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COMPOSITION OF ALKALI SILICA GEL AND ETTRINGITE IN CONCRETE RAILROAD TIES: SEM-EDX AND X-RAY DIFFRACTION ANALYSES

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ABSTRACT

Alkali silica gel and ettringite observed in concrete railroad ties were analysed by SEM-EDX and X-ray diffraction. The compositions, represented in the Si-Ca-Na + K system, of clear gel were in the range of 53 to 63 atomic% Si and 20 to 30 atomic% Ca. The K + Na contents were constant and about 15% (excluding oxygen, water and trace elements). Analyses of crystallized gel showed a constant ratio between Si, Ca and Na + K of 70 : 15 : 15. Analyses of the Si and Ca content, of crystallized gel in cracks inside the aggregate particles, and clear gel at the mouth of the cracks and in air voids revealed a compositional difference with the crystallized gel as higher Si and lower in Ca. The content of Si decreases and Ca increases in gel away from the aggregate particles. The gel compositions are in the range published in the literature. The composition of ettringite is close to stoichiometrical values for ettringite, however, slightly lower in sulfur. The X-ray diffraction analyses identified the ettringite as crystalline.

Introduction

The alkali silica gel and ettringite analyzed in this study were found in 4 to 9 years old, steam cured, prestressed concrete railroad ties.

The concrete was made with ASTM type III cement with an alkali content of 0.8-0.9% Na_2O eq. The cement content of the concrete is about 440 kg/m^3 with an average water to cement ratio of 0.42. Air entraining agent, plastizising and retarding admixtures were used in the concrete mix.

The analyzed samples are from concrete ties showing crack patterns typical for alkali silica reaction. Longitudinal cracks are found on the surface of the ties. Map cracks are found near the shoulders of the ties where the crack pattern is not modified by the prestressing. The alkali silica reactive aggregates in the concrete are various mylonites (1) of which a microcrystalline quartz-rich feldspatic schist (Figure 1) is the most commonly observed aggregate containing

FIG. 1.
Alkali silica reactive mylonite aggregate of the concrete. Abbreviations: Q = Quartz, F = Feldspar, M = Mica. The field of image measures 4.1 x 6.1 mm. Crossed Polarizers.

FIG. 2.
Clear alkali silica gel in air voids and in a crack through a mylonite aggregate (arrow). The field of image measures 1.1 x 1.6 mm. Ordinary light.

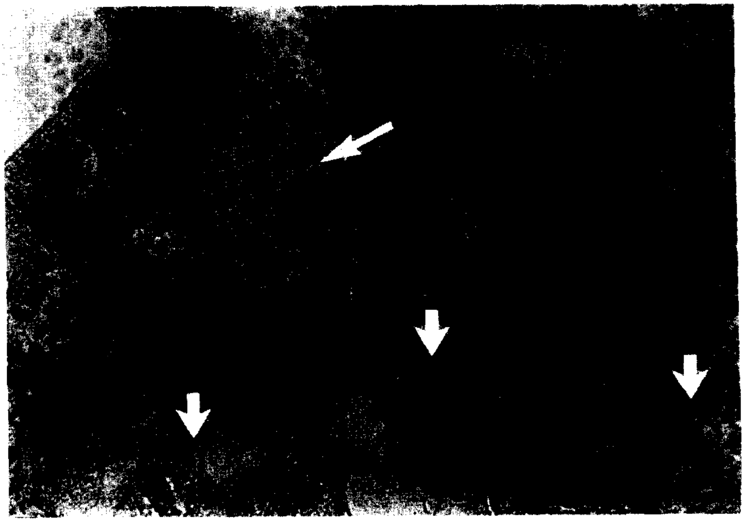

FIG. 3.
Ettringite in air voids and at the interface between the aggregate and cement paste (arrows). The field of image measures 0.4 x 0.6 mm. Ordinary light.

cracks with alkali silica gel. A mylonitized rock with a more granitic composition is, however, also found to be alkali silica reactive. A recent study on these mylonitic aggregates (2) established that alkali silica reaction occurs along grain boundaries of the microcrystalline quartz in the mylonites.

Alkali silica reaction products, such as clear gel (Figure 2), occur in cracks through the aggregates (mylonites), in cracks through the cement paste and along the rim or filling the air voids. Moreover, rosette-like crystals of alkali silica reaction product showing birefrigence (the socalled crystallized gel) occur inside the cracks in the coarse aggregate particles. Ettringite, generally needle shaped, occurs in cracks through the cement paste, at the interface between aggregates and cement paste and along the rim or filling the air voids (Figure 3).

The purpose of the present work is to verify the composition of the by microscopy identified pure depositions of gel and ettringite by SEM-EDX and X-ray analyses. Mixtures of ettringite and alkali silica gel were seen both in the optical microscope and in the SEM-EDX, however, analyses of the mixtures are not included in this paper. Discussion about the age relation between alkali silica gel and ettringite are not included in this paper but resently published by Johansen et al. (3).

Experimental

SEM-EDX Analyses. A majority of the SEM-EDX analyses were performed on an ADEM Scanning Electron Microscope equipped with an EDX-detector[1]. The analyses were performed

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at 20 kV accelerating voltage and a beam current in the range of 1 to 3 nA and 60 second time. The results were ZAF-corrected. Few SEM analyses where analysed on a JEOL 733 Superprope equipped with an EDX-detector[2]. The accelerating voltage was 15 kV and the beam current 2.01 nA. The JEOL program PACX was used for ZAF correction and intrumental control. The instrument was calibrated on known mineral standards prior to analysis.

The samples used for the SEM-EDX determination of the composition of alkali silica gel and ettringite were 20 µm thick, epoxy-impregnated, polished thin sections (4). The thin sections were carbon-coated. Areas with gel (Figure 2) and ettringite (Figure 3) were identified under an optical microscope in transmitted light. The same areas were relocated in the SEM and a total of more than 448 points in 129 thin sections were analysed. The combined use of optical microscopy and SEM-EDX on railroad ties has been published by Thaulow et al. (5).

X-ray Diffraction Analyses. Two kinds of X-ray diffraction analyses were performed[3] on ettringite:

a) Powder diffraction analysis done on a Philips PW 1050 diffractometer with a vertical goniometer.
b) Gandolfi Method done on a Gandolfi camera manufactured by Officina Eletrotechnica de Tenno.

CuKα radiation was used in both methods.

Ettringite was collected from the surface of two fractured concrete cores. The ettringite was situated (i) in air voids, (ii) on coarse aggregate surfaces, and (iii) on the imprints of coarse aggregates in the cement paste. In each case of analyses the ettringite was carefully scraped off with a thin, pointed needle and/or with a new scalpel.

The ettringite for powder diffraction was collected in a small agate mortar. The ettringite was first cleaned of larger pieces of material that were obviously not ettringite such as quartz and micas. To reduce background scatter the sample was then placed on a non-reflecting, single-crystal quartz plate. Finally the ettringite was ground with an agate pestle to get a large even surface of ettringite on the plate.

The ettringite for Gandolfi analysis was collected from a single air void in each case. Only very small quantities were needed. The glass needle mount was wetted in resin which had not been mixed with hardener. In this way the scraped off ettringite stuck on to the end of the needle. The mount was then checked under the microscope before being put in the camera. The exposure time for each sample was 12 hours.

Results and Discussion

SEM-EDX Analyses. The average compositions (by atomic %) of clear gel, crystallized gel and ettringite are found in Tables 1 and 2. The relative composition of alkali silica gel and ettringite are plotted in the Si-Ca-K+Na ternary diagram of Figures 4 and 5, respectively. The analyses in these diagrams are normalized to 100% excluding trace elements, water and oxygen.

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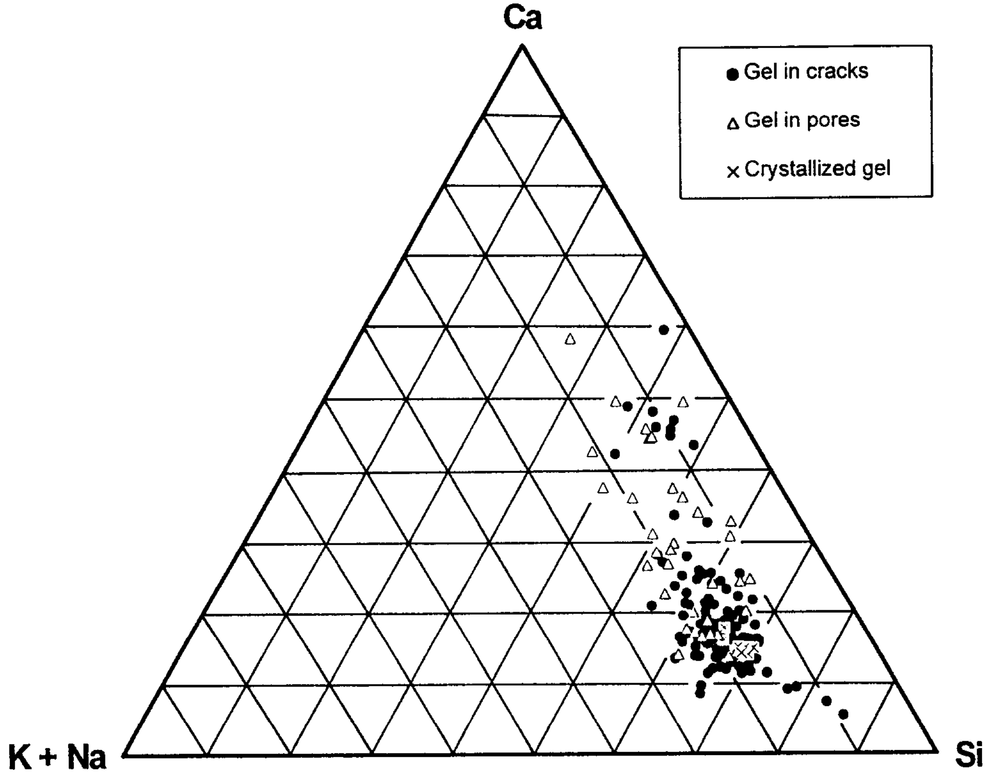

FIG. 4.

Ternary diagram (Si-Ca-K + Na) showing the composition of clear gel in cracks and in air voids and crystallized gel in cracks inside the aggregates (atomic% excluding water, oxygen and trace elements).

Alkali Silica Gel. In all the samples where alkali silica reaction products were observed in the optical microscope the SEM-EDX analyses confirmed the observation and typical gel compositions were found. Furthermore gel was found by SEM-EDX in microcracks in few thin sections where the magnification of the optical microscope (630x) was not high enough to positively identify alkali silica reaction products.

The composition of the 129 analysed samples of clear alkali silica gel are similar to earlier published results (6, 7, 8, 9, 10, 11) with high and varying contents of silica, lower and varying contents of calcium and low and relatively constant contents of sodium+potassium (Figure 4, Table 1).

Most of the analysed clear gel samples (Figure 4) fall within the range of 53-63% Si and 20-30% Ca, however, as seen on Figure 4 a large spread of 75-40% Si and 60-25% Ca are observed for all samples. The K + Na content is more and less constant about 15% (Figure 4).

The composition of the crystallized alkali silica reaction product seems to have fixed proportions of Si, Ca and Na + K corresponding to 70% Si, 15% Ca and 15% K + Na (Figure 4). This is in accordance with earlier results (8).

TABLE 1

Chemical Composition: Average, Standard Deviation, Minimum and Maximum Values of Clear and Crystalline Gel (oxygen and trace elements included)

GEL COMPOSITION

CLEAR GEL

	Atomic%	Na	Mg	Al	Si	S	K	Ca	Fe	O
IN PASTE CRACKS n = 118	Average	2.64	0.52	0.91	24.49	0.49	3.93	7.54	0.45	60.86
	Stdev	1.28	0.46	0.76	2.84	0.35	1.15	3.80	0.36	1.22
	Min	0.37	0.10	0.10	12.87	0.10	0.73	1.89	0.10	56.97
	Max	6.28	2.28	3.00	31.60	2.72	7.30	20.53	1.90	64.50

	Atomic%	Na	Mg	Al	Si	S	K	Ca	Fe	O
IN PORES n = 36	Average	2.49	0.50	0.91	21.72	0.42	4.41	12.30	0.40	58.40
	Stdev	1.03	0.36	0.74	3.80	0.21	1.87	5.08	0.29	4.13
	Min	0.75	0.13	0.10	11.55	0.10	1.29	5.23	0.12	42.91
	Max	5.25	1.17	2.67	28.55	0.84	9.99	25.73	1.14	61.59

CRYSTALLIZED GEL

	Atomic%	Na	Mg	Al	Si	S	K	Ca	Fe	O
IN AGGREGATE n = 9	Average	1.63	0.08	0.08	26.06	0.06	4.66	5.66	0.19	61.58
	Stdev	0.49	0.15	0.20	0.66	0.05	0.52	0.48	0.32	0.37
	Min	1.09	0.00	0.00	24.77	0.00	4.17	5.26	0.00	61.04
	Max	2.50	0.44	0.61	26.98	0.15	5.55	6.83	1.02	62.19

As shown in the ternary diagram of Figure 4 the composition of gel in cracks and in pores constitute a band extending from the crystallized gel towards the Si-Ca side of the ternary diagram with Ca/Si ratios around 1.7. The series of compositions extending from the crystallized gel area towards the Si corner are considered to be due to interference of Si of the aggregates in close proximity to the analysed gel.

The average compositions of Si and Ca (Table 1) are different in the three gel types analysed. Depending on contact of the gel with aggregates or paste the amount of Si and Ca either increases or decreases. In contact with aggregates the Si content is highest in the crystallized gel (26.06 atomic%) decreasing to 24.49 atomic% in the gel in paste cracks and further to 21.72 atomic% in gel in pores. The opposite trend is observed for Ca. The highest Ca content is found in gel in pores (12.3 atomic%), decreasing to 7.54 atomic % in gel in cracks and to 5.66 atomic% in crystallized gel in aggregates.

The marked difference of especially Ca in clear gel in cracks versus gel in air voids (Table 1) have been, beside in these samples, observed in a number of other gel samples analysed. It has been noted that gel in close contact with cement paste in general are more Ca-rich in older than in younger concretes and that the content of Ca in gel in cracks increases away from the aggregate particles (11). It is therefore believed that the quantity of the Ca content of gel is a result of a reaction between gel and paste, the position of the gel relative to the aggregate particles and that it is time dependent giving a more calcium-rich gel with time irrespective of the position of the gel. However, relatively to the position, the gel in direct contact to the

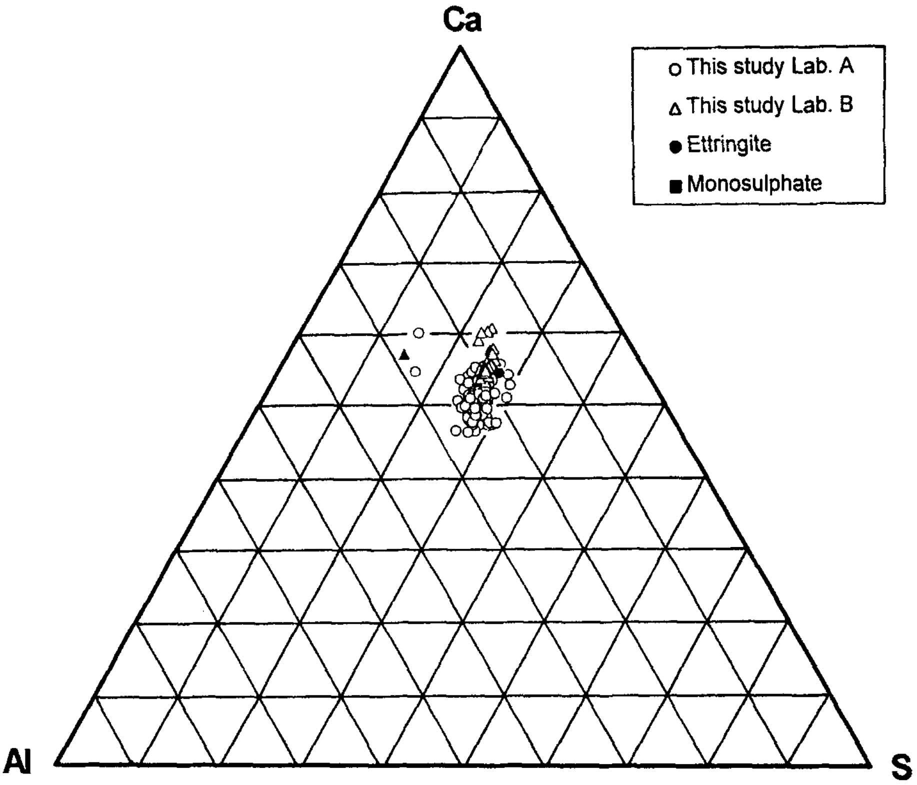

FIG. 5.
Ternary diagram (Al-Ca-S) showing the composition of ettringite of this study, stochiometrical ettringite and monosulphate (atomic% excluding trace elements and oxygen).

cement paste will initially have a higher content of calcium in contrast to the crystallized gel which always is observed to be situated in cracks inside coarse aggregate particles.

Ettringite. The ettringite analyses are shown in Table 2 and presented in the triangular diagram of Figure 5 together with stoichiometric ettringite, $3CaO.Al_2O_3.3CaSO_4.32H_2O$ and monosulphate $3CaO.Al_2O_3.CaSO_4.12H_2O$.

The ettringite identified in the optical microscope was confirmed to be ettringite by the SEM-EDX analyses. Of all the analysed samples only two of the analyses were close to monosulphate in composition, the majority of the 139 analyses showed a composition close to that of ettringite (Figure 5).

The ettringite composition is independent of the position in paste cracks, in interfacial cracks or in pores (Table 2). The composition of the three ettringite types is similar, however, none of the analyses are of pure stoichiometric ettringite composition (Table 2). They are all slightly lower in sulphur, higher in Al and Ca and contains some Si. It is believed that this deviation from pure stoichiometric composition may reflect a substitution of SO_4^{2-} by SiO_4^{4-} in the

TABLE 2

Chemical Composition: Average, Standard Deviation, Minimum and Maximum Values of Ettringite in Paste Cracks, Interfaces and Pores (atomic%, oxygen and trace elements included, water excluded)

ETTRINGITE COMPOSITION

	Atomic %	Na	Mg	Al	Si	S	K	Ca	Fe	O
IN PASTE CRACKS n = 43	Average	0.24	0.00	8.62	0.61	9.37	0.24	19.14	0.05	61.73
	Stdev	0.26	0.02	0.73	0.71	0.74	0.12	1.32	0.04	0.63
	Min	0.00	0.00	6.74	0.00	6.02	0.11	17.30	0.00	58.60
	Max	0.99	0.16	10.37	4.27	10.39	0.69	24.76	0.17	62.36
IN INTERFACE n = 13	Average	0.22	0.03	8.60	0.99	9.24	0.29	18.83	0.15	61.76
	Stdev	0.19	0.11	0.77	0.84	0.44	0.15	0.80	0.30	0.31
	Min	0.00	0.00	7.19	0.00	8.26	0.14	17.21	0.00	61.22
	Max	0.55	0.38	10.66	2.42	9.98	0.59	19.85	1.13	62.17
IN PORES n = 58	Average	0.30	0.05	8.57	0.53	9.41	0.32	19.04	0.07	61.68
	Stdev	0.31	0.30	0.72	0.73	0.93	0.28	1.03	0.19	0.70
	Min	0.00	0.00	6.44	0.00	4.26	0.00	17.20	0.00	58.34
	Max	1.17	2.19	10.77	2.77	10.44	1.96	21.49	1.39	62.64

ettringite lattice. The extra negative charges may have been balanced by the extra Al og Ca present.

X-ray Diffraction of Ettringite. The ettringite observed and analysed during optical microscopy and SEM-EDX, respectively, has been positively identified as crystalline ettringite by both X-ray diffraction methods.

Ettringite peaks can be identified in all diffractograms. The peaks were, however, not very strong in one of the samples and the content of other minerals, notably portlandite ($Ca(OH)_2$), quartz, feldspar and mica, probably complicated the identification.

The gandolfi film made from both samples (pore) also positively identifies ettringite (Figure 6).

Conclusions

The following conclusions can be drawn from the study of alkali silica gel and ettringite found in concrete railroad ties:

*The SEM-EDX analyses confirmed the optical identification of alkali silica reaction products and that of ettringite in a large number of thin sections from concrete railroad ties.

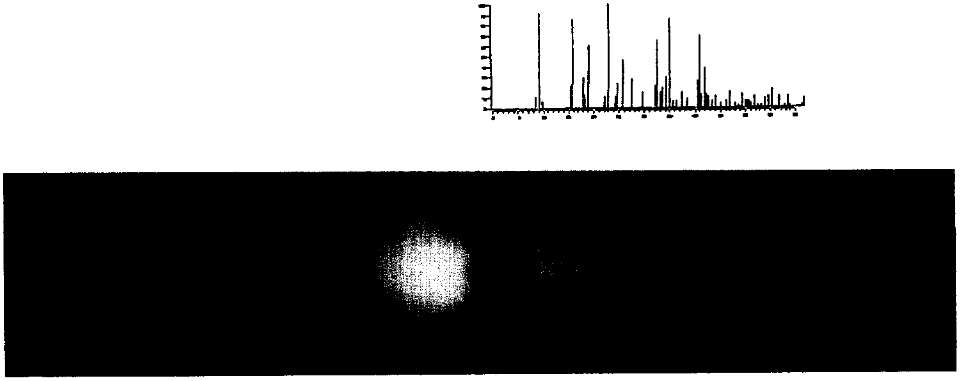

FIG. 6.
Positive print of Gandolfi film of one of the samples. Ettringite lines from the JCPDS index are inserted for comparison.

*Gel in air voids were in most cases found to be richer in calcium compared to gel in cracks in aggregates due to the possible reaction between gel and cement paste.
*The amount of calcium in the gel is strongly dependent on the position of the gel (in contact with cement paste or not).
*Crystallized alkali silica product which is never observed in contact with the cement paste has a constant composition.
*The ettringite analysed had compositions close to stoichiometrical with some Si present. The S content was thus a little lower than the theoretical composition. It is believed that SO_4^{2-} is subtituted by SiO_4^{4-} in the ettringite lattice.
*Material with the composition of monosulphate was identified in two cases only.
*The powder diffraction method and the Gandolfi method positively identified the ettringite observed by optical microscopy and by SEM as crystalline ettringite.

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