Mössbauer Effect Study of the Hyperfine Structure of the Different Phases of Iron in the Portland Cement Produced in Qatar

by

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ABSTRACT

Various samples of the raw materials used in the manufacture of Portland cement in Qatar, the clinker produced and the cement itself were studied by using Mössbauer Effect and X-ray diffraction analysis in order to investigate the hyperfine structure of the iron forms present and the distribution of these forms among the different phases of the cement. The results obtained revealed the presence of five forms of iron in the cement clinker (a) Fe^{3+} ions in octahedral sites existed in the ferrite phase (C_4AF). (b) Three forms of iron were found in the tricalcium silicate solid solution (alite); these are: Fe^{2+} in tetrahedral sites, Fe^{3+} in tetrahedral sites and Fe^{3+} in octahedral sites. (c) The fifth form of iron was found in the belite phase ($\beta - C_2S$) as a lattice stabilizer and occupies a low-spin state Fe^{II} in octahedral site. The content of each form was referred to the total iron present in the cement.

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صور الحديد في الاسمنت البورتلاندي القطري

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أجريت في هذا البحث دراسات على كل من المواد الخام المستخدمة في صناعة الاسمنت البورتلاندي القطري ، كلنكر الاسمنت وكذا الاسمنت البورتلاندي باستخدام مطياف ظاهرة موسباور وتحاليل حيود الاشعة السينية لمعرفة التركيب فوق الدقيق لصور الحديد وتوزيعها بين الأطوار المختلفة للأسمنت ، وذلك بهدف التوصل الى دور الحديد والاستفادة منه في صناعة الاسمنت بدولة قطر .

ولقد دلت النتائج التي تم التوصل اليها على وجود خمس صور للحديد في كلنكر الاسمنت وهي :

١ ـ ايونات الحديد الثلاثي في مواقع ثمانية التآزر الموجودة في طور الفريت .

٢ ـ ثلاث صور للحديد موجودة في المحلول الصلب لسليكات ثلاثي الكالسيوم (طور الاليت) وتشمل ايونات حديد ثنائي في مواقع رباعية التآزر وايونات حديد ثلاثي في مواقع رباعية التآزر واخرى ثمانية التآزر .

٣ ـ صورة من الحديد الثنائي وجدت في طور سليكات ثنائي الكالسيوم (طور البيليت) في حالة مستوى لي منخفض في مواقع ثمانية التآزر .

هذا ولقد نسبت محتويات الصور المختلفة الى المحتوى الكلي للحديد الموجود في الاسمنت .

Introduction

Some useful applications of the ME technique in the field of studying cement have been reported recently. Ference *et al.* [1] showed that the hydration of 'brownmillerite' (4CaO. AL$_2$O$_3$. Fe$_2$O$_3$), which was believed to be the only iron bearing phase of Portland cement, can be easily studied by ME, and Wittmann [2] used this technique in the determination of the degree of hydration of cement. Vertes *et al.* [3] showed that an addition of excess Ca(OH)$_2$ helps in making the charge distribution more symmetrical around the iron atoms in brownmillerite. Another application was done by Setzer *et al.* [4], who studied the surface energy and mechanical behaviour of hardened cement paste by using the ME technique. Mohan *et al.* [5] studied the ME spectra of C$_3$S preparations annealed at 1550°C and pointed out that this phase of cement can dissolve at least 0.5 wt % iron oxide, and approximately 1 in 10 iron atoms will be present as Fe^{2+}.

In the present work, the ME technique was used to investigate the hyperfine structure of the iron forms present in the Portland cement clinker produced by the Qatar Cement Factory; and to find the distribution of these forms among the different phases of cement. This study, however, is only the first step in a major project aimed at utilizing the role of the hyperfine structure of iron in cement industry in Qatar.

Experimental

Various samples of the raw materials used in the manufacture of Portland cement in Qatar (limestone, clay, iron ore, gypsum), the Portland cement clinker raw meal, the clinker produced and the Portland cement produced were provided by the Qatar Cement Factory at Umm Bab.

Studies by the Mössbauer Effect (ME), X-ray diffraction analysis (XRD) and chemical analysis were done on the representative samples of those materials.

The ME absorbers were prepared from the finely powdered and sieved materials. Pressed discs in a 5 ton piston of about 11mg/cm^2 iron for the ore sample and 1.5-2mg/cm^2 iron for the other samples were used.

The experiments were commonly done in the transmission geometry at room temperature. The 14.39 KeV gamma rays from 70mCi [57]Co source in a palladium matrix were incident on the absorber, then detected with a proportional detector and then stored in a multichannel analyzer of 1024 channels. The channel for zero Doppler velocity between source and absorber was specified by using a lazer system; and the ME curves were fitted using a computer.

Results and Discussion

The ME spectrum of the iron ore, which is added by 1% to 19% clay and 80% limestone to form the Portland cement clinker raw meal, revealed the presence of two magnetic patterns and a non-magnetic one as shown in Fig. 1. The principal magnetic pattern which represents 77.5% of the total iron present in the ore has the ME parameters characteristic of haematite α-Fe$_2$O$_3$ [6] as indicated in Table 1. The second magnetic pattern constitutes 19% of the total spectrum and has the ME parameters characteristic of geothite α-FeOOH [7]. The paramagnetic pattern constitutes only 3% of the total spectrum and
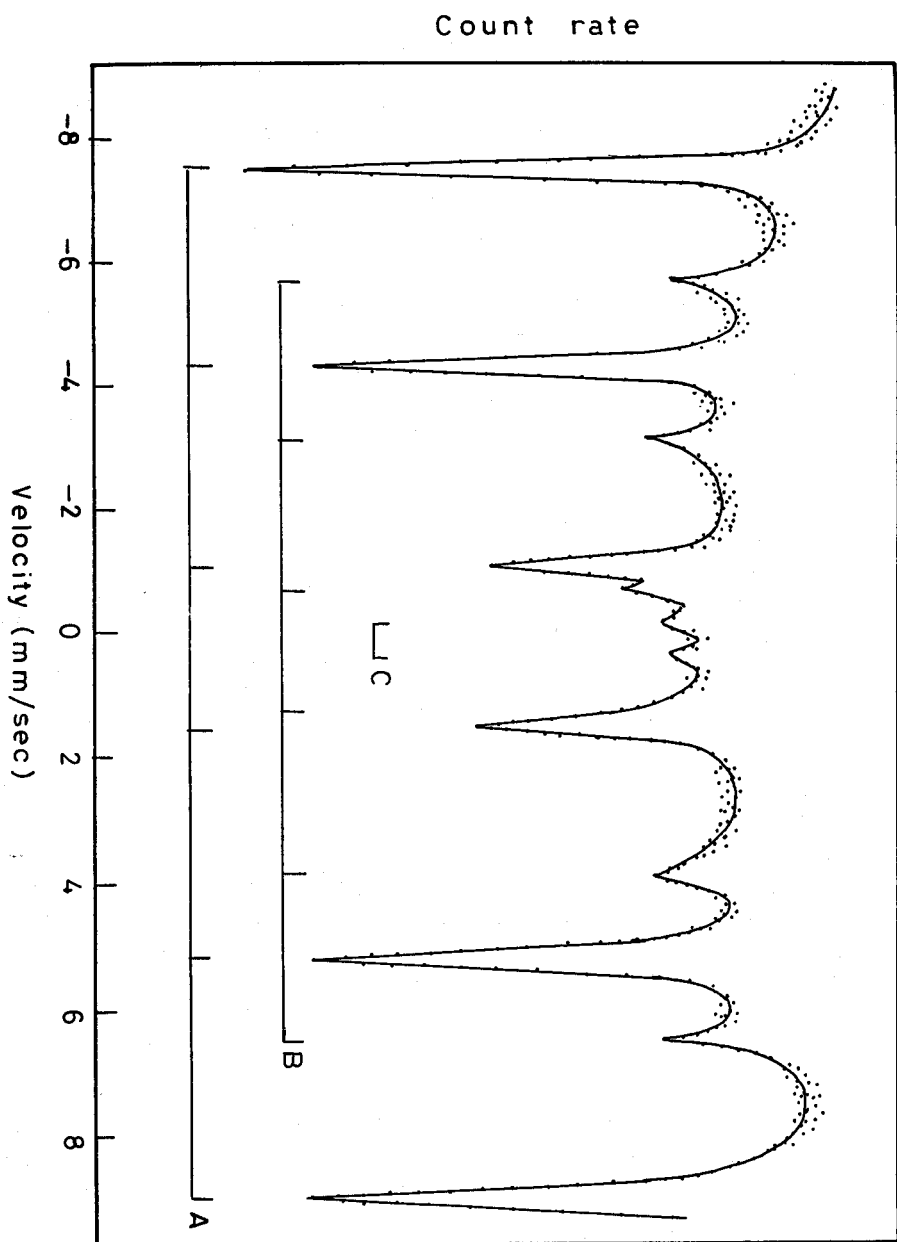
Count rate

Fig. 1: The ME spectrum of Iron ore sample

TABLE 1

The ME parameters of the different materials used in the manufacturing of Portland cement.

Sample	Component	I.S. mm/sec	Q.S. mm/sec	H KOe	State of iron	% of the total iron
Iron Ore	A	0.63	0.54	517	Magnetic Fe^{3+} (O)	77.5
	B	0.45	0.33	365	Magnetic Fe^{3+} (O)	19.2
	C	0.20	0.52	–	Non-mag. Fe^{3+} (T)	3.3
Clay	A	0.25	0.60	–	Non-mag. Fe^{3+} (T)	54.4
	B	0.20	1.00	–	Non-mag. Fe^{3+} (O)	12.9
	C	0.28	1.58	–	Non-mag. Fe^{3+} (O)	12.2
	D	1.20	2.33	–	Non-mag. Fe^{2+} (O)	20.4
Clinker	A	0.25	1.78	–	Non-mag. Fe^{3+} (O)	24.75
	B	0.19	1.34	–	Non-mag. Fe^{3+} (T)	30.69
	C	0.14	1.78	–	Non-mag. Fe^{3+} (O)	21.78
	D	0.50	1.59	–	Non-mag. Fe^{2+} (T)	12.87
	E	−0.12	1.54	–	Non-mag. Fe^{II} (O)	9.9

Error in velocity scale = ± 0.025 mm/sec.
Error in fields = ± 2.5 kOe
(O) = Octahedral sites
(T) = Tetrahedral sites
I.S. with respect to Pd Matrix

has a quadrupole splitting of 0.52 mm/sec and an isomer shift of 0.20 mm/sec. These parameters are characteristic of ether pyrite FeS_2 or the Oxyhydroxide $\beta-FeOOH$ since these two compounds have nearly the same ME parameters at room temperature [8].

The spectrum of the clay sample (Fig. 2) showed a very broad and non symmetric doublet together with a single peak at the velocity 2.37 mm/sec. The assymetry of the doublet and the deviation of its two lines from the Lorentz shape indicate the presence of more than one superimposed paramagnetic pattern, resulting from the presence of the iron ions in more than one paramagnetic form in the sample. To resolve such a spectrum, several factors were utilized to make the initial guess:

a) The width of the single peak at the velocity 2.37 mm/sec.
b) The presence of genuine shoulders (which appeared due to the high resolution of the detector used, good statistics and suitable sample thickness).
Hence the spectrum was resolved into four different doublets as reported in Table 1 and shown in Fig. 2. This was the minimum number of doublets that gave an acceptable χ^2.

The presence of several iron components in the clay sample studied, is in agreement with the fact that clays usually have several iron forms as previously reported [9, 10].

A very small content of iron, which was not detected using chemical analysis, was observed in the limestone ME spectrum but could not be analysed.

All the iron components obtained in the spectra of both the clay and the iron ore were present in the spectrum of the clinker raw meal. On the other hand the clinker sample,
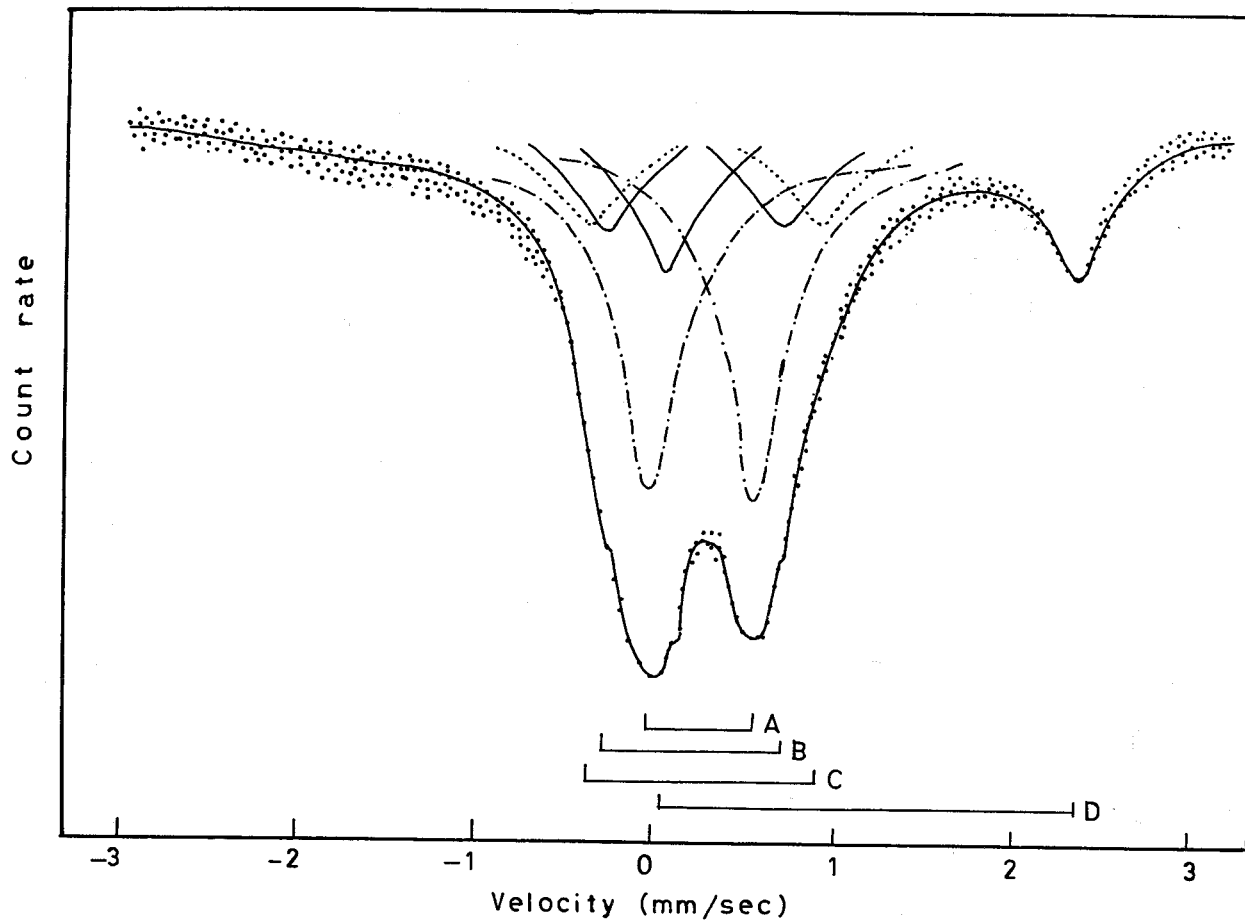
83

Fig. 2: The ME spectrum of a clay sample

which was produced by burning the meal up to 1400-1500°C, then cooled by quenching in a stream of cold air, showed a completely different spectrum from that of the meal sample. This is due to the decomposition of the former iron phases and the formation of new ones.

The results obtained from the X-ray diffraction measurements of the clinker (Fig. 3) showed the presence of the lines characteristic of the clinker phases: C_3S, C_2S and C_3A. From the X-ray results of the clinker and the chemical analysis of the cement, the phase composition of the cement was determined (Table 2).

TABLE 2

Phase composition of Portland cement

C_3S	57.52%
$\beta-C_2S$	16.81%
C_3A	8.65%
C_4AF	9.72%
MgO	2.40%
Gypsum	4.30%
Total:	99.40%

The ME spectrum of the clinker (Fig. 4) showed a doublet of large quadrupole splitting and broad and shouldered lines. This spectrum could be analysed into five different components as given in Table 1 and shown in Fig. 4. The component (A) constitutes 24.75% of the total spectrum, i.e. of the total iron present in the sample, and has ME parameters characteristic of Fe^{3+} ion in octahedral site [7]. This component is related to the ferrite phase (C_4AF), known as Brownmillerite, where the iron is located in the crystal structure of this phase as Fe^{3+} ions in octahedral site [1].

Three components (B, C and D) seemed to belong to the formation of one characteristic phase. The component (B) constitutes 30.69% of the total iron present and has ME parameters characteristic of Fe^{3+} ions in tetrahedral site; component (C) constitutes 21.78% of the total iron and has the parameters characteristic of Fe^{3+} ions in octahedral site; and component (D) constitutes 12.87% of the total iron and may be due to the presence of Fe^{2+} ions in tetrahedral site. The value of the isomer shift of component (D) is somewhat smaller than the values characteristic of Fe^{2+} ions but at the same time it is much larger than the values characteristic of Fe^{3+} ions in either tetrahedral or octahedral sites in clinker. Iron ions in clinker usually are characterized with relatively small isomer shifts and large quadrupole splittings due to the contribution of the different clinker phases [2, 5, 10, 11]. Hence component (D) is attributed to the presence of Fe^{2+} ions in tetrahedral site.

Components (B, C and D) could be attributed to the tricalcium silicate solid solution (C_3S), known as the alite phase. This confirms the results obtained by Mohan [5], that C_3S phase in cement contains three different forms of iron as $Fe^{3+}(O)$, $Fe^{3+}(T)$ and Fe^{2+}
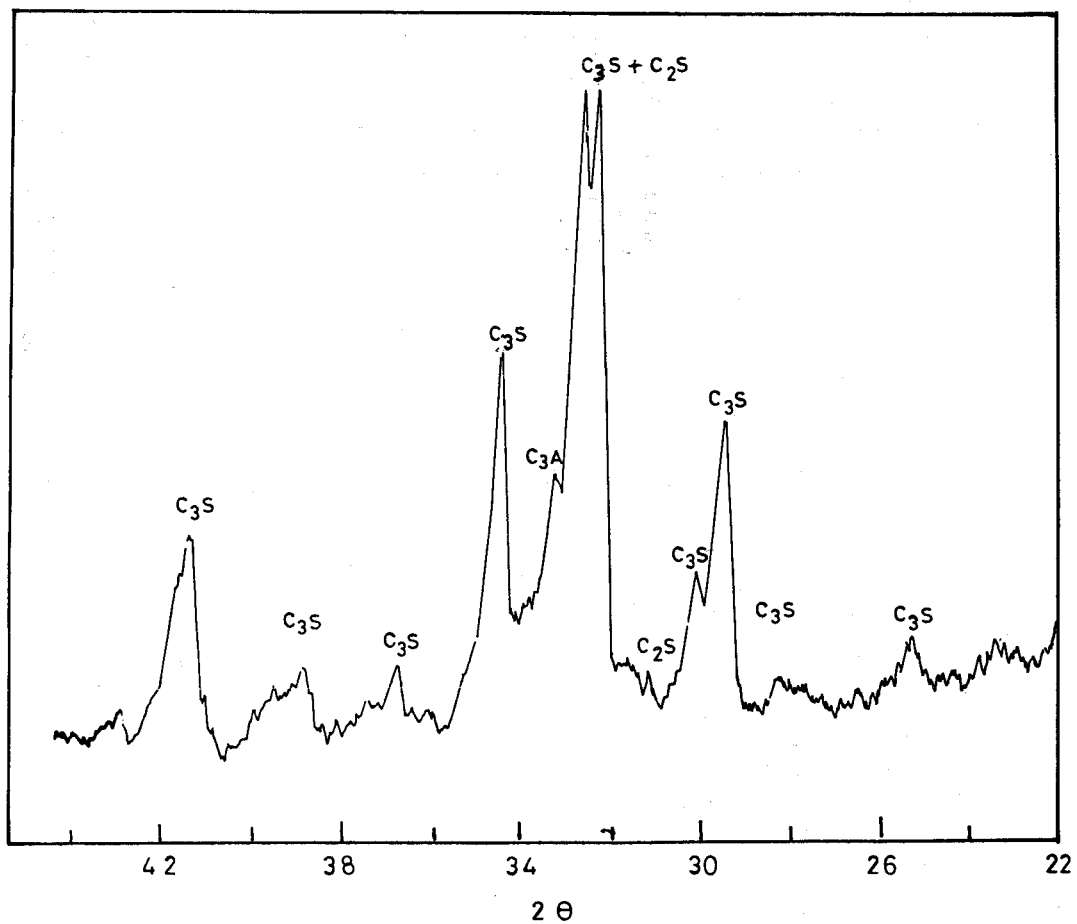
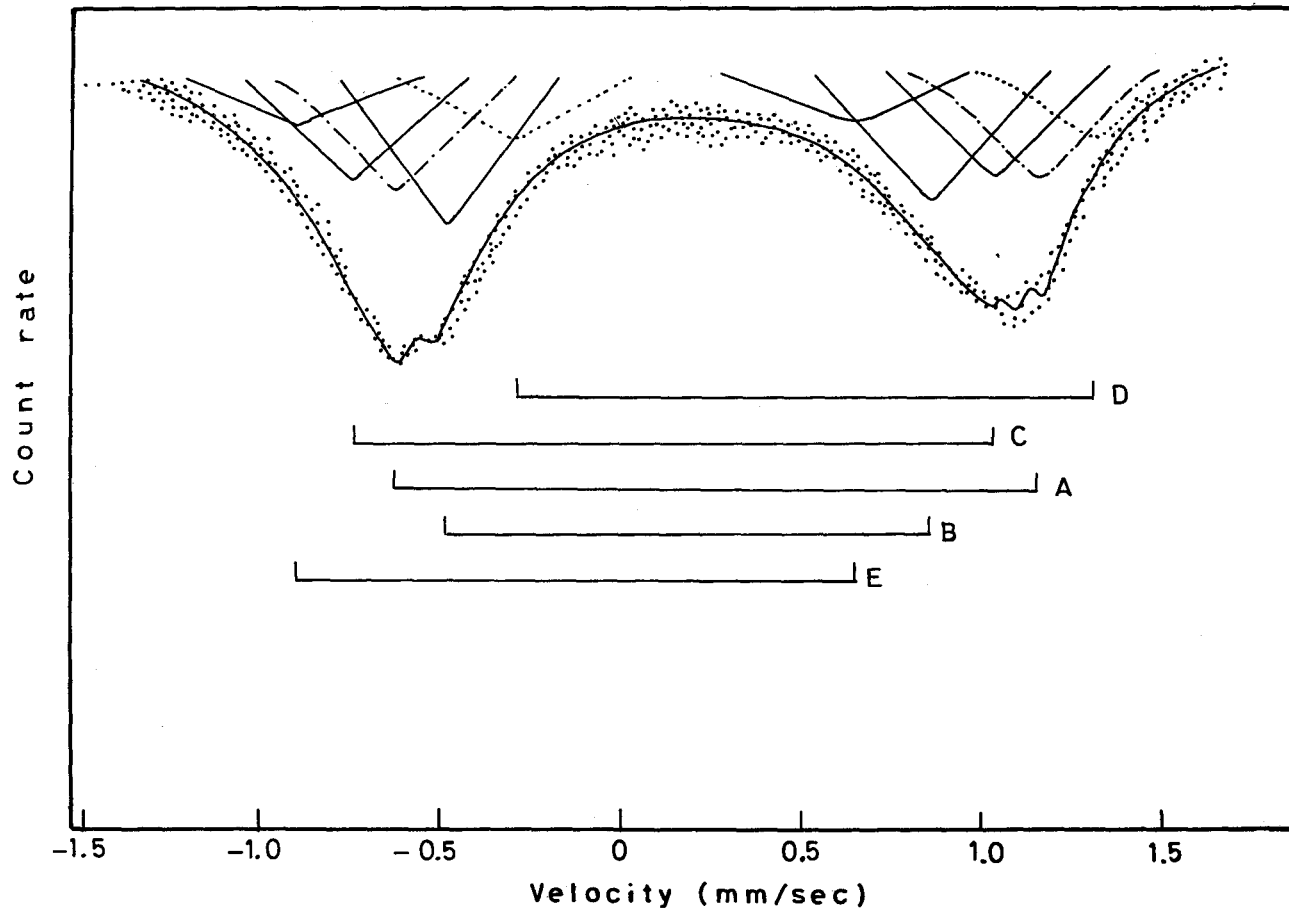*Fig. 3:* X-ray diffraction pattern of the Portland cement clinker

Fig. 4: The ME spectrum of the clinker

The fifth component (E) may be related to the belite phase ($\beta-C_2S$) as a lattice stabilizer, where this component has ME parameters characteristic of Fe[II] ions occupying a low-spin state in octahedral sites [12]. It is well known that occupation of ferrous ions in a low-spin state; i.e. the coupling of the d-electrons in the three orbitals of low energy (t_{2g}), occurs in complexes having strong ligand field as in the case of halogen ions surrounding the iron ion [13]. Since the belite phase ($\beta-C_2S$) dissolves some chromium and boron ions as lattice stabilizers, so this low-spin state iron form can be related to such stabilization effect.

No Mössbauer line could be detected on measuring gypsum indicating that gypsum does not contain any lattice impurities of iron. Thus a sample of Portland cement (96% clinker + 4% gypsum) gave the same spectrum as the clinker.

Combining the results of phase composition with the ME results, it is found that equal weights of the three phases C_4AF, C_3S and C_2S can dissolve 4.32 : 1.93 : 1 wt % iron respectively.

Conclusion

The results of this investigation revealed the presence of five forms of iron in the Portland cement clinker, and related each form and its quantity to the corresponding phases of the clinker (C_4AF, C_3S and $\beta-C_2S$); while it was believed previously that C_4AF was the only iron-bearing phase of Portland cement. These results prove that ME technique is a very effective tool in studying the hyperfine structure of iron in cement and in estimating qualitatively and quantitatively the distribution of this iron, which constitutes only 3.2 wt % of the cement, among the different phases of cement.

A more detailed study on the role of iron in the properties of cement and the changes in these properties with the variation of iron forms, i.e. the role of iron in cement industry, are needed in time and this is the object of the successive studies in our laboratory.

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