THE USE OF RED TROPICAL SOILS AS POZZOLANAS:
REACTIONS, PRODUCTS AND PROPERTIES

by

Charles Amobi Nwakanma, B.Eng (Civil)

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Department of Civil Engineering
The University of Leeds

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ABSTRACT

Nineteen red tropical soils from the States of Paraiba and Pernambuco which are located in the North East of Brazil were treated with high calcium lime, they reacted showing a wide range of variation of maximum unconfined compressive strengths with 4.5% or 6.0% lime generally required to produce maximum strength.

The reaction between the soil and lime is mainly a diffusion controlled process. Most of the reaction takes place within five to seven days and the reaction within this period obeys Jander's diffusion equation for solid state reactions. Based on the constant rate of reaction obtained from this equation and on the quantity of the reactive components of the soil, an activity index, A_i, is proposed and its validity tested against the unconfined compressive strength of the soil-lime system. A valid statistical correlation is presented linking A_i value with the empirical reactivity parameter of Thompson.

Identification of the types of the reaction products by x-ray diffraction which is greatly aided by the use of a semi-automated computer search program reveals that the soils form cementitious reaction products varying from dense and close textured calcium silicates of the tobermorite-like type through alumino-silicates to calcium alumino-ferri-silicates with relatively larger voids when the soils are treated with lime and cured for two years at 22°C. The increase in strength of the soil-lime system not only depends on the volume of the reaction products but also on their types and purity.

Other constituents of the soil-lime system affect the strength to varying degrees. While the increase in the amount of unreacted material at the expense of cementitious reaction products is not desirable, an amount of unreacted material is essential for other engineering requirements other than strength to be satisfied. Unlike other cemented composites, the strength of the soil-lime system is not related to the overall porosity of the system.

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CHAPTER 1

INTRODUCTION

Approximately one-third of the land surface of the earth is contained within the huge belt limited by the tropics of Cancer and Capricorn. Befitting attention is now being given to tropical weathering and the resulting soil products which are the dominant features of the landscape.

The nomenclature of the soils of the tropics has increased not only in size but in complexity. The confusion and controversy originated by the very nomenclature proposed by researchers in their desire to precisely define these materials have led to underutilization of the data gathered on their hehaviour. Terms like laterite, lateritic soil, latosol, ferricrete, ferruginous soil, ferrisol, oxisol, ferrasol, etc. have been used for the same type of material in one case and applied to various types of materials in other cases.

Attempts have been made to find common grounds for agreement. However, most of the attempts have not drawn a clear distinction between classification and nomenclature. To the engineer, it is enough that nomenclature be an ordered system of naming which reflects peculiar physical properties of the soils while classification be a tool for predicting their engineering behaviour. Hence in this work, use is made of the term "red tropical soils" and this is broadly a soil which fits the definition of "laterite" given by Sivarajasingham et al (1). Thus it includes 'highly weathered material (a) rich in secondary forms of iron, aluminium or both; (b) poor in humus; (c) depleted of bases and combined silica; (d) with or without non-diagnostic substances such as quartz, limited amounts of weatherable primary minerals or silicate clays ...." The term "laterite" is restricted to the original definition given by Buchanan (2) who wrote " ... it is full of cavities and pores and contains a very large quantity of iron in the form of red and yellow ochres. In the mass, while excluded from the air, it is so soft that any iron instrument readily cuts it, and is dug up in square masses with a pick axe, and is immediately cut into the shape wanted with a trowel or large knife. It very soon after becomes as hard as a brick.... As it is usually cut into the form of bricks for building, in several of the native dialects it is called the brickstone (Itica cullu) ... The most proper English name would be Laterite, from lateritis, the appelation that may be given to it in Science."

However, the word "laterite" will also appear where passages are quoted from works in which the term is used.

Red tropical soils have been used to a large extent on a "trial and error" basis. They have been used successfully as subgrades and as sub-bases or bases of low quality; in some instances the aggregates comprising red tropical soils have served as suitable mineral components of concrete and asphalt.

Their availability and abundance make them very attractive as sources of "stabilized" or improved engineering materials. To improve their engineering properties and expedite construction they are usually treated with cement, lime and rarely bitumen. Reports of successful treatments as well as failures are abundant. There is no doubt that contradictory results have their origin in the empirical nature of the techniques employed for their improvement.

This is particularly true of the use of lime to upgrade the engineering properties of red tropical soils. Although the studies of lime-soil systems are numerous for temperate soils, knowledge of the response of tropical soils to lime treatment is scanty and limited. Like any other branch of applied science, progress on the efficient and economic use of red tropical soil-lime systems will only be possible when the fundamental mechanisms of the reactions and the nature of the reaction products are properly elucidated. This will provide a basis for adequate technology for maximising the successful utilization of the lime treated soils under varying conditions and permit more refined engineering decisions to be made.

CHAPTER 2

GENERAL LITERATURE REVIEW

Each chapter of this thesis is commenced with a review of pertinent literature and methods. This chapter therefore summarises literature on some aspects of pedology and engineering behaviour of the soils.

2.1 Genesis and Composition

Red tropical soils can be formed in-situ or transported. When formed in-situ, parent rocks like basalt, sandstone and schist are decomposed under a warm and humid climate of the tropics (3,4,5,6). Expansion and contraction associated with high and low temperatures which occur during the dry and wet seasons respectively, leave cracks in huge masses of rocks through which warm surface water rich in carbon dioxide and bacteria filter. This chemically active water decomposes the rocks (aluminous silicates). An upward suction of moisture to the surface in the dry season and drainage of rainwater over the gentle and moderate relief of the tropics remove the dissolved minerals of the parent rock in solution. This process of relative accumulation is called leaching. The residuum comprises minerals like aluminium, iron, titanium, manganese, chromium and vanadium oxides, quartz and clay minerals. The types of minerals depend on the parent rock (7 - 10) while their nature depends on other soil forming factors like topography, drainage and climatic - vegetational conditions.

Aluminium exists in the form of gibbsite ($\alpha Al(OH)_3$), boehmite ($\gamma AlO(OH)$) and in amorphous forms. The chemical composition of amorphous alumina and other amorphous mineral constituents of red tropical soils are not known.

Iron occurs commonly as goethite ($\alpha Fe_2O(OH)$), haematite (αFe_2O_3), lepidocrocite ($\gamma FeOOH$). Maghemite (γFe_2O_3) and magnetite (γFe_3O_4) have also been reported (9, 11).

Titanium minerals include rutile, anatase and ilmenite. Chromium and vanadium are resistant primary minerals and their oxides can be present in small amounts depending on the type of the parent rock unlike manganese oxide which readily goes into solution in acidic conditions and is subject to removal by leaching. However, concentrations of manganese in forms like lithiophorite and birnessite are present or occur where drainage is poor or it is absent. Silica occurs as quartz, which can be residual or alluvial, and in the amorphous form. The clay mineral that occurs most commonly in the soils is the 1:1 type, i.e., kaolinite and/or halloysite. Kitagawa et al (12) and Yoshinaga and Aomine (13) have reported allophane (poorly defined combinations of silica and sesquioxides usually regarded as hydrates of alumino silicates (14, 15)) as the dominant clay mineral of young volcanogenous soils (soils derived mainly from pyroclastic materials) occuring in the tropics. Solid state reaction within an amorphous gel has been postulated to be the process of formation of kaolinite (16) with a slow rate of crystallisation. On the other hand, Kitagawa (15) postulated, from calculations of the chemical composition of allophanes, that halloysite could be the end member of the amorphous - allophane series. This and the fact that metahalloysite is difficult to distinguish from kaolinite suggests that the clay reported as kaolinite by many could be metahalloysite especially where such clay occurs alongside amorphous minerals. Illite and montmorillonite are rare in red tropical soils.

Further complications arise when the distribution and nature of the minerals within the profile are considered. There is little agreement by pedologists on the mechanism responsible for the distribution of the minerals. The concept of the soil as a residuum with relative immobile constituents was modified by a second phase of formation which involves the resolution of the residuum by groundwaters. The recognition of pallid zones underlying some of the soils led to the concept of red tropical soils as precipitates. The enriched zone was believed to be caused by the precipitation of iron and alumina in solution, with capillarity and the seasonal fluctuations of the water table being the mechanisms responsible for this (7, pp. 91 - 108). Thomas (17) postulated the removal of "rock alteration products" from deep within by ionic diffusion as a possible mechanism. Recent models proposed include the detritus models and those which compromise between the residuum and precipitation concepts.

It is difficult, if not impossible to discount groundwater as an important factor which determines the nature and type of some of the constituents of red tropical soils (18, 19). Harder (19) found among other things, for synthetic clay mineral formation that:

a) amorphous hydroxides of Al, Fe, Mn, Mg, Zn, Co, Ni, etc., are capable of coprecipitating SiO_2 even from very dilute (weathering) solutions.

b) the most important factor for silica mineral formation is the silica concentration in the solution which should not be too high or too low. Silica minerals form only in those precipitates from solutions undersaturated with respect to amorphous silica (100 ppm SiO_2 at 20°C); lower silica content allows formation of quartz or feldspar while higher contents makes the precipitate stay amorphous even after long ageing times.

c) a sufficiently slow rate of precipitation is necessary for the synthesis of clay minerals. The precipitation can be as a result of changing pH. These findings suggest that in tropical conditions clay minerals cannot be formed in the wet season since the silica content of the groundwater is generally very low whereas their formation is possible during the dry season below the water table level. The presence of allophanes and/or amorphous minerals is an indication that during their formation the silica content of the groundwater was too high for quartz or clay mineral formation.

2.2 Classification

Geologists, pedologists, agriculturalists and engineers are interested in different aspects of behaviour of the soils and consequently have classified them from their professional view points. This is reflected in the great volume of work devoted to classification which unfortunately is confusing and of limited use to a civil engineer. Ideally, a classification should serve not only as a tool to transmit information but also as a tool to predict behaviour when experience is not available.

Early attempts to classify red tropical soils used chemical content as a basis. Martin and Doyne (20) introduced the concept of silica - alumina ratio as a measure of laterization; a concept that has since been modified. Dury (21) named duricrusts on the basis of their chemical content, the name being compounded from those of the minerals present, thus:-

Silitic	SiO_2
Siallitic	SiO_2, Al_2O_3
Fersilitic	Fe_2O_3, SiO_2
Fersiallitic	Fe_2O_3, FeOOH, SiO_2, $Al_2O_3nH_2O$, AlOOH
Ferrallitic	Fe_2O_3, FeOOH, $Al_2O_3nH_2O$, AlOOH
Ferritic	Fe_2O_3, FeOOH
Fermagnitic	Fe_2O_3, MnO_2
Tiallitic	TiO_2, $Al_2O_3nH_2O$,
Allitic	$Al_2O_3nH_2O$, AlOOH

These are at the best systems of nomenclature as they lack scientific precision. They have not taken into account the following which influence any classification with engineering validity.

a) Pedological and geological factors such as parent rock, genesis and environment.

b) The type and, more important, nature of the mineralogical constituents of the soil "for it is the form in which the chemical contents occur which varies consistently in accordance with the physical properties of the soils" (7, pp. 17).

D'Hoore (22) used the terms ferruginous, ferralitic and ferrisol to describe these soils depending solely on climatic conditions, using annual rainfall intensity as a measure. Lyon Associates (9) noted that most of the samples they tested showed a good correlation between the index properties and D'Hoore's pedological classification. Their other report (10) related South American soils to the FAO - UNESCO classification which is a compromise retaining some traditional pedological terms like pedosols and recent popular terms like vertisols and andosols. These classifications can only be used as a very rough guide to the properties of the soils.

Attempts by engineers to use particle size and plasticity, which have proved adequate classification parameters for temperate zone soils, have been unsuccessful because the conventional methods for determining these parameters do not yield reproducible results (4, 5, 6, 23 - 28). This has led to a search for other consistent parameters for classification of red tropical soils. De Graft-Johnson et al (18) and Gidigasu (29) have shown that 'lateritic gravels' and fine grained 'laterite' soils can be classified on the basis of geology, amount of clay, linear shrinkage and climatic conditions while Wesley (28) showed that basic engineering properties are related more closely to mineralogical composition than to pedological classification. It thus seems that for any single quantifiable parameter to be suitable for classifying these soils, it must incorporate the intrinsic and apparently extrinsic properties of the soils. Such apparent extrinsic properties are climatic condition or the behaviour of the soils in an environment of particular conditions.

2.3 Physical and engineering characteristics

2.3.1 Texture

Variations in particle size distribution with methods of pretreatment and testing which have been widely reported can be accounted for by a number of reasons. Wet sieving, for instance, has been shown to increase the silt and clay fraction from 7% to 20% (30) while the dispersant used affects the percentage of the clay fraction. The problem does not seem to be with dispersion but preventing the dispersed particles from re-flocculating (28), hence Quinones (31) found that a halloysitic clay from Kenya dispersed with sodium oxalate gave 20% to 30% clay fraction but with sodium hexametaphosphate gave 40% to 50%. The sedimentation test is further affected by the method of drying. Moh and Mazhar (23) reported less clay in oven dried samples than in air-dried or as received samples with increased silt and sand fraction. Most workers believe that the coarse fractions of the soils result from micro-aggregations of the clayey constituents by sesquioxides (4, 25, 27). Pretreatments like wet sieving, dispersion and remoulding dismembers some of the aggregations into finer clayey clusters due to the friable nature of the sesquioxidic cementing agents while drying results in an irreversible process of dehydration of the amorphous constituents and hydrated halloysite with the free iron and alumina cementing and coagulating the clay particles (24, 25, 28). The indurated soils are less affected by pretreatment than the fine grained soils although they (indurated soils) have high content of fines and therefore do not fit into the classification system for temperate zone coarse-grained soils.

2.3.2 Atterberg Limits

The nature of the predominant clay mineral influences the levels of plasticity of the soils (9). For example, montmorillonitic tropical clays of Ghana were found to plot above the A-line while the halloysitic clays over volcanic ash plot below the A-line although both are very plastic. However, the coarse grained soils show a less erratic plasticity characteristics; most plot above the A-line with liquid limits generally below 60%. Apart from the nature of the clay it is also observed that the position of the sample within the soil profile influences the plasticity (32). Due to differential weathering, movement and deposition of dissolved materials, the variation of plasticity with depth is very difficult to predict even in two similar profiles on different topographical sites.

Another problem associated with the determination of Atterberg limits is the effect of pretreatment and handling. Sherwood (33) found that the liquid limit increased with increased working while the plastic limit was not significantly affected. The usual explanation is that remoulding or working breaks down the aggregations of clay particles by sesquioxides. While remoulding could break down friable and weak aggregations of clays, it does not seem likely that the average energy associated with mixing can break down the normal bond between the clay and sesquioxides. It has also been suggested that mixing affects the allophanes and amorphous constituents by releasing the water held in the structure of these minerals (28, 34). This explanation also seems to fall short of the energy input required to release water held in minerals.

Drying is said to partially or completely convert the clay fraction to a non-reactive silt-like fraction with reduction or total loss of plasticity (8). Gidigasu (27) noted that wet forest zone materials and deep layer dry savanah zone soils are more sensitive to changes in plasticity than highly dessicated top soils from the dry savanah zone when they are dried. Red tropical soils generally have low colloidal activity.

2.3.3 Density and compaction characteristics

When compacted from dry to wet, the dry density increases with increasing moisture content up to a maximum beyond which the dry density decreases. With increased compactive effort, the maximum dry density generally increases and the optimum moisture content generally decreases. The moisture-density relationships are influenced by factors which can be divided into two broad groups. The first group of factors derive from genesis while the second derive from pretreatment prior to testing. The failure to consider all the factors in any single study has placed limitations on the applicability of the results available on their density and compaction characteristics.

The most important genetic factor is texture or grading. This is illustrated by the fact that the gravels have maximum dry densities ranging between 1842 - 2323 kg/m^3 and optimum moisture content between 6 - 16%; while for sandy clays the maximum dry densities are 1602 - 1922 kg/m^3 and optimum moisture content 16 - 24%. The maximum dry densities for clays are generally below 1602 kg/m^3 with the optimum moisture content above 24%. Compaction breaks down weak aggregations in the soils (4, 5, 24, 35). Studies on the effect of reusing materials, which results in further breakdown of weak aggregations, on the compaction characteristics of some red tropical soils show that whereas the maximum dry density is increased, the optimum moisture content appears unaffected (35). Whether higher or lower densities are obtained after compaction depends on whether the breakdown leads to an improvement or deterioration of the grading.

Pretreatment such as drying (air or oven) affects the densities and optimum moisture contents of the soils irrespective of texture. Generally, drying gives higher maximum dry density and lower optimum moisture content than values obtained at their natural moisture contents (9, 25, 27). As has been pointed out, drying alters the state of some of the mineral constituents, irreversibly and as such the density determined from a dried sample of such soils is, in effect, for a different material. Hirashima (36) reported that for Hawaiian 'lateritic soil' formed under conditions of continuous high moisture content in the profile there was no peak when the material was compacted wet to dry but when after drying it was compacted dry to wet, a peak occurred. This illustrates the need to test samples from areas with high regular rainfall in their undried state.

2.3.4 Strength Characteristics

The strengths of red tropical soils are usually determined by unconfined compression strength test (U.C.S), California bearing ratio test (C.B.R), triaxial and penetration tests; UCS and CBR being more popular. In their untreated state, genesis and pedology influence significantly the strength of the soils. Lyons Associates (9) using D'Hoore's pedological classification (22) found that ferruginous soils have higher CBR values than ferrisols which in turn have higher values than ferrallitic soils. The most important genetic factor is texture. Unusually high internal friction has been reported for even the clayey soils (4, 24, 25, 30, 35). To evaluate the hardness of laterite concretions, Nova-Ferreira and Correia (37) proposed a hardness index which is a modified form of the fineness modulus used in assessing mineral aggregates; while de Graft-Johnson et al (18) converted grading into a single parameter called the fineness index which is a modification of the hardness index. They (18) showed a significant correlation to exist between the CBR and this index for some 'lateritic' gravels. The hardness index apparently excludes 'soft' concretions which contribute to strength despite their breakdown during compaction while the fineness index does not take into account the breakdown of the concretions.

Other genetic factors such as mineralogy and the profile position of the sample can be tied into texture as far as their effects on strength are concerned. For example, mineralogy will influence the breakdown of the aggregations during compaction manifesting in improvement or deterioration of the final texture after compaction.

2.3.5 Swelling, permeability and consolidation characteristics

Since the occurrence of swelling minerals is rare in the soils, they are not susceptible to excessive swelling. Swelling is affected by their moisture content and apparently, drying. The higher the moisture content, the less the swell while oven-dried samples prior to compaction seem to swell less than samples compacted at their natural moisture content (38).

While in-situ the porous and granular type of the soils are highly permeable but exhibit low permeabilities when compacted or remoulded (6). Typical in-situ permeability values range from 10^{-2} to 10^{-1} cm/sec but decrease to 10^{-4} to 10^{-6} cm/sec after compaction. Malomo (39) found that the strength of red tropical soils depends on the level of the stress applied and that they change from over-consolidated clay behaviour at low moisture content to normally consolidated clay behaviour at higher moisture contents. He attributed this to particle degradation. He suggested that the phenomena of breakdown of aggregations under stress occurs more readily with increase in moisture content. Hence samples with higher moisture contents will breakdown or disaggregate more than those compacted at lower moisture content.

2.4 Pozzolanic properties of red tropical soils

2.4.1 Red tropical soils as pozzolanas

BS 892 defines a pozzolana as "a naturally occuring or artificial material which has in itself little or no cementing property but which will combine with lime in the presence of water to form a stable insoluble compound having cementitious properties". Literature abound to show that most clayey soils of the tropics as well as temperate zone clays satisfy this definition. The study of the pozzolanic properties of clayey soils have generally been termed "lime soil stabilization". This term is usually associated with highway engineering simply because the soils so treated have been used in sub-bases, bases and foundations of highway structures. The additional use of red tropical soil-lime systems in parts of superstructures as blocks, bricks and in concrete (3) calls for the use of a term broader than "soil stabilization". In view of this and the fact that they satisfy the BS 892 definition given above, red tropical soils are considered as pozzolanas in this work.

2.4.2 Soil-lime reactions

2.4.2.1 Manifestations of the reactions

The reactions which occur when lime is mixed with a clayey soil in presence of water account for the changes in its engineering properties. These changes are broadly recognised as two phases:-

a) a phase resulting in improved workability and reduced plasticity (amelioration);

b) a phase resulting in strengthening (cementation). Among the many mechanisms proposed to account for amelioration are (i) flocculation due to cation exchange, (ii) carbonation, (iii) pH-dependent increase in cation exhange capacity (cec), (iv) adsorption of calcium hydroxide molecules, (v) pozzolanic reaction leading to diffuse cementation. It is unanimously agreed that "pozzolanic reaction" is responsible for the phase resulting in strengthening.

2.4.2.2 Amelioration in clays

Diamond and Kinter (40), Stocker (41) and the Transportation and Road Research Board, USA (42) have very exhaustively reviewed and summarised current opinion. Cation exchange and carbonation cannot be discounted but have been accepted as auxiliary effects, under appropriate circumstances, inadequate for the explanation of the changes associated with amelioration. They are unavoidable lime consuming processes.

Hilt and Davidson (43) in proposing the pH-dependent cec theory, which involves "a crowding of additional cation to the surfaces of the clay" after the normal cation exchange, noted that significant increase in the unsoaked strength of the soil-lime system occurs only after a certain threshold lime content is exceeded. The threshold they termed the "lime retention point". This implies that "pozzolanic reaction" (responsible for strength increase) can only take place beyond the lime retention point which is usually measured after two hours. Further clarification of the lime retention point was given by Ho and Handy (44) who observed that "lime retention requires an alkaline pH, little or no retention occurs below pH 11.0 and retention is maximum at about pH 11.75. Calcium hydroxide provides a near optimum ratio of Ca^{++} and OH^{-} ions, Mg^{++} and Na^{+} ions are relatively ineffective". They further advanced the following fundamental explanation of the lime retention point phenomena. "The cec of clays is ordinarily measured at pH 7.0. At high pH's, more cations are adsorbed, perhaps because of increasing dissociation of weakly acidic SiOH-groups exposed on clay crystal edges and is usually attributed to isomorphous substitutions in the clay mineral structure". They went on to say "The increased adsorption of Ca^{++} to clay surfaces at high pH may be the cause of better bonding between particles, evidenced by bigger flocs, higher suspension viscosity and high plastic limit". They concluded that "the lime-montmorrillonite reactions are divided into three levels. In the first, the total cec is ordinarily measured at pH 7.0. In the second, the additional lime retention is dependent on an alkaline pH. In the third, after Ca^{++} holding capacities are fulfilled, pozzolanic reaction with additonal lime can proceed".

While admitting that pH-dependent cation exchange can and does occur, Stocker (45, pp. 35) questioned the validity of the claim that this phenomenon sufficiently accounts for amolioration. He argued that pH-dependent cation exchange consumes less, much less than ½% lime if the soil pH is initially 7, less still if the pH is even greater initially. Based on Jackson's (46) identification of five ranges associated with the removal of protons from different sites (see Table 2.1) he postulated pozzolanic reaction leading to diffuse cementation as the mechanism responsible for amelioration. He stated that when pH-dependent cation exchange is maximised pH is around 10 or 11 and at this value rapid dissolution

Table 2.1 Removable protons as a function of pH (After Jackson (46)).

Range	pH	Removable protons
Range I	Approx. pH < 4.0	Exchangeable H^+ or H_3O^+
Range II	Approx. pH 4.0 - 5.6	Exchangeable Al^{+++}
Range III	Approx. pH 5.6 - 7.6	Positive hydroxyl alumina polymers (containing $Al-OH_2$ terminal groups).
Range IV	Approx. pH 7.6 - ≈ 10	Residual, weaker, $Al-OH_2$ groups in hydroxyl alumina and possibly layer silicate edges.
Range V	Approx. pH > ≈ 10	Alumino silicate dissolution reaction.

and reaction (Range V, Table 2.1) is initiated leading to generation of tiny cementitious reaction products, at, or near the edges, responsible for amelioration. He rather favours diffusion as a mode of attack than dissolution and believes lime retention point to be the quantity of lime used up in reaction in two hours by which time many of the physical changes are maximised.

The adsorption theory of Diamond and Kinter (47) recognises the reaction of lime with clay but suggests that this is preceeded by physical adsorption of calcium hydroxide molecules on to the clay surfaces, a largely reversible process. This theory is in closer agreement with that of Stocker, the difference being that while Diamond and Kinter see amelioration and strengthening as being accounted for by two distinct mechanisms, Stocker believes one mechanism is responsible for both. Current opinion therefore seems to recognise cec, carbonation and pH-dependent cec as processes that take place but each is insufficient to explain amelioration. Amelioration in clays therefore seems to be a result of one or a combination of these processes supplemented by formation of tiny reaction products.

2.4.2.3 Amelioration in red tropical soils

If amelioration in red tropical soils is not explained by the theories enumerated for clays, the deviation should be as a result of the presence of the following:-

a) the colloidal fraction (fraction less or equal to clay size consisting of clay minerals, amorphous oxides and/or allophanes).

b) the very poor crystallinity of the clays.

c) the crystalline iron compounds.

The effects of these on cec, physical adsorption and pozzolanic reaction leading to diffuse cementation theories are examined. The carbonation theory is omitted because it is independent of the three factors enumerated.

Unusually high cec have been reported for red tropical soils (48, 49, 50) which do not contain high cec crystalline clay minerals such as montmorillonite, vermiculite, and illite. Crystalline oxides of aluminium and silicon have low capacities and cannot account for this apparent abnormality nor could poor crystallinity of the clay present. The 'culprit' therefore seems to be the colloidal fraction. Fieldes et al (51) showed that the capacities of the colloidal hydrous oxides of aluminium and titanium were so high that if they are present in small quantities they could cause the high cec observed in red tropical soils. Because the differential thermal analysis curves of the laboratory precipitated colloidal hydrous oxide of aluminium contained various endothermic peaks similar to the unusual peaks of the soils, he concluded that the principal exchange material in the soils was amorphous hydrous aluminium oxide. Capacities for the colloidal hydrous oxides of iron and silica were lower but considerable. These findings imply that where allophanes are present (they have low Si/Al ratio) in the soils, high cec may be expected. Birrell et al (52) not only confirmed this expectation but further concluded that "physical adsorption of cations by soils containing allophane, palagonite and certain amorphous oxides is responsible to a greater or less extent for the apparent high cec shown by these soils...". He was led to suspect "some kind of adsorption mechanism" because he observed that the cec depended on the strength of the leaching solution and the cation used, and that the exchange complex was extremely easily hydrolysed.

It is therefore reasonable to say that cec in collodial fraction takes place and is pH-dependent because the allophanes and amorphous minerals are likely to have surfaces characterised by broken bonds (53). The exchange capacity will depend on the composition of the equilibrium liquid since the surface potential will be determined by the pH of the equilibrium liquid. This has been demonstrated by Aomine et al (54) who showed that the cec of allophane separated in an alkaline medium (pH 10.5) was about three times that of the same fraction separated in acid medium (pH 3.5). Following a method of approach similar to that of Birrell et al, Diamond and Kinter (47) concluded among other things that calcium hydroxide is physically adsorbed from solution at a very rapid rate by calcium-saturated clay and that this process which is largely reversible at very early stages is soon followed by reaction to produce calcium silicate hydrates. They measured adsorption isotherms at 5 mins. for bentonite and 10 mins. for kaolinite suspensions. It thus appears that pH-dependent cec through physical adsorption of cations takes place in the collodial fraction of red tropical soils. The question then is, is this the process responsible for amelioration or is it the begining of the process?

The answer can be found by considering the time required for amelioration in practice and that required for physical adsorption. The low concentration region of the isotherms of Diamond and Kinter fitted the B.E.T. adsorption equation theory. If 5 mins. or 10 mins. is suitable for this process in crystalline clays and

15 mins. is suitable for the determination of cec (an indirect measure of adsorption) of allophanes as shown by Aomine et al (54) then it is likely that pH-dependent cec through adsorption seems to be the initiation of the process actually responsible for amelioration. Diamond (55) demonstrated that lime reacts almost instantaneously with hydrous alumina of high specific area to generate tetracalcium aluminate hydrate. Recently, De Carvalho (56) found that while amorphous silica and alumina contents were significant, pH-dependent cec is an excellent indicator of a soil's lime reactivity. Lime reactivity is as is measured by Thompson (57) i.e. the difference between the strengths of the lime treated soil and the untreated soil. Since strengthening is a result of the formation of some cementitious reaction products, pH-dependent cec through adsorption appears therefore to be the initiation of the actual, probably one, process responsible for both amelioration and strengthening. Amelioration in red soils containing amorphous minerals appears to be a result of the rapid reaction of the collodial fraction to produce cementitious reaction products with the initiation of the process of reaction manifesting (at very early stages) in pH-dependent cec through adsorption of lime.

2.4.2.4 The reaction process

The reaction rate between soil and lime is influenced by a number of factors among which are:-

(i) the fineness or specific surface area of the minerals
(ii) solubilities of the minerals
(iii) pH of the medium
(iv) intimacy of the mix (mineral + lime)

(v) temperature.

In a practical red tropical soil-lime system, factors iii, iv, v, are controllable and since the pH depends on the percentage of lime used, factors i and ii are considered at the optimum lime % for maximum strength (pH is nearly that of saturated lime water, 12.4).

As has been suggested in the foregoing section 2.4.2.3, very rapid early reaction takes place between lime and the colloidal fraction. The mechanism is not yet clear. While investigators like Eades et al (58, 59) postulate a 'through-solution' reaction mechanism, others like Stocker (45) favour reaction through solid state transformation. The probable mechanism or combination of mechanisms responsible for strengthening in red tropical soils is a subject of Chapter 5. However, the order of reaction of the minerals can be postulated. If two minerals react, the finer one is or both are the faster is the reaction. The collodial fractions of the soils are very fine as measured by their high specific surface areas (50, 53) and hence will be more reactive than the crystalline constituents of the soil. They are also more soluble. Using a monomer model, Marion et al (60) showed that at different pH, there is considerable difference in the total soluble alumina that can exist in equilibrium with the different aluminium compounds found in soils. For instance, at a pH of 10 the total soluble alumina increases in the order of the aluminium compounds Kaolinite > Gibbsite > Halloysite > Amorphous $Al(OH)_3$. This order is significant if solubility is a measure of reactivity. From the view point of chemical composition only Kitagawa (15) concluded that halloysite may be the end member of the allophane series.

Fieldes (34) distinguished between the various forms of allophanes and indicated that they age to clay in the sequence:- allophane B → allophane AB → allophane A → metahalloysite → kaolinite. This order holds for the increasing specific surface areas of the minerals. Using solubility and specific surface areas as factors for assessing reactivity the following order of decreasing reactivity of some minerals found in red tropical soils follows:- Amorphous Si, Al > Allophanes > Metahalloysite > Halloysite > Gibbsite > Kaolinite. The role and position of crystalline iron minerals is more difficult to assess since in an alkaline medium such as that provided by red tropical soil-lime system, iron oxides are insoluble. Their roles will be considered in latter chapters.

2.4.2.5 The reaction products

Chemically, the reactions that take place when lime reacts with soil minerals can be represented by the following over simplified equations.

$$Ca(OH)_2 \rightarrow Ca^{++} + 2(OH)^- \quad \ldots \quad (2.1)$$

$$Ca^{++} + 2(OH)^- + SiO_2\text{(Soil silica)} \rightarrow CSH \quad \ldots \quad (2.2)$$

$$Ca^{++} + 2(OH)^- + Al_2O_3\text{(Soil alumina)} \rightarrow CAH \quad \ldots \quad (2.3)$$

$$\text{Kaolinite + lime} \rightarrow \text{CSH and/or CAH and/or CASH} \quad \ldots \quad (2.4)$$

$$\text{Montmorillonite + lime} \rightarrow \text{CSH and/or CASH} \quad \ldots \quad (2.5)$$

where C = CaO; A = Al_2O_3; S = SiO_2; H = H_2O; F = Fe_2O_3.

Equation (2.1) represents the dissociation of hydrated lime in water. The solubility of lime at normal temperature is low; approximately 0.20 gm/100 ml. This means that most of the lime added remain as solid particles. The dissociated and undissociated lime react with the soil minerals to produce calcium silicate hydrates, calcium aluminate hydrates and calcium aluminosilicate hydrates as indicated by equations 2.2 - 2.5. The main factors controlling the development and type of reaction products are the inherent properties and characteristics of the soil.

Reaction products identified generally as calcium silicate hydrates have been reported (58, 59, 61, 62, 63). Others have reported calcium silicate hydrates as belonging to one of the three sub-groups:

a) tobermorite gel which has a high C/S ratio and is attributed with strength gains that occur in hydrating cements.

b) CSH (1) has a low C/S ratio than tobemorite and is generally found in poor crystalline or gel form.

c) CSH (2) has a high C/S ratio but with doubtful properties (40).

Handy and Glenn (64), Ormsby (65) and Diamond et al (66) reported the formation of CSH (1) and CSH (gel). Ruff and Ho (67) went further to state that strength gain of lime-clay mixtures is due to the presence of the different phases of the complex reaction: lime + clay → CSH (gel) → CSH (2) → CSH (1) → tobermorite; the further the reaction went, the higher the strength. The formation of calcium aluminate hydrates alongside calcium silicate hydrates was also reported by some of the authors quoted. Some authors (40) have suggested that the aluminium present in some products is as a result of isomorphous substitution for silicon within the calcium silicate hydrate lattice. The identification of quaternary compounds (compounds in the lime-silica-alumina-water system) have been limited. Ariizumi et al (68) reported gehlenite, similar to that reported by Benton (69), to form at normal temperature when lime was used to treat loam soils consisting mostly of amorphous clay mineral and allophane. It thus appears that quaternary phases in which silicon and aluminium atoms occur in distinquishable lattice position are produced when lime reacts with calcined clay or with amorphous clay minerals and allophanes. It may therefore be speculated that in red tropical soils treated with lime, quaternary compounds of lime-silica-alumina and possibly lime-silica-alumina/-iron may be formed.

The reaction conditions chosen by different workers can account for the apparent differences in the reaction products reported for the same clays treated with lime. Many used pastes or systems of high liquid content, high lime/clay ratio and high curing temperatures.

2.4.3 Engineering characteristics of lime treated red tropical soils

This has been aptly summarised by de Graft-Johnson (8). The ameliorative effects have been discussed in sub-sections 2.4.2.2 and 2.4.2.3. There is a fair agreement that lime decreases the plasticity index by considerably increasing the plastic limit of the soil. The compaction characteristics of treated soils show that increasing the lime content decreases the maximum dry density and increases the optimum moisture content.

The effect of lime on strength varies according to the type and quantity of the reaction products formed. While some soils form products that increase their strengths significantly, others form products associated with small strength increase (70). Curing temperature and time affect the amount of reaction product and hence the strength. Sherwood (33) reported that red tropical soils containing high proportions of aluminium oxide may show a decrease in strength with time due to the formation of CAH_{10} and C_2AH_8 which later change to a more stable and weaker form C_3AH_6. Unless this is the only reaction product, which is unlikely, the reduction in strength may be masked by a general increase in strength. With lime treatment most red tropical soils lose the little swell they had and permeability is greatly reduced.

2.5 Chapter Summary

a) The formation of clay minerals under tropical weathering conditions is discussed and it is noted that because of the low silica content of groundwaters in the wet season, clay minerals cannot form but their formation is possible during the dry season below the water table level.

b) The reasoning that mixing releases the water held in the amorphous constituents or breaks aggregations of clay size particles to explain the changes that occur in the index properties as a result of increased mixing is questioned.

c) Red tropical soils satisfy the definition of pozzolanas and their versatile use after treatment with lime calls for the use of a term broader than "soil-stabilization" to describe the lime treatment of the soils.

d) Following the theories advanced for amelioration in clays and the explanations given for the high cation exchange capacity in red tropical soils, it is suggested that amelioration in those soils which contain amorphous minerals is due to the rapid reaction of the colloidal fraction with lime. This reaction produces cementitious products with the initiation of the process of reaction manifesting (at very early stages) in pH-dependent cation exchange possibly through adsorption.

e) Finally the order of reaction of some of the minerals in the soils is postulated viz:- amorphous silica, alumina > allophanes > metahalloysite > halloysite > gibbsite > kaolinite. These reactions could lead to the formation of quaternary compounds.

CHAPTER 3

SCOPE OF THE INVESTIGATION

The preceeding chapters show the lack of information on the fundamental properties of red tropical soils and red tropical soil-lime systems despite the actual and potential wide utilization of the soils in both the natural and lime treated states. The response of red tropical soils to lime treatment is assessed only by empirical methods. Methods with theoretical basis, tested by laboratory results are desirable; furthermore where experience is not available, as in most countries where red tropical soils occur, a simple classification system with engineering validity will be beneficial.

An understanding and eventual solution to these problems will be facilitated by the following objectives set out in this work:

a) to examine and if possible determine the mechanism of reaction between the soil and the lime,

b) to study the nature and types of the reaction products and their relative effects on the strength of soil-lime systems and,

c) to investigate the contributions, if any, of the other constituents of the red tropical soil-lime systems to strength.

It was decided to use the unconfined compressive strength (UCS) of the soil-lime systems as a measure of the effects of the reactions and reaction products since strength is one of the most important engineering properties considered in a soil-lime mixture.

The mineralogical and chemical compositions of the soils and soil-lime systems are studied using x-ray diffraction, x-ray fluorescence and thermal analysis while the micromorphology of the reaction products is assessed by scanning electron microscopy. The mechanisms of the soil-lime reactions are studied in detail and the role of the type and volume of the reaction products and quantity of other constituents of the system are assessed in relation to the changes of unconfined compressive strength.

CHAPTER 4

PROPERTIES OF THE MATERIALS USED IN THE INVESTIGATION

4.1 Introduction

The purpose of this chapter is to give a brief description of the location and environmental characteristics of the area, sampling procedure, chemical and mineralogical composition, and some of the engineering properties of the soils used. The origin and chemical composition of the lime used to treat the soils is also given.

4.2 Location and environmental characteristics of the area

The nineteen soils were collected from the states of Paraiba and Pernambuco which are located in the North East of Brazil. Figure 4.1 shows the area in relation to the world. Three distinct climatic conditions prevail over the area. A section (A in Fig. 4.2) enjoys a hot and humid climate with mean annual temperature ranging between 22°C to 26°C. Annual precipitation in this section range between 700 mm - 1500 mm with about 80% humidity. While another section (B in Fig. 4.2) is hot and humid as well, irregular rainfall (annual precipitation around 800 mm) gives it an arid characteristics. The third section (C in Fig. 4.2) is dominated by very hot climate with temperatures never below 24°C. It is semi-arid with low annual precipitation of around 400 mm.

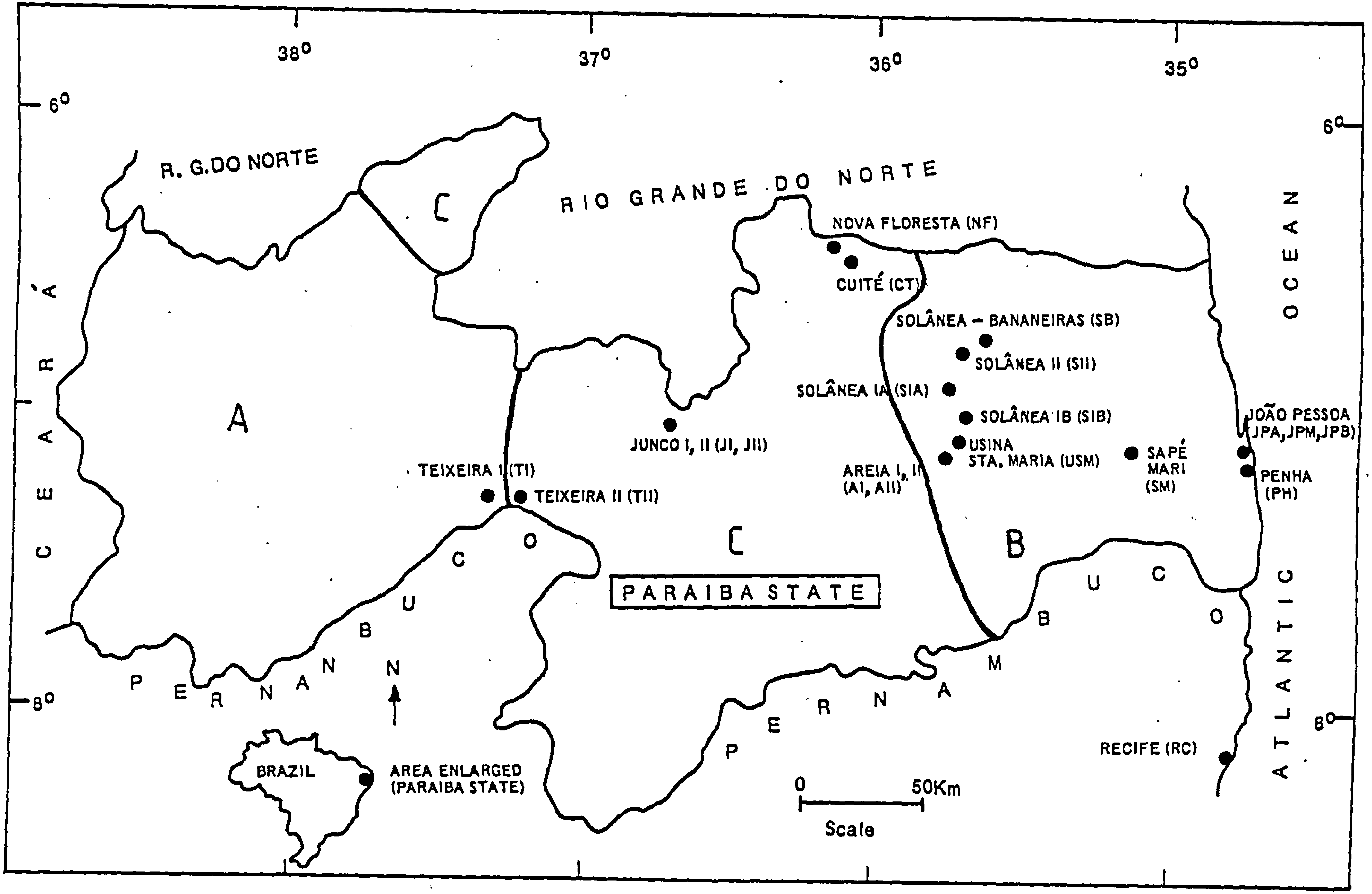
4.3 Sampling

The localities in the states of Paraiba and Pernambuco from which the samples were collected are shown in Fig. 4.2. The

Fig. 4 1 Area of research in relation to the world


TROPIC OF CANCER
EQUATOR
TROPIC OF CAPRICORN
BRAZIL
AREA OF RESEARCH

Fig. 4.2 Details of area of research showing also the climatic zones A, B, C referred to in the text


38°
37°
36°
35°
6°
8°
R. G.DO NORTE
RIO GRANDE DO NORTE
CEARÁ
OCEAN
ATLANTIC
PERNAMBUCO
A
B
C
C
NOVA FLORESTA (NF)
CUITÉ (CT)
SOLÂNEA – BANANEIRAS (SB)
SOLÂNEA II (SII)
SOLÂNEA IA (SIA)
SOLÂNEA IB (SIB)
USINA STA. MARIA (USM)
AREIA I, II (AI, AII)
SAPÉ MARI (SM)
JOÃO PESSOA (JPA, JPM, JPB)
PENHA (PH)
RECIFE (RC)
JUNCO I, II (JI, JII)
TEIXEIRA I (TI)
TEIXEIRA II (TII)
PARAIBA STATE
N
BRAZIL
AREA ENLARGED (PARAIBA STATE)
0
50Km
Scale

choice of samples was based on such factors as experience, local information and the performance of those materials that have been used in roads and dams. The samples, normally taken from the B horizon, were placed in polythene bags and sealed before being taken away for storage.

Samples were named after the towns or the nearest town from where they were taken. Throughout this study, samples are identified by the abbreviations for the names of the towns followed by roman numeral to indicate where more than one sample is collected from a town (see Table 4.1). The samples from the city of João Pessoa (JP) are identified according to their positions in the profile, i.e., A (acima = top), M (meio = middle), and B (abaixo = base); hence JPA, JPM, JPB. All the samples used for the study were less than 2 mm with the sieving done according to BS 1377 (71). Where the clay size fraction (< 0.002 mm) was needed it was obtained by sedimentation under gravity using Stoke's law and dried at 60°C to avoid possible changes in the material characteristics.

4.4 Chemical and mineralogical composition

The total silica, alumina, iron and other oxides in the clay size fraction were determined by x-ray fluorescence and the results are shown in Table 4.2. The results show that total silica and alumina each constitutes about a third of the total minerals (including water) in the clay fraction of the soils except JPA, SIA, and JII in which iron is substantial (about one third). Total iron in most of the rest of the soils account for about one-tenth of the total mineral constituents. The silica/alumina and silica/sesquioxide ratios range between 1.05 to 2.67.

Table 4.1 Nomenclature of the soils

Soil Name	Soil Symbol
João Pessoa Acima	JPA
João Pessoa Meio	JPM
João Pessoa Abaixo	JPB
Cuité	CT
Areia I	A I
Areia II	A II
Solanea IA	S IA
Solanea IB	S IB
Solanea II	S II
Nova Floresta	NF
Junco I	J I
Junco II	J II
Teixeira I	T I
Teixeira II	T II
Recife	RC
Usina S. Maria	USM
S. Bananeiras	SB
Penha	PH
Sape Mari	SM

Table 4.2 X-ray Fluorescence Analysis of the Soil-Fraction less than 0.002 mm (% by weight based on samples dried at $60^{o}C$)

Soil Symbol	% SiO_2	% Al_2O_3	% Fe_2O_3	% TiO_2	% MnO	% MgO	% CaO	% K_2O	% P_2O_5	% Na_2O	% Wt. Loss at 1000° C	Total	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{R+TiO_2}$
JPA	36.04	35.88	6.23	3.42	0.01	0.28	0.53	0.05	1.46	0.94	15.99	100.83	1.70	1.53	1.35
JPM	35.32	30.00	13.85	2.96	0.01	0.42	0.54	0.60	1.52	0.79	13.96	99.98	2.00	1.54	1.36
JPB	22.80	21.84	36.96	0.38	0.01	0.34	0.51	0.05	2.58	1.92	12.64	100.03	1.77	0.86	0.84
CT	38.40	34.20	9.85	1.65	0.00	0.41	0.57	0.30	0.15	0.34	14.61	100.48	1.90	1.61	1.51
AI	37.40	34.16	9.31	2.70	0.03	0.25	0.52	0.08	1.00	1.02	14.14	100.61	1.86	1.58	1.43
AII	35.50	34.06	8.82	2.74	0.02	0.10	0.50	0.04	1.65	1.50	14.92	99.85	1.77	1.52	1.29
SIA	36.14	31.20	7.98	1.19	0.01	0.25	0.50	0.34	2.94	1.29	17.85	99.69	1.97	1.69	1.61
SIB	31.98	20.25	30.37	1.02	0.02	0.18	0.68	0.16	2.00	1.00	13.07	100.73	2.67	1.37	1.31
SII	39.82	34.34	6.52	1.95	0.01	0.22	0.48	0.13	1.34	0.94	14.18	99.93	1.97	1.75	1.62
NF	35.06	30.86	13.56	1.98	0.01	0.15	0.53	0.16	1.83	1.18	15.00	100.32	1.93	1.50	1.39
JI	33.56	28.54	18.10	3.88	0.01	0.54	0.54	0.46	0.77	1.74	12.60	100.75	1.99	1.42	1.23
JII	26.64	20.76	34.88	1.30	0.04	0.66	0.58	0.56	1.89	0.96	12.00	100.27	2.18	1.05	1.00
TI	39.14	32.18	10.82	1.01	0.02	0.63	0.75	0.74	1.16	1.20	12.07	99.72	2.06	1.70	1.63
TII	31.38	27.48	18.31	1.36	0.01	0.33	0.53	0.81	3.53	4.14	13.01	100.89	1.94	1.36	1.29
RC	40.70	34.94	5.45	1.75	0.00	0.34	0.50	0.17	2.71	2.08	11.80	100.44	1.98	1.79	1.68
USM	40.28	34.96	4.18	2.36	0.00	0.17	0.52	0.10	0.88	0.37	15.92	99.74	1.95	1.82	1.65
SB	42.02	35.50	4.87	0.95	0.00	0.20	0.50	0.19	1.06	0.60	13.77	99.66	2.00	1.85	1.78
PH	30.92	30.86	9.50	4.00	0.02	0.30	0.59	0.09	5.34	4.12	14.76	100.50	1.70	1.42	1.21
SM	34.04	30.76	8.97	2.30	0.00	0.28	0.55	0.13	5.30	3.40	14.48	100.21	1.88	1.58	1.44

Table 4.3 shows the constituents, in the clay size fractions of the soils, which are extractable by 0.5N sodium hydroxide. The extracts represent the different minerals in the amorphous states (56). An examination of the percentages of the amorphous silica shows that there is a wide range of values from 2% for SIA to 11% for SII whereas the range of values is narrower for amorphous alumina (from 3% to 8%). Amorphous iron is nearly non-existent in RC but has the highest percentage value of 2.5 in JPA.

The mineralogical composition was determined by x-ray diffraction; it will be discussed in detail in Chapter 6. These results are shown in appendix A.1; they reveal the presence of the clay mineral kaolinite with quartz, haematite and goethite present.

4.5 Morphology and distribution of minerals

A discussion of the morphology of the minerals identified in the soils is carried out in this section with a view to examining their possible roles in the soil-lime reactions.

4.5.1 Kaolinite

The kaolinite as shown by x-ray diffraction is disordered, giving a slight shift in the (001) reflection (d-spacing ≈ 7.21Å as against d-spacing of 7.14Å for well crystallised kaolinite). The disordered clay mineral has been reported as kaolinite rather than metahalloysite purely from x-ray diffraction peaks. Metahalloysite is difficult to distinguish from disordered kaolinite. It has been suggested that the presence of partially hydrated halloysite can be detected by heating the soil to about 400°C and observing the 7.20Å d-spacing (72). An enhancement of the peak indicates the presence of partially hydrated halloysite

Table 4.3 Constituents in the clay size fractions extractable by 0.5 N NaOH (as determined by De Carvahlo (56)).

Soil Name	Soil Symbol	Constituents extracted by 0.5N NaOH		
		%SiO_2	%Al_2O_3	%Fe_2O_3
João P. Acima	JPA	2.81	3.10	0.46
João P. Meio	JPM	10.91	7.97	0.68
João P. Abaixo	JPB	6.71	6.11	2.51
Cuité	CT	7.84	4.12	0.80
Areia I	AI	8.11	6.95	1.07
Areia II	AII	9.69	5.89	0.62
Solanea IA	SIA	2.08	3.28	1.01
Solanea IB	SIB	4.13	3.97	0.79
Solanea II	SII	11.29	7.56	0.21
Nova Floresta	NF	8.31	7.02	0.43
Junco I	JI	5.02	6.11	0.78
Junco II	JII	6.69	4.07	2.05
Teixeira I	TI	8.12	6.98	0.30
Teixeira II	TII	4.68	4.02	0.87
Recife	RC	9.21	6.16	0.10
Usina S. Maria	USM	3.71	4.41	0.19
S. Banareiras	SB	8.19	6.84	0.28
Penha	PH	2.91	3.80	0.29
Sape Mari	SM	7.98	6.48	0.78

in the sample. Thermally, goethite reacts at this temperature and since the x-ray diffraction peaks are affected by the presence and state of the iron compounds (39), such a method of differentiation may not apply to the soils. Methods for the determination of the degree of crystallinity and distinction between kaolinite and metahalloysite include x-ray diffraction, infra-red and thermal analysis. The crystallinity of the soils have been studied using infra-red spectroscopy (73) and by the use of kinetic thermogravimetric methods. Both methods show that the kaolinites present in the red tropical soils studied are poorly crystallised. These studies did confirm that clay mineral halloysite is absent.

4.5.2 Silica

X-ray diffraction shows silica to occur in crystalline form as quartz and in kaolinite. In the clay size fraction the range of total silica is narrow (Table 4.2). Thus it will appear that if the soils react with lime according to the total silica not much difference in the strengths of the lime treated soils will be observed. Relatively, the range of values of the amorphous silica is wider and if the soils should react with lime in proportion to the amorphous silica present, the range of values of their strengths will be wide. It is important to point out that high values of amorphous silica are not necessarily associated with high values of total silica.

4.5.3 Alumina

No other form of crystalline alumina e.g. gibbsite, boehmite was detected. Crystalline alumina occurs only in kaolinite. The range of values of total alumina is narrow whereas it is fairly wide in the amorphous state. As in the case of silica, amorphous alumina does not vary as the total alumina.

4.5.4 Iron minerals

Iron exists in the soils as haematite, goethite and in the amorphous state. The range of values of total iron is very wide whereas the range is narrow for the amorphous state. A relationship seems to exist between the values of the amorphous and total iron in most of the soils. It would appear that the higher the value of the total iron, the greater is the value for the amorphous iron. It thus seems that iron as measured in terms of total or amorphous will have the same effect (if any) on the lime reactivity of the soils.

4.6 Physical and engineering properties

Table 4.4 shows the textural composition, compaction and strength characteristics of the soils and soil-lime mixtures. The conditions under which the maximum strengths of the soils were determined are given since strength is the engineering property used in assessing the lime activity of the soils in this study.

4.6.1 Strength determination

Each soil was treated with 0, 1.5, 3.0, 4.5 and 6.0% lime (by weight of soil). The strength of the soil is measured for each lime percentage at different moisture contents. For any particular lime content, the soil was mixed with water, statically compacted into a 5.08 cm diameter x 5.08 cm high split mould using energy equivalent to the BS intermediate compactive effort (approx. 1090 KJ/m^3). The density and moisture contents were determined. The moisture content was varied and the procedure repeated. The compacted specimens were cured at 22^oC for 28 days when their strengths were determined in unconfined compression.

Table 4.4 Physical and engineering properties of the soils used for the investigation

Soil Name	Soil Symbol	Textural Composition			Compaction and Strength Characteristics							Lime Reactivity
		Sand 2mm-0.06mm	Silt 0.06-0.002mm	Clay < 0.002mm	Natural Soil			Lime Treated Soil				
					max. density kg/m^3	moisture content for max. density %	unconfined compressive strength MN/m^2	max. density kg/m^3	moisture content for max. density %	unconfined compressive strength MN/m^2	Lime for max. U.C.S. %	
JOAO P.ACIMA	JPA	79	14	7	1911	10.35	0.29	1901	10.50	1.21	4.5	0.92
JOAO P.MEIO	JPM	60	12	28	2029	13.20	1.80	1944	16.20	5.39	6.0	3.59
JOAO P.ABAIXO	JPB	81	10	9	1861	7.70	0.10	1880	10.10	0.51	4.5	0.41
CUITE	CT	68	20	12	1983	13.85	0.41	1904	15.35	1.14	4.5	0.73
AREIA I	AI	50	20	30	1839	17.35	1.55	1812	18.55	2.05	4.5	0.50
AREIA II	AII	65	18	17	1982	14.20	0.51	1788	17.25	1.60	4.5	1.09
SOLANEA IA	SIA	66	18	16	1980	11.00	0.55	1918	14.70	0.59	4.5	0.04
SOLANEA IB	SIB	86	7	7	1873	4.80	0.08	1950	6.75	0.21	6.0	0.13
SOLANEA II	SII	56	20	24	1982	10.25	0.80	1936	11.35	2.96	4.5	2.16
NOVA FLOREST	NF	68	19	13	2061	13.30	0.50	1966	15.25	0.99	4.5	0.49
JUNCO I	JI	58	32	10	1939	10.10	0.52	1888	13.80	1.14	4.5	0.62
JUNCO II	JII	76	15	9	2079	12.35	0.20	2046	12.10	0.78	6.0	0.58
TEIXEIRA I	TI	48	30	22	1834	13.95	1.26	1782	15.40	3.22	6.0	1.96
TEIXEIRA II	TII	41	28	31	1753	16.60	1.28	1719	16.85	1.75	6.0	0.47
RECIFE	RC	60	10	30	1918	12.80	0.89	1880	14.40	2.59	6.0	1.70
USINA S.MARIA	USM	46	20	34	1742	17.30	1.85	1710	18.40	2.10	4.5	0.35
S.BANANEIRAS	SB	49	13	38	1916	12.50	1.92	1851	13.45	3.91	4.5	1.99
PENHA	PH	64	15	21	1828	14.30	1.11	1777	16.50	0.84	4.5	0.00
SAPE MARI	SM	58	19	23	1918	15.30	0.94	1865	17.10	2.49	6.0	1.55

For a lime content, the optimum moisture content was determined and the strength corresponding to this moisture content on a strength vs moisture content plot was taken as the unconfined compressive strength for that lime content. The UCS vs lime content was plotted and the optimum lime content and maximum UCS determined. The values are shown in Table 4.4; it can be seen that there is a wide range of values of maximum strength produced by 4.5% or 6.0% lime.

4.6.2 Lime reactivity

Lime reactivity is used as defined by Thompson (57). It is the difference between the maximum unconfined compressive strength of the lime treated soil and the maximum UCS of the natural soil cured for 28 days at 22°C. The values are shown in Table 4.4.

4.7 Lime used

A commercial hydrated calcitic lime produced under the name of Brancal, meaning white lime, by the company Argilas e Minérios Nordestinos S.A. of João Pessoa, Paraiba, Brazil was used in treating each soil. The chemical composition of lime is given as (after De Carvalho (56)):-

CaO	68.1%	
$Ca(OH)_2$	89.9%	(calculated by molar ratio from CaO present)
MgO	1.68%	
SiO_2	1.19%	
$Al_2O_3 + Fe_2O_3$	1.06%	
Loss on ignition	28.9%	

4.8 Chapter Summary

a) The nineteen soils investigated were sampled from an area of North-East Brazil with the climate varying from hot and humid to very hot and semi-arid.

b) The soils contain kaolinite as the clay mineral with quartz, haematite, goethite and amorphous silica, alumina and iron present.

c) While amorphous silica and alumina do not vary as the total silica and alumina respectively, amorphous iron generally varies as the total iron.

d) When treated with hydrated calcitic lime, the soils show a wide range of variation of maximum strengths with 4.5% or 6.0% generally required to produce maximum strength.

CHAPTER 5

POZZOLANIC ACTIVITY AND MECHANISM OF REACTION OF RED TROPICAL SOIL-LIME SYSTEMS

5.1 Introduction

This chapter presents a study of the mechanisms of the reaction that takes place when red tropical soils are mixed with lime. Because these soils contain many minerals in various forms, such mechanisms and indeed the reaction compounds are very complex. Nevertheless, their understanding is essential for the development of improved methods of red tropical soils utilization.

5.2 Review of pertinent literature and methods

Two principal methods have been used to study soil-lime reactions. One method is based on the ability of the soil to react with lime and the other on the mechanism responsible for such reactions. The review is therefore treated under two sub-sections.

5.2.1 Ability of the soils to react with lime

The classical method of assessing pozzolanic materials for use with cement is that proposed by Fratini (74) and modified by Rio (75). This method involves the determination of the amount of lime left in solution after a mixture of the pozzolana and Portland cement is kept in water at approximately 28°C for eight days. Qualitatively, a reactive material is that which leaves a low calcium ion concentration at the end of this period.

Soil engineers have assessed reactions between soil and lime by measuring a change in some engineering property of the soil. Hilt and Davidson (43) utilised the changes in plasticity as a measure of the initial early reaction, while Thompson (57) used changes in strength as a measure of a soil's lime reactivity. He defined lime reactivity as the difference between the unconfined compressive strength of a soil treated with lime for maximum strength, cured for 28 days at 22.8^{o}C and the strength of the untreated soil. This method has been used by De Carvalho (56), and Harty and Thompson (70), among others, to assess the lime reactivity of red tropical soils. While the use of such an indirect method to study soil-lime reaction is acceptable and useful, there is need to explore the use of the fundamental reaction properties such as reaction rate, volume of reaction products etc. Such reaction property as rate (which is measurable at ordinary temperatures) can provide full or partial information on the mechanism of reaction.

The methods in actual use for studying the reactions of other pozzolanas fall into two broad groups; a method based on solid state transformation and a method using a suspension of the pozzolanic material in a solvent. The former employs high temperature to effect the reaction between the material and lime. Because of this, the method is useful in studying the kinetics of Portland cement clinker phases as recently demonstrated by Mackenzie and Banerjee (76).

Various materials, conditions of experiment and methods of analysis have been used in the second group by researchers who employ monodisperse suspensions. The materials include silica and alumina in various states, pulverised fuel ash (PFA), and naturally occuring soils in suspension of either lime solution or hydrofluoric acid (or a mixture of hydrofluoric acid and nitric acid). Barret et al (62) and Taylor (77) used different types of amorphous silica in lime solutions while Greenberg (78) used both amorphous silica and quartz in lime solution for his investigation. Diamond and Kinter (47) used clays (kaolinite and montmorillonite) in calcium hydroxide solution. The use of compounds other than lime has so far been confined to workers studying the reactions of PFA. Hydrofluoric acid was used by Raask and Bhaskar (79) in place of a mixture of the acid and nitric acid which they considered too aggressive on PFA. The use of such selective solvent as hydrofluoric acid which dissolves only silica is not desirable in the study of red tropical soil-lime reactions because the soils contain other reactive minerals apart from silica. Thus the use of the soil in lime solution is preferred.

Lime solution is generally used because it is easier to follow the removal of lime from solution not only at early periods of reaction but throughout the duration of the reaction. The progress of the reaction has been followed in a number of ways. The conventional volumetric analysis as used by Diamond and Kinter (47) is time consuming, cumbersome and hazardous. Greenberg (78) followed the depletion of lime by a method based on the reduction in electrical conductivity of the solution as reaction proceeds. He assumed, in this method, that conductance is directly proportional to the concentration of calcium hydroxide; the reaction products and silica were said not to contribute to the conductivity of the solution. In red tropical soils this assumption needs verification because of the presence of iron compounds.

Recently, Barret et al (62) followed the progress of the reaction using atomic absorption spectrophotometry to determine silica and lime. This method is neat and fast and is therefore favoured for use in red tropical soil-lime solution system.

5.2.2 Mechanisms of reaction - the reaction models

Strengthening in soil-lime system is a result of cementitious reaction products generated by the reaction between the lime and the soil minerals (pozzolanic reaction). The mechanism responsible for pozzolanic reaction is not clear. Two views emerge from literature. While some postulate a dissolution of the soil minerals to precede reaction, others favour a reaction through a diffusion controlled process. So far, a qualitative approach has been employed to study the mechanism. Scanning electron microscopy and sometimes transmission electron microscopy have been used by most workers. Useful as these techniques are, the interpretation of the microphotographs is difficult and calls for much experience. Even where experience exist, the interpretation of the same microphotograph may differ very widely indeed. Hence it is felt that mechanisms based on mathematical models should be considered. This if used in conjunction with photographic evidence should give a better resolution of the problem. The mathematical theories of the two mechanisms are thus considered.

The derivation of the equations governing dissolution was presented by Greenberg (78) and recently more lucidly by Raask and Bhaskar (79). The rate of dissolution of a given mass is assumed proportional to its surface area, thus:-

$$\frac{dw}{dt} = -CA \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5.1)$$

where $\frac{dw}{dt}$ = dissolution rate at time t

C = rate constant

A = total surface area.

For uniform sized spherical particles equation (5.1) becomes

$$\frac{dw}{dt} = -C_1W^{2/3} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5.2)$$

where W = weight of undissolved material at time t

i.e. $C_2t = Wo^{1/3} - W^{1/3} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5.3)$

i.e. $C_3t = 1 - Wm^{1/3} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5.4)$

where $Wm = \frac{W}{Wo}$

and Wo = weight of undissolved material at time zero.

Equation (5.4) is valid for a monodisperse suspension.

For materials of particle size normally distributed, equation (5.4) becomes

$$C_4t = 1 - Wm^{\frac{1}{4}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5.5)$$

For materials of particle size log normally distributed, equation (5.4) becomes

$$C_5t = 1 - Wm^{1/5} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (5.6)$$

Hence if the dissolution theory is valid, experimental results on lime consumption with time should obey equation (5.5) or (5.6).

Kinetic models for solid state reactions based on diffusion controlled processes have been considered by Jander (80), Ginstling and Broumshtein (81) and Carter (82). Jander's model is the simplest but does not consider the effect of the varying volume of reaction products on the rate of formation of new reaction products as does Carter's. Jander based his model on the reaction which occurs between two spherical particles and on the assumption that the rate of thickening of the reaction products is inversely proportional to its thickness, thus:

$$\frac{dy}{dt} = \frac{k}{y} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.7)$$

where dy/dt = rate of thickening of the reaction products

k = rate constant

y = thickness of the reaction products.

Integrating equation (5.7):

$$y^2 = 2kt \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.8)$$

The volume of unreacted material V, at a time t is given by:

$$V = \frac{4}{3}(r-y)^3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.9)$$

or

$$V = \frac{4}{3}r^3(1-x) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.10)$$

where r = radius of reacting sphere

x = fraction of sphere which has reacted.

From equations (5.9) and (5.10):

$$y = r[1 - (1-x)^{1/3}] \quad \ldots \quad \ldots \quad \ldots \quad (5.11)$$

Substituting y from equation (5.8) in (5.11) gives

$$[1 - (1-x)^{1/3}]^2 = \frac{2kt}{r^2} = Kt \quad \ldots \quad \ldots \quad (5.12)$$

Equation (5.12) is the well known Jander equation from which the rate constant of reaction can be determined. The equation can be written as:

$$F(x) = [1 - (1-x)^{1/3}]^2 = Kt \quad \ldots \quad \ldots \quad (5.13)$$

Hence a plot of F(x) against time should give a straight line.

It may be worthwhile to point out that neither of the two models considered truly represents the actual practical red tropical soil-lime system, since the lime in the system is partly dissociated and partly solid.

5.3 Experimental method

The reaction between soil and lime was studied by a method similar to that used by Barret et al (62) which consists basically in measuring the amount of lime left in solution at predetermined time intervals using atomic absorption spectrophotometry. The detailed procedure is as follows:-

a) Preparation of lime solutions by mixing 0.15 gm or 0.10 gm of hydrated lime with CO_2 free distilled water;

b) Mixing 2.5 gm of soil with appropriate concentration of lime solution so as to obtain either 6% or 4.5% lime concentration in the soil. These percentages correspond to the optimum percentages of lime required for maximum strength (see Table 4.4). Thus a soil requiring 6% for maximum strength is mixed with lime concentration of 1.5 gm/l while 1.0 g/l is used for that requiring 4.5% lime for maximum strength;

c) Placing the mixtures of soil and lime solution in plastic containers tightly sealed to prevent the carbonation of the lime;

d) Storing the sealed containers in an oven at a constant temperature of 25°C;

e) Shaking the containers periodically and measuring the lime concentrations at predetermined times. To measure lime concentration by atomic absorption it is necessary to have very clear solutions. To achieve this, an aliquot of the soil-lime mixture is taken after the containers have been shaken. The aliquot is centifuged at 2,500 rpm for 5 - 10 mins. and the lime concentration is determined from 1 ml of the supernatant.

A preliminary study was conducted with two soils using three different size fractions of each, i.e. 2 mm - 0.074 mm, 0.074 mm - 0.002 mm and < 0.002 mm. This was done to determine the reactive fractions and to assess the magnitude of contribution to lime consumption by the coarser fractions of the soil. It is a known fact that many of the coarser particles in red tropical soils are only aggregations of the clay size fractions (3, 4) and thus they may influence the overall soil-lime reactions.

The results of this preliminary study are presented in Table 5.1. The clay fraction is 3 to 5 times as reactive as the sand fraction and 2 to 3 times as reactive as the silt fraction. The two soils used in the preliminary study represent the most reactive and one of the least reactive of the nineteen soils. The ratios quoted above will increase further, in favour of the clay size fraction, when all the fractions are mixed together in presence of lime since they will be exposed to a "competition" for lime which was not necessary when each fraction was separately mixed with lime. Therefore it is apparent that by using only the clay size fraction, a representative result can be obtained for any of the soils. Consequently, the study was conducted with the clay size fraction of each of the nineteen soils.

5.4 Measurement by atomic absorption spectrophotometer

5.4.1 Basic principles

If a solution containing a metallic ion is aspirated into a flame, such as air-acetylene flame, an atomic vapour of the metal

Table 5.1 Fraction of lime consumed at varying times for different fractions of two of the soils investigated

Soil Name and Soil Symbol	Soil Fraction	Fraction of Lime reacted after				
		1 Day	2 Days	4 Days	5 Days	7 Days
João P. Meio (JPM)	2 mm - 0.074 mm	0.062	0.091	0.098	0.102	0.113
	0.074 mm - 0.002 mm	0.124	0.140	0.162	0.168	0.198
	< 0.002 mm	0.298	0.367	0.461	0.517	0.589
Areia I (AI)	2 mm - 0.074 mm	0.030	0.065	0.082	0.096	0.117
	0.074 mm - 0.002 mm	0.102	0.115	0.146	0.172	0.196
	< 0.002 mm	0.092	0.147	0.289	0.314	0.342

will usually be formed. Some of the atoms of the metal may be raised to an energy level sufficiently high to emit the characteristic radiation of that metal. This phenomenon is utilised in the emission flame photometry technique. However, an overwhelmingly larger percentage of the atoms of the metal will remain in the non-emitting, "ground" state. These ground-state atoms can receive light radiation of their specific resonance wavelength (generally the wavelength being the same wavelength they would emit if excited). Thus, if light of this wavelength is passed through a flame containing atoms of the metal, part of that light will be absorbed, and the absorption will be proportional to the density of the atoms in the flame. This phenomenon is exploited in atomic absorption spectroscopy.

5.4.2 Features of an atomic absorption spectrophotometer

An atomic absorption spectrophotometer consists essentially of the following components:

a) a stable light source, emitting the sharp resonance line of the element to be determined;

b) a flame system into which the test solution may be aspirated at a steady rate. The temperature of this flame should be sufficient to produce an atomic vapour of the required metal from the compounds present in the test solution;

c) a monochromator lens to isolate the resonance line and focus it upon a photomultiplier;

d) a photomultiplier that detects the intensity of the light energy falling upon it, and which is followed by facilities for amplification and readout.

The light source is usually a lamp having a hollow cathode made of the element to be determined. The emission from this lamp is modulated so that its radiation only, and not that emitted from the flame by some of the atoms of the element in the test solution, will be recorded in the galvanometer signal of the readout.

5.4.3 Operation of a spectrophotometer

In using an atomic absorption spectrophotometer to determine the elements in a test solution, a calibration curve for that element has to be constructed first. A meter or the needle reading is adjusted to read zero when a blank solution (distilled water) is sprayed on to the flame. In this condition, the "unobstructed" light of the hollow-cathode lamp passes on to the photomultiplier. When standard solutions of the element to be determined (i.e. solutions in which the concentrations of the element are known) are sprayed on to the flame, part of the light from the lamp is absorbed resulting in a diminution of light intensity falling upon the photomultiplier. The readings of the meter are noted and a graph of concentration of the element againstmeter reading is plotted.

The test solution is sprayed on to the flame and the reading of the meter is noted. From the calibration curve, the concentration of the element in the test solution can be determined.

5.4.4 The atomic absorption spectrophotometer used

A Perkin-Elmer (603 series) atomic absorption spectrophotometer owned by the Scientific Division of the Central Electricity Generating Board at Harrogate was used for the elemental analysis in this study. The instrument is capable of being calibrated internally so that the concentration of the element being measured in parts per million (ppm) is read directly on a digital display. The reading displayed is an average of the readings over a time interval which is chosen by the operator. One minute time interval was used.

5.4.5 Calcium determination

When an air-acetylene flame system is employed, depression of calcium response occurs in the presence of aluminium, magnesium and phosphate ions. Such depression can be due to the formation of refractory compounds that are not dissociated in the flame. This interference is overcome by the addition of lanthanum chloride.

To determine calcium, 1 ml of the supernatant solution of the centrifuged aliquot was made up to 50 ml and the ppm of calcium determined after 1, 2, 4, 5, 7, 14, 21, 28 days at the following standard conditions.

Wavelength:	211 uv
Slit setting:	4(1.4 nm)
Light source:	hollow-cathode lamp
Flame type:	air-acetylene, oxidising (lean blue)

Because of the possible presence of aluminium lanthanum chloride was added each time a measurement was made.

The fraction of lime reacted after time t is calculated as follows:

$$\text{Extractable calcium at time } t = \frac{\text{ppm x vol. used x d.f}}{\text{sample wt. x } 10^3} = Ca(t)$$

where d.f = dilution factor

$$= \frac{\text{final diluted volume in ml.}}{\text{volume of aliquot taken for dilution in ml.}}$$

$$\text{Calcium as } Ca(OH)_2 = \frac{74.08}{40.08} \times Ca(t) = y \quad \ldots \quad (5.14)$$

$$\therefore \text{ Fraction of lime reacted} = 1 - \frac{y}{0.15} \quad \ldots \quad (5.15)$$

or

$$= 1 - \frac{y}{0.10} \quad \ldots \quad (5.16)$$

The values of these fractions as a function of time are given in Table 5.2.

5.5 Results and discussion

The results of the soil-lime reaction measurements are discussed below.

5.5.1 Lime consumption

The relations between lime reacted or consumed and time, obtained in the study, are presented in Figs. 5.1 and 5.2; for clarity of presentation, the soils have been divided in four groups as shown in the figures. The shapes of the curves are similar to those obtained by Diamond and Kinter (47) for adsorption of calcium hydroxide by kaolinite vs time in mins.,by Barret et al (62) for the depletion of lime by amorphous silica vs time in days and Greenberg (78) for consumption of lime by amorphous silica (measured by specific conductance of the solution) vs time (mins).

The relations between lime consumption and time in Figs. 5.1 and 5.2 show that lime is consumed at a "fast" rate in the initial stages of the reaction, that is, up to five to seven days. After this period the consumption continues but at a much reduced rate. This continuing consumption is in line with the general opinion that pozzolanic reaction is time dependent and therefore strength development is gradual but continuous for long periods

Table 5.2 Fraction of lime consumed at various times by the soils

SOIL SYMBOL	FRACTION OF LIME REACTED AFTER							
	1 DAY	2 DAYS	4 DAYS	5 DAYS	7 DAYS	14 DAYS	21 DAYS	28 DAYS
JPA	0.218	0.28	0.404	0.449	0.49	0.510	0.502	0.53
JPM	0.324	0.378	0.458	0.538	0.60	0.623	0.640	0.651
JPB	0.146	0.206	0.298	0.324	0.420	0.434	0.451	0.467
CT	0.20	0.227	0.289	0.333	0.362	0.359	0.371	0.380
AI	0.111	0.164	0.278	0.298	0.320	0.333	0.356	0.372
AII	0.20	0.253	0.324	0.38	0.394	0.410	0.425	0.437
SIA	0.125	0.167	0.25	0.28	0.291	0.310	0.308	0.326
SIB	0.191	0.233	0.35	0.40	0.421	0.437	0.445	0.462
SII	0.34	0.413	0.52	0.56	0.580	0.587	0.598	0.589
NF	0.262	0.324	0.404	0.422	0.417	0.434	0.447	0.458
JI	0.167	0.27	0.43	0.48	0.52	0.527	0.532	0.547
JII	0.19	0.217	0.50	0.52	0.533	0.547	0.558	0.562
TI	0.247	0.32	0.41	0.45	0.437	0.462	0.473	0.482
TII	0.33	0.417	0.46	0.48	0.52	0.533	0.538	0.546
RC	0.20	0.20	0.253	0.262	0.289	0.292	0.298	0.316
USM	0.156	0.173	0.224	0.28	0.301	0.318	0.333	0.345
SB	0.191	0.227	0.317	0.346	0.396	0.407	0.416	0.427
PH	0.20	0.431	0.44	0.493	0.498	0.510	0.519	0.523
SM	0.20	0.271	0.316	0.369	0.381	0.389	0.398	0.407

Fig. 5.1 Relations between consumption of lime and time for the nineteen soils investigated.

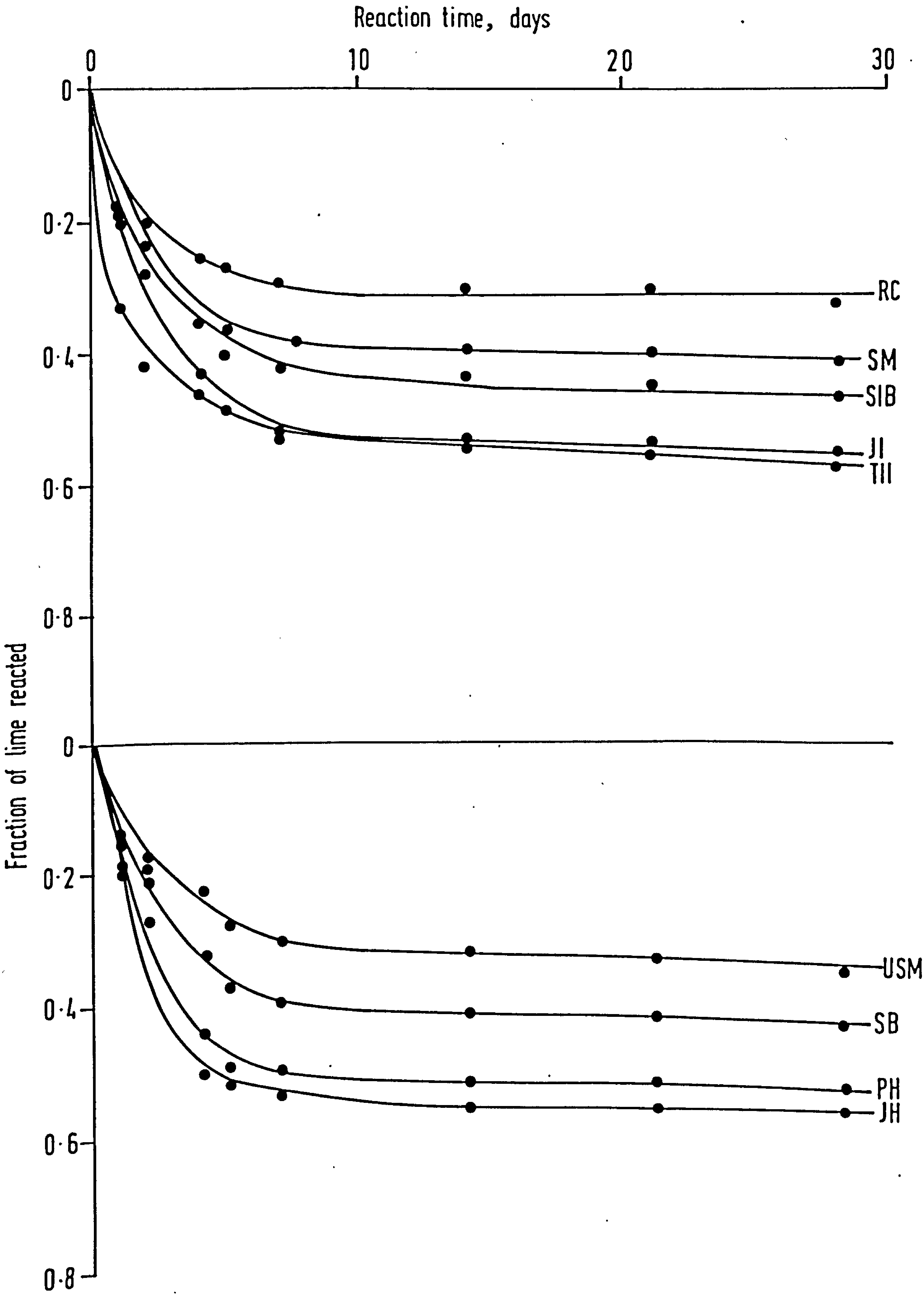
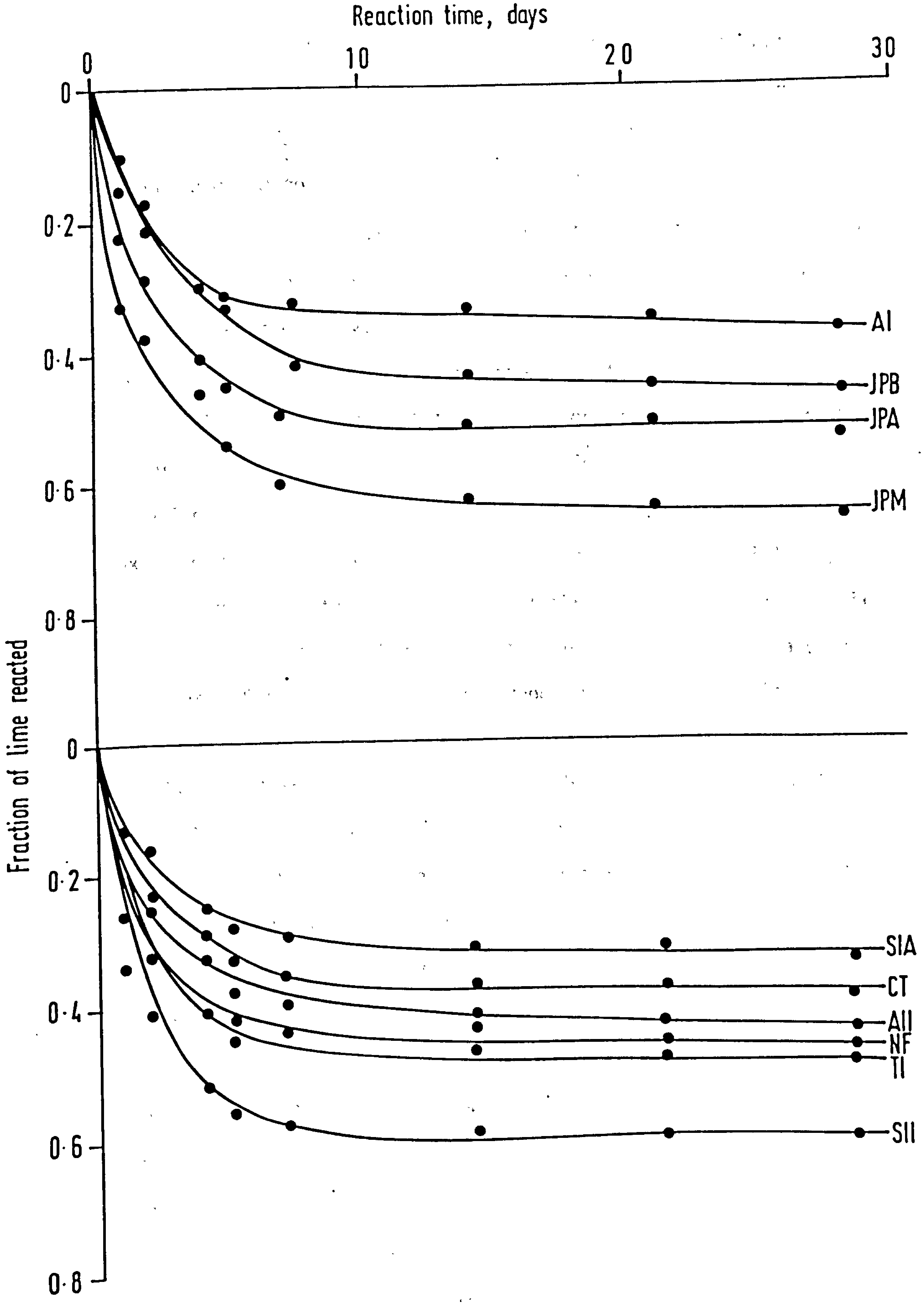

Reaction time, days
0
10
20
30
0
0·2
0·4
0·6
0·8
Fraction of lime reacted
RC
SM
SIB
JI
TII
0
0·2
0·4
0·6
0·8
USM
SB
PH
JH

Fig. 5.2 Relations between consumption of lime and time for the nineteen soils investigated


Reaction time, days
0
10
20
30
Fraction of lime reacted
0
0·2
0·4
0·6
0·8
AI
JPB
JPA
JPM
0
0·2
0·4
0·6
0·8
SIA
CT
AII
NF
TI
SII

of time. The ratios of the unconfined compressive strengths of lime treated soils after curing for 28 days to their strengths after curing for about 7 days for moderately reactive soils have been reported to vary between 2 and 3 (70). If this substantial increase in strength is totally a result of the formation of more cementitious reaction products, this should result in substantial lime consumption between 7 and 28 days because the amount of lime which disappears from the solution equals that which reacts with the soil to produce cementitious reaction products. However, the figures show that further lime consumption after the initial rapid period of about 7 days is limited. It is interesting to point out that the total lime consumption between 7 and 28 days corresponds only to eight percent of the lime consumed during the initial seven days. Therefore, it appears that the increases in strength of a soil-lime system beyond the seven day period cannot be totally explained in terms of generation of pozzolanic reaction products. Thus it is suggested that the increase in strength shown by these soils beyond seven days is mainly due to the changes that take place in the structure of the cementitious products formed during pozzolanic reaction, i.e., hydration and increases in crystallinity of the reaction products.

5.5.2 Mechanism of reaction

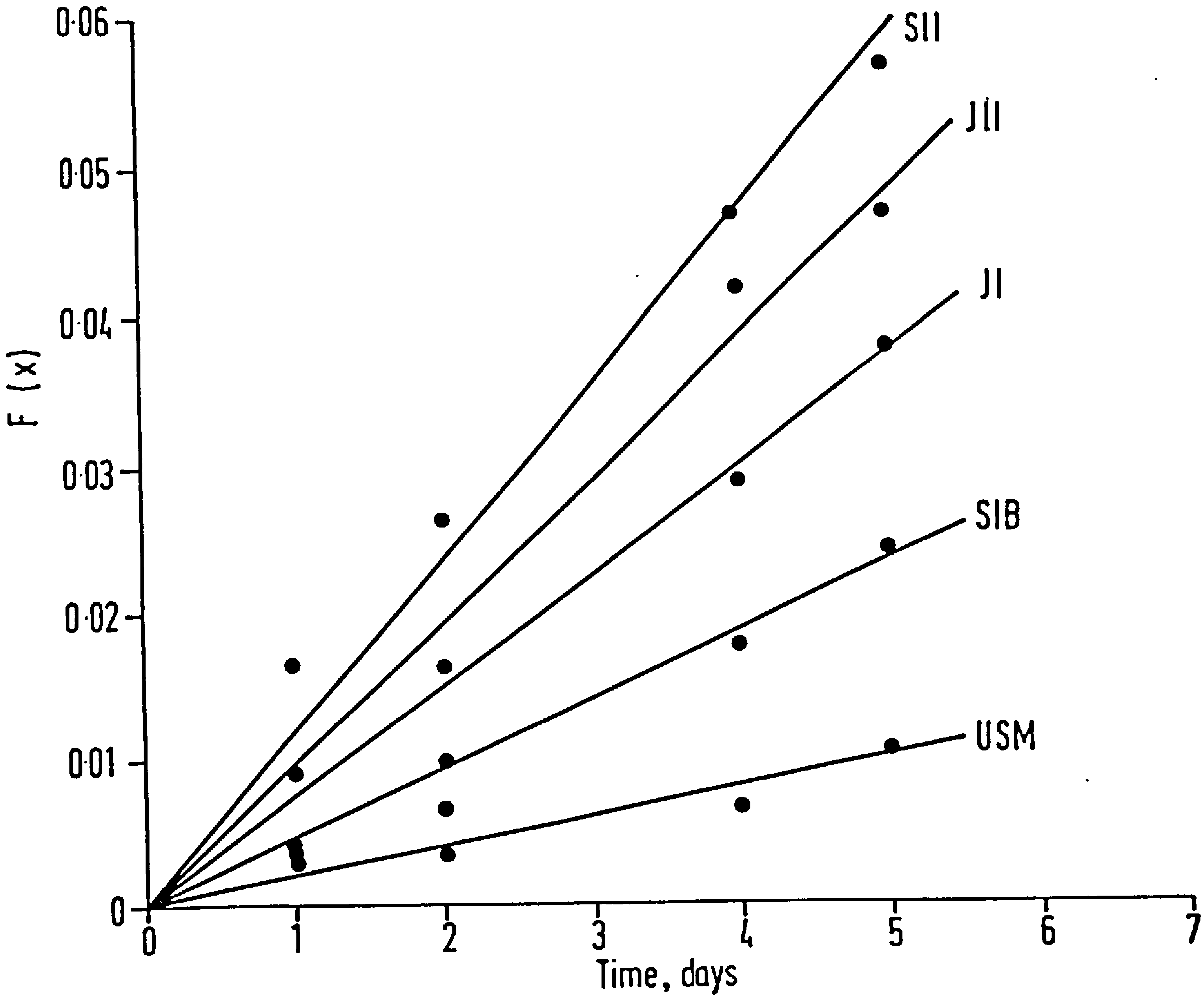
The numerical values of the lime consumption vs time relations were used to test the reaction mechanisms based on the mathematical models discussed previously. It was found that the experimental results do not follow the relations based on the equations which represent the dissolution theory, despite the fact that the experimental conditions were such as to give monodisperse suspensions for which the equations are intended to be valid. This finding coincides with the results of Raask and Bhasker (79) who reported that the dissolution model was not applicable to pulverised fuel ashes.

Since the volumes of the reaction products formed with time were not measured, the experimental data were tested with Jander's diffusion controlled model. The experimental results were found to approximate very closely to the values obtained with the function F(x) according to equation (5.13). It may be pertinent to point out that Mackenzie and Banerjee (76) used Ginstling and Brounshtein's equation (81) also based on a diffusion model to analyse the formation kinetics of tricalcium aluminate (C_3A). They found that the fraction of lime reacted vs time obeyed the equation and they deduced the rate constant of reaction from the relationship. The experimental points and the theoretical lines are shown in Figs. 5.3 and 5.4. They were plotted from values of F(x) in Table 5.3. The point at which the experimental results deviate from the mathematical model coincides with the time at which the rate of lime consumed changes i.e., 5 - 7 days. The linearity of the plots in Figs. 5.3 and 5.4 up to 5 or 7 days is taken as an indication of a degree of satisfactory fit. Fig. 5.5 shows the relation between F(x) and time for the total period of time investigated for some of the soils. The deviation of the plots after 5 - 7 days may be explained by the fact that one of the weaknesses of the Jander model is its inability to incorporate the effect of the varying volume of reaction products being formed and therefore their influence on the reacting system. It is apparent then, that the increased volume of reaction products

Table 5.3 Numerical values of the first term of Jander's equation F(x) for various times of reaction

SOIL SYMBOL	THE FUNCTION F(x) ACCORDING TO JANDER'S EQUATION							
	1 DAY	2 DAYS	4 DAYS	5 DAYS	7 DAYS	14 DAYS	21 DAYS	28 DAYS
JPA	0.00619	0.0108	0.0251	0.0325	0.0404	0.0448	0.0432	0.0495
JPM	0.015	0.0214	0.0341	0.052	0.0693	0.0785	0.0833	0.0876
JPB	0.00263	0.00548	0.0124	0.015	0.0276	0.0302	0.0328	0.0358
CT	0.00514	0.00676	0.0115	0.016	0.0194	0.019	0.0205	0.0217
AI	0.0015	0.0034	0.0108	0.0124	0.0146	0.016	0.0186	0.0206
AII	0.00514	0.00858	0.0150	0.0217	0.0236	0.0260	0.0284	0.0304
SIA	0.0019	0.00349	0.00836	0.0108	0.0117	0.0135	0.0133	0.0152
SIB	0.00465	0.00716	0.0179	0.0245	0.0277	0.0304	0.0318	0.0348
SII	0.0167	0.0265	0.0471	0.0573	0.0631	0.0640	0.0658	0.0686
NF	0.0093	0.015	0.0251	0.0279	0.0271	0.0299	0.0321	0.0341
JI	0.00349	0.0099	0.0292	0.0384	0.0471	0.0488	0.050	0.0538
JII	0.0046	0.0161	0.0426	0.0471	0.0502	0.0538	0.0568	0.0579
TI	0.00814	0.0146	0.0265	0.0321	0.0304	0.0348	0.0370	0.0388
TII	0.0156	0.0171	0.0345	0.0384	0.0471	0.0502	0.0515	0.0536
RC	0.00514	0.00514	0.0084	0.0093	0.0115	0.0118	0.0124	0.0141
USM	0.00302	0.00376	0.0066	0.0108	0.0127	0.0141	0.016	0.0173
SB	0.00465	0.0068	0.0142	0.0174	0.0239	0.0256	0.0269	0.0287
PH	0.00514	0.0164	0.0309	0.0411	0.0421	0.0448	0.0469	0.0478
SM	0.00514	0.010	0.0141	0.0202	0.0218	0.0229	0.0242	0.0256

Fig. 5.3 Relations between the first term of Jander's equation F(x) and time of reaction up to 5 days


0·06
0·05
0·04
0·03
0·02
0·01
0
F (x)
SII
JII
JI
SIB
USM
0
1
2
3
4
5
6
7
Time, days

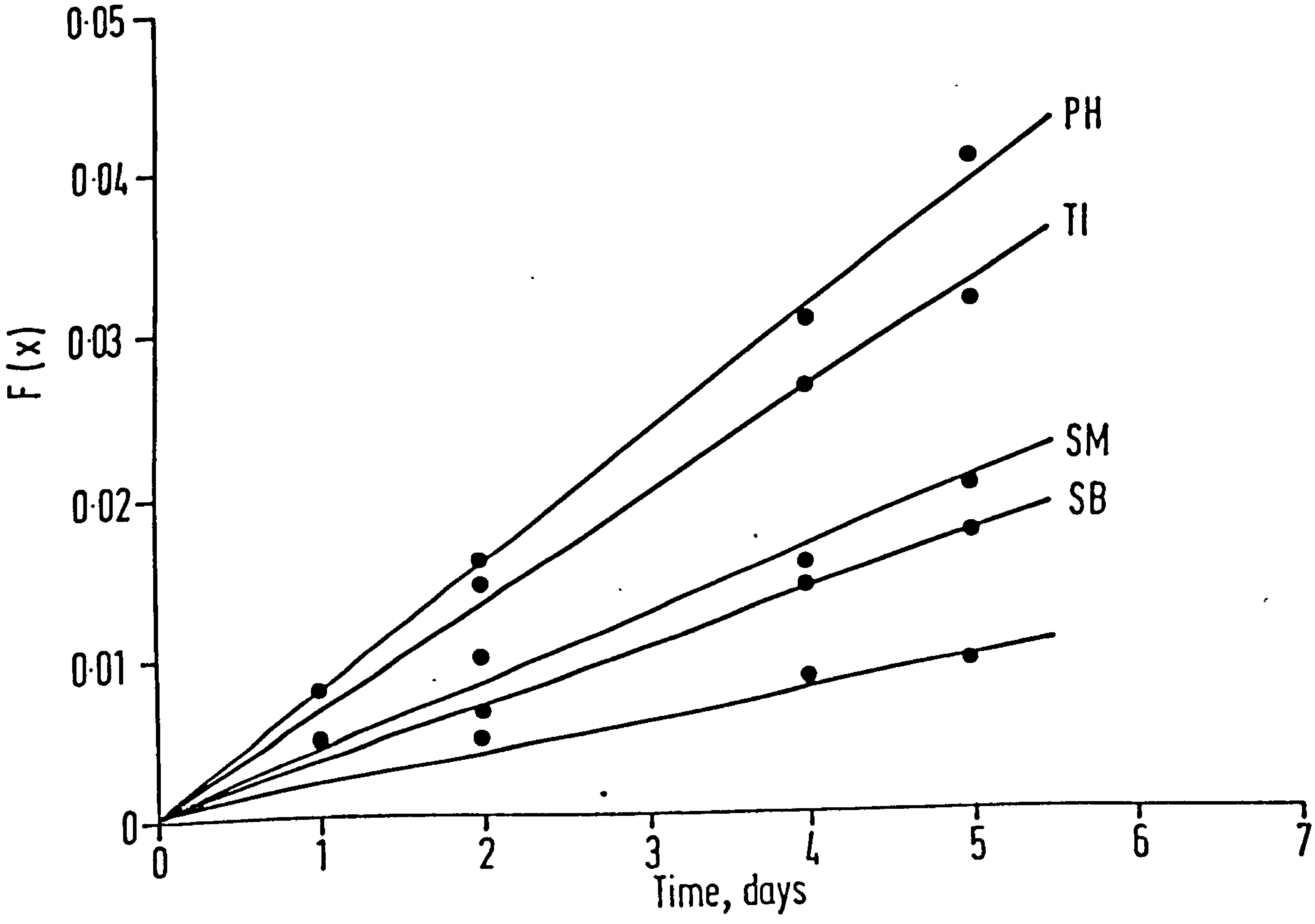
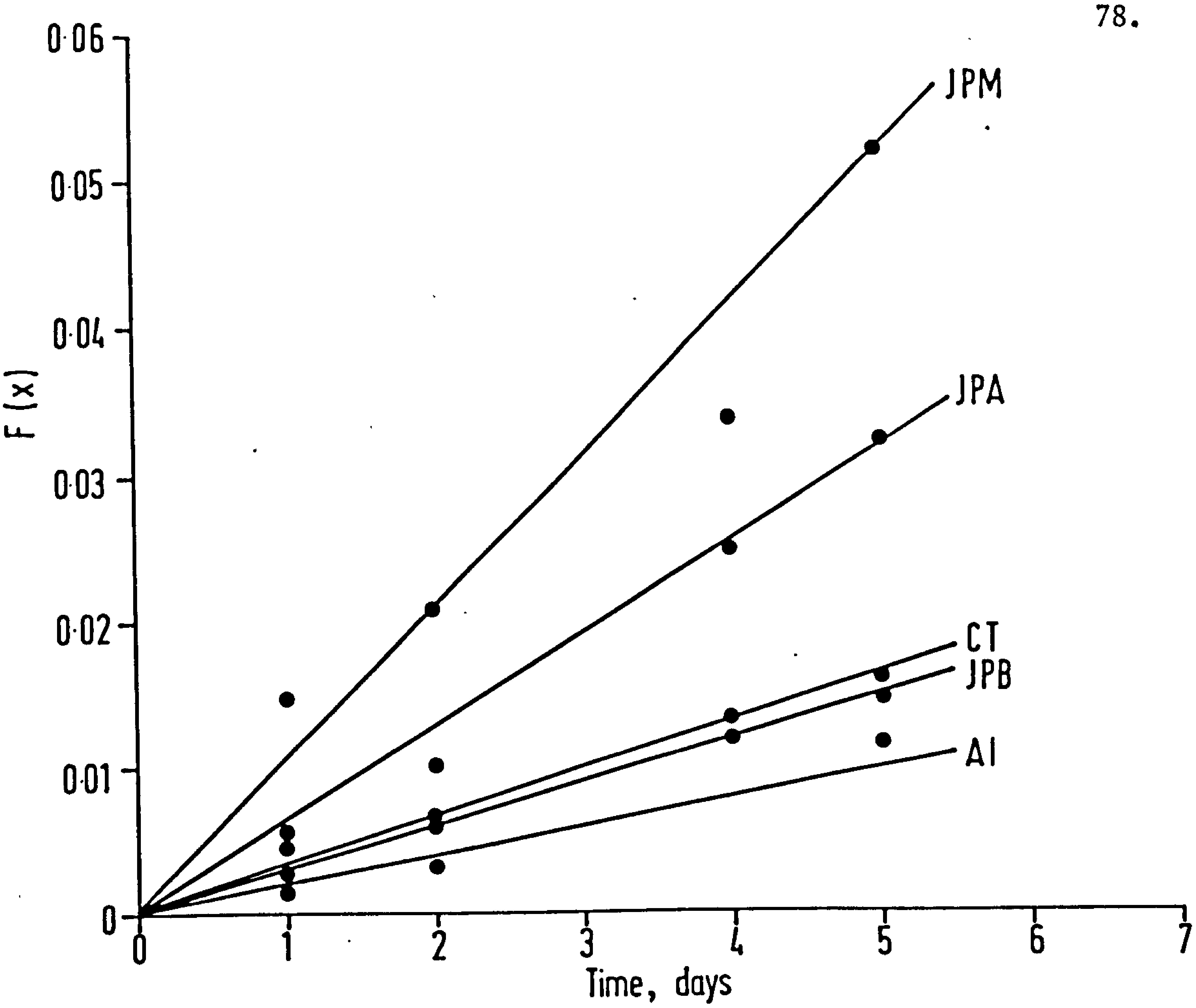

0·05
0·04
0·03
0·02
0·01
0
F (x)
PH
TI
SM
SB
0
1
2
3
4
5
6
7
Time, days

Fig. 5.4 Relations between the first term of Jander's equation F(x) and time of reaction up to 5 days


0·06
0·05
0·04
0·03
0·02
0·01
0
F (x)
JPM
JPA
CT
JPB
AI
0
1
2
3
4
5
6
7
Time, days

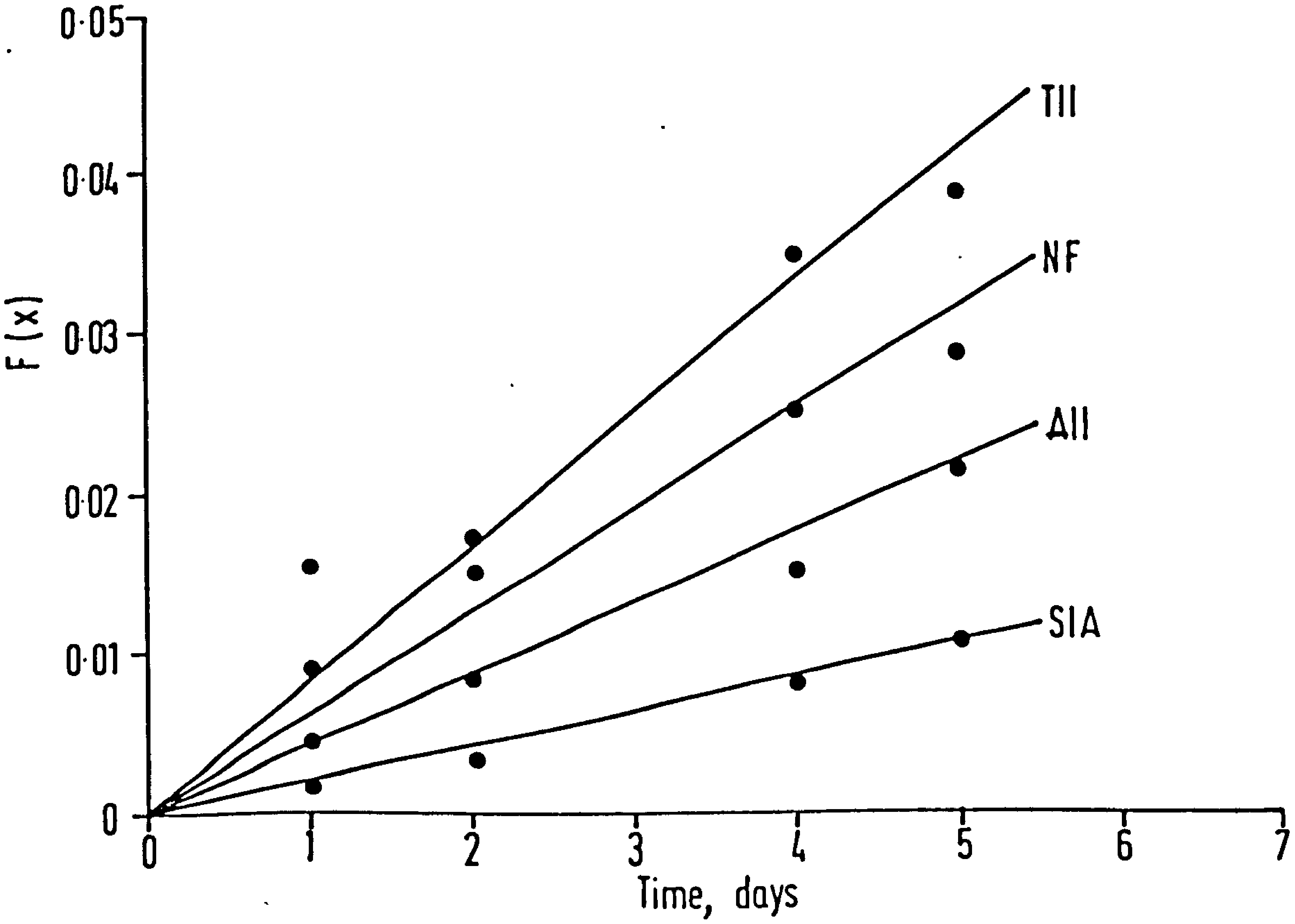
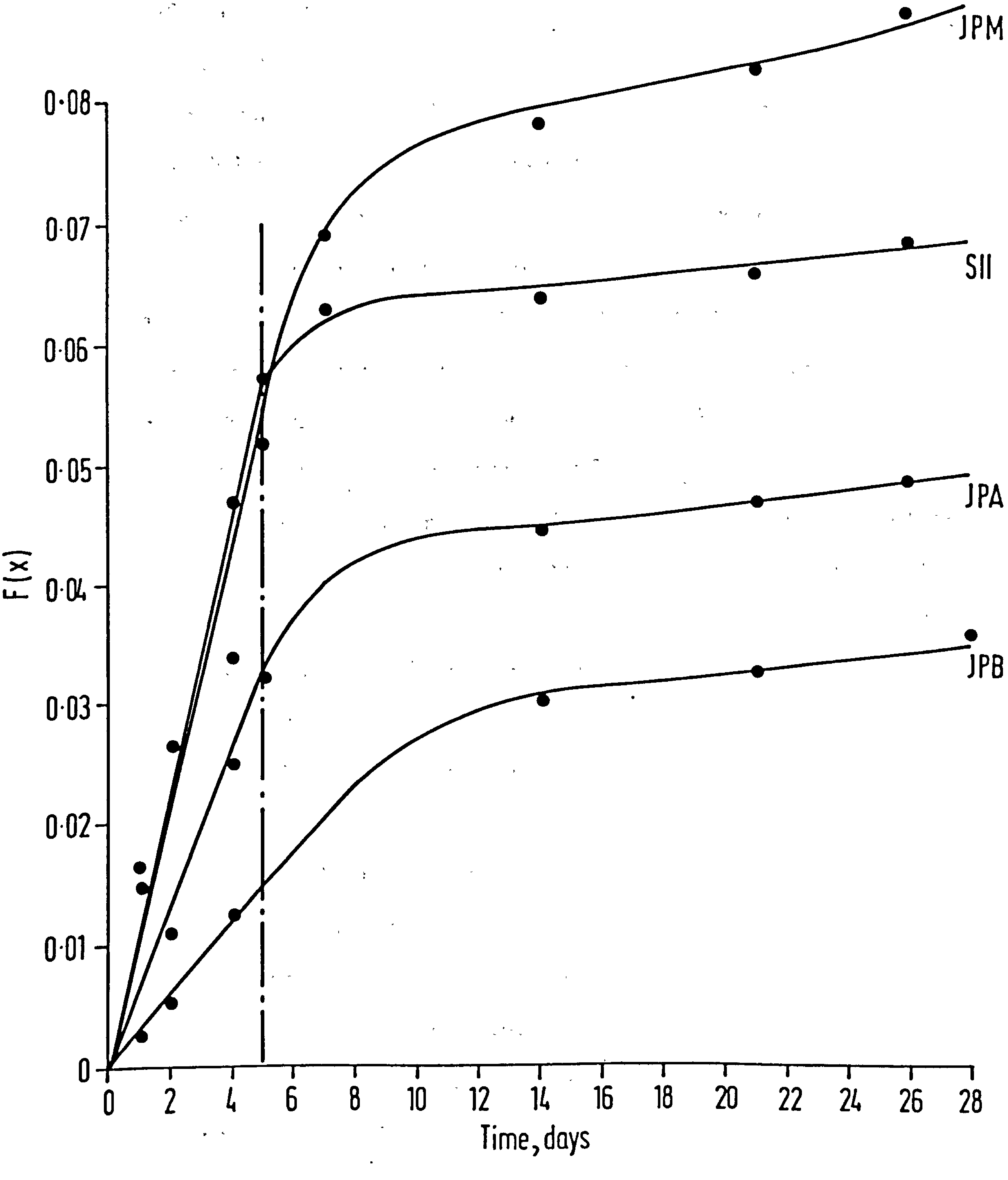

0·05
0·04
0·03
0·02
0·01
0
F (x)
TII
NF
AII
SIA
0
1
2
3
4
5
6
7
Time, days

Fig. 5.5 Relations between the first term of Jander's equation $F(x)$ and time of reaction up to 28 days for four of the soils


JPM
SII
JPA
JPB
F(x)
0
0·01
0·02
0·03
0·04
0·05
0·06
0·07
0·08
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Time, days

reduces the rate of diffusion as shown in Fig. 5.5.

While caution must be exercised when deducing mechanistic information from mechanistic reasoning, it seems most likely that the rate of reaction in red tropical soils is controlled by a diffusional process. While this may partially support Stocker's (45) deductions, dissolution is difficult to discount as a possible mechanism through which amorphous minerals present in the soils react with lime (62). In reviewing the reactions of aggregates in Portland cement concrete, Hansen (83) discussed the dissolution of quartz and siliceous minerals in general and concluded that the dissolution of silica involves:

a) Consecutive penetration of the electron cloud of an O^{2-} ion by two protons to form OH^- ions; penetration of two OH^- ions into the electrical field of the Si^{4+} ion to produce the unstable $Si(OH)_4$ group (monosilicic acid),

b) two more OH^- ions enter the $Si(OH)_4$ electrical field to form an $Si(OH)_6^{2-}$ ion,

c) the $Si(OH)_6$ ion being 6 coordinated can no longer form bonds with the other silicon atoms in the silica lattice which are 4 coordinated,

d) for proper screening (electrically) this ion combines with two protons to give the molecule $H_2Si(OH)_6$ which is free to migrate i.e., to dissolve.

For dissolution to occur, therefore, the material should be able to provide surfaces consisting of oxygen and unbonded OH^- ions as required by step (a). After cation exchange is satisfied, the available OH^- ions from the dissociation of the very small percentage of the lime added to the soil is limited. Fripiat (84) concluded that the 'hydroxyl' surfaces of amorphous silica and alumina hydrates were unlike true hydroxyl surfaces; they could more correctly be described as oxygen surfaces permeated by a cloud of delocalised protons. In characterising some soil allophanes, De Mumbrum and Chester (85) noted that soil allophanes have chemical and structural characteristics similar to the mettalic silicates of aluminium and manganese and appear to be highly hydrated, to have many exposed, unbonded OH groups and that their amorphous nature suggests "solid-solutions" of alumina and silica. Therefore, it will appear that these accounts of the "abnormal" state of existence of the surfaces of amorphous minerals and the OH^- ions will satisfy the pre-requisite for dissolution (step a) as given by Hansen (83). As a consequence, the amorphous silica and alumina of the red tropical soils used in this investigation might initially and for a short period react through a dissolution mechanism. Because there is no sharp transition from a non-crystalline to crystalline state in these soils, it is difficult to draw a line beyond which dissolution is unlikely to occur.

The rate of reaction of the crystalline minerals is lower, the mechanism not withstanding. Hence their reaction with lime will follow in the presence of reaction products formed by a more rapid reaction outlined above. The situation of the clays more or less resembles the state of the clay minerals when cement is used to treat soils containing only crystalline clay minerals. Taking the red tropical soil-lime system as a whole, it appears that apart from a short rapid reaction of the amorphous minerals possibly through dissolution, the reaction is mainly a diffusion controlled process.

5.5.3 Pozzolanic activity

The pozzolanic activity of a soil is defined as the ability of some or all of its constituents to react with lime to produce cementitious products. This ability is directly related to the type and quantity of the reactive constituents and the reaction rate. The latter depends on such factors as degree of crystallinity, surface area or fineness of the reactive constituents, pH of the reaction medium, temperature, intimacy of mixing etc. Thus a determination of the rate constant of reaction under particular experimental conditions is an indirect measure of these factors.

From equation (5.13) in sub-section 5.1.2, the slopes of the lines presented in Figs. 5.3 and 5.4 give the quantity $\frac{2k}{r^2}$. Assuming the same mean radius for the clay fraction of all the soils investigated, the slopes of the lines in Figs. 5.3 and 5.4 are measures of the rate constants of reaction. Since the clay size fraction is the most reactive, the quantity of the reactive constituents is expressed by the fraction of material smaller than 0.002 mm although it is recognised that most of the active components in the clay are really the amorphous and semi-crystalline materials.

It is proposed here that the pozzolanic activity of a red tropical soil should be expressed by an activity index which is related to the rate constant and the percentage of the reacting compounds by the following equation:

$$Ai = Kn^x \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.17)$$

where Ai = activity index

K = rate constant

n = fraction less than the clay size

x = a constant depending on the type of reacting compound in the clay fraction.

Although the introduction of the constant x may seem arbitrary, it is based on the fact that different soils may have different types of reacting compounds within their clay size fractions. For red tropical soils these compounds are silica, alumina and possibly iron; thus x is defined as a positive number whose function is to convert the reactive silica, alumina and iron to equivalent silica. It is proposed that x takes a value of 2.

$$\text{Hence } Ai = Kn^2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.18).$$

The values of the rate constants and the activity indexes for the soils using equation (5.18) are presented in Table 5.4. The Ai values range from 0.12×10^{-4} per day to 4.08×10^{-4} per day, giving a wide range for classification purposes.

The usefulness of the activity index should be proved against other accepted parameters. This was done by correlating the activity index with the unconfined compressive strength of the soil-lime systems and also by investigating its relation with the well-known lime reactivity parameter of Thompson (57).

5.5.4 Activity index and unconfined compressive strength

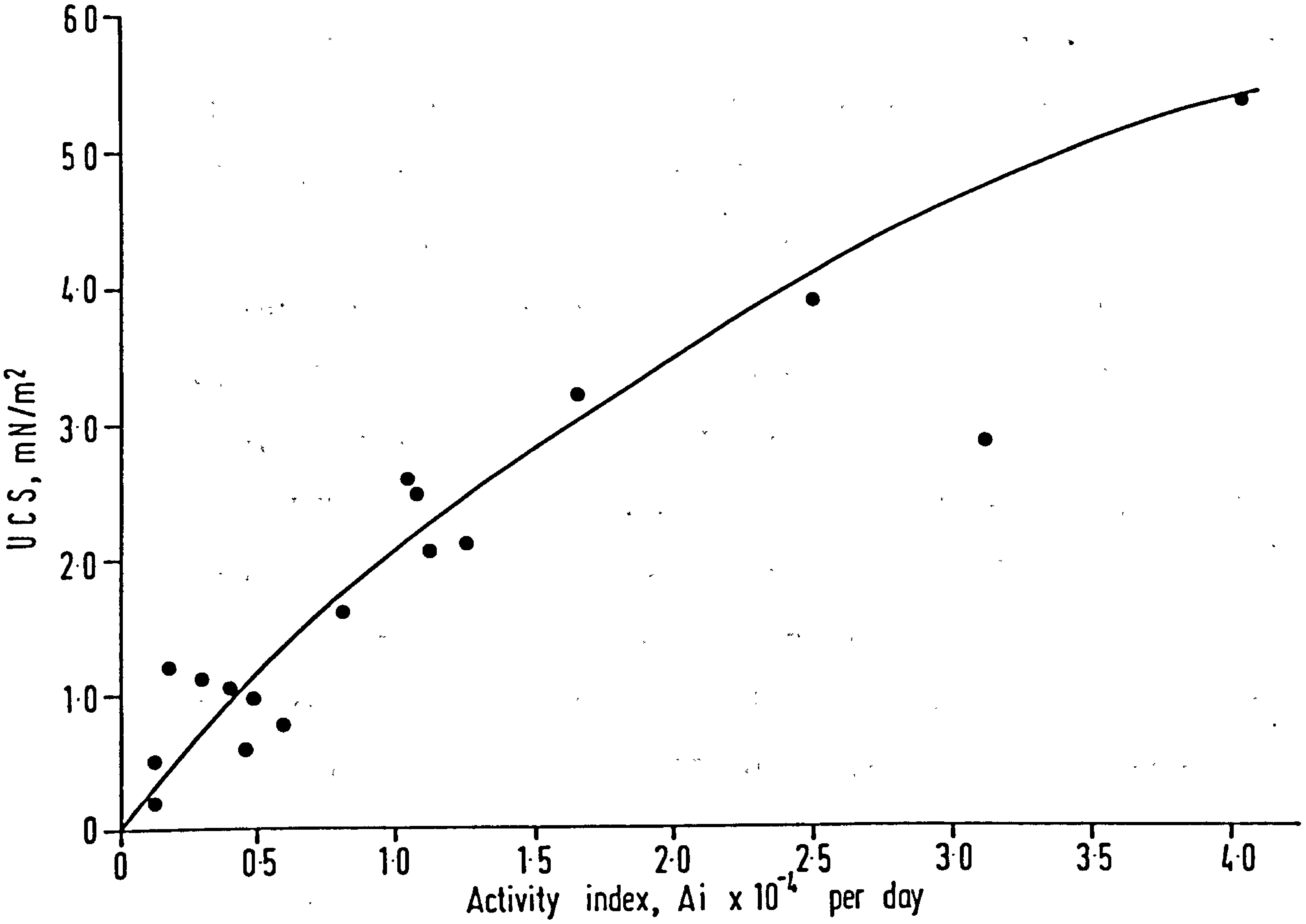
The relationship between the activity index Ai, and the unconfined compressive strength (UCS), is shown in Fig. 5.6 with the UCS as the dependent variable and Ai as the independent variable. A stepwise multiple regression analysis was used to relate Ai to UCS. The aim was to produce a linear combination of

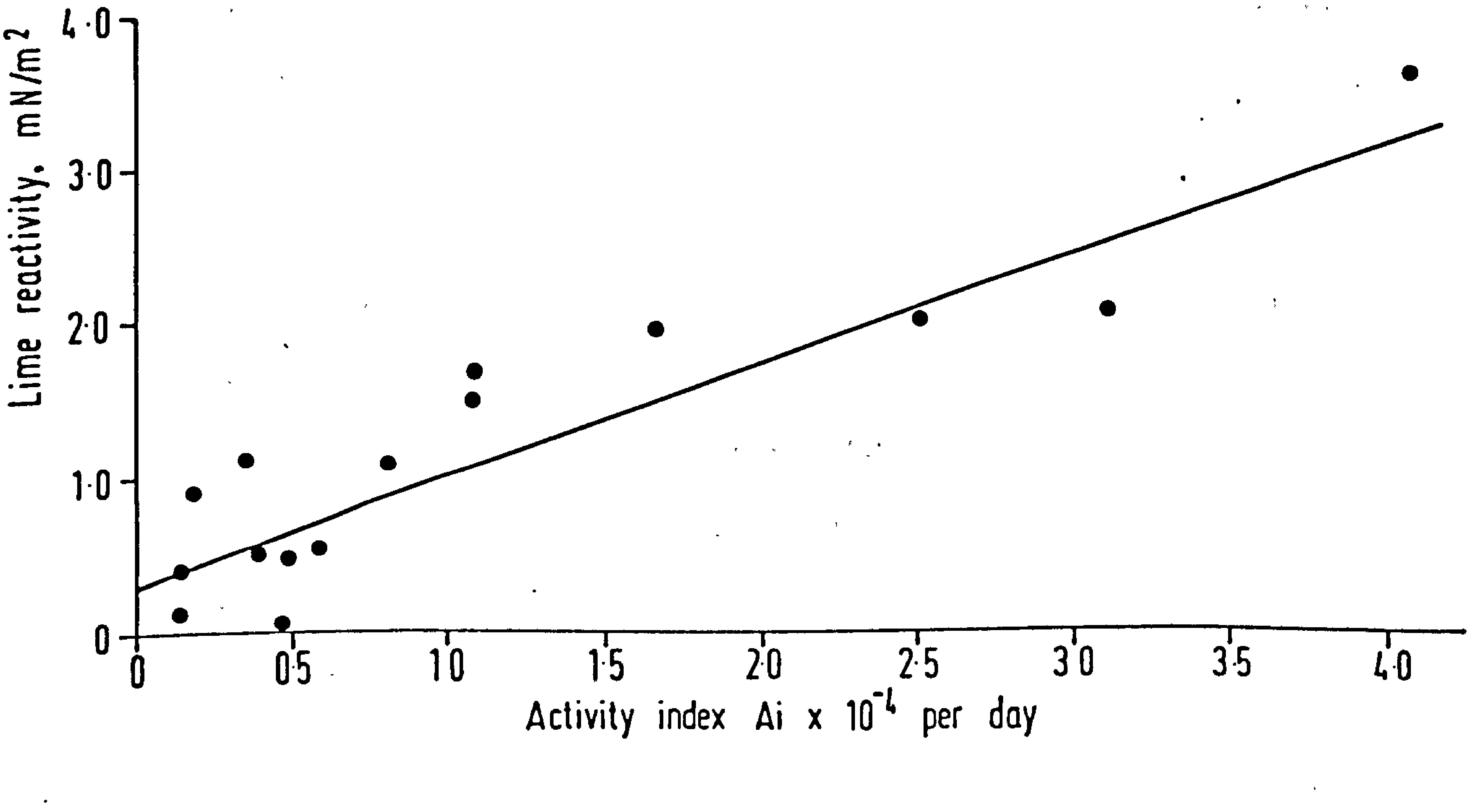
Table 5.4 Rate constants and activity indexes for the soils investigated

Soil Symbol	"Rate Constant" K per day	Pozzolanic Activity Index Ai x 10^{-4} per day
JPA	0.0035	0.172
JPM	0.0052	4.08
JPB	0.0015	0.12
CT	0.0016	0.291
AI	0.00124	1.116
AII	0.00234	0.791
SIA	0.00108	0.461
SIB	0.00245	0.120
SII	0.00543	3.13
NF	0.00279	0.472
JI	0.00384	0.384
JII	0.00471	0.567
TI	0.00340	1.646
TII	0.00384	3.689
RC	0.00118	1.062
USM	0.00108	1.248
SB	0.00174	2.512
PH	0.00411	1.812
SM	0.00202	1.07

Fig. 5.6 Relation between activity index and the unconfined compressive strength of the red tropical soils

Fig. 5.7 Relation between the activity index and the reactivity parameter of Thompson


6·0
5·0
4·0
3·0
2·0
1·0
0
U C S, mN/m²
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
Activity index, Ai x 10⁻⁴ per day


4·0
3·0
2·0
1·0
0
Lime reactivity, mN/m²
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
Activity index Ai x 10⁻⁴ per day

Ai and/or powers of Ai which correlates as highly as possible with the UCS. It was assumed that UCS is either a linear function of Ai or a power function which can be expressed by polynomials. The Statistical Package for the Social Sciences (SPSS 5), a ready computer programme available in Leeds University computer, was used for this purpose. The equation of best fit which expresses the relation between UCS and Ai was found to be:

$$UCS = 1.639\ Ai + 0.0135\ Ai^2 - 0.0276\ Ai^3 + 0.33 \quad \ldots \quad (5.19)$$

where UCS = unconfined compression strength in MN/m^2

Ai = activity index x 10^{-4} per day.

This equation is statistically highly significant with a multiple correlation coefficient of 0.973 at 95% confidence. The standard error is 0.359.

Seventeen out of the nineteen soils investigated seem to behave in the pattern as shown by equation (5.19). The deviations of the two soils (Teixeira II and Penha) may be due to error in their strength determinations or due to the type and cementing quality of the reaction products formed (a subject of chapter six).

5.5.5 Activity index vs Lime reactivity

Figure 5.7 shows the variation between activity index and lime reactivity as defined by Thompson (57). A stepwise multiple regression was used to find the lime of best fit with lime reactivity as the dependent variable and the activity index as the independent variable. Unlike equation (5.19), the best fit is given by

$$LR = 0.72Ai + 0.278 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.20)$$

where LR = lime reactivity in MN/m^2

Ai = activity index x 10^{-4} per day.

The standard error of prediction is 0.468.

This equation is highly significant with a correlation coefficient equal to 0.88 at 77% confidence. Three soils (Teixeira II, Penha, Areia I) out of the nineteen investigated, probably due to the reasons given in sub-section 5.4.4, do not obey this relation.

The linear relationship of equation (5.20) suggests that the activity index and lime reactivity have a common basis. Lime reactivity is a measurement (strengthwise) of the effect of the reaction products formed by reactions the characteristics of which determine the activity index. On the other hand, the polynomial nature of equation (5.19) suggests that the total strength of the soil-lime system is not determined solely by the reactions between soil and lime i.e., the reaction products do not exclusively determine the strengths of red tropical soils when they are treated with lime for optimum strength. The activity index thus seems to be a valid representation of the pozzolanic activity of red tropical soils investigated in this study.

5.5.6 Activity index and classification

As pointed out in Chapter 2, section 2.2, the parent material from which the soils are derived and climatic conditions which are significant for classification of red tropical soils influence or determine "the type and nature of their mineralogical constituents". De Graft-Johnson et al (18) and Gidigasu (29) showed that 'lateritic' gravels and fine grained 'laterite' soils can be classified on basis of geology, amount of clay content, linear shrinkage and climatic conditions. In proposing the activity index the clay content (n) and the type of reacting compounds (the factor x) have been considered and used. Furthermore the reaction rate which may indirectly measure the nature of the reacting compounds was used in defining the activity index. Thus the activity index which incorporates the significant parameters for classification purposes, may be a valid parameter for the classification of the soils.

The engineering characteristics used for classification will vary depending on the objectives and field service environment. The criteria for classification can be broadly divided into two:

a) that based on situations where immediate improvement in plasticity, improved workability, immediate strength increase and reduced swell potential are required;

b) that based on a 'long time' strength improvement associated with cementation by reaction products.

Classification based on criterion (a) is not considered here as the engineering properties used in (a) were not determined for this work.

Classification based on strength usually divides the soils into groups based on ranges of strengths. The range varies according to the use to which the material will be put, for example, the range will be higher for base materials than for subbase materials since stresses and durability conditions differ for various depths in the road pavement. The strength ranges so chosen can be validated only on basis of experience and actual field performance. Literature is virtually non-existent on the actual field performance of red tropical soils treated with lime. The result has been that workers who attempt to classify the soils have chosen arbitrary ranges. Harty and Thompson (70) divided the twenty-six soils they investigated into five arbitray groups on basis of their 28-day cured strengths after lime treatment for maximum strength. Minimum values of UCS suggested by other workers as an indication of lime treated soil's suitability vary very widely. For instance, for use as road bases the Central Road Research Institute of India suggests a minimum UCS value of 150 p.s.i ($\approx$ 1.03 MN/m^2) while Clare and Mohan (86) used 300 psi ($\approx$ 2.06 MN/m^2) for assessing the suitability of "stabilized laterites" from Nigeria.

It is not the intention here to add a few more arbitrary ranges without field validity. However, because the activity index is obtained much faster than strength at 28 days, it may be worthwhile to illustrate its potential use as a classifying parameter. In doing this, use is made of the American Association of States Highway Officials (AASHO) requirements for assessing suitability of lime treated temperate soils for use in road pavement sections. For use as a sub-base (minimum strength of 0.70 MN/m^2) an activity index of approximately 0.4×10^{-4} per day is required while for suitability as base (minimum strength of 1.03 MN/m^2) an activity index of approximately 0.75×10^{-4} per day is required. Based on this, a tentative classification of the lime treated soils investigated, for use as road materials is proposed in Table 5.6.

5.6 Uses of and using the activity index

The activity index is much faster to determine than the lime reactivity. It also requires less labour and materials. These facts cannot be overlooked where skilled labour and/or

Table 5.5 Tentative classification of red tropical soil-lime for use in road structures

GROUP	Activity Index Ai x 10^{-4} per day	Unconfined Comp. Strength MN/m^2	Reactivity	Possible Use
1	0 - 0.50	0 - 1.00	Non reactive to Poor	Subgrade, Subbases of low volume roads
2	0.50 - 1.00	1.00 - 2.00	Reactive	Subbases
3	> 1.00	> 2.00	Highly reactive	Bases

material is scarce. This index is not only useful in estimating the strength and lime reactivity of soil-lime mixtures but also potentially useful for classification purposes.

However, it should be exphasized that estimates made using the Activity Index is subject to error, the error increases with decreasing Ai value. It is therefore suggested that forecasts based on the index should serve as initial estimates and as useful aid in selecting materials, followed by actual laboratory and/or field strength testing. Much care and thought should accompany the use of the regression equations for soils other than red tropical soils as they may not be applicable because of the role played by the amorphous constituents of the red tropical soils.

5.7 Chapter Summary

a) Formation of reaction products as represented by lime consumption takes place during the initial five to seven days; therefore the gains in strength beyond this period appear to be due mostly to the hydration and increased crystallinity of the reaction products.

b) Under the experimental conditions, the bulk of the reaction between soil and lime is a diffusion controlled process apart from the initial rapid reaction of the amorphous minerals possibly through dissolution.

c) The activity index based on the diffusion model and the quantity and type of the reacting compounds of the soil is statistically related to the unconfined compressive strength of the soil-lime system.

d) A highly significant statistical linear correlation links the empirical lime reactivity as defined by Thompson and the proposed Activity Index. This suggests a common basis for the two methods and therefore allows the use of either of the two for assessing the pozzolanic properties of the soils.

e) The activity index is faster to obtain than lime reactivity and is potentially very useful tool for classifying red tropical soils if field performance of the soil-lime system is not available. It does not replace laboratory testing but serves mainly to help in recognising the active soils.

CHAPTER 6

RED TROPICAL SOIL-LIME REACTION PRODUCTS

6.1 Introduction

The mineralogical composition of the soils and their reactions with lime have been considered in the preceeding chapters. The reactions lead to the formation of cementitious products which may be partly responsible for amelioration, but definitely responsible for strengthening in those soil-lime systems that show increase in strength.

In this chapter, the nature, type and characteristics of the reaction products in such a complex system as red tropical soil-lime are considered. The mineralogical composition of the soils points out to the possible formation of CAH_{10} and/or C_2AH_8. These compounds are known to form during the hydration of some high alumina cement and later convert to C_3AH_6 (a more stable form) resulting in decreased strength. The role of iron in the reactions needs to be assessed. Lea (87) observed that "some ferric iron compounds in aggregate, for example, appear to react with lime without deleterious effect, but there is evidence that oxidation of ferrous iron is one factor contributing to the deterioration of some dolerite concretes". Could this be true of red tropical soil-lime systems?

Thus the objectives of this chapter are:

a) to identify and possibly quantify the cementitious reaction products.

b) to examine the influence of the reaction products on strength.

Only the main cementitious reaction products are considered; other products of reactions such as calcium carbonate are considered in latter chapters.

6.2 Pertinent literature and methods

The subject of this sub-chapter is treated under three sections.

6.2.1 Identification of reaction products

The products formed by reactions between lime and clays have been extensively studied. In Chapter 2, sub-section 2.4.2.5, the formation of hydrates of calcium aluminates and silicates (of the tobermorite-like type) when clays are treated with lime has been noted. On the contrary, there is virtually no literature on the reaction products of red tropical soil-lime systems.

The methods used for the identification of reaction products can be broadly grouped as:-

a) methods based on radiation, (b) thermal analysis,
c) chemical methods and (d) optical methods. The method of electron optics is considered in Chapter 8. X-ray diffraction (XRD) is a typical example of radiation methods while differential thermal analysis and thermogravimetry usually are typical thermal methods. Volumetric chemical analysis of extracts is used to chemically determine the constituents and overall composition of the reaction products.

Thermal methods are based on weight loss/weight gain or exothermic/endothermic reactions of compounds heated in a known atmosphere. The temperatures at which the reactions occur characterize the compounds and are therefore used to identify them qualitatively. These methods are therefore limited to those compounds that react when heated in a known environment. Like many other methods they do not resolve most overlaps i.e. do not identify minerals that react to heat at the same temperature and same environment when they are present in a mixture.

Chemical methods determine the overall chemical composition of the products but do not give information on the composition of the individual minerals constituting a material.

The most widely used method of identification is XRD. The principle of the use of XRD in soil mineral analysis is based on the fact that the orderly atomic structure of the crystals present in a soil causes them to behave to x-rays as a diffraction grating would to visible light. The atoms near the beam of single wavelength vibrate and re-emit x-rays as if their source were the atom itself. Similarly the atoms in the deeper layers are penetrated by the x-rays and behave as the surface atoms. At some angle of incidence of the x-rays the reflections from the successive layers reinforce one another to give a diffracted beam which obeys Bragg's equation:

$$n\lambda = 2d \sin \theta \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6.1)$$

where λ = wavelength of x-rays

d = spacing (basal) between each of the diffraction planes

θ = angle of incidence of x-rays

n = order of reflection, usually 1 for the diffracted beams to reinforce one another.

If the crystals of a mineral are rotated in an x-ray beam, the possible sets of the diffracting planes of its atoms can be obtained as each set of planes momentarily satisfies Bragg's equation and gives a diffracted beam. In a practical x-ray diffractometer, this is achieved by grinding the crystals so that their random orientation ensures that a few will be in the correct position for any set of planes. The angle θ is usually increased from low to high values while the diffracted beam is monitored. Typical diffraction traces are shown in Fig. 6.1 and Fig. 6.2.

The limitation of this method is that it can only be used for crystalline minerals; it cannot identify amorphous reaction products. XRD like any other method, seldom achieves unambiguous identification of the reaction products due to the pattern similarities of many closely related hydrated silicates, alumino-silicates and alumino-ferri-silicates. However such ambiguities are resolved with the aid of some of the methods mentioned earlier as supplements. Hence in this work it was decided that identification will be done by XRD and supplemented by thermogravimetry (TG), scanning electron microscopy SEM (Chapter 8), and chemical extraction analysis. Because the results of TG not only serve to identify but may be used to quantify products of the soil-lime system, like lime and calcium carbonate, (not considered here) they will be discussed in Chapter 9.

6.2.2 Quantification of the reaction products

The quantitative determination of reaction products is difficult, their precise composition is seldom known and they occur in a mixture of many other minerals. In this investigation, three methods of approach based on different principles are considered i.e., thermal, chemical and radiation.

Thermal methods, employ the selective reaction of the cementitious products in an atmosphere, monitoring the weight changes that occur during the reactions and quantifying the reactive product from the stoichiometry of the transformation. Principal thermoponderable reactions met in cement chemistry, like the equilibria solid-gas thermal reactions of the hydration-dehydration (see eqn. 6.2), carbonation-decarbonation (eqn. 6.3) types, have been used to measure some constituents of cement (88).

$$\underset{\text{solid}}{Ca(OH)_2} \rightleftharpoons \underset{\text{solid}}{CaO} + \underset{\text{gas}}{H_2O} \quad \ldots \quad \ldots \quad \ldots \quad (6.2)$$

$$\underset{\text{solid}}{CaCO_3} \rightleftharpoons \underset{\text{solid}}{CaO} + \underset{\text{gas}}{CO_2} \quad \ldots \quad \ldots \quad \ldots \quad (6.3)$$

By adapting the equations, 6.3 for instance, tricalcium silicate (C_3S), a cement clinker component, can be quantified if ground cement is heated in carbon dioxide atmosphere. Theoretically, it will react with CO_2, after the possible elimination of free lime, according to the following equation:

$$C_3S + CO_2 \rightarrow C_2S + CaCO_2 \quad \ldots \quad \ldots \quad (6.4)$$

This equation is a simplified representation of the actual complex reaction involved. By measuring the weight changes C_3S can be quantified using equation 6.4. Similarly by first reducing the alumino-ferrite phase of a cement clinker in a hydrogen atmosphere according to equation 6.5 and oxidising the reduced

$$C_4AF + 3H_2 \rightarrow C_4A + 2Fe + 3H_2O \ldots \quad (6.5)$$

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \quad \ldots \quad \ldots \quad (6.6)$$

(oxygen results from the dissociation $2CO_2 \rightleftharpoons 2CO + O_2$)

iron in a CO_2 atmosphere (eqn. 6.6) at 1000^oC, the iron content of the ferrite phase can be estimated. While TG holds out a potential method of quantifying reaction products of soil-lime systems, it can be seen from the examples given that the use of TG requires a knowledge of the actual chemical composition of the reaction product which is not certain.

Chemical methods of quantification depend on the ability to extract the cementitious products using a selective solvent. The quantification consists of the determination of the different minerals in the extracts. The methods used for separating reaction products in pozzolanas from the unreacted material rely on a method proposed by Steopoe (89) and described in old German works. The method is based on the fact that whereas the silicates and aluminates in a pozzolana are relatively insoluble in dilute hydrochloric acid under certain conditions, the silicates and aluminates in the reaction products are extremely acid soluble under the same conditions and thus may be extracted. It is only the optimum conditions for maximum extraction that different users of this method have changed. Ruff and Ho (67) used 50 mls of 0.2N Hcl in extracting 0.5 gm of lime treated soil dried in vacuum. They employed an extraction time of 30 minutes. The acid concentration is such as to give a final supernatant pH of between 1 and 2 because not only is aluminium ion stable at this pH range (it slowly polymerizes and precipitates as $Al(OH)_3$ at pH > 4.5) but also the rate of polymerization of the silicic acid dissolved is minimum in this range (90). Gray (90) used the same conditions as Ruff and Ho (67). The following modified Steopoe's method as communicated to the author by Jambor (91) was tried out and found to give a final supernatant pH of about 1.45 for red tropical soils.

The hardened lime-pozzolana paste is ground to a fineness approximately < 90μm. One gramme of the ground paste is gradually poured, under constant stirring, into a beaker containing 60 ml of HCl (density 1.12) and cooled by water at 12 - 13°C. The solution is left to clear up for 10 mins. and is filtered and the extract analysed.

Quantitative determination by XRD, makes use of a standard mineral whose composition is the same as that of the mineral to be quantified in the soil (72). Using varying quantities of the standard mineral (by weight), the diffraction intensities (above the background) at a selected d-spacing are measured preferably using the areas under the peaks as measures of intensities. A calibration graph is drawn by plotting the intensities as ordinates against the weights of the standard minerals as abscissa. The test sample (soil-lime mixture) is x-rayed and the intensity of the peak at corresponding d-spacing above the background is measured. Using this value of intensity for the test sample and the calibration graph, the weight of the mineral can be determined. Because the x-ray absorption rate varies with the constituents present, the intensity of a mineral present in the test sample depends on other minerals present (diluents) in the soil.

The use of an internal standard in addition to the standard mineral almost completely eliminates the error due to the x-ray absorption by the sample. The peak intensities of the standard mineral and the test samples are measured relative to the corresponding peak intensity of the internal standard. Any mineral can be used as an internal standard provided that:

a) it is not present in the test sample,

b) it has a peak intensity as close as possible to the d-spacing at which the diffraction intensities are measured for the standard mineral and the test sample.

Calcium fluoride, ammonium chloride, quartz have been used as internal standards (72). Recently, Tuncer et al (92) modified this method. Their modification comprises the comparison of the XRD peak intensities of the mineral in the sample with the intensities of the same peak in specimens that are a mixture of the original soil sample and known additional amounts of the mineral to be quantified, i.e. the component being determined is used as an internal standard. This modification relies on precisely knowing the composition of the mineral to be quantified so that the peak of the mineral in the test sample and the internal standard are coincident. This is very difficult, if not impossible to achieve in red tropical soil-lime systems. Hence this modification was not adopted.

6.2.3 Reaction products and strength

The study of the effects of the amount of silicates, aluminates, alumino-silicates and alumino-ferri-silicates on strength has been extensively carried out on concretes and mortars. Their effects on the strengths of clay-lime systems have not been studied as extensively while such studies are non-existent for red tropical soil-lime systems.

The strength of a cementitious paste depends on the type and quantity of binders present. Kalousek and Prebus (93) associated plate-like tobermorite with high strength and low shrinkage and CSH I as well as fibrous CSH II with low strength and high shrinkage. Powers (94, 95) attributed strength to cement gel and proposed that it is proportional to the third power of the volume of gel present. He empirically determined the relationship to be:

$$S = \sigma_o V^3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6.7)$$

where S = strength of cement paste

σ_o = strength of gel of maximum density without capillary voids

V = proportion of volume occupied by gel in a unit volume of cement paste.

Some other investigators have found the strength of concrete to be a power function of the quantity of hydration products. Among them is Schiller (96) whose formula

$$P = K \log \frac{e_k}{e} \quad \ldots \quad \ldots \quad \ldots \quad (6.8)$$

where e_k = critical porosity for which the strength, $P = 0$,

K = coefficient independent of over-all porosity but dependent on pore shape and nature of crystal contacts,

can be modified to apply to the calculation of strengths of cement pastes, mortars and concretes.

Ruff and Ho (67) found that the strength gain of lime-clay mixtures cured at different temperatures is due to the presence of the different phases of the complex reaction,

lime + clay → CSH(gel) → CSH(II) → CSH(I) → tobermorite.

The further the reaction proceeded, the higher the strength. They found no consistent relationship between time, temperature, strength and the silica/alumina ratios of the reaction products but in order to achieve high strengths they noted that the apparent calcium oxide/silica ratio had to be less than 2.

Jambor (63, 97) working on lime-pozzolana pastes found the following relationship to exist between strength and volume of new binding materials formed depending on type of the binding material.

$$S = av^3 + bv^2 + cv + \ldots \qquad \ldots \qquad \ldots \qquad (6.9)$$

where S = strength

v = volume of hydration products of types I - V

a,b,c = constants,

Type I ≡ tobermorite-like phases

Type II ≡ CSH(1)

Type III ≡ 70 to 80% gehlenite hydrate (C_2ASH_n) and 20 to 30% of CSH(1)

Type IV ≡ 70 to 80% hydrogarnet ($C_3AS_nH_{6-2n}$) and 20 to 30% of CSH(1)

Type V ≡ C_3AH_6 and/or hydrogarnet phase.

The effects of the different types of cementitious materials is further illustrated by Alexander et al (98) who found that the strength of mortars is most sensitive to C_3A content of the cement.

Most work done on the influence of the quantity and type of cementitious products on the strength of pastes has been on mortars and concretes. Very little has been done in this direction for practical soil-lime systems. In his investigations Jambor employed the following conditions not normally used in a practical soil-lime system:-

a) He used among other pozzolanas, activated kaolin made by burning washed kaolin for 2 hours at 650°C.

b) All his pozzolanas were ground to less than 90 microns.

c) He used high percentages of lime viz. 34%, 50%, 66%.

These conditions led to almost complete reaction between the lime and the pozzolanas for his XRD traces detected only weak lines of unreacted pozzolanas. Hence the strengths of the lime-pozzolana systems he measured were attributed to the new binding materials formed.

6.3 Experimental methods

The lime treated soils used were the broken pieces of the mixture that gave maximum strength as outlined in Chapter 4. They were tested after curing for about 2 years. Details of the methods used for x-ray (qualitative and quantitative) and chemical analyses are given in sections under this sub-chapter.

6.3.1 Chemical analysis

Selective chemical extraction of the reaction products was performed using the modified Steopoe's method communicated to the author by Jambor (91); the details of which were given in section 6.2.2. The lime treated soil was ground to less than 75 microns. No selective method of extraction leaves other constituents perfectly intact especially in cementitious pastes made from siliceous admixtures with high alumina and iron oxide (R_2O_3) contents and forming low contents of the reaction products (97). In view of this, similar chemical treatment was applied to the natural soil. The extracts were analysed using atomic absorption spectrophotometry as described in Chapter 5. The acid soluble calcium, silicon, aluminium and iron in both the lime treated and the untreated soils were measured under the standard conditions shown in Table 6.1 The elements were calculated thus:

$$\text{Extractable element} = \frac{\text{ppm x volume used x d.f}}{\text{sample weight x } 10^3} = \text{Ca or Al or Si or Fe}$$

where d.f = dilution factor

$$= \frac{\text{final diluted volume in ml.}}{\text{volume of aliquot taken for dilution in ml.}}$$

Calcium as CaO $= \frac{56.08}{40.08}$ Ca = 1.40 Ca

Silicon as SiO_2 $= \frac{60.09}{28.09}$ Si = 2.14 Si

Aluminium as Al_2O_3 $= \frac{101.96}{26.98}$ Al = 3.78 Al

Iron as Fe_2O_3 $= \frac{159.70}{55.85}$ Fe = 2.86 Fe

The values of the elements as oxides in the reaction products were obtained by subtracting the results for the untreated soils from those for the treated soils.

6.3.2 Qualitative XRD

Identification of the reaction products was carried out by XRD using molybdenum Kα radiation obtained from a Phillips x-ray diffractometer. Molybdenum Kα radiation was used in preference to a copper Kα radiation because it gives better diffraction peaks for iron-rich materials such as red tropical soils (39). The operating conditions are 42 KV, 14 mA, scanning rate of 1^{o} per minute, rate meter of 4 and time constant of 4. Among the factors that affect the intensity of a diffraction peak are particle size, chemical composition, crystal imperfection, sample packing, x-ray absorption, crystal orientation and amorphous substances (72). Methods adopted for the controlable factors are as follows:

Particle size was controlled by gently grinding the soil-lime mixture with a rubber pestle to pass a 75 micron sieve. Control on sample packing was effected by investigating the variation of the diffraction peak at $2\theta = 10^{o}$ with different weights of the soil contained in a sample holder of a constant volume. The area

Table 6.1 Standard conditions used to determine iron, calcium, aluminium and silicon in the extracts by atomic absorption spectrophotometry

Element	Iron	Calcium	Aluminium	Silicon
Wavelength	248 uv	211 uv	309 uv	252 uv
Slit setting	3(0.2 nm)	4(1.4 nm)	4(0.7 nm)	3(0.2 nm)
Light source	Hollow Cathode Lamp			
Flame type	Air-acetylene flame oxidising (lean, blue)		Nitrous oxide-acetylene reducing (rich, red)	

Fig. 6.1 X-ray diffraction traces for NF showing the lime treated and the natural soils. Shaded areas represent positions of new peaks.

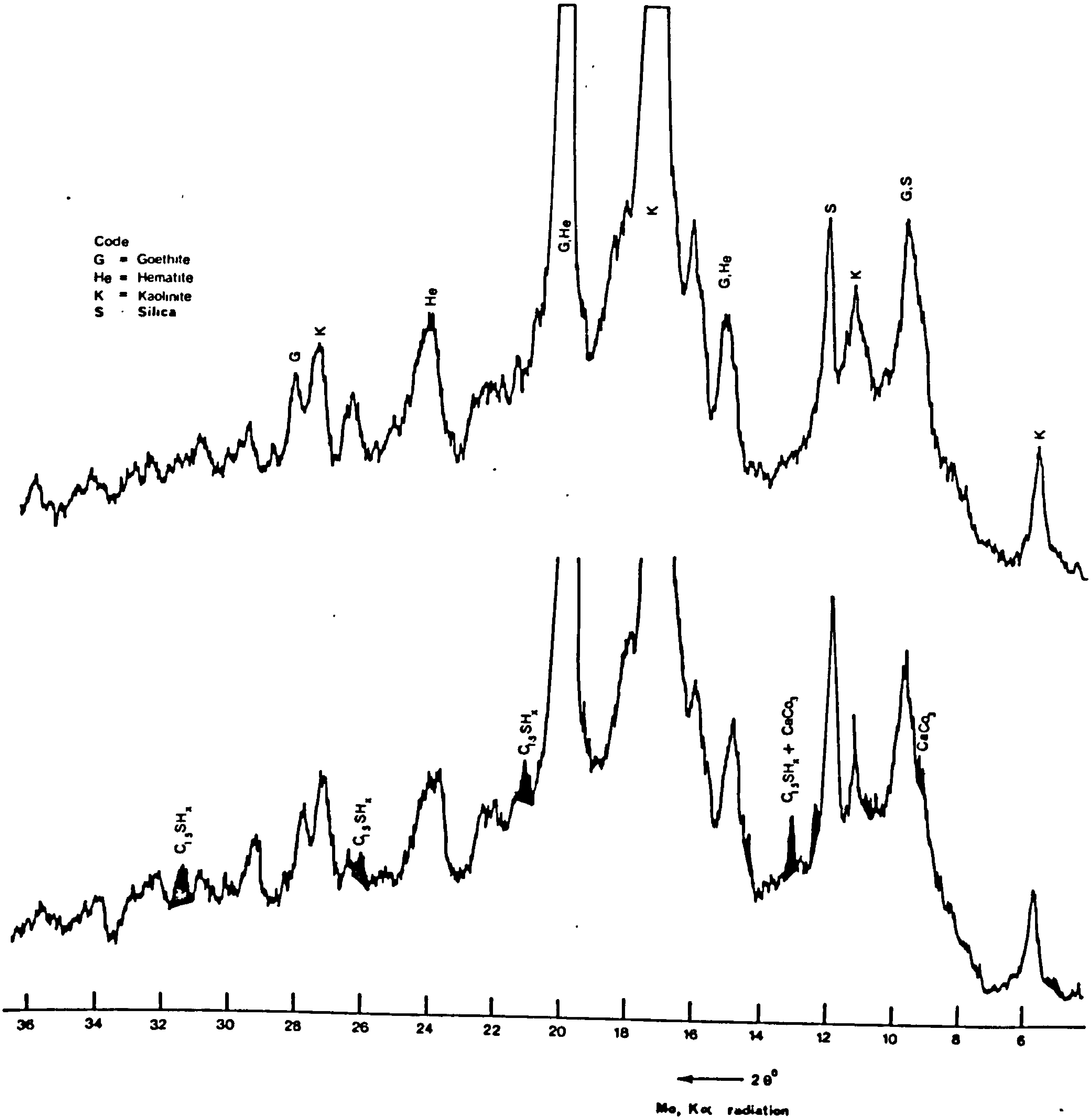
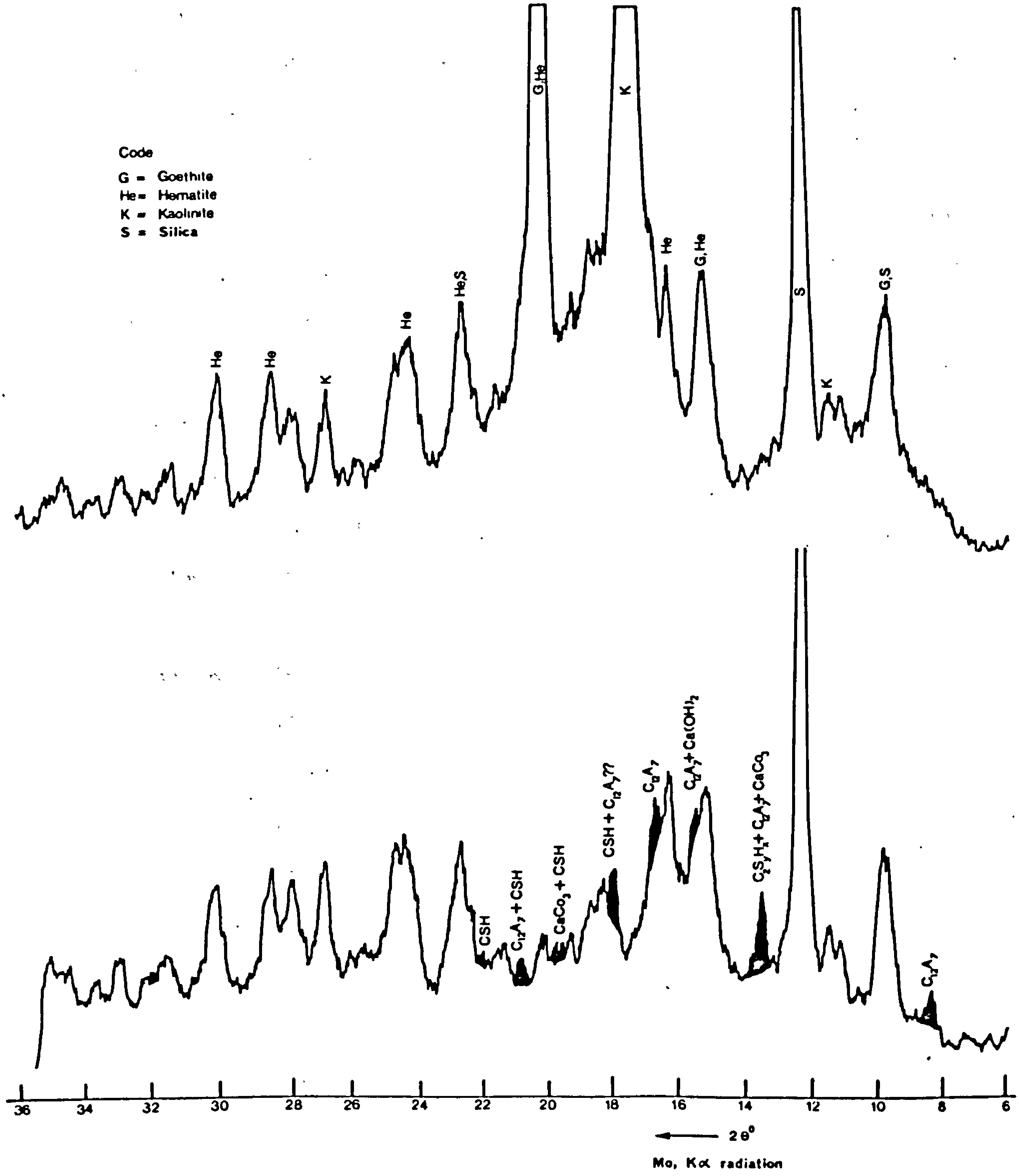

Code
G = Goethite
He = Hematite
K = Kaolinite
S · Silica
G
K
He
G,He
K
G,He
S
K
G,S
K
$C_{1.5}SH_x$
$C_{1.5}SH_x$
$C_{1.5}SH_x$
$C_{1.5}SH_x$ + $CaCO_3$
$CaCO_3$
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
← 2θ°
Mo, Kα radiation

Fig. 6.2 X-ray diffraction traces for SIA showing the lime treated and natural soils. Shaded areas represent positions of new peaks.


Code
G = Goethite
He = Hematite
K = Kaolinite
S = Silica
He
He
K
He
He,S
G,He
K
He
G, He
S
K
G,S
CSH
C12A7 + CSH
CaCO3 + CSH
CSH + C12A7??
C12A7
C12A7 + Ca(OH)2
C2SyHx + C12A7 + CaCO3
C12A7
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
← 2θ°
Mo, Kα radiation

of the peak was measured in each case with a planimeter. The results are presented in Fig. 6.3 and show that the maximum peak occurs when about 0.5 grams of the soil is used in that particular sample holder. This weight of soil was therefore used throughout the investigation.

The XRD of the lime treated and natural soil of each sample was run. Typical results are shown in Figs. 6.1 and 6.2 for soils NF and SIA. The diffraction traces for some of the rest of the soils are shown in appendix A1. By comparing the XRDs of the lime treated and natural soils the 2θ values at which new peaks occur were abstracted (shown shaded in the figures). These 2θ values were fed into a computer search program similar to that used by Willoughby et al (61). Details of the search program are given in Chapter 7. The search was for the strong peaks of ASTM standard hydrates of calcium silicates, aluminates, alumino-silicates and alumino-ferri-silicates whose composition include elements present in the initial reactants. The possibility of peaks overlapping those of the unreacted soil minerals was taken into consideration.

6.3.3 Quantitative XRD

The method of internal standard was used.

6.3.3.1 The internal standard used

Ammonium chloride was used as the internal standard because it has a diffraction peak at $2\theta \approx 15^o - 16^o$ which does not overlap the peaks of the minerals in the soil. The position of this peak is near to the d-spacings at $2\theta = 13^o - 14^o$ used to quantify the test sample. The XRD tracing of the ammonium chloride is shown in appendix A1.

6.3.3.2 Standard minerals used

Naturally occuring silicates (okenite), alumino-silicate (prehnite) and alumino-ferri-silicate (epidote), obtained from the Department of Earth Sciences of Leeds University, were used as standard minerals for the lime treated soils forming silicates, alumino-silicates and alumino-ferri-silicates respectively. The peaks of the standard minerals at $2\theta \approx 13^o - 14^o$ were used. Naturally occuring minerals were preferred to their chemically synthesized counterparts because they are more likely to be impure as discussed later. Their chemical compositions were studied by x-ray fluorescence and are shown in Table 6.2 while their XRDs are shown in Appendix A1.

6.3.3.3 d-spacing used for peak measurement in the test samples

Most calcium silicates, aluminates, alumino-silicates and alumino-ferri-silicates have diffraction peaks at 2θ equal to 13^o approximately. The intensity of this peak was used as a measure of the reaction products in each test sample. Lime and calcium carbonate have peaks in this region as well. Chemical and thermo-gravimetric analyses showed the lime treated soils to contain appreciable quantities of unreacted and carbonated lime (see Chapter 9). The reaction products obtained as a percentage of the lime treated soil were corrected for the presence of unreacted and carbonated lime.

6.3.3.4 Procedure

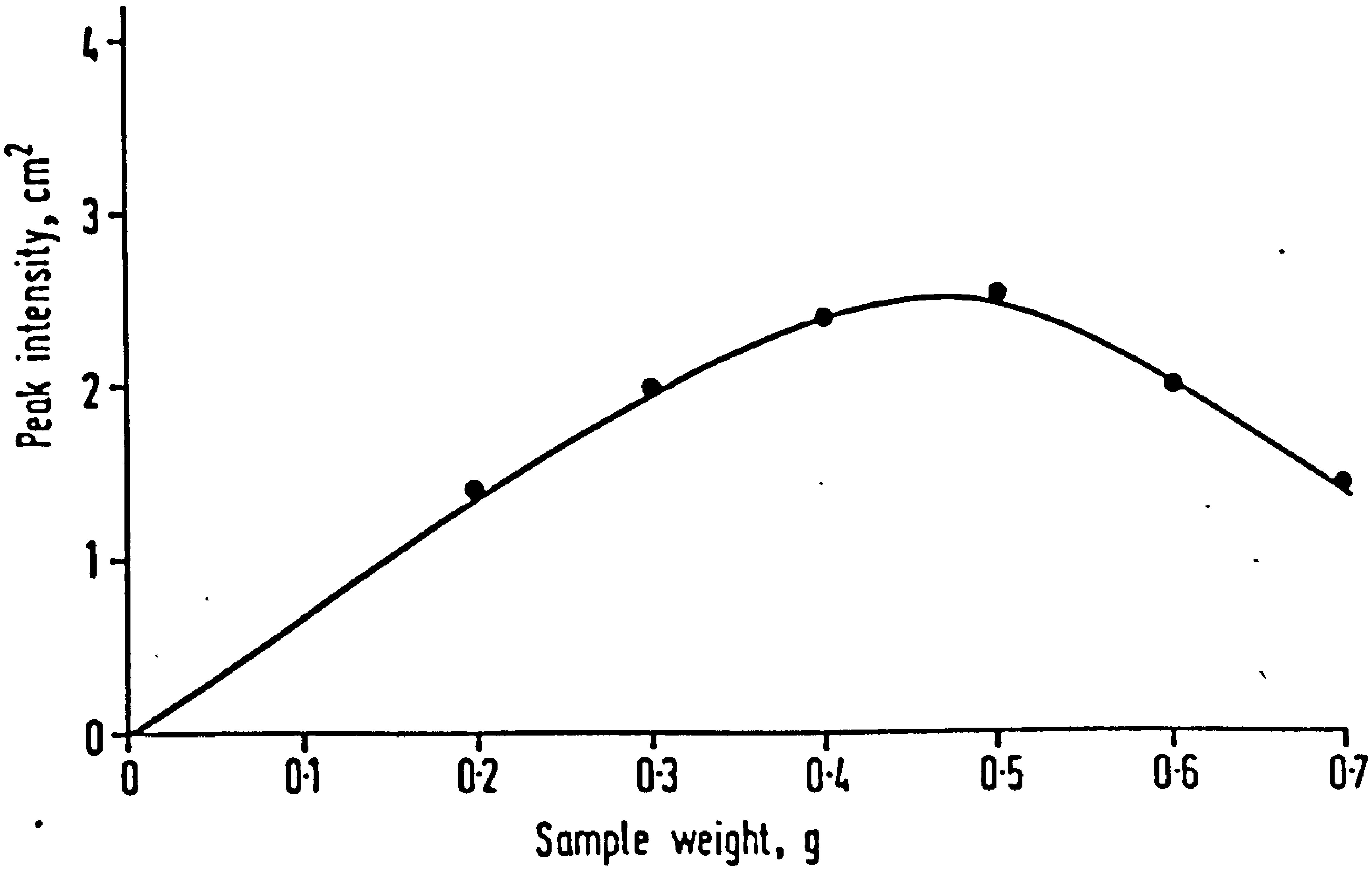
A constant quantity (0.15 gm) of the internal standard (g_i) was added to 0.05, 0.075, 0.10, 0.125, 0.15 and 0.20 gms of the standard mineral (g_m). Untreated soil (diluent) was added to make up each mixture to weigh 0.5 gms. All three materials were

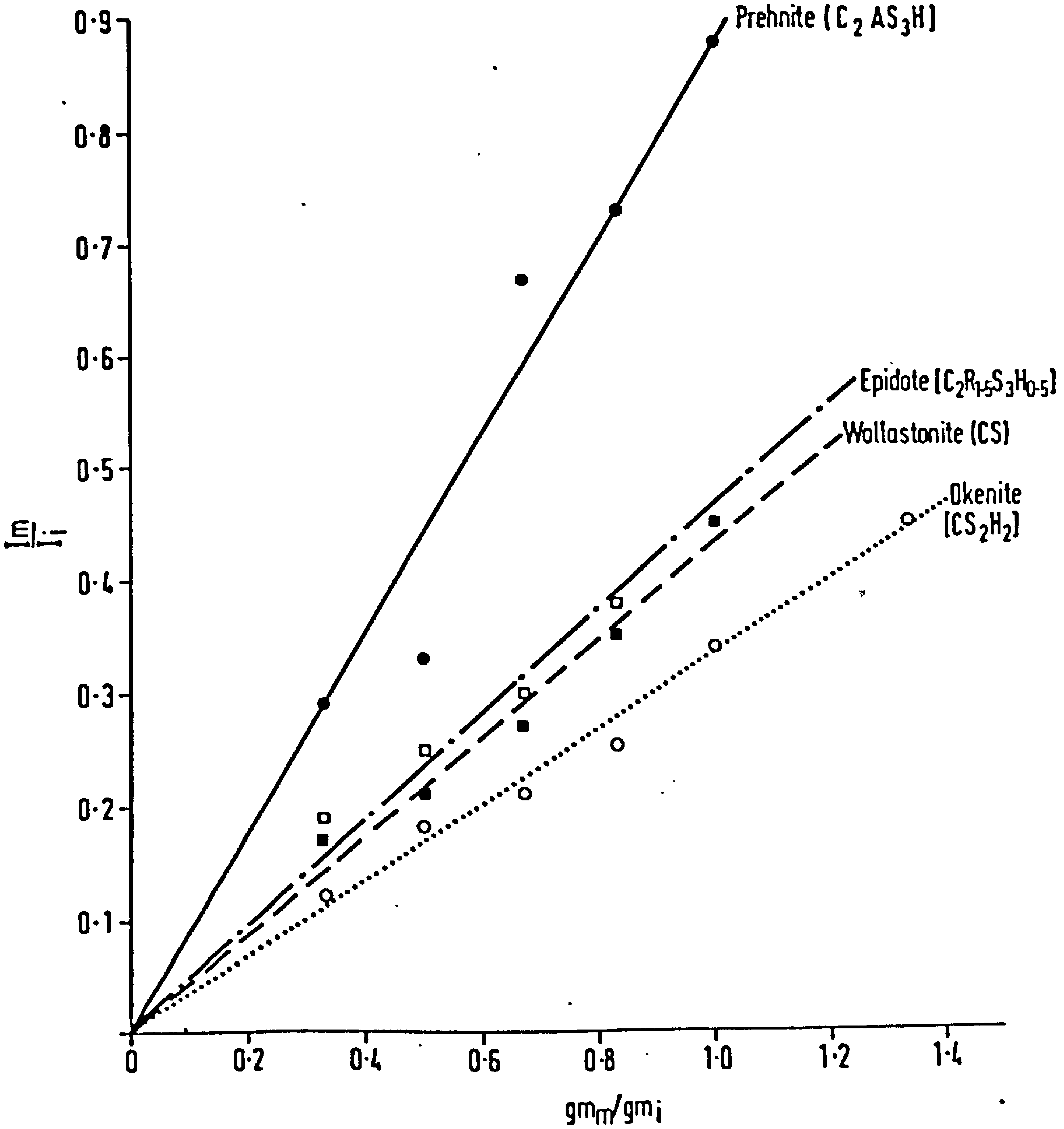
Table 6.2 Chemical analysis by XRF of minerals used as standards in XRD quantification by the method of internal standard

	OKENITE	PREHNITE	EPIDOTE
SiO_2	56.61	41.40	39.65
Al_2O_3	0.638	22.40	23.18
Fe_2O_3	0.042	0.99	11.48
CaO	23.28	24.29	20.07
H_2O	18.28	3.68	10.20

Fig. 6.3 Variation of peak intensity with density or packing of soil sample

Fig. 6.4 Calibration curves for the standard minerals used in quantifying the reaction products


Peak intensity, cm^2
0
1
2
3
4
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
Sample weight, g


Prehnite (C_2AS_3H)
Epidote [$C_2R_{1.5}S_3H_{0.5}$]
Wollastonite (CS)
Okenite [CS_2H_2]
$\frac{I_m}{I_i}$
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
gm_m/gm_i

thoroughly mixed and x-rayed. The intensities of the peaks of the standard mineral (I_m) occuring between $2\theta = 13^o - 14^o$ and of the internal standard (I_i) occuring between $2\theta = 15^o - 16^o$ were measured with a planimeter. The ratios I_m/I_i and their corresponding g_m/g_i values were calculated. A calibration curve of I_m/I_i as ordinate vs. g_m/g_i as abscissa was plotted for each standard mineral (see Fig. 6.4).

To quantify the reaction products in each soil, 0.15 gm of the internal standard was mixed with 0.35 gm of the lime treated soil and x-rayed under the same conditions as for the mixtures used for the calibration curve. The intensities of the peaks at $2\theta \approx 13^o$ for the reaction products and at $2\theta = 15^o - 16^o$ for the internal standards were measured and the ratio I_m/I_i calculated for each test sample. Using these values and the calibration curves the weights of the reaction products in the soils are determined. The calibration curve used for each soil depends on whether that soil forms silicates, alumuno-silicates or alumino-ferri-silicates as determined from their qualitative XRDs. The volumes occupied by the reaction products per unit volume of compacted lime treated soil were calculated using the following relative densities for the powdered standard minerals:
0.43 for okenite, 0.32 for prehmite and 0.29 for epidote.

6.4 Results and discussions

The results are given and discussed under appropriate sections.

6.4.1 Identification of reaction products

The computer search program greatly aided the identification of the reaction products. Tables A - E in Appendix A2 show the

ASTM x-ray data for calcium salts concordant with the new lines observed in the lime treated soils. It can be seen that it is difficult to distinguish between the many closely related silicates, alumino-silicates and/or alumino-ferri-silicates.

6.4.2 The identified products

Table 6.3 shows a summary of the likely minerals formed by each soil reacting with lime. The Table is prepared from Tables A - E in Appendix A2. The mineral, plomberite gel, (ASTM ref 10 - 416) seems to be formed in most of the soils. The ASTM index characterises the mineral as "a natural gel, poorly crystallised and probably of mixed hydrates". Its chemical composition is given as (%):- SiO_2 = 40.4, CaO = 32.6, Al_2O_3 = 2.4, Fe_2O_3 = 0.8, MgO = 0.3, H_2O = 23.3. The next most common minerals in the soils is tobermorite of the type $xCaO.SiO_2.yH_2O$ (ASTM ref 6 - 0010) with $x \sim 1$, y not known. This is also characterised as a "poorly crystallised, mixed hydrates; probably contains interstratified mixed hydrates, x-ray pattern is very variable especially d = 12.5Å".

From the characteristics of the two silicates that occured in most of the soils it appears that after about two years curing, most of the reaction products are still in poorly crystallised states but cystalline enough to be detectable by x-rays. It would also appear that most of the silicates do not occur in pure forms; they seem to be mixed hydrates. It was for this reason that naturally occuring minerals were preferred to their chemically synthesized counterparts as standards for quantitative XRD. The mixed nature of the hydrates would suggest ionic substitution in the lattice of the tobermorite formed. Kalousek (99) reported that "up to 5 - 6% aluminium was substituted before a hydrogarnet C_3ASH_4 was detected by XRD as a second phase"; below this percentage he observed that "the tobermorite with substituted aluminium exhibited the same XRD pattern as the aluminium-free tobermorite except for a small increase in values of basal spacings with increasing amount of aluminium". Diamond (100) substituted up to 10% aluminium before detecting a hydrogarnet by XRD. Using goethite as a source of iron, Diamond et al (101) were able to substitute iron into the lattice of tobermorite. Copeland et al (102) reacted high-lime tobermorite gel with aluminates, ferrites and sulphates at room temperature and found that iron substituted in amount of 7.1%. They pointed out that the results of iron substitution into tobermorite were not very reproducible. The mineralogical composition of red tropical soils strongly favours ionic substitution by aluminium or iron or both in the lattice of the calcium silicates formed thus bringing about the inpure nature of the reaction products. Only soil SI seems to have formed a hydrogarnet and it thus appears that aluminium does not substitute in large enough amount as to make a second phase x-ray detectable in most of the soils.

Some soils like JI, RC, USM, CT have formed mostly aluminates and alumino-silicates. In few other soils alumino-ferri-silicates have been identified. None of the soils formed iron compounds only as a distinct phase in contrast to the formation of calcium silicates and calcium aluminates. It would therefore appear that the role of iron seems to be to substitute into the silicates, aluminates and/or alumino-silicates formed as distinct phases. Indeed it is also noteworthy that the formation of quarternary compounds of lime-silica-alumina-iron hydrates in which silicon, aluminium and iron occur in distinguishable lattice positions is not detected in most of the soils.

Table 6.4 shows the results of the chemical analysis of the reaction products from which their approximate overall compositions are calculated as shown in Table 6.5. Their approximate overall compositions show clearly that iron is substituted in different quantities in the silicates and alumino-silicates. Because only the overall composition of the reaction products can be calculated from the chemical extractions rather than the chemical composition of the different phases that make up the overall products, the amount of iron required to substitute to enable the detection of a quartenary ferrite phase by XRD cannot be determined. No CAH_{10} or C_2AH_8 was detected to form in any of the soils.

6.4.3 Consecutive and multiple reactions

Table 6.3 shows that nearly all the soils form more than one product. Thus most of the reactions are of the second order generally represented as:-

$$A + B \rightarrow C + D \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6.10).$$

In his study of lime-quartz pastes, Taylor (103) gave a general picture of the reaction that takes place. He was of the opinion that surface reactions on quartz gave a lime rich substance similar to CSH (II). If the overall C/S ratio is low, the reaction proceeds until all lime is depleted. The CSH (II) then reacts with more quartz to give CSH (I) with low C/S ratio which recrystallises to tobermorite depending on time and temperature.

Table 6.3 Summary of likely minerals formed

(with % of strong peaks present in brackets)

SOIL SYM-BOL	SILICATES							ALUMINATES		ALUMINO-SILICATES			FERRI-SILI-CATE	ALUMINO-FERRITE		ALUMINO-FERRI-SILICATE
	$C_2SH_{0.5}$ 15-642	C_3SH_2 11-502	CSH_{N-X} 0.85-1.5 10-416	C_xSH_y 6-0010	$C_6S_4H_3$ 3-560	C_2SH 3-594	C_3SH_2 3-669	C_5A_3 11-357	$C_{12}A_7$ 9-413	Cal. Al. Sil. Hyd. 19-52	$CAS_7H_{7.5}$ 19-211	C_2ASH 16-388	Cal. Iron Sili-cate 19-231	C_6A_2F 11-190	C_4AF 11-124	Cal. Al. Iron Sil. Hydr. 10-447
PH			√(90)	√(100)												
JPM			√(90)				√(90)									
TII			√(100)	√(100)												
SB				√(80)		√(80)										
NF			√(90)													
JPB			√(90)	√(80)												
JPA			√(90)		√(100)			√(95)								
SIB												√(90)				
JI	√(80)										√(100)					
SII		√(90)	√(90)												√(80)	
RC										√(90)						
USM			√(60)							√(80)						
CT									√(90)							
AI			√(80)	√(90)										√(70)		
AII			√(80)										√(90)			
SM							√(80)							√(70)		
TI																√(90)
SIA									√(85)							
JII																√(90)

Table 6.4 Chemical analysis of the acid soluble reaction products

SOIL SYM-BOL	Chemical Composition (%)						IN PRODUCT (mols) AS			
				CaO in						
	SiO_2	Al_2O_3	Fe_2O_3	$Ca(OH)_2$	$CaCO_3$	hydra-tion pro-ducts	CaO	SiO_2	Al_2O_3	Fe_2O_3
PH	4.24	8.78	3.41	0.30	1.65	22.62	0.40	0.071	0.086	0.021
JPM	11.56	17.35	1.05	0.26	0.67	15.70	0.28	0.192	0.170	0.0066
TII	9.37	13.27	3.68	0.42	1.20	38.45	0.69	0.156	0.130	0.023
SB	14.25	14.90	1.58	0.45	1.40	25.74	0.46	0.237	0.146	0.0099
NF	5.26	11.63	13.48	0.34	1.68	22.55	0.40	0.088	0.114	0.084
JPB	7.06	6.94	1.05	0.76	0.40	24.69	0.21	0.118	0.068	0.0066
JPA	8.99	15.51	5.78	0.43	0.70	14.14	0.25	0.15	0.152	0.036
SIB	7.32	10.61	15.75	1.29	2.16	35.33	0.63	0.122	0.104	0.098
JI	10.79	15.92	11.81	0.61	1.53	21.67	0.39	0.18	0.156	0.074
SII	16.69	15.10	3.68	0.72	1.69	39.47	0.70	0.278	0.148	0.023
RC	10.66	16.53	0.26	0.34	1.50	25.0	0.45	0.177	0.167	0.0016
USM	14.0	23.68	2.28	0.53	1.52	33.86	0.60	0.233	0.232	0.014
CT	9.63	13.68	5.51	0.79	1.61	27.99	0.50	0.16	0.134	0.034
AI	16.56	27.35	4.90	0.68	1.52	30.31	0.54	0.276	0.268	0.031
AII	8.47	21.02	3.24	0.66	1.40	33.47	0.60	0.141	0.206	0.0203
SM	14.38	23.88	7.09	0.45	1.55	31.64	0.56	0.24	0.234	0.044
TI	24.52	31.23	10.33	0.89	1.16	37.41	0.67	0.408	0.306	0.065
SIA	5.13	6.94	3.15	1.40	1.01	25.22	0.81	0.085	0.068	0.020
JII	12.58	11.84	5.78	0.83	1.10	23.40	0.42	0.209	0.116	0.036

Table 6.5 Approximate overall chemical composition of reaction products

SOIL SYMBOL	CaO/SiO_2	Al_2O_3/SiO_2	Fe_2O_3/SiO_2	Approx. overall composition
PH	5.67	1.22	0.30	$C_{5\cdot 67}\ SA_{1\cdot 22}\ F_{0\cdot 30}\ H$??
JPM	1.46	0.89	0.03	$C_{1\cdot 46}\ SA_{0\cdot 89}\ F_{0\cdot 03}\ H$?
TII	4.42	0.83	0.15	$C_{4\cdot 42}\ SA_{0\cdot 83}\ F_{0\cdot 15}\ H$?
SB	1.94	0.62	0.04	$C_{1\cdot 94}\ SA_{0\cdot 62}\ F_{0\cdot 04}\ H$?
NF	4.57	1.30	0.06	$C_{4\cdot 57}\ SA_{1\cdot 30}\ F_{0\cdot 06}\ H$?
JPB	5.78	0.58	0.06	$C_{5\cdot 78}\ SA_{0\cdot 58}\ F_{0\cdot 06}\ H$?
JPA	1.67	1.01	0.24	$C_{1\cdot 67}\ SA_{1\cdot 01}\ F_{0\cdot 24}\ H$?
SIB	5.16	0.85	0.81	$C_{5\cdot 16}\ SA_{0\cdot 85}\ F_{0\cdot 81}\ H$?
JI	2.17	0.87	0.41	$C_{2\cdot 17}\ SA_{0\cdot 87}\ F_{0\cdot 41}\ H$?
SII	2.52	0.53	0.08	$C_{2\cdot 52}\ SA_{0\cdot 53}\ F_{0\cdot 08}\ H$?
RC	2.54	0.92	0.009	$C_{2\cdot 54}\ SA_{0\cdot 92}\ F_{0\cdot 009}H$?
USM	2.58	1.00	0.06	$C_{2\cdot 58}\ SAF_{0\cdot 06}\ H$?
CT	3.13	0.84	0.22	$C_{3\cdot 13}\ SA_{0\cdot 84}\ F_{0\cdot 22}\ H$?
AI	1.96	0.97	0.11	$C_{1\cdot 96}\ SA_{0\cdot 97}\ F_{0\cdot 11}\ H$?
AII	4.26	1.46	0.14	$C_{4\cdot 26}\ SA_{1\cdot 46}\ F_{0\cdot 14}\ H$?
SM	2.34	0.98	0.19	$C_{2\cdot 34}\ SA_{0\cdot 98}\ F_{0\cdot 19}\ H$?
TI	1.64	0.75	0.16	$C_{1\cdot 64}\ SA_{0\cdot 75}\ F_{0\cdot 16}\ H$?
SIA	5.48	0.80	0.23	$C_{5\cdot 48}\ SA_{0\cdot 80}\ F_{0\cdot 23}\ H$?
JII	2.01	0.56	0.17	$C_{2\cdot 01}\ SA_{0\cdot 56}\ F_{0\cdot 17}\ H$?

This sequential reaction suggested by Taylor implies that for some reactions of red tropical soils, equation 6.10 can be expressed as a consecutive reaction of the form

$$A + B \xrightarrow{k} C \xrightarrow{1} D \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (6.11)$$

where k is the rate constant for the first step and 1 is the rate constant for the second step (67). If $1 \geq k$, C is not formed and if $1 < < k$ a negligible amount of D will form. If k is slightly higher than 1, both C and D will be present. These inequalities will, possibly hold only for those red tropical soils that form one type of product, say silicates. Where more than one type of product is formed, say silicates and alumino-silicates, the consequences of the inequalities between 1 and k as applied to equation 6.11 are not valid. They would rather apply to the multiple reactions represented by equation 6.12.

$$\left.\begin{array}{l} A + B \xrightarrow{k} C \\ A + B \xrightarrow{1} D \end{array}\right] \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (6.12)$$

The implication of equation 6.12 is that the reactions can be simultaneous irrespective of the values of k and 1. The behaviour of the mixture from the point of view of strength will depend on whether C or D is in greater quantity at any particular time. These facts, in addition to the effect of the volume of reaction products formed with time, may explain the shapes of the kinetic function-time curves shown in Fig. 5.5. The figures show two distinct reaction rates. One reaction rate occurs between 0 - 5 or 7 days and the other thereafter to 28 days. It would appear that one rate is k and the other 1. Where consecutive reaction occurs then k corresponds to reaction rate measure between 0 - 5 or 7 days whereas where multiple reactions occur the greater of

Table 6.6 Quantification of reaction products of the lime-soil systems from XRD

SOIL SYMBOL	I_m (cm^2)	I_i (cm^2)	$\frac{I_m}{I_i}$	$\frac{g_m}{g_i}$	g_m	Vol. per 0.35 gm of lime treated soil	Vol. per cc of compacted soil (%)
PH	0.50	7.1	0.07	0.205	0.031	0.072	3.36
JPM	0.80	5.6	0.12	0.36	0.054	0.126	6.96
TII	1.00	12.50	0.08	0.24	0.036	0.084	3.97
SB	1.10	10.00	0.11	0.31	0.047	0.108	5.65
NF	0.70	10.0	0.07	0.20	0.030	0.070	3.69
JPB	0.50	11.10	0.045	0.13	0.02	0.045	2.57
JPA	0.40	6.20	0.065	0.19	0.029	0.066	3.54
SIB	0.80	6.20	0.13	0.15	0.023	0.07	3.64
JI	0.80	5.20	0.096	0.20	0.030	0.075	3.82
SII	0.50	5.0	0.10	0.30	0.045	0.105	5.30
RC	0.60	4.30	0.14	0.225	0.034	0.105	5.59
USM	0.50	8.0	0.063	0.13	0.020	0.05	2.33
CT	0.50	5.6	0.089	0.10	0.015	0.035	1.81
AI	0.40	4.40	0.091	0.27	0.041	0.094	4.60
AII	0.40	4.70	0.085	0.18	0.027	0.093	4.60
SM	0.70	7.80	0.09	0.27	0.041	0.094	5.01
TI	0.70	6.40	0.11	0.23	0.035	0.12	5.73
SIA	0.60	15.0	0.04	0.04	0.006	0.019	1.02
JII	0.50	6.60	0.076	0.15	0.023	0.052	3.04

the two rates is represented by the 0 - 5 or 7 days rate in Fig. 5.5.

6.4.4 Volume of reaction product vs strength

Table 6.6 shows the volumes of the crystalline reaction products as measured by the internal standard method. The volumes were plotted against the total strength of the soil-lime mixtures, the resultant relation is shown in Fig. 6.5. Its shape is similar to that obtained by Jambor (63, 97) who also showed that the strength of lime-pozzolana pastes depended on the type of reaction product formed. In any of the systems under study, a substantial amount of the soil is unreacted, it may contribute to the overall strength of the lime treated soils. It will therefore be logical to ascribe increase in strength to the type and volume of the reaction products. Hence Fig. 6.6 shows a plot of lime reactivity as measured by increase in strength against volume of the reaction products. It can be seen that with the reaction products broadly divided as:

type I - silicates
type II - silicates and alumino-silicates
type III - alumino-silicates and/or alumino-ferri-silicates,

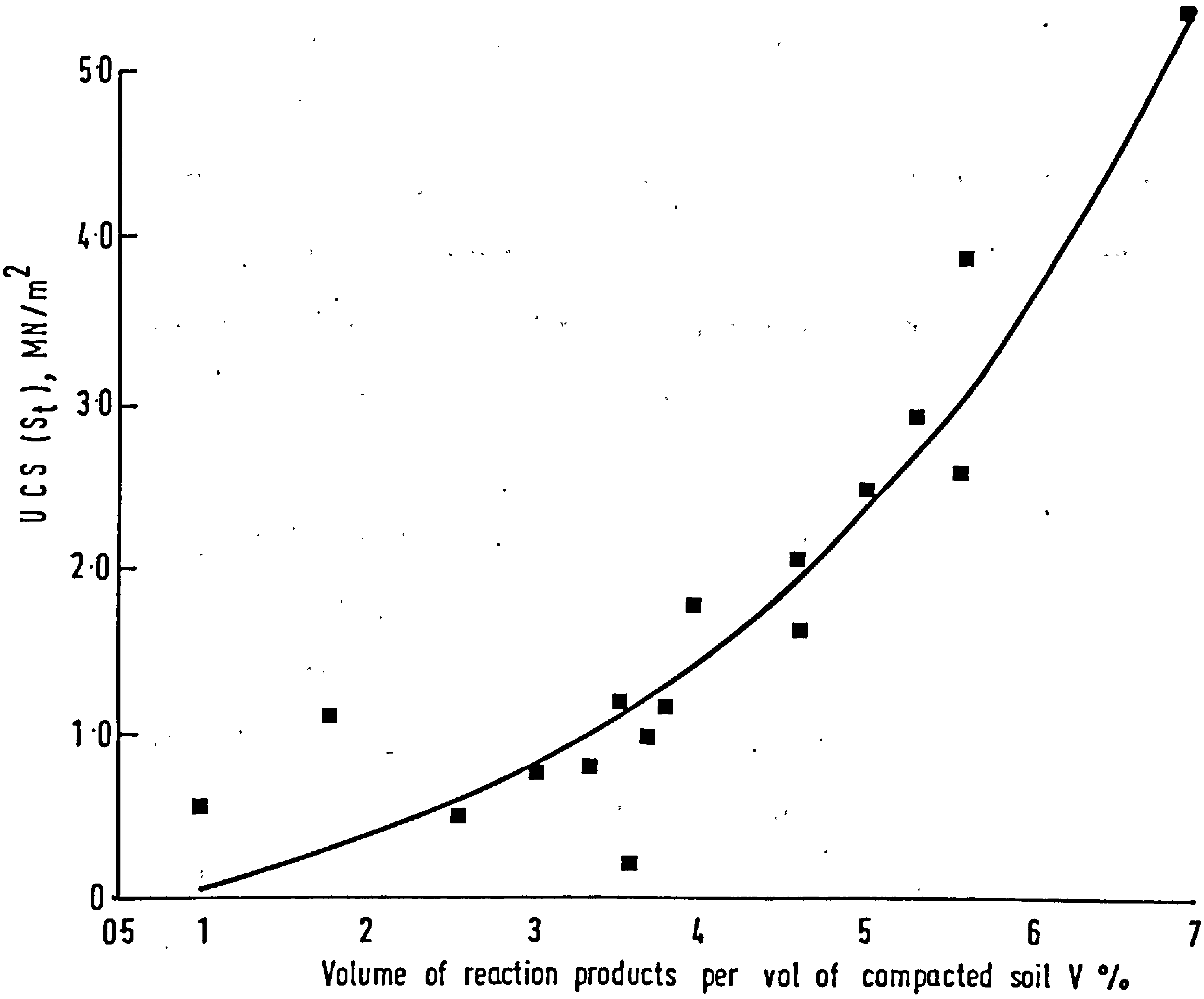
a family of curves can be drawn.

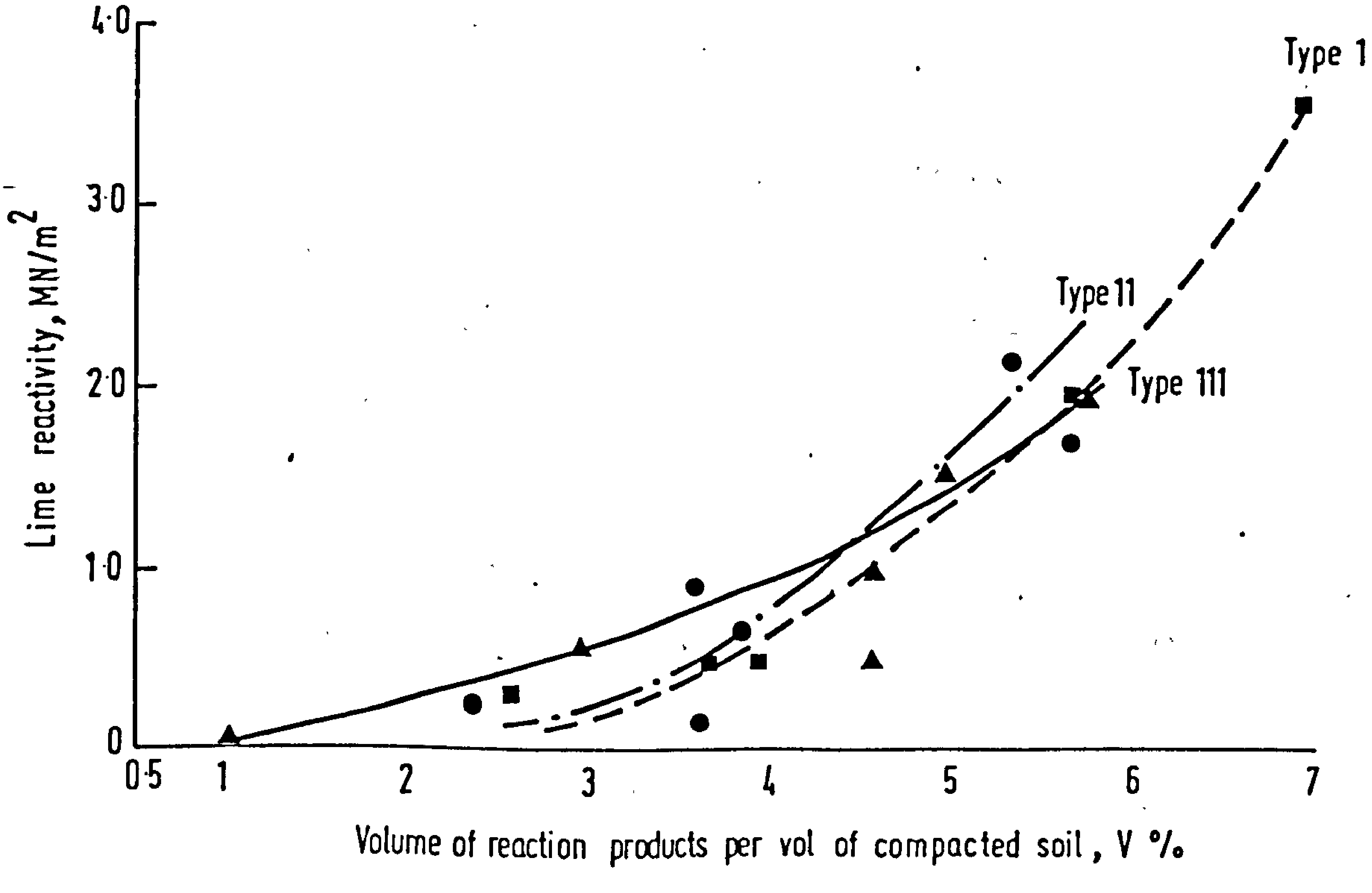
The total strength of a red tropical soil treated with lime has two components viz.

a) Some fraction of the strength of the natural soil (S_o) at the same moisture content as the treated soil. This component depends on cohesion and grain to grain contact (4, 24, 25). The reaction products will reduce the effects of cohesion and friction; the extent depending on the volume of the reaction products. This

Fig. 6.5 Relation between volume of reaction products and total strength of the soil-lime systems

Fig. 6.6 Relation between volume of reaction products and lime reactivity parameter of Thompson


5·0
4·0
3·0
2·0
1·0
0
U C S (S_t), MN/m^2
0·5
1
2
3
4
5
6
7
Volume of reaction products per vol of compacted soil V %


4·0
3·0
2·0
1·0
0
Lime reactivity, MN/m^2
Type 1
Type 11
Type 111
0·5
1
2
3
4
5
6
7
Volume of reaction products per vol of compacted soil, V %

component of total strength is represented by $k(v)S_o$ where k is a reduction factor.

b) The strength of the reaction products which depends on the volume and type of reaction product present. This component is a power function of the volume which can be represented by a polynomial of third degree as suggested and demonstrated by Jambor (63).

Hence total strength (S_t) can be written as

$$S_t = k(v)S_o + av^3 + bv^2 + cv \quad \ldots \quad \ldots \quad \ldots \quad (6.13)$$

where v is the percentage volume of the reaction products in a unit volume of lime treated, compacted soil and a, b, c are constants. The following boundary conditions apply to k.
(i) when $v = 0$, $k = 1$; (ii) when $v = 100$, $k = 0$. Equation 6.13 assumes that S_t is an arithmetic sum of the two components.

Assuming that $k \approx 1$ for small volumes, a stepwise multiple regression was carried out between lime reactivity as the dependent variable and v, v^2, v^3 as the independent variables on one hand and between total strength as the dependent variable and v, v^2, v^3 as the independent variables on the other. Multiple regression has been similarly used by Alexander et al (98) to study how strength and hydration are related to the composition of Portland cement. The regression equations obtained for the soil-lime mixtures are:

a) For total strength:

$$S_t = 0.0136v^3 + 0.0552v^2 - 0.4338v + 1.368 \quad .. \quad (6.14)$$

For increase in strength:

b) type I: $S_t - S_o = 0.0183v^3 - 0.0791v^2 + 0.184v + 0.0156$ (6.15)

c) type II: $S_t - S_o = 0.0482v^3 - 0.3374v^2 + 0.7361v + 0.0248$ (6.16)

d) type III: $S_t - S_o = 0.0799v^2 - 0.1477v + 0.06263$ ... (6.17)

Equation 6.14 is highly significant (multiple R = 0.929) at 86% confidence with standard error of 0.5340. While equations 6.15, 6.16, 6.17 are significant (multiple Rs = 0.996, 0.905, 0.930 respectively) at 99%, 82%, 86.5% confidence and with standard errors of 0.1974, 0.4116, 0.3359 respectively, they can not be used for prediction purposes because the number of samples in each group do not ensure a statistically significant population.

From Fig. 6.6 it can be seen that for small volumes of reaction products, within the experimental range, the order of strength increase is type III > type II > type I whereas at larger volumes the order is reversed. This contrasts Jambor's findings. A possible explanation that can be offered is that ionic substitution in the lattices of the silicates seem to reduce their effective binding strength and this reduction is more pronounced in small volumes than in larger volumes.

6.4.5 Overall C/S, A/S ratios vs strength

The overall C/S ratio (Table 6.5) was plotted against the total unconfined compressive strength and lime reactivity (Thompson parameter) as shown in Figs. 6.7 and 6.8 respectively. From these figures, it can be seen that a relationship appears to exist between the overall C/S ratio and the total strength on one hand and lime reactivity on the other for type I reaction products. The lower the C/S ratio the higher the strength. Ruff and Ho (67) found a similar pattern for lime-bentonite-water mixtures and concluded that high strength is achieved if the apparent C/S ratio is less than 2. A similar conclusion cannot be drawn here. No consistent relationship appears to exist for types II and III reaction products which are results of multiple reactions.

Figures 6.9 and 6.10 show the plot of total strength, lime reactivity vs A/S ratio. No consistent relationship can be found between this ratio and strength or lime reactivity for any of the types of the reaction products.

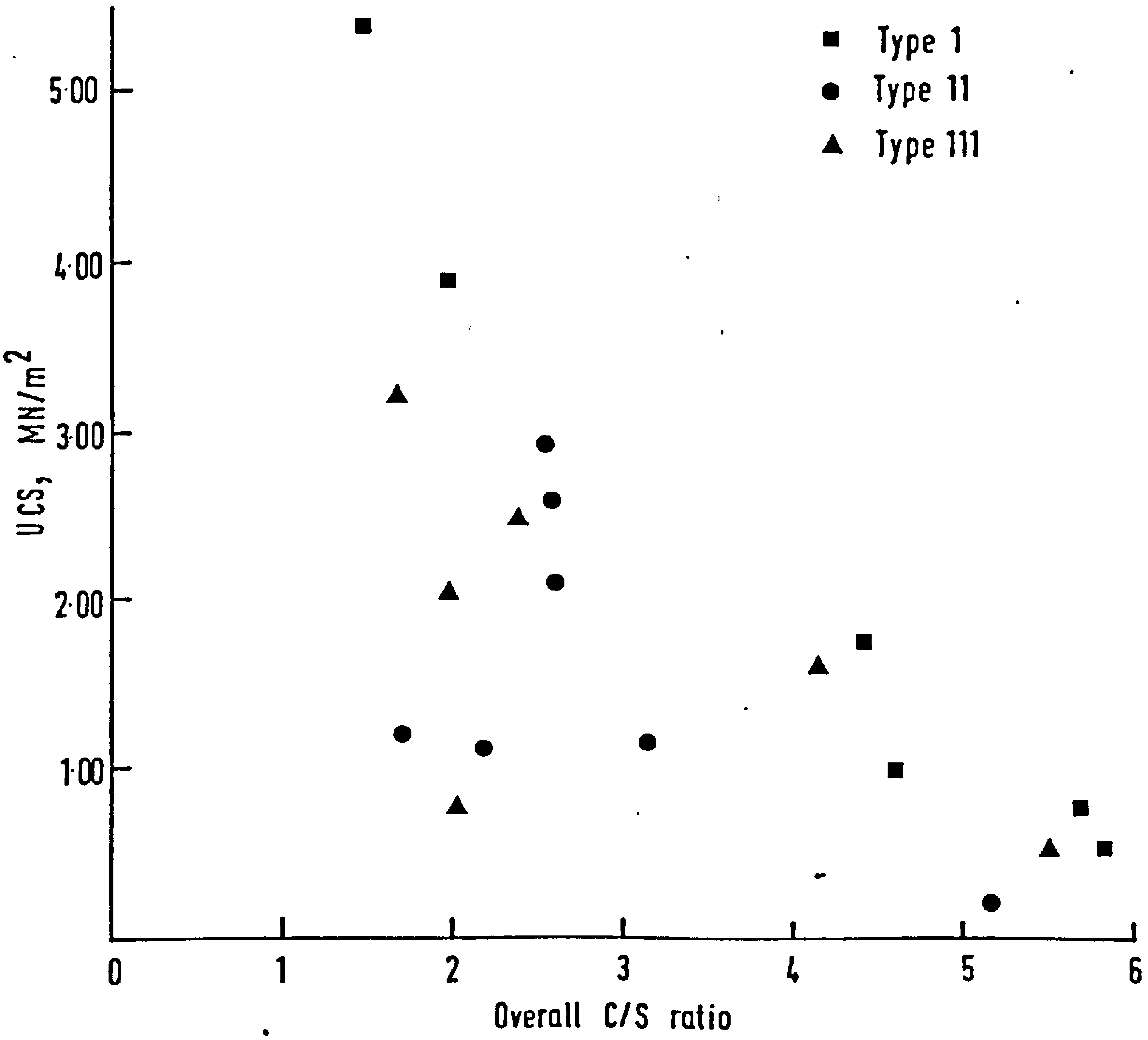
6.4.6 The relation between the activity index and volume of reaction products

The relation between the activity index and the volume of reaction products is shown graphically in Fig. 6.11. It can be seen that for a relationship to exist between them, the type of reaction product formed has to be taken into account. This can be explained by the fact that the activity index depends on the fraction of lime reacted, the time and the quantity and type of the reactive clay size fraction of the soil. On the other hand, the volume of the reaction products depends only on the fraction of lime reacted and time. Hence any relationship between the activity index and volume of the reaction products must take into account the effect of the quantity and type of the reactive clay size fraction. The effect of this parameter in a soil-lime reaction is not only the volume but also the type of the reaction products.

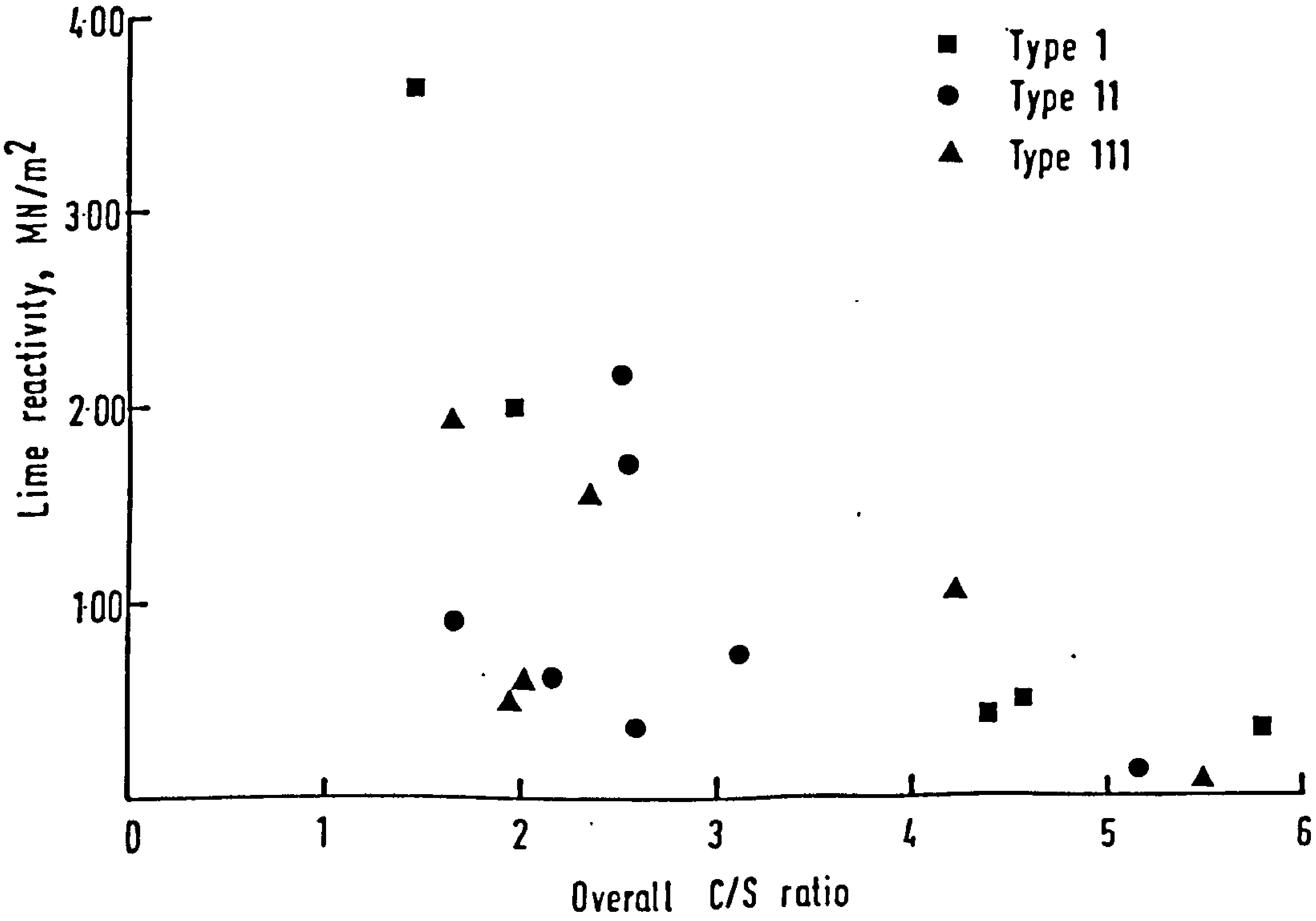
The lime reactivity parameter of Thompson was found to be similarly dependent on the volume and type of the reaction products. In Chapter 5, it was found from statistical analysis that lime reactivity is a linear function of the activity index, A_i. The similarities of Figs. 6.6 and 6.11 not only supports the variation between the activity index and lime reactivity but also confirms the conclusion that the former is the theoretical

Fig. 6.7 Relation between overall C/S ratio and total strength of the soil-lime systems

Fig. 6.8 Relation between overall C/S ratio and lime reactivity parameter of Thompson .



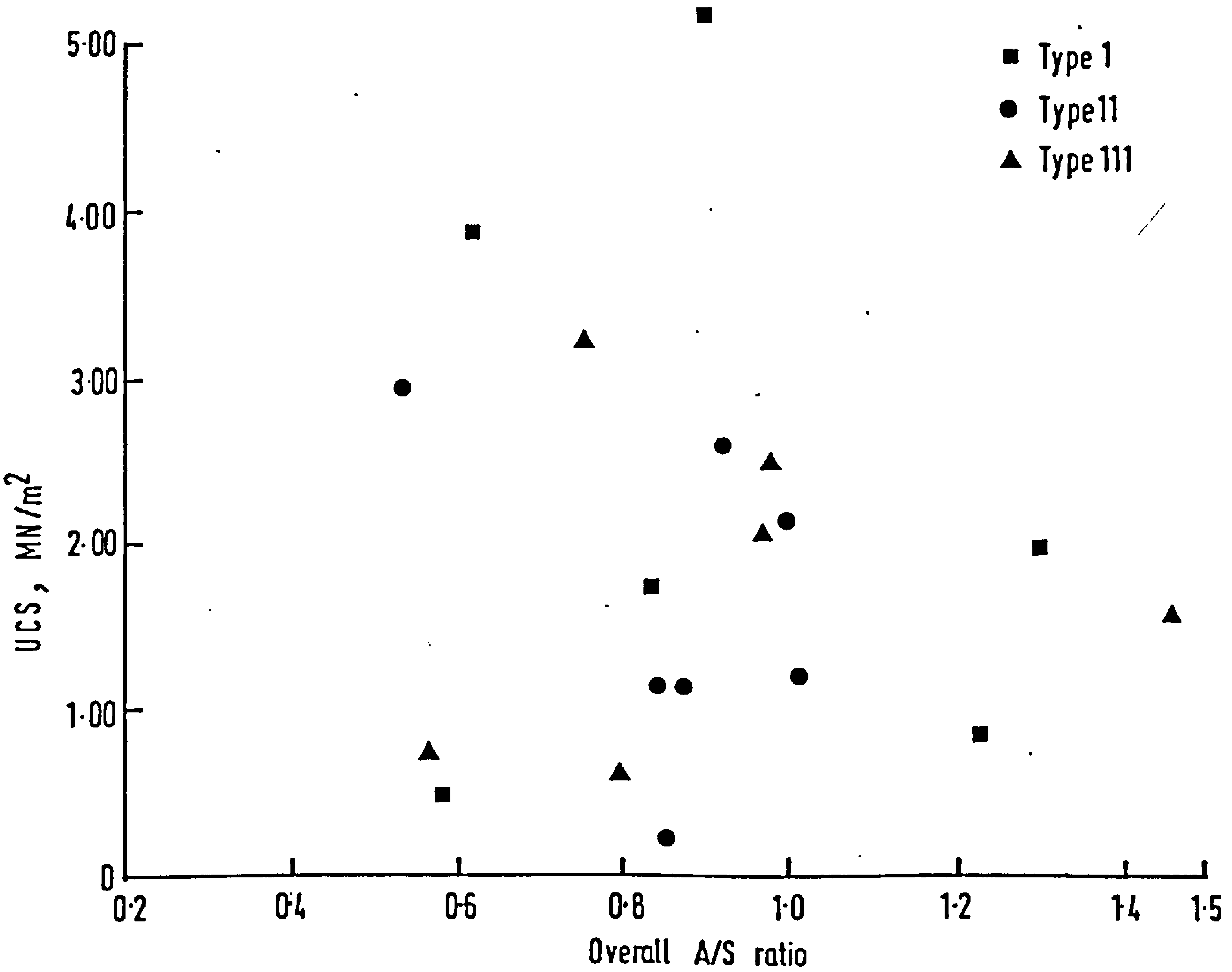
■ Type 1
● Type 11
▲ Type 111
UCS, MN/m^2
5·00
4·00
3·00
2·00
1·00
0
1
2
3
4
5
6
Overall C/S ratio



■ Type 1
● Type 11
▲ Type 111
Lime reactivity, MN/m^2
4·00
3·00
2·00
1·00
0
1
2
3
4
5
6
Overall C/S ratio

Fig. 6.9 Relation between overall A/S ratio and total strength of the soil-lime systems

Fig. 6.10 Relation between overall A/S ratio and lime reactivity parameter of Thompson


5·00
4·00
3·00
2·00
1·00
0
UCS, MN/m^2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·5
Overall A/S ratio
■ Type 1
● Type 11
▲ Type 111

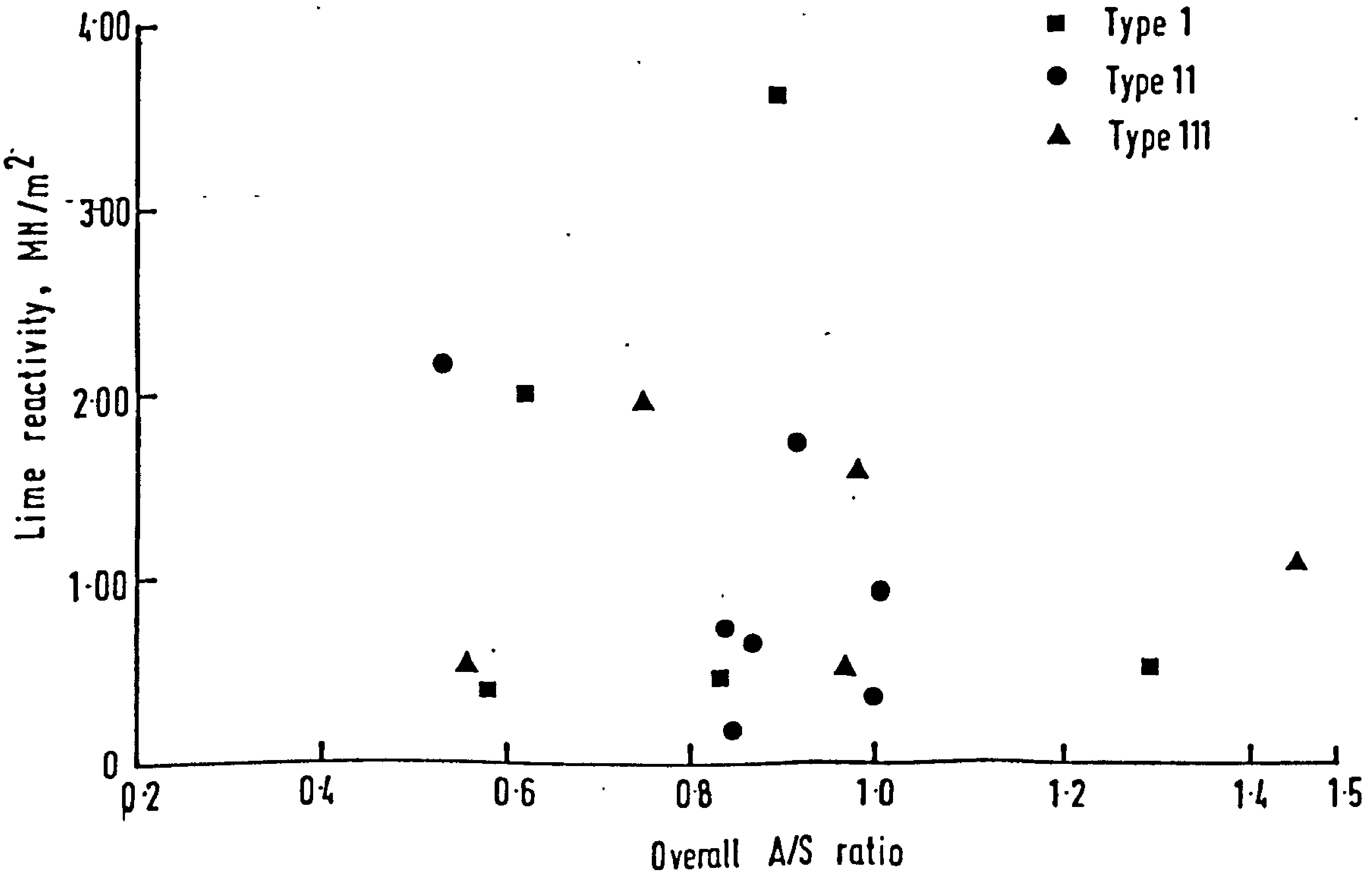
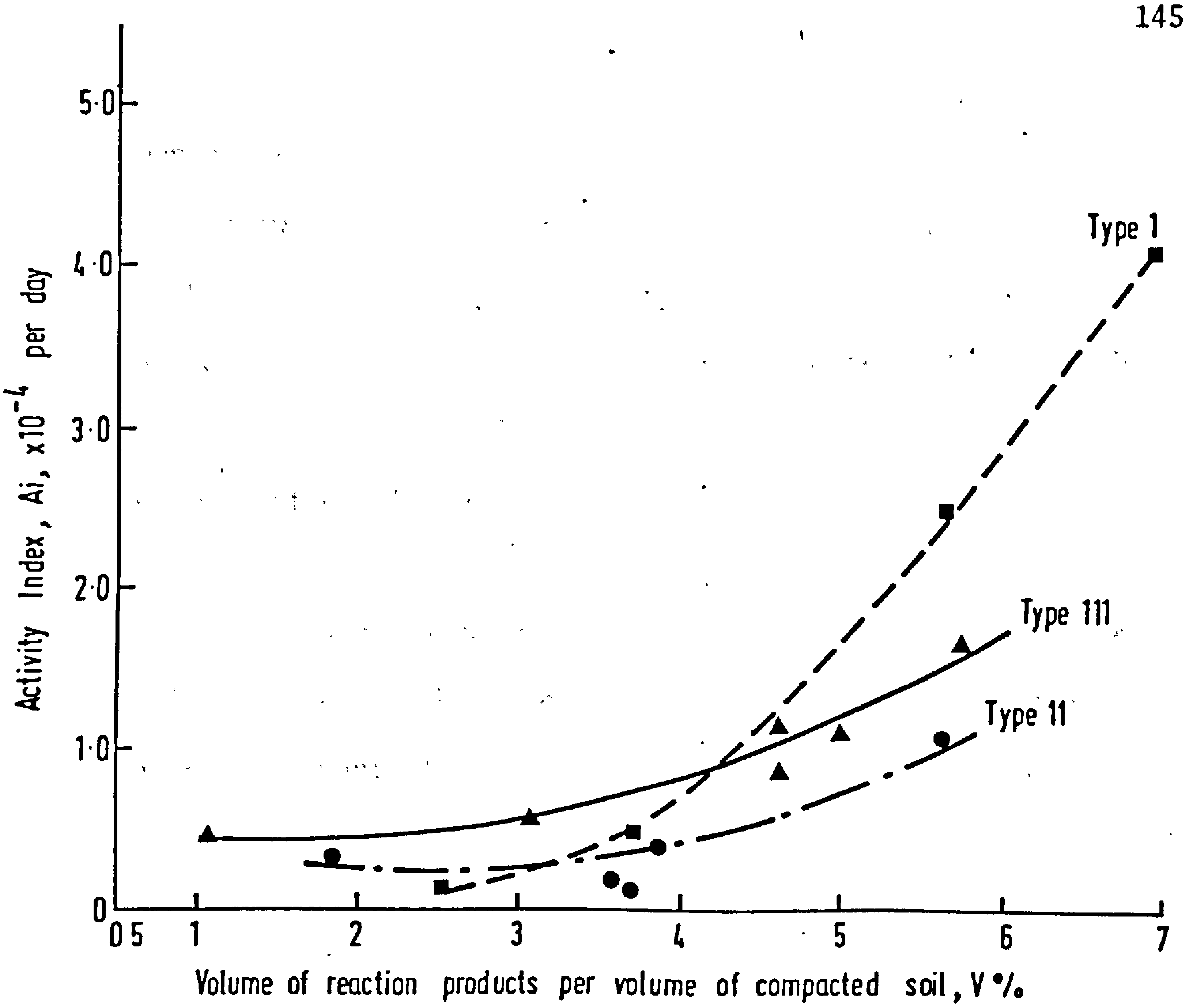
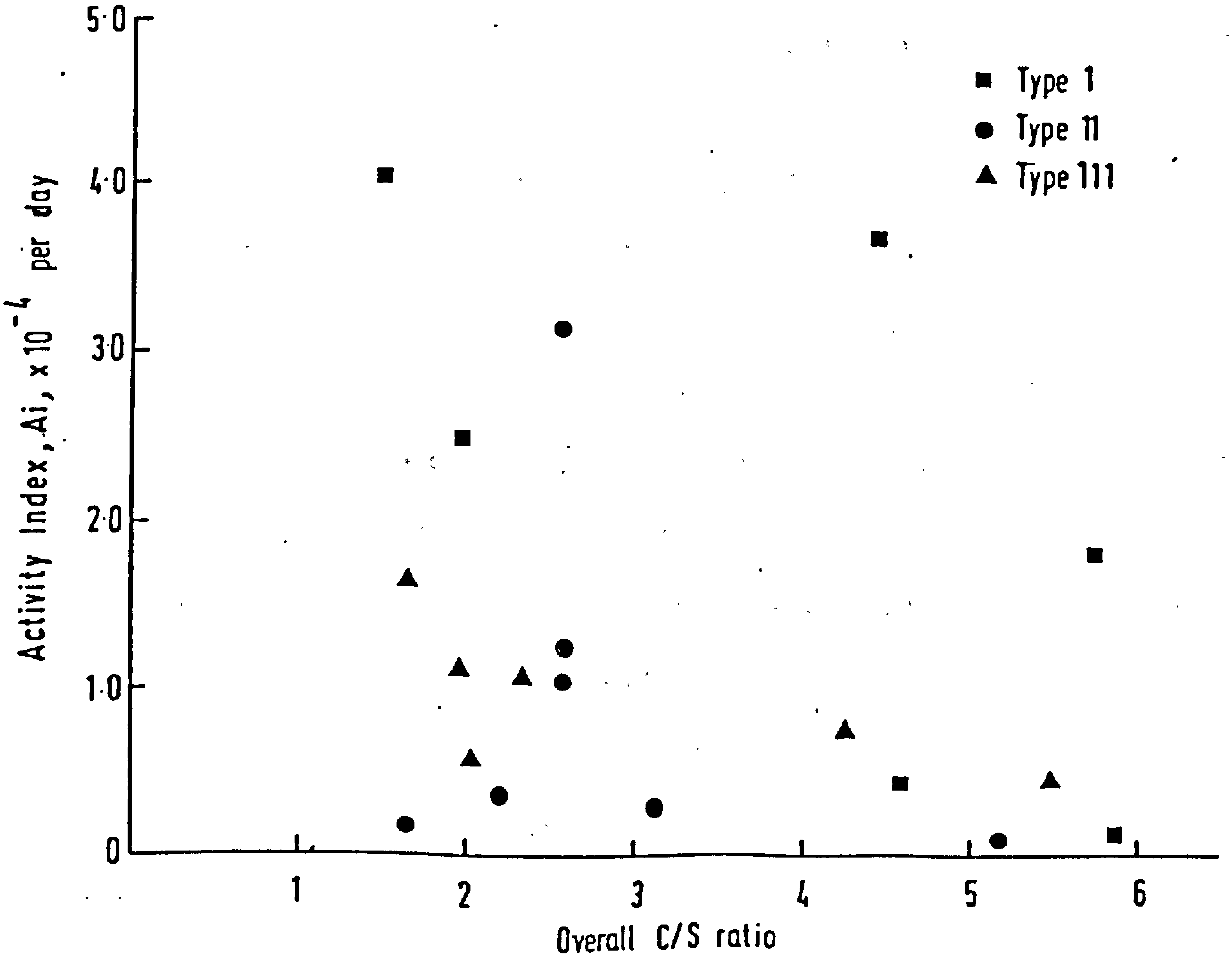

4·00
3·00
2·00
1·00
0
Lime reactivity, MN/m^2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·5
Overall A/S ratio
■ Type 1
● Type 11
▲ Type 111

Fig. 6.11 Relation between volume of reaction products and the activity indexes of the soils

Fig. 6.12 Relation between overall C/S ratio and activity indexes of the soils


Activity Index, Ai, x10^-4 per day
5·0
4·0
3·0
2·0
1·0
0
0 5
1
2
3
4
5
6
7
Volume of reaction products per volume of compacted soil, V %
Type 1
Type 111
Type 11


Activity Index, Ai, x 10^-4 per day
5·0
4·0
3·0
2·0
1·0
0
1
2
3
4
5
6
Overall C/S ratio
■ Type 1
● Type 11
▲ Type 111

counterpart of the latter. The only difference that seems to exist between Figs. 6.6 and 6.11 is that relative to the position of the curves that form type I reaction products, the curve for the soils that form type II reaction products in Fig. 6.11 has been displaced downwards. At the present state of knowledge of the properties of the activity index, no explanation can be offered for this.

Using a stepwise multiple regression analysis with the activity index as the dependent variable and the volume as the independent variable, it is found that the activity index (Ai) is a power function of the volume of reaction products (v) which can be expressed as:

a) For type I products:

$$A_i = -0.003v^3 + 0.163v^2 - 0.395v + 0.0105 \quad \ldots \quad (6.18)$$

b) For type II products:

$$A_i = 0.0306v^3 - 0.216v^2 + 0.440v + 0.0028 \quad \ldots \quad (6.19)$$

c) For type III products:

$$A_i = 0.0295v^3 - 0.226v^2 + 0.6122v + 0.0115 \quad \ldots \quad (6.20)$$

where A_i = activity index x 10^{-4} per day

v = percentage volume of reaction products.

Equations 6.18, 6.19 and 6.20 are statistically highly significant (multiple Rs = 0.9984, 0.9775 and 0.9816 respectively) at 99.7%, 95.5%, 96.4% confidence and with standard error of estimate of 0.201, 0.126, 0.144 respectively. These statistics show that the activity index correlates better with volume of reaction products than does the lime reactivity parameter of Thompson. The equations cannot be used for prediction purposes because the number of samples in each group do not ensure a statistically significant population. Soils TII, USM, SII and PH do not comply with the results in this section.

6.4.7 Activity index vs C/S ratio

Figure 6.12 shows the variation between the activity index and the overall C/S ratio. No consistent relationship appears to exist between them.

6.5 Limitations of the methods used

The user of the information presented in this chapter should be aware of the following:

a) XRD measures only minerals with specific order; short range order or amorphous reaction products cannot be quantified whereas if the reaction products are in this state they will contribute to the strength of the soil-lime systems.

b) The minerals used as standards are not exactly the same as the reaction products whose exact chemical compositions are not even known.

c) The reaction products were classified very broadly into three categories. Since their strengths depend on their specific types (97, 98) a better classification would be to further divide the broad groups into groups comprising more specific minerals. The method of identification used cannot resolve this problem. The possible effect of ionic substitution as pointed out in the silicates makes the resolution of this problem worthwhile.

6.6 Chapter Summary

While recognising the limitations of the test methods and materials used, this chapter shows that for the soils studied:-

a) Cementitious reaction products varying from silicates of the tobermorite-like type through alumino-silicates to alumino-ferri-silicates are formed by consecutive or multiple reactions.

b) Where silicates of the tobermorite-like type are formed ionic substitution in the lattice of such silicates owing to the mineralogical composition of the soils is pointed out.

c) The role of iron seems to be to substitute into silicates and aluminates formed as reaction products.

d) With the reaction products broadly calssified as

type I - silicates

type II - silicates and alumino-silicates

type III - alumino silicates and/or alumino-ferri-silicates,

the functional relationship between increase in strength and volume of reaction products is:

$$S_t - S_o = av^3 + bv^2 + cv \text{ for types I and II}$$

$$S_t - S_o = bv^2 + cv \text{ for type III}$$

where S_t = total strength of lime treated soil in MN/m^2

S_o = strength of the natural soil in MN/m^2

a, b, c = constants

v = percentage volume of reaction product in a unit volume of compacted soil.

When the total strengths of the soil-lime systems are considered, the functional relationship between total strength and volume of reaction products is:

$$S_t = av^3 + bv^2 + cv + k$$

where S_t = total strength of lime treated soil in MN/m^2

v = percentage volume of reaction products in a unit volume of compacted soil

a, b, c, k = constants.

e) Ionic substitution in the lattice of silicates seem to have a more pronounced effect on strength for small values of v than larger values.

f) No consistent relationship exists between overall C/S, A/S ratios and strength for types II and III reaction products whereas there appears to be one between C/S ratio and strength for type I reaction products.

g) The activity index is a power function of the volume of reaction products and the functional relationship between them can be expressed as:

$A_i = av^3 + bv^2 + cv$ for types I, II and III reaction products,

where A_i = activity index x 10^{-4} per day

v = percentage volume of reaction products in a unit volume of compacted soil

a, b, c = constants.

A better correlation exists between the activity index and volume of reaction products than between the lime reactivity parameter of Thompson and the latter.

h) No consistent relationship appears to exist between the activity index and the overall C/S ratio.

CHAPTER 7

SEMI-AUTOMATED IDENTIFICATION OF CRYSTALLINE REACTION PRODUCTS

7.1 Introduction

Typical XRD of some of the lime treated and natural soils are shown in Figs. 6.1 and 6.2 and Appendix A. Identification of the reaction products involves:

a) abstracting the 2θ values of the Bragg angle at which new peaks occurred by comparing the two traces;

b) calculating the d-spacings associated with each value of θ using equation 6.1;

c) estimating the intensity ranks or calculating the relative intensity value of each peak;

d) checking the d-spacings and their intensities against those of standard minerals.

A mineral is inferred if the measured d-spacings and their intensities correlate totally or very strongly with its diffraction patterns usually available in powder diffraction files (pdf).

This chapter therefore reviews methods available for searching the pdf. The methods are adapted for use in matching new peaks that occur in a soil-lime system with the pdf data base. A pdf data base is a set of minerals in a powder diffraction file whose diffraction patterns are stored in the computer and used as a basis to evaluate the measured diffraction patterns.

7.2 Review of literature and methods

Of the various automated systems available for identifying correlations between measured diffraction patterns and pdf data base, the Johnson-Vand system (104) has been promoted by the Joint Committee on Powder Diffraction Standards and is now widely used in many countries. The principal features of this program are critically outlined.

7.2.1 The d-spacings and intensities

The input data are of the d-spacing - relative intensity type. Hence the operator has to compute the d spacings from the θ - values and quantitatively measure their relative intensities before he can operate the program. It would be much better if the measured diffraction patterns can be input as θ, 2θ or functions of θ. In a mixture of minerals where peaks overlap, quantitative measurement of intensities is difficult because the area under each of the overlapping peaks is difficult to define. In such systems therefore, there is a case for the replacement of the relative intensity values by intensity ranks using the strong to very weak scale.

7.2.2 Error width or window

An allowance for an error made for every observation in the measured data depends on the apparatus used to obtain the data. Thus in the program is specified an error window (IW) given by

$$IW = \left(\frac{1}{d} - \frac{1}{d+\Delta d}\right) \times 1000 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7.1)$$

where d = d-spacing and Δd is the tolerable variation on either side of d.

Hughes (105) confirmed Johnson's findings that for Nonius focusing camera IW = 2; for Debye Scherra camera IW = 3; for a $\frac{1}{8}^{\circ}$ per minute continous scan on a diffractometer IW = 4; while for a $\frac{1}{100}^{\circ}$

step scan IW = 2. The operator of the program therefore has to input a value for IW which is used to calculate the error window, Δd, for each d-spacing. If no value of IW is specified, the program takes it to be 2.

It appears more rationale to assign error in measurement to each Bragg angle of the measured data. The value of the error window should depend on the variations in the measured diffraction patterns rather than on the position of the peaks of the measured diffraction pattern (d-spacing) and the instrument used. For instance, where a broad peak occurs, the error window should be greater than if a very sharp peak had occurred at the same value of d-spacing. Broadening of peaks is more a result of the mineral structure of the x-rayed material than the result of the instrument used (72).

7.2.3 Data base

The program holds about 20,000 compounds in the data base. Thus when employed to identify crystalline reaction products of soil-lime systems (broadly known to be silicates, alumino-silicates and alumino-ferri-silicates of calcium), it searches through a data base consisting of irrelevant compounds. This results in the use of unnecessary computer time. Futhermore, when such large data base of irrelevant compounds are used, huge magnetic file tapes are required and large computers which can handle such large data base are expensive to run. As far as time is concerned, the program is not suitable for the identification of a single phase compound. Johnson and Vand (104) concede that for identification of a single phase, as far as time is concerned, an experienced person will win easily while the chances are even

even for a two phase mixture. For a three or more phase mixture, the program will win.

7.2.4 The "elements present" option

Chemical elements or radicals known to be present or absent in the material x-rayed, can be inserted in the input and the output will be biased accordingly. Such elements or radicals are punched in the "elements present" card. Any compound that contains at least one of the "elements present" and gives a reasonable line match is considered by the program as a chemical fit. Thus if oxygen were included in the "elements present" card, every oxide, hydroxide, hydrate, carbonate, bi-carbonate etc. that gave reasonable line matches will be considered possibilities.

7.2.5 The program procedure

In the program search, the computer takes the d-spacing values with an error bar and their relative intensities and tries to fit the most likely compound to them. It then subtracts the ASTM d-spacings and their relative intensities of the first compound considered most likely from the measured d-spacings and their relative intensities. Using the residue, it tries to fit the next most likely mineral. The process is repeated until most of the measured diffraction patterns have been accounted for. A list of the ten most likely mineral phases present in the descending order of reliability is printed out.

Thus the program nearly eliminates completely the human involvement in such identification. In a good review of the merits and demerits of automated searches, Hughes (105) observed that no automated search can be as reliable as an experienced manual searcher. Automated systems can at their best serve as assistants. The problem with manual searching is the tedium associated with it. A way out of the problem is to reduce the number of likely minerals to be considered to a minimum. In achieving this reduction, it will be desirable to leave some of the parameters for identification for use by the manual interpreter of the results. Hence a blend of the automated and manual searches is desirable (106), backed up by other methods such as elemental analysis.

A semi-automated method of identification was therefore preferred for use in this investigation. This method is described in the following sub-chapter.

7.3 Features of the semi-automated search used

The system proposed and used for the research comprises a first stage of an automated search followed by a second of a careful manual interpretation and assessment of the results of the automated search. It is orientated to aid identification of reaction products in a practical soil-lime system but can be adapted for the identification of other crystalline minerals.

7.3.1 The automated search

The basic function of the automated search is to eliminate those compounds in the data base which do not match the measured diffraction data on the basis of d-spacings only. Usually two diffraction peaks match if their d-spacings and intensities are coincident or differ within tolerable limits. Where the minerals in a mixture have their peaks overlapping, it is very difficult to quantitatively measure their intensities. In lime treated soils many minerals are present and peaks overlap (see Figs. 6.1, 6.2). Hence it was decided that intensity ranks rather than intensity values should be used as measure of intensity. It was also decided that this parameter should be employed when manual interpretation is carried out; thus the use of d-spacings only in the automated search. To make the search adaptable for identification under other or simpler circumstances a provision was made for the use of intensity as well as d-spacing for the search.

The automated package consists of a search program, a data base and an input data as different and nearly independent subroutines. The idea of their "independence" is to permit the user freedom to replace the data base with the relevant minerals without virtually altering the program. Furthermore, it was hoped that this will facilitate provisions for the use of any suitable source of radiation.

7.3.1.1 The data base

The data base consists of all the available calcium silicates, aluminates, alumino-silicates, alumino-ferri-silicates, ferrites, i.e. all the calcium salts that contain some or all of the initial elements present in the reactants. Their diffraction patterns were derived from the strong peaks of the minerals occuring in the ASTM powder diffraction file held in The Houldsworth School Applied Sciences (Leeds University). Strong peaks were selected for use in identification in order to filter out matching weak reflections otherwise an alarming number of ASTM minerals will be printed which have some lines in common with the measured pattern. The number of strong peaks entered or stored for each mineral in the data base varied according to how many d-spacings of the mineral have high relative intensity values.

The d-spacings of the strong peaks and their relative intensity values were punched on cards and the peaks of each mineral arranged in the descending order of their d-spacings. Each mineral was identified by its ASTM file number punched on a card which precedes the card/s containing its d-spacings and their intensities. One hundred and sixty minerals were used as data base. Provided the number of minerals in any proposed data base is less than two hundred, the new set can overwrite the old without alterations in the program. If it is greater than two hundred, its dimension in the program should be increased accordingly. The data base was coded XRAYDATA2.

7.3.1.2 The input data

The first card of the input data field contains the username of the operator and the code of the input, XRAYDATA. On the next three cards are entered a description of the test material (e.g. JPM, 6% lime treated, cured 28 days at 22°C) and the detailed conditions of the XRD such as chart speed, number of counts per second, rate meter etc. The fifth card contains the value of the wavelength of the radiation used. Thus it does not matter what the radiation source is provided its wavelength is known. If two constraints (d-spacing and the intensity) are considered necessary to identify a peak in the automated search, a constant error width for the measured intensity values is punched on the fifth card after the value of the wavelength of the radiation. The error width must be an integer.

The next set of cards contain the diffraction patterns of the new peaks observed. The patterns are input as 2θ values of the Bragg angle. The value of 2θ at which a new peak occurs is referred to as θ_2. The error window in measurement of θ_2 is input as 2θ values, referred to as θ_1, θ_3. θ_1 is the lower limit (using the magnitudes of the angles as a measure and measuring from 0^o) and θ_3 the upper limit of θ_2. Thus a new peak is described in the input by θ_2, θ_1, θ_3 punched in this order on a card. If the intensity of a peak is measured and is to be considered in the automated search, its relative value (%) is punched immediately after θ_3 on the same card that contains θ_2, θ_1, θ_3 values of the peak. The input is terminated by punching three negative values of θ_2, θ_1, θ_3 on the last card.

7.3.1.3 Design of the search program

The algorithm for the search program is outlined in Fig. 7.1. Measured values of θ_2, θ_1, θ_3, their intensity values if measured, a constant error width for the intensity values and the wavelength of the radiation used are entered on cards. Using these, the computer calculates the d-spacings d_1, d_2, d_3 corresponding to θ_1, θ_2, θ_3 respectively. A standard mineral is read and its d-spacings and intensities (if applicable) checked against the measured values. A count of the matching peaks is kept. If no value of intensity is given for a peak, the program ignores any specified intensity error width. It finally expresses the number of matching peaks as a percentage of the total strong peaks of that mineral. The search program is coded XRAYPROG and is written in Fortran language.

7.3.1.4 The output

The following phrases used in displaying the output are defined or described:

a) "Calculated spacings" refers to the d-spacings calculated using the values of θ_2.

b) "Intensity" refers to the measured intensity of a new peak.

c) "Standard spacing" refers to the d-spacings of the strong peaks of a mineral in the data base.

d) 'Relative intensity" refers to the intensity of a standard spacing.

The output shown in Table 7.1 consists of the following information:

a) the details of the sample and the conditions of x-ray are listed;

b) θ_1, θ_2, θ_3 and their associated d-spacings are listed in that order;

c) the matching peaks of the measured diffraction pattern and the diffraction pattern of the data base mineral are tabulated. The details of the tabulation for each mineral are thus:- First the data base mineral is identified by its ASTM reference number referred to and written as "card number". The "standard spacings" and their "relative intensities" are listed. The "calculated spacing" and its "intensity" are written on the same line (horizontally) as the "standard spacing" and its "relative intensity" if both match. If no "intensity" values are measured for the new peaks, the value 0 is printed under "intensity" when a "calculated spacing" matches a "standard spacing". Finally the total number of matching peaks is expressed as a percentage of the total strong peaks of that mineral. This is printed as "percentage of strong peaks present". The output is coded XRAYOUT.

Fig. 7.1 Algorithm for seach program


START
Read lamda, intensity limit
30
L : 1, 50
Read input data $\theta_2, \theta_1, \theta_3$
θ_2 = –ve?
yes
50
no
40
J : 1, 3
Compute spacings D (L, J)
40
Write θs and spacings
30
50
Decrease L L←L – 1
Read MN
400
MN : 1, MN
Initalise kount kount = 0
Read and write card No
Read No of items on card
Read and write STD spacing and intensity
70
I : 1, L
80
J : 1, N
∝
∝
Calc. spacing < STD. spacing?
yes
80
no
Set IJ = J–1
IJ = 0?
yes
Set IJ = 1
no
Spacing limits satisfied?
yes
Intensity given?
no
no
yes
IJ = J?
no
Set IJ = J
Intensity limits satisfied ?
Increment Kount by 1
Write results
yes
no
70

Table 7.1 Part of typical output of the search program

```
XRAYDATA FOR ROMAN ROAD

DR WHITE

MOLYBDENUM TUBE
--------------------------------------------------------------------------------------------


THETA1  SPACING1     THETA2  SPACING2     THETA3  SPACING3
 5.67     15.58       5.76     15.34       5.90    14.97
 6.30     14.02       6.40     13.80       6.62    13.34
 9.50      9.30       9.55      9.26       9.65     9.16
10.60      8.36      10.70      8.26      10.80     8.19
12.00      7.37      12.30      7.19      12.60     7.02
13.60      6.51      13.80      6.41      14.00     6.32
16.55      5.35      16.65      5.32      16.75     5.29
17.85      4.97      17.90      4.95      18.05     4.91
19.25      4.61      19.30      4.60      19.40     4.57
20.55      4.32      20.70      4.29      20.85     4.26
22.40      3.97      22.65      3.92      22.80     3.90
24.40      3.65      24.55      3.62      24.80     3.59
26.50      3.36      26.70      3.34      26.80     3.32
28.10      3.17      28.25      3.16      28.30     3.15
29.00      3.08      29.10      3.07      29.20     3.06
29.80      3.00      29.90      2.99      30.05     2.97
31.90      2.80      32.00      2.80      32.10     2.79
34.30      2.61      34.40      2.61      34.65     2.59
34.85      2.57      34.90      2.57      34.95     2.57
--------------------------------------------------------------------------------------------


CARD NUMBER    9-469

STANDARD
SPACING          21.00  8.80  7.40  3.56  3.07  3.05  2.98  2.93  2.77  2.15  1.80

RELATIVE
INTENSITY          100    80    40    80    60    60    50    80    50    40    80

CALCULATED                  STANADARD   RELATIVE
SPACING      INTENSITY      SPACING     INTENSITY

   3.07          0            3.07         60

   2.99          0            2.98         50


PERCENTAGE OF STRONG PEAKS PRESENT =    18.2
--------------------------------------------------------------------------------------------


CARD NUMBER    7-302

STANDARD
SPACING          19.00  9.40  7.65  4.65  4.13  3.80  3.47  3.14  2.83  2.63  1.84  1.75

RELATIVE
INTENSITY          100   100    40    40   100    40    40   100   100   100    70    60


CALCULATED                  STANADARD   RELATIVE
SPACING      INTENSITY      SPACING     INTENSITY


PERCENTAGE OF STRONG PEAKS PRESENT =    0.0
--------------------------------------------------------------------------------------------
```

7.3.2 Manual interpretation

The first step taken in interpreting the output is to consider that mineral with the highest "percentage of strong peaks present". The "calculated spacings" used in its identification are subtracted from the listed "calculated spacings" at the top of the output. The remainder of the calculated spacings are used to check the next mineral with the highest "percentage of strong peaks present" and in so doing overlapping peaks are taken into account. The procedure is repeated until all the listed calculated spacings have been assigned.

Because of overlapping peaks, intensities of the new peaks were measured by intensity ranks, in this study, using a very strong to very weak scale. The intensity ranks were incorporated during the above manual interpretation procedure. For example, a "standard spacing" having 100 relative intensity should match a "calculated spacing" having a very strong intensity rank.

7.4 Running the package

To run the package, a data base consisting of the relevant minerals of interest is read in. The input XRAYDATA is also read in. The cards in the input are punched thus:-

Card number 1: IN : USERNAME, XRAYDATA
2: XRAYDATA FOR ....
3: Details of the test sample and the
}
4: conditions of the x-ray
5: LAMDA = insert wavelength and next intensity error width (integer)
6: θ_2 θ_1 θ_3 (intensity if measured)
7: θ_2 θ_1 θ_3 (intensity if measured)

Table 7.2 The computer program in Fortran language

```
      MASTER XRAY
      REAL LAMDA
      DIMENSION II(200)
      DIMENSION D(200,3),DS(20),INT(20)
      DIMENSION THETA(3),TITLE(10)
      DIMENSION THETB(3)
      DN(LAMDA,ARG) = 0.5*LAMDA/SIN(0.5*ARG)
      CONST=0.0174532925
      WRITE(5,700)
      DO 20 I=1,3
      READ(1,10) TITLE
      WRITE(5,600) TITLE
   20 CONTINUE
      WRITE(5,800)
  800 FORMAT(1H ,120(1H-),//)
      WRITE(5,905)
  905 FORMAT(1H0,6HTHETA1,2X,8HSPACING1,5X,6HTHETA2,10H  SPACING2,
     +5X,6HTHETA3,10H  SPACING3)
   10 FORMAT(10A8)
      READ(1,15) LAMDA,LIM
   25 FORMAT(3F0.0,I5)
   15 FORMAT(6X,F6.4,I2)
      DO 30 L=1,200
      READ(1,25) THETA(2),THETA(1),THETA(3),II(L)
      IF (THETA(2) .LT. 0.0) GO TO 50
      DO 40 J=1,3
      THETR(J)=CONST*THETA(J)
      D(L,J)=DN(LAMDA,THETB(J))
   40 CONTINUE
      WRITE(5,900) (THETA(J),D(L,J),J=1,3)
  900 FORMAT(F6.2,5F10.2)
   30 CONTINUE
   50 L=L-1
      WRITE(5,800)
      READ(2,500) MN
      DO 400 II=1,MN
      KOUNT=0
      READ(2,55) CARDH
      WRITE(5,56) CARDN
   55 FORMAT(A6)
      READ(2,60) N
   60 FORMAT(I0)
      READ(2,65) (DS(I),INT(I),I=1,N)
   65 FORMAT(20(F0.0,I0))
      WRITE(5,805) (DS(I),I=1,N)
  805 FORMAT(1H0,'STANDARD'/1H ,'SPACING',T16,15F7.2)
      WRITE(5,810) (INT(I),I=1,N)
  810 FORMAT(1H0,'RELATIVE'/1H ,'INTENSITY',T16,15I7)
      WRITE(5,460)
  460 FORMAT(//,1H0,'CALCULATED',T26,'STANADARD',3X,'RELATIVE'/
     +1H ,'SPACING',T14,'INTENSITY',3X,'SPACING',4X,'INTENSITY')
  110 FORMAT(1H0,F7.2,6X,I5,5X,F7.2,5X,I5)
  600 FORMAT(1H0,10A8)
  700 FORMAT(1H1)
      DO 70 I=1,L
      DO 80 J=1,N
      IF(D(I,2).GE.DS(J)) GO TO 302
   80 CONTINUE
  302 IJ=J-1
      IF(IJ.EQ.0) IJ=1
   75 IF(DS(IJ).LT.D(I,1) .AND. DS(IJ) .GT. D(I,3)) GO TO 112
      IF(IJ.EQ.J) GO TO 70
      IJ=J
      GO TO 75
  112 IF(II(I).EQ.0) GO TO 115
      IF(IABS(II(I)-INT(IJ)).GT.LIM)GO TO 70
  115 KOUNT=KOUNT+1
      WRITE(5,110) D(I,2),II(I),DS(IJ),INT(IJ)
   70 CONTINUE
   56 FORMAT(1H0,'CARD NUMBER  ',T17,A6,/)
  500 FORMAT(I0)
      COUNT=KOUNT
      X=N
      PERC=100.0*COUNT/X
      WRITE(5,920) PERC
  920 FORMAT(//,1H0,'PERCENTAGE OF STRONG PEAKS PRESENT = ',
     +F7.1)
      WRITE(5,800)
  400 CONTINUE
      STOP
      END
```

Last card: $-\theta_2$ $-\theta_1$ $-\theta_3$.

The formats are shown in the program on Table 7.2. After the input is read in, two job cards are required to operate the program.

Card number 1: Job name,: username, JD (specify job time)

2: contains the following below:-

```
PROG FORTRAN XRAYPROG, FILE* CRO = XRAYDATA, FILE*
CR1 = XRAYDATA2, FILE* LPO = XRAYOUT, TL 59
```

All cards are punched from line 1.

7.5 Test search identification

The package successfully identified a mixture supplied by National Bureau of Standards (America) to the Central Electricity Generating Board (CEGB) in Harrogate for assessing the merits and the demerits of automated search against manual search. Quartz and calcium silicate hydrate (CS_2H_2) were identified. Identification was enhanced by omitting the intensity values from the input but considering them in the manual interpretation.

7.6 Chapter Summary

a) A computer search program is developed to aid in eliminating the many clsosely related silicates, aluminates, alumino-ferri-silicates and alumino-silicates formed when red tropical soils are treated with lime.

b) A manual interpretation of the results of the automated search backed up by possible elemental analysis is necessary for the final and conclusive identification of the reaction products.

c) The data base minerals against which the new peaks observed in the XRD are checked can be replaced or edited to contain minerals relevant in the search without altering the search program.

d) The search program is capable of handling input data for the peaks of the new diffraction patterns and their error windows as 2θ values of Bragg's angle.

e) The program is flexible and can either use the d-spacings alone or the d-spacings and their intensities to match the peaks.

CHAPTER 8

SCANNING ELECTRON MICROSCOPY OF THE SOIL-LIME STYSTEMS

8.1 Introduction

Microscopic methods which are in use for studying the atomic lattice structure or the fabric appearance of specimens can be broadly divided into two i.e. optical microscopy and electron microscopy. While optical microscopes use light energy to form magnified images of specimens, electron microscopes use high energy electrons for the same purpose. The electron image formed by electron microscopes can be observed visually on a fluorescent screen, recorded on photographic plate or film or even stored on video tapes for subsequent processing and reconstruction by a digital computer (100).

Electron microscopes are usually classified as conventional transmission electron microscopes (TEM) or high voltage electron microscopes (HVEM) and scanning electron microscopes (SEM). The SEM has achieved, recently, a high resolving power and versatility. Due to this, only the SEM was used in the microscopic investigation of the lime treated soils. The SEM is therefore considered in detail.

8.2 Basic principles and the design of the SEM

The basic purpose of scanning electron microscopy like most other forms of microscopy is to render finer details in the specimen visible to the naked eye. To achieve this in the SEM, electrons from a heated filament are accelerated by a high voltage, usually of the order of 5 - 50 kV, and passed down the centre of an electron optical column. The electrons are formed into a probe by a set of magnetic lenses and focused onto the surface of a solid specimen. The probe scans the surface of the specimen in square tiny sections in the same way as a spot can scan a commercial television screen (100).

Scanning is achieved by passing a current from a generator through the scan coils (located between the magnetic lenses) and through the corresponding coils of a cathode ray tube so as to produce an identical but larger image of the surface on its viewing screen. The probe that strikes the specimen surface causes electrons to leave the surface. These in turn strike a collector and an electron current signal is set up. The signal is amplified and used to control the intensity of the cathode ray tube. There is an exact point to point match between the section on the specimen surface and that on the cathode ray tube screen. The intensity of each point on the image on the cathode ray tube screen is a direct measure of the number of electrons collected from the corresponding point of the specimen surface.

Specimens are usually mounted on stubs that fit directly into the specimen stage in the specimen chamber. They can be moved laterally, tilted and rotated in the SEM while being examined. Non-conducting specimens are usually coated with a conducting material for proper electrical contact and to prevent charging occuring when they are being examined in the SEM.

8.3 The SEMs used in the investigation

A Cambridge 'Stereoscan' 600 scanning electron microscope was used in investigating some of the lime treated soils, while some other soils were studied using a Joel SEM, model JSM 35 available in the Scientific Section, Central Electricity Generating Board at Harrogate.

8.4 Sample preparation

A sample of the lime treated soil to be examined was fractured and dried in vacuum. The side remote from the fractured surface was gently ground flat on a sand paper. The flat surface was mounted on a stub with Araldite.

The mounted specimen was placed on the substrate holder of a Hummer 11 coating apparatus and given a five minute coat of gold-palladium. In good working conditions, no substrate manipulation is necessary when Hummer 11 is used as the sputtering is a diffuse process and allows deposition around corners and in recesses to prevent spot charging in the SEM. The coater used was not in perfect working conditions and sometime left the edges of the specimen uncoated. When this happened the edges were given a paint of silver to ensure electrical contact between the conducting coat and the support stub. The specimen was examined in the SEM immediately or stored in a desicator until required for examination. In the latter circumstance, the specimen was given one to two minutes coat prior to examination in the SEM.

8.5 Results and discussion

The electron micrographs obtained with the Cambridge Stereoscan 600 and Joel JSM 35 are shown in plates 8.1 to 8.10.

Plates 8.1 and 8.2 show the electron micrographs of soil T II obtained with the Joel JSM 35. They reveal dense microstructures in which plates have striated and oriented appearance with intersecting morphology. The close textured massive structures of interlocking rods, long fibres and plates of well crystallised C-S-H can be seen. Amorphous reaction products could be seen to be mixed with some of the well crystallised C-S-H in plates 8.1b, 8.2a and 8.2b. These micrographs are similar to those presented by Abo-El-Enein et al (107) who studied the morphology of autoclaved clinker and slag-lime pastes in presence and absence of silica sand. By analogy to the results of the micrographs obtained by Abo-El-Enein et al, it appears that the C-S-H in the soil-lime systems are results of reactions between lime and amorphous silica which are probably as reactive, at ordinary temperature, as slag-lime and silica pastes at elevated temperatures.

Plates 8.3 and 8.4 are electron micrographs of soil T II obtained with Joel JSM 35. Plate 8.3a shows how the reaction products, whose close up is shown in plate 8.3b, bond two adjacent mineral particles together. Plate 8.3b shows the reaction product to be well crystallised, dense and hexagonal plate like crystals. They are similar to the micrographs of "stepped clusters of imperfectly developed plate like crystals of gehlenite hydrate with foreshadowed hexagonal limitation" shown and described by Jambor (108) as reaction products between activated kaolin (kaolin heated to 500°C) and lime. Gehlenite hydrate (C_2ASH_n) can possibly form due to the reaction between amorphous alumina, silica and lime (68, 69). Soil J II contains appreciable amounts of amorphous silica and alumina. Plate 8.4 shows similar reaction products (to that shown in plate 8.3) cementing and binding a particle to the surrounding soil minerals.

Plate 8.1 (a)

Electron micrograph of soil T II showing dense microstructure with plates of C-S-H having striated and oriented appearance.

Plate 8.1 (b)

A close up of Plate 8.1 (a) revealing some amorphous reaction products in presence of the well crystallised C-S-H.


25 302 0024 0010.0U


25 662 0025 0001.0U

Plate 8.2 (a)

Electron micrograph of soil T II showing interlocking rods and plates of well crystallised C-S-H.

Plate 8.2 (b)

Plate 8.2 (a) at a higher magnification showing not only the well crystallised plate-like structure but also rod like long fibres.


25 402 0027 0010.0U

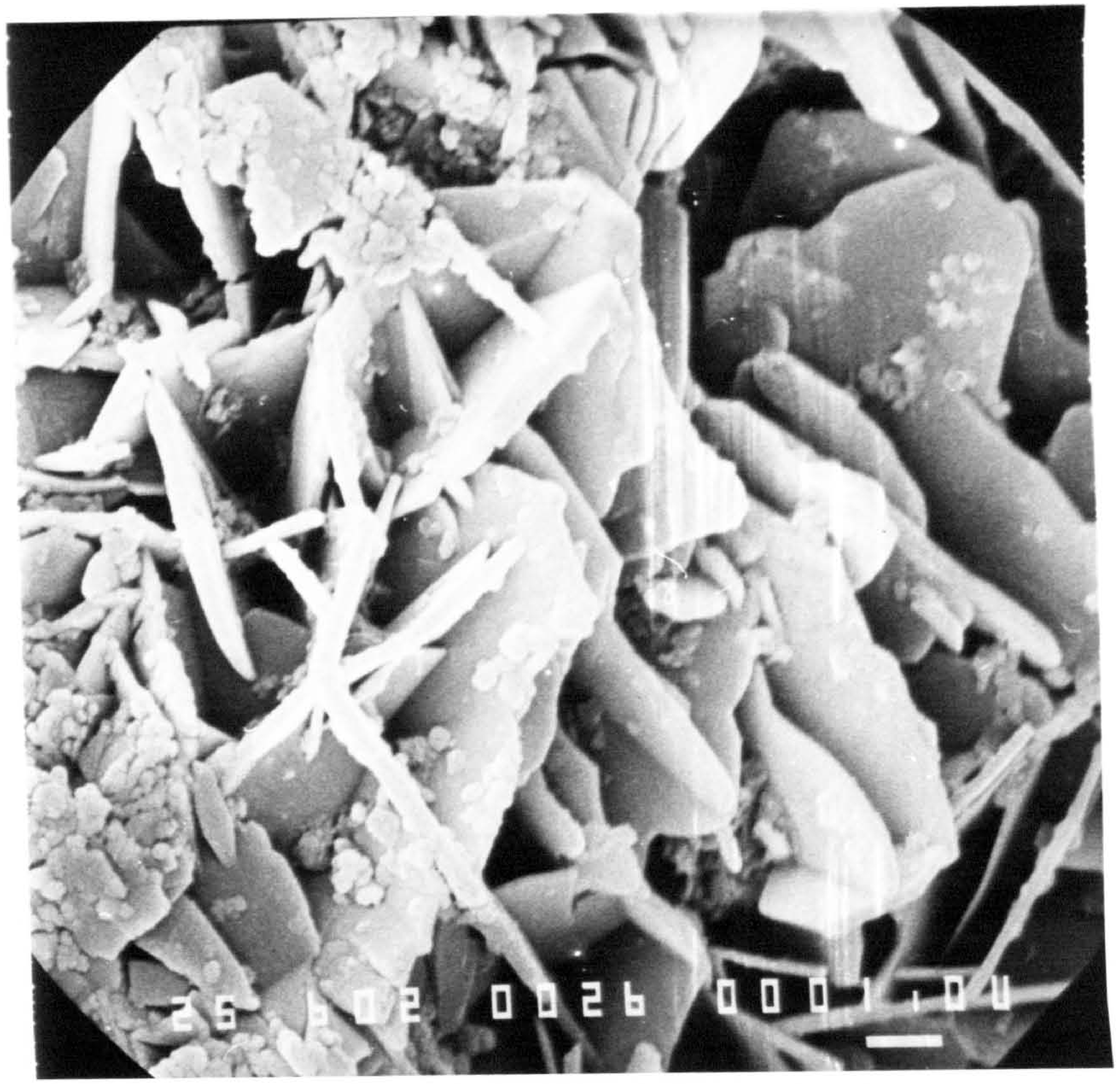
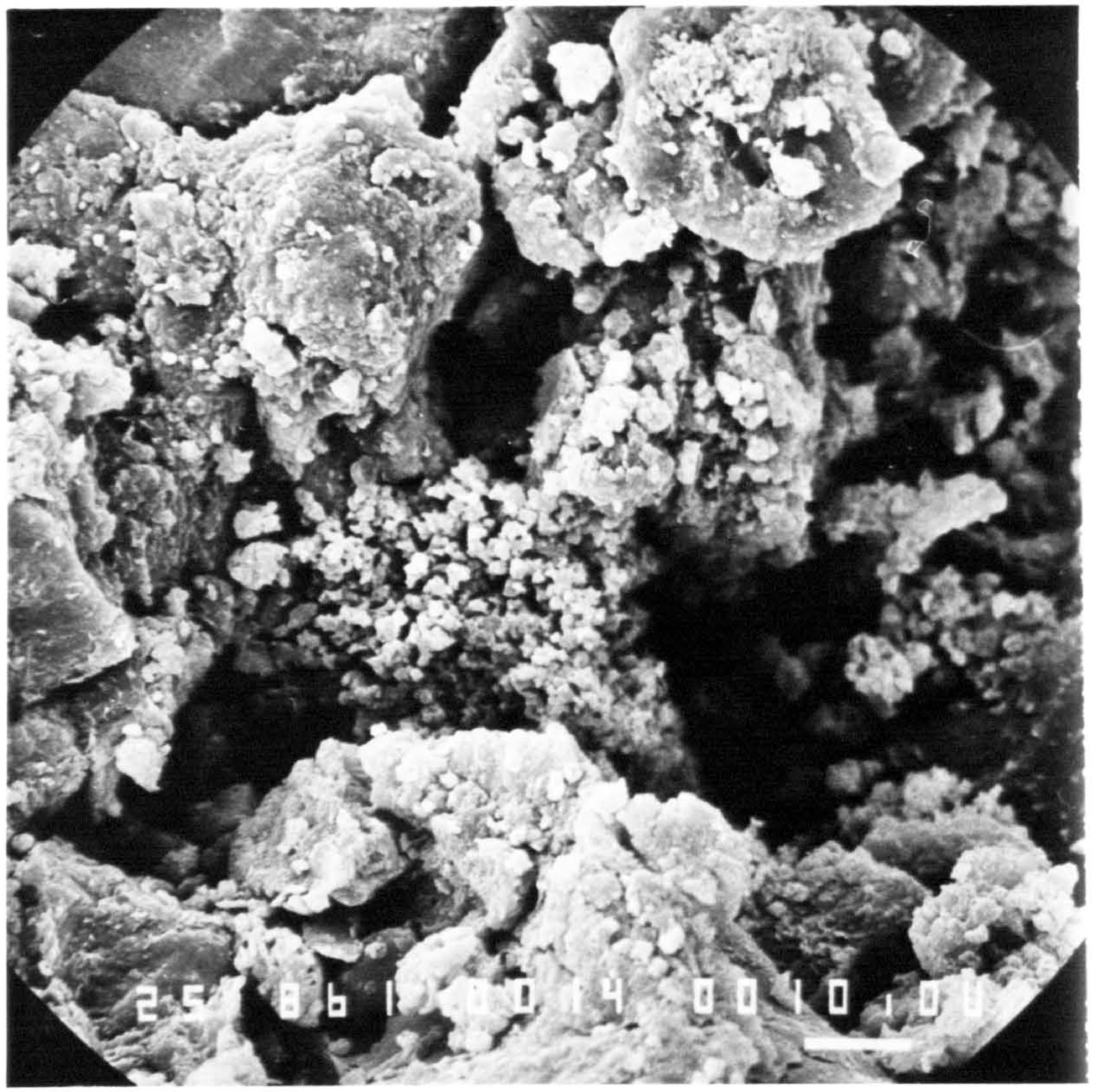

25 602 0026 0001.0U

Plate 8.3 (a)

One of the ways through which cementitious reaction products increase the strength of the soil-lime system is binding adjacent soil particles. This fact is illustrated by Plate 8.3 (a), an electron micrograph for soil T II.

Plate 8.3 (b)

This is a close up of Plate 8.3 (a). It shows the reaction products to be well crystallised, dense and hexagonal. These are probably hexagonal crystals of gehlenite hydrate.


25 861 0014 0010.0U

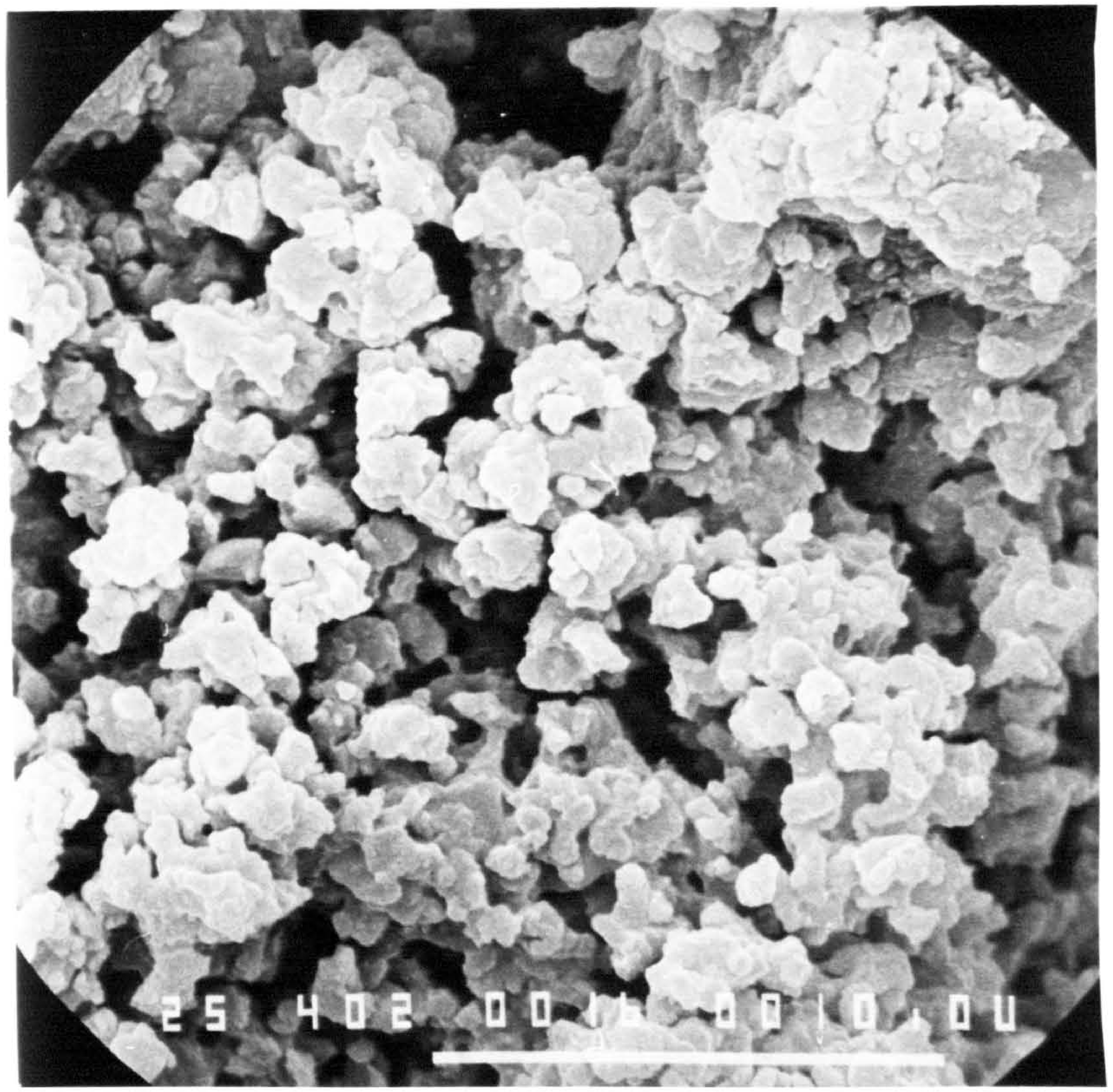
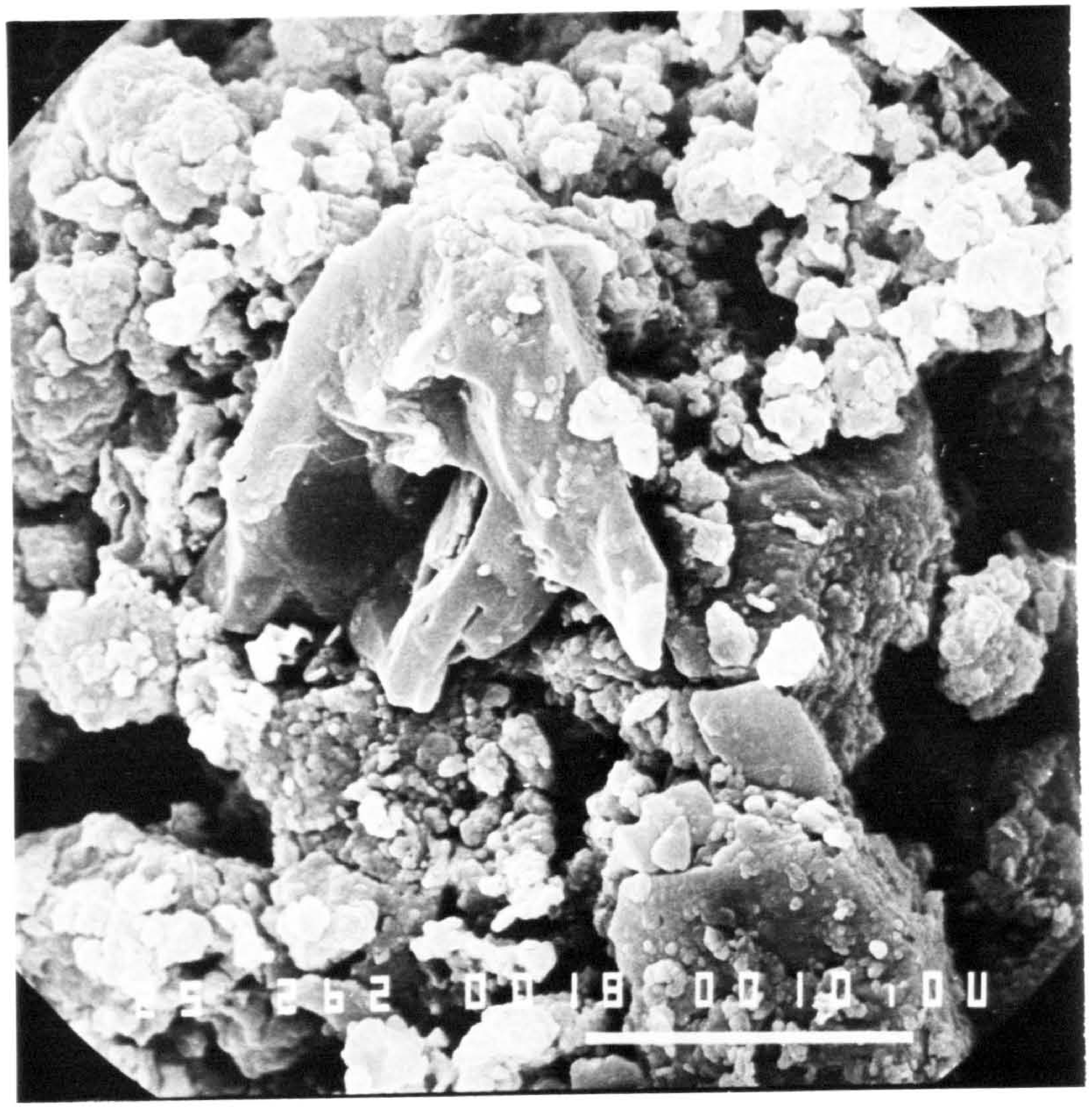

25 402 0016 0010.0U

Plate 8.4 (a)

In contrast to the function of the reaction products described in Plate 8.3 (a), strength increase in a soil-lime system can be a result of the unreacted material being embedded in the reaction products just as aggregates are embedded in concrete or sand in mortar. Plate 8.4 (a), a scanning electron micrograph of soil T II illustrates this fact.

Plate 8.4 (b)

A close up of Plate 8.4 (a) reveals most of the reaction products to be that described in Plate 8.3 (a).


25 262 0018 0010.0U

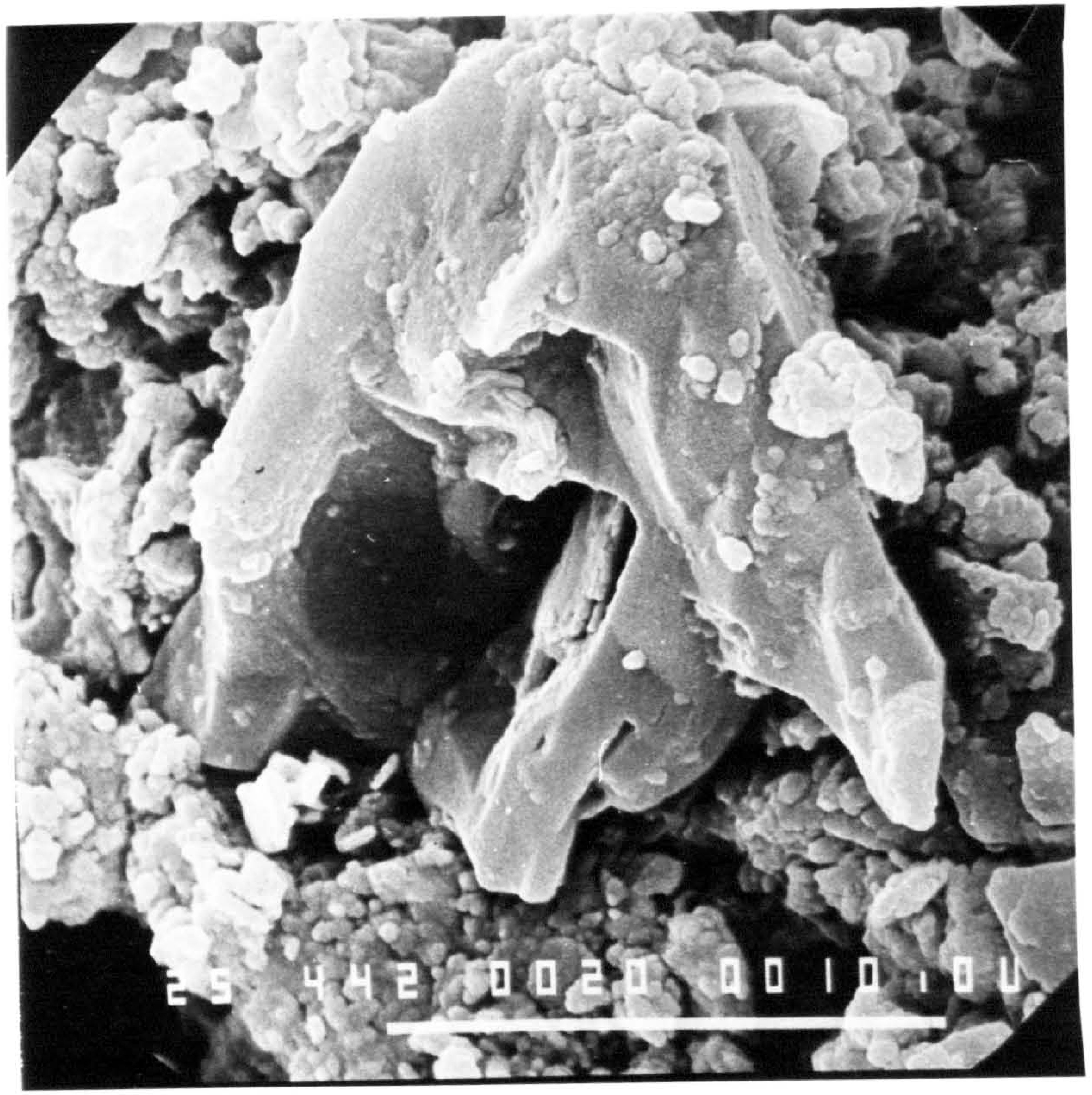
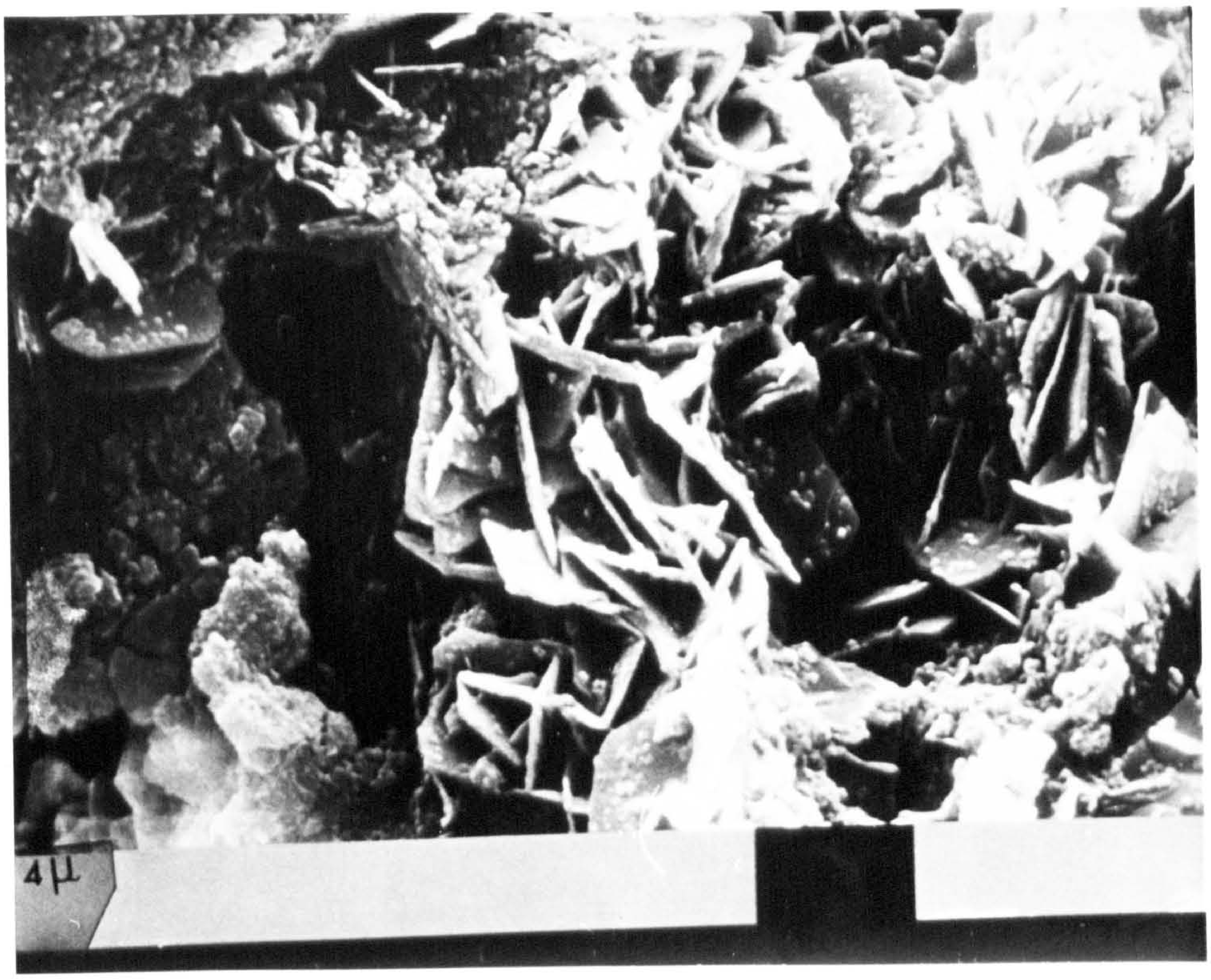

25 442 0020 0010.0U

Plate 8.5 (a)

Electron micrograph for soil A II showing the formation of massive plates of C-S-H. Plate like calcium ferrites can be seen on the left hand side and top right hand side of the plate.

Plate 8.5 (b)

Plate 8.5 (a) at a higher magnification.


4µ

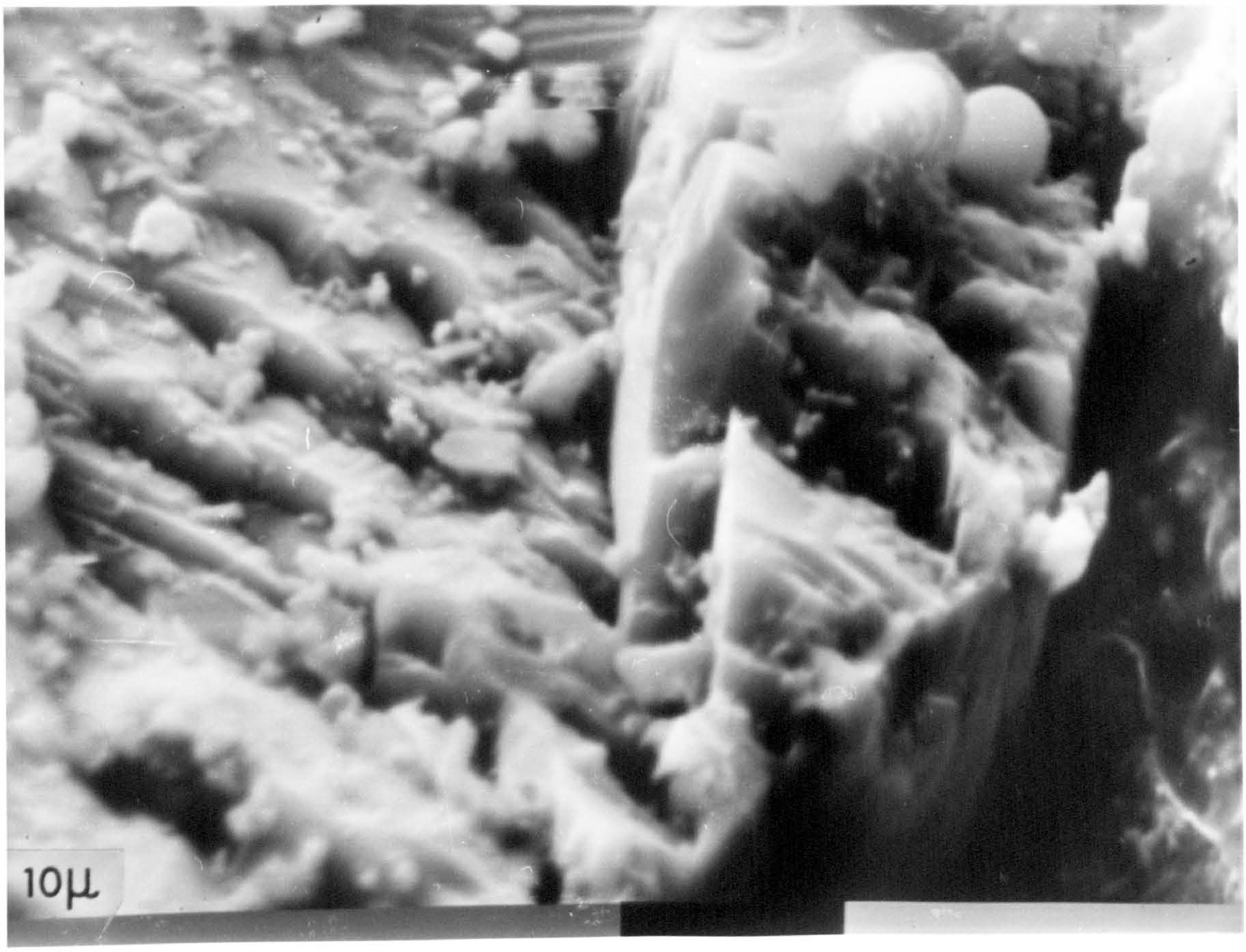

2µ

Plate 8.6 (a)

This clearly shows well crystallised plates of calcium alumino-ferri-silicates formed by treating soil J II with lime. This product was also detected by x-ray diffraction.

Plate 8.6 (b)

Plate 8.6 (a) at a higher magnification.


10μ


4μ

Plate 8.7 (a)

This shows how the calcium alumino-ferri-silicates formed by soil J II help to give strength to the soil-lime system by bonding and interlocking the unreacted mineral particles of the soil.

Plate 8.7 (b)

A close up of Plate 8.7 (a) showing the calcium alumino-ferri-silicates.


10μ

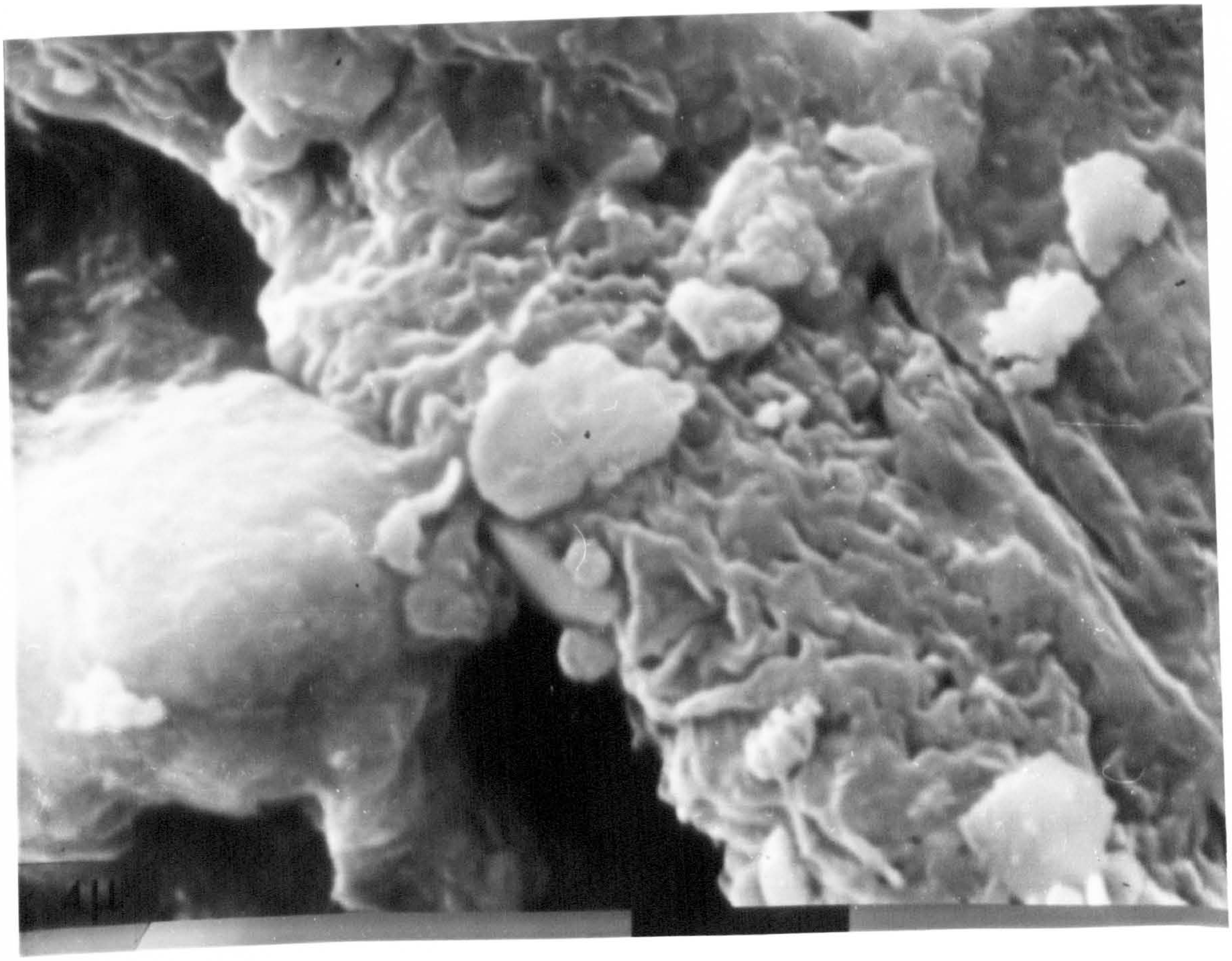

1μ

Plate 8.8 (a)

This Plate shows that not all the reaction products are crystalline even after curing for about two years at 22°C. These poorly crystallised reaction products formed by soil J II have cementitious properties.

Plate 8.8 (b)

A higher magnification of Plate 8.8 (a). Notice the presence of relatively large voids revealed in the microstructure.


20µ

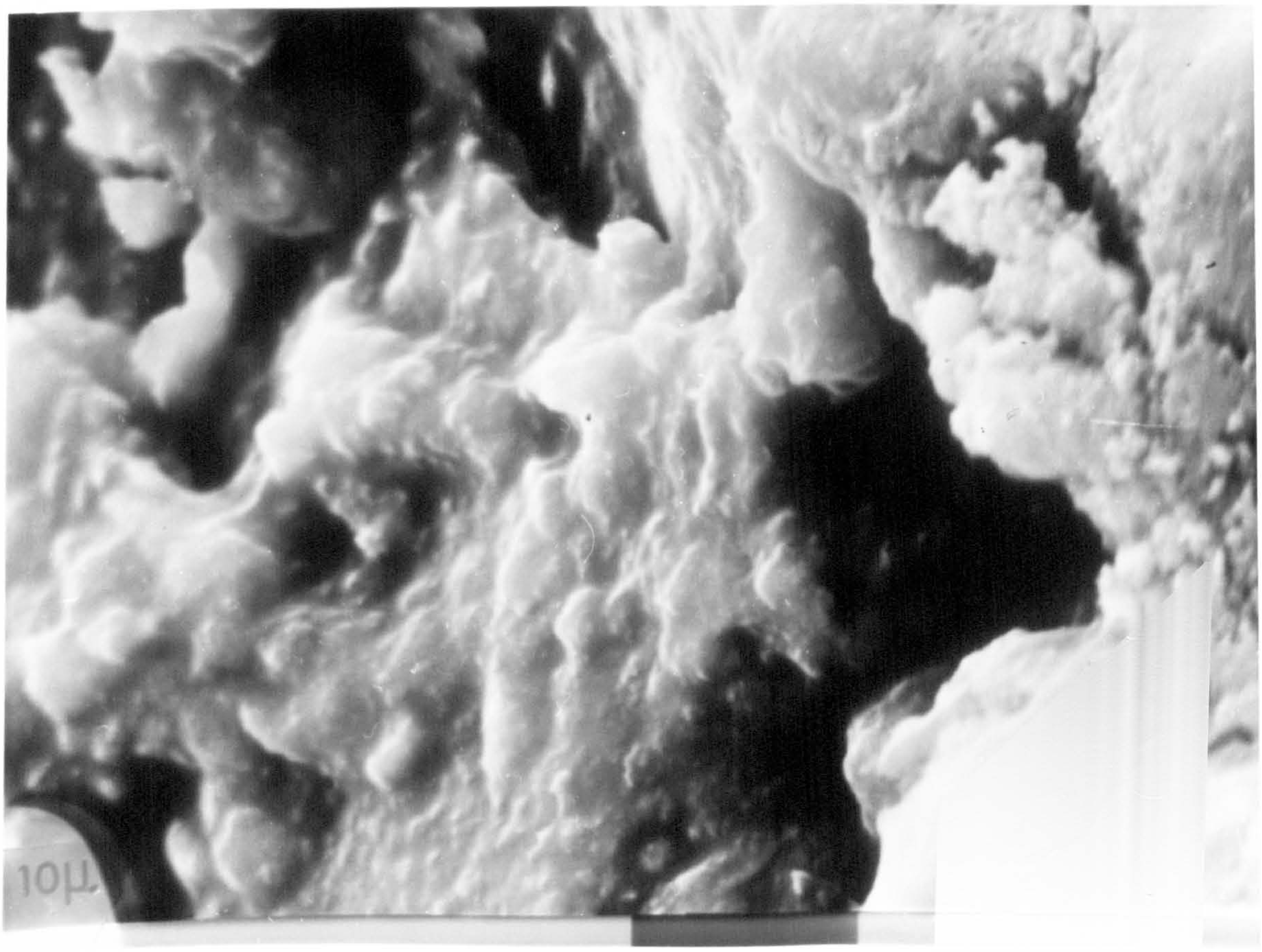

10µ

Plate 8.9 (a)

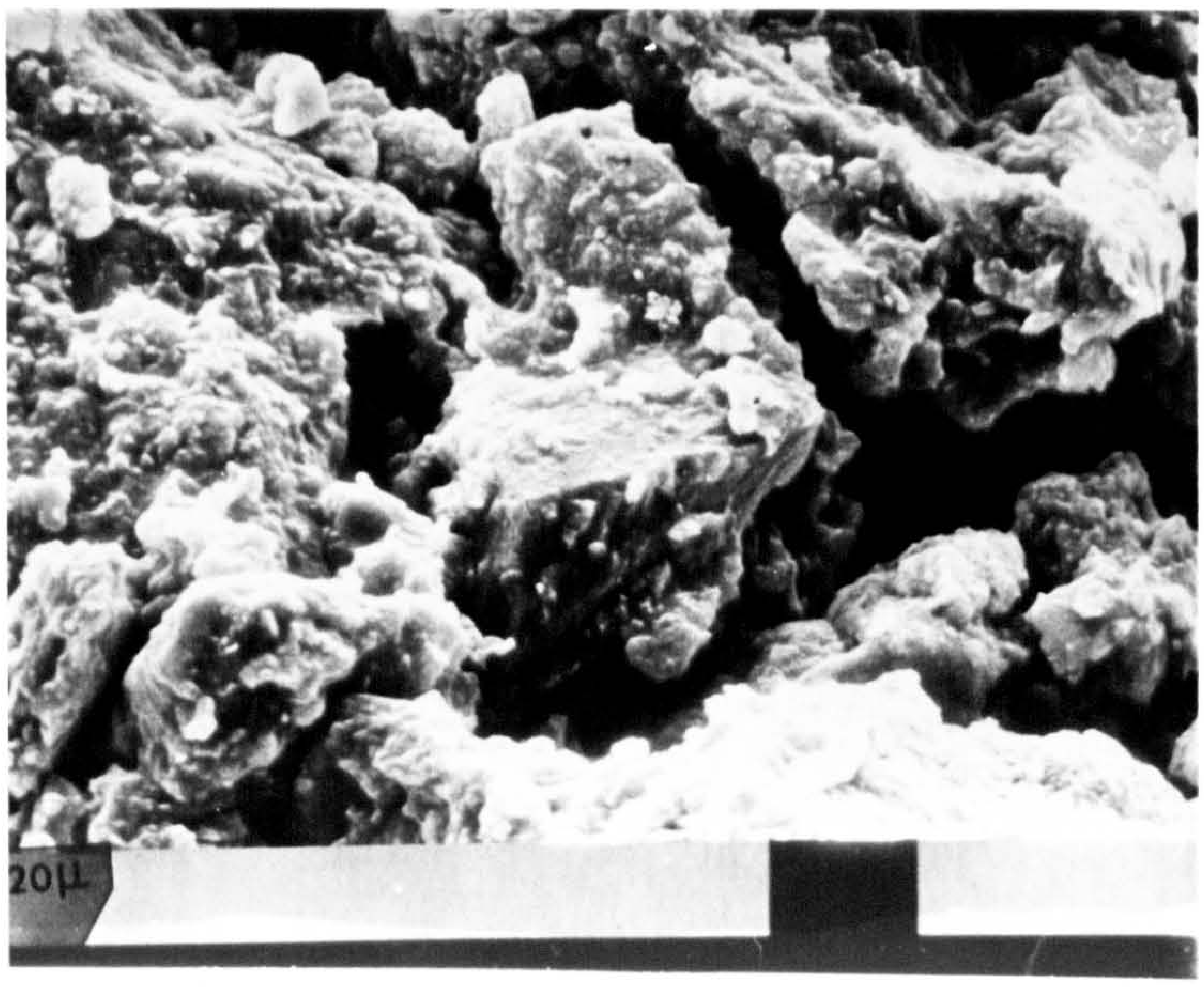
Electron micrograph for soil J II after treatment with lime showing the presence of amorphous reaction products.

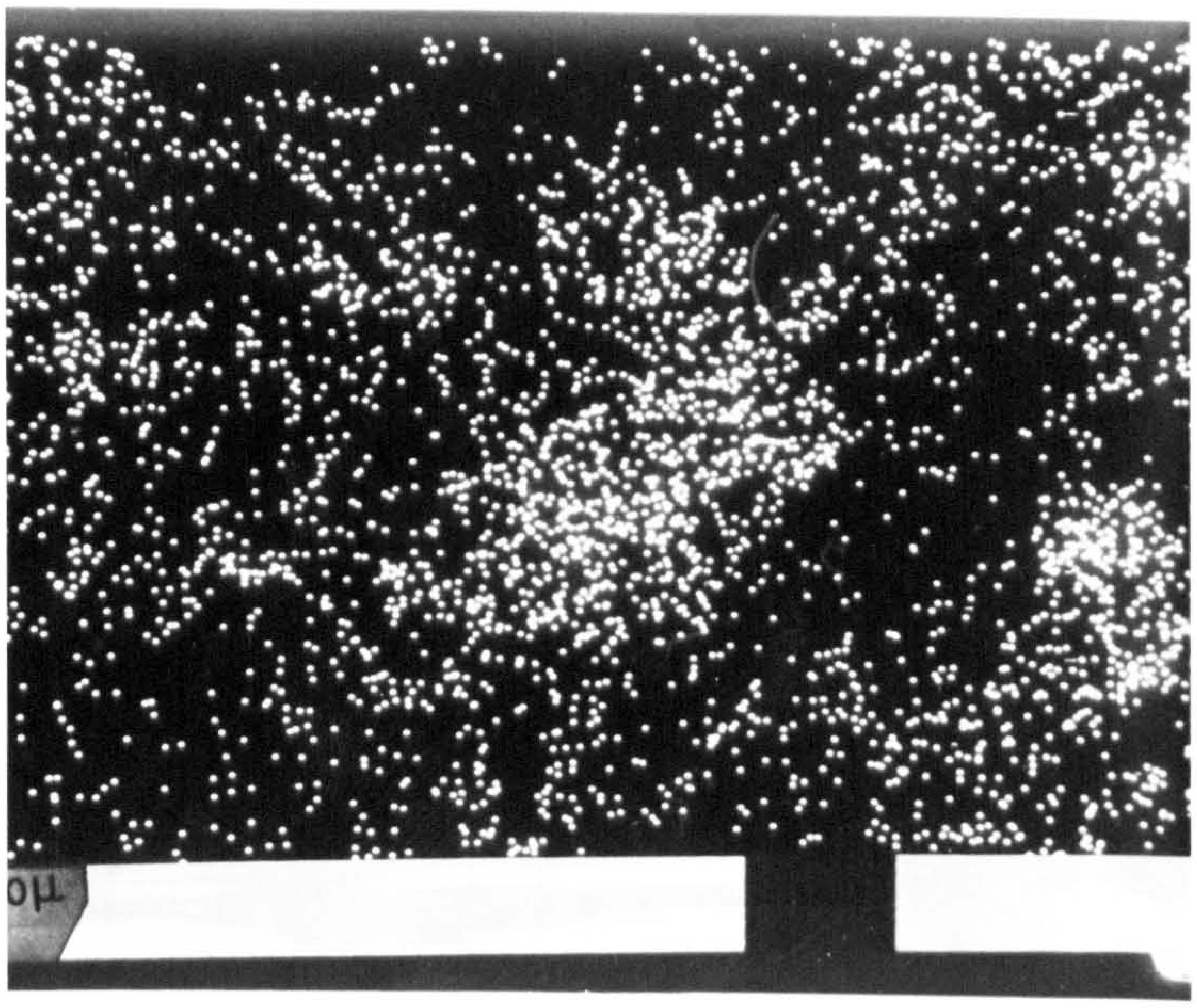
Plate 8.9 (b)

Energy-dispersive (elemental) map of Plate 8.9 (a) for calcium. Calcium can be seen to be present over the whole surface but highly concentrated in the middle.

Plate 8.9 (c)

Elemental map for silicon. That for aluminium is similar. This map shows very little silica or alumina to be present in the middle thus showing that most of the calcium in the middle is present as unreacted lime.


20μ


0μ

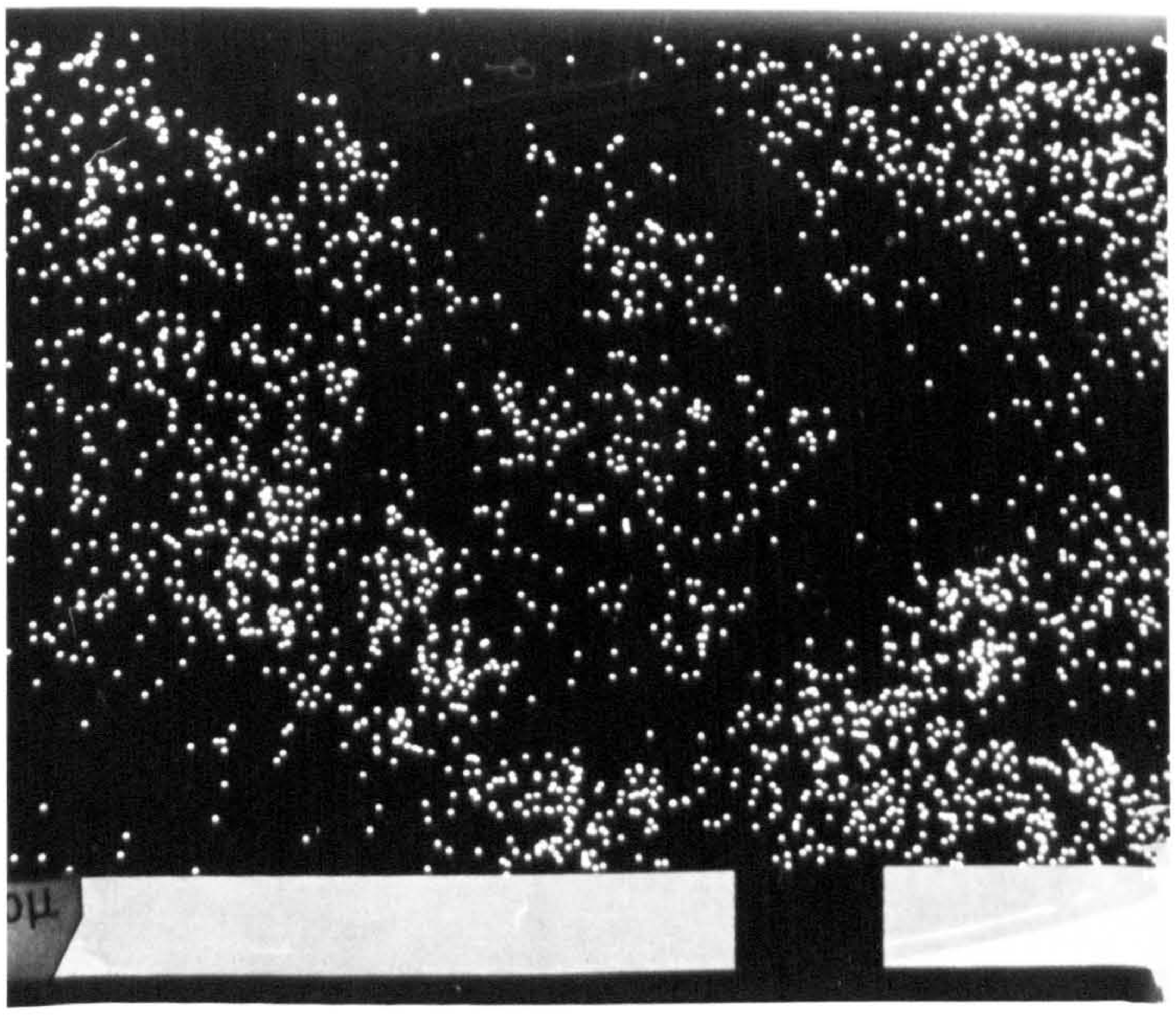

0μ

Plate 8.10 (a)

Electron micrograph for soil J II showing the presence of amorphous reaction products to the left hand side of the micrograph.

Plate 8.10 (b)

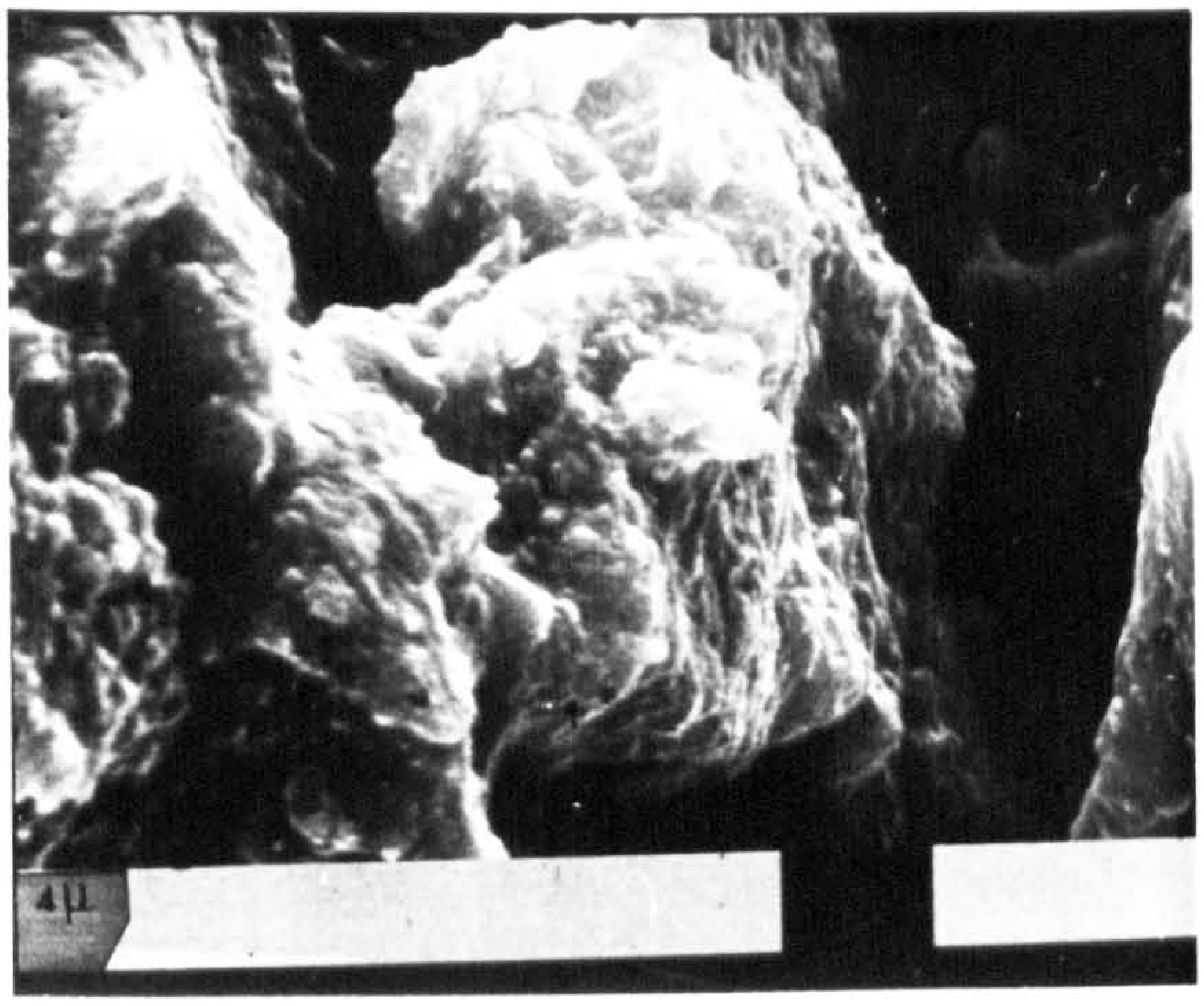
Energy-dispersive (elemental) map for calcium showing clearly the presence of calcium products on the left hand side of the micrograph.

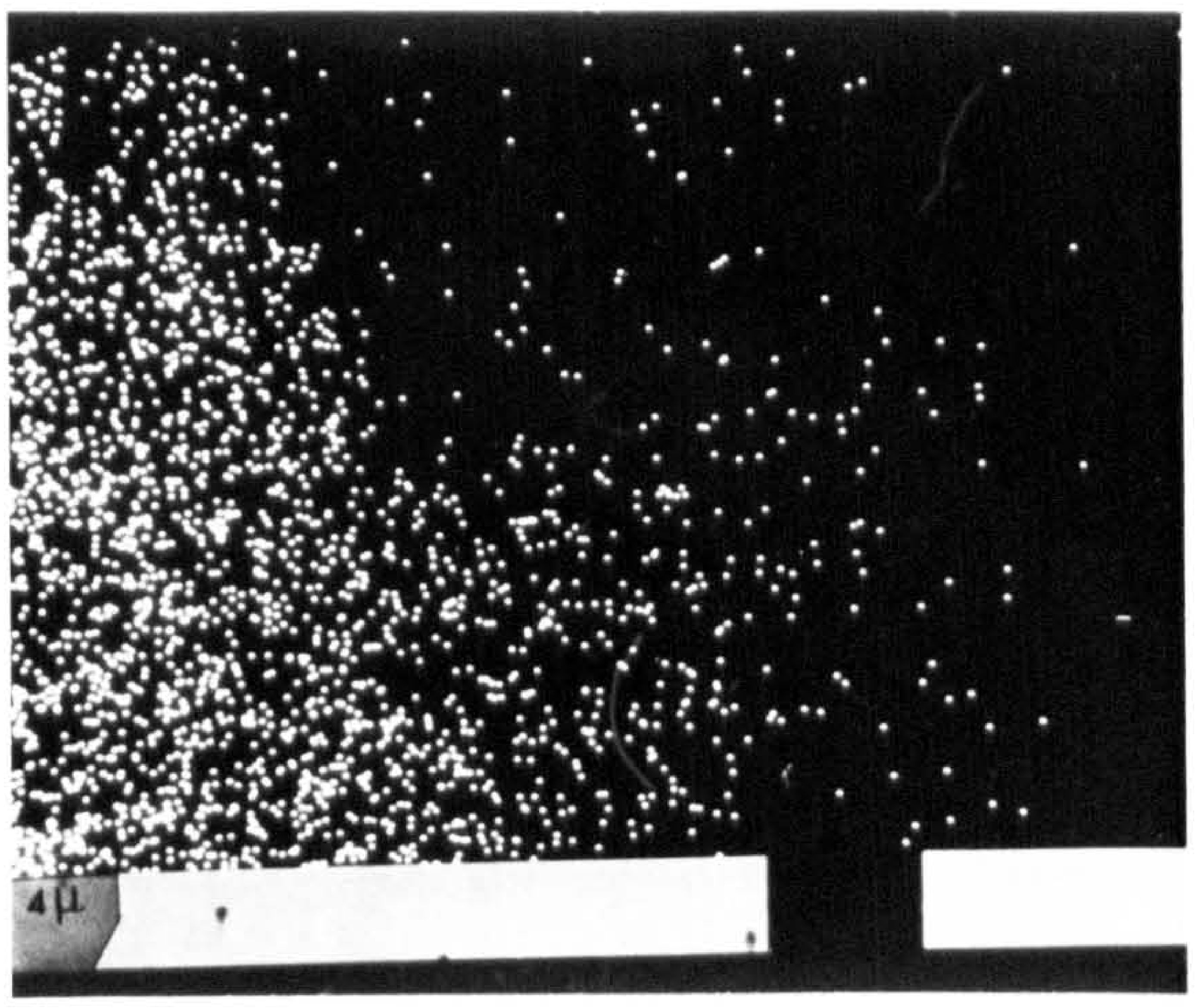
Plate 8.10 (c)

Elemental map for silicon or aluminium. Their distribution is similar to that of calcium showing the left hand side of Plate 8.10 (a) to be probably amorphous reaction products.

Plate 8.10 (d)

Elemental map for iron. The uniform distribution of iron, unlike the distributions for calcium, silicon and aluminium, suggests that the iron is unreacted or probably substitutes into the reaction products on the left hand side.


4μ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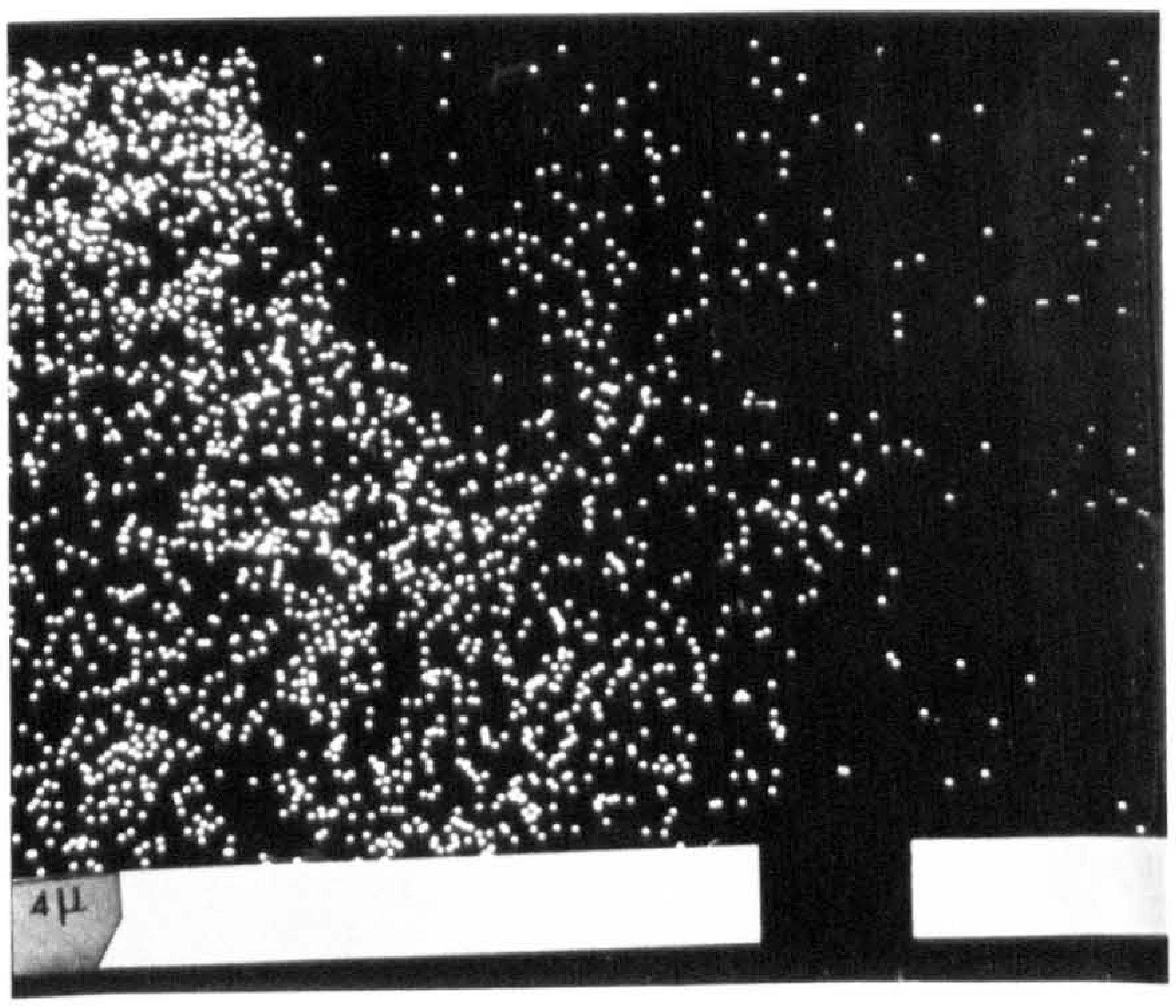
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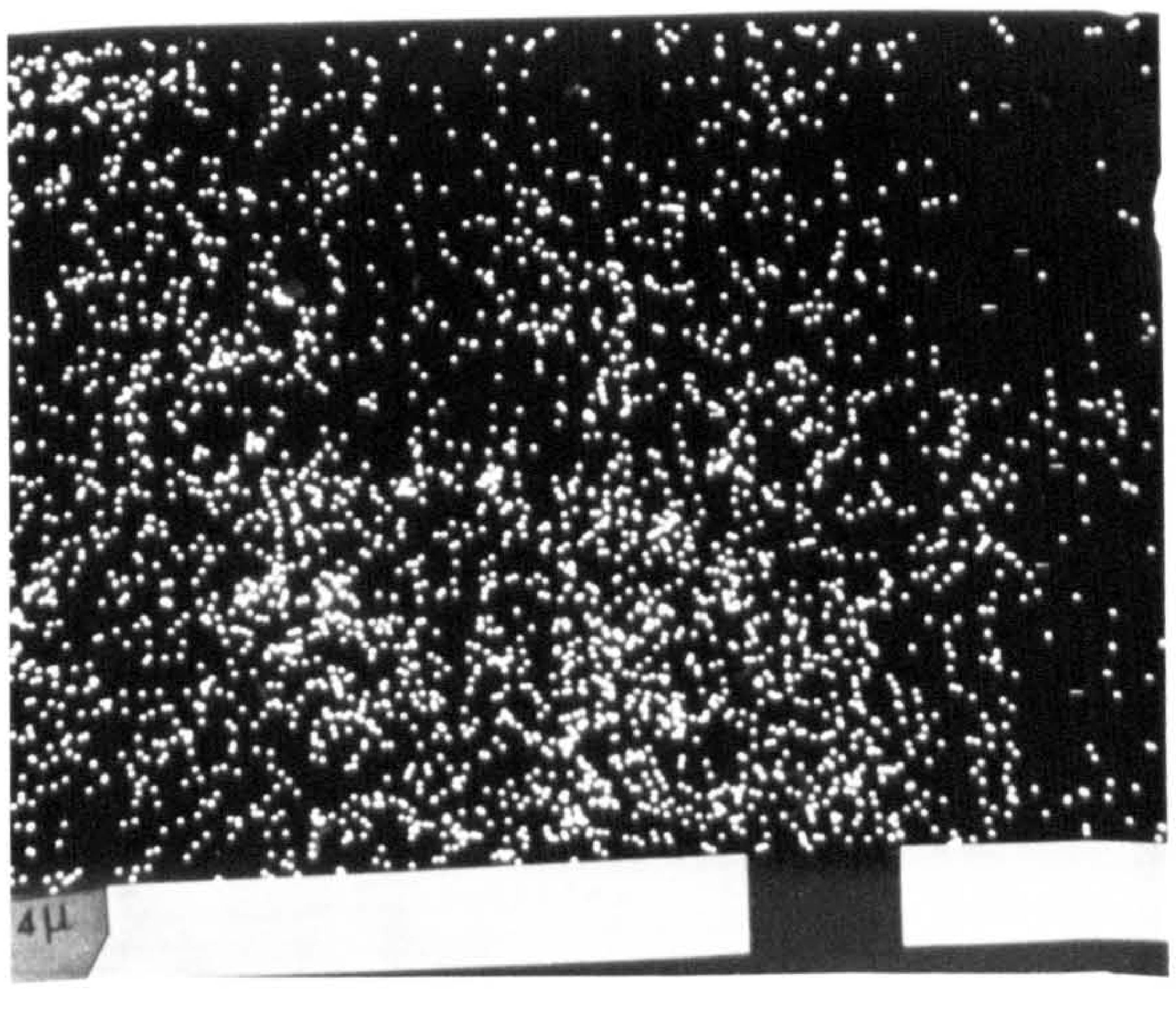

4μ

Plate 8.5 obtained using a Cambridge Stereoscan SEM 600 shows the formation of massive plates of C-S-H and plate like calcium ferrites (left hand side and top right hand side, plate 8.5a) by the soil A II. The morphology of the left hand side and top right hand side of plate 8.5a are very similar to the morphology of the calcium ferrite, C_4F, as reported by Rogers and Aldridge (109).

The rest of the plates i.e. 8.6 to 8.10 were obtained using Cambridge Stereoscan 600 for the soil J II after treatment with lime and curing for two years at 22°C. Plate 8.6 shows clearly plate like alumino-ferri-silicates with a morphology similar to that presented by Uchikawa and Uchida (110) and Roy et al (111). One of the ways by which cementitious reaction products help to increase the strength of a lime treated soil is by bonding and interlocking the unreacted mineral particles of the soil. Plate 8.7 illustrates this phenomenon and shows how the plate like alumino-ferri-silicates achieve this in the soil J II. Notice the relatively large voids in the microstructure.

Not all the reaction products can be crystalline even after curing for about two years at 22°C. This fact is illustrated in plate 8.8 which shows supposedly poorly crystallised reaction products exhibiting cementing properties in their state. Relatively large voids also characterise the microstructure.

Plate 8.9 shows the micrograph and energy-dispersive (elemental) map, of the fractured surface, for calcium, silica and alumina. The calcium element distribution map, Plate 8.9b, shows that except at the middle, calcium compounds are more or less uniformly distributed over the surface. Plate 8.9c shows the elemental map for silica. The elemental map for alumina is similar to that for silica. It can be seen in Plate 8.9c that there is little or no silica or alumina at the centre (where there is a high concentration of calcium). Thus most of the calcium compound at the centre of Plate 8.9a is unreacted or carbonated lime. Apart from the centre, silica and alumina are almost as uniformly distributed as calcium which suggests that reaction products without recognizable morphology are present. This supports the fact that poorly crystallised or amorphous reaction products are still present after about two years curing. While such products could be uniformly distributed over an area of the lime treated soil, it is not necessarily true to say that such products are uniformly distributed over all the surfaces of the lime treated soil as suggested by Ormsby and Kinter (65). Plate 8.10 highlights this fact and stresses the need for thorough mixing of the soil and lime. The element map (Plate 8.10 (d)) shows that iron is either unreacted or substitutes into the calcium alumino-silicate (left hand side, Plate 8.10 (a)).

8.6 Chapter Summary

a) Red tropical soils form reaction products which include calcium silicates, alumino-silicates and alumino-ferri-silicates.

b) While some of the reaction products have discrete morphology after about two years curing, others still remain in amorphous states.

c) The C-S-H are associated with dense and close textured massive microstructure whereas the alumino-silicates and alumino-ferri-silicates usually occur with relatively large voids in the microstructure. This suggests that the microstructure is function of both the volume and type of the reaction products.

CHAPTER 9

OTHER CONSTITUENTS OF RED TROPICAL SOIL-LIME SYSTEMS

9.1 Introduction

Apart from the main cementitious reaction products already discussed in previous chapters, there are other constituents in a red tropical soil-lime mixture. These may be other reaction products or unreacted residues. They include calcium carbonate, unreacted lime, unreacted soil and voids. They also influence the behaviour of the system. This chapter then reviews the available methods for the determination of calcium carbonate, unreacted lime and porosity of the systems studied. It presents separately a review of thermogravimetric analysis and finally presents the results together with the discussion of the findings.

9.2 Literature review and methods

While engineers recognise the presence of unreacted lime, carbonated lime and voids in lime-pozzolana mixtures, they have made little efforts to quantify them and thus quantitatively assess their influence on the system. Valuable information such as the efficiency of curing methods can be obtained from the quantitative determination of unreacted and carbonated lime.

9.2.1 Calcium carbonate

In practice, lime is mixed with the soils in presence of air. While some of the lime reacts with the soil minerals, another fraction of the added lime reacts with the carbon dioxide of the air to form calcium carbonate according to equation 9.1.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \ldots \quad \ldots \quad \ldots \quad (9.1).$$

The estimation of carbon dioxide in cement materials is not a difficult problem and this is the basis for the estimation of carbonated lime in soil-lime mixtures. Standard gas volumetric, gravimetric and chemical methods are well established. Gravimetric and chemical methods are hazardous, time consuming and cumbersome (90). Gas volumetric methods are therefore favoured and considered in more details.

Carbon dioxide in silicate "rocks" is usually determined by the decomposition of the carbonate by an acid. Early methods relied on qualitative tests for carbon dioxide (112). The tests involved the observation of bubbles when hydrochloric acid is added to a test tube containing the ground sample and hot water. Later these methods were modified to a quantitative one. This involved absorbing and weighing the carbon dioxide evolved when the sample is decomposed by acid. Methods of this type required about 45 minutes for a single determination. Shapiro and Brannock (112) developed a rapid method for quantitative determination of carbon dioxide in silicate "rocks". They used a carbon dioxide tube with a side arm for catching and measuring the gas evolved. Their method is described in detail in appendix B.1. Ormsby and Kinter (65) used this method to measure carbonated lime in lime-montmorillonite-water systems.

9.2.2 Unreacted lime

The detection of free calcium hydroxide in soil-lime systems is potentially very important since it can be used as a parameter to measure the reactivity of the pozzolanic materials which are contained in a soil.

Classically, free or uncombined lime in ordinary Portland cement, clinkers and in presence of calcium silicate hydrates is determined by selective dissolution of the lime from such mixtures. The organic solvents employed vary from glycerol-alcohol through ethylene-glycol to acetoacetic ester-isobutyl alcohol mixtures. One such method is the ASTM method C114-77 (113) for the determination of free lime in Portland cement and clinker. The method does not differentiate between free calcium oxide and free hydrated lime. It is based on the solution of free lime in a hot solution of glycerol and alcohol and subsequent titration of the dissolved lime with an alcoholic solution of ammonium acetate. The method is described in Appendix B.3.

Methods that employ organic solvents such as the ASTM method C114-77 invariably attack calcium silicate hydrates and aluminates when they occur with free lime (114). Pressler et al (114) found that hydrates prepared at lower temperatures and with higher molar C/S ratio were more vulnerable to attack. Of the calcium silicate hydrates they prepared by hydrothermal reaction between CaO and silica gel at 120°, 180° and 240°C, the worst case of organic solvent attack was that prepared with a molar C/S ratio of 1.5 at 120°C. To overcome this problem, they modified an acetoacetic ester-isobutyl alcohol method said to be originally due to Franke. The details of their modified method is given in Appendix B.4. They found their method to give accurate results for calcium hydroxide in presence of calcium silicate hydrates in which calcium was firmly bound, but the solvent attacked the calcium when it was weakly bound.

While their method gave satisfactory results, it was time consuming, requiring at least three hours for each determination.

Presseler et al (115) proposed two further modifications of their method in order to shorten the time of testing and to reduce the amount of sample required. In their modified methods, details of which are given in Appendix B.5, a single extraction is performed on each 0.1 gm portion of the sample.

In one case of the two modifications proposed, the ratio of the solvent volume to sample weight was varied from 500 to 3000 ml/gm. They found it convenient to use six 0.1 gm portions of a sample for analysis. The time of each extraction was thirty minutes and all six extractions could be done simultaneously. They called this method the solvent variation method (SVM). Longer but equal times such as one hour may be used in extracting each of the six sample-solvent ratios. In the second case of modification, the ratio of the solvent volume to sample weight was held constant at 1000 ml/gm while the time of extraction was varied from one portion of the sample to another. This they called the time variation method (TVM). In all other respects, the TVM was the same as the SVM. In both methods, the number of extractions can be varied according to need. While the TVM uses less solvent than the SVM, the SVM requires less time than the TVM.

In any extraction, all, or at least a large part of the free lime may be removed and simultaneously a small amount of the combined calcium (in the reaction products). Let the free lime, which is easy to extract, be designated by C_e and the small amount of combined lime, which is difficult to extract, by C_n. It is for the latter that a correction should be made. The rate of reaction of C_n with ethyl acetoacetate is given by

$$-\frac{dC_n}{dt} = k_1 C_n a \qquad \dots \quad \dots \quad \dots \qquad (9.2)$$

where a is the amount of ethyl acetoacetate and k is the rate constant.

Under the conditions of the SVM, the solvent-sample ratio is so large that the amount of C_n extracted with the lower ratios and those extracted by higher ratios can be assumed constant in equation 9.2 without introducing significant errors. For equal extraction times, equation 9.2 becomes

$$\Delta C_n = k_2 a \qquad \dots \quad \dots \quad \dots \quad \dots \qquad (9.3)$$

where a is proportional to the volume of solvent per gram of sample (V_s).

Hence equation 9.3 can be written as

$$\Delta C_n = k_2^1 V_s \qquad \dots \quad \dots \quad \dots \qquad (9.4)$$

Because of the high solvent-sample weight ratios used in SVM, all the free lime is removed in one extraction. The total calcium removed in an extraction, C_t , is given by

$$C_t = C_e + \Delta C_n \qquad \dots \quad \dots \quad \dots \qquad (9.5)$$

Substituting for ΔC_n:

$$C_t = C_e + k_2^1 V_s \qquad \dots \quad \dots \quad \dots \qquad (9.6)$$

Equation 9.6 shows that a plot of C_t against V_s should give a straight line with the intercept, C_e, equal to the free lime. If all C_e is not removed in one extraction, probably for a very low value of V_s, C_t is low and the point falls below the line defined by the other points. If this happens, this point is disregarded and the straight line drawn using other points obtained for higher values of V_s. In all the samples they (115) tested, C_e was removed by V_s ratio of 1000 or greater. However if the contrary should happen they recommend the use of the highest values of V_s or the extraction of the samples for one hour instead of thirty minutes.

The TVM makes use of equation 9.2 in another way. The average of the initial and final amounts of ethyl acetoacetate (a_i, a_f respectively) used is, as assumed, equal to a in equation 9.2. For constant solvent volume-sample weight ratio (V_s) but variable time, equation 9.2 becomes

$$\Delta C_n = k_3 t \quad \ldots \quad \ldots \quad \ldots \quad (9.7)$$

where t is the time and k_3 is a constant. Combining equation 9.7 with equation 9.5 gives

$$C_t = C_e + k_3 t \quad \ldots \quad \ldots \quad (9.8)$$

Equation 9.8 indicates a straight line relationship between C_t and t whose intercept is C_e, free lime.

9.2.3 Porosity

Porosity, n, is defined as the fraction of the total volume that is air and evaporable water. Because in using lime treated soils in construction attempts are made to exclude water and the fact that rate of loading of such structures is so slow that there is no pore water pressure build up, the inclusion of evaporable water in the definition of porosity is not unreasonable. Hence porosity as defined is used as a measure of voids in red tropical soil-lime systems studied in this work. Total porosity will therefore be calculated using the dry densities of the soil-lime systems.

Many investigators have either directly or indirectly related the strength of hardened cement pastes to porosity. Powers and Brownyard (95) found that:

$$S = 827.4 \frac{V_m}{W_o} - 24.8 \quad \ldots \quad \ldots \quad \ldots \quad (9.9)$$

where S = strength of hardened paste

V_m = the constant in the BET surface area equation.

V_m is proportional to the surface area of the cement gel which in turn is proportional to the amount of cement gel. W_o is the original water content after bleeding.

Schiller (96) after studying the strength of highly brittle materials found that

$$P = k \log \frac{e_k}{e} \quad \ldots \quad \ldots \quad \ldots \quad (9.10)$$

where e_k = critical porosity for which the strength, $P = 0$

k = coefficient independent of overall porosity but dependent on pore shape and nature of crystal contacts.

The definition of k in Schiller's equation suggests that strength of highly brittle materials do not depend on the overall porosity but on pore structure.

Recently, Hoff (116) showed that for cellular concrete,

$$\sigma = \sigma_o(1 - n)^b \quad \ldots \quad \ldots \quad \ldots \quad (9.11)$$

where σ = strength

σ_o = theoretical strength at zero porosity

n = overall porosity

b = a power exponent.

He was able to determine σ_o and b for cellular concretes made using only Portland cement, water and preformed foam which provided the air contents.

Most relationships between strength and volume of voids can be written in the form of equation 9.11. If a relationship similar to that expressed by equation 9.11 can be found for red tropical soil-lime systems, it would then be possible to relate a desired design strength to the porosity of the systems which in turn is a function of the moisture content of compaction, soil-lime density and specific gravity of the soil particles. This would provide some freedom in the selection of a soil-lime design criteria for a particular requirement.

9.3 Thermogravimetry

9.3.1 Introduction

Thermal analysis is a technique which determines some parameter of a system or material as a function of temperature. This implies that the system or material must be reactive to heat and that such a reaction should be measurable. The property of the material used as a measure of the reaction classifies the different methods of thermal analysis.

Such properties of the material measured in thermal investigations have been described by Mackenzie (117). They include:

a) Mass changes usually measured in thermogravimetry (TG), derivative thermogravimetry (DTG), isobaric and isothermal weight curves.

b) Energy changes usually measured in differential thermal analysis (DTA), differential scanning calorimetry (DSC) and heating curves.

c) Dimensional changes

d) Mechanical changes

e) Electrical changes

f) Magnetic changes

g) Optical changes

h) Emitted sound

i) Evolved volatiles.

The measurements can be carried out under static, quasistatic or dynamic temperature conditions depending on how the temperature of the heat source changes with time.

The most widely used techniques applied for the analysis of soils are thermogravimetry (including derivative thermogravimetry) and differential thermal analysis. The former is considered in more details.

9.3.2 Basic principles

When a material is heated from room temperature to 1000 - 1500°C, reactions occur which can lead to either a weight loss or a weight gain. Such changes can be made to take place either in air or in a chosen environment. Thermogravimetry allows to constantly measure such changes in weight as a function of time or temperature.

Some of the important changes that take place when a soil or clay is heated are (39, 118):

a) Dehydration: Water lost from a heated soil sample can be:
  (i) Pore water: this is normally held in the pores and is usually lost at about 105°C.
  (ii) Adsorbed water: this is water adsorbed by the surfaces of the clay or other minerals in the soil due to hydrogen bonding between the clay minerals and water molecules. It is lost at up to 240°C and is a reversible process.
  (iii) Hydroxyl water: this water is lost when the OH ions in the crystal lattice of a mineral are disrupted and

transformed to H_2O. This results in a complete destruction of the mineral structure.

b) Decomposition: carbonate materials in the soils decompose at characteristic temperatures to give off carbon dioxide.

c) Oxidation and reduction: some components of a soil can be made to oxidise or reduce in a controlled atmosphere.

The temperature ranges at which some of the changes can take place are characteristic of minerals undergoing the changes. The temperature at which the event is maximum is used to identify and possibly quantify the mineral. Thus the use of this technique in soil analysis requires an arrangement to measure the weight changes. This is provided by the thermobalance.

9.3.3 Instrument design

A thermobalance has three essential components: the balance, the thermal and recording components (118). The balance component makes use of the same weighing arrangements as are used in a laboratory balance. The change in weight can be measured either by deviation (deflection balances) or by the value of the restoring force required to return to the original null-position (compensation or null-point balances). More often than not, it is the thermal resistance of the sample holder which limits the temperature of thermogravimetric measurements (88). Temperature regulation can be effected either by heating at a constant rate or according to a definite thermal cycle. Electric ovens are usually used for high temperatures with the heating elements made of nichrome resistor or platinum or alloy of platinum or graphite; the type used depending on the desired maximum temperature. The recording component records the temperature and changes in weight.

The type of balance and method of temperature regulation influences the type or types of recorders to be used.

Modern thermobalances have facilities for working either under vacuum or in a controlled atmosphere. The gases evolved during reaction may be collected and analysed. In some thermobalances, facilities also exist which permit simultaneous DTA and TG experiments on the same chart thereby offering a further picture to further clarify the thermal events that occur in the system studied.

Temperature measurements in TG are chiefly inluenced by the position of the collector, the crucible or the sample container and the material being studied (88). Such material properties as weight, thermal conductivity, heat of reaction, fineness, density and sintering can start a temperature gradient thereby disturbing temperature measurement. Measurement of weight changes are influenced by those factors which exert actions on the balance of the weighing devices. Such factors are gaseous buoyancy (a pressure function of temperature exerted on the weighing devices by the gaseous atmosphere) and convection. These factors that affect TG measurements must either be taken into account or suppressed in the instrument design.

9.3.4 Thermogravimetric analysis of soils and clays

One of the problems with chemical analysis of soils and clays is that the solvents employed are not strictly selective; hence in-situ methods of analysis such as x-ray diffraction and TG are potentially powerful. Not much attention has been given to the use of TG in qualitative and quantitative analysis of soils and clays in the past. Theoretically, any constituents of soils and clays that react thermally can be identified and possibly quantified. Such constituents are organic matter, hygroscopic or pore water, adsorbed water, clay minerals, calcium carbonate, lime, goethite and gibbsite.

Schnitzer et al (119) used the thermobalance to study a number of soils differing widely in origin and compositon. They were able to detect and in some cases quantify hygroscopic moisture, organic matter, inorganic carbonate and lattice water in clays. They pointed out the presence of hydrous oxides of iron and aluminium as possible sources of error in quantifying some of the other constituents of the soils. For example, it is difficult to quantify organic matter when goethite or gibbsite is present. Similarly allophanes and amorphous minerals will cause high values for hygroscopic moisture while the presence of kaolinite will interfere and cause absolute positive error of 1.5% in carbonate measurements.

Longuet (88) and Biffen (120) have used the thermobalance to determine free calcium hydroxide and calcium carbonate in a number of calcium silicate hydrates with a good accuracy. The systems or mixtures Biffen (120) studied were not complex because the thermal events associated with calcium hydroxide and calcium carbonate were fairly distinct thus eliminating the problem of overlaps. Quantitative interpretation of overlapping thermal events is not easy and to effectively utilise the full potentials of the TG, this problem calls for resolution.

9.4 Experimental methods

Under this sub-chapter, the methods chosen and used to quantitatively determine the carbonated and unreacted lime are described including the modifications made. The methods of calculation of the porosity and unreacted soil are also given. The thermobalance used is described and the experimental conditions stated. All lime treated samples used were vacuum dried for seven days.

9.4.1 Calcium carbonate

Calcium carbonate in the lime treated soils was determined by the gas volumetric method od Shapiro and Brannock (112). Carbonated lime was also determined by thermogravimetric analysis. The method of Shapiro and Brannock was slightly modified owing to availability of materials.

Shell Tellus 27 oil was used in place of motor oil S.A.E. No. 10. In calibrating the carbon dioxide tube, a one gram mixture of an untreated red tropical soil and varying amounts of calcium carbonate (analytical grade) was used because the National Bureau of Standards standard sample No. 79 was not available. 1:1 hydrochloric acid and 3% mecuric chloride were used. The other steps as outlined for the "calibration of the carbon dioxide tube" were unchanged.

9.4.2 Unreacted lime

The ASTM method for the determination of free lime in clinkers and cements, C114-77 (113) was tried for the measurement of unreacted lime in the soil-lime systems. This method was found to be unsatisfactory. The slight pink colour which is an indication of the end point of the titration was impossible to determine because of the red or reddish-yellow colour of the soils. Because of this, a method which provides for the titration of the clear filtrate of the solvent after lime has been solubilized in it was preferred. The solvent variation method (SVM) of Pressler et al (115) was therefore used. SVM was preferred to TVM because time was considered more essential than the volume of the solvent. The multiple extraction heating mantle with temperature regulating controls used for the extraction of the free lime in the lime-soil mixtures is shown in Plate 9.1. Along side the mantle in Plate 9.1 is the equipment used for vacuum filtration.

9.4.3 Porosity

The overall porosity, n, of each lime treated soil at a moisture content for maximum dry density and strength was calculated using its dry density and the specific gravity of the soil particles.

$$n = \left(1 - \frac{\gamma_d}{G_s}\right) \times 100 \qquad \ldots \quad \ldots \quad \ldots \qquad (9.12)$$

where γ_d = dry density

G_s = specific gravity of the soil particles

n = porosity in percentage.

No attempt was made to measure or determine the pore size distribution of each lime treated and compacted soil.

9.4.4 Unreacted soil

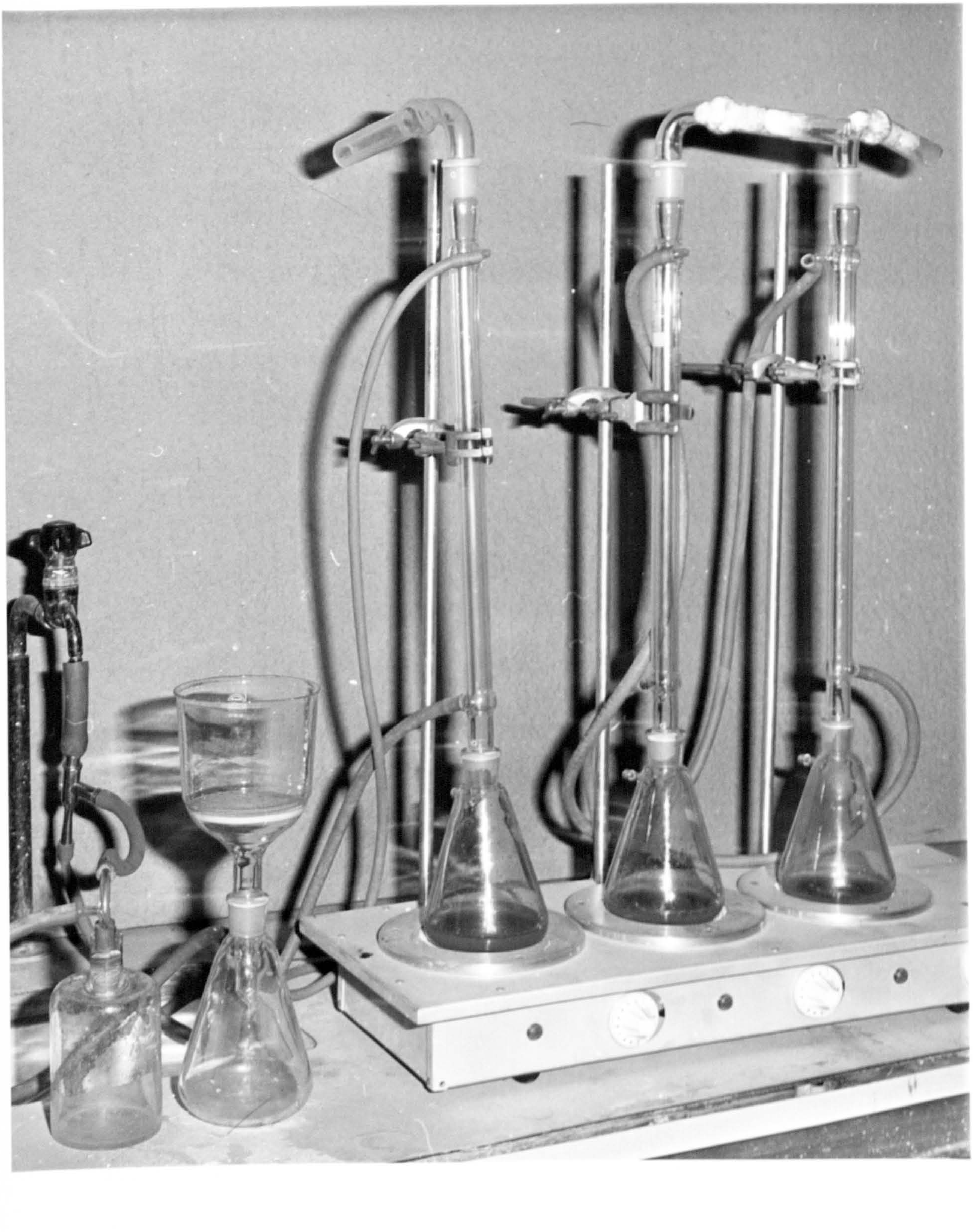
The unreacted soil was qualitatively assessed by TG and quantified by the difference between 100% and the sum of the volumes of reaction products, overall porosity, carbonated and unreacted lime.

9.4.5 Thermogravimetric analysis of lime treated red tropical soils

The TG analysis of the soil treated with lime for maximum strength was carried out using a Stanton TR 02 thermobalance to quantify carbonated and unreacted lime and to identify the

Plate 9.1

Apparatus used for the multiple extraction of unreacted lime. Alongside the heating mantle is the set up for vacuum filtration.



unreacted minerals in the soils.

The instrument is a beam form of the deflection type thermobalance consisting of a capacitance-follower plate which measures the beam movement and records the change in weight for a pre-determined beam movement (39). The furnance wall temperature, change in weight and time are simultaneously recorded on the same output. Three different linear heating rates are obtainable while temperature measurement is effected by a platinum rhodium-platinum thermocouple with the hot junction on the furnance wall. The furnance is a vertical 50 mm bore with nichrome bifilar windings capable of reaching a maximum temperature of 1000°C.

Samples were ground to pass B.S. sieve 75µm and heated in static air using silica crucibles. The calculated heating rate was 4°C/minute. 0.5 gm of the ground sample of each lime treated soil was used.

9.5 Results and discussion

9.5.1 Calcium carbonate by gas evolution

As can be seen from Table 9.1, the carbonated lime as obtained from gas evolution is in general lower than the values obtained from TG measurements. This may be due to the fact that despite the relative insolubility of carbon dioxide in oil when compared with the use of sodium chloride solution or water as the supernatant liquid in the carbon dioxide tube, some carbon dioxide evolved may have solubilized in oil. In using the method of Shapiro and Brannock (112), care must be taken to avoid foaming of the soil-acid solution while at the same time ensuring that the temperature is high enough to allow the decomposition of the carbonate by acid.

Table 9.1 Constituents of red tropical soil-lime systems other than cementitious reaction products

SOIL	LIME for max strength % (a)	S.G	Overall porosity % by vol.	UNREACTED LIME		CARBONATED LIME			$\frac{a-(b+c)}{a}$ %	UNREACTED SOIL % vol.
				% Wt. (b)	% vol.	GAS VOLUME % Wt.	T.G % Wt. (c)	T.G % vol.		
JPA	4.5	2.99	36.42	0.57	0.26	1.35	1.51	0.46	44.9	59.3
JPM	6.0	3.10	37.29	0.35	0.15	1.15	1.28	0.44	62.5	55.2
JPB	4.5	3.04	38.16	1.0	0.45	0.90	0.68	0.26	62.7	56.6
CT	4.5	2.94	35.24	1.05	0.47	1.35	1.81	1.06	46.7	61.4
AI	4.5	2.95	38.58	0.90	0.40	1.30	1.31	1.00	50.9	55.4
AII	4.5	3.09	42.14	0.87	0.39	1.25	1.14	0.92	55.3	52.0
SIA	4.5	2.95	34.98	1.85	0.83	1.45	1.60	1.59	23.3	61.6
SIB	6.0	2.92	33.22	1.70	0.76	2.20	2.31	1.42	33.3	61.0
SII	4.5	2.72	28.82	0.95	0.43	1.175	1.28	1.11	50.0	64.3
NF	4.5	3.05	35.54	0.45	0.20	1.675	1.85	1.10	48.9	59.5
JI	4.5	2.86	33.99	0.80	0.36	1.45	1.62	1.00	46.10	60.8
JII	6.0	3.16	35.25	1.10	0.49	1.80	1.21	0.72	44.80	60.5
TI	6.0	2.75	35.20	1.17	0.52	1.20	1.28	0.76	59.20	57.8
TII	6.0	2.82	39.04	0.55	0.25	2.20	2.42	0.79	50.50	56.0
RC	6.0	2.81	33.10	0.50	0.20	2.15	2.28	0.99	53.70	60.1
USM	4.5	2.69	36.43	0.70	0.31	1.95	1.68	1.00	47.1	60.0
SB	4.5	2.69	31.19	0.80	0.27	1.25	1.38	0.92	51.6	62.0
PH	4.5	2.80	36.54	0.40	0.18	1.70	1.82	1.08	50.70	58.8
SM	6.0	2.99	37.62	0.60	0.27	1.60	1.81	1.02	59.80	56.1

9.5.2 Unreacted lime by extraction

Figures 9.1 and 9.2 show the results of the extraction plotted according to equation 9.6. It can be seen that apart from possibly CT a solvent volume-soil weight ratio of 500 is usually sufficient to take all the unreacted lime into solution. Each point was obtained from the average of two titrations, the values of which were equal in most cases. The values of the intercepts i.e. the unreacted lime are given in Table 9.1. It can be seen that after about two years, more of the lime that has not reacted with the soil has carbonated than remain as free lime. Carbonation is a continuing process as long as there is unreacted or free lime and air in the pores.

Figure 9.3 shows the variation between strength and the reacted lime as a percentage of the amount of lime added. It can be seen from the figure that soils in which more of the added lime reacted have higher strengths. A similar relationship exists between lime reactivity and the amount of reacted lime as shown in Figure 9.4. These relationships are not linear but are similar to those found to exist between volume of reaction products and strength (Figure 6.5). This suggests that the percentage of lime reacted may be related to the volume of reaction products. This possibility was investigated by plotting the percentage of lime reacted V_S volume of reaction products. This is shown in Figure 9.5.

Using a stepwise multiple regression analysis (Statistical Package for Social Sciences, SPSS 5) a quantitative relationship between the strength, lime reactivity, activity index (each considered as a separate dependent variable) and the percentage

Fig. 9.1 Weight of lime Vs volume of solvent used in extraction

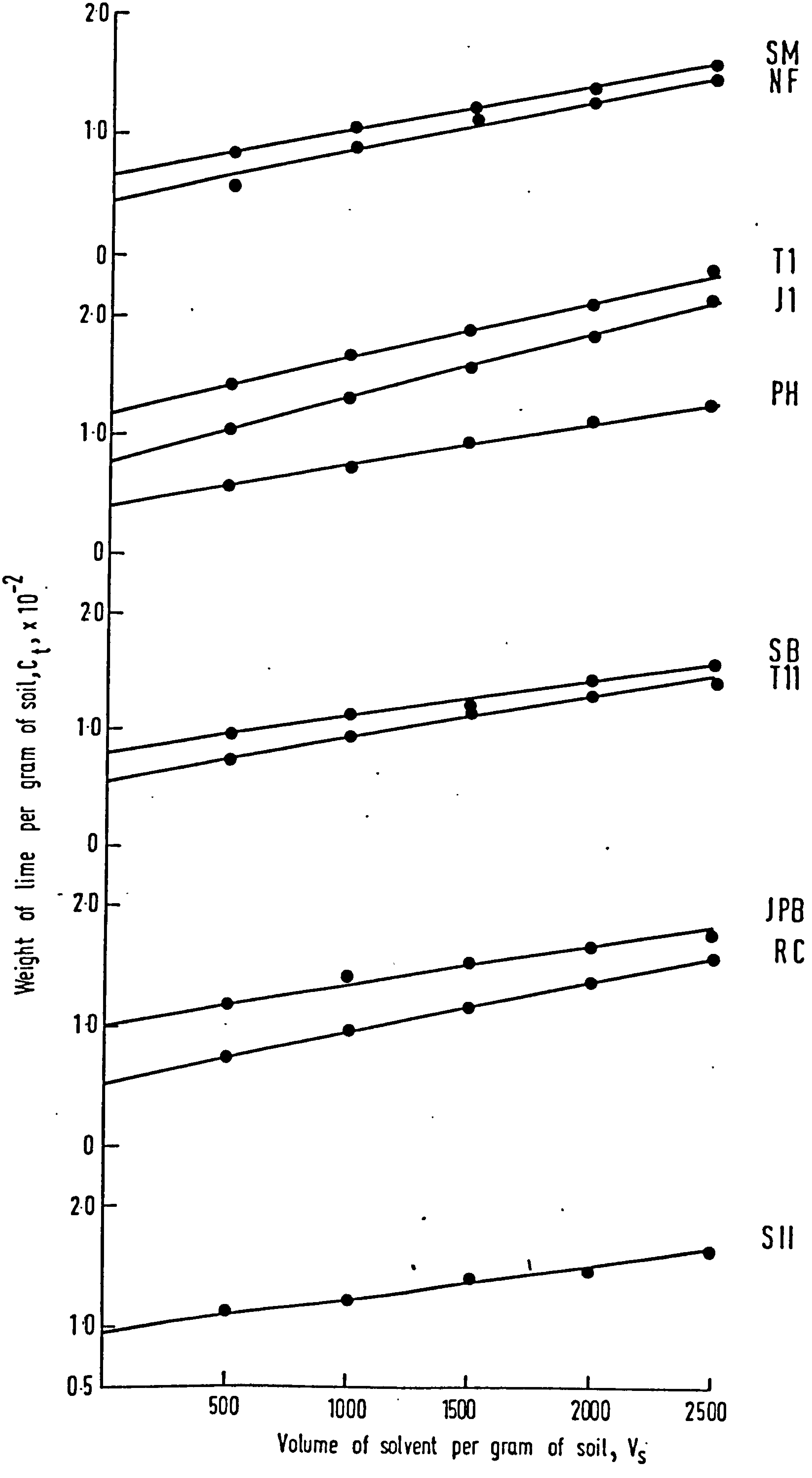

SM
NF
T1
J1
PH
SB
T11
JPB
RC
S11
2·0
1·0
0
0·5
500
1000
1500
2000
2500
Weight of lime per gram of soil, C_t, x 10^{-2}
Volume of solvent per gram of soil, V_s

Fig. 9.2 Weight of lime Vs volume of solvent used in extraction

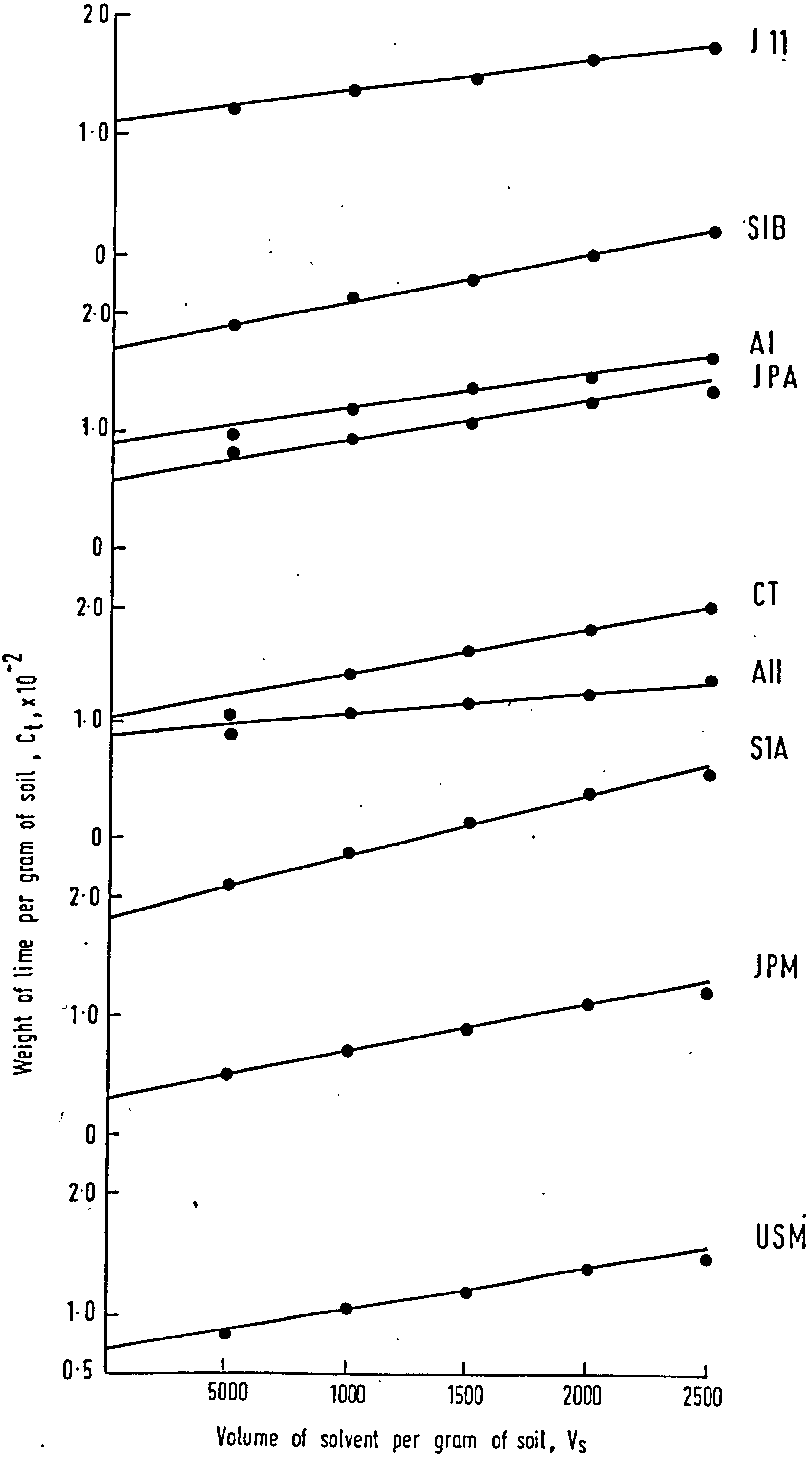
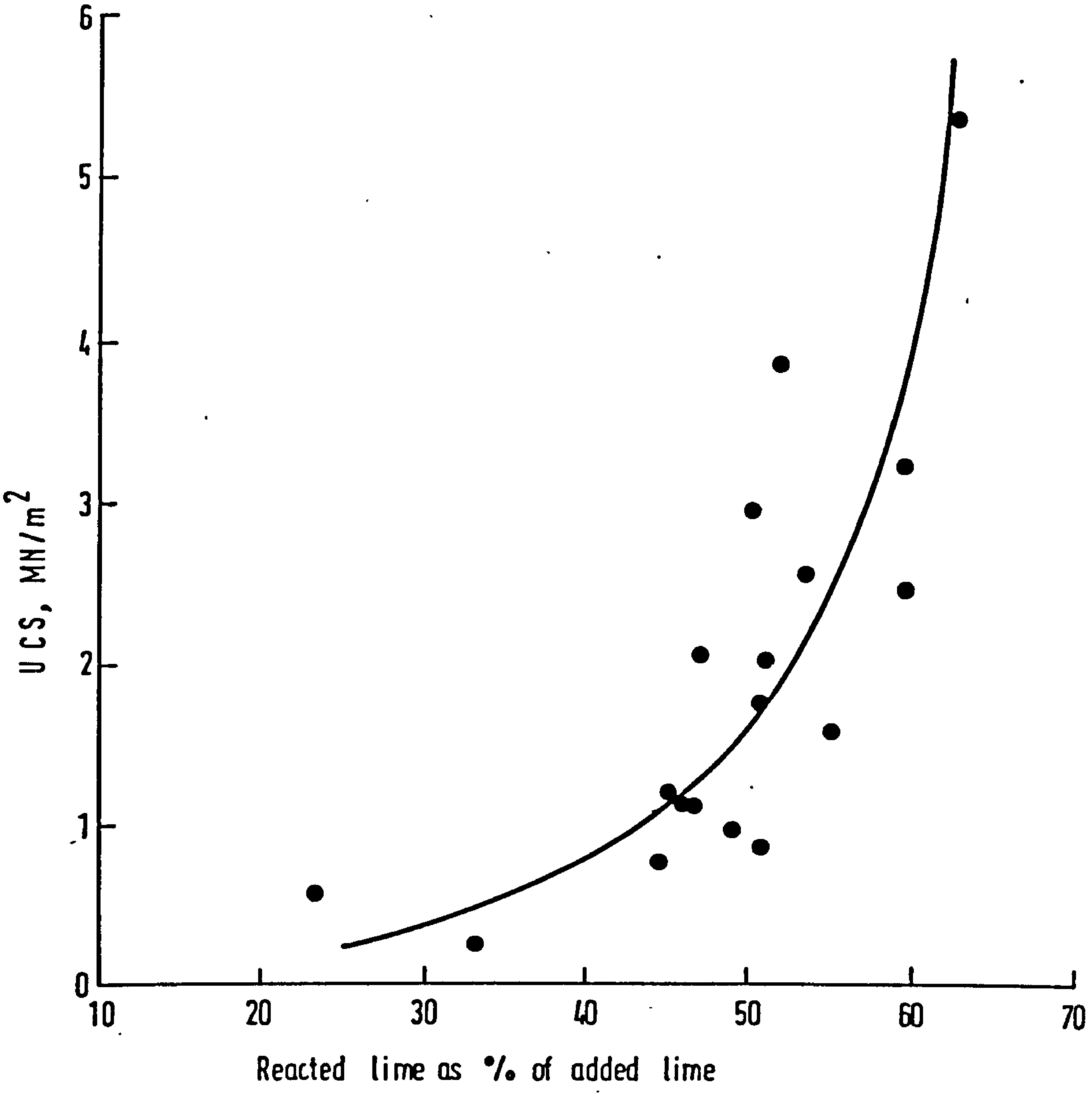

J 11
SIB
AI
JPA
CT
AII
S1A
JPM
USM
2·0
1·0
0
2·0
1·0
0
2·0
1·0
0
2·0
1·0
0
2·0
1·0
0·5
5000
1000
1500
2000
2500
Weight of lime per gram of soil, C_t, x 10^{-2}
Volume of solvent per gram of soil, V_s

Fig. 9.3 Relation between strength and reacted lime as % of added lime

Fig. 9.4 Relation between lime reactivity and reacted lime as % of added lime


U C S, MN/m^2
0
1
2
3
4
5
6
10
20
30
40
50
60
70
Reacted lime as % of added lime

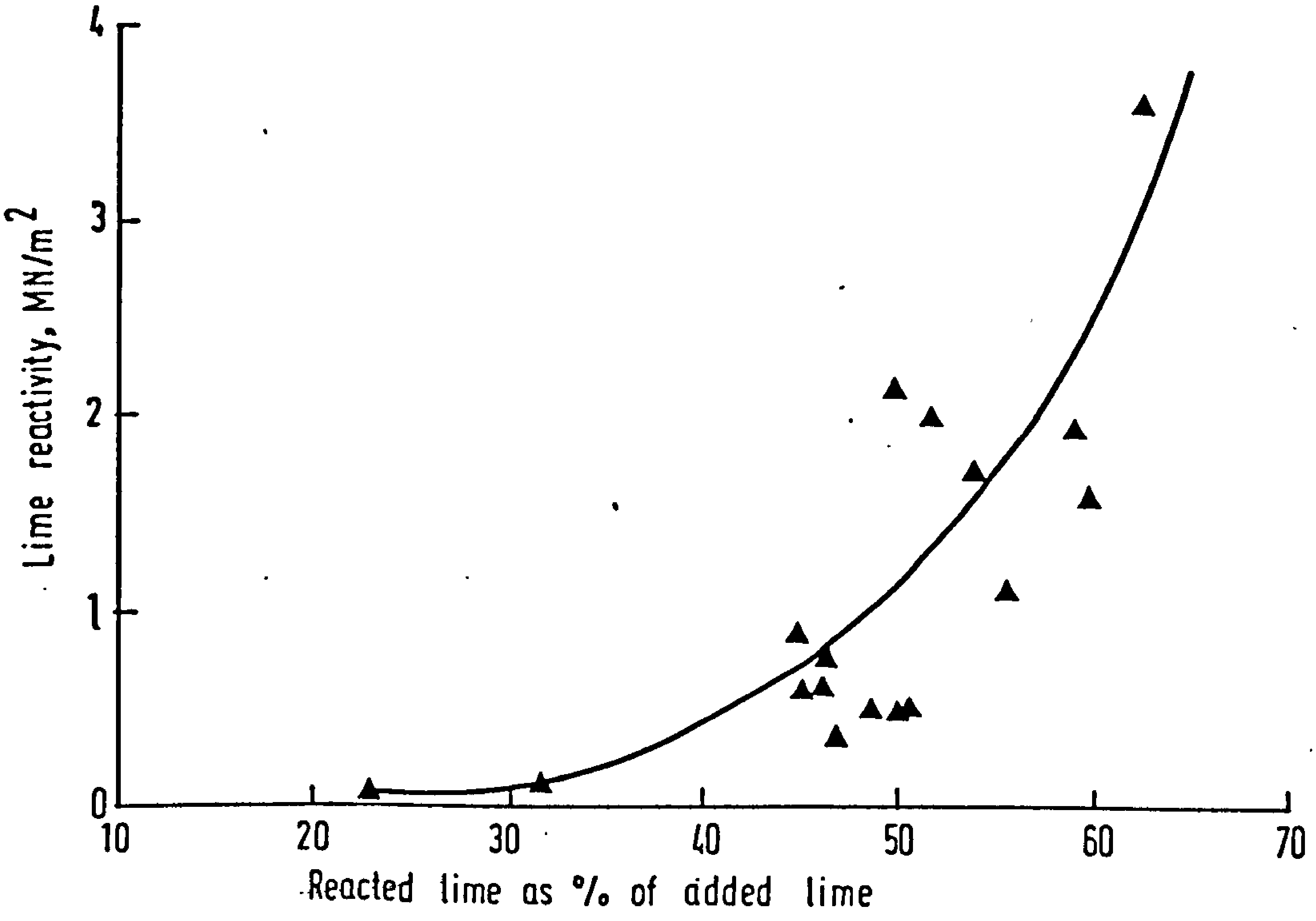
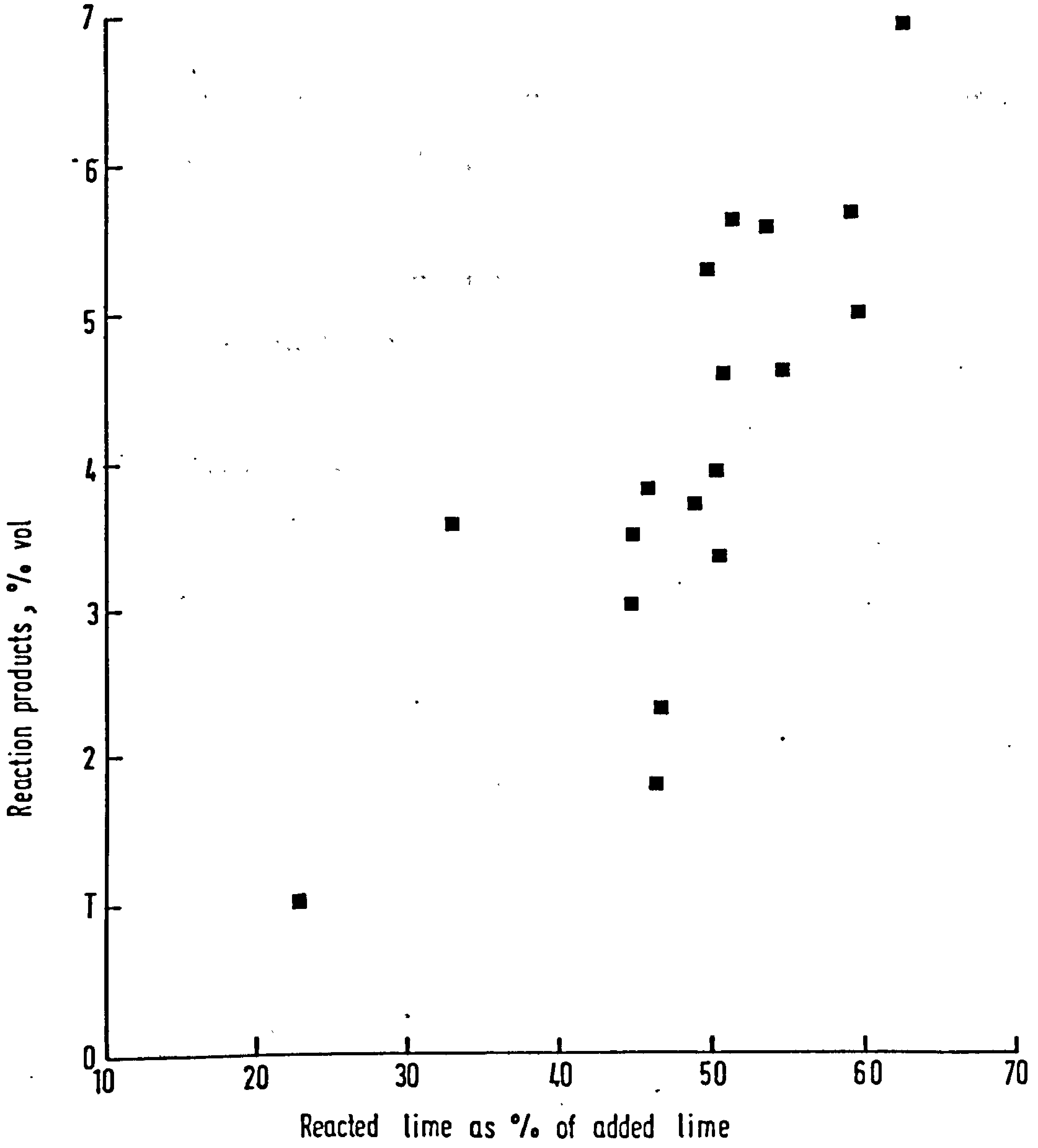

Lime reactivity, MN/m^2
0
1
2
3
4
10
20
30
40
50
60
70
Reacted lime as % of added lime

Fig. 9.5 Relation between volume of reaction products and reacted lime as % of added lime


Reaction products, % vol
0
1
2
3
4
5
6
7
10
20
30
40
50
60
70
Reacted lime as % of added lime

of reacted lime as the independent variable was investigated. The following equations and statistics were obtained for their lines of best fit:

a) Between strength and percentage of reacted lime:

$$S_t = -0.0013\,1^2 - 0.0394\,1 + 0.4885 \quad \ldots \quad (9.13)$$

multiple R = 0.572, confidence level = 32.7%, error of estimate = 1.149.

b) Between lime reactivity and percentage of reacted lime:

$$LR = 0.0014\,1^2 - 0.0663\,1 + 0.8295 \quad \ldots \quad (9.14)$$

multiple R = 0.6038, confidence level = 36.4%, error of estimate = 0.7818.

c) Between activity index and percentage of reacted lime:

$$A_i = 0.0003\,1^2 + 0.0237\,1 - 0.6064 \quad \ldots \quad (9.15)$$

multiple R = 0.385, confidence level = 15%, error of estimate = 1.196

where

S_t = total strength of the soil-lime system
1 = percentage of reacted lime
LR = lime reactivity
A_i = activity index

Equations 9.13, 9.14 and 9.15 are not significant. The poor correlation may be due to the fact that the percentage of lime reacted does not take into account the type of reaction products formed. This parameter has been shown to influence the strength of the soil-lime system and was considered in defining the activity index.

9.5.3 Unreacted soil

The relation between strength and volume of unreacted material in the lime treated soils is shown in Fig. 9.6. The sum of the volumes of pores, unreacted lime and carbonated lime in each specimen is denoted by t. Where a figure is written beside a point, this represents the value of t applicable to that point. This is written beside those points whose t do not lie within the ranges indicated by either of the three lines.

When t is kept 'constant' (varying within a certain limit e.g. t = 39.47 ± 0.60 or 36.40 ± 1.0 or 31.47 ± 1.11), the strength decreases with increasing volume of unreacted material. This finding is similar to that reached by Jambor (63) for unreacted residues of pozzolanic admixtures who concluded that unreacted residues do not help the strength of the system. The relationships in Fig. 9.6 can be explained by the fact that increase in the volume of the unreacted soil (when the volume of other phases is 'constant') is accompanied by a reduction in the volume of the reaction products. This shows that when only the unreacted soil and reaction products are allowed to vary in a red tropical soil-lime system, more strength is generated if more reaction products are produced than if less reaction products (resulting in more unreacted soil) are produced.

This explanation does not mean that unreacted soil is harmful to the system; rather it can be said that it is an inferior imparter of strength than the reaction products. Infact in practice, an amount of unreacted soil is indispensable in the system if a red tropical soil-lime mix is to satisfy other requirements other than strength. Ringsholt (121) writing on how to select samples of the most suitable red tropical soils for the production of "Latorex" (products of lime treated laterites) building elements noted that while the clayey "laterite" gives a high strength, it is difficult to pressure mould into blocks and can easily develop cracks. A well graded red tropical soil with adequate amount of clay seems ideal.

9.5.4 Porosity vs strength

Figure 9.7 shows a plot of overall porosity vs strength according to equation 9.11. No relationship of the form in equation 9.11 exists between the overall porosity of the systems and their strengths. Some other investigators (63) have found similarly for hardened lime pozzolana pastes. Rather, strength is found to be related to the pore structure which can be approximated by average pore size. The smaller the average pore size, the higher the strength of the system.

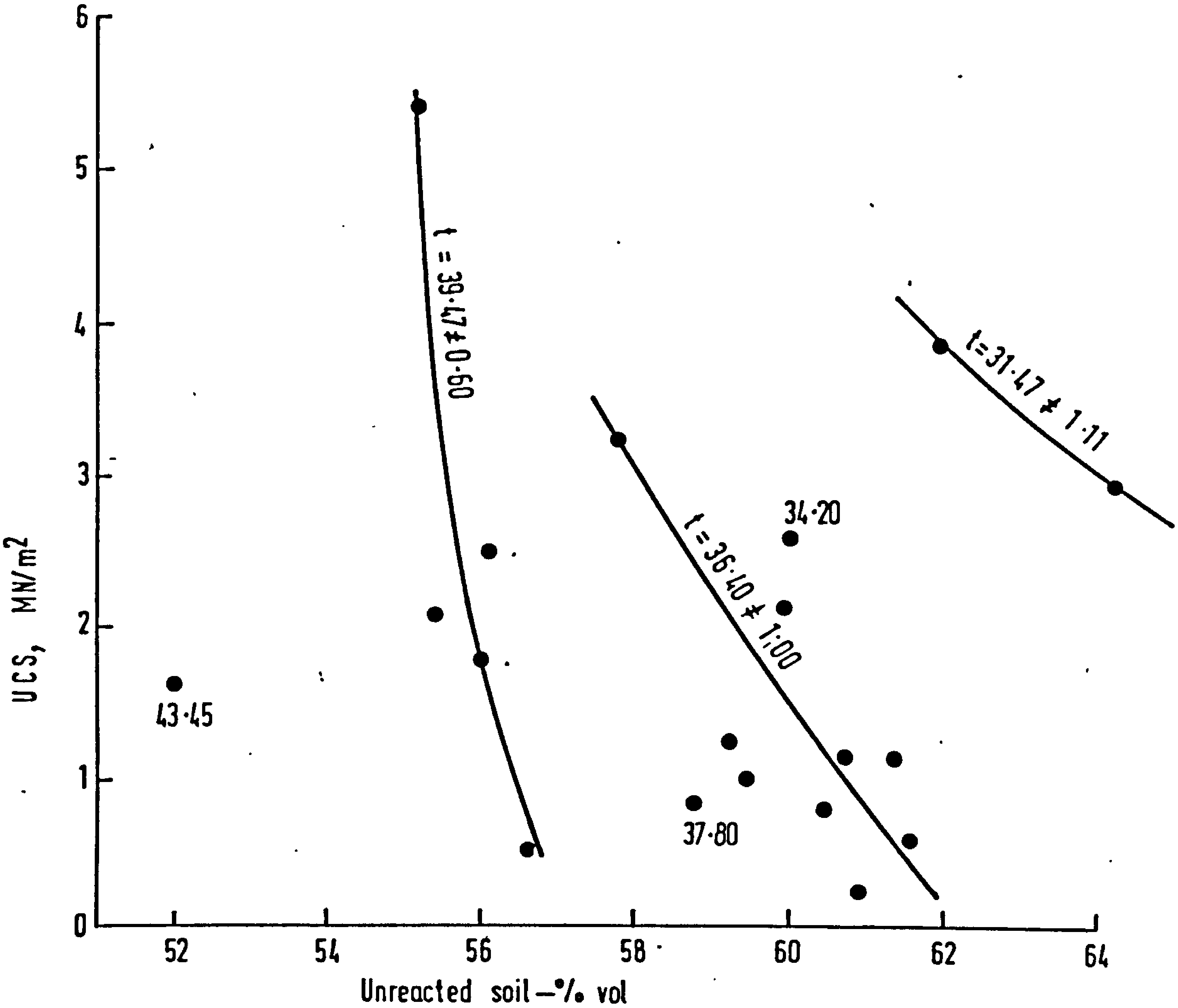
Pore size distributions and/or the average pore sizes of hardened lime-pozzolana pastes depend on the type and volume of the newly formed reaction products contained in the paste as well as on its overall porosity (63). Materials that contain the same type of reaction products have similar pore size distributions. The differences in their average pore sizes are more or less proportional to the volume of reaction products and overall porosity with the average pore size decreasing with increasing volume of reaction products. Pore size distribution differs with different types of reaction products, even when the soil-lime system contains the same volume of reaction products and total porosity.

9.5.5 Thermogravimetry and Derivative Thermogravimetry

Typical thermogravimetry (TG) and the derivative thermogravimetry (DTG) curves of the soils are shown in Figs. 9.8 and 9.9 for two of the soils. The TG and the DTG of the rest of the soils

Fig. 9.6 Relation between strength and volume of unreacted soil

Fig. 9.7 Relation between strength and overall porosity


6
5
4
3
2
1
0
UCS, MN/m²
52
54
56
58
60
62
64
Unreacted soil—% vol
t = 39·47 ± 0·60
t=36·40 ± 1·00
t=31·47 ± 1·11
34·20
43·45
37·80

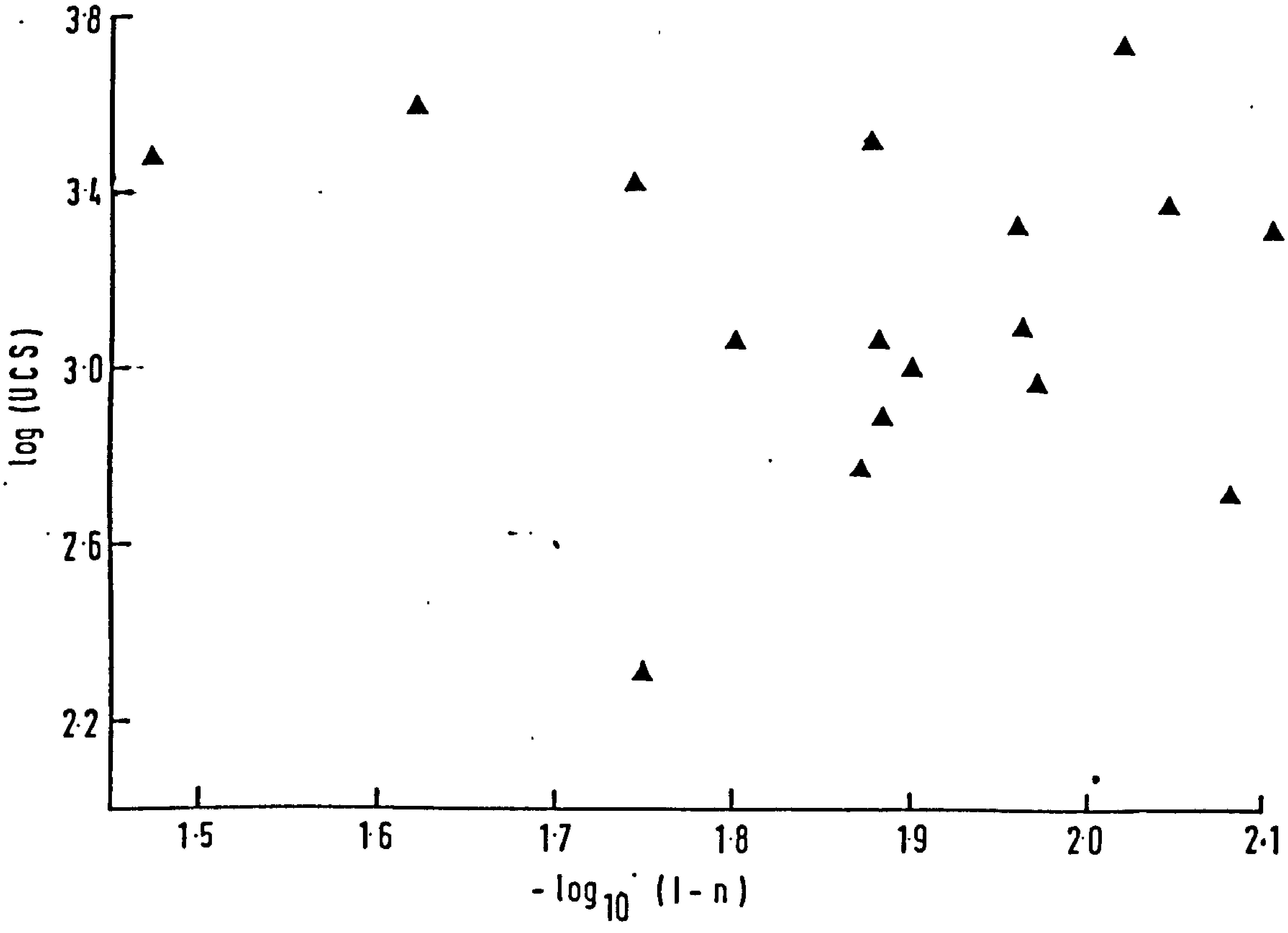
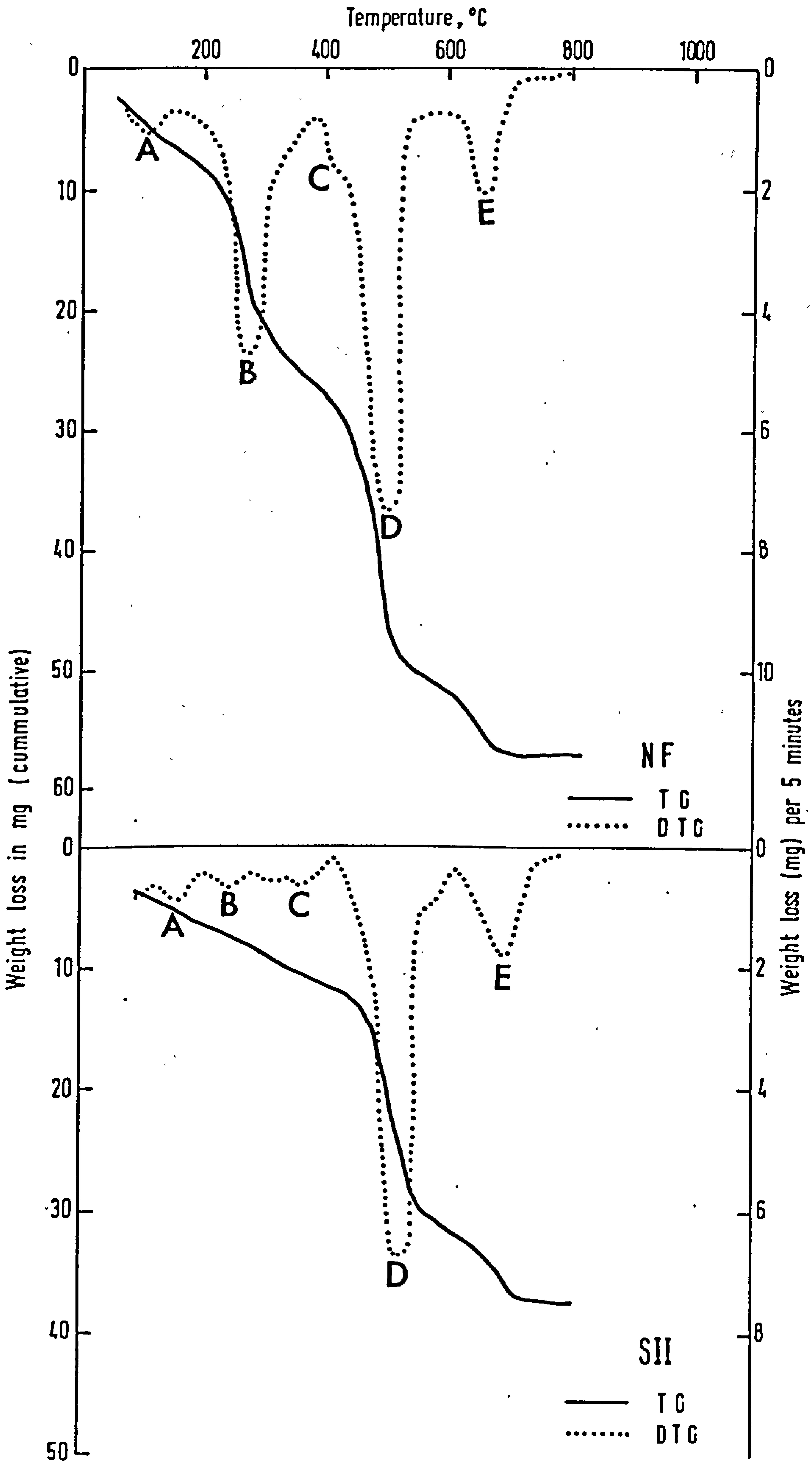

3·8
3·4
3·0
2·6
2·2
log (UCS)
1·5
1·6
1·7
1·8
1·9
2·0
2·1
- log₁₀ (1 - n)

Fig. 9.8 TG and DTG curves of lime treated soils

Fig. 9.9 TG and DTG curves of lime treated soils


Temperature, °C
200
400
600
800
1000
Weight loss in mg (cummulative)
Weight loss (mg) per 5 minutes
0
10
20
30
40
50
60
0
2
4
6
8
10
A
B
C
D
E
NF
T G
D T G
0
10
20
30
40
50
0
2
4
6
8
A
B
C
D
E
SII
T G
D T G

are presented in Appendix B.6.

The TG curves were obtained by plotting the cummulative weight loss vs temperature while the DTG curves were obtained from the TG curves by plotting weight changes in five minute intervals. The period of five minutes was chosen for convenience since a time marker pen incorporated in the recording mechanism marks off five-minute periods in the TG traces. This method of obtaining the DTG appears to be a simple and satisfactory way of obtaining a derivative curve from the TG result produced by a Stanton balance (39).

Five weight loss peaks numbered A to E are present in all the lime treated soils, although they are present in varying quantities.

Peak A occurs at 100° - 120°C. This is due to the loss of combined (hygroscopic and adsorbed) water in the specimen.

Peak B occurs at 280° - 320°C. The peaks give a dip on the TG curve. The possible thermal events taking place can be either the burning of organic matter contained in the soils or the dehydration of goethite or the structural water loss in gibbsite. The soils contain very little organic matter and not even traces of gibbsite, hence the latter event i.e. dehydration of goethite accounts for peak B. Goethite is dehydrated to form haematite. This event is more pronounced in some soils than in others showing that such soils contain more goethite than others even after the soils have been treated with lime.

Peak C occurs at 400° - 440°C and is due to the decomposition of the unreacted lime to give off water. The event appears as a small peak in the DTG of some samples while in others it is "swallowed" up by event D thereby conferring a skew on peak D. The decomposition temperature depends on the amount of lime present. Biffen (120) showed that for large samples of calcium hydroxide (1.223 gms) the range of the decomposition temperature is between 395° to 649°C while for small samples (0.104 gm) it is between 425° to 534°C. This suggests that the smaller the sample of calcium hydroxide, the less the range of decomposition temperature. The peak temperature and size of peak C shows that the unreacted lime in the soils are very small indeed. The use of decomposition peak temperature as a possible parameter for quantifying lime in complex systems as the ones considered in this study may be worthy of investigation.

The DTG curves in Figs. 9.8 and 9.9 and the temperature ranges quoted by Biffen (120) show that the decomposition of lime is overlapped by the thermal event having peak D in the samples. This is confirmed by the fact that at the temperatures where peaks C occur in the DTG, no dips can be observed in the TG curves. This is unlike peaks A, B, D, E which show dips in the TG curves where they occur. Biffen (120) also showed that the water of hydration driven off calcium silicates comes off very slowly in the region where calcium hydroxide would give off water. When lime occurs in presence of calcium silicate hydrate, the dip on the TG curve due to the presence of lime could readily be observed. By taking the vertical distance from the point at which the straight-line curve (of the TG) due to the evolution of the combined water from the calcium silicate hydrates starts to change to the point where the straight line resumed and calculating the calcium hydroxide from the loss in weight of water equivalent to this vertical distance, he obtained a good estimate of the amount of calcium hydroxide in all cases. The estimation of calcium hydroxide in the samples studied from the TG curve was not carried out because the small quantities involved are overlapped by peak D.

Peak D occurs at 480° - 500°C and is due to the dehydroxyllation of the unreacted kaolinite. The curves show that the unreacted kaolinite vary in quantity from sample to sample.

Peak E which occurs at 670° - 700°C is due to the decomposition of the carbonated lime in the samples. A greater part of this event is not overlapped. This is subtantiated by the dip it produces in the TG curve. The carbonated lime in each sample was calculated by converting the weight of carbon dioxide given off to equivalent weight of calcium hydroxide. This was done by multiplying the weight of carbon dioxide by 1.6818. The figure of 1.6818 was obtained from the stoichiometry of the reactions:

$$\underset{100}{CaCO_3} \;\underset{\equiv}{\rightarrow}\; CaO + \underset{44}{CO_2} \qquad \ldots \quad \ldots \quad \ldots \qquad (6.3)$$

$$\therefore\ y_{mg} \text{ of } CO_2 \text{ (from TG)} = \frac{100}{44}\, y\ CaCO_3$$

$$\underset{74}{Ca(OH)_2} + CO_2 \;\underset{\equiv}{\rightarrow}\; \underset{100}{CaCO_3} + H_2O \qquad \ldots \qquad (9.1)$$

$$\therefore\ \frac{100}{44}\, y\ CaCO_3 = \frac{74}{100} \cdot \frac{100}{44}\, y\ Ca(OH)_2 = \frac{74}{44}\, y\ Ca(OH)_2$$

$$\text{i.e. } y_{mg} \text{ of } CO_2 \text{ (from TG)} = 1.6818\ y\ Ca(OH)_2.$$

The measured values of the carbonated lime from the TG are shown in Table 9.1 and compare very well with values obtained by gas evolution method.

9.6 Chapter Summary

a) Carbonated lime measured by carbon dioxide evolution is usually less than that obtained by TG measurements in the soil-lime systems.

b) Because of the colour of red tropical soils, the ASTM method for determining free lime in Portland cement and clinkers cannot be applied to determine the unreacted lime in the soil-lime systems. On the other hand, the solvent variation method proposed by Presseler et al (115) can be used. In this method, a solvent volume - soil weight ratio of 500 is usually enough to extract all the unreacted lime.

c) The accumulation of unreacted soil at the expense of reaction products is not desirable for increase in strength. However, an amount of unreacted material is required to overcome cracking of the soil-lime to some extent and to give optimal working conditions in practice.

d) Strength does not depend on the overall porosity but probably depends on the microstructure of the soil-lime system. The microstructure can be represented by pore structure which in turn can be approximated by the average pore size. The average pore size depends on the type and volume of the reaction products.

e) The unreacted material consists of goethite, kaolinite, quartz and haematite. Quartz and haematite do not show on the TG which offers a potential in quantifying the unreacted kaolinite and goethite.

f) Unreacted lime is difficult to quantify from TG results because it is overlapped by the dehydroxylation of kaolinite whereas carbonated lime can be quantified with reasonable accuracy.

CHAPTER 10

CONCLUSIONS

The following general conclusions regarding the reactions that take place, the reaction products formed and their influences on strength of red tropical soil-lime systems emerge by collectively considering the Chapter summaries.

When lime is mixed with the soils in presence of water, rapid initial reaction takes place between the non-crystalline constituents of the soils and lime. This reaction which could be responsible for amelioration is followed by a slower reaction between lime and the crystalline and non crystalline clay minerals; the less crystalline the clay, the more likely it is to react. In totality, the reaction is mainly a diffusion controlled process and most of the reaction takes place within seven days. Depending on the nature of the amorphous constituents of the soil, the rapid and slower reactions produce cementitious reaction products of various types and the strength of the soil-lime system is increased with increasing crystallinity of the reaction products. The cementing abilities of the reaction products are sensitive to varying degrees to ionic substitution within the lattice of the reaction products. Strengths of the systems depend mainly on the type and volume of the reaction products. A well graded red tropical soil with excess of fines seems to be ideal for lime treatment.

In addition to the broad conclusions given above, the following specific conclusions drawn from the evidences presented in this thesis are given in detail:

1. Red tropical soils are pozzolanas and hence react with lime. Their activity is associated mainly with their clay size fraction.
2. Most of the reactions that take place occur during the initial period of five to seven days. This implies that most of the reaction products are generated within this period; therefore the gain in strength beyond this period is due mostly to the increased degree of crystallinity of the reaction products formed during the initial five to seven days period. In practice therefore, new methods of curing which accelerate the crystallinity of the reaction products are required to bring about rapid strength in the soil-lime systems.
3. While some components of the clay size fraction could react through dissolution of the minerals, the mechanism of reaction between the soils and lime is mainly a diffusion controlled process which can be expressed by Jander's diffusion equation for solid state reactions. The reactions could be multiple i.e. where more than one mineral in the clay size fraction react with lime to form two or more different, distinct products or consecutive, in which case one reaction product initially formed changes from one form to the other.
4. Based on the quantity of the active components and the rate constant of reaction obtained from Jander's equation, an activity index which is statistically related to the unconfined compressive strengths of lime treated soils can be obtained. A highly significant statistical linear correlation

links the empirical reactivity parameter of Thompson and the activity index. This finding is of significance since it allows the use of either of the two values for assessing the pozzolanic properties of red tropical soils. The advantages of the activity index are that it is a parameter based on a theoretical model and it can be obtained faster than the reactivity value which requires not only time but great input of labour.

5. The cementitious reaction products formed by the reactions vary from calcium silicates of the tobermorite-like type through calcium alumino-silicates to calcium alumino-ferri-silicates.
6. X-ray diffraction is a suitable technique for identifying the reaction products. Identification is greatly aided by the use of a semi-automated computer search program which helps in eliminating the many closely related calcium silicates, alumino-silicates and alumino-ferri-silicates that can be formed when the soils are treated with lime.
7. Iron substitutes into the lattice of the silicates and alumino-silicates. The strengths of the silicate forming soils are more sensitive to ionic substitution than those of the soils that form alumino-silicates especially at small volumes of the reaction products. This results in the calcium alumino-silicates and alumino-ferri-silicates imparting more strength than calcium silicates at low volumes.
8. The strengths depend on the type and volume of the reaction products. Where silicates and alumino-silicates are formed,

the strength can be expressed as a cubic polynomial of the volume of reaction products whereas a quadratic relation gives the best fit for strength vs volume of reaction products for alumino-ferri-silicate forming soils.

9. While some of the reaction products have discrete morphology after about two years curing at 22°C, others still remain in amorphous states.
10. Electron microscopy study shows that the calcium silicate hydrates formed by some of the soils have dense and close textured massive structures while the alumino-silicates and alumino-ferri-silicates usually occur with relatively large voids in the microstructure.
11. Thermogravimetry offers a quick, simple and neat method for the determination of carbonated lime in the systems while unreacted lime can be accurately determined by extraction methods that provide for the analysis of clear filtrates.
12. Increase in the quantity of unreacted material at the expense of the reaction products is not desirable. On the other hand, an amount of unreacted material may be necessary for requirements other than high strength.
13. Unlike other cemented systems, strength is not directly related to overall porosity in the red tropical soil-lime systems studied.

CHAPTER 11

SUGGESTIONS FOR FUTURE RESEARCH

This thesis is a pioneer research in this field of red tropical soils and as such no attempt has been made to solve some of the problems which were identified and recognised during the study. Results obtained in this work can be improved upon if the problems are resolved. It is therefore suggested that investigations should be made into the following:-

1. The improvement of the activity index proposed in this work. This can be done by measuring the effect of the varying volume of reaction products with time on the determination of the rate constant of reaction. The reactions in the soil-lime system can be arrested at predetermined times using any suitable technique and the volume of the reaction product measured. Using these measurements and the corresponding fractions of lime reacted, the rate constant of reaction can be determined.
2. Any method that can overcome the use of standard minerals in quantifying the reaction products will be invaluable. The use of thermogravimetry in a controlled atmosphere is promising. This is worthy of investigation as it seems useful in quantification and identification of the reaction products.
3. The use of TG to determine the reacted and unreacted constituents of the soil. This should be investigated for it offers an indirect method of measuring some of the reactive

constituents in the clay size fraction. For example, if the reacted kaolinite can be determined from TG and the amount of calcium silicate and/or alumino silicate formed is quantified, it may be possible to quantify the amorphous silica and alumina. The advantages of such in-situ methods over selective extraction methods are obvious.

4. Separation of the overlapping peaks in the DTG. This will enable the quantification of unreacted lime in the soil-lime mixture thus offering an alternative method of measuring the fraction of lime reacted in order to determine the activity index.
5. The classification of the reaction products into different types should be improved. The groupings should contain those soils that form known quantities of specific reaction products or known fractions of the different phases in the mixture that forms a group. This will help to improve the strength - volume of reaction products relationships which will lead to better equations for forecasting purposes.
6. There is room for improving the semi-automated computer search program. The output can be improved to provide such information as the name and chemical formula of the ASTM standard minerals in the data base, an abstract showing the standard minerals with high "percentage of strong peaks present" in their descending order etc.
7. Porosimetric investigation of the soil-lime systems is recommended. This can be linked to strength and moisture content thus enabling more latitude in the soil-lime mix design using different criteria applicable for different uses of the soil-lime systems.

REFERENCES

1. Sivarajasingham, S., Alexander, L.T., Cady, J.G. and Cline, M.G. "Laterite", Advanced Agronomy, New York, Vol. 14, pp. 1 - 60, 1962.

2. Buchanan, F. "A journey from Madras through the countries of Mysore, Kanara and Malbar," Vol. 2, pp. 436 - 461, London, 1807.

3. Nanda, R.L. "Laterite as a highway construction material," Indian Road Congress Journal, Vol. 36, pp. 371 -389, 1975.

4. Townsend, F.C., Manke, P.G. and Parcher, J.V. "The influence of sesquioxides on lateritic soil properties," Highway Research Record, No. 374, pp. 80 -91, 1971.

5. Townsend, F.C., Manke, P.G. and Parcher, J.V. "Effect of remoulding on properties of lateritic soils," Highway Research Record, No. 284, 1969.

6. Bawa, K.S. "Laterite soils and their engineering characteristics," Journal Soil Mechanics and Foundation Division, A.S.C.E., Vol. 83, Nov. 1957.

7. McFarlane, M.J. Laterite and Landscape, London, Academic Press, 1977.

8. De Graft-Johnson. "Engineering Characteristics: General Report", 7th Int. Conf. S.M.F.E., Speciality Session on Engineering Properties of Lateritic Soils, Mexico, Vol. 1, pp. 1 - 43, 1969.

9. Lyon Associates, Inc. U.S.A. "Laterite and Lateritic Soils and Other Problem Soils of Africa; An Engineering Study for Agency for International Development," Report AID/CSd - 2164, June 1971.

10. Lyon Associates, Inc. U.S.A. "Laterite, Lateritic Soils and Expansive Soils of South America; An Engineering Study for Agency for International Development, 1977.

11. Faniran, A. "Maghemite in the Sydney duricrusts," American Mineralogist, Vol. 55, pp. 925 - 933, 1970.

12. Kitagawa, Y., Kyuma, K. and Kawaguchi, K. "Clay mineral composition of some volcanogenous soils in Indonesia and the Philippines," Soil Science and Plant Nutrition, Vol. 19, No. 3, pp. 147 - 159, 1973.

13. Yoshinaga, N. and Aomine, S. "Allophane in some ando soils," Soil Science and Plant Nutrition, Vol. 8, No. 2, pp. 6 - 13, 1962.

14. Yoshinaga, N. "Chemical composition and some thermal data of eighteen allophanes from ando soils and weathered pumices," Soil Science and Plant Nutrition, Vol. 12, No. 2, pp. 47 - 54, 1966.

15. Kitagawa, Y. "A short discussion on the chemical composition of allophanes based on the data of Yoshinaga in 1966," Soil Science and Plant Nutrition, Vol. 19, No. 4, pp. 321 - 324, 1973.

16. De Kimpe and Fripat, J.J. "Kaolinite crystallization from H-exchanged zeolites," American Mineralogist, Vol. 53, pp. 218, 1968.

17. Thomas, M.F. Focal Problems in Geography: Tropical Geomorphology, London, Macmillan Press, 1974.

18. De Graft-Johnson, J.W.S., Bhatia, H.S. and Yeboa, S.L. "Influence of geology and physical properties on strength characteristics of lateritic gravels for road pavements," Highway Research Record, No. 405, pp. 87 - 104, 1972.

19. Harder, H. "Clay mineral formation under lateritic weathering conditions," Clay Minerals, Vol. 12, pp. 281 - 287, 1977.

20. Martin, F.J. and Doyne, H.C. "1: Laterite and lateritic soils in Sierra Leone," Journal of Agricultrual Science, Vol 17, pp. 530 - 547, 1927.

21. Dury, G.H. 'Rational descriptive classification of duricrusts," Earth Science Journal, Vol. 3, No. 2, pp. 77 - 86, 1969.

22. D'Hoore, J.L. Soil Map of Africa and Explanatory Monograph, Communication for Technical Co-operation in Africa, Publication 93, 1964.

23. Moh, Z.C. and Mashar, F.M. "The effects of methods of preparation on the index properties of lateritic soils," Speciality Session on the Engineering Properties of Lateritic Soils, Proc. 7th Int. Conf. S.M.F.E., Mexico, Vol. 1, pp. 23 - 35, 1969.

24. Terzaghi, K. "Design and performance of the Sasumua dam," Proc. Institution of Civil Engineers, Vol. 9, pp. 369 - 394, 1958.

25. Clare, K.E. and O'Reilly, M.P. 'Road construction over tropical red clays," Conf. on Civil Engineering Problems Overseas: Institution of Civil Engineers, Paper No. 12, pp. 243 - 256, 1960.

26. Newill, D. "A laboratory investigation of two red clays from Kenya," Geotechnique, Vol. 11, No. 4, pp. 302 - 318, 1961.

27. Gidigasu, M.D. and Yeboa, S.L. "Significance of pretesting preparations in evaluating index properties of laterite materials," Highway Research Record, No. 405, pp. 105 - 114, 1972.

28. Wesley, L.D. "Some basic engineering properties of halloysite and allophane clays in Java, Indonesia," Geotechnique, Vol. 23, No. 4, pp. 471 - 494, 1973.

29. Gidigasu, M.D. "Parameters for classification of fine grained laterite soils of Ghana," Highway Research Record, No. 374, pp. 57 - 76, 1971.

30. Schofield, A.N. "Lime stabilization of nodular clayey pea-laterite in Nyasaland," Dept. of Science and Industrial Research (U.K.), Road Research Laboratory, Overseas Bulletin, No. 3, pp. 1 - 15, 1957.

31. Quinones, P.J. "Compaction characteristics of tropically weathered soils," Ph.D. thesis, University of Illonis, 1963.

32. Baldovin, G. "The shear strength of lateritic soils," Proc. Speciality Session on Engineering Properties of Lateritic Soils, 7th Int. Conf. S.M.F.E., Mexico, Vol. 1, pp. 129 - 142, 1969.

33. Sherwood, P.T. "The properties of cement stabilized materials," Road Research Laboratory, Report LR 205, 1968.

34. Fieldes, M. "Clay mineralogy of New Zealand Soils: 11 - Allophane and related colloidal materials," New Zealand Journal of Science and Technology, Vol. 37, pp. 337 - 350, 1955.

35. Matyas, E.L. "Some engineering properties of Sasumua Clay," Proceedings Speciality Session on the Engineering Properties of Lateritic Soils, 7th Int. Conf. S.M.F.E., Mexico, Vol. 1, 1969.

36. Hirashima, K.B. "Highway experience with thixotropic volcanic clay," Proceedings Highway Research Board, Washington, Vol. 28, pp. 481 - 496, 1948.

37. Novais-Ferreira, H. and Correia, J.A. "The hardness of lateritic concretions and its influence in the performance of soil mechanics tests," Proceedings 6th Int. Conf. S.M.F.E., Montreal, Vol. 1, pp. 82 - 86, 1965.

38. Brand, E.W. and Hongsnoi, M. "Effects of method of preparation on compaction and strength characteristics of lateritic soils," Proceedings Speciality Session on Engineering Properties of Lateritic Soils, 7th Int. Conf. S.M.F.E., Mexico, Vol. 1, 1969.

39. Malomo, S.S. "The nature and engineering properties of some red soils from N.E. Brazil," Ph.D. thesis, Dept. of Civil Engineering, Leeds University, 1977.

40. Diamond, S. and Kinter, E.B. 'Mechanisms of soil-lime stabilization: an interpretative review," Highway Research Record, No. 92, pp. 83 - 102, 1965.

41. Stocker, P.T. 'Diffusion and diffuse cementation in lime and cement stabilized clayey soils - summary of an interpretative review," Australia Road Research, Vol. 3, No. 9, p. 9, 1969.

42. Transportation and Road Research Board, "State of the art; Lime stabilization," Transportation Research Circular, No. 180, pp. 1 - 12, 1976.

43. Hilt, H.G. and Davidson, D.T. "Lime fixation in clayey soils," Highway Research Board, Bulletin No. 262, pp. 20 - 32, 1960.

44. Ho, C. and Handy, R.L. "Characteristics of lime retention by montmorrillonitic clays," Highway Research Record, No. 29, pp. 55 - 69, 1963.

45. Stocker, P.T. "Diffusion and diffuse cementation in lime and cement stabilized clayey soils," Australia Road Research Board, Special Report, No. 8, 1972.

46. Jackson, M.L. "Aluminium bonding in soils: a unifying principle in soil science," Soil Science Society of America, Vol. 27, p. 1, 1963.

47. Diamond, S and Kinter, E.B. "Adsorption of calcium hydroxide by montmorillonite and kaolinite," Journal of Colloid and Interface Science, Vol. 22, pp. 240 - 249, 1966.

48. Kelley, W.P. and Page, J.B. "Criteria for the identification of the constituents of soil colloids," Proceedings Soil Science Society of America, Vol. 7, pp. 175 - 181, 1943.

49. Tanada, T. "Certain properties of the inorganic colloid fraction of Hawaiian soils," Journal Soil Science, Vol. 2, pp. 83 - 96, 1951.

50. Krishna Murti, G.S.R., Sarma, V.A.K. and Rengasamy, P. "Amorphous ferri-alumino silicates in some tropical ferruginous soils," Clay Minerals, Vol. 11, pp. 137 - 145, 1976.

51. Fieldes, M., Swindale, L.D. and Richardson, J.P. 'Relation of colloidal hydrous oxides to the high cation exchange capacities of some tropical soils of the Crook Islands," Soil Science, Vol. 74, pp. 197 - 205, 1952.

52. Birrell, K.S. and Gradwell, M. "Ion-exchange in some soils containing amorphous mineral constituents," Journal of Soil Science, Vol. 7, No. 1, pp. 103 - 143, 1956.

53. Van Olphen, H. 'Meetings: Amorphous clay materials," Science, Vol. 171, pp. 91 - 92, 1971.

54. Aomine, S. and Jackson, M.L. "Allophane determination in ando soils by cation exchange capacity delta value," Soil Science Society of America, Proceedings, Vol. 23, pp. 210 - 214, 1959.

55. Diamond, S. "Rapid reaction of lime with hydrous alumina," Nature, Vol. 204, pp. 183, 1964.

56. De Carvalho, J.B.Q. "The soil properties affecting lime stabilization of tropical red soils from N.E. Brasil," Ph.D. thesis, Department of Civil Engineering, Leeds University, 1979.

57. Thompson, M.R. "Lime reactivity of Illinois soils," Proceedings American Society of Civil Engineers, S.M.F.E. Division, Paper SM 5 (4907), pp. 67 - 92, 1966.

58. Eades, J.L., Nicholas, F.P. Jr. and Grim, R.E. "Formation of new minerals with lime stabilization as proven by field experiments in Virginia," Highway Research Board, Bulletin No. 335, pp. 31 - 39, 1963.

59. Eades, J.L. and Grim, R.E. 'Reaction of hydrated lime with pure clay minerals in soil stabilization," Highway Research Board, Bulletin No. 262, pp. 51 - 63, 1960.

60. Marion, G.M., Hendricks, D.M., Dutt, G.R. and Fuller, W.H. "Aluminium and silica solubility in soils," Soil Science, Vol. 121, No. 2, pp. 76 - 85, 1976.

61. Willoughby, D.R., Gross, K.A., Ingles, O.G., Silva, S.R. and Spiers, V.M. "The identification of reaction products in alkali-stabilized clays by electron microscopy, x-ray and electron diffraction," Australia Road Research Board, Proceedings, Vol. 4, Part 2, Paper No. 430, pp. 1386 - 1407, 1968.

62. Barret, par P., Menetrier, B. and Cottin, B. "Study of silica-lime solution reaction," Cement and Concrete Research, Vol. 7, pp. 61 - 68, 1977.

63. Jambor, J. 'Relation between phase constitution, overall porosity and strength of hardened lime-pozzolana pastes," Magazine of Concrete Research, Vol. 15, No. 45, pp. 131 - 142, 1963.

64. Glenn, G.R. and Handy, R.L. "Lime-clay mineral reaction products," Highway Research Record, No. 29, pp. 70 - 82, 1963.

65. Ormsby, W.C. and Kinter, E.B. "Strength development and reaction products in lime-montmorillonite-water systems," Public Roads, Vol. 37, No. 4, pp. 136 - 148, 1973.

66. Diamond, S., White, J.L. and Dolch, W.L. "Transformation of clay minerals by calcium hydroxide attack," Proceedings 12th National Conference on Clay and Clay Minerals, Vol. 12, pp. 359 - 379, 1964.

67. Ruff, C.G. and Ho, C. "Time-temperature strength-reaction product relationships in lime-bentonite-water mixtures," Highway Research Record, Vol. 139, pp. 42 - 60, 1966.

68. Ariizumi, A., Maki, T. and Oba, M. "On stabilization of Kanto loam by means of lime gypsum admixtures," Annual Report of Roads, Japan Roads Association, Tokoyo, pp. 22 - 31, 1962.

69. Benton, E.J. "Cement-pozzolana reactions," Highway Research Board, Bulletin No. 239, pp. 56 - 65, 1960.

70. Harty, J.R. and Thompson, M.R. "Lime reactivity of tropical and sub tropical soils," Highway Research Record, No. 442, pp. 102 - 112, 1973.

71. British Standards Institution: BS 1377, Methods of Testing Soils for Civil Engineering Purposes, London, The Institution, 1975.

72. Jackson, M.L., Soil Chemical Analysis - Advanced Course, Published by author, Department of Soils, University of Wisconsin, Madison 6, pp. 233 - 237, 1956.

73. Cabrera, J.G. and De Carvalho, J.B.Q. "The crystallinity of kaolinite in red tropical soils," Presented for publication to Soil Science, 1979.

74. Fratini, N. "Lime content in cement mixtures: 11 evaluation of pozzolana cements," Annalytical Chemistry (Rome), Vol. 39, p. 41, 1949.

75. Rio, A. "Ion-exchange activity of natural pozzolanas," Annalytical Chemistry (Rome), Vol. 42, p. 526, 1952.

76. Mackenzie, J.D. and Banerjee, R.K. "Formation kinetics of Portland cement clinker phases: 1 - Tricalcium aluminate," Transcations and Journal of British Ceramic Society, Vol. 77, pp. 88 - 92, 1978.

77. Taylor, H.F.W. "Hydrate calcium silicates. Part 1-Compound formation at ordinary temperatures," Journal of Chemical Society, Vol. 726, pp. 3682 - 3690, 1950.

78. Greenberg, S.A. "Reaction between silica and calcium hydroxide solutions. 1, Kinetics in the temperature range 30^o to 85^oC," Journal of Physical Chemistry, Vol. 65i, pp. 12 - 16, 1961.

79. Raask, E. and Bhasker, M.C. "Pozzolanic activity of pulverised fuel ash," Cement and Concrete Research, Vol. 5, No. 4, pp. 363 - 376, 1975.

80. Jander, W. "Reactions in solid-state at high temperatures: 1, Rate of reaction for an endothermic reaction," Ceramic Abstracts, Vol. 7, No. 9, pp. 644, 1928.

81. Ginstling, A.M. and Brounshtein, B.I. "Concerning the diffusion kinetics of reaction in spherical particles," Journal Applied Chemistry, U.S.S.R., Vol. 23, pp. 1327 - 1338, 1950.

82. Carter, R.E. "Kinetic model for solid state reactions," Journal Chemical Physics, Vol. 34, No. 6, pp. 2010 - 2015, 1961.

83. Hansen, W.C. "Basic chemistry of reactions of aggregates in Portland cement concrete," Journal of Materials, Vol. 2, pp. 408 - 431, 1967.

84. Fripiat, J.J. "Surface properties of alumino-silicates," Proceedings 12th National Conference on Clays and Clay Minerals, pp. 327, 1964.

85. De Mumbrum, L.E. and Chester, G. "Isolation and characterization of some soil allphanes," Soil Science Society of America, Proceedings, pp. 355 - 359, 1964.

86. Clare, K.E. and Mohan, D. "An examination of five soils and an aggregate from Nigeria," Road Research Laboratory, Road Note, No. 882, 1947.

87. Lea, F.M. The Chemistry of Cement and Concrete, Revised Edition of Lea and Desch, Arnold, p. 569, 1970.

88. Longuet, P. "The use of thermogravimetric measurements in cement chemistry," Proceedings 5th International Symposium on the Chemistry of Cement, Tokyo, Part 1, 1968.

89. Steopoe, A. "Investigation concerning reactivity of Roumanian trasses in trass-lime and trass-cement mortars," International Association for Testing Materials, Zurich, Vol. 1, p. 918, 1931.

90. Gray, M.N. "Soil stabilization with lime and secondary chemical additives," Ph.D. thesis, Department of Civil Engineering, Leeds University, U.K., 1972.

91. Jambor, J. Institute of Construction and Architecture of the Slovak Academy of Sciences, Bratrslava, Czechoslovakia. In private communication, July 7, 1977.

92. Tuncer, E.R., Paulson, S.K., Demirel, T. and Lohnes, R.A. "A method for quantitative determination of soil minerals by x-ray diffraction," Transportation Research Record, Vol. 560, pp. 75 - 80, 1976.

93. Kalousek, G.L. and Prebus, A.F. "Crystal chemistry of hydrous calcium silicates III, morphology and other properties of tobermorite and related phases," Journal of the American Ceramics Society, Vol. 41, No. 4, pp. 124 - 133, 1958.

94. Powers, T.C. "Structure and physical properties of hardened Portland cement pastes," Journal of the American Ceramic Society, Vol. 41, No. 1, pp. 1 - 6, 1958.

95. Powers, T.C. and Brownyard, T.C. "Studies of the physical properties of hardened Portland cement paste," Journal of the American Concrete Institute, Proceedings, Vol. 18, Nos. 2 - 8, 1947.

96. Schiller, K. "Strength of highly brittle porous materials," Nature, Vol. 180, pp. 862 - 863, 1957.

97. Jambor, J. "Written discussion," Proceedings 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 111, pp. 541 - 557, 1968.

98. Alexander, K.M., Taplin, J.H. and Wardlaw, J. "Correlation of strength and hydration with composition of Portland cement," Proceedings 5th International Symposium on Chemistry of Cement, Tokyo, Vol. 111, pp. 152 -166, 1968.

99. Kalousek, G.L. "High temperature curing of concrete under high pressure," Proceedings 5th International Symposium on Chemistry of Cement, Tokyo, Vol. 111, pp. 523 - 540, 1968.

100. Diamond, S. "Tobermorite and tobermorite-like calcium silicate hydrates: their properties and relationships to clay minerals," Ph.D. thesis, Purdue University, Lafayette, 1963.

101. Diamond, S., White, J.L. and Dolch, W.L. "Effects of isomorphous substitution in hydrothermally synthesized tobermorite," The American Mineralogist, Vol. 51, pp. 388 - 401, 1966.

102. Copeland, L.E., Bordor, E., Chang, T.N. and Weise, C.H. "Reactions of tobermorite gel with aluminates, ferrites, and sulphates," Journal of Portland Cement Associations, Research and Development Laboratory, Vol. 9, pp. 61 - 67, 1967.

103. Taylor, H.F.W. The Chemistry of Cement Hydration, Progress in Ceramic Science, Pergamon Press, New York, Vol. 1, pp. 89 - 145, 1961.

104. Johnson, G.G. Jnr. and Vand, V. "A computerized powder diffraction identification system," Industrial and Engineering Chemistry, Vol. 59, No. 8, pp. 18 - 31, 1967.

105. Hughes, T.E. "Experience in the use of the ASTM diffraction search program," Lecture to the Crystallography Group of the Institute of Physics at the University of Hull, 6th April, 1972.

106. O'Connor, B.H. and Bagliani, F. "A semi-automated system for identifying crystalline materials with powder diffraction data," Journal of Applied Crystallography, Vol. 9, pp. 419 - 423, 1976.

107. Abo-El-Enein, S.A., Gabr, N.A. and Mikhail, R.Sh. 'Morphology and microstructure of autoclaved clinker and slag-lime pastes in presence and absence of silica sand," Cement and Concrete Research, Vol. 7, No. 3, pp. 231 - 238; No. 4, pp. 363 - 368, 1977.

108. Jambor, J. "Influence of phase composition of hardened binder pastes on its pore structure and strength," Proceedings of the International Symposium on Pore Structure and Properties of Materials, Prague, Part 11, pp. D75 - D96, 1973.

109. Rogers, D.E. and Aldridge, L.P. 'Hydrates of calcium ferrites and calcium alumino ferrites," Cement and Concrete Research, Vol. 7, No. 4, pp. 399 - 410, 1977.

110. Uchikawa, H. and Uchida, S. "The hydration of $11CaO . 7Al_2O_3 . CaF_2$ at 20^oC," Cement and Concrete Research, Vol. 2, No. 6, pp. 681 - 695, 1972.

111. Roy, D.M., Gouda, G.R. and Bobrowsky, A. 'Very high strength cement pastes prepared by hot pressing and other high pressure techniques," Cement and Concrete Research, Vol. 2, No. 3, pp. 349 - 366, 1972.

112. Shapiro, L. and Brannock, W.W. 'Rapid determination of carbon dioxide in silicate rocks," Analytical Chemistry, Vol. 27, No. 11, pp. 1796 - 1797, 1955.

113. American Society for Testing and Materials, Annual Book of ASTM Standards, Chemical analysis of hydraulic cement, ASTM C 114 - 77, "Free Calcium Oxide in Portland Cement and Clinker," ASTM part 13, pp. 110 - 112, 1977.

114. Pressler, E.E., Brunauer, S. and Kantro, D.L. "Investigation of the Franke method of determining free calcium hydroxide and free calcium oxide," Analytical Chemistry, Vol. 28, No. 5, pp. 896 - 902, 1956.

115. Pressler, E.E., Brunauer, S., Kantro, D.L. and Weise, C.H. 'Determination of the free calcium hydroxide contents of hydrated Portland cements and calcium silicates," Analytical Chemistry, Vol. 33, No. 7, pp. 877 - 882, 1961.

116. Hoff, G.C. "Porosity-strength considerations for cellular concrete," Cement and Concrete Research, Vol. 2, pp. 91 - 100, 1972.

117. Mackenzie, R.C. "Highways and byways in thermal analysis," Analyst, Vol. 99, pp. 900 - 912, 1974.

118. Wendlant, W.W. Thermal Methods of Analysis, 2nd Edition, J. Wiley, New York, 1974.

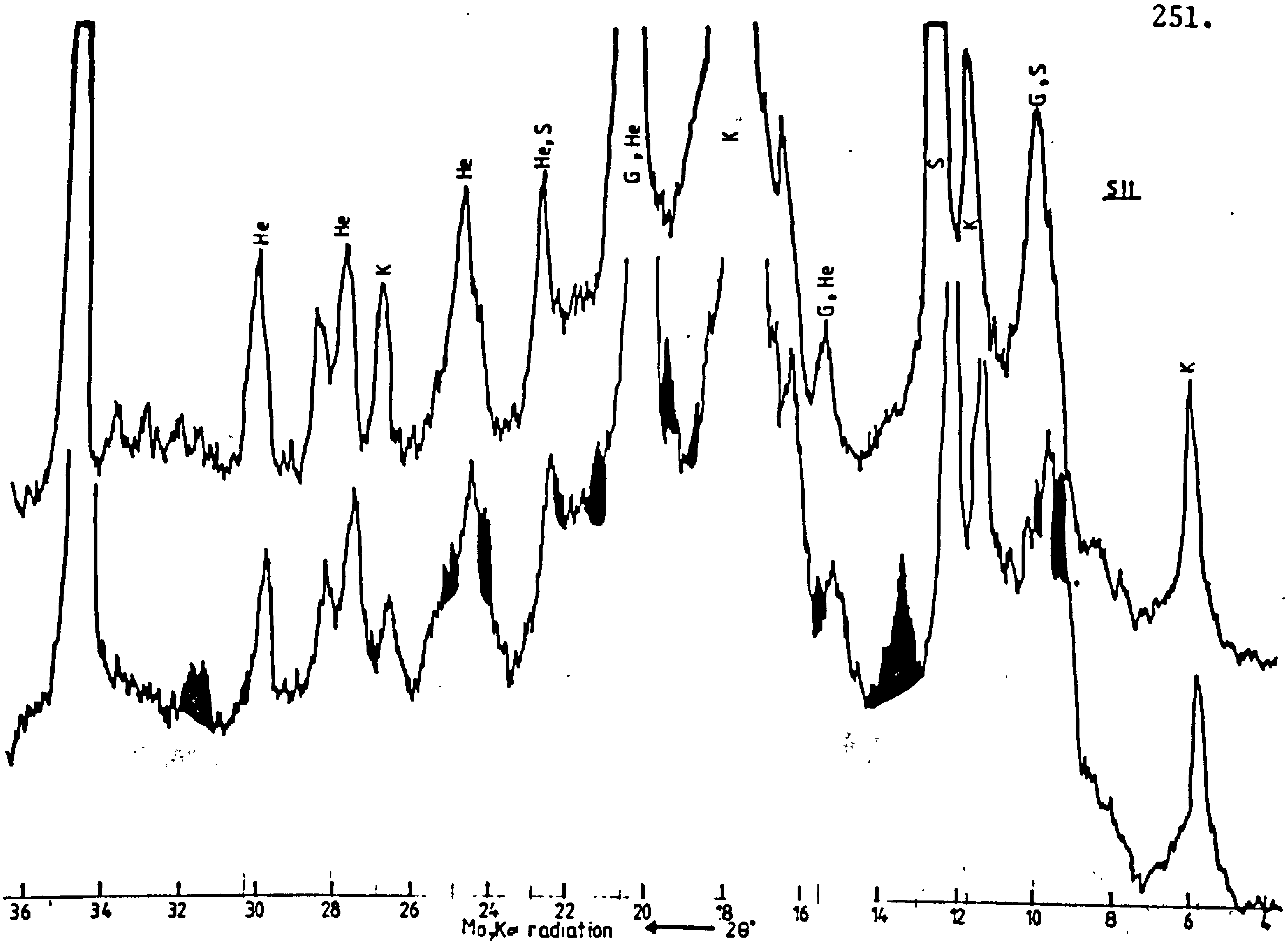
119. Schnitzer, M., Wright, J.R. and Hoffman, I. "Use of the thermobalance in the analysis of soils and clays," Analytical Chemistry, Vol. 31, No. 3, pp. 440 - 444, 1959.

120. Biffen, F.M. "Determination of free lime and carbonate in calcium silicate hydrates by thermobalance," Analytical Chemistry, Vol. 28, pp. 1133 - 1136, 1956.

121. Ringsholt, T. "Short guidance on the selection of suitable lateritic soils for production of LATOREX," Building Materials Laboratory - Technical Information, The Technical University of Denmark, 1975.

APPENDIX A 1

X-ray diffraction traces for some of the soils showing the lime treated and natural soils. Shaded areas represent positions of new peaks.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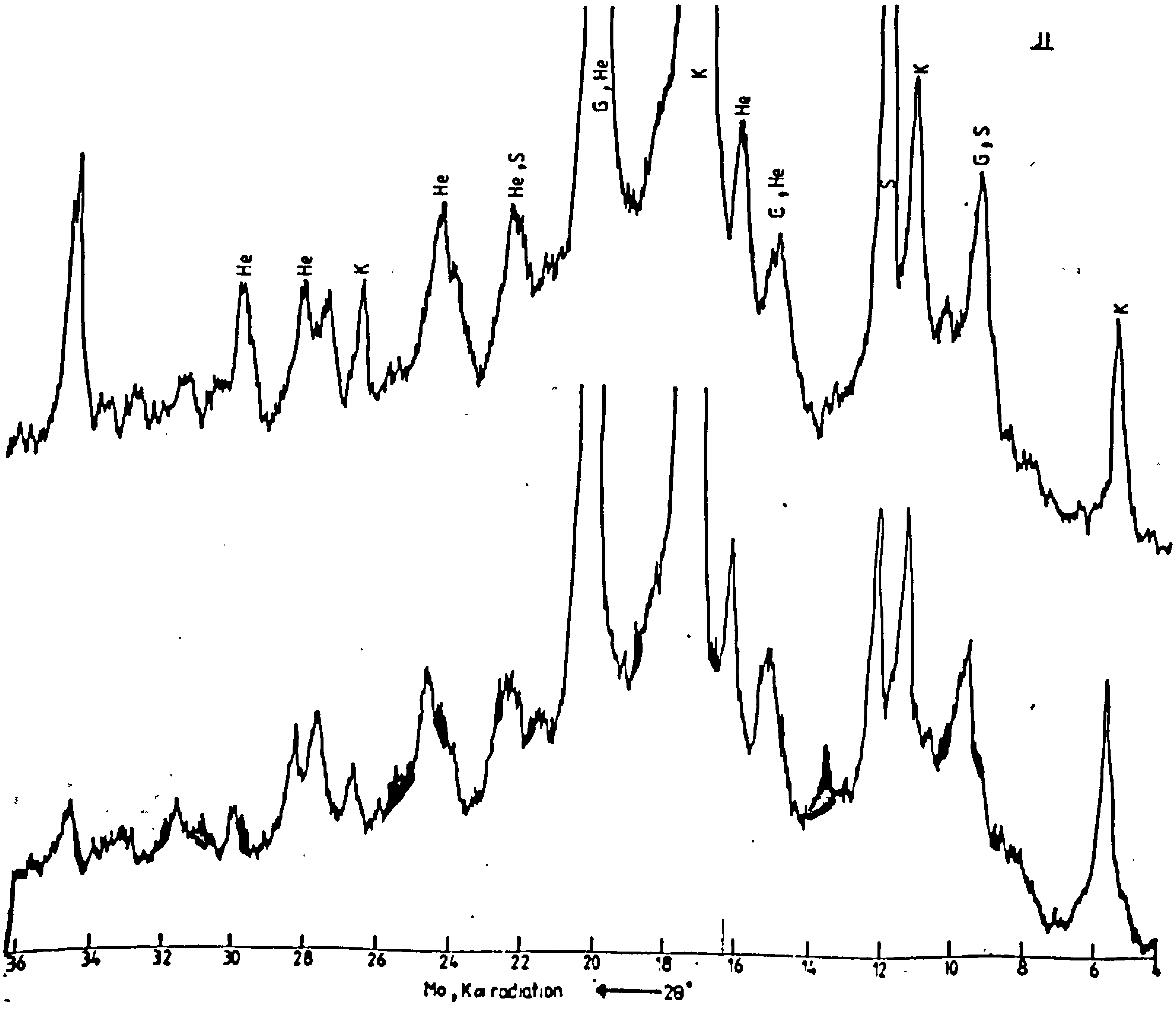
Mo,Kα radiation ← 2θ°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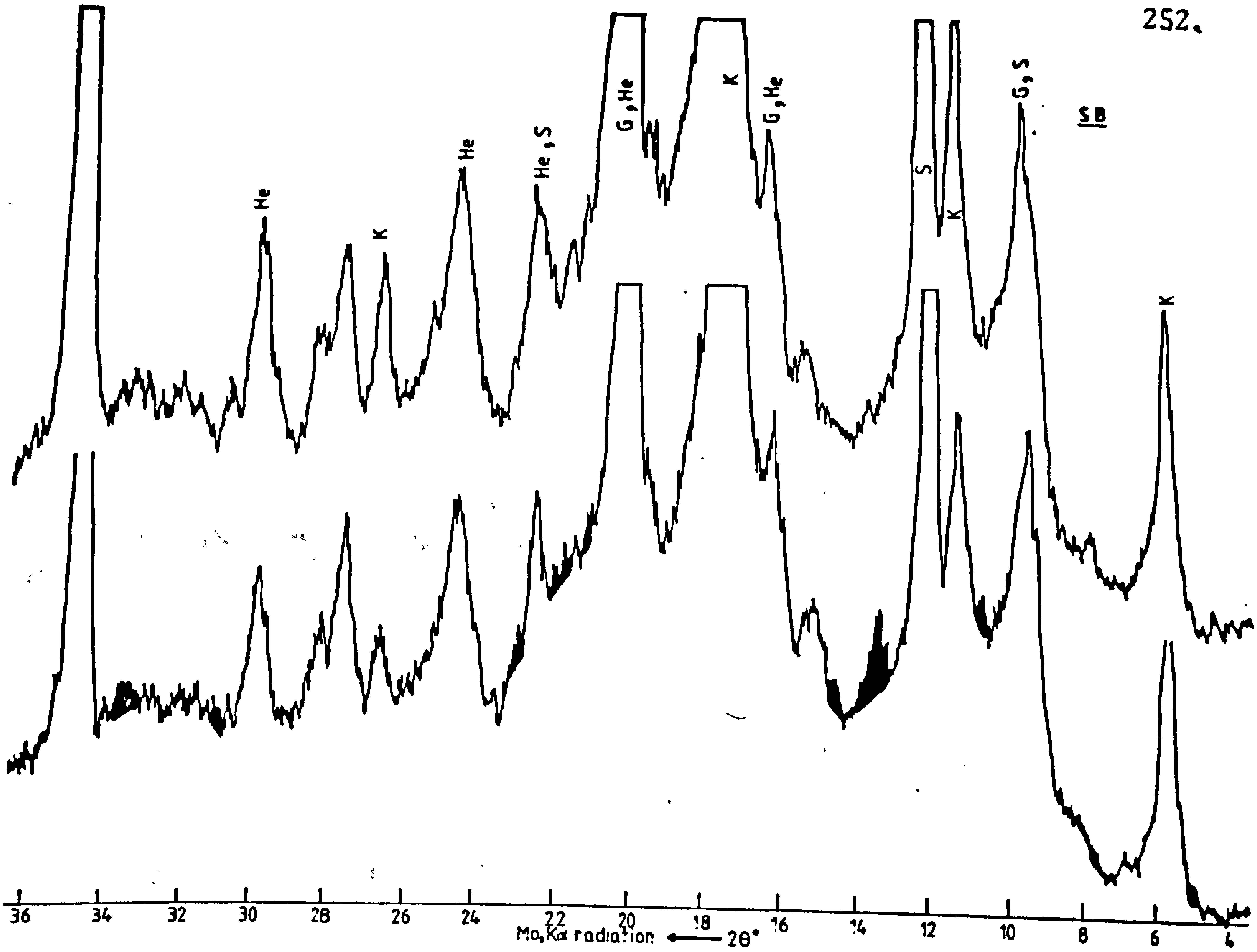
Mo,Kα radiation ← 2θ°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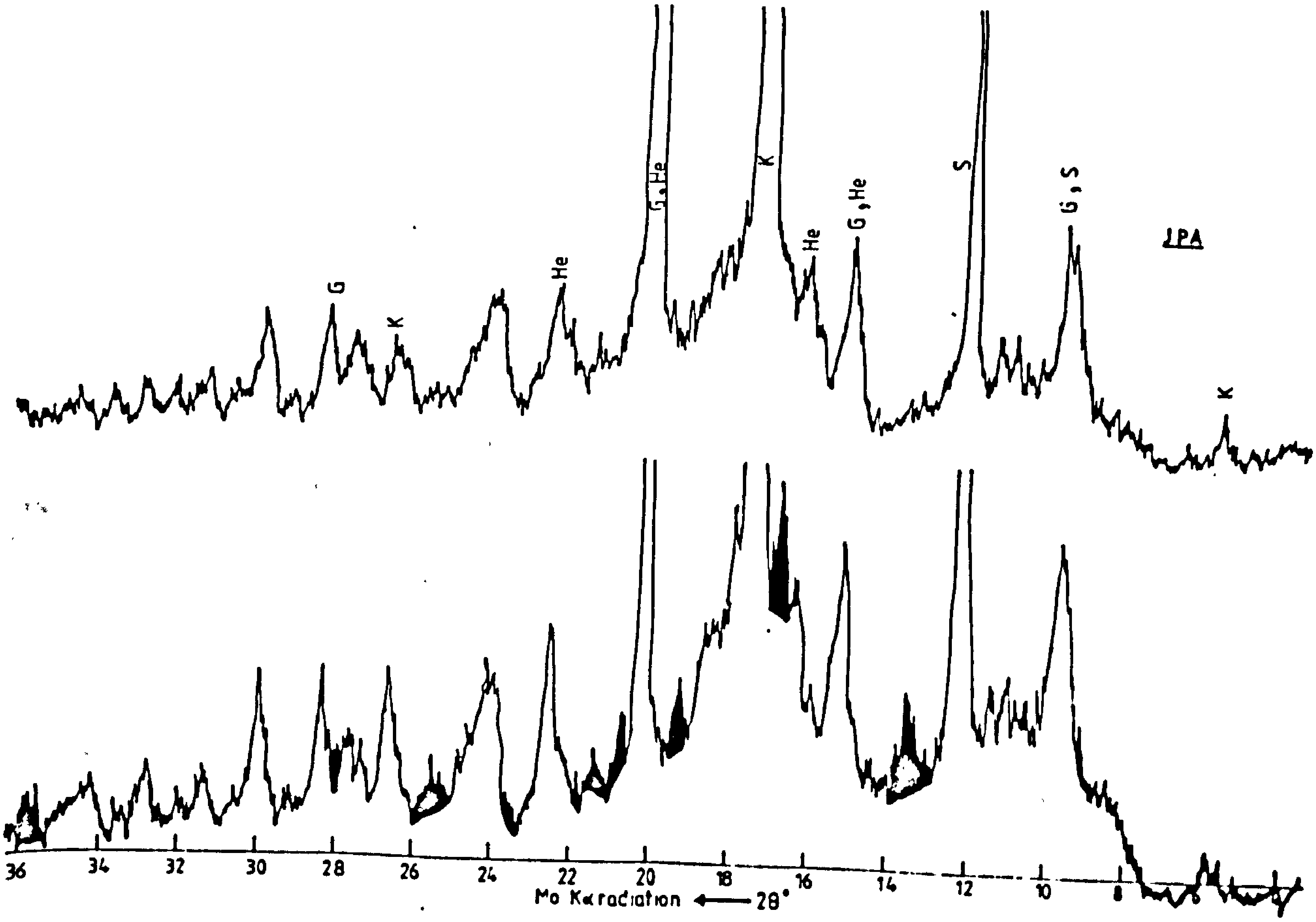
Mo, Kα radiation ← 2θ°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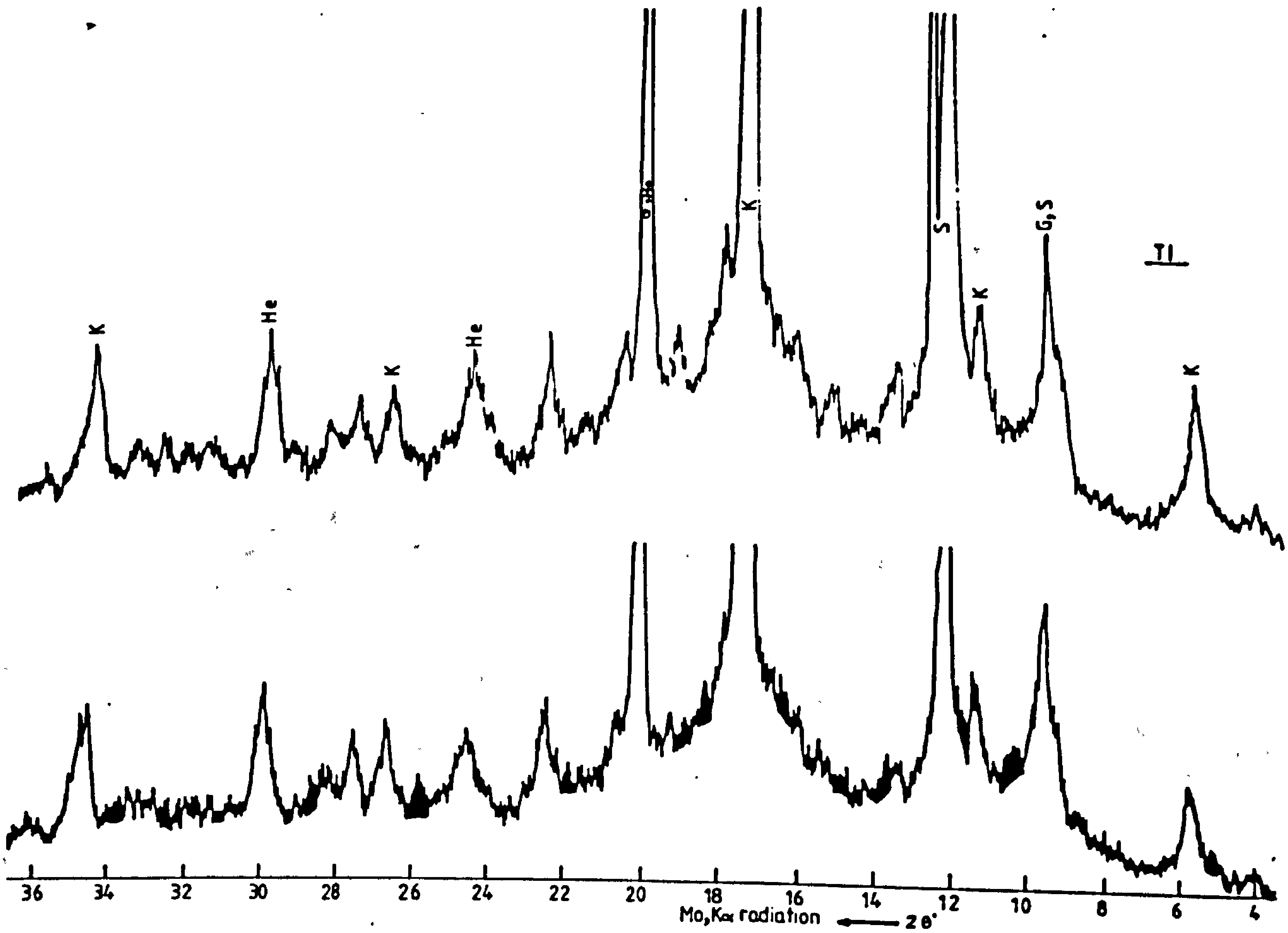
Mo Kα radiation ← 2θ°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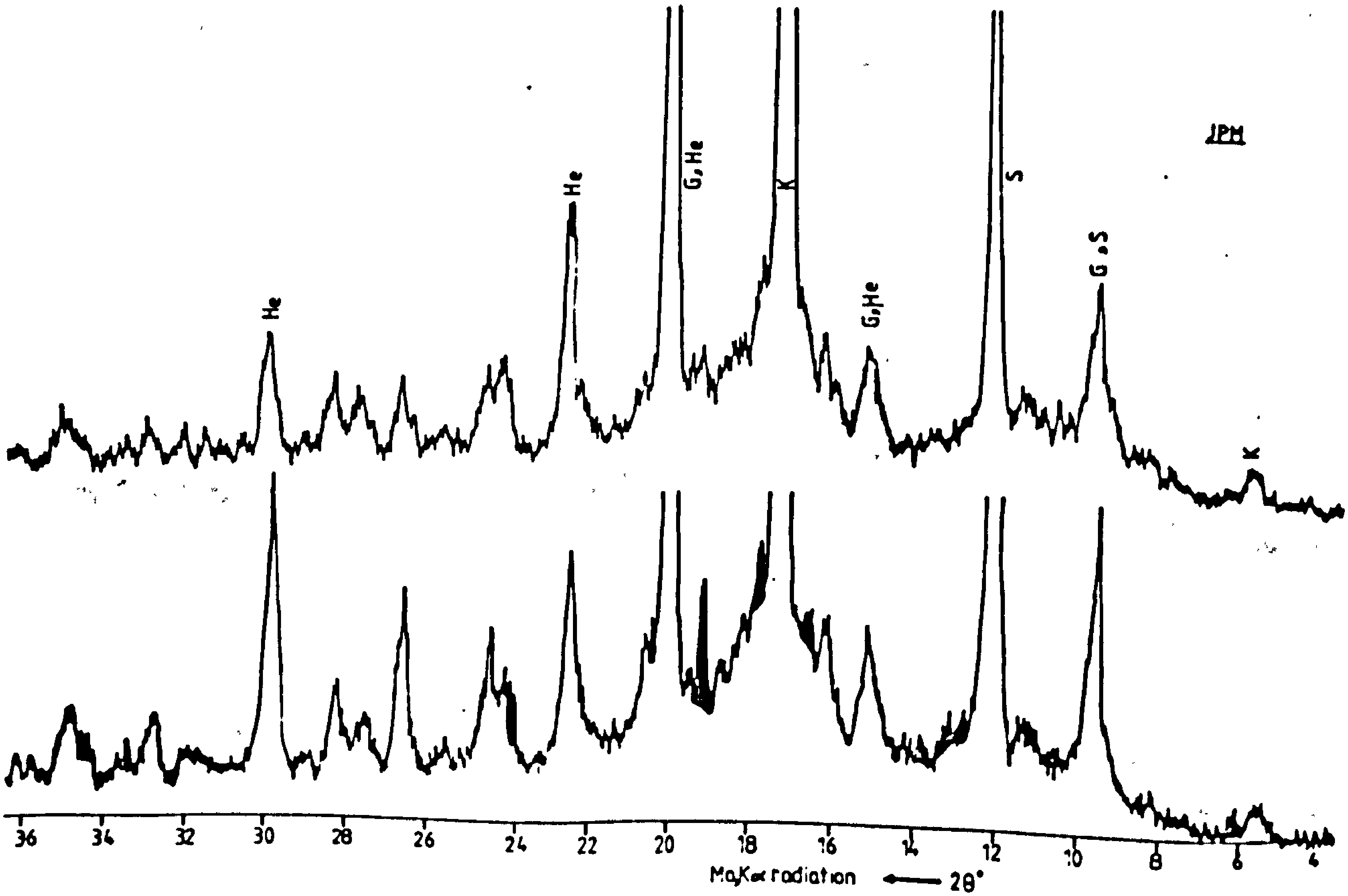
Mo,Kα radiation ← 2θ°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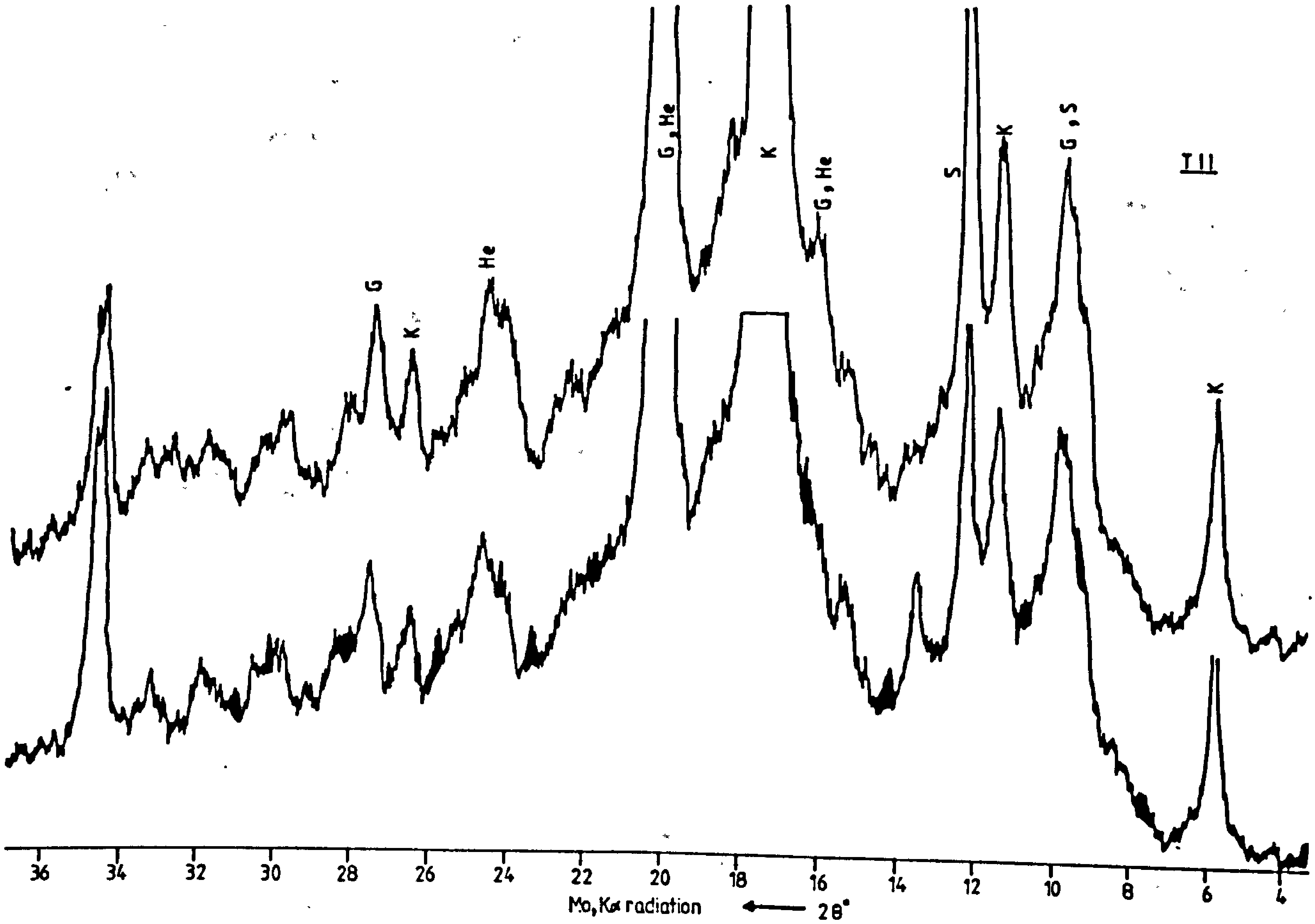
Mo,Kα radiation ← 2θ°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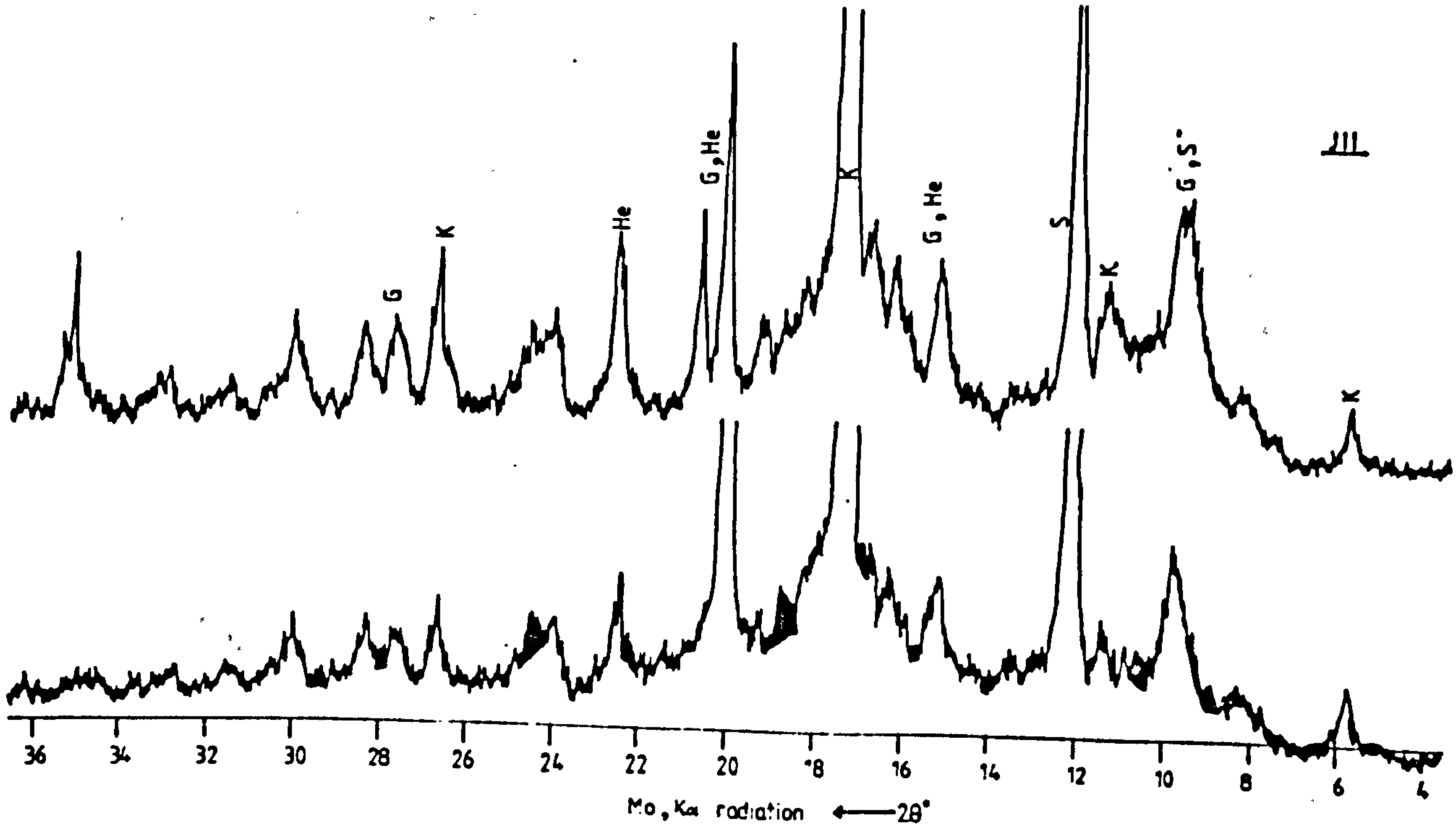
Mo, Kα radiation ← 2θ°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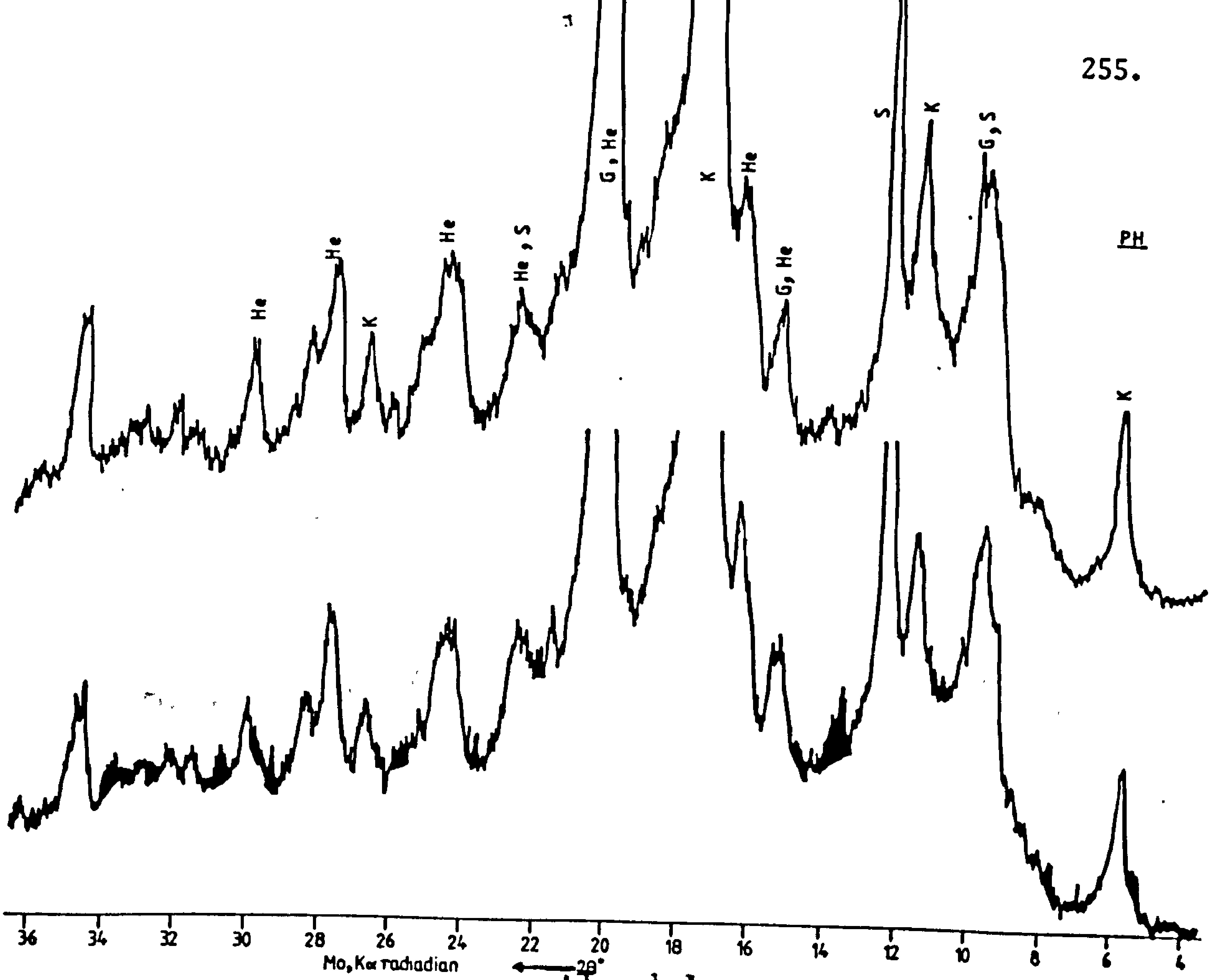
Mo, Kα radiation ← 2θ°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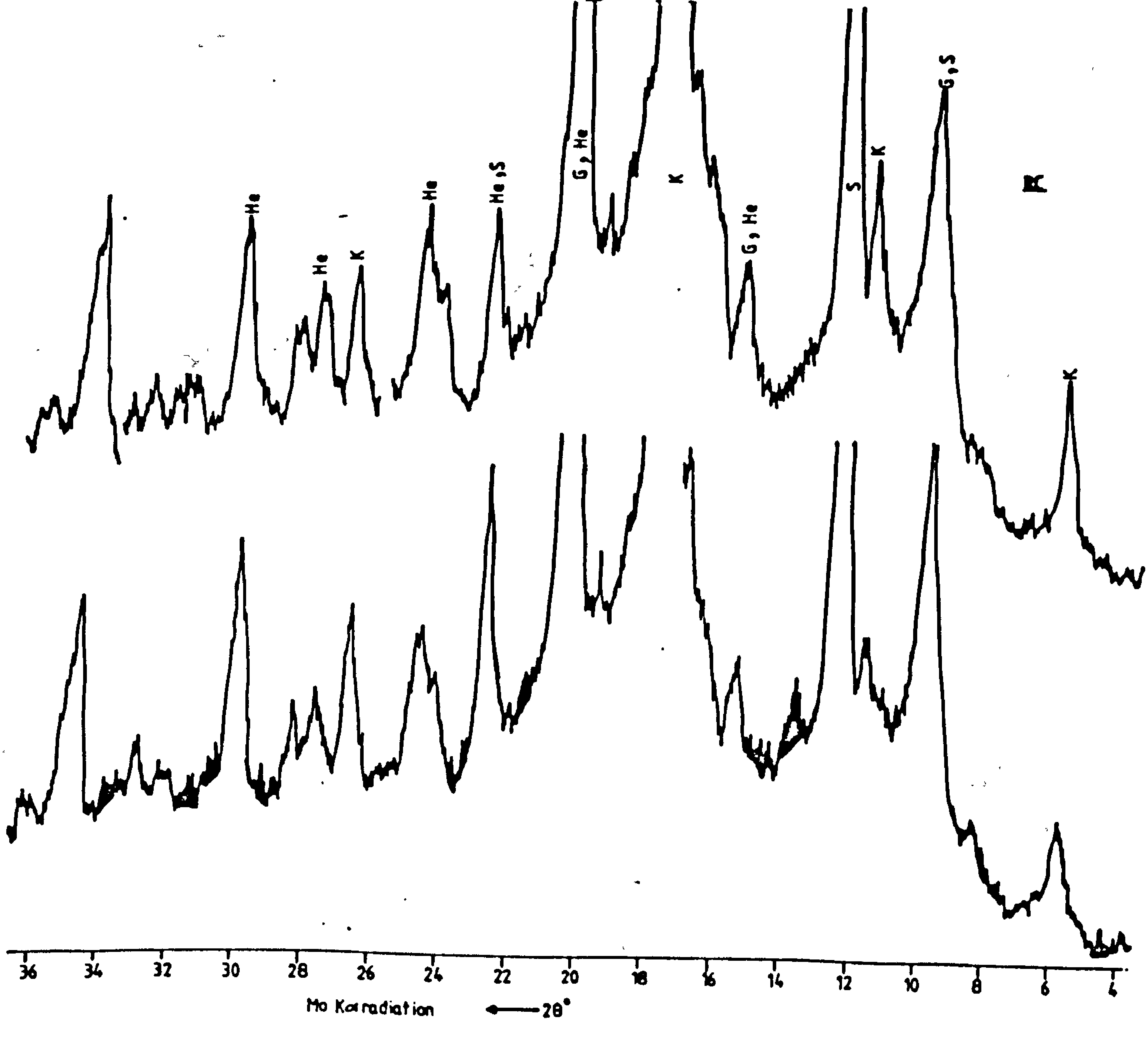
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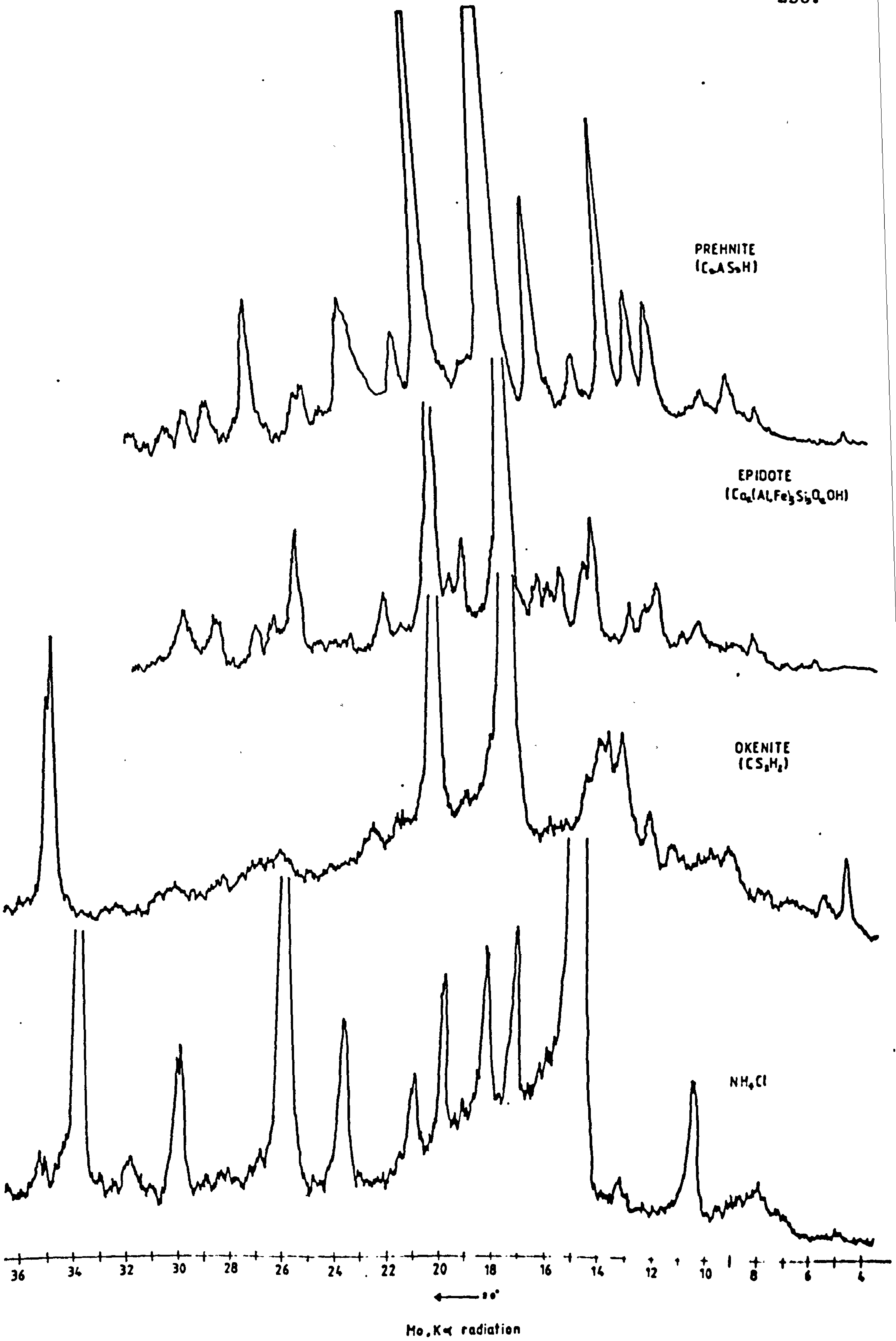
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EPIDOTE
(Ca₂(Al,Fe)₃Si₃O₁₂OH)
OKENITE
(CS₂H₂)
NH₄Cl
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← 2θ°
Mo, Kα radiation

APPENDIX A 2

ASTM powder x-ray data for calcium salts concordant with new lines observed in the lime treated soils

TABLE A

NEW LINES OBSERVED				CALCIUM SALTS						
TII TEIXEIRA II	RC RECIFE CAPITAL	JPA J. PESSOA-ACIMA	SIB SOLANEA I	C_xSH_y ($x\sim1$; $y=?$) 6-0010	$C_{0.85-1.5}SH_{N-X}$ 10-416	Cal. Al. Sil. hydrate 19-52	$C_6S_4H_3$ 3-560	C_5A_3 11-357	C_2ASH 16-388	$CaFeSiO_4$ 11-477
12.73				12.5(10)						
5.36	5.09				5.48	5.50				5.58
		4.29					4.30			
			3.61						3.61(9)	3.67
		3.19					3.22	3.15		
3.02	3.00	3.09	3.00	3.07(10)	3.17-3.01(10)	3.09(10)	3.10(10)			
	2.94	2.96				2.99(10)	2.98	2.93(10)		2.96(10)
2.87	2.82	2.82	2.78	2.80(8)	2.81(10)	2.81	2.86	2.89(9)	2.79(10)	
			2.59						2.56	2.61(9)
2.45		2.46						2.47		
		2.28					2.25(8)	2.33		
2.03		2.14	2.12		2.07		2.07(8)	2.14	2.08	
1.88	1.91	2.01	1.86	1.83	1.83	1.84	1.94	2.08		1.83
1.70	1.73	1.72		1.67	1.67	1.67	1.70	1.78		
			1.50					1.59	1.56	
1.41	1.41	1.38		1.40	1.40			1.41		

TABLE B

NEW LINES OBSERVED				CALCIUM SALTS							
SB S. BANANEIRAS	JI JUNCO I	SII SOLANEA II	NF NOVA FLORESTA	$C_{0\cdot85-1\cdot5}SH_{N-x}$ 10 - 416	C_3SH_2 11-502	C_6A_2F and/or C_4AF 11-190/ 11-124	$CAS_7H_{7\cdot5}$ and/or CAS_7H_6 9-211/ 19-213	$C_2SH_{0\cdot5}$ 15-642	C_xSH_y (x~1, y=?) 6-0010	C_2SH 3-594	CAS_2H_4 20-452
13.14									12.5(10)		
	9.26						9.15				
		8.15			8.6(10)						
		7.83				7.24					
	4.63		4.38				4.66				4.27
	4.12						4.06(10)			4.22	
	3.98							3.96(10)			
			3.30		3.26						3.34 (10)
	3.16		3.12				3.19	3.10			3.19
3.05	3.00	3.02		3.17-3.01(10)	3.01 (10)		3.04		3.07(10)	3.04 (10)	
2.80	2.76	2.83	2.82	2.81(10)	2.88/ 2.84	2.77	2.77	2.77	2.80	2.84	
2.45		2.63				2.67/ 2.63(10)			2.40	2.47	
2.25		2.17/ 2.09		2.07	2.08	2.04		2.03		2.35	
1.93		1.93	1.94			1.92				1.90	
1.87	1.88		1.84	1.83	1.87	1.81		1.88	1.83	1.85	
1.78/ 1.60	1.69	1.64/ 1.52	1.58/ 1.31	1.67		1.57/ 1.53		1.72	1.67	1.80/ 1.66	

TABLE C

NEW LINES OBSERVED				CALCIUM SALTS							
PH PENHA	AI AREIA I	AII AREIA II	SM SAPE MARI	C_xSH_y (x~1: y=?) 6-0010	$C_{0\cdot85-1\cdot5}SH_{N-x}$ 10 - 416	C_6A_2F and/or $C_2A_{2/3}F_{1/3}$ 11-190/ 16-410	Cal. Al. Iron Sil. hydrate 10-447	$C_{12}A_7$ 9-413	Cal. Iron Sil. hydrate 19-231	Cal. Iron Sil. CaFeSi O 16-701	C_3SH_2 3-669
12.73				12.5(10)							
5.29					5.48						8.8
		4.25						4.89	4.17		
	3.74	3.64					3.79		3.58		
			3.26							3.24	3.33
3.01	3.08	3.02	3.02	3.07(10)	3.17-3.01(10)			3.00	3.01(8)		3.04
	2.96		2.96				2.90(10)			2.97(10)	2.92 (10)
2.76	2.78			2.80	2.81(10)	2.76	2.74	2.68 (10)			
	2.60	2.45	2.57			2.65/2.62 (10)	2.64	2.45		2.56/2.53	
	2.14		2.25		2.07	2.19/2.14	2.21	2.19		2.22	2.09
	1.97	1.92	1.92			2.04/1.91		1.94	1.90	1.99	1.88
1.87	1.86	1.81	1.91	1.83	1.83(10)	1.81			1.82(10)	1.87	1.87
1.61		1.67	1.66	1.67	1.67			1.66	1.61	1.63	1.70
	1.58		1.59			1.57/1.53	1.59	1.60		1.61	
		1.54	1.56						1.57	1.50	
1.41	1.43		1.43	1.40	1.40					1.40	

TABLE D

NEW LINES OBSERVED				CALCIUM SALTS						
TI TEIXEIRA I	CT CUITE	USM USINA STA. MARI	JPM J. PESSOA -MEIO	$C_{0.85-1.5}SH_{N-x}$ 10 - 447	Cal. Al. Iron Sil. hydrate 10-447	$C_2A_{0.5}H_{6.5}$ 16 - 339	$C_{12}A_7$ 9-413	Cal. Al Sil. hydrate 19-52	C_3SH_2 3-669	$CaCo_3$ 5-0586
7.83						7.92(10)			8.8	
		5.43		5.48				5.5		
	4.97						4.89			
3.88	3.78	3.88			3.79	3.99				3.86
			3.50							
			3.34						3.33	
2.98	2.98	3.02	3.05	3.17-3.01(10)	2.90(10)		3.00	3.09(10)	3.04	3.04 (10)
2.76			2.90	2.81(10)	2.74	2.87/2.70	2.68(10)	2.99/2.81	2.92(10)	
2.51		2.57/ 2.46			2.64/2.45	2.46	2.45			2.50
2.23	2.20		2.28		2.21	2.24				2.29
2.18	2.13	2.19	2.19		2.19		2.19			
			2.10	2.07		2.05			2.09	2.10
1.87	1.92		1.90	1.83			1.95	1.85	1.88	1.91/ 1.88
	1.66	1.77	1.70	1.67		1.66	1.66	1.68	1.77/1.70	
1.59	1.62	1.62	1.62		1.60		1.60			
1.44		1.42/ 1.41	1.45/1.36	1.40		1.44				

TABLE E

NEW LINES OBSERVED			CALCIUM SALTS						
JPB J. PESSOA-ABAIXO	SIA SOLANEA IA	JII JUNCO II	C_xSH_y 6-0010	Cal. Al. Sil. hydrate 19-52	$C_{0.85-1.5}SH_{N-x}$ 10-416	$C_{12}A_7$ 9-413	$CS-C_3S_2$ 9-210	Cal. Al. Iron Sil. hydrate 10-447	$CaCo_3$ 5-0586
	4.88					4.89 (9.5)			
		3.85						3.79	3.86
3.02	3.02	2.92	3.07 (11)	3.09 (10)	3.17-3.01 (10)	3.00	3.07 (10)	2.90 (10)	3.04 (10)
2.83			2.80	2.99/2.81	2.81 (10)		2.97/2.81 (10)		
	2.62	2.68				2.68 (10)		2.64	
	2.43	2.40				2.45		2.45	2.50
	2.27						2.28		2.29
	2.09	2.19			2.07	2.19	2.14/2.07	2.21	2.10
	1.97					1.95	2.00		1.93
1.84	1.86	1.84	1.83	1.85	1.83		1.83 (10)		1.88
1.74/1.61		1.67	1.67	1.68	1.67	1.66	1.67	1.60	
		1.40							
1.31			1.40		1.40				
1.14			1.11						

NOTE:- The figures underlined and in brackets show the very strong peaks of the new mineral formed and the calcium salts from ASTM respectively.

APPENDIX B.1

Shapiro and Brannock's Method for Rapid Determination of Carbon Dioxide in Silicate Rocks

APPENDIX B.1

Shapiro and Brannock's Method for Rapid Determination of Carbon Dioxide in Silicate Rocks

a) The carbon dioxide tube consists of a borosilicate glass test tube, 180 mm diameter x 150 mm long to which they attached a side arm of borosilicate glass 10 mm outside diameter x 200 mm long, with a closed end. The side arm was attached at 45 mm from the bottom of the test tube.

b) They used an electric heater with a regulator to heat the sample and the liquid in the lower portion of the carbon dioxide tube.

c) The carbon dioxide tube was calibrated as given in appendix B.2.

d) To determine the carbon dioxide content of a sample, 1.0 gm of the sample powder was transferred to the bottom of the test tube and procedures of steps 2 - 7 of the "Calibration of carbon dioxide tube" in appendix B.2 followed.

e) The percentage of carbonate in the sample was estimated from the scale on the side arm..

After trying three different supernatant liquids viz. distilled water, 20% sodium chloride solution and motor oil S.A.E. No. 10, they found that distilled water and 20% sodium chloride solution were usable but inferior to oil because of the greater solubility of carbon dioxide in water and the sodium chloride solution. Boiling in the lower part of the tube was also easier to control with oil. 200 mm side arm length was found best for the recovery of evolved gas while a boiling time of at least two minutes was adequate. Mecuric chloride was used to eliminate the interference of iron which would otherwise react with hydrochloric acid to produce hydrogen.

APPENDIX B.2

Calibration of Carbon Dioxide Tube

APPENDIX B.2

Calibration of Carbon Dioxide Tube

1. Weigh 1.03 gms of "National Bureau of Standards" standard sample no. 79 and transfer, by means of a dry funnel to the bottom of the carbon dioxide tube.

2. Add 2 ml. of the mecuric chloride solution and tap the tube to free entrapped air bubbles.

3. Add oil to the oil-level mark, 110 mm from the bottom of the tube.

4. Tilt the tube so that the oil completely displaces the air from the side arm. Then return the tube to a position such that the main part of the tube is vertical.

5. Add 2 ml. of 1:1 hydrochloric acid, and tilt the tube so that the side arm is vertical to allow any carbon dioxide produced to enter the side arm.

6. Mount the carbon dioxide tube on a clamp attached to a support so that the side arm is vertical, and insert the lower part of the tube through the hole in the cover of the heater with the interface of the aqueous and oil phases just at the level of the cover (the heater should be preheated so that the temperature around the lower part of the tube can be maintained at about 185°C). Allow the aqueous phase to boil for about 2.5 minutes.

7. Remove the tube from the heater and allow tap water to flow down the outside of the side arm for 15 seconds (the water temperature should be between 15° and 25°C).

8. Remove from the stream of tap water, hold the tube with the side arm upright, and mark the position of the meniscus on the

side arm. This is the 1% mark.

9. Repeat steps 1 to 8 using 0, 0.206, 0.412, 1.54 and 2.06 gms of the standard sample to obtain calibration marks equivalent to 0, 0.2, 0.4, 1.5, 2.0% carbon dioxide respectively.

10. The tube can now be marked off by interpolation to give marks for each 0.1% carbon dioxide.

APPENDIX B.3

ASTM C114-77 Method for the Determination of Free Lime in Portland Cement and Clinker

APPENDIX B.3

ASTM C114-77 Method for the Determination of Free Lime in Portland Cement and Clinker

To one gram of the finely ground sample in a 200 or 250 ml flat bottom flask is added 60 ml of the solvent (glycerol and alcohol) and a few glass beads to agitate the solution while it is boiling. A reflux condenser is attached and the flask and its contents boiled over a suitable source of heat (use of open gas flame for boiling the solvent-sample mixture presents a fire hazard). The condenser is removed and the soil titrated while still near boiling. A slight pink colour indicates the end point of the titration.

The flask and contents with the condenser attached are returned to the hot plate and boiled. The titration and boiling cycles are repeated and may be as frequently as five minutes but not exceeding twenty minutes in the early stages. The final end point of the titration is when the pink colour persists for about ten seconds. The free lime present is calculated as equal to $EV \times 100$ where,

E = lime (CaO) equivalent of the ammonium acetate solution in gm/ml (1 ml $\equiv$ 0.005 gm CaO) and

V = ml of ammonium acetate solution required by the sample.

APPENDIX B.4

Modified Franke Method for Determination of Free Lime in Portland Cements

APPENDIX B.4

Modified Franke Method for Determination of Free Lime in Portland Cements

Reagents:

a) Acetoacetic ester (ethyl acetoacetate), anhydrous grade.

b) Isobutyl alcohol, anhydrous grade.

c) Thymol blue indicator; chemical name, thymol sulfonphthalein.

d) 60% perchloric acid.

Solution preparations:

a) Solvent: 450 ml of ethyl acetoacetate and 3 litres of isobutyl alcohol.

b) Indicator: 0.1 gm of thymol blue indicator powder dissolved in 100 ml of isobutyl alcohol.

c) Titration: to obtain approximately 0.2 N perchloric acid, 21.8 ml of 60% perchloric acid is made up to 1000 ml with isobutyl alcohol.

Standardization of the acid solution:

This follows in principle, the ASTM method of standardizing ammonium acetate solutions, C114-77 (113).

Equipment:

a) Water-cooled condensers, preferably with standard-taper inner joints to fit 200 ml Erlenmeyer flasks; and upper adapter tubes to fit absorption tubes containing soda-lime and ascarite.

b) Buchner-type borosilicate glass filtration funnel of

350 ml capacity and F grade porosity.

c) Equipment for vacuum filtration.

Procedure:

Sieve and grind the sample of cement according to the standard ASTM (113) procedure for free lime determination. Measure 70 ml of the prepared solvent solution (acetoacetic ester and isobutyl alcohol) and transfer into a 200 ml Erlenmeyer flask. Weigh accurately 1 gm of the prepared sample of cement and transfer into the flask. Adjust the flask in position to a water-cooled condenser, fitted with an upper adapter tube containing soda-lime and ascarite and reflux at boiling temperature on a hot plate for 3 hours. Remove the flask, stopper and cool. Filter with vacuum on a 350 ml filter funnel, receiving the filterate in a second flask. Wash the flask and residue in the funnel with 50 ml of isobutyl alcohol, using a policeman to guide the flow. Add 10 to 12 drops of the indicator solution to the filterate and titrate with the standard 0.2 N perchloric acid solution to a distinct reddish tinge.

APPENDIX B.5

Solvent Variation and Time Variation Methods for free lime determination

APPENDIX B.5

Solvent Variation Method

Reagents, solution preparations and equipments as in the modified Franke method (Appendix B.4). Procedure is as before but with the following modifications:

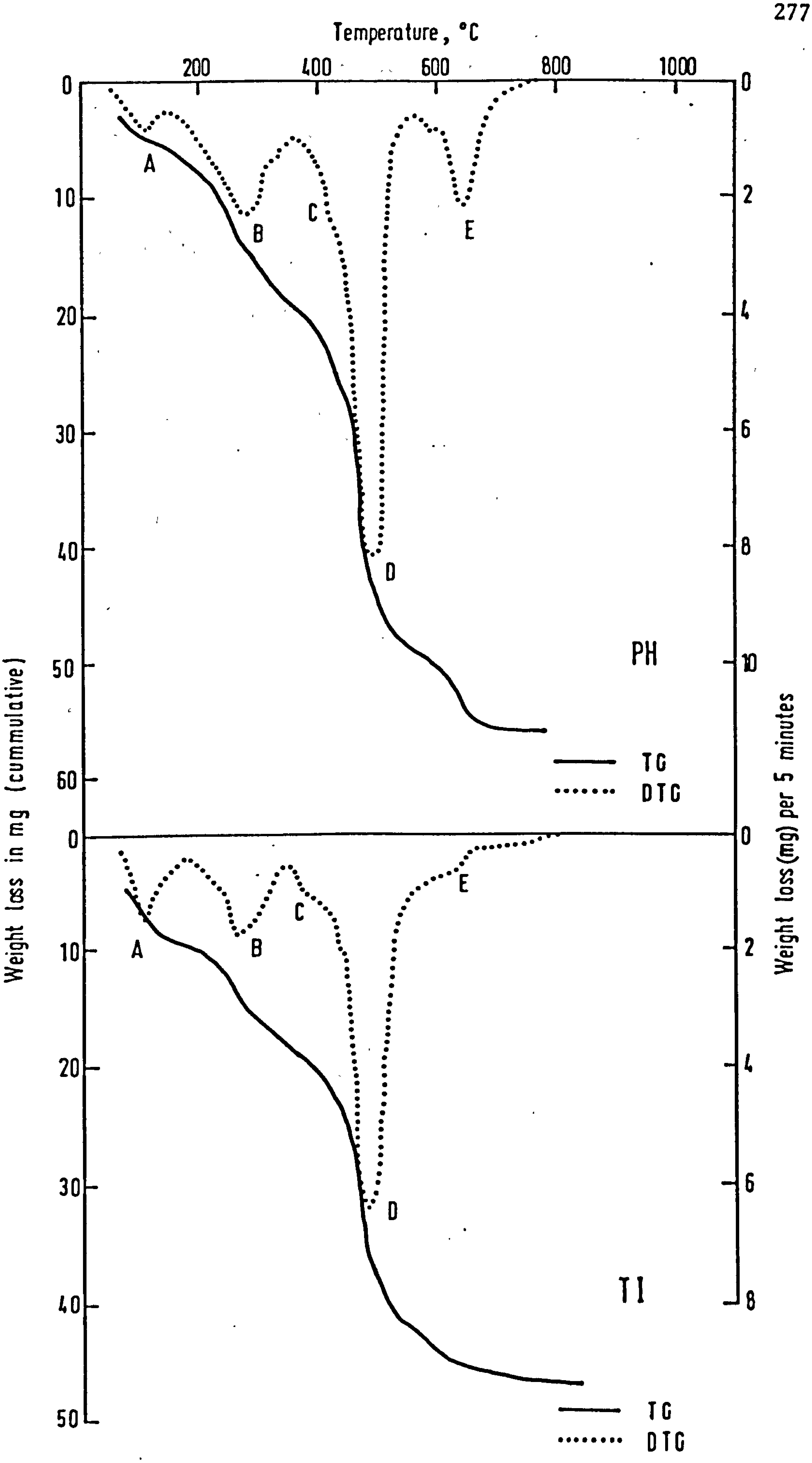
Volumes of solvent used are 50, 100, 150, 200, 250 and 300 ml. Six 0.1 gm portions of sample are weighed out. Each solvent-sample mixture is refluxed for 30 minutes.

Time Variation Method

As above, but volume of solvent used is always 100 ml. Six 0.1 gm portions of sample are weighed out. Two solvent-sample mixtures are refluxed for 1 hour, two for 1.5 hours and two for 2 hours.

APPENDIX B.6

TG and DTG Curves of some of Lime Treated Soils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800
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60
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10
20
30
40
50
Weight loss (mg) per 5 minutes
0
2
4
6
8
10
0
2
4
6
8
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B
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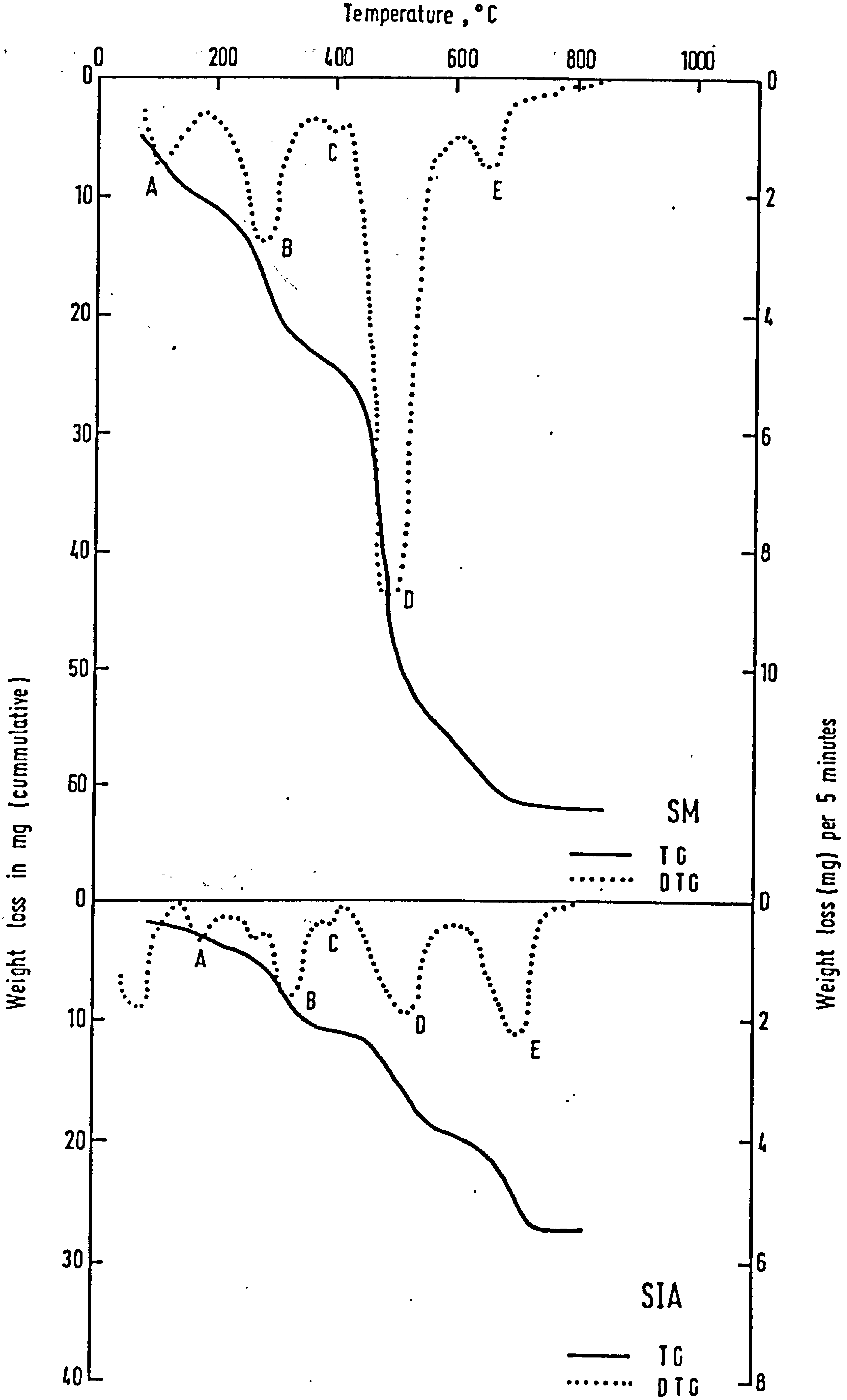
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Weight loss (mg) per 5 minutes
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0
2
4
6
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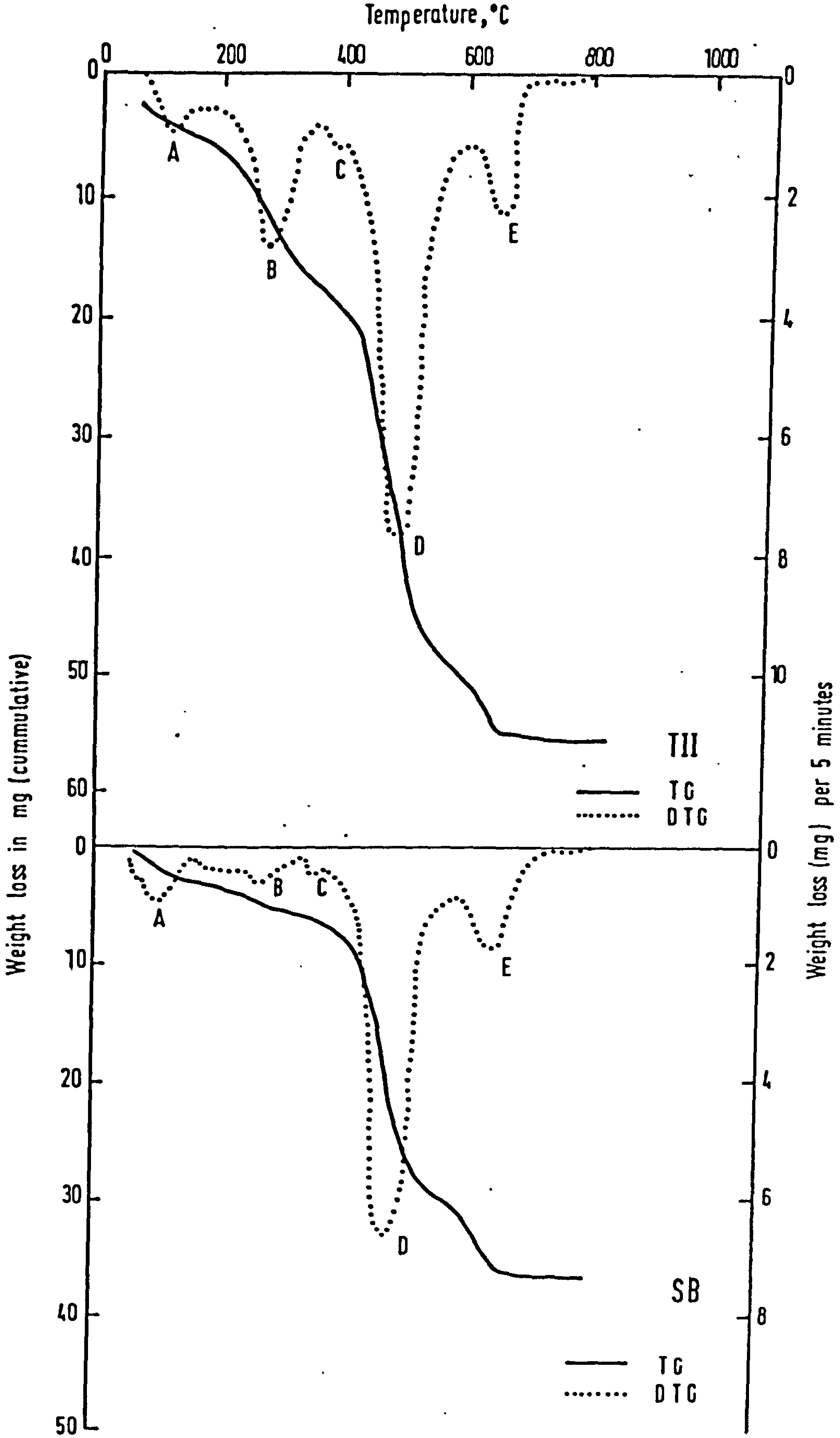
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30
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50
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Weight loss (mg) per 5 minutes
0
2
4
6
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A
B
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E
TII
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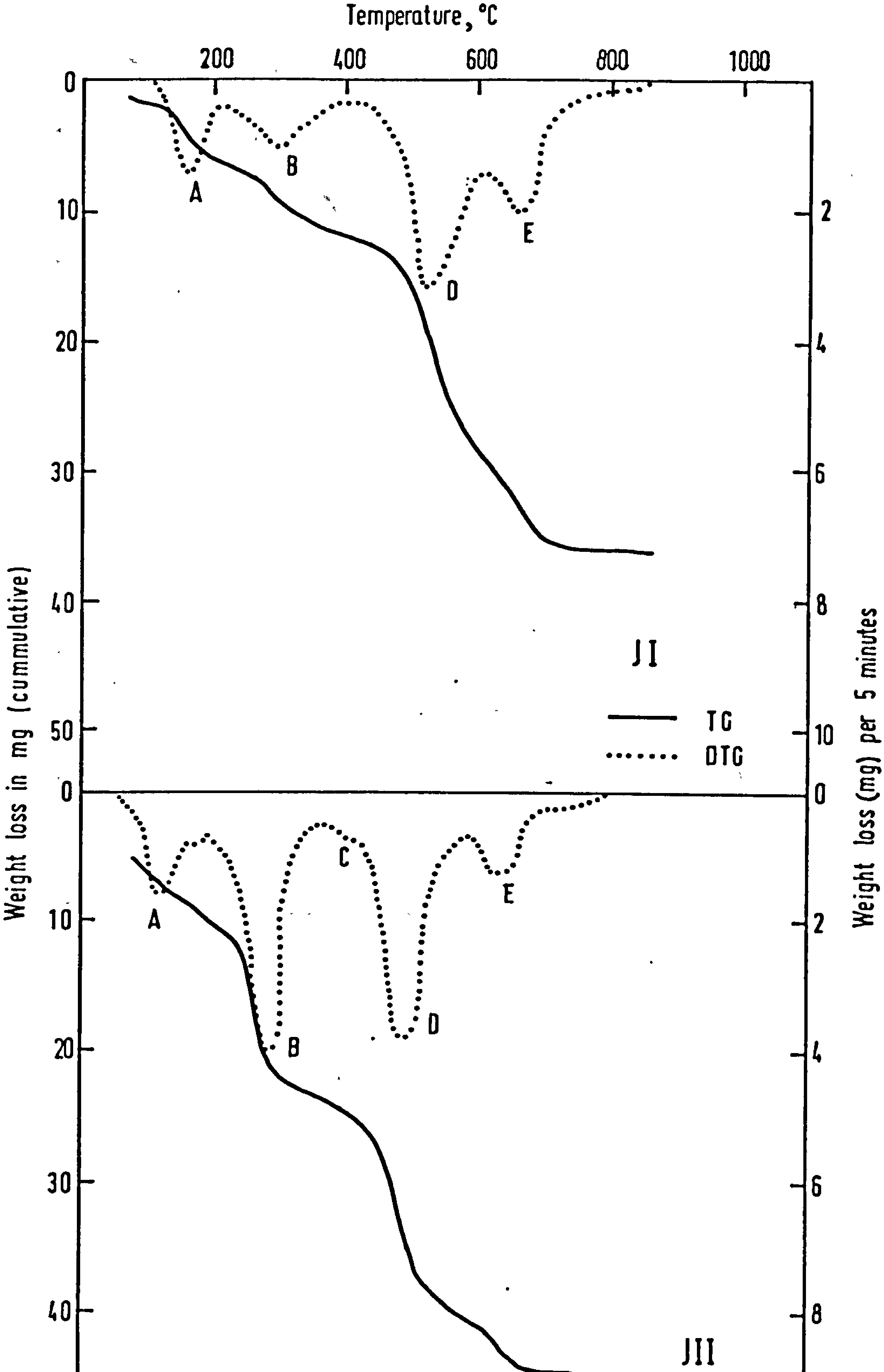
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40
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10
20
30
40
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Weight loss in mg (cummulative)
2
4
6
8
10
0
2
4
6
8
10
Weight loss (mg) per 5 minutes
A
B
D
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TG
DTG
A
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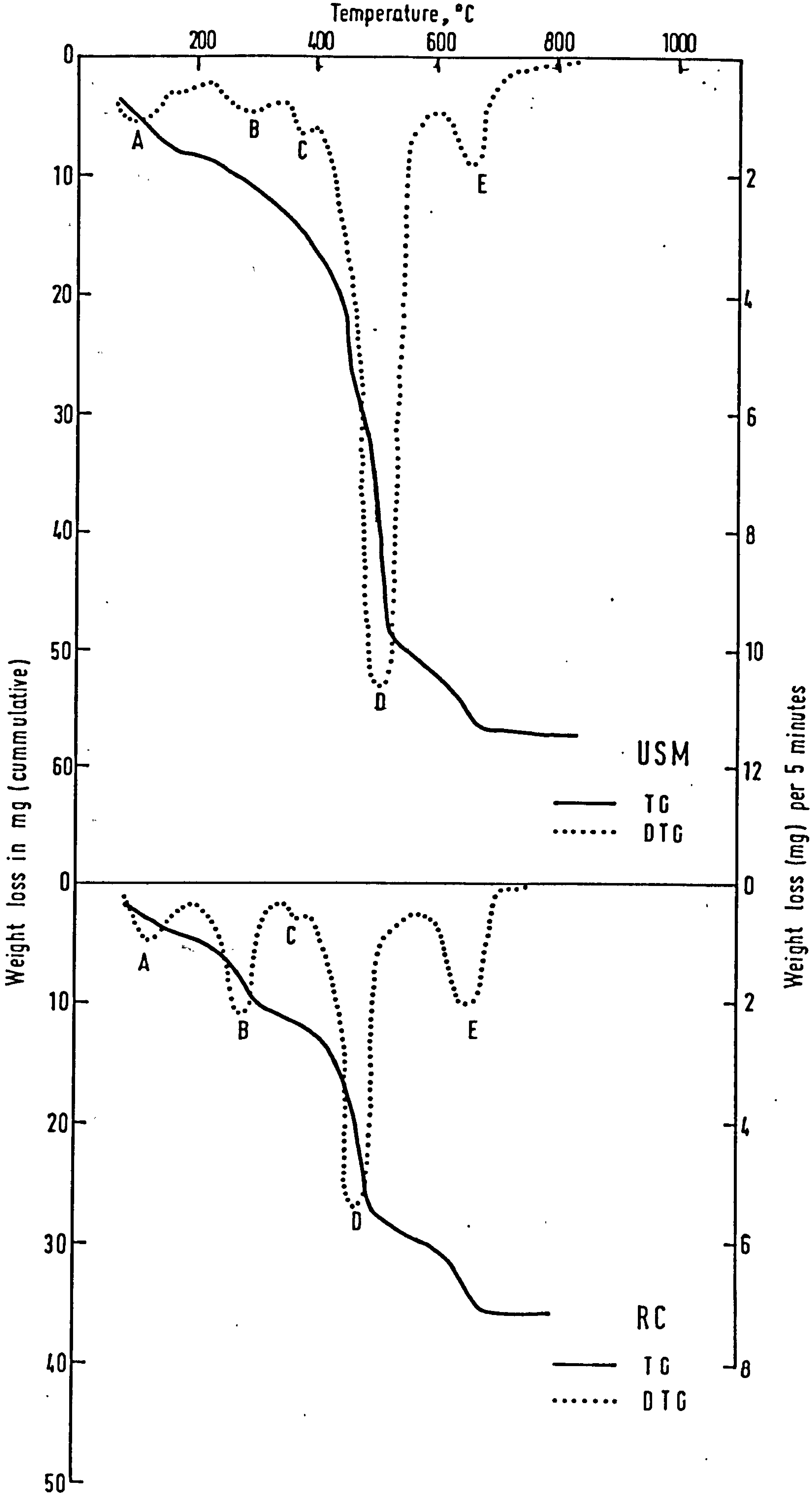
TG
DTG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4
6
8
10
12
0
2
4
6
8
Weight loss in mg (cummulative)
Weight loss (mg) per 5 minutes
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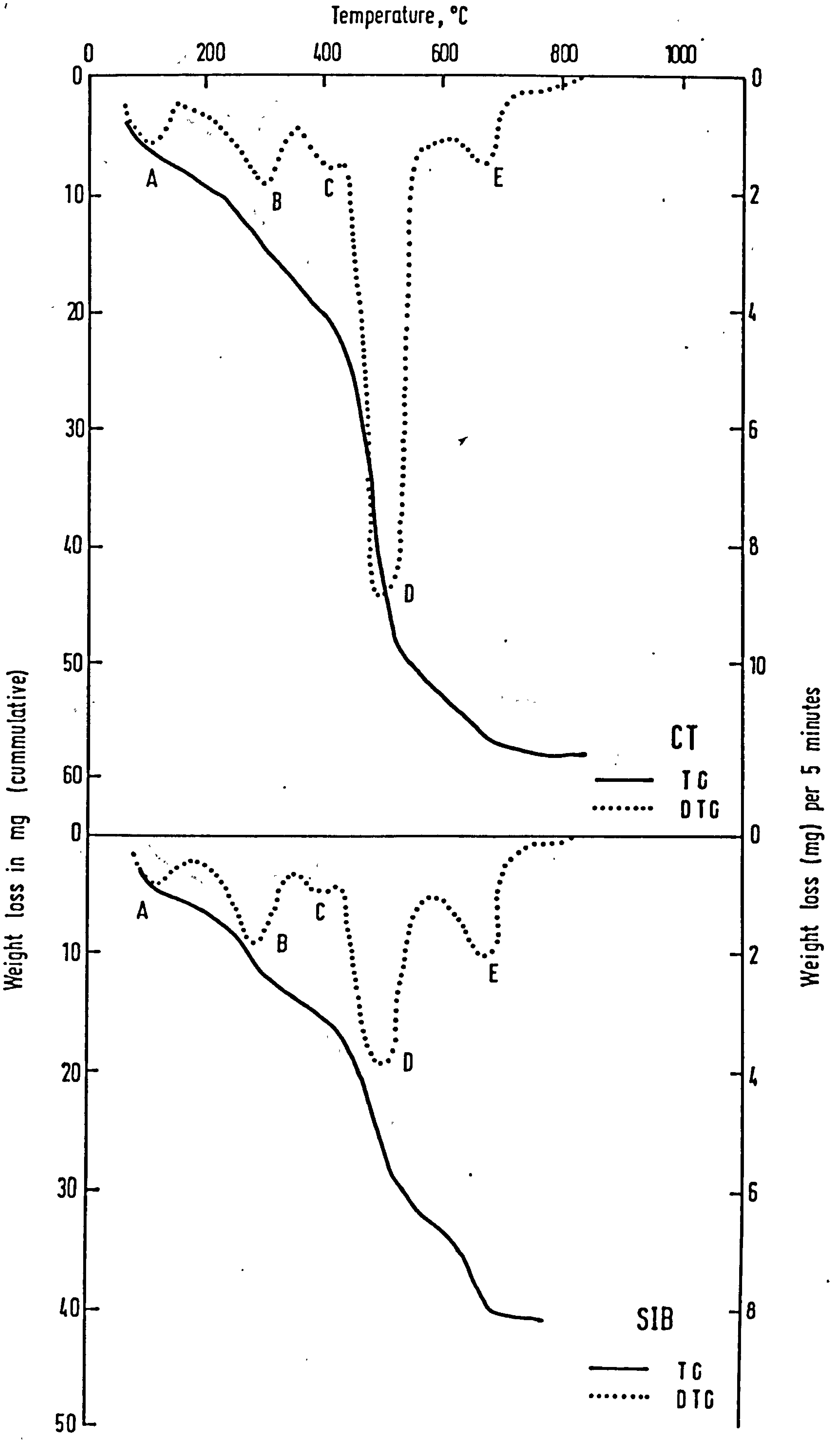
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30
40
50
Weight loss (mg) per 5 minutes
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2
4
6
8
10
0
2
4
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8
A
B
C
D
E
CT
TG
DTG
A
B
C
D
E
SIB
TG
DTG


Temperature, °C
0
200
400
600
800
1000
Weight loss in mg (cummulative)
Weight loss (mg) per 5 minutes
0
10
20
30
40
50
60
0
10
20
30
40
50
0
2
4
6
8
10
0
2
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C
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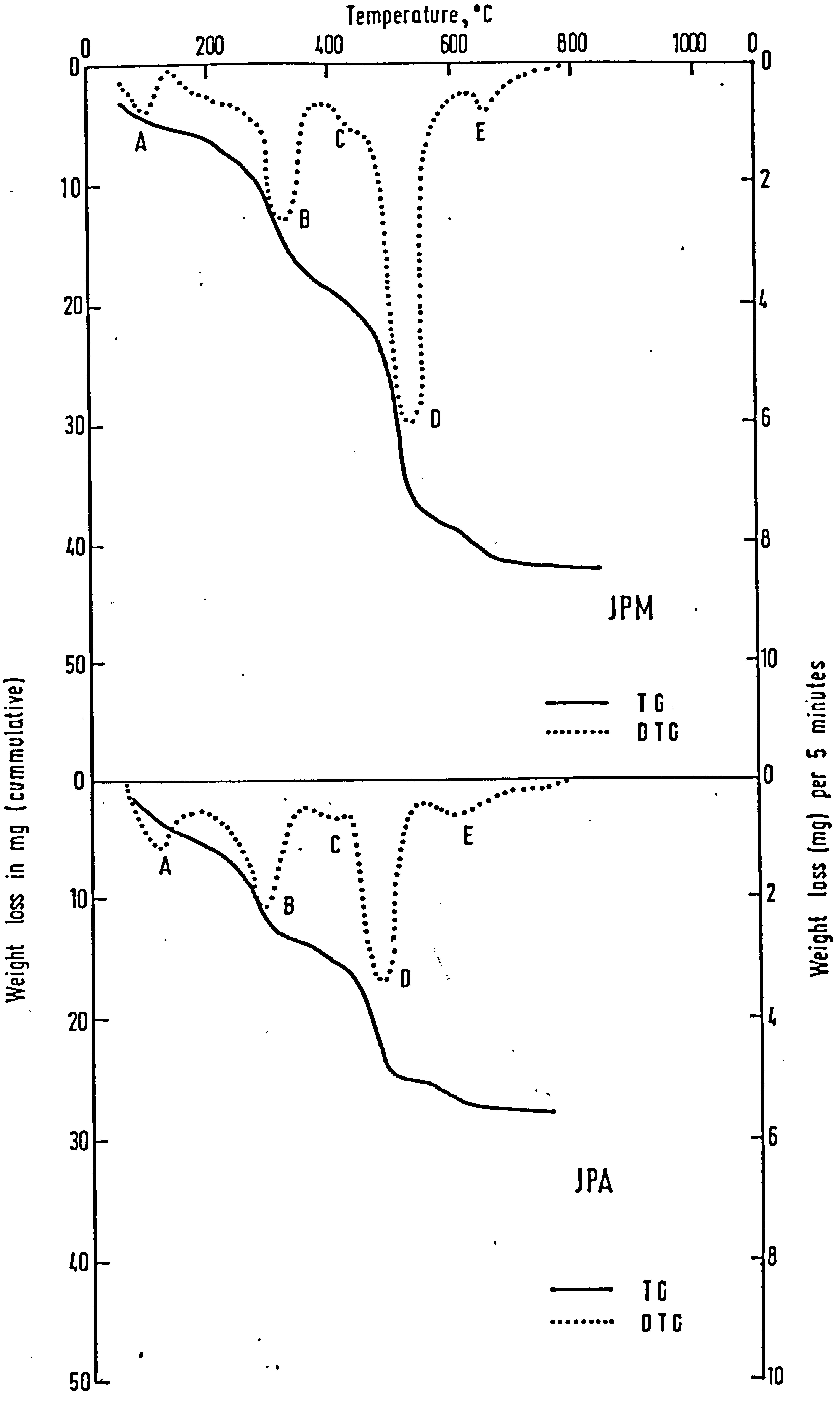
TG
DTG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10
20
30
40
50
Weight loss (mg) per 5 minutes
0
2
4
6
8
10
0
2
4
6
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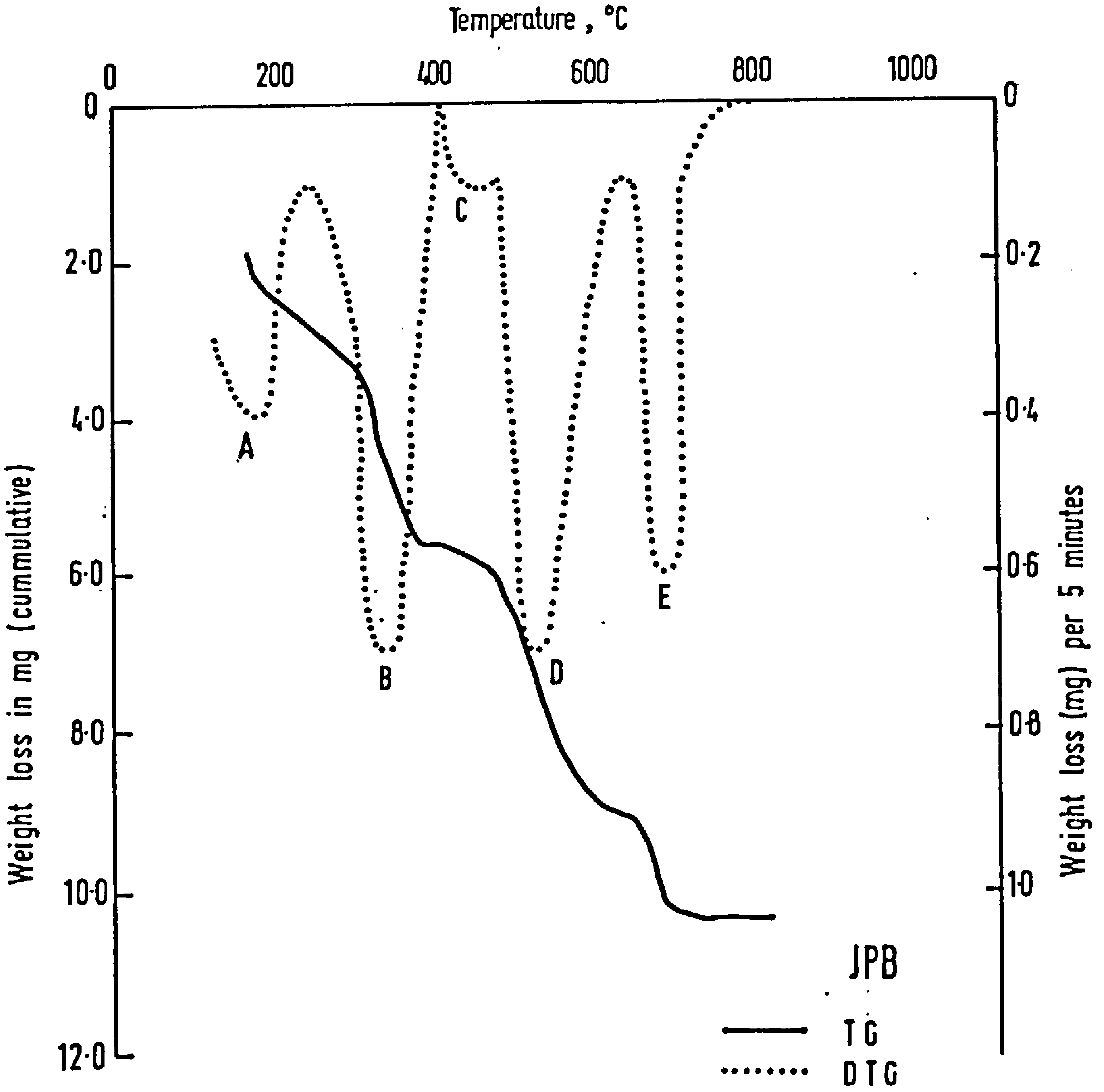
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Weight loss (mg) per 5 minutes
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