IR-SPECTROSCOPY, A MODERN METHOD TO TEST THE ALKALI REACTIVITY OF SILICA AGGREGATES

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Earlier work in testing methods of alkali silica reaction is extended to IR-spectroscopy. With the IR-spectroscopy we are able to measure directly the quantity of OH-oscillators in silica aggregates. All reactive silicas contain a high quantity of OH-oscillators on lattice defects or internal interfaces. Measuring the IR-intensities of the OH stretching region between 3800 cm^{-1} and 2800 cm^{-1} the alkali reactivity of silica aggregates can be tested. Silica aggregates with high infrared absorptions are alkali reactive too.

INTRODUCTION

The last 35 years have seen dozens of papers published on testing methods of the alkali silica reaction. A summary of the usual testing methods e.g. is published in the papers of Hirche [1] and Schriftenreihe der Zementindustrie [2]. The most research methods have immense disadvantages. E.g. the mortar bar test, ASTM standard C227 must be observed 6 months to get expansion results. Partly you can't reproduce field parameters in laboratory. Petrographic examination, ASTM standard C295 or examination of solubility of silica aggregates, ASTM standard C289 yield only qualitative results.

Hirche [1] has described a physico-chemical model showing the correlation of reactive silanol groups on interfaces and expansion of silica aggregates. Only the amorphous and microcrystalline (krypto-crystalline) silica in the aggregates causes expansion in concrete. All these silicas have lattice

single group

double group

Fig. 1. Hydroxyl-groups on SiO_2 - interfaces (HOCKEY, PETHICA (1961))

defects or interfaces in a high degree. The quantity of the original lattice defects increases in crushed aggregates through further destruction of the SiO_2-lattice. The interfaces are covered with hydroxyl ions. Hockey and Pethica [3] have pointed out that OH double groups exist in vacuum only to a temperature of 200 °C. Thereafter OH single groups arise with reversible oxygen links. Approximate 400 °C the SiO_2-lattice rearranges producing irreversible oxygen links (see Fig.1.). Thermogravimetric and infrared measurements, Hirche [1] support the existence of hydroxyl groups in both forms.

The quantity of hydroxyl groups (= OH-oscillators) on SiO_2-interfaces and SiO_2-lattice defects can be measured with IR-spectroscopy. Silica aggregates with high infrared absorptions in the OH stretching region between 3800 cm^{-1} and 2800 cm^{-1} cause extensive alkali-silica reaction. It should be pointed out that this paper does not treat all problems of IR-spectroscopy on silicas, but instead, the conclusions based on this work are important by demonstrating a rapid and simple testing method.

EXPERIMENTAL

The infrared spectra were measured on a Perkin-Elmer Model 225 infrared spectrophotometer using KBr plates. The KBr plates pressed after heating 20 mg aggregate sample and 180 mg KBr to the invastegating temperature (vacuum 10^{-4} Torr). Before heating the mixture of aggregate and KBr was grinded in an agate mill.

Partly it was calculated the so called total absorption of the infrared spectra, Brügel [4] (see Table I).

$$A = \frac{1}{c\cdot d}\int_{a_1}^{a_2} \ln\frac{J_o}{J}\, d\nu \approx \frac{1}{c\cdot d}\left[\ln\frac{J_o}{J}\,\Delta\nu\right]_{a_1}^{a_2};$$

A = total absorption (cm/mol)
c = aggregate concentration in KBr plate ($\mathrm{mol/cm^3}$)
d = thickness of KBr plate (cm)
I_o, I = intensities
ν = frequency ($\mathrm{cm^{-1}}$)

The PL1 source program which was used to compute the total absorption of the OH stretching region between 3800 $\mathrm{cm^{-1}}$ and 2800 $\mathrm{cm^{-1}}$ has been described previously, Hirche [1].

RESULTS

This study of the effect of silanol groups in an aggregate on the alkali silica reaction was conducted in four series listed in Table I. In all cases, the infrared spectra from

Table I. The tested aggregates and the total absorption

No.	aggregate	origin	total absorpt. $10^6\cdot$cm/mol 20 °C	275 °C	535 °C
1	Quartz	Fa. Merck	0.49	0.20	0.10
	Pyrexglass	Fa. Schott	1.31	0.57	0.15
	Flint	Nordfriesland	2.24	1.24	0.35
2	Opal I	–	–	–	–
	Opal II	Czechoslovakia	–	–	–
	Opal III	–	–	–	–
	Opal IV	Australia	–	–	–
3	Flint I	Schleswig	–	–	–
	Flint II	Nordfriesland	–	–	–
4	opal.SandstoneI	Heiligenhafen	–	–	–
	opal.SandstoneII	Bultwisch	–	–	–

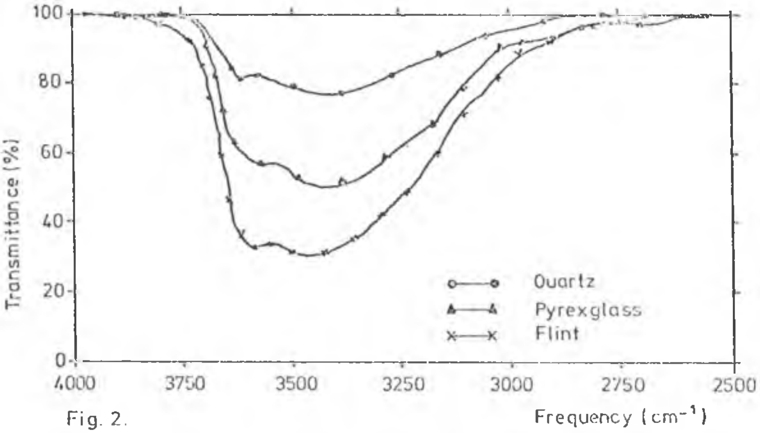

Fig. 2.

IR-Spectroscopy on silica-aggregates; temperature of sample 20°C.

4000 cm^{-1} to 2500 cm^{-1} were recorded.

Figure 2, Figure 3 and Figure 4 show the different infrared spectra of Quartz, Pyrexglass and Flint in Series 1. For Pyrexglass we must take Duranglass of the Fa. Schott because we couldn't get Pyrexglass. Duranglass and Pyrexglass have approximately the same composition. The alkali reactive aggregates Pyrexglass and Flint are measured with higher total absorptions as the inactive Quartz. As temperature of the KBr plates is increased the total absorptions of all three aggregates decreases. The quantity of silanol groups

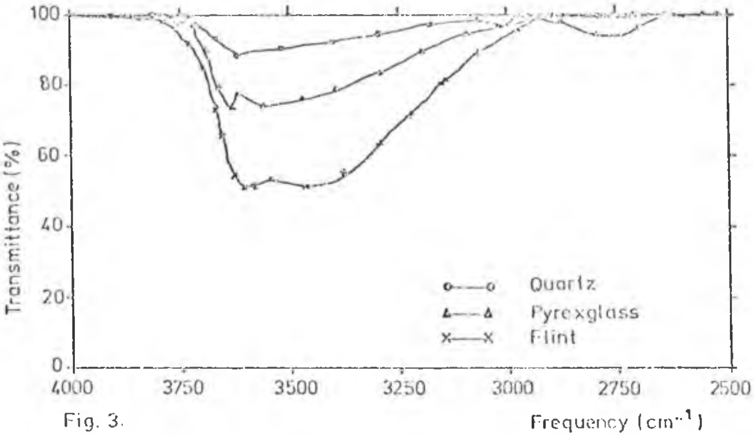

Fig. 3.

IR-Spectroscopy on silica-aggregates; temperature of sample 275°C.

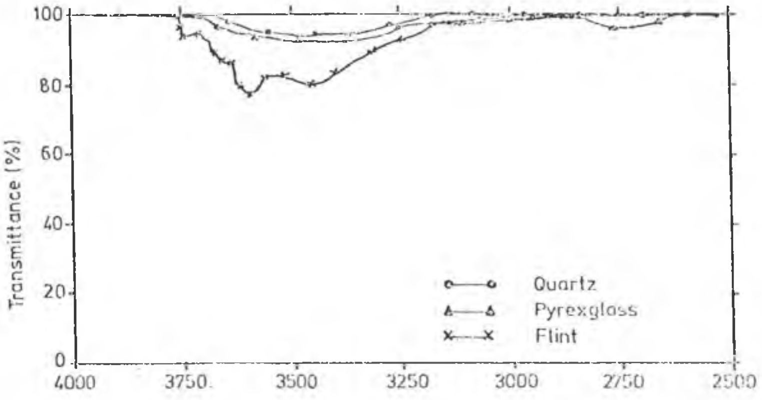

Fig. 4.

IR-Spectroscopy on silica-aggregates; temperature of sample 535°C.

decreased in aggregate.

Figure 5 shows the infrared spectra of different opals. Laboratory research gave the result that mortar bars with the aggregates Opal I - III expanded small. Opal IV was high alkali reactive.

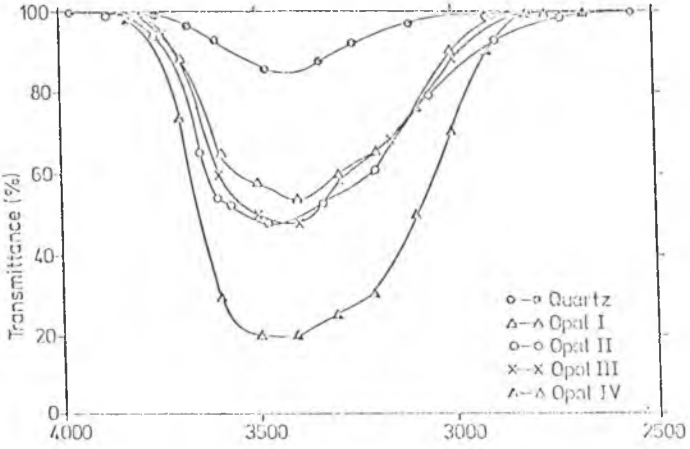

Fig. 5.

IR-Spectroscopy on opaline aggregates; temperature of sample 20° C.

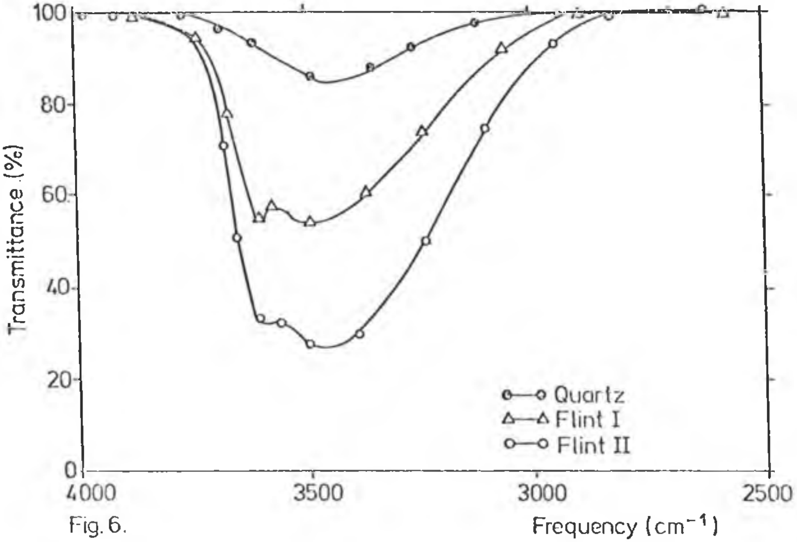

Fig. 6.

IR-Spectroscopy on flint aggregates; temperature of sample 20° C.

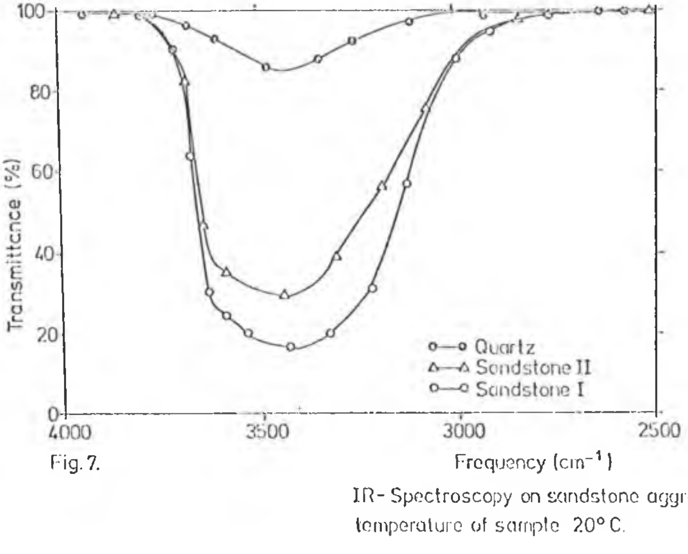

Fig. 7.

IR-Spectroscopy on sandstone aggregates; temperature of sample 20° C.

In the same way, Segnit, Stevens and Jones [5] distinguish more crystalline opals with few hydroxyl groups and more amorphous opals containing plenty hydroxyl groups.

Figure 6 and Figure 7 show the infrared spectra of Series 3 and Series 4. The alkali reactive aggregates Flint and opaline Sandstone produce a very greater deal of infrared absorption as the inactive Quartz.

DISCUSSION

Attempts were made to test the hypothesis that silica aggregates with high infrared absorptions in the OH stretching frequencies from 3800 cm^{-1} to 2800 cm^{-1} cause expansion in concrete through reaction of the alkalies on these silicas. The results of the experimental show that all alkali reactive samples lay over a certain level of infrared transmittance. We aren't able to give a reference line now. More experimental work must be done. Maybe we can say that all silica aggregates with total absorption greater than $8x10^5$ cm/mol are dangerous.

Altough there are problems to get representative grain mixtures with homogeneous crushing behaviour or that more reactive shells of silica aggregates can produce an unexpected local expansion or that the invastegated sample is very small the described testing method of alkali silica reaction is fairly exact and practicable.

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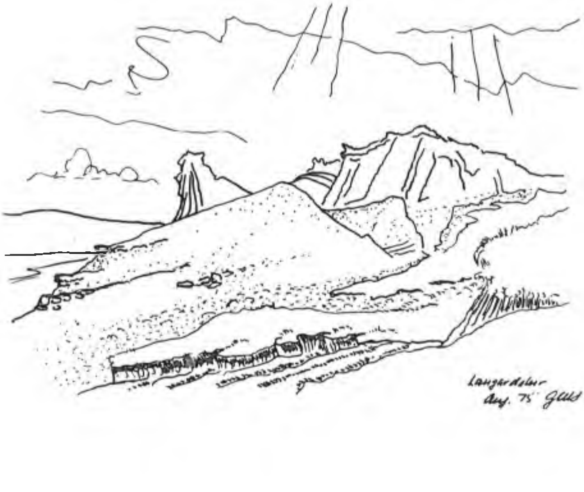
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