Pergamon

Cement and Concrete Research 31 (2001) 3–6

CEMENT AND CONCRETE RESEARCH

Long-term wear on outside walls of buildings by sulfur dioxide corrosion

Ayhan Demirbaş[a,*], Temel Öztürk[b], Faik Özgür Karataş[b]

[a] *P.K. 216, TR-61035 Trabzon, Turkey*
[b] *Department of Chemical Education, Karadeniz Technical University, 61335 Akçaabat, Trabzon, Turkey*

Received 3 March 1999; accepted 5 October 2000

Abstract

The effect of sulfate ions on the corrosion of concrete on outside walls of buildings was studied. The corrosion rate was very high during the early years and decreased with time. Corrosion-induced cracking of concrete can be simulated by sulfate formation with sulfur dioxide (SO_2) at the concrete interface for a long period. Excessive alkali sulfate formation at the concrete surface causes destructive volume expansion. In general, the age of concrete is highly correlated with its sulfate content and water solubility. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfate attack; Surface layer; Corrosion

1. Introduction

The presence of fluorides, chlorides, sulfates, and sulfur in the raw feed enhances the corrosion rate of reinforcing steels in concrete [1–4]. Atmospheric pollution is a major cause of concrete deterioration, especially in industrial areas. The sulfur dioxide (SO_2) in the air combines with rainwater to form sulfurous acid. This reacts with lime compounds in the concrete, forming calcium sulfate. Calcium sulfate is only slightly soluble in water and is deposited on or near the surface, forming a skin. The calcium sulfate then crystallizes behind this skin, and differential movements between it and the concrete underneath loosen the concrete and cause disintegration.

The highest concentration of SO_2 in the atmosphere is in industrial areas. Polluted air causes wear or erosion, and an originally smooth surface can be weathered away leaving coarse exposed aggregate highly susceptible to deterioration due to corrosion of the reinforcement. Pozzolans or slags increase the long-term corrosion-resisting characteristics of concrete [5–7]. Alkalis in Portland cement clinker occur as sulfates and, depending on the amount of SO_3 available, may also be present in calcium silicate and aluminate phases. Introduction of alkalis into clinker minerals may modify their crystal structure, which, in turn, can change their hydraulic reactivity.

Alkalis in cement are found primarily as alkali sulfates or as solid solution substituents in calcium aluminate or in belite [8].The alkali sulfates most commonly formed are potassium sulfate (arcanite, K_2SO_4), sodium potassium sulfate (aphthitalite, $Na_2SO_4{\cdot}3K_2SO_4$), and calcium potassium sulfate (calcium langbeinite, $2CaSO_4{\cdot}K_2SO_4$) [9]. Calcium sulfate occurs either alone or as $2CaSO_4{\cdot}K_2SO_4$ subject to the prior formation of double alkali sulfates [10].

Direct combustion of high-sulfur coals, especially lignites, produces flue gases containing large amounts of SO_2, which is one of the major atmospheric pollutants. Combustion of high-sulfur lignites is one of the fundamental reasons for problems with SO_2 emissions. SO_2 is one of the most corrosive air pollutants evolving mostly from the combustion of fossil fuels in transport vehicles, industrial furnaces, and thermal power plants. In many countries, the main sources of SO_2 are oil- and coal-fired power plants, which have produced about more than half of SO_2 discharge. Developing countries, especially great metropolis cities, undergo serious SO_2 pollution during winter because domestic heating depends mostly on coal, lignite, fuel-oil, and petroleum coke, which may have high sulfur contents. The average sulfur

---

* Corresponding author. Tel.: +90-462-2487429; fax: +90-462-2487344.

E-mail address: ayhandemirbas@hotmail.com (A. Demirbaş).

0008-8846/01/$ – see front matter
PII: S0008-8846(00)00447-6

Table 1
Average monthly concentrations (ppm) of SO_2 and PM in air

Year	Pollutant	January	February	March	April	May	June	July	August	September	October	November	December
1991	SO_2	101	79	66	43	34	27	20	21	29	30	47	78
1991	PM	116	81	85	58	41	21	16	17	20	32	80	96
1992	SO_2	87	84	72	47	30	22	20	21	24	24	81	108
1992	PM	90	86	82	47	35	31	21	23	22	33	105	123
1993	SO_2	145	133	81	50	44	24	25	23	27	31	77	134
1993	PM	139	107	62	48	41	26	17	19	23	42	69	142
1994	SO_2	99	103	82	53	24	27	24	24	34	25	55	87
1994	PM	116	92	69	54	32	11	13	16	23	28	55	91
1995	SO_2	77	70	52	37	25	19	20	23	25	25	68	94
1995	PM	87	54	59	50	34	15	17	20	25	29	73	116
1996	SO_2	57	109	73	43	21	21	20	20	20	26	64	53
1996	PM	89	100	59	35	22	20	15	14	21	23	72	57
1997	SO_2	58	65	61	41	25	22	20	23	22	26	75	70
1997	PM	65	67	59	45	26	23	21	23	24	29	97	101
1998	SO_2	67	77	74	34	27	22	23	24	26	28	33	73
1998	PM	71	80	84	36	23	21	24	22	25	27	57	75

Source: Data from Trabzon Environment Head Office.

content of Turkish lignites is relatively high, and direct combustion of these fuels produces flue gases containing large amounts of SO_2, which is one of the major atmospheric pollutants.

This work is planned to study the effect of SO_2 corrosion caused wear and tear at the concretes taken from outside walls of different buildings.

2. Materials and methods

Samples were supplied from outside surfaces of walls by scraping up to 1–2-mm depth of different aged buildings in Trabzon.

In order to recover Na^+, K^+, and Ca^{+2} ions and other water-soluble constituents, the samples (2–4 g) were extracted with hot water at 311 K for 1 h.

The air-dried samples were ground by passing a screen of 250 mesh before analyses. Ca^{+2} ion was determined by compleximetric titration methods [11]. A flame photometer (Biotechnica Instruments, Model 8T 624D) was used for the determination of Na^+ and K^+ concentrations [12,13]. Sulfate contents of the samples were determined according to ASTM D2795-69.

3. Results and discussion

Results from SO_2 and particle matter (PM) measurements are given in Table 1. The average contents of alkalis with in different aged concretes are presented in Table 2. The average water solubilities of with different aged concretes at 311 K are shown in Table 3.

From Table 2, using linear regression analysis, the age of concrete (AC) or age of building can be compared with the chemical composition data. Linear regression of the AC with sulfate content of concrete (SCC) taken from the inside of the wall resulted in a square of the correlation coefficient (r^2) of .9546. In general, the SCC increases with an increase in AC, and the AC is highly correlated

Table 2
Average contents of alkalis in with different aged concretes (wt.% of used sample)

	Ca^{+2} content		SO_4^{+2} content		Na^+ content		K^+ content	
Age of building (years)	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
7	4.51	5.90	7.26	8.94	0.34	0.43	0.54	0.78
10	3.64	6.36	5.74	9.63	0.22	0.48	0.46	0.84
16	3.37	6.81	4.65	12.08	0.24	0.57	0.33	0.82
25	2.72	7.40	3.10	13.48	0.08	0.49	0.19	0.86
34	1.17	7.85	2.76	15.61	0.05	0.54	0.12	0.90
43	0.48	8.36	1.58	16.80	0.03	0.52	0.09	0.91
56	0.45	8.81	1.12	17.35	0.02	0.58	0.04	0.93
64	0.23	9.62	0.92	18.91	<0.01	0.56	0.01	0.92
86	0.12	10.78	0.45	21.61	<0.01	0.58	<0.01	0.95

with SCC. For the model including the SCC, the regression equation is

$$AC = 9.0629 + 0.1550(SCC) \tag{1}$$

where AC is the age of concrete or building (year) and SCC the sulfate content of concrete (wt.% of used concrete). For Eq. (1), correlation coefficient (r) is .977.

From Table 3, using linear regression analysis, the AC can be compared with the water-solubility data. Linear regression of the AC with water solubility of corroded concrete (WSCC) obtained from the inside of the wall resulted in a square of the correlation coefficient (r^2) of .9686. In general, the WSC increases with an increase in AC. For the model including the WSC, the regression equation is

$$AC = 17.6775 + 0.3364(WSC) \tag{2}$$

where AC is the age of concrete or building (year) and WSCC the water solubility of corroded concrete (wt.% of used concrete). For Eq. (2), correlation coefficient (r) is .984.

Gypsum ($CaSO_4 \cdot 2H_2O$) on the surface layer of concrete may be formed by reaction between $CaCO_3$ in concrete and SO_2 and H_2O in the air. The solubility of calcium carbonate is very low so as to be virtually negligible, but the solubility of sulfates, in long period, is very important (Tables 2 and 3). Most of the soluble portion occurs as sulfate, with the sulfate often derived from sulfurous impurities in the kiln fuel rather than from the cement raw materials [8].

Sulfates in solution attack concrete and cause expansion, deterioration, and eventual disintegration. In the early stages of attack, there is little visual evidence of any change in the concrete, although there may be some reduction in strength as the chemical actions proceeds. This is accompanied by a slight expansion, which may not be apparent in the concrete itself, but may cause trouble at points of restraint. As the attack proceeds, there is usually some change in color from the normal cement gray, and cracking occurs, starting from the surface in dense concrete, but penetrating much deeper in more porous concrete [14].

Sodium and potassium in cement may conveniently be divided into "water-soluble" and "water-insoluble" portions on the basis of extent of dissolution in a standard shaking test (ASTM Standard Method of Test C 114-69). This test method involves shaking a suspension of cement in 10 parts of water for a 10-min period and filtering out the dissolved portion for analysis. Potassium generally predominates over sodium in sulfate form. The alkali sulfates dissolve very quickly in water.

Table 3
Average water solubilities of different aged concretes at 311 K (wt.% of used sample)

Age of building (years)	7	10	16	25	34	43	56	64	86
Outside of wall	12.51	10.80	8.42	7.53	6.42	5.06	3.45	1.12	0.61
Inside of wall	18.92	21.74	22.84	25.07	28.13	34.56	36.76	41.58	44.21

4. Conclusion

Sulfates in solution attack concrete and cause expansion, deterioration, and eventual disintegration. The rate of attack depends on the following factors.

(1) Easily soluble sulfates such as those of sodium, potassium, magnesium, and ammonium, react more vigorously than calcium sulfate.

(2) The higher the concentration of sulfates in the solution, the more serious the attack is. The severity of attack is increased in circumstances in which a flow of sulfate-bearing water brings a continuous supply of the salt into contact with the concrete.

(3) Temperature may also be a factor as the activity of sulfate solutions increases with temperature. If the pH value drops below 6, the rate of attack is likely to increase.

(4) Permeable concrete, particularly if one side is in contact with moist soil containing sulfates and the other side is open to the air so that evaporation occurs, is attacked throughout its thickness resulting in an overall expansion and complete disintegration.

(5) Attack proceeds along the lines of cracks particularly when the movement of moisture along any crack is encouraged by one-sided water pressure or evaporation from a free surface.

(6) Sulfates of sodium, potassium, magnesium, and ammonium may cause serious damage to Portland cement in the presence of moisture. This begins by expansion within the concrete, which may be enough to cause general expansion in the structural member. Cracking and disruption follow. Cracks provide a path for soluble chemicals to migrate into the interior of the structure causing deterioration of the concrete.

Data from Table 3 show that corrosion-induced cracking of concrete can be simulated by sulfate formation with SO_2 at the concrete interface for a long period. Excessive alkali formation at the concrete surface causes destructive volume expansion. The volume expansion, especially length change, increased from 0.05% to 0.067% with increasing alkalis, as Na_2O equivalent, from 0.65% to 0.78% in cement mixes for 723 days [14,15]. In general, corrosion increases with increase sulfate content and Ca^{+2}, K^+, and Na^+ ion concentrations.

Sulfate salts attack concrete only when they are in a solution. Because concrete is porous, and any foreign material can penetrate into the concrete as water-soluble, the best prevention is to stop the penetration of these chemicals by stopping the capillarity, e.g., by using dense, low w/cm ratio concrete. Concrete materials may provide a permanent internal seal, which forms a hydrostatic block, barring the migration of moisture. Concrete impermeability may be increased by the strength of the concrete at the surface. This will retard attack of harmful chemicals at the surface, protecting the vulnerable interior of the concrete, thereby increasing the life expectancy and safety of the structure.

References

[1] M.L. Escudero, A. Macias, Corrosion of reinforcing steel in mortar of cement with CaF_2 as a minor component, Cem. Concr. Res. 25 (1995) 376–386.

[2] M.L. Allan, Probability of corrosion induced cracking in reinforced concrete, Cem. Concr. Res. 25 (1995) 1179–1190.

[3] H. Yalçin, M. Ergun, The prediction of corrosion rates of reinforcing steels in concrete, Cem. Concr. Res. 26 (1996) 1593–1599.

[4] P. Gu, S. Elliot, J.J. Beaudoin, B. Arsenault, Corrosion resistance of stainless steel in chloride contaminated concrete, Cem. Concr. Res. 26 (1996) 1151.

[5] M. Maslehuddin, A.İ. Al-Mana, H. Sariçimen, M. Shamim, Corrosion of reinforcing steel in concrete containing slag or pozzolans, Cem. Concr. Aggregates 12 (1990) 24–31.

[6] A. Aslan, F.Ö. Karakaş, A. Demirbaş, Influences of lignite ash additives on strength, setting, expansion, and hydration properties of cement, Energy Educ. Sci. Technol. 1 (1998) 102–110.

[7] A. Demirbaş, Y. Erdoğan, H. Genç, M. Tüfekçi, A. Aslan, A. Ayas, S. Karslioğlu, Physical and technological properties of cement admixtures, Energy Educ. Sci. Technol. 1 (1998) 31–36.

[8] S. Diamond, A review of alkali–silica reaction and expansion mechanisms: 1. Alkalis in cements and in concrete pore solutions, Cem. Concr. Res. 5 (1975) 329–346.

[9] I. Jawed, J. Skalny, Alkalis in cement: a review: I. Forms of alkalis and their effect on clinker formation, Cem. Concr. Res. 7 (1977) 719–730.

[10] H.W. Pollitt, A. Brown, Proc. 5th Int. Symp. Chem. Cem. Tokyo, vol. 1, 1968, p. 322.

[11] H. Gülensoy, Kompleksometrinin Esaslari ve Kompleksometrik Titrasyonlar, İstanbul University, İstanbul, 1977 (in Turkish).

[12] Y. Erdoğan, A. Demirbaş, H. Genç, Partly-refined chemical by-product gypsums as cement additives, Cem. Concr. Res. 24 (1994) 601–604.

[13] A. Demirbaş, Recycling of lithium from borogypsum by leaching with water and leaching kinetics, Res. Conserv. Recycl. 25 (1999) 125–131.

[14] A. Demirbaş, N. Yazici, A. Şahin, Calculation of compressive strengths of concrete from cement with admixture, Energy Educ. Sci. Technol. 2 (1999) 15–20.

[15] G.G. Carette, V.M. Malhotra, Characterization of Canadian Fly Ashes and Their Relative Performance in Cocrete. CANMET Report 86-6E, 1986.