 R.Q.D. - Rock Quality Designation
 ⊥ 80-90° } Attitude of Prominent Fractures
 √ 60-80° }
 < 30-60° }
 < 0-30° }
 F Fast } Relative Rate of Descent of Barrel
 S Slow }

+ Gain } Water Recovery Level
 - Loss }
 Constant Flow }
 Inconsistent }

F Fresh } Weathered State
 FW Faintly Weathered }
 MW Medium Weathered }
 HW Highly Weathered }
 CW Completely Weathered }
 RS Residual Soil }

Standing Water Level 24-11-81

alunite (Fig. 3.3a). The appearance of secondary minerals in relatively fresh material is indicative that salt saturated solutions pass through the preferential flow paths offered by joints and laminae. Very fine pyrite is also present in unweathered shale.

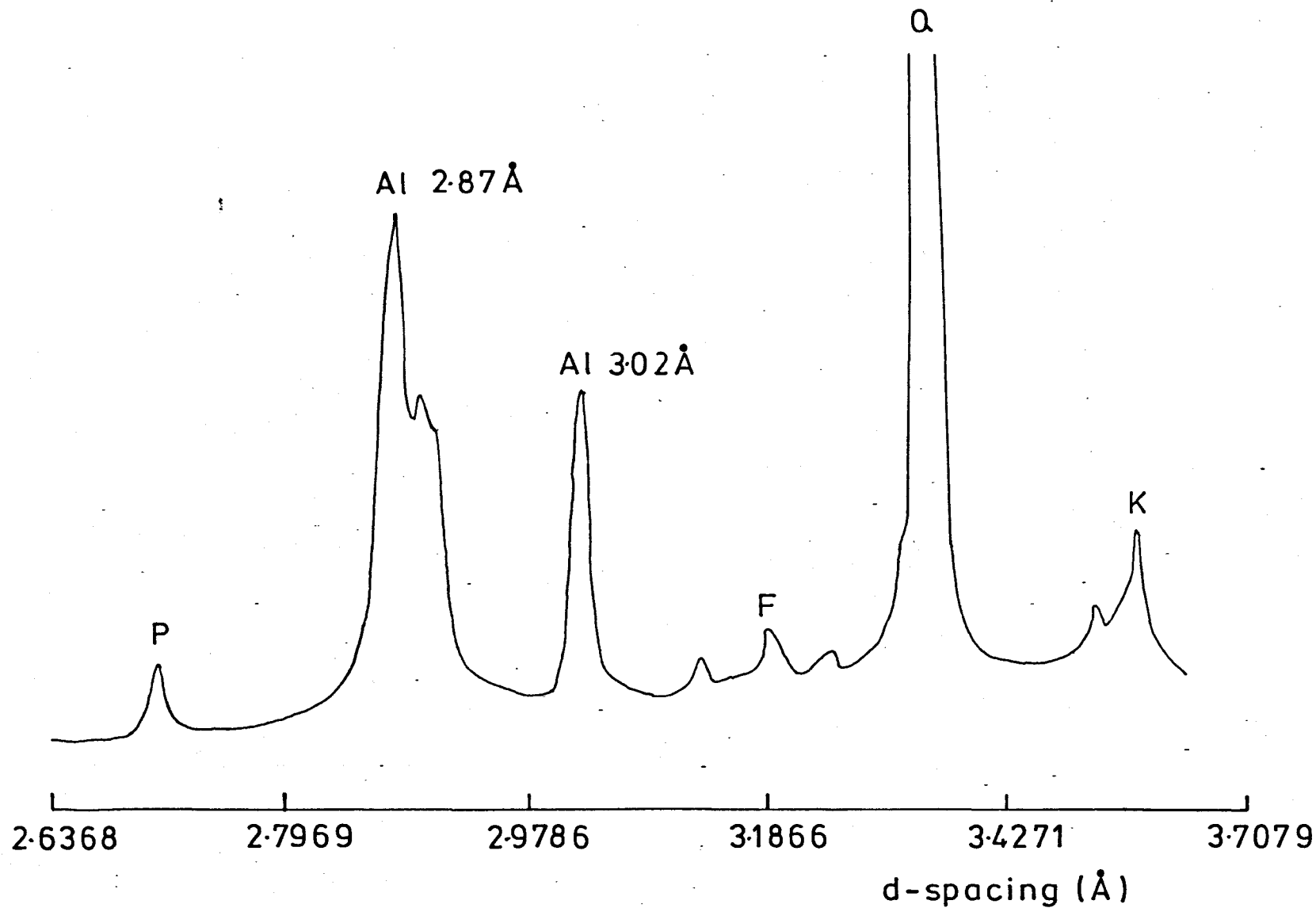
Plate 3.2 shows a slide of unweathered material in which repeated light and dark layers are discernible. The lighter areas appear to be characterised by low quartz contents, fine clay and disseminated opaque material which is probably organic matter. The darker layers contain greater amounts of opaque material, coarser quartz crystals and fine clay. Colour differences between the layers may be related to the greater preferred orientation which appears to be exhibited by the clay minerals and organic matter in darker layers. Similar layer definition was observed by Spears (1969) in the Mansfield Marine Band.

Immediately above the fresh material the shale is fragmented, rounded and oxidised (Fig. 3.2). This was interpreted to be the disturbed zone along which movements of the landslide are concentrated. The presence of iron oxides on fragments and along partings within fragments testifies that weathering solutions pass through this zone and may attack the fresh shale below.

The material becomes more fragmented above the slip zone and fracture surfaces are stained an orange colour. Fracture frequency increases from zero at around 26 m to numerous small partings at surface levels. No systematic change in their orientation was recorded. At about 20.9 m, coarser-grained silt and sandstone fragments indicate the lowest levels of the Mam Tor Beds. The interbedded shales became increasingly difficult to recover in the core and at depths down to 3.8 m they tended to disintegrate completely during drilling, only returning to the surface as clay coatings around more competent silt and sandstone core.

X-ray diffraction analyses of shales at depths of 27.7 m, 26 m, 23.4 m and at the surface at Mam Tor show that pyrite becomes increasingly

3.3a X-ray diffraction trace of Edale Shale from a depth of 26 m at Mam Tor showing the major alunite peaks.



Al - alunite; Q - quartz; K - kaolinite; F - feldspar; P - pyrite.

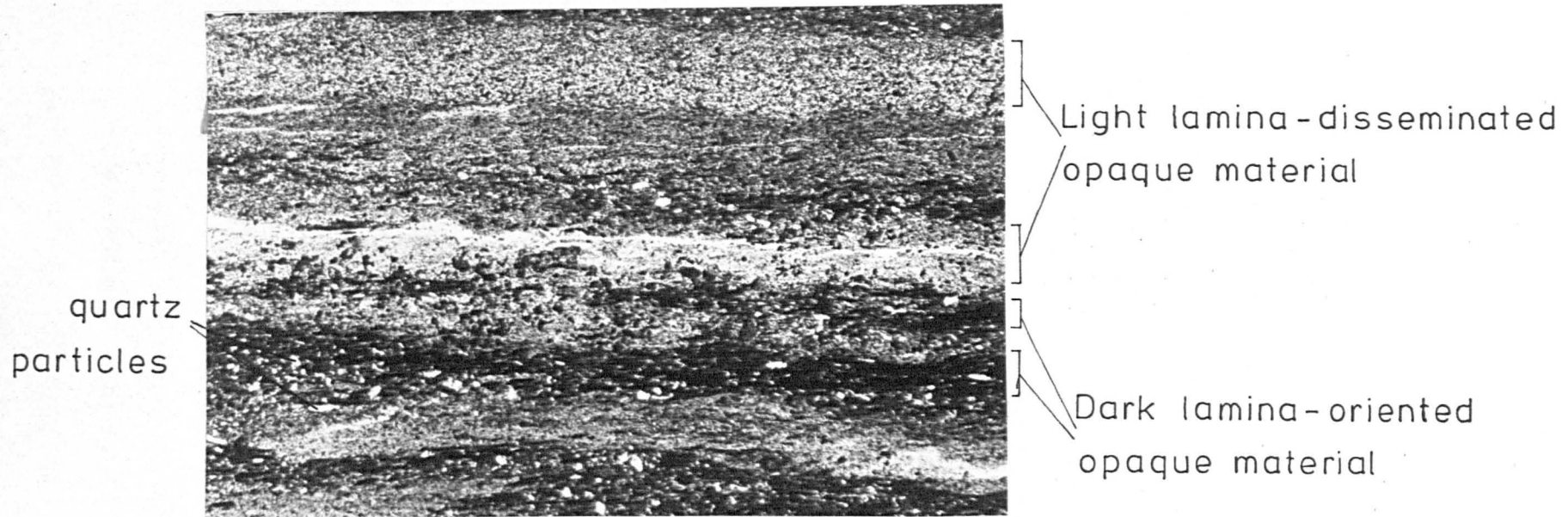


PLATE 3.2 Thin section of fresh Edale Shale from a depth of 27.7 m.

1mm

Clay	0 m	23.4 m	25 m	27.7 m	Quarry
Kaolinite	16	21	9	17	23
Illite	22	21	24	23	21
Expanding minerals	56	52	63	57	50
Chlorite	6	6	3	3	6

TABLE 3.1 Relative proportions of clay minerals in Edale Shale from different depths within the Mam Tor borehole. Material from Hope Valley Cement Works is included.

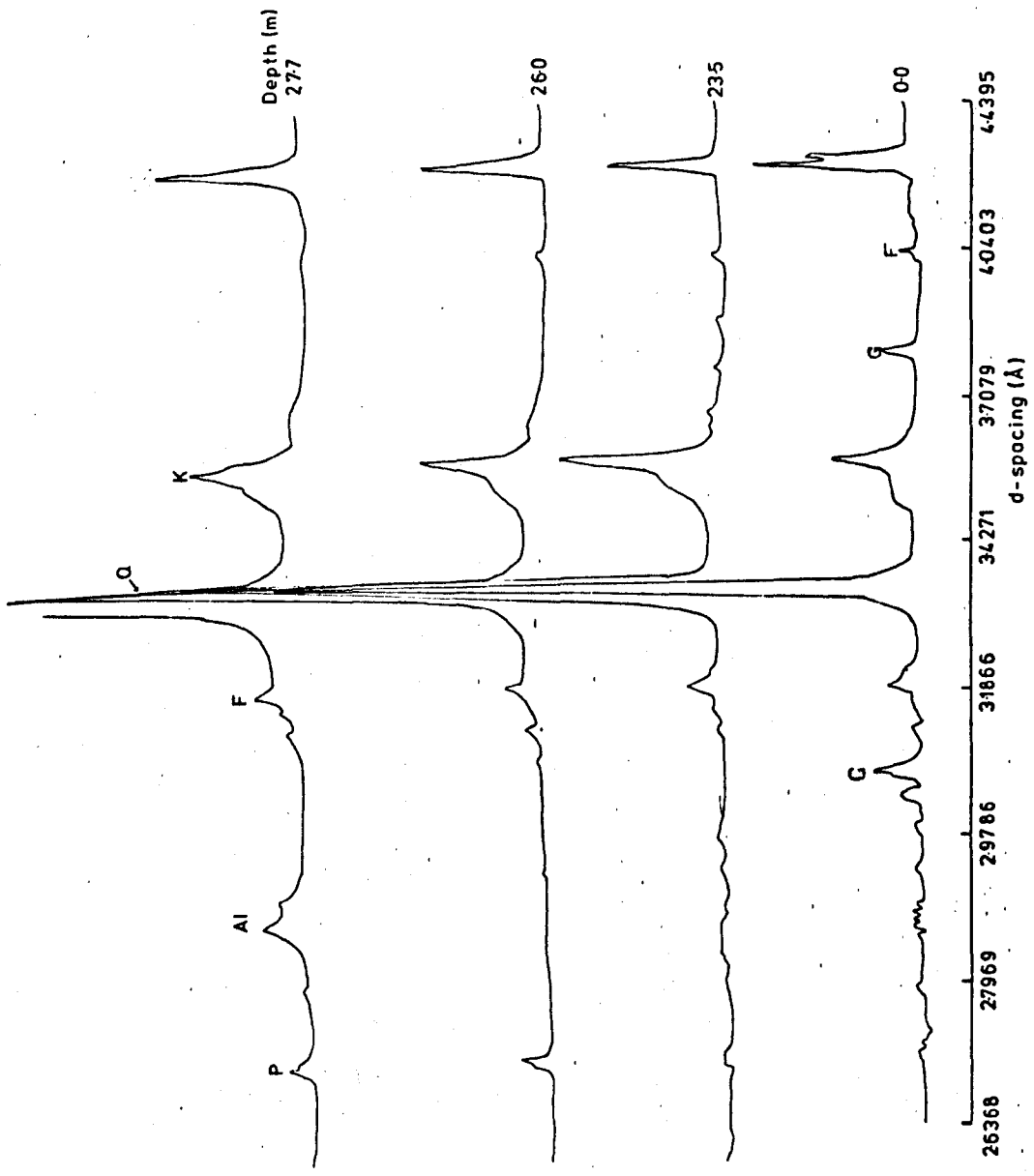
important with depth, particularly below the slip plane in fresh shale (Fig. 3.3b). Hematite was identified in surface specimens and at 26 m, in the region of the slip zone. Gypsum is abundant in surface samples but is not present in other samples at depth. Quartz and feldspars occur in all samples with quartz as the major component.

A semi-quantitative analysis of the clay minerals (Fig. 3.3c) using the method of Weir et al. (1975) gave the relative proportions shown in Table 3.1. The figures given are not precise due to the difficulties inherent in quantitative X-ray diffraction work, thus it is only possible to infer trends from the data rather than determine precise variations in clay minerals with depth. In fact, no certain trends are identifiable, although it appears that chlorite increases towards the surface with a general reduction in expandable minerals. It is likely that a concomitant increase in kaolinite would also occur as recorded in weathering studies elsewhere, for example by Spears & Taylor (1972), Taylor (1973) and Loughnan (1969).

Also included in Table 3.1 are the relative proportions of the clay minerals in Edale Shale obtained from the quarry at Hope Valley Cement Works. From the higher kaolinite and lower expandable clay content of this sample compared with that at Mam Tor, the quarry shale appears to have experienced weathering perhaps to an even greater degree than the surface material at Mam Tor. Contrary to the latter, however, shales from the quarry contain pyrite which is surprising, although the absence of oxidising bacteria may hinder breakdown. This was also the opinion of Vear (1981). The presence of diagenetic pyrite is therefore not a reliable indicator of the weathering grade of the shale. Gypsum and iron oxides are abundant but again, since their source is uncertain owing to storage of the shale in wet, oxidising conditions, the presence of these minerals does not testify that they have been deeply weathered in situ.

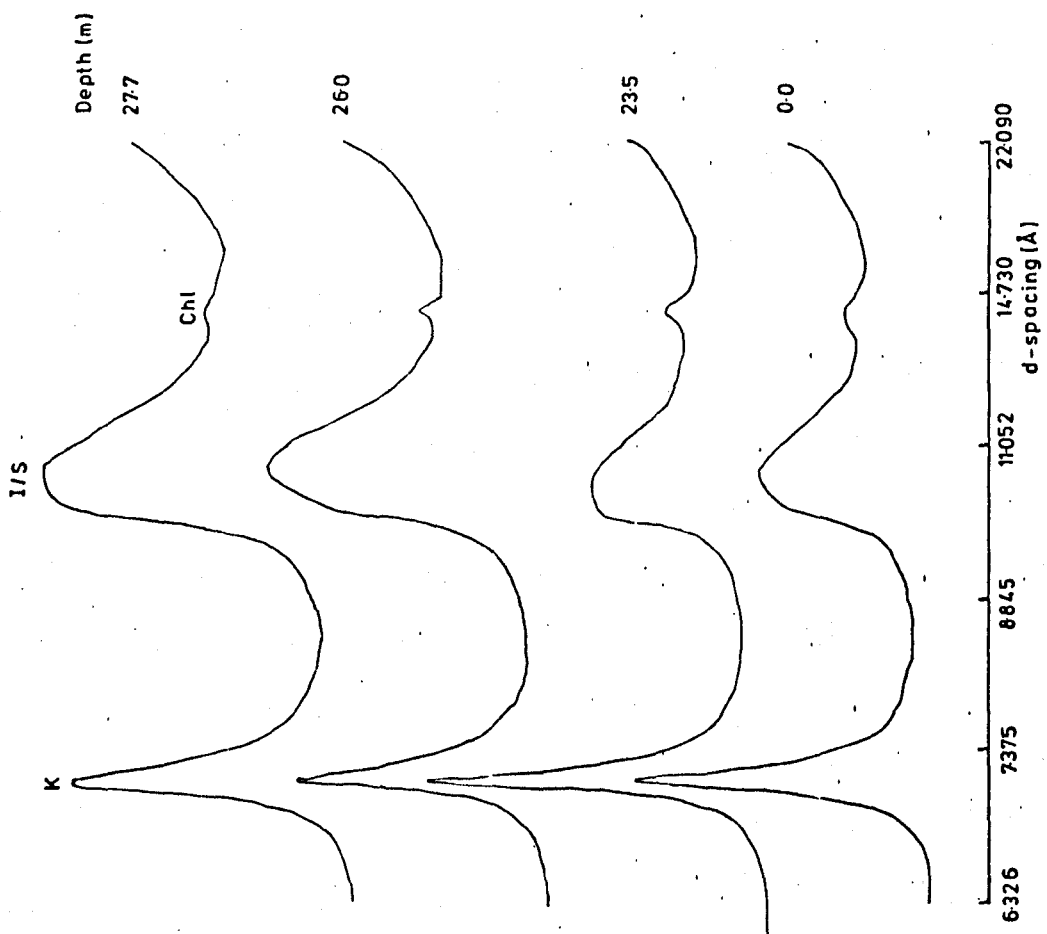
FIG. 3.3b X-ray diffraction traces of Edale Shale taken from the Mam Tor borehole at depths of 0, 23.5, 26.0 and 27.7 m (whole-sample traces).

K - kaolinite; F - feldspar; G - gypsum; Al - alunite; P - pyrite;
Q - quartz



3.3c X-ray diffraction traces of Edale Shale from depths of 0, 23.5, 26.0 and 27.7 m in the Mam Tor borehole showing major peaks for clay minerals in < 2 μm -size material.

K - kaolinite; I/S - illite/smectite mixed layer clays; Chl - chlorite



3.2 Engineering properties of Edale Shale

The properties investigated in this section were residual shear strength expressed as the apparent residual angle of friction (ϕ_{ra}') and plasticity. The reasons for choosing these particular properties are discussed in Chapter 1. The concept of residual shear strength is discussed in Appendix B.1 and the techniques used to determine these properties are described in section 6.5 and Appendix A.2 respectively. Measurements were made on Edale Shale from the Hope Valley Cement Works and from surface exposures at Mam Tor.

The results are shown in Table 3.2. The values for ϕ_{ra}' were obtained under a normal stress of 294 kN m^{-2} which is estimated to be the normal force experienced by Edale Shale at a depth of 22.5 m within the landslide. The results show that weathered shale at Mam Tor has a higher ϕ_{ra}' than the less weathered material from the Hope Valley Cement Works. This is interpreted to reflect a higher quartz content in the weathered material. Spears & Taylor (1972) noted that quartz tends to concentrate during weathering due to preferential removal of fine material. In later studies in this project (Section 4.5), shale from Mam Tor was found to have a higher silica content than the Cement Works material, which indicates that it probably contains larger amounts of quartz.

ϕ_{ra}' for the shale aggregate did not appear to be very sensitive to a tenfold reduction in the strain rate nor was it affected by the initial grain size distribution of the shale.

In more detailed studies of the engineering behaviour of Edale Shales, T.H. Al-Dabbagh (pers.comm.) concluded that the shear strength and plasticity properties of this material are variable over the area of its outcrop. This is probably attributable in part to differences in the degree of weathering at different locations. Other causes of variation in shear strength may include differences in particle size distribution and mineralogy. He also investigated the residual shear strength and

Sample	ϕ_{ra}°	LL%	PL%	PI%	Initial Moisture Content %	Final Moisture Content %
Relatively unweathered Edale Shale (Hope Valley Cement Works) <2 mm, strain rate 0.48 deg. per min.	21.5	28	14	14	27	-
As above < 850 μm	22.5 ^o	28	15	13	18	25
As above < 425 μm	22.0	37	20	17	11	20
As above < 425 μm , strain rate 0.048 deg. per min.	21.7	-	-	-	11	20
Weathered Edale Shale from Mam Tor < 425 μm , strain rate 0.48 deg. per min.	24 24	39 38	23 23	16 15	31	-

Normal stress 294 kN/m^2

c_r' assumed to be zero

Material properties:

Initial bulk density of shale aggregate = 1.94 Mg m^{-3}

Initial dry density of shale aggregate = 1.43 Mg m^{-3}

Initial void ratio = 0.87

Initial porosity = 0.46

Final bulk density (after consolidation in ring shear apparatus) = 2.75 Mg m^{-3}

Final dry density = 1.87 Mg m^{-3}

Final void ratio = 0.43

Final porosity = 0.30

Table 3.2 Residual shear strength and plasticity of Edale Shale aggregate in different weathering states, size fractions and rates of strain

plasticity of fresh shale from a depth of 27.7 m in the Mam Tor borehole. Lower strengths and higher plasticity values were recorded relative to surface material. This is probably a function of the lower quartz contents with respect to clay minerals at depth compared with those in weathered surface shale.

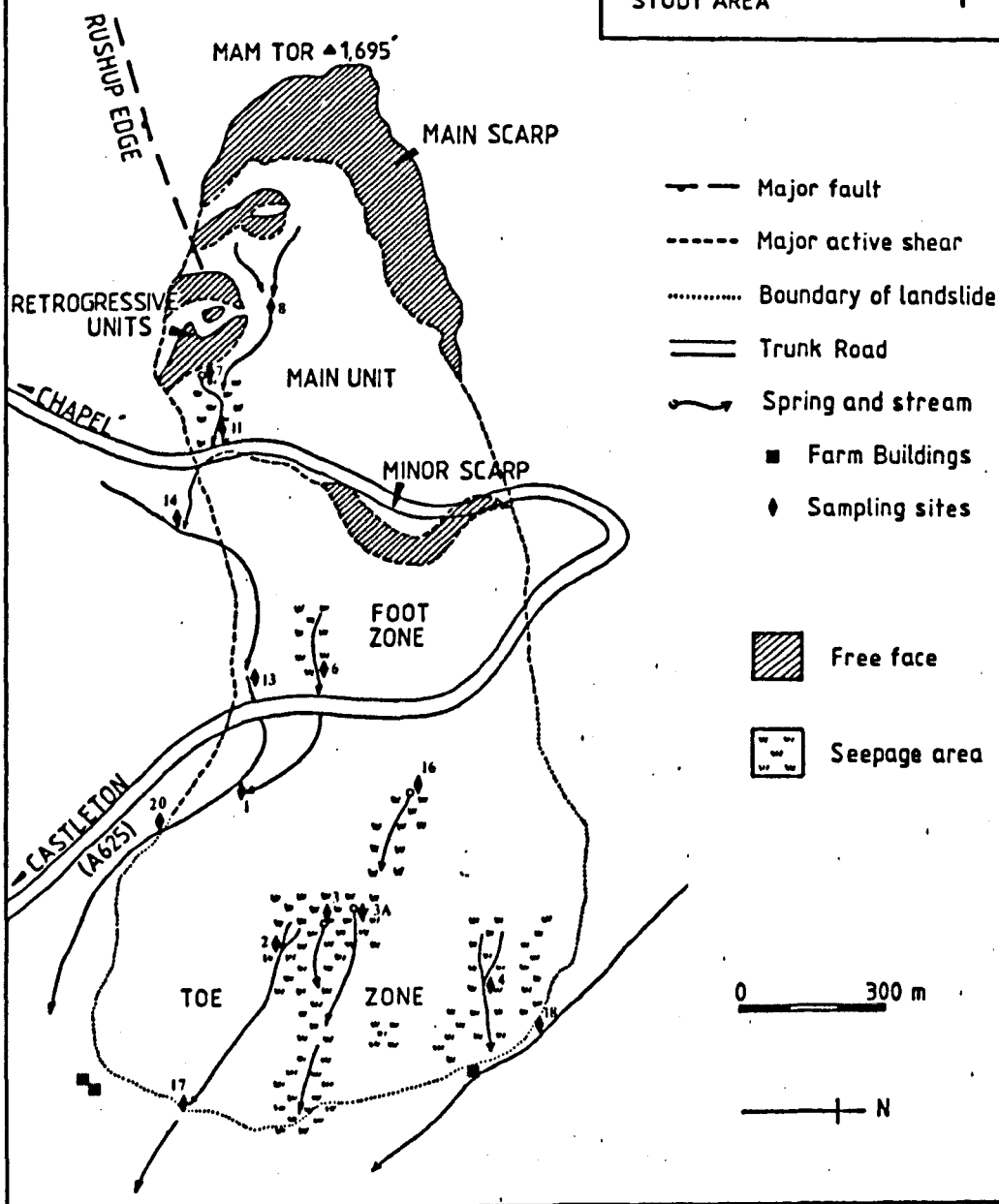
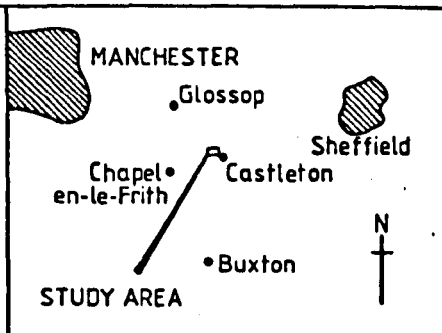
3.3 The landslide at Mam Tor

This project is mainly concerned with the properties of materials and how they are affected by weathering. Studies of geomorphological interest at Mam Tor are the topic of a separate investigation (T.H. Al-Dabbagh, personal communication). However, the occurrence of Edale Shale at this major landslide (Fig. 1.6) provided an ideal opportunity to consider the findings of laboratory studies in the context of slope stability. Furthermore, a comprehensive study of the weathering system at Mam Tor has been carried out by Vear (1981). Information derived from his studies contributes to the interpretations given in this project of continued instability of the landslide.

Fig. 3.4 shows the geomorphological features of importance at Mam Tor and a cross-section through the landslide is illustrated in Fig. 3.5. The landslide has a rotational main unit about 400 m long by 300 m wide and a translational toe 400 m in length. In terms of Skempton & Hutchinson's (1969) classification, the slide is a complex rotational slump with a translational toe. The exact geometry of the rotational slip surface is not certain but it is concave in form and from the borehole in the main unit, the maximum depth of the disturbed zone is approximately 26 m (Fig. 3.5). From borehole data (Fig. 3.2), the Mam Tor Beds have been backtilted from a regional dip of 5° to values of 45° in the affected area.

The back scarp, shown in Plate 3.1 is about 108 m high and is cut on its southern flank by a fault (Fig. 3.4) which brings the Edale Shales into juxtaposition with the Mam Tor Beds. Instability of the shales is

Fig 3.4 Location and Major Geomorphological Features of the Landslide at Mam Tor, Derbyshire from Vear & Curtis (1981), fig.1



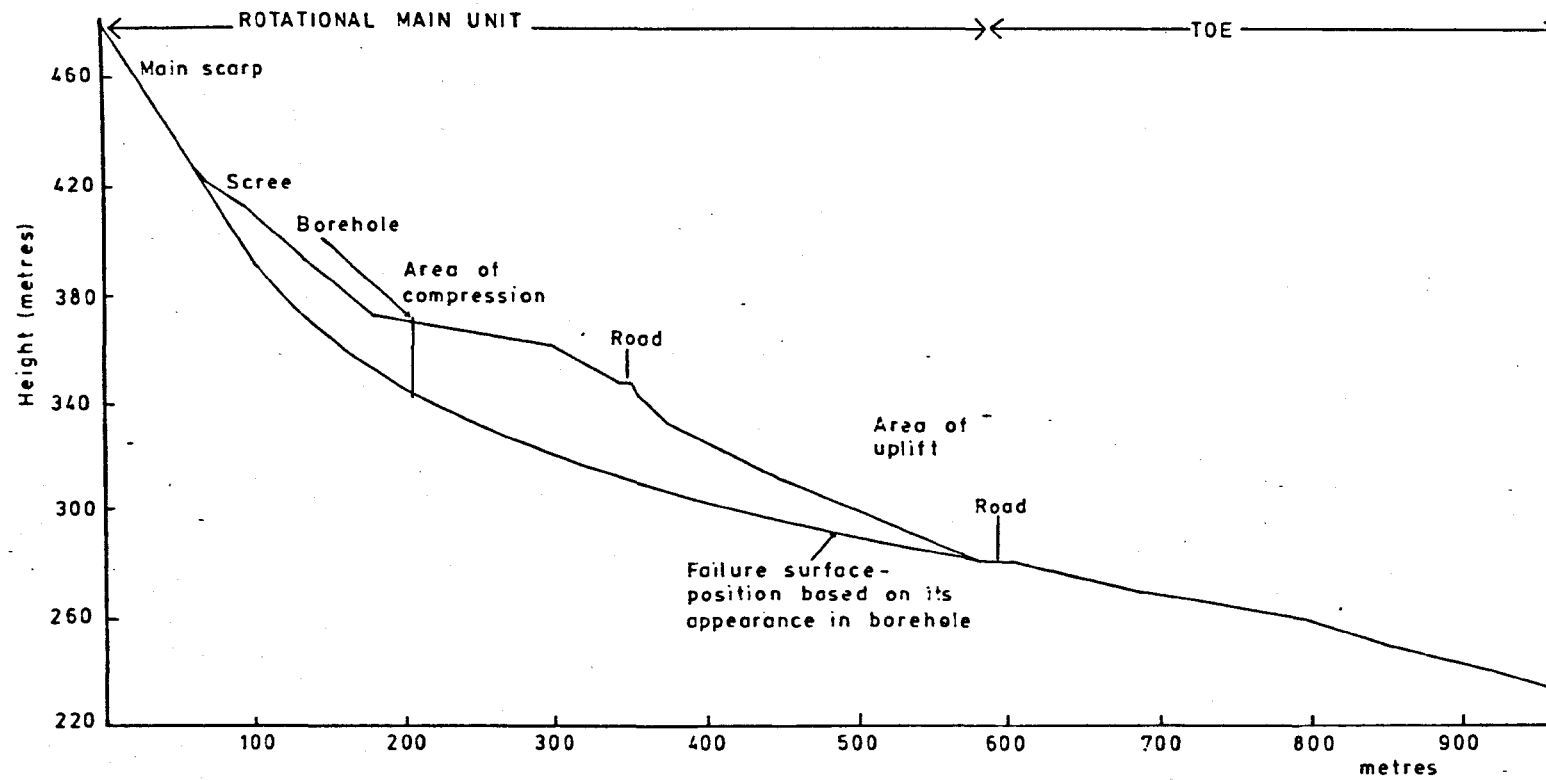


FIG. 3.5 Cross-section through the landslide at Mam Tor.

evinced by the occurrence of a number of retrogressive scarps within these beds on the southern side of the landslide. Similar retrogressive activity is not apparent in the Mam Tor Beds in the main scarp. Instead, scarp retreat here is mainly achieved by disintegration of the interbedded shales. Large sandstone blocks are left unsupported which results in rock falls. The top of the main unit is partially covered with scree material at the base of the scarp.

The central area of the main unit has a hummocky appearance due to the compression of material affected by rotational slumping (Plate 3.3). The lower part of the main unit, however, shows uplift features (Plate 3.4). The centre of rotation of the slumped unit is, therefore, judged to be located between the two roads (Fig. 3.5).

The material forming the translational toe is derived from the rotational unit and is very unsorted. A piezometer installed in this area shows that the groundwater level is frequently at the surface, hence the soil mass remains saturated for most of the year. The mode of movement of the toe is debatable and, following the descriptions of Skempton & Hutchinson (1969), this feature has been variously termed earthflow or mudflow during field discussions (Plate 3.5).

Instability of the landslide appears to be intermittent. Frequent small movements occurring during wet seasons are interspersed every few years by major failure events. Little data are available on the scale of movements. A surveying project was set up using theodolite and electronic distance measuring equipment (EDM) to measure rates of displacement of various points on the landslide over the three-year period of this research. The survey was initiated with a view to estimating the scales of movement of major or minor failures which might occur during the time of the survey. It was also intended to ascertain which parts of the slide were

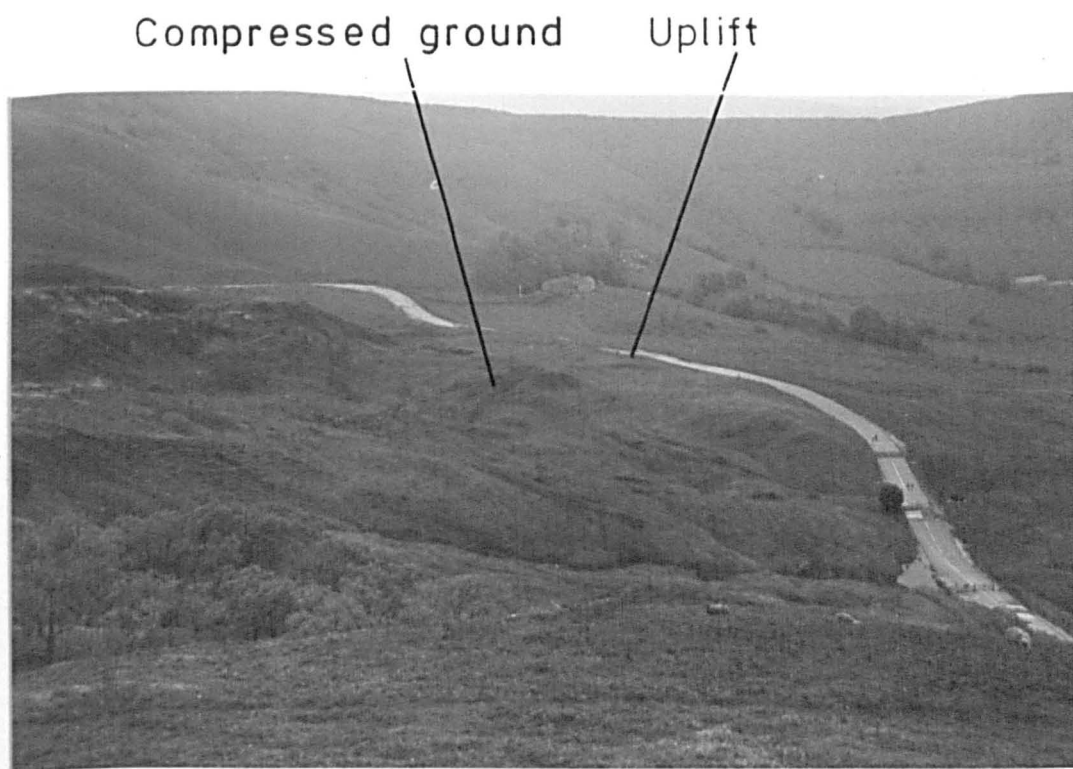


PLATE 3.3 Area of compression on the main unit of Mam Tor.



PLATE 3.4 Lifting of the foot of the rotational main unit, Mam Tor.



TOE

PLATE 3.5 Toe region of Mam Tor.

most active in order to obtain some evidence for explaining instability of the whole slide. Unfortunately, no obvious discrete failure events were recorded. There did appear to be a slow, steady creep, however, with the toe region giving the fastest rates of horizontal movements of about 0.2 m per year. The pattern of instability suggests that the factor of safety is permanently close to unity so that a small reduction could initiate movement. Increases in groundwater level may trigger small, frequent movements but a less frequently occurring condition is required to explain the relatively occasional major movements.

3.4 Weathering processes at Mam Tor

3.4.1 Physical weathering

At Mam Tor, rapid degradation in exposures of Edale Shale is very evident on the retrogressive scarp faces of the landslip. One of these scarps is shown in Plate 4.1. At the top of the slope, shales are exposed in a steep free face. Here, they are thinly bedded with a shallow dip of 5° to the northwest and exposure to the weathering environment has obviously resulted in preferential parting parallel to bedding planes, as seen in Plate 3.6. The whole face is stained yellow and orange through the deposition of goethite and limonite, with gypsum crystals deposited along some of the partings. Joints cut the rock vertically at approximately 30 cm intervals and are filled with iron oxides and abundant gypsum crystals. Iron-staining is present to depths of 23 m as shown in the borehole but gypsum is only present in large amounts in surface exposures, probably because evaporative concentration of waters is required for precipitation. A scree slope occurs below the top face. At the highest part of the scree, individual shale pieces are about 2-3 cm in diameter and 1 mm thick. Plate 3.7 shows that the pieces are polygonal in shape

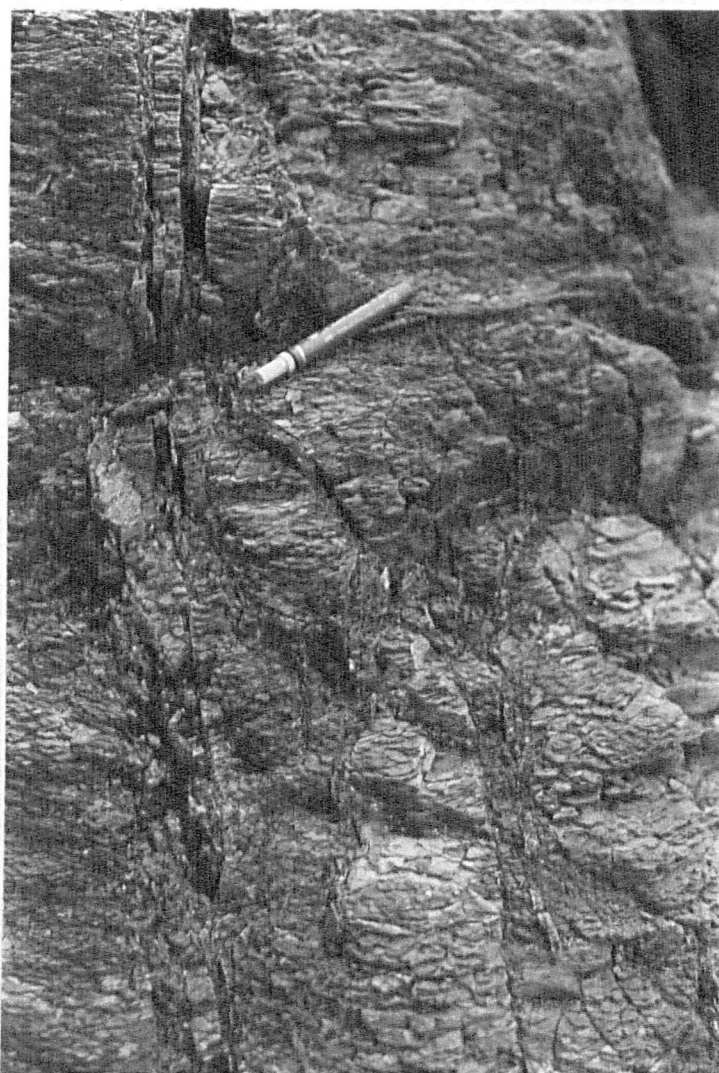


PLATE 3.6 Parting along joints and bedding planes at the top of the retrogressive scarp.

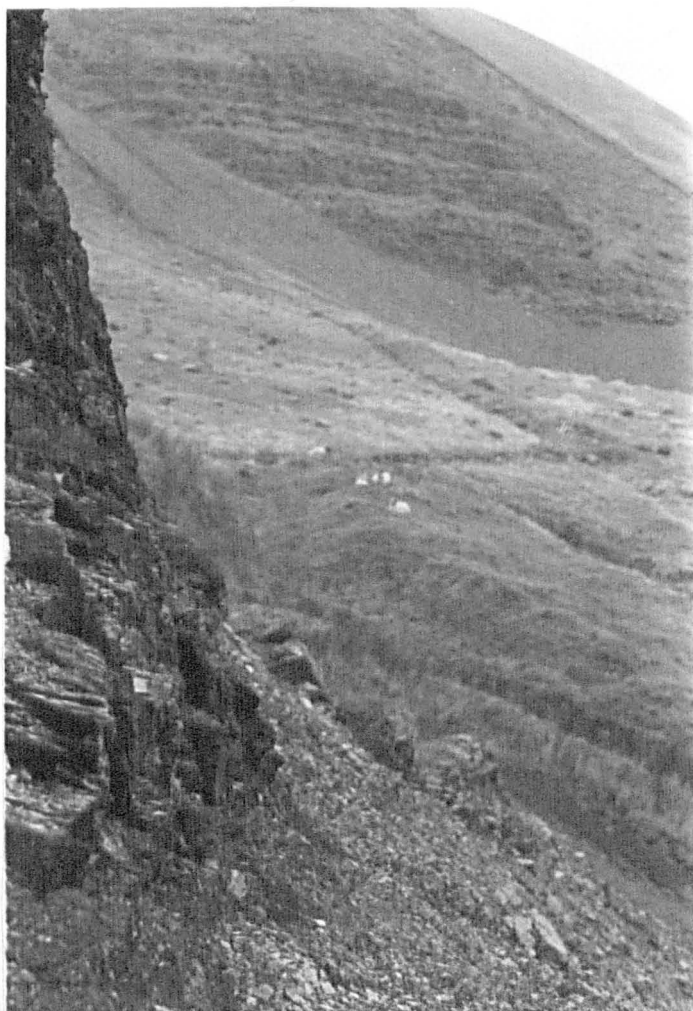


PLATE 3.7 Newly weathered shale at the top of the scarp.

with a tendency to flake along bedding planes and contract into smaller pieces on bedding surfaces. They are frequently coated in goethite and limonite. Mid-slope, the aggregate size is about 5 mm in diameter and 0.5 mm thick. The particles are still polygonal in shape but show lesser tendency to part along bedding planes. At the scree bottom, the soil is very wet due to runoff accumulation and seepage, probably from the nearby fault crush (Plate 3.8). Here, individual particles are hardly discernible and where identifiable, measure only about $\frac{1}{4}$ mm in diameter with little staining except on coarser pieces (Plate 3.9). The soil has a clayey consistency. At higher levels on the slope, similar clayey material also occurs just a few centimetres beneath the coarser surface detritus.

Rock disintegration on the scarp disrupts the rock structure in a style very similar to physical breakdown observed in other shales and mud-rocks, e.g. Kennard et al. (1970), Taylor & Spears (1970). Commonly noted modes of breakdown include parting along bedding planes, polygonal contraction on bedding surfaces and by joint expansion. The tendency for this material to part preferentially along bedding planes and to develop fissility may be attributed to the finely laminated structure described in section 3.2.

3.4.2 The effect of salt precipitation on the disintegration of some rock types

The effect of gypsum precipitation in joints and along bedding planes is uncertain. Continued filling of the discontinuities in this manner may accelerate rock breakdown by prising the material apart. Weathering by salt crystallisation is common in coastal and arid environments and the causes and effects of this process are well documented, for example Cooke (1979), Cooke & Smalley (1968), Wellman & Wilson (1965). The effectiveness of salt weathering is dependent on rock properties, salt



PLATE 3.8 Fault crush seepage at bottom of scarp.



PLATE 3.9 Finely broken down shale at the bottom of the scarp.

properties and environmental conditions. According to Cooke (1979), rapid disintegration in affected rocks is observed when crystal growth pressures in the porespace have to be relieved by adjustment of the rock structure which results in weakening of the whole rock fabric.

A small experiment was carried out to investigate the effects of crystal growth on the disintegration of certain rocks (Lammerton 1982). A sample of a sandstone, silty mudstone, shale and mudstone were immersed in a solution of 14% sodium sulphate (Na_2SO_4) for 1 hour. The samples were then dried at 60°C for 4 hours and at 30°C for 19 hours. The percentage of each sample remaining at the end of every cycle was determined by weighing, selecting only those particles with a mass greater than 1g. The results are shown in Fig. 3.6. Statistical analysis of the results showed that the precipitation of salts in the samples did not increase the rate of disintegration significantly when compared with the same rock types immersed in distilled water and subjected to the same drying procedure. In the mudstone, salt precipitation appears to reduce the rate of breakdown and in the sandstone, a gain in weight was recorded. These observations suggest that for some rock types, the presence of salt may actually hinder rather than help breakdown by acting as a cement for material on either side of a joint or bedding plane.

A similar observation was made by Cooke (1979) who noted that weathered fragments could adhere to the main rock particle through the cementing action of crystalline salts. He also found that in rocks showing an overall weight gain due to salt crystallisation, weight loss was detected after they had been leached.

The influence of gypsum precipitation in the shales at Mam Tor may therefore be twofold; discontinuities may be prised apart yet disintegration of the affected rock is possibly retarded if the developing crystals hold rock fragments together.

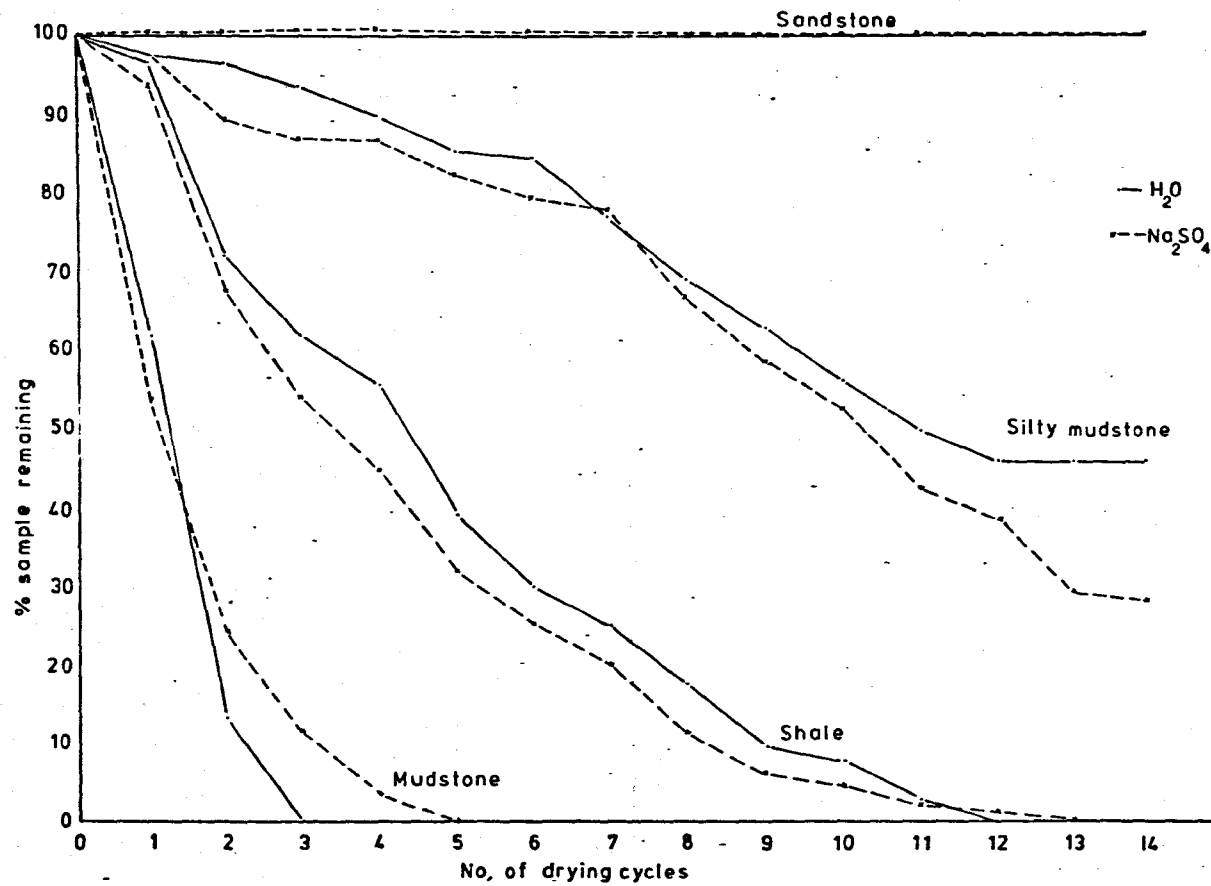


FIG. 3.6 Results of experiment on rock disintegration due to salt crystallisation.

Physical weathering clearly reduces intact shale to a fine aggregate. Spears & Taylor (1972) considered that this type of disintegration is dominant over chemical processes in the degradation of shales. Chemical weathering proceeds on much longer timescales relative to physical breakdown. Furthermore, chemical reactions are often effective only after physical processes have reduced material to a fine aggregate, thereby creating a large surface area available for reaction.

There is little doubt, however, that chemical weathering may have a significant effect on the properties of some rocks. The precipitation of secondary minerals in shales beneath buildings as documented by Penner et al. (1966), Quigley & Vogan (1970) and Grattan-Bellew & Eden (1975) attest to the importance of this chemical process under suitable conditions.

3.4.3 Chemical weathering at Mam Tor

The nature and extent of chemical reactions at Mam Tor were investigated in detail by Vear (1981). The temperature, pH and conductivity of a number of seepages around the landslide area were measured at weekly intervals over a period of about 2 months. Water samples collected from selected seepages were analysed by atomic absorption spectrophotometry to determine the concentrations of Ca, Mg, Na, K and Al. Cl^- , HCO_3^- , SO_4^{--} and total iron concentrations were also measured.

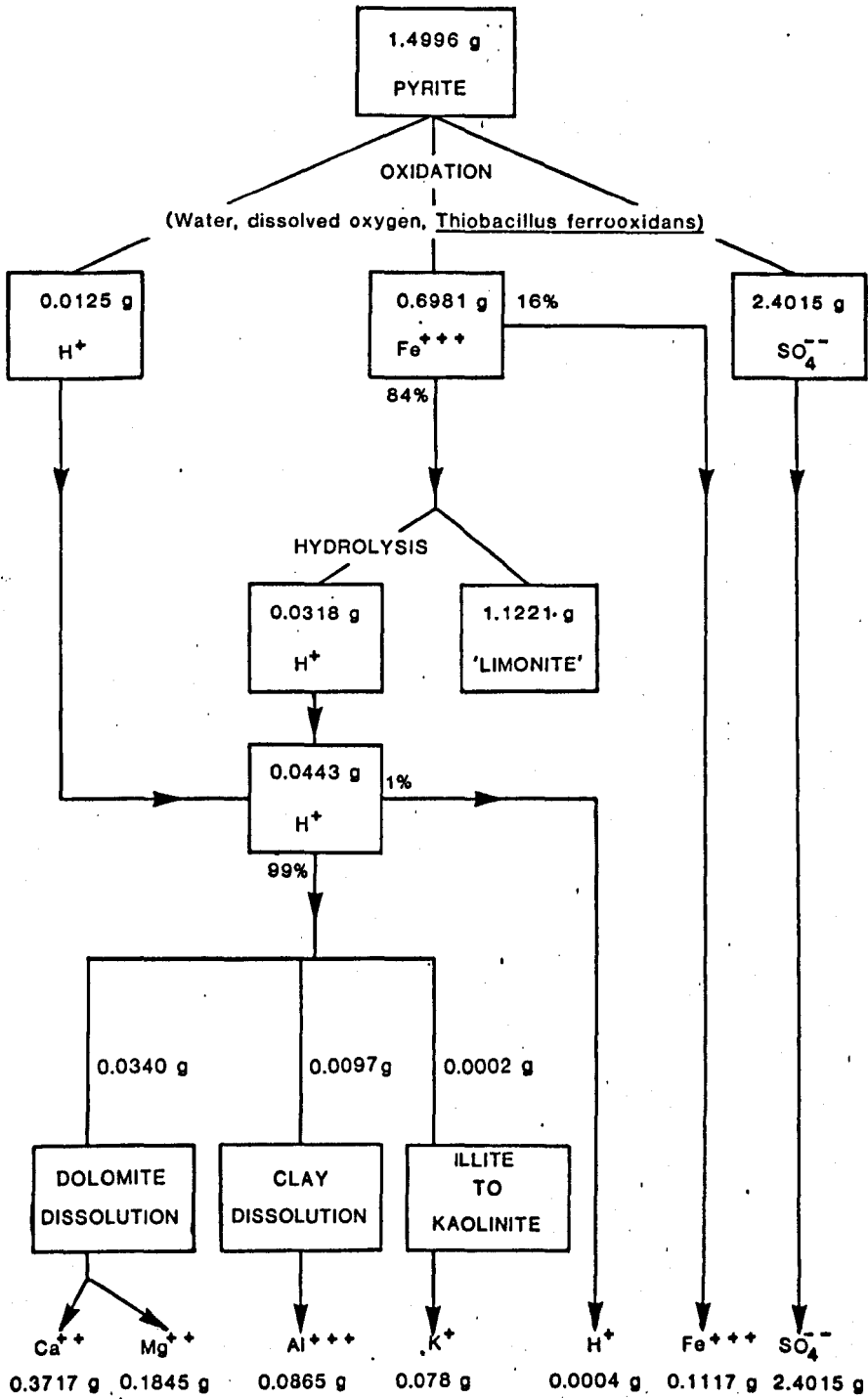
The samples possessed similar chemical compositions although their levels of dilution varied due to mixing with surface runoff. One sample, taken from a fault crush seepage (Fig. 3.3; site 7) showed very little response to surface temperature or rainfall fluctuation which suggests a relatively lengthy residence at depth. Analyses of these waters provided evidence for chemical reactions in the shale at depth since they were least diluted by surface runoff.

Fig. 3.7 shows the reactions which Vear & Curtis (1981) postulated to account for the composition of the waters emerging at the fault crush seepage. The composition of these waters is given on the bottom line of the diagram. Assuming that no gypsum is precipitated within the fault zone, 1.4996 g of pyrite must be oxidised by each litre of water, probably aided by bacterial activity, in order to produce the quantity of sulphate shown. This reaction would also release 0.0125 g of H^+ into solution and 0.6981 g of iron, yet only 0.1117 g Fe^{3+} emerges in the surface seepage; the remainder must, therefore, be deposited at depth, probably as hydrated ferric oxide. This would acidify the system considerably by the addition of another 0.0318 g H^+ . Of the total 0.0443 g H^+ generated, only 0.0004 g H^+ appears in the seepage. 99% of the available H^+ must, therefore, be consumed in mineral reactions as suggested by the large concentrations of other cations. Ca and Mg are probably explained by the dissolution of carbonates, Al by clay decomposition and K by degradation of illite to kaolinite. The relative importance of these H^+ consuming reactions were attributed as follows:

Carbonate dissolution	77%
Silicate decomposition	22%
Potassium release	< 1%

Clearly, the scale of chemical alteration is very great. The extreme reactivity of sulphide minerals has been acknowledged for a long time, particularly in the context of acid mine drainage but the results of Vear & Curtis (1981) indicate that other reactions consequent upon the generation of sulphuric acid after pyrite oxidation take place at strictly comparable rates. More than 99% of the acid produced at depth is consumed in mineral transformations before reaching the surface. Since meteoric water is likely to be focussed along fracture zones with the slide it follows that sulphide oxidation and dissolution, together with silicate

FIG. 3.7 Weathering processes at Mam Tor (from Veal & Curtis 1981).



and carbonate decomposition, will also be concentrated within discontinuities.

Vear (1981) showed that for each litre of water emanating from the fault crush seepage, 0.7 ml of void space could be created in the shale by mineral dissolution reactions, assuming that no gypsum or jarosite precipitation occurs within the system. If secondary mineral precipitation is considered, there is an increase in volume within the overall system. Furthermore, the volume increases are unlikely to occur uniformly. With respect to slope stability, the differential strains set up by localised volume increases possibly accelerate a reduction in the factor of safety and may aid progressive failure.

3.5 Summary

Edale Shale is a Carboniferous shale which outcrops in an area close to Sheffield. It exists in a variety of weathering states over the area of its outcrop and this is reflected in the range of values obtained for residual shear strength in different samples.

The availability of recently quarried Edale Shale in large quantities from Hope Valley Cement Works facilitated its use in the experimental work on changes in the physical properties of shales during weathering.

Whilst this research is not directly concerned with slope stability problems, the occurrence of Edale Shale within an active major landslide at Mam Tor provided an ideal opportunity to observe the process of shale weathering in a natural situation and to consider the results of laboratory studies in the context of slope stability.

Mam Tor is also a location where the chemical weathering system can be monitored. It is thus an important source of chemical data for comparing the conclusions of laboratory tests with natural processes.

CHAPTER IV

THE GRAIN SIZE PROBLEM

4.1 Definition

The grain size or particle size distribution of a rock or soil influences its residual shear strength (ϕ_r') and plasticity properties. Since changes in particle size by weathering are frequently reported, for example by Cooke & Doornkamp (1974, p.272), Prior and Graham (1974) and Shamburger et al. (1975), ϕ_r' and plasticity are also likely to alter in response to a reduction or increase in particle size.

Uncertainty arises, however, over the meanings of the term grain size, particle size and clay fraction. As with the term shale, geologists and engineers frequently differ in their interpretation of these expressions; geological classifications of detrital sediments and sedimentary rocks are constructed on the basis of differences in grain size distribution of the constituent fundamental particles (Table 1.1) but in soil mechanics, grain size usually applies to the dimensions of aggregates. In engineering, the terms silt-size and clay-size thus have dual meanings and may refer to aggregates, as well as individual particles, which measure $< 63 \mu\text{m}$ and $< 2 \mu\text{m}$ in diameter respectively (Scott 1978). This explains why engineers frequently report increased clay-contents with weathering since the breakdown of clay aggregates into individual particles produces a larger proportion of material $< 2 \mu\text{m}$ in size.

A clear distinction is required between the grain size distribution of constituent particles and the sizes of aggregations in a soil. Here, the former is termed fundamental particle (or grain) size distribution and the second, aggregate size.

Three problems need clarification: (i) How are these properties each measured?; (ii) Which property exerts the greatest influence on the engineering behaviour of weathered material?; (iii) Is fundamental grain size ever approached during weathering?

4.2 Measurement of fundamental particle size distribution

The standard method for particle size analyses is carried out by sedimentation after pre-treatments to remove organic matter and cements (B.S. 1377, 1975). Currently recommended methods of analysis, such as the pipette or hydrometer methods are, however, generally recognised as unsatisfactory, particularly for determination of the $< 2 \mu\text{m}$ fraction. This is primarily due to the difficulties encountered in sample disaggregation. The failing is perhaps most problematic in indurated mudrocks which contain large quantities of strongly aggregated, fine material that has been subjected to deep burial and diagenesis. Pettijohn (1975) points out the serious limitations of applying sedimentation to ancient shales for this reason.

Sedimentation techniques assume that all particles in suspension are spherical and obey Stokes Law. Large discrepancies, however, have been shown to exist between the percentages of material less than $2 \mu\text{m}$ determined by sedimentation and values obtained using other methods. Dumbleton (1967) found that the total clay contents of Keuper Marl measured by mineralogical analyses ranged between 50-90% in contrast to 15-35% obtained using a British Standard sedimentation test. Martin & Lambe (1956) found an extreme discrepancy in a montmorillonitic soil which had 85% clay by mineralogical composition but only 2% by weight of particles finer than $2 \mu\text{m}$. Such differences are caused by cementation and flocculation. The majority of well-lithified rocks appear to contain aggregates of fine material which are larger than $2 \mu\text{m}$ which

leads to the recording of anomalously low fines contents and high silt contents. Although pre-treatments are recommended in, for example, the B.S. 1377 (1975) test, to remove or counteract the effects of aggregation, they do not always bring about complete dispersion of the rock components and may also destroy or modify the original size distribution. The former problem was illustrated by Sherwood (1967) during attempts to obtain a particle size analysis for Keuper Marls. He obtained low fines contents ($< 2 \mu\text{m}$) even after pre-treatments and mechanical working. Resistant aggregation was attributed to a silica cement. Other cements commonly encountered in sediments include carbonates, iron oxides and organic matter. In view of the difficulties of attempting direct measurements of fine material in rocks, it may be more useful to obtain an indirect estimate using an appropriate parameter which varies in direct response to changes in the fines content.

Chemical composition is one factor which is related to rock mineralogy and may therefore provide a good indication of the fundamental grain size distribution of a rock in terms of the proportions of material measuring less than $2 \mu\text{m}$, assuming that this fraction is predominantly clay.¹ The latter condition permits use of Si and Al measurements to indicate variations in the quantity of $< 2 \mu\text{m}$ material present since these elements are fundamental in clay structures.

Other work using chemical parameters has also attempted to determine relationships between composition and grain size distribution. Spears (1964) stated that: "quartz content would appear to be an expression of the sediments grain size" and used a free silica/combined silica ratio to indicate proportions of quartz to clay minerals. Pettijohn (1975) found that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio changed as grain size varied since SiO_2 values fell when the quartz content decreased and Al_2O_3 values rose with a concomitant increase in clay content. Other ratios have also been

¹Not all clays are $< 2 \mu\text{m}$ in size. Chlorite and kaolinite particles may be up to $10 \mu\text{m}$ in diameter

used. Spears, Taylor & Till (1971) found that total clay abundance in colliery spoil could be indicated by variations in K_2O and Al_2O_3 while Spears & Kanaris-Sotiriou (1976) described a continuous variation of TiO_2/Al_2O_3 with grain size.

4.3 Relationship between chemical composition and grain size distribution in unconsolidated sediments

In unconsolidated sediments the amount of material $< 2 \mu m$ in size ($\% < 2 \mu m$) can be truthfully measured by physical techniques. This hypothesis formed the basis of an investigation which aimed to establish a relationship between grain size distribution and chemical composition. It was tested by taking ten unconsolidated sediments whose grain size had been measured and determining their major element compositions by X-ray fluorescence (XRF). The chemical data was then related to the $\% < 2 \mu m$ fraction for each sample.

The samples were selected from a batch of over 200 sediments derived from the Humber Estuary. Grain size distributions of the whole batch had been previously determined by withdrawal analysis (Humphries, pers. comm.) after pre-treatments to remove iron oxides, carbonates and organic matter and subsequent dispersion in 3% calgon. The selected samples gave a range of percentages for the $< 2 \mu m$ fractions from 0% to about 38%; sample numbers and their respective $< 2 \mu m$ percentages are shown in Table 4.1.

The sediments had been stored in saline water in plastic bottles for a number of years. A representative sample of material was extracted from each bottle using a syringe and dried at $110^{\circ}C$ on an evaporating dish. Each sample was ground in an agate mortar, homogenised by splitting and quartering and then divided into six equal parts using a sample splitter. Two parts were terna-crushed for one minute to obtain a fine powder and stored in glass screw-top jars.

	Sample no.	% < 2 μ m	Na ₂ O %	Total %
Run 1 Pre-leaching	56	0	1.11	99.58
	143	2.57	0.89	99.87
	170	2.60	1.41	99.07
	142	5.65	1.39	100.04
	117	10.07	2.23	100.45
	200	15.39	3.38	97.07
	210	16.38	2.18	98.95
	245	22.71	2.63	97.41
	157	33.49	4.37	94.77
	138	37.44	6.06	90.83
Run 2 Post-leaching	56	0	0.60	99.87
	143	2.57	0.45	100.40
	170	2.60	0.47	100.65
	142	5.65	0.58	100.78
	117	10.07	0.83	100.25
	200	15.39	0.97	100.55
	210	16.38	1.05	99.83
	245	22.71	0.94	100.00
	157	33.49	1.16	99.37
	138	37.44	0.85	99.21

TABLE 4.1 < 2 μ m, Na₂O and analysis total percentages for pre- and post-leaching runs.

4.3.1 Chemical analyses

Samples were prepared for elemental analysis by XRF as outlined in Appendix A5. For the first batch of analyses, several sets of results fell widely outside the acceptable limits of 99.50% to 100.49% for composition totals. The errors appeared to be related to sodium content with high sodium percentages giving low totals. Alkali chlorides are a recognised source of ignition loss (Norrish & Hutton 1969) and since these samples were derived from an estuarine environment, excessive losses would appear to be explained by the volatilisation of sodium chloride. To reduce this possible source of error, the samples were leached twice with distilled water on Whatman 542 hardened ashless filter papers before oven drying at 105°C. The dried sediments were removed from the filter papers as a cake, repowdered and stored in glass jars. As some sediment remained on the filter papers they were ashed at 450°C for four days. Since after this time no significant weight loss was recorded it was assumed that the filter papers had decomposed. The sediments which remained after ashing were remixed with the powdered portions of the samples and each one was homogenised on a turbular apparatus for ten minutes. The homogenised sediments were then desiccated overnight and a second set of discs prepared for analysis. Ignition losses were greatly improved after washing and sodium percentages were also reduced significantly suggesting that a sodium salt had contributed to the errors in the first batch of analyses. A comparison between the totals and sodium percentages for both runs is shown in Table 4.1 and the major element analyses for the post-washing run are presented in Table 4.2.

Sample no.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	CaO	MgO	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	S	Loss on ignition	Total
56	83.38	3.17	1.96	0.98	3.75	0.70	0.60	0.23	0.03	0.09	0.03	4.96	99.87
143	79.77	4.04	3.19	0.92	4.11	0.93	0.45	0.27	0.10	0.15	0.04	6.43	100.40
170	78.60	4.51	3.40	1.01	3.53	1.05	0.47	0.42	0.05	0.09	0.26	7.24	100.65
142	78.05	4.95	3.89	1.10	3.79	1.14	0.58	0.43	0.07	0.18	0.07	6.43	100.75
117	64.54	9.68	5.10	1.81	4.93	1.81	0.83	0.73	0.11	0.29	0.24	10.19	100.25
200	64.59	9.84	5.08	1.89	4.55	1.90	0.97	0.77	0.11	0.25	0.13	10.46	100.55
210	59.58	11.06	6.02	2.11	5.20	2.16	1.05	0.90	0.15	0.33	0.17	10.99	99.83
245	52.63	13.72	6.62	2.34	6.63	2.63	0.94	0.95	0.13	0.25	0.29	12.57	100.00
157	47.76	15.20	8.38	2.47	5.25	2.85	1.16	1.18	0.19	0.48	0.38	14.07	99.87
138	51.08	13.94	6.31	2.26	0.60	1.72	0.85	0.87	0.03	0.18	1.00	20.37	99.21

TABLE 4.2 Humber sediments - chemical analyses using XRF

4.3.2 Mineralogical analyses

Two types of analyses were carried out: (i) by X-ray diffraction to obtain qualitative information on the minerals present; and (ii) the pyrosulphate fusion method of Trostel & Wynne (1940) to determine the amount of silica present as quartz.

The diffraction traces were run from 4° to $44^{\circ} 2\theta$ at a scan rate of 1° per minute. The results are shown in Fig. 4.1. Empirical appraisal of the traces indicates that the proportion of clay increases relative to quartz from sample 56 to sample 138 confirming the trend shown by the withdrawal analysis results; Other minerals identified include calcite, dolomite and feldspars with small amounts of rutile.

Using the fusion method of Trostel & Wynne (1940) the proportion of total silica which could be attributed to quartz was measured. The amount of silica combined in clays and feldspars was calculated simply by subtracting the quartz percentage from the total silica percentage obtained in the XRF analysis. This not only provided a means of interpreting the silica and alumina values obtained by XRF but also served as an independent estimate of the clay content of the samples. Unfortunately, the results were not strictly accurate since no allowance was made for any silica combined in feldspar. The Trostel & Wynne (1940) procedure involves a pyrosulphate fusion followed by dissolution of the fusion in alkalis leaving free silica for gravi-metric estimation. The procedure is outlined in Appendix A7. It has been successfully applied to the determination of quartz in sedimentary rocks, for example by Till & Spears (1969), and combined with a hydrofluosilicic acid treatment by Chapman, Syers & Jackson (1969) to measure the quartz contents of a variety of soils, sediments and rocks.

FIG. 4.1a X-ray diffraction traces of Humber Sediments (whole sample specimens nos. 56, 117, 143, 170, 142). The % < 2 μ m fraction is shown for each sample.

K - kaolinite; Ill - illite; Q - quartz; F - feldspar;
Ca - calcite; M - mica; D - dolomite

NO.142

565%

D

Ca

F M

Q

Q

Ca

F

III

K

NO.170

260%

NO.143

257%

NO.117

1007%

NO.56

0%

30

25

20

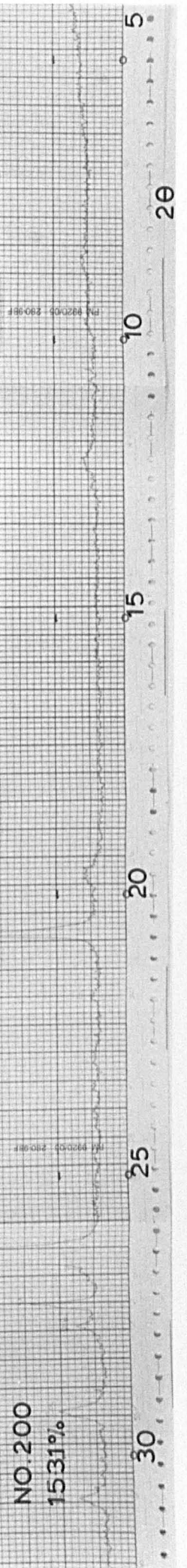
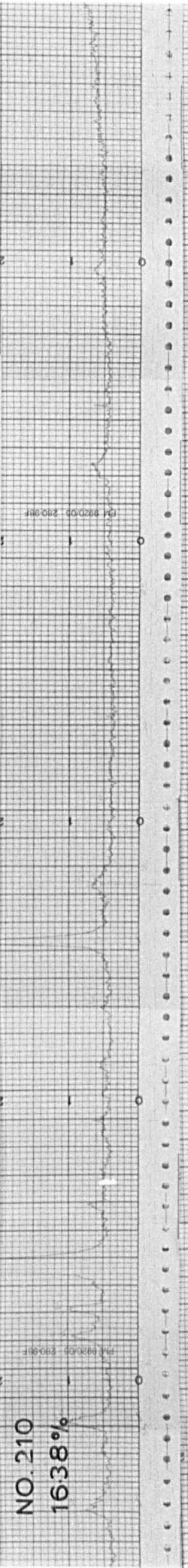
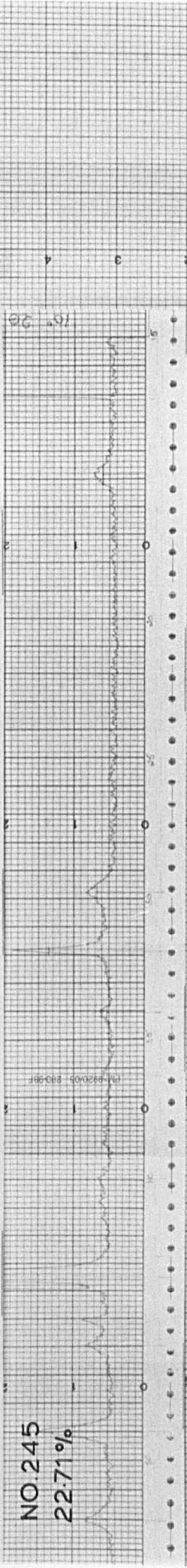
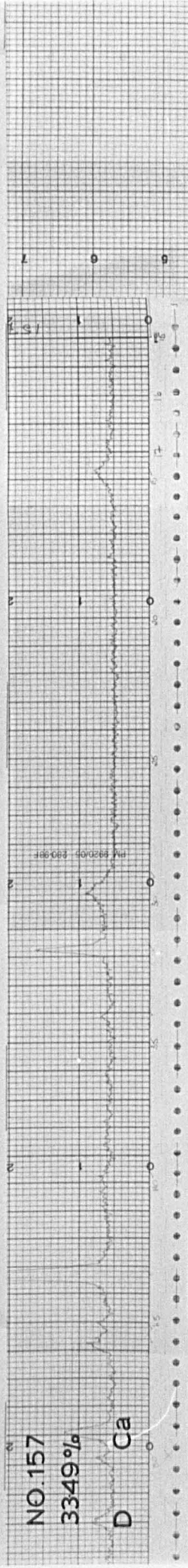
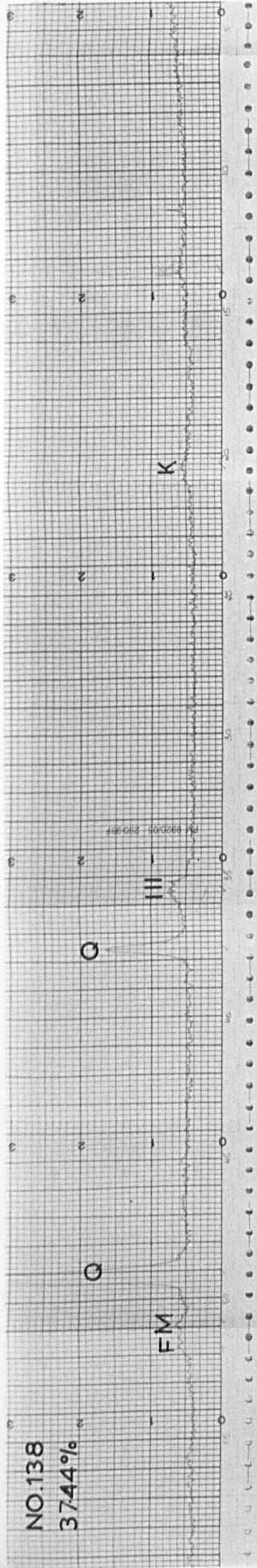
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10

5

FIG. 4.1b X-ray diffraction traces of Humber sediments (whole sample specimens nos. 200, 210, 245, 157, 138). The % < 2 μ m fraction is shown for each sample.

K - kaolinite; Ill - illite; Q - quartz; F - feldspar;
Ca - calcite; M - mica; D - dolomite



The values obtained using the pyrosulphate fusion method for the Humber sediments are shown in Table 4.3. Bound silica in clays was calculated by subtracting the free silica percentages from the total silica values.

Results from the first run of this experiment were promising. However, the second run produced unsatisfactory results giving free silica values that were frequently greater than the total silica percentage given by XRF analyses! The problem was initially attributed to contamination by foreign particles and steps were taken to reduce this problem as explained in Appendix A7. Impurity corrections were made to all samples as recommended by Trostel & Wynne (1940), but the values obtained for weights of impurities present were far in excess of the acceptable level of 0.002 g, as shown in Table 4.4. Spears (pers. comm.) suggested that inadequate washing of the fusion with hot distilled water was probably the major cause of error. In view of the amount of time required to perform this method, coupled with doubts about the reproducibility of the results, it was decided to abandon this part of the experiment. No reliable data was therefore obtained on the proportions of total silica present as quartz.

4.3.3 Correlation between chemical and size fraction data

In section 4.3.1, the possibility of using variations in Si and Al contents to indicate the proportion of $< 2 \mu\text{m}$ size material in sediments and sedimentary rocks was considered.

Fig. 4.2 shows the relationship between total SiO_2 percentages obtained by XRF and the $< 2 \mu\text{m}$ size fractions measured by withdrawal analyses. Fig. 4.3 shows a similar plot for the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio calculated from the XRF data. The graphs are of the predicted forms.

Sample no.	Run no.	% < 2 μm	Total % SiO_2 (XRF)	% free SiO_2 (fusion)	% bound SiO_2
56	1	0	83.38	83.80	0.4
	2			91.2	-
	3			87.6	-
143	1	2.57	79.77	75.0	4.7
	2			84.0	-
	3			82.0	-
170	1	2.60	78.60	79.4	-
142	1	5.65	78.06	70.2	7.8
	2			77.8	-
	3			81.4	-
117	1	10.07	64.54	60.6	3.9
200	1	15.89	64.59	58.4	6.2
210	1	16.38	59.58	57.0	2.6
	2			62.6	-
	3			55.2	4.4
245	1	22.71	52.63	43.6	9.0
157	1	33.49	47.76	31.6	16.2
	2			40.2	7.6
	3			28.4	19.4
138	1	37.44	51.08	38.2	12.9
	2			44.4	6.7
	3			33.0	18.1

TABLE 4.3 Determination of free silica using K-pyrosulphate fusion (Trostel & Wynne 1940).

Run no.	Sample no.	% free SiO ₂	Impurities (g)
1	56	83.8	0.284
2		91.2	0.083
3		87.6	0.080
1	143	75.0	0.217
2		84.0	0.154
3		82.0	0.039
1	170	79.4	0.250
1	142	70.2	0.223
2		77.8	0.171
3		81.4	0.053
1	117	60.6	0.168
1	200	58.4	0.166
1	210	57.0	0.134
2		62.6	-
3		55.2	0.033
1	245	43.6	0.147
1	157	31.6	0.049
2		40.2	0.040
3		28.4	0.021
1	138	38.2	0.081
2		44.4	0.027
3		33.0	0.024

TABLE 4.4 Correction for impurities after free silica determination of Trostel & Wynne (1940).

FIG. 4.2 Relationship between SiO_2 content and < 2 micrometre size

fraction for Humber sediments.

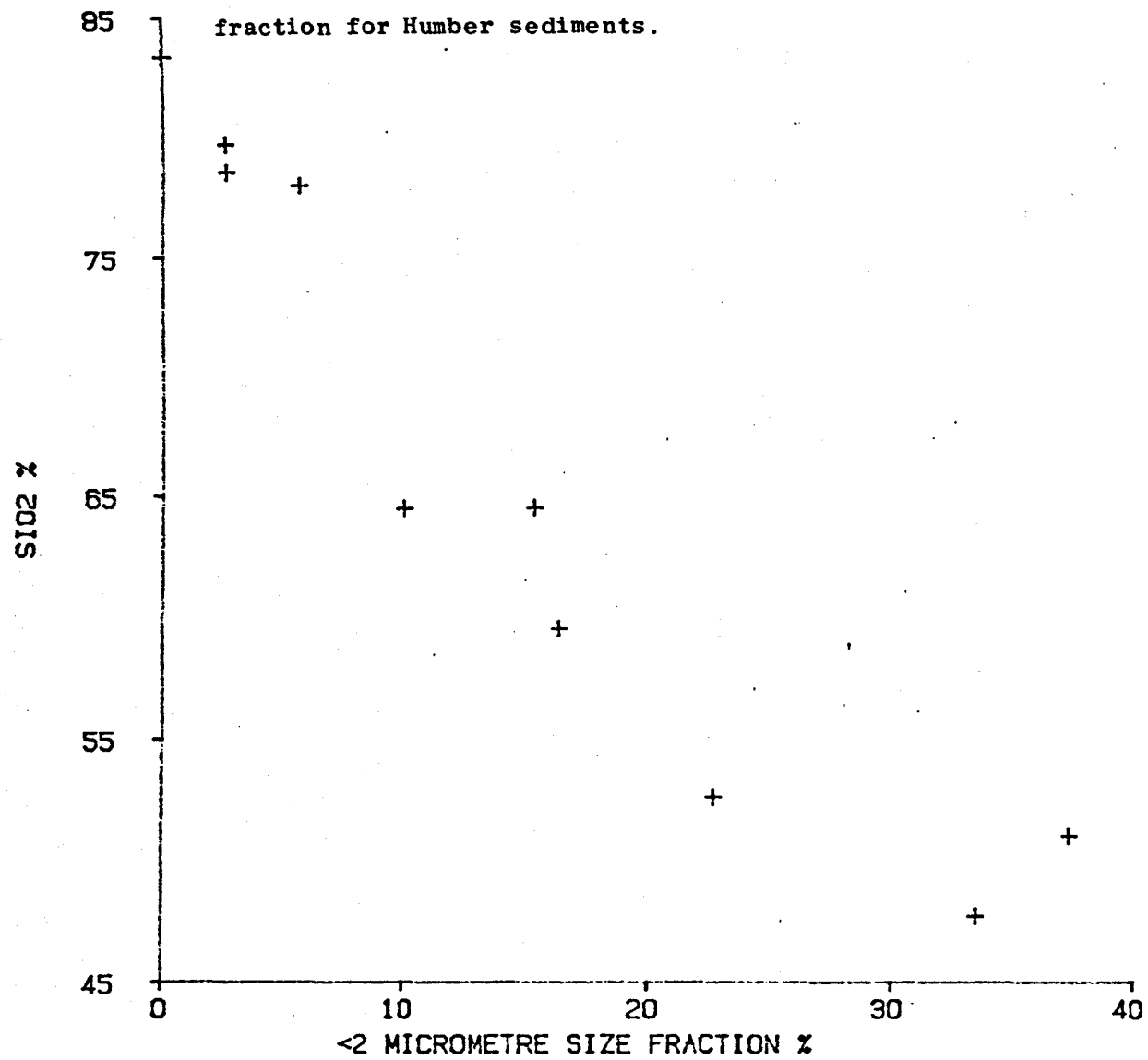
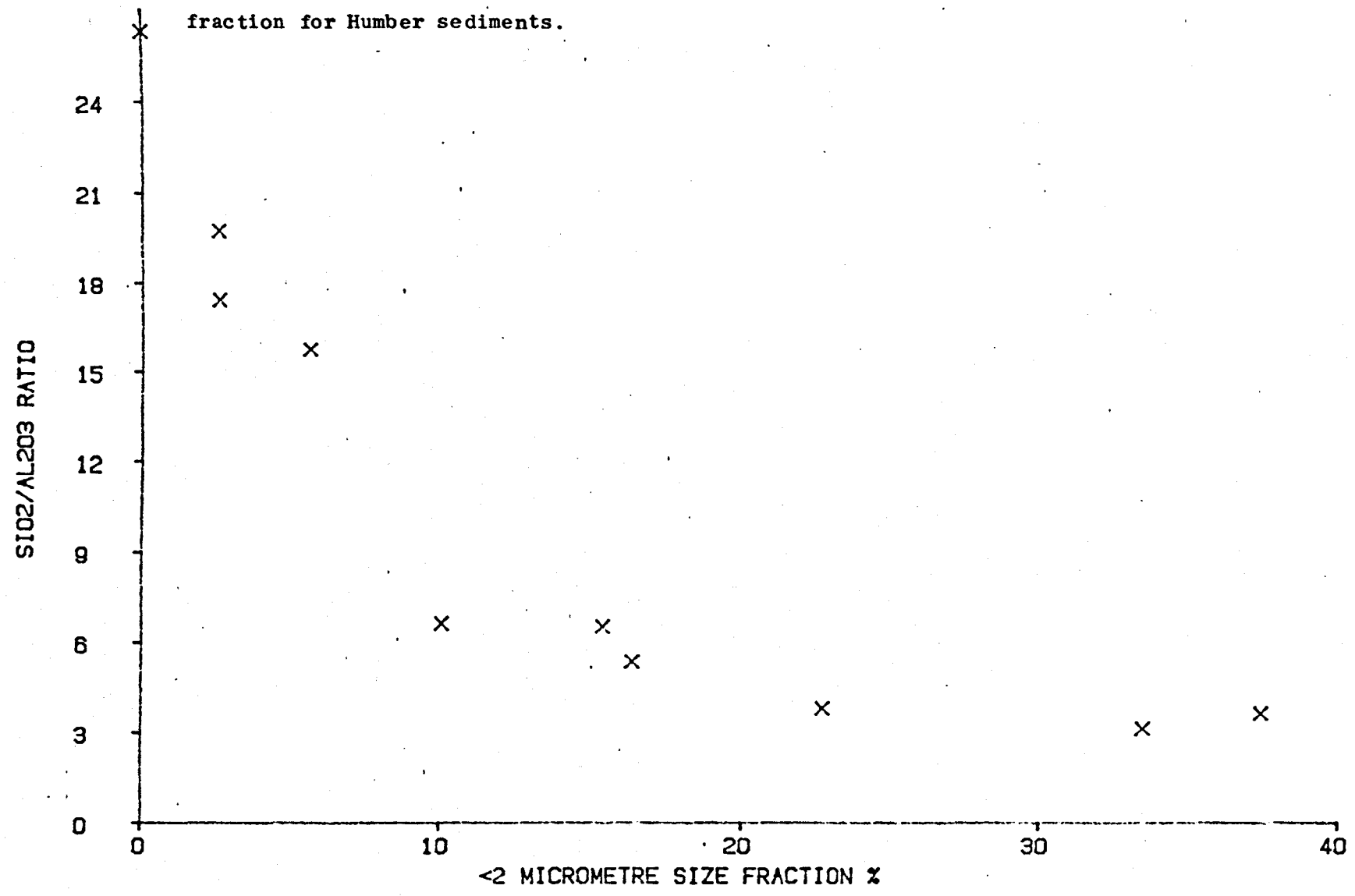


FIG. 4.3 Relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and < 2 micrometre size fraction for Humber sediments.



SiO_2 percentages reduce rapidly as the proportion of quartz decreases with increasing amounts of $< 2 \mu\text{m}$ size material. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios also decrease in response to greater quantities of clay minerals in the fine fraction.

Transformation of the $\text{SiO}_2\%$, $< 2 \mu\text{m}$ size fraction and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio data to a natural log base produced linear relationships. Regression analyses on the logged values are presented in Figs. 4.4, 4.5 and 4.6 and in Table 4.5. Figs. 4.4 and 4.5 are regressions of the form "X on Y" where X is $\text{SiO}_2\%$ or $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio respectively and Y is $< 2 \mu\text{m}$ fraction. Fig. 4.6 is a "Y on X" regression. While the correlations for both SiO_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio are good, the best fit line was obtained using the ratio. The reproducibility of values for the ratio was also found to be superior to that of the SiO_2 percentages as shown in Table 4.6 where the pre-leaching and post-leaching data sets (see section 4.2.2) are compared. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was therefore selected for use in further statistical work.

The data suggest that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is an indication of the grain size distribution; low $\text{SiO}_2/\text{Al}_2\text{O}_3$ values correspond with relatively larger $< 2 \mu\text{m}$ fractions and vice versa, higher ratios indicate lower proportions of $< 2 \mu\text{m}$ material. Equation 4.5 (see Table 4.5) can be used for the Humber sediments investigated here to obtain an estimate of the $< 2 \mu\text{m}$ fraction percentages using the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. A comparison of measured and calculated values is given in Table 4.7. A Students t-test indicated that there is no significant difference between the means at the 95% confidence level.

FIG. 4.4 Relationship between SiO_2 and $< 2 \mu\text{m}$ size fraction - logged data.

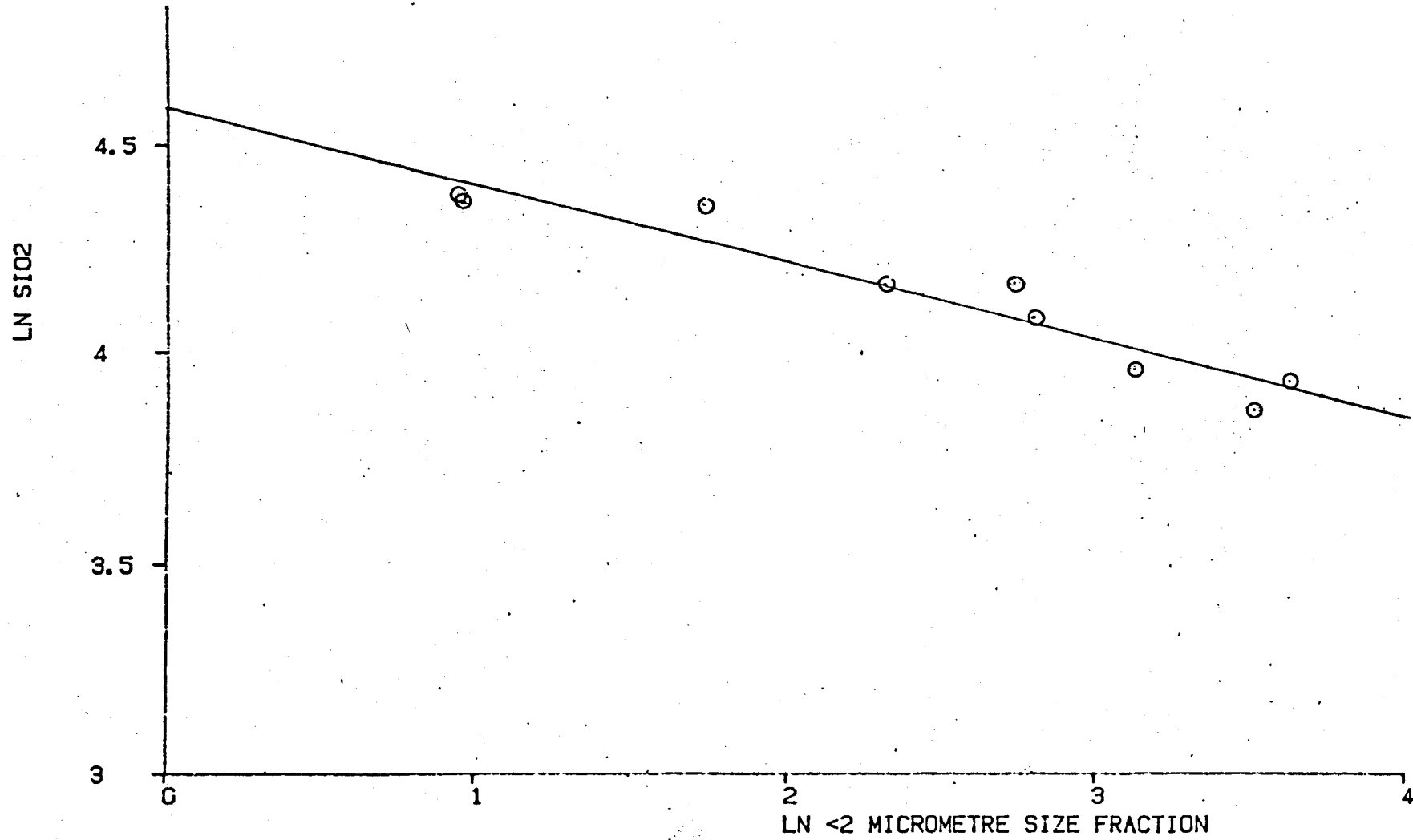


FIG. 4.5 Relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $< 2 \mu\text{m}$ size fraction -

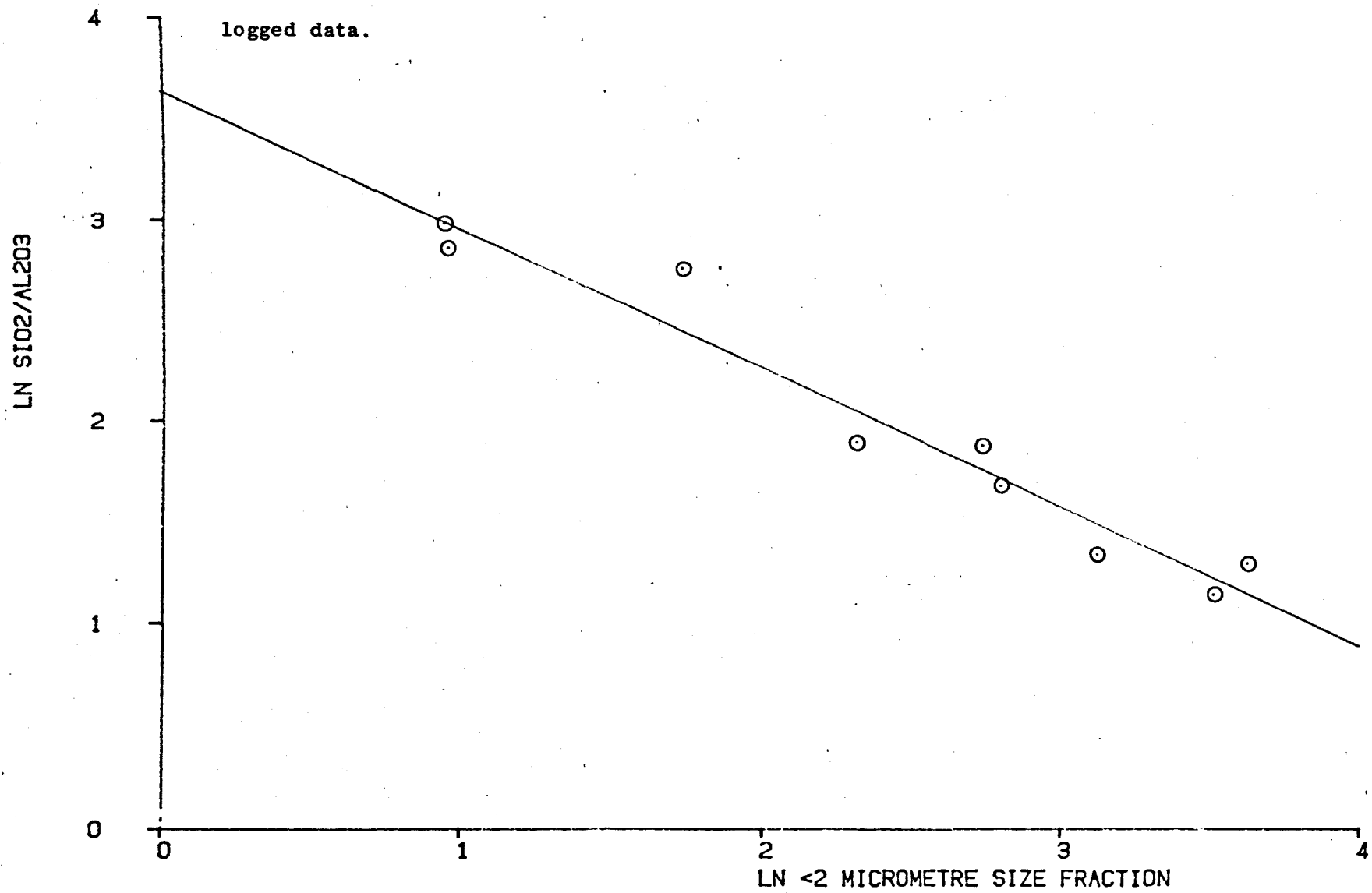
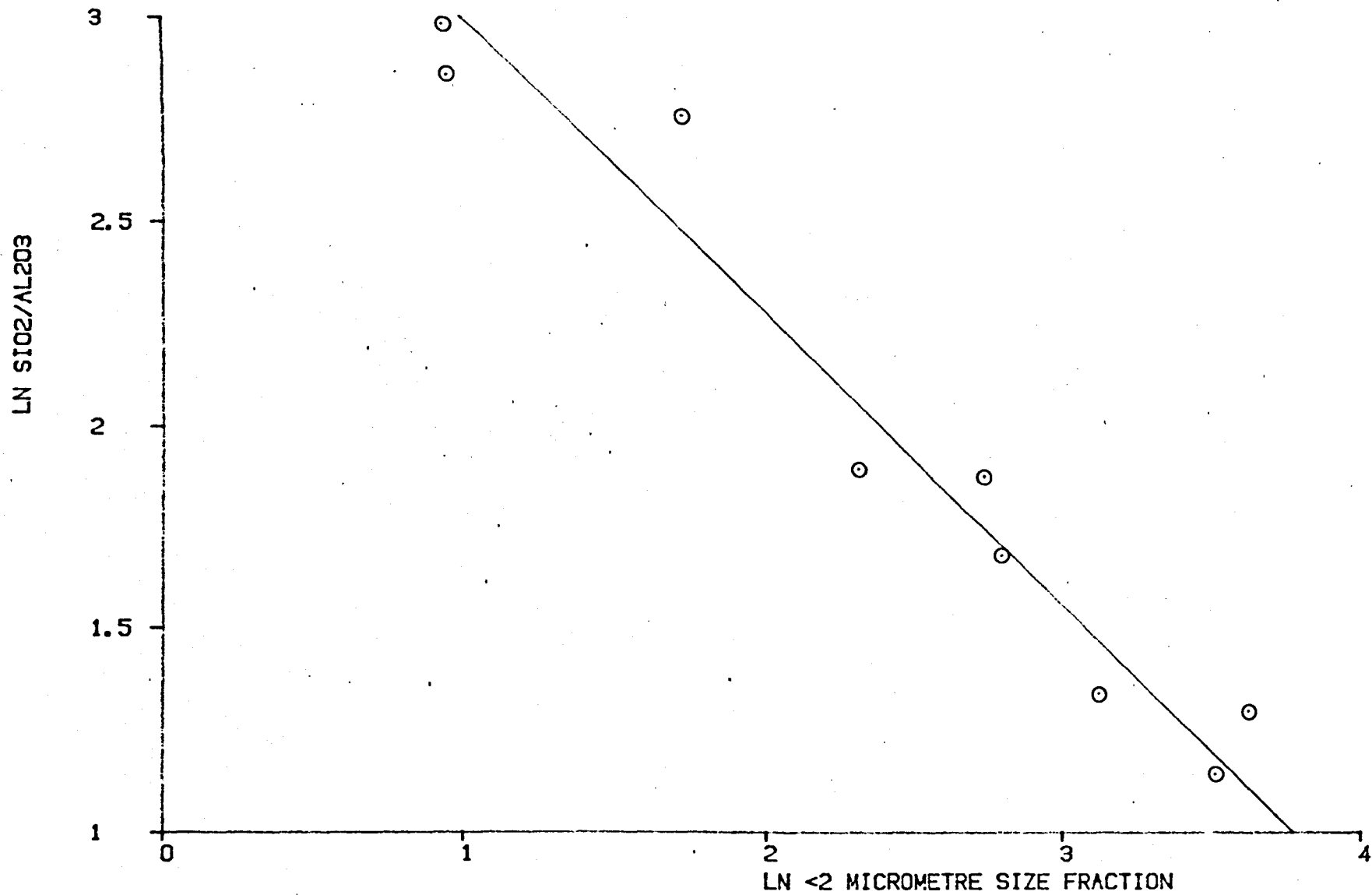


FIG. 4.6 Relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $< 2 \mu\text{m}$ size fraction - logged data; Y on X regression.



Element oxide and material	Goodness of fit	Correlation coefficient	Regression equation	Fig. no./ Equation no.
SiO ₂ (Humber)	0.913	-0.956	$\ln \text{SiO}_2 = 4.590 - 0.185 \ln < 2 \mu \text{ fraction}$	4.3
SiO ₂ /Al ₂ O ₃ (Humber)	0.950	-0.975	$\ln \text{SiO}_2/\text{Al}_2\text{O}_3 = 3.639 - 0.686 \ln < 2 \mu \text{ fraction}$	4.4
SiO ₂ /Al ₂ O ₃ (Humber)	0.950	-0.975	$\ln < 2 \mu \text{ fraction} = 5.159 - 1.384 \ln \text{SiO}_2/\text{Al}_2\text{O}_3$	4.5
SiO ₂ /Al ₂ O ₃ (Plastic clay)	0.936	-0.967	$< 2 \mu \text{ fraction} = 101.217 - 32.710 \ln \text{SiO}_2/\text{Al}_2\text{O}_3$	4.8
SiO ₂ /Al ₂ O ₃ (Ball clay)	0.899	-0.948	$\ln < 2 \mu \text{ fraction} = 4.726 - 0.201 \text{SiO}_2/\text{Al}_2\text{O}_3$	4.9

TABLE 4.5 Statistical data on the relationships between the < 2 μ size fraction and chemical composition.

Sample no.	SiO ₂ % pre-leaching	SiO ₂ % post-leaching	SiO ₂ /Al ₂ O ₃ pre-leaching	SiO ₂ /Al ₂ O ₃ post-leaching	Measured % < 2 μm
56	82.95	83.38	26.93	26.30	0
117	62.09	64.54	6.46	6.67	10.07
138	40.25	51.08	3.67	3.66	37.44
142	76.33	78.05	15.29	15.76	5.65
143	78.23	79.77	19.13	19.74	2.57
157	41.44	47.76	3.11	3.14	33.49
170	75.95	78.60	17.45	17.43	2.60
200	58.26	64.59	6.43	6.56	15.39
210	56.57	59.58	5.32	5.39	16.38
245	49.01	52.63	3.99	3.84	22.71

TABLE 4.6 Comparison of the reproduceabilities of SiO₂% and SiO₂/Al₂O₃ ratio.

Sample no.	Measured % < 2 μ m	Calculated % < 2 μ m
56	0	1.88
143	2.57	2.80
170	2.60	3.33
142	5.65	5.83
117	10.07	12.59
200	15.39	12.87
210	16.38	16.92
245	22.71	27.07
157	33.49	35.67
138	37.44	28.84
Mean	14.63	14.58

Equation 4.5

$$\ln < 2 \mu \text{ fraction} = 5.159 - 1.384 \ln \text{SiO}_2/\text{Al}_2\text{O}_3$$

TABLE 4.7 Comparison of measured and calculated values for % < 2 μ m size fraction in the Humber sediments. Measured values after Humphries (pers. comm.).

4.4 Analysis of some ball and china clays and Edale Shale

4.4.1 Ball and China Clays

Some physical and chemical properties of various blends of Tertiary ball and plastic clays and also china clays have been investigated by Watts, Blake, Bearne & Co. p.l.c. of Newton Abbott. The data obtained include chemical analyses obtained using XRF and particle size distributions. The mineralogies of the ball and china clays do not differ significantly except that the china clays have lower mean quartz contents and contain well-ordered kaolinite in contrast to the disordered or partially disordered kaolinite of the ball clays.

Particle size distributions were determined by a Sedigraph 5000 particle size analyser after the clays had been broken down to pass an $\frac{1}{8}$ mesh sieve, then added to a mixture of 50 ml water, 5 ml sodium hydroxide solution and 5 ml of Calgon, homogenised for two minutes and finally passed through a 300 μm mesh sieve.

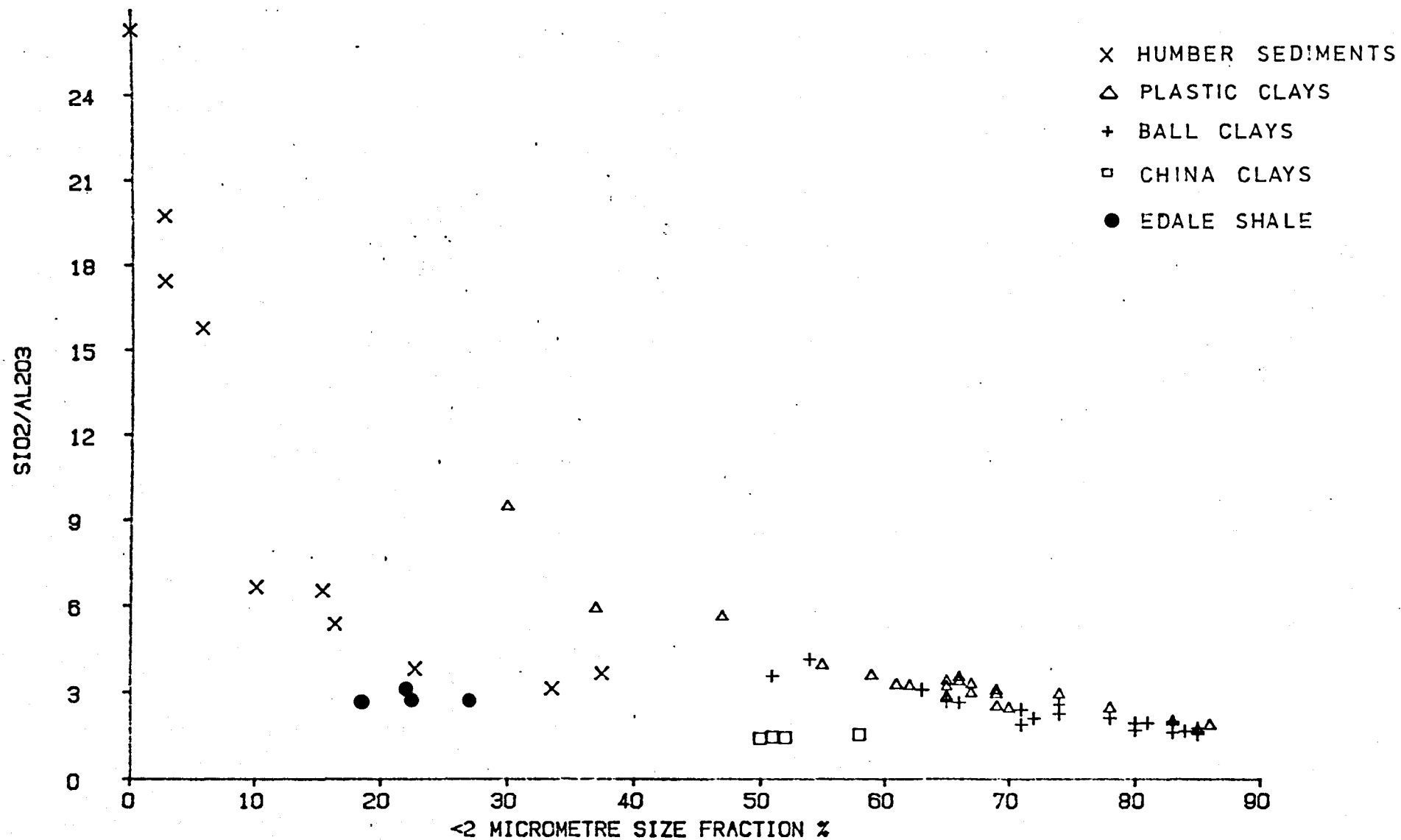
From the data provided (WBB, 1982), plots of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios against % < 2 μm fraction were compared with similar plots for the unconsolidated Humber sediments. These are presented in Fig. 4.7.

4.4.2 Edale Shale

Glass discs of Edale Shale from Hope Valley Cement Works Quarry and four samples from the surface of a weathered retrogressive scarp at Mam Tor were prepared by the method outlined in Appendix A5. Their chemical compositions were determined by XRF and the results are shown in Table 4.8. For the quarry material, four runs were carried out because unreliable results were obtained from the first two attempts in that losses on ignition were excessive. This was attributed to the large quantities of organic matter, sulphur and possibly carbonate present in

FIG. 4.7

COMPARISON OF HUMBER DATA WITH EDALE SHALE AND WBB STANDARD CLAYS



Material	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	MnO	P ₂ O ₅	S	Ignition loss	Total	Measured < 2 μm %	$\frac{SiO_2}{Al_2O_3}$	Calculated < 2 μm %
Edale Shale - quarry untreated	46.02	15.16	0.65	5.34	1.02	1.29	1.42	0.52	0.12	0.10	0.65	43.69	116.00	22.0	-	-
Edale Shale - quarry untreated	57.99	19.01	0.82	6.69	1.31	1.72	1.77	0.73	0.14	0.13	0.83	30.32	121.45	22.0	-	-
Edale Shale - quarry ignited	63.46	20.82	0.87	7.35	1.39	1.74	1.94	0.75	0.15	0.20	0.17	0.030	98.89	22.0	3.05	37.17
Edale Shale - quarry ignited	64.15	21.16	0.88	7.40	1.44	1.70	1.95	0.86	0.15	0.17	0.17	0.030	100.13	22.0	3.02	37.69
Edale Shale - Mam Tor No. 1 ignited	61.83	23.85	0.95	2.55	0.52	1.14	2.63	0.36	0.01	0.06	0.45	6.62	100.97	18.6	2.59	46.61
Edale Shale Mam Tor No. 2 ignited	55.38	20.93	0.83	8.50	2.33	1.10	2.50	0.30	0.01	0.15	1.56	6.47	100.07	-	2.64	45.39
Edale Shale - Mam Tor No. 3 ignited	57.87	22.12	0.89	7.78	1.25	1.28	2.63	0.35	0.03	0.13	0.92	4.59	99.82	27.0	2.62	45.88
Edale Shale - Mam Tor No. 4 ignited	61.09	23.02	0.94	7.16	0.15	1.27	2.73	0.37	0.01	0.16	0.34	4.63	101.88	22.5	2.65	45.16

TABLE 4.8 Chemical analyses and measured and calculated < 2 μm % for Edale Shale.

the material. Before the second two runs, the shale was ignited at 100°C for about 3 hours to remove volatile substances and glass discs were prepared from the ignited, desiccated rock powder. The subsequent analysis totals were satisfactory. The Mam Tor samples were also pre-ignited before disc-making.

From the chemical data, a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for each sample was calculated and using Equation 4.5 values for the $< 2 \mu\text{m}$ percentage were computed. These results are included in Table 4.8. Clearly, the measured and calculated values for $< 2 \mu\text{m}$ are very different. This contradicts the conclusions for the Humber sediments in which differences between measured and calculated values for $< 2 \mu\text{m}$ were apparently insignificant. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are plotted against measured $< 2 \mu\text{m}$ fractions on Fig. 4.7 along with the results for the Humber sediments and ball, plastic and china clays.

4.4.3 Relationships between $< 2 \mu\text{m}$ fraction and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in different sediments

Inspection of Fig. 4.7 reveals that the data sets plot in four distinct groups:

- (i) Ball and plastic clays
- (ii) China clays
- (iii) Humber sediments
- (iv) Edale shale

Each group exhibits a different relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and % $< 2 \mu\text{m}$ fraction.

As already mentioned, the Humber data conform to a log-log correlation (Table 4.5). The curve for the plastic and ball clays, however, is considerably shallower. The best fit regression lines for these materials are log-linear in form as presented for Figs. 4.8 and 4.9 and in

FIG. 4.8 Relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and < 2 micrometre size fraction - plastic clay.

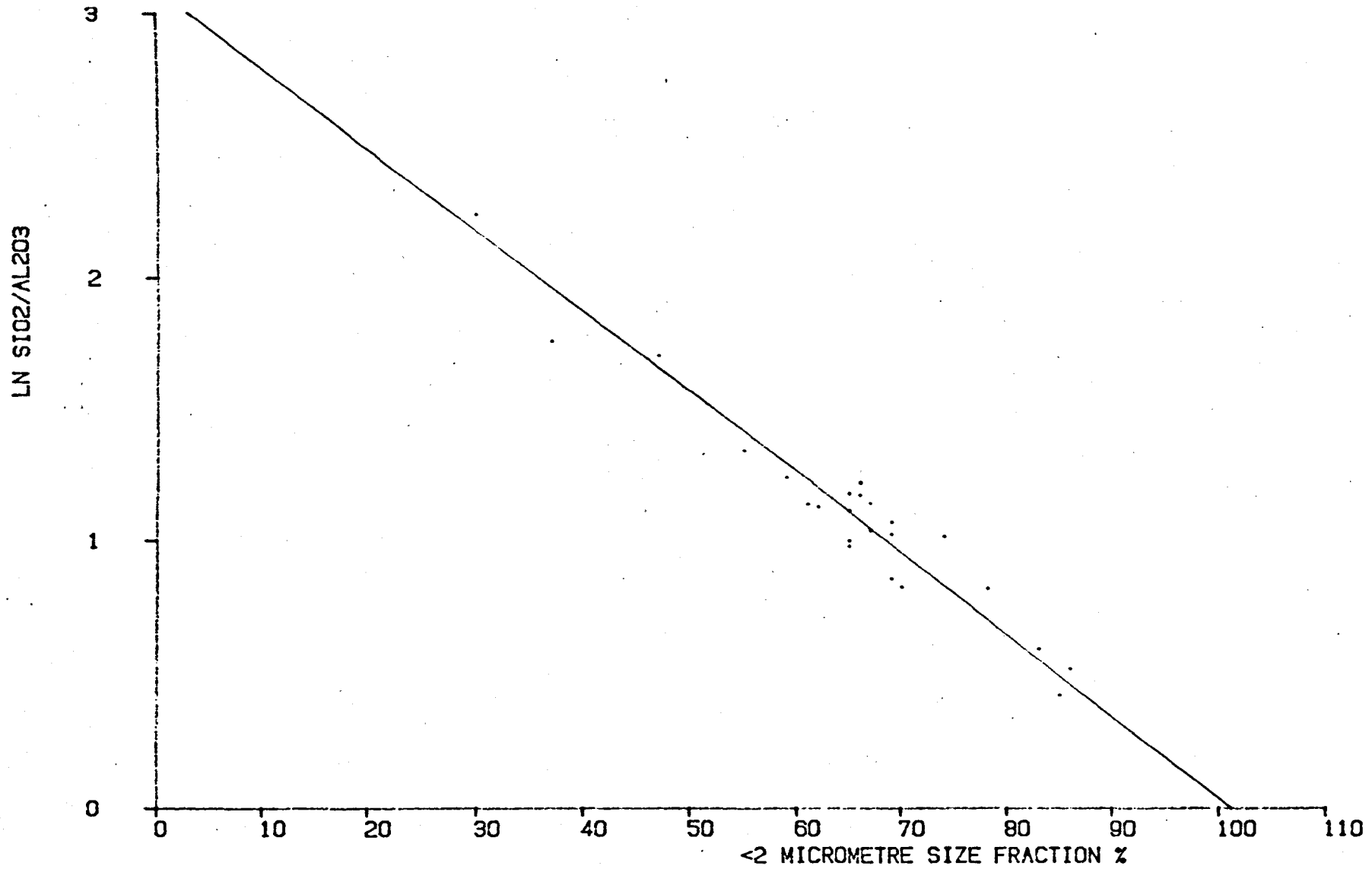


FIG. 4.9 Relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and < 2 micrometre size fraction - ball clay.

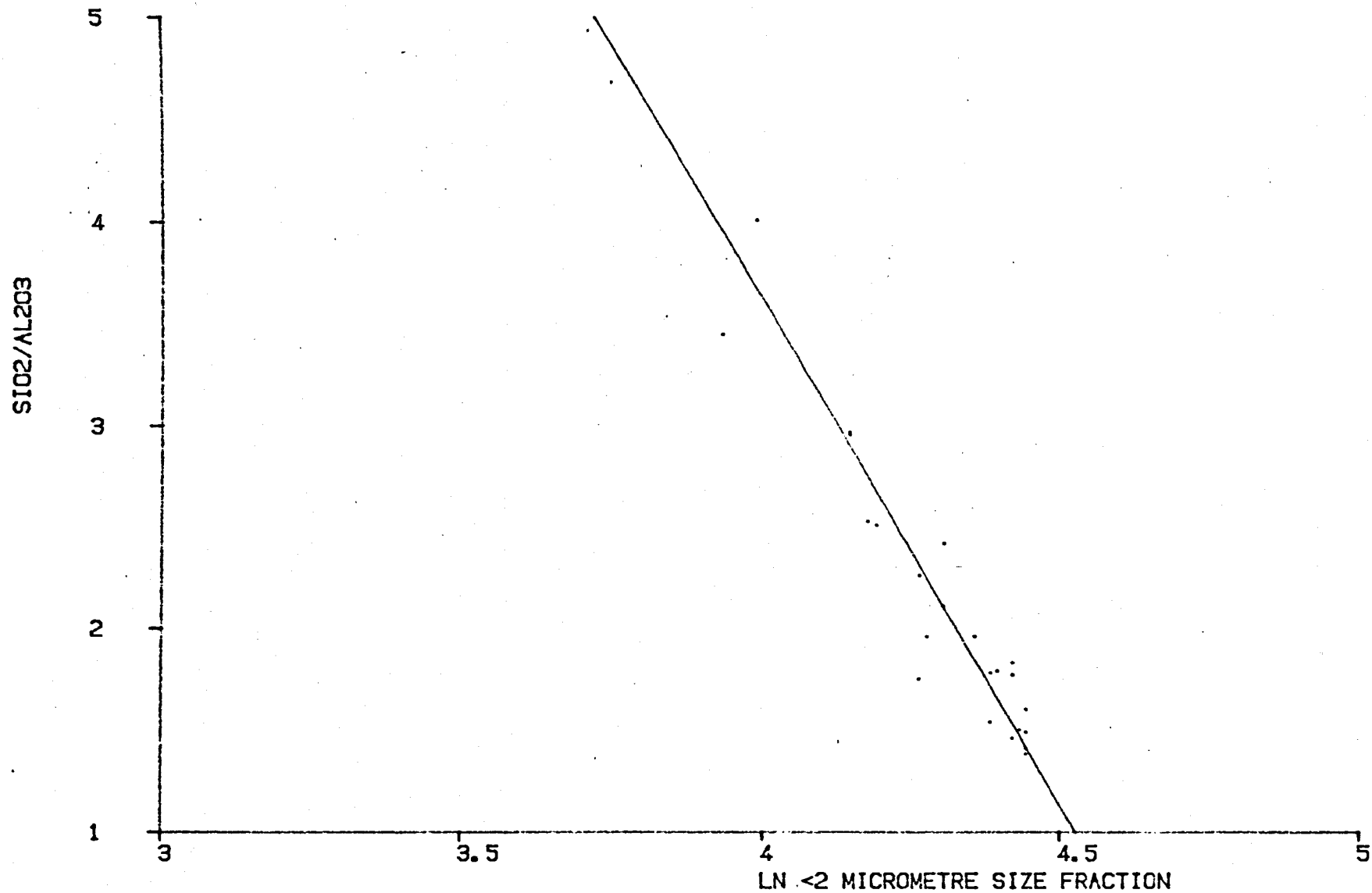


Table 4.5 (Equations 4.8 and 4.9). Clearly, the correlations exhibited by the clays are different from that shown by the Humber sediments and even the clays differ slightly between themselves; the ball clays have a best fit correlation of $\ln X$ on Y compared to the X on $\ln Y$ regression for the plastic clays. This suggests that Equation 4.5, derived for a set of unconsolidated Humber sediments, is not necessarily valid for all detrital sediments and sedimentary rocks.

Referring back to Fig. 4.7, if the Humber curve is extrapolated then it would appear to intersect the curves for the plastic and ball clays around a value of 70% for the $< 2 \mu\text{m}$ fraction. Unfortunately, data for the Humber sediments did not include samples with $< 2 \mu\text{m}$ percentages greater than 38% so the convergence for the two data sets is tentative. The divergence of the ball and plastic clays from the Humber samples at low percentage $< 2 \mu\text{m}$ fractions probably reflects differences in the compositions of the $< 2 \mu\text{m}$ size materials. The ball and plastic clays show higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios than the Humber sediments for the same $< 2 \mu\text{m}$ percentage.

It would have been interesting to investigate the clay curve at lower % $< 2 \mu\text{m}$ fractions to assess the influence of quartz content on the rate of change of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio but unfortunately, no suitable data were available.

The china clays and Edale Shale points fall into separate groups with comparable characteristics. Each cluster occurs within a narrow range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios with a measured variation in % $< 2 \mu\text{m}$ fractions of about 10%. This may reflect the lack of reproducibility inherent in physical methods of particle size analysis, particularly in dealing with old, indurated rocks or with clays where flocculation in saline solutions is a problem. The latter is important in coulter

counter work which was employed by WBB for their clay size analyses and may explain why the measured % < 2 μm fraction for the china clays was so low.

By comparison with the Humber data, the china clays and Edale shale results should plot at higher percentages for the < 2 μm fractions. Using the graph (Fig. 4.7) values of about 65% and 87% respectively for the shale and china clay would be expected. These figures are confirmed if the equations in Table 4.5 are used to calculate % < 2 μm fractions. For the china clays, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are closest to those of the ball clays hence equation 4.9 seems the most appropriate. This gives values of between 87.1 and 84.8%. Similarly, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios for the shales are comparable with the plastic clays, so using equation 4.8, values between 64.7 and 69.3% are obtained.

These results suggest that a more accurate estimation of the proportion of fines in a sample can be achieved by employing a composition indicator rather than physical measurement due to the difficulties of adequate disaggregation with well-lithified sediments. The exact relationship between chemical composition, in terms of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, and < 2 μm fraction percentages appears to depend on the type of sediment, even in those with quite similar fundamental grain size distributions. This may reflect variations in the mineralogical compositions of the fine fractions which would have a significant influence on chemical composition and hence the sensitive relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and < 2 μm fractions. A more rigorous analysis of the relationship between chemical composition and the proportion of < 2 μm size material in sediments and sedimentary rocks must be performed on many different samples with a wide range of fines contents before a useful and meaningful method of prediction can be properly constructed.

4.4.4 Relationship with other elements

Figs. 4.10 to 4.14 show plots of the $< 2 \mu\text{m}$ size fraction against percentages of some other elements present in the samples. All data for the Humber sediments, plastic, ball and china clays and Edale Shale are presented.

Generally, no significant correlations are shown for the shales or clays indicating the absence of any systematic variation in other minerals in these samples. In the unconsolidated sediments, however, there do appear to be trends, particularly in the Fe_2O_3 plot (Fig. 4.10). Iron may be present in a number of forms such as coatings on silt and sand grains, as colloidal particles stabilised by organic matter (Moore et al., 1979) and within the lattice structures of clay minerals, thus its relationship with the $< 2 \mu\text{m}$ size fraction is liable to be complex. The trends for Ca and Mg (Figs. 4.11 and 4.12) may reflect changes in minerals such as calcite and dolomite while K (Fig. 4.13) is probably associated with the clay fraction. TiO_2 (Fig. 4.14) like quartz, is detrital and its variation in sediments is commonly similar to that of free silica (Spears, 1964). Titanium (Ti) is thus expected to be a good indicator of fundamental grain size distribution in terms of the proportion of $< 2 \mu\text{m}$ material present, although it is apparently not the case for the sediments analysed here.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio clearly remains the most reliable parameter indicating variations in grain size distribution in detrital sediments and sedimentary rocks.

4.5 Effect of physical weathering on the grain size distribution residual shear strength and plasticity of Edale Shale

Residual shear strength and plasticity have been shown to vary with clay fraction. This is shown in Figs. 4.15 and 4.16. However, the

Key for Figs. 4.10 to 4.14

× Humber sediments

△ Plastic clays

+ Ball clays

□ China clays

● Edale shale

FIG. 4.10 Relationships between Fe content and < 2 micrometre size fraction.

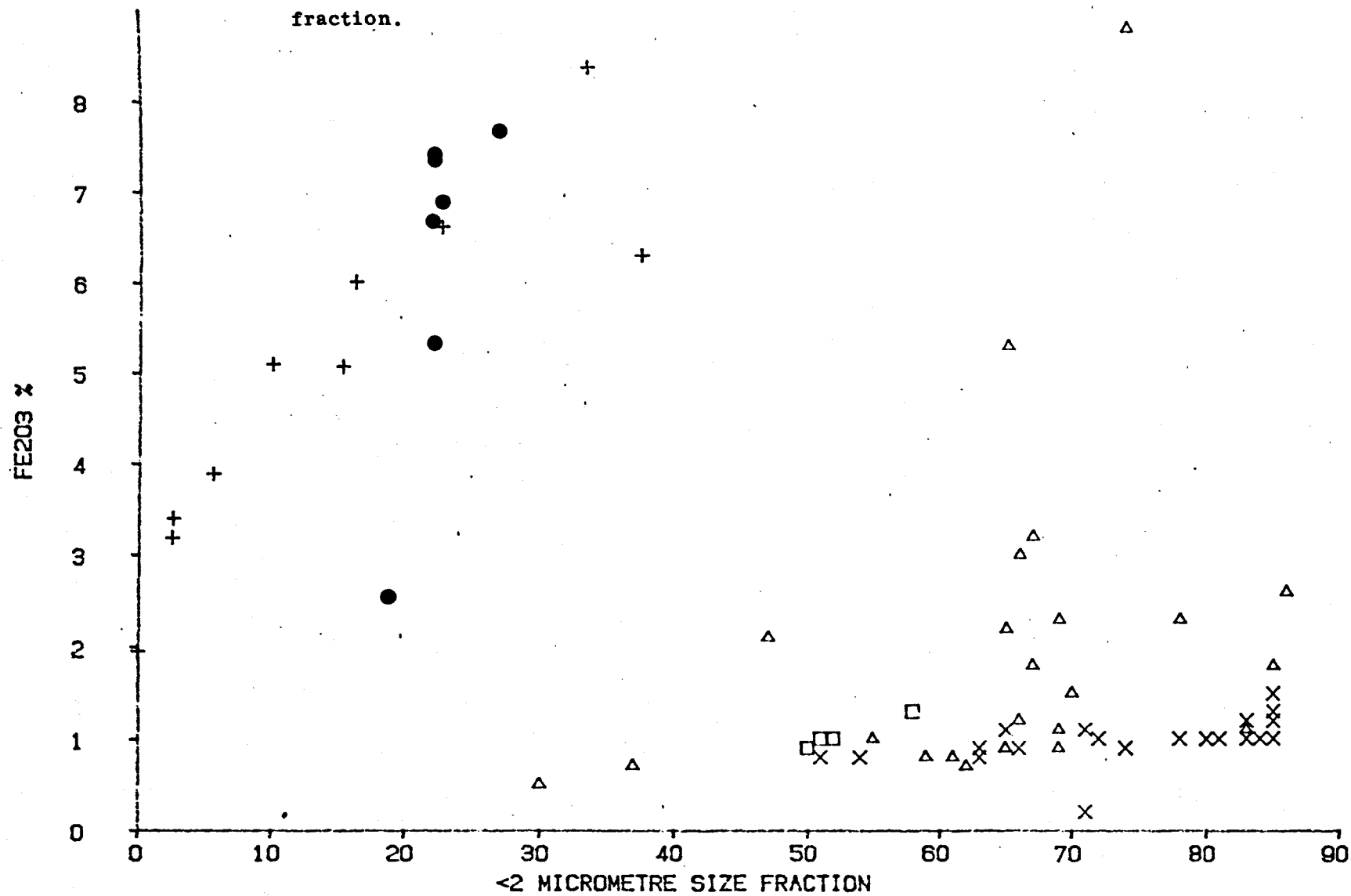


FIG. 4.11 Relationships between Ca content and < 2 micrometre size fraction.

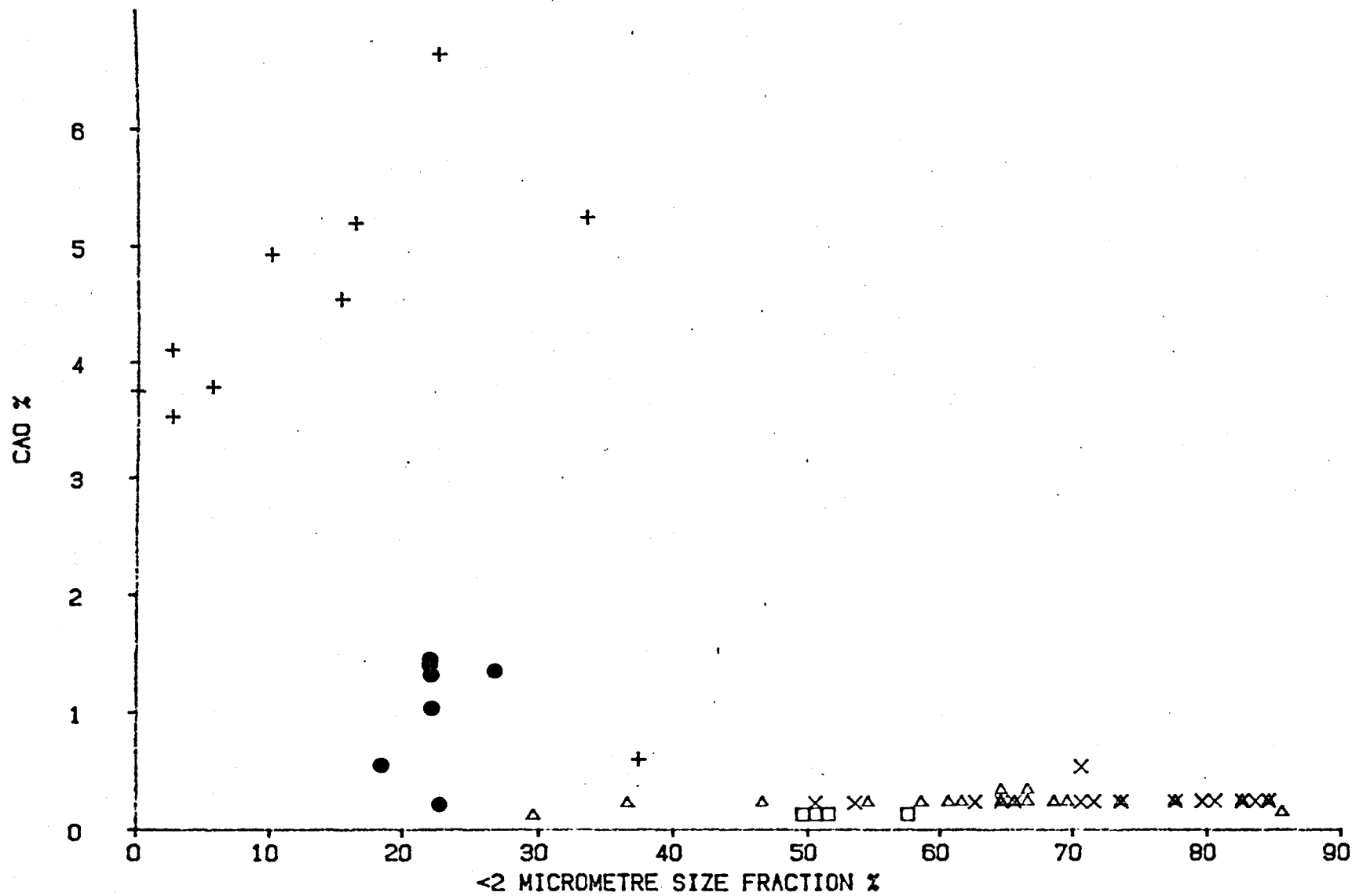


FIG. 4.12 Relationships between Mg content and < 2 micrometre size fraction.

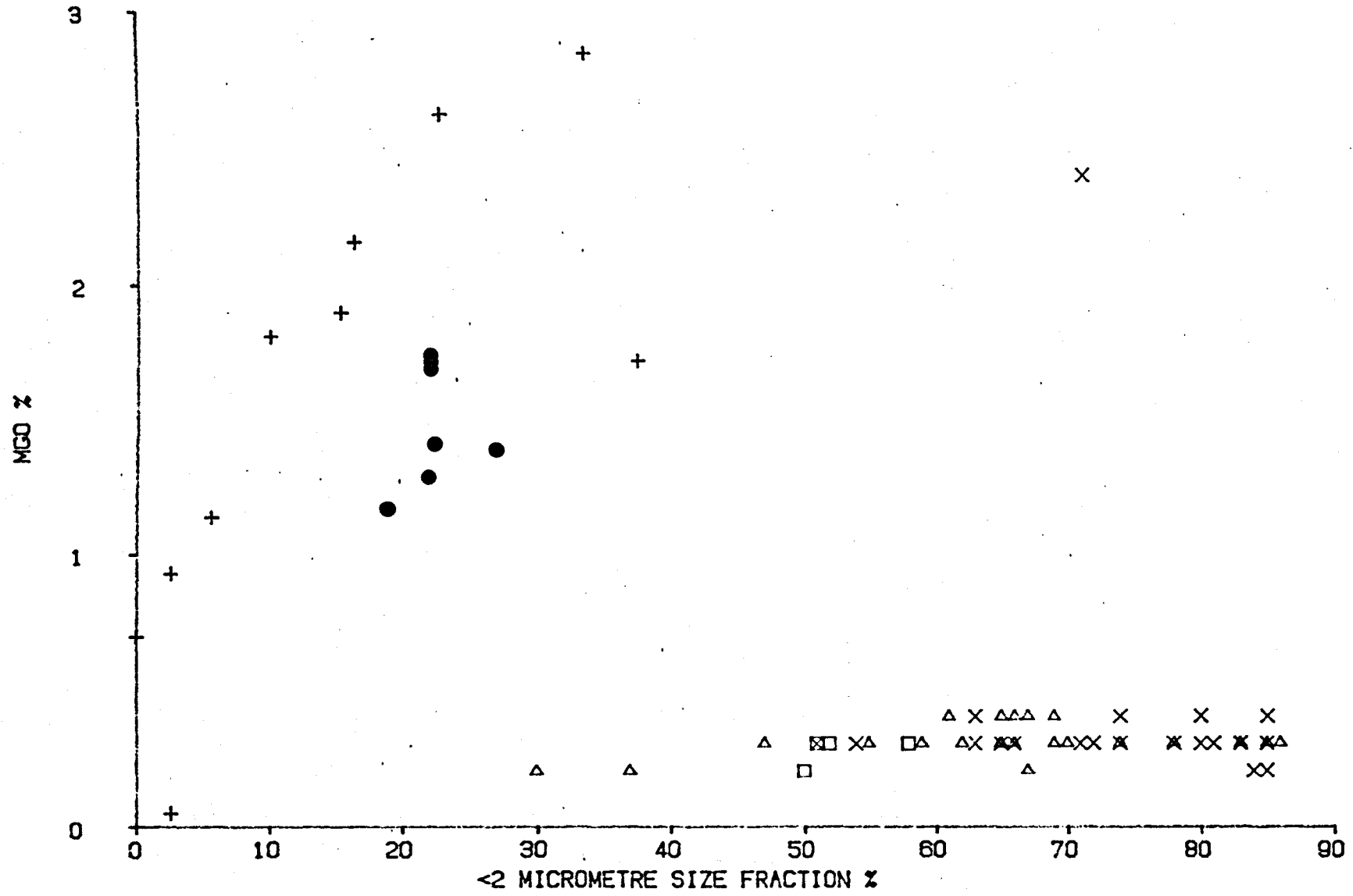


FIG. 4.13 Relationships between K content and < 2 micrometre size fraction.

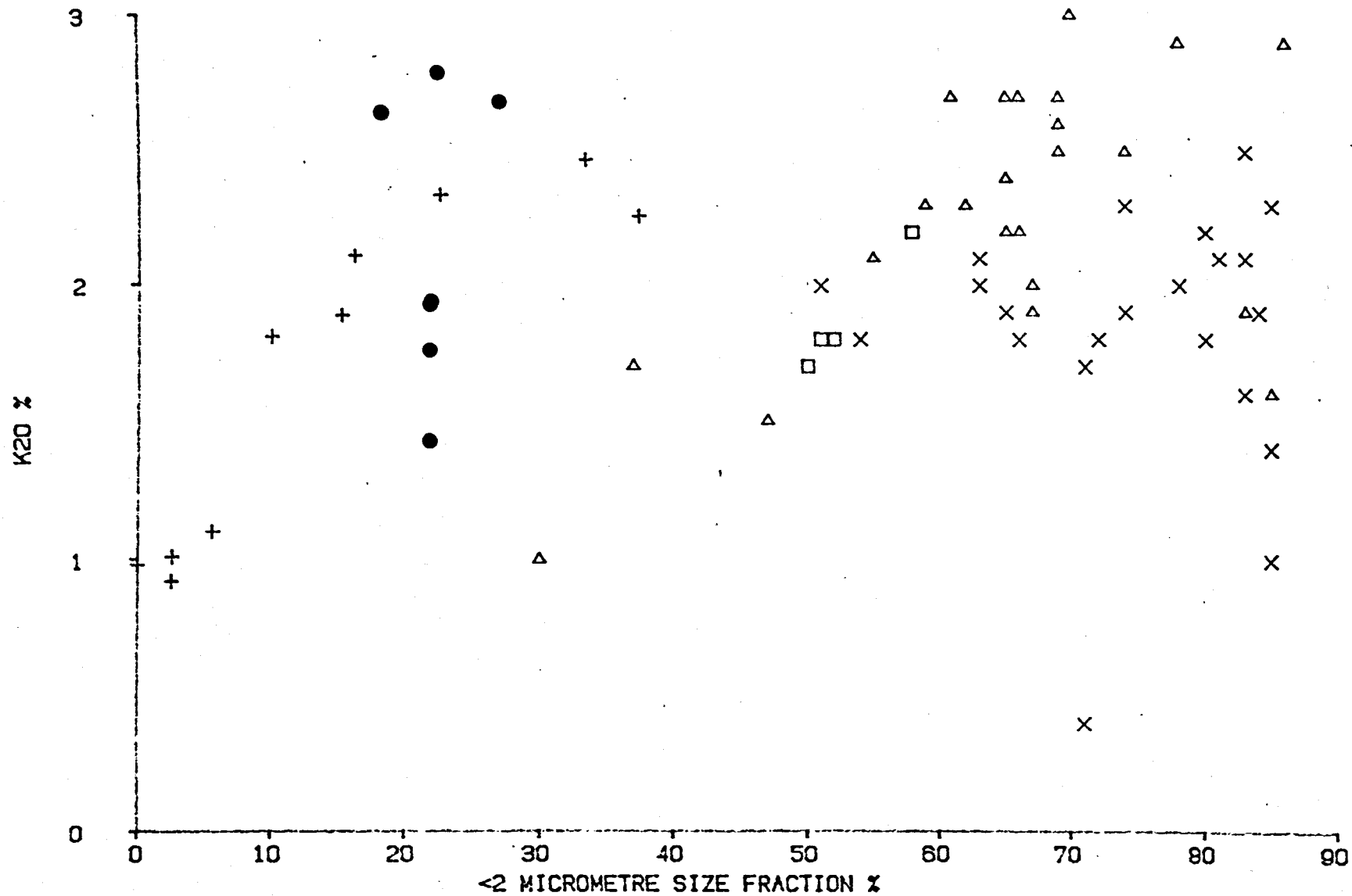
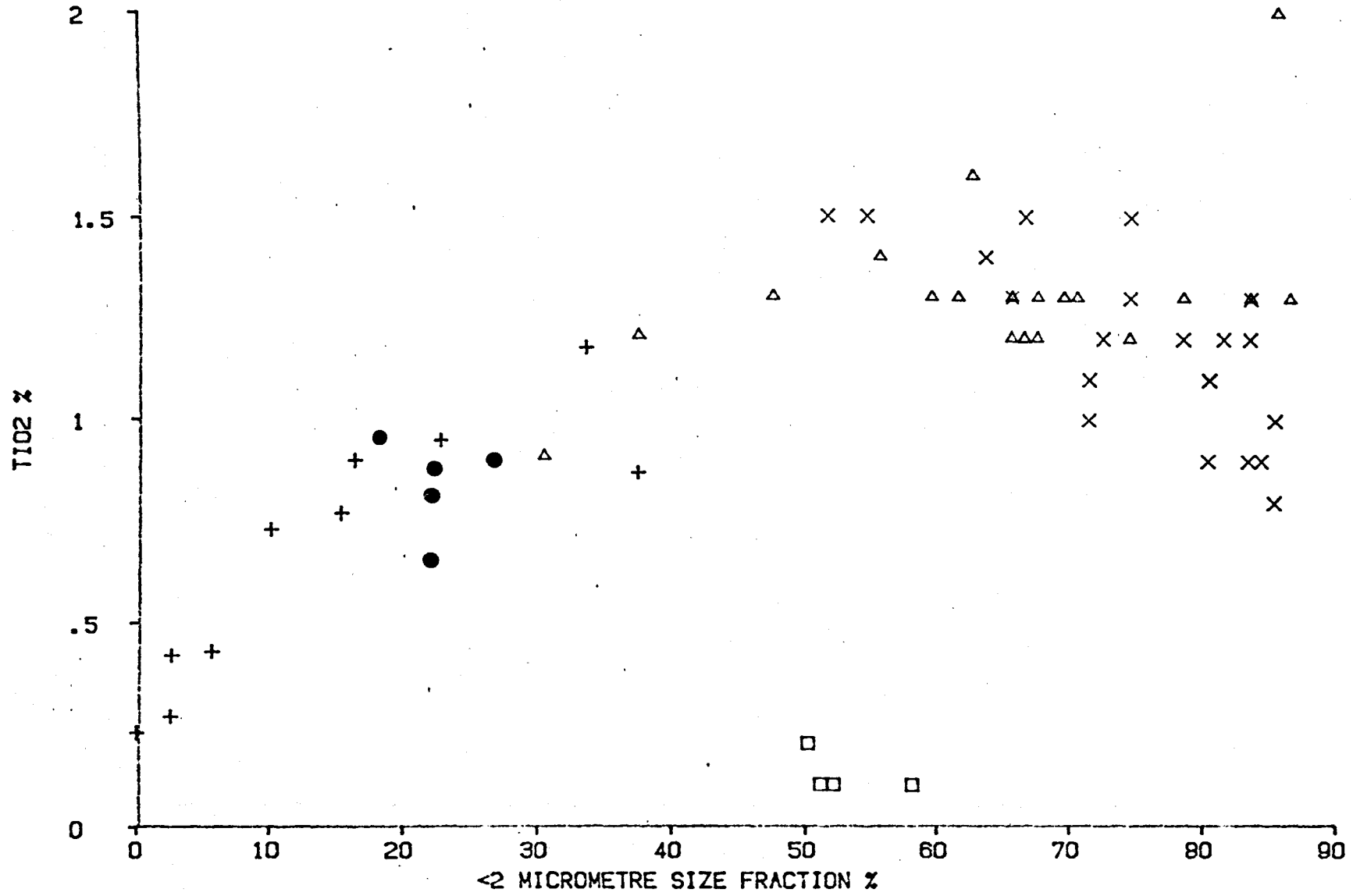


FIG. 4.14 Relationships between Ti content and < 2 micrometre size fraction.



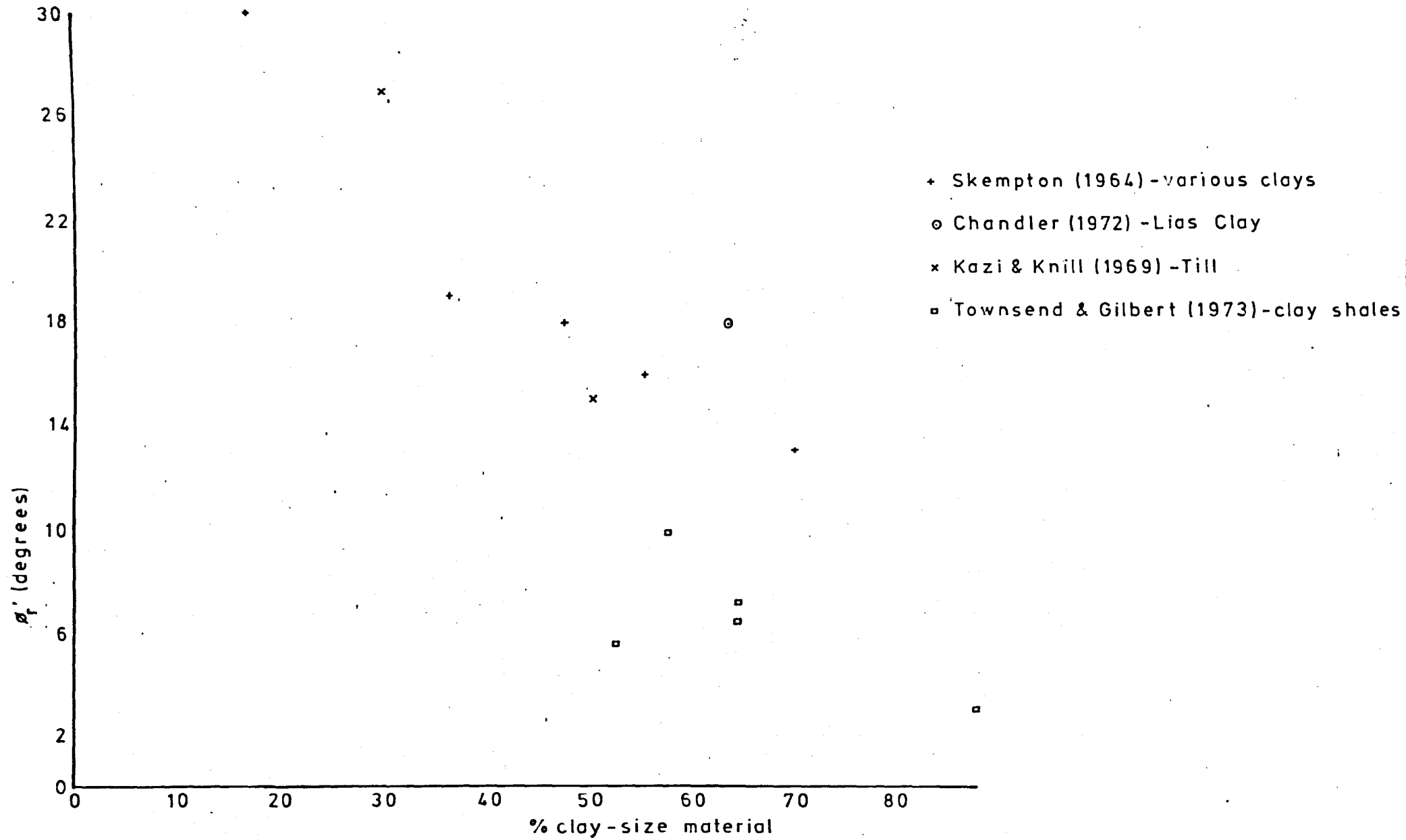


FIG. 4.15 Influence of clay content on ϕ_r' .

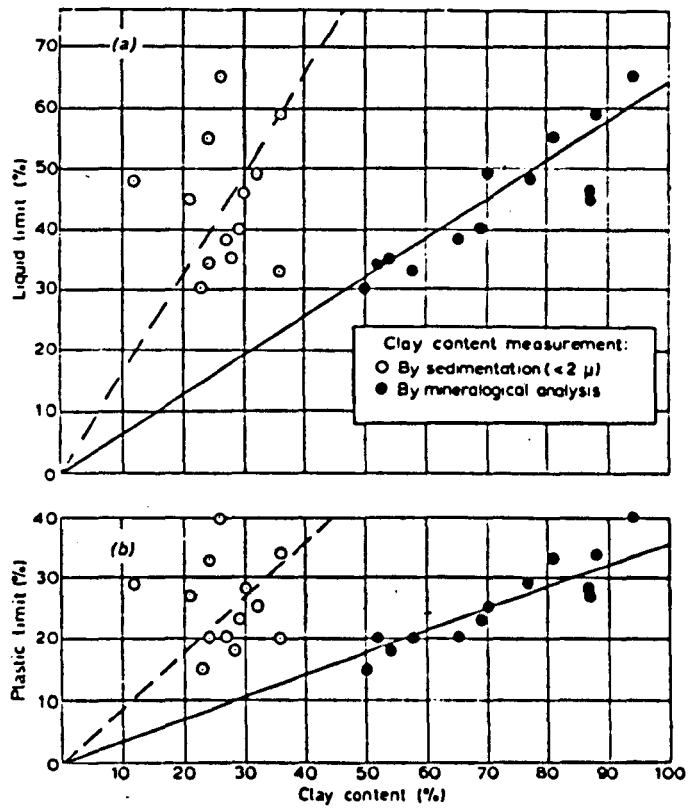


FIG. 4.16 Relation between the liquid and plastic limits of Keuper Marls and their clay content as measured by two different methods - from Dumbleton & West (1966, Fig. 11).

percentage of $< 2 \mu\text{m}$ size material in a soil is usually measured by physical methods which do not always give reliable results. Using the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as an indication of the proportion of $\% < 2 \mu\text{m}$ fraction, a more meaningful relationship may be obtained between fundamental grain size distribution and residual shear strength and plasticity.

Since physical weathering reduces aggregate size it is interesting to determine whether material of fundamental grain size is produced by comparing $\% < 2 \mu\text{m}$ fraction values obtained using the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio with the results of sedimentation tests. The effects of physical weathering on the physical properties of a soil may then be assessed with reference to changes in aggregate size.

The influence of physical weathering on the plasticity and residual shear strength of Edale Shale were investigated using four samples of this material from various levels on a retrogressive scarp at Mam Tor. Values for $\% < 2 \mu\text{m}$ fraction determined by sedimentation are denoted $< 2 \mu$ (sed.) and values calculated using the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio are $\% 2 \mu$ (calc.). The scarp is shown in Plate 4.1 and the samples in Plates 4.2-4.5.

Sample 1 was taken from the top face, sample 2 from newly fallen shale at the top of the scree, sample 3 from mid-slope scree and sample 4 from the scree bottom. The shale was assumed to be least weathered at the top of the slope and a systematic physical degradation of material downslope was observed. The scarp thus provided a site suitable for investigating the effects of short term weathering on various rock characteristics. It was assumed that on the scree at least, physical processes were dominant and that chemical weathering had had little opportunity to effect major mineralogical changes within the material. Another advantage of using this site was that the material was almost

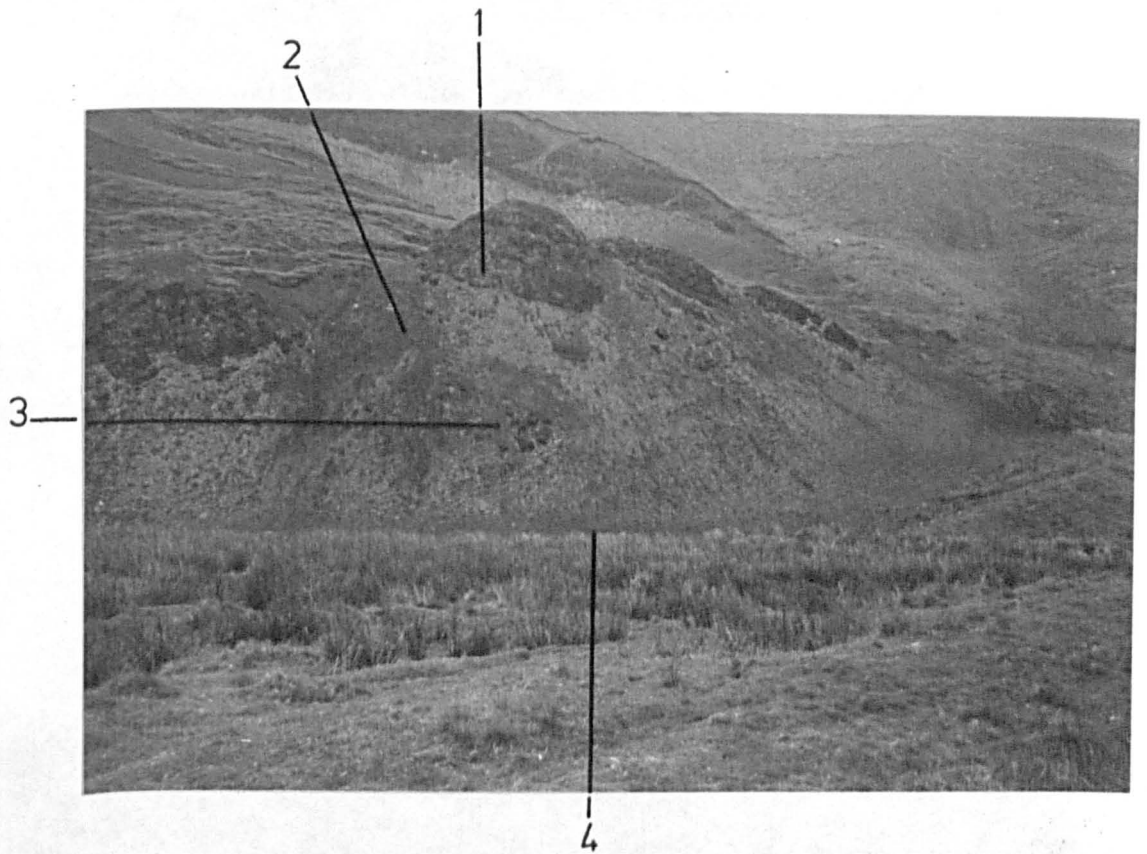


PLATE 4.1 Retrogressive scarp at Mam Tor showing sites from which samples were selected.

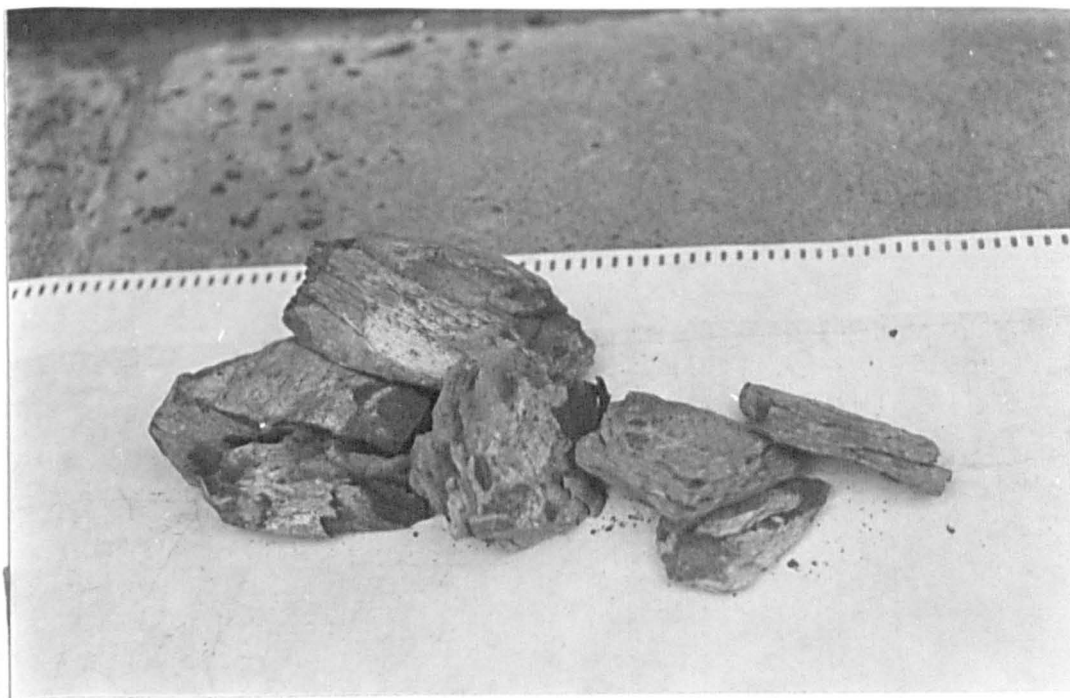


PLATE 4.2 Sample 1 - material from face at top of scarp.



PLATE 4.3 Sample 2 - material from top of scree.

0 25cm

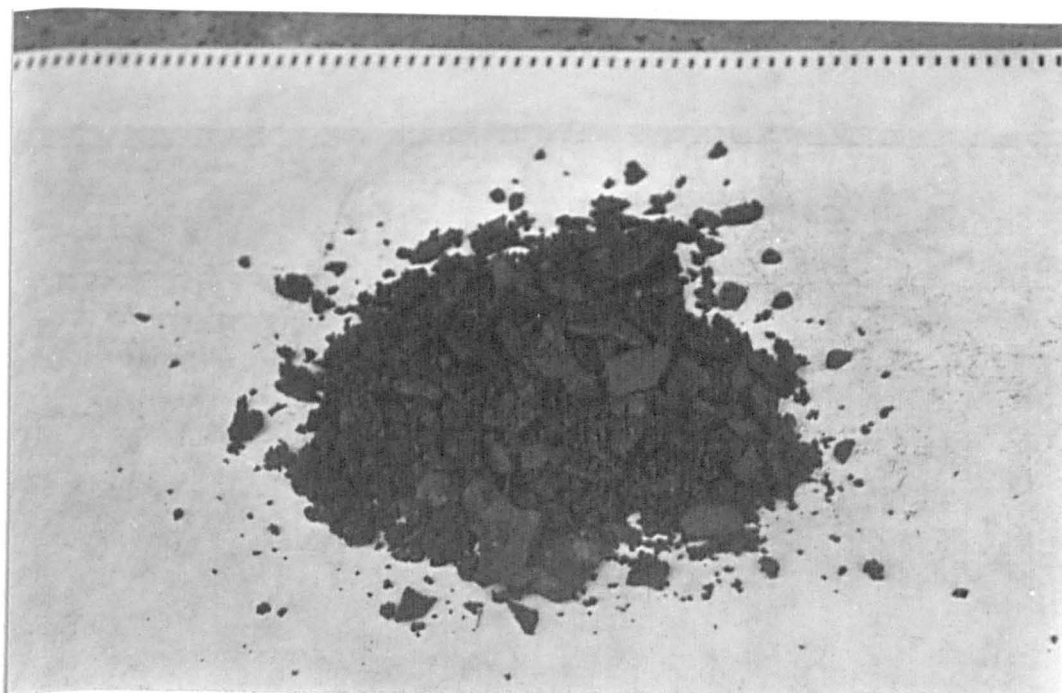


PLATE 4.4 Sample 3 - material from mid-scee.

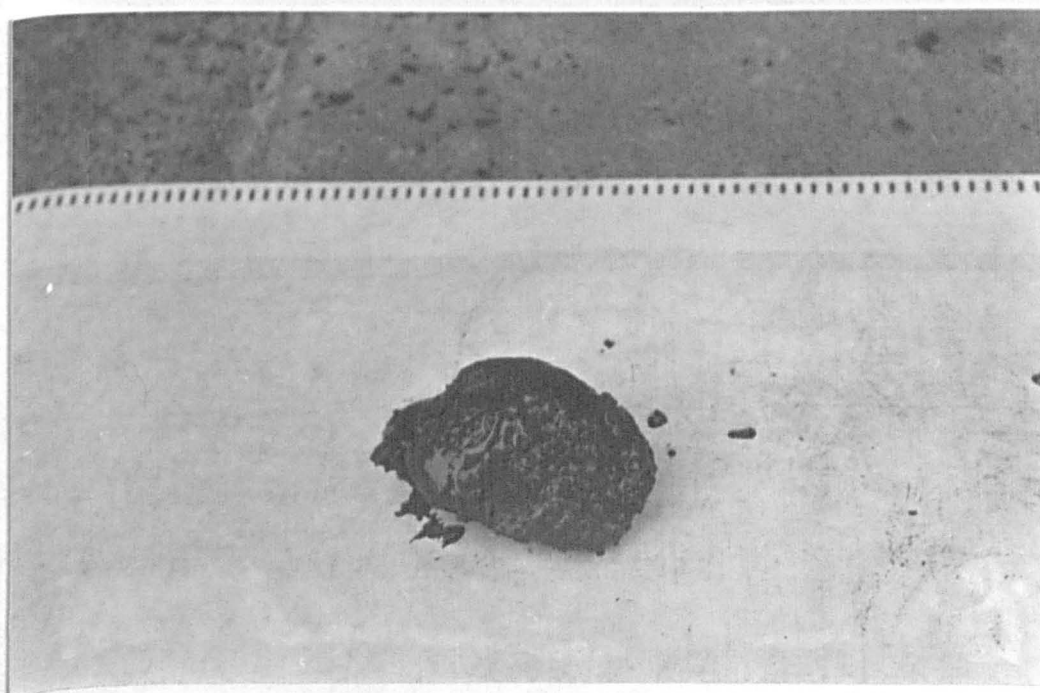


PLATE 4.5 Sample 4 - material from bottom of scree.

0 25cm

certainly derived from the scarp and that breakdown was sufficiently rapid for present day processes to be responsible for degradation. Contamination by material from other sources and preferential removal of certain components were, however, unknown factors considered in the interpretation of results.

4.5.1 Chemical and mineralogical analyses

Glass discs of samples 1-4 were prepared after ignition by the method described in Appendix A5 and chemical analyses obtained by XRF. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were calculated from the results and are presented in Table 4.9. Using these values, the % < 2 μm size fraction was calculated using equation 4.8 (Table 4.5). Although the amount of fine material in the sample predicted by this equation is a cautious estimate, relative differences between the values are important since this is assumed to indicate changes in the proportion of < 2 μm material.

Each sample was also analysed by X-ray diffraction. Smear mounts were prepared for both whole rock specimens and < 2 μm size separations as described in Appendix A4. There were apparently no differences between the samples in terms of bulk mineralogy except that samples 1, 2 and 3 contained gypsum and sample 4 did not. The soluble minerals, including gypsum, have presumably been removed from material at the base of the scree. The relative proportions of clay minerals were determined from the < 2 μm size XRD traces using the method of Weir *et al.* (1975) and the results are presented in Table 4.9. It should be noted that for the reasons given in Appendix A4, the percentages obtained are tentative and should be regarded only as a guide to the mineral proportions. The trends shown are more important.

	Top face 1	Scree top 2	Mid-scree 3	Bottom scree 4
SiO ₂ /Al ₂ O ₃ < 2 μm (calc)	2.59 70.09	2.64 69.46	2.62 69.71	2.65 69.34
% kaolinite	14	6	9	16
% illite	12	6	12	21
% expandable	73	86	77	61
% chlorite	-	1	2	2
% < 2 μm by sedimentation - no pre-treatment	18.6	6.6	25.8	22.2
% < 2 μm by sedimentation - organic matter removed	18.6	3.3	27.0	22.5
Plastic limit %	28	29	30	30
Liquid limit %	45	45	46	46
*(Apparent) resi- dual shear stress	65.18	52.34	63.07	69.23
φ _{ra} '	12.5°	10.1°	12.7°	13.2°
Displacement to Peak Strength (mm)	4.1	3.4	3.9	3.4

*mean values; assume c_r' = 0

TABLE 4.9 Summary of physical, chemical and mineralogical properties of Edale Shale from a scarp at Mam Tor.

4.5.2 Physical and engineering properties

The samples were air dried on a metal tray and disaggregated by a mortar and pestle prior to sieving through a 1.18 mm mesh. Each sample was subdivided by rotating sample splitter and apportioned as follows:

- 30 g - sedimentation, no pre-treatment
- 30 g - sedimentation, organic matter removed
- 200 g - liquid limit
- 20 g - plastic limit
- 40 g - residual shear strength

The sedimentation tests were carried out by the pipette method (B.S.1377, 1975) on shale dispersed with calgon as outlined in Appendix A3. The removal of organic matter was performed using hydrogen peroxide. The results of the tests are given in Table 4.9 and Fig. 4.17.

The plastic and liquid limits of each sample were determined using the B.S. 1377 rolling thread and cone penetrometer methods.

Residual shear strengths were expected to provide a more sensitive indicator of possible weathering effects on physical properties. The samples were tested using a Bromhead Ring Shear apparatus for which samples were prepared by the procedures described in Chapter 6. A strain rate of $0.48 \text{ deg. min.}^{-1}$ was used. Consolidation prior to shearing indicated that this rate was sufficiently slow to maintain drained conditions during the tests. Peak strength occurred at displacements of 3-4 mm as shown in Table 4.9. Vertical displacements indicated only slight settlement during shearing but the rate of settlement increased dramatically towards the end of each test, probably because of soil extrusion from the sample holder.

All results, in terms of the residual shear strength parameters ϕ_{ra}' are given in Table 4.9 where the effective normal stress used was 294 kN m^{-2} and c_r' is assumed to be zero.

ORGANIC MATTER
REMOVED

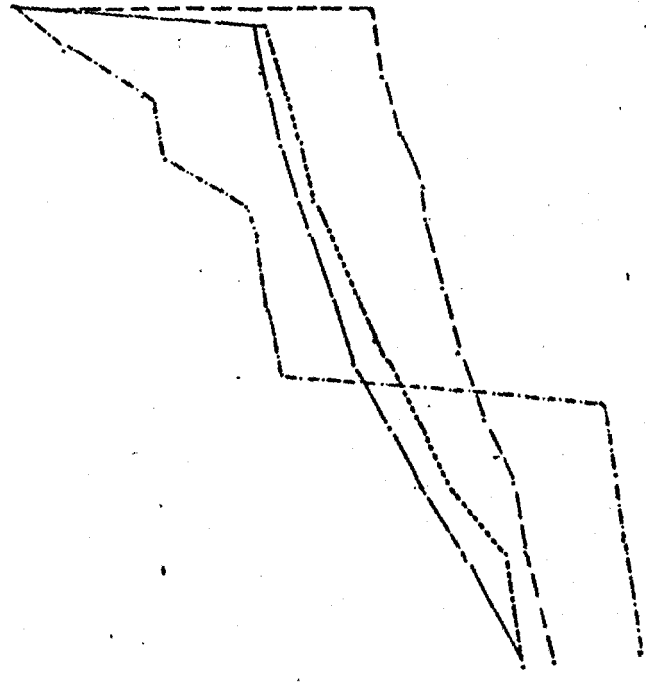


FIG. 4.17 Grain size distributions of samples 1-4 determined by sedimentation.

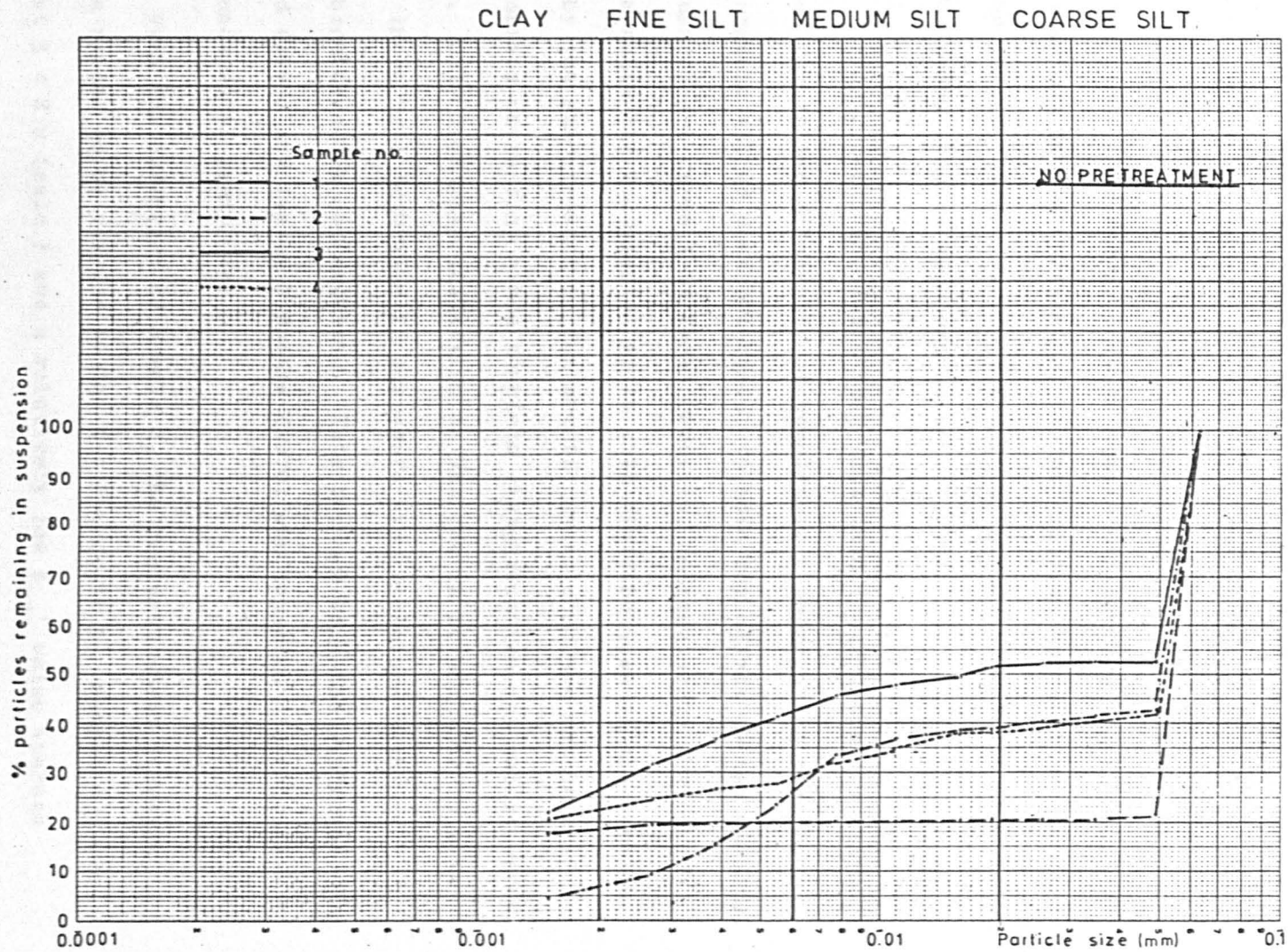
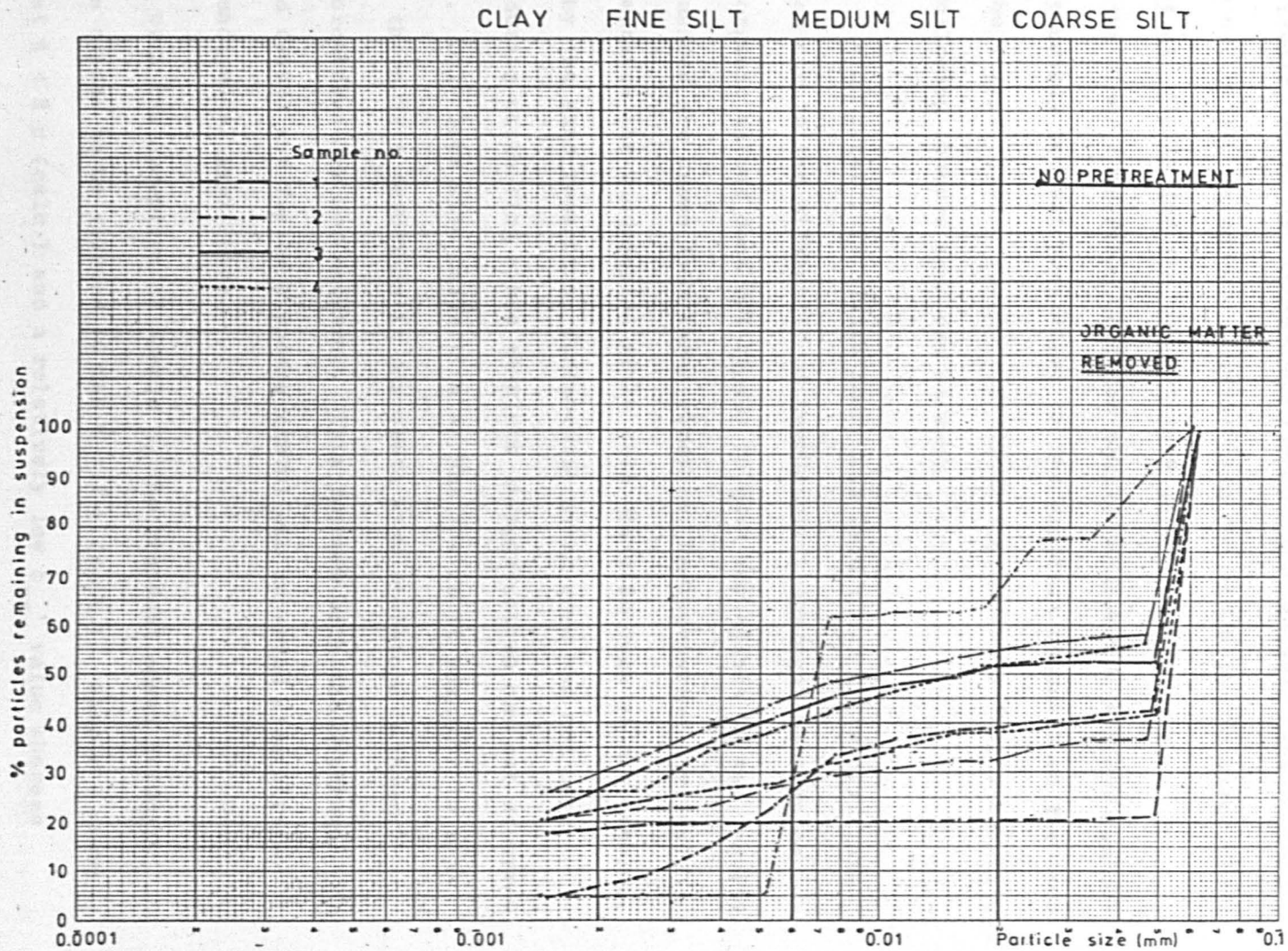


FIG. 4.17 Grain size distributions of samples 1-4 determined by sedimentation.



4.5.3 Discussion

With reference to Table 4.9, between sample variation of all properties, appears to be small and unsystematic in terms of the assumed weathering pattern on the scarp. The properties showing the least conclusive changes are clay mineralogy and plasticity. Although the former apparently varies, firstly, there are no defined trends, and secondly, the figures quoted do not differ by amounts greater than 20% which is the error given by Weir *et al.* (1975) for the quantitative analysis technique.

For the other properties, between sample differences are not systematic and possibly reflect variations in the original material on the free face of the scarp. Within sample variations appear to be fairly consistent and the following observations can be made:

(1) % < 2 μ (sed.) is always much less than % < 2 μ (calc.). This is expected due to the difficulty of completely disaggregating samples. Removing organic matter does not appear to have any affect on the results. Two conclusions are drawn from these comments. Sedimentation obviously fails to measure the fundamental grain size distributions of the samples. Clearly, by the same reasoning, fundamental grain size has not been attained during weathering since complete disaggregation has not occurred naturally. Only from site inspection at Mam Tor is it possible to realise that there is a reduction in aggregate size downslope although complete breakdown has not occurred. This concurs with the findings of Kennard (1967) and Taylor & Spears (1970) who reported slow attainment of fundamental grain size.

(2) With the exception of sample 2, the residual shear strength parameters appear to be related to the % < 2 μ (calc.). Sample 1 shows the largest % < 2 μ (calc.) and a relatively low ϕ_{ra} value whereas sample 4 has the smallest % < 2 μ (calc.) and correspondingly, a higher

ϕ_{ra}' value. Sample 3 has intermediate values. These results seem reasonable since higher ϕ_{ra}' values would be expected to correlate with lower $\% < 2 \mu$ (calc.). However, variations in the amount of fine material present are possibly less significant than changes in bulk mineralogy. Quartz contents are also reflected in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio with higher ratios implying larger amounts of quartz. Kenney (1967) found residual shear strength to be primarily dependent on mineralogical composition and Spears & Taylor (1972) reported a close correlation between residual shear strength parameters and quartz content in Coal Measures rocks. Since the magnitude of residual shear strength is independent of initial grain size and water content, differences in the values of τ_{ra}' and ϕ_{ra}' may be related to mineralogy, provided comparisons are between samples tested under similar normal stress conditions. In samples 1, 3 and 4, therefore, quartz content may exert an influence on engineering properties. Sample 2, however, does not conform to this conclusion. The most obvious explanation for the rather low ϕ_{ra}' value is that the expandable clay component of this sample is apparently large. Although the clay percentages in Table 4.9 were said to be unreliable, sample 2 does seem to have a distinctly larger proportion of expandable clay than the other samples which may clearly influence residual shear strength (Kenney 1967).

The apparent influence of quartz content on ϕ_{ra}' is also illustrated by differences in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of Edale Shale from Mam Tor and from Hope Valley Cement Works. The latter material has a ratio of about 3.0 (Table 4.8) while the value for Mam Tor material is around 2.6 (Table 4.9).

Table 3.2 shows that for Cement Works and Mam Tor shale respectively, ϕ_{ra}' values are 22° and 24° . The higher value for Mam Tor is interpreted to reflect larger quantities of quartz.

4.6 Conclusions

With reference to the objectives of this section, the following points can be made:

1(a). Physical methods of particle size analysis do not always measure the fundamental grain size distribution truthfully. They are particularly unreliable when dealing with indurated, fine-grained material or with clays where dispersion of individual particles is difficult.

(b). A statistical correlation appears to exist between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and % < 2 μm size fraction in detrital sediments and sedimentary rocks. The exact relationship varies for different samples but in general variations in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio may indicate differences in grain size distributions for a given set of sediments.

2. Fundamental grain size is apparently not attained during rapid weathering of shales.

3. Changes in the residual shear strength and plasticity of shales do not appear to be dependent on their state of physical breakdown. Instead, mineralogy seems to exert a much stronger influence on properties like residual shear strength.

CHAPTER V

RATES OF CHEMICAL REACTION IN SHALES

5.1 Introduction

The oxidation of sedimentary pyrite can be rapid, particularly when aided by bacterial action (Penner et al. 1966). The potential for subsequent chemical reaction with the surrounding rock mass is apparently great; Vear & Curtis (1981) and Van Breeman (1972) reported that in natural acid weathering systems, reaction with fresh materials could consume 97-99% of available acid. However, the timescales for reactions involving newly generated acids are uncertain. Natural systems are frequently too complex for precise investigation due to their multi-component nature and because many different reactions involving different components of a particular system occur simultaneously.

In view of the possible implications of chemical weathering for engineering properties, an estimation of the rapidity with which significant changes in the rock-porewater system may occur would be valuable. A series of simple, closed system experiments were, therefore, conducted to ascertain whether reactions comparable to those occurring naturally could be reproduced under laboratory conditions. Ultimately, controlled investigations of reaction rates were carried out.

5.2 Leaching experiments

Two sets of experiments were carried out using Edale Shale obtained from the Hope Valley Cement Works and sulphuric acid at a concentration of 2.4 g l^{-1} commensurate with that of naturally generated acids at Mam Tor (Vear & Curtis 1981, Site 7).¹

In the first set (Experiment 1), two 10 g samples of shale crushed to $500 \mu\text{m}$ were placed in conical flasks containing 250 ml of acid

¹This concentration is neither maximum nor minimum. Maximum acid concentration is expected locally in the vicinity of pyrite oxidation. Minimum values occur if acid is neutralised by rock reaction.

(Experiments 1.I and 1.II). The mixtures were stirred continuously for 1 week during which time the acid was changed once, after 48 hours. Aliquots of 20 ml were removed at intervals and placed in polythene bottles.

The concentrations of Ca, Mg, K, Na, Fe, Si and Al in each extraction were measured by atomic absorption spectrophotometry (AAS) and the change in pH with time was also monitored. The results are presented in Table 5.1 and the styles of cation release are plotted in Fig. 5.1a & b. The concentrations of most ions increased rapidly initially but slowed dramatically within a few hours. Ca and Mg were released in the greatest quantities, Na and Si in the smallest amounts and Al in relatively intermediate concentrations. These results corresponded with a reduction in H^+ concentration in solution indicating that the rate of ion dissolution decreased as acid was consumed. Fe, however, was not released in the same way since its concentration continued to increase as reaction proceeded.

Whole rock smear mounts of the pre- and post-leaching shale were analysed by X-ray diffraction. The traces are shown in Fig. 5.2 and display no obvious changes in the mineralogy after reaction, except for the removal of gypsum.

In the second experiment (Experiment 2), different masses of shale were reacted with acid to observe the effect on the rate of reaction of increasing the surface area of solid available and to estimate the time-scales of reaction. 1, 3, 10, 30, 50 and 100 g of crushed shale were each placed in 250 ml of acid and the mixtures stirred for 24 hours. Again, 20 ml aliquots were removed at intervals approximating to a logarithmic timescale and analysed as before. The acid consumed¹ by the end of the 24 hour period by different masses of shale is shown in Table 5.2 and the acid consumption is plotted against ratios of H^+

¹Acid consumption is measured in terms of H^+ (mg) used in reaction

		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Fe	Al ³⁺	Si ⁴⁺	pH
1.I	mins. 0	0.00	0.00	0.00	0.00	0.00	0.48	2.6	1.5
	10	0.757	4.53	87.75	52.3	14.90	3.81	4.1	1.6
	40	0.868	5.39	110.5	67.1	33.40	5.80	2.7	1.6
	80	0.962	5.63	122.6	73.8	56.80	7.65	3.3	1.7
	160	1.029	5.98	129.3	81.5	87.80	8.95	3.5	1.7
	320	1.273	6.26	124.9	87.0	125.8	10.27	5.0	1.7
	24 hours	1.460	6.80	120.7	107.9	278.1	14.18	4.6	1.9
	48 hours	3.457	8.32	109.6	126.0	432.1	20.55	8.3	2.1
	* 54 hours	3.567	11.47	-	136.0	485.3	22.37	9.0	1.6
	5 days	4.205	11.84	114.30	152.2	572.5	27.49	12.4	1.7
	6 days	4.073	12.11	151.05	180.5	942.6	42.67	20.0	1.7
	7 days	5.807	-	128.7	148.2	659.1	39.79	16.2	1.7
1.II	mins. 0	0.00	0.00	0.00	0.00	0.036	0.90	1.7	1.5
	10	0.833	4.67	93.4	54.80	15.6	3.81	0.1	1.6
	40	0.021	-	-	-	-	-	2.9	1.5
	80	0.960	5.68	119.8	74.60	64.15	7.87	5.7	1.7
	160	1.056	5.94	125.1	83.05	100.6	9.49	4.1	1.7
	320	1.209	6.11	121.6	87.55	138.2	10.60	3.7	1.7
	24 hours	1.526	6.62	115.5	109.15	286.1	13.90	12.4	1.9
	48 hours	3.637	8.29	104.1	125.8	416.4	20.70	11.1	2.1
	* 54 hours	3.921	9.51	105.90	131.9	458.9	22.97	15.6	1.6
	5 days	3.612	10.72	105.90	141.4	450.9	29.27	15.7	1.7
	6 days	5.341	10.30	105.90	143.1	551.8	30.93	19.3	1.7
	7 days	5.566	10.02	105.90	144.95	562.1	32.57	23.1	1.8
Vear & Curtis (1981)	13	5.4	385	178	111	86	-	3.4	

*Acid changed after 48 hours. The results are cumulative for total cations released during reaction.

TABLE 5.1 Cation composition of solutions at selected times - concentrations in $\mu\text{g ml}^{-1}$.

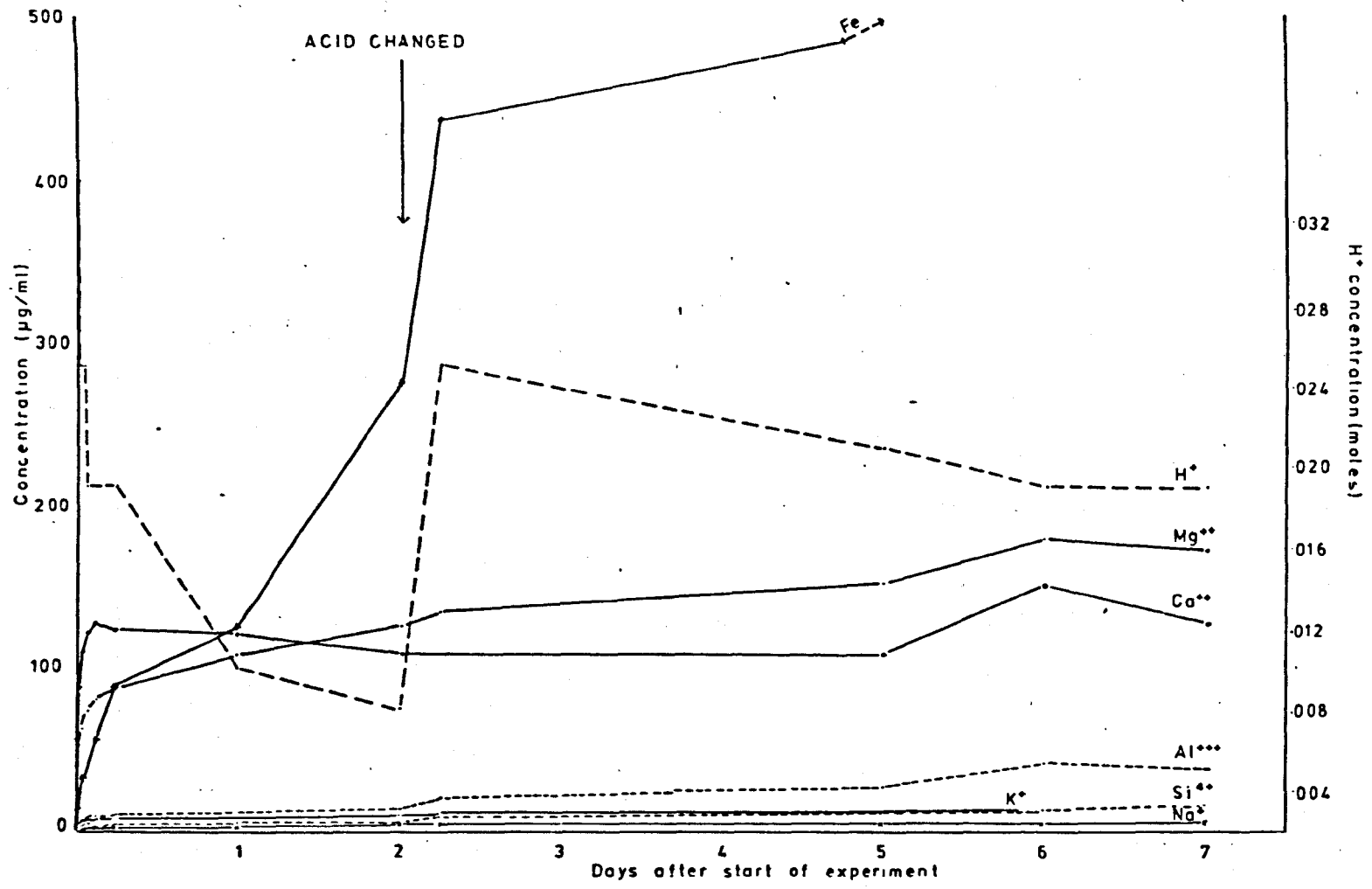


FIG. 5.1a Change in H⁺ and cation concentration with time - Experiment 1.I.

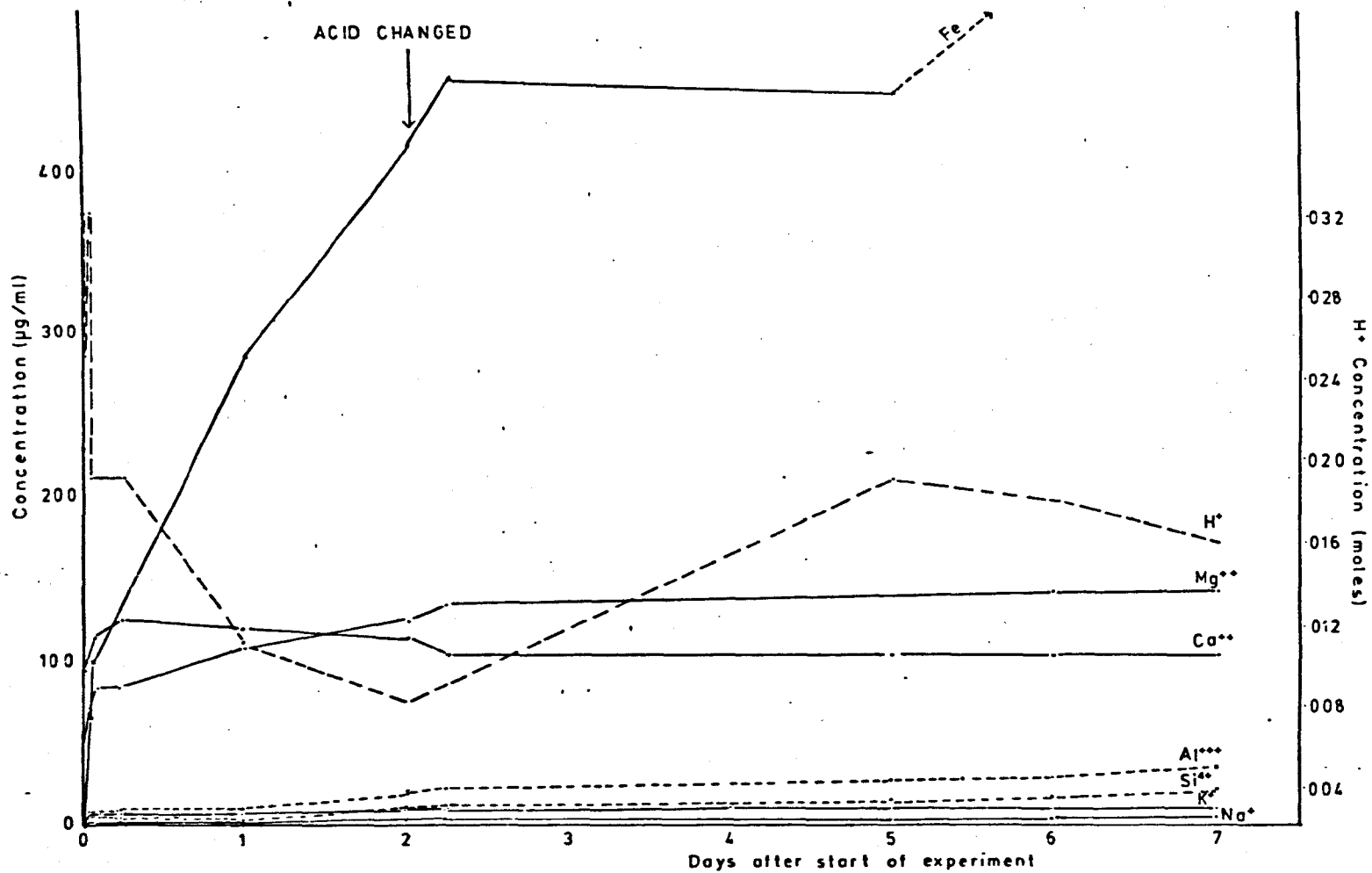
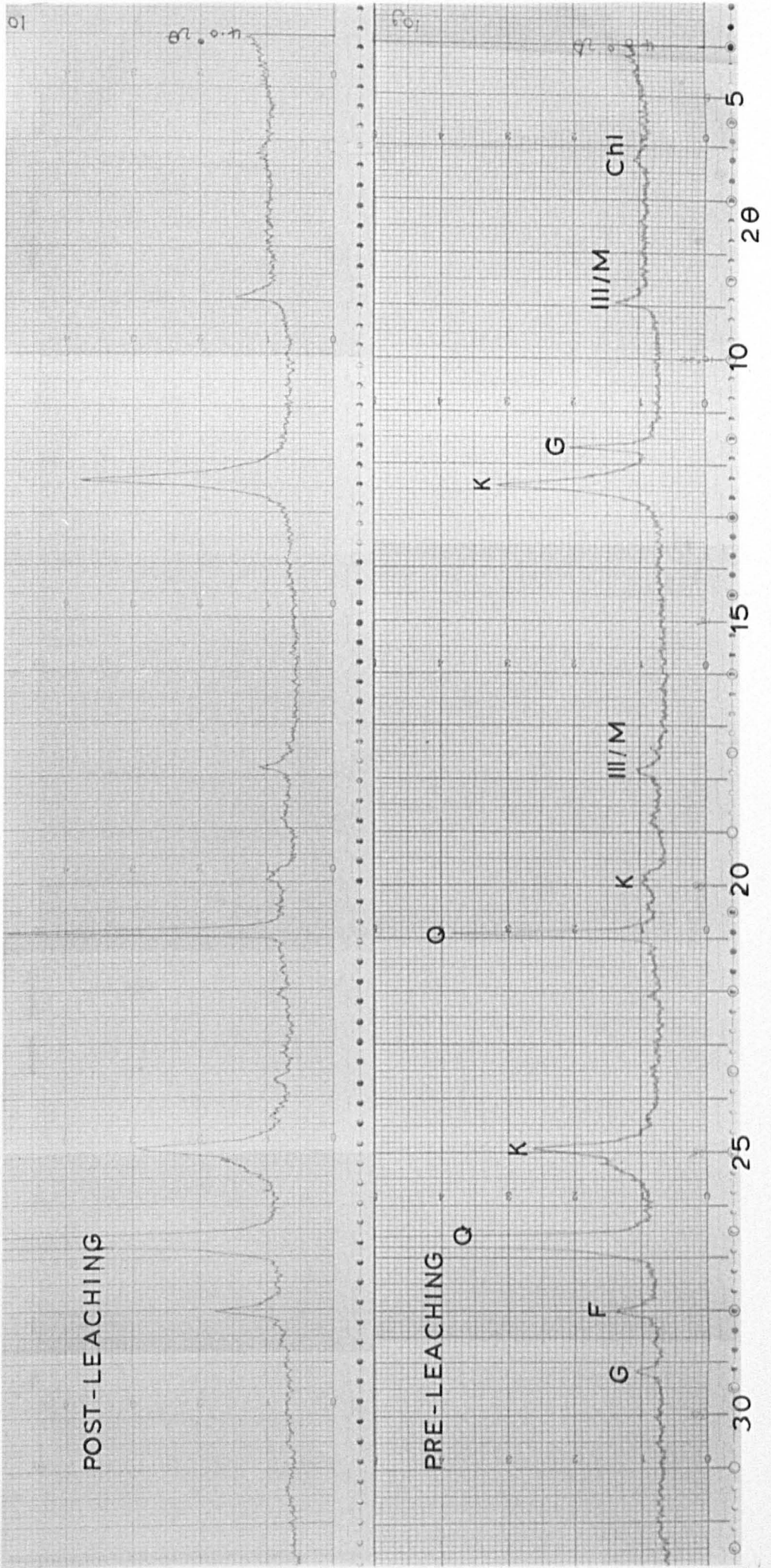


FIG. 5.1b Change in H⁺ and cation concentration with time - Experiment 1.II.

FIG. 5.2 X-ray diffraction traces of pre- and post-leaching shale.

Chl - chlorite; Ill/M - illite/mica; G - gypsum;
K - kaolinite; Q - quartz; F - feldspar



Mass of shale	$ \text{H}^+ /\text{shale}$ mg/g	Acid consumed in 24 hours
100 g	0.08	99.9%
50 g	0.16	98.0%
30 g	0.27	94.4%
10 g	0.80	60.2%
3 g	2.67	29.2%
1 g	8.00	20.6%

TABLE 5.2 Acid consumption for different solid:solution ratios (Experiment 2).

$ \text{H}^+ /\text{shale}$ mg/g	(minutes) ^{t$\frac{1}{2}$}
0.08	0.36
0.16	2.4
0.27	2.6
0.80	52
2.67	235
8.00	710

TABLE 5.3 Estimation of reaction half-lives using Fig. 5.4 (Experiment 2).

concentration to mass of shale ($|\text{H}^+|/\text{shale}$, mg/g) in Fig. 5.3. The amount of acid consumed in reaction appears to increase with the amount of shale present.

The change in H^+ concentration with time is shown in Fig. 5.4 and indicates that reaction was initially very fast, then slowed considerably within an hour or two, depending on the quantity of shale used. In Fig. 5.5, the same data were plotted with a logarithmic timescale and approximately straight-line relationships were obtained. The half-lives of the reactions were estimated from Fig. 5.5 at the point where the H^+ concentration had reduced to half its initial value and the times for the half-lives are included in Table 5.3. Reaction half-lives are seen to vary from hours to less than minutes in duration, depending on the ratio of acid to sample.

5.3 Discussion

The concentrations of ions in solution determined by Vear (1981) for a seepage which apparently drains a fault crush zone (Site 7) at Mam Tor are included in Table 5.1. If compared with the total concentration of ions present in solution at the end of one week in Experiment 1 (Fig. 5.6) broadly similar patterns of cation release are observed. In particular, Ca and Mg are present in larger amounts than K and Na with Al occurring at intermediate concentrations. The behaviour of Fe is, again, anomalous since it is released in greater quantities in the laboratory experiments compared with values obtained at Mam Tor.

Although on a qualitative basis the relative concentrations of ions in solution are generally similar, quantitative comparisons cannot be made because of the differences in the solid-solution ratios and contact times under experimental and natural conditions; longer contact times would probably occur in the field, depending on solution flow rates, and

FIG. 5.3 Acid consumption for different $|\text{H}^+|/\text{shale}$ ratios
(Experiment 2).

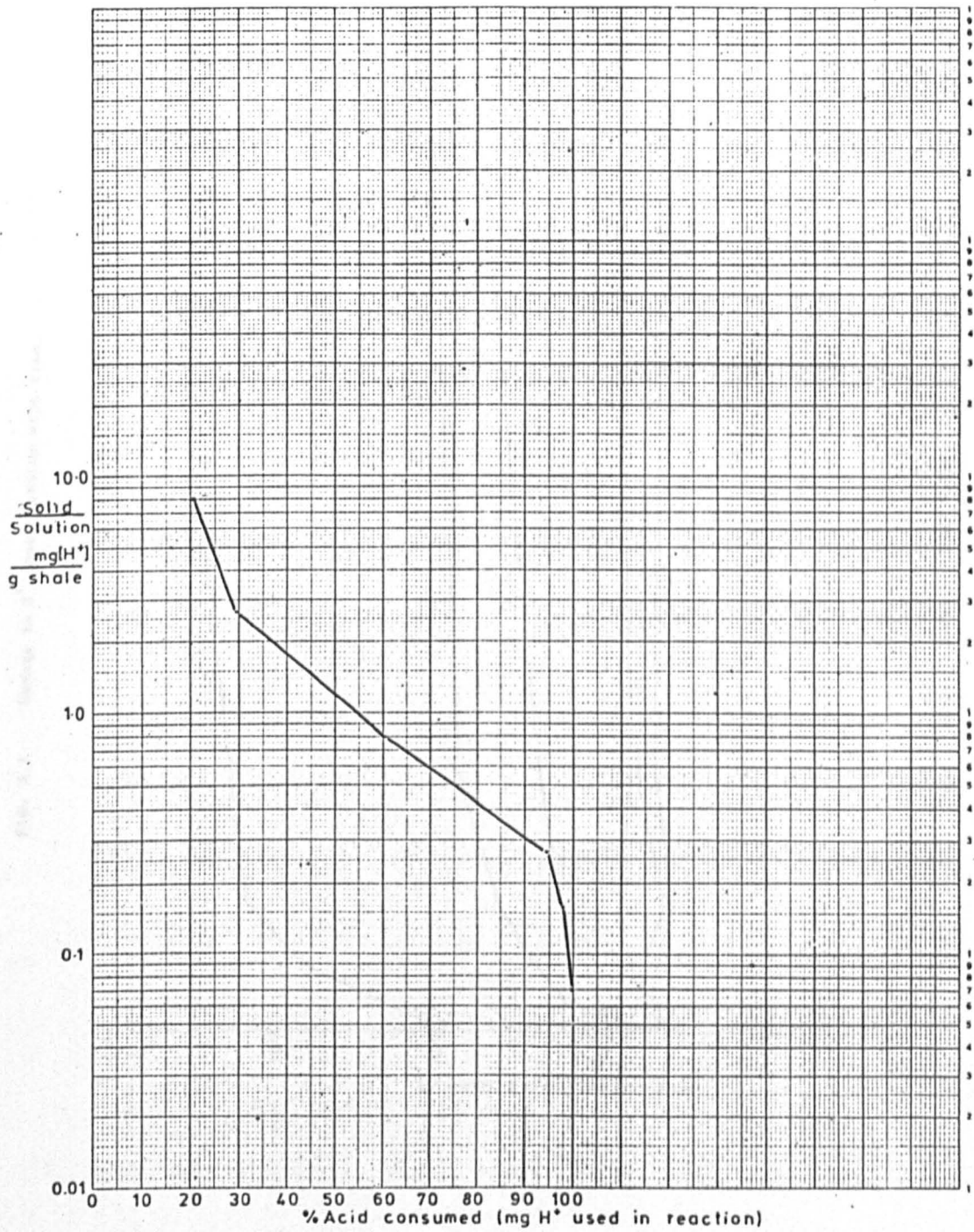
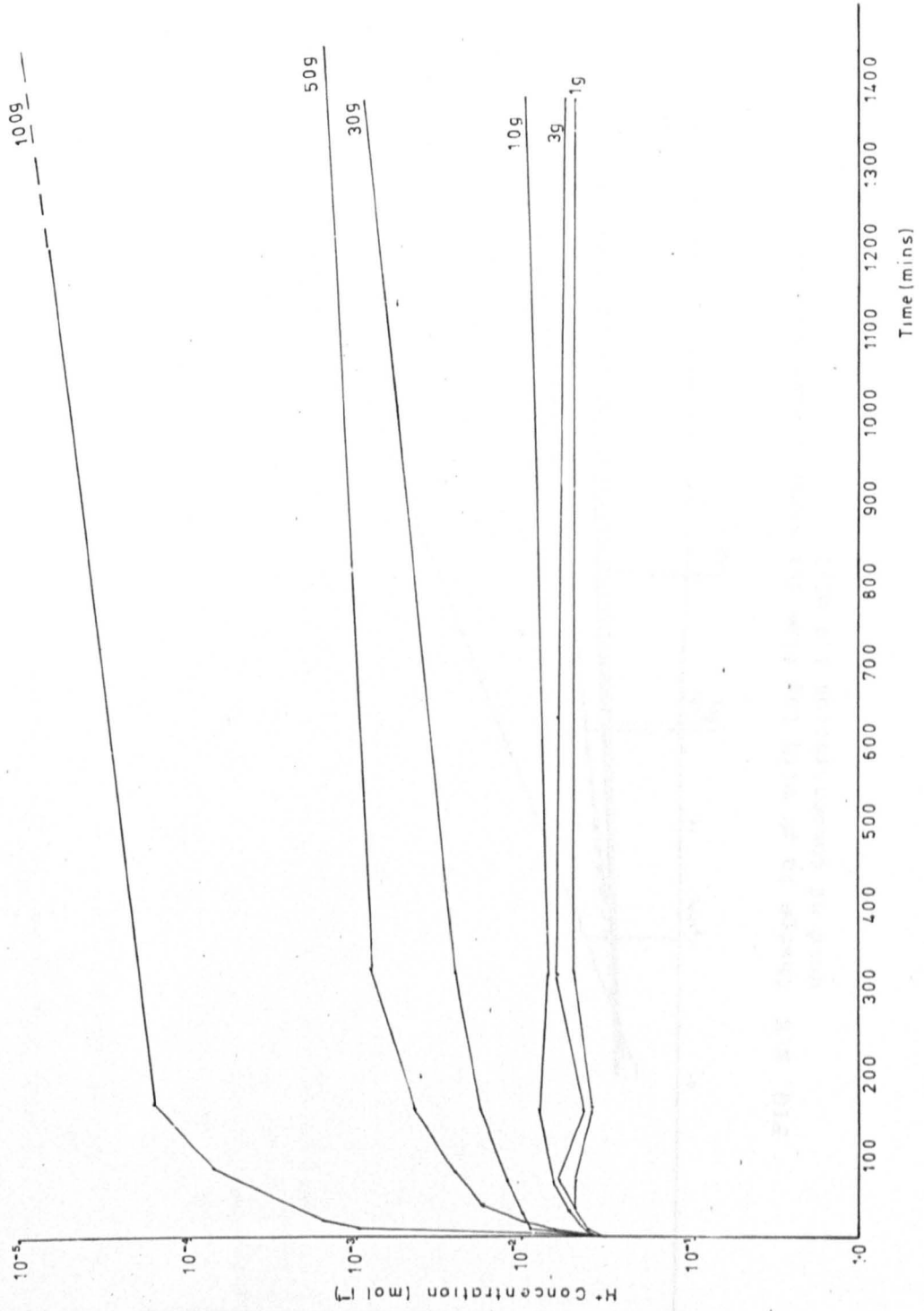


FIG. 5.4 Change in H^+ concentration with time.



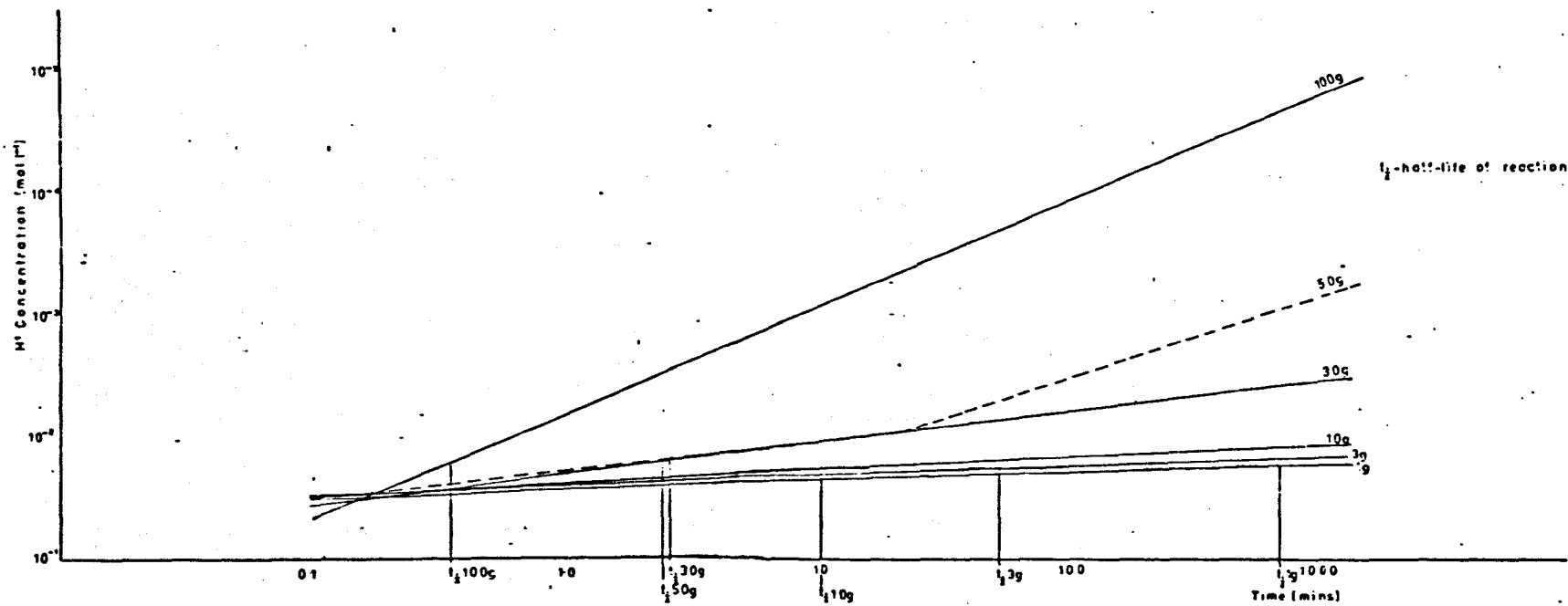
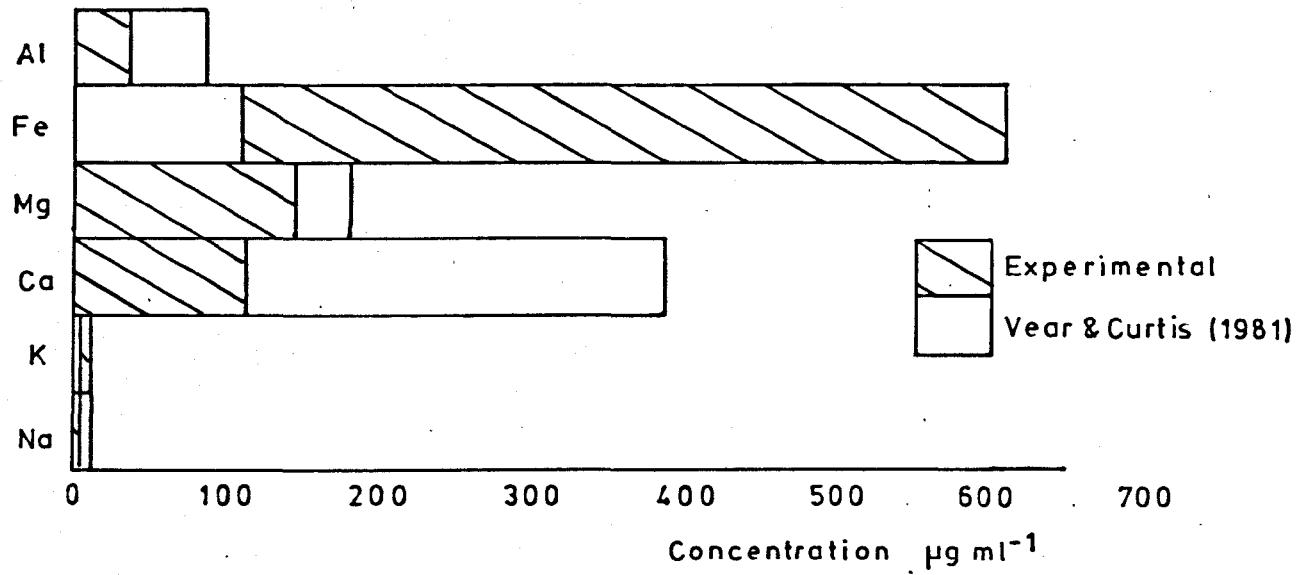


FIG. 5.5 Change in pH with log time for various masses of shale in acid of concentration 1.4 ml/l.

FIG. 5.6 Comparison between concentration of ions in solution after 1 week (Experiment 1) and in groundwater at Mam Tor (Vear & Curtis 1981).



larger solid to solution ratios are anticipated. Furthermore, the starting material used in experimental work was slightly weathered rather than fresh, containing detrital, diagenetic and secondary minerals within one sample. Detailed analyses of exactly which shale constituents were involved in reactions were inappropriate since the ions released to solution could have derived from a number of minerals. Pyrite, iron oxides and hydroxides and even clay minerals, for example, could provide sources of iron while Ca may originate from both gypsum and carbonates.

Results obtained in other work, for example on the acid leaching of pyritic soil and colliery spoil by Van Breeman (1973) and Struthers (1964) in which the major solution components were Ca and Mg with Al, Fe and K forming only relatively minor constituents, indicates that the patterns obtained in the experimental work are common in most weathering situations involving pyritic materials. It is of interest that Barnhisel & Rotromel (1974) also found that for low solid to solution ratios, the pH of reaction solutions changed only slightly. They recorded final pH values of about 2.0 and 1.4 in 0.01 and 0.1 N systems respectively, results comparable to those obtained here. These findings would appear to support the premise that the natural generation of acids following pyrite oxidation can be reproduced in the laboratory.

The tests clearly show too that initial reaction of fresh acid with shale is very rapid and that the half-lives of reaction are short with an order of only minutes. The reactions are heterogeneous, that is, they take place in more than one phase since gases, liquids and solids are all involved. They certainly do not approximate first order kinetics, that is, more than one molecule of each substance is concerned in the rate-controlling process.

Most previous studies of alteration rates reported in the literature involve simpler systems comprising only one mineral. Of particular note

are Lin & Clemency (1981a & b), Busenberg & Clemency (1976) and Wollast (1967), from which it appears that the dissolution of even a single mineral is complicated. Frequently, dissolution occurs in distinct stages characterised by different styles of reaction. In acid dissolution studies on micas, Schnitzer & Kodama (1976) discovered that a unique order for the release rate of ions could not be distinguished. In multi-component assemblages like shales the complexity of reaction is much greater so that it is impossible to contemplate explicitly all the simultaneous processes, in spite of suggestions by Dibble & Tiller (1981) that this is a more fruitful approach!

Berner (1978) points out that laboratory experiments on the rate control of mineral dissolution are not of universal applicability. His experimental values are generally higher than the equivalent natural ones. He was, however, considering open systems where the flushing rate of solution could affect the speed of mineral dissolution. In contrast, in the closed systems used in these experiments reaction rates are controlled by other factors but the limitations of extending results to extra-laboratory situations are still relevant since natural reaction conditions are frequently indeterminate.

Fig. 5.3 indicates that at ratios of H^+ concentration to mass of shale ($|H^+|/shale$) of about 0.1 mg/g, the shale buffered reaction so that nearly all the H^+ available was consumed extremely rapidly. In contrast, a ratio of $|H^+|/shale$ of 8 mg/g only just reduced the H^+ concentration to half its initial value over a time-scale of hundreds of minutes. In this latter case, the surface area of shale available for reaction was probably limiting. The amount and state of disaggregation of materials thus appears to exert a strong influence on chemical reaction rates. Petrovitch (1981) noted that mechanical comminution affected mineral dis-

solution rates by reducing grain size and creating additional surface area through structural damage. In situations where grinding and abrasion of particles occurs, as is probably the case in shear zones, the potential for rapid chemical weathering is thus augmented.

The rapidity with which fresh acids can attack shale may have important consequences in engineering terms. The present research demonstrates that under favourable conditions of H^+ concentration and material surface area, significant reaction can take place within minutes. Other factors may, of course, influence chemical activity. Curtis (1976a), for example, notes that realistic weathering should take into account both the generation of, and subsequent involvement of anions in the overall weathering processes. Curtis (pers. comm.) also considers, however, that in systems where a large facility for chemical weathering exists, involving both organic and inorganic acids, a high H^+ concentration is the common factor. H^+ concentration hence appears to exert a major influence on chemical weathering.

The evidence for reaction has been based on modification of solution composition. Dramatic changes in solution may, therefore, accompany chemical weathering, even if the material undergoing weathering does not appear to experience radical or even detectable alteration. This is evident from the lack of change shown on XRD traces of the starting and finishing materials in the experiments. The short term implications of changes in the cation compositions of porewaters in shales will be considered in the following chapter. The longer term effects are amply illustrated by the precipitation of sulphates such as gypsum and jarosite which can cause rock expansion (Penner et al. 1966; Quigley & Vogan 1970). In terms of engineering structures, such activity can occur well within the lifetime of a structure. The effect of secondary mineral precipitation

on the physical properties of shales was not studied in detail, although it was observed in Edale Shale at Mam Tor as a result of the continuation of the chemical processes discussed.

The degree of mineral alteration necessary to produce significant changes in physical properties remains uncertain. Since chemical weathering also results in physical breakdown, disaggregation may influence certain properties like plasticity or shear strength. This is supported by the work of Laguros et al. (1974) who found that ultrasonic disaggregation of some shales induced changes in their engineering properties to behaviour which simulated that of field-weathered material without any mineral degradation occurring.

5.4. Conclusions

It has been confirmed in laboratory experiments that the pattern of cation release during artificial acid weathering of shales can be similar to that found in natural weathering systems. Meaningful reactions are, therefore, reproducible under laboratory conditions. This has facilitated a study of the rates of chemical reactions which probably occur in the vicinity of acid generation under natural conditions.

The initial attack of acids produced by pyrite oxidation on fresh shale can apparently occur extremely rapidly. The dominant factor limiting reaction, at least in the closed systems used, appears to be the surface area of shale.

During chemical weathering, the composition of the active solutions will be changed markedly, even if there is little apparent effect on the mineralogy of the solid material. This may affect the engineering properties of shales in the short term; continued release of ions into solution can certainly create problems in a matter of a few years due to the precipitation of salts within weathered rock masses.

CHAPTER VI

THE EFFECT OF POREWATER COMPOSITION ON RESIDUAL SHEAR STRENGTH AND PLASTICITY

6.1 Introduction

In Chapter 5, laboratory simulated chemical weathering reactions involving sulphuric acid and Edale Shale were found to modify the acid composition markedly. Furthermore, the alteration in composition occurred rapidly and did not appear to be accompanied by mineralogical changes in the 'weathered' shale. Although in natural systems the effects of chemical weathering in shales on physical properties are obviously significant over time periods of years, the implications of the short term modifications in porewater composition are less well understood.

Various investigations into the influence of different solutions and variations in salt concentrations on selected physical properties of pure clay minerals have been conducted elsewhere. Li (1978) investigated the effects of sodium and calcium chloride solutions at varying concentrations on the mechanical properties of kaolinite and bentonite. Moum & Rosenqvist (1961) studied the relationships between mechanical properties of montmorillonite and illite and electrolyte composition while Mesri & Olson (1970) investigated the response of shear strength of montmorillonite in the presence of different cations. The influence of clay composition and system chemistry on clay strength was researched by Nagaraj & Rao (1973).

In materials which contain large quantities of clay minerals, such as shales, it is possible that changes in porewater composition may affect the physical behaviour of those materials. However, since shales

contain other minerals besides clays, the degree to which physical properties would be affected is uncertain.

Some work has been carried out on natural soils, particularly on sensitive or 'quick' clays (defined as soils in which the ratio of undisturbed strength to remoulded strength is high), for example, by Moun et al. (1971), Rosenqvist (1962), Talme (1968). The shear strengths of these deposits were found to be severely reduced after saline porewaters which were resident in the clays during their deposition in seawater were replaced by freshwater after uplift into a non-marine environment. Ramiah et al. (1970) and Winterkorn & Moorman (1941) reported that changes in the physical properties of silty clays could be induced by cation exchange and that the response depended on the cations involved.

The effect of changes in the cation composition of porewaters on certain engineering properties of Edale Shale were thus investigated in this work. The influence of acid solutions was also studied since sulphuric acid production is ubiquitous wherever pyritic shales are weathered.

The properties selected for measurement were residual shear strength and plasticity. These were chosen because of their importance in the context of slope stability. In addition, the methods by which residual strength and plasticity are determined could be modified to meet experimental requirements. In the case of residual shear strength, a Bromhead Ring Shear apparatus was adapted to permit a throughflow of different solutions during shear strength tests. For plasticity, standard techniques were employed, using a cone penetrometer for liquid limit determinations and the rolling-thread method for plastic limit measurements (BS 1377 (1975)). Before each test, samples of shale were left to soak in different solutions for a period of 24 hours.

6.2 Residual shear strength

A reduction in strength from peak strength is consistently observed after failure in sheared materials. Bjerrum (1967) described residual shear strength as the ultimate strength attained by a sample sheared beyond failure and which remains constant for further straining. The concepts of residual shear strength and the parameters of cohesion (c) and angle of friction (ϕ) are discussed in Appendix B1.

According to Skempton (1964), the first determination of the residual shear strength of a clay was published by Tiedmann in 1937 while credit is given to Haefeli for emphasising the practical importance of this property during the early days of its recognition. Skempton (1964) primarily attributed the development of residual shear strength to: "the development of thin bands or domains in which the flaky clay particles are orientated in the direction of shear". Intuitively, the shear strength of randomly orientated particles is greater than that of particles lying in a parallel arrangement because they offer less resistance to movement. Skempton (1964), Petley (1966) and Hermann & Wolfskill (1966) considered that an increase in water content within sheared material also contributes to the drop in strength from peak to residual. In addition, Hutchinson et al. (1973) noted that particle breakdown occurs on natural shear planes, mainly due to the destruction of clay aggregates. This would aid potential for reorientation.

The alignment of platy minerals along planes of sliding has been observed in subsequent work on shear strength. An optical technique based on the birefringence properties of clay minerals was used by Morganstern & Tchalenko (1967a & b) to investigate the microstructures developed in natural shear zones and in clays subjected to laboratory shear tests. Strong particle orientation was present, particularly in

samples from natural slips which exhibited two sets of shear-induced structures, a family of continuous shear planes in the direction of movement and discontinuous en echelon planes inclined to the continuous ones. Petley (1966) and Skempton & Petley (1967) attributed slickensides and polishing on slip surfaces to particle orientation and noted that these features corresponded with the attainment of residual shear strength along the slip planes.

Lupini et al. (1981) recorded the evolution of the post-failure structure in clay mixtures subjected to shear tests and showed a progressive orientation of clay particles along the shear surface. Partial orientation was achieved in the zones immediately adjacent to the slip surface.

Skempton (1964) considered that full orientation of clay particles was inhibited in samples containing quartz grains which explains the higher residual shear strengths of silty materials compared with those containing larger quantities of clay minerals. Lupini et al. (1981) went on to propose three modes of residual shear behaviour depending on particle size and friction properties. Two shearing mechanisms were described, turbulent shear and sliding shear. The former case is dependent on particle rolling and translation and the latter by sliding. A turbulent mode occurs in soils dominated by 'rotund' particles or by platy minerals with high friction coefficients, and gives high residual shear strength. A sliding mode is characteristic of materials containing predominantly platy minerals which form low-strength, strongly orientated shear surfaces. When no particle shape dominates, both turbulent and sliding shear occur. Examinations of the post-failure structures in specimens exhibiting intermediate behaviour revealed not one, poorly orientated surface but a number of well-formed, discontinuous

shear surfaces in which well-orientated zones were seen to terminate against groups of sand grains.

The influence of mineralogical composition on the residual shear strengths of soils is well documented. Bjerrum (1967) commented that the value of the residual friction angle, ϕ_r , depends on the size, shape and mineralogy of the constituent particles. Skempton (1964), Spears & Taylor (1972) and Voight (1973) recognised the significant effect of clay content on shear strength and plasticity with increasing quantities of $< 2 \mu\text{m}$ material (or alternatively, a decrease in quartz content) effectively lowering the value of ϕ_r . This is shown in Fig. 6.1. Borowicka (1965) reported that in soils with clay contents greater than 43%, silty particles are apparently embedded in a mass of colloidal material and do not exert any influence on shearing properties. Below 43%, there are insufficient colloidal particles to form a slickensided area covering the whole shear plane and this effect is enhanced with decreasing clay content.

The residual shear strength of soils is clearly dependent on the friction properties of constituent minerals. Lambe & Whitman (1979) stated the basic laws of friction, which are fundamental to shear resistance, as follows:

(a) the shear resistance between two bodies is proportional to the normal force between them;

(b) the shear resistance is independent of the dimensions (shape) of the two bodies.

In terms of soils, residual shear strength is dependent on the normal stress imposed on a soil mass. This has been confirmed in a number of studies, for example, by Bromhead (1978) on landslides in London Clay, Hutchinson et al. (1973) on Etruria Marl in Staffordshire and

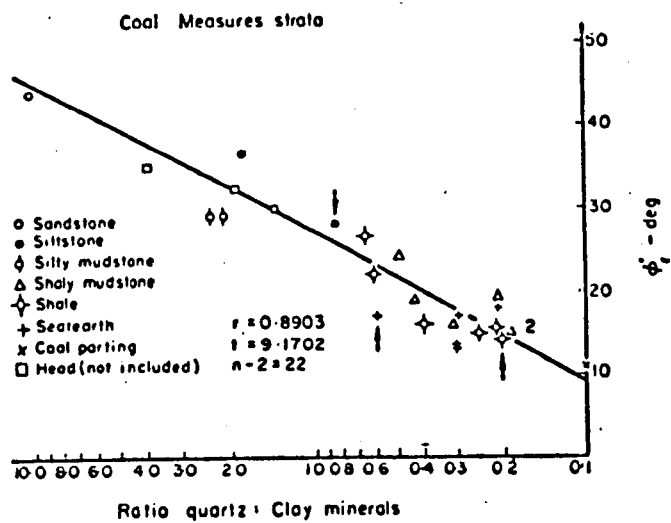


FIG. 6.1

Quartz:clay minerals ratio against ϕ_r' ; from Spears & Taylor (1972, p. 752).

Chattopadhyay (1972) for some pure clay minerals. The residual shear strength of overconsolidated clays has been shown to be independent of stress history, original structure and water content (Skempton 1964). This also applies to overconsolidated shales, as assumed by Fleming et al. (1971).

6.3 The residual strength of clay minerals

The presence of clay minerals has been noted to exert a considerable influence on the residual shear strength of soils, particularly those in which they constitute a large portion of the soil mass. An examination of the factors governing the residual shear strength properties of clay minerals is therefore pertinent.

6.3.1 Residual shear mechanism

The source of residual shear strength in clay minerals is attributed to friction developed along cleavage planes at interparticle contacts (Morganstern 1967; Chattopadhyay 1972). Mitchell (1969) pointed out that interparticle contacts are the only significant region between minerals where effective normal stresses and shear stress can be transmitted. The mode of shearing is by sliding, as shown by Morganstern (1967) and Lupini et al. (1981).

6.3.2 Factors affecting the residual shear strength of clays

Kenney (1967) carried out a comprehensive investigation into the effect of mineral composition on the shear strength of both artificial and natural soils and concluded that the residual shear strength of a soil is dependent on mineral composition and the ion concentration in the pore fluid. He also found that it is not necessarily dependent on grain size or plasticity. The residual shear strengths of the clay minerals were found to decrease in the following order:

micas > kaolinite > montmorillonite

The strength properties of the micaceous minerals and montmorillonite were strongly dependent on system chemistry but kaolinite was less sensitive. Chattopadhyay (1972) gave the following values of ϕ_r' for some mono-mineralic soils:

Quartz	35°
Attapulgite	30°
K-mica	17-24°
Kaolinite	12°
Illite	10°
Montmorillonite	4-10°

This order is similar to that of Kenney (1967). Chattopadhyay (1972) interpreted the values to reflect bonding forces along cleavage planes, noting that these have to be overcome at interparticle contacts during shear at large strains. Campinella, quoted by Mitchell (1969), tentatively suggested that a level of strain is attained at which the numbers of bonds that form and rupture are equal.

An important conclusion drawn by Kenney (1967), Lambe (1958) and Kondner & Vendrell (1963) is that certain minerals exert a greater influence on the behaviour of a soil than is indicated by the proportion of that mineral present in the soil mass. This is particularly applicable to notably reactive minerals such as members of the smectite family.

The effect of ion composition and concentration on the behaviour of clay minerals has been studied extensively. One of the earliest studies on the effect of cation composition on soils was by Winterkorn & Moorman (1941) who discovered that the shear strength of a natural soil is higher in the presence of K ions than with Na ions. This is supported by Moom & Rosenqvist (1961) who measured the shear strength of K-montmorillonite

while Mesri & Olson (1971) found that the shear strength of Ca-montmorillonite is higher than that of Na-montmorillonite. Different cations were observed by Matsuo (1957) to reduce the strength of natural soils in the following order:

NH_4 , H, K, Fe, Al, Mg, Ba, Ca, Na, Li

while Kenney (1967) considered that the ϕ_r' value of illite and montmorillonite was increased by cations of higher valency and greater polarisability in the order:

$\text{Ca}^{++} > \text{K}^+ = \text{Na}^+$

He also concluded that ϕ_r' for illite and montmorillonite increases with the ion concentration. For kaolinite, Li (1978) recorded reductions in shear strength with increasing concentrations of NaCl although in bentonite, shear strength apparently increased with concentration of NaCl. In tests on saturated, remoulded montmorillonite and kaolinite, Warkentin & Yong (1962) measured reduced shear strengths with increasing concentration of NaCl but in the presence of varying concentrations of Ca and Na solutions, the residual shear strengths of silty clays were found to remain unchanged by Ramiah et al. (1970). Chattopadhyay (1972) considered increased NaCl concentrations to have no effect on the ϕ_r' of kaolinite but to enhance markedly ϕ_r' for montmorillonite. Studies on the influence of salt concentration and cation composition on the shear strength of sensitive or 'quick' clays in Canada and Norway concur that increases in shear strength accompany both increased salt concentrations and replacement of monovalent with divalent cations in pore fluids (Kenney et al. 1967; Bjerrum 1954; Moum et al. 1971; Torrance 1974, 1979).

This resumé of previous studies has elucidated some factors which are considered to govern shear strength in clay minerals. Generally, it appears that:

(a) the residual shear strength of clay minerals is sensitive to changes in porewater composition and concentration;

(b) residual shear strength of clays depends on the type of clay mineral;

(c) in natural soils and clay mineral mixtures certain clay minerals have a profound influence on the shear strength of a sample. The magnitude of their effect is greater than indicated by their relative amounts present in the sample.

6.4 The importance of residual shear strength in slope stability

The relevance of residual shear strength in slope stability problems concerning clays and shales is evident from many case studies of failures. According to Skempton (1964), residual shear strength is invariably found to be mobilised along a slip surface after failure has occurred and all subsequent movements on an existing slip surface are thus controlled by the residual shear strength, irrespective of the type of material involved.

Skempton & Hutchinson (1969) reviewed a number of studies on slides on pre-existing slip surfaces. At Folkestone Warren on the south Kent coast, large landslides have occurred at regular time intervals in sea cliffs consisting of Cretaceous chalk overlying Gault clay and sandy Folkestone beds. Several massive slides as well as smaller, more frequent slides are thought to have been activated by marine erosion and continued post-failure displacements are governed by the residual strength along the slip surface. An account, attributed to Henkel & Yudhbir (1966), of a slide in the River Beas Valley in northern India showed that for failure of a block 92 m wide to have occurred during the monsoon period of 1964, the limiting strength must have been approaching residual, particularly along the many tectonic shear zones present in the strata.

In Early & Skempton's (1972) investigation of the landslip at Walton's Wood, Staffordshire, it was concluded that slope failure took place along the pre-existing slip planes of an old landslide which had formed during the last glaciation (Chapter 1). The equilibrium of the slope prior to the 1961 failure was thus controlled by residual shear strength. In London Clay, Skempton & Hutchinson (1969) noted that residual strength actually accounts for the maximum observed stable slope inclination of 10° .

Control of slope stability by residual shear strength is not restricted to slides on old shear surfaces. A gradual reduction of strength within a mass to residual value by the process of progressive failure may lead to the development of sliding planes. A major failure is likely to ensue if stresses are high and the strength is sufficiently reduced. Although Bjerrum (1967) stated that the ultimate stability is controlled by residual strength only, Skempton (1964) considered that a slip will occur before residual strength is reached everywhere within the whole mass. The plastic strains which occur during creep failure (see section 2.8) also reduce soil strength to residual value, according to Nelson & Thompson (1974), and creep rates are then governed by residual shear strength.

Residual shear strength may be developed along discontinuity surfaces. Skempton & Petley (1967) found that in fissured, over-consolidated clays, small shearing movements of only a few millimetres after joint formation are probably sufficient to reduce ϕ' to its residual value. This is important in the context of progressive failure; the role of joints and fissures in aiding progressive failure was discussed in section 2.8. If these structures present areas within a soil mass which have already attained residual strength then the onset of major failure is accelerated.

Residual shear strength is clearly of fundamental importance to slope stability. Short term changes in residual strength may, therefore, be considerably significant if they stimulate further phases of reduced slope stability or acceleration of a major failure event. In the following sections the magnitude of changes in the apparent residual shear strength of shale aggregates (ϕ_{ra}') which might be induced by alterations in porewater composition and concentration are investigated.

6.5 Measurement of residual shear strength by ring shear apparatus

There are three main laboratory methods available for the determination of the residual shear strength of a soil:

- (i) Ring shear apparatus
- (ii) Direct shear box
- (iii) Triaxial apparatus

The direct shear box method is described in detail by Terzaghi & Peck (1967) and the triaxial test by Bishop & Henkel (1978). The tests described in this section were carried out by the ring shear method.

6.5.1 Advantages and disadvantages of the ring shear test

Traditionally, the residual shear strength of a soil has been determined using the direct shear box. There are, however, significant inherent disadvantages with this method. As noted by Terzaghi & Peck (1967) the foremost shortcoming arises from the change in area of the sliding surface as the test proceeds which leads to an unequal distribution of shearing stresses. Changes in the area of contact between upper and lower halves of the split sample and the non-simultaneous development of shear failure at all points on the potential surface of sliding are also unsatisfactory. In addition, particles aligned along the shear surface are subject to reorientation with each reversal of the direction of shear.

These problems are eliminated in the ring shear apparatus in which residual shear strength is measured by continuous shear of an annular sample. Displacements of any magnitude are attainable, thus field conditions may be simulated more closely.

In terms of results, values of residual shear strength obtained by the ring shear method are generally lower than those from direct shear tests and the triaxial method. Bishop et al. (1971), for example, gave values of ϕ_r' for blue London Clay of 9.3° , 10.5° and 13.5° , respectively, obtained by the ring shear, triaxial and reversal shear box methods. These authors also observed that the shear surface produced in the ring shear apparatus is more highly polished and smoother.

The method does, however, possess significant sources of error. Soil extrusion is a particular problem giving rise to uncertain experimental conditions, including a redistribution of the normal and shear stresses during testing. The derivation of equation B.21 depends on the assumption of a uniform distribution of normal stresses, although Bishop et al. (1971) showed that for $\phi_r' < 20^\circ$ the error is likely to be about $\pm 2^\circ$, even for "the most extreme and unlikely non-uniform stress-distributions considered". Conversely, La Gatta (1970) found that measured shear strengths could be reduced by 15% when soil extrusion was permitted while Heley & MacIver (1971) reported high values for ϕ_r' due to preferential removal of disaggregated, well-oriented clay particles. Extrusion also produces irregularities on the shear surfaces and prevents accurate determination of volume change of a specimen. The problem cannot be eliminated but may be reduced by adding large loads in increments (Bromhead 1979) by adopting slow strain rates and by trimming specimens to 1 mm below the top of the sample recess.

Bromhead also pointed out that inaccuracies in load measurement on tangential load proving rings may arise from differences in the stiff-

ness of the rings which can throw an unbalanced load on to the centreing pin (Fig. 6.2) and cause friction. To reduce this effect, matched proving rings were used. A similar effect may result from uneven settling of the loading platen. Such friction, however, has two components which are largely self-compensating. The simplicity of design of modern ring shear apparatus make them a useful tool in soil strength measurement. There are few disadvantages inherent in their use provided that interpretation of results takes account of the potential sources of error.

6.5.2 Structure and operation

The model used in this work was a Bromhead Ring Shear apparatus produced by Wykeham Farrance Engineering Ltd., number WF 25850.

The structure of the apparatus is shown in Fig. 6.2. An annular soil sample 5 mm thick and with inner and outer diameters of 70 mm and 100 mm respectively, is confined radially between concentric rings and is compressed vertically between two porous sintered bronze friction discs. The top disc is attached to a loading platen (11) to which a normal force is applied by means of a counter-balanced 10:1 ratio lever loading system (12, 10, 13, 32). A rotation is imparted to the sample holder (23) by a variable speed motor and gearbox transmitting through a worm drive. That part of the sample in contact with the lower porous friction disc is forced to rotate with the sample holder while the soil in contact with the top stationary loading platen opposes any rotation until, eventually, the stresses within the soil mass result in failure. A shear surface forms close to the upper disc which is artificially roughened to prevent slip at the soil/disc interface. The torque transmitted through the sample is reacted by a pair of matched proving rings bearing on a cross arm attached to the loading platen and the resultant moment is monitored on dial gauges or transducers attached to a chart recorder.

KEY FOR FIG. 6.2

- 1 Consolidation dial gauge arm and datum post
- 2 Load hanger
- 3 Lever loading arm
- 6 Bearing adjustment rods
- 8 Proving ring bracket
- 10 Loading yoke
- 11 Sample turret assembly
- 12 Yoke screw adjustment
- 13 Counter balance weight
- 15 Oil filler plug
- 16 Oil level plug
- 17 Gear change lever
- 23 Adjustable degree scale
- 30 Beam jack

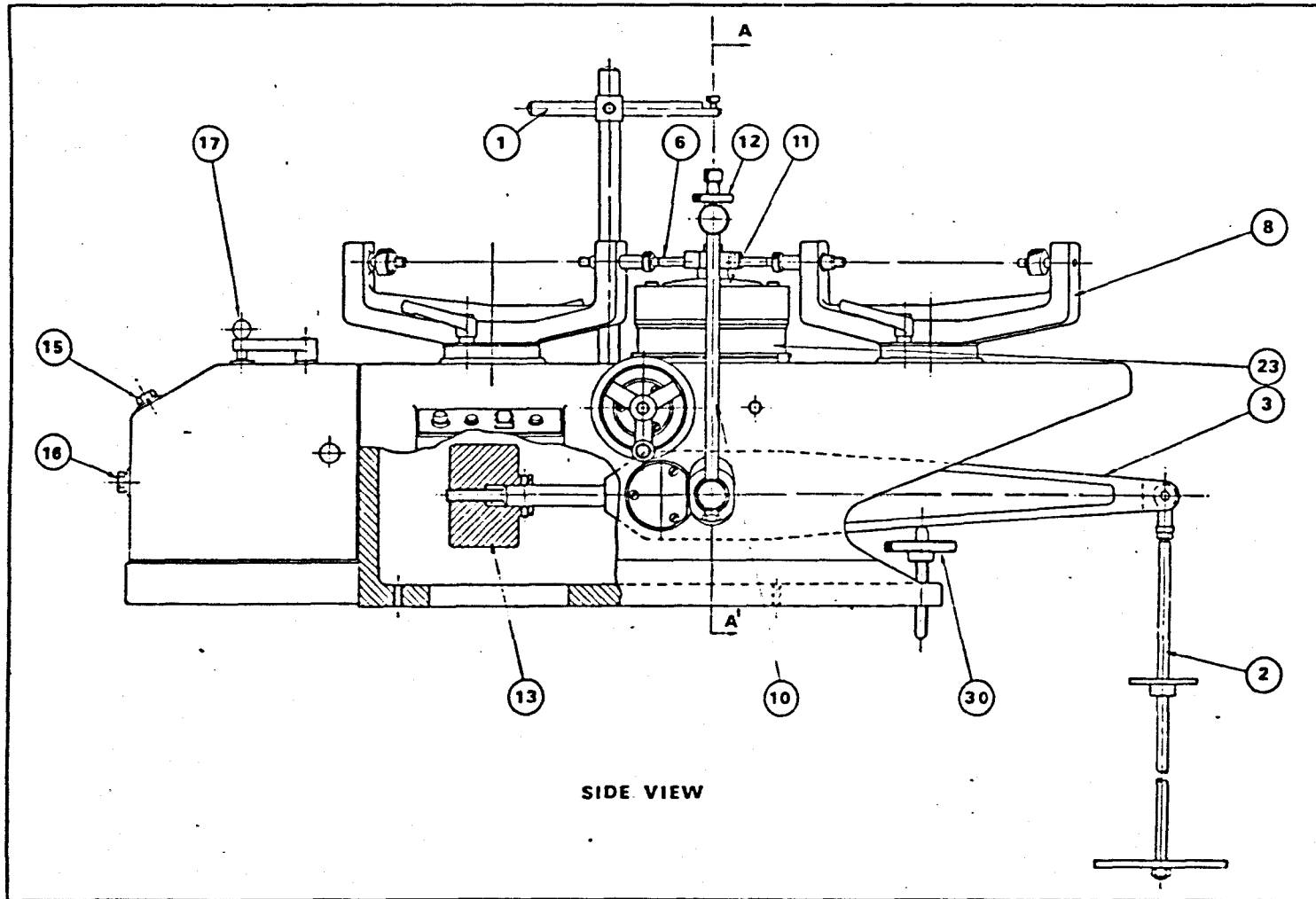


FIG. 6.2 Structure of the Bromhead Ring Shear Apparatus (from the Wykeham Farrance Technical Manual).

The apparatus is rate of displacement controlled since its purpose is to investigate the post-peak section of the stress-displacement curve (Bishop et al. 1971). In the Bromhead design, use of a double drained sample only 5 mm thick permits very rapid rates of shear while still maintaining fully drained conditions in the specimen. Although according to Skempton & Bishop (1950), Casagrande showed that the peak strength of clay depends to an appreciable extent on the rate at which it is sheared, La Gatta (1970) found that increasing the strain rate 100 times had no effect on the residual shear strength of undisturbed, remoulded and crushed shales provided fully drained conditions are maintained and rheological or viscous shear strength elements are not induced.

6.5.3 Sample preparation

In the tests described, material $< 425 \mu\text{m}$ was used for ease of remoulding and to reduce the time required for attainment of the residual condition. The latter is an important consideration when machine time is limited. The soil was prepared by crushing in a mortar and pestle and sieved to select material $< 425 \mu\text{m}$ in size. The coarser fraction was discarded.

Tests on Edale Shale prepared in this manner but of different size distributions showed residual shear strength to be independent of initial grain size. The results are as follows:

Size distribution	ϕ'_{ra}
$< 2 \text{ mm}$	21.5°
$850\text{-}500 \mu\text{m}$	22.5°
$< 425 \mu\text{m}$	22.0°
$< 425 \mu\text{m}$	21.7°

The normal stress was 294 kN m^{-2} and c'_r is assumed to be zero.

The sample was remoulded at a water content corresponding approximately with the liquid limit so that in comparative work, all samples would be in a similar state at the beginning of tests. Subsequent changes in moisture content could then be related to physical changes in the material. Also, Terzaghi & Peck (1967) noted that near to the liquid limit, the resistance of clay to both slow and quick consolidated shear increased linearly in proportion to pressure on the surface of sliding.

The sample was then packed into the sample holder, taking care not to trap air, and trimmed to 1 mm below the top of the recess. The sample holder was replaced into the apparatus. The loading platen with attached torque arm was placed over the sample. The water bath was filled with distilled water to at least the level of the top of the sample holder in order to keep the soil saturated.

6.5.4 Consolidation

The tests were performed on drained, consolidated samples. Before shearing commenced, the sample was subjected to 100% primary consolidation under the normal load to be applied throughout the test. The definition of consolidation is given in Appendix B2.

A normal stress of 294 kN m^{-2} was calculated to be the normal pressure experienced by Edale Shale at an approximate depth of 22 m within Mam Tor, assuming a water table of 15 m. A hanger weight of 12 kg was required to provide this normal stress.

After ensuring that the lever arm jack (30, Fig. 6.2) was in contact with the lever arm to prevent a normal load being transmitted to the sample, the loading yoke (10) was placed above the torque arm and brought into contact with the loading platen by adjustment of the knurled yoke screw (12). The vertical dial was brought to bear on top of the loading yoke. After placing the appropriate weights on top of the loading yoke,

the zero reading on the vertical dial was recorded and the lever arm jack unscrewed to apply the normal load to the sample. Vertical dial readings were taken at 10,50,30 seconds and at 1 minute, 2,4,15 and 30 minutes then at 1,2 and 4 hours. In addition, readings were taken at 20 to 24 hours by which time primary consolidation was generally completed. Vertical compression of the sample was plotted on a square-root time basis and the coefficient of consolidation determined by the method described in Appendix B3. The water in the water bath was maintained level with the top of the sample holder to prevent the soil drying out.

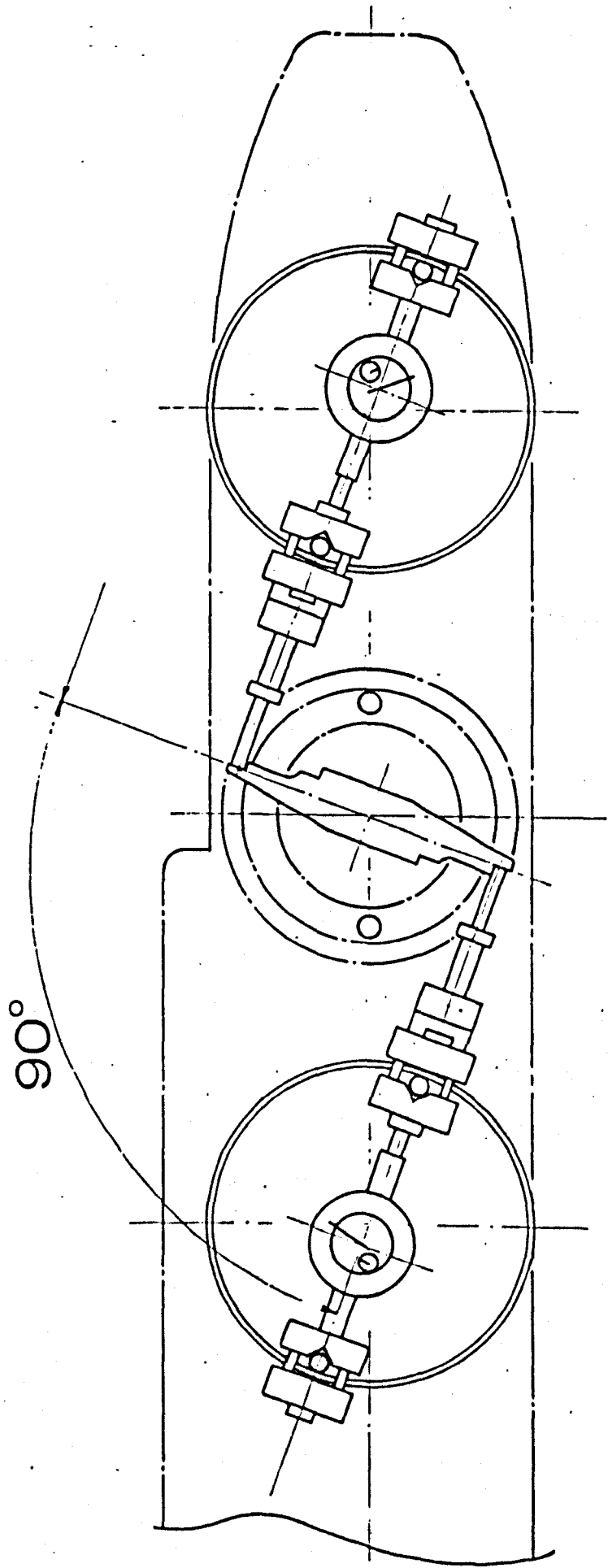
6.5.5 Residual shear strength measurement

The maximum strain rate permissible to maintain fully drained conditions during shearing was calculated using the coefficient of consolidation (section 6.5.4 and Appendix B4).

The proving rings were brought to bear on the torque arm, ensuring that the angle of contact with each plunger was 90° at a separation of 150mm (Fig. 6.3). The stress dial readings for the proving rings were zeroed and the vertical displacement and sample holder positions checked. Shearing was initiated after selection of the appropriate motor speed to give the required strain rate. Dial deflections (stress and vertical dials) and sample holder rotation were monitored every minute until a 'peak' stress was recorded. Overnight, stress transducers on the proving rings provided continuous records on a chart recorder which was calibrated from daytime readings.

Shear stress dial readings were converted to shear stress values using the working expression given by Equation B.20 in Appendix B.6. c_r' was assumed to be zero since weathering normally reduced effective cohesion to very low values. Work by Buist *et al.* (1979) for example, on Lower Coal Measure mudstones measured c_r' to be zero. The assumption was confirmed to be valid for weathered Edale Shale by T.H. Al-Dabbagh (pers.comm.). In any case the value of c_r' is not critical in comparative

FIG. 6.3 DIAGRAMMATIC VIEW OF TORQUE ARM POSITIONING



work where the normal stress is not changed.

Clay reorientation is probably the most significant factor in the post-failure evolution of a shear surface. Large displacements are thus required for full development of the residual condition and to achieve this, Bishop et al. (1971) devised a speed up-slow down routine in order to accumulate shear strain. This procedure was adopted for some tests but for certain cases (see section 6.6.3) slow strain rates had to be maintained. Cumulative angular rotation of the sample holder was converted to an equivalent displacement in millimetres by multiplying the number of degrees rotated by a conversion factor which is derived in Appendix B8.

A graph of shear stress versus displacement was plotted following the recommendation of La Gatta (1970) that displacement is plotted on a logarithmic scale to accentuate the shape of the curve. In this way, residual shear strength is defined with least ambiguity.

From the stress-displacement curve, the value of residual shear stress was recorded and used to derive residual shear strength in terms of ϕ_{ra}' .

6.5.6 Sample analysis and maintenance of apparatus

After shearing, the water bath was drained and the apparatus dismantled. Removal of the loading platen permitted observation of the sample. Obvious colour changes, consistency changes and the presence of polishing and slickensides were noted in particular.

The sample holder was cleaned thoroughly after each test using a wire brush. The porous discs were also declogged by immersion in detergent in an ultrasonic bath. This was particularly important after test-

ing fine-grained material because the pores block easily and cease to drain efficiently. Stubborn clay particles were more effectively removed by immersion and ultrasonic treatment in paraffin followed by detergent and rinsing in water.

6.6 Effect of porewater composition on the residual shear strength of Edale Shale

6.6.1 Experimental requirements

Previous measurements to determine the response of residual shear strength to porewater composition have been achieved by remoulding portions of a sample in various solutions or by leaching a specimen with different solutions outside the testing apparatus. The experiments of Olson & Mitronovas (1962), Nagaraj & Rao (1973) and Chattopadhyay (1972) provide examples of these practices. However, changes in the physical properties of materials tested using these techniques have to account for the possible consequences of sample variation and disturbance. A more appropriate experimental design allows solutions to be introduced to a sample during shearing. In this way there is no need to remove or change a specimen in mid-experiment and the effects of sample variation and disturbance are eliminated.

6.6.2 Modifications to the ring shear apparatus

Direct measurements of residual shear strength in the presence of different solutions were facilitated by modifying the drainage system of the Bromhead ring shear apparatus. Figure 6.4 shows the alterations that were made.

Four new vertical channels were drilled to connect with the existing horizontal drainage channels. Brass nipples were tapped into the tops of the new channels as inlets for solutions. The four circumferen-

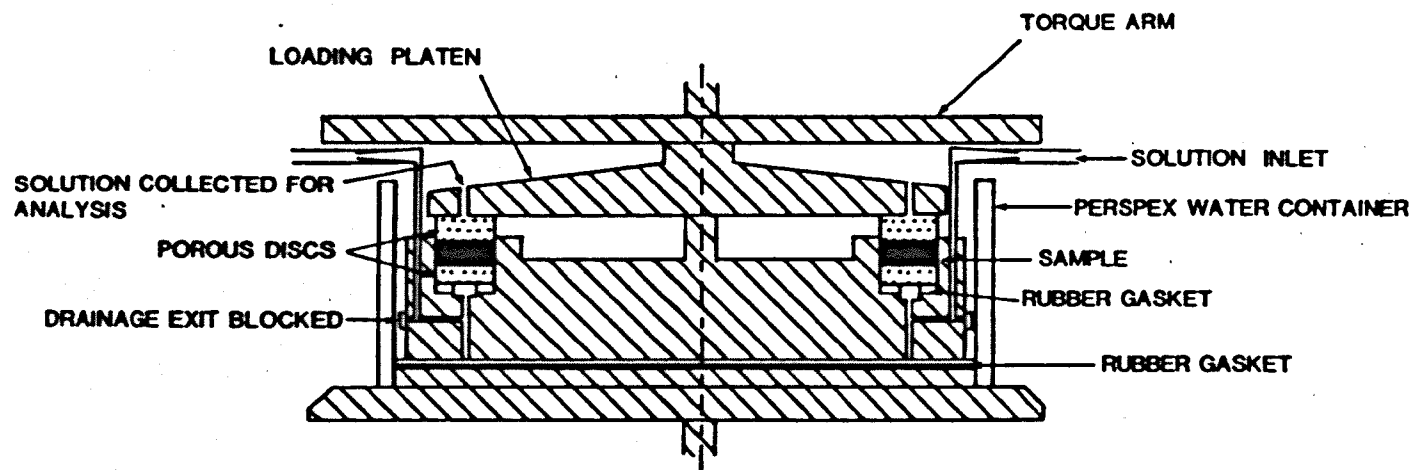


FIG. 6.4

Cross-section through the sample holder showing alterations to the drainage system.

tial drainage exists were then blocked with cap screws and PTFE tape and a double thickness rubber gasket was placed underneath the sample holder to prevent leakage from the lower vertical drainage channels.

Solutions were stored in a reservoir at a constant head of 1 m. Two flow systems were designed for introducing solutions to the samples. In the initial system solution passed down a length of stiff nylon tubing of 4 mm inner diameter and into a four-way manifold from which the flow was directed to each of the four brass nipples (Plate 6.1). Since drainage into the water bath from the lower drainage channels was prevented, solution was forced to flow upwards through the lower porous disc, the sample and the upper porous disc to reappear from drainage outlets in the loading platen. Here, it was collected by suction into a test tube for subsequent analysis. Before operation, the flow system was de-aired by disconnecting each tube from its inlet and allowing solution to flow out into a waste receptacle.

Once solution emerged from the loading platen the flow was established and shearing could then commence.

Since the four tubes were connected to the rotating sample holder, twisting was a problem and every 90° of rotation it was necessary to disentangle the tubes to prevent them wrenching off the nipples. To relieve this problem, a more compact flow system was designed using flexible perspex tubing and small plastic T-pieces (Plate 6.2). The new arrangement was sufficiently small to fit on top of the loading platen beneath the torque arm. Only one feeder tube was used and by pre-wrapping this round the centre pin, the apparatus could be left unattended for periods up to 60 hours with no risk of twisting.

Sample erosion or even liquefaction were potential problems due to the application of a 1 m head of water at the base of the sample (Fig. 6.4a). However, Fig. 6.4b shows that under a normal stress of 294 kN m^{-2}

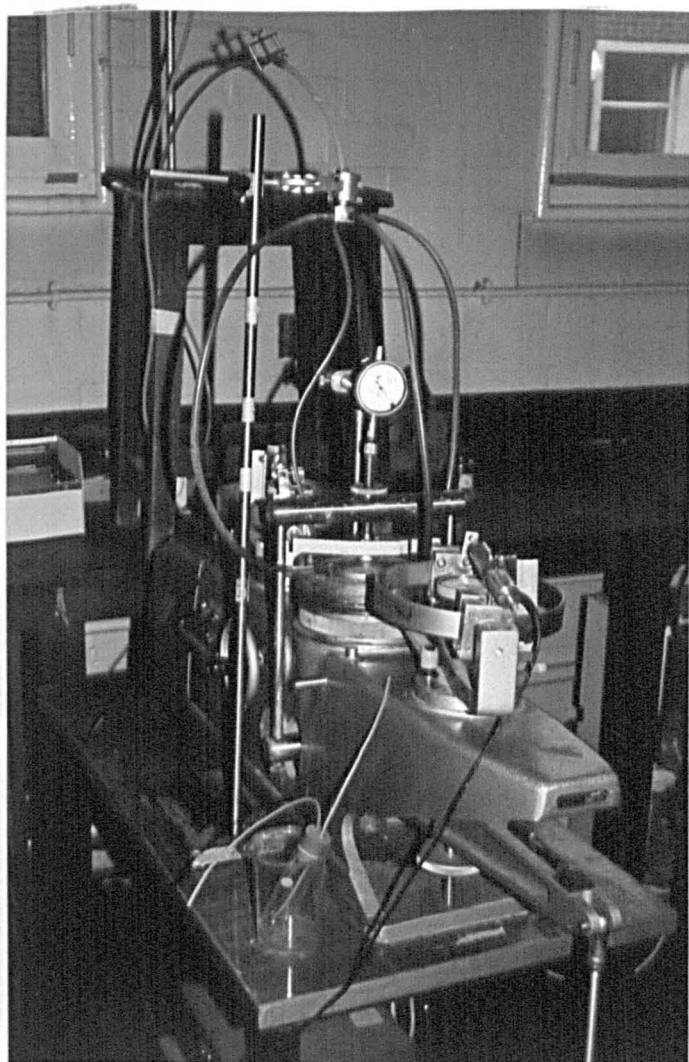


PLATE 6.1 Flow system with four-way manifold

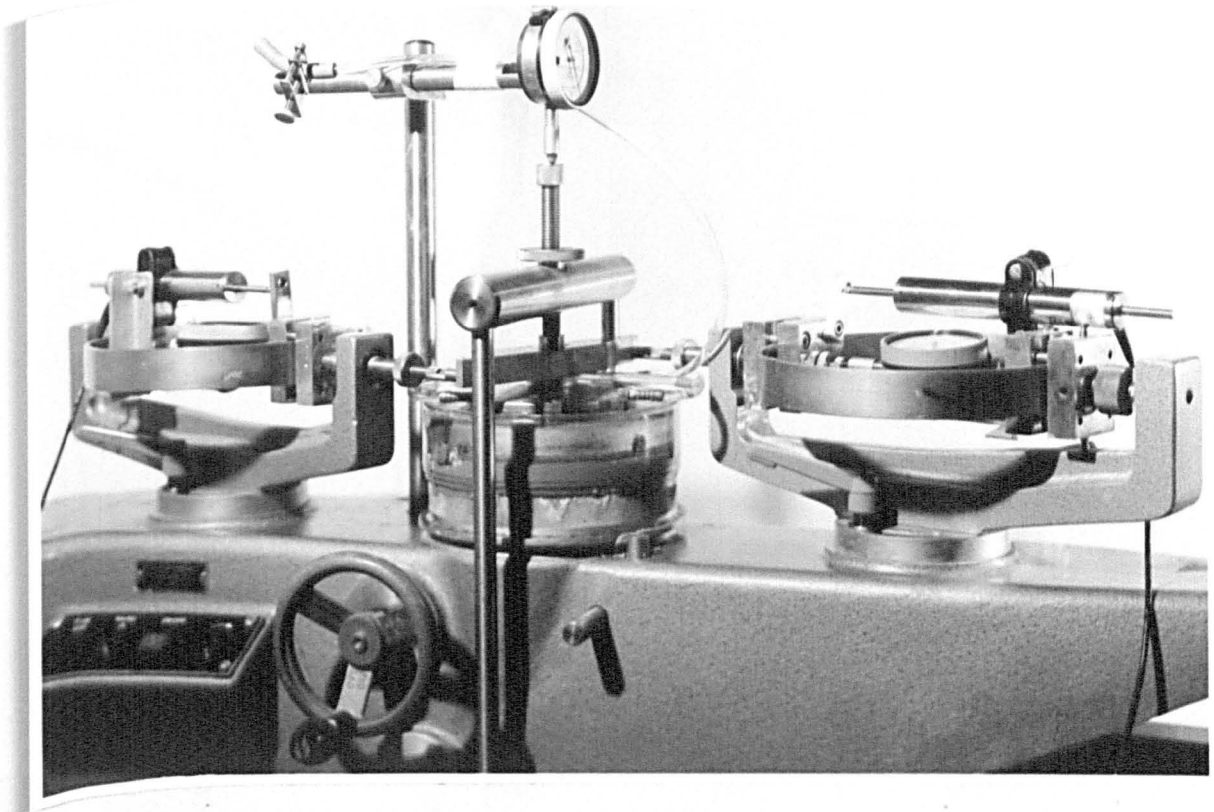
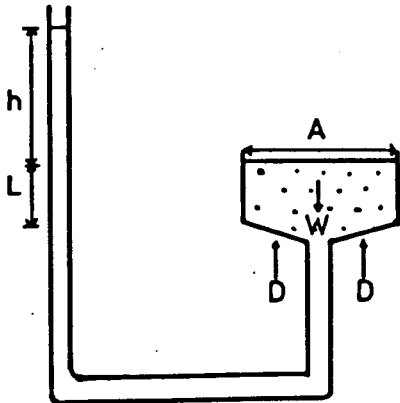


PLATE 6.2 Compact flow system and sample holder.

Fig. 6.4a Liquefaction of a soil sample due to the pressure of 1 m head of water applied at the sample base.



- h - head of water of unit weight
- L - height of sample through which head is dissipated
- D - hydrodynamic pressure
- W - weight of one unit of volume of saturated soil
- A - cross sectional area of soil sample

At equilibrium: $D \uparrow - W \downarrow = 0,$

since $D = (h + L) \gamma_w$

and $W = \frac{G + e}{1 + e} \gamma_w LA$ Where G is the specific gravity of the soil particles

at the base of the sample:

$$(h + L) \gamma_w A = \left(\frac{G + e}{1 + e} \right) \gamma_w L.A.$$

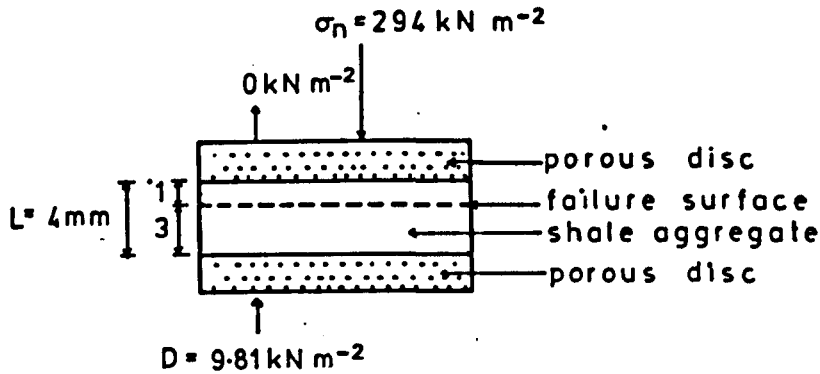
thus $\frac{(h + L)}{L} = \frac{G + e}{1 + e}$

and $\frac{h}{L} = \frac{G - 1}{1 + e}$

Assume $G = 2.67^1$ for shale aggregate and an average void ratio of $e = 0.67$, $\frac{h}{L}$ is equal to 1.00. Hence, when the hydraulic gradient approaches unity, a 'quick' condition occurs.

¹This value was calculated for Edale Shale

Fig. 6.4b Effect of upward seepage on the effective normal stress on a sample 4 mm high



$D = \text{pressure due to 1 m head of water} = \rho_w g h$

where ρ_w is the density of water = 1 Mg m^{-3}

g is 9.81 kN m^{-2}

h is 1 m

L is approximate length of flow path through the sample = 4 mm

Thus $D = 9.81 \text{ kN m}^{-2}$ and $\frac{h}{L}$ is 250.

Assume the failure surface to be 1 mm below the top of the sample. On the failure surface, the maximum pressure (if head is dissipated through the sample and not in the porous disc) is:

$$\frac{1}{4} \times 9.81 = 2.90 \text{ kN m}^{-2}$$

If the effective normal stress on the failure surface is 294 kN m^{-2} , an upward pressure of 2.90 kN m^{-2} incurs a change in the effective normal stress of 0.99%. This is considered to be negligible.

a hydraulic gradient of 250 was unlikely to erode the sample. In addition the effect of an upward pressure of water was calculated to have a negligible effect on the normal effective stress on the shear plane, assuming that most of the head of water was dissipated in the porous disc below the sample. Observations that suggest this assumption was viable include the slow rate of outflow of solution from the upper drainage holes such that solution had to be sucked out for subsequent analysis. The rate of change of ϕ_{ra} on introduction of a new solution was also slow (p.111). When the flow system operated with no sample in place the solution 'welled-up' through the lower porous disc. It did not flow sufficiently rapidly to cause a 'fountain' effect. Furthermore, the shear strengths obtained in tests performed with distilled water in the unmodified apparatus (Table 3.2) are comparable with initial shear strength values for distilled water under a flow regime (Table 6.1).

Strain rates for the tests in the modified apparatus were calculated using equation B16 (Appendix B5) for single drainage conditions.

For initial tests, a slow strain rate of $0.032 \text{ deg. min}^{-1}$ was selected. Faster rates up to $0.12 \text{ deg. min}^{-1}$ were attempted for subsequent tests in order to reduce test duration. However, solution tended to escape from the gap between the sample holder and loading platen instead of emerging from the upper drainage exits which suggested that the flow was avoiding the sample and taking a path around the sides instead. A small rubber gasket was inserted below the lower porous disc to guide the solution to the centre of the sample but continued escape of solution at a fast rate rendered the experiment impractical. Slower strain rates of $0.032 \text{ deg. min}^{-1}$ were thus selected again for further tests.

6.6.3 Experimental procedure

The same method of sample preparation and experimental procedure were followed for tests using the modified apparatus as for the normal tests described in sections 6.5.3 and 6.5.5.

For each sample, the residual condition was initially established with distilled water. A new solution was then placed in the reservoir and changes

in the shear stress were monitored until a new residual shear strength was attained. The sample was then flushed with distilled water and a different solution introduced to the sample.

6.4.4 Results of ring shear tests using different solutions

Three sets of experiments were carried out using Edale Shale from the Hope Valley Cement Works Quarry. The solutions used included Na and K nitrates,¹ sulphuric acid at a concentration of 0.14% commensurate with that used in the weathering experiments (section 5.2) and groundwater from the fault crush seepage at Mam Tor (section 3.5.3).

In the first set of experiments, NaNO_3 and KNO_3 were chosen because Na^+ and K^+ cations are known to exert different influences on clay mineral properties such as expandibility, plasticity and shear strength. Rosenqvist (1955, 1962) Kenney et al. (1967) and Talme (1968), for example, found that in materials with large quantities of illite, plasticity and shear strength are lower in the presence of Na^+ ions than K^+ ions.

NaNO_3 at a concentration of 0.1 molar was flowed through the sample and after recording a new residual value the sample was flushed with distilled water followed by 0.1 molar KNO_3 . In the second run of this test the solutions were introduced in the reverse order to check the results obtained in the first run. At the end of this test, NaNO_3 at a higher concentration of 1.0 molar was used to determine whether residual shear strength is sensitive to solution concentration. The results for these experiments are given in Table 6.1 and plotted in Fig. 6.5.²

The results show that ϕ_{ra} of Edale Shale appears to be sensitive to the cation composition of the porewaters and to the concentration of the ions present, at least in the case of NaNO_3 . KNO_3 apparently increases and NaNO_3

1. Nitrates were used as the least complexing anion in order to reduce anion effects during cation exchange reactions.

2. A linear displacement scale is used in figs. 6.5, 6.6a & b, 6.8 to emphasise changes in apparent residual shear strength with different solutions.

Solution	Concentration	ϕ_{ra}' (degrees)
Distilled water	-	22°
NaNO ₃	0.1 molar	20°
NaNO ₃	1.0 molar	19°
KNO ₃	0.1 molar	23°
H ₂ SO ₄ (approximate values for two runs)	0.14 %	25-27°
*Groundwater	-	18-19°

ϕ_{ra}' values are average of two runs where $c_r' = 0$

*Only one run carried out. Value of ϕ_{ra}' with distilled water 19° in this test.

Material Properties:

Initial bulk density of shale aggregate = 1.94 g cm⁻³
 Initial dry density of shale aggregate = 1.43 g cm⁻³
 Initial void ratio = 0.87
 Initial porosity = 0.46

Final bulk density (after consolidation in the
 ring shear apparatus) = 2.75 g cm⁻³
 Final dry density = 1.87 g cm⁻³
 Final void ratio = 0.43
 Final porosity = 0.30

Table 6.1 Response of residual shear strength of Edale Shale to different solutions.

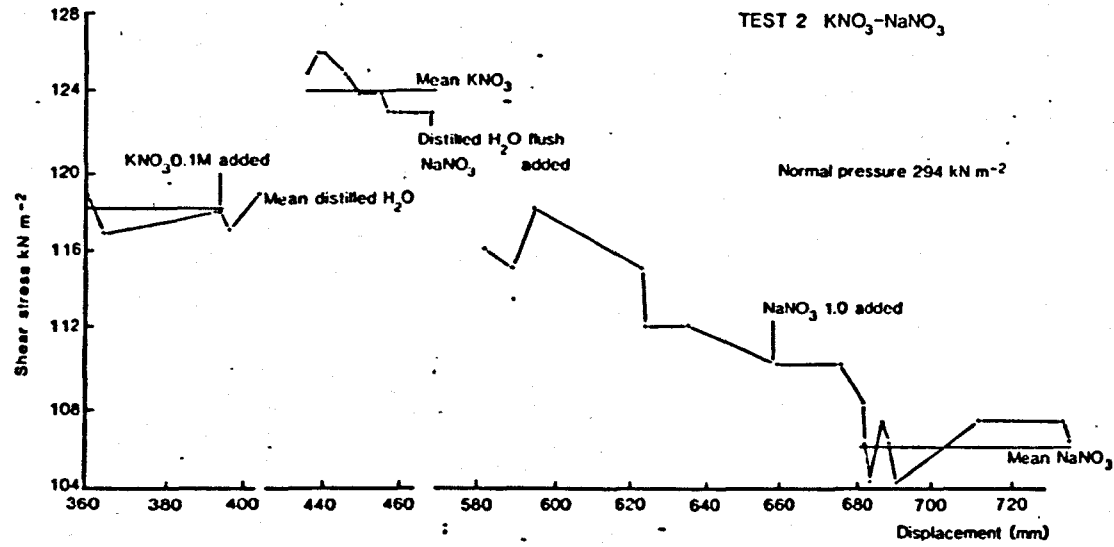
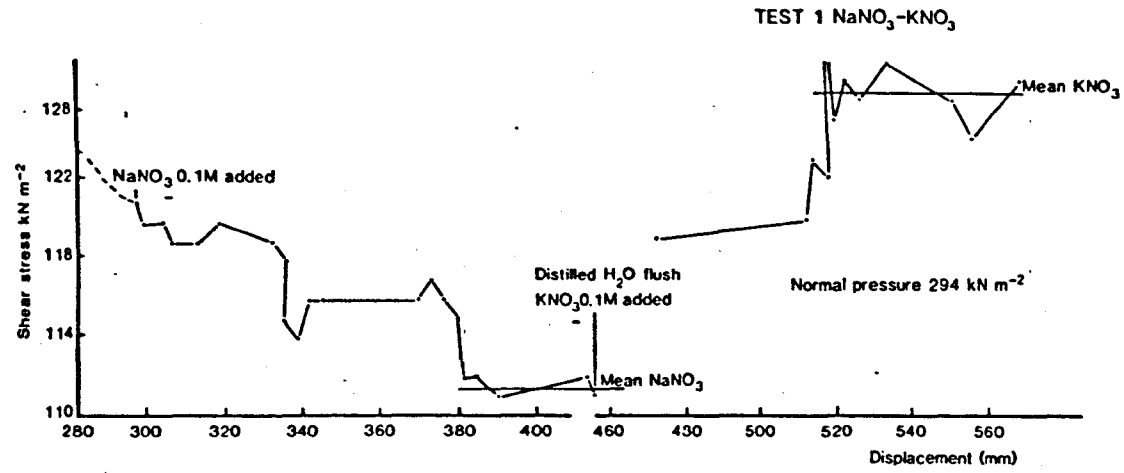


FIG. 6.5

The influence of NaNO_3 and KNO_3 on the residual shear strength of Edale Shale.

reduces ϕ_{ra} ' with respect to the values obtained with distilled water. An increase in the concentration of NaNO_3 produced a further reduction in ϕ_{ra} '. The response time of changes is not known precisely, but is certainly less than 15 hours and is, therefore, regarded as rapid. The changes in ϕ_{ra} ' appear to be reproducible and independent of the order in which solutions are introduced.

For the second set of experiments in which sulphuric acid was passed through the sample ϕ_{ra} ' began to increase after about 20 hours. The results are included in Table 6.1. Distilled water was flushed through the sample after about 72 hours and a return to the original ϕ_{ra} ' was observed after 1 hour. A second run was carried out with acid of the same concentration and a new ϕ_{ra} ' obtained after 69 hours (Figs. 6.6a & b).

Solutions collected from the loading platen outlets were analysed by atomic absorption spectrophotometry and the solution composition for the first acid test is shown in Table 6.2a. The same pattern of cation release occurred as observed for the weathering experiments discussed in section 5.2. However, the actual quantities present are different¹ and this is interpreted to reflect differences in the contact times and solid-solution ratios of the two experiments.

The sheared sample was allowed to dry after the experiment and was then prepared for XRD analysis (Appendix A.4) to investigate changes in shale mineralogy resulting from exposure to acid solutions. As seen from Fig. 6.7, no obvious differences between pre- and post-sheared shale are apparent. Again this concurs with the findings of the experiments in section 5.2.

Eight further runs involving acid were attempted but each one was abandoned for a variety of reasons as indicated in Table 6.2b.

The third experiment investigated the effect of a natural acidic solution from Mam Tor on residual shear strength. The results are given in Table 6.1 and Fig. 6.8. Table 6.3 presents the compositions of the pre- and post-flow solution compositions. As expected, the initial concentrations of cations in the groundwater are much higher than for the acid. It is interesting to compare the compositions of the acid and groundwater after flow through the sample.

1. The excessively high iron content is probably due to acid contact with the bronze porous discs.

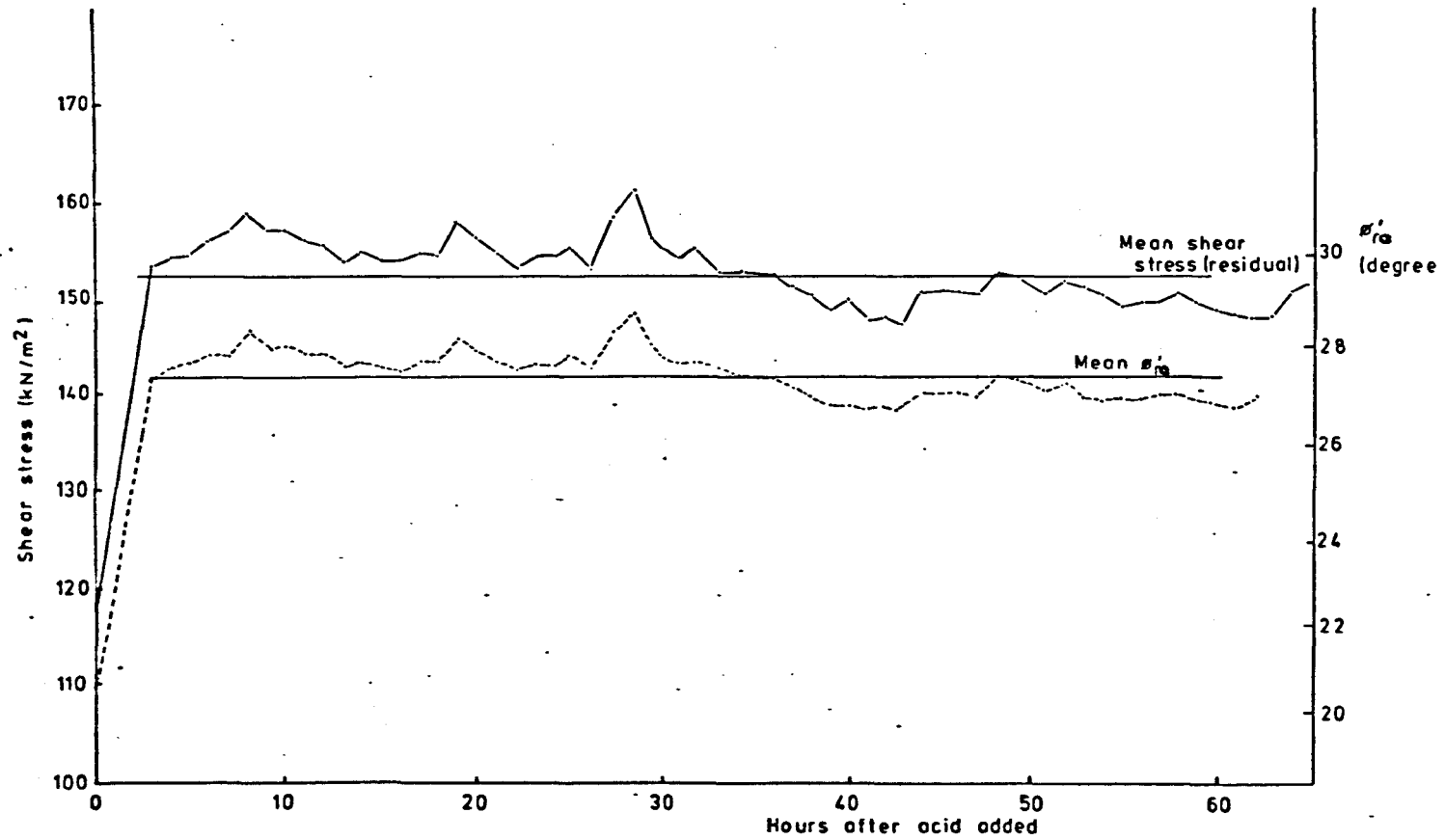


FIG. 6.6a The effect of sulphuric acid on the residual shear strength of Edale Shale

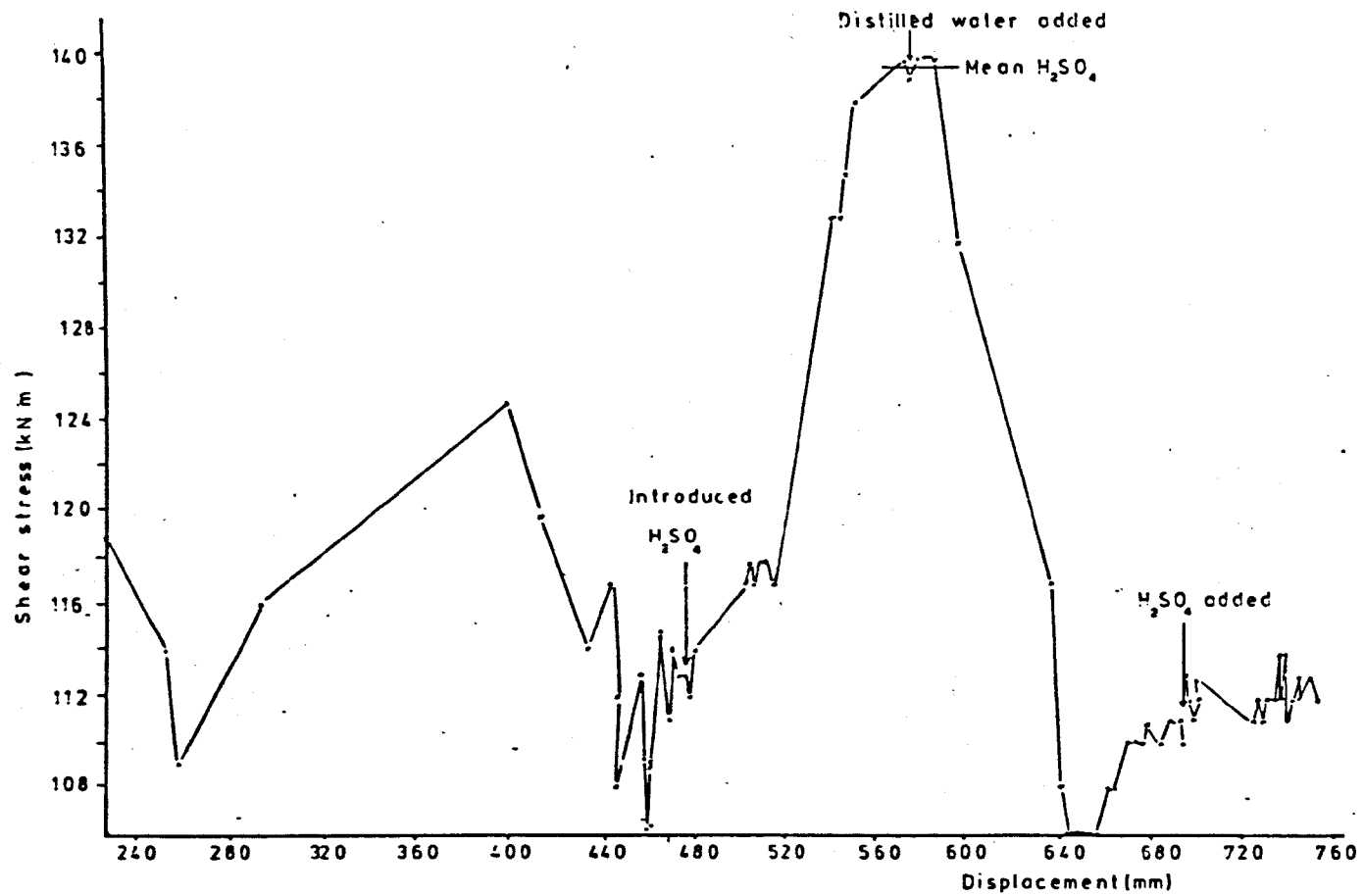


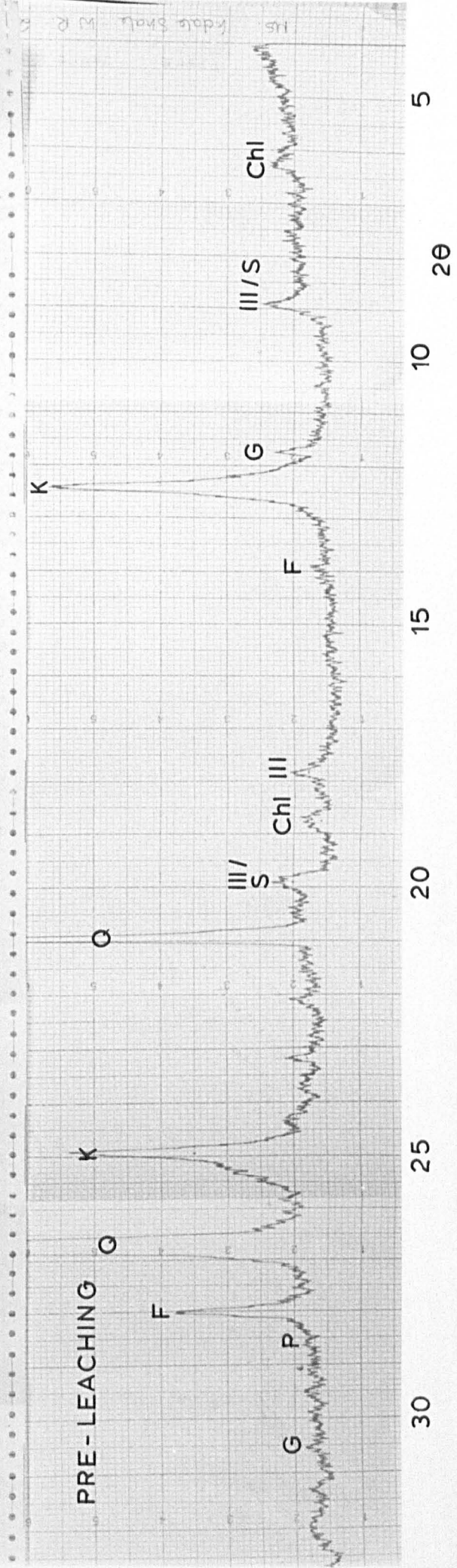
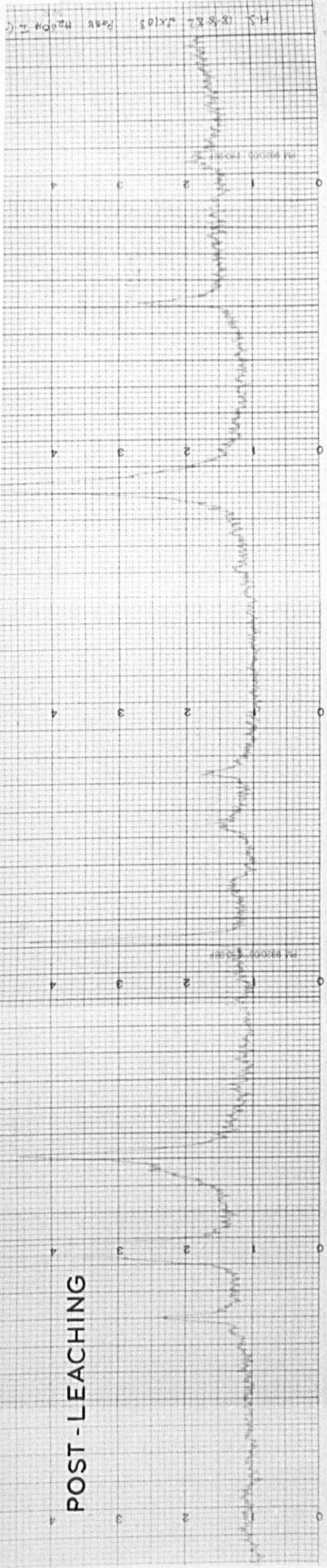
FIG. 6.6b The effect of sulphuric acid on the residual shear strength of Edale Shale

Cation	Blank H ₂ SO ₄ 0.14% (µg/ml)	Post-flow H ₂ SO ₄ (µg/ml)	After 1 week in leaching experiment (section 5.2) (µg/ml)
Na	0.101	2.83	5.69
K	0.065	13.21	10.02
Ca	1.863	443.82	117.3
Mg	1.486	61.64	146.5
Fe	0.421	9.85	610.6
Si	-	-	19.6
Al	0.055	0.5	19.7
pH	1.5	-	1.7

TABLE 6.2a Compositions of acid solution before and after flow through the sample compared with composition of acid solution after leaching experiment.

FIG. 6.7 X-ray diffraction traces of Edale Shale before and after shear strength tests with acid.

Chl - chlorite; Ill/S - illite/smectite mixed layers;
G - gypsum; K - kaolinite; F - feldspar; Q - quartz;
P - pyrite



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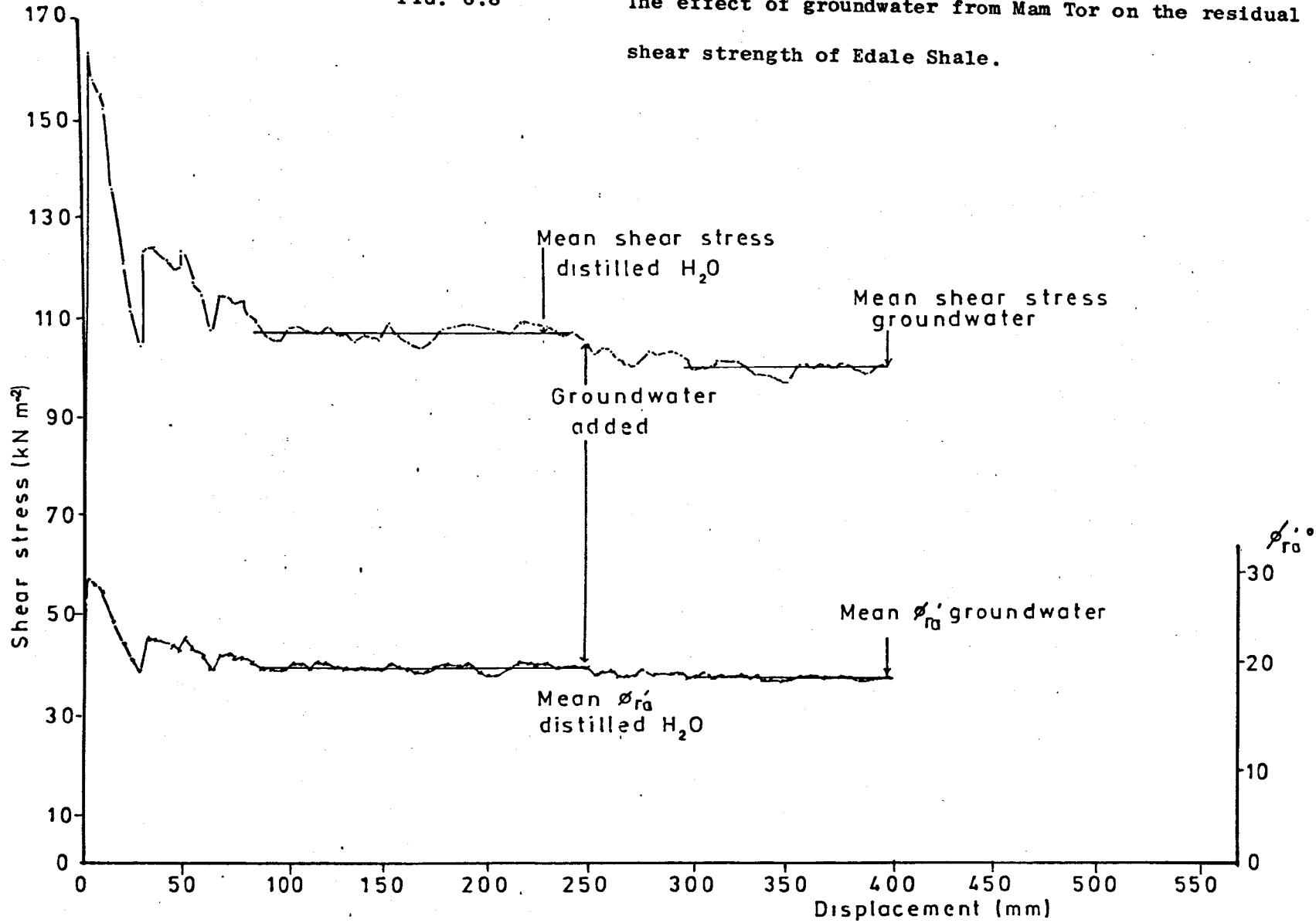
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Run no.	Reason for failure of experiment	Remedy
1	Successful	-
2	Successful	-
3	Acid leaking between loading platen and sample holder - no change in ϕ_r recorded.	Set up fresh experiment. More compact flow system installed.
4	As for run 3	Porous discs cleaned ultrasonically. Gasket placed below lower disc.
5	As for run 3	Increased reservoir height to give 1.3 m head of water. Flow pressure now greater.
6	As for run 3	Set up fresh experiment
7	Leakage from circumferential drainage outlets.	Inserted screws with larger caps and PTFE tape.
8	No change in ϕ_r	Set up fresh experiment
9	T-piece smashed	Renewed T-piece
10	Leakage from loading platen and sample holder.	Used slow strain rates (0.032 degrees/min)

TABLE 6.2b Experimental problems

FIG. 6.8

The effect of groundwater from Mam Tor on the residual shear strength of Edale Shale.



Cation	Pre-flow groundwater $\mu\text{g ml}^{-1}$	Post-flow groundwater $\mu\text{g ml}^{-1}$
Na	13.17	14.61
K	7.43	30.47
Ca	260.12	349.92
Mg	23.50	70.83
Fe	8.28	11.70
Si	-	-
Al	82.12	1.55
pH	3.4	-

TABLE 6.3 Compositions of groundwater before and after flow through the sample.

With the exception of Al, the same order of cation concentrations are observed in both solutions suggesting that the potential for reaction between sheared sample and groundwater is not very great, probably because the groundwater has been previously neutralised by rock reaction at depth within Mam Tor.

Unfortunately, limited machine time precluded arrangement of an extensive testing programme. In view of the problems encountered during the experiments the results obtained are regarded as preliminary in nature. However, they imply that changes in residual shear strength can be induced by short-term modifications in porewater composition and concentration.

6.7 Post-shearing sample analysis

After removing the loading platen, bright orange deposits, probably iron oxide, that had been extruded from the sheared sample were observed on the inner and outer edges of the sample holder. Well-developed shear surfaces with a slickensided and polished appearance were only occasionally observed near the top of the sample.

Sheared samples appeared to have a more clayey, 'soapy' feel than presheared material indicating that clay mineral aggregates had been broken down during the shearing process. To determine the relative particle size distributions in terms of aggregate dimensions in sheared and unsheared shale, samples of material from a polished zone and from an adjacent, non-sheared area were each prepared for Coulter counter analysis. The principles of this system are discussed by Kubitschek (1960).

The sample holder containing a post-test specimen was observed under a binocular microscope. Polished areas were easily identified. Material from the shear surfaces was lifted away with a scalpel blade and immediately placed in a solution of calgon (1.5 g L^{-1}) to prevent clay flocculation. Sufficient material was collected to make a 'cloudy' suspension in the calgon. The same procedure was followed for obtaining unsheared samples.

A small amount of suspension was placed in a phial of 10% NaCl, disaggregated sonically and analysed on a Coulter counter, of Coulter Electronics Ltd., model number ZBI, in the Department of Genetics, Sheffield University. A $50 \mu\text{m}$

aperture probe was used in the analysis. The results are shown in Fig. 6.9.

The machine was calibrated with beads measuring $1.15 \mu\text{m}$ in diameter. This was the smallest calibration available for the apparatus used. For the shale, particle diameters of $0.45 \mu\text{m}$ and $0.52 \mu\text{m}$ were obtained for sheared and unsheared material respectively. Compared with a calibration of $1.15 \mu\text{m}$ these values are probably too low to be reliable. In addition, the lower limit of accuracy of the $50 \mu\text{m}$ probe is estimated to be 2% of the aperture diameter, or $1 \mu\text{m}$.

Similar specimens of sheared and unsheared material prepared in the manner described were sent to Coulter Electronics Ltd., for analysis using a $30 \mu\text{m}$ aperture probe. The lower limit of accuracy for this probe is $0.6 \mu\text{m}$. Figure 6.10 shows that, again, the particle sizes of sheared and unsheared material are too small for accurate determination using the equipment available.

Edale Shale thus appears to contain a large proportion of material less than $0.6 \mu\text{m}$ in size, but no distinction can be made between unsheared and sheared material within the accuracy limits of the experimental methods available.

6.8 Effect of porewater composition on the plasticity of Edale Shale

6.8.1 Plasticity and its importance as an engineering property

The consistency of a soil depends on its water content. There are four consistencies, solid, semi-solid, plastic and liquid, which are defined by the shrinkage, plastic and liquid limits. Figure 6.11 shows that at water contents below the shrinkage limits (SL), a soil is solid and semi-solid between the shrinkage limit and plastic limit (PL). At water contents above the plastic limit, a soil behaves plastically. The highest water content for plasticity occurs at the liquid limit (LL) when a soil will flow under its own weight if subjected to a small disturbing force. The differences between the water contents at the plastic and liquid limits is the plasticity index (PI).

FIG. 6.9

Measurement of particle size by Coulter counter analysis -

50 μm aperture probe

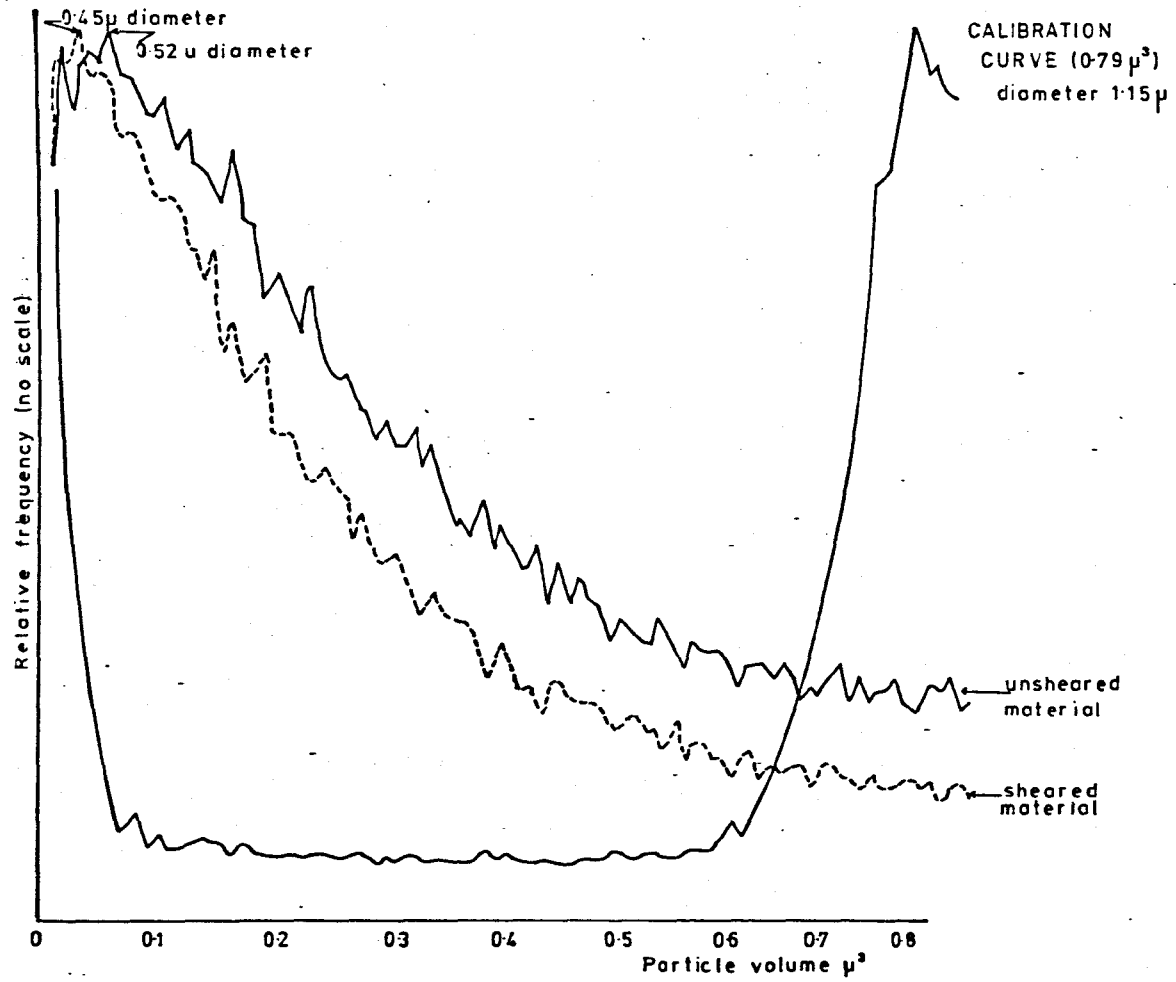


FIG. 6.10

Measurement of particle size by Coulter counter analysis -
30 μm aperture probe (Coulter Electronics Ltd.).

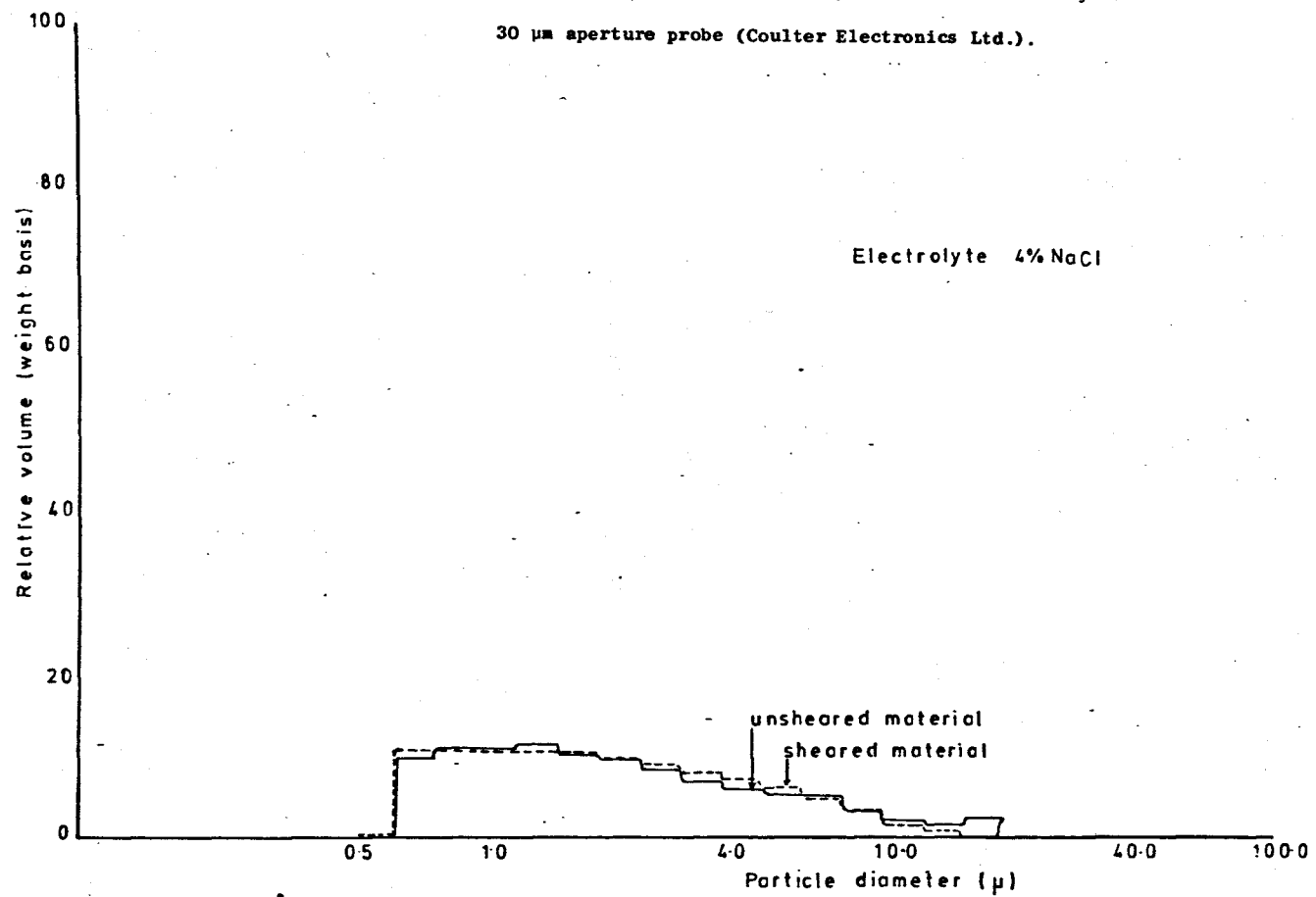
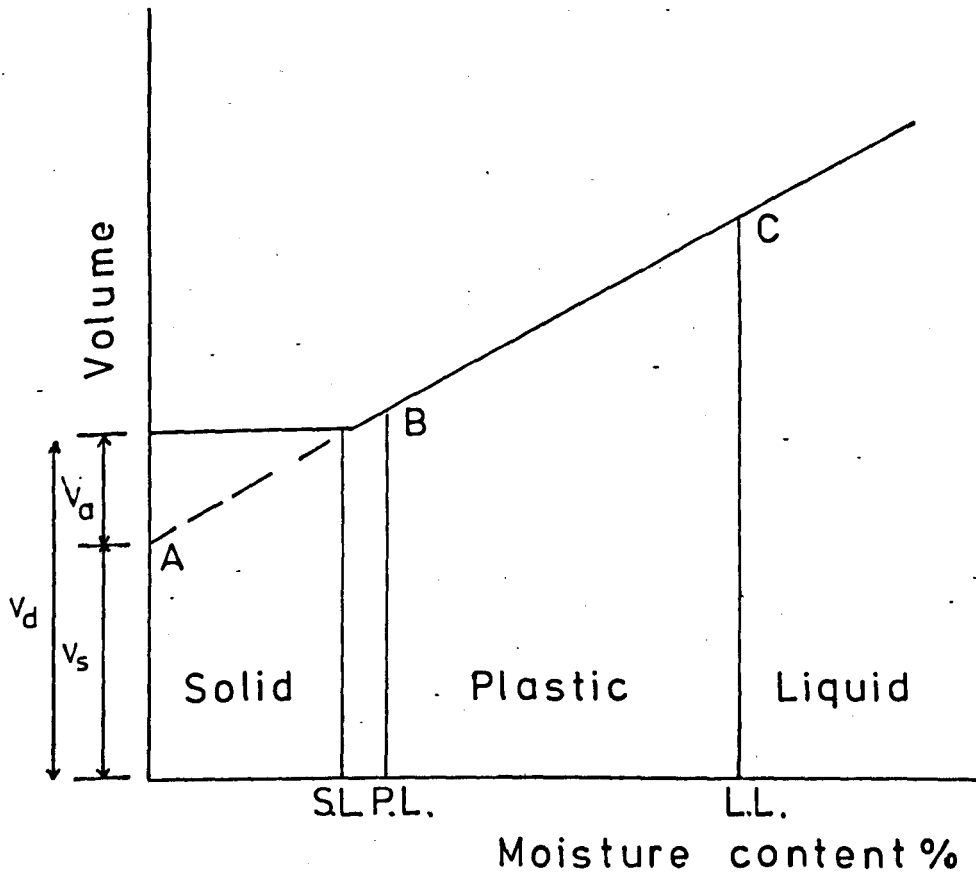


FIG. 6.11

Behaviour of a soil in relation to water content;
from Whalley (1976, p. 20).



V_a - volume of voids

V_s - volume of solid

V_d - total soil volume

SL - shrinkage limit

PL - plastic limit

LL - liquid limit

Plasticity Index = PL - LL.

In slope stability problems it is important to understand how a particular soil will respond at a certain water content. Each soil possesses characteristic plasticity limits because this property is influenced by factors which are different for every soil. Dumbleton & West (1966) considered that mineralogical composition, shape and size distribution of component particles, particle interaction with water and dissolved salts and the effect of cementing determine soil plasticity.

With respect to mineralogical composition, moisture contents at the plastic and liquid limits are generally higher with increasing clay contents, as shown in Fig. 4.16. Dumbleton & West (1966) stated that "plasticity is the most outstanding characteristic of clay soils".

Different clay minerals have different plasticity limits. Grim (1962) listed some mono-mineralic clay soils in decreasing order of plastic limit as attapulgite > montmorillonite > halloysite > illite > kaolinite and for liquid limits, Li and Na montmorillonite > attapulgite > Ca, Mg, K, NH_4 montmorillonite > illite > kaolinite > halloysite. These orders reflect the relative abilities of the clay minerals to adsorb water. As with residual shear strength, expandable clays such as montmorillonite tend to exert a greater influence on the plasticity of a soil than other clay minerals. Grim (1962) and Rosenqvist (1962) noted that changes in plasticity are mainly effected by changes in the liquid limit since this is more sensitive than the plastic limit.

Poorly crystalline or even amorphous minerals give enhanced limits, for example, amorphous material in the Champlain clays of Canada was found by Henderson & Carson (1978) to be responsible for the high plasticity of this clay. Organic matter has a similar effect.

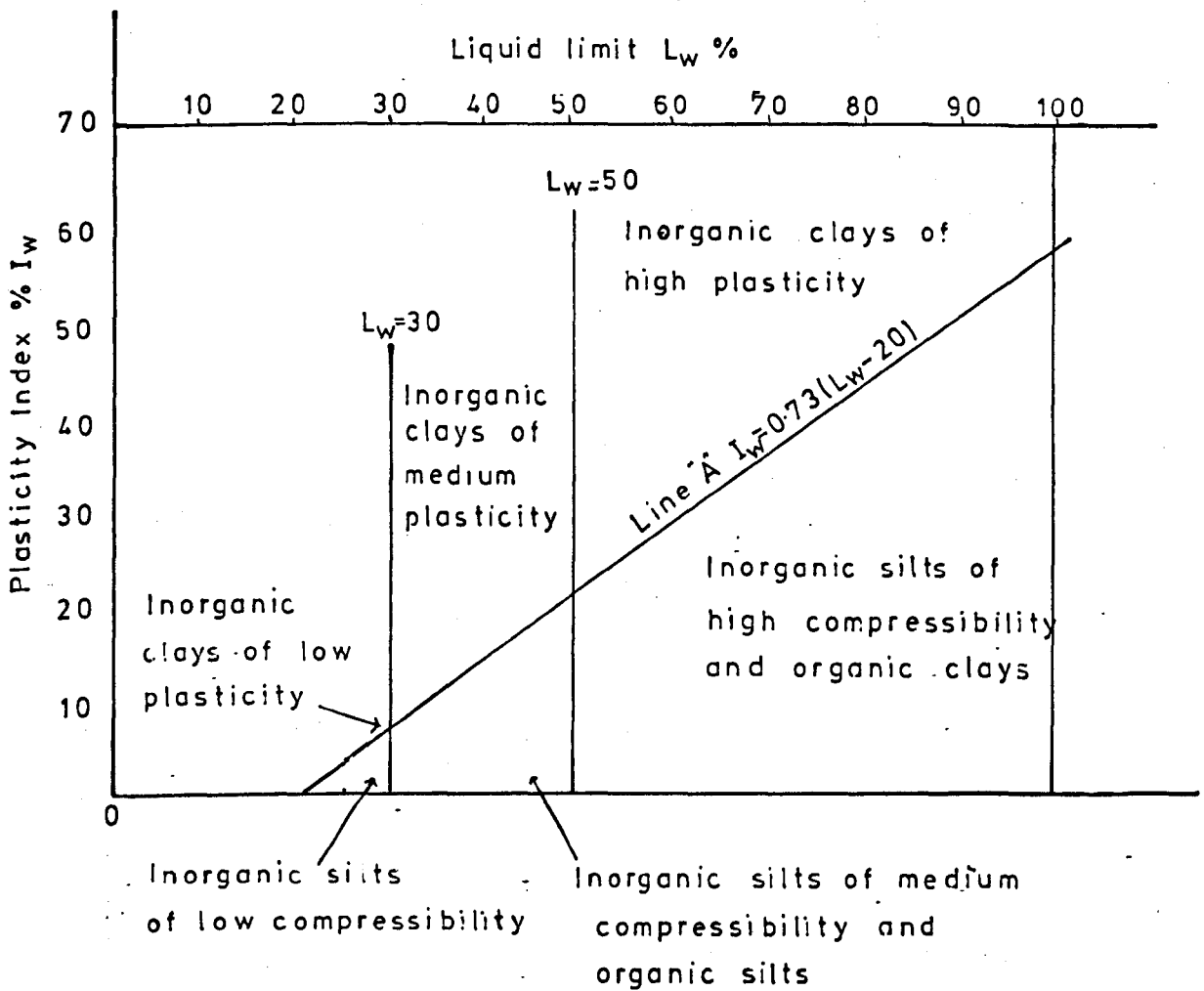
A convenient way of distinguishing between soils of different types is to use a Casagrande plasticity chart of plasticity index plotted

against liquid limit. A large number of soils plot on or near a line, called the A-line, which cuts the liquid limit axis at 20% and has a slope of 0.73 (Fig. 6.12). The position in which a soil plots gives a general idea of its engineering behaviour and certain types of soil plot in characteristic positions as shown in Fig. 6.12. Soils which fall below the A-line have a relatively high liquid limit in relation to their plasticity index (Dumbleton & West 1966).

Particle size influences plasticity. Smaller particles offer a larger surface area for water adsorption and also tend to have less well-ordered crystal lattices, particularly if their small size is produced by grinding. The effect of cementing and aggregation is also important; inadequate breakdown of aggregates may give values which are too low because of the increased effective particle size.

Porewater chemistry has been found to affect plasticity in clay minerals and in natural soils. The results of other studies are given in Table 6.4. As salt concentration in the porewaters increases, the liquid limit and plastic limit both decrease with the liquid limit showing the greater effects. Different salts appear to influence plasticity to different degrees, depending on the clay type. Li (1978) showed that the liquid limit of kaolin and bentonite were lower in the presence of NaCl than CaCl_2 . For hydrous mica, Kenney (1967) found that the liquid limit was lower with NaCl than with KCl while Winterkorn & Moorman (1941), in tests on Putnam clay, reported the highest liquid limit to occur with Na and the lower with K. Rosenqvist (1962) found that in illites the liquid limit increases with increasing size of the monovalent ion, thus $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$, but in montmorillonite the response changed to $\text{K} < \text{Rb} < \text{Cs} < \text{Na} < \text{Li}$. Matsuo (1957) produced a plasticity chart showing that cation exchange in soils changes their consistency in a certain order (Fig. 6.13).

FIG. 6.12 Casagrande Plasticity Chart.



Material	Salt solution	Concentration	PL %	LL %	References
Kaolinite	NaCl	0 g/l	31.4	46.5	Li (1978)
		10 g/l	31.3	43.5	
		50 g/l	31.0	40.8	
		100 g/l	31.0	39.8	
Kaolinite	CaCl ₂	0 g/l	31.4	46.5	Li (1978)
		10 g/l	31.2	44.8	
		50 g/l	31.0	42.7	
		100 g/l	31.0	41.4	
Bentonite	NaCl	0 g/l	62.4	540	Li (1978)
		10 g/l	62.8	280	
		50 g/l	62.0	125	
		100 g/l	62.2	88	
Bentonite	CaCl ₂	0 g/l	62.4	540	Li (1978)
		10 g/l	62.0	290	
		50 g/l	62.2	115	
		100 g/l	62.0	95	
Putnam clay	HCl	0.05 N	30	57	Winterkorn & Moorman (1941, Fig. 2)
	NaOH	-	31	89	
	KOH	-	28	53	
	Mg(OH) ₂	-	25	56	
	Ca(OH) ₂	-	27	62	
	Al(OH) ₃	-	27	60	
Na-Hydrous mica	NaCl	0 g/l	33	51	Kenney (1967)
K-Hydrous mica	KCl	30	39	99	
		0	39	72	
Na-Montmorillonite	NaCl	30	46	118	
		0	53	1325	
Na-Grundite	NaCl	30	45	620	
		0	46	164	
		30	43	130	

TABLE 6.4 Results of some investigations into the effect of system chemistry on plasticity

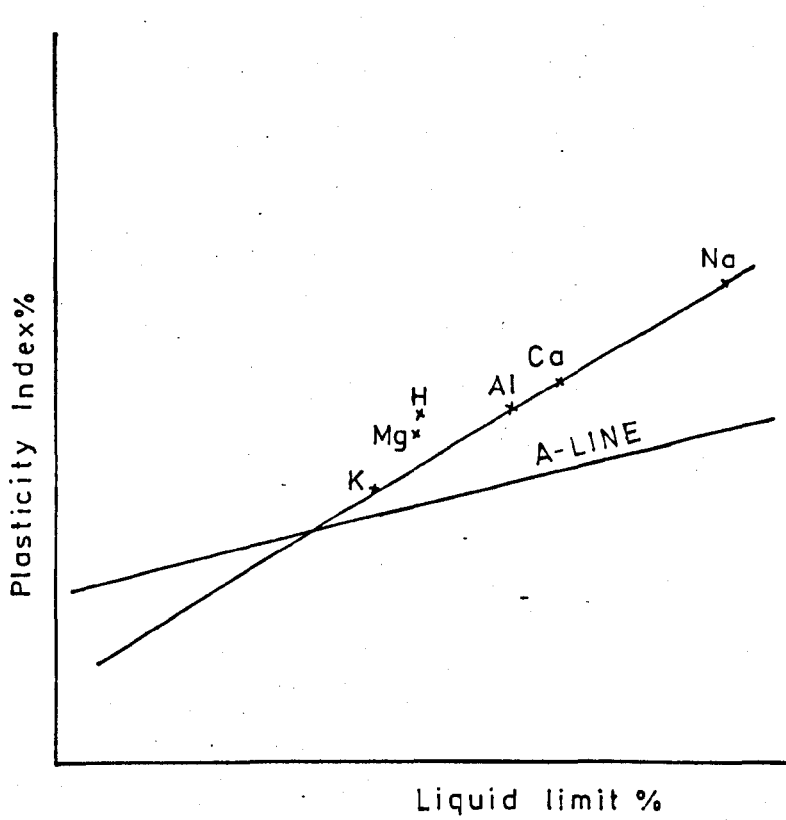


FIG. 6.13

Change in consistency of a soil due to cation exchange
(Matsuo 1957).

Although some studies, for example Kenney (1967), on the engineering properties of soils have concluded that there is no correlation between plasticity and residual strength, Voight (1973) considers that a relationship does exist between these properties since mineralogical factors affect both plasticity and residual strength alike. Fig. 6.14 shows a curve of plasticity index plotted against residual strength coefficient ($\mu_r = \tan \phi_r$) for a large number of different types of natural soils. The diagram suggests that materials with high residual strength coefficients possess low plasticity. Voight's principal conclusion was that plasticity index appears to be a useful guide to the residual strength of natural soils. Rethati (1971) also generalised in a similar context by stating that the higher the absolute value of the plastic limit, the less favourable are the engineering characteristics of the soils.

With regard to slope stability, it is evident that a change in the behaviour of a soil at a given water content may result from modification of porewater composition. Such changes will be critical if the water content of the soil is already close to the liquid limit.

6.8.2 Measurement of plasticity

Plasticity is usually expressed in terms of 'water' content and standard methods such as B.S. 1377 (1975) prescribe that distilled water is used in all tests.

Olson & Mitronovas (1972) considered water-content to mean the "weight of pore fluid (water plus dissolved salts) divided by the weight of solids" for their experiments on illite with different electrolyte concentrations. Theoretically, this should still represent moisture content since salts precipitated on drying will be included in the dry weight. Warkentin (1961) redefined liquid limit completely in order to

- Sample localities are:
1. Selnes
 2. Manglerud
 3. Asrum
 4. Labrador
 5. Ottawa
 - 6, 7. Sandnes
 8. Little Belt
 9. Bear paw
 10. Pierre
 11. Pepper
 12. Cucharacha
 - 13-18. Vaiont
 19. Walton Wood
 - 20, 21. Guildford
 - 22-24. Acherfield
 - 25, 26. Weald
 - 27-28. Manglea
 29. Wraysbury
 30. London
 - 31, 32. Gault
 33. Chalk
 - 34-36. Keuper marl
 37. Lias
 - 38-40. Appalachian colluvium
 39. Upper Coal Measures

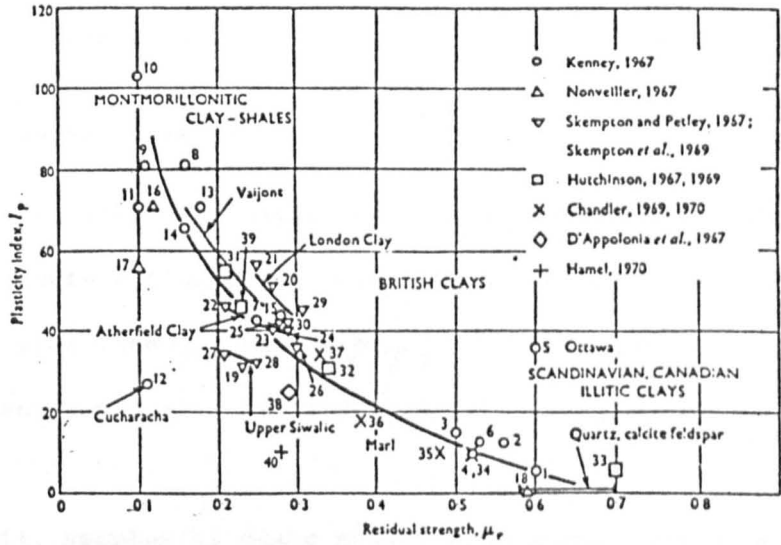


FIG. 6.14 Plasticity Index plotted against residual strength coefficient, μ'_r ; from Voight (1973).

provide a more useful explanation for the influences of different ions, salt concentration and pH on this property. The reinterpretation was stated as the distance between particles or between structural units of clay minerals at which, "forces of interaction between the clay particles become sufficiently weak to allow easy movement of particles or units relative to each other".

In the following experiments the definition of Olson & Mitronovas (1972) is adopted for the term water content.

6.8.3 Plasticity tests on Edale Shale

The plastic and liquid limits of Edale Shale were determined by the methods described in Appendix A.2 using the same solutions as in the residual strength tests plus $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$. The results obtained for these tests complement residual shear strength data obtained in the ring shear tests.

For the liquid limit, samples of Edale Shale, with a particle size less than 425 μm , were remoulded in the solutions for 40 minutes following the recommendation of Dumbleton & West (1966) for strongly aggregated soils. This was carried out in a Kenwood Food Mixer. The samples were left in an airtight tin for about 24 hours every time solution was added before testing with a cone penetrometer. The duration of a complete liquid limit determination was therefore prolonged over a period of 5 days per sample. This was considered necessary, however, to give time for the solution and sample to equilibrate.

For the plastic limits, tests were carried out by the rolling thread method (B.S. 1377, 1975) after an initial saturation period of 24 hours.

Appraisal of the results presented in Table 6.5 for both limits shows that the plastic limit is highest in the presence of distilled water and the liquid limit is highest with acid. The limits decrease

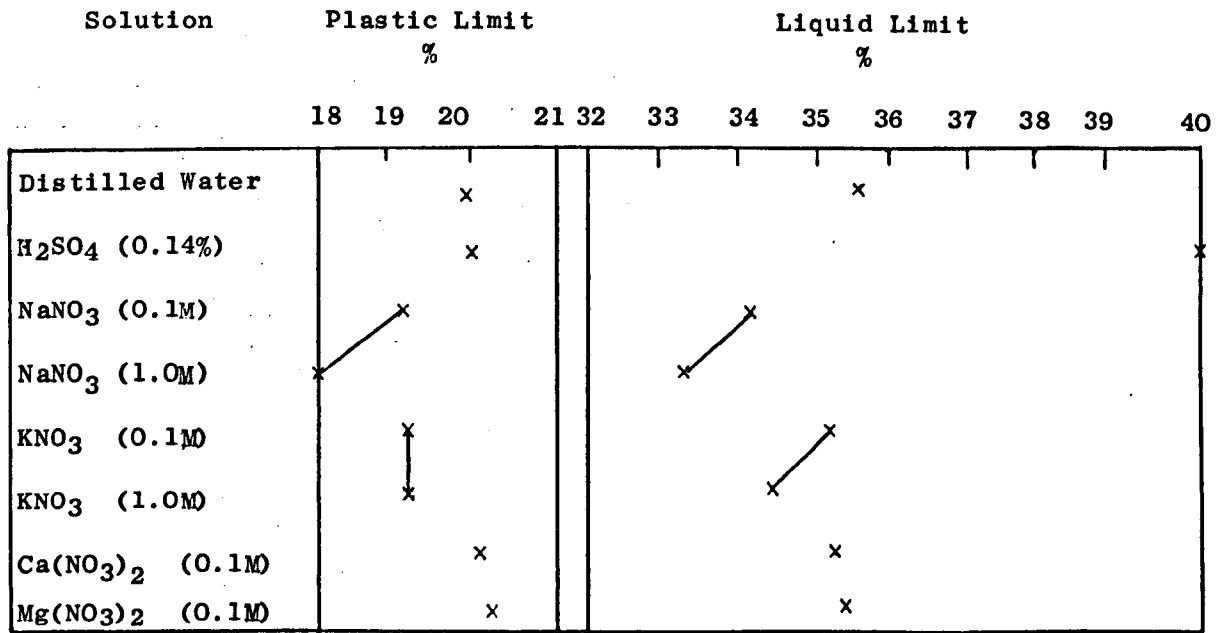


Table 6.5 Plasticity determinations on Edale Shale with different solutions

with increasing salt concentration and increase according to ion type in order $\text{Na} < \text{K} < \text{Ca} < \text{Mg}$. The liquid limit is affected to a greater extent than the plastic limit in terms of solution composition and concentration. The plasticity index shows a reduction accordingly.

6.9 Discussion

It is appropriate here to summarise the deductions that can be made from the results of the strength and plasticity tests.

1. Residual shear strength and plasticity properties of Edale Shale are sensitive to short term changes in porewater composition and concentration.
2. The responses of residual shear strength and plasticity to different solutions are comparable with those exhibited by clay minerals, although the magnitude of the changes are not as great.
3. The changes induced in the residual shear strength of the shale by different salt solutions are apparently rapid, reversible and independent of the order in which the solutions are introduced.
4. The residual shear strength and plasticity index of the shale appear to be increased in the presence of acid.

Taking the second point first, it is perhaps expected that in shales, which comprise large quantities of clay minerals, engineering properties will be partially dictated by the behaviour of the clays under the prevailing chemical conditions. However, the presence of other minerals, particularly quartz and possibly well-cemented aggregates, will inevitably dilute this influence to some extent. The contribution of clay minerals to soil behaviour also depends on the clay types since expandable minerals, such as smectites, apparently exert a much greater influence than non-expandable ones like kaolinite (section 6.3.2). As pointed out by Bolt (1956), it is difficult to quantify how much of the behaviour of a mineral mixture is attributable to each mineral constituent.

6.9.1 Effect of salt solutions

The rapid and reversible changes in residual shear strength in the presence of different salts almost certainly involve cation exchange in clay minerals with corresponding changes in bonding energies. Exchange reactions are probably limited to cations satisfying charge imbalances on the external clay surfaces rather than in interlayers, particularly in illites and kaolinite. This is supported by the studies of Haan et al. (1965) on diffusion of potassium into an illite over various time periods up to 16 months. It was concluded from these investigations that cation exchange in this mineral is restricted to cations close to the edges of individual particles and that more centrally located ones require very many years to contribute to porewater composition in soils.

The physical behaviour of clay platelets is governed by attractive and repulsive forces. Van Olphen (1963) explained that in many clay systems platelets assume a parallel arrangement whereby large surface areas are able to interact at comparatively short distances. At close separations the major contributory factor in layer repulsion is hydration energy derived from either or both adsorbed water and from hydrogen bonding between water molecules and clay surfaces. At greater plate distances, long range particle interaction involves electrical double layer repulsion, or osmotic swelling, due to pressures arising from differences in ionic concentration between clay plates and external solution. As shown by Norrish (1954) in an examination of swelling in montmorillonite, the transition between the two types of interaction is sharp. Fig. 6.15 shows how clay layers separate initially in distinct stages followed by a phase of continuous separation at much larger distances.

Although work by Norrish (1954) on osmotic swelling is concerned with montmorillonite, Norrish (1973) considered that other clay minerals should

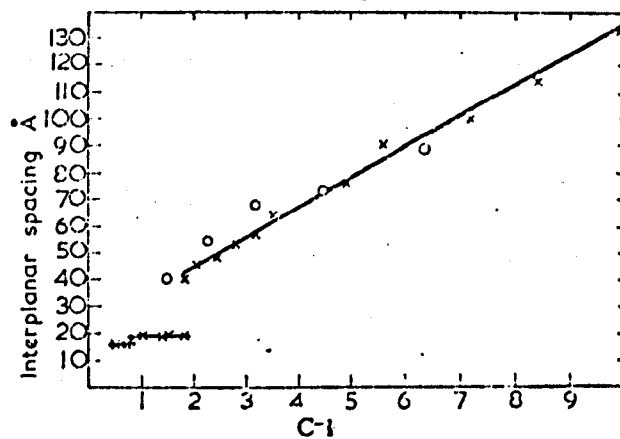


FIG. 6.15

Lattice expansion of montmorillonite, x NaCl solutions

o Na₂SO₄ solutions; from Norrish (1954, Fig. 5).

$C^{-1/2}$ is the reciprocal of the square root of concentration of solution.

behave qualitatively in the same manner. Quantitatively, however, their behaviour is modified by differences in particle shape, size and surface charge density since these factors influence the magnitude of repulsive and attractive forces.

Low & Margheim (1979) criticised the concept of osmotic swelling as a cause of clay expansion in water and proposed that swelling pressures were primarily due to a reduction in potential energy of adsorbed water as a result of its interaction with adjacent layer surfaces.

However, certain engineering characteristics of clay-electrolyte systems, dependent on clay expansion, are more generally attributed to osmotic swelling and hydration, for example by Bolt & Miller (1956), Bolt (1956) and Warkentin & Schofield (1962) for consolidation properties.

In terms of shear strength, osmotic swelling and hydration probably influence effective normal stress and hence, the angle of internal friction, ϕ . This was considered to be true for illites by Sridharan & Venkatappa (1979) and for kaolinite and montmorillonite by Warkentin & Yong (1962) and Mesri & Olson (1970). Chattopadhyay (1972) proposed a modified shear stress equation to account for the effect of physico-chemical environment on clay shear strength:

$$\tau_{res} = [\sigma_N' - (R-A)] \tan \phi_r'$$

where σ_N' is the apparent effective stress

$R-A$ is the net interparticle stress due to the physico-chemical environment

τ_{res} is the residual shear stress

$\tan \phi_r'$ is the residual angle of friction

$(R-A)$ is apparently predicted well by double layer repulsion, particularly in Na-montmorillonite, although for less reactive minerals, the physico-chemical environment probably has less effect.

Taylor (1959) considered that the formation of double layers between clay particles provides a reasonable basis for interpreting the mechanical behaviour of soils with a large clay mineral content.

The changes in residual shear strength of Edale Shale with different cations may be explained, at least in part, by hydration and osmotic processes within the clay fraction. Residual strength is higher for K than for Na. According to Rosenqvist (1955), the attractive forces between clay plates are mainly due to Van der Waal's forces and are proportional to the polarisability of the adsorbed cations. Since K has a larger polarising influence than Na and also has a lower hydration energy, it follows that repulsive forces in the presence of K are less effective than with Na. Residual shear strength is thus higher with K in the porewaters than with Na.

Greater repulsive forces are experienced with Na because it has a high hydration energy. An increase in the concentration of Na in the porewaters presumably increases the available hydration energy and hence clay layer separation is enhanced. The observed shear strength is thus lower because the repulsive force is large (Lambe 1958).

This response appears to be typical of illite and kaolinite minerals although not of others, such as smectites, for which increased concentrations of ions reduces repulsion by modifying their inherent repulsive tendency (Yong & Warkentin 1966). Reduced shear strengths in these minerals were attributed by Warkentin & Yong (1962) to easier particle readjustment under the applied shearing forces as a result of inhibited particle repulsion.

The effects of electrolytes on shear strength are often considered to be due to changes in particle or aggregate arrangements, for example by Warkentin & Yong (1962), Rosenqvist (1955), Mesri & Olson (1970), but

this seems inappropriate in the case of residual shear strength since this property is supposedly reliant on a parallel orientation of clay plates. Nagaraj & Rao (1974) were of the opinion that where clay aggregation is favoured by the physico-chemical environment, packet structures develop and these assume a parallel arrangement without any significant distortion within the fabric elements. The magnitude to which residual shear strength is affected then depends on the stability, size and nature of the fabric elements. It was found that in the presence of Na, double layers were formed between individual particles, hence fabric elements were smaller and residual strength lower than that recorded with Ca, where double layers were depressed and clay aggregates larger. Differences of plastic limit are explained by Warkentin (1961) in terms of particle rearrangement. In low swelling clays under neutral conditions (pH 6.5), the interparticle attraction forces cause particles to assume face-to-face arrangements with some edge-to-face contacts. With increasing salt concentration, particularly of monovalent ions, the structure changes to face-to-face arrangements in which the void space between particles is lower and the liquid limit decreases. With divalent ions, however, edge-to-face flocculation is favoured, the void space increases and so does the liquid limit. For swelling clays, the dominant interparticle force is repulsion. Increasing salt concentration with monovalent cations reduces repulsion and hence the liquid limit decreases. With divalent ions, such as Ca, increasing the concentration does not reduce the liquid limit appreciably according to Warkentin (op. cit.). This is explained by the formation of particle units, or tactoids, which are not very sensitive to changes in salt concentration.

An alternative explanation is given by Grim (1962) who proposed that plasticity is primarily governed by the structure and orientation

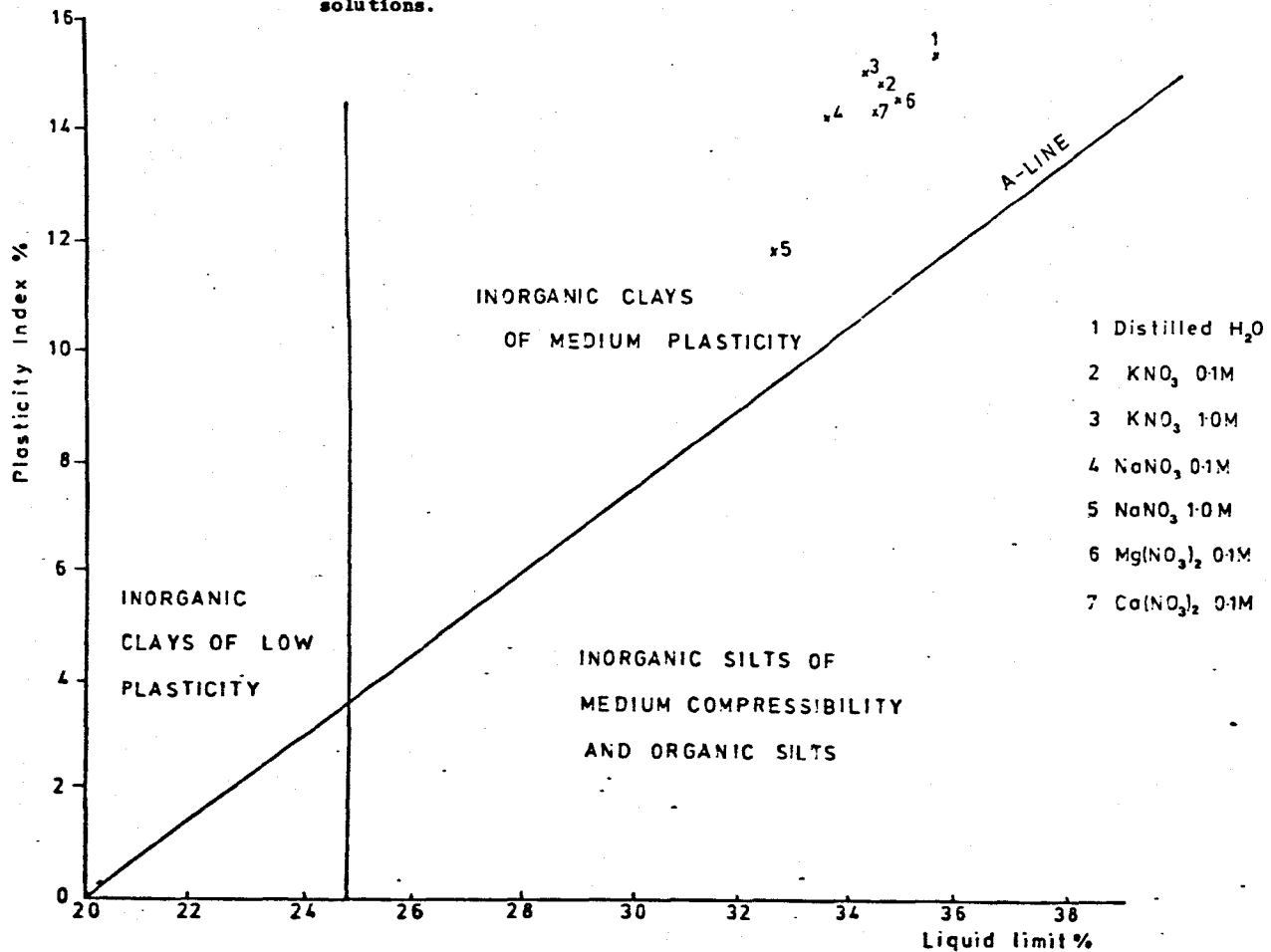
of adsorbed water on clay mineral surfaces and that adsorbed cations affect plasticity by their influence on adsorbed water orientation.

The plasticity properties of Edale Shale in the presence of different cations are comparable with those predicted for illites and kaolinites as reported by Rosenqvist (1955) and Li (1978). In Fig. 6.16 the values are presented on a plasticity chart where they plot in the region corresponding to medium plastic clay (Fig. 6.12). The consistency changes indicated on the chart do not follow the same relationship with the cation type as those shown by Matsuo (1957) which may reflect differences in soil compositions. The residual shear strength properties also appear to be explained by considering the behaviour of illites and kaolinites with different porewater compositions and concentrations. This is perhaps unexpected in view of the large proportion of 'swelling' clays in Edale Shale since this clay type has been reported to exert a considerable influence on the behaviour of clay mineral mixtures. However, as stated by Taylor (1959), "owing to the wide variations found in the texture, composition and geological history of natural soils, it is hardly to be expected that any single theoretical treatment is likely to give a universal interpretation of the influence of chemical factors on the mechanical properties of soils in general".

6.9.2 Effect of acidic solutions

It is perhaps surprising to record an apparent increase in ϕ_r' and plasticity in the presence of sulphuric acid. As for salts, the rapid and reversible response in ϕ_{rs}' suggests that short term changes in inter-particle bonding occur. With acidic solutions, this is likely to involve reactions with H^+ ions. Feigenbaum & Shainberg (1975) considered that where H^+ is present in solution, a rapid exchange may occur between the

FIG. 6.16 Plasticity chart for Edale Shale with different solutions.



adsorbed cations on clays and H^+ to form H^+ -clay. Norrish (1973) also proposed that H^+ ions act as an exchange cation, although only in dilute solutions.

The longer term effect of acid weathering on residual shear strength and plasticity is uncertain but it would seem reasonable to expect further, permanent strength increases from the nature of the reactions that occur. Strength increases on weathering have been reported elsewhere, for example, by Gould (1960) who found that ϕ_r' increased from 12.5 to 17.5° in an unweathered Tertiary marine clay to 24 to 27° in weathered material. Talme (1968) also measured higher strengths in a Norwegian 'quick' clay after the addition of hydrochloric acid.

In Chapter 2 the evolution of materials with greater thermodynamic stability in the weathering environment was discussed. Chemical weathering reactions in shales tend to produce mineral compositions dominated by quartz, kaolinites and Al or Fe-oxides and hydroxides; the latter occur either as free gibbsite or goethite or as interlayers in clays like chlorite or smectites and vermiculites. All these products possess typically higher strengths than the original shale constituents, particularly expandable smectites and illites. Kidder & Reed (1972) found that hydroxy-aluminium interlayering greatly reduced the swelling properties of expandable clays and Gray (1970) and Foster & Gazzard (1975) reported that the presence of hydroxy-aluminium interlayering greatly increased soil strength.

Amorphous material, such as iron oxides, may also be produced during weathering (Chukrov 1972; Yong et al. 1980). Yong et al. (1979) considered amorphous material to possess a negative charge and found that it increased the physical stability of some sensitive Canadian clays. In other systems, therefore, amorphous material may contribute to strength by its bonding properties.

6.9.3 Implications of short term changes in porewater composition to slope stability at Mam Tor

The residual strength and plasticity of Edale Shale are affected by changes in the cation composition, concentration and pH characteristics of the porewaters. The change in physical properties is probably due to the influence of different cations in the porewaters (including H^+) on interparticle bonding, particularly between clay minerals. ϕ_{ra}' is reduced in the presence of Na and increased by K relative to values obtained with distilled water. ϕ_{ra}' also appears to be increased markedly with acid at a concentration commensurate with that reported by Vear & Curtis (1981) to be generated under natural weathering conditions at Mam Tor, Derbyshire.

Clearly, the compositions of weathering solutions are modified progressively by continued reaction with surrounding rock. Groundwater emerging in surface seepages at Mam Tor, for example, has a large concentration of K, Ca and Mg with smaller quantities of other cations and has a pH of around 3.4. The combined influence of these chemical factors will affect the residual shear strength of Edale Shale within the landslide and particularly along the slip surface where weathering solutions are thought to percolate. This is suggested in the residual shear strength test conducted with groundwater taken from Mam Tor.

It is not possible to make quantitative predictions for the effect of porewater composition on residual shear strength for the whole slide particularly as weathering processes are not at the same stage everywhere. On a broad scale, however, a reduction in ϕ_{ra}' of 1° for Edale Shale under an effective normal stress of 294 kN m^{-2} produces a 5% drop in the factor of safety (Appendix B.9) assuming limiting equilibrium to be controlled by residual shear strength. This is obviously significant,

particularly if the factor of safety is already close to unity. A concurrent rise in porewater pressures, top loading of the rotational main unit by blocks falling from the back scarp, removal of support to the main unit after movements of the translational toe or changes in slip plane geometry due to material dissolution may trigger a major movement.

CHAPTER VII

CONCLUSIONS

The geochemistry and physical structure of shales renders them unstable in the weathering environment. The components of shales which accumulate during deposition and diagenesis are diverse, consequently subsequent degradation by weathering involves chemical and physical processes which operate simultaneously but do not proceed at the same rate.

The problems presented to engineering by shales are varied and appear to be strongly related to the geochemical properties of these materials. Low strength, salt precipitation and swelling are notable examples. Successful prediction of the scale and nature of potentially unsatisfactory physical behaviour in a rock requires an understanding of the rates and type of physical and chemical reactions likely to occur in weathering conditions. Links between geochemical and engineering properties should therefore be researched. Natural shale-water systems are, however, too complex to analyse in detail. Instead, laboratory investigations under controlled conditions provide useful information on specific physical and chemical properties.

In laboratory experiments using Carboniferous Edale Shale conclusions were drawn on the rate and nature of chemical reactions involving shales and sulphuric acid. The effects of changes in porewater composition and concentration on residual shear strength were studied. The influence of physical breakdown on residual shear strength was also considered together with the problems of measuring particle size distribution in shales.

7.1 Chemical reactions in shales

Sulphuric acid is produced wherever pyrite oxidation occurs. Experiments described in Chapter 5 in which different masses of shale were reacted with sulphuric acid showed that the pattern of cation release during

artificial acid weathering of shales can be similar to that found in natural weathering systems. Meaningful reactions are, therefore, reproducible under laboratory conditions. This has facilitated a study of the rates of chemical reactions which probably occur in the vicinity of acid generation under natural conditions.

The initial attack of acids produced by pyrite oxidation on fresh shale can apparently occur extremely rapidly. Half-lives for the reactions involving different shale masses varied from 0.36 minutes (ratio of H^+ to shale 0.08 mg/g) to 710 minutes (ratio of H^+ to shale 8.00 mg/g). Exact figures for the same reactions in the vicinity of natural pyrite oxidation cannot be estimated because the solid solution ratios are not known. Although the void ratio of the shale may give an indication, the local concentration of acid produced is not known and natural systems have open rather than closed flow regimes. The main conclusion to be drawn here is that reactions involving fresh acid are rapid and are limited, at least in the closed systems used, by the surface area of the shale. Hence, in situations where particle breakdown is occurring, such as in shear zones, reaction may be accelerated by the increased surface area available for contact with acid waters.

During chemical weathering, the composition of the active solutions will be changed markedly, even if there is little apparent effect on the mineralogy of the solid material. This may influence the engineering properties of shales in the short term; continued release of ions into solution can certainly create problems in a matter of a few years due to the precipitation of salts within weathered rock masses.

7.2. Effect on engineering properties

The major property investigated in this work was residual shear strength. This was selected because it is the strength mobilised along a slip plane after failure and thus controls post-failure stability.

Residual shear strength was expressed in terms of apparent residual angle of friction (ϕ_{ra}) because:

(a) the normal stress was not changed during tests, hence ϕ_{ra} values are not true ϕ_r for Edale Shale.

(b) displacement during shear was probably insufficient to establish a full residual condition in terms of particle orientation and breakdown.

Measured ϕ_{ra} was probably an intermediate "minimum shear resistance". Attempts to differentiate sheared from unsheared material on the basis of grain size were unsuccessful. Coulter counter analysis merely indicated that both sheared and unsheared shale aggregate contained large quantities of material $< 0.6 \mu\text{m}$ in size.

It was found that ϕ_{ra} and plasticity in Edale Shale are sensitive to short term changes in porewater composition and concentration. Na^+ reduced ϕ_{ra} and K^+ increased ϕ_{ra} relative to the value obtained with distilled water. An increase in concentration of Na^+ ions magnified the reduction in ϕ_{ra} . The responses of ϕ_{ra} and plasticity with different cations in solution are comparable with those shown by clay minerals. However the magnitude of the changes is relatively lower. Hence, for a rock containing large quantities of clay minerals its physical behaviour appears to be influenced by the behaviour of the clay minerals. The presence of other minerals, particularly quartz, probably reduces the clay effect.

The changes induced in ϕ_{ra} by different cations are rapid, reversible and independent of the order in which the solutions are introduced. These observations suggest that cation exchange in clay minerals occurs with corresponding changes in bonding energies.

Acid apparently increases ϕ_{ra} and the plasticity index. This is almost certainly due to short term changes in interparticle bonding involving H^+ ions.

Changes in ϕ_{ra} and plasticity in Edale Shale do not appear to be dependent on their state of physical breakdown. Mineralogy exerts a stronger influence than aggregate size distribution. The relative quantities of quartz and clay minerals are probably most important. Modifications in ϕ_{ra} may be due to porewater composition in the short term and mineralogical alteration in the long term.

7.3 Measurement of particle size distribution

Physical methods of measuring fundamental grain size distributions, particularly the $< 2 \mu\text{m}$ fraction are not reliable for indurated rocks. A statistical correlation between the proportion of $< 2 \mu\text{m}$ size material and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio determined by X-ray fluorescence analysis was established using unconsolidated Humber sediments. Similar relationships were found for Plastic, Ball and China clays. However, the exact mathematical relationship for a particular rock appears to depend on the composition of the $< 2 \mu\text{m}$ size fraction.

For Edale Shale, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was used to estimate the amount of less than $2 \mu\text{m}$ material present. Values over 70% obtained from a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio versus percentage $< 2 \mu\text{m}$ size fraction plot indicate that physical methods of measurement seriously underestimate the amount of fine material present.

Estimates of percentage $< 2 \mu\text{m}$ material in Edale Shale in different stages of physical breakdown were obtained by a sedimentation technique and by calculation using the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Discrepancies between the results showed that fundamental grain size distribution is not obtained during rapid physical weathering.

7.4 Chemical weathering systems

Although natural systems are not readily analysed in detail, for laboratory studies like those discussed in this work, it is helpful to divide weathering processes into individual components for separate investigation.

With respect to chemical weathering, Fig. 7.1 illustrates how in general terms two distinct components are recognisable, the solid phase and solution phase. Weathering modifies both phases in a cyclic manner. Positive feedback is operative whereby initial weathering reactions control subsequent reactions which create new conditions to influence further weathering.

Generally, it appears that the physical properties of materials depend on the extent of weathering as the solids are modified. For any given solid state, however, independent values for physical properties are obtained depending on porewater composition. Field properties of weathered shales, therefore, depend on:

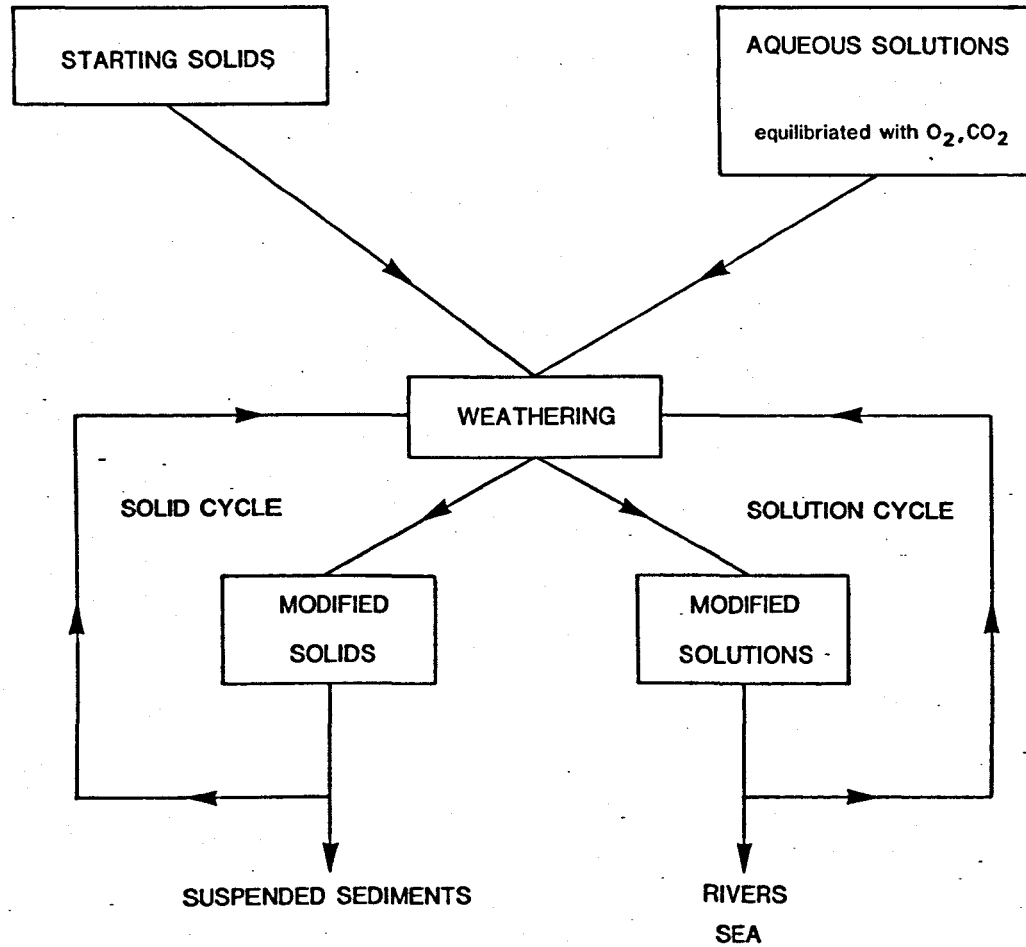
- Evolution of the solid phase
- Evolution of the solution phase

7.5 Links between weathering and slope stability

The weathering system at Mam Tor which is described by Vear & Curtis (1981) (Chapter III) can be represented in terms of the general weathering model as shown in Fig. 7.2.

Steward & Cripps (1983) discussed changes in the physical properties of weathered shale at Mam Tor as a result of the operation of this system. In the solid phase in cycle 1, a net decrease in bulk density occurs due to the removal of diagenetic pyrite while in the complementary solution phase the potential for weathering is enhanced by acid generation. Further mineral dissolution in cycle 2 combined with clay leaching continues to reduce the bulk density while the ion concentration of acidic solutions increases from the products of the reactions. In cycle 3, precipitation of secondary minerals from saturated solutions increases bulk density. Cation exchange occurs, particularly in the clay minerals. In the fourth cycle, slower reactions involving detrital minerals alter

FIG. 7.1 COMPONENTS OF WEATHERING



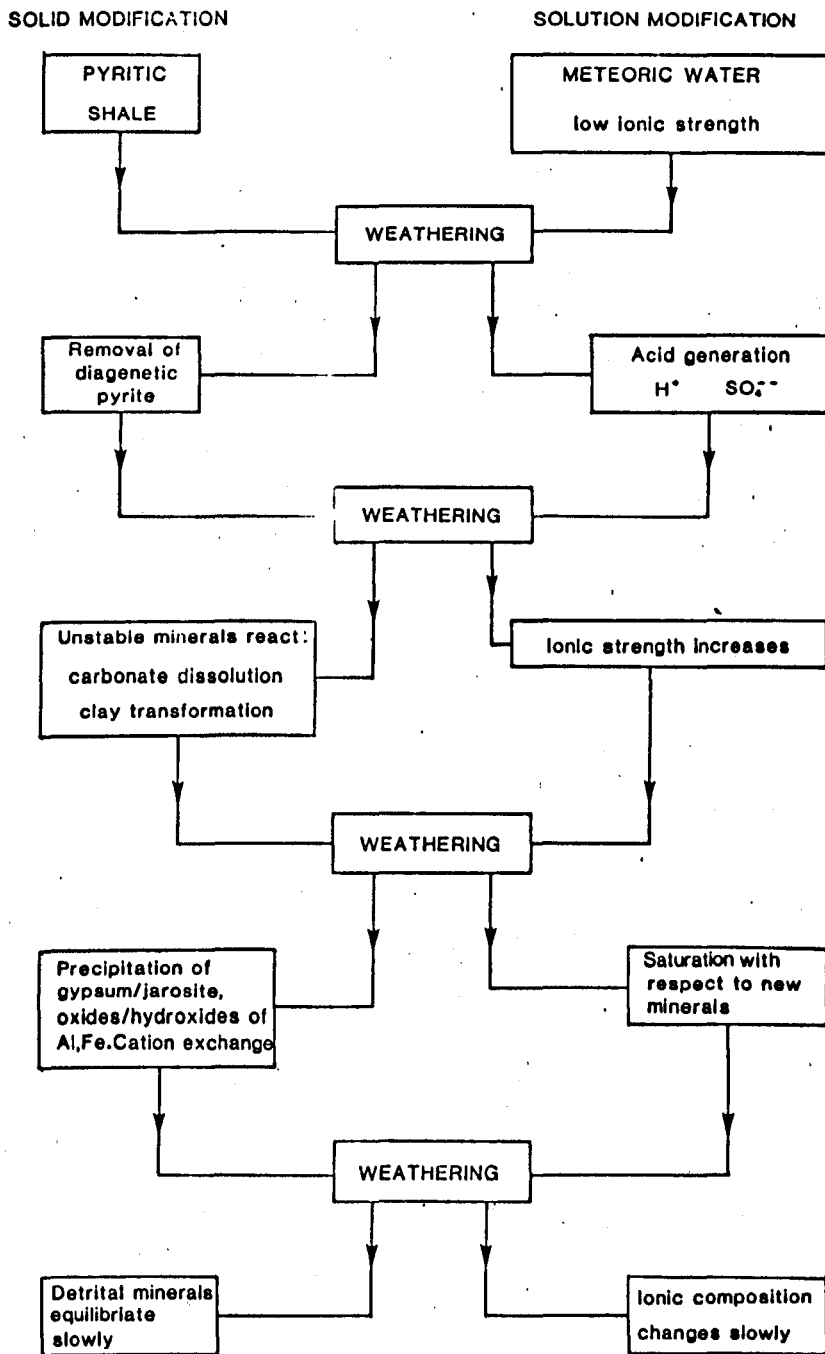


FIG. 7.2 Representation of the weathering system at Mam Tor -
from Steward & Cripps (1983).

the composition of porewaters over a long time period and the physical properties of the weathered shale probably change very slowly.

These cycles operate simultaneously over all parts of the landslide, although one process is likely to be dominant in time at a particular location and may play a large part in determining the physical properties of the rock mass at that site.

The waters draining Mam Tor are rich in Ca, Mg and K, hence pore-water composition may play a part in determining residual shear strength.

Weathering reactions do not invariably reduce strength, as shown in the experiments with KNO_3 and acid. Rock quality may deteriorate, however, due to the effects of other chemical weathering processes. At Mam Tor, the most significant of these in terms of bulk material properties is probably the volume changes which accompany mineral dissolution and precipitation. The passage of each litre of acidic water through the rock mass involves a net loss of material, not taking account of secondary salt precipitation (Vear & Curtis 1981). This loss is unlikely to occur uniformly and probably modifies the permeability characteristics of the rock mass so that access to unweathered material is enhanced.

Gypsum crystals accompanied by abundant goethite are commonly observed along bedding planes and joints in surface exposures of Edale Shale. Their role in aiding physical breakdown is uncertain (Chapter III) but it is possible that by continued precipitation they may force discontinuities apart. At depth, jarosite may be precipitated rather than gypsum with similar consequences, setting up local stresses within the rock mass.

Information regarding the properties of Edale Shale at depths down to about 28 m was obtained from a borehole in the rotational main unit of the landslide and is described in Chapter III. Evidently, oxygenated

meteoric waters or acidic waters produced at shallow depths percolate through the slip zone and attack fresh rock. Continued physical disintegration combined with chemical activity along the slip zone may reduce the factor of safety of the landslide over a period of years to a critical failure condition.

In other investigations, for example by Subramaniam & Carr (1981), Prior & Graham (1974) and Early & Skempton (1972) which are described in Chapter I, evidence of chemical activity along slip zones was reported. Changes in the engineering properties of material on these shear surfaces may be occurring in the manner speculated for Mam Tor. If the factor of safety reaches values close to one, other destabilising influences may then trigger failures.

7.6 Final comment

Division of a weathering system into separate components provides a clearer indication of the relationships between geochemical processes in both time and space. If quantifiable, the contributions made by each geochemical component would be of value in predicting the likely physical behaviour of a given shale-water system. As yet, however, this is not possible.

APPENDIX A

PRACTICAL TECHNIQUES

The general procedures adopted for tests and analyses in this work are outlined in this appendix. Where standard methods have been used, reference is made to the original documentation and only possible sources of error with precautionary measures additional to those in the prescribed methods have been included. Modifications to standard procedures in order to improve or adapt particular techniques are described in greater detail.

The following methods are included:

- A.1 Determination of moisture content
- A.2 Determination of plasticity limits
 - A.2.i Liquid limit
 - A.2.ii Plastic limit
 - A.2.iii Plasticity index
- A.3 Determination of grain size distribution in sediments by the pipette method
- A.4 Method of specimen preparation for X-ray diffraction analysis
 - A.4.i Powder mount
 - A.4.ii Smear mount
 - A.4.iii Quantitative determination of clays using X-ray diffraction
- A.5 Determination of chemical composition by X-ray fluorescence
- A.6 Determination of the chemical composition of solutions by atomic absorption spectrophotometry
- A.7 Determination of quartz (free silica) in sediments by the method of Trostel & Wynne (1940).

A.1 Determination of moisture content

Moisture content (w) is defined by BS 1377 (1975) as the mass of water which can be removed from the soil, usually by heating at 105°C , expressed as a percentage of the dry mass. Determination of w is fundamental in a number of engineering tests including plasticity measurements and in pre- and post-shearing moisture content determinations.

A clean dry container with a lid was weighed to the nearest 0.01 g (W_c). The sample was placed in the container and weighed (W_w). All matrix water was evaporated by oven-drying at $105\text{--}110^{\circ}\text{C}$ for about 24 hours until no further change in weight was recorded. During drying the container lid was placed loosely over the sample to prevent contamination by foreign particles.

After drying, the sample was cooled in a desiccator and weighed (W_d).

The moisture content was calculated by equation A1.

$$w = \frac{W_w - W_d}{W_d - W_c} \times 100\% \quad \text{A1}$$

Values for w were rounded to the nearest integer.

A.2 Determination of plasticity limits

A.2.1 Liquid limit (LL)

Two methods were employed for the determination of the liquid limit. In initial tests the Casagrande percussion cup was used but this was later replaced by a cone penetrometer apparatus.

Both methods are outlined in detail in BS 1377 (1975) and Vickers (1978) who also give accurate descriptions of the apparatus. The cone penetrometer is the preferred method by the BS 1377 (1975) because it is easier to carry out, gives more reproduceable results, is less dependent

on operator judgement and the apparatus can easily be maintained in correct adjustment.

Differences between the results are considered to be slight by Vickers, although Norman (1958) found that the cone penetrometer gave higher values than the Casagrande apparatus.

Sample preparation for both methods was the same. Soil was dried sufficiently to permit disaggregation by a rubber pestle and mortar. The material used was sieved through a 425 μm mesh and a minimum of 200 g retained for testing. The dried soil was mixed with distilled water on a clean flat glass plate to form a thick paste which was then left in an airtight container for 24 hours to allow the water to permeate the soil thoroughly.

A.2.11 Plastic limit (PL)

The plastic limit was determined using the rolling thread method prescribed by BS 1377.

Other, more controlled methods were considered, particularly regarding use of the cone penetrometer. For comparative purposes, however, the current standard method was used. Application of updated procedures will inevitably require a redefinition of the plastic limit as advocated by Wroth & Wood (1978) who took the limit at a point where the shear strength of a sample was 100 times its strength at the liquid limit.

A.2.11i Plasticity index (PI)

The standard definition was used:

$$\text{PI} = \text{LL} - \text{PL}$$

A.3 Determination of grain size distribution in sediments by the pipette method

Determination of grain size distribution by sedimentation may involve up to four stages of preparation and testing, including the measurement of the specific gravity of the material to be analysed, removal of cementing compounds, dispersion of the constituent particles and the sedimentation test itself.

A.3.i Measurement of specific gravity

The BS 1377 (1975) procedure was followed for this determination.

A.3.ii Removal of organic matter

The BS 1377 (1975) method was employed using 20 vol. H_2O_2 as an oxidant.

A.3.iii Dispersion of particles

The BS 1377 (1975) technique was followed initially. This involved shaking soil (pre-treated if organic matter was removed) in 100 ml of distilled water with 20 ml 2% calgon on an end-over-end tumbler for 4 hours, followed by wet-sieving on mesh 63 μm . The standard procedure recommends that the soil retained on the sieve should be oven-dried and resieved on appropriate mesh sizes to assess the proportions of gravel and sand present. In practice, however, the 63 μm sieve became very congested during the initial washing because of the large quantities of fine material in the soil. The whole sample was, therefore, suspended in distilled water and analysed by sedimentation.

A.3.iv The sedimentation test

This was carried out in an Andreasen Cylinder, one of which is shown in Plate A1. The cylinders were graduated in centimetres and had fixed

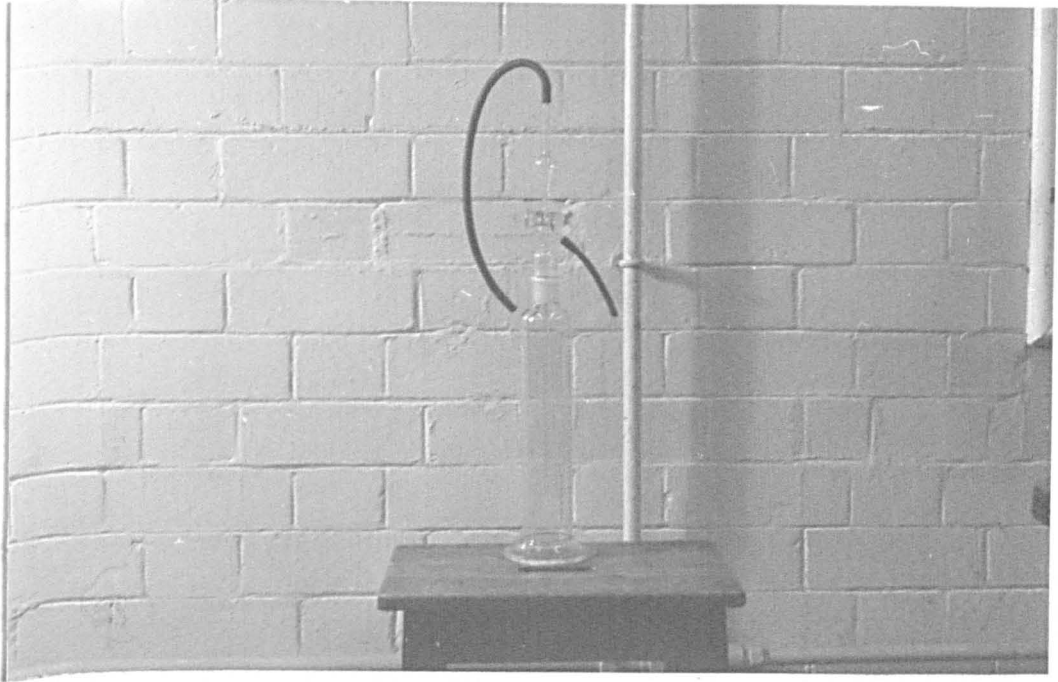


PLATE A.1 Andreasan cylinder.

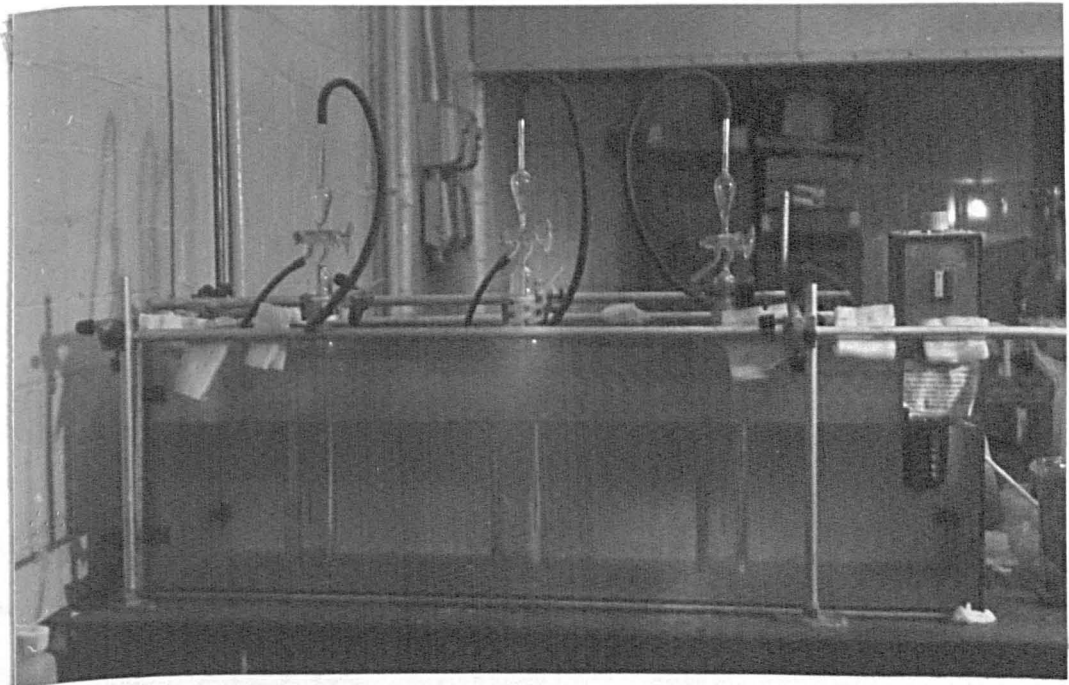


PLATE A.2 Cylinders in water bath to maintain a constant temperature during sedimentation.

10 ml pipettes. They were placed in a water bath and maintained at constant temperature throughout tests (Plate A2).

Each soil-water mixture to be analysed was washed completely into the appropriate cylinder and the depth made up to 20 cm with 25 ml 2% calgon and distilled water. One hour before the tests commenced the water bath was switched on and the temperature allowed to equilibrate at 21.5°C. All four samples were analysed simultaneously.

Sedimentation is the process whereby a steady fall of particles occurs through a liquid at rest. The particle sizes at a given depth at a given time are determined from Stokes Law which relates the velocity of a particle falling through a liquid to the radius of the particle, its specific gravity and the viscosity of the liquid. For a spherical particle, the relationship is expressed in equation A4.

$$V = \frac{H}{T} = \frac{2}{9} \frac{(\gamma_S - \gamma_L)g \cdot r^2}{\eta} \quad A4$$

where V = velocity of falling particle (cm S⁻¹)

H = distance through which particle falls (cm)

T = time taken to fall H cm (s)

g = acceleration due to gravity

r = radius of particle (cm)

η = viscosity of liquid (poise)

γ_S = specific gravity of particle

γ_L = specific gravity of liquid

Stokes Law can be modified to allow for the non-spherical nature of particles but for most practical problems, use of equivalent spherical diameter (esd) is assumed to be satisfactory.

The velocity of a falling particle should be limited so that turbulence is not created in the suspension. This condition is satisfied if Reynolds number does not exceed 0.2, at which point Stokes equation

has an error of 5%. In terms of particle size this dictates an upper limit of 0.2 mm esd above which Stokes Law is inaccurate.

Using this law it is possible to calculate the times at which particles of a given size range will be present at a given depth. Generally, a depth of 10 cm is used and sampling times calculated so that particles finer than medium silt (20 μ), fine silt (6 μ) and clay (2 μ) would be present at that depth. Conversely, it is possible to calculate the particle size ranges which will be present at a given depth at specific times using the same equation. The latter approach seemed more practical to use when more than one test was run simultaneously because it allowed greater flexibility with withdrawal times and a timetable was constructed to ensure systematic sampling. In this work, four samples were analysed together and a sampling plan implemented which allowed 17 minutes between the start of one test and commencement of the next.

Each test was started by inverting the cylinder ten times and timing for settlement of the suspension was started as the cylinder was returned to the upright position after the tenth inversion. The pipettes were inserted and remained in place for the duration of the test. This avoided any disturbance to the suspensions consequent upon the pipettes being lowered and raised at each sampling event.

Samples were withdrawn at intervals on a log-time basis, at 1.5, 3, 5, 10, 15 and 30 minutes, 1 hour, 2, 4, 8 and 24 hours, following the procedure recommended by Ackroyd (1956). Exactly 10 ml of the suspension was drawn into the pipette on each occasion and the contents were washed into a pre-weighed 25 ml beaker. All the beakers were dried at 105°C to evaporate the water, allowed to cool and then weighed to determine the mass of soil particles present.

The maximum particle sizes present at the given times at 20 cm depth were calculated using equation A5 from Akroyd (1956):

$$\text{Particle size} = F \frac{\text{Effective depth (cm)}}{\text{Time (min)}} \quad (\text{mm}) \quad \text{A5}$$

where F is a factor derived from Stokes Law based on temperature and specific gravity of the soil.

The amount of soil particles remaining could be expressed as a percentage by weight of the amount of soil dispersed in the original suspension using equation A6.

$$p = \frac{100 \times W_t}{W_o} \quad \text{A6}$$

W_t is weight of soil per ml at a depth of 20 cm after time t

W_o is weight of soil per ml in the original liquid

Account was taken of the amount of dispersant, i.e. 2% calgon, in the original liquid and so equation A6 became modified to equation A7 which was used in the final calculation:

$$p = \frac{100 (W_D - W_c)}{W_o} \quad \text{A7}$$

where W_D is g/ml of dried soil + 2% calgon

W_c is g/ml of 2% calgon

W_o is g/ml of soil in suspension

The following points about application of Stokes Law were noted by Vickers (1978):

(a) The range of applicability is restricted to particle sizes between 0.2 mm and 0.002 mm esd falling through water. For larger particles there is a risk of turbulence while smaller ones may be susceptible to Brownian motion.

(b) Particles often do not resemble spheres.

(c) An infinite extent of liquid is assumed to exist around each particle and its free fall is supposedly unaffected by the tube although this is thought to be negligible if the concentration is maintained less than 50 g/1000 ml and the tube is in excess of 50 mm diameter.

(d) The value used for specific gravity is an average value and may well be in error. This concerns clay minerals particularly since adsorbed water can amount to $\frac{2}{3}$ of the particle volume and the true specific gravity of the solid matter will be lower than the average. For reliable results, high temperatures drying must be avoided.

(e) Certain soils change their particle size characteristics in suspension. Illite and montmorillonite may break down on stirring.

(f) Temperature variations in the environment may cause convection currents within the suspension.

(g) Some soils do not disperse easily. This has been shown to be a large problem in indurated rocks, for example in ancient shales by Pettijohn (1975) or in Keuper Marl by Davis (1967).

The sedimentation test is considered adequate for most practical problems involving soils but its value for measuring particle size distributions of fine-grained, well-cemented rocks should be viewed with caution.

A.4 Methods of specimen preparation for X-ray diffraction analysis

A.4.1 Powder mount

A rock or coarse soil sample was crushed in a cast iron mortar and pestle. A small amount of the powder produced by crushing was ground to a talc consistency in an agate mortar. This was stored in a plastic phial if not used immediately.

To prepare a powder specimen for analysis, a clean glass slide was placed over the rectangular recess of the powder holder and secured with sellotape. Powder was added to the recess in small amounts, ensuring that each layer was distributed evenly. When the holder was full, the top surface was levelled flush with the top of the recess and an aluminium backing clipped over the sample. The glass slide could then be removed and after checking that the specimen was perfectly compressed with the exposed surface even, the holder was inserted in the sample chamber of the diffractometer for analysis.

A.4.ii Smear mount

Gibbs (1965) compared different methods of preparing oriented specimens of clays in $< 2 \mu\text{m}$ fraction and found that the only procedures capable of producing homogeneous specimens are the smear, rapid suction and pressure methods. In other methods, for example sedimentation, separation of different minerals often occurs resulting in concentrations of components in different parts of a specimen. This is particularly important in quantitative work where thick, homogeneous samples are required in order to give meaningful relative intensities of reflection.

Smear mounts were used in the analysis of both whole rock and selected size fraction specimens. For whole rock smears, a powder was prepared in the same way as for a powder mount. A small amount of this material was then further ground in an agate mortar with a drop of distilled and deionised water. After wet-grinding, sufficient distilled and deionised water was added to produce a thick suspension of material. This was taken up into a dropper pipette and two or three drops placed on one half of a clean glass slide. The suspension was smeared evenly along and across one half of the slide and left to dry at room temperature.

For the preparation of $< 2 \mu\text{m}$ size fraction smears, a rock or coarse soil sample was disaggregated in a cast iron mortar and pestle. About 5 g of this material was placed in a glass centrifuge tube with calgon of concentration 1.5 g l^{-1} . The mixture was shaken and then centrifuged for about 15 minutes or until the supernatant liquid was clear. Occasionally, the liquid was discoloured or a film of organic matter was seen floating at the surface but provided no particulate material remained in suspension the liquid was discarded and the solid resuspended in calgon. The process continued until any clay particles ceased to flocculate rapidly. The centrifuged solid was then washed in distilled-deionised water.

Separation of different size fractions from suspension is related to size and density and to the viscosity and temperature of the suspension medium. To separate out a particular particle size, a suspension can be centrifuged for a given time depending on the temperature of the medium. The supernatant then contains particles of the required size and finer. This procedure was followed to obtain the $< 2 \mu\text{m}$ size fraction. The required material was removed from suspension by centrifuging for about 1 hour or until the supernatant was clear. The unwanted liquid was discarded and the solid was mixed with a drop of distilled de-ionised water. A few drops of the mixture were placed on one half of a clean glass slide and smeared as before. The smear was left to dry at room temperature.

A.4.iii Quantitative determination of clays using X-ray diffraction

The relative proportions of the clay minerals were determined using the method of Weir *et al.* (1975) in their study of Nile Delta clays. The procedure takes the 7.1 \AA kaolinite reflection as an internal standard and recommends that diffractometer traces are recorded from Ca and

Mg-saturated specimens, dried in air, solvated in ethylene glycol at 20°C and heated to 300°C to collapse expanding minerals to 10 Å.

For quantitative analyses oriented specimens of the < 2 µm fraction are used. In this work, the samples were prepared as a smear in the manner described above. The intensities of mineral reflections were measured using peak areas. This was achieved by tracing peak shapes onto good quality draughting film and then cutting them out for weighing; the masses of the cuttings were recorded as representations of mineral reflections.

Following Weir et al. (1975), the intensities were adjusted by simple proportion to equalise that of kaolinite from the three traces (air dry, glycolated and heated for each sample). The proportion by weight of the mineral phases were then calculated using the simplifying assumptions:

(1) On a weight for weight basis, expanding minerals collapsed to 10 Å and give the same reflection intensity as illite.

(2) Chlorite gives a reflection twice the intensity of illite.

(3) Kaolinite gives a reflection 2.5 times the intensity of illite.

Hence, from normalised intensities:

I_I	gave the proportion of illite
$I(I + Ex) - I_I$	gave the proportion of expandable component
$I_K/2.5$	gave the proportion of kaolinite
$I_{chl}/2$	gave the proportion of chlorite

The relative percentages were then calculated. Weir et al. (1975), however, considered that the results were only reproduceable to within 20% of the amounts present.

This method was rapid for the determination of the relative proportions of clay minerals in a sample but the accuracy was clearly questionable.

A.5.1i Precautions

X-ray fluorescence is a very reliable method of analysis providing the general operating conditions and preparation procedures recommended by Norrish & Hutton (1969) are adhered to. Perhaps the most common source of error occurs during the weighing of the disc components which gives erroneous analysis totals. The accuracy and reproducing of analyses is also influenced by the quantity of unstable components in samples, including alkali chlorites, sulphur, carbonates and organic matter. All samples were oven-dried before fusion to avoid excessive vapourisation of water and various treatments were carried out to reduce losses from other volatile substances.

Preleaching of samples suspected of containing problematic alkali chlorites improved subsequent analysis tools. Pre-igniting material with large quantities of organic matter or carbonate removes much of the troublesome components and the ignited material can be fused as usual with no further losses. Sulphur is lost completely from fusions made in graphite crucibles (Norrish & Hutton 1969). In platinum crucibles, sulphate is not lost but some other forms of sulphur may not be retained. Additional oxidising agent may be used to convert these forms to sulphate.

Even after precautions have been taken to reduce errors, duplicate tests may not give exactly the same results owing to slight variations in the weighing of constituents or from physical differences between discs. Careful preparation ensures that these differences are not of major importance provided that the rock powder used is homogeneous.

The application of matrix corrections to account for variability in absorption and enhancement of radiation is important bearing in mind sample variability and the degree of precision required. As variability increases, matrix corrections become more necessary but can only improve

results significantly where experimental errors are much smaller than the corrections. In the spectrometer used in these investigations, matrix corrections were pre-programmed using Philips proportionality factors.

A.6 Determination of the chemical composition of solutions by atomic absorption spectrophotometry

The instrument used in this work was a Perkin-Elmer 460. The principles of operation are outlined in the manufacturer's handbook, Perkin Elmer (1976).

The risk of contaminating samples before analysis is very high and strict precautions were taken to reduce this possibility. All glassware, tops and pipettes were washed in chromic acid and rinsed three times in distilled water. Polythene screw top bottles were used for storing solutions due to the risk of silica release inherent with glass vessels. The utmost care was taken to keep fingers away from the sample and from surfaces which would be in contact with it due to the sensitivity of sodium determinations.

Some samples had to be diluted for the measurement of certain elements in order to maintain concentrations within the linear range of the machine calibration. The dilution factors varied for different elements and specimens.

The precipitation of iron from solution was counteracted by adding nitric acid. The combining of calcium with another anion was overcome by providing lanthanum as a competing cation. Where an element not being measured fell within the absorption spectrum of the element of interest, reduction of the radiation detector slit width or moving to a different wavelength reduced the problem.

A.7 Determination of quartz (free silica) in sediments by the method of Trostel & Wynne (1940)

Initially, the procedure proposed by Trostel & Wynne (1940) was followed exactly, including impurity corrections. Severe reproducibility problems were experienced, however, with results showing large positive errors. Several amendments were thus made to the method as follows:

(a) The method assumes that amorphous quartz does not dissolve and that silica crucibles are therefore suitable for use during the fusion stage. Platinum crucibles were used in repeat tests to eliminate the possibility of crucible dissolution.

(b) Carbonisation of filter papers was carried out over burners to facilitate better control over the speed of drying and ignition.

(c) A liner was placed in the furnace to prevent particles spalling from the sides from falling into the dishes during filter paper ignition.

(d) The permissible range of temperature during fusion was 85-90°C; at 75°C solution of silicic acid was incomplete but if boiling occurred, quartz was partially dissolved. Care was taken to avoid freezing of salts over the melt since this would prevent the subsequent procedures from working effectively. Judgement on the completeness of each stage in the procedure was subjective, however, and errors in the results were eventually attributed to this problem. The greatest source of error was thought to occur during the washing of the quartz residue with HCl and distilled water. Insufficient removal of iron and other impurities probably made a large contribution to the positive errors which arose.

APPENDIX B

DEFINITIONS OF TERMS AND DERIVATIONS OF EXPRESSIONS

B.1 Definition of shear strength in a soil

Shear strength is essentially the resistance of a soil to increasing shear strain in response to an increasing shear stress.

Figure B.1a considers the behaviour of the soil element shown in Fig. B.1b which is subjected to a simple shear force, τ , and a normal compression force, σ_n . As the applied shear stress increases, the resistance of the element to deformation also increases. At the yield point, significant plastic strain begins to occur and the increase in resistance to total deformation can only continue to a limited extent. When the maximum shear stress that the element can withstand has been reached (τ_{max}), failure occurs and with continued strain the shearing resistance decreases until a nearly constant residual shear strength develops.

The same failure pattern is observed in soil masses under the influence of shearing stresses. The initial peak, or maximum strength is due to particle interlocking and perhaps some physical bonding. After failure, many bonds have been broken and platy particles may become re-orientated to positions which offer least resistance to the applied shear stresses. The source of residual shear strength is, therefore, mainly frictional forces along the shear surface.

It is convenient to consider shear strength as consisting of two components, cohesion, c , and friction which is usually expressed as $\sigma_n \tan \phi$, where σ_n is normal stress and ϕ is the angle of shearing resistance. The derivation of these parameters is illustrated in Fig. B.2. As the normal stress in a soil increases, as it would with depth within a soil mass, the shear stress at which failure occurs also increases. This

FIG. B.1a Behaviour of a soil element subjected to shear stress relationship between shear stress and shear strain.

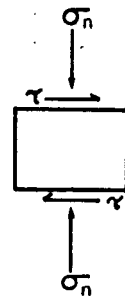
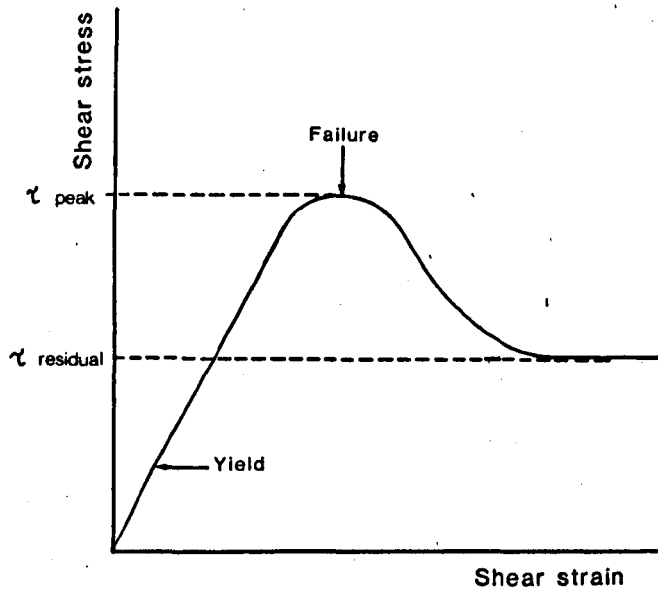


FIG. B.1b A soil element under a shear stress.

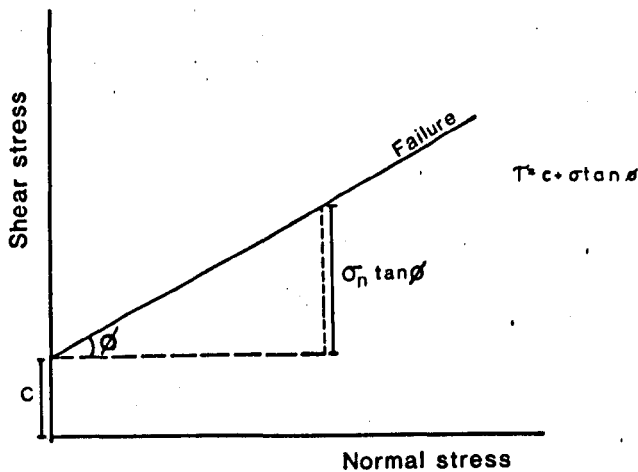


FIG. B.2 Relationship between shear stress and normal stress in a soil element undergoing shear failure.

is because the frictional properties of a soil are dependent on the normal stress. All points on the failure envelope therefore represent the combination of normal and shear stresses which will cause failure in a given mass. The relationship between the stresses is approximately linear, expressed by the Coulomb equation:

$$\tau = c + \sigma_n \tan \phi \quad \text{B1}$$

At higher σ_n , in coarse and dense materials, the failure envelope curves upwards as yield dominates over discrete shearing.

Figure B.2 shows the most common plot characteristic of a soil with both cohesion and friction properties. The c intercept represents cohesion due to particle interlocking and to the electrical forces within clays.

Cohesion is independent of normal stress. At the extremes of stress behaviour are the cohesionless soils, which may include some sands, and soils with no friction component which, it can be argued, is displayed by some clays.

Post-failure behaviour of a soil mass is controlled by the residual condition and the Coulomb equation is simply expressed in terms of residual shear strength parameters:

$$\tau_r = c_r + \sigma_n \tan \phi_r \quad \text{B2}$$

The general Coulomb equation is only valid for dry soils, however, because the presence of water modifies the transmission of normal stresses through the solid material. This is taken into account by considering effective stresses. Stresses applied to a saturated soil will be borne partly by the porewater and partly at intergranular contacts. Increasing the normal load reduces pore space and so increases the porewater pressure. The magnitude of the pressures depends on drainage conditions. The normal stress is corrected for this in terms of the effective stress, σ' , where

$$\sigma' = \sigma_n - u$$

B3

σ_n is total normal stress

u is porewater pressure

Equation B1 (Coulomb equation) is redefined as

$$\tau = c + (\sigma_n - u) \tan \phi$$

$$\tau = c' + \sigma' \tan \phi'$$

B4

where c' and ϕ' are cohesion and angle of shearing resistance with respect to effective stress. The corresponding residual parameters are c'_r and ϕ'_r . The effective stress modification is thought to be sufficiently accurate for all practical purposes and is approximately valid for a wide variety of materials and conditions of loading (Scott 1980).

When porewater pressures are fully dissipated, effective stress is equal to the total normal stress, hence shear strength tests are frequently carried out under fully drained conditions.

It is possible to increase the strength of a soil by suction pressures or negative porewater pressures. This will occur in the presence of thin films of water between particles through capillary and surface tension forces.

B.2 Derivation of c_v , coefficient of consolidation

Consolidation is defined by Terzaghi & Peck (1967) as a gradual decrease in water content at constant load. The coefficient of consolidation, c_v , indicates the rate of dissipation of porewater pressures in a consolidating sample. c_v is required in calculations to determine the maximum strain rate for which a sample will remain fully drained during shear tests (see section B.1).

Consider a small soil sample undergoing compression in a vertical direction (Fig. B.3).

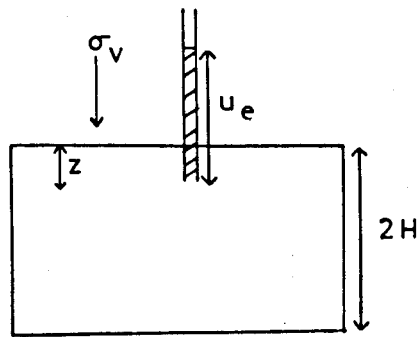


Fig. B.3 Vertical section through a thin horizontal slice of a consolidating layer.

Various assumptions are necessary to derive c_v :

- (a) Consolidation takes place in one dimension;
- (b) Flow of porewaters is only in a vertical direction;
- (c) Strain is only in a vertical direction;
- (d) The horizontal dimension over which a change in volume of the soil occurs is very great compared with the thickness of the specimen.

This one dimensional problem is the simplest case and assumes also that total stress is constant with time, i.e.

$$\frac{d\sigma_v}{dt} = 0$$

Initial excess pore pressures are supposed to be uniform with depth and drainage occurs at both the top and bottom of the consolidating stratum.

These conditions are met providing that the vertical stress is applied in a time that is very small compared with the consolidation time so that literally no consolidation occurs before loading is complete.

The total vertical stress at any point will then be constant during the consolidation process.

For this problem, Lambe & Whitman (1979) showed how it is convenient to convert Terzaghi's consolidation equation (Equation B5) by introducing non-dimensional variables, Z and a time-factor, T.

$$c_v \frac{d^2 u_e}{dz^2} = \frac{du_e}{dt} - \frac{d\sigma_v}{dt} \quad \text{B5}$$

where c_v is coefficient of consolidation

u_e is excess pore pressure

z is depth

t is time

σ_v is total vertical stress

$$\text{Let } Z = \frac{z}{H} \quad \text{B6}$$

$$\text{and } T = \frac{c_v t}{H^2} \quad \text{so that } c_v = \frac{TH^2}{t} \quad \text{B7}$$

where z and H are measured from the top of the consolidating stratum and where

H is half the thickness of the consolidating stratum

T is a non-dimensional time factor

$$\text{Equation B5 becomes } \frac{d^2 u_e}{dZ^2} = \frac{du_e}{dT} \quad \text{B8}$$

$$\text{where } \frac{d\sigma_v}{dt} = 0$$

Of particular interest is the total compression of the stratum at each stage of the consolidation process which may be found by summing the vertical compressions at the various depths. This compression is conveniently expressed by the average consolidation ratio, U:

$$U = \frac{\text{compression at time-factor } T}{\text{compression at end of consolidation}}$$

Now, for Equation B8 a solution is needed which satisfies the following conditions:

initial condition at $t = 0$

$$u_e = u_o \text{ for } 0 < Z < 2 \quad \text{where } u_o \text{ is initial excess pore pressure}$$

boundary condition at all t

$$u_e = 0 \text{ for } Z = 0 \text{ and } Z = 2$$

The solution is

$$u_e = \sum_{m=0}^{\infty} \frac{2u_o}{M} ((\sin M_Z) e^{-M^2 T}) \quad \text{B9}$$

$$\text{where } M = \frac{\pi}{2} (2^m + 1)$$

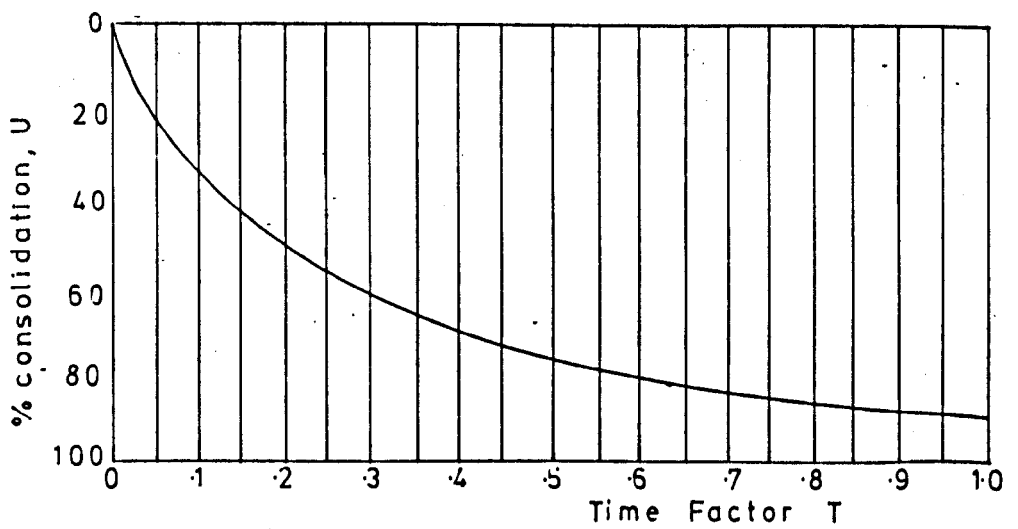
m is a dummy variable taking values 1, 2, 3 . . . (Taylor 1948).

Integration of Equation B5 gives an expression for U as a function of T which is shown in Fig. B4. Here, the consolidation ratio $U_z = 1 - \frac{u_e}{u_o}$ is graphed as a function of Z and T .

Final settlement is estimated then Fig. B4 is used to find settlement at various times during consolidation. U initially increases rapidly but the rate of settlement then slows. Since U approaches 1 asymptotically, theoretically consolidation is never complete.

B.3 Calculation of c_v

For each specimen to be tested, a separate determination of c_v is required. This is achieved by monitoring settlement of a sample after loading under a particular normal stress. The investigation is carried out either in a consolidation apparatus, called an oedometer, or in



U : average consolidation ratio

$$U = \frac{\text{compression at time } T}{\text{compression at end of consolidation}}$$

FIG. B.4 Average consolidation ratio, U , plotted against Time Factor, T (after Lambe & Whitman 1979, p. 411).

shear strength testing equipment prior to the commencement of shearing. Settlement generally takes place in two stages which are distinguished from their different rates of consolidation. Primary consolidation is relatively rapid and is usually completed after 24 hours, although it may be extended to 48 hours or occasionally longer (Akroyd 1964). Secondary consolidation is much slower and occurs because the mineral skeleton of a sample has time-dependent stress-strain properties. The effects of this secondary stage are generally very small and are not accounted for in the calculations to determine c_v .

The change in thickness of a sample with time is obtained during one increment of load. In practice, the form of the compression curve is similar to the theoretical curves but does not fit exactly the models that are predicted by consolidation theory. Fitting methods are therefore used to give the best possible estimates for c_v .

The primary consolidation curve may be approximated by a square-root time curve or a logarithmic curve. Construction is based on that part of the curve which is required to determine times to 50% consolidation (t_{50}) and 90% consolidation (t_{90}) for the log method and square root time method respectively. In each case, total settlement is found by extrapolation.

Both procedures contain arbitrary steps that compensate for differences between observed and theoretical behaviour. A correction for the zero point is usually required because of seating errors or because air may be trapped in the consolidating sample, and arbitrary determination of 50%, 90% and 100% consolidation is required since compression has the continued secondary stage after excess pore pressures have been dissipated.

The two methods, however, yield different results. The square root method usually gives larger values for c_v and is therefore the preferred method in strain rate calculations.

Square-root method

The square-root based consolidation curve is shown in Fig. B5. It comprises an initial steep section which approximates a straight line followed by a curved lower part with a shallower gradient. The observed curve is corrected by drawing a tangent to the straight line portion to intersect the vertical axis at zero time. This intersection defines d_s , the corrected zero point. A second line is drawn through d_s with an inverse slope of gradient 1.15 times that of the first tangent. Theoretically, this line should cut the observed compression curve at 90% compression, hence the t_{90} can be found.

Now, from the curve of U against T in Fig. B4, a value for T of 0.848 is found at 90% compression. Substitution of this value in Equation B7 gives

$$c_v = \frac{0.848 H^2}{t_{90}} \quad \text{B10}$$

c_v can thus be computed by substituting t_{90} in Equation B10.

Log method

The log based consolidation curve is shown in Fig. B6. Typically, the curve consists of two straight line portions connected by a curved section. The observed curve is adjusted by drawing two tangents to the straight portions. Intersection of these curves defines the point at which 100% consolidation is assumed (d_{100}). The corrected zero point, d_s , is located by laying off above 0.1 minutes point, a distance equal to the vertical distance between this point and one at which the time is 4 times greater. 50% compression is defined halfway between d_s and d_{100} .

Referring to Fig. B4, T takes a value of 0.197 for 50% compression, hence substitution in Equation B7 gives

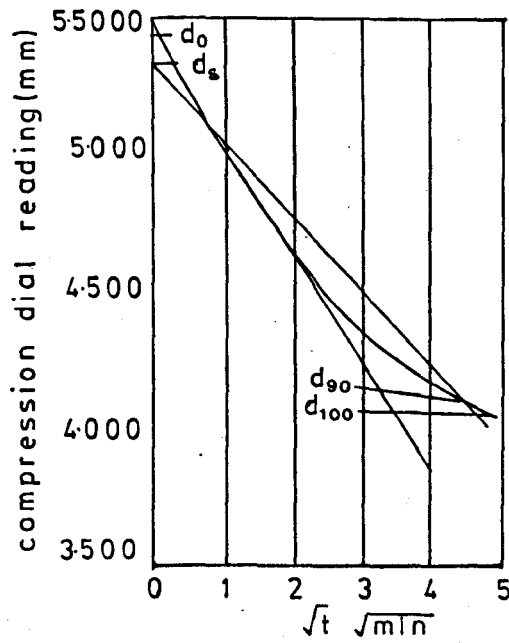


FIG. B.5 Consolidation curve - square root base (from Lambe & Whitman 1979, p. 412; after Taylor (1948)).

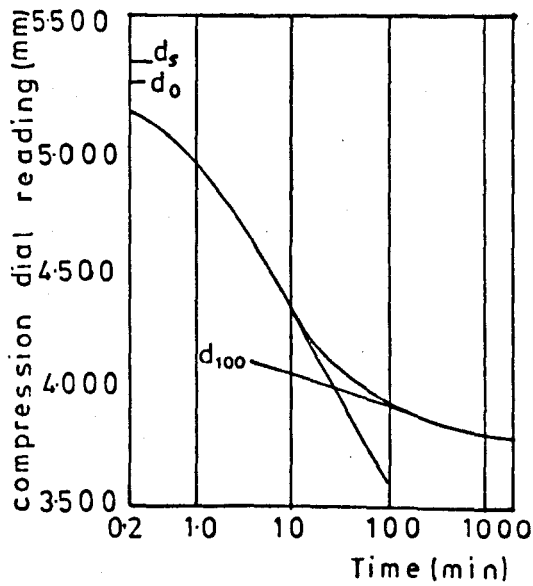


FIG. B.6 Consolidation curve - logarithmic base (from Lambe & Whitman 1979, p. 412; after Taylor (1948)).

$$c_v = \frac{0.197 H^2}{t_{50}}$$

B11

c_v is calculated using Equation B11.

B.4 Calculation of the strain rate

Once full dissipation of excess porewater pressures has occurred the effective stress borne by a sample is equal to the total normal stress. c_v is now used to determine the maximum strain rate for which a sample will remain fully drained during shearing.

First, the time to failure, t_d , is required and is calculated from consolidation theory (Gibson & Henkel 1954; Bishop & Gibson 1963). The average degree of consolidation at failure is expressed:

$$\bar{U}_f = 1 - \frac{H^2}{\eta c_v t_f} \quad \text{B12}$$

where \bar{U} is average degree of consolidation

H is half height of sample

c_v is coefficient of consolidation

η is a factor depending on drainage conditions at sample boundaries

t_f is time to failure

A theoretical degree of pore pressure dissipation of 95% is sufficient to ensure a negligible error in measured strength. The requisite time to failure may be written:

$$95\% = 1 - \frac{H^2}{\eta c_v t_f}$$

$$\rightarrow \frac{H^2}{\eta c_v t_f} = 1 - 0.95$$

$$\rightarrow \frac{H^2}{\eta c_v t_f} = 0.05$$

$$\begin{aligned} \rightarrow \quad t_f &= \frac{H^2}{0.05 \eta c_v} \\ \rightarrow \quad t_f &= \frac{20H^2}{\eta c_v} \end{aligned} \quad \text{B13}$$

In the Bromhead Ring Shear Apparatus which was used in this work for measuring shear strength, the sample is drained from both the top and bottom. For this condition, η has a value of 3 (Bishop and Henkel 1978).

Substituting in Equation B13, the expression becomes:

$$t_{fd} = \frac{20H^2}{3c_v} \quad \text{B14}$$

where t_{fd} is time to failure under drained conditions. The rate of strain is found from Equation B15.

$$R = \frac{E_{fd}}{t_{fd}} \quad \text{B15}$$

where R is strain rate.

E_{fd} is maximum strain under fully drained conditions.

A value of E_{fd} may have to be assumed if it has not been previously determined in shear strength tests on the same material.

B.5 Calculation of strain rate for single drainage

For single drainage, η has a value of 0.75 (Bishop & Henkel. 1978).

$$t_{fd} = \frac{H^2}{0.038 c_v} \quad \text{B16}$$

For rate of strain, Equation B15 is used.

B.6. Derivation of the shear stress calculation for the Bromhead Ring Shear Apparatus

Conventionally, when residual shear stress has been reached, the distribution of shear stress across the sample is assumed to be uniform. The torque T , transmitted through the sample is:

$$T = \text{Force} \times \text{Area} \times \text{Radius}$$

where $T = \text{torque}$. T is summed over the radius $R_1 \rightarrow R_2$, where R_1 and R_2 denote inner and outer radius of the sample respectively:

$$T = \int_{R_1}^{R_2} (2\pi R^2) dR \quad \text{where } \tau = \text{shear stress}$$

$$T = \frac{2\pi}{3} \left[R^3 \right]_{R_1}^{R_2}$$

$$T = \frac{2\pi}{3} (R_2^3 - R_1^3) \quad \text{B17}$$

Since the torque is given by the mean load on the proving rings multiplied by the distance between them, torque can also be expressed as:

$$T = \frac{(F_1 + F_2)L}{2} \quad \text{B18}$$

where F_1 and F_2 are the loads on the proving rings

L is the length of the torque arm

Equation B17 can be rewritten as:

$$\tau = \frac{3T}{2\pi(R_2^3 - R_1^3)} \quad \text{B19}$$

Substituting Equation B18 into Equation B19, a working expression for shear stress is obtained:

$$\tau = \frac{3(F_1 + F_2)L}{4\pi(R_2^3 - R_1^3)} \quad \text{B20}$$

B.7 Derivation of expression for residual angle of friction

The normal effective stress on the sample can be written:

$$\sigma' = \frac{P}{\pi(R_2^2 - R_1^2)}$$

where σ' = normal effective stress

p = normal load

Now, from $\tau_r = c_r' + \sigma_n \tan \phi_r'$, $\tan \phi_r' = \frac{\tau_r}{\sigma_n}$, assuming $c_r' = 0$

$$\rightarrow \tan \phi_r' = \frac{3(F_1 + F_2)(R_2^2 - R_1^2)L}{4(R_2^3 - R_1^3)P}$$

B21

B.8 Derivation of conversion factor, degrees to millimetres, for the Bromhead Ring Shear Apparatus

Sample holder rotation is measured in degrees.

Average circumference of soil sample is:

$2\pi r$ where r is the average radius of the soil annulus

Outer radius = 50 mm

Inner radius = 35 mm

thus the average circumference is $\frac{170\pi}{2}$ mm

Each degree of rotation is $\frac{170\pi}{2 \times 360}$ mm

$$= \underline{0.742 \text{ mm degree}^{-1}}$$

B.9 Definition of the factor of safety

The factor of safety (F) is a standard of comparison between the restraining and sliding forces acting on a soil mass. The definition given by Scott (1980) is expressed as:

$$\tau = \tau_f / F \rightarrow F = \frac{\tau}{\tau_f}$$

B.22

which means that F measures the factor by which shear strength would have to be reduced to bring a structure to a state of collapse,

$F < 1$ signifies that the structure is unstable

$F = 1$ indicates that the structure is in a critical state on the point of failure

$F > 1$ shows that the structure is stable

A simplified Bishop conventional method was used to estimate a factor of safety for Mam Tor. In this method, a cross-section of the slope under consideration is divided into a number of slices. Each slice is treated as shown in Fig. B7.

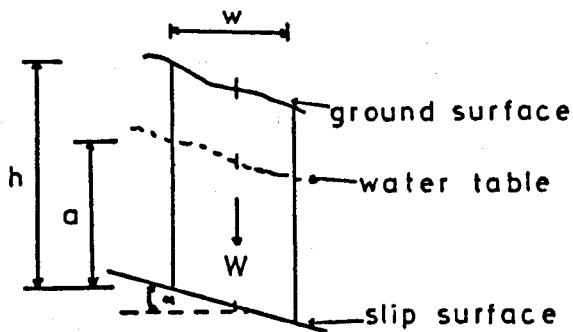


FIG. B7 Slice used for the determination of Factor of Safety by the Bishop Conventional Method.

The factor of safety is calculated using equation B23

$$F = \frac{\sum(W \cos \alpha - u)}{\sum(W \sin \alpha)} \tan \phi'$$

where W = weight of soil mass = $\gamma h w$

and γ = soil density

h = height of slice

w = width of slice

α = angle of slip surface to horizontal
within slice area

u = porewater pressure = $a w \gamma_w$

and γ_w = unit weight of water = 1.0 Mg m^{-3}

a = height of water table in slice

ϕ' = effective angle of friction

Cohesion is assumed to be 0 kN m^{-2}

REFERENCES

- AKROYD, T.N.W. (1964). Laboratory Testing in Soil Engineering. Geotech., Monograph No. 1, 233 pp.
- ALLEN, J.R.L. (1960). The Mam Tor Sandstones: a turbidite facies of the Namurian deltas of Derbyshire. J. Sed. Petrol., 30, 193-208.
- APTED, J.P. (1977). Effects of weathering on some geotechnical properties of London Clay. Ph.D. Thesis, Univ. of London.
- ASHBY, D.A. & PEARSON, M.J. (1978). Mineral distributions in sediments associated with the Alton Marine Band near Penistone, South Yorkshire. International Clay Conference 1978, Developments in Sedimentology, 27, Elsevier, Ed. by Mortland, M.M. & Farmer, V.C.
- ATTEWELL, P. & TAYLOR, R.K. (1971). Investigations, tests and experiments on the mechanical strength and breakdown characteristics of certain overconsolidated clay shales. Interim and final reports on DA-ERO-591-70-G002, European Research Office, U.S. Army.
- BADGER, C.W., CUMMINGS, A.D. & WHITMORE, R.L. (1956). The disintegration of shales in water. J. Inst. Fuel, 29, 417-423.
- BARNHISEL, R.I. & ROTROMEL, A.L. (1974). Weathering of clay minerals by simulated acid coal spoil-bank solutions. Soil Sci., 118, 22-27.
- BELL, F.G. (Ed) (1978). Foundation engineering in difficult ground. Butterworth & Co. Ltd., Ch. 6 Taylor, R.K. Properties of mining wastes with respect to foundations, 175-203.
- BELL, F.G. (1980). Engineering Geology and Geotechnics, Newnes-Butterworth. Ch. 5, Foundations for buildings, 199-248.
- BÉRARD, J. (1970) Black shale heaving at Ottawa, Canada: Discussion. Can. Geotechn. J., 7, 113-114.
- BERKOVITCH, I., MANACKERMAN, M. & POTTER, N.M. (1959). The shale breakdown problem in coal washing. Part 1: Assessing the breakdown of shales in water. J. Inst. Fuel, 32, 579-589.

- BERNER, R.A. (1978). Rate control of mineral dissolution under earth-surface conditions. Am. J. Sci., 278, 1235-1252.
- BISHOP, A.W. (1967). Progressive failure - with special reference to the mechanism causing it. Proc. Geot. Conf. Oslo, Vol.II, 142-150.
- BISHOP, A.W. (1973). Stability of some tips and spoil heaps. Q. Jl. Engng Geol., 6, 335-377.
- BISHOP, A.W. & GIBSON, R.E. (1963). The influence of the provisions for boundary drainage on strength and consolidation characteristics of soils measured in the triaxial apparatus. ASTM STP 361 (Laboratory shear testing of soils), 435-451.
- BISHOP, A.W., GREEN, G.E., GARGA, V.K., ANDRESEN, A. & BROWN, J.D. (1971). A new ring-shear apparatus and its application to measurement of residual strength. Geotechnique, 21, 273-328.
- BISHOP, A.W. & HENKEL, D.J. (1978). The measurement of soil properties in the triaxial test. Arnold, 2nd Edn., pp. 189.
- BISHOP, A.W., WEBB, D.L. & LEWIN, P.I. (1965) Undisturbed samples of London Clay from the Ashford Common Shaft: Strength - effective stress relationships. Geotechnique, 15, 1-31.
- BJERRUM, L. (1954). Geotechnical properties of Norwegian Marine Clays. Geotechnique, 4, 49-69.
- BJERRUM, L. (1967). Progressive failure in slopes of overconsolidated plastic clay and clay shales. J. of the Soil Mechs. and Found. Div. ASCE 93, SM5 Proc. Paper 5456, Sept., 1-49.
- BLATT, H., MIDDLETON, G. & MURRAY, R. (1972). Origin of sedimentary rocks. Prentice-Hall, 2nd Ed. London.
- BOLT, G.H. (1956). Physico-chemical analysis of the compressibility of pure clays. Geotechnique, 6, 86-93.
- BOLT, G.H. & MILLER, R.D. (1956). Compression studies of illite suspensions. Proc. Soil Sci. Soc. Amer., 19, 285-288.

- BORROWICKA, H. (1965). The influence of the colloidal content on the shear strength of clay. Proc. 6th Int. Conf. Soil Mech., Montreal, 1, 175-178.
- BRITISH STANDARDS INSTITUTION (1975). Methods of test for soils for civil engineering purposes. B.S. 1377, 1975, GR10.
- BROMHEAD, E.N. (1978). Large landslides in London clay at Herne Bay, Kent. Q. Jl. Engng. Geol., London, 11, 291-304.
- BROMHEAD, E.N. (1979). A simple ring-shear apparatus. Ground Engineering, 12, 40-44.
- BUIST, D.S., BURNETT, A.D. & SANDERS, M.K. (1979). Engineering properties and slope stability of Lower Coal Measures rocks from Monk Wood cutting, Unstone-Dronfield Bypass, Derbyshire. Engng. Geol., 14, 11-28.
- BURWELL, E.B. (1950). Geology in dam construction, Part I (article in Applications of geology to engineering practice, Berkey Volume). Geol. Soc. Am., 11-31.
- BUSENBERG, E. & CLEMENCY, C.V. (1976). The dissolution kinetics of feldspars at 25°C and 1 atm. CO₂ partial pressure. Geochim. Cosmochim. Acta, 40, p. 41.
- CANCELLI, A. (1977). Residual shear strength and stability analysis of a landslide in fissured overconsolidated clays. Bulletin of the Intern. Assoc. of Engng. Geol. Symposium No. 16, Landslides and Other Mass Movements, 193-197.
- CHAPMAN, S.L., SYERS, J.K. & JACKSON, M.L. (1969). Quantitative determination of quartz in soils, sediments and rocks by pyrosulfate fusion and hydrofluosilicic acid treatment. Soil Sci., 107, 348-355.
- CHANDLER, R.J. (1969). The effect of weathering on the shear strength properties of Keuper Marl. Geotechnique, 19, 321-334.

- CHANDLER, R.J. (1972). Lias clay: weathering processes and their effect on shear strength. Geotechnique, 22, 403-431.
- CHATTOPADAHYAY, P.K. (1972). Residual shear strength of some pure clay minerals. Ph.D. Thesis, University of Alberta, Edmonton.
- CHRISTENSEN, F.W. (1970). Isotropic tensional and compressional strain patterns in tabular shaped bodies. Proc. 2nd Congress Int. Soc. Rock Mechs., Belgrade 1, 265-269.
- CHRUKHROV, F.V., ZVYAGIN, B.B., ERMILOVA, L.P. & GORSHKOV, A.I. (1972). New data on iron oxides in the weathering zone. Proc. Int. Clay Conf., Madrid, 397-404.
- COLLINSON, J.D. & WALKER, R.G. (1967). Namurian sedimentation in the High Peak. In Geological Excursions in the Sheffield Region, University of Sheffield, 80-89. Ed. R. Neves & C. Downie.
- COOK, M.G. & RICH, C.I. (1963). Negative charge of dioctahedral micas as related to weathering. Proc. Clays & Clay Mins. 11th National Conf., 47-65.
- COOKE, R.V. (1979). Laboratory simulation of salt weathering processes in arid environments. Earth Surface Processes, 4, 347-359.
- COOKE, R.V. & DOORNKAMP, J.C. (1974). Geomorphology in Environmental Management: An introduction. Clarendon Press, Oxford, 379 pp.
- COOKE, R.V. & SMALLEY, I.J. (1968). Salt weathering in deserts. Nature, 220 (5173), 1226-1227.
- CRIPPS, J.C. & TAYLOR, R.K. (1981). The engineering properties of mud-rocks. Q. J. Eng. Geol., London, 14, 325-346.
- CURTIS, C.D. (1976a). Stability of minerals in surface weathering reactions: A general thermochemical approach. Earth Surface Processes, 1, 63-70.
- CURTIS, C.D. (1976b). Chemistry of rock weathering: fundamental reactions and controls. In Geomorphology and Climate, Ed. Derbyshire, E., London, Wiley,

- CURTIS, C.D. (1977). Sedimentary geochemistry: Environments and processes dominated by an aqueous phase. Philos. Trans. Roy. Soc. London, A286, 353-372.
- CURTIS, C.D., LIPSHIE, S.R., OERTEL, G. & PEARSON, M.J. (1980). Clay orientation in some Upper Carboniferous mudrocks, its relationship to quartz content and some inferences about fissility, porosity and compactional history. Sedimentology, 27, 333-339.
- CURTIS, C.D. & SPEARS, D.A. (1968). The formation of sedimentary iron minerals. Economic Geology, 63, 257-270.
- DAVIS, A.G. (1967). Mineralogy and phase equilibrium of Keuper Marl. Q. Jl. Engng. Geol., London, Vol.1, 25-38.
- DIBBLE, W.E. & TILLER, W.A. (1981). Non-equilibrium water/rock interactions, 1. Model for interface controlled reactions. Geochim. Cosmochim. Acta, 45, No. 1, 79-92.
- DIDYK, B.M., SIMONEIT, B.R.T., BRASSELL, S.C. & EGLINTON, G. (1978). Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature, 272, 216-222.
- DUMBLETON, M.J. (1967). Origin and mineralogy of African Red Clays and Keuper Marl. Q. Jl. Engng. Geol., London, Vol.1, 39-45.
- DUMBLETON, M.J. & WEST, G. (1966). Some factors affecting the relation between the clay minerals in soils and their plasticity. Clay Minerals, 6, 179-193.
- EARLY, K.R. & SKEMPTON, A.W. (1972). Investigations of the landslides at Walton's Wood, Staffordshire. Q. Jl. Engng. Geol., London, 5, 19-41.
- EVANS, L.J. & ADAMS, W.A. (1975). Chlorite and illite in some Lower Palaeozoic mudstones of mid-Wales. Clay Mins., 10, 387-397.
- FASISKA, E.J., WAGENBLAST, H. & DOUGHERTY, M.T. (1974). The oxidation mechanism of sulphide minerals. Bull. of the Assoc. of Engng. Geologists, Vol. XI, No. 1.

- FEIGENBAUM, S. & SHAINBERG, I. (1975). Dissolution of illite - a possible mechanism of potassium release. Proc. Soil Sci. Soc. America, 39, 985-990.
- FLEMING, R.W., SPENCER, G.S. & BANKS, D.C. (1970). Empirical study of behaviour of clay shale slopes. (two volumes). U.S. Army Engineering Nuclear Cratering Group, Livermore, California.
- FOSTER, D.H. & GAZZARD, I.J. (1975). The influence of polymeric hydroxy-aluminium cations on the consolidation, shear strength and consistency limits of clay soils. Geotechnique, 25, 513-525.
- GEOLOGICAL SOCIETY ENGINEERING GROUP (1970). The logging of rock cores for engineering purposes. Working Party report. Q. Jl. Engng. Geol., London, 3, 1-24.
- GIBBS, R.J. (1965). Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. Am. Miner., 50, 741-751.
- GIBSON, R.E. & HENKEL, D.J. (1954). Influence of duration of tests at constant rate of strain on measured 'drained' strength. Geotechnique, 4, 6-15.
- GOULD, J.P. (1960). A study of shear failure in certain Tertiary marine sediments. Proc. Res. Conf. Shear Strength Of Cohesive Soils (A.S.C.E.) June, 615-642.
- de GRAFT-JOHNSON, J.W.S., BHATIA, H.S. & VEBOAH, S.L. (1974). Some swelling characteristics of the marine shales of Accra, Ghana. Proc. 3rd Int. Conf. 'expansive soils', Haifa, Israel, Jerusalem. Academic Press, Vol. 2, 55-63 (Abstract).
- GRATTAN-BELLEW, P.E. & EDEN, W.J. (1975). Concrete deterioration and floor heave due to biogeochemical weathering of underlying shale. Can. Geot. J., 12, 372-378.
- GRAY, D.H. (1970). Electrochemical hardening of clay soils. Geotechnique, 20, 81-93.

- GRIM, R.E. (1968). Clay Mineralogy, 2nd Edition. International Series in Earth and Planetary Sciences, McGraw Hill, 596 pp.
- GRIM, R.E. (1962). Applied Clay Mineralogy. International Series in the Earth Sciences, McGraw-Hill.
- de HAAN, F.A.M., BOLT, G.H. & PIETERS, B.G.H. (1965). Diffusion of K^{40} into illite during prolonged shaking. Soil Sci. Soc. America Proc., 29, 528-530.
- HAEFELI, R. (1965). Creep and progressive failure in snow, rock, soil and ice. Proc. 6th Int.Conf.Soil. Mech., Found. Eng. Montreal, Vol.3, 134-148.
- HEDBERG, H.D. (1936). Gravitational compaction of clays and shales. Amer. Jour. Sci. Ser. 5, 31, 241-281.
- HELEY, W. & MacIVER, B.N. (1971). Engineering properties of clay shales. Report 1: Development of classification indexes for clay shales. U.S. Army Engineer Waterways Experimental Station, Vicksburg, Mississippi Technical Report S-71-6.
- HENDERSON, W.H. & CARSON, M.A. (1978). Changes in the plasticity of a sample of Champlain Clay after selective chemical dissolution to remove amorphous material. Can. Geot. J., 15, 609-617.
- HENKEL, D.J. & SKEMPTON, A.W. (1954). A landslide at Jackfield, Shropshire, in a heavily overconsolidated clay. Geotechnique, 5, 131-137.
- HEPWORTH, R.C. (1965). Heaving in the subgrade of highways constructed on the Mancos Shale. Trans. Soc. Min. Eng., June, 124-141.
- HERMAN, H.G. & WOLFSKILL, L.A. (1966). Residual shear strength of weak shales. Technical Report No. 3-699. Engineering properties of nuclear craters, Report 5, Cambridge, Massachusetts, Massachusetts Institute of Technology, 37 pp.
- HERSTUS, J. (1971). Influence of weathering on effective values of shear strength of Miocene Clay. Proc. 4th Conf. on Soil Mechanics & Foundation Engineering, Budapest, 135-142.

- HUTCHINSON, J.N., SOMERVILLE, J.H. & PETLEY, D.J. (1973). A landslide in periglacially disturbed Etruria Marl at Bury Hill, Staffordshire. Q. Jl. Engng. Geol., London, 6, 377-404.
- JACKSON, M.L. (1963). Interlayering of expansible layer silicates in soils by chemical weathering. 11th National Conf. on Clays & Clay Mins.
- JOHNSON, S.J. (1969). Report of Chairman of Speciality Session No. 10, Engineering Properties and Behaviour of Clay Shales. Proc. of the 7th International Conf. Soil Mechs. Found. Eng., Vol. 3, p. 483.
- KELLER, W.D. (1957). Principles of chemical weathering. Lucas Bros., Columbia, Missouri,
- KELLER, W.D. (1963). Diagenesis in clay minerals - a review. Clays & Clay Mins., 13, 136-157.
- KENNARD, M.F., KNILL, J.L. & VAUGHAN, P.R. (1967). The geotechnical properties and behaviour of Carboniferous shale at the Balderhead Dam. Q. Jl. Engng. Geol., London, 1, 3-24
- KENNEY, T.C. (1967). The influence of mineral composition on the residual strength of natural soils. Proc. Geot. Conf. Oslo, Vol. 1, 123-129.
- KENNEY, T.C., MOUM, J. & BERRE, T. (1967). An experimental study of bonds in a natural clay. Proc. Geotech. Conf. Oslo, Vol. 1, 65-69.
- KIDDER, G. & REED, L.W. (1972). Swelling characteristics of hydroxy-aluminium interlayered clays. Clays & Clay Mins., 20, 13-20.
- KONDNER, R.L. & VENDRELL, J.R. (1963). Clay mineral effects on the stress-strain response of soils in direct shear. Proc. 11th National Conf. Clays & Clay Mins., 252-268.
- KRAUSKOPF, K.B. (1967). Introduction to Geochemistry, McGraw-Hill, 719 pp.
- KUBITSCHKEK, H.E. (1960). Electronic measurement of particle size. Research, 13, 128-136.

- KUENEN, P.H. (1941). Geochemical calculations concerning the total mass of sediments in the earth. Amer. Jour. Sci., 239, 161-190.
- KUZNETZOV, S.I., IVANOV, M.V. & LYALIKOVA, N.N. (1963). Introduction to Geological Microbiology, McGraw-Hill Co., 252 pp.
- LA GATTA, D.P. (1970). Residual strength of clays and clay-shales by rotation shear tests. Harvard Soil Mechanics Series, No. 86, Harvard University, Cambridge, Massachusetts.
- LAGUROS, J.G., SUBODH KUMAR & ANNAMALAI, M. (1974). A comparative study of simulated and natural weathering of some Oklahoma shales. Clays & Clay Minerals, 22, 111-115.
- LAMBE, T.W. (1958). The engineering behaviour of compacted clay. J. Soil Mech. & Fdn. Div. ASCE Proc., Vol. 84, SM2, 1-35.
- LAMBE, T.W. & WHITMAN, R.V. (1979). Soil Mechanics, S.I. Version Series in Soil Engineering, J. Wiley & Sons, USA.
- LAMMERTON, S. (1982). Unpublished undergraduate thesis, Department of Botany, University of Sheffield.
- LEIN, A.Y. (1978). Formation of carbonate and sulphide minerals during diagenesis of reduced sediments. In Krumbein, W.E., Environmental Biogeochemistry and Geomicrobiology, Vol. 1, The Aquatic Environment, 339-354, Ann Arbor Science.
- LEUSSINK, H. & MÜLLER-KIRCHENBAUER, H. (1967). Determination of the shear strength behaviour of sliding planes caused by geologic features. Proc. Geotech. Conf. Oslo, Vol. 1, 131-137.
- LI, C.H. (1978). Some effects of salt concentration in the porewaters on mechanical properties of some clays. M.Sc. Thesis, University of Wales.
- LIN, F.C. & CLEMENCY, C.V. (1981a). Dissolution kinetics of phlogopite, I. Closed system. Clays & Clay Minerals, 29, No. 2, 101-106.
- LIN, F.C. & CLEMENCY, C.V. (1981b). The kinetics of dissolution of muscovites at 25°C and 1 atm. CO₂ partial pressure. Geochim. Cosmochim. Acta, 45, 571-576.

- LOUGHNAN, F.C. (1973). Chemical weathering of the silicate minerals, Elsevier, New York
- LOVE, L.G. (1965). Micro-organic material with diagenetic pyrite from the Lower Proterozoic Mount Isa shale and a carboniferous shale. Proc. Yorks. Geol. Soc., 35, 187-202.
- LOW, P.F. & MARGHEIM, J.F. (1979). The swelling of clay, I. Basic concepts and empirical equations. Soil Sci. Soc. Amer. J., 43, 473-481.
- LUPINI, J.F., SKINNER, A.E. & VAUGHAN, P.R. (1981). The drained residual shear strength of cohesive soils. Geotechnique, 31, 181-213.
- McKEE, E.D. & WEIR, G.W. (1953). Terminology for stratification and cross-stratification in sedimentary rocks. Bull. Geol. Soc. of America, 64, 381-390.
- MARTIN, R.T. & LAMBE, T.W. (1956). Soil composition and its influence on the engineering behaviour of fine-grained soils. Clay Minerals Bulletin, 3, 137-150.
- MATSUO, S. (1957). A study of the effect of cation exchange on stability of slopes. Proc. 4th International Conf. on Soil Mechs. & Found. Engng., London.
- MEAD, W.J. (1936). Engineering geology of dam sites. Trans. 2nd Int. Congr. Large Dams, Washington D.C., 4, 183-198.
- MESRI, G. & OLSON, R.E. (1970). Shear strength of montmorillonite. Geotechnique, 20, 261-270.
- MITCHELL, J.K., SINGH, A. & CAMPANELLA, R.G. (1969). Bonding, effective stresses and strength of soils. Proc. ASCE Journal of the Soil Mech. and Foundations Div., Vol. 95, No. SM5, 1219-1246.
- MOORE, R.M., BURTON, J.D. & WILLIAMS, P.J. le B. (1979). The behaviour of dissolved organic material, iron and manganese in estuarine mixing. Geochim. Cosmochim. Acta, Vol. 43, No. 6, 919-926.

- MORGANSTERN, N.R. (1967). Shear strength of stiff clay. Proc. Geot. Conf. Oslo, Vol.11, 59-69, Norwegian Geotechnical Institute, 1968.
- MORGENSTERN, N.R. & EIGENBROD, K.D. (1974). Classification of argillaceous soils and rocks. Proc. J. Geol. Div. Amer Soc. Civ. Engrs. 100, 1137-56.
- MORGANSTERN, N.R. & TCHALENKO, J.S. (1967a). Microscopic structures in kaolin subjected to direct shear. Geotechnique, 17, 309-328.
- MORGANSTERN, N.R. & TCHALENKO, J.S. (1967b). Microstructural observations on shear zones from slips in natural clays. Proc. of the Geotech. Conf. 1967, Oslo, Vol.1, 147-152.
- MOUM, J., LØKEN, T. & TORRANCE, J.K. (1971). A geochemical investigation of the sensitivity of a normally consolidated clay from Drammen, Norway. Geotechnique, 21, 329-340.
- MOUM, J. & ROSENQVIST, I.TH. (1961). Mechanical properties of montmorillonitic and illitic clays related to electrolytes of the porewater. Proc. 5th International Conference on Soil Mechanics and Foundation Engineering, Paris, Vol. 1, 263-267.
- NAGARAJ, T.S. & RAO, S.N. (1973). Influence of clay composition and system chemistry on residual strength of saturated remoulded clays. Indian Geotechnical Journal, 4, 161-173.
- NAKANO, R. (1967). On weathering and change of properties of Tertiary mudstones related to landslides. Soil and Foundation, 7, 1-14.
- NELSON, J.D. & THOMPSON, E.G. (1974). Creep failure of slopes in clays and clay shale.. Symp. Soil Engng & Engng. Geol., April 1974, 177-195.
- NIXON, P.J. (1978). Floor heave in buildings due to the use of pyritic shales as fill material. Chemistry & Industry, 4, 160-164.
- NORMAN, L.E.J. (1958). A comparison of values of liquid limit determined with apparatus having bases of different hardness. Geotechnique, 8, 79-183.
- NORRISH, K. (1954). The swelling of montmorillonite. Trans. Faraday Soc., 18, 120-134.

- NORRISH, K. (1972). Factors in the weathering of mica to vermiculite. Proc. Int. Clay Conf. Madrid, 417-432.
- NORRISH, K. (1973). Forces between clay particles. Proc. Int. Clay Conf. Madrid, Ed. Serratosa, J.M., Division de Ciencias, C.S.I.C.
- NORRISH, K. & HUTTON, J.T. (1969). An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochim. Cosmochim. Acta, 33, 431-453.
- OERTEL, G. & CURTIS, C.D. (1972). Clay-ironstone concretion preserving fabrics due to progressive compaction. Geol. Soc. Am. Bull., 83, 2597-2606.
- OLLIER, C.D. (1969). Weathering - Geomorphology Text 2. Oliver & Boyd, pp. 304.
- OLSON, R.E. & MITRONOVAS, F. (1962). Shear strength and consolidation characteristics of calcium and magnesium illite. Clays & Clay Minerals, 9, 185-209.
- PACES, T. (1978). Reversible control of aqueous Al and Si during the irreversible evolution of natural waters. Geochim. Cosmochim. Acta, 42, 1487-1493.
- PARRY, R.H.G. (1972). Some properties of heavily overconsolidated Oxford Clay at a site near Bedford. Geotechnique, 22, 485-507.
- PENNER, E., EDEN, W.J. & GILLOTT, J.E. (1966). Floor heave due to biochemical weathering of shale. Proc. 8th Int. Conf. Soil Mech. Found. Engng., Moscow 2, 151-158.
- PENNER, E., EDEN, W.J. & GRATTAN-BELLEW, P.E. (1972). Expansion of pyritic shales. Canadian Building Digest, Division of Building Research, National Research Council of Canada, 152.1-152.4.
- PERKIN-ELMER (1976). Analytical methods for atomic absorption spectrophotometry. Perkin-Elmer, September 1976.

- PETLEY, D.J. (1966). The shear strength of soils at large strains. Ph.D. Thesis, University of London.
- PETROVITCH, R. (1981). Kinetics of dissolution of mechanically comminuted rock-forming oxides and silicates. Geochim. Cosmochim. Acta, 45, 1665-1674.
- PETTIJOHN, F.J. (1975). Sedimentary Rocks, 2nd Edition, Harper & Row, 628 pp.
- POTTER, P.E., MAYNARD, J.B. & PRYOR, W.A. (1980). Sedimentology of Shale Study Guide and Reference Source, Springer-Verlag, New York, Heidelberg, Berlin. 306 pp.
- POWERS, M.C. (1959). Adjustment of clays to chemical change and the concept of the equivalence level. Clays & Clay Minerals, 2, 309-326.
- POWERS, M.C. (1967). Fluid-release mechanisms in compacting marine mud-rock and their importance in oil exploration. Am. Assoc. Petrol. Geol. Bull., 51, 1240-1254.
- PRIOR, D.B. & GRAHAM, J. (1974). Landslides in the Magho district of Fermanagh, Northern Ireland. Engng. Geol., 8, 341-359.
- QUIGLEY, R.H. & VOGAN, R.W. (1970). Black shale heaving at Ottawa, Canada. Can. Geot. J., 7, 106-113.
- RAISWELL, R. (1971). The growth of Cambrian and Liassic concretions. Sedimentology, 17, 147-171.
- RAMIAH, B.K., DAYALU, N.K. & PURUSHOTHAMARAJ, P. (1970). Influence of chemicals on residual strength of silty clay. Soils and Foundations, 10, 25-36.
- RAMSBOTTOM, W.H.C., STEVENSON, I.P. & GAUNT, G.D. (1967). Fossiliferous localities in the Namurian rocks of Edale. In Geological excursions in the Sheffield region, University of Sheffield, 75-80. Ed. Neves & Downie.
- REICHE, P. (1950). Quoted in Loughnan, F.C. (1973), Chemical Weathering of the Silicate Minerals, Elsevier, p. 1. New York.

- RETHATI, L. (1971). Correlations associated with liquid and plastic limits of soils. Proc. 4th Conf. on Soil Mechanics, Budapest, 273-282.
- ROSENQVIST, I.Th. (1955). Investigations in the clay-electrolyte water system. Norwegian Geotechnical Institute, Publ. No. 9.
- ROSENQVIST, I.Th. (1962). The influence of physico-chemical factors upon the mechanical properties of clays. Clays & Clay Minerals, 9, 12-27.
- RUSSELL, D.J. & PARKER, A. (1978). Geotechnical, mineralogical and chemical interrelationships in weathering profiles of an over-consolidated clay. Q. Jl. Engng. Geol., London, 12, 107-116
- SCHNITZER, M. & KODAMA, H. (1976). The dissolution of micas by fulvic acid. Geoderma, 15, 381-391.
- SCHWERTMANN, V. (1971). Transformation of hematite to goethite in soils. Nature, 232, 624-625.
- SCOTT, C.R. (1980). An Introduction to Soil Mechanics and Foundations, 3rd edition, Applied Science Publishers, London, 406 pp.
- SCOTT, J.S. & BROOKES, E.W. (1968). Geological and engineering aspects of Upper Cretaceous shales in Western Canada. Paper 66-37, Geological Survey of Canada, Department of Energy, Mines and Resources, Ottawa.
- SHAMBURGER, J.H., PATRICK, D.M. & LUTTEN, R.J. (1975). Design and construction of compacted shale embankments. Report No. FHWA-RD-75-61 Vol. 1 Survey of problem areas and current practices. Prepared for Federal Highways Administration, Washington D.C. (NTIS, Springfield, Virginia).
- SHAW, D.B. & WEAVER, C.E. (1965). The mineralogical composition of shales. J. Sed. Petrol., 35, 213-222.

- SHERWOOD, P.T. (1967). Classification tests on African red clays and Keuper Marl. Q. Jl. Engng. Geol., London, 1, 47-55.
- SKEMPTON, A.Q. (1964). Long-term stability of clay slopes, 4th Rankine Lecture. Geotechnique, 14, 77-102.
- SKEMPTON, A.W. & BISHOP, A.W. (1950). The measurement of shear strength in soils. Geotechnique, 2, 90-108.
- SKEMPTON, A.W. & HUTCHINSON, J.N. (1969). Stability of natural slopes and embankment foundations. Proc. 7th Int. Conf. on Soil Mechs. & Foundn. Eng., Mexico, 291-340.
- SKEMPTON, A.W. & PETLEY, D.J. (1967). The strength along structural discontinuities in stiff clays. Proc. Geotech. Conf. Oslo, 2, 29-46.
- SPEARS, D.A. (1964). The major element geochemistry of the Mansfield marine band. Geochim. Cosmochim. Acta, 28, Vol. 2, 1679-1696.
- SPEARS, D.A. (1969). A laminated marine shale of Carboniferous age from Yorkshire, England. J. Sed. Petrol., 39, 106-112.
- SPEARS, D.A. (1976). The fissility of some Carboniferous shales. Sedimentology, 23, 721-725.
- SPEARS, D.A. (1980). Towards a classification of shales. J. Geol. Soc. London, 137, 125-129.
- SPEARS, D.A. (1981). Classification of fine-grained sedimentary rocks - Discussion. J. Sed. Petrol., 51, 1031-1032.
- SPEARS, D.A. & AMIN, M.A. (1981). Geochemistry and mineralogy of marine and non-marine Namurian black shales from the Tansley Borehole, Derbyshire. Sedimentology, 28, 407-417.
- SPEARS, D.A. & KANARIS-SOTIRIOU, R. (1975). Titanium in some Carboniferous sediments from Great Britain. Geochim. Cosmochim. Acta, 40, 345-351.
- SPEARS, D.A. & TAYLOR, R.K. (1972). The influence of weathering on the engineering properties of in situ Coal Measure rocks. Int. J. Rock Mech. Min. Sci., 9, 729-756.

- SPEARS, D.A., TAYLOR, R.K. & TILL, R. (1971). A mineralogical investigation of a spoil heap at Yorkshire Main Colliery. Q. Jl. Engng. Geol., London, 3, 239-252.
- STEWART, H.E. & CRIPPS, J.C. (1983). Some engineering implications of chemical weathering of pyritic shale. Q. J. Eng. Geol., London, 16, 281-289
- STOW, D.A.V. (1981). Fine-grained sediments: Terminology. Q. Jl. Engng. Geol., London, 14, 243-244.
- STRUTHERS, P.H. (1964). Chemical weathering of strip mine spoils. Ohio Journal of Science, 64, 125-131.
- SUBRAMANIAM, A.S. & CARR, R.W. (1983). A55 Pwll Melyn slip and remedial works: a case history. Q. Jl. Engng. Geol., London, 16, 53-63.
- TALME, O.A. (1968). Clay sensitivity and chemical stabilisation. Rapport från Bygghorsknigen Stockholm, Report 56, 192 pp.
- TAYLOR, A.W. (1959). Physico-chemical properties of soils: ion-exchange phenomena. J. Soil Mech. & Fdn. Div. Proc. ASCE, 85, SM2, 19-30.
- TAYLOR, R.K. (1973). Letter to the Editor: Investigation of the landslide at Walton's Wood, Staffordshire (1972). Q. Jl. Engng. Geol., 7, 101.
- TAYLOR, R.K. (1978). Properties of mining wastes with respect to foundations. In Bell, F.G. (Ed.) Foundation engineering in difficult ground, Butterworth & Co. Ltd., 175-203.
- TAYLOR, R.K. & SPEARS, D.A. (1970). The breakdown of British Coal Measure rocks. Int. J. Rock Mech. Min. Sci., 7, 481-501.
- TAYLOR, R.K. & CRIPPS, J.C. (in press). Mineralogical controls on volume change. In Ground Movements in Engineering, Ch. 9, Ed. Attewell, P. & Taylor, R.K. Pub. Blackie, Glasgow.
- TAYLOR, R.K. & SPEARS, D.A. (1972). The geotechnical characteristics of a spoil heap at Yorkshire Main Colliery. Q. Jl. Engng. Geol., London, 5, 243-263.

- TAYLOR, R.K. & SPEARS, D.A. (1973). Discussion: Lias clay: weathering processes and their effect on shear strength. Geotechnique, 23, 132-133.
- TAYLOR, R.K. & SPEARS, D.A. (1981). Laboratory investigation of mudrocks. Q.Jl. Engng. Geol., London, 14, 291-309.
- TERZAGHI, K. & PECK, R.B. (1967). Soil Mechanics in Engineering Practice. 2nd Edn., John Wiley & Sons, New York, 729 pp.
- TILL, R.A. & SPEARS, D.A. (1969). Determination of quartz in sedimentary rocks using XRD. Clays and Clay Minerals, 17, 323-327.
- TORRANCE, J.K. (1974). A laboratory investigation of the effect of leaching on the compressibility and shear strength of a Norwegian Marine Clay. Geotechnique, 24, 155-173.
- TORRANCE, J.K. (1979). Post-depositional changes in the porewater chemistry of the sensitive marine clays of the Ottawa area, Eastern Canada. Engng. Geol., 14, 135-147.
- TOURTELOT, H.A. (1960). Origin and use of the word shale. Am. J. Sci., 258-A, Bradley volume, 335-343.
- TOURTELOT, H.A. (1979). Black Shale - its deposition and diagenesis. Clays & Clay Minerals, 27, 313-321.
- TROSTEL, L.J. & WYNNE, D.J. (1940). Determination of quartz (free silica) in refractory clays. Am. Ceramic Soc. Journal, 18-22.
- TWORT, A.C. (1964). The new Tittesworth Dam. J. Inst. Water Engineers, 18, 125-180.
- VAN BREEMAN, N. (1972). Soil forming processes in acid sulphate soils. In: Dost, H. (Ed.) Acid Sulphate Soils, Proc. Int. Symp. on Acid Sulphate Soils, Wageningen, Netherlands.
- VAN BREEMAN, N. (1973). Dissolved aluminium in acid sulphate soils and in acid mine waters. Soil Sci. Soc. America Proc., 37, 694-697.
- VAN OLPHEN, H. (1963). Introduction to Clay Colloid Chemistry. Wiley, New York, 146-153.

- VEAR, A. & CURTIS, D.C. (1981). A quantitative evaluation of pyrite weathering. Earth Surface Processes and Landforms, 6, 191-198.
- VEAR, A. (1981). The geochemistry of pyritic shale weathering within an active landslide. Ph.D. Thesis, University of Sheffield, Depts. of Geography and Geology.
- VICKERS, B. (1978). Laboratory Work in Civil Engineering; Soil Mechanics, Crosby Lockwood Staples, London, 145 pp.
- VOIGHT, B. (1973). Correlation between Atterberg plasticity limits and residual shear strength of natural soils. Geotechnique, 23, 265-267.
- WALL, G.J., WILDING, L.P. & MILLER, R.H. (1974). Biological transformations of clay sized sediments in simulated aquatic environments. Proc. 17th Conf. Great Lakes Res., 207-211.
- WARKENTIN, B.P. (1961). Interpretation of the upper plastic limit of clays. Nature, 190, 287-288.
- WARKENTIN, B.P. & SCHOFIELD, R.K. (1962). Swelling pressure of Na-montmorillonite in NaCl solutions. J. Soil Sci., 13, 98.
- WARKENTIN, B.P. & YONG, R.N. (1962). Shear strength of montmorillonite and kaolinite related to interparticle forces. Clays & Clay Minerals, 9, 210-218.
- WATTS, BLAKE, BEARNE & CO. plc (1982). Summary of technical data - Ball Clays, Plastic Clays, China Clays. October 1982, Newton Abbot, Devon.
- WEAVER, C.R. & BECK, K.C. (1975). Clay water diagenesis during burial: How mud becomes gneiss. The Geological Society of America, Sp. Pap. 134, 93pp.
- WEIR, A.H., ORMEROD, E.C. & MANSEY, I.M.I.E.L. (1975). Clay mineralogy of sediments of the western Nile Delta. Clay Minerals, 10, 369-387.
- WELLMAN, H.W. & WILSON, A.T. (1965). Salt weathering, a neglected geological corrosive agent in coastal and arid environments. Nature, 205, (4976), 1096-1098.
- WHALLEY, W.B. (1976). Properties of materials and geomorphological explanation. Theory & Practice in Geography, Oxford University Press, 58 pp.

- WINTERKORN, H.F. & MOORMAN, R.B.B. (1941). A study of changes in physical properties of Putnam Soil induced by ionic substitution. Proc. Highway Res. Board, 21, 415-434.
- WOLLAST, R. (1967). Kinetics of the alteration of K-feldspar in buffered solutions at low temperature. Geochim. Cosmochim. Acta, 31, 635-648.
- WROTH, C.P. & WOOD, D.M. (1978). The correlation of index properties with some basic engineering properties of soils. Can. Geot. J., 15, 137-146.
- WYKEHAM FARRANCE ENGINEERING LTD. The Bromhead Ring Shear WF25650.
Technical manual.
- YUALON, D.H. (1961). Mineral composition of the average shale. Clay Minerals Bulletin, 5, 31-36.
- YONG, R.N. & WARKENTIN, B.P. (1966). Introduction to Soil Behaviour, Macmillan, N.Y., 451 pp.
- YONG, R.N., SETHI, A.J. & LA ROCHELLE, P. (1979). Significance of amorphous material relative to sensitivity in some champlain clays. Can. Geotech., 16, 511-520.
- YONG, R.N., SETHI, A.J. & LA ROCHELLE, P. (1980). Significance of amorphous material relative to sensitivity in some Champlain clays: reply. Can. Geotech. J., 17, 636-638.
- ZARUBA, Q. & MENCL, V. (1969). Landslides and their control, (Elsevier, Amsterdam), 205 pp.