



X-RAY DIFFRACTOMETRIC INVESTIGATION OF THE STATE OF CRYSTALLIZATION IN THE CEMENT MATRIX PHASE OF A VERY OLD CONCRETE

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In connection with the problem of isolating nuclear waste materials for almost indefinite times, the possibility of autogenous changes in the crystallinity and microstructure of the cement binder in concrete, taking place after very long times of curing under non-corrosive conditions, should be considered. In order to explore these possible changes, a concrete from the wall of a water tunnel, built 1914, was studied by means of X-ray crystallographic methods. The records were compared with those given by different cement pastes of younger ages, although fully hydrated.

The data indicate no major changes in the cement matrix phase of the old concrete, but reservation should be made for the disturbing and shadowing XD effects from the aggregate materials, which are difficult to separate completely from even the finest particle fractions of the mortar. Certain slight indications of fiber formation, in combination with theoretical considerations on C-S-H crystal structures, based on the character of XD-records from the pure pastes, have been used for some speculations on what might happen structurally in the C-S-H gel phase, if given long enough times for conversion.

Key words: concrete, old age, cement paste, crystalline state.

1. BACKGROUND

As is well known, it has become urgent to form an opinion on the relative merits of different alternative methods for the disposal of waste materials from nuclear energy plants by effectively isolating them from their environment for all future time. One way would be to store the waste, possibly after some kind of processing, in closed and sealed concrete containers, which are then placed, and further isolated in some way, deep underground in rock tunnels or shafts. In this connection, it is of course of some interest to consider the long-time durability of concrete materials under the prevailing conditions. One must try to judge, if the effective life-time of concrete, used for this purpose, can be extended considerably beyond that which is normally demanded for the material - maybe 50 or 100 years, depending on the type of construction, and on the composition and proportioning of the concrete. However, one cannot safely exclude the possibility that, after a very long period of time - perhaps of the character of initiation time, in analogy with the one preceding the corrosion of steel reinforcement in concrete - there may occur cer-

tain changes in the crystallinity or pore structure of the cement binder. Such changes may lead to a serious decrease in some essential material property, such as resistance to penetration by radioactive ions, or resistance to corrosion, scaling, or cracking. The properties and behaviour of cement and concrete, with special consideration of changes occurring after long times, have been discussed in considerable detail by Bergström, Fagerlund, and Rombén /1/, in a literature review compiled in cooperation with the Swedish Project Nuclear Fuel Safety (KBS), and recommendations on the choice of materials, construction methods, etc, are also given.

It can be stated that "with the right concrete properly used, concrete constructions have an extraordinarily good durability" (Warris /2/). However, there is practically no experimental evidence to be found in the literature either for or against this statement. For natural reasons, constructional concrete of a reasonably modern type has not yet reached an age of more than 50 years, and cement or concrete samples of a high age, preserved under laboratory conditions, seem to be non-existent - the oldest moisture-conditioned cement paste samples in our laboratory stores are at present 15 years old. During the time that concrete has existed as an extensively used building material, the quality control has predominantly been focused on the initial hardening stage, up to the 28-day strength test. After this has been passed, it has been generally and tacitly assumed that a normal concrete, properly placed and conditioned in a non-corrosive environment, is only improving in quality, density, and strength.

The damages that have been observed in concrete constructions - and these are unfortunately too common - are mostly associable with deviations of some kind: corrosive environment, errors in the proportioning, construction and placing, or harmful components in the cement or aggregate. As far as is known, one has never considered the possibility of long-time damage caused by an autogenous conversion of the cement gel into a well-crystallized compound, which would then be a change inherent in the matrix, perhaps proceeding very slowly, but still inevitable, for reasons of a demand for attainment of thermodynamic equilibrium.

Studies made on the changes with age, up to 50 years, taking place in concretes of different types, and in mortar and paste, have mainly been concerned with the development of strength (Wascha and Wendt /3/, Walz /4/, and others).

The trend in the changes in strength values, as observed by Wascha and Wendt, is an increase up to 25 years, but between 25 and 50 years the tendency is not clear. Considerable reductions, about 50 per cent, were observed in certain cases, especially with respect to tensile strength, but the cause of this trend was not discussed. Similar decreases have been observed for the tensile splitting strength of cement pastes in the range of relatively low water/cement values (about 0.40) and at considerably lower ages (cf. e g Grudemo /5/). This tendency to increasing brittleness of concrete at higher ages is also pointed out by Bergström et al /1/, and may be connected with the slow growth of the micro-crack systems in the matrix. It is open to question, if the effective compressive strength is also seriously affected in the long run by this process, as well as the permeability to water, and

heavy nuclide ions dissolved from the waste materials. The diffusivity of such ions in cement pastes and mortars of various types are at present being investigated by KBS.

No systematic studies have as yet been made, as far as is known, on the development of microstructure and recrystallization in the cement binder phase of concrete at high ages. A number of ancient lime-silica mortars were studied by XD methods by Mchedlov-Petrosyan, Vyrodov and Papkova /6/, who report the presence, in unknown quantities, of several of the well-crystallized C-S-H minerals occurring rarely in certain rocks, and in hydrothermal preparations at temperatures above 150°C. It must be considered remarkable that as many as five of these compounds (denominated e g C₂SH(A), C₂SH(B), C₂SH(C), tobermorite, CSH(B)), should appear simultaneously in the same mortar. Considering the difficulty of verifying with certainty the presence of even one of these constituents in XD records from multi-phase mixtures containing mainly calcite, and unfortunately lacking nearer experimental details on the records, on which these findings are based, one cannot help feeling inclined to regard them with some scepticism.

2. X-RAY DIFFRACTOMETRIC ANALYSIS: PREREQUISITES, MATERIALS STUDIED, CONDITIONS OF SAMPLE PREPARATION, CHARACTER OF DATA OBTAINED, ETC

In connection with problems arising for the possible use of containers for a safe storing and isolation of nuclear waste materials for indefinite times, CBI has been consulted at various occasions by Project KBS (Nuclear Fuel Safety). It was considered to be of interest to try to detect possible changes with age in the cement matrix of very old concrete. One method selected for this purpose was X-ray diffractometry (XD). XD traces were recorded for powder samples consisting of different parts of an old concrete, especially for the finest particle fractions of the subdivided mortar, and the XD patterns and intensities were compared mutually and with records given by standard components of defined composition and higher purity, such as cement pastes of lower ages, and various aggregate materials.

The concrete material chosen for this study was taken from a concrete wall in a tunnel for water at the Porjus hydroelectric power plant. The wall was cast 1914, about 200 mm thick directly against the rock and covered on the inside by a cement mortar layer, then in contact with flowing water until a few years ago. The concrete in the 100 mm cores taken out from the wall contained some part of coarse aggregate (about 40 mm granite rock particles), and a mortar consisting of about 70 per cent sand, with particles from a few mms down to about 0.1 mm, in which the fine sand fraction was comparatively large. Mortar samples were extracted by sawing, chiselling, crushing and gentle grinding, then sieving (mesh widths employed; 320, 125, 37 and in some cases 20 µm), then further ground, sieved, and ground again down to sizes suitable for XD work. It was found that the binder phase adhered quite strongly to the sand particles, which made it difficult to separate the matrix phase from the aggregate phase, since upon more vigorous grinding even small fragments of the fine sand were broken loose. Thus, substantial fractions of rock minerals,

about 10 per cent feldspar and about 5 per cent quartz, could not be excluded from even the finest sieve fractions, and there was proportionately more of them in the more normal sieve fractions.

As has been indicated above, the investigation aims at detecting and identifying possible changes with age in the weak and diffuse diffraction effects given by the calcium silicate hydrate (C-S-H) gel phase in the matrix, such as the intensification and sharpening of the XD maxima, the change of 2θ angular positions of the peaks, the possible appearance of new peaks from components formed after long time, etc. As is shown more in detail in the diagrams, the XD patterns of the well-crystallized aggregate components consist of a series of sharp maxima with peak heights which, relatively speaking (in 100 per cent diagrams), are 20 to 50 times higher than the maxima from gel components. Even with only 5 to 10 per cent of aggregate minerals present in a mixed sample, the records are dominated completely by the aggregate lines. Especially in the presence of feldspar of variable composition and structure, and consequently giving XD patterns which are difficult to analyse, the more relevant XD effects are disturbed and masked to a high degree, particularly in the important 2θ range around 30° , which contains a great number of closely-spaced maxima originating from feldspar.

3. ESTIMATE OF STRENGTH PROPERTIES

The quality of the Porjus 1914 concrete mortar appeared to be quite satisfactory. Inspection in the microscope of cut and finely ground surfaces of the mortar did not reveal any internal corrosion or cracking. On the contrary, the cohesive strength in the matrix-to-sand interfaces seemed remarkably high. An attempt was made to measure the Vickers' hardness H_V of the matrix, by indentation of the small paste areas that could be found between the closely-spaced fine-sand particles. This gave $H_V = 300$ to 350 MPa, which according to previous experience would correspond to an original water/cement ratio of about 0.45. No information on the water/cement ratio actually used is given in the work description from 1914. The corresponding value of the compressive strength could be estimated to at least 40 MPa, according to comparison data available for mortars with quartz sand aggregate (cf. FIG 1, taken from a still unpublished report.)

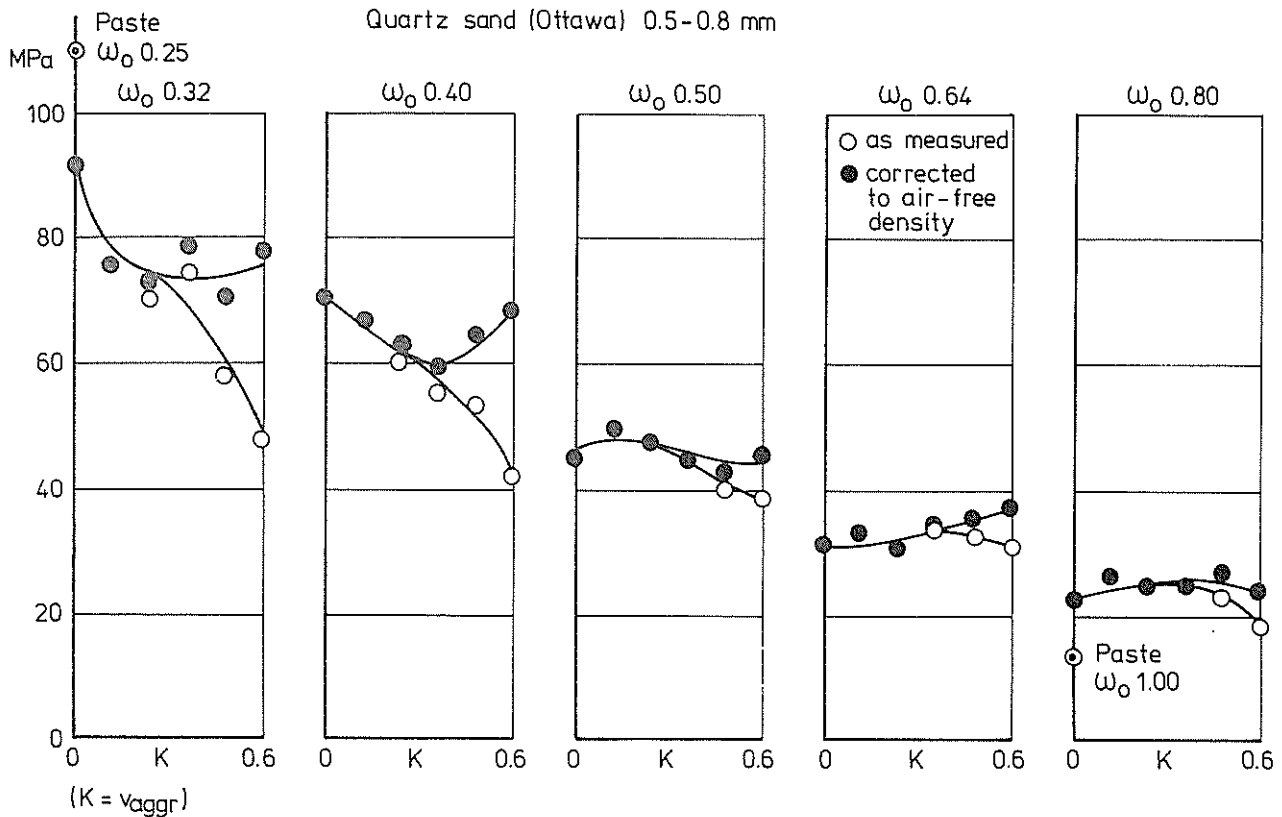


FIG 1. Compressive strength (\emptyset 20 x 20 mm cylinder) of mortars with quartz sand aggregate.

4. ANALYSIS OF XD RECORDS FOR THE PORJUS CEMENT MORTAR

FIGS 2-8 are reproductions of the variation of XD intensity with the scattering angle $2\theta^\circ$ for different relevant 2θ ranges: the low-angle (6-14) region with basal reflexions observed, the medium angle (24-36) region, where the strongest reflexions are generally located, and a region about 50° , which is of interest on account of the possible presence of so called fiber reflexions, corresponding to $1/4$ of the repeat unit 7.2 to 7.3 Å of the type of silica chain present in fibrous C-S-H compounds possibly formed, or alternatively to $1/2$ of the distance between Ca ions in CH layers. The diagram lines are directly copied from the XD recorder traces, as accurately as possible, however with a smoothing of the ripple, the fast statistical variation of the X-ray intensity about an average value for a certain angle.

FIG 2 shows a comparison of two superimposed diagrams, one from the fine fraction of the gently crushed and ground mortar, and one from the sand fraction, from which the paste sticking to the surfaces has been removed by dissolution in HCl (1:4 dilution). Judging from the intensities, the material giving the solid curve contains 15 to 20 per cent CH - calcium hydroxide (portlandite), and fine-fraction fragments of aggregate materials: quartz (Q - about 8 per cent) and feldspar (F - probably a couple of different varieties, together perhaps 15 per cent), the rest of the material, more than 50 per cent, consisting of cement

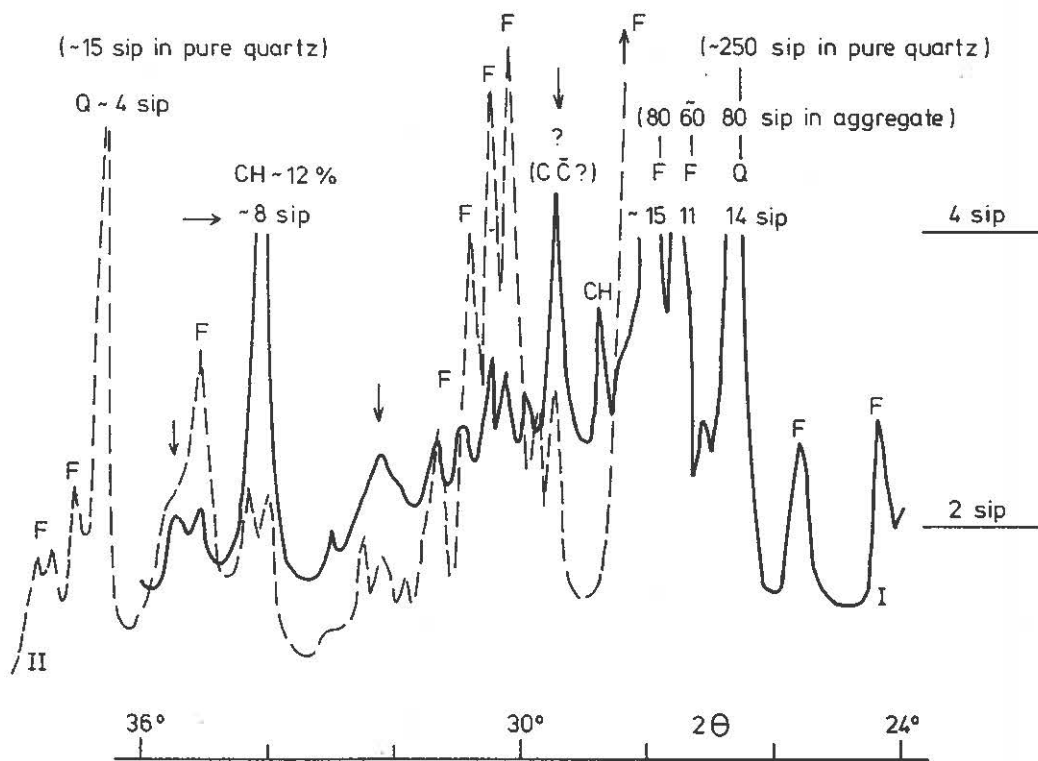


FIG 2. XD records for 68 years' old mortar, fine fraction ($<40 \mu\text{m}$, about 6 per cent of total weight, ((I) full line) compared with aggregate fraction, washed in HCl ((II) broken line).

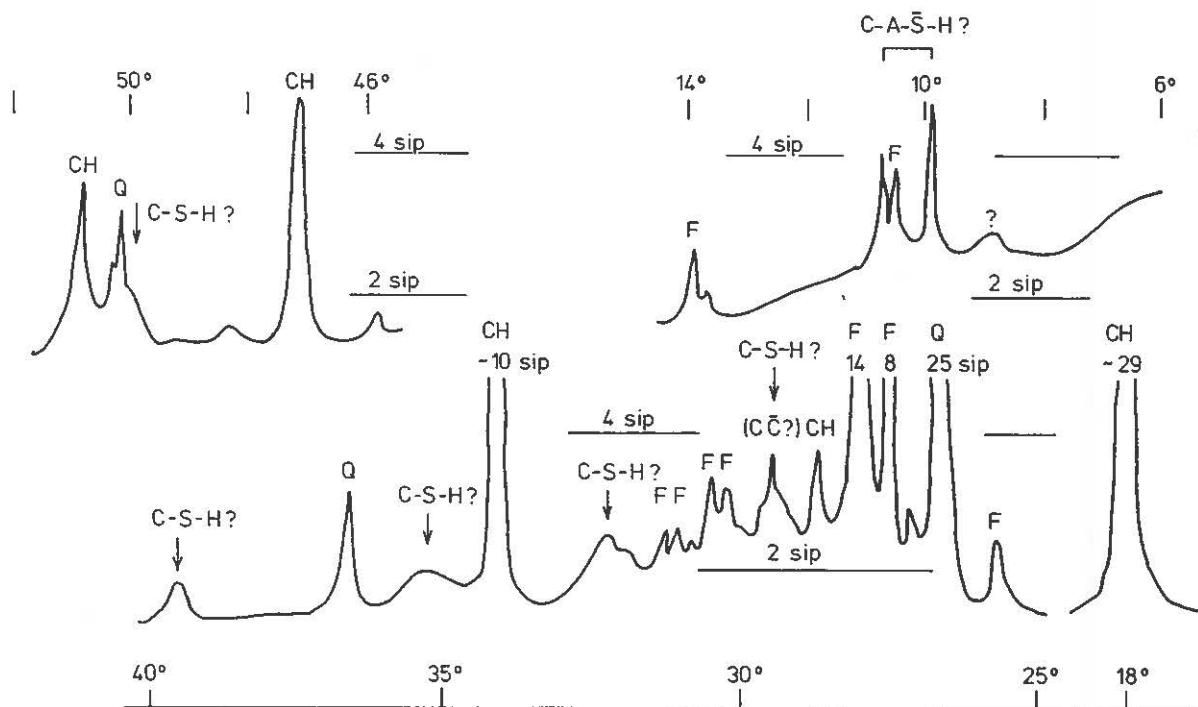


FIG 3. XD record of fine fraction ($<40 \mu\text{m}$) of old cement mortar, for various 2θ ranges of interest.

gel phase. The aggregate part of the mortar (dashed curve) corresponds to nearly 30 per cent quartz, and probably more than 60 per cent feldspar, the rest consisting of small amounts of layer minerals (muscovite mica, biotite) and possibly some Fe-containing minerals. It can be seen that the aggregate lines are still predominating in the four-times gel-concentrated fine-fraction curve. but in certain ranges, at about 29° and at 31 to 35° , the fine-fraction record runs above that of the aggregate. The diffraction effects in these ranges (denoted by arrows directed downwards) would then correspond to reflexions from C-S-H gel, and can also be observed in the records from pure cement pastes of different types, cf. FIG 9 etc. The peak denoted by γ , at $29^\circ 4'$, however, could very well be caused partly by carbonation, since the only strong peak for CC - calcite is situated just at this angle, the peak height in the diagram corresponding to less than 2 per cent calcite.

FIG 3 shows the most important interferences for a similar preparation from the fine fraction of the mortar. The low-angle curve (top right) shows a couple of feldspar peaks, and also a couple of basal reflexions (at $2\theta = 9.9$ and 10.7) probably from calcium monosulfoaluminate hydrate in two different states of hydration (cf. discussion for FIG 7). In these powder preparations, the CH crystals are markedly lamellar, and the basal reflexion ($00\cdot1$) at $18^\circ 06'$ will therefore become very much intensified, on account of the effect of orientation parallel to the sample surface, which effect has turned out to be very persistent and difficult to eliminate. The peak height of this reflexion, 27 sip ^x according to FIG 3, is therefore too large to be used in calculating a reasonable value of the CH content of the sample (for unoriented, 100% pure CH, the corresponding peak height is about 43 sip). More correct values for the CH content can be obtained from the "oblique" reflexions for CH $10\cdot1$ at $34^\circ 1'$, and CH $10\cdot2$ at $47^\circ 1'$, with 100 per cent values 52 sip and 17 sip, respectively. These peaks in FIG 3 correspond to CH contents of 22 and 26 per cent in the matrix phase of the preparation (corrected for about 25 per cent aggregate particles). Since these values are probably on the low side, on account of a negative effect of orientation, the real CH content can be expected to be nearly 30 per cent. This value is approximately normal for the maximum CH content that is reached after rather short time in a standard cement paste of medium water/cement ratio. These data indicate that no appreciable leaching of Ca ions from the Porjus cement matrix has taken place, in spite of its contact with water for very long times.

The diffraction effects denoted C-S-H? in FIG 3 are the low and broad maxima that are left, after the lines from the better-crystallized components of the preparation, aggregate and CH, have been identified. They can be taken to indicate some kind of formation of structure, of an unknown and rather ill-defined type. An attempt can be made to estimate the size of the structural units involved, from the approximate expression

$$t = (B^2 - B_0^2)^{-1/2} \cdot 160 \text{ \AA} \text{ with } B_0 = \text{apparatus constant} = 0^\circ 10' 20''$$

^xsip = "Si peak", a unit for peak intensity, 1 sip = 1 per cent of the peak intensity for the $28^\circ 44'$ peak of Si metal, as measured about simultaneously for a standard Si powder sample.

where B = width at half maximum height of the peaks in this case is estimated to at least 0.6° , giving $t_{\max} = 300 \text{ \AA}$. This value is of the same order of magnitude, or rather smaller than, the corresponding values of the sizes of structural elements in different types of pure cement pastes, as is evident from FIGs 9-15. Thus, no pronounced tendency to growth of the crystalline elements in the gel phase of the Porjus mortar can be detected.

If similarly, and quite tentatively, the hump-like rise of the background in the records between about 25° and $34^\circ 2\theta$ is regarded as a very broad maximum, with $B = 4$ to 5° , the size of the corresponding structural units would be 30 to 40 \AA . A similar diffuse peak in the scattered electron intensity at the equivalent lattice distance of about 3.0 \AA (corresponding to $2\theta = 29.75^\circ$ for X-rays) is a normal effect in electron diffraction patterns from C-S-H gel particles, according to Grudemo /7/. This effect can hardly be interpreted as a sign of a beginning formation of microcrystals, but rather as a tendency of the ions, and especially oxygen with a variable number of protons attached (as in oxide hydrates of the C-S-H type), to arrange themselves in atomic planes with an approximate distance of 3 \AA . This implies a certain deviation from the purely statistical distribution of lattice plane distances in a gel material.

FIGs 4-6 give a comparison of records for a series of different fine fractions in the various 2θ ranges of interest. Of the reflexions observed in the low-angle region (FIG 4), the diffuse peak at about 9° may be partly an artefact, caused by the use of thin-layer (0.3 mm) specimen holders (it disappeared more or less with the use of ordinary holders for 1 mm powder thickness). The peaks at 10.5° and $13.9-7^\circ$, originating from feldspar, quite naturally increase in intensity in the coarser particle fractions. The peak at 9.9° , with its satellite at 10.7° , most probably originates from so called monosulfate - $C_4\text{ASH}_{12}$ - and is strongest in the intermediate fractions. It turned out, according to FIG 7, that a moderate heat treatment - 110°C for 30 min - caused the 9.9° peak to disappear, and the 10.7° peak to grow considerably in intensity. In another preparation, a mortar fraction less than 125 μm , gently dried and stored isolated for about a month, a third strong peak appeared at 10.9° , together with 9.9° and 10.7° peaks, but had disappeared again in a repeated run the next day (result of a prolongation of the X-ray irradiation?). These changing reflexions have been observed earlier by different investigators, appearing for the hexagonal layer lattice of $C_4\text{ASH}_n$ with different discrete states of the structure of water molecules in positions between monomolecular layers (variable states of drying, and with $n = 12, 8$ (or rather 7.5) and perhaps 6.

It is natural that this type of C-A-S-H minerals should be formed in old concrete, probably as a product of disintegration of the mineral ettringite - $C_6\text{AS}_3\text{H}_{32}$ - initially formed, since the cement was at that time manufactured with a comparatively high content of aluminate ($C_3\text{A}$ and its alkalicontaining varieties, $C_2(\text{A},\text{F})$ of variable composition). This compound may keep stable in the moisture-saturated conditions in the concrete, but may be dehydrated, and possibly also carbonated, upon exposure to other ambient conditions during the preparation of samples.

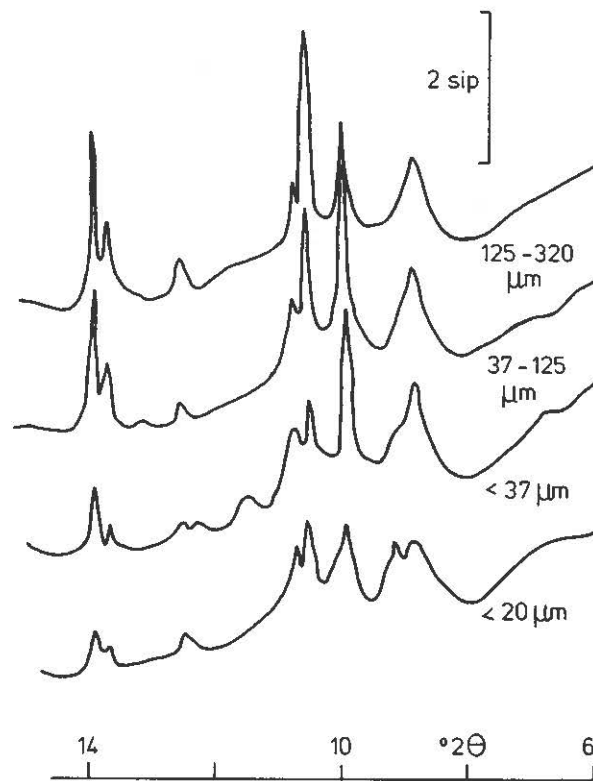


FIG 4. XD records for different finer fractions ($<40 \mu\text{m}$, together about 20 per cent of mortar mass) of old cement mortar, 2θ range 6 to 14° .

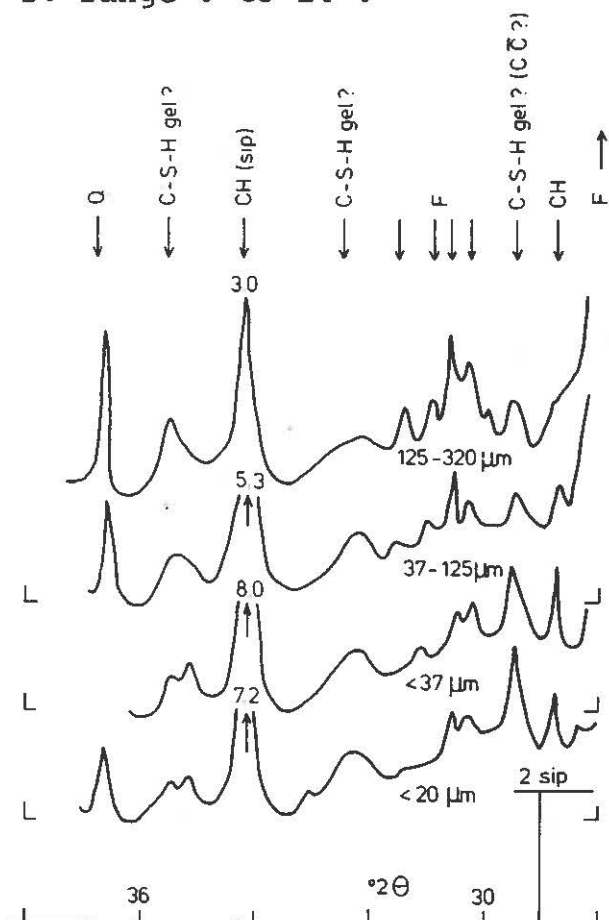


FIG 5. As FIG 4, 2θ range 28 to 38° .

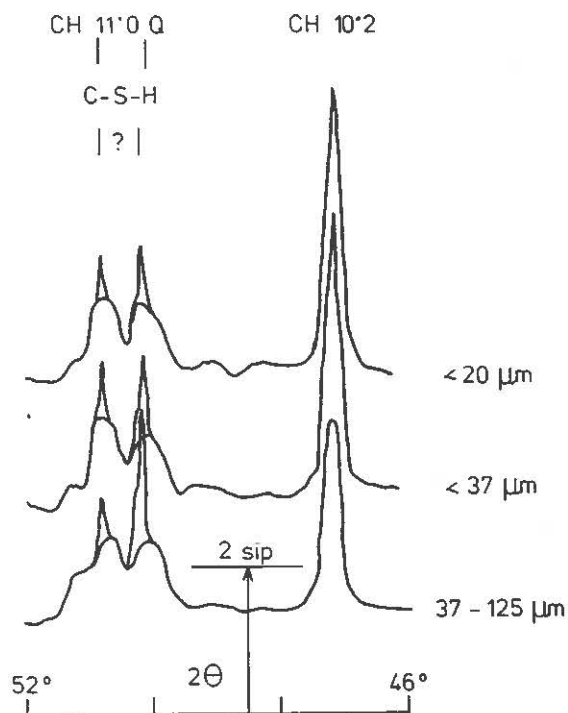


FIG 6. As FIG 4, 2 θ range 46 to 52°

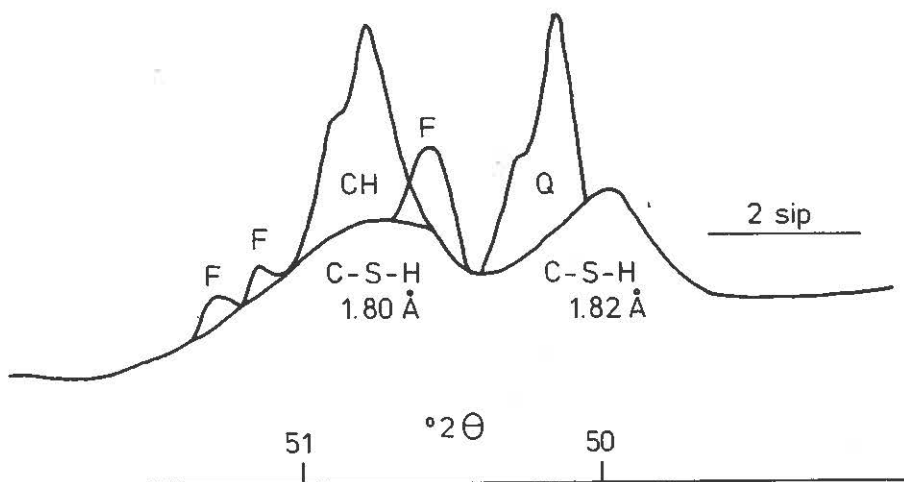


FIG 6a. Old cement mortar, <20 μm fraction, high-resolution XD analysis of 49 to 52° 2 θ region.

The recordings of FIG 5, for the 28 to 37° range, show mainly that the content of aggregate particles (F,Q) increases in the coarser fractions, while CH and C-S-H gel decrease. This is also the tendency visible in FIG 6, for the 46 to 52° range.

It is of interest to note, in FIG 6, that there seems to be two diffuse maxima at 50°0 and 50°8 (corresponding to about 1,82 and 1,80 Å), with superimposed sharper peaks from quartz and CH, respectively. A single diffuse line at about 50°0 is normally observed for long-time-hydrated cement pastes of different types (cf e g FIGs 11-15). This has earlier been identified as a fibre reflexion, corresponding to b/4 (index 040) in a fibrous crystal structure containing so-called dreierketten, such as tobermorite, foshagite, hillebrandite and others, with the b unit equal to three links of polymerized SiO₄ tetrahedra, or alternatively half the chain unit in a proton-bound so-called Bernal chain /8/.

The possibility of detecting a continued polymerization of SiO₄ units in cement pastes of high age has been discussed thoroughly in the cement literature of later years, most recently by Dent Glasser et al /9/, who analysed an about 8 ys. old cement paste by means of so-called trimethylsilylation methods. Polymer complexes up to Si₉O₂₆ have been detected by this method, the reliability of which is still questioned by the authors referred to.

The observation of the appearance of two fibre reflexions in the Porjus matrix material has a degree of reliability similar that of the observation of high-polymer peaks in chromatograms. An attempt to resolve the peaks in the 49 to 52°2θ region is shown in FIG 6a. Admittedly, the double diffuse peak is weak, and the analysis is brought to the limit of resolution. However, it might indicate the presence of structural complexes (cryptocrystals) with partly polymerized, partly hydrogen-bonded SiO₄ chains, perhaps with chain units 7.20 Å (4x1.80) and 3.64 Å (2x1.82), respectively. With due reservation for the inconclusive evidence, it can be stated that if a process of polymerization of this nature cannot be detected until after several decades, the time required for reaching some kind of equilibrium ought to be considerably longer, and the effect of the structural changes associated with this conversion cannot be surveyed or predicted.

5. ADDITIONAL OBSERVATIONS FOR THE PORJUS CONCRETE

Several XD recordings were made for aggregate materials: sand from the mortar, washed in HCl, larger stones in the aggregate, material from the adjacent rock. These records were used to check the XD effects for aggregate fragments in the finer fractions of the mortar. These materials consisted of normal granite rock, mainly agglomerates of feldspar and quartz, with smaller quantities of dark particles or black, glistening flakes in small inclusions. The latter were probably (cf FIG 8) of the smectite (2:1) type (mica, peak at 8°8), or of the kandite (1:1) type (kaolinite-like, peak at 12°5). The latter may contain Fe, judging from the high background intensity.

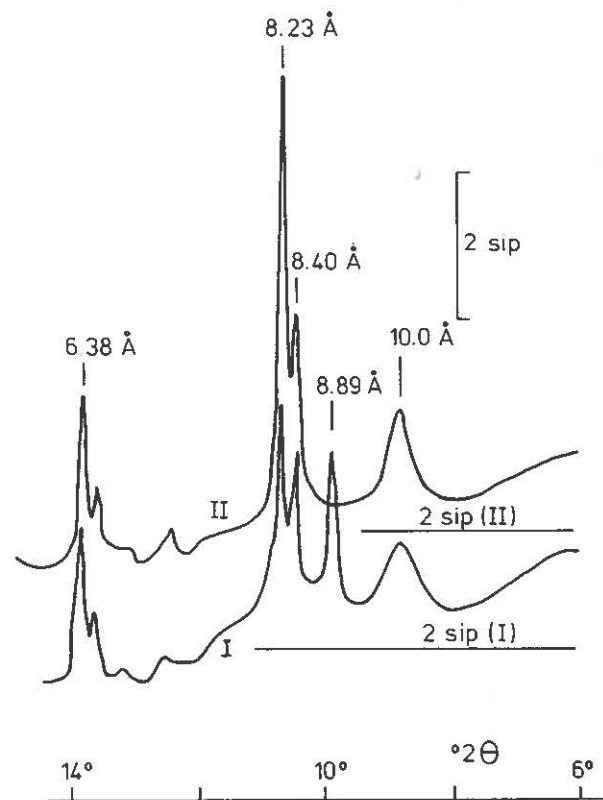


FIG 7. Low-angle region of XD for old cement mortar, fine fraction, ($<40\ \mu\text{m}$, mixture of several sieve preparations). I. before II. after treatment in dry heating cabinet 110°C for $1/2\ \text{hr}$.

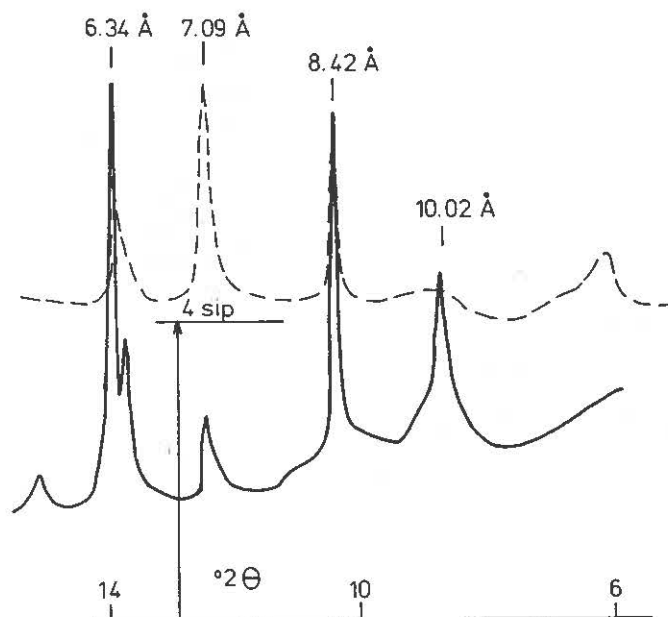


FIG 8. XD records for old cement mortar, sand fraction (0.32 to 0.5 mm, after crushing and light grinding of mortar), washed in HCl, low-angle region $6\ \text{to}\ 14^\circ 2\theta$. (---comparison with dark and glittering, flaky material, prepared-out from the near-by rock).

The strongest quartz interferences are situated at $26^{\circ}64$, $20^{\circ}87$, $50^{\circ}14$, and $36^{\circ}55$ 2θ , with the 100 percent peak heights 255, 55, 28 and 15 sip, respectively. The strongest feldspar peaks lie at $27^{\circ}94$ (strongest in this type of feldspar) and $27^{\circ}46$ 2θ , with unknown and strongly variable 100 percent values about 100 sip (in certain feldspar standards available the peak near $27^{\circ}5$ was the strongest one). In addition, as seen in FIG 2 and FIG 8, feldspar has a great number of weaker peaks in practically all regions of 2θ .

XD records were also made for fine fractions prepared-out from the cement mortar coating the concrete wall on the inside (towards the water, peeling-off in some parts of the tunnel) and on the outside (between concrete and rock). The compositions of these materials were found to be about the same: in addition to 10 to 15 per cent feldspar + quartz there was 12 to 16 per cent CC - calcite, possibly a product of carbonation of CH initially formed, but not observed in the mortar coatings. The rest of the mass should thus consist of gel material (cement gel?) that had not carbonated in the moisture-saturated environment.

6. COMPARISON XD RECORDS FOR PURE PASTE MATERIALS

FIG 9 shows the 26 to $36^{\circ}2\theta$ region in the records from a series of white cement pastes, of initial water/cement ratios (ω_o) between 0.32 and 1.32 (with water separation at the higher ratios prevented by increasing addition of aerosil SH_x - colloidal silica), and moist-hydrated in closed vessels for about 5.5 years. These pastes are practically completely-reacted, except for the 0.32 paste, where about 10 per cent cement still remains (cf the diagram for the anhydrous cement in scale 1:10, $A = C_3S$ - alite, $B = \beta C_2S$ - belite, white cement is about 85 per cent alite, about 7 per cent belite, the rest C_3A and gypsum, with negligible amounts of ferrite phase). The diagrams contain CH patterns of normal intensities (no appreciable leaching of Ca ions to the surface), weak peaks from ettringite (E), and a few C-S-H gel peaks, at $29^{\circ}3$, $31^{\circ}8$, $50^{\circ}0$, and possibly $35^{\circ}0$. These agree approximately with the maxima denoted C-S-H in the diagrams from the fine fractions of the Porjus mortar (ca FIGs 5 and 6). The presence of basal reflexions in the 6 to 12° range could not be established with certainty.

FIG 9a gives the variation of observed peak heights with water/cement ratio for the two strongest CH interferences and the strongest gel peak. The latter seems to increase about linearly with ω_o , depending among other things upon the fact that both the quantity and the crystallinity of the gel is expected to increase with the quantities of colloidal silica added. Simultaneously, the quantity of CH should decrease slightly. This trend is also shown by the curve for CH $10^{\circ}1$, which reaches a maximum at ω_o 0.5 to 0.7, where the peak height corresponds to about 34 per cent CH, in good agreement with values observed for C_3S pastes according to Grudemo /10/.

The curve for the basal reflexion intensity, on the other hand, rises steeply with ω_o , which in this case cannot be explained as the effect of an increasing degree of crystal orientation, since the XD records were made directly from the diamond-saw-cut sur-

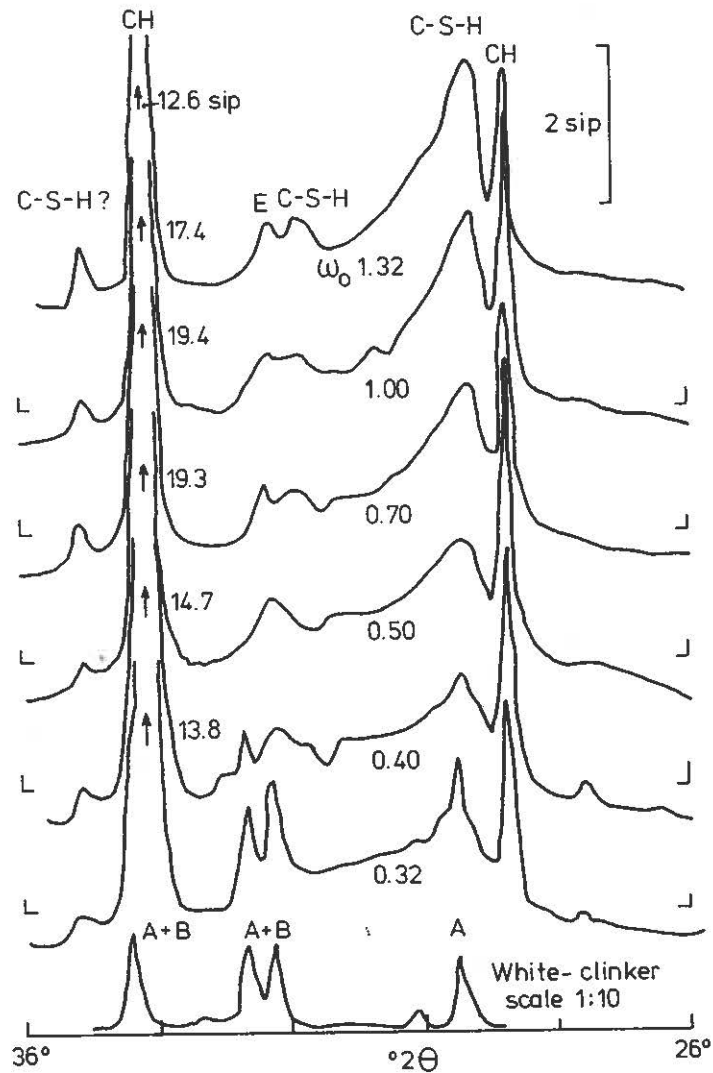


FIG 9. XD records for white cement pastes, of initial w/c ratios 0.32 to 1.32 (aerosil/c 0 to 0.08), 5.5 years' hydrated.

faces of paste plates, not from powder. A possible explanation, which, however, may seem rather artificial, could be an increased tendency to stratification of monolayers of CH and C-S-H with a distance between layers of about 4.9 Å. Such a structure would contribute to an increase of the peak at about 18° only, since this distance happens to coincide with the inter-layer distance in the CH crystal.

FIGs 10-15 show the profiles of the most important reflexions, in a high degree of resolution and enlargement, for a number of pure pastes: standard cement of different water/cement ratios, rapid-hardening cement, components C_3S and βC_2S , all after about 15 years of moist hydration. All the samples were cast as plates, 5 mm thick, which after the long time of preservation in saturated lime solution (initially water) were covered with a layer of CH crystals, in some cases amounting to several per cent of the total weight.

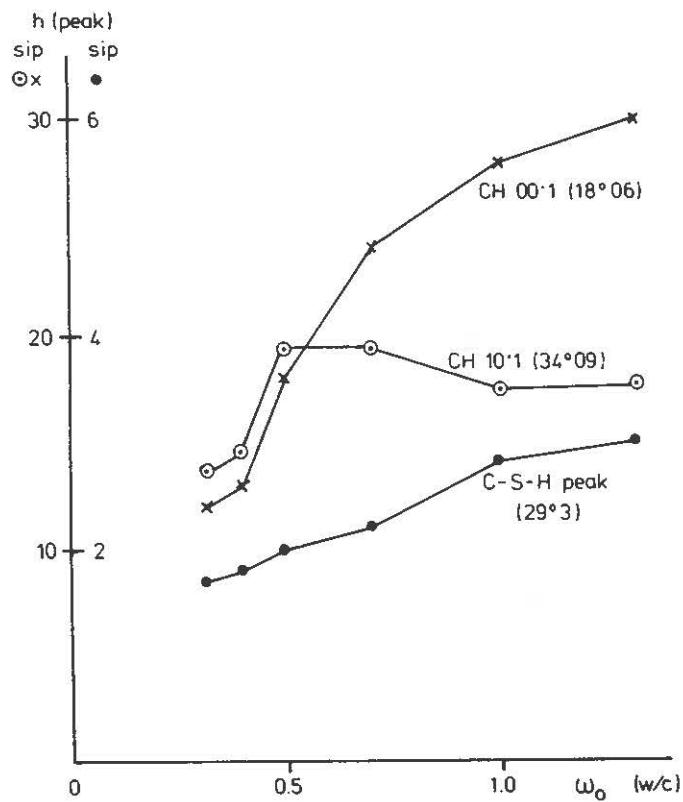


FIG 9a. XD intensities for certain peaks in the diagrams of FIG 9.

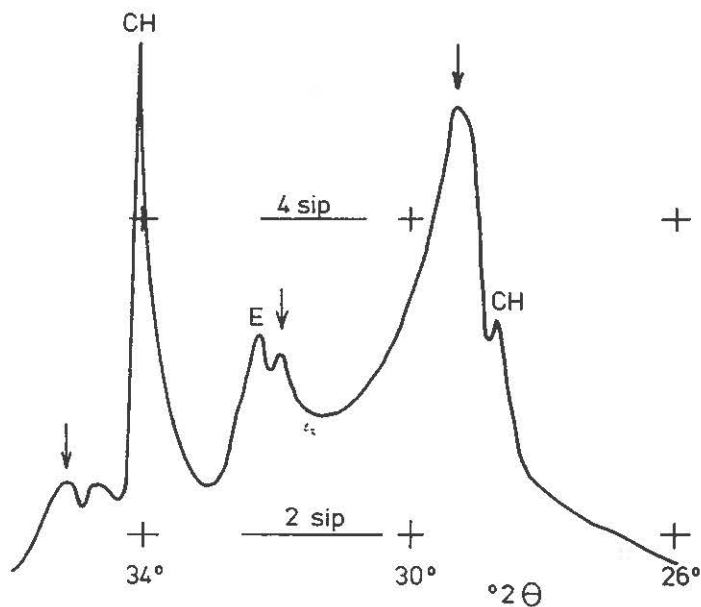


FIG 10. XD record for PC paste (Limhamn Standard), w/c 0.50 - 15.5 ys. hydrated (5 mm plate in CH sol., surface CH crystals removed).

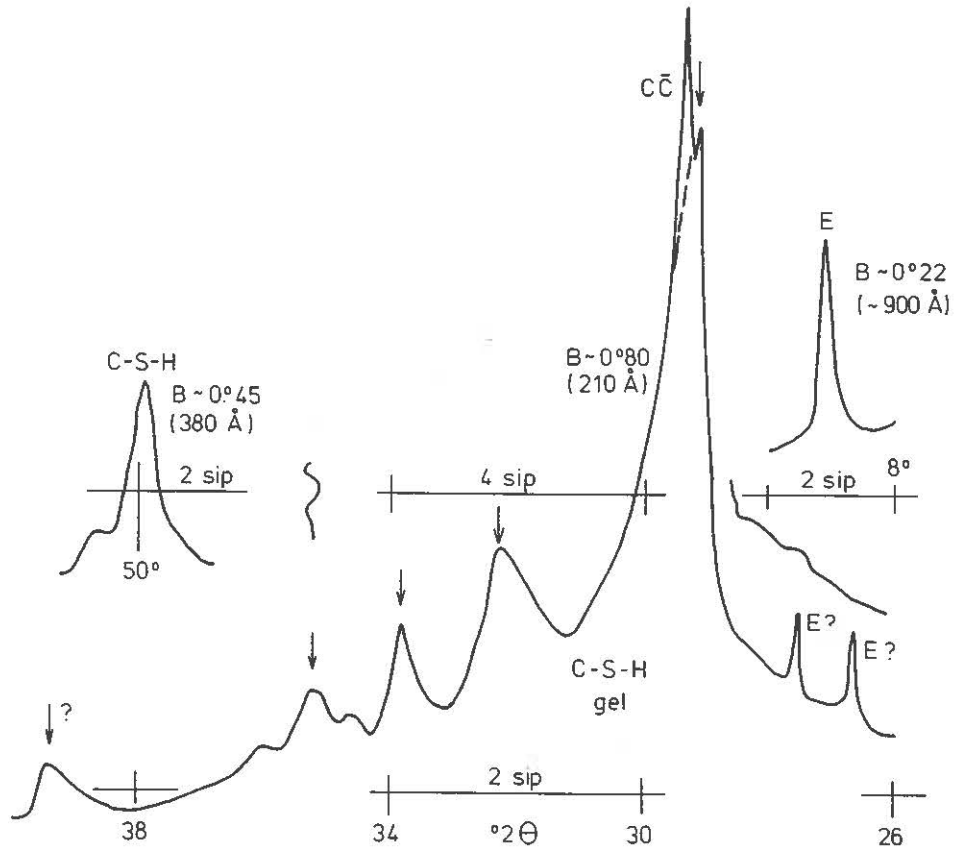


FIG 11. As FIG 10, w/c 1.0 (ae/c 0.06) - 14.8 ys. hydrated

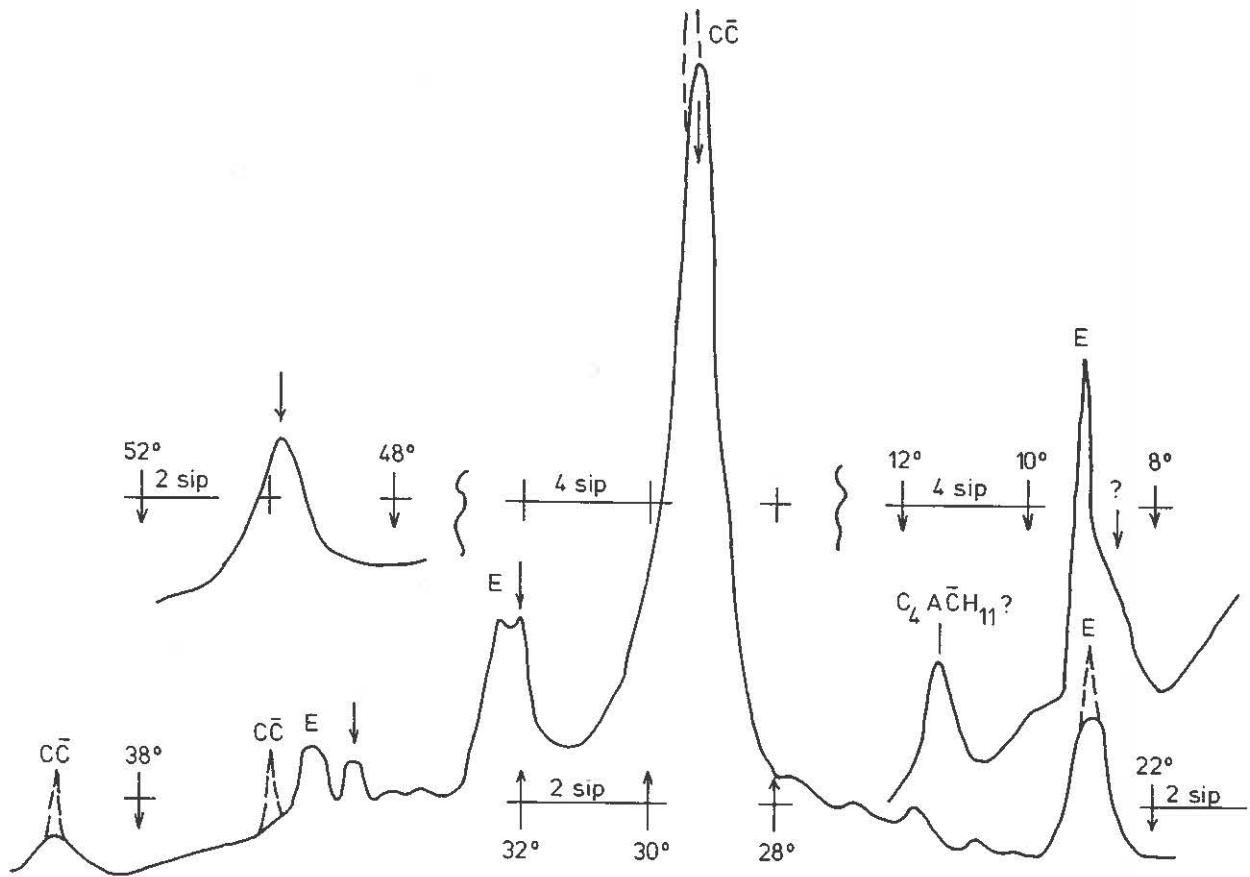


FIG 12. As FIG 10, w/c 1.25 (ae/c 0.08) - about 15 ys. hydrated

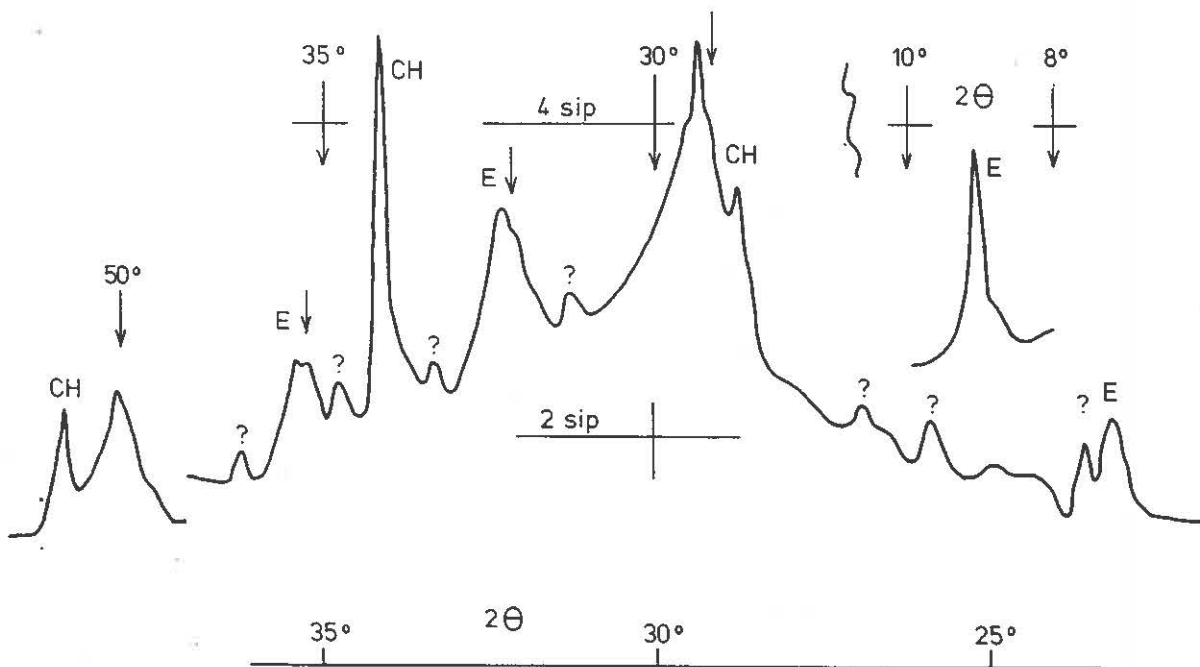


FIG 13. XD record for PC paste (Limhamn Rapid-Hardening), w/c 0.40 - about 15 ys. hydrated (5 mm plate in CH sol., surface layer of CH crystals removed).

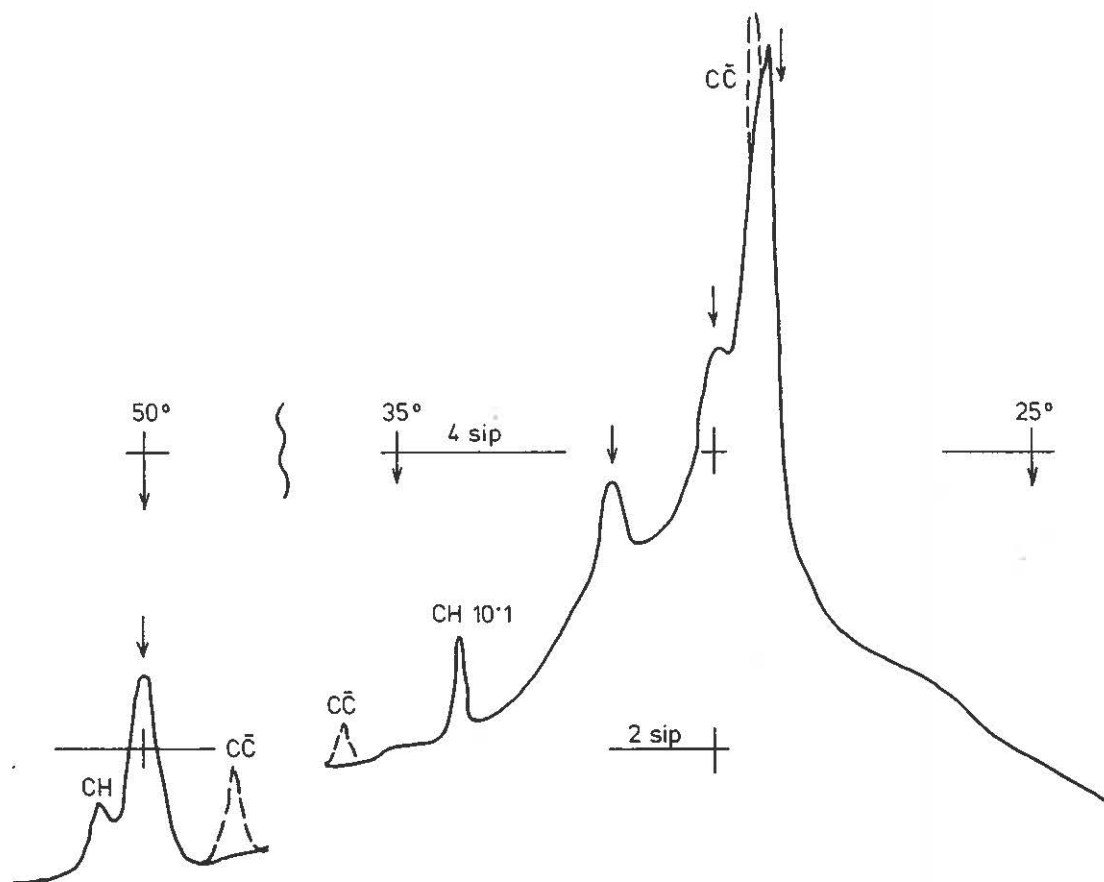


FIG 14. XD record for C_3S paste, w/c 1.25 (ae/c 0.08) - about 15 ys. hydrated³ (5 mm plate in CH sol., thick layer of CH crystals removed from surface to be irradiated).

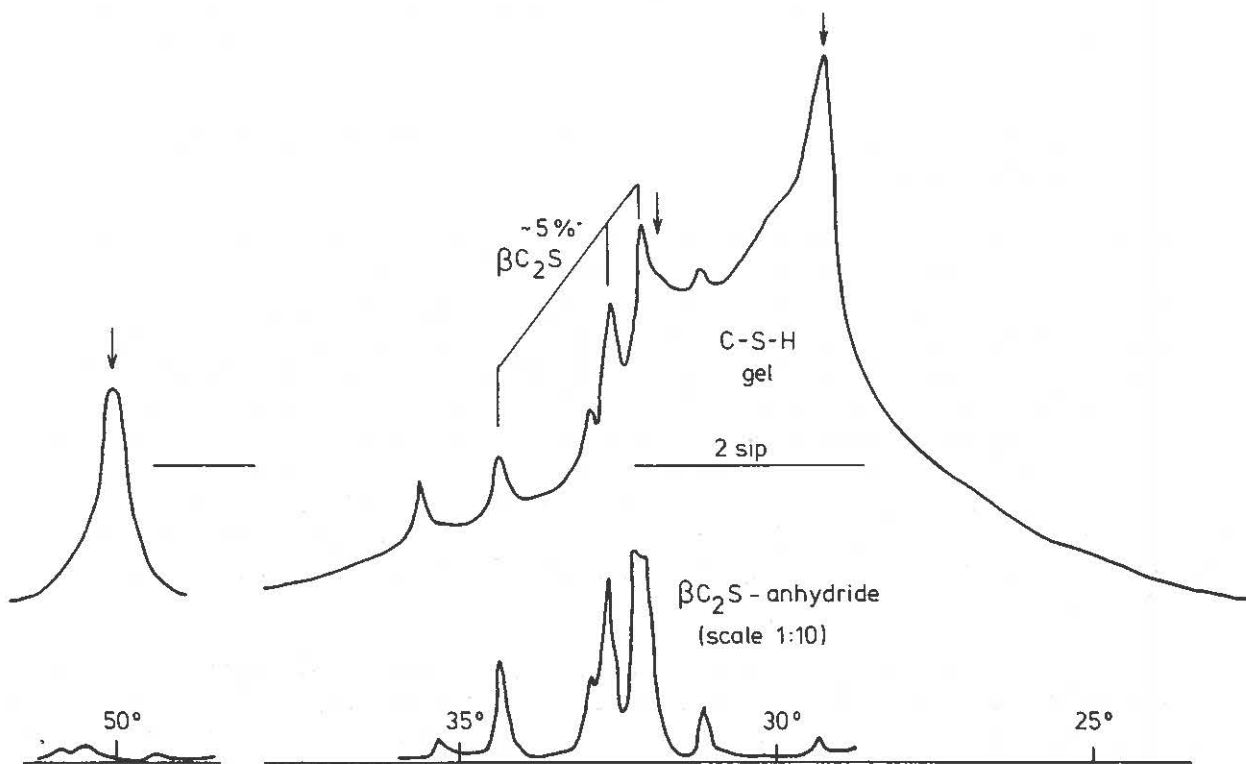


FIG 15. XD record for belite ($C_{108}S_{52}A$) paste, w/c 0.63 - 14.6 ys. hydrated (5 mm plate in CH sol., very thin layer of CH crystals removed).

This layer was scraped away, and the underlying surfaces were dried in ethyl alcohol and examined by XD. Thus, the objects are more or less deprived of their natural CH content, as caused by the cement reaction, which causes the XD interference effects of the C-S-H gel to come out stronger and more distinct. In addition, the dissolution and removal of CH from the capillary spaces may have promoted the formation of better-crystallized C-S-H gel in the solution-filled pores left behind.

The intensity distributions observed for the different objects in this series are rather similar, generally speaking: a maximum intensity at $29^{\circ}2 - 4$, more or less pronounced and with a half-maximum width B corresponding to a crystal size of 200 Å or less, a secondary maximum at about 32° , and less pronounced peaks at 35° and $39^{\circ}5$, and finally a fibre reflexion at about $50^{\circ}0$. The latter peak is never very high (less than 1.5 sip), but can be relatively sharp, e g for the belite paste, where its width seems to indicate a crystal size (fibre length?) of nearly 400 Å. An inspection of the low-angle regions in these records shows only indistinct signs of the presence of basal reflexions (to be associated with layer lattices), similar to those observed for e g tobermorite in light-weight concrete (e g Siporex), or the reflexions in synthetic C-S-H preparations (cf /10/). Possibly, the rise in intensity at about $8^{\circ}8$ (10.0 Å) in FIG 12 (superimposed by the sharp ettringite peak at $9^{\circ}1$) may correspond to such a basal reflexion.

Due to the special circumstances of curing and specimen preparation, as related above, the CH reflexions are weak or absent. It can be further noted that even after 15 years of reaction, there is still about 5 per cent unreacted material left in the belite paste (FIG 15).

7. HYPOTHESIS FOR THE FORMATION OF C-S-H STRUCTURES IN CEMENT SYSTEMS

The phase diagram of the ternary oxide system $\text{CaO} - \text{SiO}_2 - \text{H}_2\text{O}$ is a complex one, and is still not very well known in its details. The conversions between different stable states upon changes in the state variables seem to take place at an extremely slow rate, especially at lower temperatures and in condensed systems, such as pastes. According to the latest list, given by Taylor /11/, the phase diagram would contain about 30 minerals, with C/S ratios varying from 0.5 (nekoite, okenite) to 3.0 (tricalcium silicate hydrate), and with more or less well-known crystal structures. Many of them have been found in rocks, and several have been synthesized in hydrothermal reactions, preferentially at temperatures above 150°C .

The C-S-H phase formed in the course of cement hydration has earlier been supposed to resemble tobermorite, containing $(\text{SiO}_3)_n$ chains, but in later years, the structure has been found to more analogous to that of jennite, which contains a mixture of $(\text{SiO}_3)_n$ chains and Si_2O_7 dimers as structural elements.

It has been suggested by Gard and Taylor /12/, that a crystalline phase of the jennite type is the thermodynamically-stable C-S-H phase in portland cement systems at normal temperatures. A conversion of the type of deglassing of the condensed colloidal cement gel would therefore be possible. However, this transformation obviously proceeds extremely slowly.

It was suggested already long ago (Taylor /13/), that the lattice distances 3.06, 2.82, and 1.82 Å (or 3.02, 2.80, 1.80 Å in the original paper) would correspond to interferences with cross-grating indices $hk = 11, 20$, and 02 , respectively, of a rectangular, face-centered unit cell with $a = 5.64$, $b = 3.64$ Å. Such a cell might be derived from the orthohexagonal base unit cell of the CH lattice, with dimensions 6.22×3.59 Å (see FIG 16, top), by supposing a row of Ca-OH octahedra, of composition $\text{Ca}(\text{OH})_4$, replaced by some kind of silicic acid chain (as in FIG 16, middle). To the left is shown a fully-polymerized chain of the three-link type, to the right a chain with free SiO_4 tetrahedra linked by proton bonds. Because of the diminution in width of the substitution units, this would lead to a cell that is contracted in one direction, regardless of the type of chain involved, or of the occurrence of mixed-type chains. The layer elements formed in this way, of composition $\text{C}_2\text{S}_3\text{H}_n$ to CSH_n , may be superimposed according to FIG 16, bottom. The dashed lines are an indication of Ca ions in interstitial-layer positions, which must be assumed in order to make the total composition $\text{C}_{1.5}$ to 2SH_n .

These suggestions for lattice structures are of course more or less speculative. It is not known if a hypothetical structure of this composite type can be imagined to convert in the direction towards a higher degree of crystallinity, or if a continued structural conversion and change in the morphology of the material may lead to deterioration caused by associated changes in the physical properties, such as strength and permeability.

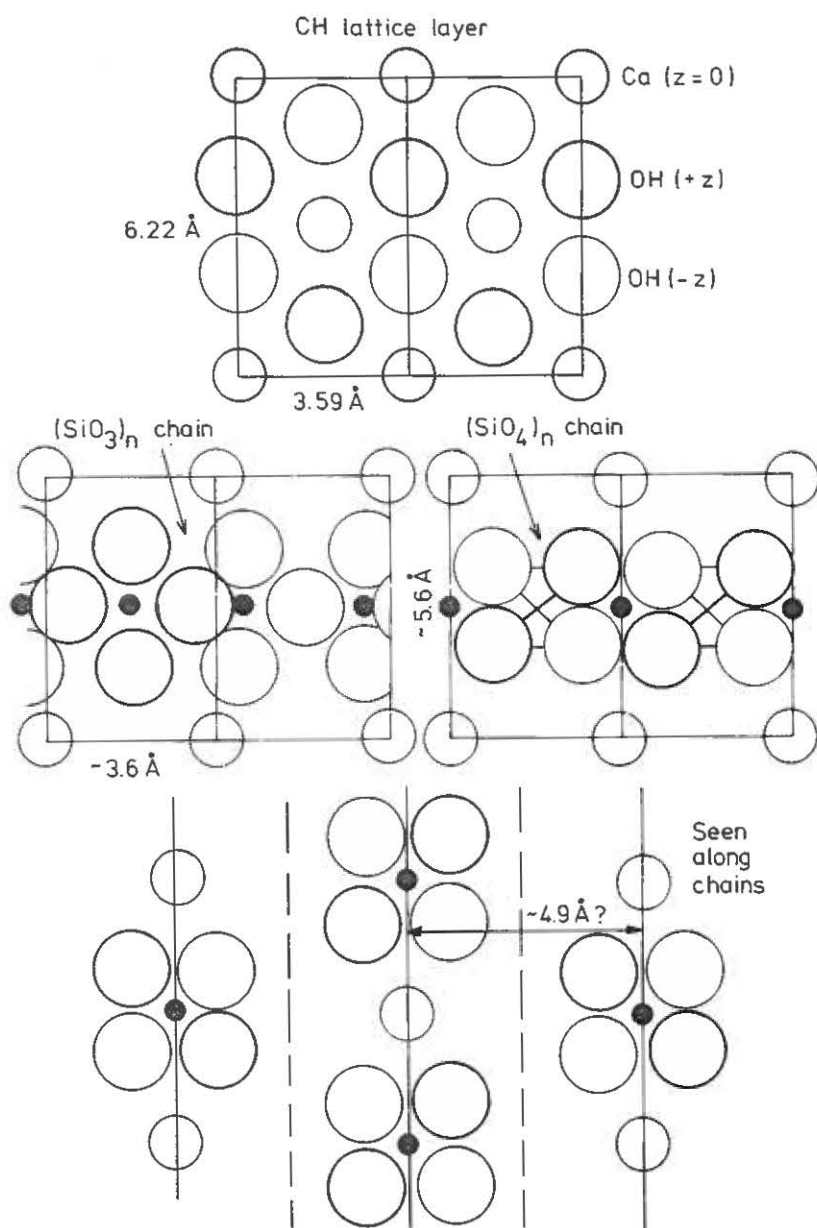


FIG 16. Sketches of CH lattice layer, and of hypothetical structures of crystal formation in C-S-H gel.

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