THE RELATIONSHIP BETWEEN FLINT MICROSTRUCTURE AND ALKALI-SILICA REACTIVITY

P L Rayment
Building Research Establishment

Flint is a known alkali silica reactive rock type in the
UK but there are considerable differences in the
reactivity of individual flint fragments. In this study
flint samples from a number of sources were investigated
in order to discover reasons for these differences. A
disordered crystalline silica phase was the most alkali
soluble material present but porosity was the determining
factor in alkali-silica reactivity. Cortex fragments were
more reactive than unweathered flint fragments.

INTRODUCTION

Results from laboratory experiments and observations of concrete structures
in the field, as reported at several of the previous AAR conferences, have
shown that flint is an alkali-silica reactive rock type in the UK. Flint
mainly consists of different silica phases, most of the crystals being too
small to be resolved by optical microscopy. Silicified fossil skeletal
material may be scarce or common and areas of coarser chalcedony and quartz
occasionally occur. Flint is an important and often major constituent of
the Quaternary sands and gravels in Southern England and East Anglia and is
also abundant in marine-dredged aggregates, particularly those from the
English Channel and the southern part of the North Sea. All the flint
fragments within these sands and gravels have been derived ultimately from
flint deposits occurring within the Upper Cretaceous Chalk rocks. Flint
within nodules in the Chalk is black or greyish-black, although
paler-coloured areas may be present. A weathered outer layer, known as the
cortex, usually surrounds the flint. However, some flint nodules show
little development of a cortex. The cortex is white and porous, provided
there has been no secondary deposition of substances by percolating
groundwaters. Flint fragments in sands and gravels may consist solely of
cortex or unweathered flint or alternatively comprise a mixture of both.
The fragments are sometimes stained brown due to the deposition of
secondary iron oxide. Cortex fragments are common in the flint-rich
natural sands of the UK, both land-based and marine-dredged. Gravel
deposits show quite a variation in the proportions of cortex and
unweathered flint present. Also in gravels, unlike sands, fragments
consisting only of cortex are rare.

Hobbs showed that, given a certain set of conditions, some siliceous
materials, such as Beltane opal, produce maximum expansion when a

particular amount of the reactive material is present (1). The amount in
known as the pessimum proportion. In the case of flint, however, a study
of British sands and gravels by Rayment et al (2) showed that, when the
relationship between flint content and reactivity of aggregates from
various locations was compared, it was not possible to correlate a
particular amount of flint with maximum expansion. This strongly suggests
that individual flint fragments within sands and gravels differ in
reactivity so that the reactivity of a particular sand or gravel aggregate
depends upon the reactivities of the individual flint fragments of which it
is composed. There is also geological evidence to suggest that flint
fragments differ in reactivity. Curry (3) reported that some flint
fragments in a Palaeogene gravel had been attacked by alkaline solutions
whereas other fragments had remained unchanged.

The work described in this paper presents the results obtained so far
in a study investigating the relationship between flint microstructure and
alkali-silica reactivity. The flint samples examined came from a variety
of sources including insitu nodules from the Upper Chalk, fragments from
river, glacial and Quaternary Head gravel deposits and particles from a
River Thames sand.

INVESTIGATION OF FLINT MICROSTRUCTURE

Flint samples were studied by optical and scanning electron microscopy
using rough samples, polished thin sections (30μm thick) and polished
blocks, in which the samples were mounted in epoxy resin. In transmitted
light microscopy, information about microstructure was often increased by
examining the polished thin sections without a mounting medium and
coverslip. In scanning electron microscopy both the secondary electron and
backscattered electron modes were used, although the latter mode was found
to be particularly useful in the microstructural investigations.

Lepispheric microstructure was an important feature within the vast
majority of flint samples examined, although evidence for its occurrence
sometimes only came from a careful study of the sample using a variety of
different methods of observation. The term lepispheric texture was first
used by Wise and Kelts (4) to describe the spheres composed of bladed
crystals of opal-CT which occur in deep-sea chalks. Opal-CT is a silica
phase with X-ray characteristics between those of cristobalite and
tridymite. Figure 1 shows lepispheres in Beltane opal. Energy dispersive
X-ray microanalysis showed that the spheres consisted of silica and the
bladed morphology of the crystals is typical of opal-CT (Figure 2).
Clayton (5) described similar spheres occurring in flint nodules within the
Chalk in the south of England, although in the nodules he examined the
spheres consisted of quartz crystals and not opal-CT. He identified two
main types of lepispheric microstructure occurring in flint nodules. In
the open lepispheric structure, lepispheres formed a loose framework
between which an interstitial silica phase occurred. In the closed
lepispheric state, the lepispheres were tightly packed and little
interstitial silica occurred. Jeans (6) recorded opal-CT lepispheres in
flint nodules within the Lower Chalk in Buckinghamshire, Berkshire and
Wiltshire. No opal-CT lepispheres were found in any of the flint fragments
examined in this study.

Open lepispheric microstructure was often easily seen in the cortex
fragments from the various sources investigated in the present study. This
was due to the complete or partial removal of the interstitial silica from

between the spheres. The silica crystals in the interstitial phase were
extremely small and recent transmission electron microscope studies have
shown that the crystals contain many lattice defects. The lepispheres
usually varied from 10μm to 30μm in diameter but, within a particular flint
fragment, spheres of one particular size predominated (Figure 3). Each
sphere consisted of a number of anhedral equant quartz crystals. The
crystals were about 2μm to 5μm across but were very much smaller around the
outside of the lepispheres (Figure 4). The centres of the spheres
contained a different type of silica which was more easily removed by
natural weathering. This suggests that it may be the same silica phase as
that occurring between the lepispheres. Removal of the silica gave the
lepispheres a characteristic hollow appearance. The flint fragments in the
sands and gravels showed that the final stage in the natural weathering of
flint is the gradual removal of the lepispheres themselves. At this stage
of weathering the lepispheric microstructure starts to become obscured.

The cortex fragments in sands and gravels sometimes contained iron
oxide which occurred between the lepispheres and in the centres of the
spheres, filling up the spaces left by the removal of some or all of the
more easily weathered silica phase. Iron oxide also occurred in more
severely weathered flints. The distribution of iron oxide within the
cortex fragments was often far from uniform.

Lepispheric microstructure was only indicated in the unweathered flint
by the occurrence of spheres protruding into voids or situated within
microfossil chambers. Alkali etching, produced by immersion in potassium
hydroxide solution, revealed an open lepispheric microstructure in some of
the unweathered flint fragments (see section on flint reactivity).

INVESTIGATION OF FLINT REACTIVITY

Reactivity was investigated in two ways. Firstly flint fragments, usually
as polished blocks, were immersed in a 1N solution of potassium hydroxide
which also contained a source of calcium ions. The flint samples were
allowed to react for 7 days at 60°C. The appearance of the flint before
and after attack was noted and also the amount of gel produced. Secondly
studies were made of the change in appearance of sand-sized flint particles
after undergoing alkali attack for varying lengths of time within actual
concrete specimens. The specimens consisted of concrete prisms
(75*75*200mm) which contained an inert limestone coarse aggregate, a high
alkali content (7kg Na_2O_e/m^3) and a reactive sand. The same Thames Valley
sand was used as in the microstructural investigations so some correlation
could be made between the appearance of the flint before and after alkali
attack. The flint in the Thames Valley sand showed a range of weathered
states from dense unweathered flint to very porous cortex particles. Some
cortex fragments contained secondary iron oxide and had reduced porosity.
The concrete prisms were stored under hot (38°C) humid conditions.
Polished thin sections (30μm thick) were made at 2, 3, 11 and 24 months of
age and examined by optical and scanning electron microscopy.

The results from the alkali immersion tests on the unweathered flint
fragments showed that the interstitial silica was the most reactive silica
phase present in the flint, since it was preferentially removed by the
potassium hydroxide (Figure 5a and 5b). The rate of removal of the
interstitial silica phase was not the same for all the flint samples, being
greatest for a light grey flint fragment from a Quaternary Head gravel.
The lepispheres, in contrast, showed only a slight etch. Some flint

fragments from the glacial gravel showed very little change after alkali immersion. This implies that either there was little or no interstitial silica present, i.e. a closed lepispheric structure, or the interstitial silica was in a less reactive form. The unweathered flint fragments which were preferentially attacked produced some calcium alkali silica gel but amounts were substantially less than that produced by the cortex fragments. This shows that the porosity of the flint is extremely important in determining the amount of gel produced. Although the more reactive interstitial silica phase was present in at least some of the unweathered flint fragments, the lack of porosity significantly reduced the rate of gel production. It was not possible to see the microstructural changes undergone by the cortex fragments after alkali immersion because of the large amounts of gel produced.

The results from the thin section examinations of the flint particles within concrete showed that the reactive flint consisted of cortex material. Particles of flint cortex with open lepispheric texture were attacked, sometimes quite severely. Cortex fragments entirely filled with large concentrations of iron oxide were not attacked, presumably because the iron filled up all the porosity, thereby preventing attack on the lepispheres and any remaining interstitial silica. Areas of cortex free of iron oxide or containing reduced amounts were reactive since they still possessed the necessary porosity. Unweathered flint particles showed no significant signs of attack. However there was some evidence that, if unweathered flint with an open lepispheric microstructure became cracked, dissolution of the interstitial silica could start to occur along the length of the crack.

In many ways alkali attack on flint particles simulates natural weathering, i.e. removal of interstitial silica followed by attack on the lepispheres. Therefore, for any given flint in a concrete it is not possible to know the exact state of weathering of the flint prior to alkali attack. This makes the identification of reacting particles difficult especially in the early stages of the reaction.

Reacting flint fragments were identified at very early ages (2 and 3 months) by the presence of a rim which usually occurred at or within 40μm of the cement boundary (Figure 6). The rim occurred around flint particles in all the size fractions but in some of the larger flint fragments it only occurred around part of the flint. It was not present where the porosity of the flint was low, such as in unweathered areas or regions rich in iron oxide. No such rim was seen in the flint particles prior to reaction in the concrete, even though over 100 flint particles were examined during the microstructural investigations of the Thames Valley sand. The rim varied in thickness from 7μm to 30μm and its inner and outer edges were not clearly defined. The rim had a denser structure than the rest of the flint and quantitative analyses showed that it consisted of silica with smaller amounts of calcium (2 to 9 wt% CaO). Potassium amounts were always much lower than calcium and were sometimes not detectable. A mechanism for the formation of this rim in reacting particles is suggested. Because of their larger size, calcium ions diffuse into reacting flint particles more slowly than the potassium and hydroxyl ions. The solubility of silica is reduced in the presence of calcium so as the dissolved silica from the reacting flint particles diffuses outwards it meets a region of higher calcium ion concentration and some of the silica comes out of solution, entrapping calcium ions as it is deposited. Calcium alkali silica gel usually occurred in the cement close to flint fragments with a rim. Also analyses

of cement hydrates surrounding the rimmed flint fragments showed unusually
high levels of silica.

In the concrete sectioned at 11 months, large amounts of silica had
been removed from the reacting flint particles. Figure 7 shows part of a
reactive flint particle in which lepispheres have been attacked, leaving
remnant lepispheres just discernible in a few areas. In some reactive
flint particles the lepispheres showed signs of attack from within as well
as from outside. Many reactive flint particles possessed a fairly wide
zone of reaction product, which occurred towards the more peripheral
regions of the flint. The reaction product often masked the rim at the
flint/cement border. The reaction product zone had raised levels of
silicon, calcium and potassium in comparison with the rest of the flint.
The amounts of calcium and potassium oxide were not very large, however,
and each tended to be below 5 wt%. Where cracks traversed the reaction
product zone a very thin layer of crystalline reaction product covered the
crack walls. At 24 months attack on the flint fragments was more extensive
than at 11 months. In some reactive flint fragments the lepispheric
microstructure was obliterated and fossil skeletal remains were often the
only recognisable structures left within the reacted flint. Large amounts
of reaction product occurred both within and outside the reactive flint
fragments. The crystalline reaction product was much more abundant than at
11 months and again it only occurred within reactive flint fragments. It
was present in cracks, both large and small, and in small pockets, the
latter rarely occurring in the central areas of the flint particles. The
crystalline reaction product consisted of 58.9% SiO_2, 14.6% CaO, 12.5% K_2O
and 1.9% Na_2O (mean of 15 analyses).

CONCLUSIONS

The vast majority of flint samples studied possessed an open lepispheric
microstructure. A crystalline silica phase with many lattice defects
occurred interstitially between spheres composed of quartz crystals. The
interstitial silica had a high degree of structural disorder and a very
small crystal size so was the most easily removed phase, both by natural
weathering and alkali dissolution. However, porosity was found to be the
most important factor determining the alkali-silica reactivity of flint,
since porous cortex fragments were more reactive than unweathered flint.
At a certain level of porosity the small quartz crystals around the outside
of the lepispheres were attacked by alkaline solutions. The occurrence of
iron oxide in the central areas of some lepispheres shows that solutions
can travel along crystal boundaries into the very centres of the spheres.
This explains why lepispheres showed signs of attack from within as well as
from around their outer surfaces. As silica dissolution progressed the
remaining quartz crystals in the lepispheres were attacked and the
lepispheric microstructure became obliterated.

There must be a certain level of porosity at which a maximum rate of
silica dissolution occurs. Too little porosity results in reduced amounts
of alkalies getting into the flint and if there is too much porosity there
will be less silica available for dissolution. The deposition of secondary
materials, such as iron oxide, reduces the porosity. Cortex fragments
completely filled with large concentrations of iron oxide showed no
evidence of reactivity.

In order to avoid alkali-silica reaction in concrete structures it is
essential that as much information as possible be available to the

contractor concerning the reactivity of any flint to be used in the
concrete mix. At present, because of the differences in reactivity shown
by flint fragments, it is not always possible to accurately predict the
reactivity of a particular aggregate combination. The results from this
work have shown flint cortex to be the main reactive type of flint. In the
future it may be possible to correlate amounts of flint cortex with
different levels of reactivity, particularly for gravel deposits. It
should then be easer to avoid aggregate combinations which are potentially
expansive.

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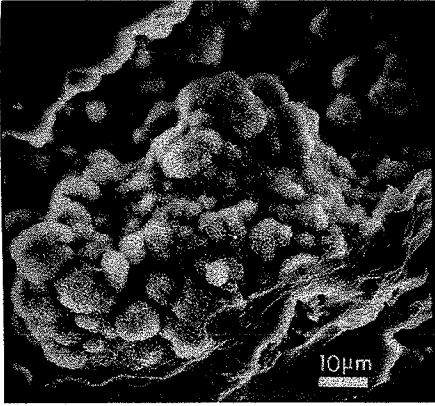
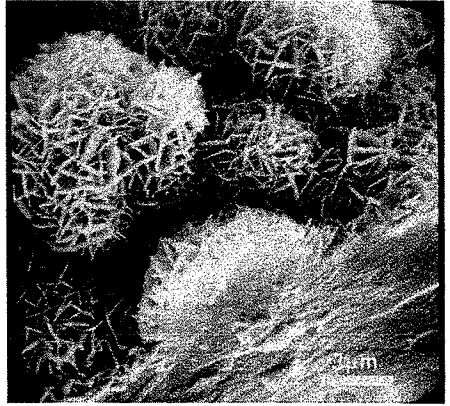Figure 1 Opal-CT lepispheres in Beltane Opal. SEM micrograph in secondary electron mode (SE)

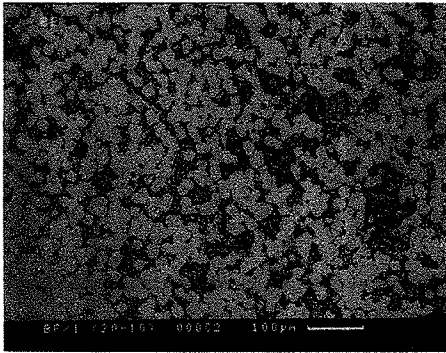Figure 2 Bladed crystals of opal-CT (SE)

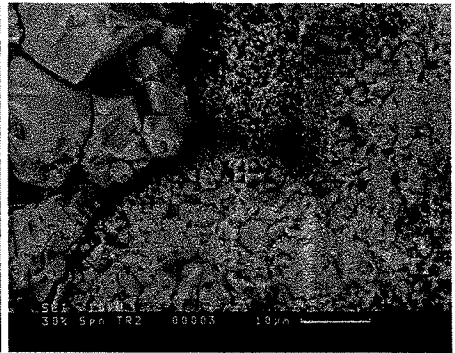Figure 3 Quartz lepispheres in a fragment from a gravel. SEM micrograph in backscattered electron mode (BSE)

Figure 4 Lepispheres formed of quartz crystals. Larger quartz crystals fill void at top left (BSE)
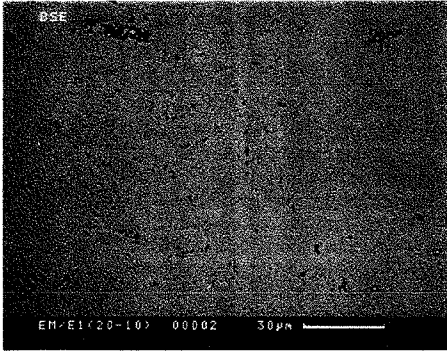
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Figure 5a Flint fagment from a
gravel before immersion in
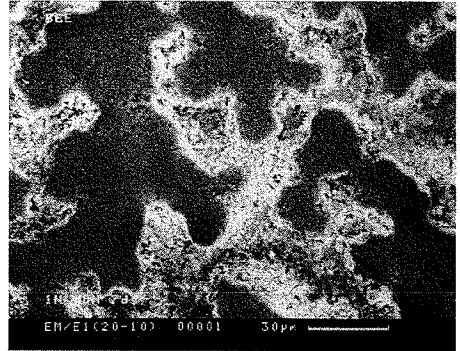alkaline solution (BSE)

Figure 5b The same flint after
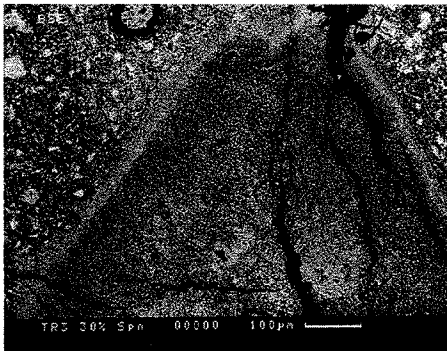immersion in alkaline solution
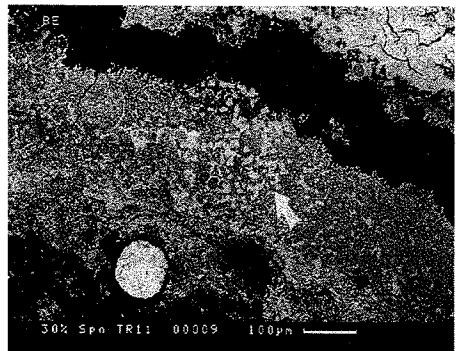(BSE+SE)

Figure 6 Rim around a reactive
flint particle (BSE)

Figure 7 Remnant lepispheres in
a reactive flint particle
(arrowed)