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Surface composition of anhydrous monocalcium aluminate, $CaAl_2O_4$

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Electron spectroscopy (ESCA) and electron spin resonance (ESR) have been used to study the surface of synthetic calcium monoaluminate, $CaAl_2O_4$. There are differences between annealed and quenched samples; the surface of the annealed material has the expected composition, while that of the quenched specimen has an apparently non-stoichiometric surface with high aluminium levels. Aluminium–oxygen groups are probably associated with unpaired electrons which make up the deficiency in negative charge. Suggestions are made regarding substitution processes by various impurity ions.

1. Introduction

Monocalcium aluminate, $CaAl_2O_4$ ($CA^†$), is the main component of aluminous cement [1] and its hydration gives rise to the rapid set and early strength of this material. Heller [2] and Dargill [3] have described the crystal structure of CA. It is based on that of the β-tridymite form of SiO_2, in which aluminium replaces silicon in each oxygen tetrahedron. The charge balance is made up by inserting Ca(II) ions in the cavities between the tetrahedra. It is thus a "stuffed tridymite" structure, and the large size of the Ca(II) ion causes considerable distortion of the framework. There are six types of AlO_4 tetrahedra, all distorted, and all linked together so that the oxygen atoms are all in "bridging" positions. There are three types of calcium sites: Ca_I and Ca_{III} are irregularly six-coordinated and Ca_{II} is nine-coordinated. Studies have suggested that Fe(III) substitutes for Al(III) [4, 5]. There appears to be no published evidence for substitution of Ca(II) by Fe(III) in such aluminates.

Electron spectroscopy for chemical analysis (ESCA) has been used in the study of cements in two ways: some papers concentrate on the hydration of individual phases [6–12], while others examine the surfaces of the anhydrous compounds [13, 14]. The hydration of dicalcium silicate, $C_2S^†$, and tricalcium silicate, $C_3S^†$, has been followed, showing the reduction in calcium concentration in the surface layers with time of hydration [6–10]. Similar work using ESCA to examine the surface of hydrating tricalcium aluminate, $C_3A^†$, has been published [10, 12]. This work uses calibration curves to relate peak height to elemental concentration and the calibrating standards are assumed to have a surface composition which is the same as that of the bulk. The present work is a continuation of that carried out on the anhydrous silicates [13], tricalcium aluminate and calcium aluminoferrite ($C_4AF^†$) [14], and uses sensitivity factors rather than calibration curves. Sensitivity factors have been published (see [15]) and their use reduces assumptions about the surface—bulk properties of the materials, while introducing others about the transfer of the sensitivity factors for elements from one compound to another [13].

2. Experimental details

2.1. Starting material

Monocalcium aluminate was synthesized from Analar calcium carbonate and Analar aluminium nitrate, by firing stoichiometric quantities at 1630 K and following the progress of the reaction with X-rays. It was observed that the material fired at 1630 K was pale blue in colour when removed from the furnace, and thereby effectively quenched. It remained coloured for several weeks at room temperature. Annealing of this material at 1300 K for 24 h produced a white sample. Samples were pressed into discs 13 mm diameter, at a pressure of 20 tons in.$^{-2}$, and refired before examination in the ESCA spectrometer.

2.2. ESCA spectroscopy

Spectra were measured using an Escalab 5 Electron Spectrometer manufactured by Vacuum Generators Ltd, using either Al$K\alpha$ radiation (1486.6 eV) or Mg$K\alpha$ radiation (1254.4 eV). Both atomic composition and chemical shifts were measured, the latter by using the carbon peak at 284.7 eV as reference. This was always present due to contamination. The proportion of total carbon as carbonate, where this was present, was estimated by measurement of the relative peak areas on a high resolution scan.

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† Cement nomenclature: A = Al_2O_3, C = CaO, F = Fe_2O_3, S = SiO_2.

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TABLE I Uncorrected surface analyses (at %)

	Annealed		Quenched		Theory
	Height	Area	Height	Area	
Ca	12.1	13.2	10.3	10.9	14.3
Al	22.2	21.5	37.2	38.0	28.6
O	49.8	49.3	47.8	46.7	57.1
C	15.9	15.9	4.4	4.4	

2.3. ESR spectroscopy

Spectra were obtained at room temperature and at 77 K on Varian E3 or E109 spectrometers for unirradiated, irradiated and heat treated samples, using DPPH as reference.

2.4. Thermoluminescence (TL)

A Teledyne Isotopes TLD7300 instrument was used to determine the TL curve. A Stanton–Redcroft temperature controller (Type LVP-C) was used to control the heating rate.

3. Results

3.1. ESCA spectroscopy

Table I gives the complete surface analyses for the annealed and quenched compounds. No elements were detected other than those given. The analytical figures were determined from both peak heights and peak areas, and the separate results are given in Table I. Table II gives the corrected analyses: these are corrected by subtraction of organic carbon, followed by the calcium carbonate equivalent of the inorganic carbon. The composition was then recalculated to 100 at %. The analyses in Table II have been converted to atom ratios for Table III. Charge ratios (derived by giving each element its normal valency and sign) have been calculated and are included in Table II. It can be seen from Table III that the surface composition of the annealed specimen is very close to the theoretical for both sets of measurements, whereas the quenched specimen has a surface of very different composition. This difference shows itself in a decrease in calcium and oxygen and an increase in aluminium content. Chemical shift data are given in Table IV.

3.2. Thermoluminescence

The TL spectrum obtained from the quenched material is shown in Fig. 1. The spectrum is complex and consists of four peaks at about 338, 383, 454 and 532 K. The last peak is considerably more intense than the others. Data concerning this spectrum will be presented elsewhere [16], and will not be discussed further.

TABLE II Corrected surface analyses (at %)

	Annealed		Quenched		Theory
	Height	Area	Height	Area	
Ca	13.7	14.9	10.8	11.4	14.3
Al	28.2	28.8	38.9	39.7	28.6
O	58.0	56.3	50.0	48.8	57.1
+/−	1.0	0.97	1.38	1.45	

TABLE III Atom ratios (corrected data)

	Annealed		Quenched		Theory
	Height	Area	Height	Area	
Ca/Al	0.48	0.52	0.28	0.29	0.50
Ca/O	0.24	0.26	0.22	0.23	0.25
Al/O	0.49	0.51	0.78	0.81	0.50

3.3. ESR spectra

The ESR spectra from CA, treated in various ways, are shown in Figs 2 to 7. Assignments are given in Tables V and VI.

The spectra are complex and overall consist of a group of resonances around 1200 to 1400 G, some less well-defined around the "free spin" region (g = 2.0023), and some broad features in the 4200 to 6200 G region. Some of these arose from impurity ions present in both the annealed and quenched samples, and these will be discussed in terms of the substitution processes taking place, and others indicate that electron centres exist which go some way towards explaining the analytical results on the quenched material.

4. Discussion

4.1. Annealed specimen

4.1.1. Surface composition

It is apparent from the analyses (taken as figures or ratios) that the surfaces of the specimen held at 1300 K has a composition very close to the theoretical. The +/− ratio is therefore very close to unity. The small discrepancies between experimental and theoretical values are not thought to be meaningful in the light of the assumptions made in the use of sensitivity factors. CA therefore behaves differently from the silicates and C_3A previously studied [13, 14] in which there is a general increase in the concentration of the smaller cationic species (silicon or aluminium) and a reduction in calcium at the surface. The difference may be explained on the basis of the crystal structures. CA has a fully condensed network of AlO_4 tetrahedra, while the silicates and C_3A have a range of structures, all of which are capable of further condensation, e.g. orthosilicate groups can condense to pyrosilicate. The change in formal charge on such condensed groups requires less calcium for neutrality and this appears to be the main driving force behind the redistribution of ions. Obviously, in a fully condensed system, this mechanism cannot operate. It is clear that no loss of CaO on ignition has occurred, as has been suggested in other systems [17].

4.1.2. Chemical shift results [18]

The shift data given in Table IV are as expected for the oxidized forms of the elements, and there are no significant details to be discussed.

TABLE IV Chemical shift data (binding energies, eV)

	Annealed	Quenched
Ca2p	346.6	347.1
Al2p	73.0	73.3
O1s	529.8	530.3

Shifts are relative to C1s = 284.7 eV

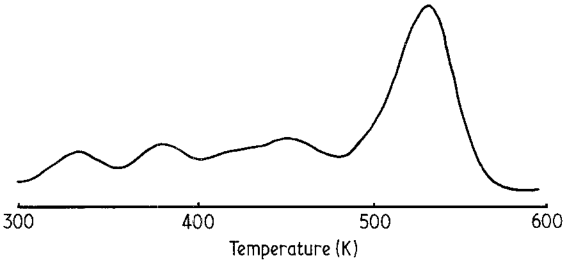


Figure 1 Thermoluminescence curve for quenched CA.

4.1.3. ESR spectra

The spectra obtained from the annealed specimen are associated with various impurity ions present at low levels in the material (see Fig. 2).

4.1.3.1. 1200 to 1400 G resonances. Lines in the 1200 to 2000 G region (Fig. 3i to ix) were assigned to high-spin Fe(III) in low-symmetry environments for the same reasons as previously outlined for tricalcium aluminate [19]. There appear to be at least three such environments for Fe(III) in CA. Assignments are shown in Table V, with *g* values calculated relative to DPPH. Overlap of peaks made further assignments impossible. Because only a low concentration of Fe(III) is present (probably not > 100 p.p.m.), these ions are likely to be found only in Al(III) sites in the sample studied. Substitution of Fe(III) in the distorted AlO_4 tetrahedra in CA would produce rhombic spectra as seen, but the ESR data indicate only three sites with any certainty.

4.1.3.2. 700 to 1100 G resonances. The group of resonances in the 700 to 1100 G region (Fig. 3a to f) may be due to Mn(II) in low-symmetry environments [20]. There appear to be three sets of resonances in this region and these may correspond to Mn(II) substituted in Ca(II) sites in CA. The structure of this aluminate appears to bear out this assignment because there are three different distorted Ca(II) sites.

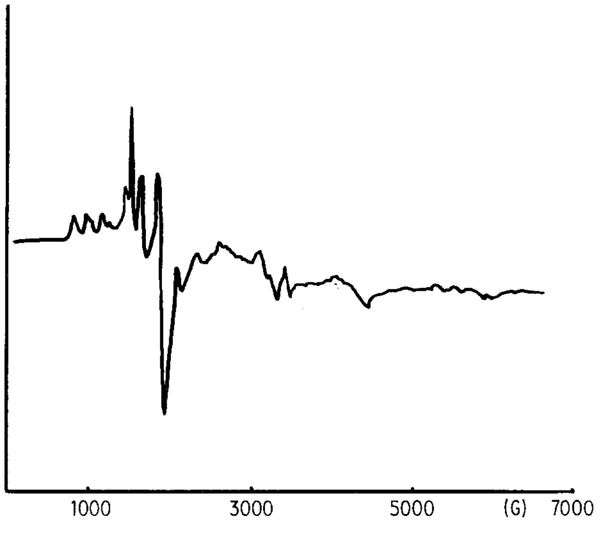


Figure 2 ESR spectrum for annealed CA. Range 0 to 7000 G, temperature 77 K.

TABLE V Assignment of 1200 to 1400 G resonances

Line	Site	Relative Intensity	*g* values
(i)	A	18.0	4.98 (∥)
(ii)	B	31.0	
(iii)	C	42.0	4.71 (∥)
(iv)		16.5	4.39 (∥)
(v)		19.0	
(vi)		5.0	4.18 (⊥)
(vii)		14.0	
(viii)		25.0	
(ix)	C	67.5	3.62 (⊥)
(x)	B	37.0	3.50 (⊥)
(xi)	A	8.0	3.24 (⊥)
(xii)			2.0

4.1.3.3. 5700 G resonances. In the 5700 G region (Fig. 4) a number of resonances are seen on a broad background. The main resonance occurred at $g = 1.47$. This may be associated with Pb(III) ions. However, they are most probably extra transitions for high-spin Fe(III) centres. This spectral region showed no significant changes on irradiation or annealing.

4.2. Quenched specimen

4.2.1. Surface composition

Table II indicates that the quenched specimen has a surface which is considerably enriched in aluminium and depleted in calcium and oxygen. The Ca/O ratio, however (Table III), is still close to the theoretical value, suggesting that aluminium has in some way intruded into the surface. Loss of CaO would produce the same result [17] but the same material when annealed has not lost CaO. The charge ratio is much greater than unity and suggests that the surface is non-stoichiometric. Because such non-stoichiometry is unlikely in a system with no variable valence ions, there are two ways in which the discrepancy might be explained, and the +/− ratio accounted for. Both of these require that extra "negative" species are present to correct the +/− ratio. It is possible that hydride ions are present: this was effectively discounted by the results of a laser ionisation mass analysis (LIMA) study, which showed virtually no such ions to be present. The most likely possibility (in line with the blue colour of the material) is that the apparent non-stoichiometry is caused by the presence of unpaired electrons. This was investigated in the ESR study.

4.2.2. Chemical shift results [18]

As with the annealed specimen, there are no significant features in the shift data.

4.2.3. ESR results (Fig. 5)

4.2.3.1. Free spin resonances. Fig. 6 shows features in the $g = 2$ region with a superimposed *g*-marker signal

TABLE VI Effects of irradiation and annealing on the $g = 2.0$ resonance

Line	Unirradiated	Irradiated	338 K	378 K	448 K
(xii)	0.89	2.78	2.29	1.86	0.82

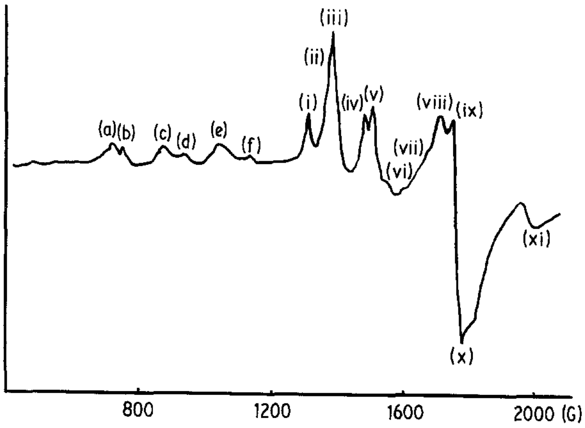


Figure 3 ESR spectrum for annealed CA. Range 1200 ± 800 G, temperature 77 K. For meaning of symbols, see text.

(DPPH) at $g = 2.0035$. Some of the low-field lines are thought to be due to low-spin Fe(III), but there are too many features for iron to be the only contributor, in our view. The set of lines covered by α in the figure could be due to hyperfine coupling to ^{27}Al ($I = 5/2$) in –Al–O· "hole" centres. Such features have frequently been observed in silica containing substitutional Al, but the poor definition makes full assignment difficult. The broad assymmetric line (XIV) having $g \sim 1.975$ and $g \sim 1.935$ is probably due to Ti(III) impurities.

4.2.3.2. Effects of irradiation. On ultraviolet irradiation ($\lambda = 253.7$ nm) and subsequent annealing of the sample the intensities of the Fe lines ($g = 1200$ to 1400) did not change significantly. Fe(III) ions are, therefore, apparently not implicated in the thermoluminescence of CA in the temperature range studied. In the free spin region (Fig. 7) a new broad resonance (xii) was found after irradiation ($g = 2.0$). There were no other significant changes in this region. Results for this resonance are given in Table VI. The intensity of the new resonance (xii) was measured against an invariant resonance (xiii) for comparison. On annealing, the extra resonance gradually diminished and was lost at 448 K; it is therefore connected with the first three peaks of the TL spectrum.

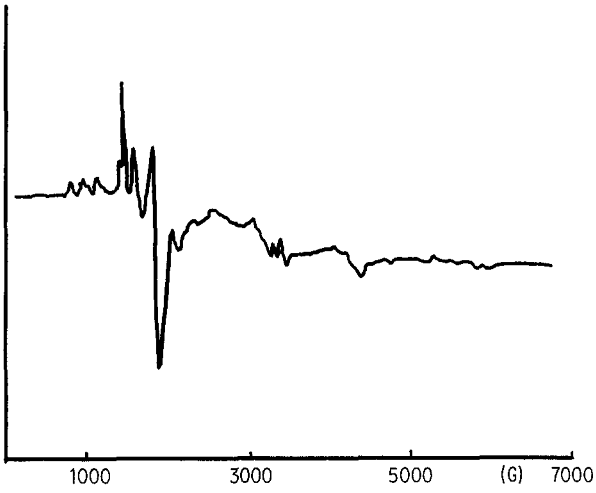
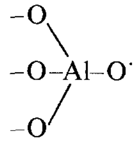


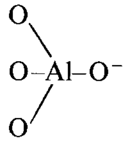
Figure 5 ESR spectrum for irradiated CA. Range 0 to 7000 G, temperature 77 K.

4.2.3.3. Mechanism of trapping/thermoluminescence. Fe(III) ions are not implicated in trapping for the reasons mentioned in the previous section.

The central broad resonance described above, which is connected with the TL spectrum, is not easy to identify, because many systems give resonances in this region [21]. The most likely possibility is some form of surface "F"-centre of the type



and there is some spectral evidence for this. Such a centre could arise from surface



groups by loss of an electron. Such traps would be most likely to occur at the surface, given the requirement of a non-bridging oxygen. Such a site would be

Figure 4 ESR spectrum for annealed CA. Range 5700 ± 2000 G, temperature 77 K.

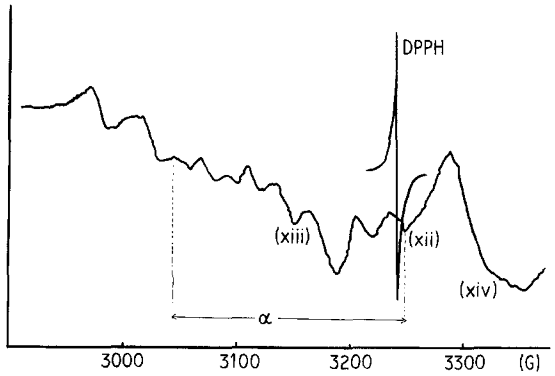


Figure 6 ESR spectrum for CA irradiated and annealed at 573 K. Range 3150 ± 250 G, temperature 77 K. For meaning of symbols, see text.

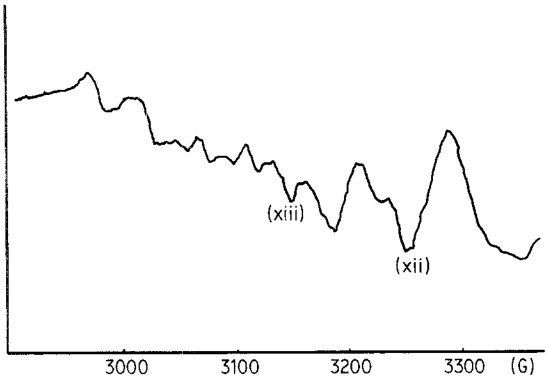
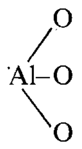


Figure 7 ESR spectrum for irradiated CA. Range 3150 ± 250 G, temperature 77 K. For meaning of symbols, see text.

coloured. A centre of the type



would achieve a reduction in oxygen levels at the surface, but should produce a very large sextet splitting centred on $g = 2$ which was not detected. The quenched specimens seems likely, therefore, to have a structure which is disrupted in some way (so as to give non-bridging oxygens). This is probably related to the increased aluminium levels. The structure is being further investigated.

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