Durability of Concrete Structures in Denmark

A Study of Field Behaviour and Microscopic Features - by G. M. Idorn

Thin section examinations

The technique used for the preparation of thin sections, Ervin Poulsen (542) and P. E. Andersen and B. Hjorth Petersen (501), makes it possible to identify most of the components of the concrete and to distinguish them from the impregnating medium. The identification covers determination of both the optical character and the morphology, including particle size of mineral grains, aggregates and polymineral substances. Observations discussed in the present treatise and in the related reports have been substantiated on this basis.

The stabilization of structure and components of the concrete which is part of the thin section preparation limits the possibilities of undertaking accurate measurements of refractive indices etc. However, the measurements that are possible are usually sufficient when the results are evaluated by an experienced observer and considered together with morphological characteristics, comparative measurements on powder mounts, and possibly supplemented by X-ray data, etc.

Certain reservations are necessary with regard to the complex hydrates found as secondary precipitates in disintegrated concrete. These are usually termed calcium aluminate sulphate hydrates by the writer on the basis of the following characteristics.

1. Acicular and needle-shaped, very thin crystallites, normally about 50 to 300 microns in length. Occurring singly or in bundles, frequently in radiating aggregates.
2. Low refractive index and only slightly birefringent. Parallel extinction, negative elongation.
3. Frequent in specimens of concrete that have been exposed to sulphates but may also abound in any concrete that is in an advanced state of decomposition.

These characteristics can also apply to a number of variants of calcium aluminate hydrates (544), which may possibly occur instead of or together with the calcium aluminate sulphate hydrate.

The term 'gel' is used to describe a secondary precipitate in cracks and voids. Gel has the following characteristics.

Optically isotropic, transparent to translucent, colourless. Refractive index very much lower than impregnating medium. Often shows cracking due to drying shrinkage.

In most cases, the gel is alkali-silica gel originating from alkali-aggregate reaction in particles of porous and possibly also dense flint aggregate, but there may be a certain content of Ca^{++} in this substance (544) pp. 28 to 32. This is not apparent from the optical characteristics, and the somewhat vaguer term, gel, is therefore used. In porous, very decomposed particles of porous flint the alteration product, gel, cannot be optically distinguished from the basic material, porous, opaline flint, but the extent of the reaction suggests that the remaining substance is gel.

Both primary components, such as cement particles, and calcium hydroxide and secondary precipitates, e. g. calcite, may occur in such minute particle

sizes or be so concealed by discharging gel or by the surrounding cement paste that complete identification is not possible. In such cases, the term 'carbonate-like substance' is used. Definite identification can be relied upon in the following cases.

Calcium hydroxide ($Ca(OH)_2$).
β-dicalcium silicate (β-C_2S).
Calcite ($CaCO_3$).
Aragonite ($CaCO_3$).
Gypsum ($CaSO_4$, $2H_2O$).
Brucite ($Mg(OH)_2$).

Other authors have identified further substances, especially secondary precipitates.

There is a rather small range of minerals in Danish aggregates, as these are limited to glacial and marine, eroded materials from Fennoscandia, mixed with cretaceous chalk, limestone and flint. The flint may be mainly dense, chalcedonic flint or mainly porous, opaline flint, see H. Gry and B. Søndergaard (534). In past and present studies, the writer has only specified the structure of flint particles in broad outline.

Examinations of thin sections rather than of fragments and powder mounts of selected substances provide an opportunity to study components and entire structures, including crack formations, in their 'natural' state. Such studies may make a useful contribution to the recognition and evaluation of the course of secondary processes in the concrete. By using thin sections made from concrete cores it is possible to obtain a representation of the microstructure of the concrete in situ.

It has been considered important in the present work to follow and interpret crack formations related to reacted aggregate particles. Crack structures that seem specifically to reflect the effects of freezing/thawing are also treated, and, of course, crack formations that have no particularly significant origin also appear.

The photographs etc. previously published, especially in (2681), (2910), (2911) and (3971), on the disruption and dissolution of reacted aggregate particles, have been supplemented in this treatise by certain later observations, and the entire material has been reevaluated to illustrate the nature of alkali-aggregate reaction and other types of deterioration.

It was originally intended to include a summary and evaluation of observations on quantities and morphology of calcium hydroxide in mortar and concrete, but these observations have now been discussed separately and in more detail by H. H. Bache et al. (3979).

Many observations are available on deeper chemical alterations due to the aggressive action of penetrating solutions, especially sulphates, and these observations are also evaluated to illustrate present hypotheses on chemically conditioned disintegration of concrete. The possibilities of complex action by the aggressive influences are discussed. Too little use has perhaps been made in the investigations of such supplementary aids as traditional chemical analyses, modern X-ray technique, DTA, etc. Similarly, for more quantitative descrip-

tions of the various types of reaction, no measure has yet been found for the permeability and porosity etc. of both sound and deteriorated cement paste and of the common rocks, especially limestone and flint.

Observations on alkali-aggregate reaction

A review of earlier petrographic observations on alkali-aggregate reaction leads to the following grouping of the descriptions.

1. Crack formations and chemical alteration in reacted particles, classified according to type of rock (porous flint, dense flint, composite rocks).
2. Formation and precipitation of gel.
3. Development of crack patterns in mortar and concrete.
4. Hypotheses on alkali-aggregate reaction from a petrographic viewpoint.

Crack formations and chemical alteration in reacted particles. Considered according to its mode of formation, flint is, in the main, structurally isotropic and mono-mineral, and the alkali-reactive component is simply the siliceous principal component. This means that the petrographic reaction picture (for a given particle size and alkali concentration) must mainly depend on

1. Mineralogical dominance of either opaline silica (amorphous and therefore reacting relatively quickly) or microcrystalline, chalcedonic silica and therefore reacting more slowly.
2. Rock structure, i. e. permeability, porosity, particle size, internal specific surface.
3. Particle shape.
4. Characteristics of surrounding cement paste and mortar.

We shall see in which respects the observations provide information in more detail of this classification.

Fig. 16 shows three particles of porous flint with partial dissolution of the mineral substance and internal main-cracks, the appearance of which shows that the remaining structure of the material has retained considerable solidity and mechanical strength. As a macroscopic parallel to this reaction picture, reference can, for instance, be made to the formation of pop-outs shown in (2910) figs. 75 and 76, and to the porous flint particles in a section of core No. 54.5.30 from the Oddesund Bridge, shown in (2911) figs. 8 and 9.

Fig. 17 shows part of a reacted, porous flint particle, in which very extensive dissolution of the main amorphous mass of the mineral substance has taken place. The remaining, undissolved chalcedonic constituents, e. g. fossil remains, have not provided sufficient reinforcement to prevent intensive deformation and drying shrinkage of the substance remaining. This reaction picture has a macro-scopic parallel in (2911) figs. 12 and 13.

Fig. 18 shows a particle that must originally have consisted of porous flint and that represents total dissolution of the mineral substance and replacement by viscous gel. The gel shows truly deformation and crack structures because of

unimpeded shrinkage during preparation. This example is from the concrete of a caisson cast in 1912 in Aalborg Harbour. It is possible that the very long re-action time, combined with the action of sea water (penetration of sodium, magnesium and sulphate ions), etc. has led to total dissolution, including any original chalcedonic components. However, these special exposure factors are not present in similar examples, see for instance (3971) figs. 42 and 43. Macro-scopic parallels are compact exudations of expanding, viscous gel on surfaces and sections etc. of cores and on concrete surfaces, see e. g. Plum et al. in (2932).

The photographs shown have been selected from the entire observation material available as typical examples of the gradation of the internal structural de-composition of porous flint. The effect on the surrounding matrix also indicates a certain systematism of the reaction process.

Fig. 19 shows a particle of porous flint with extensive internal alteration, but without crack formations due to expansion, i. e. without visible, mechanical effects of reaction in the surrounding paste.

Fig. 20 shows a similar situation, but in this case, the surrounding cement paste seems to be impregnated with exuding gel, a dark zone having formed around the particle, giving a less distinct cement paste than usual. There are weak, indistinct cracks along the particle in this case.

Fig. 21, which shows part of the particle in *fig. 18*, demonstrates the fact that if sufficient 'softening' of the structure of porous flint takes place during altera-tion to gel, drying during preparation (or possibly natural drying under at-mospheric exposure) may cause the rim of the particle to crack away from the surrounding cement paste or - more often - may cause the cement paste to crack conformally with the rim of the particle. The figure shows the remarkable fact that the formation of a clear reaction rim does not necessarily mean that the crack is placed as a division between the rim area and the interior of the particle. This phenomenon is common in reacted porous flint particles (3971).

Fig. 22 represents the reaction picture of porous flint that might immediately be expected. The formation of gel in the particle structure has led to expansion, with consequent radiation of gel-filled cracks into the surrounding matrix. The picture has numerous parallels in (3971). A macroscopic parallel is (2911) fig. 9. It should be noted that in thin sections, the crack picture, which can be adduced to expansion during gel formation, can be superimposed by crack formations due to drying shrinkage (preparation), so that the primary mechanism is difficult or impossible to ascertain in the individual cases.

Fig. 23 is an example of this. In other cases too, see for instance (3971), the sequence of expansion and drying shrinkage is difficult to deduce convincingly from the observations available.

Most reacted particles of porous flint show uniform structural alteration from the particle rim towards the centre. However, some particles, see *figs. 18* and *21*, and (3971), do show a distinct reaction rim, ordinarily of a thickness of about 0.1 to 0.3 mm. Macroscopic parallels to particles without and with reaction rims are, for example, figs. 9 and 12 and plate VIII in (2911). The reaction rims in the cases mentioned seem to consist of isotropic gel of the same type as in the interior of the particles, although the rims are frequently less birefringent than the gel inside the particle, which indicates total dissolution in the rim zone before the precipitation of gel.

Figs. 24 and *25* show a part of the particle in *fig. 18*, with shrinkage cracks in the interior gel substance of the particle and in the cement paste along the rim of the particle. *Fig. 25* emphasizes the distinct isotropy of the substance in the rim zone. (3971) figs. 42, 43 and 44, illustrates the same phenomenon. In the last two figures, the interior gel mass of the particle is seen to surround spherulitic calcite precipitates, while the gel substance in the rim zone is completely isotropic. It is characteristic of the reaction rim phenomena mentioned that the actual edge of the particle stands out clearly against the surrounding cement paste.

In a few cases, instead of a sharp, distinct particle rim, a rim zone is seen, which indicates intensive interaction between the components of the cement paste and the particle substance. The main mass of all the particles in question seems to have been completely transformed to viscous gel, and the particles have been located in badly decomposed parts of the concrete.

Fig. 26 is a typical example of this reaction picture. (3971) figs. 55/56, 77/78 and 89/90 show similar phenomena.

Zonal discoloration along particle surfaces and along internal crack formations is the last of the typical phenomena of reaction observed. This is observed in some porous particles but not in others.

Particles with typical phenomena of this type are shown in *fig. 16* above. Figs. 45, 50, 51 in (3971), are other examples. It appears that the 'discolored' zones along the internal cracks of the particles frequently fail to become impregnated during slide preparation. This may be due to gel formation of the same kind as along the rim zones of the particles, cf. *fig. 24* and others. In such cases there may be a question of secondary 'rim zones', since the internal main cracks can be said to divide a reacting particle into several smaller particles.

It has been characteristic of the material investigated that particles of porous flint have not been observed without more or less extensive symptoms of reactivity. (It must be remembered that the material is selected from structures and concrete samples showing megascopic and macroscopic symptoms of deterioration due to alkali-aggregate reaction, while apparently undamaged concrete has not been included).

As far as concerns particles of dense flint seen in ruptured surfaces, cut sections and thin sections, by far the majority, regardless of particle size, have shown no symptoms of structural decomposition. In many cases, where cracks cross surfaces of mortar or concrete, the porous flint particles seem to have determined the course and intensity of cracking, while the dense flint particles have acted as inert rock. It also seems to be characteristic of unreacted dense flint particles that there is a good bond between their surfaces and the surrounding cement paste. (The reservation often made in practice that the 'smooth' surface of the flint is a weakening factor is therefore not confirmed by a closer structural study. There seem to be no grounds for considering the surface of ordinary sedimentary, coarse and fine particles of dense flint to be 'smoother' than the surface of igneous rocks etc.).

The typical examples of the effect of reactions in dense flint, which are described in the following, have therefore been selected from the study of many particles and represent a mere fraction of the flint particles present in the samples and mounts in question.

Fig. 27 shows a dense, black homogeneous flint particle in badly deteriorated concrete. The particle is traversed by thin, closed main-cracks, which may have occurred as a result of internal expansion during invisible dissolution of, and formation of gel in, the mineral structure. (The cracks cannot have arisen before the concrete was cast because the particle could not in that case have kept its shape and size during mixing and casting). Similar, slight crack formations in uniform, dense flint are shown in (3971).

Fig. 28 shows a very similar, 'faintly developed' crack formation in dense flint, embedded in flint. The flint in question is a cylindrical bar of black, dense flint, and stored for some months until a cement paste of high alkali concentration and stored for some months until external fractures showed up together with surface deposits of gel. A faint, light zone is visible in the flint particle, and this must be assumed to represent diluted, i. e. partly dissolved, mineral substance.

Fig. 29 shows a particle of dense flint from a factory chimney examined on a consultation basis. The particle is traversed by thin cracks along which advanced dissolution of the mineral substance has taken place. The same course of reaction has occurred along the particle rim.

In the test series, mentioned above, with production of alkali-aggregate reaction in cylindrical and prismatic flint bars, see (2681) pp. 6 to 13, dissolution action of the mineral substance had taken place along the rims of the particles of dense, black flint that were not traversed by internal main-cracks. See also (1897) discussion p. 804.

Fig. 30 can in continuity of the above, still be regarded as a representative illustration of the crack-producing action of alkali-aggregate reaction in reacted particles of dense flint. The broad, open main-cracks, which have carried gel from altered mineral substance out into cracks radiating from the particle into the surrounding cement paste are repeatedly encountered in (3971). It is frequently noted that the course of cracks and crack ramifications inside the particles follow parts of the particle that seem originally to have had relatively high porosity or opaline content (pigmentation), i. e. relatively low mechanical strength (3971).

Limited, porous parts of dense flint often appear, and the reaction picture may then be typical of dense flint in the dense, chalcedonic part of the particle and of porous flint in the porous and possibly opaline, dense part; and a cracked, some cases this means an uncracked, undissolved, dense part. In other cases, open, straight main-deformed and partly dissolved, porous part. In other cases, open, straight main-cracks are seen traversing the dense parts, associated with ramified, irregular disruption and deformation of the softened porous structure.

Figs. 31 and *32* are examples of these phenomena, and (2910) fig. 93, shows another typical case.

Some particles have limited porous parts showing such intense reactivity that the zones seem to have produced cracks and consequent further reactivity in the particles as a whole (3971). It is possible that intensive alteration of dense flint may in some cases result in the material having an appearance that cannot be distinguished from originally porous structures.

Figs. 33, 34 and *35* show that in some particles of reacted, dense flint, unusual micro-crack formations can be seen in the rim zones.

Fig. 36 shows similar surface cracking in a magnification of the rim zone of the particle *fig. 29*. In this case, the crack structure is obscured by accompanying dissolution of the flint substance of the particle. This is reminiscent of the dissolution in dense flint shown in *fig. 28*.

Fig. 37 shows a thin section of a flint pebble from a submarine deposit near the Skaw, Jutland. This flint had not been used for concrete, and both the rim crack formations and dissolution along the rim cracks can only have resulted from natural action, i. e. wave action and slow silica dissolution.

Fig. 38 gives a magnification of the rim zone.

Fig. 39 shows a thin section of a flint pebble from the same deposit. The phenomena of rim corrosion are so weak in this case that they can only be seen at high magnification, as shown in *fig. 40*.

Fig. 41 is a partly ground thin section of a flint pebble from the same deposit. In its original form, this pebble looked like ordinary dense, black flint. The thin section shows a rim zone, which appears to be dense and black, covering a zone of oxidation around a dense, grey flint substance. The submarine milieu from which the pebble comes consequently seems to have had a reducing effect. The layer of oxidation must be assumed to originate from an earlier deposition of the flint on land in a moraine or glacial deposit, since this milieu is often characterized by very brown flint.

Fig. 42 is a thin section of a flint particle from a glacial or glaciofluvial deposit. The slightly pigmented character of the surface indicates browning due to oxidation, which has given the flint a brown surface but has not penetrated very far.

Fig. 43 shows a black, dense, submarine flint, a typical gravel pit flint and the freshly broken surface of flint from a primary deposit. The submarine flint has a distinctly scarred and pitted surface, no doubt in thin section showing rim cracks and dissolution like the flint of the same origin shown in *figs. 37* and *38*. Incidentally, it seems likely that this kind of flint surface is mainly a result of surf-erosion, the severe symptoms exhibited being the combined effects of impact and wear.

The gravel pit flint, which is dense and typically grey, shows an abraded but smooth, 'waxy' surface. The broken face of the third flint particle shows a very even and smooth surface.

It is natural to assume that a corroded particle surface such as the submarine flint pebble may be the seat of alkali-aggregate reactivity, resulting in further crack formations and further dissolution of substance. However, although such corrosion phenomena can occur in flint already subjected to natural weathering, it is also remarkable that a pure, smoothly ground surface of dense flint can be intensely affected by alkali-aggregate reaction, as for example shown in *fig. 28*. In interpretations of petrographic observations of these phenomena in thin sections of concrete it is necessary to bear in mind all the possibilities mentioned, and indeed also their possible combinations.

Fig. 44 shows a situation similar to the rim dissolution of dense flint in *fig. 26*. This shows a flint particle in a thin section of lime-mortar from a six centuries old church wall near Randers in Jutland. The mortar could be seen to have been repeatedly limewashed. In the course of time this treatment has resulted in the intense rim corrosion shown, which is very reminiscent of the rim formation in alkali-aggregate reaction.

Fig. 45 shows a quartz particle in the same thin section. This particle seems to have been exposed to a corresponding, although somewhat weaker chemical reaction between the quartz and the surrounding substance. Identification of the reaction product is impossible.

Fig. 46 shows a flint particle from a thin section of Roman mortar from Caesarea in Israel. The particle shows rim corrosion very similar to that in the particle shown in *fig. 44*. In this case also, the alteration must be assumed to be an expression of reaction between surrounding lime and the flint substance. It must be remembered that hydrated calcium silicate has previously been stated to occur in mortars from ancient times, cf. (3981). The thin section from Caesarea also shows extensive formations of reaction products located around the particle rim. Further there is an almost totally dissolved feldspar particle. R. Malinowski et al. (3980) state that a microscopic investigation of thin sections of this Roman concrete reveals symptoms of rim reactions between aggregate particles and matrix. Basalt particles are 'invaded' by calcite, which replaces olivine and plagioclase (while pyroxene is not attacked) and forms a type of reaction rim. A similar 'reaction rim' may also occur around particles of chert and terracotta (crushed tile - writer's remark). The authors consider it probable that this 'contact calcitization' has contributed to the coherence of the mortar.

Intense reactivity that has led to rim corrosion of flint has previously been observed by the writer (2787) fig. 12. In this case, there was reason to consider aggressive carbon dioxide combined with sulphates to be the deleterious agent.

The observations of intense rim corrosion in flint exposed for centuries to reaction with lime solutions are an indication of the fact that much weaker reactions of the same type, which may occur in concrete under 'normal' conditions, perhaps lead to the formation of good bond between the flint aggregate and adjacent cement paste. A possible beneficial effect of this type has previously been suggested by K. Mather and Th. Kennedy (3982). A so-called 'beneficial reactivity' is perhaps a frequent phenomenon. However, in principle, it is only a short step from such reactions to weakening dissolution of flint substance in particle rim zones and possible formation of expanding gel in the particle structure, and no means have yet been found of limiting the reaction process to the desired effects or knowing when deleterious action may occur.

In the classical literature on alkali-aggregate reaction, the phenomenon of 'reaction rims' has been treated by various authors.

D. McConnell et al. (2571) and R. C. Mielenz and L. P. Witte (3994) show photomicrographs of reacted particles with 'clarified rims'. The possibility is examined of special rim structures developing in aggregate particles before production of the concrete, for example, in geological weathering. The secondary 'coating' of sedimentary aggregate materials is also discussed with a view to avoiding confusion with 'reaction rims'. Reactive coatings (e. g. opaline silica) may, however, occur on inactive aggregate particles, in desert regions and other locations. L. S. Brown (2913) has found distinct 'reaction rim' formation on reacted aggregate particles in specimens of deteriorated concrete. In one case with intensely expansive reactions in concrete cast with glass as aggregate, a 'reaction rim' split off from the interior of reacted particles, while the bond between the surrounding cement paste and the outer rim of the particle remained unbroken. This phenomenon is shown in (2913) figs. 7 and 8, cf. also

figs. 26 and 113 in (3971). Jones (538) shows 'clarified reaction rims' around particles of hard, but porous, silicified Danish chalk. In this case, the aggregate particles had been crushed for tests on the expansion of mortar bars, so it is certain that the reaction rim is a consequence of processes in the mortar. The reaction rim phenomena in the particles mentioned are, moreover, reminiscent of (2911) fig. 12.

In Denmark, calcareous flint is the only important polymineral, reactive aggregate. Sedimentary, porous flint with no lime content must be considered to have formed by postglacial (or glacial) leaching of originally calcareous, porous flint. Therefore, the non-calcareous flint is relatively more frequent in regions with a preponderance of glaciofluvial deposits, while lime contents are more likely to have been preserved in moraine deposits and in primary deposits such as Erslev flint.

In the calcareous, porous flint, only the SiO_2-substance (and perhaps only a part of this) is dissolved during alkali-aggregate reaction. The mechanical crack picture must therefore mainly be similar to the reaction picture in dense flint, i. e. open main-cracks occur after intense reaction, see several examples in (2910). However, even when the quantity of limestone is low in relation to the quantity of porous flint in particles of this type, a certain distortion of the mineral structure is still seen, as for example in (2681) fig. 7, (2910) fig. 8, and (3971) fig. 116, and others. The calcareous flint mentioned (and by and large also chert and siliceous limestone) has a principally homogeneous structure. Certain foreign, reactive rocks are distinctly heterogeneous, and this is reflected in the mechanical effects of the reactions.

The Swedish phyllite rocks in the Norrland dam concrete (2910) show a distinguishable stratification, see e. g. (2910) fig. 28. Crystalline quartz grains are scattered in the rock, which also contains mica and various other minerals. Soluble, amorphous silica was not detected. It looks as though shear stresses along the lamination have influenced the crack development. Another remarkable phenomenon is the precipitation of gel along the sides of the main-crack in the particle, see (2910) figs. 28, 29 and 30. As previously stated, this is very rare when flint is the reacting rock. It might be explained by the fact that the reactive silica is only a minor constituent of the rock structure. A third noteworthy phenomenon in this case of alkali-aggregate reaction is the extensive formation of calcium aluminate sulphate in the cracks passing through the concrete. There seems to be no likely source of sulphates other than the rock itself (however, the content of pyrite was not investigated). The significance of the presence of sulphate will be discussed later.

Norwegian concrete that had been subject to alkali-aggregate reaction was examined by H. Musæus (3922), who found that the reactivity could be traced to a phyllitic rock. The writer carried out a preliminary examination of thin sections of the concrete in question, and *figs. 47, 48, 49, 50, 51, 52* and *53* show reaction phenomena in phyllite aggregate particles.

Fig. 47 shows a particle of which quartz is the main constituent (amorphous silica may be present as a binding compound). A faint, longitudinal orientation of the mineral structure can be seen, and the main-crack through the particle follows this direction. A certain sub-division of the fracturing can be distinguished.

Fig. 48 shows a triangular particle, which has quartz grains scattered in an amorphous ground mass. Dissolution and subsequent drying shrinkage have resulted in more irregular cracking, similar to the distortion found in porous flint.

Fig. 49 shows a compact, rounded particle containing very small amounts of quartz, the main constituents being argillaceous substances. The rather weak structure shows main cracks with partial dissolution of the mineral structure. A certain lamination is also indicated.

Fig. 50 shows an oval particle with interior dissolution and cracking, indicating a degree of strength and solidity of the structure similar to that found in many porous calcareous flints.

Fig. 51 shows an oblong particle of a strongly foliated structure, containing bands of coarse crystalline quartz. The cracks can be seen to follow the directions of stratification of the rock, and it is obvious that the structural strength of this rock was considerable, even after the reaction. The feature of reactivity in this particle may be described as open, folded main-cracks.

Fig. 52 shows a wedge-shaped, highly stratified particle of quartz, mica and some argillaceous material. The crack formations mainly follow the direction of the stratification. It is noteworthy that a crack through the surrounding mortar traverses the particle.

Fig. 53 shows how the traversing crack penetrates the stratified particle structure. Cracks form along the strata after which tensile failure occurs in the remaining layers according to a statistical 'placing' of weak areas and stress concentrations. Thus, failure in a stratified mineral, with dissolution of substance in the longitudinal direction is very similar to tensile failure in fibrous materials such as, for example, wood.

A mortar bar cast with a Norwegian basaltic sand (part of investigations carried out at the University of Oslo) was sent to the writer for preparation of a thin section when the bar had expanded and shown gel exudations. *Figs. 54 to 61* incl, demonstrate the effect of reactivity in basalt grains of a heterogeneous, polymineral structure, where the reactive constituent is probably volcanic glass.

Fig. 54 shows a triangular particle with a distinct, somewhat ramified, traversing main-crack. Gel has precipitated in an open surface void underneath the particle. Above the particle, the crack continues out into the surrounding mortar, and a void has become filled with gel.

Fig. 55 shows the void (originally an air bubble formed against the side of the mould during casting of the mortar bar), with gel deposits along the wall. The flat, innermost part of the void is the surface of the basalt particle.

Fig. 56 shows the passage of the main-crack through the basalt particle and out into the surrounding mortar, where it traverses a spherical void (0.2 mm dia.) now filled with gel. The cement paste surrounding this bubble appears dark due to impregnation with leaching gel.

Fig. 57 shows a basalt particle with such extensive internal dissolution and structural decomposition that irregular, internal map-cracking occurs together with apparently secondary cracks inside the particle rim. Numerous gel-filled cracks radiate out from the particle into the surrounding mortar.

Fig. 58 shows a detail of the rim zone of the particle, with extensive crack formation. The rim zone consists of a 50 to 80 micron thick homogeneous, submicroscopic or isotropic substance. The crack development is not easily deduced in a complex case such as that in question, but this much can be said: Slanting upwards towards the left of the particle there is a main-crack, which ramifies in the rim zone and then follows a more diffuse course (rather indistinct in the photograph) as gel-filled cracks in the surrounding paste. To the right there is a corresponding opening of the rim by microcracks, but the main cracking leading to these from inside the particle seems to have been intensified - or, by virtue of the structural decomposition, formed - through shrinkage before or during drying of the mount.

Fig. 59 shows an oblong, rounded, rather fine-grained basalt particle with cracks following the longitudinal stratification.

Figs. 60 and *61* show two rather coarse-grained basalt particles with such badly corroded rim zones and intensive gel impregnation of the surrounding paste that the reaction picture is very reminiscent of the particle shown in *fig. 26* etc. *Fig. 61* shows gel in two adjacent bubbles, together with a secondary crack (presumably due to drying shrinkage) running through these bubbles and straight through the particle.

Figs. 62 and *63* show a reacted shale particle in a concrete sample from Nebraska, USA, which was given the writer by L. S. Brown, through the Portland Cement Association. The distinctly stratified structure of rather weak material that has dissolved during the reaction shows main-cracks oriented partly in the direction of the strata and partly towards the corners of the particle. The parallel crack structures 'collect' in the corners, and from here, ramified and gel-filled cracks run out into the surrounding mortar. The particle is a typical example of reaction phenomena in an angular particle shape and a fine-grained, homogeneous, stratified structure which is mechanically weak and partially reactive. Comparison with the Danish 'dog's liver', see (2681) figs. 50, 51 and 52, seems natural. These particles were also of an argillaceous rock, although not stratified. The cracking took place mainly during drying subsequent to their reaction with sodium hydroxide.

It will be seen from the illustrations to this survey of reaction phenomena in and at reacted aggregate particles that there is a conspicuous difference in the particle shape in relation to the mineral structure.

Particles of porous flint have a distinct tendency to be rounded, with an ellipsoidal perfect shape. This is a natural consequence of the fact that this fine-grained, rather soft and porous rock in Danish aggregates mainly comes from marine or glaciofluvial sediments (sand and gravel deposits).

Particles of dense flint come from the same deposits, but especially in material subjected to marine erosion, the hardness, brittleness and homogeneity of the dense flint make the perfect shape, tetrahedral or flat, lense-shaped, in both cases with worn edges. Among the polymineral rocks (basalt and phyllite), both the above-mentioned particle shapes are seen, together with more irregular, angular particles that have been only slightly eroded after breaking off from the primary deposit. The particle shape has been taken into consideration in recording the typical phenomena of reaction given in the diagrams in *plates XIII, XIV* and *XV*.
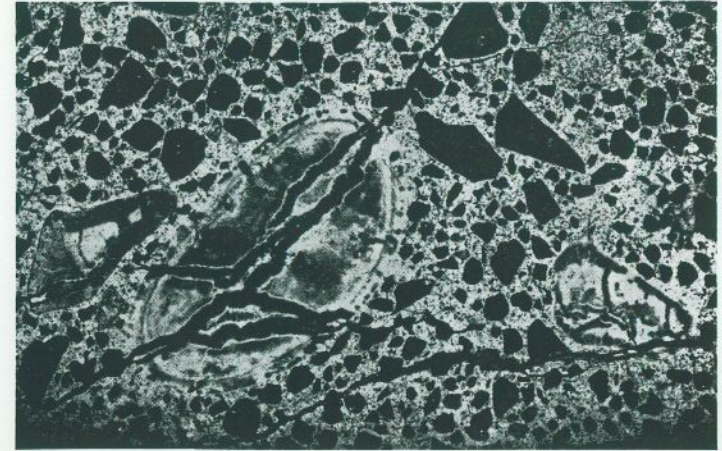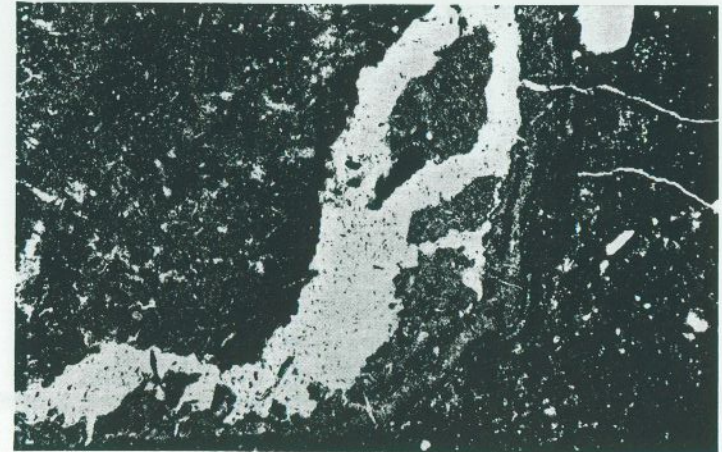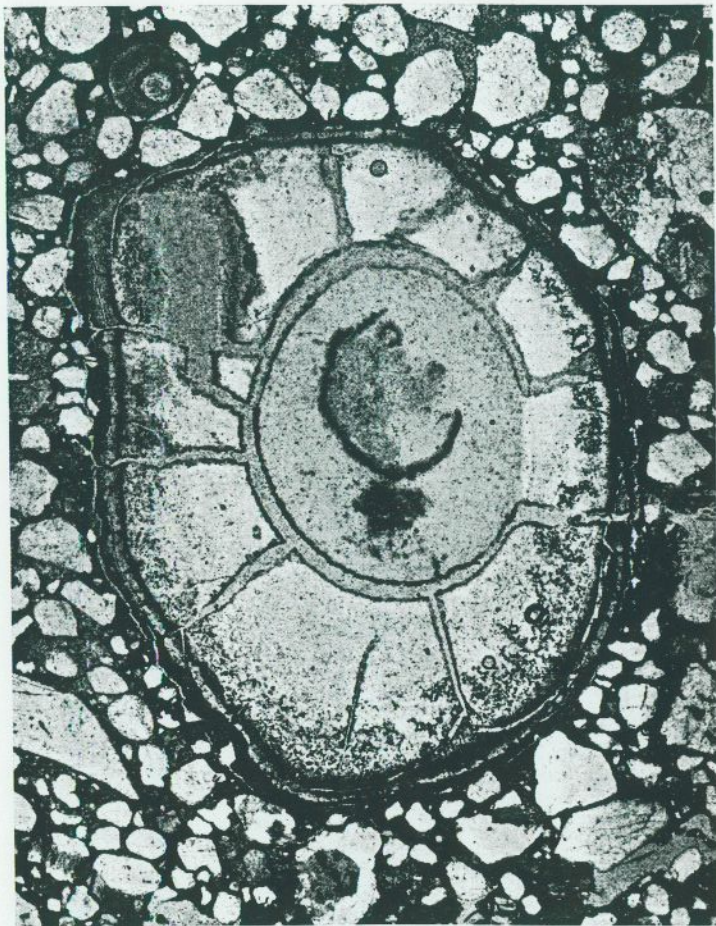

Fig. 16. Three reacted particles of porous flint (the mottled effect is due to impregnation with araldite) in thin section made from a concrete core, Oddesund Bridge. The mineral substance is partially dissolved, but the main-cracks show that a certain solidity and mechanical strength are retained. There is marked zonal dissolution along the main-cracks which continue into the surrounding mortar. From (3971). Thin section No. 54.5.30-10. V.

Key to the symbols in figure texts is to be found on page 120.

Fig. 17. Reacted pebble of porous flint in thin section of concrete core, Oddesund Bridge. Extensive dissolution of the amorphous main mass of the mineral substance has taken place. The undissolved chalcedonic fossil remains have not prevented deformation and drying shrinkage of the residual material. From (3971). Thin section No. 54.5.13-5. O.

[1 mm]

Fig. 18. Reacted particle of porous flint completely altered into a viscous gel which has dried and shrunk without impediment during the laboratory treatment of the concrete. The completely dissolved particle may originally have included chalcedonic components, since the concrete in question is from a concrete caisson cast in 1912 in the harbour of Ålborg and has been exposed to sea water since that time. From (2917). Thin section No. BFL 4-3. ○.
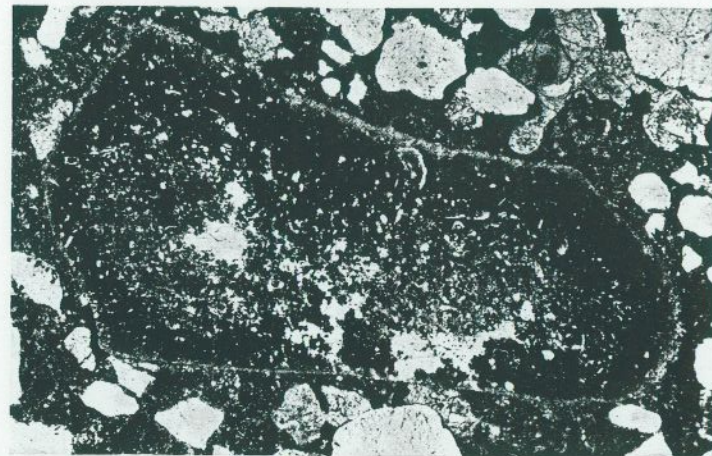

[1 mm]

Fig. 19. Reacted particle of porous flint in thin section of concrete core, Oddesund Bridge. The interior structure of the flint is highly dissolved and altered into a dark gel, but there are no cracks in the surrounding matrix. Thin section No. 54.5.70-4. ○.

Fig. 20. Reacted particle of porous flint in thin section of concrete core, Oddesund Bridge. The interior structure of flint is highly dissolved and altered into gel. There are no cracks due to swelling pressure in the surrounding matrix, but there is a dark zone of cement paste adjacent to part of the particle boundary. This indicates impregnation of the cement paste with exuding gel. A few indistinct cracks from a quartz particle to the flint indicate drying shrinkage of the remnant of the particle. From (3971). Thin section No. 54.5.30-8. ○.


[0.5 mm]

1 mm
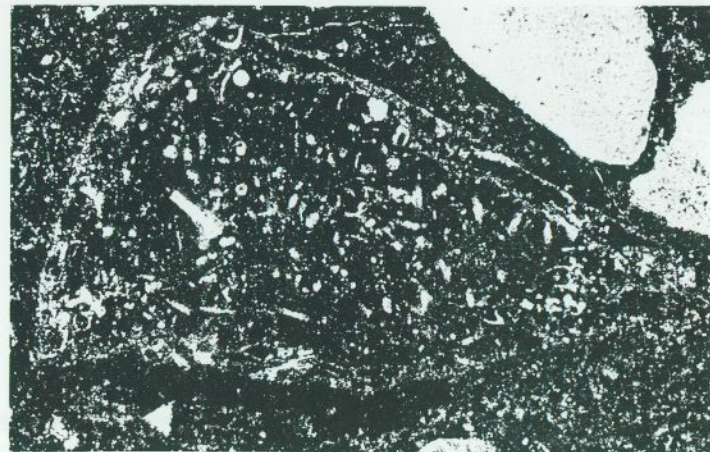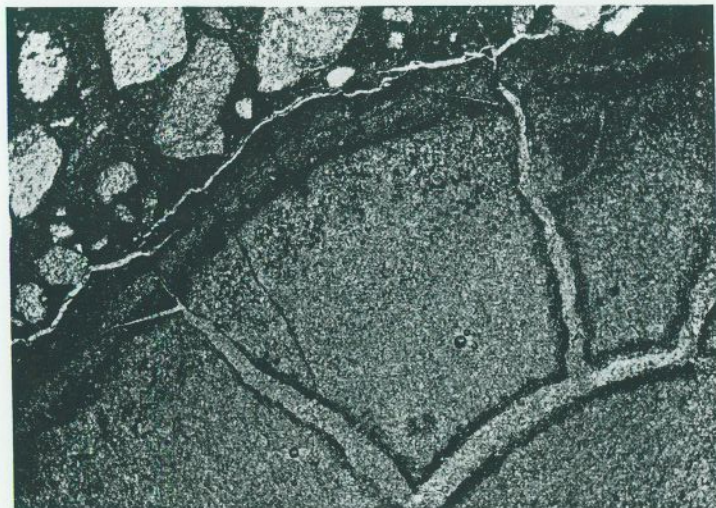
1 mm

Fig. 21. *Part of reacted porous flint particle shown in fig. 18. Excessive drying shrinkage of the 'softened' mineral substance has caused the particle rim to crack away from the surrounding cement paste or, at some places, the cement paste to crack conformably with the particle rim. There is no cracking between the reaction rim and the interior of the particle. Thin section No. BFL 4-3.* ○.

Fig. 22. *Reacted particle of porous flint in thin section of concrete core, Oddesund Bridge. The particle, with its gel-filled cracks radiating into the surrounding matrix, is typical of alkali-aggregate reaction. Chalcedonic parts of the particle (light areas in the picture) have remained unaltered and solid during reaction. The very light part in the interior of the particle is where part of the mineral substance has been abraded during preparation of the thin section. From (3971). Thin section No. 54.5.13-3.* ○.
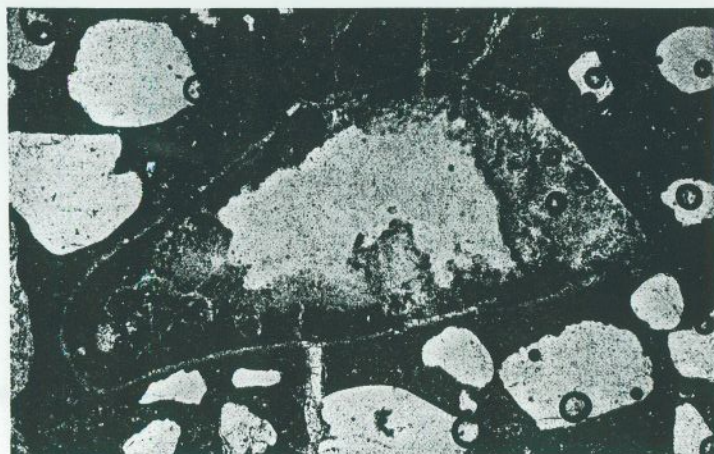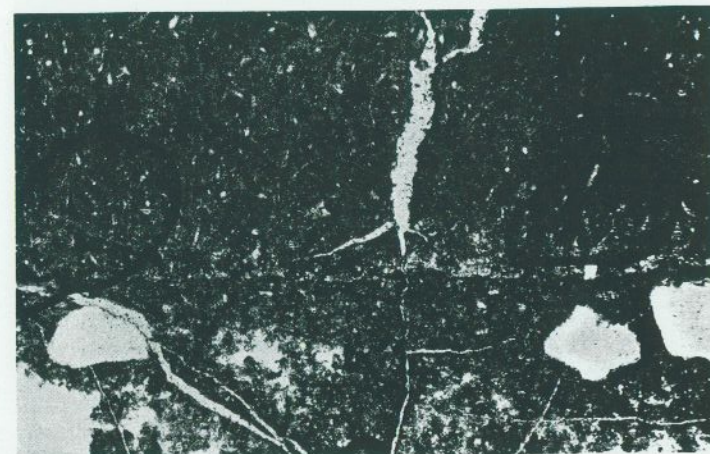
1 mm

Fig. 23. *Detail of reacted pebble of porous flint in thin section of concrete core, Oddesund Bridge. Swelling of the particle has produced a crack in the paste perpendicular to the rim of the particle. Subsequent shrinkage has caused parts of the paste 'to follow the particle', and a system of secondary cracks in the paste has been superimposed on the original expansion crack. A succession like this of shrinkage following expansion must be excepted when swelling gel has developed in porous flint. The dark rings are air bubbles which have developed between the cover glass and the thin section during some years' storage in the laboratory. From (3971). Thin section No. 54.5.13-5.* ○.

Fig. 24. *Detail of reacted particle of porous flint in fig. 18 and 21. Cracks due to drying shrinkage are seen in the altered interior of the particle and in the cement paste along the particle boundary. There is no tendency to cracking between the reaction rim and the interior of the particle. Thin section No. BFL 4-3.* ○.
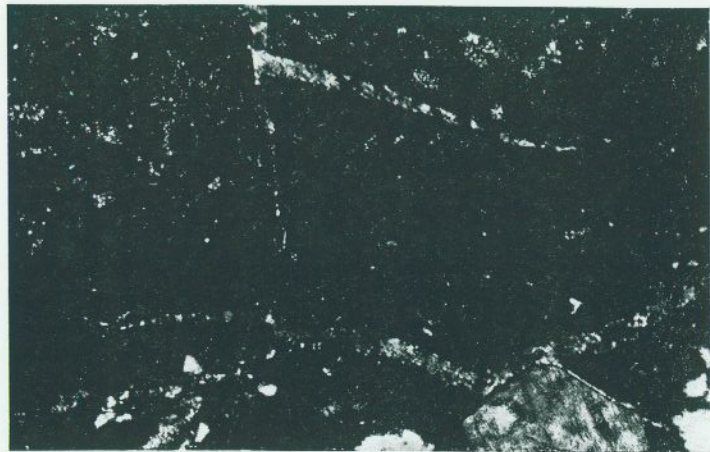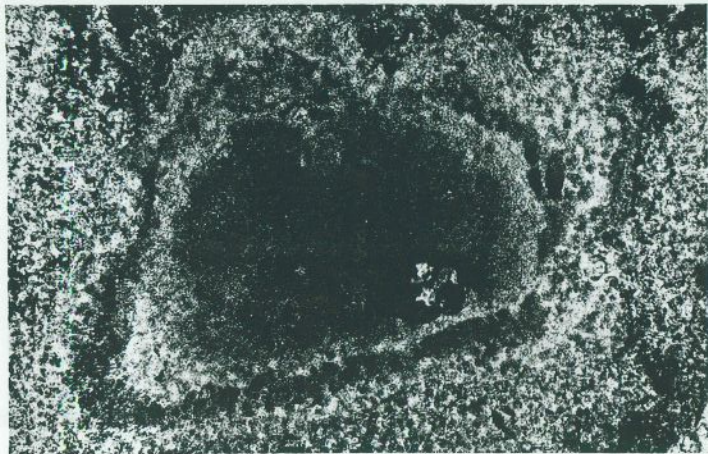

0.1 mm

Fig. 25. As fig. 24, polars crossed. The distinct isotropy of the reaction rim is shown, contrasting the optical character of both the cement paste and of the interior of the particle. Thin section No. BFL 4-3. Ø.

Fig. 26. Reacted particle of porous flint in thin section of concrete specimen from the outside of exterior wall of bascule pier, Oddesund Bridge. The interior of the particle has been altered to isotropic gel. The rim area contains much secondary crystalline calcite. Elsewhere, the thin section shows strong evidence of intense alkali-aggregate reaction and sulphate attack. From (3971). Thin section No. I-440-[54.5.101]. O.
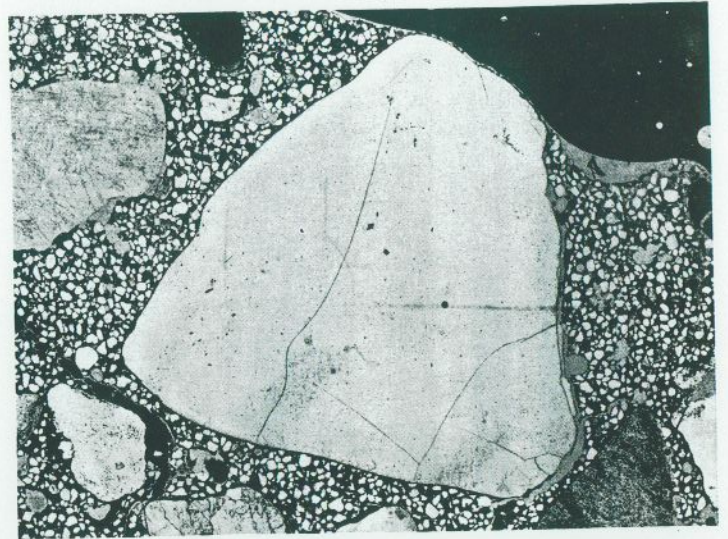
Fig. 27. Pebble of dense black, homogeneous flint in thin section from concrete specimen in groyne block, north barrier of the Lim Fiord. The pebble is traversed by narrow, almost closed main-cracks which cannot have been present when the concrete was placed. Minor cracks extend only a short distance inwards from the boundary, and gel is present in the crack which separates part of the periphery of the pebble from the surrounding mortar. The phenomena described are considered evidence of moderate alkali-aggregate reaction. From (2910). Thin section No. G 19-34-[44.13.1-(5908)]. II.
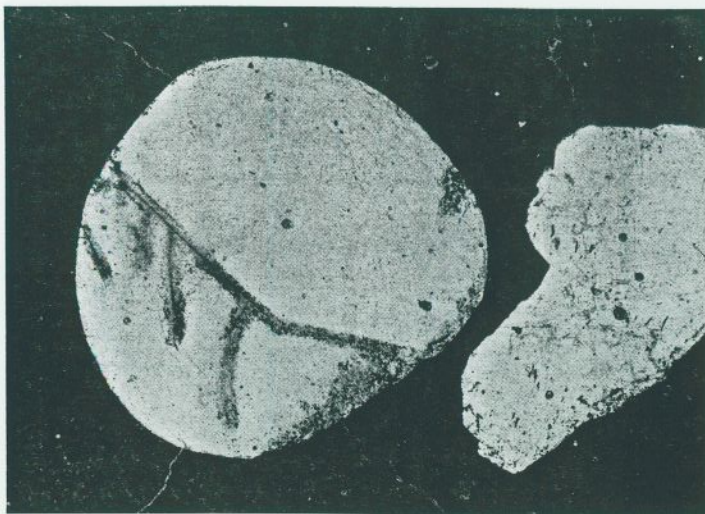
Fig. 28. Reacted pebble of dense black, homogeneous flint in a test prism in which a prepared cylindrical flint bar had been embedded in Portland cement mortar of 6.0 per cent eqv. Na_2O (NaOH was added to the mixing water to provide this concentration). The thin section was prepared by sectioning the prism perpendicular to the axis of the flint bar, when cracking of the prism had been observed together with exudation of gel through the cracks. The photograph shows poorly developed main-cracks traversing the pebble, with zonal dissolution of the mineral substance along the cracks and at some places at the boundary. From (2681). Thin section No. G 20-93-[F 59.2.(3-4)b]. II.
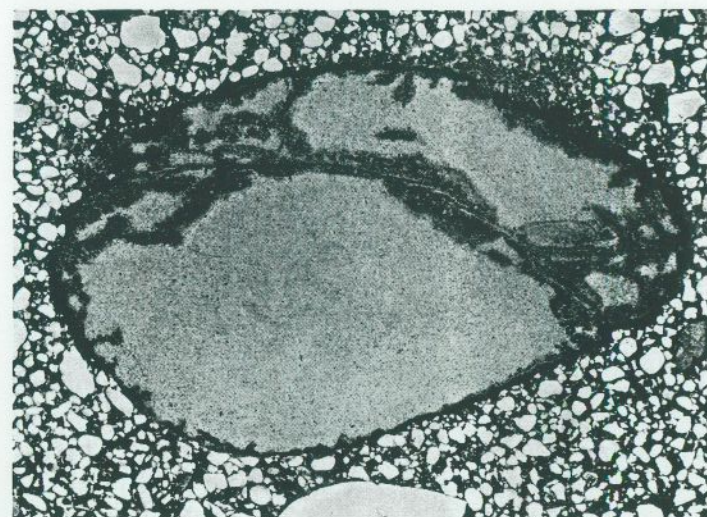
Fig. 29. Reacted pebble of dense flint in thin section of concrete specimen from factory chimney. The pebble is traversed by narrow, open cracks along which advanced alteration of the mineral substance has taken place. Alteration has also been severe in a narrow zone at the rim of the pebble (rim corrosion). At some places a main-crack separates the reaction rim from the interior of the pebble, i. e. the bond between the boundary and the surrounding paste has been stronger than that between the altered mineral substance and the reaction rim. The alteration may have been the first step of reaction if the pebble originally contained relatively porous parts where cracking could then follow the mechanical weakening of the structure. Or, a traversing crack may have developed in the pebble as a result of the accumulated hydraulic pressure in the submicroscopic pores of the flint and visible alteration can have accompanied the crack development as the second phase of reaction. Thin section No. BFL 4-6. II.

1 mm

5 mm

Fig. 30. *Reacted particle of dense flint in thin section of concrete core, Oddesund Bridge. The picture is typical of alkali-aggregate reaction in dense flint in Danish concrete. The broad, open main-cracks have allowed gel to 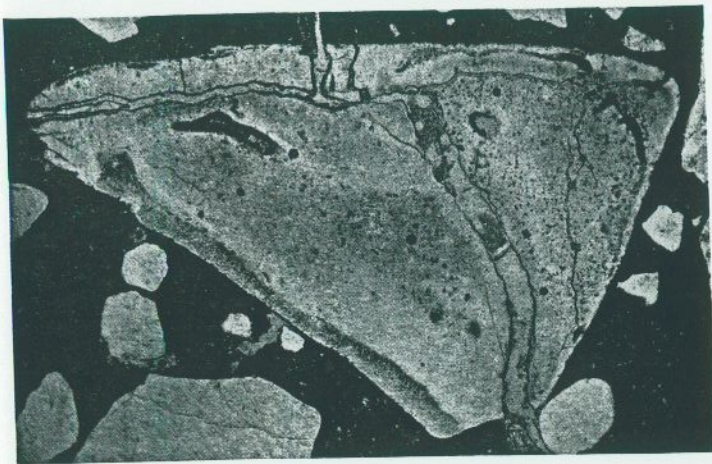flow from the altered rock into cracks radiating into the surrounding cement paste. Inside the particle the pattern of cracking may have been determined by the presence of relatively porous and possibly opaline parts of the particle. From (2681). Thin section No. 54.5.13-6.* ○.

Fig. 31. *Reacted pebble of flint partly porous calcareous (dark in picture) and partly dense chalcedonic (light in picture), in thin section of concrete specimen from groyne block, north barrier of the Lim Fiord. The porous part is severely cracked, and partial dissolution and weakening of the mineral substance can be seen. The boundary of this part of the pebble is at some places almost 'opening up' towards the surrounding mortar. The dense part of the flint appears to be almost unaffected. From (2910). Thin section No. G 22-[44.13.2-(5908)].* ||.

1 mm

Fig. 32. *Reacted pebble of partly porous, partly dense chalcedonic flint in thin section of concrete specimen from groyne block, north barrier of the Lim Fiord. (The same thin section as the pebble shown in fig. 31). The porous part of the flint shows intense dissolution and thorough cracking of the mineral substance. The dense part shows a clear cut, wide open main-crack continuing into the surrounding mortar. The increase in volume of the pebble caused by the cracking must mean a movement of the surrounding matrix. Thin section No. G 22-[44.13.2-(5908)].* ||.

Fig. 33. *Reacted pebble of dense chalcedonic flint in thin section of concrete core, Oddesund Bridge. The photograph shows a detail of the pebble where a traversing main-crack reaches the boundary via a 'delta' of curved and ramified cracks. This fractured area contains a concentration of pigmented substance, i. e. opaline, porous flint. It is mechanically weak compared with the compact chalcedonic substance forming the larger part of the pebble. A narrow gel-filled, slightly carbonated zone (in fact, a peripheral crack) is seen between the boundary of the pebble and the surrounding mortar. Thin ramifying cracks extend from this space into the mortar. The dark rings are air bubbles which have developed between the cover glass and the thin section during some years' storage in the laboratory. From (3971). Thin section No. 54.5.13-1. O.*

Fig. 34. *Reacted pebble of dense chalcedonic flint in thin section of concrete from the interior of bascule pier below water level, Oddesund Bridge. The picture shows extensive main-cracking in the boundary area of the pebble, and alteration of the boundary itself to a pigmented, amorphous substance extending into the adjacent cement paste. This is the phenomenon designated rim corrosion, see also fig. 29. Thin section No. G 22-[54.5.118]. O.*
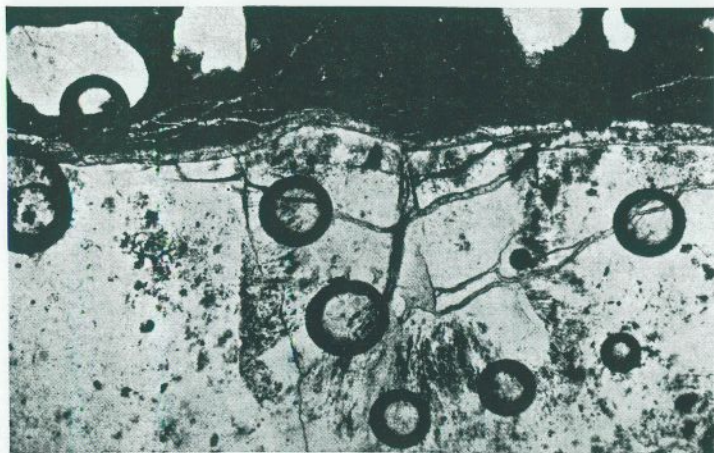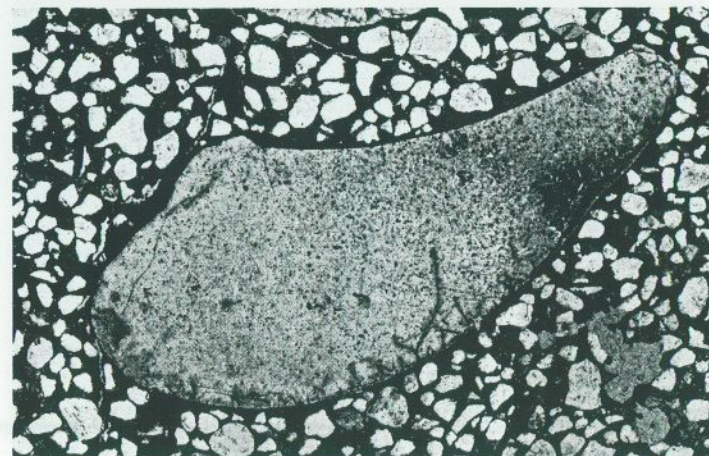
Fig. 35. *Reacted pebble of dense chalcedonic flint in thin section of concrete specimen from groyne block, north barrier of the Lim Fiord. Narrow cracks emphasized by dissolution of the adjacent mineral substance are numerous on one side of the pebble. Gel is present in connecting cracks in the mortar. From (2910). Thin section No. G 19-34-[44.13.1-(5908)]. II.*

1 mm
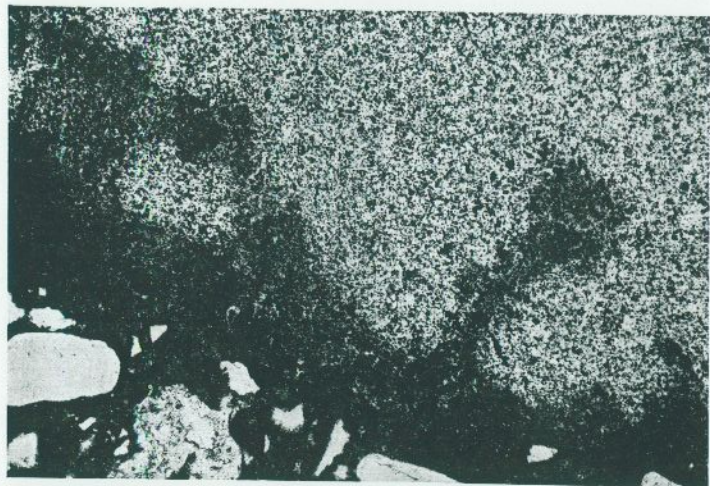
1 mm

Fig. 36. *Detail of boundary of the reacted pebble of dense flint shown in fig. 29. Extensive rim corrosion has taken place and the exact location of the edge of the particle is obscured. The alteration of the flint has progressed inwards along cracks similar to those shown in figs. 34 and 35. Thin section No. BFL 4-6.* ○.

Fig. 37. *Unreacted pebble of dense chalcedonic flint from submarine gravel deposit off the Skaw, Jutland. The thin section was made of the pebble in its natural condition. Thus, the rim cracks and the apparent dissolution along the cracks must be due to natural action, i. e. surf impact and slow silica dissolution by sea water. The surface character shown may be an important factor in the development of bond strength in sound concrete. In cases of alkali-aggregate reaction, the surface character may facilitate the development of gel in pebbles of dense flint. Thin section No. BFL 3-13.* ‖.
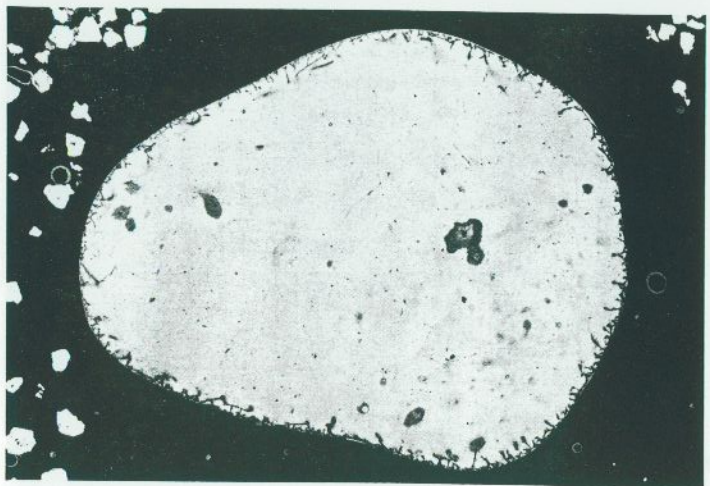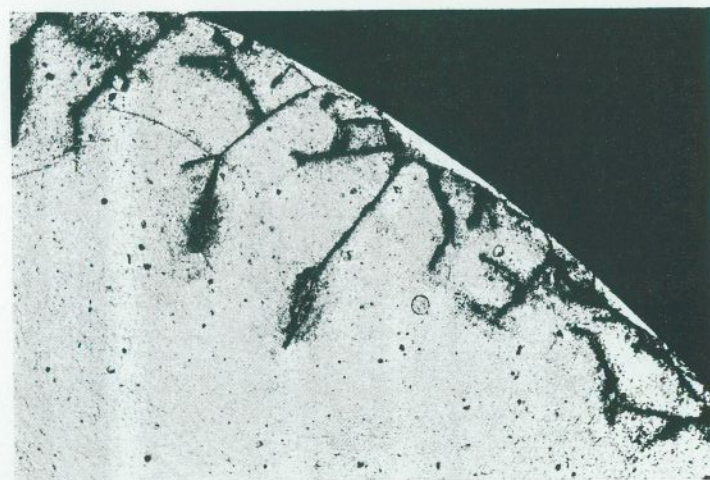
Fig. 38. *Detail of the boundary of the pebble in fig. 37. The picture emphasizes the type and extent of the microscopic surface cracking and the slight dissolution of mineral substance along the cracks. These phenomena represent the mechanism by which dense flint pebbles are rounded and comminuted by marine erosion. Polymineral or laminated rocks etc. can be expected to show other phenomena of erosion to be predominant. Thin section No. BFL 3-13.* ○.

Fig. 39. *Unreacted pebble of dense chalcedonic flint from the same deposit as the pebble shown in figs. 37 and 38. The thin section was made from the pebble in its natural condition. In this case the surface cracking is indistinct. Thin section No. BFL 3-12.* ‖.

10 mm

10 mm

0.5 mm
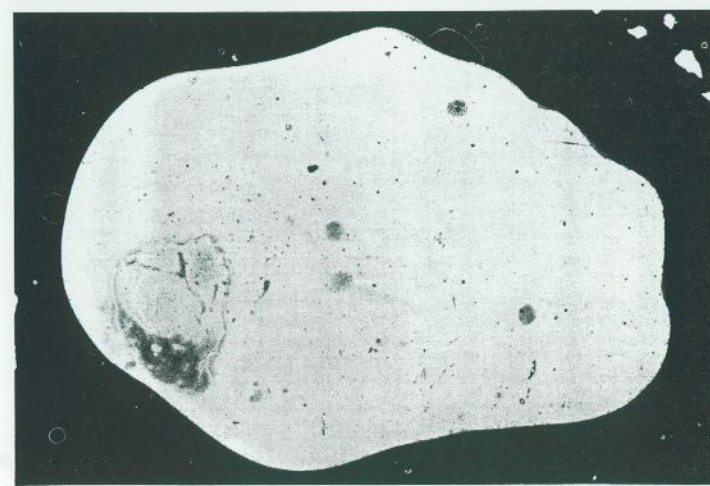
5 mm
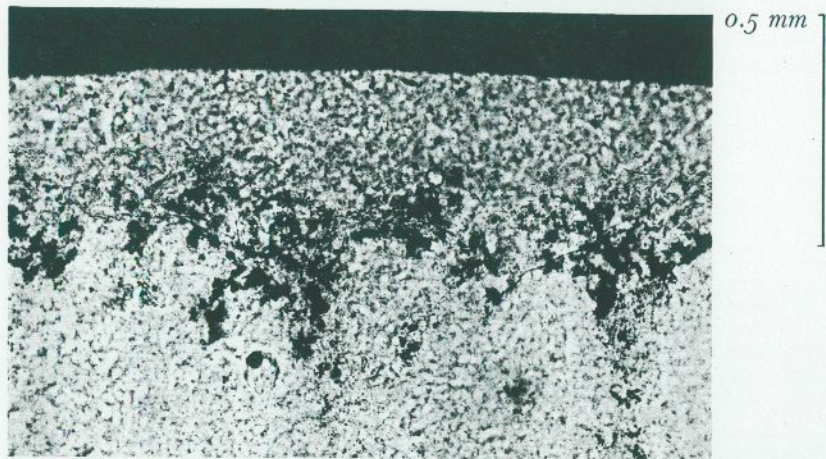
Fig. 40. Detail of boundary of the pebble shown in fig. 39. The microscopic surface cracking at the edge is not as deep as with the pebble shown in figs. 37 and 38. Thin section No. BFL 3-12. ◯.

Fig. 41. Unreacted pebble of dense chalcedonic flint from submarine deposit off the Skaw. The section was made from the pebble in its natural condition and was not ground down to usual thickness (20 microns). The pebble originally had the appearence of ordinary dense black flint. Preparation of the section revealed that the black colour was confined to the outermost surface layer. Inside, as can be distinguished in the picture, is a narrow brown zone around the grey interior mass of dense flint. It must be assumed that the originally grey flint was first stained brown in a glacial deposit on land by the penetration of ground water containing ferric iron. Later, in the marine deposit, reduction of the outermost layer must have taken place. Thin section No. BFL 5-2 (unfinished). ∨.
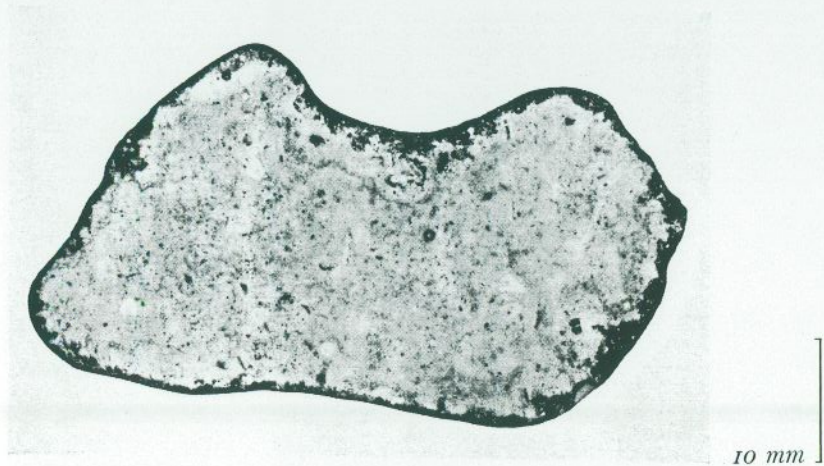
Fig. 42. Unreacted pebble of dense flint from glacial or glaciofluvial deposit on land. The thin section was made from the pebble in its natural condition. The darker zone at the edge shows where brown staining caused by the penetration of ground water containing dissolved ferric iron has occurred. The surface of the pebble was smooth. Thin section No. BFL 5-3. ||.

Fig. 43. Two pebbles and a broken fragment of dense flint demonstrating the character of natural surface corrosion shown in figs. 37-42. The pebble to the left is from a submarine deposit and shows severe surface scarring and pitting, reflecting impact and wear from surf erosion. The gravel pit pebble in the middle shows an abraded but smooth surface, partly even waxy. The broken faces of the piece of primary flint taken from a limestone formation, show very even and smooth surfaces. (There is some evidence from archaeology that flint submerged since the Stone Age in acidic fresh water can attain a quite polished surface).

10 mm

100 mm

0.5 mm
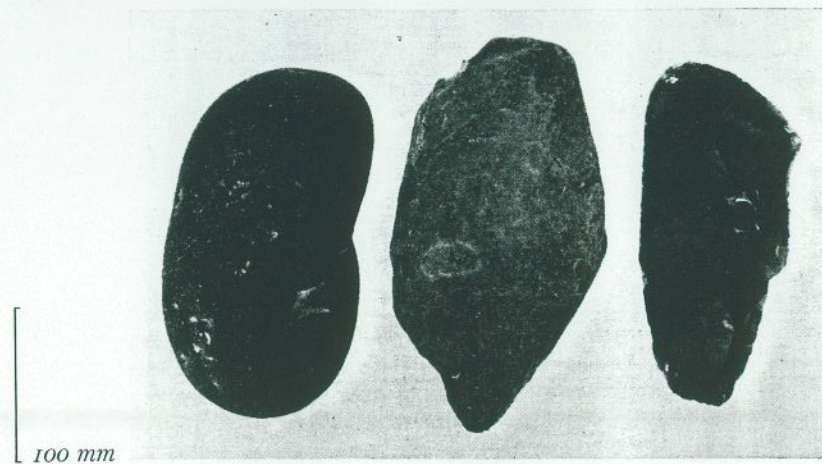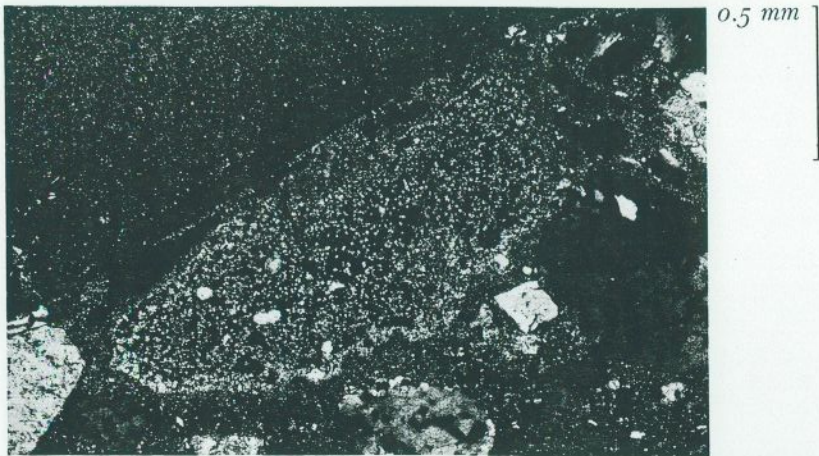
Fig. 44. Particle of dense flint in thin section of a lime mortar from a 600 years old wall of church near Randers, Jutland. It must be assumed that repeated repair work and lime-washing of the mortar in the course of time have enhanced reaction between calcium hydroxide and the flint substance. The extensive rim corrosion of the particle is attributed to this reaction. A slight reactivity of this kind may take place invisibly in ordinary concrete and contribute to the development of bond between any acidic rock particle and the adjacent matrix. Thin section No. BFL 2-9b. Ø.

Fig. 45. Quartz particle in the thin section of mortar from church wall, fig. 44. The quartz has probably been affected by the same kind of reaction as the flint in fig. 44, but in this case the result must be designated rim corrosion. Previously published by P. Nepper-Christensen (5522). Thin section No. BFL 2-9b. Ø.

0.1 mm
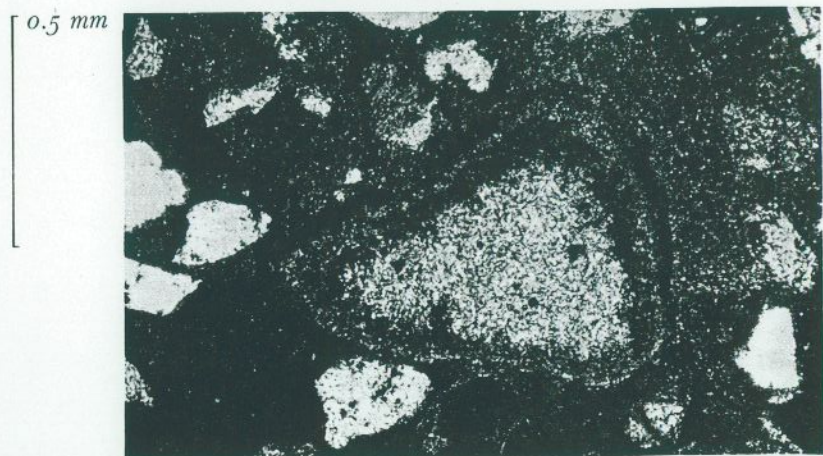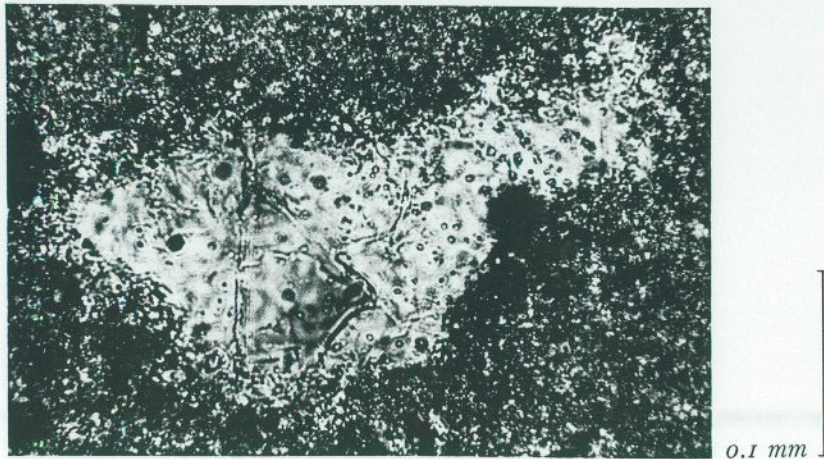
Fig. 46. Particle of dense flint in thin section of Roman mortar from Caesarea, Israel. The particle shows severe rim corrosion similar to the phenomenon in fig. 44. Hydrated calcium silicates are presumably primary reaction products, but the optical character of the altered rim substance does not allow microscopic identification. The same thin section showed intense rim corrosion of the quartz grains and advanced dissolution of a plagioclase particle. Thin section No. BFL 3-48. Ø.

0.5 mm

Fig. 47. Oblong particle of phyllitic rock, with quartz as the main constituent, in thin section of Norwegian concrete with alkali-aggregate reaction. The longitudinal main-crack follows the indistinct stratification in the rock structure. Subsidiary cracks in the same direction can be distinguished. Thin section No. Rosenqvist 60. O.

0.5 mm
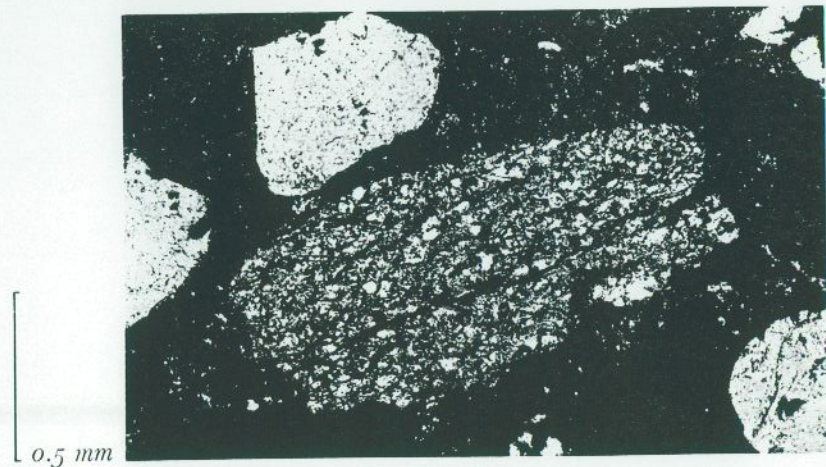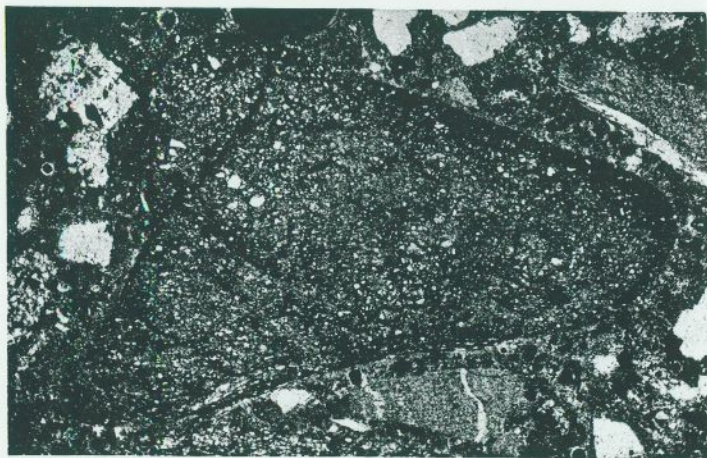
Fig. 48. Triangular pebble of phyllitic rock in thin section of Norwegian concrete with alkali-aggregate reaction. The particle has quartz grains scattered in the rather amorphous ground mass. The reaction has resulted in mechanical weakening and irregular cracking and distortion similar to that found after reaction in some types of porous flint. Thin section No. Rosenqvist 58. ○.

Fig. 49. Compact rounded particle of phyllitic rock in thin section of Norwegian concrete with alkali-aggregate reaction. The main constituents are argillaceous substances which contain a few scattered quartz grains. The shapes of the traversing main-cracks and of the subsidiary narrow cracks indicate partial dissolution and mechanical weakening of the rock structure during the reaction. Thin section No. Rosenqvist 58. ○.
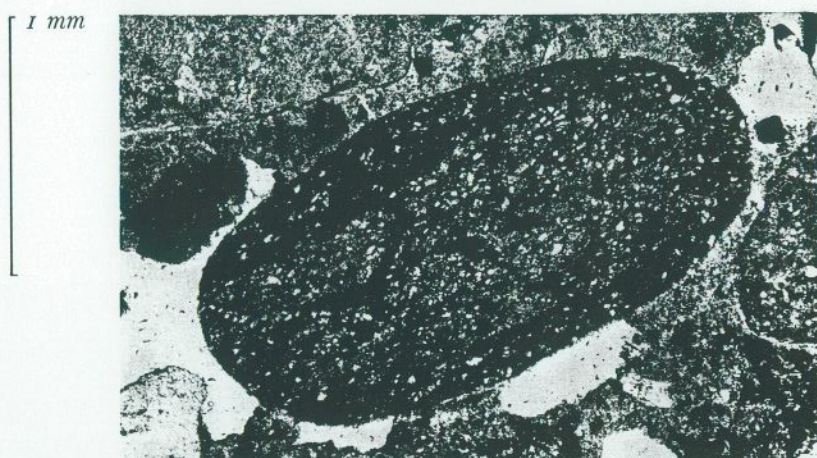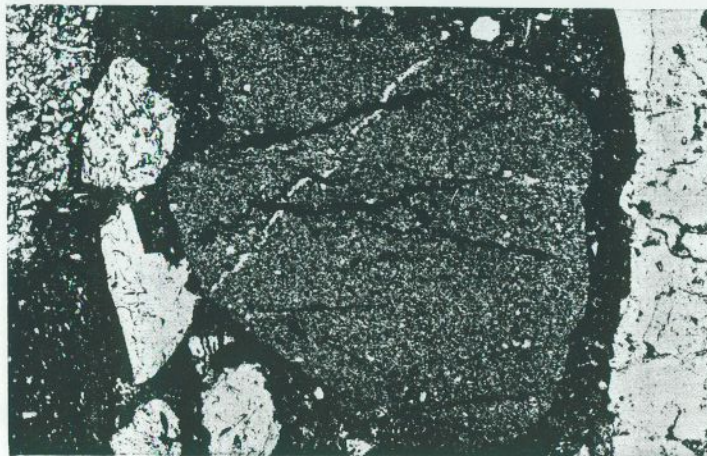
Fig. 50. Oval particle of phyllitic rock in thin section of Norwegian concrete with alkali-aggregate reaction. The particle shows a distinct dark reaction rim and interior dissolution and disruption of the structure, very much as when porous, calcareous flint has reacted. Thin section No. Rosenqvist 58. ○.

Fig. 51. Oblong pebble of a strongly foliated phyllitic rock, containing banded crystalline quartz, in thin section of Norwegian concrete with alkali-aggregate reaction. Narrow, open main-cracks follow the direction of the foliation of the structure which to a great extent seems to have kept its mechanical strength, very much as when dense flint reacts. Thin section No. Rosenqvist 58. ○.

0.5 mm

1 mm
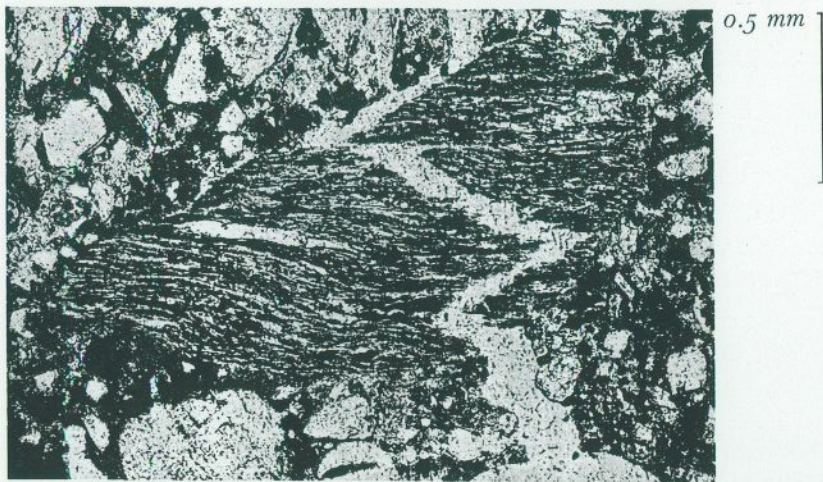
Fig. 52. *Wedge-shaped particle of laminated phyllitic rock in thin section of Norwegian concrete with alkali-aggregate reaction. Dissolution and cracking have followed the direction of the layers of the rock structure. A connecting crack traverses the particle. Thin section No. Rosenqvist 56.* ○.

Fig. 54. *Triangular particle of basaltic rock in thin section of Norwegian mortar bar which had expanded due to alkali-aggregate reaction. (Only basaltic particles showed evidence of reaction). A distinct, somewhat ramified traversing main-crack continues into the surrounding mortar. A void, originally an air bubble on the bar surface and situated adjacent to the reacted pebble, is lined by the exuded gel. Thin section No. Rosenqvist 627/3-60.* ‖.

Fig. 53. *Detail of particle shown in fig. 52. The photograph shows how the dissolution has 'opened up' the laminated structure of the rock. The traversing crack has taken a random, zig-zag course through the reacted particle, like a tensile fracture in the fibrous structure of wood. Thin section No. Rosenqvist 56.* ○.

Fig. 55. *Detail of particle in fig. 54. Gel is lining the wall of the bubble at the boundary of the reacted basalt particle. The gel shows the typical 'glass-fragment' appearance. Thin section No. Rosenqvist 627/3-60.* ○.

0.1 mm

0.5 mm

0.5 mm
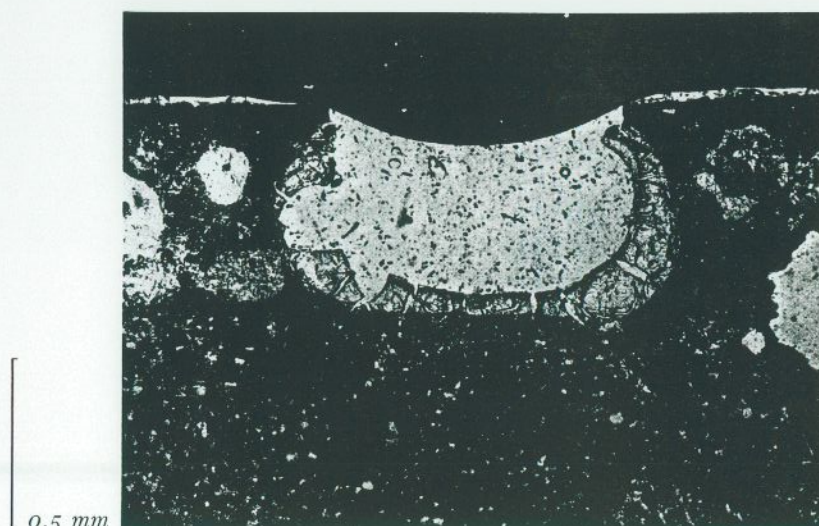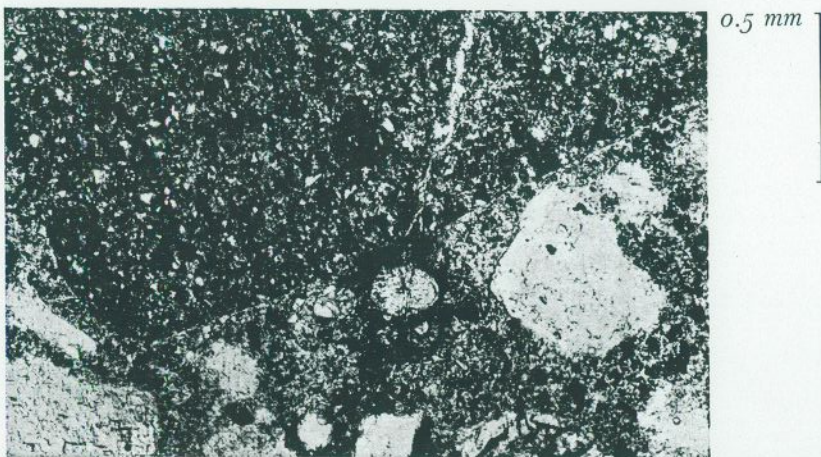
Fig. 56. Detail of particle in fig. 54, showing the traversing main-crack continuing into the surrounding mortar. The crack crosses a spherical void (0.2 mm dia.) completely filled with gel. The cement paste along the crack appears dark due to impregnation with gel. Thin section No. Rosenqvist 627/3-60. O.

Fig. 57. Rounded, compact pebble of basalt in thin section from the Norwegian mortar bar which had expanded due to alkali-aggregate reaction. The pebble shows extensive internal cracking and dissolution of the mineral substance. Cracks radiate out into the surrounding mortar where they are gel-filled. Thin section No. Rosenqvist 627/3-60. ||.

1 mm

0.1 mm
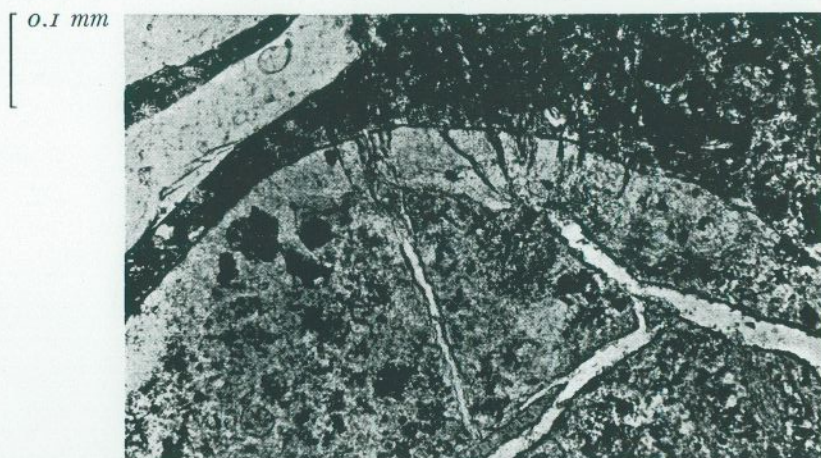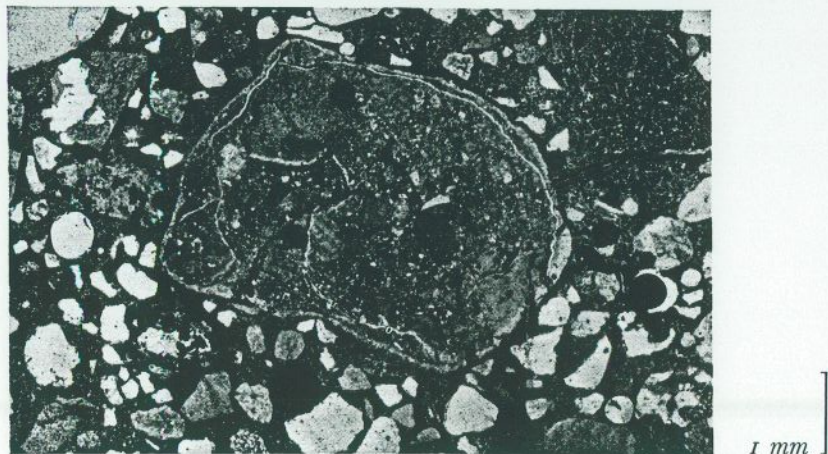
Fig. 58. Detail of basaltic pebble in fig. 57. A narrow rim zone has been altered to an isotropic substance, i. e. a reaction rim. Main-cracks from the interior of the pebble ramify through the reaction rim and continue (less distinctly) in the surrounding paste where they contain gel exuded from the pebble. Shrinkage during drying may have influenced the crack development. Thin section No. Rosenqvist 627/3-60. O.

Fig. 59. Oblong particle of rather fine-grained basalt in thin section of Norwegian mortar bar which had expanded due to alkali-aggregate reaction. The particle shows longitudinal, though indistinct cracking, extending into the surrounding mortar at one end of the particle. Thin section No. Rosenqvist 627/3-60. O.
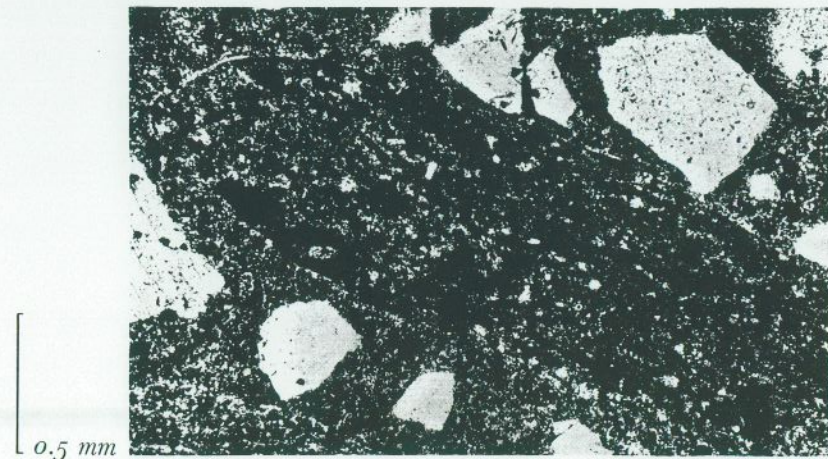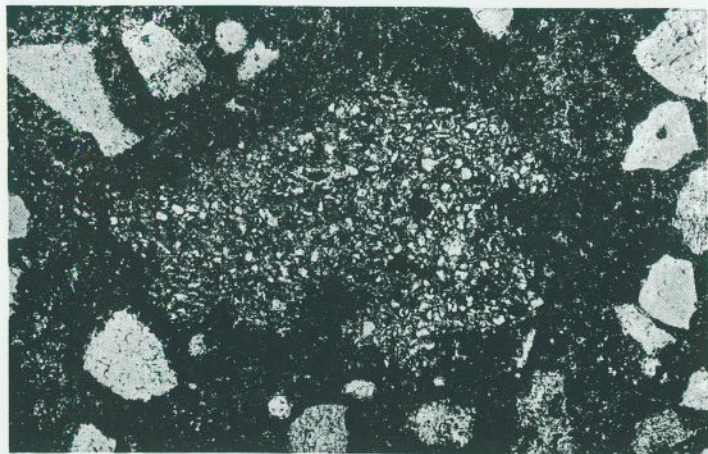
0.5 mm

0.5 mm

Fig. 60. *Particle of basalt in thin section of Norwegian mortar bar which had expanded due to alkali-aggregate reaction. The particle shows severe rim corrosion. The surrounding cement paste is gel-impregnated. Thin section No. Rosenqvist 627/3-60.* ○.

Fig. 61. *Particle of basalt in thin section of Norwegian mortar bar which had expanded due to alkali-aggregate reaction. The particle shows severe rim corrosion, and the surrounding cement paste is impregnated with gel. Gel has precipitated in two air bubbles close to the particle, while other smaller bubbles in the vicinity have remained empty. Thin section No. Rosenqvist 627/3-60.* ○.
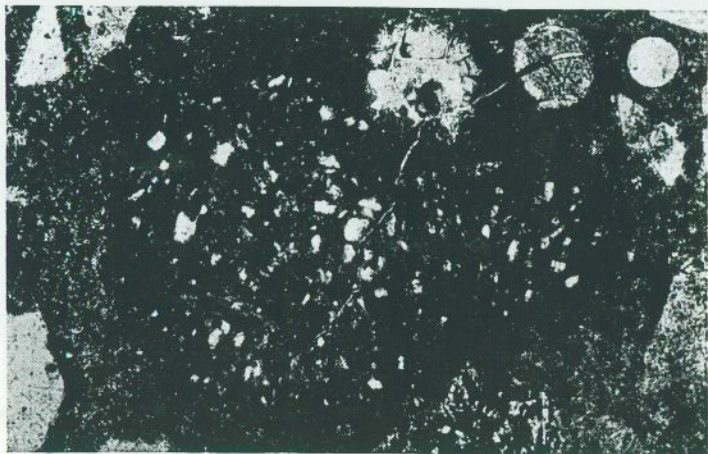
0.5 mm

1 mm
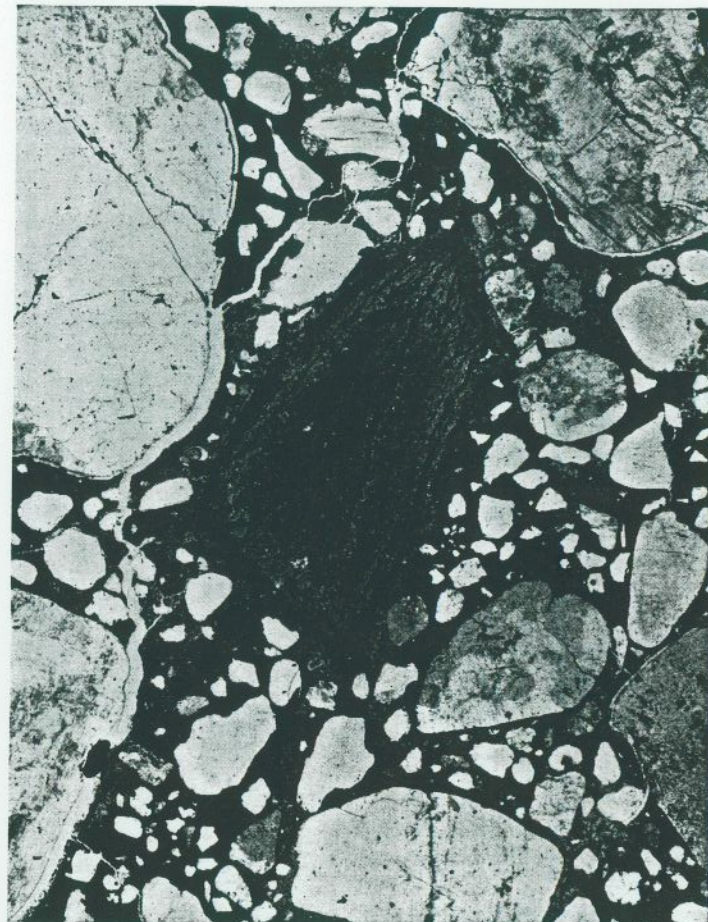
Fig. 62. *Reacted shale particle in thin section of concrete from Nebraska, USA. The rather weak, stratified rock shows main-cracks which follow the direction of the strata, bending and gathering towards the corners of the particle. Ramified gel-filled cracks continue into the surrounding mortar. A reaction rim can be distinguished at the boundary of the particle. Thin section No. BFL 4-2.* ||.

Fig. 63. Detail of reacted shale particle, fig. 62. The extensive cracking in the interior of the particle, the main directions of the cracks, and the dark reaction rim, are easily discernible. Thin section No. BFL 4-2. ○.

Key to the symbols in figure texts

○ Transmitted light. Exposure in the microscope. Polars not crossed. Light areas represent transmittance of light.

∅ Transmitted light. Exposure in the microscope. Polars crossed. Light areas represent transmittance of light.

‖ Transmitted light. Exposure with thin section in the enlarger. Polars not crossed (polarizing filters mounted on the enlarger). Light areas represent transmittance of light.

✕ Transmitted light. Exposure with thin section in the enlarger. Polars crossed (polarizing filters mounted on the enlarger). Light areas represent transmittance of light.

∨ Reflected light. Direct camera exposure of object.

Plate XIII shows the principal types of reaction phenomena in porous flint. It is characteristic that most of the particles of porous flint in the material investigated showed symptoms of chemical action, i. e. dissolution of a greater or smaller part of the mineral structure.

Plate XIV shows the principal types of reaction phenomena in dense flint. It is characteristic that most particles of dense flint in the material investigated showed no symptoms of reaction.

Plate XV shows the principal types of reaction phenomena in angular and rounded, stratified and homogeneous particles of phyllite and basalt, in which soluble silica is only a minor constituent of the rock.

To the left of *plate XIII*, the sketches show reaction phenomena inside particles. The series on the right continues with sketches showing effects in the surrounding paste. 1 and 2 show that if the particle structure is strong enough (or is reinforced by a content of inactive calcite), the reaction may cause the formation of internal, open main-cracks. In some cases, as shown in 2, these are accompanied by zonal discoloration, which presumably represents infilling of the porous structure along the main-cracks, thereby preventing the impregnating medium from penetrating into the body of the substance.

3 represents a porous flint, the structure of which has not been sufficiently rigid or open to form main-cracks, but firm enough for more irregular cracks to become visible. Having regard to the rather weak particle structure, which is partly dissolved during the reaction, it is probable that shrinkage of the remaining gel/mineral substance, either before or during the preparation, has been a contributory cause of the formation of the crack system.

4 represents a comparatively unusual reaction picture, characteristic in that the particle rim is partly broken and has a 'ragged' appearance out towards the surrounding cement paste and that the particle structure is, moreover, partially dissolved (as in 3).

5 represents such advanced dissolution and alteration of the porous structure that only insoluble chalcedonic residues are left as visible solids within the boundaries of the particle. This reaction picture is frequently accompanied by shrinkage phenomena.

6 represents an equally dissolved structure, but without remaining solid components. In this case, the 'perfect shape' comes from drying shrinkage, i. e. an uncracked core subjected to triaxial compressive stresses, relieved by tensile failure resulting in severance of the core from the outer parts, which remain in uninterrupted bond with the surrounding paste. This reaction picture, more or less obscured, is rather common, and corresponds to the interior of the particle having been altered to a mechanically isotropic gel that has hardened and dried out either before preparation (during natural exposure or storage of sample) or during preparation.

7 shows extensive internal dissolution (as in 5 or 6), accompanied by a dark rim zone in the cement paste surrounding the particle. From the observation material available, this phenomenon must be interpreted as an exudation of low-viscosity gel into surrounding cement paste of sufficient porosity to absorb the gel.

8 is a general representation of particles of porous flint with visible, internal chemical alteration, but with no cracks in the surrounding cement paste orig-

inating from the periphery of the particle. This reaction picture may, for instance, occur when a section cut at random through the particle does not include crack formations (very likely in irregular, long or flat particles).

9 and 10 show the most common consequence of the formation of expansive gel in reacting particles. At certain locations along the periphery, depending on the particle shape, the strength and density of cement paste, the morphology of the concrete, and the physico-chemical and mechanical conditions of equilibrium, etc, cracks are formed that radiate out into the surrounding mortar and concrete. This reaction picture is essential for the concept 'deleterious, harmful, expansive' alkali-aggregate reaction. The special, narrow rim of gel around the particle in 10 is frequently observed. Its presence cannot be explained on the basis of reaction phenomena in the particle in question, but it seems most likely that this is a case of gel exuding from other particles and entering a crack that has followed the rim of the particle instead of traversing it.

11 and 12 represent frequently observed combinations of crack formations like those mentioned above and shrinkage due to drying either before or during the preparation.

13 is an unusual reaction picture, found only in special circumstances, and represents a profound alteration of the particle rim zone and the adjacent cement paste. The boundary between particle and paste is indistinct, and the boundary between the particle core and its rim lies within the altered rim zone.

At the left of *plate XIV* there are sketches of phenomena inside particles of dense flint and in their rim zones, while the series on the right represents mechanical effects of expanding reactivity in surrounding paste.

14 simply shows the most common appearance of particles of dense flint in the entire observation material, i. e. no symptoms of reaction. 15 shows a particle with a narrow, closed crack. One or more cracks in a particle of such appearance are presumably an expression of the fact that weak alkali-aggregate reaction has taken place, but more convincing proof that the reaction has been of exactly this kind is absent. The open main-cracks shown in 16 and 17, in the latter case with zonal discoloration, can more surely be regarded as the result of internal expansion, since with the very considerable strength and rigidity of the dense flint, it is difficult to imagine a shrinkage of the particles that could equalize the growth of the cracks to the volume of the particle.

As far as 14-17 are concerned, it must be remembered that they may represent the reaction picture in four cross-sections of a very long particle - this has, in fact, been observed in the experiments described in (2681).

18 shows a rather unusual reaction picture for dense flint, possible particle dissolution and dilution of the dense flint substance from the rim inwards during formation of viscous gel. The phenomenon has been observed and described both in laboratory tests and in field concrete, but the conditions indicate that a special chemical balance in the concrete (possibly an extremely high Na^+/Ca^{++} ratio compared with ordinary concrete) is required for the reaction to follow this course.

19 represents an invisible and hypothetical, 'weak' rim reaction that may be supposed to improve the bond between the particle and the surrounding cement paste.

Plate XIII. *Typical phenomena of alkali-aggregate reaction in particles of porous flint. The sketches on the left (1 to 7) show phenomena inside particles, the sketches on the right (8 to 13) show effects of reaction on surrounding paste. 1 and 2 show particles which still have an internal structure strong enough to cause the development of open main-cracks. Partial dissolution of the rock substance always occurs with porous flint, and is indicated by dotting. 3 to 6 show advanced internal dissolution, 7 shows gel impregnation of the surrounding paste. 8 to 10 show the mechanical effects of particle swelling. 11 and 12 represent subsequent drying shrinkage. 13 shows an unusually extensive alteration of the particle rim. Range of particle size: About 3 to 32 mm.*

20 shows a somewhat more extensive rim reaction resulting in the formation of a visible corrosion rim. This phenomenon can be interpreted as a further development of the reaction picture in 19, and this is confirmed by numerous observations. The fact that layers of $Ca(OH)_2$ are often observed around aggregate particles means that the chemical reactions along the rim of a dense flint particle may involve more than just alkali-aggregate reaction in general.

21 (= 14) shows an unreacted particle without cracks in the surrounding paste. As mentioned earlier, particles of dense flint occur in this condition in the majority of cases.

22 shows a thin, closed crack that must be imagined to continue through the particle, see 15. In such cases, there may be a question of purely physico-mechanical phenomena with no connection with alkali-aggregate reaction, and the features of reaction of many particles in the same thin section or specimen must be considered before drawing any conclusions.

23 and 24 (compare 9 and 10 for porous flint) show the typical reaction picture for particles of dense flint in which expansive gel has formed, causing the surrounding paste to crack and gel to flow out into the cracks. The gel rim surrounding the particle in 24 (cf. 10) is only observed occasionally, although it is not exceptionally rare.

25 and 26 are micro rim corrosion phenomena, illustrated earlier in the case of dense flint eroded by marine action and of a basalt particle in sedimentary sand in Norwegian mortar. In 26, the microcrack zone on the surface of the particle has been the seat of rim corrosion phenomena corresponding to those shown in 18 or 20 or both.

On the left of *plate XV*, a series of angular, stratified particles is sketched in which the reactive component is only a minor constituent. 27 shows interior cracking corresponding to dense flint, 28, reaction in a weaker material (as 3 or 4 in *plate XIII*), and 29, a reaction course involving formation of a reaction rim. 30 shows definite tensile failure in a particle of almost fibrous structure. The random course of the tensile failure through the strata of the particle is quite pronounced. Rounded particles with crack phenomena like 27 and 28 are shown in sketches 31 and 32. 33 and 34 show special types of reaction for basalt particles. It will be seen that the phenomena correspond well to those described above for porous and dense flint. It seems likely that reaction in polymineral rocks with only a minor content of reactive substance require a particularly high alkali content or an unfavourable chemical or physical (high temperature and humidity) situation before a deleterious effect due to expansive reaction is apparent.

It is of considerable interest to note that the symptoms of reaction in porous and dense flint and in heterogeneous reactive rocks are so uniform that the differences can be explained by the differing structures of the rocks, as is clearly seen from the figures in *plates XIII, XIV* and *XV*. Further, this confirms that the critical factor in crack formations in porous flint is not frost action, but predominantly alkali-aggregate reaction. This can be concluded from the fact that the common reaction symptoms for porous and dense flint cannot, in the case of the dense flint, be due to frost; moreover, such symptoms have been produced in laboratory tests that have not included exposure to freezing and thawing.
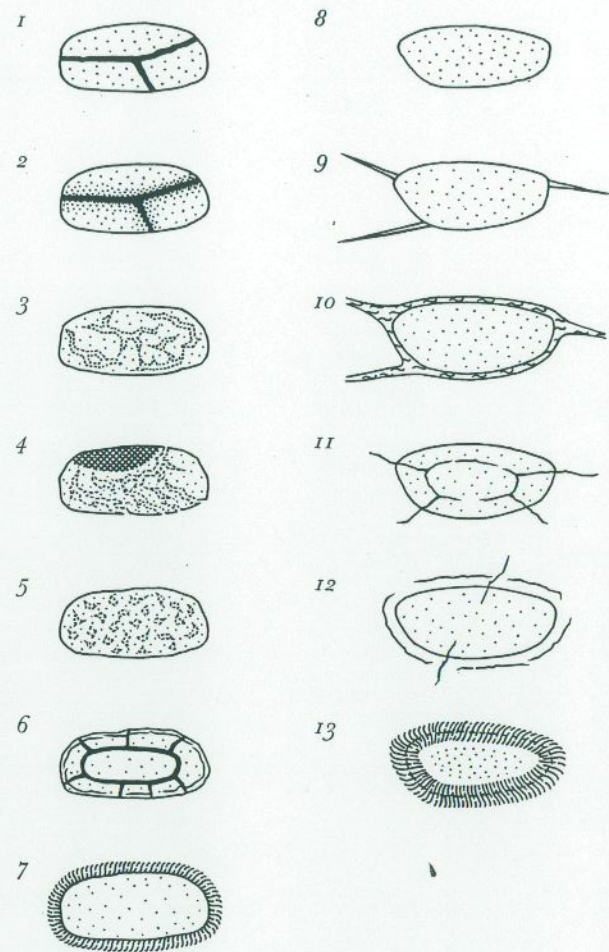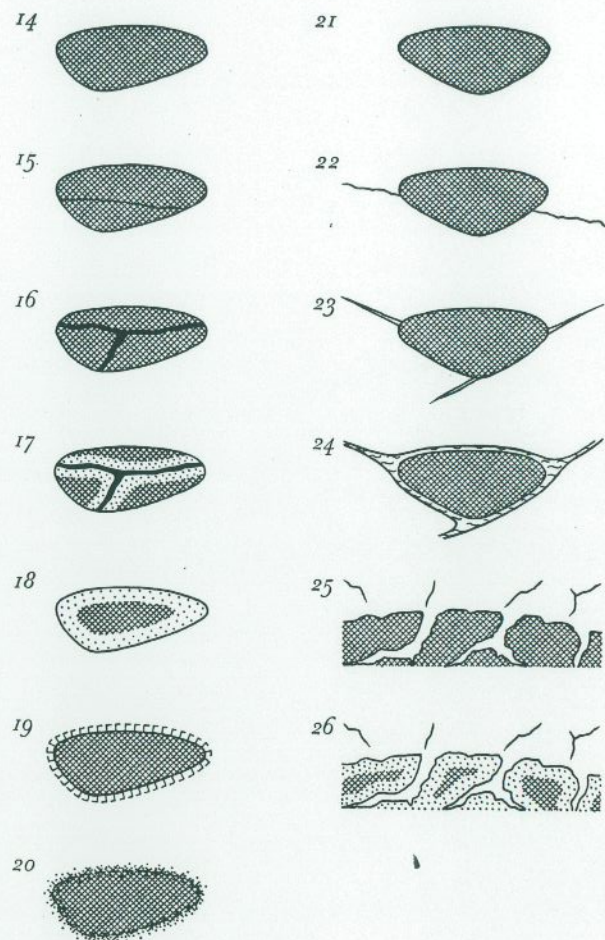

Plate XIV. Typical phenomena of alkali-aggregate reaction in particles of dense flint. The sketches on the left (14 to 20) show phenomena inside particles, the sketches on the right (21 to 24) show effects of reaction on surrounding paste. 25 and 26 represent reaction in the actual surface layer of large pebbles. 14 and 21 are reminders that most particles of dense flint show no signs of reaction. 15 and 22 represent indistinct effects of reaction. 16 and 17 show common types of open main-cracks. 18 shows dissolution of rock substance from the external boundary, an uncommon feature. 19 indicates invisible improvement of the bond between particle and paste, and 20 shows more extensive rim corrosion found only in exceptional cases. 23 is the most typical pattern of cracking in surrounding paste. 24 shows the same, but with a gel rim around the particle. Range of particle size: About 3 to 32 mm.

The sketches show a pronounced difference in the effect of reactions depending on whether the particle structure is so dense that mechanical rigidity is preserved during gel formation, or whether it is so open and soluble that the chemical process totally destroys the internal rigidity of the particle during gel formation. The physico-chemical conditions as a whole and the time of reaction etc. naturally determine which of these two reaction pictures is observed, but there are insufficient data in the present investigations to permit a more quantitative assessment of these conditions. However, a few qualitative considerations may be put forward to indicate how the physico-chemical-mechanical effects of the reactions throw some light on the mechanism.

Plate XVI shows, in idealized sketches, how expansion in reacting particles causes crack development. 1 and 2 are porous, homogeneous flint that is totally transformed to swelling gel, which exerts uniformly distributed pressure on the wall of the cement paste around the particle. At a certain expansion pressure, the tensile strength of the cement paste is exceeded. As is usual in brittle bodies, cracks form, with decreasing thickness from the particle rim out into the surrounding cement paste. During failure, the swelling gel runs out into these cracks and precipitates there. Round (i. e. spherical) particles may cause failure anywhere along the wall of the adjacent cement paste, provided that this is homogeneous. Triangular (i. e. tetrahedral) particles primarily cause cracks to issue from corners (i. e. edges) with the greatest stress concentrations. Secondary failure probably occurs along the edges (also in the following cases).

3 and 4 show the idealized crack formation in the case where the outermost rim zone of the particle forms a non-swelling reaction rim (corresponding mechanically to a ring that shrinks around a stable core), while the interior is transformed into homogeneous, swelling gel. The crack pattern in the rim zone after failure corresponds to the rupture conditions in a rim zone of cement paste adjacent to the particle wall in 1 and 2, i. e. the non-expansive particle rim is subjected to triaxial tensile stresses. It should be noted that this reaction rim must crack *before* rupture can take place in the surrounding cement paste.

5 and 6 show the idealized crack formations in the case where the particle rim zone constitutes the homogeneous, expansive mass, the chemical alteration working inwards from the outside. In this case, the interior mass of the particle remains uncracked (triaxial compression), while cracks form in the cement paste as in 1-2 and 3-4.

7 and 8 show the idealized crack picture in the case where the swelling gel has formed throughout a particle of dense, homogeneous structure that retains its rigidity during the reaction process. It is most probable that the failure in a spherical particle is primarily severance following a great circle because even a very slight inhomogeneity anywhere would create a notch effect that must lead to stress equalization via failure. In a triangular (tetrahedral) particle, the rupture lines must be assumed to run along the medians. The cracks in the surrounding cement paste must assume a course in accordance with this. As a result of the compression and diffusion conditions, the swelling gel must be assumed to flow out and condense in the cracks in the surrounding cement paste.

9 to 12 incl. show secondary effects of drying shrinkage in and around particles of porous flint that has been transformed into gel during absorption of water
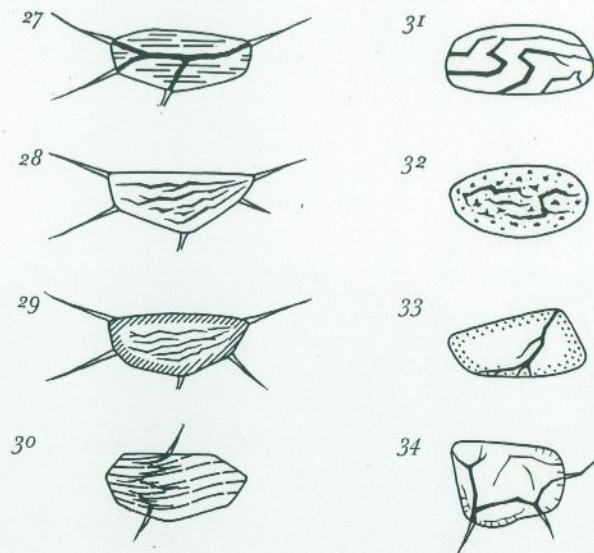
Plate XV. *Characteristic phenomena of reaction in polymineral rocks in which soluble silica is only a minor constituent. 27 to 30 are angular pebbles of stratified rocks (schists, phyllites, etc.). The extent of internal disruption depends on the solidity of the rock structure as a whole. The cracks follow the path of dissolution, i.e. mechanical weakening. 31 and 32 show rounded, foliated rocks with characteristic features of cracking and dissolution. 33 and 34 represent a homogeneous rock (basalt) with cracking very much like that in dense flint. Range of particle size: About 3 to 32 mm.*

and expansion. It must be imagined that crack formations and a certain gel exudation in cracks has taken place as the primary course of reaction. 9 simply shows a contraction (condensation) of gel within the space of a particle under conditions in which the adhesion of the gel mass to the cement paste is poor along the rim. 10 shows a homogeneous gel mass with adhesion to the particle wall greater than the internal tensile strength of the mass. The uncracked core has been subjected to triaxial compressive stresses due to drying. 11 and 12 indicate the shrinkage phenomenon when the cement paste nearest the particle becomes partly or entirely included in the zone of shrinkage cracking during contraction of the gel mass. These last two crack pictures show cracks in the cement paste following a course out from the centre of the particle, i. e. the shrinkage cracks may be superimposed on primary expansion cracks.

It is important to remember that drying shrinkage in cement paste (or mortar) can give rise to crack patterns around both inactive and reactive aggregate particles which are of the same appearance as the patterns described for cracks issuing from expanding aggregate particles in a non-shrinking cement paste or mortar. This circumstance may be an important factor in the final disruption of the surfaces of concrete exposed to internal expansive reactions and external drying. Further, as weak, badly cured concrete exposed to intensive drying tends to crack purely as a result of shrinkage stresses, it will be seen that in the final stages of field deterioration there may well be a question of 'both this and that', and attempts to distribute responsibility for the deterioration are often valueless and misleading.

The sketches in *plates XIII* to *XVI* show only the idealized particle shapes: spherical (porous flint) and tetrahedral (dense flint). However, the observation material shows that long and flat particles are common (besides, of course, the more irregularly rounded or angular particle shapes that are the most common). (2910) and (3971) contain sufficient examples of reacted particles of these shapes to permit sketches of typical crack pictures as shown in *plate XVI*. In both types of particles the main orientation of the crack formations is diametrical or diagonal, in the same direction as the main orientation of the particle. Cracks in the surrounding paste therefore follow this stress orientation.

Crack formations in flint, caused by water absorption with subsequent freezing, have been described in (2928). *Fig. 64* is reproduced from fig. 2 of this paper. Ice accumulations have formed in voids or highly porous interior zones of dense flint pebbles (fist size or larger). Rupture has followed due to swelling pressure. The crack mechanism is thus the same as when swelling gel ruptures a particle from the inside, regardless of the fact that in these cases it is a question of purely physical processes. Mielenz (43) has previously shown fracturing of aggregates exposed to freezing. In connection with the development of expansive alkali-aggregate reaction in dense flint, it is interesting to observe that water is able to diffuse through the flint structure into a porous core. Probably, Na+ and OH⁻ can therefore also diffuse into the mass.

Formation and precipitation of gel. The following observations on the formation and behaviour of gel during alkali-aggregate reaction in concrete and mortar are available from field inspections and macroscopic core examinations, see previous chapters, and from many mortar bar tests, e. g. Jones (1479) and Plum et al. (2932).

Swelling of rounded and angular pebbles
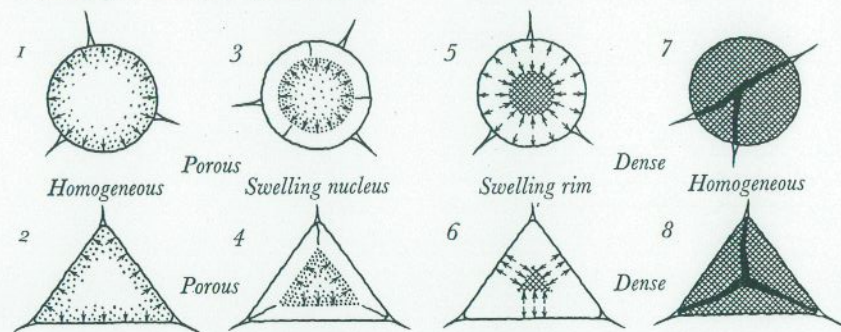
Shrinkage of gel and of reacted flints
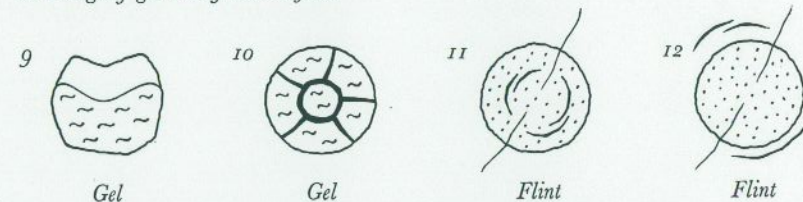
Swelling in flat or oblongated pebbles
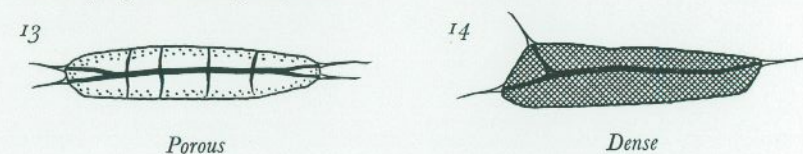
Plate XVI. Idealized sketches of the mechanical effects of alkali-aggregate reaction. The upper two series of pictures show on the extreme left hydraulic pressure exerted by liquid gel, which has replaced a solid, porous flint structure. On the extreme right is shown the explosive effect of accumulated pressure in a still solid structure. Left centre shows the features of a non-swelling reaction rim, and right centre the effect of swelling in the rim zone. Gel precipitated in voids and reacted porous flint exhibit severe shrinkage cracking after drying, as shown in the third series of sketches. Flat and elongated flint pebbles show cracking patterns determined by the particle shape as shown in the last pair of sketches. Range of particle size: About 3 to 32 mm.

1. The formation of viscous gel and its transport through cracks to concrete surfaces depends on temperature conditions and the presence of the necessary humidity. At temperatures below about 20 °C, only small quantities of gel seem to form. Higher temperatures accelerate the formation of gel and increase its fluidity considerably. Gel formed inside the concrete only seems able to reach concrete or mortar surfaces and collect in drops at very high relative humidities. The lower limit for the relative humidity in this respect is presumably in the region of 98-100 per cent RH. However, measurements have not been taken on surfaces of structures, and only insufficient measurements are available from laboratory tests.

2. Gel precipitations are mainly pure alkali-silica complexes that condense during drying. Development of gel varies in intensity. After transport through cracks in cement paste in contact with a liquid phase saturated with $Ca(OH)_2$, gel precipitations often contain only small quantities of Ca^{++}; they are thus mainly pure, hydrous, alkali-silica complexes (544). Alkali carbonates may occur in small quantities as impurities. Drying causes condensation, and in free air there later occurs a slow leaching process. The condensation causes a change in the character of the material from watery-sticky or resinous and yellow or brown to porcellaneous, white, hard and brittle. After a certain, undefined period of drying, the process seems to be irreversible.

3. Watery gel seems to flow out over concrete surfaces through existing or possibly newly formed cracks, e. g. (2910) figs. 75 and 76, although there are examples of viscous gel having exercised expansive pressure, e. g. (543) fig. 11, and (2911) with corresponding photomicrographs in (3971) of thin sections made from a concrete core, and other observations. There is thus also the possibility of crack formations in alkali-aggregate reaction arising due to swelling of gel that has flowed out from the point of formation, i. e. not confined in the structure of the particle. It is also possible for very viscous gel to exude into the structure of the concrete mass without exerting swelling pressure. Exudations of watery gel on surfaces of mortar bars are thus often observed without being accompanied by crack formations see e.g. Plum et al. (2932). During the field inspections for DCAR, fresh gel exudations were sometimes observed on top of old, dried exudations. It has similarly been noted in the laboratory that the formation of gel takes a long time. This means that the structural differences described earlier (*plates XIII to XVI*) between slightly reacted flint with main-cracks and a mostly still preserved, rigid particle structure on the one hand, and intensively reacted flint with a mainly disintegrated or dissolved particle structure on the other, may only represent intermediate phases. The observations from both field inspections and investigations of concrete samples in Denmark (543), (544), (2910), (2911), (3971) et al, and from the tests on flint rods cast in cement paste indicate that a supply of alkali ions (Na^+ or K^+, or both) beyond that provided by the cement is necessary to obtain very severe dissolution of flint, especially of dense flint, and considerable production of gel. In the case of the Oddesund Bridge (2911) and (3971), excessive gel produc-

tion has been demonstrated in the concrete below the water level, where there is a constant supply of Na^+ due to seepage of sea water, and partly transformation and precipitation of the calcium hydroxide of the cement paste as hydrated calcium sulphate and formation of magnesium hydroxide, so that the Na^+/Ca^{++} ratio is considerably higher than in ordinary concrete, and is still increasing.

4. In only a few cases have thin sections been prepared of gel precipitations formed over reacted aggregate particles in concrete surfaces. (3971) figs. 62 to 74 are an example of a gel 'pop-out' formed over a porous, reacted flint particle near the surface of a concrete core during storage in the laboratory. (3971) figs. 103 to 120, are examples of unusually concentrated gel deposits in concrete fragments, and (3971) figs. 121 to 127 show an unusually concentrated surface precipitation of gel, hydrated calcium sulphate and magnesium hydroxide.

Apart from these exceptional gel formations, the thin sections investigated, especially in (2910) and (3971), show the following characteristic modes of occurrence of precipitated gel.

a. As a lining or filling substance in cracks ramifying from reacted aggregate particles. *Fig. 22* and *30* show examples of this type of deposits. In a few cases, remains of the original particle structure have been found carried out into newly formed cracks showing the suddenness of the crack formation. Gel in cracks usually shows typical 'glass mosaic' shrinkage cracking.

b. Filling large, irregular voids arising from poor compaction or dissolution of cement paste. *Fig. 65* is an example of this.

c. Filling or lining air bubbles entrapped in the concrete or mortar matrix during casting. *Figs. 55, 61* and *66* show typical examples. Gel in voids always seems to have a clear, optically isotropic appearance with perfect shrinkage cracking after drying. In some cases, where air bubbles have primarily been partly filled with gel, a secondary precipitation of calcium aluminate sulphate has been observed (2910).

d. Impregnation of cement paste adjacent to reacted aggregate particles. Although conclusive, optical identification of gel precipitated in this way is not possible, the circumstances leave no doubt that the impregnation medium is gel. Examples are dealt with above in the discussion of dissolution and formation of gel in reacting aggregate particles. *Figs. 20* and *61* are examples of this mode of occurrence.

e. Lining of cracks *inside* reacted aggregate particles. As mentioned above, the typical feature is that cracks in reacted pebbles are empty, and consequently that on disruption, the surplus gel has moved out into the extended cracks in the surrounding concrete. However, in rocks containing silica as a minor constituent, gel has been found lining the interior fractures (2910) figs. 27 to 30. In rare cases of severe deterioration, gel has also been found to precipitate in interior cracks in flint, see *fig. 67*.

It seems that gel often condenses in ramifying cracks after erupting from the swelling particle, but as previously mentioned, it is not likely that this is due to absorption of Ca++ in the complex from the cement paste. (It must be remembered that storage and preparation of concrete specimens entail condensation). The thin section observations do not indicate secondary expansion caused by gel concentration in cracks and irregular voids. Incidentally, gel-filled expansion cracks radiating out from original air bubbles that have later become filled with gel have not been seen either, e. g. see *fig. 66* and (2681) figs. 48 and 49, (2910) fig. 19, and (3971) fig. 66. However, as previously mentioned, field inspections and core examinations do show that exuding gel *can* exert swelling pressure.

In some reacted pebbles a certain amount of apparently secondary calcite has been observed in the rim zone nearest the surrounding paste, e. g. (2681) fig. 3, or distributed in the remaining gel substance occupying the space left in a thoroughly reacted, porous flint particle, see figs. 43 and 44 in (3971). This can be explained by assuming that Ca++ has diffused into the reaction site from the surrounding paste together with the alkali and hydroxide ions. The reaction rims previously mentioned do not, in thin sections, show any sign of containing lime. However, this does not prove that there is no calcium in the precipitate.

A rather peculiar phenomenon is shown in (3971) figs. 11 and 12, and mentioned in the caption to fig. 51 of the same paper. Just at the 'mouth' of a traversing crack in a flint pebble where it starts to be occupied by gel, there is a distinct 'cork' of carbonated gel filling the crack. Does this mean that an osmotic cell has been formed, allowing gel to escape from the interior and alkali hydroxide to penetrate into the particle? (Before preparation, the traversing cracks must be expected to have been filled with a liquid and not a gaseous phase). In the cases mentioned, this carbonation phenomenon is very distinct, but at most crack-mouths only indistinct carbonation, or none at all, can be seen. Again, this does not prove the absence of Ca++ from the gel complex.

In some accumulations of gel on concrete surfaces or in very deteriorated concrete, seams of calcium carbonate can be seen along gel deposits (2910). In these cases the gel appears to be somewhat deteriorated, although calcite and gel are still distinguishable.

Development of crack patterns in mortar and concrete. Thin sections of mortar and concrete usually cover such small areas that it is not possible to make studies of cracks radiating from aggregate particles or traversing large particles. However, in the investigations carried out by the writer or in which he has participated there are, in some cases, large thin sections in which the crack pattern could be followed. In (544) earlier observations are reported of

1. Radiating cracks from a single reacting aggregate particle.
2. Cracks extending from one reacting particle to another, forming a wide, continued fracture.
3. 'Map-cracks' in a concrete surface, extending only a short distance into the concrete. Fractures follow haphazard courses deeper in the mass.

In (2910) figs. 1, 2, 79/80, 83/84 and 88/89 show larger thin sections with examples of the propagation of cracks both from large isolated particles of porous flint and between several closely packed particles. Figs. 88 and 89 in particular

show how parallel cracks can run between reactive particles close to a concrete surface (cf. also the macroscopic equivalent in the same paper, figs. 77 and 78). Figs. 79/80 and 83/84 correspond more to the pop-out formation, which is shown macroscopically in figs. 75 and 76 of the same paper. Figs. 1 and 2 show unusually disintegrated concrete, but in particles of porous flint, the correlation between internal crack formation and dissolution and radiating cracks is conspicuous. (This cannot be seen on broken surfaces, but to a certain degree on sawn surfaces after polishing, and even better in thin sections).

In (2911) it is shown how the relationship between cracking and the location of reactive aggregate particles can be brought out by carefully sketching of the features of sawn and polished surfaces or cores. The tendency for cracks to form sub-parallel to the concrete surface in concrete walls in the caisson of the Oddesund Bridge is shown in sketches of the cores, while especially plate VIII of core 54.5.30 shows how the pattern of the cracking is dependent on the location of reactive particles of porous flint. Plate X shows corresponding phenomena. Several pictures in (3971) confirm these macroscopic observations mentioned.

Figs. 68 and *69* show a thin section - about 5×8 cm of one half of core No. 54.5.13 (2911). The sketch shows the most important cracks and reacting particles of porous and porous/dense flint. They confirm that concentrations of porous flint tend to form interconnecting cracks.

Fig. 70 shows a thin section of concrete from a road surface in Nebraska, USA, containing the reacted shale particle shown in *figs. 62* and *63*. This concrete is cracked over the entire thin section, with the main orientation of the cracks sub-parallel to the surface, despite the fact that the section does not contain many reacted aggregate particles.

It is reasonable to imagine a gradation in the crack intensity from a single particle, with as one extreme porous, reacted flint without accompanying crack formations in surrounding mortar, and the other extreme dense, reacted flint that through presumably violent internal reaction produces cracks, which wedge their way a shorter or longer distance into the surrounding material. However, the thin sections in the writer's investigations are unsuitable for a more detailed differentiation of the stages between these two extremes. For this purpose, special experiments are called for. All the same, the observation material does indicate that both the number and size of the reactive particles affect the crack intensity.

Fig. 71 shows a thin section (containing the particle shown in *fig. 18*), representing concrete that has been exposed for many years to a steady supply of Na+ from surrounding sea water. The reacted particles are extensively dissolved, the cracks are wide and deep, and there are considerable quantities of precipitates. This concrete must, in a way, be regarded as representing an advanced stage of disintegration, since alkali-aggregate reaction has helped to 'open up the concrete' for continued reaction and supplementary sulphate attack.

It should be noted, with regard to the descriptions of cracking given, that all samples were taken from near the surface of concrete structures. Deep inside a concrete mass the stresses will have a decreasing ability to release cracking.

Hypothesis on alkali-aggregate reaction from a petrographic viewpoint. It was originally intended to utilize the available petrographic observation material to illustrate earlier hypotheses on the physico-chemical nature of alkali-aggregate

reaction and its mechanical mode of operation, cf. Powers & Steinour (3991), (3992), (3993), and Verbeck & Gramlich (1498), and Hansen (3958). However, it seems, for many reasons, that the return for a study in this respect would be rather poor.

Firstly, the complex influence on concrete of the varying basic conditions (concrete composition, variations in material properties, etc.) result in considerable uncertainty in detailed quantitative studies regarding a single, selected factor such as, for example, alkali-aggregate reaction.

Secondly, the reactive aggregates vary considerably in structure etc. and are very different from the aggregates used elsewhere in more theoretical studies.

Thirdly, the thin section provides only a two-dimensional picture, thus leaving uncertainty regarding interpretation of three-dimensional phenomena.

Fourthly, the microscope is not sensitive enough to permit the reaction to be followed in sufficient detail for its physico-chemical nature to be understood, since the distinction between microscopic and submicroscopic phenomena must be regarded as quite arbitrary.

These observations do not, however, mean that the theoretical papers mentioned above do not include analyses and evaluations that can, and should be correlated with the writer's observations, inter al. because the theoretical treatment of alkali-aggregate reaction mainly concerns the physico-chemical alteration of reacting aggregate particles and, to a certain degree, the mechanical effects of these alterations. It is from this that the macroscopic and megascopic effects on structures must be derived.

There are only a few references in the literature to the importance of temperature in alkali-aggregate reaction. Powers & Steinour (3992) drew attention to the fact that Conrow obtained accelerated expansion in concrete after 7 days' heating to 130 °F in an oven, followed by storage in water. Verbeck & Gramlich (1498) found that temperature had a marked influence on the osmotic pressure in their experiments with opal and sodium hydroxide. The increase in pressure was negligible at 50 °F in the course of 12 days, but was considerable after 1-2 days at 100 °F. Also Stanton (4029) studied the effect of temperature and found that storage at 100 °F gave approximately twice the expansion obtained with storage at 70 °F for mortar bars with Californian reactive sand. Jones (1481) obtained corresponding results.

Rosenqvist (private communication to the writer), cf. p. 91 and *figs. 54* to *61*, has recently found that basaltic sand from the Oslo area, which has never given rise to observed reactivity in concrete structures, produces expansion and gel development in mortar bars made with local cement (high alkali content) during storage at 40 °C.

In Denmark recently (spring 1965), gel precipitations and pop-outs on surfaces of precast concrete panels have been observed after only a few hours' steam-curing at 80-90 °C. It seems unlikely that visible reaction will occur in ordinary concrete production without heating with the cement and aggregates used. Moreover, it appears that the reaction ceases as soon as the first heat-conditioned 'discharge' has taken place.

It has previously been noted by the writer, cf. p. 64, that gel precipitations on concrete surfaces of structures in Denmark mainly develop during the summer. It seems reasonable to assume that the effect of increases in temperature on the rate and course of the reaction is kinetically and thermo-dynamically controlled (incidentally, more quantitative investigations with the temperature as parameter are lacking). However, it must be remembered that the solubility of calcium hydroxide decreases with increasing temperature (3979), so that the relative Na^+/Ca^{++} concentration in the liquid phase of the cement paste increases considerably with increasing temperature. This effect is presumably an accelerating factor in alkali-aggregate reaction, even under natural temperature variations. It must be borne in mind that the available quantity of eqv. Na_2O is consumed more rapidly at elevated temperatures than at a constant, lower temperature, and a rapid consumption of a given quantity of alkalies must cause the reaction to cease. The relationship between the reaction course and time for concrete structures has been referred to by the writer in Bredsdorff et al. (1897) pp. 756-58.

The observations now available, especially from concrete in structures in Denmark, confirm earlier findings of an accelerating action caused by the addition of solutions of alkali ions to increase the alkali content of the cement. Both alkali hydroxides and alkali salts show this effect, see inter alia Vivian (5468) and Davis (5469). The observations from the concrete of the Oddesund Bridge (2911) and (3971) can be interpreted to mean that a constant supply of SO_4^{--} and Mg^{++}, together with Na^+, causes a lasting further development and intensification of the reaction. The fact that the quantity of calcium hydroxide in the cement paste is gradually reduced as Ca^{++} is precipitated as gypsum, aragonite, calcite, etc, whilst Na^+ etc. is still being supplied from outside, must be assumed to contribute to the above effect. This provides confirmation 'that variations in the amounts of calcium hydroxide present profoundly influence the course of reaction', Verbeck & Gramlich (1498). Incidentally, when there is no possibility of supplementary alkalies being supplied, deleterious reactivity to any noticeable extent occurs only exceptionally in field concrete in Denmark. Even in the concrete of the Oddesund Bridge, the reaction is much less severe in concrete above the sea water level than below.

The present field inspections and thin section observations do not reveal directly phenomena that can either confirm or disprove the validity of empirical relationships established on the basis of results of mortar bar tests, Powers & Steinour (3992), Poulsen (3993), concerning the influence of the size and quantity of the reactive aggregate particles on the course of reactions. As one extreme with respect to the influence of the particle size it may be mentioned that field observations of structures on the west coast of Jutland, made with pozzolanic cement, (531) mainly confirm the preventive action of finely ground reactive, opaline material. On the other hand, there is no indication of a critical upper limit for particle size as regards reactivity. There are many examples in the observation material of reactive particles of gravel (i. e. > 4 mm □) having reacted, but they are limited to concrete that has been exposed to an increase in alkali concentration over a period of years. Under these circumstances, even pebbles of dense flint have shown intensive and swelling gel formation. These conditions must, however, be regarded as extreme. In concrete without special or continuous addition of alkalies, limited reaction occurs in particles of porous flint, presumably independent of their size, but visible effects will arise but rarely. Individual particles lying near surfaces do, however, often cause limited

pop-out formation. The reaction ceases soon after the initial stage as a consequence of the reduction in the alkali concentration.

In recent years there has been a distinct tendency to use concrete with lower w/c-ratios than at the time when most of the structures inspected by the writer were erected. This causes greater tensile strength to the cement paste and a lower flow rate of the liquid phase in the concrete, cf. Verbeck & Gramlich (1498), pp. 1112-1114, and less liquid phase is available for fluidation of gel. These factors in combination must be expected to lead to less visible effects of reactivity.

In the descriptions of thin section observations on reacted aggregate particles, reference has frequently been made to the existence of an impregnated zone in the cement paste outside reacted particles. This corresponds well with the theories put forward regarding the development of osmotic pressure as a reaction mechanism. The gel-impregnated paste presumably functions as a semipermeable membrane in a cement paste that is in itself too porous to have any filtering or membrane effect. In many cases, the expansive pressure then seems to act hydraulically from a fluid or viscous, homogeneous reaction mass during total disintegration of the mineral structure of the particle.

In particles of dense flint it seems that the formation of gel first takes place somewhere inside the particle (perhaps in a relatively porous part). When sufficient pressure develops the particle itself shatters primarily, resulting in open main-cracks. In the experiments described earlier, (2681), in which particles of dense flint were cast in mortar bars, very dense, homogeneous, black flint was used. This, together with the exceptionally high alkali concentration, may explain why, in these cases, the dissolution of the flint mass started at the periphery.

Powers & Steinour (3991) describe gel as expansively swelling, even when it has flowed out from the site of reaction into cracks and voids. The gel pop-out from Assens Harbour (543), and corresponding phenomena observed in stored cores (3971) pp. 14-19, are examples of a direct effect of this nature. On the other hand, the extent to which gel precipitated in cracks can continue to contribute to expansion of these cracks, cannot be determined on the basis of the thin section observations, since these represent a fixed stage.

Gel in cracks is often found associated with calcium hydroxide, or calcium carbonate as calcite or aragonite. Occasional observations have been made of a 'cork' of secondary calcite, where open main-cracks in reacted aggregate pebbles run into gel-filled cracks in surrounding cement paste (it is unusual to find cracks inside reacted particles filled with gel), see p. 132. Minute deposits of calcite that seem to be newly formed have in some cases been observed along the rims of reacted particles, possibly the remains of a lime-alkali-silica complex. However, apart from these weak indications, the present observations cannot be said to have thrown any light on the theories regarding the formation of a lime-alkali-silica complex in the rim zones of reacting particles, as distinct from a pure alkali-silica complex inside the particles.

Observations on reactions involving sulphates

Earlier literature contains few observations on thin sections of concrete destroyed by sulphate attack. This is undoubtedly due for the most part to the fact that the structure of concrete attacked chemically in this way is so weakened that it was not possible to prepare thin sections before the development of modern methods of impregnation. Therefore, also in recent years, many research workers have preferred X-ray identification to supplement binocular and powder mount observations and identification. However, only the thin section technique permits a study of the morphology of substances precipitated during chemical alteration of the original components of the cement paste and allows any structural effects of these alterations to be traced.

Foreign and older Danish investigations of chemical deterioration involving sulphates have previously been described by the writer (530), (531), (543), (544) and (2704). Thin section observations were first used by the writer in (2787), which describes the phenomena of disintegration in a concrete foundation that had been exposed for a number of years to the action of ground water containing a considerable quantity of sulphate and also presumably aggressive carbon dioxide. The symptoms of deterioration included

1. Excessive amounts of calcium aluminate sulphate as well-developed formations of acicular crystallites in cracks and voids.
2. Excessive amounts of calcite as well-developed formations of scalenohedrons etc. in voids.
3. Calcium aluminate hydrate as well-developed hexagonal, plate-shaped crystals in voids.
4. Extensive dissolution of cement paste.
5. Rim corrosion on surfaces of aggregate particles.
6. Absence of calcium hydroxide and dicalcium silicate particles.

It was obvious that the secondary precipitates mentioned must have been formed at the expense of the original components of the cement paste. Considerable leaching also seemed to have taken place, but as the original degree of compaction of the concrete was not known, this could only be evaluated qualitatively. It was interesting to observe formations of calcium aluminate sulphate in voids in concrete, since this indicated that crystallization mainly takes place where there is sufficient room, rather than causing disruption in the cement paste during the crystalline growth, as sometimes assumed earlier. There was no indication of such disruption in the material. The mechanism of disintegration could therefore be described as dissolution and leaching of cement paste components, combined with precipitation of secondary constituents (inferior to cement paste from the point of view of bond between aggregates and matrix). The morphological characteristics of these constituents indicated, moreover, that the processes had taken place over a long period of time and with slow crystallization, possibly with repeated cycles of dissolution and precipitation.

(3981) (German edition (4072)), describes thin section observations of calcium aluminate sulphate in concrete (with hydraulic lime as bonding agent), cast about 1650 at Port d'Antibes in the South of France. In this case, the structure and strength of the concrete were well preserved despite extensive precipitations

in voids. The observations are considered to show that the presence of calcium aluminate sulphate does not in itself indicate deleterious attack on the cement paste.

In the series of Progress Reports published by the writer, the following thin section observations on sulphate action were presented.

(2681)   Mortar bars stored in Na_2SO_4.
(2910)   Concrete from groyne 7, north barrier at the Lim Fiord. Highway bridge, North Jutland. Concrete from Swedish dam. Precipitation from East-Asiatic dock bottom.
(2911) & (3971) Concrete from pier 7, underwater, Oddesund Bridge.

Supplementary observations from investigations carried out at the Concrete Research Laboratory Karlstrup have been preliminarily presented as

(2930)   'Investigation of chemical action in concrete works at Fredericia Harbour'.
(4083)   'Investigation of concrete from chimney in Egypt'.

The results of tests on mortar bars (2681) stored in 10 per cent Na_2SO_4 found the highest content of calcium aluminate sulphate in bars made with pozzolanic cement. These had expanded less than bars made with ordinary Portland cement (not containing calcium aluminate sulphate). Calcium aluminate sulphate was found as minute aggregates of crystallites in the cement paste, but not in voids and cracks. Calcium hydroxide was found in all the bars, regardless of content of pozzolan and whether expansive reactions had occurred. Unhydrated C_2S, on the other hand, was only found in bars made with ordinary Portland cement. Carbonation occurred near cracks that opened out towards the surface. The bars which had expanded showed a tendency for the individual sand particles to separate from the surrounding paste through 'peripheral cracks'.

The most interesting and bewildering result of these observations is that there were no *visible* symptoms of chemical alteration involving sulphates in the bars cast with ordinary Portland cement which showed the greatest expansion, whereas significant amounts of calcium aluminate sulphate were found in the bars cast with pozzolanic cement which had expanded least. It could be that submicroscopic calcium aluminate sulphate in the paste, not detectable in the microscopic examination, or chemical alteration of the cement paste itself may be responsible for the swelling of the paste. However, the rather compact microscopic formations of calcium aluminate sulphate, distributed in the expanded cement paste, represent the best indication of an expansive action of the precipitate in the writer's observations.

These phenomena might possibly have been explained had it been possible to obtain more information on the complex solubility conditions, but as a whole, more comprehensive tests, with accompanying quantitative and petrographic analyses are required to obtain more than phenomenological information from the results.

Formations of calcium aluminate sulphate like those described above distributed throughout the solid cement paste, have not since been observed by the writer in concrete attacked by sulphates. On the other hand, peripheral cracks are a more common phenomenon of deterioration in concrete, but it

must be remembered that they can also come when the dilation of the paste has physical causes, e. g. frost action, cf. p. 145.

Fig. 72 is a reproduction of a conspicuous example of the mode of occurrence of calcium aluminate sulphate in the deteriorated concrete foundation described in (2787). The cement paste is highly dissolved around the bubble, and there can be no question of the precipitate filling the available space, so that purely mechanical rupture of this wall cannot have taken place.

Fig. 73 shows calcium aluminate sulphate occurring adjacent to a partly dissolved phyllite particle (alkali-aggregate reaction was also involved in this case).

Only in cases of excessive attack in sea water has the writer observed calcium aluminate sulphate to accumulate on aggregate surfaces, see (2911) fig. 14, but in this case the morphology of the precipitate ('tennis balls') indicates that separation of the aggregate pebble from the surrounding matrix took place prior to the crystallization, and not as a result thereof. However, Terzaghi (2914) reports an abundance of ettringite in seams around aggregate pebbles and attributes the measured expansion and the cracking of the examined concrete structure to this crystallization. The writer has observed calcium aluminate sulphate in seams around aggregate pebbles in the concrete with phyllite aggregate (2910), and Bastiansen et al. (595) observed the same kind of precipitation around alum-shale pebbles in Norwegian concrete. In the latter two cases, however, the source of the sulphate is constituents of the aggregate pebbles, and the concentration of the reaction product may be partly or totally due to this fact. It must also be borne in mind that crystallization around aggregate pebbles may occur after expansion of paste which has formed a peripheral crack.

According to the writer's observations, calcium aluminate sulphate occurs most frequently as radiating bundles of very thin, acicular or needle-shaped crystallites, growing inwards from the walls of voids, pores, air bubbles, or cracks in the concrete. Microcracks have not been observed leading into the surrounding matrix in a way likely to indicate expansive pressure due to the crystallization. Further, the bundles of crystallites are not usually compact enough to fill the available space, so pressure can hardly have been exerted during the growth of the solid crystallites. (This does not preclude the possibility of hydraulic pressure having been generated in liquid-filled spaces during the crystallization process, but the observations yield no information on this). It must also be remembered that even in concrete that has never been exposed to sulphates or that has not deteriorated at all, calcium aluminate sulphate will in the course of time accumulate in voids and cracks etc. (544) and (3981).

Calcium aluminate sulphate and similar precipitates are flocculent, and the individual crystallites are brittle when handled for preparation etc. Only the more compact 'tennis balls' in air bubbles contain so many 'point contacts' between the crystallites that a certain strength exists in the aggregation as a whole. However, this is still very easy to crush. Hence, the compound will not replace mechanical strength lost through decomposition of the original matrix. On the other hand, if grown in original voids, it cannot be considered detrimental to the strength of the concrete.

Special symptoms of chemical decomposition of concrete involving sulphates originating from an external source (sea water) are exhibited by the concrete samples from pier 7 of the Oddesund Bridge, partly from the outer pier side, below water level, and partly from the inner pressure chamber. The condition of this concrete has been described in detail by the writer (2911), (3971). The chemical alteration of the cement paste is at an advanced stage. Not only is $Ca(OH)_2$ and C_2S dissolved, but also part of the cement-gel substance (although there are local unattacked concentrations of cement paste). Calcium aluminate sulphate precipitates are found scattered in voids and cracks, but the principal secondary precipitates are gypsum and magnesium hydroxide. Further, calcium carbonate is frequently found precipitated as aragonite. From the morphology of the substances, crystallization can be seen to have taken place over a long period in the liquid phase and sometimes via repeated crystallization and dissolution. Two generations of crack formations can definitely be identified, which indicates that crack formations have occurred in situ during the process of deterioration. Especially in the material from the inner chamber of the Oddesund Bridge, the percolation of water through the concrete, probably from as far back as the time of erection, is a factor that must have influenced the extent of the alterations. During this percolation, the ions, especially Na^+, Mg^{++} and SO_4^{--}, that have participated in the chemical reactions, have been supplied continuously, and a considerable precipitation of reaction products has occurred on the inner walls of the concrete (3971) fig. 121 and following. On this background, leaching can be said to be a contributory factor in the deterioration.

Figs. 74, 75, 76, 77 and *78* show characteristic precipitations of gypsum, magnesium hydroxide and aragonite to illustrate the disintegration of cement paste under the conditions mentioned. Precipitations of calcium carbonate in the form of calcite in these samples are probably due to carbonation during drying after removal from the structure.

Surface coatings of aggregates have been observed with gypsum as the precipitate, see *fig. 74*. In this case gypsum may have replaced calcium hydroxide by a slow solid phase reaction, but this would probably be exceptional. Most frequently gypsum is found as a replacement substance in dissolved or diluted cement paste, with a tendency to parallel orientation of the anhedral microscopic crystals. *Fig. 75* is a typical example of such crystalline aggregates. It is noteworthy that the traversing crack has cut some of the gypsum crystals, thus indicating that the formation as a whole is a weak zone in the matrix, compared with surrounding areas of less deteriorated cement paste.

The characteristic mode of occurrence of magnesium hydroxide is as bands, fan-like or spherulitic formations of very thin, intergrowing, parallel fibres with nuclei or bases of much smaller, irregular growing crystallites, see *fig. 76*, (2911) and (3971). The rate of crystallization has been relatively high at the beginning, but seems to have decreased as the precipitation proceeded towards the interior of the void or crack. A similar mode of crystallization is demonstrated for calcium hydroxide in (3971) and commented upon by Bache et al. (3979). Sometimes magnesium hydroxide forms a coating around aggregate pebbles (2911). In other cases the banded formations form 'caves' in which other substances, e. g. gypsum and aragonite have crystallized (3971). (The

banded and spherulitic formations bear a marked similarity to the crystallization of natural tobermorite from liquid solutions in amygdales in dolerite rocks, see Jørgensen (6092)).

The micro-texture of the magnesium hydroxide indicates it to be a rather tough and hard substance of considerable strength, especially in the longitudinal direction of the fibres. Bands of magnesium hydroxide may thus act as a reinforcing, structural component in a deteriorated matrix, although it seems unlikely that the substance increases the impermeability of a concrete under deterioration since accumulation and crystallization seem to take place in the visible liquid-filled spaces rather than in the submicroscopic pore system of the cement gel.

There is no evidence at all that precipitation of magnesium hydroxide may cause expansive pressure and fracturing in the microstructure of concrete and thus act as a primary contributor to the deterioration.

Figs. 77 and *78* show aragonite in cracks. This compound has so far been observed by the writer only in voids and cracks in the underwater concrete from the Oddesund Bridge (3971). The lathlike crystals form fan-shaped radiating aggregates in larger spaces and 'lattices of girders' in cracks. The 'point-and-edge-contact' texture is very spectacular, for instance in (3971) figs. 85 and 86, and indicates only a slight and brittle bond. (However, even this kind of bond is stronger than open, empty cracks).

The hydrated calcium aluminate referred to by the writer (2787) has not been observed in more recent examinations, and other investigators have not so far reported observations of this precipitate. Its existence and the significance of its occurrence thus still require confirmation. It is, however, reasonable to expect the development of hydrated calcium aluminates when aggressive carbon dioxide causes severe deterioration of concrete.

Figs. 79 and *80* show how sulphuric acid attack may result in complete replacement of the cement paste by an intergrowing aggregation of microscopic gypsum. The fractures in the gypsum paste are characteristic of a material of little intrinsic strength. This is also shown by the 'softness' and deformability of the fresh, moist concrete specimens and by the weak, brittle condition of dried specimens. Again, the 'point-and-edge-contact' structure of the gypsum matrix can be expected to provide poor mechanical properties, inferior to the toughness and strength of the submicroscopic gel structure of the original cement paste. Magnesium hydroxide did not occur in this case. Calcium aluminate sulphate was present as an interstitial precipitation in cement paste in the concrete from a factory chimney (4083). The cement paste had been partly replaced by an aggregate-like mass of calcium aluminate sulphate. Gypsum too was abundant in the paste, but at the same time, calcium hydroxide and unhydrated C_2S occurred. Thus, in this concrete there was not only alkali-aggregate reaction - see p. 87 and *fig. 29* - but also an intermediate stage of alteration involving sulphates, probably originating from the chimney smoke. The Colombo dock specimens (2910) included euhedral gypsum crystals, obviously developed in a liquid phase. It seems clear from the available information and from the morphology of the specimens of incrustations examined that liquid seeping upwards through the concrete has first precipitated calcite on the dock floor, and this calcite has covered further supplies of liquid

in which gypsum has crystallized. A further supply of liquid has broken through the calcite surface, precipitated new calcite and so on. High temperature must have been an important factor in this case. (Incipient crystallization of gypsum in incrustations was found in the pressure chamber specimens from the Oddesund Bridge, (3971). Magnesium hydroxide was the alternate precipitate in this case).

Summing up, the precipitates discussed may be found in the following ways

1. In original voids, air bubbles, etc, in the cement paste.
2. As replacement for crystalline calcium hydroxide in the cement paste.
3. As replacement for dissolved cement paste.
4. In fractures, developed during deterioration, sometimes in more than one generation.

Swelling of paste as a result of sulphate attack is indicated by peripheral cracks, which represent a destruction of bond quite different from the interaction in the boundaries of aggregate particles met in alkali-aggregate reaction.

It has not proved possible on the basis of the writer's microscopic observations to obtain much new information on the chemistry of sea water attack and other kinds of sulphate attack. This is because the quantities of interacting substances, the characteristics of the concrete and physical conditions, temperature variations and hydraulic gradients, are unknown. It seems convincingly demonstrated that extensive development of the secondary precipitates mentioned can only take place when an external, continuously replenished source of sulphates (and magnesium) is in contact with the concrete.

Poulsen and Idorn (2794) showed that the brackish water in Copenhagen Harbour caused leaching of the permeable mass concrete of one caisson of Knippels Bridge. The concentration of Ca^{++} and the pH-value were greater in the water that had passed through the concrete than in the surrounding harbour water, whereas changes in the concentrations of alkalies and sulphates were negligible.

Water that percolated through the caisson walls and mass concrete of the Oddesund Bridge was found by Kjær (5483) to have undergone considerable changes in composition during the passage through the concrete. Large quantities of Mg^{++} and SO_4^{--} were found to be consumed by the concrete, whereas the Ca^{++} concentration did not change. These results support the writer's conclusion about the severity of the action of sulphates and magnesium in concrete, whereas the chemical analysis of the water provides little information on extent of alkali-aggregate reaction, and does not show any decrease in the Ca^{++} concentration in the concrete. It must also be remembered that Ca^{++} can participate in profound alterations of the concrete, even with very serious mechanical effects, without any change in the total Ca^{++} concentration. This is because there is a multitude of available sources of supply of Ca^{++} ions in the concrete itself, namely:

1. $Ca(OH)_2$ in solution and in crystalline (and possibly amorphous) phase of the cement paste.
2. β-C_2S which yields $Ca(OH)_2$ by hydration or Ca^{++} by acid attack.
3. $CaCO_3$ as secondarily precipitated calcite or aragonite.
4. $CaCO_3$ as limestone in aggregate pebbles, especially in calcareous porous flint in which the siliceous structure has been affected by alkali-aggregate reaction.
5. Ca^{++} from other rock types or mineral grains.

Some of these sources of calcium are activated by changes of temperature and others by alterations in the chemical conditions in the concrete. If, for instance, a steady supply of alkalies is delivered to the concrete from surrounding sea water and at the same time Ca^{++} from the cement paste is utilized by reaction with sulphate, the Na^+/Ca^{++} proportion will be so much increased compared with the normal conditions that alkali-aggregate reaction must be expected to become very severe and deleterious, and this is exactly what the petrographic examination of the underwater specimens from the Oddesund Bridge tells us. It is remarkable that further sulphate attack is by no means impeded in this way. On the contrary, with continuous dissolution of the paste and cracking, it is enhanced, not least due to the increased rate of percolation. As a general conclusion, one could say that in many cases of severe alkali-aggregate reaction the possibility of sulphate attack should also be examined thoroughly, and vice versa. In the cases with the Norwegian rocks (alum shale and phyllite) precipitation of secondary sulphates, derived from dissolution of substances in the aggregates was observed. This should probably be considered as a weakening of the structure intensifying the mechanical effects of the alkali-aggregate reaction.

The concrete has been exposed to a unilateral hydraulic pressure in a number of the cases dealt with here. In other cases, evaporation combined with capillary suction and a diffusion gradient may provide similar propitious conditions for deleterious chemical processes. Exposure of this kind can cause extremely rapid deterioration, Rosenqvist (593).

Some remarks are called for on the macro-effects in field concrete of the chemical and structural alterations referred to above. Although expansion is a significant effect of sulphate attack in laboratory experiments (in extreme exposure also warping and eventually disintegration), there are not many records of gross structural expansion ascribed to sulphate attack, especially not from ordinary sea water. On the contrary, most concrete withstands sea water exposure very well when of adequate initial quality, Wakeman et al. (5516) and discussions (5517). However, in severe cases of special kinds of sulphate attack, e. g. Terzaghi (2914) and Bastiansen et al. (595), considerable expansion has been found to have taken place; expansion may also have played a part in the spalling of the Swedish dam concrete (2910).

Weakening and decomposition of the matrix are more common symptoms than expansion and lead to a mushy consistency of moist concrete and to a brittle condition of dried concrete. The designation 'seriously disintegrated' for some groyne blocks, (531) and (544), refers to this kind of deterioration. (2787) and many other papers describe similar advanced cases in which expansions are not on record, whereas destruction of the binding properties of the cement paste and of the bond between matrix and aggregate particles is evident and advanced.

In the underwater concrete from the Oddesund Bridge there are some indications that osmotic pressure may play an as yet unknown part in the deterioration. Viz:

1. The selective precipitation of large amounts of gypsum, magnesium hydroxide and calcium carbonate.
2. The unusual amounts of alkali-silica gel.
3. The local concentrations of undamaged cement paste amidst very deteriorated areas.
4. The different composition of sea water before and after percolation through the concrete.

Although the writer's examinations cannot contribute directly to the discussions of more recent hypotheses on the basic nature of sulphate reactions, it is appropriate to call the reader's attention to such interesting recent studies as presented for instance by Eitel (1491) with discussions by Spindel and Steinour (1489), Ben-Yair and Heller (5462), Chatterjii and Jeffery (2597) with discussion by Roberts and Chopra (4056). Also the studies of crystal growth in connection with the setting of gypsum etc. by Hansen (56), and Jørgensen (706), (5463), ought to be taken into consideration in planning future experimental work. Scientific investigation and descriptions of field deterioration ought to be more closely integrated in future than they have in the past.

Observations on frost damage to concrete

Freezing and thawing act on concrete primarily as a physical agent causing volume changes in aggregate particles, cement gel, calcium hydroxide and in the liquid and gaseous phases of the cement paste. Under certain circumstances alternate swelling and contraction of the concrete as a whole also take place. Secondarily, the thermal gradients provide changes in the solubility of the solid components, especially of the calcium hydroxide. Thirdly, if the volume changes in the concrete or its components lead to fracture, atmospheric air, water or external solutions may enter the concrete, thus providing further chemico-physical influence and decomposition.

The first thin section examination of frozen concrete carried out by the writer is the concrete with 'peacock traces' (2681). This not very well described concrete had been exposed to frost at a very early stage of hydration (as green concrete) and showed intensive development of ice lenses. The traces of ice lenses are well preserved in the thin section, and ice formations along aggregate boundaries can be seen to have destroyed areas of bond between aggregate and cement paste. A thorough carbonation of the paste had taken place, but this phenomenon must be interpreted with caution because the concrete had been kept indoors uncovered for some years before the thin section preparation.

The concrete bar frozen after three hours' prehardening (2910) represents a case of a well defined concrete, damaged at an early age. Again, plenty of ice lenses, although microscopic, were found all over the concrete. They

were located as subparallel formations of microfractures in paste areas, but were also frequent along the boundaries of aggregate pebbles. Calcium hydroxide was plentiful in the spaces left after the ice development and showed accumulated crystallization, probably very much as the ice would have appeared if preserved before and during the thin section preparation.

Figs. 81 and *82* show the microscopic residues from ice lenses in the thin section.

Detrimental agents other than freezing/thawing could also be excluded in the Greenland concrete specimens (2910) (a high degree of water saturation was provided by means of a natural tidal exposure, Lind Pedersen (5466)). This concrete had been adequately hardened before being exposed to frost. Accordingly, the evidence of damage seen in the thin sections does not comprise spaces left by ice lenses, but

1. Scarring from the surface inward, consisting of microfractures and extensive carbonation of the cement paste.
2. Cracks separating aggregate pebbles and cement paste, apparently developed after accumulation of ice on surfaces of aggregate pebbles. Connecting cracks from one pebble to another.
3. Exceptional accumulations of crystalline calcium hydroxide in spaces in the interior of the concrete.
4. Sound, undamaged appearance of the cement paste in the interior of the concrete.

Figs. 83 and *84* show scarring of the concrete surface with subsequent carbonation. *Fig. 85* shows bond cracks with a connection crack, and *figs. 86* and *87* show exceptional crystallization of calcium hydroxide.

It is interesting that the Baltic concrete (2789) showed field evidence of deterioration very similar to that described above for the Greenland concrete. In both cases the aggregates consisted of excellent, frost-resistant rocks, and freezing/thawing in a coastal exposure was the only important factor of deterioration. Hence, we can expect the microscopic evidence of frost attack in the Baltic concrete to be the same as in the Greenland specimens. As yet, however, this has not been checked.

Bache et al. (3979) have discussed in a general way the conditions governing the accumulation of crystalline calcium hydroxide in spaces - and especially in original air voids - in concrete. It must be remembered that temperature cycles which do not traverse the freezing point, and a variety of chemical processes may also induce crystallization. Furthermore, the time factor must be considered in examinations of this kind. (2681) figs. 6, 22 to 28, and 61 to 66, and (3971) figs. 40, 53 to 54, 58 to 59, and 111, show modes of occurrence of calcium hydroxide.

In the general description of symptoms of frost attack to be looked for in thin sections, we still lack a detailed study of a pop-out caused by freezing of pore water in a pebble of porous limestone or flint, or any rock type of similar structure. Also the effect of pre-drying or saturation of such aggregates before the casting of the concrete requires investigation.

Observations on shrinkage effects in concrete

The characteristic feature of cracking in concrete with shrinkable aggregate has recently been studied by Roper et al. (3600). They examined concrete made with South African aggregates. These have been described for instance by Stutterheim (2655) as causing excessive cracking and deflection in concrete structures in arid regions in South Africa. The petrographic examination showed an abundance of cracks along the boundaries of the aggregate pebbles, often best developed in the longitudinal direction of the particles. Radiating cracks were much less frequent than boundary cracks. Sometimes the cracks followed the aggregate-paste interface, sometimes they passed through the surrounding paste, and in some cases they were found entirely within the aggregate particles.

The writer has not specifically studied deterioration due to excessive shrinkage of aggregates in Danish concrete, but there are observations comparable to the above description.

The cracking around a shrinking aggregate particle surrounded by a relatively stable matrix, must to a first approximation have the same appearance as expansion of a matrix surrounding a relatively stable aggregate particle. Thus the writer's description of boundary cracks, developed in expanded mortar bars during exposure to sulphate attack (2681) corroborate the observations by Roper and co-authors. However, we must remember that in one case we are dealing with true swelling, and in the other case with true shrinkage. (Incidentally, the megascopic feature of severe aggregate shrinkage in concrete seems to be typical map-cracking, see e. g. Stutterheim (3325) fig. 3. Hence, careless interpretation of symptoms of field failure may give very misleading conclusions).

An 'artificial' case of aggregate shrinkage in a stable matrix is presented in (2681) figs. 50 to 52. Silicified, argillacious limestone particles were embedded in araldite, weakened by reaction with sodium hydroxide and afterwards exposed to drying in the open. Severe cracking, typical of drying shrinkage, took place in the particles, whereas the matrix, being much stronger than the rock substance, did not crack during the swelling of the particles or during the subsequent drying shrinkage.

Fig. 88 shows the crack pattern within one of the particles. The compressed interior is separated by a wide, open fracture from the boundary area, which is firmly adhering to the surrounding matrix.

(2681) figs. 48 and 49, show a rather similar pattern of cracking in dried gel precipitated in a void in a broken piece of concrete. (2911) figs. 12 and 13, show the effect of drying on the decomposed structure of porous flint. Polygonal map-cracking of the remaining interior substance has taken place, very much like in drying clay. A crack separates the interior of the particle from the boundary.

Fig. 18 in the present paper shows the pattern due to drying shrinkage in an aggregate particle that has been completely altered into gel after decomposition of the original porous flint. The boundary cracks run partly within the particle (along the reaction rim) and partly in the matrix. Similar fracture phenomena involving shrinkage of aggregate particles are shown in (3971). However, in most of these cases alkali-aggregate reaction has probably antedated the shrink-

age and made the rock substance weak and deformable, much of the cracking being due to swelling pressure.

This complexity calls for considerable caution in interpreting the features of cracking in any microscopic examination of this kind.

Nepper-Christensen (5482) has measured the shrinkage and swelling characteristics of dense flint and basaltic rocks. In practice, however, neither structural deflections nor cracking due to exposure to changing humidity have so far been reported in Denmark.

The ageing of concrete

Extreme cases of 'ageing' are represented by Roman concrete. In the writer's examination of thin sections of Roman concrete from aqueducts in the South of France (3981), the most conspicuous evidence of ageing was the complete filling of air voids with calcite. Incidentally, the mechanical strength of the concrete indicated that a good bond between the aggregate and the matrix had been maintained. In the Roman concrete from the aqueduct at Caesarea, Israel, supplied by Dr. Ben-Yair, the following observations were made.

1. Complete carbonation of the paste.
2. Deep and intensive rim corrosion in a flint particle, see *fig. 46*.
3. Distinct rim corrosion in a good many quartz grains, often together with boundary cracks and apparently precipitation of a reaction product, possibly a hydrated calcium silicate.
4. Partial solution of a feldspar grain.

Malinowski et al. (3980) also examined the Caesarea mortar and other Roman concrete and mortar from Israel, and their observations corroborate the above. The lime mortar from the church in Jutland, see p. 88 and Nepper-Christensen (5522) is another example of true 'ageing' of mortar, and the symptoms of alteration are very similar to those mentioned above.

The concrete from Port d'Antibes, stated by the harbour authorities to have been cast during the time of Vauban 1650-1700, (3981), showed the remarkable combination of excellent preservation and extensive formations of calcium aluminate sulphate in voids.

The Danish roofing tile dating from 1884 (3981) represents an extreme case of ageing of a concrete - or rather mortar - cast with Portland cement. The 16-mm thick tile had been in position on a roof from 1884 until 1955, but showed no sign of deterioration apart from abrasion of the upper surface. Carbonation was limited to the surface layers, and both calcium hydroxide and β-dicalcium silicate were plentiful in the interior. The mortar appeared to have been cast as a dry, rich mix and well compacted. These characteristics, combined with the particular exposure conditions of the tile must be responsible for the almost complete absence of signs of ageing.

Figs. 89 and *90* show a full-width section of the thin section (which represents a complete cross-section of the roofing tile), illustrating the characteristics of the mortar mentioned above.

Ageing as a contributory cause of final disintegration, or as a designation for very thorough deterioration either of old concrete or of concrete that has been in poor condition right from the start, is represented in the writer's investigations by

1. The concrete foundation from the southern harbour district of Copenhagen (2787).
2. Groyne No. 71 at the north barrier of the Lim Fiord, Jutland (544) and (2910).
3. The highway bridge, North Jutland (544) and (2910).
4. Knippels Bridge in Copenhagen (2796), (2795), (2794), (2793) and (2792).

A description has already been given on p. 137 of how the symptoms of deterioration of the concrete foundation indicated a combined attack of aggressive carbon dioxide and sulphates as the predominant cause of failure. The duration of the deleterious exposure and the apparent poor initial quality of the concrete make it possible in this case to characterize the following phenomena as evidence of ageing.

1. High degree of dissolution or alteration of the original cement paste, involving total absence of calcium hydroxide and β-C_2S, and a high degree of porosity.
2. Highly elaborated and extensive crystallization of secondary compounds, e. g. calcite, calcium aluminate sulphate and hydrated calcium aluminate partly as replacement for the original cement paste.
3. Remains of alteration products of original paste, not identifiable but probably consisting of impure silica gel. The substance is usually irregularly fibrous or aggregate-like with no distinct optical characteristics and appears to be a deformable and weak material with no particular binding properties.
4. Corrosion of the boundaries of aggregate particles, indicating partial dissolution of the rock substance.

The thin sections from groyne 71 (2910), may be considered to represent ageing to a less pronounced extent than the above, especially since the paste is significantly less diluted, although some alteration is indicated. Characteristic evidence of ageing in this case is

1. Extensive carbonation alternating with areas of quite isotropic paste residues without visible calcium hydroxide and β-C_2S, i. e. probably an unidentifiable silica gel.
2. Carbonation of precipitated alkali-silica gel, indicating secondary alteration of the gel substance.
3. Very extensive cracking of the concrete, indicating high permeability and low mechanical strength.
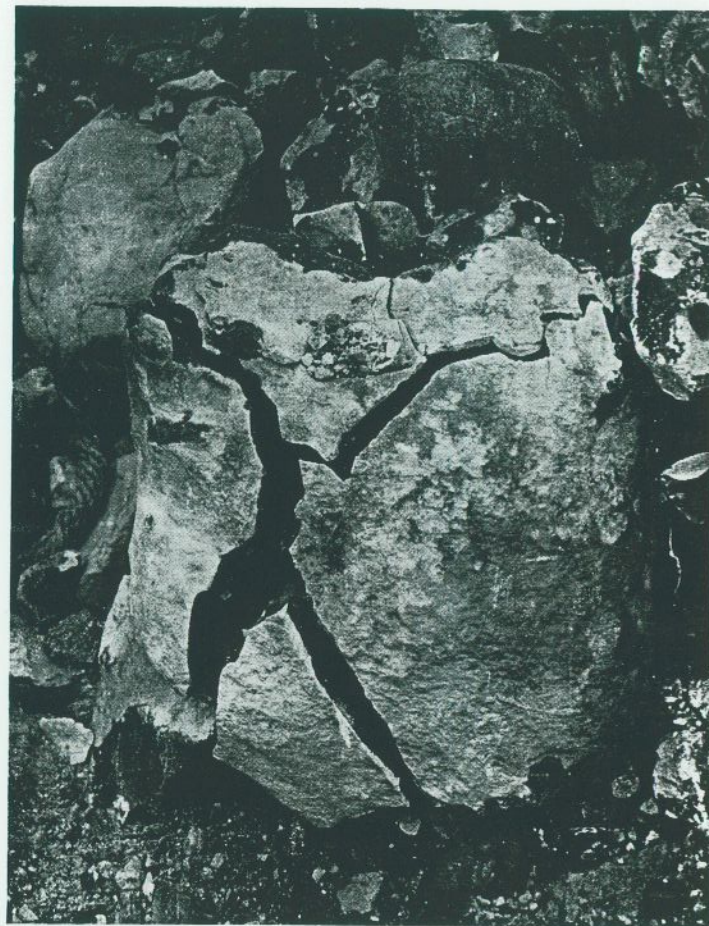
50 mm

Fig. 64. Fist-size pebble of dense flint from the foot of slope in gravel pit at Outrup, Jutland. The photograph was taken at the end of the winter as being typical of numerous examples of explosive cracking due to swelling pressure resulting from freezing of the pore water in the flint. All cracked pebbles which were opened had a porous interior, often with a hollow space, often with rust stains, indicating that the penetrating water had contained iron. The mechanism of the disruption must be considered to be very much the same as when alkali-silica gel accumulates in the pores of reacting dense flint in concrete and then imbibes water. From (2928).

1 mm
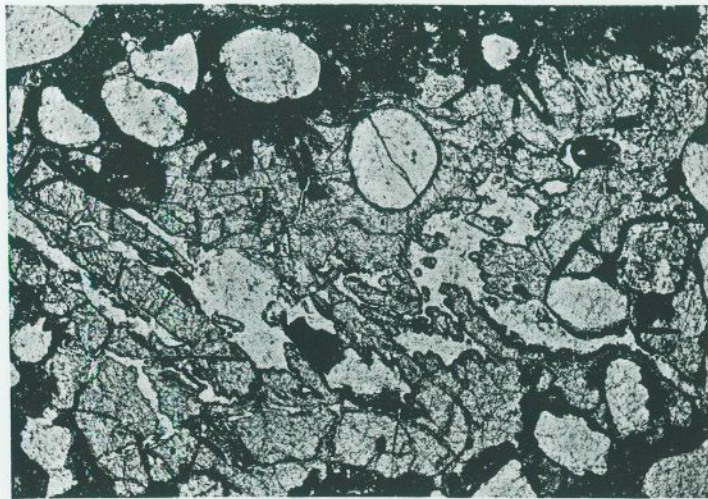
0.1 mm

Fig. 65. Detail of crack through the mortar in thin section of concrete from an interior chamber of bascule pier, Oddesund Bridge, below water level. The crack is more than half filled with transparant, isotropic gel showing typical shrinkage cracking. Some sand grains are completely surrounded by gel, indicating that severe dissolution of the cement paste has taken place prior to precipitation of the gel. From (3971). Thin section No. G 19-35-[54.5.110a]. O.

Fig. 66. Air bubble in thin section of concrete specimen from factory chimney. The bubble is located close to a reacted pebble of dense flint (the boundary can be seen in the picture) and is partly filled with gel which has seeped in from the reaction site in the pebble. The gel shows typical drying shrinkage and cracking. Thin section No. BFL 4-6. O.
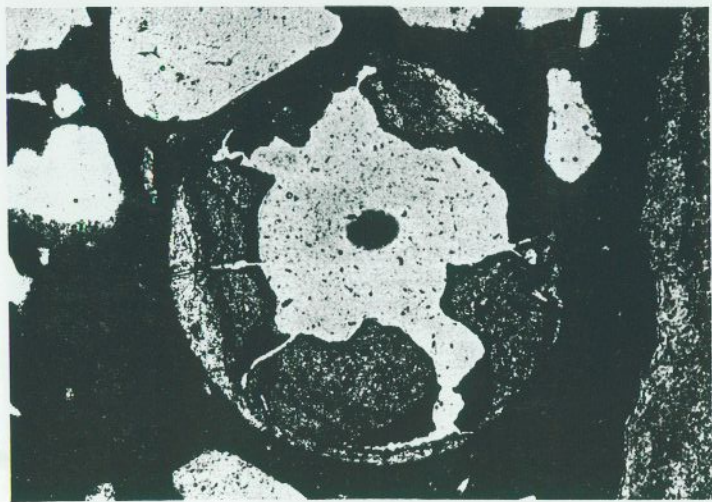
Fig. 67. Large pebble of dense, pigmented flint, in thin section of concrete from exterior wall of bascule pier below water level, Oddesund Bridge. The traversing main-crack is lined with gel, an unusual phenomenon among the writer's observations on alkali-aggregate reaction. The gel has possibly seeped into the crack from another reacted pebble. From (3971). Thin section No. I-44-[54.5.101]. O.

Fig. 68. Thin section of the longitudinal section of concrete core No. 54.5.13, Oddesund Bridge. Cracks traversing the core and pebbles of reacted porous flint can be distinguished (compare with fig. 69). The dark patch without sand grains consists of cement paste, and is probably an accidental joint. Thin section No. G 19-5-[54.5.13]. II.


0.5 mm
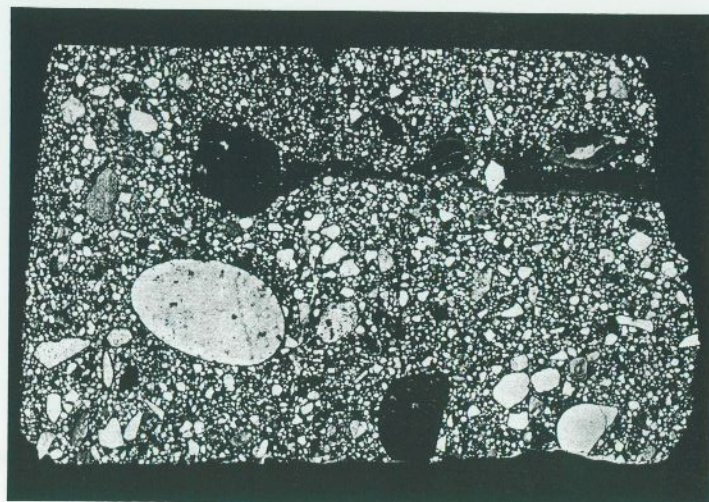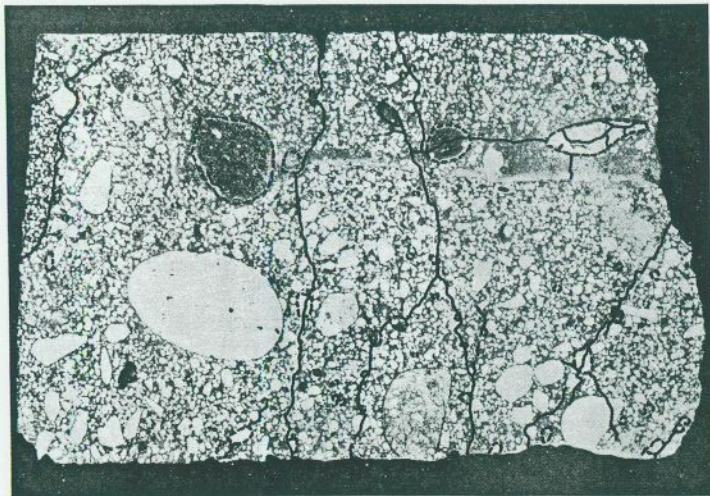
10 mm

10 mm

Fig. 69. Thin section shown in fig. 68, with the connecting cracks and the reacted pebbles and sand particles of porous flint emphasized. It can be seen that the cracks tend to pass through the reacted particles. In other words, the swelling of these particles has contributed to the development of the cracks. Thin section No. G 19-5-[54.5.13].

Fig. 70. Thin section of concrete from road, Nebraska, USA, containing the reacted shale particle shown in figs. 62 and 63. The concrete is cracked over the entire thin section, predominantly sub-parallel with the concrete surface which is one edge of the thin section, despite the fact that there are only very few reacted shale particles in the thin section. Thin section No. BFL 4-2. II.
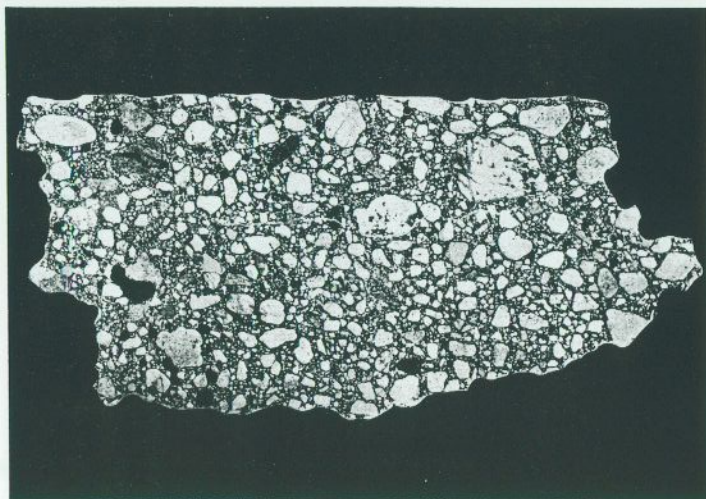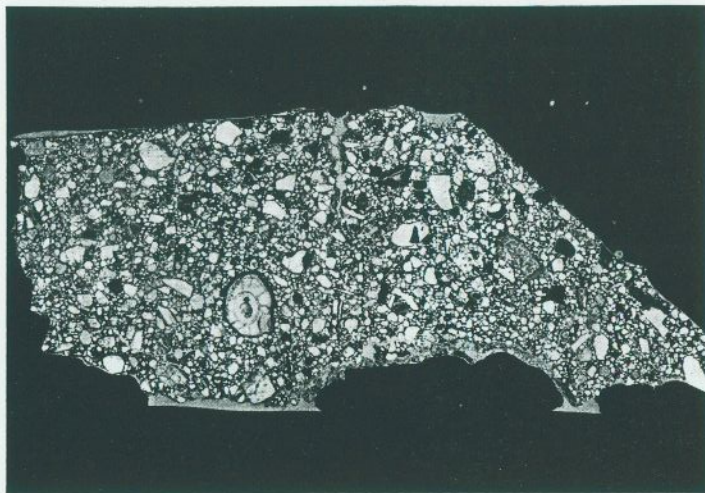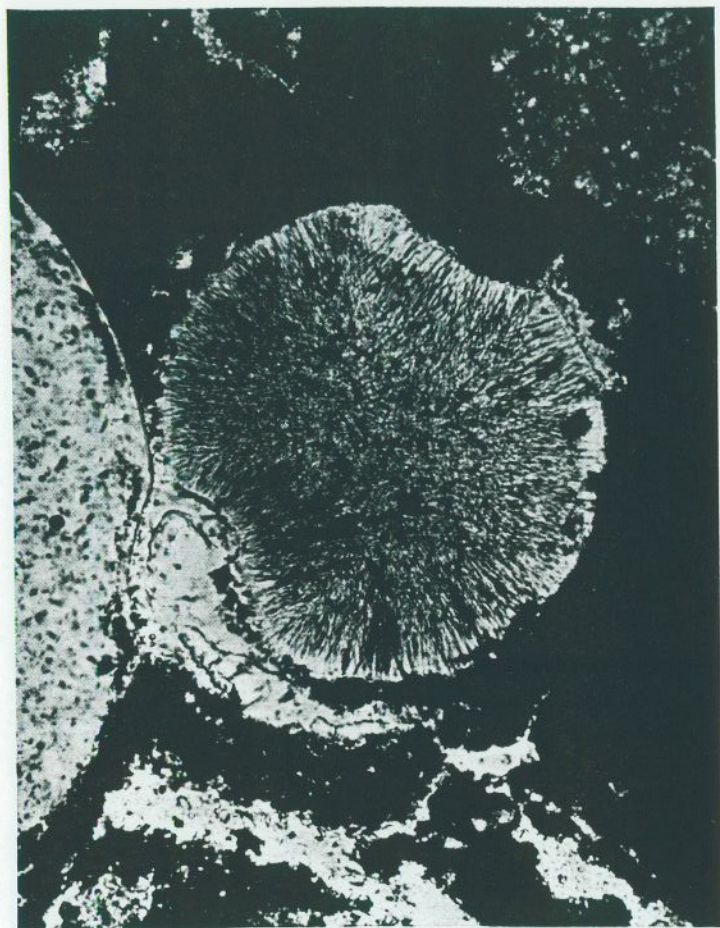

50 mm

10 mm

Fig. 71. Thin section of concrete from old caisson in the harbour of Ålborg, Jutland. The thin section contains the reacted pebble of porous flint shown in figs. 18, 21, 24, and 25. The whole section is severely cracked and contains many pebbles and sand grains of flint which are thoroughly reacted. The cement paste is partly dissolved along the cracks. This concrete has reached the stage of disintegration. Thin section No. BFL 4-3. II.
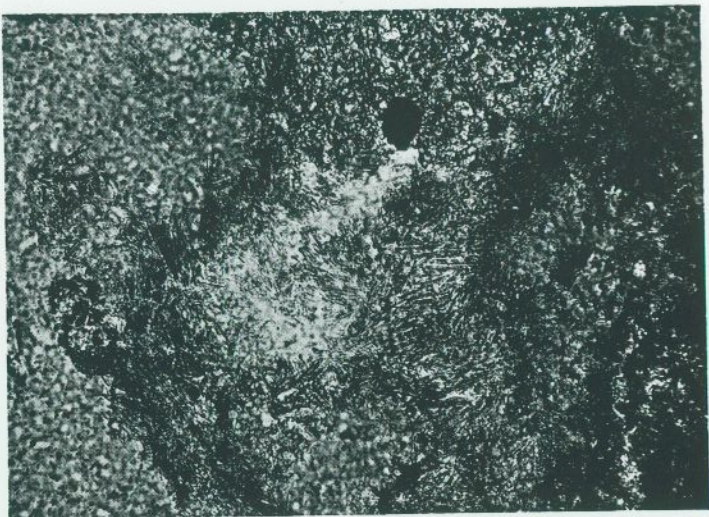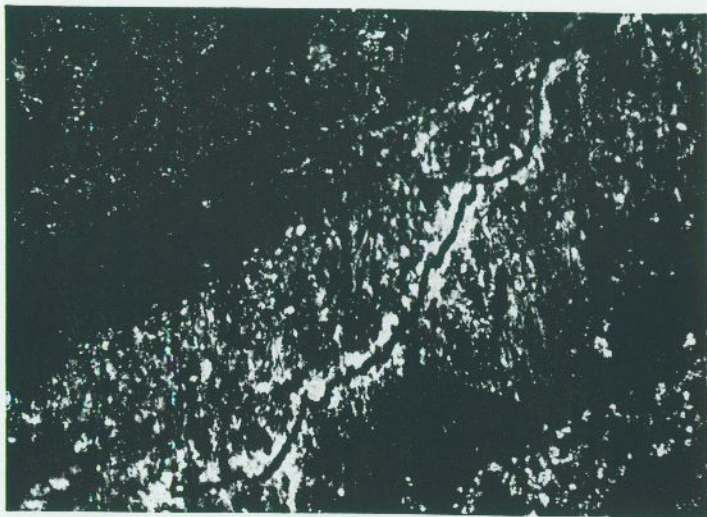
0.1 mm

0.1 mm

Fig. 73. *Open crack radiating from severely cracked phyllitic pebble in thin section of concrete from dam in Norrland, Sweden. The crack is filled with secondary, granular calcite intermingled with lath-like calcium aluminate sulphate. From (2910). Thin section No. III-1-[122/54-BET. 4].* ○.

Fig. 74. *Fractured mortar showing sand grains, cement paste and open spaces in thin section of concrete from exterior wall below water level of bascule pier, Oddesund Bridge. Anhedral and submicroscopic gypsum has crystallized adjacent to the quartz grain and in the adjoining fracture, possibly replacing calcium hydroxide. From (3971). Thin section No. I-41-[54.5.101].* ○.

Fig. 72. *Air bubble with radiating aggregation of needle-shaped crystallites of calcium aluminate sulphate in thin section of concrete specimen from deteriorated old foundation, South Harbour area, Copenhagen. The rather compact aggregation does not occupy the whole of the available space in the bubble and there are no cracks radiating from the bubble into the surrounding cement paste. Thus, the development of the compound seems to be a result of deterioration rather than a cause of the damage. The case is referred to in (2787). Thin section No. K 300/56-1.* ○.
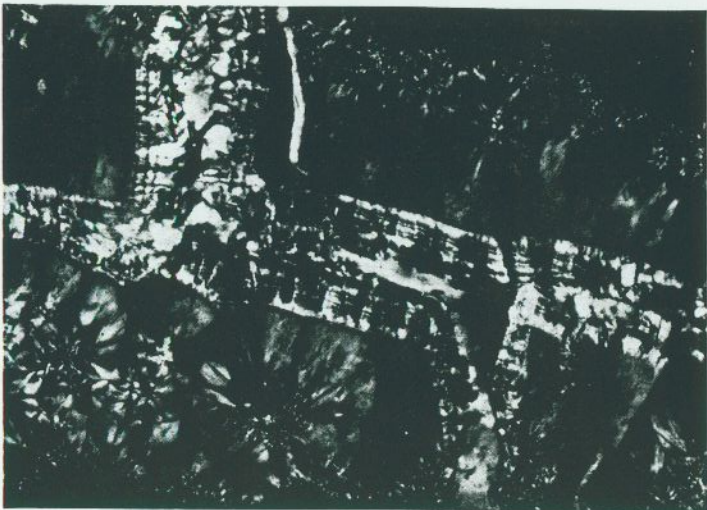

0.1 mm

0.1 mm

Fig. 75. *Area of cement paste with crystallization of gypsum in thin section of concrete from exterior wall of bascule pier below water level, Oddesund Bridge. Crystallites of gypsum have been severed by the traversing crack, showing that precipitation has taken place before the fracture. From (3971). Thin section No. 1-41-[54.5.101]. Ø.*

Fig. 76. *Secondary magnesium hydroxide in fracture in thin section of incrustation from inner wall of chamber below water level, bascule pier, Oddesund Bridge. The compound has precipitated as fibrous, banded formations. Two generations of cracking and crystallization can be distinguished. From (3971). Thin section No. G 20-51-[54.5.113]. Ø.*
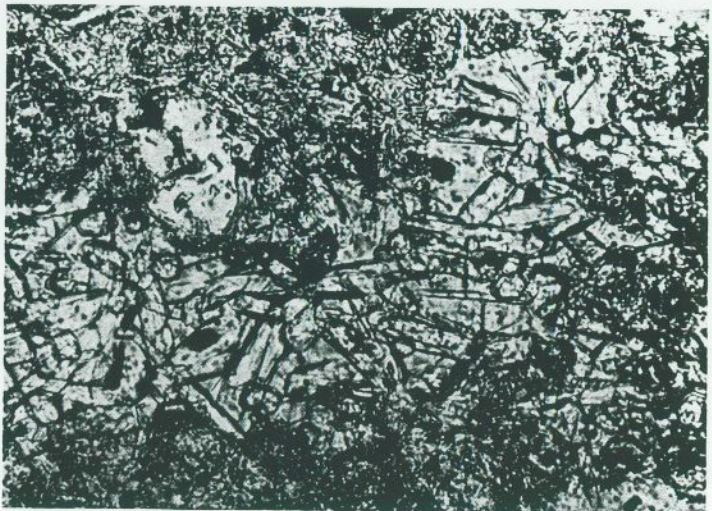

0.1 mm

0.1 mm

Fig. 77. *0.3 mm wide crack besides granitic pebble in thin section of concrete from exterior wall below water level of bascule pier, Oddesund Bridge. One half of the crack (originally, apparently the whole crack) is occupied by banded magnesium hydroxide. The other half, apparently formed by a second disruption, contains lath-like crystallites of aragonite. From (3971). Thin section No. 1-45-[54.5.101]. Ø.*

Fig. 78. *Detail of crack in the vicinity of the location shown in fig. 77. The laths of aragonite form a girder system in which the binding force can act only through 'point and edge' contacts, and therefore must result in a weak and brittle material compared with the original cement paste. From (3971). Thin section No. 1-42-[54.5.101]. O.*
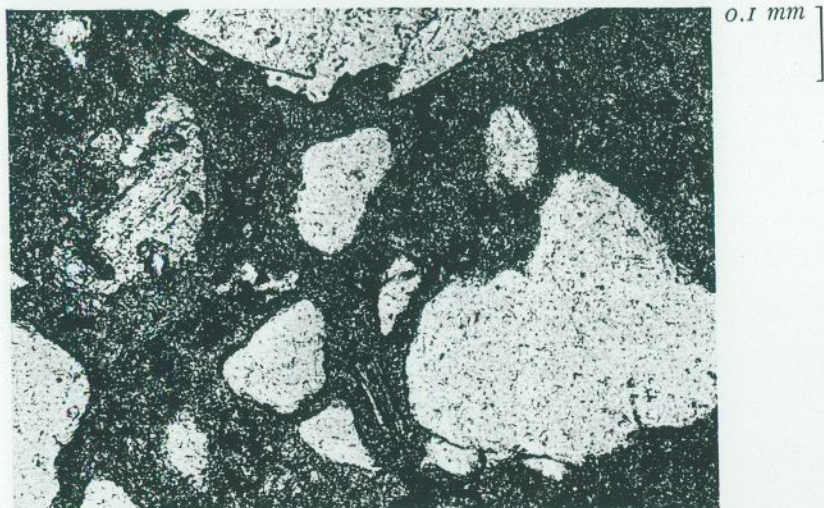

0.1 mm

0.1 mm

Fig. 79. Mortar in thin section of concrete from sulphuric acid plant in Jutland. The original cement paste is completely replaced by microcrystalline gypsum which must have been deformable in the moist condition and weak and brittle after drying. Thin section No. BFL 3-15. ○.

Fig. 80. Another location in the mortar of the thin section shown in fig. 79. The type of fracture shows the deformability of the microcrystalline matrix of gypsum in the moist condition prior to the preparation of the thin section. Thin section No. BFL 3-15. ○.

0.1 mm

1 mm
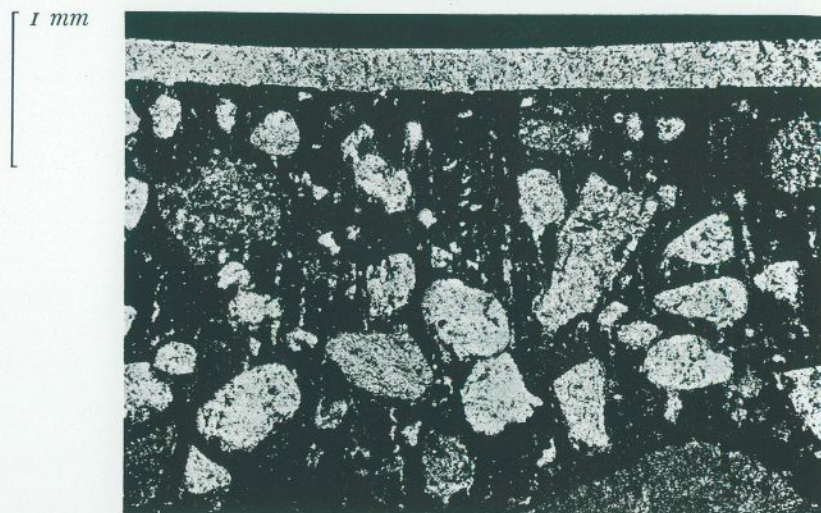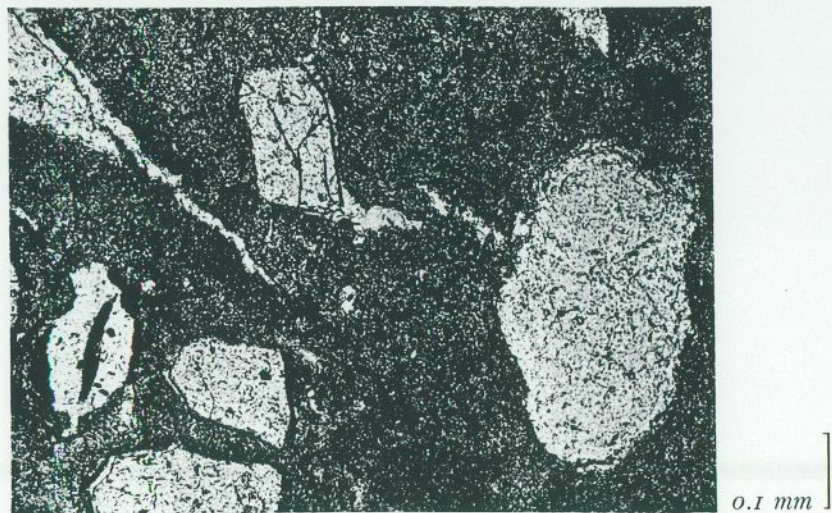
Figs. 81 & 82. Details of thin section of concrete bar which had been exposed to − 20 ℃ after three hours' prehardening at +20 ℃. Groups of imprints of ice lenses are seen in patches perpendicular to the edge of the thin section which represents the original surface of the bar. The spaces left by the ice have been occupied by secondary crystalline calcium hydroxide. Slight carbonation has occurred in patches at the original surface. Thin section No. G 22-[6001-III B-1]. Fig. 81: ○. Fig. 82: ⌀.

1 mm

1 mm
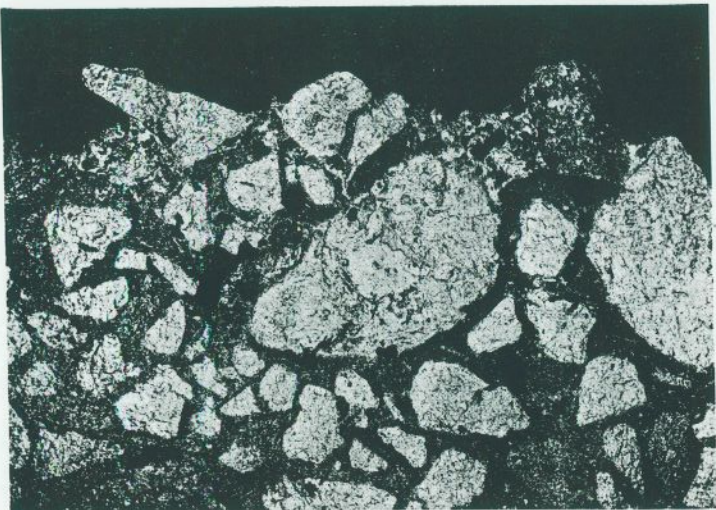
10 mm

Figs. 83 & 84. Details of thin section of experimental concrete slab from Godthåb, Green-land. The thin section is a part of the concrete surface and shows scarring of an originally smooth surface, due to severe freezing/thawing in the tidal zone. Carbonation of the paste can be distinguished. Thin section No. G 22-[5905-1 a]. Fig. 83: ○. Fig. 84: ∅.
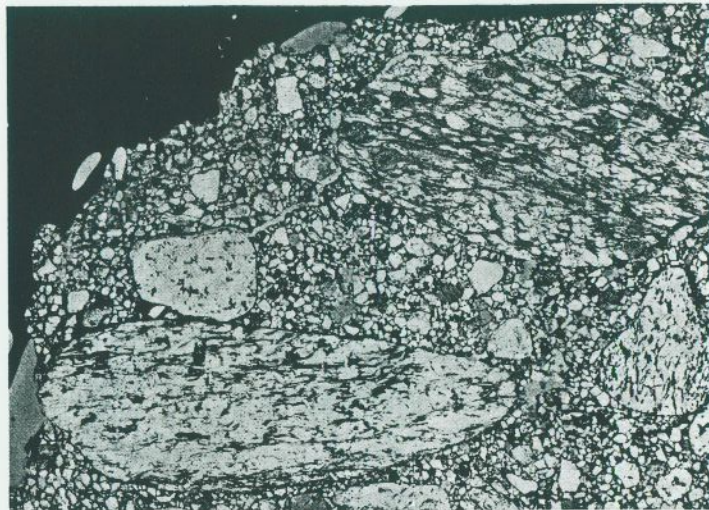
Fig. 85. Detail of thin section of experimental concrete slab from Godthåb, Greenland. The photograph shows part of the original concrete surface, now scarred by frost action, with bond cracks along granitic aggregate pebbles and a connecting crack between two pebbles. Thin section No. G 22-[5905-1]. ‖.

Fig. 86. Accumulated crystallization of subhedral calcium hydroxide between two rounded aggregate particles of quartz and feldspar in thin section of experimental concrete slab from Godthåb, Greenland. The cleavage of the calcium hydroxide appears to be parallel to the cleavage of the adjacent feldspar. However, this may not be true of the third dimension. Thin section No. G 22-[5905-1 a]. ○.

1 mm

0.1 mm

0.1 mm

10 mm

Fig. 88. *Pebble of silicified, argillaceous limestone subjected to alkali-aggregate reaction after embedment in araldite, and thereafter shrunk during drying of the weakened rock substance. The compressed interior is separated by a wide open fracture from the boundary area which has remained firmly adhering to the surrounding matrix. From (2681). V.*

Fig. 87. *Accumulated crystallization of subhedral calcium hydroxide in a space between two quartz grains in thin section of experimental concrete slab from Godthåb, Greenland. The calcium hydroxide is seen to adhere closely - in fact, almost to protrude from the boundary of one quartz grain. The basal cleavage of the calcium hydroxide can be distinguished. Thin section No. G 22-[5905-1]. Ø.*
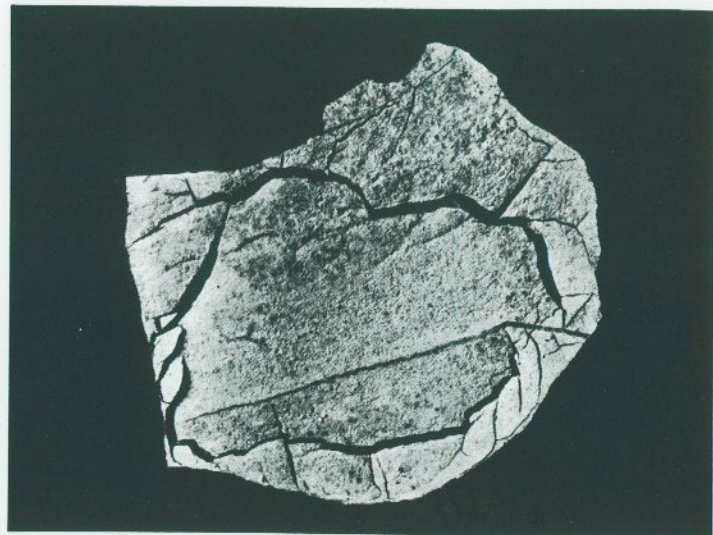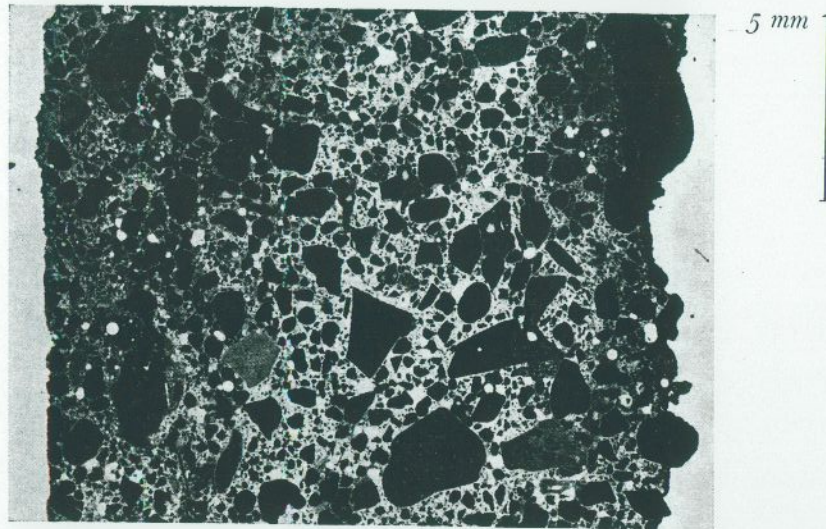
_5 mm_

Figs. 89 & 90. Details from thin section of cross section of concrete roofing tile cast in Fåborg, Funen, in 1884. The tile had been exposed to the weather on a roof until 1955, but no sign of deterioration was found except for abrasion of the upper surface. Carbonation was limited to the actual surface layers, and calcium hydroxide and β-dicalcium silicate were plentiful in the cement paste. On the whole, the concrete showed little evidence of ageing despite the time of exposure. Thin section No. BFL 4-31. Fig. 89: V. Fig. 90: X.

_5 mm_
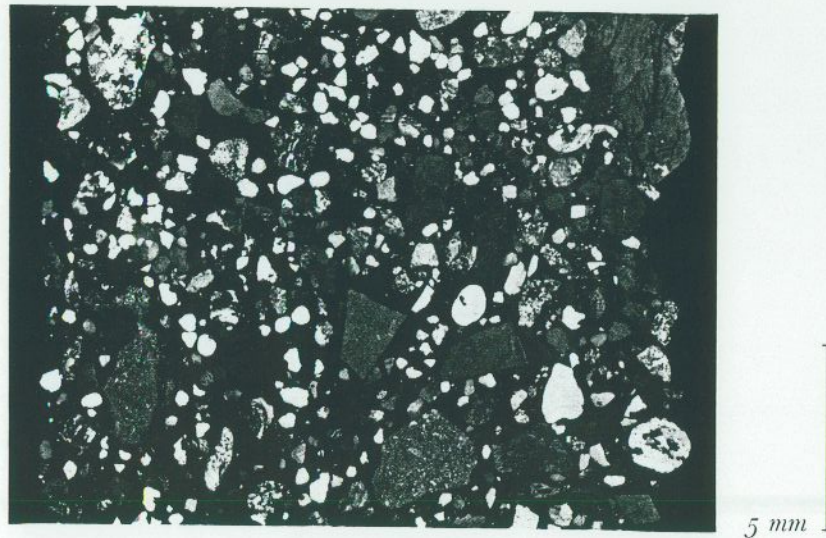
The microstructure of the concrete from the North Jutland highway bridge (2910) also shows signs of advanced decomposition. The cement paste is obviously diluted, seams of secondary calcite alternate with quite isotropic remains of original paste, and secondary calcite has also precipitated in gel formations, possibly during weathering of the gel. Very extensive, compact formations of calcium aluminate sulphate (or a similar, possibly impure compound) are frequent in cracks and in boundary zones around aggregate grains.

Knippels Bridge, one of the two bridges connecting Copenhagen with the island of Amager, was examined by Ervin Poulsen, the writer and associates in 1958 and 1959 at the request to the DNIBR by the harbour authorities. General repairs were planned, the proposed method being to inject cement mortar into the old concrete mass (cast in 1935-36) in the bridge piers to counteract increasing percolation of water from the harbour. The concrete was quite mushy at some places on the inner surfaces and very brittle when dried. Extensive exudations of calcium hydroxide, which carbonated when exposed to the air, were observed, and the percolation of water through horizontal joints was directly visible at some locations. In fact, on the basis of the first inspection, the concrete was characterized as the most severely deteriorated to date examined by the writer and colleagues. Macroscopic examinations of drilled cores and thin section examinations gave definite indications of:

1. Insufficient initial quality both as regards concrete composition and workmanship.
2. Severe percolation of water accompanied by sulphate attack and leaching.
3. Partial disintegration of cement paste into an unidentifiable fibrous substance with no binding properties.
4. Severe alkali-aggregate reaction.

The investigations were continued with a chemical analysis of the percolating water and external harbour water (2794), and by the drilling of a total of 135 metres of 7.5 cm cores for subsequent laboratory examination. Point counting of calcium hydroxide in the thin sections was attempted in an effort to measure the degree of alteration of the cement paste (2792). The water was found to dissolve calcium hydroxide during passage through the concrete and to release SiO_2, NH_4^+ and CO_2. The long cores revealed advanced deterioration at many locations within the concrete mass, and the thin section examinations confirmed

1. Pronounced decrease in the content of calcium hydroxide in deteriorated areas.
2. Presence of calcium aluminate sulphate in cracks and voids.
3. Widespread and advanced cracking all over the concrete, even in unbroken pieces of the cores, due to alkali-aggregate reaction.

The above descriptions may be summarized in the following general concept: Ageing of concrete is a process of disintegration, developing through years of exposure to natural, aggressive agents. Ageing makes concrete weak and mushy when moist and brittle and friable when dry. The aggregates are loose in the matrix or are easily loosened by hand or through natural wear and tear.

The state of ageing may be reached through attack by a variety of deleterious agents, physical or chemical, or both, and the evidence of ageing in thin section examination is the superimposed symptoms of decomposition of the original microstructure of the concrete. The most important symptoms are:

1. Absence or only indistinct remains of β-dicalcium silicate and calcium hydroxide. Isotropic or even impure, fibrous character of the remains of cement paste.
2. High degree of porosity due to dissolution of cement paste.
3. Extensive precipitation of calcite and calcium aluminate sulphate (or similar compounds).
4. Corrosion of the boundary areas of aggregate particles.
5. Weathering of alkali-silica gel, when alkali-aggregate reaction has been part of the primary deterioration.
6. Extensive microfracturing, drying-shrinkage crack-formation, boundary cracking, etc.

It goes without saying that none of these symptoms considered alone, is an indication of ageing.

Complex deterioration

The present thin section examinations were not planned from the start as an approach to basic problems of concrete deterioration. The aim has primarily been to extract as much knowledge as possible on the typical effects of deleterious agents from available observations on the behaviour of the microstructure of field concrete. The examinations have concentrated on observations on

1. Concrete and mortar from laboratory experiments with a single type of deterioration.
   Alkali-aggregate reaction - prisms of cement mortar with cast-in bars of chert and flint (2681), and reactive aggregate particles embedded in araldite (2681).
   Sulphate attack - prisms of cement mortar exposed to sodium sulphate (2681).
   Freezing/thawing - concrete bar exposed to early freezing (2910).
2. Field concrete exposed to one predominant type of deterioration, definitely excluding others.
   Sulphate attack - incrustations from harbour in East Asia (2910).
   Freezing/thawing - concrete slabs from Greenland (2910), piece of concrete with 'peacock traces' (2910).
3. Field concrete exposed to a combination of agents of deterioration.
   Groyne 71, West Jutland (2910).
   Dams, North Sweden (2910).
   Highway bridge, North Jutland (2910).
   Oddesund Bridge, Jutland (2911) and (3971).
   Concrete foundation, Copenhagen (2787).
   Knippels Bridge, Copenhagen (2796) and (2792).

Supplementary observations of case-studies from abroad and from additional studies have been referred to.

In most of the cases there are unrecorded factors, which may or must have influenced the deterioration. Variations in temperature and humidity, changes in solubility of constituents and of complex compounds etc. can thus have caused abrupt or slow deviations from the main progress of deterioration, and these deviations may have had a temporary or permanent effect. Removal of specimens from the parent concrete and preparation of thin sections may also sometimes cause changes in the microstructure, and we have seen that, for instance, cracking due to concurrent swelling and shrinkage may succeed and overlap each other. Finally, important phenomena of alteration may be quite invisible to the microscope. With these reservations in mind, it is, in the writer's opinion, still justifiable to specify the symptoms that have been found characteristic of each factor of deterioration.

Table 8 sums up the symptoms observed in thin section examinations for various agents of deterioration. The mode of occurrence is very briefly described for each constituent sought in the thin section, i. e.

Composite structure of aggregates and cement paste.
Aggregates.
Cement paste.

and the secondary precipitates

Alkali-silica gel.
Calcium hydroxide.
Calcite.
Aragonite.
Hydrated calcium aluminate.
Calcium aluminate sulphate.
Gypsum.
Magnesium hydroxide.

An indication is given of how these various symptoms correspond to one or another of the factors of deterioration under consideration

Alkali-aggregate reaction.
Sulphate attack.
Aggressive carbon dioxide.
Freezing/thawing.
Shrinkage.
Ageing.

The table also shows whether the symptoms are characteristic of slight deterioration, whether they are frequently found in the cases examined, or whether the symptoms are observed in cases of advanced deterioration. Thus, this compilation does not pretend to be a guide to microscopic phenomena of deterioration in general, but may prove useful for further investigations and in this way possibly contribute to a more satisfactory textbook on the diagnosis of concrete 'diseases'.

In cases where a variety of deleterious agents have been present it must be remembered that some processes seem to enhance each other whilst other processes are merely additive.

It seems evident, for instance, that a steady supply of sodium, magnesium and sulphate ions through the percolation of sea water strongly accelerates alkali-aggregate reaction. Concurrent with the steady supply of sodium, the concentration of calcium ions is decreased due to precipitation of calcium carbonate, gypsum and calcium aluminate sulphate, and magnesium hydroxide is formed. This seems to be the reason for the copious production of swelling gel, even in dense flint particles in the underwater concrete of the Oddesund Bridge. A similar acceleration may have been in action in the sulphide bearing, alkali-reactive phyllites from the dam in North Sweden.

The same kind of combination may be present in groyne 71, West Jutland, and the highway bridge, North Jutland, but in these cases freezing and thawing and drying shrinkage are involved rather than percolating water, and the final picture of the damage is more complex and indistinct than in the above cases.

The foundation concrete (2787) and the Knippels Bridge concrete, both in Copenhagen, provide evidence of the effects of aggressive carbon dioxide that have probably been enhanced by the presence and continuous supply of sulphates from the brackish harbour water. In the latter case, alkali-aggregate reaction was also found to be severe, and percolation of water had been excessive, probably throughout the lifetime of the concrete.

As far as the Greenland concrete slabs are concerned, it seems natural to assume that the combination of tidal exposure (sea water) with severe freezing has accelerated the disintegration. However, there are few thin section observations from other cases available for comparison because Denmark itself has a rather moderate combined frost/tide exposure.

The cases of complex deterioration in Denmark described are all of the same type in that they concern concrete that is known or has been shown to have been of low initial quality. High porosity, low solid cement paste content, inhomogeneity, initial cracking due to shrinkage and carbonation etc. are repeatedly met as factors that must have been important for the deleterious development of the disintegrative processes.

o means rarely observed
oo means often observed
x means observed in cases of severe deterioration

Constituent	Symptom of deterioration	Alkali-aggregate reaction	Sulphate attack	Aggressive carbon dioxide	Freezing/thawing	Shrinkage	Ageing
Composite structure	Connecting cracks	oo	o		x[1]	x	oo
	Peripheral cracks		oo		oo		
	Boundary cracks	oo				o	oo
	Radiating cracks	oo			oo[1]		
Aggregate particles	Unreacted dense/reacted porous	oo					
	Reacted dense and porous	oo					
	Internal cracking	oo		o	oo		
	Discoloration along internal cracks	oo					
	Dilution of substance	oo					
	Dissolution of substance	oo		oo			oo
	Reaction rim	oo					
	Corrosion (pitting) of boundary	oo		oo			oo
Cement paste	Irregular microcracks, surface		oo			oo	oo
	Irregular microcracks, interior		oo			oo	
	Sub-parallel microcracks		x				
	Sound, amorphous, with β-C_2S and $Ca(OH)_2$	oo	o	o	oo	oo	
	Diluted, β-C_2S and $Ca(OH)_2$ absent		x	oo			oo
	Impure silica gel, dissolution		x	x			oo
Alkali silica gel	In cracks in cement paste	oo					
	In cracks in aggregate particles	o					
	In voids and air-bubbles	oo					
	Impregnating cement paste	oo					oo
Calcium hydroxide	Microcrystalline in paste	oo	o	o	oo	oo	
	Accumulated crystallisation				oo		
	Euhedral crystals in voids and air-bubbles	o	o	o	oo	o	
	In cracks	oo			oo		
Calcite	Microcrystalline in paste	x	o	oo	x		oo
	In cracks	o	o	oo	oo	x	oo
	Euhedral in voids and air-bubbles		x	x			oo
	Seams in alkali-silica gel						oo
	Replacing cement paste		x				oo
	In incrustation		x				oo
Aragonite	Radiating aggregates		oo[2]				
	Euhedral, in voids and cracks		oo[2]				
Hydr. calc. aluminate	Euhedral, in voids and cracks		x				
Calcium aluminate sulphate	In cracks and voids	oo	oo				oo
	Seams along aggregate particles	oo	oo				oo
	In cement gel substance	x[3]					
Gypsum	Microcrystalline in cement paste		x				
	In cracks		x				
	Euhedral, in voids and air-bubbles		x				
	Replacing cement paste		x				
	In incrustations		x				
Magnesium hydroxide	Banded formations in cracks and voids		x[2]				
	In incrustations		x[2]				

[1] Porous aggregates.   [2] Only with sea water attack.   [3] In mortar bars.

Table 8. Compilation of microscopic evidence of concrete deterioration in relation to various causes of distresses.