

ANALYSIS OF DIFFERENT CEMENT BASED PASTES IN SO₂ AND NO₂ ATMOSPHERES¹

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Abstract

The paper explains the behaviour of cements of different composition in atmospheres rich in sulphur-dioxide and nitrogen-dioxide.

As a result of 180 day long exposition to sulphur-dioxide rich atmosphere the minimal increase of the sulphate ion compound (4%) occurred in cements containing 20% fly ash, while the maximum increase (7%) was found in cements with 40% slag content. The results for portland cements were between these two extreme values. While on the surface of portland cement samples a well-adhesive salt layer appeared, the outer 0.8-1.0 mm of samples with 40% slag peeled off by the end of the 180 day long treatment period. The main constituent of both the salt and the peeled off layer was gypsum, formed from the portlandite and the carbonate phase of the samples.

The nitrate content in 180 day old samples stored in nitrogen-dioxide rich atmosphere turned out to be between 1.1-1.4% unaffected by the composition of the cement.

Keywords: cement, deterioration, air pollution.

Introduction

Both Hungarian experience and international case studies dealing with concrete structures show that in case of buildings located in heavily polluted areas or close to heavy traffic highways considerable accumulation of sulphate or nitrate ion may occur.

According to HENSEL's [1] assumption sulphur-dioxide and nitrogen-oxides react with water, the oxygen from the air and the alkaline and alkaline earth metal-hydroxides of concrete. Among the formed sulphate and nitrate salts we find calcium-sulphate (weakly soluble); magnesium-sulphate (average solubility) and other salts (well soluble). An other common characteristic of these salts is that they dissociate in water to give

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neutral or slightly acidic pH and, as a result, the basic pH of concretes decreases. Hensel pointed out that the neutralisation becomes even faster if there is carbon-dioxide present at the same time.

SCHOLL and KNÖFEL [2] state that the damaging effect of acidic gases from the air to building surfaces occurs in the case of both liquid and dry settling, but considers the latter to be more important. This is so, because gases can penetrate deeper into the pores of porous materials if the pores are not filled with water, while in case of liquid settling the reaction takes place in the surface liquid phase. That is why the liquid settling is only a supplementary effect.

WEAVER [3] points out another harmful effect of acidic air polluting materials besides dissolution. Air polluting materials may form soluble salts in deeper layers. During the drying of building materials liquids carry these salts towards the surface, where they accumulate. More rainfall results in repeated dissolution and crystallisation. This cycle may repeat several hundred times, and if the salt is hygroscopic or it can take up crystal water then enormous pressures may build up in the pores. This may result in the disintegration of the material, but a tough crust can also be formed on the surface which can peel off afterwards. This process takes place mostly together with the formation of gypsum, and has been observed usually on outdoor limestone-surfaces.

BALÁZS and his colleagues [4] measured about six times higher gypsum content in the surface layer of a reinforced concrete bridge beam as compared to the concentration in deeper layers.

Knowing about the foregoing results and assumptions we extended our laboratory investigations on the deterioration of reinforced concrete to the effect of sulphur-dioxide and nitrogen-oxides on cements of various compositions. The fact that other research teams have been carrying out investigations parallel with us shows the importance of the topic. SCHOLL and KNÖFEL [5] analysed the parallel effect of carbon-dioxide and sulphur-dioxide on mortar samples. The samples were prepared with three different cement types (slag, portland and white) and with two different water/cement ratios (0.42 and 0.58).

The highest sulphate ion content was observed in slag based samples with 0.58 w/c ratio, but only in the outer 0–5 mm layer.

FUHR [6] analysed cements with different belite content (25–71%); his results showed that the increase of the belite content accelerates the accumulation of sulphate ions. STROHBAUCH and his colleagues [7] examined the increase of volume of cement samples on the effect of air polluting materials. Their samples were prepared with four different cements (PZ 35, PZ 45, PZ 55 and one with high aluminat content), with w/c ratios of 0.4 and 0.6. These samples were kept in different atmospheres. The most sig-

nificant change occurred in the sample with high aluminate content kept in sulphur-dioxide. These samples completely disintegrated by the end of the 180 day long treatments. The authors did not observe the formation of any new phases in nitrogen-dioxide rich atmospheres, but recognized that the parallel presence of sulphur- and nitrogen-dioxide slowed the process of sulphate formation.

Experimental

Laboratory Materials

The cement samples were made up of portland cement clinker, gypsum, slag and fly ash for the experiments. The raw materials were first ground to a specific surface area of around $350 \text{ m}^2/\text{kg}$ in a roller mill, and then were homogenised. We produced the following cement pastes: portland cement (pc), cement containing 40% slag (spc), and cement with 20% fly ash content (fpc).

The gypsum content necessary to regulate the bond time was set to result a 2% sulphate ion content in the finalised cement.

Preparation of Samples

To examine the effect of w/c ratio and porosity we prepared samples of $10 \times 10 \times 50 \text{ mm}$ with three different w/c ratios. The w/c ratio was 0.28–0.31 for the first, 0.35 for the second and 0.40 for the third series.

The samples were stored under 20°C water for the first 7 days, then in desiccator above water until the start of the experiments.

The investigations to examine the effect of air polluting materials were started 2 months after the preparation of the samples; by that time even cements containing additives had dominantly consolidated.

Experiment Atmospheres

We maintained constant gas concentrations in 200 l plastic cans shown on *Fig. 1*.

Gases were led from the containers (SO_2 , NO_2 , CO_2) into the cans through control devices. Periodically operating ventillators helped to distribute the gases inside the plastic cans.

We controlled the SO_2 and NO_2 concentration and temperature three times a day with an IMR 2500 P type gas analyser. The CO_2 concentration was measured parallely by an Orsat analyser. We compensated the

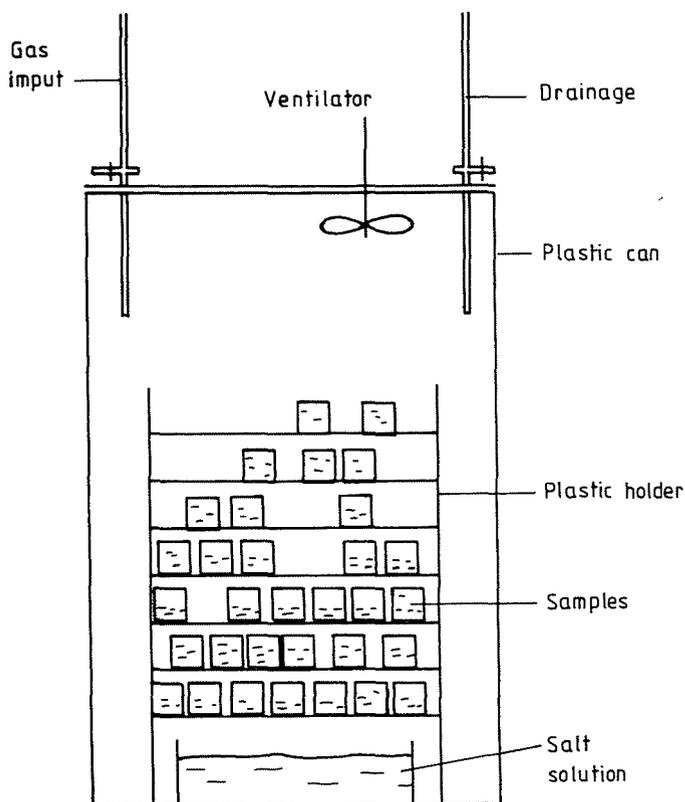


Fig. 1. Plan of the site of experiments

concentrations any time when it seemed to be necessary. The gas concentrations of the different cans were as follows:

SO ₂	atmosphere	:	200 ppm SO ₂
NO ₂	atmosphere	:	80 ppm NO ₂
CO ₂	atmosphere	:	4 volume % CO ₂

As the optimal operation temperature for the gas containers was 23 °C, we kept the laboratory at this temperature. The relative humidity of 70–75% was set by saturated ammonium-sulphate solutions kept inside the cans. The samples were stored in perforated plastic bowls; the ones that were on top of each other were separated by plastic plates. We made sure that the samples would not contact with each other.

A fourth, closed can was set up for etalon samples with a relative humidity of around 70%.

Characteristics Examined, Examination Methods

We removed 3 samples of every cement type from the cans at the age of 14, 28, 56, 90 and 180 days. Before the examinations we dried the samples at 60 °C.

10 × 10 × 10 mm pieces cut from each end of the samples were used for chemical analysis, since these were the areas that were most intensively exposed to the various atmospheres. Slices from similar environments were put together before grinding. We measured the pH values and the sulphate and nitrate ion content of each of these powders.

To identify the loss or generation of phases on effect of the various treatments, we carried out thermoanalytical examinations with Derivatograph type Q-1500 D and recorded X-ray diffraction diagrams.

Results and Evaluation

The Effect of Different Atmospheres on pH Values

The pH values measured by different times on the samples of three different cement contents are summarised in *Tables 1* and *2*. The figures clearly show that the different atmospheres had only little effect on pH, the values changed from the original average of 13 to 12.0–12.3 under 180 days. The decrease seems even smaller if we consider the values of *Table 3*; according to these figures there was hardly any difference in comparison with pH values of the etalon samples stored in normal air.

Table 1

The pH values of paste samples of different cement compositions (SO₂ series)

	Cement sign, w/c	Duration of SO ₂ exposition, days					
		0	14	28	56	90	180
pc	0.30	13.06	13.06	12.73	12.71	12.70	12.41
	0.35	13.06	13.05	12.71	12.70	12.70	12.36
	0.40	13.05	13.05	12.58	12.64	12.65	12.33
spc	0.28	13.03	12.99	12.69	12.56	12.53	12.20
	0.35	13.04	13.02	12.66	12.56	12.52	12.16
	0.40	13.00	13.00	12.66	12.56	12.52	12.18
fpc	0.30	13.05	13.05	12.69	12.68	12.56	12.29
	0.35	13.06	13.05	12.70	12.58	12.56	12.20
	0.40	13.06	13.03	12.70	12.57	12.56	12.25

However, comparing the different cement compositions we can state that the pH decrease of heterogeneous cements (spc and fpc) was slightly bigger

Table 2The pH values of paste samples of different cement compositions (NO₂ series)

	Cement sign, w/c	Duration of NO ₂ exposition, days					
		0	14	28	56	90	180
pc	0.30	13.06	13.06	12.60	12.57	12.54	12.36
	0.35	13.06	13.05	12.66	12.58	12.57	12.32
	0.40	13.05	13.05	12.63	12.58	12.55	12.32
spc	0.28	13.03	13.00	12.57	12.56	12.49	12.11
	0.35	13.04	13.00	12.58	12.53	12.46	12.03
	0.40	13.00	13.00	12.57	12.53	12.46	12.06
fpc	0.30	13.05	13.03	12.56	12.58	12.60	12.18
	0.35	13.06	12.06	12.51	12.54	12.59	12.20
	0.40	13.06	13.02	12.50	12.51	12.57	12.10

Table 3

The pH values of paste samples of different cement compositions (comparison figures after 90 days of treatment)

	Cement sign, w/c	Original values	Storage atmosphere			
			air	CO ₂	SO ₂	NO ₂
pc	0.30	13.06	12.72	12.62	12.70	12.54
	0.35	13.06	12.71	12.52	12.70	12.57
	0.40	13.05	12.71	12.48	12.65	12.55
spc	0.28	13.03	12.61	12.40	12.53	12.49
	0.35	13.04	12.59	12.30	12.52	12.46
	0.40	13.00	12.59	12.30	12.52	12.46
fpc	0.30	13.05	12.72	12.46	12.50	12.63
	0.35	13.06	12.70	12.42	12.56	12.59
	0.40	13.06	12.70	12.39	12.56	12.57

as compared to portland cement samples, and the biggest decrease was in the sample containing slag additive. The effect of water/cement ratio is also clear; 0.1% increase results in 0.05–0.1 decrease in pH value.

The above statements apply to samples from both SO₂ and NO₂ environments, though the measured figures were less for the latter.

Sulphate Ion Content in an Atmosphere Rich in SO₂

The sulphate ion content of samples stored in SO₂ are shown in *Table 4*. In the initial period the sulphate ion content slightly increased – independently from the cement quality, then the increase became more significant and more dependent from the cement composition between the age of 90–180

Table 4

Sulphate ion content of different cement paste samples, mass% (SO₂ series)

	Cement sign, w/c	Duration of SO ₂ exposition, days					
		0	14	28	56	90	180
pc	0.30	1.95	2.12	2.43	2.60	2.95	5.76
	0.35	1.96	2.16	2.44	2.61	3.10	5.80
	0.40	1.97	2.16	2.56	2.63	3.18	5.95
spc	0.28	1.50	1.58	1.64	1.81	2.32	8.34
	0.35	1.49	1.60	1.70	1.85	2.41	9.61
	0.40	1.51	1.70	1.84	1.90	2.63	8.40
fpc	0.30	1.84	2.11	2.16	2.25	3.09	4.28
	0.35	1.87	2.08	2.19	2.41	3.44	4.70
	0.40	1.86	2.16	2.37	2.57	3.36	3.10

days. By the age of 180 days the sulphate ion content of fly ash cement samples were 2.5 times, for portland cement samples approximately 3 times and for slag samples approximately 6 times higher than the original values. This sulphate content means 3, 4 and 7% sulphate ion build in respectively.

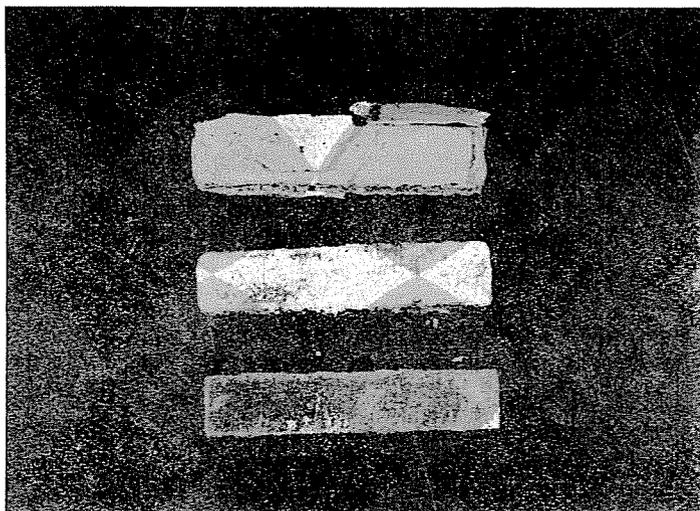


Fig. 2. Cement samples stored in SO₂ atmosphere for 90 days

We could not observe any changes on the surface of the samples until the age of 90 days. After that white or yellowish salt crusts appeared on certain samples. Fig. 2 shows the typical appearance of the various samples at the age of 180 days. The samples with slag additive suffered the most significant

damages, the outer layer of samples intended to peel off. The surface of portland cement samples was covered with well-adhering salt layer, while the salt on the surface of fly ash cement samples was less significant as compared to other types.

Nitrate Ion Content in an Atmosphere Rich in NO₂

Table 5 shows the values of the nitrate ion content measured in samples of different cement compositions. It is clearly seen that a measurable amount of nitrate ion was present by the age of 14 days. The nitrate ion contents measured at the age of 180 days were between 1.1 and 1.4%, practically independent from the cement composition. Even the effect of water/cement ratio proved to be extremely low; a 0.1% increase of w/c ratio resulted 10–20% increase of nitrate ion content.

We did not observe any changes on the surface of the different samples.

Table 5
Nitrate ion content of different cement paste samples, mass% (NO₂ series)

	Cement sign, w/c	Duration of NO ₂ exposition, days				
		0	14	28	56	90
pc	0.30	0.06	0.18	0.42	0.61	1.11
	0.35	0.10	0.20	0.37	0.59	1.15
	0.40	0.18	0.21	0.45	0.72	1.30
spc	0.28	0.10	0.12	0.40	0.59	1.25
	0.35	0.12	0.19	0.38	0.67	1.30
	0.40	0.14	0.30	0.61	0.70	1.42
fpc	0.30	0.07	0.15	0.27	0.61	1.30
	0.35	0.07	0.16	0.37	0.64	1.09
	0.40	0.10	0.20	0.53	0.68	1.40

Phase Analysis of Paste Samples Exposed to SO₂ and NO₂

Originally we recorded derivatograms of most of the samples in order to identify and measure the gypsum phase. However, the sulphate content – and the gypsum content as well – did not reach that particular level when we could have used them to identify the dehydration of gypsum from other processes that may cause water loss between 100–200 °C. The recorded decomposition peaks for portlandite (Ca(OH)₂) and calcium-carbonate however proved to be enough for quantitative evaluation.

Table 6

Figures calculated from derivatograms of samples treated with SO₂

Sign of sample	Duration of SO ₂ exp., days	Heating loss, mass%	Calculated quantities					
			Water loss of portlandite			CO ₂ loss of calcium-carbonate		
			referring to original mass%	referring to heated mass%	difference %	referring to original mass%	referring to heated mass%	difference %
pc	0	22.3	2.97	3.82	0	7.06	9.08	0
	90	23.7	2.67	3.50	-8	3.78	4.95	-45
spc	0	24.6	2.03	2.69	0	5.08	6.73	0
	90	32.5	1.21	1.79	-34	1.61	2.39	-44
fpc	0	21.6	2.31	2.95	0	6.72	8.57	0
	90	22.9	1.84	2.57	-13	3.36	4.36	-49

Table 7

Results of phase examinations of salt layers and peeled-off crusts from cement paste samples

Sample examined	Atmosphere	Heating loss mass%	Water loss of gypsum, mass% (CaSO ₄ × 2H ₂ O%)	CO ₂ loss of carbonate, mass% (CaCO ₃ %)
pc, salt layer	SO ₂ 180 days	26.20	15.65 (76.80)	2.62 (5.90)
spc, peeled-off crust	SO ₂ 180 days	31.49	17.86 (85.40)	2.76 (6.30)

Fig. 3 shows the derivatogram of an untreated portland cement sample. Peak I marks the water loss of gypsum, peak II shows that of calcium-hydroxide, peak III originates from the decomposition process of calcium-carbonate. We calculated the heating loss of the samples and the mass loss for peaks II and III by quantitative evaluation of TG graphs. *Table 6* summarises the results; we are presenting the figures of heated materials for better comparison. From these latter results we calculated the changes caused by the 90 day long exposition as compared to the original state. The decrease of the portlandite content was 8, 13 and 34% in portland cement, fly ash and slag samples, respectively. The decrease of the carbonate phase was between 45–50% in the examined samples.

Fig. 4 shows the derivatogram of yellow salt layers from surface of samples exposed to SO₂ for 180 days, while *Fig. 5* shows the results for layers peeled off from the surface of samples containing slag. The most significant peaks of the graphs are the loss of water by gypsum (I) and

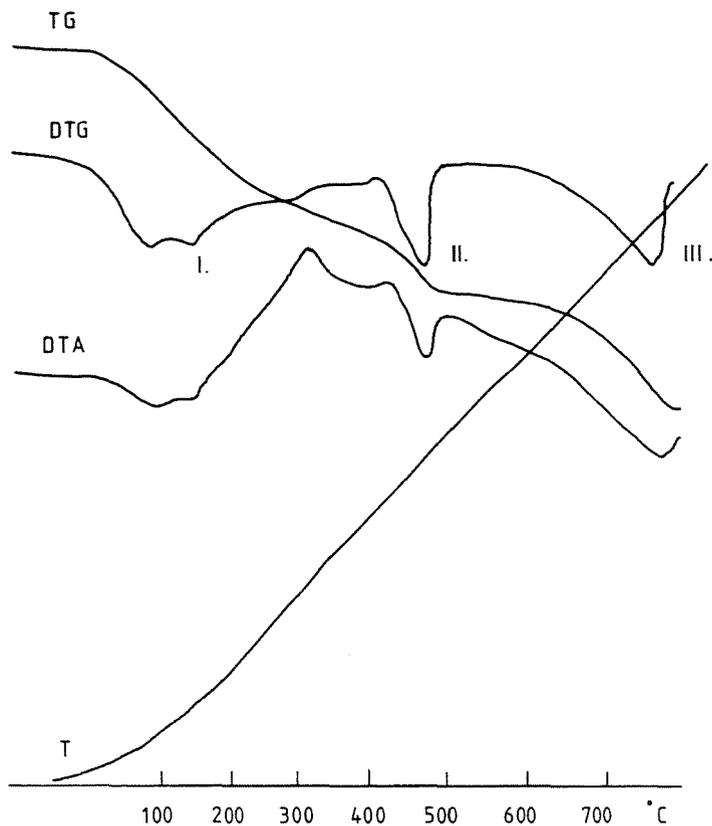


Fig. 3. Derivatogram of untreated portland cement sample

the decarbonization process (III). The gypsum and calcium-carbonate contents were calculated by evaluating TG graphs. The figures summarised in Table 7 show that the salt layer contained 75–85% gypsum and approx. 5% calcium-carbonate. We recorded X-ray diffraction diagrams of each cement type before the treatment and after 90 days of SO_2 exposition. Hardly any of the records supplied any useful information, however, that's why we present only a few of them.

The X-ray diffraction diagram of the portland cement sample (Fig. 6) showed the presence of portlandite and calcite (as crystalline phase) beside unhydrated clinker minerals. Both the untreated and the 90 day old samples had measurable gypsum content, and we identified an ettringite phase after the first 90 days. The record of the fly ash pulp sample (Fig. 7) is similar to the one of portland cement sample. Ettringite was present by the age of 90 days in this case as well.

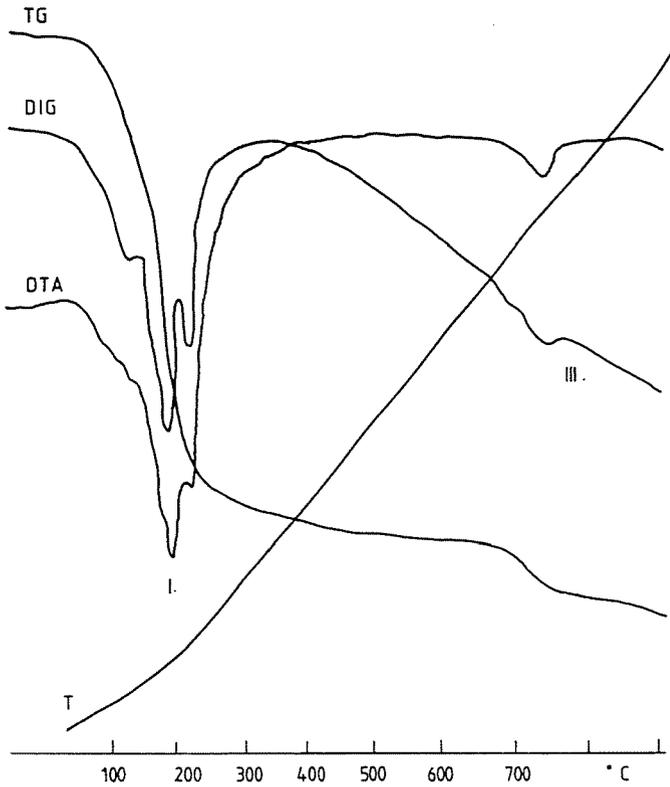


Fig. 4. Derivatogram of salt layer on the surface of portland cement samples (after 180 days of SO_2 exposition)

Unlike the other two cement compositions the X-ray diffraction diagram for the sample with slag (Fig. 8) showed unstable calcium-carbonate formations (vaterite, aragonite), as well as different calcium-aluminate-hydrates (for example monosulphate) with little intensity. The monosulphate content disappeared during the treatment, but the formation of secondary ettringite took place in the case of this cement composition as well.

Conclusions

We examined the effects of atmospheres containing extreme quantities of SO_2 (200 ppm) and NO_2 (80 ppm) on cement pulp samples of heterogeneous compositions through laboratory investigations.

We observed that the sulphate ion contents of fly ash, portland cement and slag cements were 2.5, 3 and 6 times higher after SO_2 exposition than

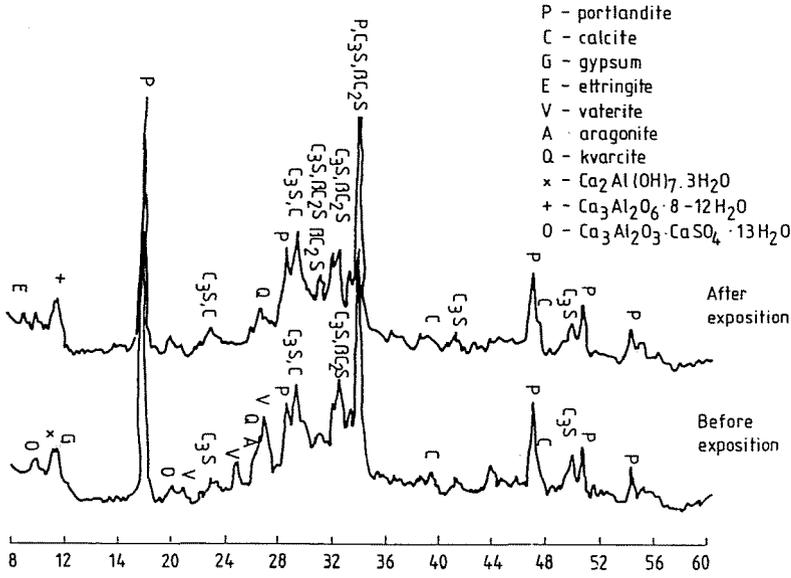


Fig. 7. X-ray diffraction diagrams of fly ash samples; untreated and after 90 days of SO_2 exposition

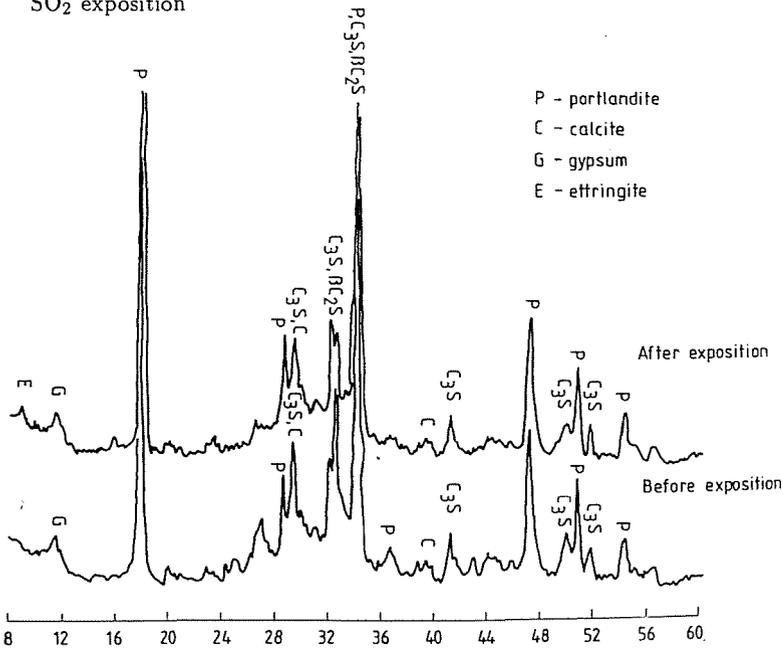


Fig. 8. X-ray diffraction diagrams of slag samples; untreated and after 90 days of SO_2 exposition

the original values. The surface of fly ash cement samples did not show any difference after 180 days, while a yellow and white salt layer of 1 mm thickness appeared on portland cement samples. Slag samples suffered the most damage; the outer 0.8–1.0 mm layer peeled off from their surface. The main constituent (75–85%) of both the well-adhesive flourishing and the peeled-off layer was gypsum; formed partly from portlandite and partly from carbonate phases (the previous completely disappeared, while the quantity of the latter decreased according to derivatograms).

The unfavourable behaviour of slag samples corresponds to the statements of other researchers, but the mentioned salt layer was not yet observed.

X-ray diffraction examinations show the formation of secondary ettringite phase in 90 day old portland cement, slag and fly ash samples. Parallel to this the monosulphate phase of the samples containing slag decreased. The nitrate ion content of cement samples exposed to NO₂ rich atmosphere was 1.1–1.4% by the age of 180 days.

Our assumption that the build-in of nitrate ions decreases the pH more than the build-in of sulphate ions (probably due to the formation of salts hydrating in acidic environment) was proved by these experiments – except for the slag samples.

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