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X-ray photoelectron spectroscopy of the cement clinker phases tricalcium silicate and β-dicalcium silicate

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Abstract

We have used X-ray photoelectron spectroscopy (XPS) to investigate both tricalcium silicate (Ca_3SiO_5, C_3S) and β-dicalcium silicate (Ca_2SiO_4, β-C_2S), the principal components of cement clinkers. In addition to showing how the two phases may be characterised and differentiated, we show how the sensitivity of these phases to atmospheric carbon dioxide and moisture may, as a result of improper sample preparation, lead to erroneous results. The observed alteration processes of the clinker minerals shed light upon the aging process of cement clinker during storage.

Keywords: Clinker; Aging; Ca_3SiO_5; Ca_2SiO_4; X-ray photoelectron spectroscopy

1. Introduction

The behaviour of the calcium silicates is of immense interest in cement chemistry due to their use as cement clinker phases, yielding calcium silicate hydrates (C-S-H) upon hydration. The C-S-H are themselves important, being the principal binding phases in ordinary Portland cement (OPC). Our interest in the calcium silicates stems from such research, and we have recently reported the use of X-ray photoelectron spectroscopy (XPS) as a means of characterising the different silicate structures within the various C-S-H phases [1]. However, a thorough understanding of the hydrated phases also necessitates an understanding of the reaction products, hence the current study.

Numerous groups have used XPS to study the hydration of the calcium silicates tricalcium silicate (Ca_3SiO_5, C_3S) [2–4] and β-dicalcium silicate (Ca_2SiO_4, β-C_2S) [5]. However, they have predominantly used the surface sensitivity of the technique to concentrate upon changes in elemental composition during hydration. Only the most recent study [2] reported Ca 2p and Si 2p binding energies, whilst Ménétrier et al. [3], despite reporting changes in O 1s binding energy and peak shape, did not comment upon changes in the Si 2p and Ca 2p spectra. Meanwhile, Okada et al. [6] published a detailed investigation of the photoelectron spectra of numerous silicate minerals, including the calcium silicate wollastonite (β-$CaSiO_3$, CS). They were able to relate the spectra to the extent of silicate tetrahedra polymerisation. Unfortunately, they did not investigate the calcium silicate clinker phases.

The sensitivity of these phases towards water and carbon dioxide is well known and has been commented upon in the studies mentioned above [2,3]. However, the extent to which hydration and carbonation may affect the spectra and thus their interpretation has not been reported. In this communication, we report a brief but thorough study of the photoelectron spectra of both alite and belite and show that without the necessary caution sample contamination may lead to erroneous results. Additionally, the observed alteration processes play an important role in the shelf life of OPC clinker.

2. Experimentation

C_3S was prepared from a 1:3 stoichiometric mixture of quartz powder and $CaCO_3$ (both Merck). The mixture was

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ground in an agate mortar, roasted at 1500 °C for 3 h and then cooled rapidly. This procedure was repeated until no reflections due to CaO could be observed by X-ray diffraction.

The product was identified, via X-ray diffraction, as a mixture of 89 wt.% triclinic (T1) and 11 wt.% monoclinic polymorphs. There were some additional reflections matching those of a rhombohedral polymorph (R), but it is more likely that they belong to superstructures of the monoclinic (M1) and the triclinic polymorphs [7–9]. The partial stabilisation of the high-temperature polymorphs (M1 and M3) in the absence of any stabilising ions, such as Mg, Al or Fe, was due to the rapid quenching of the heated sample where the rate of growth of both polymorphs may be greater than the rate of transition to the more stable crystal form.

The synthesis of β-C_2S may be achieved by repeated heating in the temperature range of α′-C_2S stability (1100–1200 °C) but often requires stabilisation at room temperature. Often, this is achieved via doping with B_2O_3 but may also be achieved via doping with Al_2O_3 and sulphate [10]. The latter situation results in a more reactive product, and as our samples were being used to synthesise various C-S-H phases, it is in this form that our samples were stabilised. A mixture of $CaCO_3$, quartz powder, $CaSO_4$ and Al_2O_3 of the composition described in Table 1 was mixed in water and heated to 700 °C. Thereafter, the sample was heated stepwise to 1400 °C, with X-ray diffraction being performed after each step (1000, 1200 and 1400 °C) to follow the disappearance of the peaks due to $CaSO_4$.

Each sample was analysed twice. In the first instance, the samples were analysed after storage in closed, although not hermetically sealed, vessels for 2 years. In the second case, samples were prepared shortly before analysis and roasted immediately prior to analysis for 1 h at 1400 and 1200 °C for alite and belite, respectively. The two analyses are from now on referred to as the aged and fresh, respectively.

Each sample was pressed onto adhesive-backed copper tape and inserted into the vacuum chamber for analysis. Analysis was performed using a VG Escascope fitted with a Mg K_α ($h\nu = 1253.6$ eV) X-ray source operating at 260 W (13 kV, 20 mA). Si_{KLL} Auger lines could be obtained by using the Bremsstrahlung from the Mg source. The intensity of these lines is ~20% of that of the Si 2p line. The details of the lines recorded are shown in Table 2.

Data were extracted from the spectra via peak fitting using XPSPeak software (available by download from http://www.phy.cuhk.edu.hk/~surface/). A Shirley background was assumed in all cases. Spectra were corrected for charging effects using the adventitious hydrocarbon peak at 284.8 eV binding energy.

Table 1
Mixture used for the production of β-C_2S

	mol%	Reagent	wt.%
Al_2O_3	1.40	Al_2O_3	1.66
SO_4	4.60	$CaSO_4$	7.29
CaO	66.00	$CaCO_3$	71.48
SiO_2	28.00	SiO_2	19.57
Σ	100.00	Σ	100.00

Table 2
Details of spectral lines recorded

Region	Start energy (eV)	End energy (eV)	Pass energy (eV)	Dwell time (ms)	Number of scans
Wide	0	1100	50	5	5
C 1s	275	305	30	50	20
O 1s	520	550	30	50	20
Ca 2p	335	370	30	50	20
Si 2p	90	120	30	50	20
Si 2s	140	163	30	50	20
Si_{KLL} (kinetic energy)	1580	1615	50	50	20

3. Results and discussion

The binding energies and peak widths (FWHM) of the fresh and aged samples are given in Table 3.

The Si 2p peaks for the fresh phases are sharp and symmetrical, with the calcium-rich alite having a slightly lower binding energy than belite. The value for alite is very similar to that reported by Long et al. [2], but alas no literature value could be found for belite. We have recently reported the influence on binding energies of calcium–silicon ratios for C-S-H phases [1]. Thus, the higher Si 2p binding energy for belite is expected. This dependency is further exemplified when considering the binding energies

Table 3
The binding energies and peak widths (FWHM) of the fresh and aged samples

	Fresh		Aged	
	C_3S	β-C_2S	C_3S	β-C_2S
Ca $2p_{3/2}$	346.55 (2.19)	346.87 (1.99)	347.31 (1.96)	347.23 (2.01)
Si $2p_{3/2}$	100.57 (2.03)	100.80 (1.98)	100.76 (2.66)	100.51 (1.66)
			102.92 (2.66)	*102.44 (2.04)*
Si 2s	151.71 (3.00)	151.92 (3.08)	151.45 (1.96)	151.33 (2.71)
			153.75 (1.96)	*153.57 (2.71)*
Si_{KLL}	1612.43	1612.14	1611.75	1612.19
			1609.19	*1609.80*
α′	1713.02	1712.95	1712.51	1712.70
			1712.11	*1712.24*
O 1s	530.34 (2.56)	530.36 (2.28)	529.91 (2.12)	530.19 (2.23)
O 1s	531.98 (1.88)	532.00 (1.95)	531.75	531.84
[O1]:[O2]	75.5:24.5	70.2:29.8	9.3:90.7	13.4:86.6
$\delta_{Ca\ 2p-Si\ 2p}$	245.99	246.07	246.55	246.72
			244.39	*244.79*

Data are presented for the Si $2p_{3/2}$ and Ca $2p_{3/2}$ binding energies. The energy separations for the $2p_{3/2}$ and $2p_{1/2}$ lines were fixed at 0.6 and 3.55 eV for silicon and calcium, respectively.

α′ is defined as the sum of the Si 2p binding energy and the Si_{KLL} kinetic energy.

Values in italics may be assigned to hydrated phases formed upon aging.

reported by Okada et al. [6] and Wagner et al. [11] for wollastonite, i.e., 102.37 and 102.16 eV, respectively.

Many authors have reported Si 2s binding energies instead of Si 2p values due to overlapping of the Si 2p photoelectron and Bremsstrahlung-induced Si_{KLL} Auger electron peaks when aluminum is present in the analysed phases. We therefore present the Si 2s binding energies for the principal clinker phases for the first time to allow comparisons to be made with other studies. Again, the same dependence upon calcium–silicon ratio may be observed, and the binding energies are considerably less than that reported by Seyama and Soma [12] for the chain silicate wollastonite, i.e., 153.1 eV.

There is little difference between the two phases when the separation between Si 2p and Ca 2p binding energies (δ_{Ca-Si}) is considered. Our values of 245.99 and 246.07 eV for C_3S and β-C_2S, respectively, are close to the value calculated using data from Long et al. [2] (245.95 eV) but are slightly greater than those reported for C_3S (T1) (245.7 eV) and β-C_2S (245.4 eV) by Regourd et al. [4] and Thomassin et al. [5], respectively. However, when the effects of aging (hydration and/or carbonation) are considered, the explanation is clear. The formation of C-S-H phases results in a shift in the Si 2p peak to higher binding energies, as the isolated silicate tetrahedra in the clinker phases polymerise. This has been reported by Mollah et al. [13], who observed an increase in Si 2p binding energy upon the hydration of dry cement clinker from 100.6 to 102.0 eV and by ourselves in a study of various crystalline C-S-H phases [1]. Such a shift is observed here for the aged phases, with a corresponding decrease in δ_{Ca-Si}. Thus, we may consider the C_3S and β-C_2S surfaces studied by Regourd et al. and Thomassin et al. to be partially hydrated.

Aging of our samples in air resulted in calcium carbonate formation, observed via a large C 1s peak at ~289.5 eV ascribed to a carbonate species, and calcium enrichment of the sample surfaces. However, interesting observations may be made regarding the Si 2p peaks. For the sake of example, Fig. 1 shows the Si 2p spectra of both fresh and aged β-C_2S. It may be clearly seen that the spectrum of the aged β-C_2S contains two components, centred at 100.51 and 102.44 eV. The former corresponds to unaltered β-C_2S, whilst the latter may be assigned to a calcium-depleted C-S-H phase. The calcium–silicon ratio of this phase was calculated from peak areas to be ~0.4 (±0.1). Similarly, for C_3S, the Si 2p spectrum could be separated into two components, centred at 100.76 and 102.92 eV. C_3S was more heavily carbonated than β-C_2S; thus, accurate quantification was not possible, but the higher binding energy implies a more calcium-depleted phase, approaching that of silica gel. There is a good agreement between these binding energies and as yet unpublished results from amorphous C-S-H phases, thus supporting our approximate quantification.

In addition to the shift to higher binding energies upon aging, the higher binding energy peaks are slightly broader than those of the unaltered clinker phases. Peak broadening may indicate a more disordered silicate structure compared with the clinker phases.

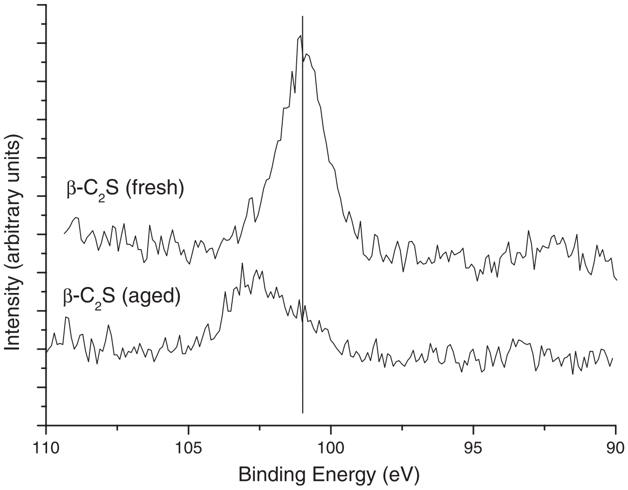

Fig. 1. Si 2p spectra of fresh and aged β-C_2S.

We suppose that storage of the clinker phases in air led to the formation of a thin hydrated layer of amorphous C-S-H, which in turn reacted with atmospheric carbon dioxide to yield calcium carbonate and a heavily calcium-depleted C-S-H phase. As the hydrated layer is extremely thin, it proffers only a limited quantity of amorphous C-S-H available for reaction. Thus, the extent of surface carbonation within this limited volume is far greater than that experienced in bulk samples.

The Ca 2p binding energies exhibit similar trends to the Si 2p energies. That for fresh C_3S is less than for β-C_2S, and both are less than those of the aged samples, which are predominantly calcite [14]. The binding energy for fresh C_3S agrees with that of Long et al. [2], who also reported a slight increase in binding energy upon hydration. Until now, we have referred to aging of the clinker phases and have not differentiated between hydration and carbonation, both of which may occur. This was intentional as unfortunately the Ca 2p binding energies of $CaCO_3$ and C-S-H phases are similar [1], so it is not possible to distinguish between the different reaction products on the basis of their Ca 2p photoelectron spectra.

Unlike the silicon photoelectron peaks, there was no increase in Ca 2p peak width upon aging of the clinker phases. However, the presence of a large excess of $CaCO_3$ may obscure any contribution from either aged or fresh clinker phases themselves. Fig. 2 shows the Ca 2p spectra from fresh and aged β-C_2S.

There is a marked difference in the O 1s spectra of the fresh and aged samples. The fresh samples exhibit two overlapping peaks, centred at ~530.3 and 532 eV. These have been assigned, in the crystalline C-S-H phases, to nonbridging and bridging oxygen atoms, respectively [1]. However, the clinker phases contain isolated silicate tetrahedra and therefore contain no bridging oxygen atoms. We

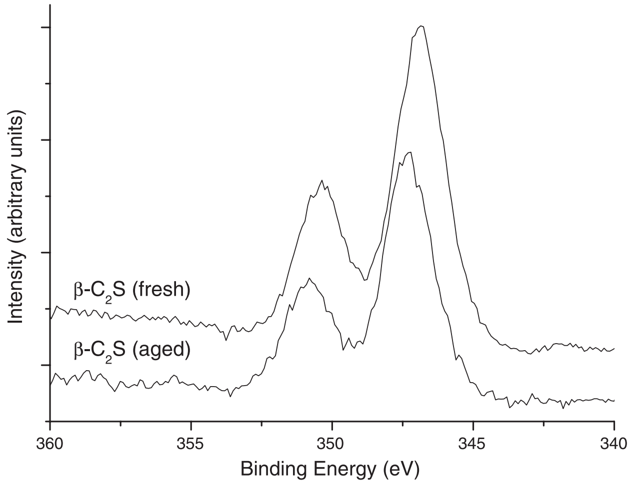

Fig. 2. Ca 2p spectra of fresh and aged β-C_2S.

therefore propose that despite roasting the samples prior to analysis partial hydration and/or carbonation had already occurred, resulting in the higher binding energy peak, which may be assigned to either bridging oxygen atoms or $CaCO_3$.

Finally, the different phases were characterised in terms of their modified Auger parameters (α'). This approach has been shown to be more accurate than shifts in photoelectron binding energies alone and is more sensitive to changes in the strength of bonding between next nearest neighbours [11,15]. We have recently used this approach to characterise a variety of crystalline C-S-H phases and showed that the modified Auger parameter may be used to distinguish the differing degrees of silicate ion polymerisation [1].

The α' values for fresh C_3S and β-C_2S were both ~1713 eV. This compares with values of 1712.43 eV for the calcium silicate wollastonite and 1711.46 eV for SiO_2 gel as reported by Wagner [11]. The C-S-H have α' values ranging ~1712.3–1712.6 eV for the phyllosilicates, 1712.55–1712.65 eV for the inosilicates and 1712.8–1712.9 eV for the nesosilicates [1]. Thus, the modified Auger parameter may be used to assess the extent of silicate anion polymerisation, and the fresh clinker phases may be correctly defined as nesosilicates, i.e., possessing isolated silicate tetrahedra.

The effects of aging were again evident when examining the α' values. As for the photoelectron peaks, two species could be identified, the first being the unaltered clinker phases and the second being a result of aging. The α' values of 1712.11 and 1712.24 eV for aged C_3S and β-C_2S, respectively, are too high to correspond to SiO_2 gel [11] and too low to correspond to a crystalline phyllosilicate phase [1]. However, the aforementioned unpublished results from amorphous C-S-H phases show that calcium-depleted phases ($C/S < 0.7$) have α' values similar to those observed here on the aged samples. Thus, in agreement with the photoelectron spectra, aging of the clinker phases in laboratory air appears to result in the formation of a calcium-depleted amorphous C-S-H phase.

4. Conclusions

XPS has been used to characterise cement clinker phases. Rapid aging of the clinker phases was observed, necessitating that the samples be roasted immediately prior to analysis.

The fresh clinker phases could be defined in terms of their isolated silicate tetrahedra, as observed via their Si 2p photoelectron spectra and their modified Auger parameter values. The first effects of aging were seen in the freshly prepared samples via the appearance of a high binding energy shoulder in the O 1s spectra, although no influence upon the Si 2p spectra could be observed at this point. Further aging of the samples led to silicate polymerisation and the formation of amorphous C-S-H and $CaCO_3$ via the reaction of the clinker phases with atmospheric water and carbon dioxide. Recent work by Suherman et al. [16] showed that NIST cement clinker reference materials show the presence of up to 16% amorphous material. We suppose that the rapid hydration of clinker phases as observed by ourselves may account for a proportion of this amorphous material.

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