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SELECTIVE DISSOLUTION OF CLINKER MINERALS
AND ITS APPLICATIONS

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Abstract

Various chemical techniques for the selective separation of calcium silicates, calcium aluminates, calcium aluminoferrites and some minor components of portland cement clinker are reviewed and discussed in view of possible applications. Unique applications include the study of clinker mineral morphology and composition by a combination of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS); the determination of alite and belite particle size distribution; the removal of interfering substances for improved quantitative x-ray diffraction analysis; and the synthesis of specific clinker minerals such as alkali substituted aluminates. The determination of hydration kinetics of components separated from industrial clinkers by the described methods is also possible.

Introduction

Portland cement clinker is a multicomponent material in which the crystalline calcium silicates are embedded in a matrix of calcium aluminates and aluminoferrites of differing composition and crystallinity. In an industrial clinker, all clinker components are known to be present in an impure form. The calcium silicates, Ca_3SiO_5 (C_3S) and Ca_2SiO_4 (C_2S), always contain small amounts of impurities present in their crystalline structures in one form or another. Thus, we refer to them as alite

and belite, respectively. The aluminate phase can occur as $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A) or as one of its structural variants containing potassium, sodium and, possibly, other elements such as silicon. The ferrite phase forms a solid solution series (Fss) in which the $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio varies depending upon the composition of raw materials and the conditions of burning and cooling. Minor components, such as magnesium and calcium oxides and various alkali sulfates, are present in free form or dissolved in the major clinker components.

The analysis of these clinker components historically is performed by x-ray diffraction analysis or optical microscopy. Although both techniques can produce reasonable quantitative analyses of the main four components present in the clinker, they cannot easily answer the questions relating to the presence of important minor components, such as alkali sulfates, because of their small concentrations. Are these compounds present in free form or as solid solutions? Are they readily available for early hydration? These and other questions are important in view of their effect upon early development of physical properties of hydrating cement and cementitious products.

A logical means of increasing the concentration of a particular clinker compound for analytical purposes is the technique of selective dissolution. In much the same way as etching techniques are used for analysis by optical microscopy, the techniques of selective dissolution are based, on a macro level, upon the preferential solubility of one or more clinker components whereas others are undisturbed by the solvent. It has been known for some time that weak acids will dissolve calcium silicates more rapidly than calcium aluminates or aluminoferrites, but it has been only in the fifties that successful attempts were made to

separate the clinker calcium silicate phases from the interstitial material. Since then an avalanche of relevant articles has appeared, suggesting selective separation methods for practically all clinker compounds.

It is the purpose of this presentation to critically review the techniques available, and to discuss their future and importance for the cement industry. It should be remembered that none of the described techniques may be completely selective, in that small amounts of "insoluble" compounds may go into the solution or "soluble" compounds may not completely dissolve under the conditions used. Therefore, data should be interpreted with care, particularly when used for quantitative purposes. Under these conditions, the techniques can be extremely valuable for research as well as for technical service purposes.

Selective Dissolution of Free CaO

Two of the most important analytical procedures needed in cement chemistry are the determinations of free CaO in anhydrous systems and of free Ca(OH)_2 in hydrated systems. They are important in following the completeness of clinker burning and the progress of cement hydration, respectively.

We do not wish to review all the relevant analytical techniques, but it is important to note some of the most useful ones which are dependent on selective dissolution. The best known is the Franke method (1), based on the solubility of free CaO or Ca(OH)_2 in a 3:20 mixture of acetoacetic ester and isobutyl alcohol, and the subsequent determination of this originally uncombined calcium by various methods, such as titration with hydrochloric or perchloric acids.

Several modifications of the Franke method were suggested by researchers at the Portland Cement Association in Chicago, who applied their modified techniques to the determination of free lime in anhydrous substances such as portland cements and clinker minerals (2), as well as free Ca(OH)_2 in an intimate mixture with calcium silicate hydrate (2, 3, 4). Their best known Franke method modifications are the "solvent variation" and "time variation" methods.

A lesser known method is that of Konarzewski and Lukaszewicz (5), published in 1932, in which free CaO in portland cement is dissolved in a 1:1 mixture of phenol and absolute ethanol under reflux for several hours. The liquid is filtered and the residue washed with ethanol. Subsequently the ethanol is removed from the filtrate by distillation, and the residue is dissolved in water. The amount of Ca(OH)_2 present is determined by titration with $\text{N}/15$ HCl using a methyl orange indicator.

One of the oldest methods for free Ca(OH)_2 determination is the glycerol-alcohol method of Emley (6). Modifications of this technique by Lerch and Bogue (7) and Lebedeva (8) were used for many years but may be subject to errors and give variable results (9).

More recently Chang and Chen (10) suggested a method involving extraction of free lime by hot anhydrous ethylene glycol followed by titration with $\text{N}/14$ HCl using phenolphthalein as an indicator. Under the optimum conditions of $80\text{--}85^\circ\text{C}$, and a cement fineness of 3000 to 5000 cm^2/g , the method is reported to take only five minutes per sample. MgO is not extracted by the ethylene glycol, and the presence of gypsum does not interfere with the analysis.

Selective Dissolution of Calcium Silicates

Separation of calcium silicate clinker components from those in the interstitial material is probably the most important result of the attempts to develop selective dissolution techniques. It makes it possible to more accurately determine the mineralogical composition of residual clinker phases by x-ray diffraction and to study the details of hydration of clinker components present in industrial products in relatively small amounts. Most of the techniques discussed result in the dissolution of calcium silicates, carbonates and free CaO, leaving in the form of an insoluble residue most of the aluminate and ferrite phases as well as some of the minor components.

Probably the very first paper on the subject is the 1904 note by Hart (11), who studied the composition of the interstitial phase obtained through removal of the calcium silicates by acetic acid. Based on results obtained, Hart hypothesized that the interstitial phase is composed of a double salt of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 + 2\text{CaO} \cdot \text{Al}_2\text{O}_3$ (i. e. C_4AF) and an "anhydrous serpentine", $3\text{MgO} \cdot 2\text{SiO}_2$. Fifty years later, Royak et al. (12, 13) have shown that acetic acid removes not only the calcium silicates but, depending on their Al to Fe ratio, also the aluminate and the aluminoferrite phases. For selective dissolution of calcium silicates, Royak and co-workers suggested boric acid. This technique has been used later also by Moore (14), Bogdanova and Spolis (15), and Akhmedov et al. (16). The method uses 400 ml of saturated boric acid solution (5%) per gram of cement. Boric acid dissolves CaO, $\text{Ca}(\text{OH})_2$, alite, belite and most of the minor components.

It was Takashima (17) in 1958 who suggested the use of salicylic and picric acids as dissolving solutions. Since then the salicylic acid-methanol method became one of the most popular selective separation techniques (14, 18-24). In this method the cement is treated with an approximately 1:5 mixture of salicylic acid and dry methanol for 30 to 60 minutes. Salicylic acid removes only the free lime, alite and belite phases, thus enabling the subsequent x-ray analysis of the total interstitial phase and its further separation by other techniques. Hjorth and Lauren (22) verified Takashima's (17) suggestion that the rates of dissolution of alite and belite in salicylic acid differ, in that the rate of alite dissolution exceeds that of belite. This enabled them to enrich the sample in belite and, using a computer model, to obtain accurate data on the amount and crystalline variety of belite present in a particular clinker or cement.

According to Hawkins and Wilson (25) it is possible to determine alite and belite concentrations in synthetic mixtures by the use of salicylic acid-methanol technique. Salicylic acid reacts stoichiometrically with CaO, pure C_2S and pure C_3S in molar proportions of 1:2, 1:4 and 1:6, respectively. The method comprises the complete reaction of C_3S and C_2S with a known amount of salicylic acid in methanol. Any insoluble residue, composed mainly of aluminates and ferrites, is determined by filtering and weighing. A known quantity of pure C_2S is then added to the filtrate in order to react with the excess of salicylic acid present. The undissolved C_2S is then determined gravimetrically. From the above data and a separate free CaO determination, the ratio of C_2S to C_3S is calculated. Due to interferences from other compounds, the authors had only limited success in applying the technique to commercial clinkers.

Hawkins and Wilson (25) also explored the possibility of separating the free CaO and alite from the remainder of the clinker by the use of an ammonium chloride (5%) in 1:4 water-ethanol solution. Because of technical problems related to precipitation of amorphous silica, the method was not successful in quantitatively determining CaO and alite. However, it was very useful for concentrating belite for further x-ray evaluation. In a modification of this procedure, Klemm and Skalny prevented the precipitation of silica by the addition of dimethylformamide (DMF). DMF is known to interact with monomeric silicate species to form a stable complex of the type $\text{Si}(\text{OH})_4 \cdot (\text{DMF})_x$. It was used by Azeem (26) in a procedure for a gravimetric sulfate determination in the presence of soluble silicate, and later by Klemm and Fetter (27) to study the polymerization kinetics of dissolved silica in geothermal brines.

The use of ammonium acetate or citrate was first suggested by Keil and Gille (28). The technique was adopted by Fratini and Turriziani (29), who employed a mixture of water (25 ml), ammonia (65 ml) and ammonium citrate (10g) to remove the calcium silicates from a 1 g cement sample. The insoluble residue was used to obtain better x-ray diffraction data for the ferrite phase. The method was used for a similar purpose also by Midgley et al (30) who additionally explored the question of the relative solubilities of calcium aluminate and aluminoferrite phases during the removal of the calcium silicates.

A significant improvement was the maleic acid technique, which was introduced by Tabikh and Weht (31) in 1971. A dry and ground sample (5 g) is mixed with anhydrous methanol (150 ml) followed by the addition of maleic acid (15 g). The mixture is stirred for 10 minutes in which time the free CaO and calcium silicates are completely removed (32).

Malic acid was also found to dissolve the calcium silicate phases in a manner similar to that of maleic acid (33). It is appropriate to mention that the analysis of the filtrate after the dissolution of calcium silicates can give useful data on the composition of these compounds, particularly in regard to alkalies and other elements present in the silicate phases.

Jander and Hoffmann (34) attempted the separation of free CaO and the four known calcium silicates (CS , C_2S , C_3S_2 and C_3S), but encountered difficulties. They did not succeed in separating C_2S from C_3S , compounds of greatest interest to cement specialists. Midgley (35) has attempted to overcome this problem by partial enrichment of C_2S utilizing the difference in the rates of hydration between these two hydraulic calcium silicates.

It is well known in sample preparation for optical microscopy that the etching of polished surfaces leads to better resolution of minerals present. This is due to preferential etching of some of the structures or, in other words, to their preferential or selective dissolution. Examples of chemicals used for this purpose are given for example in reference (36). In recent years, a compromise between surface etching (for optical microscopy) and complete dissolution (for x-ray diffraction analysis) has been used by several authors in preparation of samples for analysis by SEM and its combination with energy dispersive spectroscopy, usually referred to in the literature as EDS, EDAX, or EDXA. Yamaguchi and Takagi (37), Skalny et al (33) and Wojnarovits and Udvardi (38) used partial dissolution of bulk clinker samples to study the morphology and composition of anhydrous clinker components.

Selective Dissolution of Interstitial Phases

Although it was early recognized that the hydraulic silicate minerals in cement clinker would dissolve in weak acid solutions and, in fact, the entire ground clinker or cement is soluble in strong mineral acids such as HCl, the separation and dissolution of the interstitial aluminate and ferrite phases received more limited attention. During the high temperature clinkering reactions, these phases constitute the melt from which the silicate minerals crystallize and develop. Upon cooling, the melt differentiates into crystalline compounds, solid solutions, and amorphous glassy constituents. In addition to C_3A and Fss phases, other compounds such as $C_{12}A_7$ or $C_4A_3\bar{S}$ might be expected. The separation and removal of one or more of these phases can greatly aid in the interpretation and identification of x-ray diffraction patterns, or in the quantitative analysis of specific minerals.

In 1939, Keil and Gille (28) showed that aluminates are more soluble than ferrites in an ammonium citrate solution. Fratini and Turriziani (29), using an ammoniacal solution of ammonium citrate (pH = 11.4), removed the silicate phases from a series of commercial clinkers with different A/F ratios. They extracted 2 g cement samples with 200 ml of citrate solution for 12 hours followed by a second extraction of the remaining C_3A and ferrite residue. Analyses of these residues indicated that the higher the iron content, the greater the resistance of the aluminoferrites to partial dissolution. Using a solution of similar composition, Midgley et al. (30) studied the comparative dissolution rates of C_6AF_2 , C_4AF , C_6A_2F , and C_3A . The C_3A dissolved the fastest, followed by C_6A_2F , C_4AF , and finally C_6AF_2 which was the most resistant to the dissolving solutions.

The extraction of silicate minerals and C_3A from commercial clinkers was accomplished by Satou and Tamura (39) with a methanolic nitric acid solution. A 10 g quantity of clinker was stirred in 500 ml of 7% nitric acid solution in methanol for 30 minutes at 30°C. The resulting ferrite residue composition corresponded roughly to C_6A_2F . This residue was subsequently compared by means of x-ray diffraction patterns to blends of crystalline and glassy synthetic ferrites, which had been prepared from a melt by rapid quenching and slow annealing techniques. It was concluded that the commercial clinker ferrite residue had a crystal to glass ratio of 6:4. Takashima and Higaki (40), in an extension of earlier work (17), discovered that picric acid in methanol dissolves both silicates and clinker glass, whereas salicylic acid in methanol dissolves only the silicate phases. Therefore, the difference between the amounts of residue obtained by both extraction methods yields the amount of clinker glass present.

Royak, Nagerova, and Kornienko (12) studied the solubility of 0.1 g amounts of synthetic calcium aluminates and ferrite minerals in 100 ml of 1 N aqueous acetic acid solutions for 75 minutes at room temperature. C_3A dissolved completely, while only about 10% of C_5A_3 ($C_{12}A_7$?) and C_4AF passed into solution. However, similar treatment of commercial clinker samples revealed that, in addition to the expected solubility of the silicate phases and C_3A , 40 to 50% of the Fe_2O_3 from the ferrite phase also dissolved. This was attributed to high solubility of interstitial glassy material, whose formation is favored both by a melt containing C_3A and C_4AF , and rapid clinker cooling.

A preliminary removal of silicates with a salicylic acid-methanol solution, followed by treatment of this residue with 1 N acetic acid was

utilized by Yamaguchi and Takagi (23). The major portion of the ferrite phase remained in the final residue. This method was also used by Tomita et al. (41) and by Pollitt and Brown (42), who found that if the pH of the acetic acid was maintained between 3.5 and 3.8, the ferrite phase could be recovered after complete C_3A removal.

A hot sodium carbonate leach has been found effective in the removal of calcium aluminates from calcium silicate-aluminate sinters in which the C_2S has undergone the β to γ inversion (43, 44). Royak, Nagerova, and Kornienko (45) proposed a method for determining the phase compositions of aluminous cements by means of varying solubilities in a Na_2CO_3 solution.

The use of sugar (sucrose) as a dissolving agent was first suggested by Merriman (46) in 1924. Merriman's studies on the solubility of cements in sugar solutions developed into a test for durability called the "disintegration index", and later the "sugar-solubility test". A review of this work and the explanation of the chemistry involved was made by Lerch (47), who related the degree of Al_2O_3 extraction to other factors in the clinker such as free CaO and sulfate content.

Fateeva and Kozlova (48) found that synthetic C_3A and C_5A_3 ($C_{12}A_7$?) can be dissolved by a 10% sugar solution. The method was applied to the titrimetric calcium analysis of aluminates removed from clinker and cement by repeated washings of a boric acid residue with a hot 10% sugar solution. The calcium contents of a C_3A and C_4AF mixture were determined by Leibina (49) by the dissolution of the C_3A phase in a 10% aqueous sugar solution (18-20°C) for 5 minutes, followed by an EDTA titration of the filtrate at pH 12 using a Chrome Dark Blue indicator. It was found that about 9% of the calcium present in the ferrite phase also dissolved

and, therefore, an appropriate correction had to be applied to the calculation. A similar sugar extraction technique was used by Regourd and Guinier (50) on the salicylic acid residue of commercial cements to isolate the Fss phase for x-ray crystallographic studies.

An excellent dissolution method was developed by Gutteridge (51) at the Cement and Concrete Association in England, which removes all interstitial compounds from cement except the silicate phases. In this procedure, 3 g of cement is stirred for 2 minutes in 100 ml of boiling KOH (10%) and sugar (10%) aqueous solution. The residue is removed by filtration, washed in turn by a KOH-sugar solution and acetone, and dried. It may subsequently be used for x-ray diffraction studies or chemical analysis.

In order to simplify complicated x-ray patterns for compound identification, Moore (14) treated 1 g cement samples with 400 ml of cold distilled water for 40 minutes, followed by filtration, a methanol wash, and drying at 50°C. This treatment removed $C_{12}A_7$, a portion of the C_3A , free CaO, and gypsum. Difficulties may occur because of x-ray scattering due to the presence of hydrated gels which are often present, or to the formation of new compounds. Samples, for example, which contain $C_{12}A_7$, free CaO and $CaSO_4$ together will form ettringite under such cold water treatment. Although Moore reports that $C_4A_3\bar{S}$ is also dissolved from cement by this treatment, Mather (52) has found that, when Type K expansive cement (2 g) is stirred for 40 minutes with 800 ml of cold water containing distilled water ice cubes to maintain a 0° temperature, x-ray examination of the dried residue shows that the $C_4A_3\bar{S}$ still remains. However, when this same residue is stirred with a second 800 ml portion of cold water and ice for an additional 1 hour and 20 minutes (total of 3 hours),

all of the $C_4A_3\bar{S}$ will be extracted from residue. Takashima and Amano (18) first removed silicate phases and free CaO from cement by salicylic acid in methanol treatment, and then stirred the residue in a large volume of boiling water for 10 seconds. This treatment served to dissolve all of the C_3A and only a small part of the ferrite phase. The Fss residue was characterized by x-ray diffraction.

Analysis by Selective Dissolution of MgO

MgO is present in portland cement clinker in free form (periclase) or as a constituent of other crystalline and amorphous phases. Its excessive presence in free form is known to cause disruptive expansion of concrete. Because of its relatively low solubility in the weak acids used for selective dissolution of free CaO and calcium silicates, MgO is retained in the insoluble residue, and it can be detected by x-ray diffraction analysis. Addition of an inert internal standard prior to the acid treatment makes it possible to obtain a reasonable quantitative analysis along with the aluminate and aluminoferrites phases.

Complete separation and identification of MgO in the various phases of cement clinkers and blast furnace slags has been attempted by Bogdanova and Sitchikova (53, 54). The analysis was performed in several steps: First, using an aqueous EDTA solution at room temperature for 15 minutes, MgO present in the calcium silicate phases is dissolved, and then determined colorimetrically in the filtrate. A second cement sample is treated with ethanolic acetic acid in the presence of NH_4Cl . Subsequently, the filtrate is evaporated and the residue dissolved in HCl. The MgO in the solution is then determined as above, and represents the sum of free

MgO (periclase) + MgO in calcium silicates + approximately 5% of MgO present in the interstitial phase. MgO present as periclase is computed from the above analysis. The insoluble residue after the ethanol-acetic acid treatment is dissolved in HCl, the MgO present in the interstitial phases determined colorimetrically, and estimated using the 5% correction mentioned above.

A technique to determine the free MgO content is also reported by Mirakyan and co-workers (55). It is based on the dissolution of cement in an absolute alcohol-glycerol mixture, and subsequent formation in the presence of NH_4Cl of a binary salt. The solution is filtered, and the filtrate is titrated with EDTA to determine the amount of free MgO originally present. A selective dissolution method has been used by Royak and Nagerova (56) in determining the extent to which MgO can form solid solutions with tricalcium silicate.

Selective Dissolution of Alkali Compounds

Alkali compounds are perhaps the most common minor components found in portland cement clinker. They may be present as halides, sulfates, sulfate and carbonate double salts, and alkali-doped silicates and aluminates. Selective dissolution techniques have been used to separate and identify the various clinker phases containing alkalies.

Moore (14) found that, because alkali salts are generally water soluble, cold water leaching of cement or ground clinker removes K_2SO_4 (arcanite), $\text{K}_3\text{Na}(\text{SO}_4)_2$ (aphthitalite), $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ (calcium langbeinite), KCl, and calcium-alkali double carbonates. Zevin et al. (57) treated clinker samples with water for 30 minutes to completely remove K_2SO_4 which interfered with the quantitative x-ray diffraction determination of belite.

Pollitt and Brown (42) systematically studied the various forms of alkali present in cement and clinker by chemical separation of the various phases. Hot ethylene glycol, such as is used for the free lime determination, removed the simple alkali sulfates, but allowed the double sulfates to remain in the residue. A water leach subsequently dissolved the double sulfate, $K_2Ca_2(SO_4)_3$. The leached residue could then be analyzed for the remaining alkalies. Silicate compounds were removed by the salicylic acid-methanol technique, and the residue alkalies in the interstitial phases were then determined. Finally, the C_3A was removed by treatment with aqueous acetic acid and the alkali content of the ferrite residue was measured. This allowed calculations of K_2O and Na_2O present in sulfate compounds, and the amounts of each in the aluminate, ferrite, and silicate phases.

A comprehensive x-ray examination of alkali phases in cement clinker was conducted by Adams (58), and most compounds identified were determined either quantitatively or semi-quantitatively. The process was simplified by removal of the free CaO and silicate phases by a maleic acid-methanol extraction, followed by a study of the residue which contained alkali sulfates, double sulfates, alkali-doped calcium aluminates with suggested compositions of KC_8A_3 and NC_8A_3 . The exact stoichiometry, however, of such alkali-doped aluminate compounds is very much in doubt (59, 60). Further extraction of the maleic acid residue with aqueous acetic acid removed the aluminate phases, and indicated that 5 to 10% of the K_2O originally present in the cement may be found in the ferrite phase.

Analytical methods for the determination of minor compounds in cement and clinker by means of x-ray diffraction studies of a maleic

acid-methanol residue were reported by Mander, Adams, and Larkin (61). Alkali-doped C_3A was determined in commercial clinkers and compared to the synthetic K_2O and Na_2O -doped aluminate compounds. Although KC_8A_3 could not be successfully prepared, a material corresponding to $K_{1.07}C_{7.48}M_{0.05}F_{0.06}A_{2.79}S_{0.56}$ (62) was synthesized by a process in which white cement clinker ($\leq 2\% Fe_2O_3$) was interground with 3.5% K_2CO_3 , and heated to $1375^\circ C$ for 15 to 30 minutes. The temperature of this reclinckered sample was reduced to about $980^\circ C$ over 30 minutes, and then air quenched. After removal of the silicate phases with a maleic acid-methanol solution, the residue was estimated to contain approximately 85% KC_8A_3 .

Complete Clinker Analysis by Selective Dissolution Techniques

As has previously been shown, a large number of techniques have been developed for the chemical separation of the major phases in portland cement and clinker. In some cases the separation is quantitative, but in others it serves only to enrich a sample in one substance or another. Depending upon whether the desired separation is required for isolation of a particular mineral for a detailed x-ray diffraction study, or for a progressive chemical analysis of the various phases in a cement sample, a wide choice of procedures is available.

Because a cement can be considered in its most simple form to consist of silicate phases, which are responsible for the major strength development during hydration, and the interstitial phases, which formed the high temperature melt during the clinker formation, the separation of these two main groups of clinker components is of great importance.

For this purpose, a cement sample can be treated with a maleic acid-methanol solution of Tabikh and Weht (31) to completely remove all silicates and free CaO, retaining the aluminate and ferrite phases, MgO, and CaSO₄. On the other hand, the same cement sample can be treated with the hot aqueous KOH-sugar solution of Gutteridge (51) to completely dissolve out all interstitial phases and retain only the alite and belite.

A detailed separation procedure was developed by Bogdanova and Spolis (15) in which samples taken from along the length of a rotary kiln were first treated with 5% boric acid to remove silicates, CaCO₃ and free CaO. The residue was next extracted with a 10% sugar solution to remove calcium aluminates. This residue was subsequently reacted with 1 N HCl to dissolve the aluminoferrites and a portion of unreacted oxides from the raw meal. Any solid residue still remaining was fused with sodium borate and analyzed for the oxides present. The various residues obtained were studied by x-ray and infrared methods, as well as being chemically analyzed. A similar procedure of successive extractions of clinker minerals was used by Babachev and Petrova (63) to analyze cements containing 15 to 40% additions of sand and slag.

The analysis of cement samples differs from clinker samples generally because of the amount of calcium sulfates present. Tabikh and Weht (31) found that in an x-ray diffraction analysis, gypsum and hemihydrate peaks interfered with the measurements of other compounds of interest. Accordingly, it was their practice to heat cement samples at 450°C for 10 minutes in order to convert calcium sulfate hydrates to anhydrite. Heat treated samples were subsequently taken for maleic acid treatment.

Moreno Arus and Perez Alonso (64) removed the silicate phases of portland cement with a salicylic acid-methanol extraction, and then determined the hemihydrate and gypsum contents of the residue by DTA. Takashima and Higaki (40) found that with a picric acid-methanol solution, anhydrite and gypsum are not dissolved, but hemihydrate is quite soluble.

The boric acid dissolution technique was utilized by Ragozina and Akhmedov (65) to determine the relative amounts of free and combined CaSO_4 in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{CaSO}_4$. A new aluminosulfate compound was observed, which was believed to be $\text{C}_4\text{A}_3\bar{\text{S}}$. A selective dissolution technique was developed by Wong (52) of the Waterways Experiment Station to separate CaSO_4 from $\text{C}_4\text{A}_3\bar{\text{S}}$ in type K expansive cements. The cement sample is first extracted with a maleic acid-methanol solution, and a 1 g portion of the residue is stirred in 200 ml of a 10% NH_4Cl aqueous solution for 45 minutes. All sulfates are extracted, and the $\text{C}_4\text{A}_3\bar{\text{S}}$ remains for x-ray diffraction analysis. Adams and Larkin (66) analyzed the NH_4Cl extraction residue for its SO_3 content, and from this value calculated the amount of $\text{C}_4\text{A}_3\bar{\text{S}}$ in the cement.

The salicylic acid-methanol selective dissolution method has also been found to be useful in the study of solid solutions. Sakurai et al. (67) used the technique in the study of solid solutions of C_3S with Cr_2O_3 , Al_2O_3 and Fe_2O_3 as well as solid solutions of C_3S with fluorine, Al_2O_3 , Fe_2O_3 and P_2O_5 . Frigione and Marra (68) applied the method to determine the effects of isomorphic replacement of Fe for Al in the C_3A crystal lattice, resulting from the compound being held for an extended time at clinkering temperature.

Separation of Hydrated Compounds

The separation of hydrated cement compounds has been to a large extent reasonably non-selective. The silicate phases hydrate to a C-S-H composition, which varies in both stoichiometry and morphology depending upon such factors as water / cement ratio, temperature, and initial clinker composition. It does, however, completely decompose in strong acids, leaving an amorphous silica residue.

Tabikh et al. (69) used the maleic acid-methanol dissolution technique as a method for the determination of the cement content in concrete. In theory, all hydrated cement compounds should dissolve leaving behind a residue of sand and coarse aggregate. However, complete hydration may not be achieved, and an insoluble fraction of unhydrated ferrite phase will therefore remain. It was also found that erroneously high values for cement content are obtained when pozzolanic materials were included in the concrete.

Further work on the determination of the cement content of hardened concrete by selective dissolution was conducted by Clemena (70). It was found that some siliceous and calcareous aggregates dissolve to a limited extent in the maleic acid-methanol solution and, therefore, for most accurate results, a calibration curve may have to be prepared for each type of aggregate used.

Ettringite in hydrated cement pastes was determined by Uchikawa and Uchida (71) by an extraction technique using a 1:3 ethylene glycol-methanol solution for 1 to 2 hours at room temperature. By this procedure, ettringite could be removed, whereas monosulfate, C_3AH_6 , and $Al(OH)_3$ remain in the residue. The ettringite content of the paste was then

calculated from the analysis of Al_2O_3 found in the solution after the extraction. Daimon et al. (72) extracted $\text{Ca}(\text{OH})_2$ from hydrated C_3S pastes with a glycerol-ethanol mixture in a study of C-S-H pore structures.

Ciach et al. (73) etched the surface of hydrated C_3S paste samples with ethylene glycol for 30 minutes in order to develop the textural details of the microstructure for SEM and x-ray diffraction studies. Goto and co-workers (74) treated the surface of a hydrated C_3S paste with a 1% solution of HNO_3 in ethanol to differentiate between the so-called inner and outer C-S-H products by SEM. After a free lime extraction of the paste surface with a 4:6 glycerol-ethanol solution, two types of C-S-H phases were found which differed in their C/S ratios.

Applications

The most common application of selective dissolution is for x-ray diffraction analysis. Cement or clinker samples are treated with a solvent which removes the calcium silicates, aluminates or other selected compounds present, and the residue is subsequently analyzed. A stepwise dissolution of clinker compounds permits good qualitative and a reasonable quantitative total analysis of clinkers and cements.

It is recognized that the non-silicate phases are the ones mainly responsible for the very early reactivity of a cement with water. In order to better understand these reactions, synthetic clinker minerals and their mixtures are generally used in experimentation. However, selective dissolution of calcium silicates from industrial clinkers permits the study of the actual interstitial phases which had formed during the clinkering process.

Thus, it is possible to determine the hydration kinetics of industrial aluminate and ferrite phases under different hydration conditions, such as in the presence of admixtures or at various temperatures.

In a similar manner, the silicate phases can be isolated by the selective dissolution of aluminates and ferrites. Figure 1 shows the heat evolution patterns of calcium silicates obtained by removal of the interstitial phases from a Type I portland cement with a hot KOH-sugar solution. The differences in heat evolution reflect the retardation of silicate hydration resulting from the incomplete removal of the sugar-containing solvent from the surface of the calcium silicate minerals. A thorough washing of the residue after extraction is not enough. As seen in the calorimetric patterns, if the silicates are washed first with hot KOH and then acetone, followed by heating for 1 hour at 200°C, normal hydration occurs. However, washing with hot water and then acetone, followed by the heating treatment, results in greatly delayed hydration. Without the heating treatment to decompose any residual sucates, there is complete retardation.

On the other hand, even incompletely washed samples can be analyzed reliably by x-ray diffraction, or SEM. If crushed rather than ground clinker samples are treated with the hot KOH-sugar solution, the interstitial "glue" which binds together the silicate minerals is removed, and the free alite and belite crystals can be removed to determine their particle sizes and size distribution.

Small pieces of bulk clinker can be treated with many of the previously described chemical solutions. This results in the selective dissolution of particular phases from the surface of the clinker and thus permits an examination of the residue, with its original morphology undisturbed, by a

combination of SEM and EDS (33). This combination can be used for explaining the effects of minor components and of burning conditions on the morphology and distribution of clinker minerals and, under optimal conditions, to answer some of the unresolved questions on the mechanism of their formation and subsequent hydration.

Figure 2 shows the distribution of alite and belite crystals on a fragment of clinker which was treated with a KOH-sugar solution. The bulk clinker sample shown was treated with the dissolving solution for the same period of time normally used with a finely ground clinker or cement sample.

Figure 3 shows the remnants of a coating on belite particles, which had originally been embedded within alite crystals. The alite has been dissolved off the clinker surface by the maleic acid-methanol treatment, and the residual "egg shells" were analyzed by EDS and identified as the aluminoferrite phase. These results clearly indicate that alite was formed by crystallization from the melt, completely engulfing the slowly dissolving belite crystals.

In order to supplement high-temperature DTA and x-ray diffraction, separated clinker interstitial phases can be further studied with a heating microscope. Figure 4 shows the magnified silhouettes of compacted interstitial phases of clinkers produced from the same raw material under different conditions, and photographed at clinkering temperatures on a Leitz heating microscope. Whereas one of the samples completely melts at a temperature of 1255°C , the other shows only minor sintering at 1300°C . The use of this technique on selectively separated aluminoferrite and aluminate phases is a meaningful tool to better understand clinker melt formation, surface tension and its effect on silicate mineral crystallization processes.

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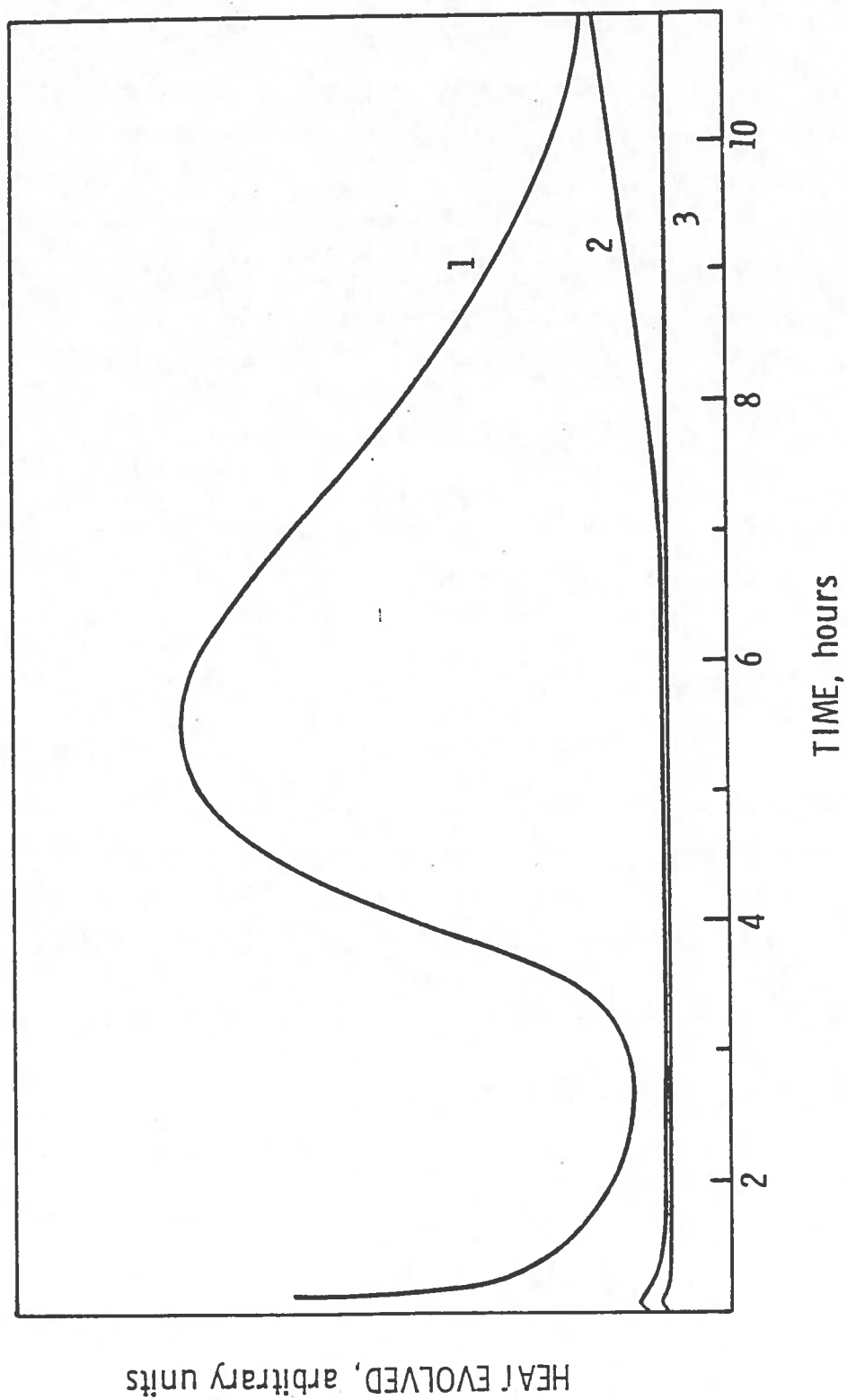


Figure 1. Heat Evolution Curves of Calcium Silicate Residue Obtained from Hot KOH-Sugar Dissolution of Interstitial Phases. Sample 1 washed with hot KOH and heated 1 hour at 200°C; Sample 2 washed with hot water and heated 1 hour at 200°C; and Sample 3 washed various ways, but not heated.

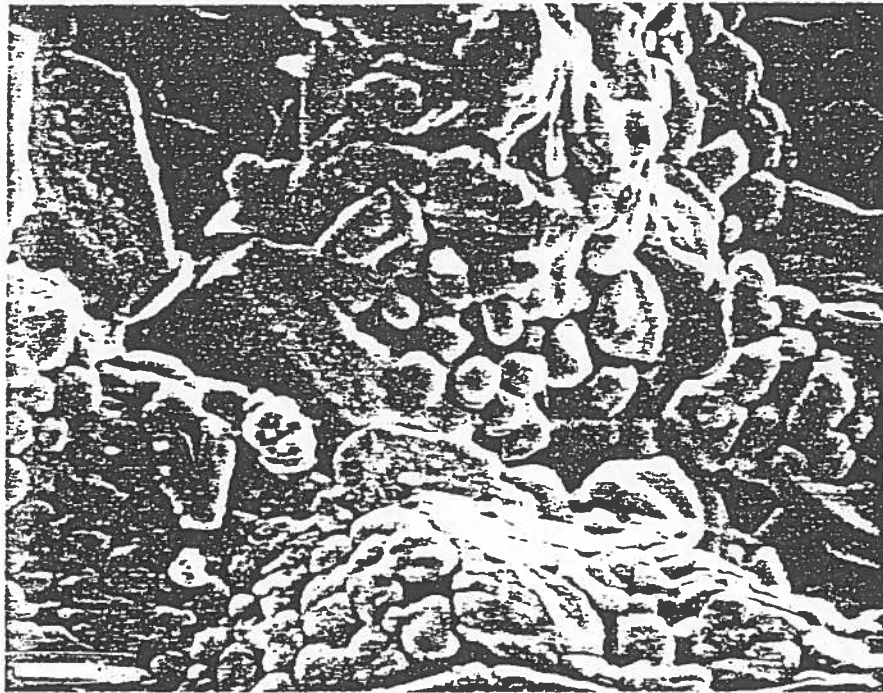
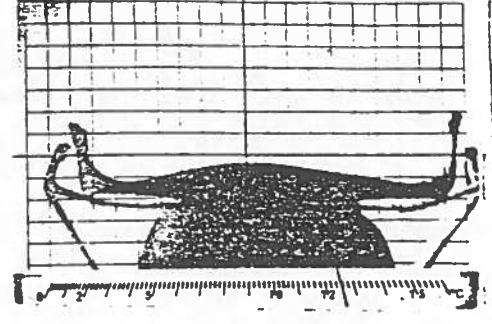
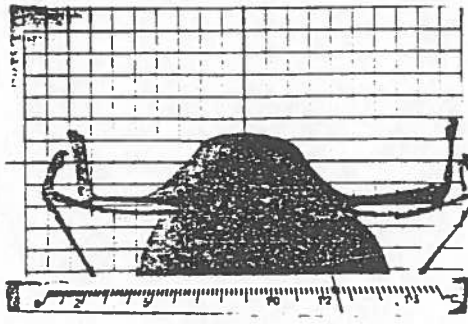
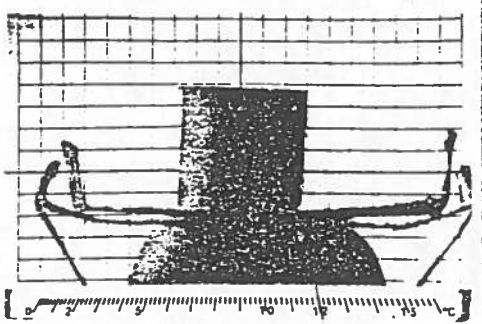


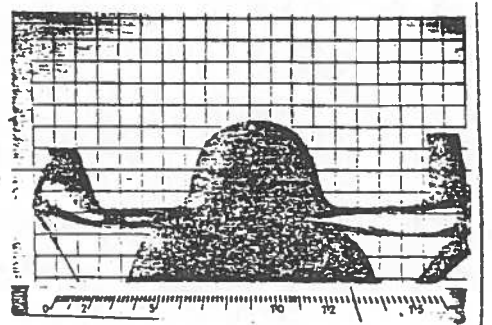
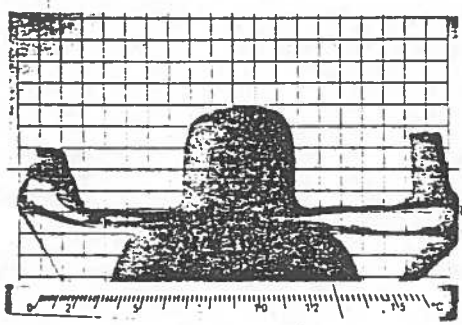
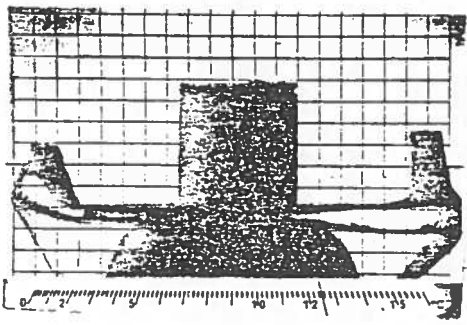
Figure 2. Portland Cement Clinker Treated with KOH-Sugar Solution to Dissolve Aluminates and Ferrites from the Surface. ($10\text{ }\mu\text{m}$ scale)



Figure 3. Portland Cement Clinker Treated with Maleic Acid-Methanol Solution to Dissolve Silicates from the Surface, and Reveal Aluminoferrite "eggshell" Embedded in Alite Crystal.



CLINKER A



CLINKER B

Figure 4. Photomicrographs of 3-mm Diameter Samples of Interstitial Phases (Maleic Acid-Methanol Residue) Removed from Different Portland Cement Clinkers and Heated to the Melting Points.