

Research Article

Mössbauer, XRD, and Complex Thermal Analysis of the Hydration of Cement with Fly Ash

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Hydration of cement with and without fly ash is studied with Mössbauer spectroscopy, XRD, and thermal analysis. Iron in cement is present as Fe^{3+} -ions and occupies two octahedral positions, with close isomer shifts and quadrupole splittings. Iron in fly ash is present as Fe^{2+} and Fe^{3+} , and the Mössbauer spectra display three doublets—two for Fe^{3+} in octahedral coordination and one for Fe^{2+} . A third doublet was registered in the hydrating plain cement pastes after the 5th day, due to Fe^{3+} in tetrahedral coordination in the structure of the newly formed monosulphate aluminate. In cement pastes with fly ash, the doublet of tetrahedral iron is formed earlier because the quantity of ettringite and portlandite is low and more monosulphate crystallizes. No $\text{Fe}(\text{OH})_3$ phase forms during hydration of C_4AF . The fly ash displays pozzolanic properties, which lead to lowering of the portlandite quantity in the cement mixtures and increasing of the high temperature products.

1. Introduction

Tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) are main clinker phases in cement. The hydration of C_3A proceeds quickly, and during reaction with gypsum, ettringite is formed and at later stages, monosulphate occurs accompanied by monocarbonate and aluminates with different composition. The hydration of C_4AF proceeds slower, but finally, there are formed hydrate products with composition similar to the products of the C_3A hydration. In the presence of lime and gypsum, AFt phase is the main product of reaction, but the progress of hydration of C_4AF is slowed down due to the formation of AFt layer at the surface of C_4AF -grains. In a subsequent step, the AFt phase converts to AFm, prior to complete consumption of calcium sulphate [1].

The distinction between iron-free and iron-containing analogues is difficult to be found by use of the widely used methods for the study of cement because the structural differences between these phases are negligible [2]. Mössbauer spectroscopy is a suitable method for the study of iron distribution in cement as well as its behaviour during the hydration process, because this approach allows to study directly

the character of the bonding, the phase state, and the electronic environments of the iron ions [3, 4].

Eissa et al. [5, 6], Afifi et al. [7], and Pascual et al. [8] have proved that iron in C_4AF is bivalent (Fe^{2+}) and trivalent (Fe^{3+}) with the latter being in tetrahedral (T) and octahedral (O) coordination. The authors have found that iron atoms are weakly bonded in strongly deformed crystal lattice, while Ekimov et al. [9] derived formulae for the distribution of the atoms in both states. The studies of Vertes et al. [10] have shown the presence of fine magnetic structure in nonhydrated brownmillerite, and Tamás and Vértés [11] have established that during hydration, this phase disappears and the whole content of iron in the solid solution being in octahedral coordination.

The studies of Pobell and Wittmann [12–14] on the hydration of Portland cement showed that the intensity of the doublets with which the Mössbauer spectrum is described changes, and after 10 years, the doublet of iron in nonhydrated cement disappeared completely [13].

Harchand et al. [15–17] and Eissa et al. [18, 19] have registered three doublets in the Mössbauer spectra of slag Portland cement—two doublets characterizing iron in octahedral and

tetrahedral state and a third one—of iron in the hardened monosulphate. The authors have proved that during hydration the relative content of iron in octahedral state lowers, while that in tetrahedral state it increases. A correlation has been found between the ratio of the iron quantity in tetrahedral and octahedral state ($\text{Fe}^{3+}(\text{T})/\text{Fe}^{3+}(\text{O})$) and the strength of the cement paste.

The conclusions of Harchand et al. [15–17] are that during hydration of sulphate-resistant Portland cement and slag Portland cement, no $\text{Fe}(\text{OH})_3$ was formed. Mössbauer spectrum of sulphate-resistant Portland cement is with two doublets—the first one is of the ferrite phase, and the second one, whose intensity increases during hydration, is of iron included in the monosulphate (AFm phases).

Hassaan et al. [20, 21] have registered two doublets in the Mössbauer spectrum of hydrating cement and have found that with time, the quantity of tetrahedral iron increases at the expense of octahedral iron. In the case of high aluminate cement, he has registered three doublets—of $\text{Fe}^{3+}(\text{O})$, $\text{Fe}^{3+}(\text{T1})$, and $\text{Fe}^{3+}(\text{T2})$, respectively. The intensity of the last two changed with time, and this was accepted as a measure for the degree of hydration of the cement paste.

Dwivedi et al. [22], Rai et al. [23], and Singh et al. [24] have proved using the Mössbauer effect the delaying effect on the cement hydration of black gram pulse and superplasticizer, while Barathan et al. [25] have studied the hydration of Portland cement with addition of silica fume and have registered the transformation $\text{AFt} \rightarrow \text{AFm}$.

The purpose of the present paper is to investigate the hydration of cement with and without addition of fly ash from TEPS by use of Mössbauer effects and other methods.

2. Material and Methods

2.1. Initial Materials. Two types of Portland cement are used—from the Bulgarian factories Zlatna Panega (PC1) and Holcim (PC2) and fly ash (FA) from TEPS Bobov Dol (Bulgaria) 100% classified under $63 \mu\text{m}$, with specific surface of the particles $s = 2.67 \text{ m}^2/\text{g}$. The chemical compositions of the initial materials are given in Table 1 and the mineral contents in Table 2.

2.2. Samples and Methods. The prepared samples are of plain cement and cement with addition of 10 wt.% of FA from the total quantity of the initial mixture with water-to-solid (W/S) ratio of 0.5. The samples were, then, hermetically closed in polymer containers up to the 24th hour of hydration, after being removed and kept in water at temperature of 20°C up to a particular age for investigation. For the samples studied in the first 24 hours, there was applied an interruption of the hydration process by drying and subsequent soaking in acetone and ether. Then, these samples were dried and grounded in the form of dust before analysis.

The specific surface of the ash particles was determined following the method of low temperature adsorption ($T = 77.4 \text{ K}$)—a variant of the BET method.

The starting materials and the hydrating cement pastes were analyzed for determination of the quantity of Fe^{2+} and

TABLE 1: Chemical composition of initial materials.

Oxides	PC1 (%)	PC2 (%)	FA (%)
SiO_2	21.59	23.91	50.40
$\text{Fe}_2\text{O}_3(\text{t})$	3.78	3.33	7.79
Fe_2O_3	3.65	3.13	5.81
FeO	0.12	0.18	1.78
TiO_2	0.15	0.21	0.71
Al_2O_3	4.29	6.15	23.07
MnO	0.04	0.13	0.06
CaO	65.41	58.52	6.69
MgO	0.99	1.17	2.09
Na_2O	0.35	0.58	1.08
K_2O	0.95	1.17	3.13
P_2O_5	0.07	0.07	0.23
SO_3	2.38	2.88	2.38
LOI	<0.05	1.88	2.37

TABLE 2: Mineral composition of initial cements.

Mineral composition, %	PC1	PC2
C_3S	57.52	58.30
C_2S	23.48	18.10
C_3A	5.54	10.20
C_4AF	11.70	11.30
Gypsum	1.76	2.10

^aThe results are for dry (105°C) samples.

Fe^{3+} . The total content of iron, $\text{Fe}_2\text{O}_3(\text{t})$, was determined by optical emission spectroscopy with a source of inductively coupled plasma (ICPAES) after alkaline melting with LiBO_2 dissolution with diluted nitric acid. The content of FeO was determined by titrating with KMnO_4 after dissolution with H_2SO_4 in the presence of Na_2CO_3 , which is a reagent suppressing the oxidation of Fe^{2+} . The content of Fe_2O_3 was determined as a difference from the total amount— $\text{Fe}_2\text{O}_3(\text{t})$ and the content of FeO multiplied by the coefficient for stoichiometric transformation ($k = 1.11$).

The Mössbauer spectroscopic investigation was performed with a spectrometer operating in a symmetric triangle and constant acceleration mode. The acceleration calibration is in relation to natural Fe-foil, and the Mössbauer source is $^{57}\text{Co}/\text{Rh}$ (^{57}Co is intruded in rhodium foil) at room temperature. The obtained data are processed by the least squares method with the “MOSFINT” program. The approximation model is a sum of doublets (tested for variants of 2, 3, or 4 doublets). The program allows approximation of the experimental data with the so-called thin approximation and with integral approximation [26, 27] and incorporation of definite bonds and constraints on the approximated parameters, for example, equal widths, boundaries of the variations, and so forth, [28, 29].

The powder XRD analysis was performed on a DRON UM1 diffractometer (Ni-filtered Cu radiation, 40 kV/25 mA). The registration of the diffraction lines was performed by a scintillation counter.

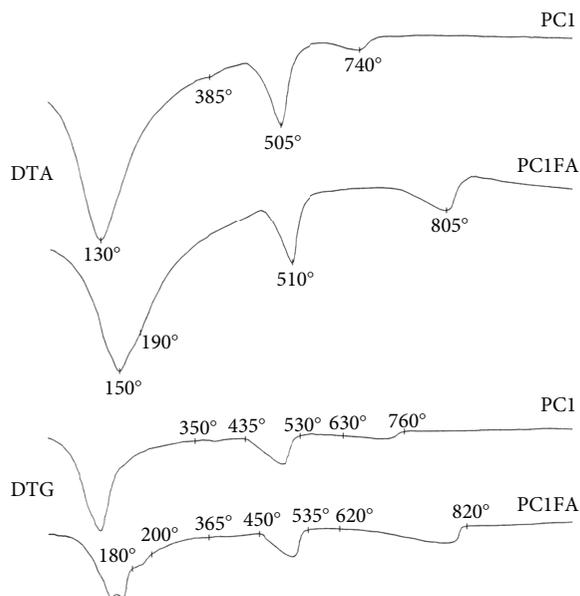


FIGURE 1: Thermal effects registered on the 48th day of hydration of samples of cement pastes PC1 and PC1FA.

TABLE 3: Weight loss during heating of the cement pastes PC1 and PC1FA on the 48th day of hydration.

Sample	Weight loss during heating, mg/g solid substance (mg/g cement), due to hydrate products in groups			
	PI	Pt	PII	Total
PC1	318.1 (318.1)	75.2 (75.2)	54.1 (54.1)	447.4 (447.4)
PC1FA	271 (301.1)	52.7 (58.6)	100 (111.1)	423.7 (470.8)

The complex thermal analysis of the samples PC1 and PC1FA was done with apparatus type 3427 MOM by heating from 20 to 1000°C with 10°C/min steps in air and Al₂O₃ as inert material; the mass of the samples was 800 mg each.

3. Experimental Results and Discussion

Complex Thermal Analysis. The thermal effects, registered on the 48th day of hydration of the samples of cement pastes PC1 and PC1FA (Figure 1) are connected with decomposition of the hydrate products and liberation of the hydrate water as follows [30, 31]: Ca-hydrosilicates, Ca-hydroaluminates, and ettringite with temperature of dehydration up to about 435–450°C, further denoted as PI products, portlandite, Pt, with temperature of the endothermic peak at about 505–510°C, and products denoted PII including calcite and Ca-hydrosilicates with temperature of dehydration higher than 620–630°C (Table 3). Effect at 180–200°C was also registered for the cement paste with fly ash addition, which probably is due to the thermal decomposition of Ca-monosulfoaluminate or less probably due to hydrocarbon aluminate.

The total content of the hydration products in the plain cement paste is higher from the respective one in the cement paste with fly ash addition, but recalculating it per 1 gram cement in the cement paste, it is seen that it is higher for the paste with addition of fly ash, most probably due to the pozzolanic reaction of the ash. The differences in the content of hydration products are more pronounced in the products with low temperature of dehydration (including ettringite in this group) as well as of portlandite in the cement paste with fly ash. As a result of the pozzolanic reaction of the ash with portlandite in the second paste, there was registered an increase of the quantity of the hydration products with higher temperature of dehydration.

Powder XRD Analysis. The powder XRD patterns of the cement pastes PC1 and PC1FA are presented on Figures 2 and 3, respectively. The phase analysis showed that after 1 day of hydration, the main peaks of portlandite are with increased intensity for the cement paste with addition of fly ash. Thus, it follows that the fly ash stimulates the hydration up to the 24th hour. With ageing of the hardening process, the same intensities lower in magnitude as a result of the pozzolanic reaction between the fly ash and portlandite.

Mössbauer Spectroscopy. The Mössbauer spectra of the initial cements (Figure 4) were processed with a model of two doublets. The obtained Mössbauer parameters (Table 4) show that in both cement samples the Fe atoms are in three-valence states and are distributed in two positions, O1 and O2, in octahedral coordination with close isomer shifts, δ_1 and δ_2 , and quadrupole splittings, Δ_1 and Δ_2 , and relative intensity, respectively, for the first and second position of $I_1 = 45\text{--}46\%$ and $I_2 = 54\text{--}55\%$. A doublet, which characterizes Fe²⁺, was not recorded.

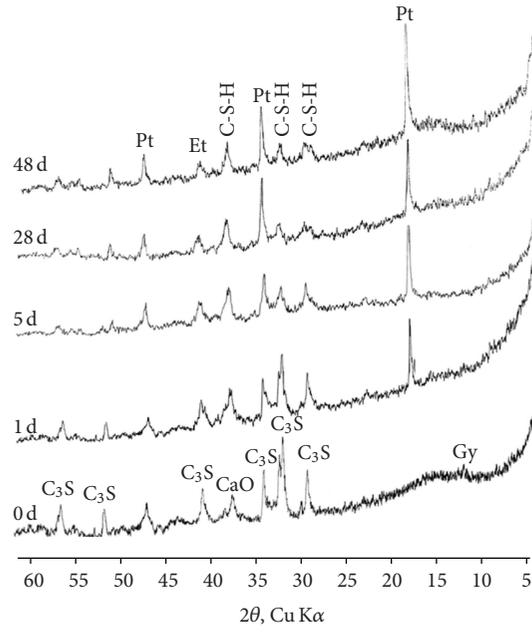


FIGURE 2: Powder XRD patterns of cement paste PC1 at different ages of hydration.

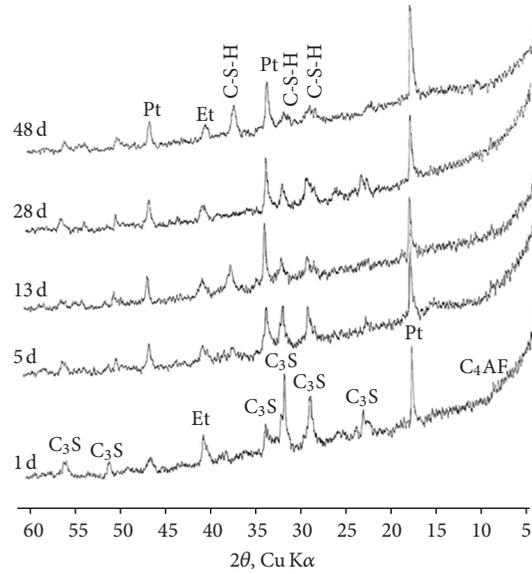


FIGURE 3: Powder XRD patterns of the cement paste PC1FA at different ages of hydration.

TABLE 4: Mössbauer parameters of the initial materials.

Sample	δ_1 (mm/s) (O1)	δ_2 (mm/s) (O2)	δ_3 (mm/s)	Δ_1 (mm/s) (O1)	Δ_2 (mm/s) (O2)	Δ_3 (mm/s)	I_1 (%)	I_2 (%)	I_3 (%)
PC1	0.22	0.27	—	1.24	1.65	—	46	54	—
PC2	0.20	0.25	—	1.21	1.60	—	45	55	—
	(T1)	(T2)		(T1)	(T2)				
FA	0.20	0.45	0.58	0.92	0.95	2.31	39	36	25

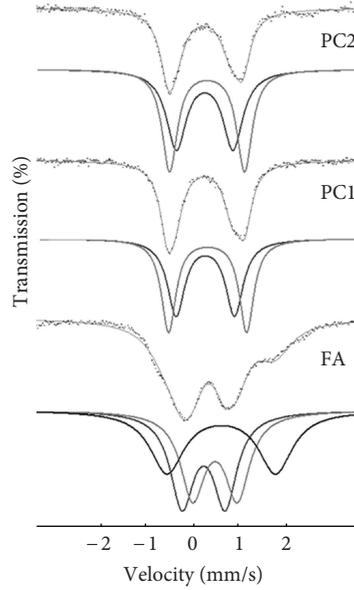


FIGURE 4: Mössbauer spectra of the initial cements and fly ash.

TABLE 5: Mössbauer parameters of the of cement PC1 at different ages of hydration.

Time of hydration	δ_1 (mm/s) (O1)	δ_2 (mm/s) (O2)	δ_3 (mm/s) (T)	Δ_1 (mm/s) (O1)	Δ_2 (mm/s) (O2)	Δ_3 (mm/s) (T)	I_1 (%) (O1)	I_2 (%) (O2)	I_3 (%) (T)
0 h	0.22	0.27	—	1.24	1.65	—	46	54	—
1 d	0.23	0.29	—	1.38	1.82	—	42	58	—
5 d	0.23	0.29	—	1.46	1.84	—	39	61	—
14 d	0.24	0.29	0.24	1.42	1.81	0.38	40	32	28
28 d	0.26	0.30	0.26	1.35	1.81	0.37	27	37	36
48 d	0.28	0.30	0.28	1.36	1.84	0.44	30	33	37

The Mössbauer spectrum of the fly ash was processed with a model based on three doublets, with the first two of which corresponding to Fe^{3+} in tetrahedral coordination, positions T1 and T2, respectively, while the third one corresponds to Fe^{2+} .

Figures 5 and 6 represent Mössbauer spectra of cements PC1 and PC2 at different ages of hydration, and Tables 5 and 6 contain the respective Mössbauer parameters. Up to the 5th day of hydration, there is registered a redistribution of the Fe^{3+} ions between the two octahedral positions, and the quantity of iron increases in position O2, which is connected with the hydration of C_4AF . The ratio of the quantities of iron ions in positions O1 and O2 in the initial cements PC1 and PC2 is, respectively, 0.85 and 0.82, and after 1 day of hydration, it is already 0.72 and 0.54, respectively. It is seen that the process of redistribution of the Fe^{3+} ions between the two octahedral positions is more intense for cement PC2, which is connected with twice greater quantity of C_3A than in cement PC1. Due to this reason, the speed of consumption of gypsum in it is higher and, thus, facilitates the hydration of

C_4AF [1, 32]. Between the 5th day, and 14th day, a doublet of three-valence iron in tetrahedral coordination (T) is formed as a result of lowering of its content in the octahedral position O2. This doublet in the cement pastes is due to the formation of iron-containing mono-sulphate-aluminate, which appears in the later stages of hydration [2, 33, 34]. The intensity of the third doublet I_3 increases up to the 48th day of hydration.

The Mössbauer parameters of the third doublet differ from these of $\text{Fe}(\text{OH})_3$ ($\delta = 0.25$ mm/s, $\Delta = 0.72$ mm/s) and its gel ($\delta = 0.45$ mm/s, $\Delta = 0.72$ mm/s) [17], which means that during hydration of the tetracalcium aluminoferrite no $\text{Fe}(\text{OH})_3$ phase is formed or it is in a negligible quantity.

Figures 7 and 8 represent the Mössbauer spectra of hydrating cement pastes with addition of fly ash, respectively, PC1FA and PC2FA, and Tables 7 and 8 contain their Mössbauer parameters. The doublet of the three-valence iron in tetrahedral coordination is formed between the 1st day and the 5th day of hydration, earlier, and compared with the pure cement pastes, and its intensity I_3 increases up to the 48th

TABLE 6: Mössbauer parameters of the of cement PC2 at different ages of hydration.

Time of hydration	δ_1 (mm/s) (O1)	δ_2 (mm/s) (O2)	δ_3 (mm/s) (T)	Δ_1 (mm/s) (O1)	Δ_2 (mm/s) (O2)	Δ_3 (mm/s) (T)	I_1 (%) (O1)	I_2 (%) (O2)	I_3 (%) (T)
0 h	0.20	0.25	—	1.21	1.60	—	45	55	—
1 d	0.22	0.29	—	1.25	1.80	—	35	65	—
5 d	0.22	0.29	—	1.33	1.82	—	37	63	—
14 d	0.24	0.29	0.29	1.35	1.81	0.45	28	52	25
28 d	0.24	0.29	0.29	1.35	1.81	0.47	26	47	27
48 d	0.24	0.29	0.29	1.33	1.81	0.47	24	47	29

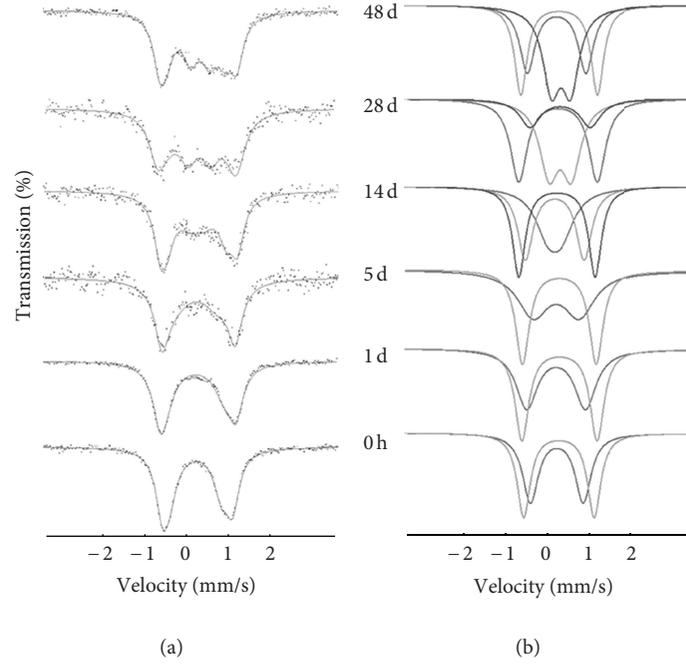


FIGURE 5: Mössbauer spectra of cement PC1 at different ages of hydration.

TABLE 7: Mössbauer parameters of the of cement PC1FA at different ages of hydration.

Time of hydration	δ_1 (mm/s) (O1)	δ_2 (mm/s) (O2)	δ_3 (mm/s) (T)	Δ_1 (mm/s) (O1)	Δ_2 (mm/s) (O2)	Δ_3 (mm/s) (T)	I_1 (%) (O1)	I_2 (%) (O2)	I_3 (%) (T)
1 d	0.24	0.30	—	1.32	1.80	—	45	55	—
5 d	0.25	0.31	0.31	1.43	1.82	0.49	32	44	24
14 d	0.25	0.31	0.31	1.39	1.82	0.47	30	42	28
20 d	0.25	0.29	0.31	1.37	1.80	0.47	29	41	30
28 d	0.25	0.29	0.32	1.35	1.83	0.44	29	38	33
48 d	0.25	0.29	0.33	1.35	1.81	0.45	28	37	35

TABLE 8: Mössbauer parameters of the of cement PC2FA at different ages of hydration.

Time of hydration	δ_1 (mm/s) (O1)	δ_2 (mm/s) (O2)	δ_3 (mm/s) (T)	Δ_1 (mm/s) (O1)	Δ_2 (mm/s) (O2)	Δ_3 (mm/s) (T)	I_1 (%) (O1)	I_2 (%) (O2)	I_3 (%) (T)
1 d	0.26	0.31	—	1.41	1.86	—	41	59	—
5 d	0.25	0.29	0.29	1.41	1.85	0.55	34	43	23
22 d	0.25	0.29	0.29	1.38	1.83	0.52	31	38	31
28 d	0.24	0.29	0.29	1.40	1.83	0.63	29	34	37
48 d	0.29	0.32	0.35	1.46	1.98	0.71	26	31	42

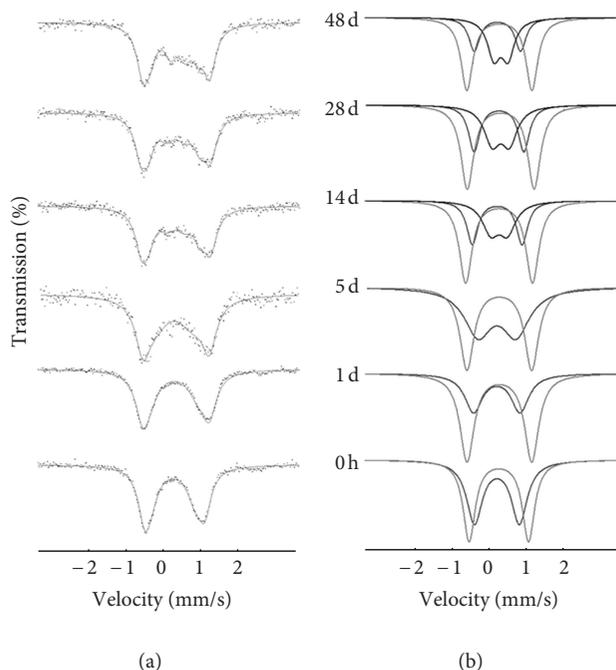


FIGURE 6: Mössbauer spectra of cement PC2 at different ages of hydration.

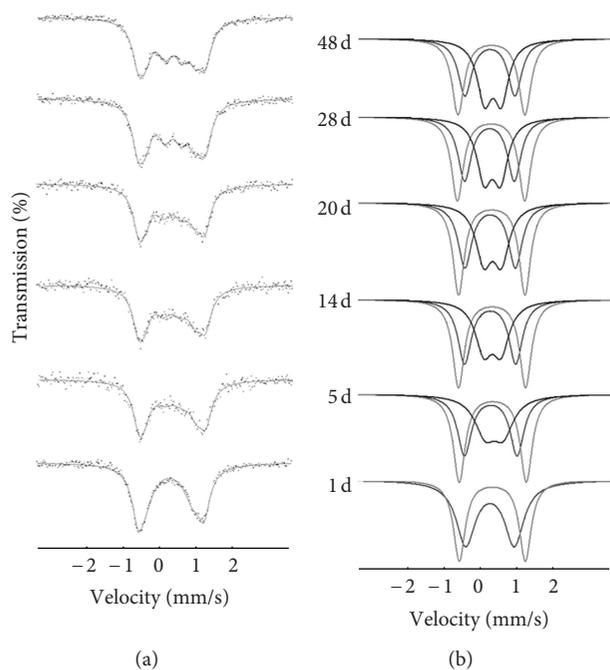
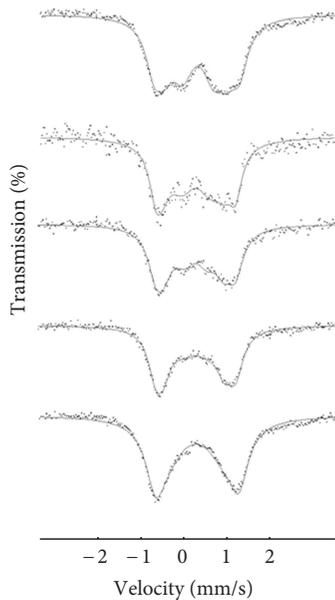


FIGURE 7: Mössbauer spectra of cement paste with addition of fly ash PC1FA at different ages of hydration.

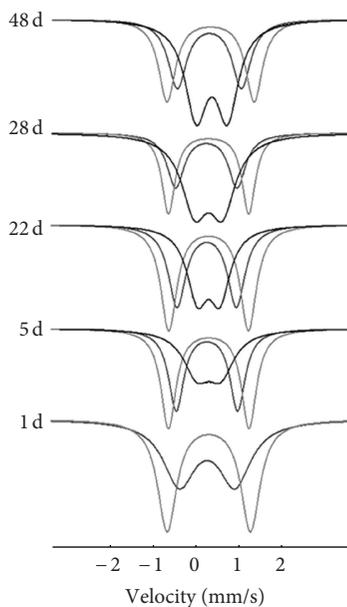
day of hydration. The reason for this is that in the presence of fly ash, a smaller amount of ettringite and of portlandite is formed after the 1st day, and the hydration of C_4AF is hampered [35]. The final result is that greater amount of monosulphate is formed because the ratio SO_4/Al_2O_3 in the system is lowered thus favouring AFm formation [36, 37].

4. Conclusions

- (1) In the initial cements, iron is present as Fe_2O_3 and FeO phases. The three-valence iron is distributed in two octahedral positions with close isomer shifts and quadrupole splittings. Due to its low concentration in



(a)



(b)

FIGURE 8: Mössbauer spectra of cement paste with addition of fly ash PC2FA at different ages of hydration.

the cement paste, iron in the FeO phase was registered only chemically.

- (2) Iron in the fly ash composition is present in bi- and three-valence form, which in the Mössbauer spectra is registered by three doublets—two for the three-valence iron in octahedral coordination and one for iron in bivalence form.
- (3) A third doublet was registered in the Mössbauer spectra of the hydrating plain cement pastes after the

5th day, which is due to the presence of three-valence iron in tetrahedral coordination in the structure of the newly formed monosulphate aluminate.

- (4) In the cement pastes with addition of fly ash, the doublet of tetrahedral iron was formed between the 1st day and 5th day of hydration because of the fact that in these cement pastes the quantity of ettringite and portlandite is low, and significant quantity of monosulphate is formed. With the increased time of hydration, the relative quantity of tetrahedral iron is also increased at the expense of octahedral iron.
- (5) No $\text{Fe}(\text{OH})_3$ phase was formed during the hydration of C_4AF .
- (6) The fly ash from “Bobov Dol” TEPS (Bulgaria) displays pozzolanic properties, which lead to lowering of the portlandite quantity in the cement pastes with fly ash and parallel increase of the quantity of the products with high temperature of dehydration.

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