aggregate particles. As far as the results obtained in this study were concerned, the fly ash did not inhibit alkali-silica reactions at all, but facilitated the mobilization of calcium into reactive aggregate particles leading to the formation of the gels with high calcium concentrations. Therefore, the reduction or elimination of expansion brought about by the addition of the fly ash appears to be attributable to the formation of gels with high calcium concentrations and/or to the reduction in the mobility of water through the fly ash-bearing cement paste matrix. However, an indication that the addition of calcined kaolin to the mortars containing the reactive aggregate almost completely inhibited alkali-silica reactions was also obtained in another series of experiments /13/. This result can be explained by the reduction in hydroxyl ion concentration of the pore solution resulting from surface reaction of the siliceous pozzolan /1/. It may be likely that the mechanisms responsible for reduction or elimination of the expansion caused by alkali-silica reactions are different for different types of pozzolans.

5. CONCLUSIONS

The application of the combined technique of quantitative EDXA analysis and microhardness measurements to direct examinations of the progressive inward chemical reaction and physicochemical absorption of pore solution in reacting aggregate particles in mortars provides the following several informations regarding alkali-silica reaction mechanisms.

(1) The intrusion of water into the affected portion inside reacting opal particles after 7 days is evidenced by a great reduction in microhardness.

(2) The solidification of the softened region within about 50 μm from the interface after 14 days found in a coarse opal grain embedded in cement paste appears to relate to the intrusion of a relatively large amount of calcium.

(3) The expansion of the mortars at least until about one month depend upon the amount of gels formed rather than upon their chemical compositions.

(4) The fly ash used in this study did not inhibit alkali-silica reactions at all, but facilitated the mobilization of calcium into reactive aggregate particles.

REFERENCES

1. DIAMOND, S., Mechanisms of alkali-silica reaction and expansion- a review and reassesment, pp.71, Unpublished, 1974.
2. KNUDSEN, T. and THAULOW, N., Cem. Concr. Res., 5, 443 - 454, 1975.
3. THAWLOW, N. and KNUDSEN, T., Sym. on Alkali-Aggregate Reactions, Preventive Measures, Reykjavik, 189 - 203, 1975.
4. POOLE, A.B., in "The Effect of Alkalis on the Properties of Concrete" Cement and Concrete Assn, London, 163 - 175, 1976.
5. DIAMOND, S., BARNEYBACK, R.S. AND STRUBLE, L.J., Proc. the 5th Int. Conf. on Alkali-Aggregate Reaction in Concrete, D252/22, pp.10, 1981.
6. KAWAMURA, M., TAKEMOTO, K. and HASABA S., Trans. of JCI, 4, 1 - 8, 1982.
7. STRUBLE L.J., MS Thesis, School of Civil Engineering, Purdue Univ., 1979.
8. DIAMOND, S., Cem. Concr. Res., 2, 617 - 632, 1972.
9. POWERS, T.C. and STEINOUER, H.H., ACI Journal, 51, 785 - 811, 1955.
10. VERBECK, G. and GRAMLICH, C., Proc. ASTM, 55, 110 - 1131, 1955.
11. OGAWA, K., UCHIKAWA, H. and TAKEMOTO, K., Cem. Concr. Res., 10, 683 -696, 1980.
12. DIAMOND, S. AND KINTER, E.B., H.R.R., 92, 83 - 92, 1966.
13. KAWAMURA, M., TAKEMOTO, K. and S. HASABA, in the course of preparation.

REACTIVE AGGREGATES AND THE PRODUCTS OF ALKALI-SILICA REACTION IN CONCRETES

Poole, A. B.   and   Al-Dabbagh, I.

Queen Mary College, University of London,
London E1 4NS.   U.K.

ABSTRACT

Potentially alkali-reactive flint particles from U.K. aggregates have been examined and compared to similar non-reactive particles using electron probe micro-analysis and scanning electron microscopy. It is found that reactivity of particles correlate with their impurity contents and with their colour. There is an indication that the micro-textures in flint also relate to reactivity.

A.S.R., Flint, Micro-analysis

1. INTRODUCTION

Although alkali-aggregate reaction in concrete has been recognised in the U.S.A. since the late 1930's is was only in 1976 that it was positively identified in some concrete transformer bases on the U.K. mainland. A number of concrete structures in South West England have now been shown to have deteriorated as a result of alkali-silica reaction between flint particles in the fine aggregate and alkalis from the cement paste.

A number of tests to identify potentially reactive aggregates have been devised with perhaps the best known being the A.S.T.M. Chemical Method, C289,and the Mortar Bar Method, C227, for alkali-silica reactivity and the Rock Cylinder Method, A.S.T.M.,C586,for alkali-carbonate reactivity. Among other methods which have been used as a screening test for checking aggregate for potential reactivity is the Gel Pat Test devised by Jones and Tarleton in 1958 /1/. This test involves the embedding of a suspect aggregate in an O.P.C. tablet which is ground to expose the aggregate and stored in a $\frac{1}{2}$N solution of KOH and NaOH.

As part of a programme of testing of alkaki reactive aggregates in the U.K. organised by Dr. Nixon of the Building Research Establishment /2/ small amounts of some 15 samples of potentially reactive and non-reactive fine aggregates from British sources were provided in order to test the validity of the pat test procedure as a screening test for potential reactivity. Several series of cement pats were prepared using these aggregates and stored in alkalis at 20°C, 30°C, 40°C and 50°C for periods up to 56 days. The results of these tests will be reported elsewhere but in general terms it was observed that very few aggregate particles reacted to produce gel under the 20°C storage condition but all 15 samples contained particles which showed reaction after storage at 50°C. The cement/ aggregate pats used in this study were then used to provide examples of potentially reactive and non-reactive material for further study.

2. EXPERIMENTAL CONSIDERATIONS

2.1 The Petrography of the Samples

Examples of reacted and non-reacted particles of aggregate were broken from the face of the cement tablets using a dental drill and other methods. These methods set a practical size limit on particles extracted of about 1 mm. Thus the petrographic descriptions summarised in Table 1 below concentrate on the mineralogical composition of the fraction of the sample with particle sizes in excess of 1 mm.

Table 1. Petrographic Data on the +1mm Size Fractions of the Samples

Sample		Maximum Grain Size mm	Percentages based on visual estimates							Principal Constituents -1mm Fraction
			Flint	Quartz	Quartzite	Iron Ore	Sandy Iron Stone	Shell	Others	
Thames Valley	1	3	70c	20	5	5	-	tr	-	Quartz (Quartzite)
	2	2	50	35	5	5	5	-	-	Quartz (Flint Quartzite)
	3	2	45	40	5	10	-	-	-	Quartz (Quartzite Flint)
Trent Valley	1	1	50*	-	50*	-	-	-	-	Quartz (Quartzite, Ironstone)
	2	5	50c	10	30	5	3	-	Igneous 2	Quartz (Quartzite)
	3	1	-	-	-	-	-	-	-	Quartz (Quartzite, Ore, Flint)
	4	5	60	5	20	15	-	-	-	Quartz (Quartzite
	5	3	15	3	73	2	2	-	Igneous 5	Quartz Quartzite
	6	5	10	3	75	5	5	-	Igneous 2	Quartz (Quartzite)
	7	4	20	10	65	5	-	-	Feldspar 2	Quartz Quartzite
Sea Dredged	12	2	10*	20*	40*	5*	-	25*	-	Quartz (Shell, Quartzite)
	14	5	10	15	57	1	2	15	-	Quartz (Shell)
	16	2	25	50	15	-	-	10	Feldspar tr.	Quartz (Shell, Quartzite)
	21	5	40	20	30	tr.	6	3	Feldspar 1	Quartz, Quartzite (Shell)
	23	2	20*	43*	-	2*	-	35*	-	Quartz (Shell)

* = Very few +1mm grains only   tr. = trace   c = chalcedony present as a minor constituent

It was observed that, although some of the ironstone particles appeared to have decayed as a result of immersion in the alkali solutions, the reacted particles associated with silicate gel were flints of various types. These flint particles were extracted from the cement matrix together with a selection of flint particles which showed no visible signs of reaction. Each particle was washed repeatedly in distilled water and dried.

Both reactive and non-reactive flints were graded according to their colour and, although this is to some extent subjective because of gradation between colours, it was possible to group the particles as follows:

Pure white:	outer porous cortex material
Cream to brown:	colour probably due to iron impurity
Grey to black:	vitreous smoky flint

Previous work relating to reactive flint particles in Denmark /3/, /4/ and the U.K. /5/ show that, although small differences can be identified between varieties of flint, there are no clear features of morphology composition or colour to distinguish potentially reactive particles from non-reactive ones.

2.2 Scanning Electron Microscopy

Particles selected in this study were broken across to provide a fresh and reasonably flat surface for study in a Hitachi S450 scanning electron microscope. The particles were mounted on stubs for use in the microscope and carbon coated. In addition to these aggregate particles a series of gels taken from the surface of reacted particles in the cement pats were dried and prepared for examination in the scanning electron microscope in a similar way. This microscope has been fitted with a Link Systems 860 series energy dispersive analytical facility which is capable of accurate quantitative elemental analyses if flat polished specimens are used. In the case of the aggregate and gels examined in this study quantitative analysis was not possible because of the roughness of the surfaces available for study. However, semi-quantitative analyses were made and by normalising results to 100% some general comparisons may be drawn between specimens. However, care in interpretation is required when drawing comparisons between results because analytical precision will be low and normalisation of results masks the presence of water and carbonate in the specimens. In order to improve the analyses, small areas of 100 micron side were analysed rather than a single point as is more usual with electron probe micro-analysis. With the gel analyses several replicate area analyses were made and the result averaged.

Scanning electron microscopy showed that the broken flint surfaces have a range of surface textures of varying roughness and contain micropores often less than 1 micron in diameter. Figures 1 and 2 are typical of the types of surface features observed and a series of photographs of this type all at the same magnification were taken of the specimens examined. The size and surface area of the voids (as a percentage of the whole surface) were determined for each specimen by using squared tracing paper.

Electron micrographs were also taken of specimens of alkali-silica gels taken from the surfaces of reacted particles. The majority of the gels have a rounded molecular appearance as is illustrated by Figure 3 while others have a spongy 'crumpled foils' type of appearance as in Figure 4. Little correlation was observed between type of flint and appearance of the gel but the spongy appearance of the gel is more common from samples that have been stored at the higher temperatures.
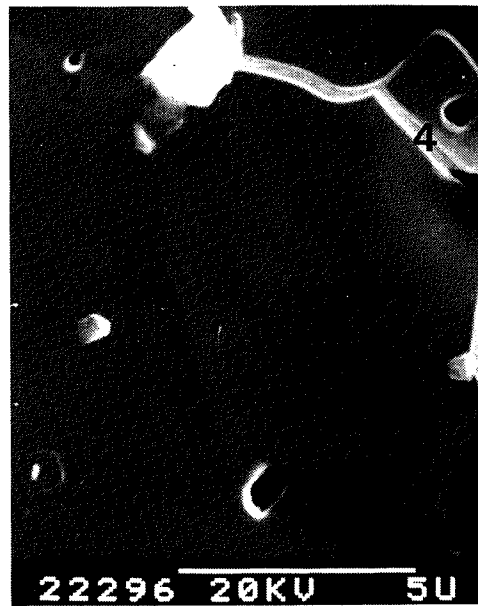
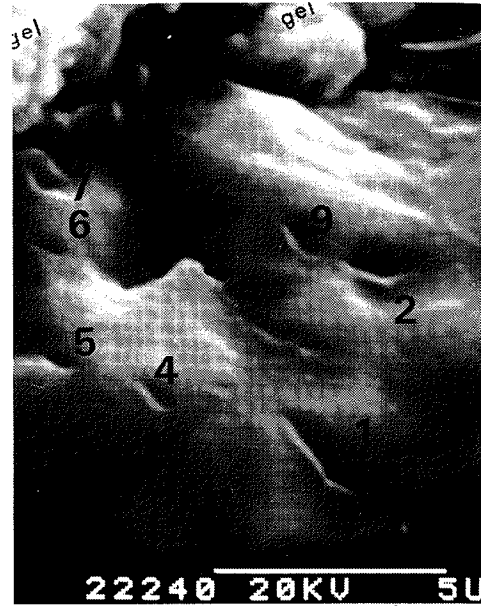Fig. 1 Non-reactive grey flint. Numbers indicate pores in the surface. Scale bar 5mμ.

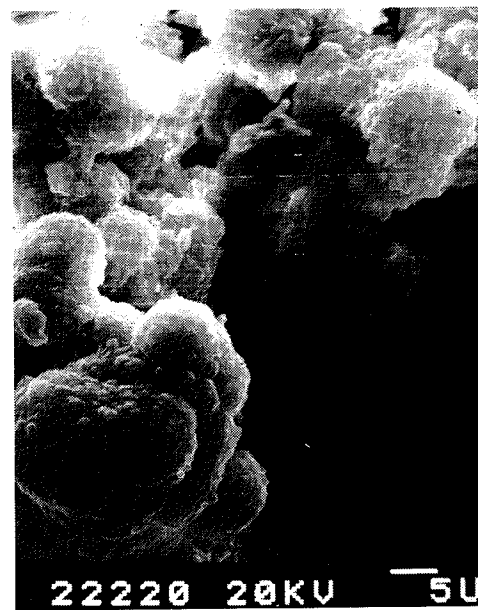Fig. 2 Cream/brown reacted flint with gel. Surface micropores numbered scale bar 5mμ.

Fig. 3 Gel produced at 30°C on flint from the Trent Valley. Scale bar 5mμ.
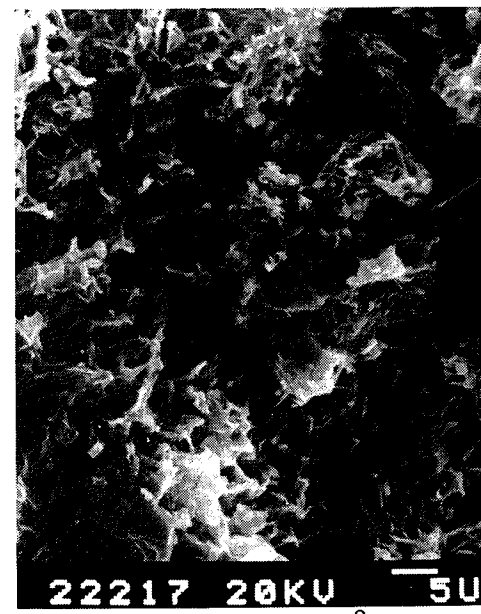

Fig. 4 Gel produced at 50°C on flint from sea dredged gravel. Scale bar 5mμ.

Table 2. Normalised Analyses of Alkali-Silica Gels

Sample		Si	Al	Fe	Ca	Na	K	S	Storage temp. °C	Morphology
Thames	1	17.9	1.45	0.00	22.2	6.06	10.1	2.85	50	nodular/foils
Valley	1	21.5	1.11	0.05	20.75	9.95	6.37	0.55	30	nodular
Trent	1	22.4	2.21	0.18	22.0	3.36	8.76	0.64	50	nodular/foils
Valley	1	24.4	0.97	0.18	20.4	5.66	7.23	0.23	30	nodular
	3	23.0	0.99	0.15	19.8	6.18	7.95	1.16	50	foils
	3	25.3	0.92	0.04	18.8	6.77	6.56	0.25	40	foils
Sea	14	16.6	1.45	0.32	22.2	8.61	11.4	1.73	50	foils
Dredged	14	19.9	1.30	0.16	12.9	21.5	4.11	0.94	30	nodular
	16	22.6	1.87	0.58	14.9	10.8	8.68	0.44	30	nodular
	16	20.7	1.77	0.30	20.3	5.57	10.1	1.30	50	foils
	16	21.8	1.15	0.12	17.2	9.29	8.93	1.43	40	nodular/foils
Wood Opal		23.7	3.70	0.31	19.3	4.48	6.87	0.14	20	nodular
Cyprus Siliceous Lst.		23.4	0.86	0.15	19.8	6.29	9.16	0.22	20	nodular
Cyprus Siliceous Lst.		15.6	1.32	0.23	34.4	3.59	8.71	0.53	30	foils

3. EXPERIMENTAL RESULTS

3.1 The Alkali-Silica Gels

A series of some 11 semiquantitative analyses of gels were made of dehydrated specimens taken from the surface of reacting particles. The normalised results of these analyses are tabulated in Table 2 together with analyses of gels produced in a similar way from specimens of wood opal and the reactive siliceous limestones from Cyprus. In order to improve analytical precision between 2 and 4 replicate analyses were made on each gel specimen and the results averaged.

The solutions used in the gel pat tests are a lime saturated mixture of sodium and potassium hydroxides thus accounting for the high lime contents of all the gels. The aluminium and iron contents derive from impurities in the aggregate particles while the ratio of sodium to potassium appears to correlate with the temperature at which the reaction took place. This ratio suggests that a greater proportion of potassium enters the gel at the higher temperatures, though total alkali in the gels is very variable and cannot be related to reaction temperature. The general similarities between all the analyses listed in Table 2 are striking and it is clear that it is not possible to correlate reactive particle type or morphology satisfactorily with gel composition under these test conditions.

3.2 The Flint Particles

Correlation of the potential reactivity of the flint particles with colour, pore size, pore area and analytical data were attempted for the various storage temperatures. As storage temperature is increased so the number of flint particles reacting also increases though, because some particles are inherently more reactive than others, it is difficult to relate rate of reaction directly to increased temperature of storage as is illustrated by the examples given in Table 3 below. It should also be noted that many flint

Sample		Storage 20°C	Storage 30°C	Storage 40°C	Storage 50°C
Sea dredged	16	3	17	29	36
Trent Valley	3	0	2	4	17
Thames Valley	1	0	0	17	20

aggregates have proved to be non-reactive in service but can be made to react under the conditions of this test provided elevated storage temperatures are used.

Under these test conditions colour and reactivity appear to show good correlation, the cream to brown coloured particles being the most reactive though some white particles also exhibit reaction at the highest temperature. This colour correlation is also reflected in the analytical results in that reactivity can be shown to correlate in a general way with both iron and aluminium impurity concentration in the flints. Iron impurity in the flint gives rise to the brown colouration observed, but whether the iron is a primary constituent of the flint or has been absorbed into its pores from the surroundings remains uncertain. Correlation between reactivity and observed porosity is uncertain but, since reactive particles absorb and fix alkalis as alkali-silica gel, there is some poor correlation between alkali concentration absorbed into the flint surfaces and reactivity. These relationships
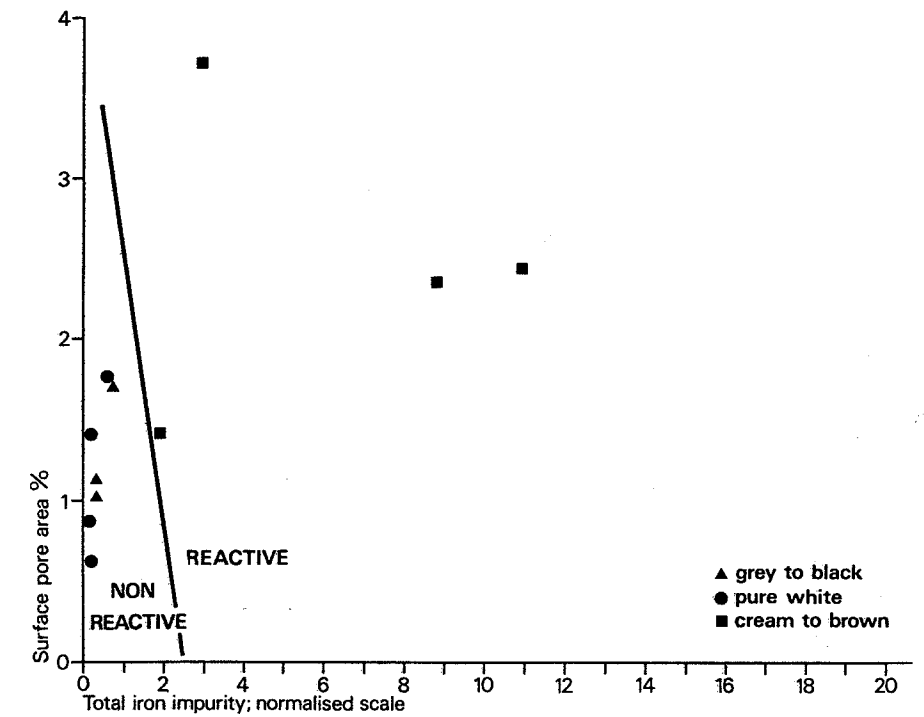
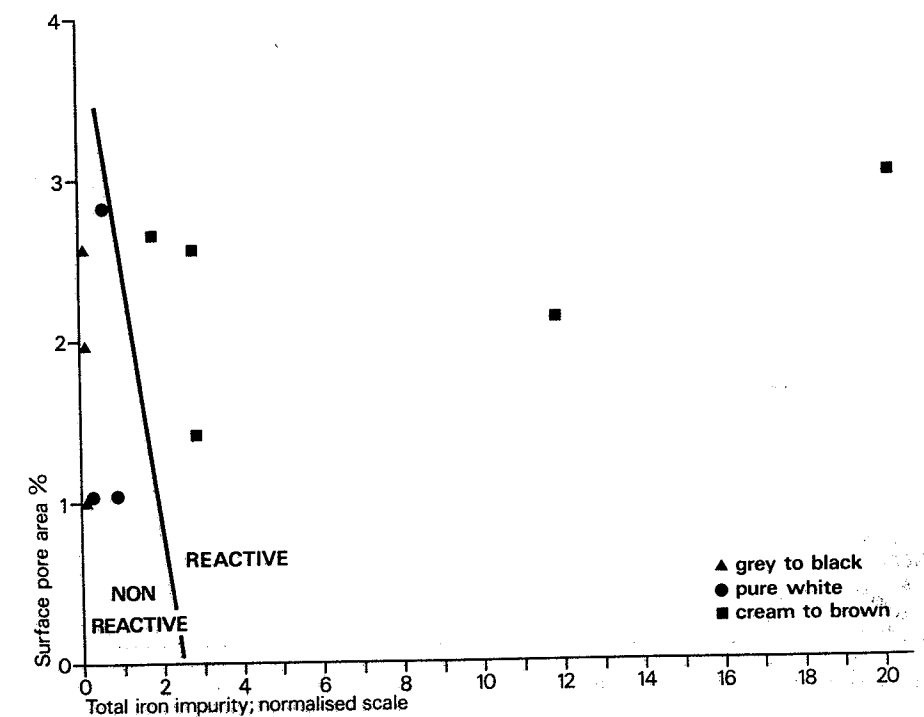Fig. 5 Iron impurity against pore area. 30°C storage temperature.

Fig. 6 Iron impurity against pore area. 40°C storage temperature.
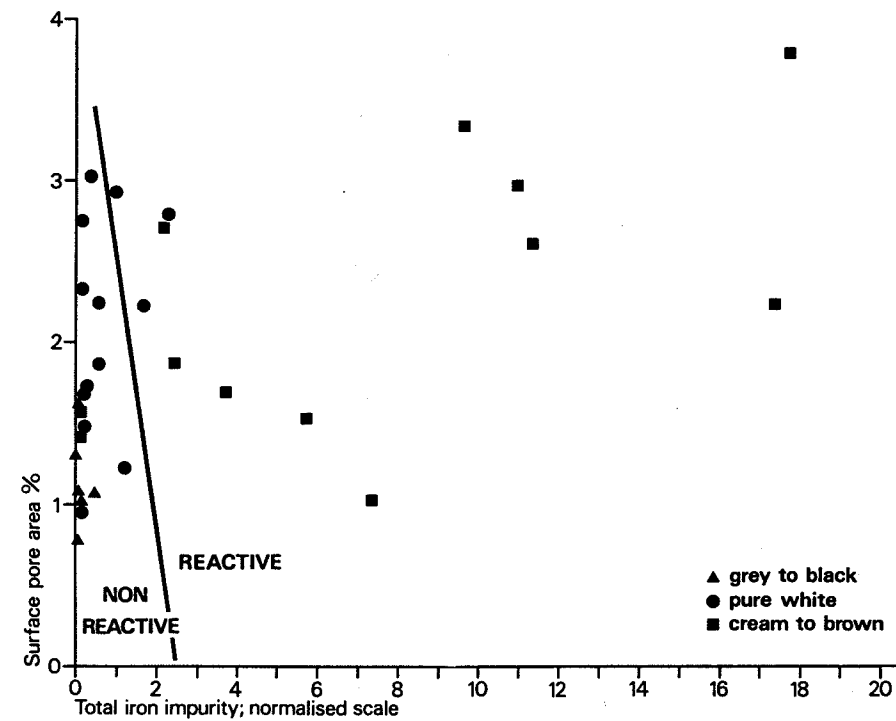
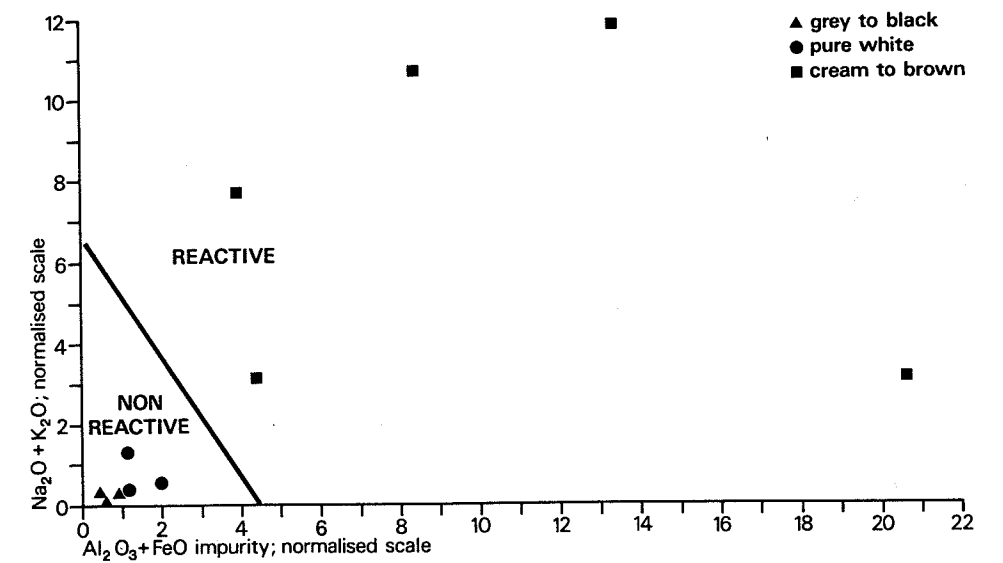Fig. 7   Iron impurity against pore area. 50°C storage temperature.
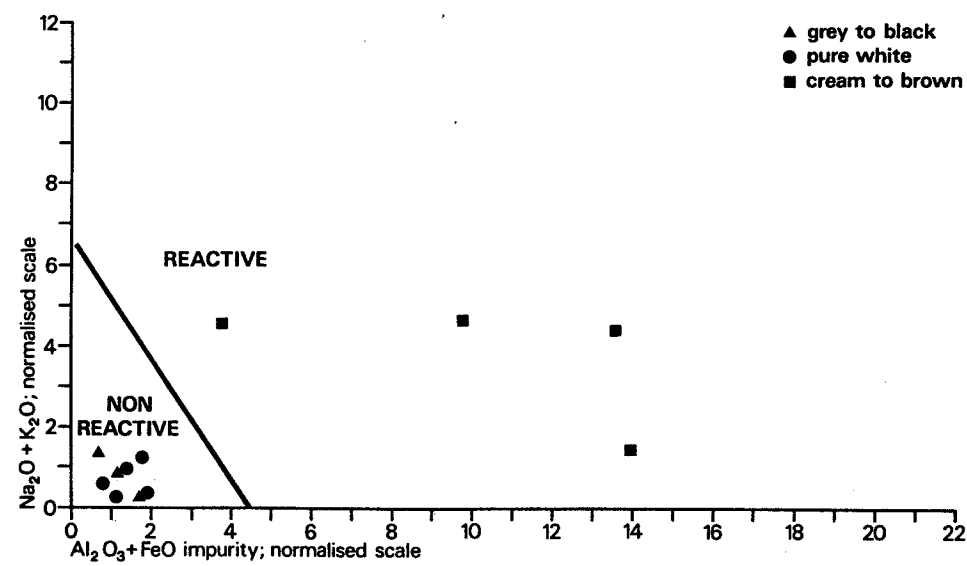

Fig. 9   Iron and aluminium against alkalis. 40°C storage temperature.

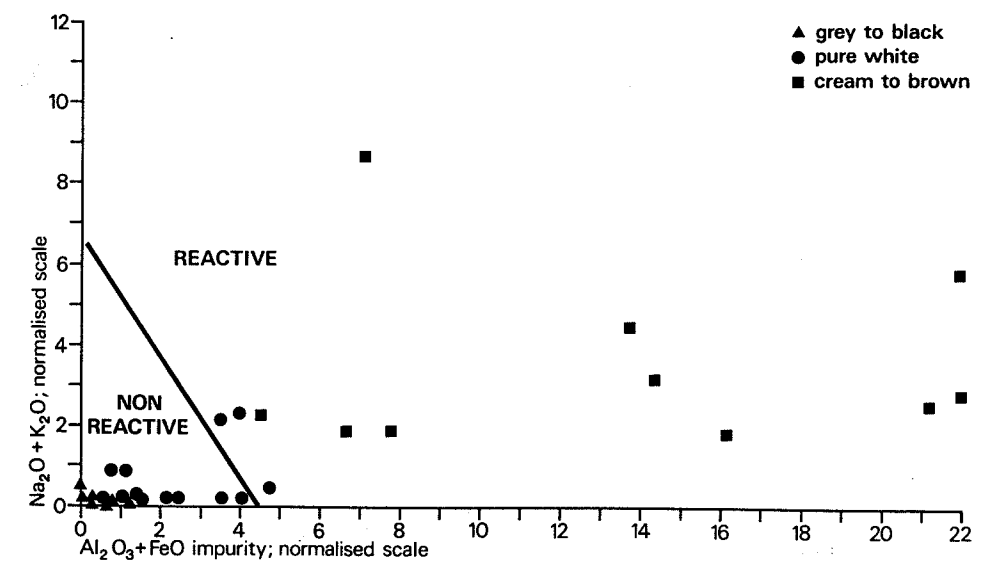Fig. 8   Iron and aluminium against alkalis. 30°C storage temperature.

Fig. 10   Iron and aluminium against alkalis. 50°C storage temperature.

are best illustrated by the scatter diagrams Figures 5, 6 and 7 which
correlate pore area against iron and aluminium impurity and Figures 8, 9 and
10 which correlate absorbed alkalis with iron impurity. These diagrams
allow two fields, non reactive and potentially reactive, to be identified.
It should be noted that the 'reactive fields' indicated are not exclusive
to reactive flint only since non-reactive cream to brown flints are present
in some test pats (particularly those at low storage temperatures) and
would plot in the 'reactive field'. No grey to black flints with low levels
of impurity were found to react, however, so the non-reactive fields in these
diagrams are exclusive of reacting particles even at the $50^{\circ}C$ storage
temperature.

4. DISCUSSION OF THE RESULTS

4.1 Morphological Consideration of the Gels

The nodular and crumpled foil types of gel morphology correlate well with the
temperature of gel formation. The differences between gels formed at different
temperatures might be expected to relate to differences in chemical composition,
rate of formation and viscosity. Analyses of the dehydrated specimens do
not show systematic variation of overall composition but the ratios of Na_2O to
K_2O do indicate that potassium enters the gel more readily than sodium at the
higher temperatures. A possible explanation of the morphological differences
may be made if the gel/solution interface is considered to be an elastic
osmotic membrane. At low temperatures the gel is produced slowly so that the
membrane swells slowly to form a series of rounded domes. At higher temperature
reaction product is produced rapidly so that the membrane (perhaps less
elastic because of compositional differences) frequently splits to allow
gel to spill out as a sheet or foil around which a new membrane develops; the
frequent splits in the membrane eventually allow a sponge-like mass of plates
and foils to develop as is observed.

4.2 Morphological Consideration of the Flints

Although the correlation between reactivity and impurity levels in flints is
well demonstrated by the gel pat experiments, the expected correlation of
reactivity and the micro-structure of the flints is by no means clear. No
real correlation of reactivity and observed pore size or proportion can be
drawn, although this may only reflect the crude observational method and
limited variation measured. However, the relative roughness or smoothness of
the fractured surfaces of the flints as illustrated by Figures 1 and 2 provides
some general correlation with the rougher surfaces being more typical of the
reactive particles.

5. CONCLUSIONS

The following conclusions may be drawn from the series of gel pat tests carried
out with aggregates containing flints:

1. The reaction producing gel becomes more rapid and more particles react
   as storage temperature is increased.

2. Cream to brown flints appear most reactive in these tests while grey
   to black flints were unreactive.

3. The reactive particles contain relatively high impurity levels of iron
   and aluminium.

4. The Na_2O/K_2O ratio is inversely proportional to reaction temperature in gel.

5. The morphology of the gel surface changes as reaction temperature rises
   possibly due to the disruption of an osmotic membrane.

References

1. JONES, F. E. & TARLETON, R. D., Reactions between aggregates and cement.
   Part VI National Building Research Paper No. 25 H.M.S.O. 1958b.
2. NIXON, P. J., Testing for alkali reactive aggregates in the U.K.
   6 Int. Conf. Alkalis in Concrete, Proceedings 1983.
3. IDORN, G. M., Durability of concrete structures in Denmark, Technical
   University of Denmark 1967.
4. BUURMAN, P. and VAN DER PLAS, L., The genesis of Belgian and Dutch flints
   and cherts, Geologie Mijnb, 50 1971: 9-28.
5. SIMS, I., Investigations into some chemical instabilities of concrete,
   Ph.D. thesis London University 1977, 175-243.