Flint Characteristics and Alkali-Silica Reactivity

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ABSTRACT

As would be expected, shape, sizes, distribution, continuity, and percentage of micropores in flint particles will affect the rates of internal reaction between the particles and alkaline solutions. Three varieties of flint particles chosen on the basis of colour were utilized to determine pore entry radii, pore size, and interior surface area distributions using mercury intrusion porosimetry. A careful visual examination was carried out of the reaction products formed on these natural aggragates after being immersed in alkaline solutions. Photographic records of the different silica gels were also obtained and compared. The results suggest that the grey/black flint has two distinct sizes of individual pore spaces which allow the ready movement of both air and solution. The pure white and cream/brown flints showed that the smaller micropores are predominant. There is also an indication that cream/brown flint is more reactive in alkaline solutions than the other two varieties, and apparently produces four distinct types of gel morphology at different temperatures under these conditions.

1.INTRODUCTION

Flint has been widely used as an aggregate for concrete for a considerable period, particularly in southern England, either as a natural gravel, typically with irregular particle shapes, or as a crushed material, which typically has equant and very angular fragments. Concrete structures using flint aggregate have been built over a long period of time and have an excellent service record, the flint a satisfactory and stable material.

The results described in this paper have been obtained as part of a detailed study of the alkali-silica reaction in the U.K. in which some physical and chemical aspects of the reaction have been investigated (Nixon and Bollinghaus, l983; Poole and Al-Dabbagh, 1983). The work on flint has concentrated on different flint aggregates, and aggregates from the Trent Valley which contained flint. Some of these were selected because it was known that they had been used in structures which had suffered as the result of alkali-aggregate reactivity, while others, notably from the Thames Valley, were regarded as a control group for the test procedures to be investigated.

The standard methods and procedures have been successfully used in the study of alkali-silica reactivity, but in this work others have been developed in an attempt to gain more information which may relate directly or indirectly to alkali-aggregate reaction and its effects.

Mercury porosimetry has been used to investigate the pore sizes and surface areas of reactive flint particles. This information, in conjunction with direct observation and measurment of pores in reactive particles, provides the basic data for consideration of ionic mobilities and migration in reacting particles. The results of this test and others will be reported and discussed elsewhere, but in general terms it was found that the differences in colour and reactivity correlated with pore size and pore volume.

2. LABORATORY STUDIES

2.1 Flint colour and reactivity

Three groups of flints (of the 1 mm size fraction) selected on the basis of colour-cream/brown, grey/black and pure white-from sea-dredged samples (14,16), Trent Valley samples (1,3) and Thames Valley sample (1) were prepared as gel pats according to the Gel Pat Test of Jones and Tarleton (1958) with ordinary Portland cement. Each pat contained about 50 particles of specific colour. The pats were placed in storage cabinets at two temperatures, 30°C and 50°C. After 7 days the cream/brown flints had begun to develop spots of white gel reaction product at both temperatures. The number of cream/brown flint particles reacting increased at the higher storage temperature, as is illustrated by the examples given in table 1 below. It was observed that dark brown staining of gels associated with the cream/brown flints was confined to the lower-temperature pats.

Table 1

Flint Sample	Percentage of Reactive Flint Particles					
	30°C days			50°C days		
	7	28	56	7	28	56
Sea dredged-14						
Cream/brown	8.0	18.0	36.0	68.0	80.0	80.0
Grey/black	0.0	0.0	0.0	8.0	8.0	8.0
Pure white	0.0	6.0	18.0	30.0	48.0	48.0
Thames Valley-1						
Cream/brown	6.0	6.0	20.0	30.0	37.0	37.0
Grey/black	0.0	0.0	6.0	0.0	0.0	9.0
Pure white	0.0	0.0	6.0	0.0	7.0	12.0
Trent Valley-1						
Cream/brown	3.0	5.0	15.0	35.0	35.0	40.0
Grey/black	0.0	0.0	3.0	7.0	11.0	11.0
Pure white	0.0	0.0	10.0	7.0	17.0	22.0

In these tests there appeared to be a correlation between reactivity and colour. The cream/brown flint particles appeared to be the most reactive, although some pure white ones also exhibited reaction at the early stages of storage at both temperatures. The grey/black flint particles became bleached to a whitish colour but no reaction product appeared to have developed on the surface.

The results of the gel pat tests carried out by Sims (1977) indicated that about half the flint particles showed signs of a reaction after five weeks immersion in alkaline solution at 50°C. These results differ from the ones obtained in this study. The grey/black flint particles showed the most frequent evidence of reaction . It was found that in some cases patchy white deposits due to carbonation or crystallization of hydroxides developed, and considerable care is required to correctly identify particles as being alkali-silica reactive when they are pale coloured. Careful observation indicated that the cream/brown flint and some of the white flint particles were associated with an accumulation of gelatinous reaction product at the time when the grey/black flint particles were associated only with a patchy white deposit. This colour correlation is reflected in the analytical results which are taken from examples of reacted and non-reacted flint particles broken from the faces of the cement tablets using a dental drill and similar techniques (Poole and Al-Dabbagh, 1983).

2.2 Pore size and surface area of flints

In this study, pore entry radii, sizes and surface area distributions were examined for each of the three different colours of flint particles using mercury intrusion porosimetry technique. The instrument used was a Micrometrics Autopore 9200 which had a range of recorded radii from 0.003 μm to 300 μm. In general, the size of the pores is inversely related to the pressure required to force mercury into the material according to the usual capillary pressure relationship. The model analogue implicit in this analysis is an assembly of round tubes of various sizes. It is recognized that this is not a correct model for porous solids, for example a void may have an entrance that is smaller than its interior. Thus the whole void volume will be recorded as being the size of the entrance .

Differences between the three types of coloured flint particles according to the relation between accumulative pore volume and pore diameters were found using this technique. The grey/black flint appeared to have two types of individual pore-spaces, macro (7.61-300 μm) and micro ($<$0.013 μm) although there is no sharp line of demarcation, giving the bimodal distribution shown in Figure 1, whilst

the other two varieties showed that micropore spaces are predominant, as plotted in Figures 2 and 3.

These results suggest that the grey/black flint allows the ready movement of both air and solutions. In the other specimens micropores predominate and will relate to migration of micropore fluids. Although there is insufficient information available to show the possible migration aspects of solutions inside the different varieties of flint, the results obtained in this study do suggest that perhaps fluids in the micropores and their migration is more important for reaction in the cream/brown and pure white flint particles than in the grey/black ones.

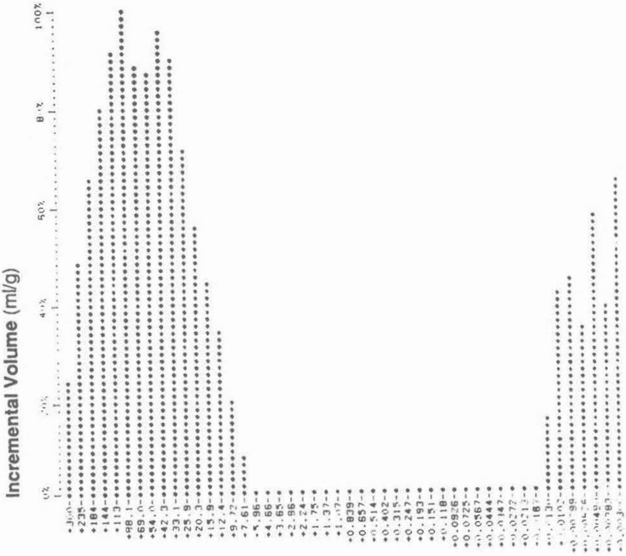


Figure 1:
The differential pore-size distribution curves for pore volume for grey/black flint.

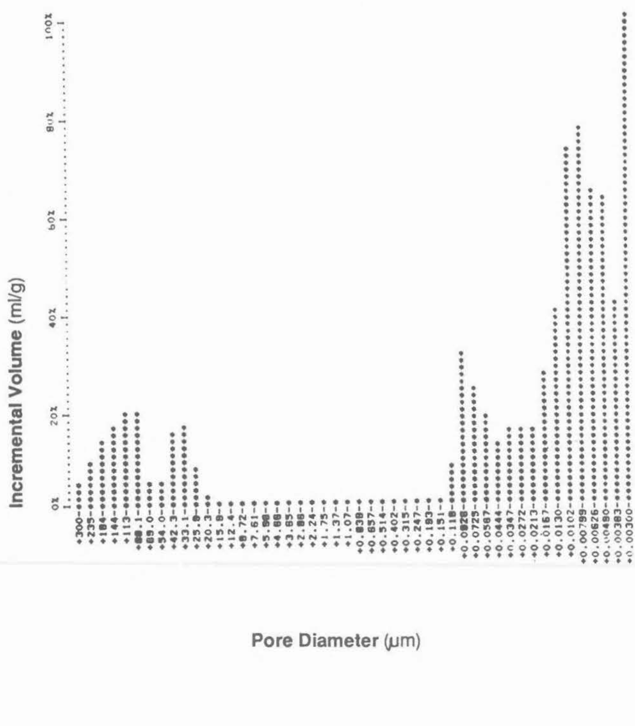


Figure 2:
The differential pore -size distribution curves for pore volume for cream/brown flint.

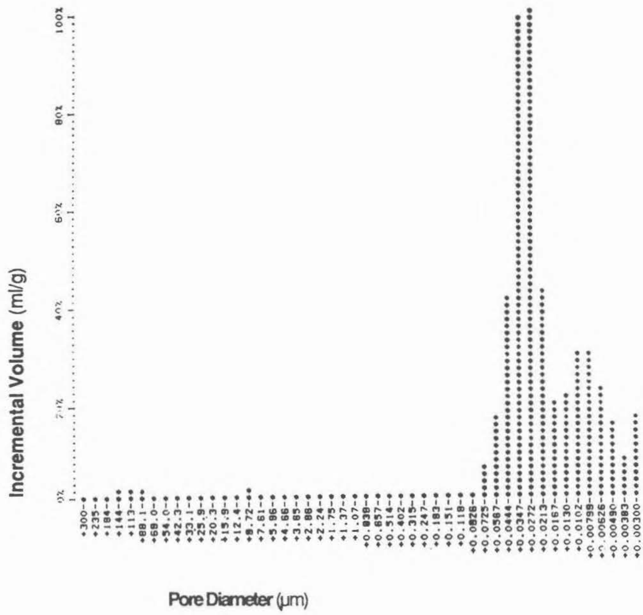


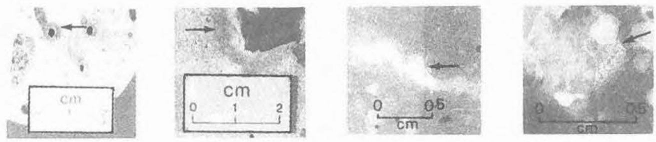
Figure 3:
The differential pore-size distribution curves for pore volume for pure white flint.

2.3 The identification of alkali-silica reaction in natural aggregates

Representative siliceous particles from a number of different aggregate types were mixed with ordinary Portland cement and prepared as gel pats since it was considered that the various micromorphological and textural features of the reactive particles might affect the development, composition and form of the gel reaction products. A careful visual examination and comparison was made of the photographs of the different silica gels. A brief summary of each specimen is given in the captions for Figures 4 and 5.

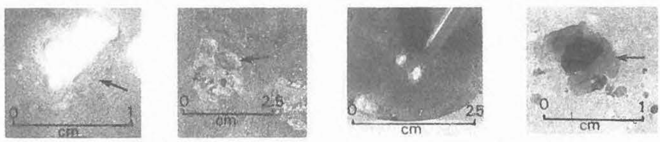
The differences, which may reflect different temperatures of storage and reaction, may be seen and compared. Cream/brown flint particles apparently produce four distinct types of gel growth. At low temperature the exudation appeared as brownish spots scattered through the cement paste around the reactive particle and associated with dark rims, as illustrated by Figures 4a and 4b. At elevated temperatures gel develops on the surface of the reactive particles. There is a distinct difference between gel developed at 30°C (Figure 4c) and that at 50°C (Figure 4d) which probably reflects differences in chemical composition and viscosity of the gel. It seems that the slow reaction at low temperatures permitted a faster diffusion of silica gel through the surrounding cement paste than at higher temperatures. Four other types of gel structure may be identified which are produced by other reactive siliceous particles. Figure 5a shows a gel with a very well-marked concentric structure developed around nucleii of gel, indicative of reactions proceeding from several points within the particle. Such concentric gels were developed on the opaline limestone from Cyprus after storage at room temperature and 30°C. Occurrence of reactive particles of aggregate, associated with silica gels, being destroyed by the reaction are illustrated in Figure 5b, which shows a Kenyan rhyolite that behaved differently from the other siliceous particles. The globular structure of silica gels apparently produced in situ by reaction of the Californian wood opal (Figure 5c) is similar to that formed on the opaline limestone from Cyprus. Figure 5d shows the brown, fluid stain-like silica gel which developed on glassy basalt particles. This example appears to have a high iron content, which is not typical of silica gels (Al-Dabbagh,1986). The colour is almost certainly due to iron compounds liberated from the basalt by the alkaline solution. As is clear from the photograph no hint of structure can be recognized .

It is clear that the composition of the reactive aggregate particles may be partly responsible for the morphological differences, but the temperature of storage and the composition of the developing gel may also have influence on them.



a. b. c. d.

Figure 4: Parts of pats of different diameters after immersion in alkaline solution, showing distinct differences between gels developed on cream/brown flint particles at different temperatures.



a. b. c. d.

Figure 5: Parts of pats after one week in alkaline solution, showing distinct types of gel structure on different siliceous particles.

3. CONCLUSIONS

Careful study of flints, including treatment with strong alkaline solutions, has provided some indications of the relations between flint reactivity and physical and chemical characteristics . The colour of flint particles is a reflexion of a number of the characteristics, including microstructure and the concentration of impurities. Colour, as might be expected, can therefore also be correlated with reactivity in that cream/brown flints were more reactive in alkaline solutions than the grey/black varieties. This correlates with the iron and aluminium impurity levels, as has already been noted (Poole and Al-Dabbagh, 1983). The differences in colour and reactivity have also ben shown to correlate with pore size and pore volume. The grey/black flint appear to contain both "macro" (7.61-300 μm) and "micro" (<0.013 μm) pores in a bimodal distribution. The cream/brown flints, on the other hand, have a predominance of the micropore sizes.

The gel reaction products also exhibit a variety of compositions and morphologies. Indeed, the relationship between gel composition, structure, mode of formation and its physical properties, particularly with respect to swelling pressure, viscosity and the effects of aging, would make an important subject for future research in this field.

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