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**EFFECT OF PHLOGOPITE MICA ON  
ALKALI-AGGREGATE EXPANSION IN CONCRETE**

by  
P. E. Grattan-Bellew and J. J. Beaudoin

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EFFECT OF PHLOGOPITE MICA ON ALKALI-AGGREGATE EXPANSION IN CONCRETE

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ABSTRACT

The tensile strength of concrete is increased by the addition of high aspect-ratio mica reinforcement. Phlogopite mica contains about 10%  $K_2O$ ; soluble  $K^+$  would contribute to the alkalinity of the pore solution in concrete enhancing its potential expansivity if it is made with alkali-expansive aggregate. Electron microprobe analysis confirms that the solubility of  $K^+$  from phlogopite in cement paste, about 0.09% is the same as in mixed calcium-sodium-hydroxide solutions. The addition of 1.5% by volume of phlogopite to concrete prisms made with alkali-carbonate expansive aggregates caused a small increase in the rate of expansion of prisms made with both high and low alkali cement. It is concluded that the addition of small quantities of phlogopite as a reinforcement in concrete is not a cause for concern, although caution should be exercised in adding larger volumes to concrete made with potentially alkali-expansive aggregate.

L'addition d'une armature de mica possédant un rapport de l'envergure à la profondeur élevé augmente la résistance à la traction du béton. Le mica phlogopite contient à peu près 10% de  $K_2O$ ; le soluble ( $K^+$ ) contribue à l'alcalinité de la solution poreuse du béton, accentuant l'expansibilité potentielle du béton composé d'un agrégat alcali-expansif. L'addition d'une quantité de phlogopite équivalant à 1.5% du volume à des prismes de béton faits d'un agrégat d'alcali-carbonate expansif a provoqué un léger accroissement de la vitesse d'expansion des prismes, que ceux-ci aient été composés d'un ciment fortement ou faiblement alcalinisé. On peut conclure que l'addition d'une petite quantité de phlogopite pour renforcer le béton ne devrait pas être un sujet de préoccupation, bien qu'on devrait exercer une certaine prudence lorsqu'on en ajoute de plus grandes quantités à un volume de béton composé d'un agrégat alcali-expansif.

### Introduction

The tensile strength and fracture toughness of portland cement paste are enhanced by the addition of small amounts of high-aspect-ratio phlogopite mica flakes. Compressive strength, in contrast, is reduced by about 30%. It is known that aggregates containing an excess of soluble alkalis can cause expansion of concrete made with expansive aggregates and even low alkali cement (1,2). The potassium content of phlogopite, derived from its chemical composition (Table 1) and expressed as  $K_2O$ , is 9.62%. Some of the potassium is known to be in an exchangeable form (3,4,5,6). Any that is soluble could potentially contribute alkali to the pore solution of the cement paste. In concrete made with alkali-expansive aggregate, therefore, the enhanced alkali content might exacerbate the alkali-aggregate reaction and contribute to a lowering of concrete strength. This study was designed to investigate possible deleterious effects of the addition of phlogopite mica flakes to concrete made with normal and alkali-expansive aggregates and high and low alkali cements.

### Experimental

#### Materials

Phlogopite mica. This is a high-aspect ratio reinforcing grade mica marketed as "Suzorite Mica."\* The flakes are generally of irregular shape with a mean width varying between 250 and 1400  $\mu m$  (Fig. 1). The physical and chemical properties of the phlogopite are shown in Table 1.

Concrete prisms. The mix design for concrete prisms,  $30 \times 7.6 \times 7.6$  cm, gauge length 25.4 cm, made at a W/C of 0.52, is given in Table 2(a). Mica comprised 1.3% by volume of the concrete; the coarse aggregate was an alkali-

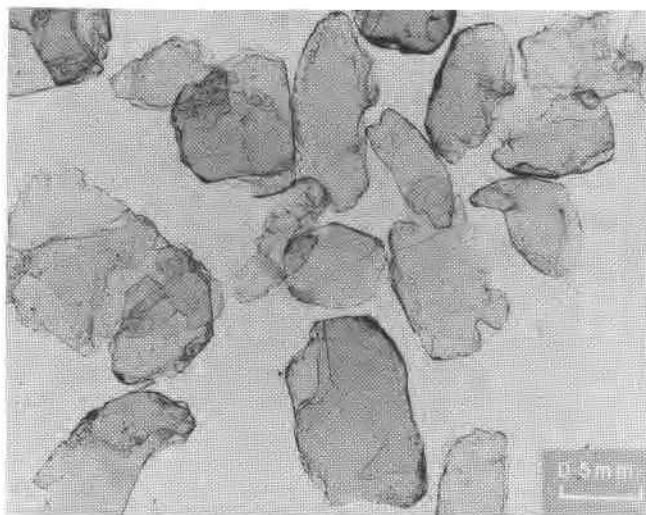


FIG. 1

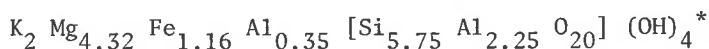
Optical micrograph showing the size and shape of typical flakes of phlogopite mica. The relative thickness of the flakes is indicated by the degree of shading.

\* Marietta Resources International Ltd., 5083 St. Denis St., Montreal, Quebec.

## PHLOGOPITE, EXPANSION, ALKALI-AGGREGATE REACTION

TABLE 1  
Physical and Chemical Properties of Phlogopite

Chemical composition:



Specific gravity: 2.90

Aspect ratio\*\*: (20 flakes)  $87 \pm 90$  (1 standard deviation)

Mean long axis of flakes:  $1019 \mu\text{m} \pm 550$

Mean short axis of flakes:  $714 \mu\text{m} \pm 156$

\* Chemical analysis by Marietta Resources International Ltd.

\*\* Aspect ratio is defined as mean width of a flake divided by its thickness

carbonate expansive dolomitic limestone from Kingston, Ontario (7); and local quartz sand was used for the sand size fraction of the aggregate. Kingston carbonate rock was selected because it causes rapid expansion when made into concrete with high alkali cement, minimizing the time needed to evaluate alkali-aggregate expansion.

Pairs of concrete prisms were made with high and low alkali cement: two pairs with Kingston aggregate containing mica, and two in which the mica was replaced by quartz sand. For comparison, an extra two pairs of prisms were made with non-expansive limestone aggregate and low alkali cement; one pair contained mica, the other pair sand.

Cement. The cements were normal portland type 1 (ASTM designation). Their total alkali and soluble alkali content are shown in Table 2(b). The solubility

TABLE 2(a)  
Mix Design For Concrete Prism

Component		Weight, grams
Cement		627
Sand		1192
Mica		63
Stone	-19 + 12.5 mm	934
	-12.5 + 9.5 mm	765
	-9.5 + 6.4 mm	340
Water		326

TABLE 2(b)

Total and Soluble Alkali Contents of Cements

	Total Alkali, %			Soluble Alkali, %		
	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O (equiv)*	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O (equiv)
High alkali cement	0.65	0.61	1.05	0.35	0.60	0.78
Low Alkali cement	0.20	0.50	0.53	0.03	0.28	0.21

\* Na<sub>2</sub>O equivalent is equal to (Na<sub>2</sub>O + K<sub>2</sub>O × 0.655)

of the alkalis was determined by ASTM method C114 (8). The soluble alkali contents were determined because they show better correlation with rate of expansion of the concrete made with expansive aggregate than do the total alkali contents. The Blaine surface area of the high alkali cement was  $372 \text{ m}^2/\text{kg}$  and that of the low alkali cement,  $338 \text{ m}^2/\text{kg}$ .

#### Calcium Hydroxide Solutions

Determination of the solubility of  $\text{K}^+$  contained in the phlogopite was carried out in solutions of saturated  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  containing 5, 10 or 25% 1N.NaOH. They were prepared with deionized water; determinations were done at 22 and 39°C.

#### Experimental Techniques

Length change of concrete prisms. The expansion of concrete prisms was determined by a modified form of CSA test A23.2-14A (9). The concrete was stored at 38°C and 100% RH. The length of the prisms representing the mean of a pair was measured twice a week for the first few weeks and then at longer intervals.

Solubility of  $\text{K}^+$  from phlogopite in calcium hydroxide solutions. The solute in the pore solution of hydrating cement paste consists largely of  $\text{Ca}(\text{OH})_2$  (10), with smaller amounts of Na, K and other elements. To simulate the potential solubility of  $\text{K}^+$  from phlogopite in cement paste, it was determined in solutions of  $\text{Ca}(\text{OH})_2$  and mixtures of  $\text{Ca}(\text{OH})_2$  and NaOH by placing 10 g phlogopite in a litre of saturated  $\text{Ca}(\text{OH})_2$  solution or a saturated  $\text{Ca}(\text{OH})_2$  solution to which 5, 10 or 25% 1N.NaOH had been added. Mixtures were placed in plastic containers and rotated during storage. Change in the  $\text{K}^+$  concentration of the solution with time was monitored by removing 10 ml aliquots at intervals and determining the concentration by atomic absorption spectrophotometer.

Change of  $\text{K}^+$  content of phlogopite contained in cement paste. In an attempt to correlate the solubility of  $\text{K}^+$  from phlogopite in cement paste with its solubility in solutions of  $\text{Ca}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2$  and NaOH, the Mg/K ratio of phlogopite was determined on flakes mixed with cement paste and those stored in the test solutions. The Mg/K ratio rather than the  $\text{K}^+$  concentration was determined because of the ease with which it could be done by electron microprobe attached to the SEM. As experiments had shown that the Mg concentration was essentially unaffected by storage of the phlogopite in  $\text{Ca}(\text{OH})_2$  solutions, changes in the Mg/K ratio must be due to changes in the  $\text{K}^+$  concentration of the mica. The determined Mg/K ratios are neither weight nor molecular ratios but ratios of the integrated intensities under the respective peaks, determined by electron microprobe; they do not necessarily correlate directly with the molecular ratios. Relative changes in the  $\text{K}^+$  concentration, however, would be reflected in the Mg/K intensity ratio.

#### Results

##### Expansion of Concrete Made with Alkali Carbonate Aggregate and 1.3% Phlogopite

It is evident in Fig. 2 that the addition of mica to a normal concrete mix has caused a small increase in the observed expansion of concretes made with both high and low alkali cement. There was only marginal increase in expansion when mica was added to a non-expansive limestone. The addition of phlogopite to concrete made with reactive aggregate and low alkali cement increased the rate of expansion from  $19 \times 10^{-3} \text{ days}^{-\frac{1}{2}}$  to  $23 \times 10^{-3} \text{ days}^{-\frac{1}{2}}$ . The addition of phlogopite to concrete made with high alkali cement resulted in a smaller percentage increase from  $53 \times 10^{-3} \text{ days}^{-\frac{1}{2}}$  to  $58 \times 10^{-3} \text{ days}^{-\frac{1}{2}}$ . It is probable that the addition of a small amount of  $\text{K}^+$  from the mica to the pore

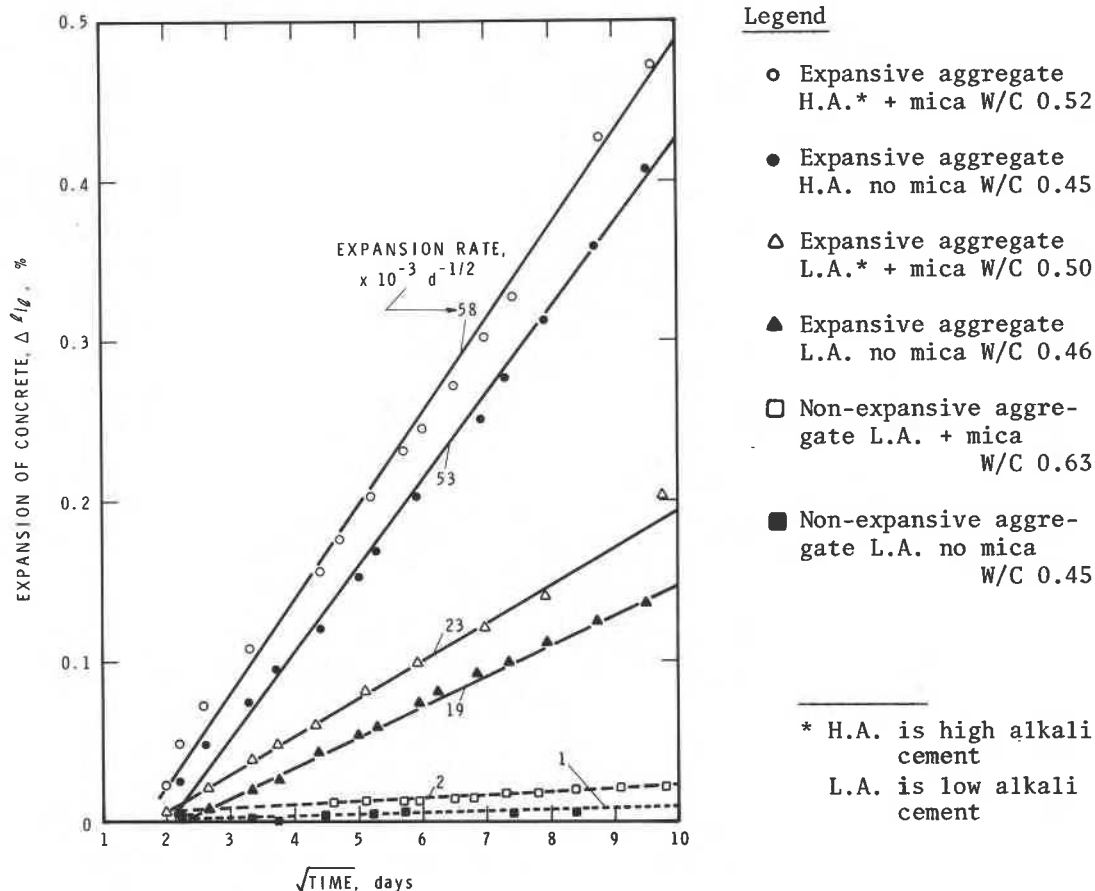


FIG. 2

Expansion of concrete prisms with time of storage at 100% RH and 38°C.

solution would have less effect on the total alkali content of the high alkali cement paste than it would on that of the low alkali cement paste because the percentage increase of the total soluble alkali would be smaller.

The effect of adding mica flakes on the expansion of concrete made with reactive aggregate is influenced by several factors:

(1) Mica flakes increase the flexural strength of the composite, tending to reduce expansion of concrete.

(2) The presence of mica in the paste fraction of concrete increases the porosity of the cement paste. This has the effect of decreasing the concentration of alkali in the saturated paste by the dilution effect, and tends to decrease the rate of reaction.

(3) The soluble alkali from phlogopite increases the alkali content of the pore solution, enhancing the rate of reaction.

(4) The increased W/C ratio when mica is added increases porosity, weakening the concrete and increasing the potential for expansion.

(5) Increase in the W/C ratio has the effect, at least in the early stages of hydration, of diluting the alkali, tending to reduce the observed expansion.

Experiment has shown that the net effect of adding phlogopite has been an increase in rate of expansion of concrete (Fig. 2). It is not possible, however, to determine the contributions of the individual factors.

#### Solubility of $K^+$ in $Ca(OH)_2$ and $Ca(OH)_2+NaOH$ Solutions

It is shown in Fig. 3 that the addition of even 5% NaOH to  $Ca(OH)_2$  solution increases the amount of  $K^+$  extracted from phlogopite, in agreement with previous observations (11). The change in the rate of extraction of  $K^+$  from phlogopite with time is shown in Fig. 4 and Table 3. The initial high rate of extraction of  $K^+$ ,  $9.72\text{ d}^{-\frac{1}{2}}$  lasts for less than a day, and the subsequent rate is very low,  $0.11\text{ d}^{-\frac{1}{2}}$ . Similar results were obtained with other solutions. In general, the addition of NaOH to  $Ca(OH)_2$  solution affects only the initial rate of extraction of  $K^+$  from phlogopite; after the first day, the rates of extraction are essentially the same for all solutions.

#### Determination of Mg/K Ratio by Electron Microprobe

The results of probe analysis of flakes of phlogopite are given in Table 4. There is an increase in the Mg/K ratio with time owing to a reduction in the amount of  $K^+$  in the mica. The Mg/K measured on phlogopite reinforcement in one-year-old cement paste was about the same as that in mica in  $Ca(OH)_2$  solution for a week or more. It is expected that the value of Mg/K for

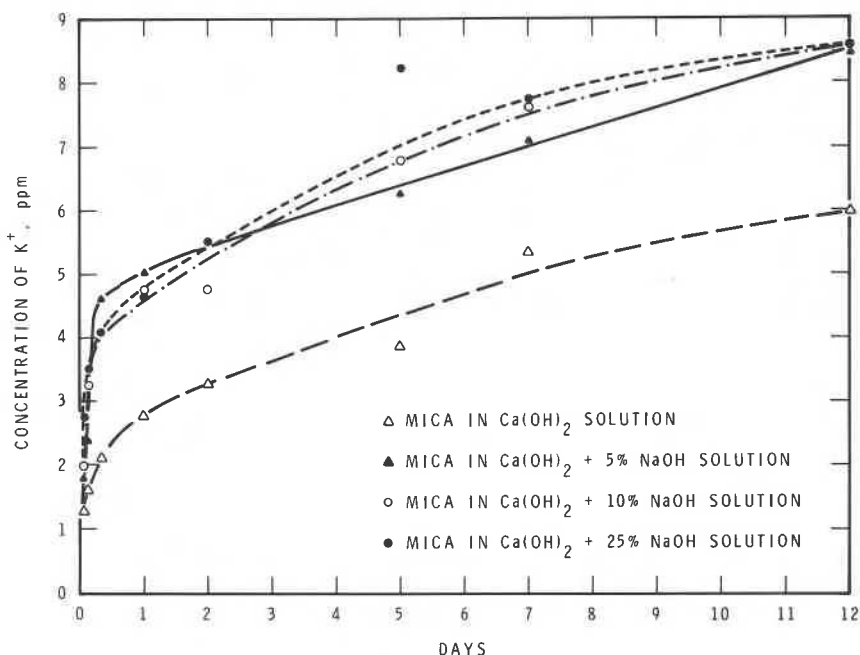


FIG. 3

Change in  $K^+$  concentration in solution of  $Ca(OH)_2$  and NaOH containing phlogopite mica as determined by atomic adsorption

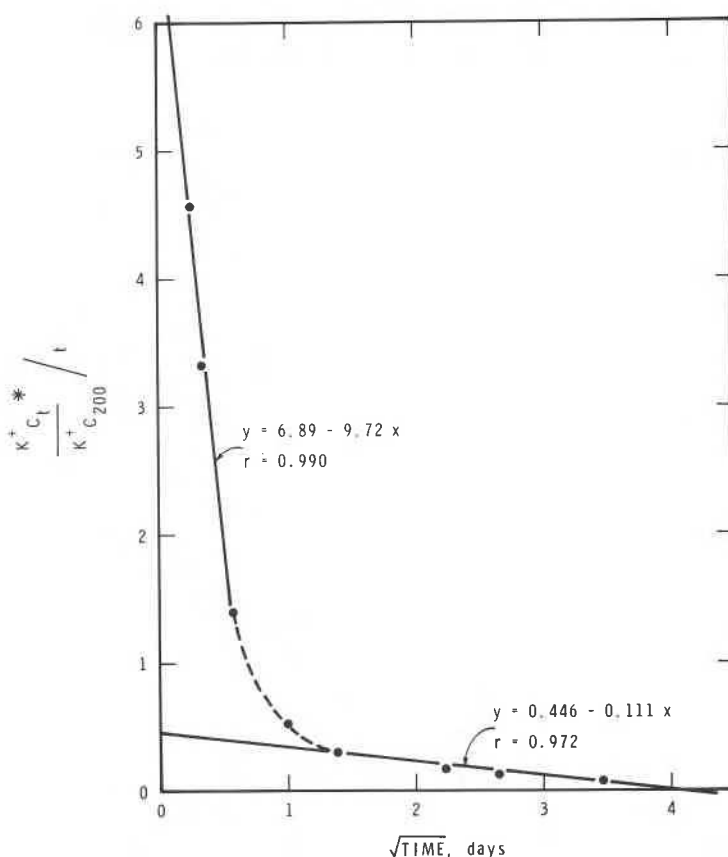


FIG. 4

Rate of extraction of  $K^+$  from phlogopite in calcium hydroxide solution containing 25% NaOH.

\*  $K^+$  concentration at time  $t/K^+$  concentration at 200 days.

phlogopite in cement paste would be essentially the same after one week as after one year. The Mg/K ratio varied considerably even within one untreated mica flake; to overcome this variation at least eight measurements were made on each sample and the results were averaged to give the listed values. The data for Mg/Al ratio in Table 4 show little change after treatment of the mica with  $\text{Ca}(\text{OH})_2$  solutions, indicating that Mg is unaffected by it and lending credibility to the technique. Increasing the temperature from 22 to 38°C does not appear to have any appreciable effect on the solubility of  $K^+$  in calcium hydroxide solutions. The value of 1.33 for Mg/K from phlogopite reinforcement in one-year-old cement paste is compatible with the values obtained from phlogopites immersed in a solution of  $\text{Ca}(\text{OH})_2 + \text{NaOH}$  for a few days. An increase of 14.6% in the Mg/K ratio\* was observed in the mica in one-day-old cement

\* Percentage change in Mg/K ratio is used here as the determination on the mica in one-day-old cement paste was done subsequent to the other determinations. The operating conditions of the electron microprobe had changed and thus the figures obtained are not directly comparable.

TABLE 3

Extraction of  $K^+$  from Phlogopite with Time in  $Ca(OH)_2$  and  $Ca(OH)_2+NaOH$  Solutions

Square		Solutions							
Time	Root	$Ca(OH)_2$		$Ca(OH)_2+5\%NaOH$		$Ca(OH)_2+10\%NaOH$		$Ca(OH)_2+25\%NaOH$	
days	Time	$K^+$		$K^+$		$K^+$		$K^+$	
		ppm	$\frac{K^+_{c_t}}{K^+_{c_{200}}}/t$	ppm	$\frac{K^+_{c_t}}{K^+_{c_{200}}}/t$	ppm	$\frac{K^+_{c_t}}{K^+_{c_{200}}}/t$	ppm	$\frac{K^+_{c_t}}{K^+_{c_{200}}}/t$
t	$\sqrt{t}$	$K^+$	$\frac{K^+_{c_t}}{K^+_{c_{200}}}$	$K^+$	$\frac{K^+_{c_t}}{K^+_{c_{200}}}$	$K^+$	$\frac{K^+_{c_t}}{K^+_{c_{200}}}$	$K^+$	$\frac{K^+_{c_t}}{K^+_{c_{200}}}$
0.067	0.259	1.25	2.87	1.75	2.61	2.00	3.14	2.75	4.56
0.117	0.342	1.60	2.10	2.35	2.00	3.25	2.92	3.50	3.32
0.33	0.574	2.10	0.979	4.60	1.39	4.10	2.34	4.10	1.38
1.00	1.000	2.75	0.423	5.00	0.50	4.75	0.50	4.65	0.517
2.00	1.414	3.25	0.25	5.50	0.275	4.75	0.25	5.50	0.306
5.00	2.236	3.85	0.118	6.25	0.125	6.80	0.20	8.25	0.183
7.00	2.646	5.35	0.117	7.10	0.101	7.65	0.115	7.75	0.123
12.00	3.464	6.00	0.077	8.50	0.071	8.65	0.083	8.65	0.080
Estimate at 200	14.142	6.50	-	10.00	-	9.5	-	9.00	-

$\frac{K^+_{c_t}}{K^+_{c_{200}}}/t$  is the ratio of the  $K^+$  concentration in the solution after time t to the estimated concentration at 200 days divided by time t.

TABLE 4

Variation of Mg/K of Phlogopite with Method and Time of Treatment

Storage Condition	Temperature °C	Time, days	Mg/K	Mg/Al
Untreated	-	-	1.16	1.56
$Ca(OH)_2$	22	7	1.33	1.45
$Ca(OH)_2$	22	14	1.36	1.59
$Ca(OH)_2$	22	30	1.39	1.60
$Ca(OH)_2+10\%NaOH$	22	14	1.32	1.57
Reinforcing in cement paste	22	365	1.33	1.58
$Ca(OH)_2$	38	7	1.27	1.56
$Ca(OH)_2$	38	21	1.41	1.55

paste compared to that in untreated mica; this is the same increase as was observed in the mica in one-year-old cement paste, confirming that most of the  $K^+$  is released from the phlogopite in the first day.

No evidence could be found by electron microprobe that  $\text{Ca}^{+2}$  replaces  $\text{K}^{+}$  in the phlogopite lattice. As the maximum amount of  $\text{K}^{+}$  extracted is of the order of 0.09%, and as each  $\text{Ca}^{+2}$  would replace two  $\text{K}^{+}$ , the maximum  $\text{Ca}^{+2}$  content of the mica would be 0.05%. This is below the resolution of the microprobe.

The optical micrograph (Fig. 1) shows that phlogopite flakes have frayed edges, and it seems probable that the  $\text{K}^{+}$  can be readily removed from the edges when the lattice is distorted, giving rise to the high early rate of extraction of  $\text{K}^{+}$  from phlogopite. Once the  $\text{K}^{+}$  from the edges has been removed, the process would slow down; any more  $\text{K}^{+}$  would involve slow diffusion to the edges.

#### Conclusions

(1) A small amount of  $\text{K}^{+}$  in phlogopite is soluble in  $\text{Ca}(\text{OH})_2$  and NaOH solutions and in the pore solution of hydrated portland cement paste.

(2) Addition of small amounts of phlogopite to concrete made with potentially alkali-expansive aggregate results in a small increase in the rate of expansion of the concrete stored under humid conditions. The increase in the rate of expansion, however, is not sufficient to cause concern about the use of phlogopite mica as a reinforcement, even in concrete made with deleteriously alkali-expansive aggregate and low alkali cement.

(3) Caution should be exercised in adding excessive amounts of phlogopite to concrete made with potentially alkali-expansive aggregates.

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