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ELECTRON PARAMAGNETIC RESONANCE STUDY OF DRY CEMENTS

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ABSTRACT

Measured X-range Electron Paramagnetic Resonance (EPR) spectra of dry cements are showing that the configuration of iron ions is mainly in Fe^{3+} oxidation state in distorted octahedral and purely tetragonal symmetry of the surrounding ligands. This is reflected in the deformation of the sextet spectra of Mn^{2+} ions (g-factor value of 2.0018, simulated as $g_{\perp} = g_{\parallel} = 2.0018$, $A_{\perp} = A_{\parallel} = 8.8$ mT, pp = 1.0 mT) by the addition of parallel component of the EPR spectrum of Fe^{3+} ion. All spectra were measured at the temperature of 293 K.

I. Introduction

Main components of the Portland cements are tricalcium silicate and dicalcium silicate, tricalcium aluminate and tetracalcium alumino ferrite. Because of the presence of a certain amount of iron and manganese in the studied cements the possibility of utilization of these components as a spin labels for following the kinetics of solidification and of hardening of the main silicate component Si-O-Si seems advantageous. It can be proposed, that in the course of the solidification process of the concrete the lowering of the mobility of particular silicate aggregates is reflected in the vigorous changes in polycrystalline quasi-isotropic character of Electron Paramagnetic Resonance (EPR) spectra of Fe^{2+}, Fe^{3+}, or Mn^{2+} ions to the anisotropic. The latter anisotropic character of the observed EPR spectra is caused by the forbidden rotation and simultaneously lowered mobility of the stiffed molecular chains, which is reflected in their different magnetic field orientation. This phenomenon can be used on following the kinetic parameters of the solidification as well as at the certain favorable conditions also for more accurate characterization of the co-ordination of particular elements of the spatial lattice formed during the hardening period [1]. For better characterization of studied cements (for the list see Table 1) the samples prior to the kinetic experiments were studied in a dry conditions by means of EPR technique. To characterize the composition of the samples the results of elemental analysis are given in Table 1.

TABLE 1

List of the Studied Cement Samples and the Results of Their Elemental Analysis

No.	Type of the Studied Cement	Chemical Composition (in weight % *)				
		Fe_2O_3	Al_2O_3	CaO	MgO	MnO
1	OPC 400 Čížkovice	2.13	6.03	64.52	0.88	0.03
2	SPC 325 Čížkovice	2.18	5.99	64.90	0.96	0.04
3	OPC 400 Mokrá	3.64	5.17	62.60	0.90	0.14
4	OPC 475 Maloměřice	3.59	5.26	61.88	1.73	0.12
5	OPC 550 Maloměřice	4.32	5.26	61.88	1.83	0.09

*Observed quantity of SiO_2 in the samples was in the range of 21.96 to 23.46 weight %.

II. Experimental

Electron Paramagnetic Resonance spectra were recorded on computer controlled (Aspect 2000 and PC AT IBM computer) X-range Bruker ER 200E spectrometer equipped with the variable temperature unit. Particular measurements were performed at the temperatures of 293 K.

III. Results and Discussion

By comparison of the electronic structure of iron and manganese it is possible to see, that their ions, i.e. Fe^{3+} ($I = 1/2$ for ^{57}Fe) and Mn^{2+} ($I = 5/2$ for ^{55}Mn, where I is nuclear spin number) have the same electronic structure of the valence electronic layer of $[Ar]3d^5$. The presence of an unpaired electron in the electronic structure of these elements is causing their paramagnetic properties, which are reflected on measuring the EPR spectra as shown in Figs. 1,2 and 3.

For evaluation of the observed EPR spectra, the spin - Hamiltonian was used in the form:

$$H = \beta B g S + S A I, \tag{1}$$

where β is Bohr's magneton, B is a vector of induction of the external magnetic field, S and I are electronic and nucleic spin operators, g is a tensor of hyperfine interaction of magnetic moments of unpaired electron with the magnetic moment of nuclei with the non-zero nuclear spin [1,2]. The parameters of this spin-Hamiltonian were calculated by deconvolution analysis of the measured experimental EPR spectra by non-linear optimization method based on minimization of an error function (F) [1,2]:

$$F = \sum_{B}[f^{exp}(B) - f(B)]^2 = \min , \tag{2}$$

where $f^{exp}(B)$ and $f(B)$ are the experimental and calculated points of the spectral line shape given as follows:

$$f(B,\Theta) = N\sum_{M_I} P(\Theta)G(B,\Theta,M_I) , \tag{3}$$

where $P(\Theta)$ is the probability of i-th spectral transition, which for the case of the axial symmetry is calculated:

$$P(\Theta) = g_\perp^2[g_\perp^2 \sin^2\Theta + g_\parallel^2(1 + \cos^2\Theta)]/(4g_{ef}^2) \tag{4}$$

where g_{ef} is given:

$$g_{ef} = [g_\perp^2 \sin^2\Theta + g_\parallel^2 \cos^2\Theta]^{1/2} , \tag{5}$$

where $g_\perp$ and $g_\parallel$ are perpendicular and parallel components of g-tensor; $G(B, \Theta, M_I)$ is a spectral line shape function, which in our case is in the form of derivative Lorentz's line function:

$$G(B,\Theta,M_I) = -\{[B - B^0(\Theta)]/\Delta B\}\cdot\{1 + [4/(3\cdot\Delta B^2)]\cdot[B - B^0(\Theta)]^2\}^{-2}, \tag{6}$$

where $B^0(\Theta)$ is the resonance induction of the transition from the projection of the nuclear spin M_I to the direction of the external magnetic field with the induction of B; Θ is the difference of the external magnetic field from the main axis of g-tensor and of the tensor of hyperfine interaction A; ΔB is the peak-to-peak width of the spectral line.

Spin-Hamiltonian for our measured axial and quasi isotropic spectra was calculated by perturbation method into the second order [1]. For the resonance induction the following expression was observed :

$$B^0(\Theta) = h\nu + M_I A_{ef} + [(h\nu + M_I A_{ef})^2 - 4\lambda_{M_I}]^{1/2}, \tag{7}$$

where A_{ef} is an effective value of the tensor of hyperfine interaction, given as :

$$A_{ef} = [A_\perp^2 g_\perp^2 \sin^2\Theta + A_\parallel^2 g_\parallel^2 \cos^2\Theta]^{1/2}/g_{ef} , \tag{8}$$

and λ_{M_I} is correction factor from the perturbation theory.

Measured values of g-factors ascribed as $g_{Fe} = 4.2289$ and $g_{Mn} = 2.0018$ are in a good agreement with the published data given in the literature, where $g_{iso} = 2.0259$ [3] for Mn^{2+} ion measured in silicon matrix and $g_\perp = 5.9930$ and $g_\parallel = 2.0054$ for Fe^{3+} ions [4]. There can be

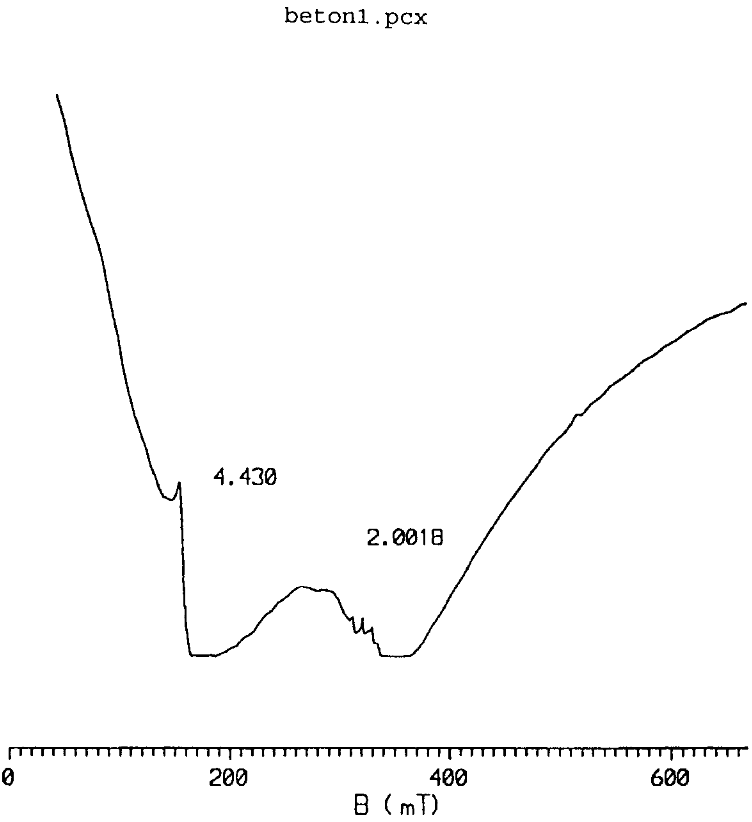

FIG. 1.
Electron Paramagnetic Resonance Spectrum of Čížkovice OPC 400 measured at 293 K. (Gain = 4x10^4, TC = 200 s, Mod = 0.5 Gpp).

proposed distorted octahedral and purely tetragonal symmetry of the surrounding ligands around the central atoms. The proposal, that the iron in the sample OPC 475 Maloměřice is present in higher amount in oxidation state III+ in octahedral and tetragonal spatial configuration is confirmed by the fact, that the increased intensity of the sextet spectrum with the g-factor of 2.0018 is probably due to the addition of the quintet spectrum of the parallel component of the EPR spectrum of Fe^{3+} ion present in tetragonal symmetry [3]. This is causing a total deformation of this multiplet as shown in Fig. 2.

Based on the calculation of multiplicity (2I + 1) one can expect in the ideal experimental conditions appearance of the sextet EPR spectrum for Mn^{2+} ions. Observed splitting constant of 8.8 mT of measured sextet spectrum ascribed to the Mn^{2+} ion (see Fig. 3) is in a good agreement with the value of 9.09 mT reported for 10^{-4} molar aqueous solution of Mn^{2+} [4], 8.3 mT reported in water free cement [5] and of 8.4 mT reported for Mn^{2+} measured in SrO matrix [6]. Based on the shape of spectrum as well as on the value of g-factor which is close to the value of a free electron (g_e = 2.002319 [2]) can be proposed octahedral configuration of surrounding ligands around the central Mn^{2+} ion for all studied cements.

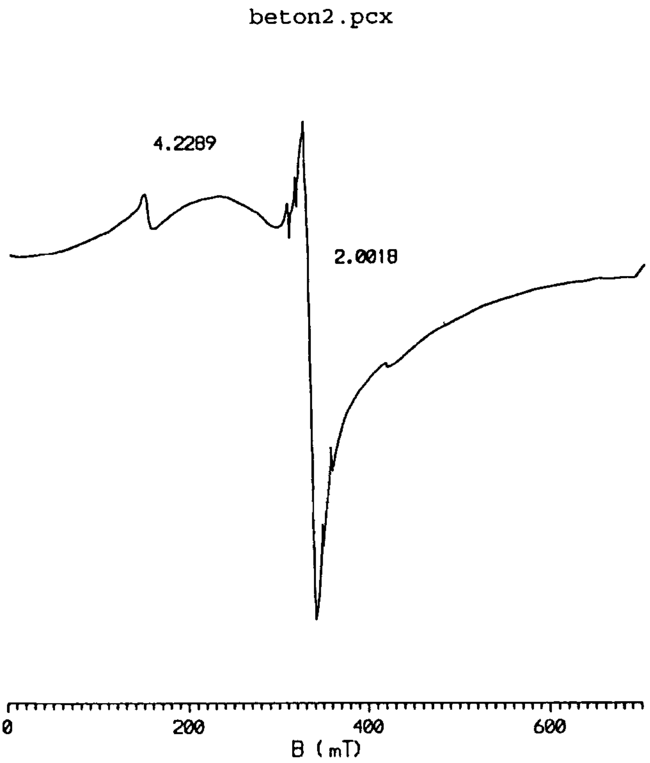

FIG. 2.
Electron Paramagnetic Resonance Spectrum of OPC 475 Malomeřice measured at 293 K.

IV. Conclusions

Based on our EPR measurements it is possible to conclude that similarly as in the investigation of the hardening during the sol-gel processes, the presence of Mn^{2+} ions in the cements can be used for the characterization of the kinetic parameters of the solidification and hardening of cement slurries.

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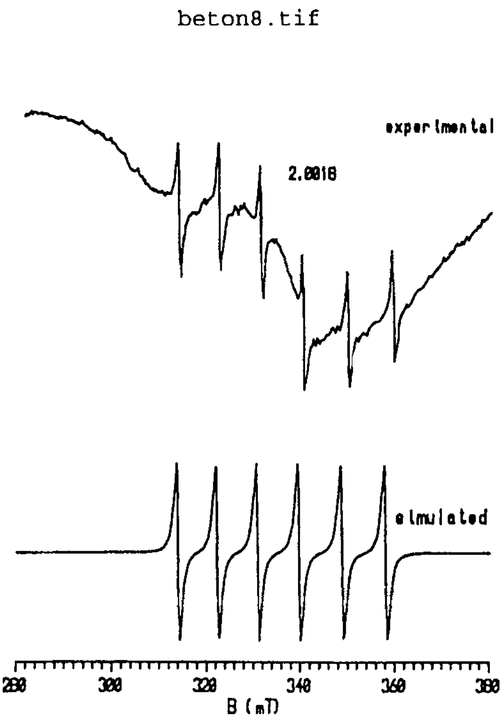

FIG. 3.

Experimental and simulated portion of EPR spectrum of Mn^{2+} ion measured for sample OPC 400 Čížkovice as shown in FIG. 1. Simulated as $g_\perp = g_\parallel = 2.0018$, $A_\perp = A_\parallel = 8.8$ mT, pp = 1.0 mT, where pp is the peak-to-peak width of the spectral line.

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