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PORTLAND ASH CEMENT DEGRADATION IN AMMONIUM-SULFATE SOLUTION

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ABSTRACT

This paper considers the sulphate corrosion of Portland cements (C_3A content in clinker 6.60% and 13.31%) and the same Portland cements where the 30% of Portland cement clinker was replaced with coal ash. The test samples were prepared according to Koch-Steinegger's method and then exposed to the influence of aggressive environment (10% $(NH_4)_2SO_4$ solution). The measurements of several properties were carried out, the results were analyzed, and a correlation among the influencing factors was suggested through mass change, bonded SO_4^{2-} content, and degradation coefficient. There was a strong influence of coal ash on degradation, also. *© 1998 Elsevier Science Ltd*

Introduction

Degradation of concrete, as well as the related protection and ensuring of concrete structures against aggressive impacts by chemical agents, regardless of whether this concerns liquid, gas, or even solid phase under certain conditions, represents a complex problem of utmost importance for the economy in general, and especially for building construction and the construction industry.

Chemical degradation of concrete is the consequence of reactions between the constituents of cement stone, i.e., calcium silicates, calcium aluminates, and above all calcium hydroxide, as well as other constituents, with certain substances from water, solutions of soil, gases, vapours, etc. The most important aggressive agents are: SO_4^{2-}, Mg^{2+}, NH_4^+, Cl^-, H^+, and HCO_3^- (1–6).

When we speak about sulphate degradation, we primarily think of the impact by sulphate ions on cement stone. The sulphate ion is the cause of one of the most dangerous corrosions—the corrosion of expansion and swelling—because it causes the occurrence of expansive compounds, the most imortant of which is ettringite, $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$, in the shape of prismatic crystals (7,8).

For the process of concrete degradation under the impact of sulphates, it is essential which cation is linked with the sulphate ion. Namely, cations linked with sulphate ions can be

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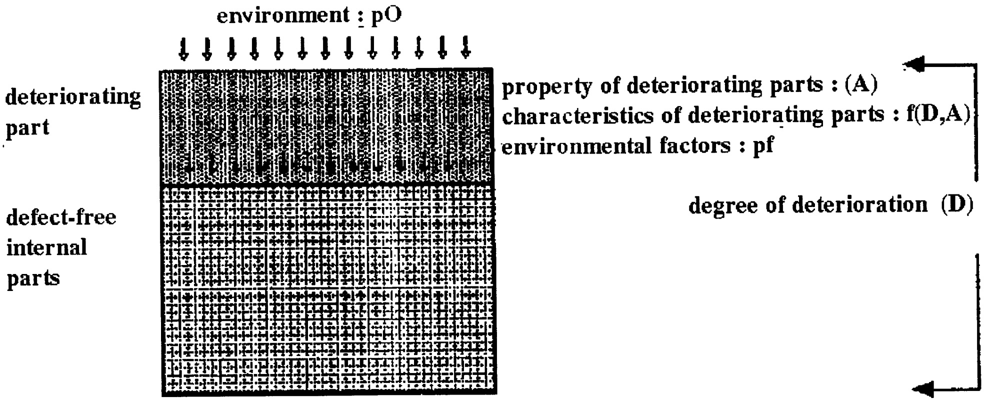

FIG. 1.
An estimation of deterioration.

divided into three characteristic groups. The first group includes alkali metals Na^+ and K^+, which give extremely soluble hydroxides, while the second group comprises metals such as Mg^{2+} and Fe^{2+}, which give poorly soluble hydroxides, and the third group consists of cations NH_4^+ and H^+, which give volatiles or hydroxide. The third group of sulphates, that is $(NH_4)_2SO_4$ and H_2SO_4, covers the most aggressive compounds. In case of impact by these compounds on concrete, there occurs not only expansion, but also intensive dissolution of cement stone.

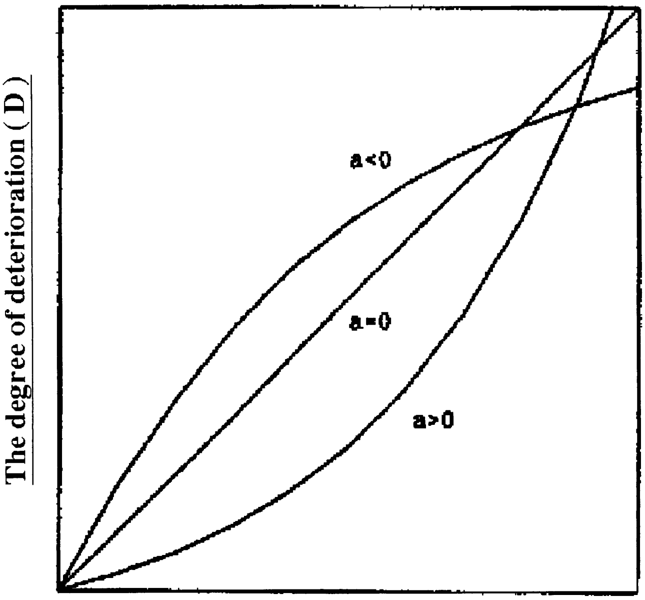

FIG. 2.
The deterioration patterns of building materials.

TABLE 1
Potential phase composition of portland cement clinker.

Potential phase composition, % mass	Portland cement clinker	
	1	2
C_3S	57.54	66.98
C_2S	13.50	12.72
C_3A	13.31	6.60
C_4AF	8.67	9.10

Proposed Degradation Model

Japanese researchers Matsufuji, Koyama, and Harada (9) proposed an estimation equation which can be used to predict the progress of deterioration for various building materials, and an attempt is made to summarize and classify the deterioration phenomena of each material used in a building.

Environmental forces have a direct effect on deterioration together with gases and liquids, which also have an indirect effect. These deterioration factors are defined as environmental factors contributing to deterioration.

Generally, the deterioration of building materials progresses as the environmental factors permeate and otherwise affect the materials. An estimation of deterioration is shown in Figure 1 with the assumption that the environmental factors, which act on defect-free internal parts, are influenced by the property of the parts that have already deteriorated.

The effect of the environmental factors (pf) depends on the environment where materials are exposed (pO) and the characteristics of the deteriorating parts between pO and pf. Also, the characteristics of the deteriorating parts can basically be presented by the function ($f(D,A)$). D is the degree of deterioration of the material itself, and A is the property of the deteriorating part. As the result, pf can be represented as shown in Eq. 1:

TABLE 2
Ash chemical composition.

Chemical composition, % mass	Ash
LOI	5.68
SiO_2	50.85
Al_2O_3	21.65
Fe_2O_3	11.56
CaO	6.52
MgO	2.65
SO_3	0.05
S	0.02
Na_2O	0.30
K_2O	0.70
Insoluble residue	76.61

TABLE 3
Cement chemical composition.

Chemical composition, % mass	Cement			
	PC1	PC2	PAC1	PAC2
SiO_2	19.67	21.01	14.00	15.64
Al_2O_3	6.95	5.33	6.23	4.88
Fe_2O_3	2.71	2.92	2.67	2.85
CaO	62.02	63.75	44.67	47.53
Insoluble residue	0.10	0.11	20.18	18.70
LOI	0.84	0.69	3.03	2.89
CaO free	0.12	0.35	0.00	0.00
CaO in $CaCO_3$	0.51	0.45	0.55	0.55
CaO in $CaSO_4$	1.40	1.18	1.41	1.08
SO_3 in $CaSO_4$	2.00	1.69	2.02	1.54
MgO	2.22	1.41	2.43	1.21
Alkalies as Na_2O	0.41	0.33	0.38	0.35
K_2O	0.40	0.33	0.22	0.30
Cl^-	ND	ND	ND	ND

$$pf = pO + f(D,A) \tag{1}$$

If we assume that the deterioration speed is proportional to *pf*, the diferential equation representing the deterioration speed (dD/dt) will be as shown in Eq. 2:

$$dD/dt = kpf \tag{2}$$

where k is the constant for proportion.

Further, if we assume that the characteristic values of deteriorating parts, $f(D,A)$ can be represented as the product of the degree of deterioration and the deteriorating material, Eq. 3 can be obtained from Eq. 2.

$$dD/dt = b + aD \tag{3}$$

TABLE 4
Cement physico-chemical properties.

Physico-chemical properties	Cement			
	PC1	PC2	PAC1	PAC2
Sieve residue at 0.09 mm sieve, % mass	1.80	2.60	5.20	6.00
Density, g/cm^3	3.14	3.17	2.88	2.85
Specific surface area, cm^2/g	3320	3100	3720	3710
Setting				
-standard consistence, % mass	25.8	23.8	28.0	27.5
-initial time, min.	165	165	240	255
-final time, min.	225	225	330	360
Soundness				
-Le Chatelier test, mm	1.0	1.5	1.0	1.0

TABLE 5
Cement strengths.

	Cement			
Strengths, MPa	PC1	PC2	PAC1	PAC2
Flexural:				
−2 days	4.4	3.7	2.5	2.1
−3 days	5.3	4.4	3.6	2.9
−7 days	7.2	7.4	6.2	4.7
−28 days	8.0	8.9	8.3	8.4
Compressive:				
−2 days	15.7	13.2	8.8	7.4
−3 days	19.8	16.0	14.9	10.4
−7 days	30.2	32.8	24.2	19.4
−28 days	40.3	50.9	39.5	44.9

where *dD*/*dt* is the deterioration speed; *b* is a constant related to *pO*; and *a* is a constant related to the properties of deteriorating parts.

From Eq. 3, considering that $D = 0$ at time $t = 0$, the degree of deterioration (D) can be represented as shown in Eq. 4 and 5.

At time $a = 0$:

$$D = bt \tag{4}$$

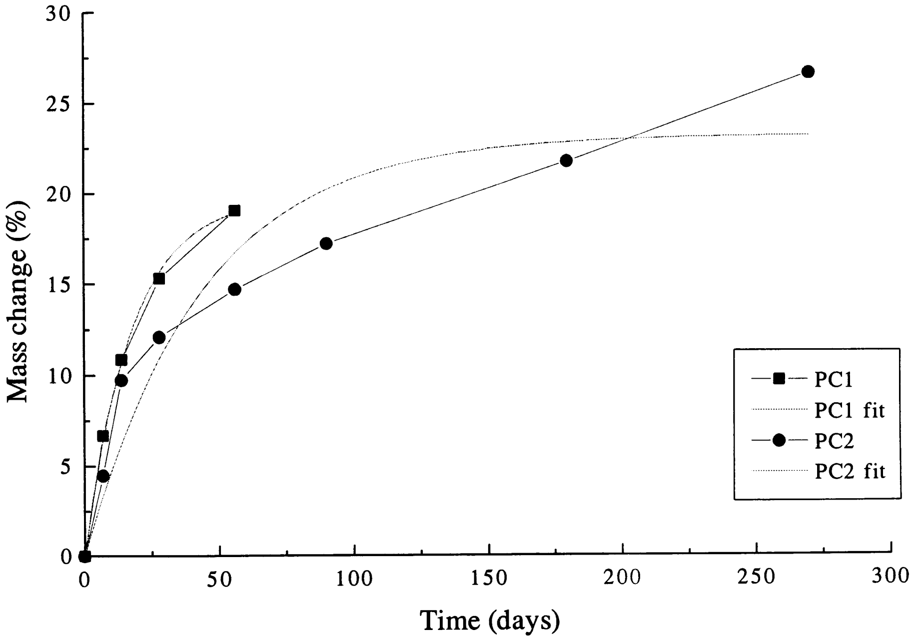

FIG. 3.
Experimental and estimated curves for mass change for Portland cements.

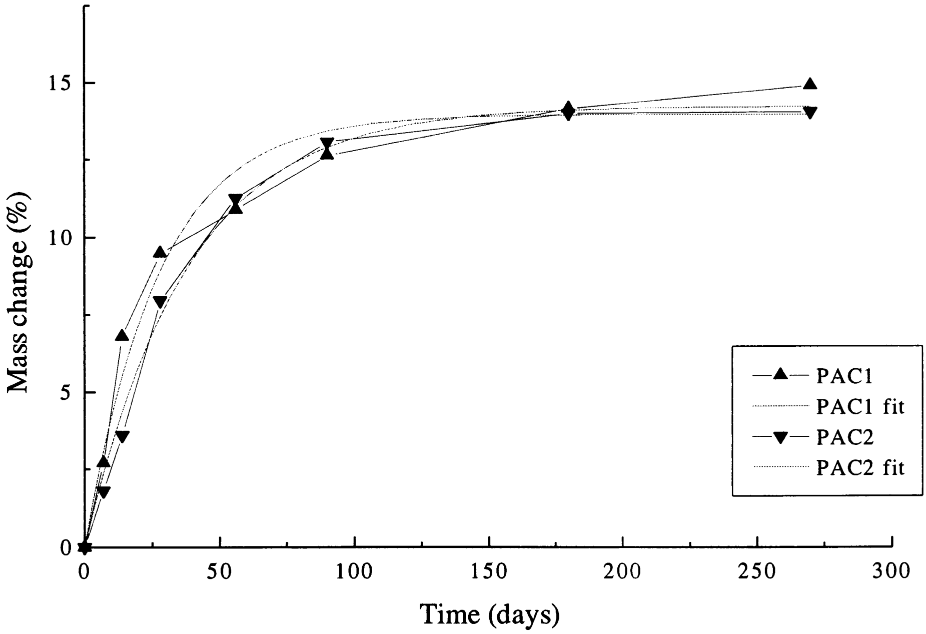

FIG. 4.
Experimental and estimated curves for mass change for Portland-ash cements.

At time $a \neq 0$

$$D = b/a(exp(at) - 1) \tag{5}$$

where D is a degree of degradation; a is a constant depend on the environment where materials are exposed; b is a constant related to the properties of deteriorating parts; and t is degradation process time.

The above results can be represented as shown in Figure 2, and the deterioration of building materials can be classified into the three patterns shown below according to the value of a.

1. Alignment type: when $a = 0$. In Eq. 3, when $a = 0$, the deteriorating parts do not affect *pf* even if deterioration has progressed. Accordingly, the deterioration effects on building materials can usually be considered to equal *pO*. In this case, deterioration speed does not depend on the current status of deterioration, so it is the simplest model for the estimation.
2. Convergence type: when $a < 0$. When $a < 0$, the speed of deterioration depends on the current degree of deterioration, but the speed is falling gradually. That is, the deteriorating parts reduce external force causing deterioration. In this type of deterioration pattern, the speed of deterioration increases at the beginning and is zero at the end.
3. Multiplication type: when $a > 0$. When $a > 0$, the speed of deterioration depends on the current degree of deterioration. In this type of deterioration pattern, the more the degree of deterioration progresses, the higher the speed becomes.

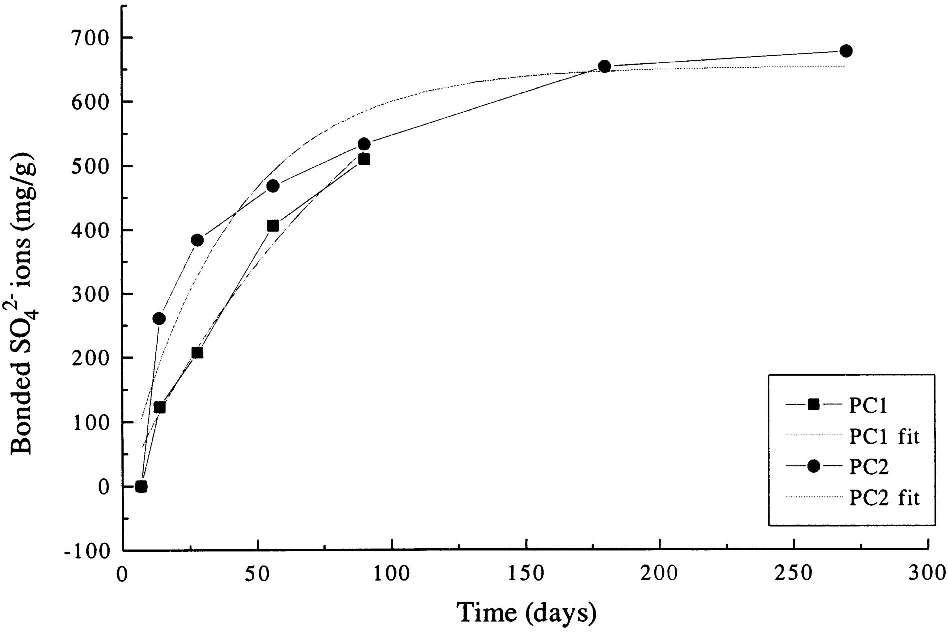

FIG. 5.
Experimental and estimated curves for the bonded SO_4^{2-} ions for Portland cements.

This paper shows the influence of the composition of Portland cement clinker and of cement on the degradation of cement stone by the impact of the aggressive environment. An ammonium sulphate solution was selected as the representative of an aggressive environment.

The results showed that there is a considerable influence by certain mineral components of Portland cement clinker, and of cement, on the degradation by the impact of the aggressive sulphate and ammonium ions. Those results require that in designing concrete that will be exposed to the impact by aggressive ions, special attention be paid to the selection of cement.

The basic idea and motivation for the present work is to widen the knowledge of degradation processes and degree of degradation in concrete. The work continues research that has been underway for several years (10).

Experimental

The program for researching degradation of cement through the impact of sulphate corrosion envisaged characterization of Portland cement and Portland ash cement manufactured in our country:

- Portland cement 1 (PC1)
- Portland cement 1 with the addition (replacement of clinker) of 30% of coal ash (PAC1)
- Portland cement 2 (PC2)
- Portland cement 2 with the addition (replacement of clinker) of 30% of coal ash (PAC2)

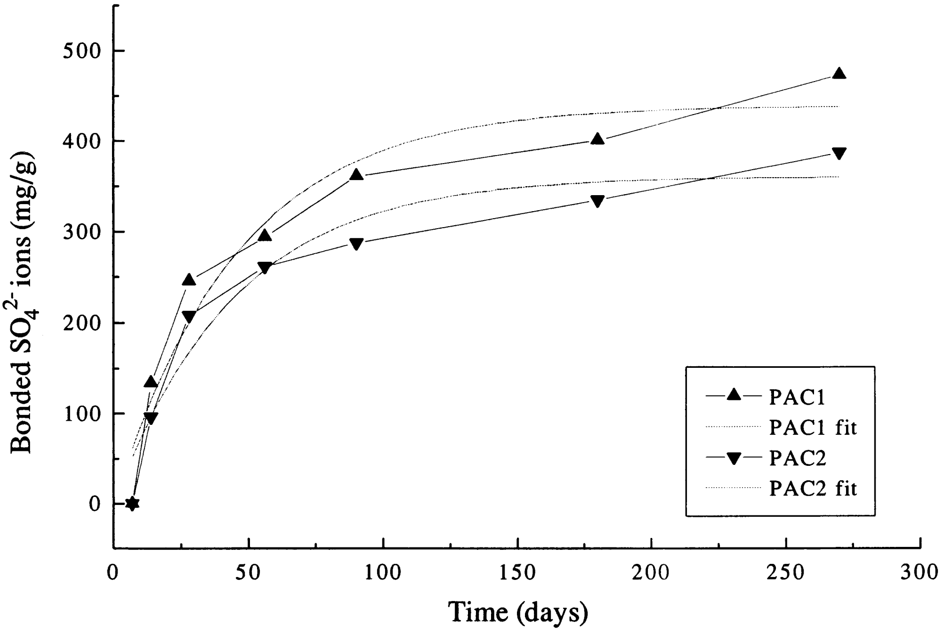

FIG. 6.
Experimental and estimated curves for the bonded SO_4^{2-} ions for Portland-ash cements.

Determination of the chemical composition of all materials, testing of physico-chemical and mechanical properties of cements, and the potential phase analysis of clinkers was performed. Testing the influence by the selected aggressive solutions on concrete was carried out. On the basis of results of the implemented tests, the first reports of the degradation of cements by ammonium-sulphate corrosion, as well as their classification, have been reported previously (11,12).

The chemical resistance of the cements was tested according to the Koch-Steinegger method (13), with mortar prisms prepared from standard sand of the former German cement standard DIN 1164 (1958) and with water/cement ratio 0.6. Before the prisms were exposed to aggressive solution, they were cured 1 day in the mould and 20 days in water. A 10% $(NH_4)_2SO_4$ solution was used instead of 4.4% Na_2SO_4 solution of the original Koch-Steinegger method. As a comparision equal number of prisms were stored in distilled water. Flexural strength was determined after 7, 14, 28, 56, 90, 180, and 270 days of storage in the aggressive solution. In previous investigations (13,14), this method was proven to be suitable especially when testing blended cements. According to the authors' criterion, the sulphate resistance was the quotient:

$$RC = \frac{\text{Flexural Strength of the Sample Stored in the Sulphate Solution}}{\text{Flexural Strength of the Sample Stored in Water}}$$

Results are presented as the mass change of the testing samples through time, by bonded SO_4^{2-} content calculated from the SO_4^{2-} content in solution, and by the degradation coefficients (*DC*) which were calculated as a supplement to the corrosion coefficients (*RC*) of the testing samples.

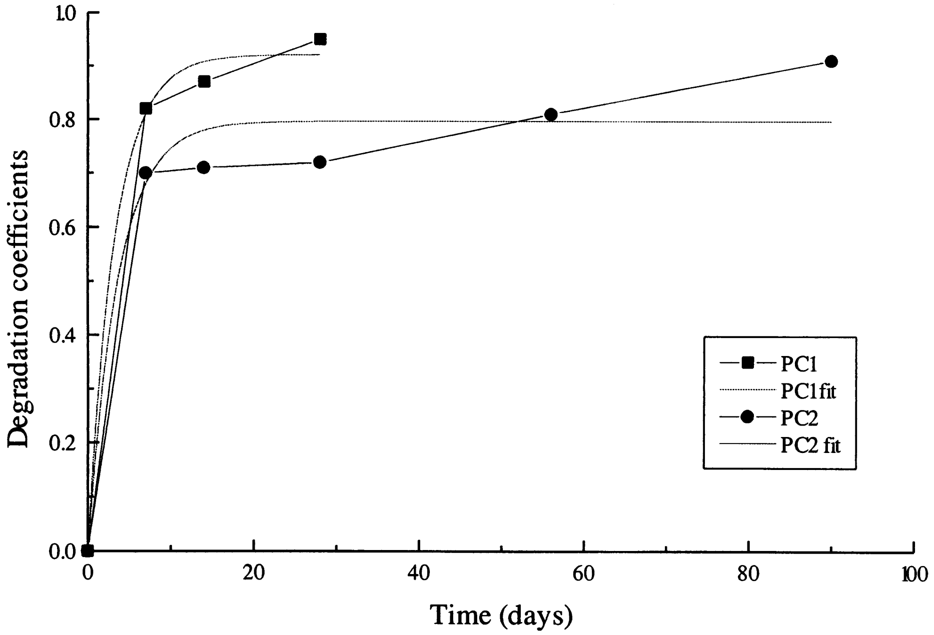

FIG. 7.
Experimental and estimated curves for degradation coefficients for Portland cements.

Other methods used in this work included:

1. Determining the strength (European standard EN 196–1)
2. Chemical analysis (European standard EN 196–2)
3. Determining the setting time (European standard EN 196–3)
4. Determining the sieve residue (European standard EN 196–6)
5. Determining the specific surface (European standard EN 196–6)
6. Calculating the potential phase analysis (ASTM C 150)

Results and Discussion

Test Specimens

The potential phase analysis for the Portland cement clinkers are given in Table 1. It can be seen that kinds of cements differ in the percentage content of C_3A in clinkers 6.60% to 13.31%, which has an effect on sulphate resistance. Ordinary Portland cement is not resistant to the influence of sulphates because it has a considerable content of tricalciumaluminate, C_3A, whose hydrates react with sulphate ions, giving expansive compounds. Portland cement with increased resistance to sulphates must have a low content of C_3A. The difference in the C_3S content is also significant with regard to sulphate resistance.

Table 2 gives the chemical composition of the mineral admixture coal ash. The chemical composition of this coal ash makes it generally suitable for application in concrete because

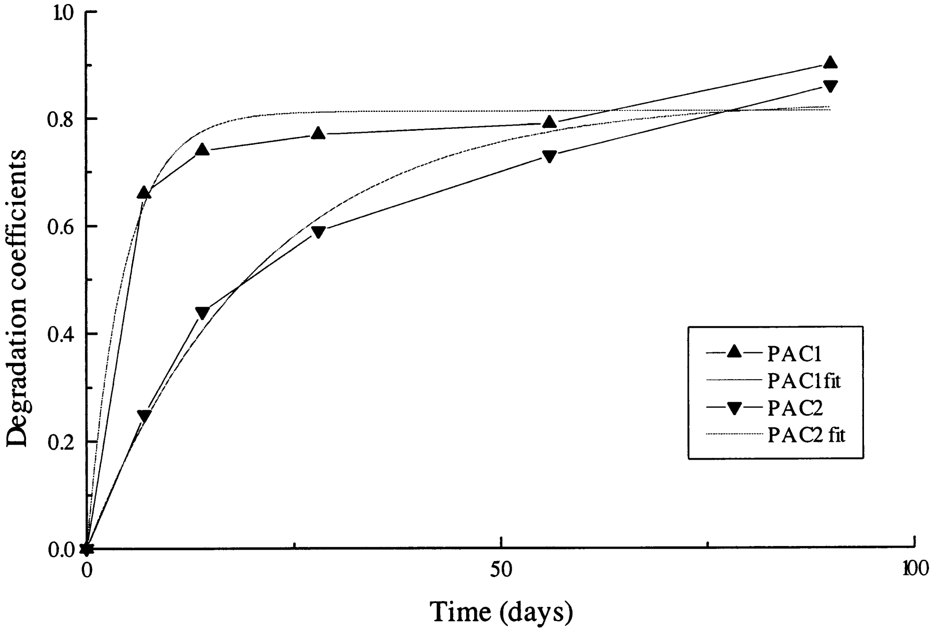

FIG. 8.
Experimental and estimated curves for degradation coefficients for Portland-ash cements.

of its high content of oxides SiO_2, Al_2O_3 and Fe_2O_3, and its low content of CaO. MgO, sulphate and alkali content are low also. Loss on ignition is higher than usual for this type of coal and boilers. XRD analysis showed that the fly ash is mostly amorphous. Quartz, feldspar and hematite are present as crystalline phases.

The chemical compositions of the cements and blended cements are presented in Table 3. As regards the chemical composition, all the cements satisfy the conditions for quality of the Yugoslav standard JUS B.C1.011. The characteristic feature is an increased content of insoluble residue in cements with the addition of ash. The addition means that, in certain percentage, Portland cement clinker is replaced with mineral admixture. Loss on ignition was higher in Portland ash cements also. Free CaO content was diminshed by adding the 30% of coal ash. Sulphate and MgO contents for cements PC2 and PAC2 were lower.

Table 4 gives selected physico-chemical characteristics of the four cements: fineness, specific surface area (after Blaine), density, standard consistence, setting time, and volume stability. The addition of ash increased the water demand for standard consistence, setting time and specific surface area, but had no significant influence on other characteristics. Sieve residue for the blended cements increased also, due to the fineness of the ash itself and insufficient intergrinding with the cement.

All characteristics were in compliance with Yugoslav standard JUS B.C1.011.

Table 5 gives values for flexural and compressive strengths of cements after 2, 3, 7, and 28 days. The addition of ash generally contributes to the increase in strengths, especially in the later phases of aging, which is its most important contribution. Due to the clinker mineralogical composition, Portland cement PC2 had a slower increase but higher later strengths.

TABLE 6
Matsufuji-Koyama equation coefficients determined for the mass change curves.

Cement	Coefficient *a*	Error	Coefficient *b*	Error	Chi^2 function
PC1	−0.05652	0.00265	1.11457	0.03605	0.07915
PC2	−0.02273	0.00567	0.52771	0.1061	6.7388
PAC1	−0.0364	0.0052	0.50765	0.06161	0.85719
PAC2	−0.02648	0.00196	0.37609	0.02286	0.22944

Sulphate Degradation Tests

The selected environment provided very strong aggressiveness, ensuring fast results. The results of tests regarding the degradation by sulphate corrosion of cements tested according to the Koch-Steinegger method are presented by mass change, bonded SO_4^{2-} content, and degradation coefficients, in Figures 3 to 8.

Figures 3 and 4 present mass change of cement mortar testing samples exposed to the aggressive ammonium-sulphate solution. Curves PC1 fit, PC2 fit, PAC1 fit, and PAC2 fit are estimated curves from Eq. 5 for the mass change.

Due to fast mass change and ettringite formation, PC1 testing samples lasted for 56 days only, but PC2 testing samples lasted for the whole 270 days. It is obvious that C_3A clinker content played an important role. Cements with the ash addition lasted for 270 days also, confirming that ash played a protective role against ammonium-sulphate solution aggressive impact.

Figures 5 and 6 present measurement of bonded SO_4^{2-} content of cement and Portland-ash cement samples from the aggressive ammonium-sulphate solution. Curves PC1 fit, PC2 fit, PAC1 fit, and PAC2 fit are estimated curves from Eq. 5 for the bonded SO_4^{2-} content.

Incorporation of sulphates from solution was rather faster with Portland cement PC2 up to 90 days. After that time, samples from Portland cement PC1 cracked and broke down due to ettringite formation, but the testing samples from Portland cement PC2 lasted throughout 270 days of examination.

Incorporation of sulphates into Portland-ash cements was much slower due to a protective layer from hydration products formed in such cements. Even here the aluminate content played an important role, so incorporation of sulphates in cement PAC2 was lower than in cement PAC1.

Figures 7 and 8 present degradation coefficients of cement and Portland-ash cement

TABLE 7
Matsufuji-Koyama equation coefficients determined for the bonded SO_r^{2-} ions curves.

Cement	Coefficient *a*	Error	Coefficient *b*	Error	Chi^2 function
PC1	−0.01009	0.00518	8.82577	1.47551	1170.70501
PC2	−0.02488	0.00516	16.27591	2.74994	3775.52424
PAC1	−0.02163	0.00427	9.50351	1.49879	1482.19593
PAC2	−0.02234	0.00444	8.06318	1.28637	1025.31065

TABLE 8
Matsufuji-Koyama equation coefficient determined for the degradation of coefficients curves.

Cement	Coefficient *a*	Error	Coefficient *b*	Error	Chi^2 function
PC1	−0.30416	0.05859	0.28005	0.04857	0.00118
PC2	−0.27524	0.10774	0.2193	0.08017	0.00602
PAC1	−0.22045	0.04832	0.17933	0.03605	0.00288
PAC2	−0.04782	0.00567	0.03977	0.00361	0.00136

samples exposed to the aggressive ammonium-sulphate solution. Curves PC1 fit, PC2 fit, PAC1 fit, and PAC2 fit are estimated curves from Eq. 5 for the degradation coefficients.

From the diagrams, it can be clearly seen that cements with the addition of 30% of ash show convincingly the best sulphate resistance. The increase of corrosion degradation in the very begining for all the cements is a normal phenomenon, because the creation of expansive compounds closes the pores, and makes cement paste impervious to aggressive ions. However, further increase in the volume within the paste very quickly results in cracking. For the Portland cement PC1 with the high content of C_3A this occured after 28 days only. Testing samples from Portland cement PC2 and cements with the ash addition lasted for 90 days.

As can be seen from Figures 3 to 8 and from Tables 6 to 8, results obtained with the Matsufuji-Koyama model for the cements with the ash addition are much better than for the Portland cements. These results suggest that, in essence, the Portland-ash cements hydration products formed a protective layer, thus slowing corrosion process and increasing durability. Portland cements, however, showed, depending on the C_3A content, either an alignment type or a multiplication type of degradation after initial period of forming the protective corrosion process products layer. This layer obviously became negligible due to the action of NH_4^+ ions, thus opening new pores and accelerating the corrosion process again.

The results of these investigations are encouraging, because the addition of ash improves sulphate resistance. For example, cement PAC1 with the addition of ash shows good resistance to the aggressive impact by sulphate solution, although this cement is, due to its high C_3A mineralogical composition, very unsuitable in that sense. It is evident from tests of PC1 and PC2 that resistance of Portland cement to sulphate aggression is directly related to its C_3A content.

Conclusions

The $(NH_4)_2SO_4$ test results allow the formulating of certain conclusions:

1. Sequence with the Matsufuji-Koyama model for the convergence type of degradation was very good for the cements with the ash addition, but, for the Portland cements, depending on the C_3A content, it was rather alignment or multiplication type.
2. The above-cited tests of cements from the current production of the domestic cement industry provided the basis for classification of these products regarding resistance to sulphate. This offers the possibility that, in certain cases, the ensuring of the integrity of structures and their elements which lie in contact with aggressive environments be implemented by way of applying the selected cement with adequate composition and

quality of concrete, thus avoiding special measures for protecting concrete such as using expensive coatings, films and linings.

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