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Influence of SO_2 deposition on cement mortar hydration

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Abstract

The chemical reactions that occur during the hydration of Portland cement can be modified in the additional presence of certain compounds, such as SO_2, which may be present in areas of high pollutant gas concentration. This paper considers mortars that have been cured for 1 and 7 days and exposed to SO_2 gas under dry and wet conditions. The role of ozone as gaseous catalyst in the reactions is studied. Fourier transform infrared spectrum analysis of the surface of the samples revealed carbonation had occurred; however, X-ray diffraction of the bulk material from the samples revealed $Ca(OH)_2$ only when the samples were exposed to dry conditions. In wet conditions, in the presence of water, the dissolution of CO_2 gas is enhanced, the carbonation of the $Ca(OH)_2$ is promoted at higher levels, and thus no $Ca(OH)_2$ is detected. Under wet conditions, the degree of salt formation was greater than in dry conditions. In the presence of water, and due to $Ca(OH)_2$ carbonation, the pH of the pore solution is lower than 12; thus SO_3^{2-} formation is favored. For the mortars exposed to dry conditions, kinetic salts such as K_2SO_4 are formed. However, in the additional presence of water, thermodynamically stable products as $K_2Ca(SO_4)_2 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$ are detected. The results of scanning electron microscopy indicated that the morphological composition of C-S-H gel resembles needle-like structures radiating from a grain. This morphology has been described by Taylor as type I.

Keywords: Sulfate; Carbonation; Mortar; Hydration

The hydration of Portland cement is a sequence of chemical reactions that occurs between clinker components, calcium sulfate, and water. The various hydration reactions proceed simultaneously at different rates and influence each other. On contact, cement and water immediately exchange ionic species between solids and liquid phase [1]. The presence of sulfate in the hydration process is important, particularly for the setting and acceleration of alite hydration. Sulfate thus affects the rate of strength development and volume stability. In most of the studies investigating the influence of sulfate in the hydration process, gypsum have been used [1–4].

In areas with high pollutant gas concentration, such as SO_2 and NO_2, sulfate formation is one of the most important deterioration processes in building materials [5]. Under these conditions, high SO_2 concentration is present initially at the sample surface. Reactions to form calcium sulfate as well as reactions with cement compounds can be occur. It is apparent from previous studies [6–8] that water plays a very important role in calcium sulfate formation in building materials.

During cement hydration an aqueous phase is present. The main composition of this phase is Ca^{2+}, OH^-, $Al(OH)_4^-$, SiO_4^{2-}, SO_4^{2-}, Na^+, and K^+. In the presence of SO_2 pollutant gas additional phases as SO_2 (aq), SO_3(aq), SO_3^{2-}, or SO_4^{2-} can also be present in the aqueous solution.

In this paper simultaneous hydration and sulfur related compounds formation within a cement mortar were studied. For this proposal mortars under 1 and 7 days cured were exposed to SO_2 pollutant gas. In this case, SO_2 (g) dissolution and oxidation proceed until the formation of SO_4^{2-}. A study of the different salts formed on the mortar surface, in addition to microstructural composition and structural analysis by scanning electron microscopy (SEM), were carried out.

1. Experimental

Cement mortar specimens of 3.5 × 2.5 × 0.8 cm, were prepared. The cement and sand composition are given in Table 1. The water-to-cement ratio used in mortar preparation was 0.6. The cement-to-sand ratio was 1:3.

After molding, but prior to exposure in the SO_2 chambers, the specimens were cured in a 90% relative humidity chamber for 1 and 7 days. Two samples of each mortars were placed in the chambers. The exposure in the conditions are shown in Table 2.

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Table 1
Chemical composition of the cement and sand

Oxide	Cement	Sand
SiO_2	20.67%	98.92%
Al_2O_3	4.31%	0.18%
Fe_2O_3	3.39%	0.06%
CaO	65.10%	0.00%
MgO	2.70%	0.28%
SO_3	2.89%	0.00%
L.I.	1.18%	0.05%
R.I.	0.27%	0.40%

After a 28-day exposure period, the samples were dried at 40°C for 24 h. Weight changes were determined. The mineralogical composition of the exposed sample was determined by X-ray diffraction (XRD). The chemical composition of the salts formed on the exposed mortar surfaces was analyzed by Fourier transform infrared spectrum (FTIR). Structural and compositional changes were examined by SEM/energy dispersive X-ray analysis (EDX).

2. Results and discussion

2.1. Weight exchange

Mortars cured 1 and 7 days were exposed to SO_2 pollutant gas for a period of 28 days; the weight changes of the samples are given in Fig. 1. The values given are the average of two samples.

The evaporation of free water from within the samples, in addition to the reactions of free water to produce hydration products, may account for any observed weight decreases for the mortars. On the other hand, weight increases can occur when salts are formed by reactions of the mortar with CO_2 and SO_2 gases. All the samples exhibited weight decrease, with the weight decreases being greater for the samples exposed to dry conditions. CO_2 (g) and SO_2 (g) reactions are enhanced in water presence. Therefore, a greater amount of salts formation would be expected, resulting in greater weight increases. Comparatively lower weight decreases were observed for the mortar cured for 7 days in comparison to the mortar cured for 1 day. After 7 days of curing the hydration process increases as free water decreases.

2.2. XRD analyses

XRD patterns for the mortars cured for 1 and 7 days and exposed under different conditions are similar to those of quartz, calcite, and alite. Additionally, $Ca(OH)_2$ was observed for samples exposed in absence of water; with water the dissolution of CO_2 is a fast step in the process.

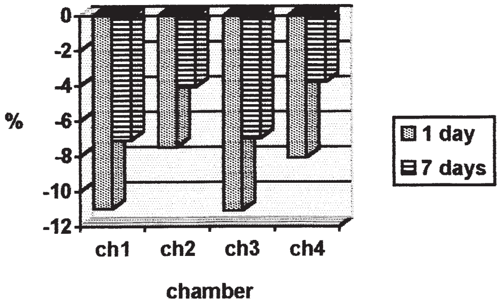

Fig. 1. Weight exchange after 4-week exposure.

From XRD diffractograms a semiquantitative $Ca(OH)_2$/$CaCO_3$ relation can be obtained to compare the carbonation of the samples exposed in the presence of water. Peaks at $2\vartheta = 23.02°$ and 18.08° from $CaCO_3$ and $Ca(OH)_2$, respectively, were selected for the semiquantitative analyses. The selected peaks are free from any interference with other compounds present in the samples. Table 3 summarizes the results. $I_{Ca(OH)2}/I_{CaCO3}$ for the mortars cured 7 days is higher than for the mortars cured for only 1 day. Longer cured time produce greater hydration, in addition to $Ca(OH)_2$ formation. In both cases, the presence of ozone was found to increase $CaCO_3$ formation.

Due to the presence of $Ca(OH)_2$, the pH of the pore solution for the dry conditions exposed samples is relatively high (about 12). At this pH level, CO_3^{2-} formation is faster than SO_3^{2-}; thus, more $CaCO_3$ is formed than $CaSO_4$. For the mortars exposed under wet conditions, the presence of water enhanced CO_2 (g) dissolution and $CaCO_3$ formation; hence, no $Ca(OH)_2$ was observed. Under these conditions the pH of the pore solution is lower, closer to pH = 7, and so SO_3^{2-} formation is enhanced.

2.3. FTIR analyses of the surface of the mortars

Compositional analyses of the surface of the samples after 28-day exposure under different conditions were studied by FTIR. In the case of the mortars cured 1 day, SiO_2 bands from quartz and CO_3^{2-} from calcite were found to be present under all exposure conditions, indicating that carbonation process occurred on the sample surfaces. As discussed previously, the high pH level of the pore solution favors the formation of CO_3^{2-} rather than SO_3^{2-}.

Table 2
Exposure conditions in the chambers

Chamber	ppm SO_2	ppm O_3	mL H_2O/L air
1	2.5		
2	2.5		70×10^{-3}
3	2.5	10	
4	2.5	10	70×10^{-3}

Table 3
Relationship of the XRD peaks of $Ca(OH)_2$ and $CaCO_3$

Sample	Exposure conditions	$I_{Ca(OH)2}/I_{CaCO3}$
Cement mortar w/c = 0.6 (1 day)	SO_2	0.2
	$SO_2 + O_3$	0.4
Cement mortar w/c = 0.6 (7 days)	SO_2	0.9
	$SO_2 + O_3$	0.6

For the mortars exposed in the chambers in the absence of water, additional bands at 1100; 990 and 617 cm^{-}1 were present. Potassium sulfate vibrations were identified at 1100 and 617 cm^{-1}. The sharp band at 990 cm^{-1} arises from SO_3^{2-} vibrations. Elfving [9] and Zappia et al. [7] were in agreement that any sulfite present in $Ca(OH)_2$ or mortar sulfation was in the form of calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$).

For those samples exposed in chambers with presence of water (wet conditions), white surfaces were formed. FTIR analyses of these areas revealed bands at 1190, 1135, 1123, 668, 643, and 615 cm^{-1}, indicating the presence of syngenite ($K_2Ca(SO_4)_2 \cdot 2H_2O$). Additionally, several bands from gypsum and potassium sulfate vibrations are detected. Further, another narrow band at 947 cm^{-1}, with a small shoulder at 960 cm^{-1} arising from SO_3^{2-} vibrations, also is detected. Some areas of the surface of the mortars exposed to wet conditions are without white deposit. In the absence of ozone, some increases in the broadness of the 1100 cm^{-1} band is observed, indicating vibrations of the SO_4^{2-} group. However, for the mortars exposed in the presence of ozone different bands from gypsum, syngenite, sulfite, and potassium sulfate were detected.

Summarizing the FTIR results of the mortars cured for 1 day and subjected to 28-day exposure in chambers under dry conditions revealed that the salts formed were K_2SO_4 and SO_3^{2-}, independent of the presence of absence of ozone. However, under wet conditions syngenite and gypsum were found in addition to K_2SO_4 and SO_3^{2-}.

The chemical compositions of the surface salts formed on the samples cured for 7 days and exposed to SO_2 were analyzed by FTIR. A broad band at 1420 cm^{-1} and strong peaks at 874 and 714 cm^{-1} arise from CO_3^{2-} vibrations from $CaCO_3$ as calcite. These bands are present in all the samples, indicating that the reaction between $Ca(OH)_2$ and CO_2 occurred. A broad band at 1000–970 cm^{-1} arises from C-S-H vibrations; additionally, two sharp peaks at 980 and 657 cm^{-1} indicated SO_3^{2-} vibrations. These findings are in agreement with previous studies [7,9], confirming the formation of calcium sulfite hemihydrate formation. The broad band at 1150–1100 cm^{-1}, together with the two peaks at 613 and 600 cm^{-1}, arise from the presence of SO_4^{2-} at the mortar surface. Similar spectra were obtained for the samples exposed to SO_2 plus ozone.

In the presence of water, in addition to CO_3^{2-}, SO_3^{2-}, and K_2SO_4 vibrations, absorptions from syngenite were identified. White deposits on the surface of the mortar were observed, FTIR analyses of which revealed relatively high concentrations of potassium sulfate. Syngenite and sulfite vibrations also were detected. FTIR analysis of the white deposits on the mortars exposed to SO_2 in the presence of wetting and ozone revealed the presence of gypsum, syngenite, and sulfite. No K_2SO_4 was detected.

As was found for the mortars cured for 1 day and exposed under dry conditions, no gypsum or syngenite were detected by FTIR. However, in the additional presence of water, both salts were detected.

The sample bulk was analyzed by XRD and the exposed surface by FTIR. No $Ca(OH)_2$ was detected at the surface due to the total carbonation of the surface. However, XRD detected free calcium hydroxide because the bulk of carbonation was incomplete. The salts formed in the mortars under SO_2 exposure were not detected by XRD because the quantities were too small and beyond the detection limit of the technique.

Table 4 shows the salts formed on the surface of the samples after 28-day exposure under various conditions. Identification was carried out using FTIR.

Jawed et al. [1] proposed that, on initial contact of cement and water, an exchange of ionic species between the solids and the liquid phase occurred. The high water solubility of calcium aluminates, sulfates, and alkalis from the clinker leads to a rapid increase in concentration of the liquid phase with respect to Ca^{2+}, OH^-, $Al(OH)_4^-$, SO_4^{2-}, K^+, and Na^+. The composition of this liquid phase is a dynamic system constantly changing with time. Neville [10] proposed that when the relative humidity is higher than 80%, little movement of water between the mortar and the ambient air occurs, which favors SO_2 gas dissolution in water and further sulfation reactions. Therefore, depending on the liquid phase conditions, different salts are formed.

For the samples cured for only 1 day and exposed under dry conditions, in addition to SO_3^{2-}, potassium sulfate was formed. However, under wet conditions, a potassium-calcium sulfate such as syngenite ($K_2Ca(SO_4)_2 \cdot 2H_2O$) was produced. According to the solubilities of the salts formed (Table 5), potassium sulfate is a kinetic product and syngenite is a thermodynamic product. Due to its high solubility,

Table 4
Salts formed on the surface of the samples after 4 weeks of exposure to different conditions

Time exposure (days)	Exposure conditions	SO_3^{2-}	K_2SO_4	$K_2Ca(SO_4) \cdot 2H_2O$ (syngenite)	$CaSO_4 \cdot 2H_2O$ (gypsum)
1	SO_2	+	+		
	$SO_2 + O_3$	+	+		
	$SO_2 + H_2O$	+	+	+	+
	$SO_2 + O_3 + H_2O$	+	+	+	+
7	SO_2	+	+		
	$SO_2 + O_3$	+	+		
	$SO_2 + H_2O$	+	++	+	
	$SO_2 + O_3 + H_2O$	+		+	+

Table 5
Solubility of different alkali and calcium salts at 25°C

Salts	Solubility (g/L)
$CaSO_3 \cdot 1/2H_2O$	0.04
$CaSO_4 \cdot 2H_2O$ (gypsum)	2.4
$K_2Ca(SO_4)_2 \cdot 2H_2O$ (syngenite)	2.5
K_2SO_4	120

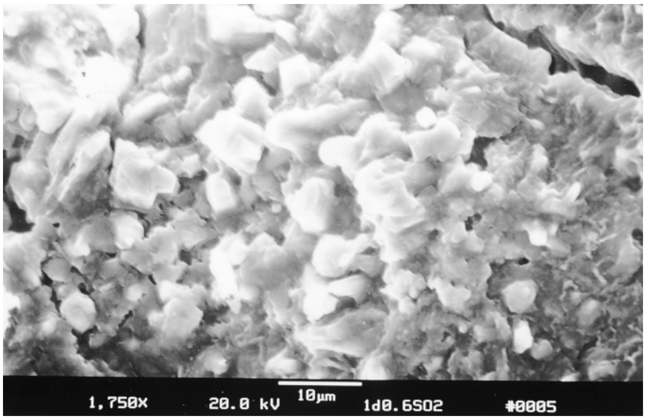

Fig. 2. SEM of the K_2SO_4 formed in the mortar cured for 1 day and exposed to dry conditions.

potassium sulfate is the product of the reaction in less aggressive conditions. Furthermore, for the samples exposed to wet conditions, which are more aggressive than dry conditions, a potassium-calcium sulfate with lower solubility was formed.

As expected, similar behavior was established for the samples cured for 7 days. In dry conditions, a kinetic control product such as K_2SO_4 was formed. However, under wet conditions, thermodynamic control products such as gypsum ($CaSO_4 \cdot 2H_2O$) and syngenite ($K_2Ca(SO_4)_2 \cdot 2H_2O$) were produced.

2.4. SEM analyses

The morphological and mineralogical composition of the exposed mortars was analyzed by SEM/EDX. For the mortar cured for 1 day and exposed under dry conditions, irregular forms growing in the sample were observed (Fig. 2). EDX analyses of these forms revealed the presence of S and K, which is in agreement with K_2SO_4 formation as indicated by FTIR. The amorphous C-S-H gel formed in the hydration reaction is shown in Fig. 3.

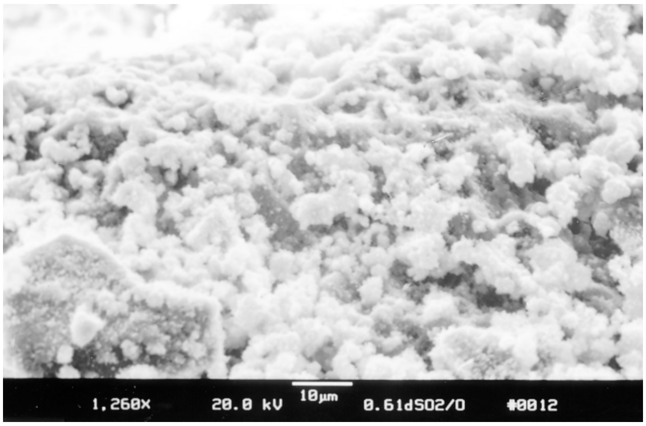

Fig. 3. SEM image of C-S-H formed in the mortars cured for 1 day and exposed to dry conditions.

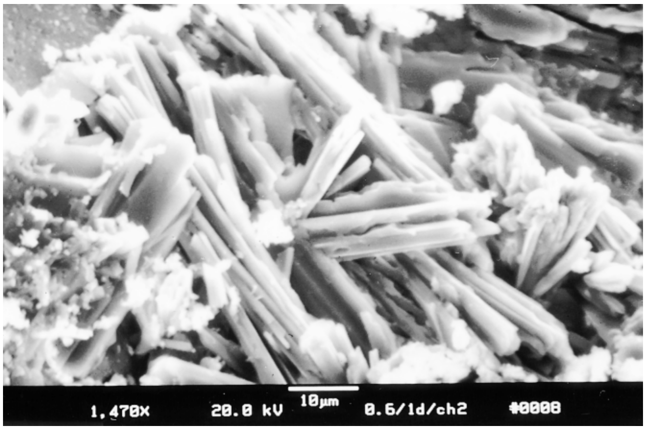

Fig. 4. SEM image of crystals formed in the samples cured for 1 day and exposed to wet conditions. Ca, S, and K are in their composition.

In the case of the samples exposed under wet conditions, another crystal with a different morphology was observed (Fig. 4). Analysis by EDX indicated the presence of S, K, and Ca, confirming syngenite ($K_2Ca(SO_4)_2 \cdot 2H_2O$) formation. The product of the hydration of the clinker silicates, C-S-H gel, is similar to that observed previously. It therefore can be concluded that the product of the hydration of the clinker silicates, C-S-H gel, has not been influenced by the presence of SO_2.

With regard to the mortars cured for 7 days and exposed under dry conditions, no crystals were observed. Similar amorphous C-S-H was detected. Subsequent analyses of the mortars exposed to wet conditions revealed large amount of crystals even at low magnifications (Fig. 5). The elemental composition of these crystals is basically S and Ca. Another crystal having a needle-like form also was observed. EDX analysis of the crystals revealed the presence of K, S, and Ca. Similar amorphous C-S-H gel formed in the hydration reaction was observed and, again, no difference in the microstructural composition of the C-S-H gel was found.

Jawed et al. [1] described torbermorite gel morphologies

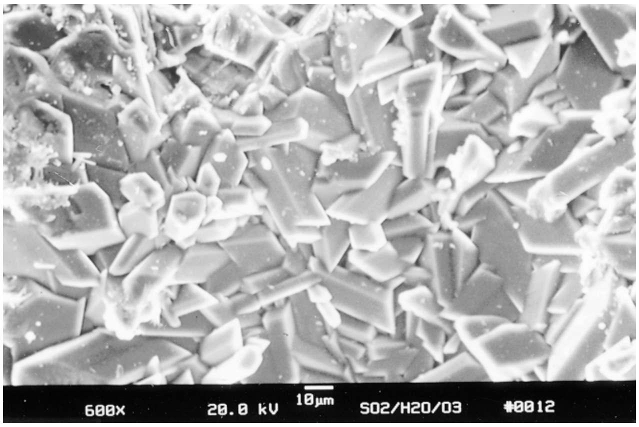

Fig. 5. SEM image of crystals formed in the samples cured for 7 days and exposed to wet conditions. Ca and S are the main components.

according to SEM and transmission electron microscopy studies. From SEM studies, the designation I to IV has been used to describe different morphologies, i.e., I for needles radiating from grain; II for reticulated morphology; III for indefinite; and IV for spherical agglomerate morphology. According to Fig. 3, 5, 6 and 8, torbermorite gel morphology correspond to type I-like needles radiating from grain. According to SEM results, no differences in the morphology of the C-S-H gel were found from mortars exposed to various conditions as well as curing time. However, different salts composition under different exposure conditions were detected. Generally, under dry conditions, SO_3^{2-} and K_2SO_4 were the main salts formed, but, under wet conditions, syngenite and gypsum also were formed.

At the moment, no relationship has been found between torbermorite gel composition and morphology and salt formation. Further research in this area is necessary.

3. Conclusions

The main conclusions of this paper can be summarized as follows:

1. Mortar cement cured for 1 and 7 days exposed to SO_2 conditions showed weight decrease due to the formation of various salts.
2. The chemical composition of the bulk mortar as determined by XRD indentified quartz, calcite, and C-S-H gel.
3. FTIR analysis of the salts formed on the surface of the mortars revealed that, under dry conditions, more soluble salt as kinetic product had formed. On the other hand, under wet conditions, less soluble salts as thermodynamic product were noted on analysis.
4. Under wet conditions, CO_2(g) dissolution in water is promoted and the carbonation process proceeds at a greater rate; thus $Ca(OH)_2$ is not observed.
5. The pH of the pore solution under dry conditions is close to 12 due to the presence of $Ca(OH)_2$. Under these conditions, very little SO_3^{2-} is formed. However, under wet conditions, without $Ca(OH)_2$, the pH of the pore solution decreases and SO_3^{2-} is formed in greater quantities.
6. According to SEM results, the morphological composition of C-S-H is type I, needles radiating from grain.

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