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X-Ray Diffraction Studies on Building Materials During 1958-59*

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Abstract

X-ray diffraction studies on building materials published during 1958-59 have been reviewed. The review covers some of the work done on clay minerals and clays, various types of cements and several miscellaneous materials as gypsum, asbestos, calcium-magnesium carbonates, etc.

Applications of X-ray diffraction methods to technical processes and study of solid state reactions have been covered. Development in instrumentation has also been dealt with.

Introduction

X-RAY diffraction studies in building materials have been considerable. General reviews and books have appeared on the work done on cements and on clay minerals—the fields in which x-ray studies had been rather intensive. In an article in the Proceedings of 1938 Symposium, W. Bussem[1] has given the summary of the x-ray work done on cements up to 1938. Important developments in next 12 years or so are available in the proceedings of the International Conference held in 1952[2]. A summary of crystal structure investigations employed in cement research has appeared in 1957[3]. Results of structural investigations have aptly found place in well known books on chemistry of cements by Lea[4] and Bogue[5]. Some x-ray work on clay minerals are available in convenient form in the texts of Grim[6] and of Brindley[7] and also in American Petrolium Institute's reference book[8]. A general review of the x-ray diffraction studies on building materials has appeared in 1958[9]. It is, therefore, considered appropriate to include the work done during the period 1958-59 in the present article.

Clay Minerals and Clays

The main work in clay minerals had been on Kaolin and metakaolin. A new concept of the transformation sequence of Kaolinite to mullite has been put forward by Drs. G.W. Brindley and M. Nakahira.[10,11] This is a notable work in this field during this period.

The series of reactions by which Kaolinite transforms to mullite is perhaps the most important in the entire field of ceramic technology and heavy clay-structural products. The first stage in the reaction series is the endothermic reaction at about 500°C which corresponds with loss of strutural water and the formation of metakaolin. An exothermic reaction at 925-950°C is generally regarded as a rapid crystallisation. Gamma alumina and mullite are thought to be formed at this stage, although appearance of mullite may be delayed. Cristobalite is formed at these or at somewhat higher temperatures. At about 1200°C a second exothemic reaction occurs in which gamma alumina disappears and mullite and cristobolite

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become more clearly defined. The new interpretation which is put forward concerns the phase which since 1928 had been known as gamma alumina. Based on results obtained from x-ray diffraction studies of minute single crystals of Kaolinite, it is suggested that the new phase is to be considered an aluminium silicon spinel with vacant cation sites. Mullite is thought to be formed by the decomposition of the spinel.

The composition of the proposed Al-Si Spinel is $Si_3\ Al_4\ O_{12}$. This differs from the composition of metakaolin $Si_4\ Al_4\ O_{14}$ by one unit of SiO_2. On this basis, the transformation of metakaolin to the spinel form requires the removal of one quarter of the SiO_2 content of metakaolin and can be written.

$$Si_4\ Al_4\ O_{14} \rightarrow Si_3\ Al_4\ O_{12} + SiO_2$$
(metakaolin) (Spinel)

The spinel phase is in defect state and has a high degree of orientation with respect to the original Kaolinite crystal, the (111) close packed oxygen planes of the spinel lying parallel to the oxygen sheets of Kaolinite and with octahedral units in parallel orientation in two structures.

The thermal effects accompanying the reaction can be interpreted as follows :

C 500°C	Endothermic reaction	Dehydration of Kaolin and formation of metakaolin $2\ Al_2O_3.\ 4Sio_2$
C 925°C	Exothermic reaction	Metakaolin layers condense to form spinel type phase to approximate composition $2Al_2\ O_3.\ 3SiO_2$ with discard of silica (about 1 in 4 SiO_2) ; a sharp transformation.
C 1050°C to 1100°C	Exothermic reaction	Spinel type structure transforms to a mullite phase, precise composition not certain, with further discard of Silica, appearing visibly as cristobalite.
1200°C—1400°C		Continued development of Cristobalite and mullite, the latter with lattice parameters consistent with composition $3Al_2\ 0_3\ 2\ Sio_2$.

The reaction sequence can be represented as follows :

$$Al_2\ O_3.\ 2\ SiO_2.\ 2H_2O. \xrightarrow[500°C]{} Al_2\ O_3.\ 2\ SiO_2 + 2H_2O.$$
(metakaolin)

$$2[Al_2\ O_3.\ 2\ SiO_2] \xrightarrow[900°C]{} 2\ Al_2\ O_3.\ 3\ SiO_2 + SiO_2$$
(Spinel)

$$2\ Al_2\ O_3.\ 3\ SiO_2 \xrightarrow[1100°C]{} 2[Al_2\ O_3.\ SiO_2] + SiO_2$$
1 : 1 mullite Cristobalite type

$$3[Al_2\ O_3.\ SiO_2] \xrightarrow[\text{about } 1400°C]{} 3\ Al_2\ O_3.\ 2\ SiO_2 + SiO_2$$
3:2 Mullite Cristobalite.

The suggestion 1:1 mullite is a tentative one.

This view regarding the possibility of existence of a defect Silicon—Spinel phase preceding the transformation of Kaolinite into mullite has been endorsed by the earlier work of Steadman and Youell[12] on the crystallography and thermal decomposition of cronstedtite. The silicon spinel phase has a high degree of orientation with respect to the original Kaolinite crystal. An oriented transformation of Kaolinite into mullite during its heat treatment has been observed earlier by G.B. Mitra [13], (002) plane of Kaolinite being converted into the (231) plane of mullite. In a subsequent communication[14] G.B. Mitra has presented experimental evidence for the existence of disordered phases proceeding the formation of mullite during the heat treatment of mullite.

Structure of Metakaolin[15] :

One major difficulty in understanding Kaolinite-mullite reaction series has been the nature of metakaolin. This material gives practically no distinct X-ray pattern and has been described as an amorphous compound, as mixed oxide, as a solid solution and as a semi-crystalline material and has been considered a source of uncertainty. In this work[15] the nature of metakaolin and its relations to Kaolinite on one hand and to the high temperature phases on the other have been considered.

The basis of estimating the structure of metakaolin has been on these lines. The lattice parameters of 'a' and 'b' of Kaolinite are retained more or less unchanged in metakaolin and the C axis periodicity disappears. The octahedral Al-O (OH) layer of Kaolinite is likely to be changed more than the tetrahedral Si-O layer by the loss of water. On these considerations it seems probable that the Si-O network Kaolinite is retained essentially unchanged in metakaolin. The distortions in the Si-O layers in Kaolin is likely to remain or even increase in metakaolin during dehydration.

In the unit cell of Kaolinite there are three layers of oxygen ions, each containing 6 oxygen ions per unit cell. This arrangement is called 6-6-6 sequence. When dehydration occurs 18 oxygen ions are reduced to 14 and the resulting structure must permit the Kaolinite layers to collapse to about 6.3 AU although it must be in an irregular manner. To conform with density it is suggested that 6-6-2 arrangement is retained in metakaolin with only two oxygen ions in the upper layer.

Structural variations of Kaolin minerals had been reported by H. Takahashi[16]. In this study the degree of crystallinity for Kaolin minerals through X-ray, thermal and other methods and the relation between structural characteristics and physicochemical properties were determined. The X-ray data reflected both internal and stacking variations. From comparison of X-ray and thermal data it is inferred that the displacement in the series from Kaolinite to fireclay is 1 dimensional with respect to 'b' axis, whereas the displacement in halloysite is two dimensional (rotational displacement). The value of base exchange capacity of Kaolinite, fireclay and halloysite are correlated with the internal disorderliness of Kaolin structure.

Exothermic reaction of metakaolin between 950°C—1000°C has been studied by T. Demediuk and W.F. Cole[17]. Using X-ray methods it is concluded that the silicate phase formed after the exothermic reaction in co-precipitated gels of Al_2O_3 and SiO_2 is a disordered phase characteristic of mullite. Heating the sample to 1200°C improved the crystallinity of mullite.

Much of the clay minerals in Recent and

Tertiary Sediments has been found to contain interlayer mixtures of three clay mineral types. An analytical method to determine the quantity of each clay mineral type has been developed by E.C. Jonas. and T.E. Brown[18]. The method involves gathering diffraction data from oriented aggregate specimens in equilibrium with 50% R.H. together with data from specimen either after heating or solvating with ethylene glycol.

Studies on clays in a general way have been earried out in various Laboratories both in India and abroad. These are of importance for specific purposes. The trend is mostly on ascertaining the major clay mineral constituents [19],[20],[21].

Quantitative analysis of silica minerals is important for many purposes. A rapid X-ray diffractometer method for quantitative determination of quartz, tridymite, and cristobolite in silica refractories has been developed by Holmquist et al[22]. Starting with high purity quartz, standards of tridymite and crystobolite were prepared. Based on the diffraction patterns of known mixture of standards, the percentages of the various silica minerals can be calculated for samples of silica refractories. Only one pattern needs to be taken for each sample and the whole determination needs much less time than the conventional methods.

Cements:

Phase equilibria in the high lime portion of the system CaO-SiO_2-H_2O has been studied by D.M.Roy[23].

The stability relationships of the phases in the system CaO-SiO_2-H_2O is important. Earlier work was concerned with the equilibria under atmospheric conditions, newer techniques have enabled to widen the scope of investigations at elevated temperature and pressures. The present study concerns stabillty relations of calcium silicate hydrates under hydrothermal conditions in the high lime region. While the total composition of hydrated cement is high in CaO content, tobermorite (ideally $4CaO.5SiO_2, 5H_2O$) or poorly crystallised structurally related hydrates are believed to form the basis of the binder in concrete and high insulated materials. From the earlier work on these systems it appears that in the high CaO portion of the system the minerals afwillite, hillebrandite, foshagite, possibly a high temperature hydrate (such as $C_2SH(D)$) corresponding to the 2 CaO: SiO_2 ratio and C_3SH_2 would be stable in the "hydrothermal" range. It is known that in the system $CaSiO_3$-H_2O-tobermorite of the CaO:SiO_2 ratio 1:1 was stable at as high as 220°C and at 15,000 psi water pressure and that an intermediate phase was formed for small interval 40°C above this temperature before giving rise to the less hydrous phase Xonotlite. Recently stability relations of dicalcium silicates and related composition were determined under hydrothermal conditions (D.M.Roy, unpublished). In this study attempt has been made to obtain information on the hydrates in the high lime portion of the system. CaO-SiO_2-H_2O and as such is an extension to the previous study at low temperatures. Of particular interest was the determination of the upper stability limits of hydrated phases where they are in equilibrium with anhydrous compounds, such as, vankanite, larnite or bredigite. A compositionl diagram of a portion of the ternary system is also given. At least three new compounds were shown to have been formed in the high CaO portion of the system at elevated temperatures. The probable composition of these phases is indicated in the compositional diagram. The new phases are relatively low in H_2O content, and they are found to be stable to a remarkably high temperature. An additional needle shaped phase was formed at temperatures around 700°C at high pressures, but data are not sufficient to describe the new phase.

Some work on the crystal chemistry of hydrated calcium silicates has been reported by G.L. Kalauseck and A.F. Frebus [24]. Three very similar hydrated calcium silicates that serve as binders for or are closly related to the binding material of autoclaved and moist air cured concrete and related products have been differentiated by electron microscopy, X-ray diffraction, D.T.A. infrared absorption and degree of stability towards acetoacetic ester and oxide-composition. Tobermorite 4-5 CaO. 5 SiO_2, $5H_2O$ is the binder of properly autoclaved concrete and related products. This phase is identified by X-ray diffraction lines at 11,3.07 and 2.97 A of strong intensity by a basal spacing at 11A and by a flat platy crystal habit. The analogous hydrates of similar CaO/SiO_2 molar ratio (C/S) and designated the 0.8 to 1.33 C/s hydrate generally shows a basal spacing 14A, occurs in crimpy foils and exhibits a strong exothermic effect in D.T.A. at 8.35°C. This phase differs remarkably from tobermorite, does not undergo any crystal binding and shows some of the physical characteristics of the clays. It is the low lime intermediate in the formation of tobermorite.

Further important work in the lime silica systems are the studies on the tricalcium silicate and its stability within the system CaO-SiO_2 by Welch and Gutt [25], phase equilibrium studies in the system CaO-Cr_2O_3-SiO_2 by Glasser and Osborn[26]. Studies in the system CaO-Al_2O_3-SiO_2-H_2O which gives new data on the polymorphism of dicalcium silicate and its stability in the system CaO-SiO_2-H_2O. by D.M. Roy[27]. X-ray analysis of preparations of the system tricalcium silicate and dicalcium silicate has been done by Yamagochi et al[28]. Heating changes of calcium silicate hydrates have been studied by Yoshii and Sudoh[29].

Dicalcium Silicate—Tricalcium Phosphate

The phase equilibrium in the system 2 CaO, SiO_2-3 CaO, P_2O_5 have been investigated by high temperature microscopy and X-ray analysis by Nurse et al[30]. The system presents a continuous series of solid solution with a melting point maximum at 2240°C. A new high temperature form of 3CaO P_2 O_5 has been discovered which does not survive quenching to room temperature, but is completely miscible with the α form of 2 CaO SiO_2. At low temperatures two compounds are formed by solid state reactions, the known silicocarnolite stable below 1450° and a new phase, stable below 1125°C having approximate composition 7 CaO. P_2 $O_5$7 2 SiO_2.

Calcium Aluminates

P.P. Budnikov and I.V. Kravchenko[31] have studied the calcium aluminate hydration process. Samples of purified mineral CaO. Al_2 O_3 were subjected to hydration under various conditions. CaO. Al_2 O_3 first formed hexagonal 2 CaO. Al_2 O_3. 8 H_2O which gradually recrystallised to cubic 3 CaO. Al_2O_3. 6 H_2O. After five months the hydration was completed and only small amounts of 2 CaO. Al_2O_3. 8 H_2O could be detected. In H_2O at 45°, the hydration and connected recrystallisation proceeded much faster. The strength of the material dropped on the initial recrystallisation but was later restored and eventually increased. G. Schippa and R. Turviziani[32] had examined the ternary solids in equilibrium in the system CaO-Al_2O_3-H_2O and excludes the possibility of formation of hexagonal metastable solids 3 CaO. Al_2O_3. (H_2O). The X-ray pattern which has been attributed to 3 CaO. Al_2O_3 12 H_2O is almost identical with that for 3 CaO. Al_2O_3. $CaCO_3$ (H_2O). The reaction between 3 CaO-Al_2O_3 and Ca So_3 1/2 H_2O has been studied by Tanaka and Swzuki[33].

The ferrite phase :

A study of the composition of ferrite phase present in commercial portland cements has

been made using X-ray diffraction techniques by H.G. Midlay[34]. Examination of 31 different samples shows that the most frequently occurring compositions lies between 4 CaO. Al_2O_3. Fe_2O_3 and 6 CaO. Al_2O. 2 Fe_2O_3. The solid solution of magnesia and ferrite phases has been studied by A. Kato[25]. He observes that the interplanar spacings of the X-ray diffraction pattern of 4 CaO. Al_2O_3. Fe_2O_3 decrease slightly with small additions of MgO but increase with large additions of MgO. This is thought to be due to the substitution of MgO for the CaO up to about 1% (Mol) and then for Fe and Al, resulting in the displacement of the composition of 4 CaO. Al_2O_3 Fe_2O_3 towards the high Fe_2O_3 and of the solid-Solid solution series as proposed by Insley.

Stability of the phase Fe_2O_3. Al_2O_3 has been studied by A. Muan[36].

Structure determination : B Wollastonite.

The crystal structure of this mineral has been investigated by Tolliday[37]. B. Wallastonite ($CaSiO_3$) comprises both triclinic wollastonite and monoclinic para wollastonite. A new type of infinite chain silicate structure has been proposed earlier for B. Wollastonite based on X-ray crystallographic work on projection. The three dimensional work on parawollastonite, which is reported here, confirms this.

The structure of grossularite, a garnet, with ideal formula Ca_3 Al_2 $(SiO_4)_3$ has been studied by Abrahams and Geller[38]. The observations that none of the oxygen polyhedra is regular (although the space group would allow the tehahedra and octahedra to be regular simultaneously) and that the octahedra are more nearly regular than the tetrahedra are very important.

The optical properties and structures of Ca0. 2 Al_2O_3 and Sr0, 2 Al_2O_3 have been reported by Boyko and Wisnyi[39]. Their results confirm the earlier observation of Hagerqvist et al.

Foshagite (4 Ca0. 3 SiO_2. H_20) resembles several other silicate minerals such as xonotlite, hillebrandite and tobermorite. In their study Gard and Taylor[40] found the composition, unit cell and the dehydration characteristics of this mineral.

Application of X-ray diffraction analysis to technical processes : H.Schloemer[41] has developed an X-ray method by which the course of cement firing process on the sintering belt can be followed with different amounts of air and air pressures above and below the sintering belt. An examination of crystalline structure shows that the crystallisation with coarse C_3S grains and with strong corrosion phenomenon gives lower value of mechanical strength than the fine crystalline constituents. To obtain finer crystals too high a temperature peak must be avoided and the sintering be so controlled that the maximum temperature isotherm appears a few meters before the point of removal of sinter from the belt.

Designing of a tunnel kiln on the basis of Laboratory tests has been indicated by West et al[42]. A shale containing lime stone was studied, using chemical, differential thermal and X-ray techniques to establish rational mineralogical analysis and reaction that occur during firing. These tests indicated the steps to be taken to overcome the defects in the final product.

Application of X-ray methods to study Solid State reactions: Naeser and Scholz[43] have studied the effect of mechanical treatment at room temperature on reactivity of solids. Repeated rolling of very fine powders at room temperature increases the reactivity. Sintering temperature of dolomite and of fine quartz was reduced by 100-200°C or the temperature of

melting was reduced considerably. Several other materials were also examined. X-ray patterns show a change in the normal spacings, a widening, narrowing or disturbance of the distances.

Folley and New berry[44] have studied the substrate with a X-ray microscope as many surface reactions are influenced by the structure and composition of substrate material.

Miscellaneous Materials

X-ray diffraction studies of many materials have been carried out in this period,for instance, α alumina[45], of mullite and glass content in clay products[46], structure of silica[47], aluminium hydroxide gels[48], hydration of MgO from vapour phase[49], α silica-water systems[50], bohmite-hydragilite mixtures[51], slag cements from Indian slags[52].

J.B. Droste and R.E.Grim[53] have used an ingeneous method to study the transformation in gypsum when it is heated. They have used an autoclave fitting into an X-ray spectrometer diffraction unit which permits continuous X-ray diffraction studies at moderately elevated temperatures to study the conversion of gypsum into hemihydrate. It is found that gypsum changes directly to the hemihydrate. There is no evidence of an intermediate phase. Also there is no evidence of an intermediate liquid phase, even a momentary one, in the transition. In fact the data strongly suggests that such a liquid stage is not present and that the transition is a direct solid state reaction.

J.R.Goldsmith and D.G.Graf[54] have obtained graphical relations between lattice constants and composition of the Ca-Mg carbonates. They have obtained values of a_o and c_o for magnesian calcites, the dolomites and a synthetic magnesite from X-ray diffractometer and film measurement. This was done to verify their earlier work on X-ray and compositional data which were used to prepare spacing versus composition curves of a number of naturally occurring magnesian calcites. In the present work several synthetic magnesian calcites have been prepared and examined by spectrochemical analysis and X-ray diffraction. In addition, compositions and spacings of synthetic magnesite and five carefully selected dolomites have been obtained in order to evaluate more accurately the composition—unit cell relationship in Ca-Mg carbonates.

The effect of firing on kankar limes has also been studied by X-ray diffraction[55].

Asbestos

X-ray diffraction patterns of asbestos fibres from Indian sources have been taken for identification purposes. The effect of processing on the crystallinity of asbestos from Indian and foreign sources as well as the set products of asbestos-cement systems has been studied[56],

Instrumentation

Recording X-ray powder diffraction patterns at temperatures over 1400°C raises diffraction problems in camera and furnace design. A new powder diffraction technique has been evolved by Aruja et al[57]. In this a thermocouple combines the function of a sample support, heating and temperature measurement. The maximum working temperature depends on the thermocouple material and is normally 1750°C using 5/20 rhodium- platinum or 1850°C with 20/40 rhodium-platimum couples.

An apparatus using the oscillating heating method while recording the X-ray powder diffraction has been evolved by Rowland et al[58]. This is a method for continuously scanning a single diffraction maximum while the sample temperature is increased at a regular

rate. This method overcomes many of the difficulties in stationary heating methods. After the diffractometer has been oscillated over a sufficient number of maxima, the resulting series of diagrams represents diffrac tion patterns at any temperature within the temperature range. The method is applicable to a variety of crystalline materials.

Conclusion

It will be seen that in the period under review X-ray diffraction methods had been quite intensively and variedly used in studying building materials. Misconcepts in some fields have been removed, new areas have been studied and technological applications made. The results obtained will not certainly produce better buildings immediately. These investigations can be of help in better understanding of technical processes, in devising new types of building materials and in more efficient use of those already existing. No attempt has been made to cover the entire field in this review as that would make the article voluminous and bringing out of the connecting principles difficult.

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