

CHEMICAL STUDIES OF ALKALI SILICA REACTION IN CONCRETE
WITH DIFFERENT FLINT CONTENTS

P J Nixon⁺, C L Page^{*}, J Hardcastle⁺, I Canham^{*} and K Pettifer⁺

⁺ Building Research Establishment, UK

^{*} Aston University, Birmingham, UK

1. ABSTRACT

Concretes have been made using different proportions of reactive flint in the aggregate and high alkali levels in the cement such that some show damaging expansion and others with greater proportions of flint do not expand. The concretes have been studied by optical microscopy, pore solution analysis and increase in amount of soluble silica. It has been found that in the concretes containing the higher proportions of flint, which do not expand, there is a greater reduction in pore solution hydroxyl ion concentration, and more solubilisation of silica. The nature of the pessimum concept of aggregate reactivity is discussed in relation to these results.

2. INTRODUCTION

The critical influence on the amount of expansion and damage in mortars and concretes, caused by the alkali silica reaction, of the proportion of reactive silica in the aggregate and the ratio of reactive silica to the available amount of alkali has long been recognised. The effect is particularly apparent with very reactive forms of silica like opal where at moderate alkali levels the greatest expansion is found when only a few per cent of opal are present in the aggregate and the expansion decreases to negligible levels as the proportion of opal increases beyond this. Thus for example Hobbs[1] investigating a particular source of opal from the Beltane Quarry in California, found that in mortars made with a cement having an equivalent sodium oxide content of about 1%, the greatest expansion was with 6% opal in the aggregate whereas expansion had decreased to negligible amounts when 16% opal was present. When the alkali content of the mortar increased Hobbs, in common with other workers, found that the amount of opal needed to produce the worst expansion also increased, ie the worst expansion was produced at a particular silica to alkali ratio.

Similar effects have been found with other aggregates and the proportion of silica producing the greatest expansion has acquired the term 'pessimum' proportion. This 'pessimum' effect has been found to be very important in the UK experience of damage caused by alkali silica reaction. The main reactive form of silica in the UK is micro and crypto-crystalline quartz in flints and cherts. Nixon[2] has reported a laboratory investigation of a particular river sand and gravel in which the predominant rock type was flint. He combined the sand/gravel in various proportions with a limestone aggregate such that the proportion of the sand/gravel varied from 10% to 100% of the whole aggregate. It was found that the maximum expansion of the concrete made with the aggregate occurred when the flint sand was present as 20% of the total aggregate. Negligible expansions were found when 60% or 100% of the aggregate was composed of the sand/gravel. The pessimum has also been found to be

important in real concrete structures. Many of the worst cases of ASR damage in the UK have occurred in concrete made with a sand containing flint or chert combined with a limestone or granite coarse aggregate. In contrast, in the south-east of England there has been extensive use of concrete made with flint sands and gravels without reported cases of damage.

In the present investigation, the mechanism underlying the pessimum effect in concrete made with a sand/gravel containing flint, has been studied in three ways: using optical microscopy, by measuring the amount of attack on the siliceous aggregate and by analysing the change in the composition of the concrete pore solution during reaction.

3. EXPERIMENTAL

3.1 Materials

The sand and gravel was from the same source in the valley of the river Thames as in previous investigations[2]; 96% of the gravel was composed of flint and 50% of the sand. The other major constituents of the sand were quartz (20%), meta quartzite (14%) and limestone (14%).

A limestone from the west of England (Cheddar) was used to vary the proportion of flint sand/gravel in the total aggregate. The total silica content of this limestone has been found by chemical analysis to be only 0.98%.

The cement used in most of the investigation was an ordinary Portland cement with an equivalent sodium oxide content of 0.96% (0.96% K_2O , 0.33% Na_2O). In some of the expansion tests however a second somewhat higher alkali Portland cement with 1.06% Na_2O equivalent (1.3% K_2O , 0.21% Na_2O) was used.

3.2 Variation of expansion with proportion of siliceous aggregates

The expansion of concretes containing this sand and gravel combined in various proportions with the limestone (and in a few cases with a granite coarse aggregate and quartz sand) have been measured at a number of alkali levels and at either 38°C or 20°C in moist conditions or outdoors. The specimens stored at 20°C or 38°C were 200 x 75 x 75 mm prisms which were stored in individual containers over water. The outdoor specimens were

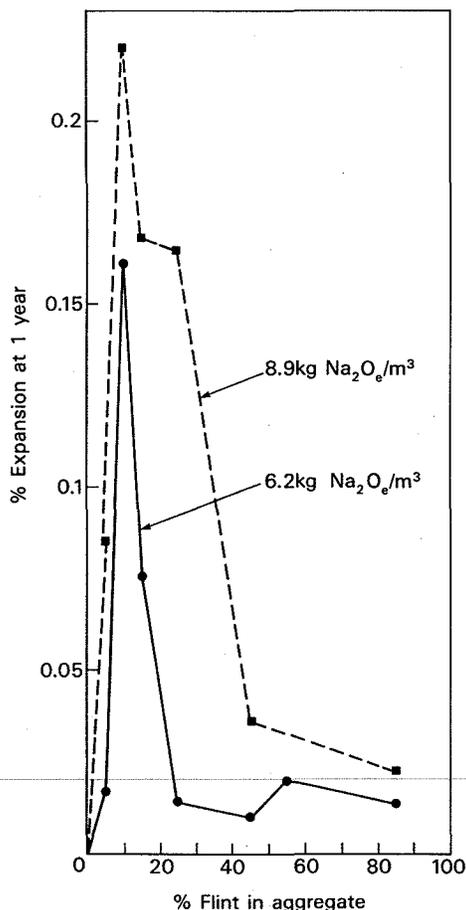


Figure 1. Effect of flint content on expansion of concrete stored in moist conditions at 38°C.

either 200 x 75 x 75 mm prisms or 100 x 100 x 500 mm prisms. The variation of expansion with content of flint for specimens stored at 38°C is summarised in Figure 1. It can be seen that the greatest expansion corresponds to a flint content of about 10%.

Increase in the alkali level of the concrete results in a broadening of the pessimum curve, ie the range of flint contents over which there is significant expansion. At 20°C significant expansion and cracking was found in the concretes containing 10 and 15% flint at both alkali levels after 2 years. No other flint contents were tested at 20°C. Outdoors, where only the complete series at the higher (8 kg/m³ Na₂O_e) alkali level was exposed, cracking was found in the 5, 10, 15, 25 and 45% flint concretes after about 5 years but no cracking was found in the mix containing 85% flint (ie all sand and gravel). Two concretes with about 5.6 kg/m³ Na₂O_e and with 10 and 15% flint in the aggregate respectively, which were also stored outdoors, had also cracked after 5 years. Overall therefore the results at 20°C and outdoors support the results obtained at 38°C in suggesting a pessimum content of flint of about 10%. The results of outdoor exposure suggest however a wider range of flint contents over which potentially damaging expansion might occur; from below 5% to above 45% but below 85%.

The increase in expansion with time for a mix containing a pessimum quantity of flint stored in moist conditions at 20°C or 38°C is shown in Figure 2.

3.3 Optical microscopic examination

A number of concretes either containing 'pessimum' proportions of flint or chert which have expanded and cracked after moist storage or alternatively with high proportions of flint or chert such that the concrete has not expanded significantly or cracked visibly after prolonged moist storage, have been compared by optical microscopic examination of thin (30 micron) sections.

In the concretes containing pessimum flint proportions which have expanded and cracked, there is clear evidence of attack on flint particles and both micro-cracks and macro-cracks (50 micron up to millimetre widths) propagate from such sites of reaction. The cracks are often filled with gel and they narrow with distance from the reactive particles. Usually the cracks pass through the cement paste but in the most severe cases non-reacting aggregate particles may also be fractured. Even in severe cases however, considerable areas of the cement paste seem un-affected by the reaction or the cracking.

An effect which is seen very commonly is darkening of the cement

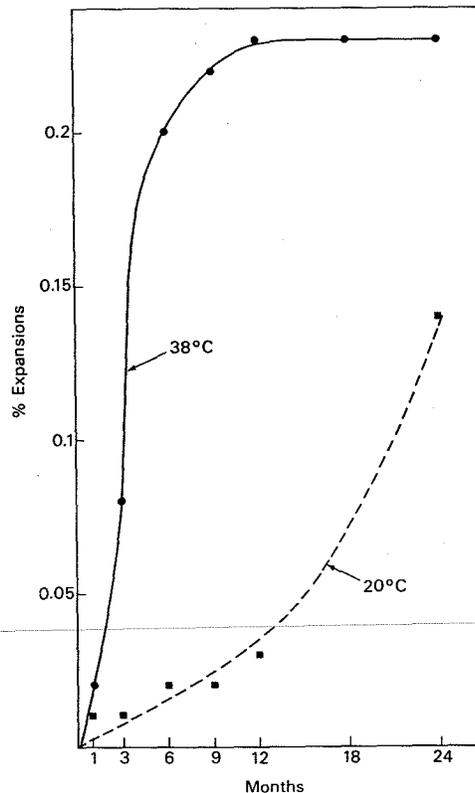


Figure 2. Expansion with time of concrete containing 10% flint.

paste in zones bordering gel-filled cracks or voids or close to reacting particles. The darkened areas look 'milky' in crossed polars and are distinctly different to the normal isotropic cement paste. It is probable, though not proven, that the effect is caused by gel impregnating pores in the paste.

Fine micro cracks with widths up to about 10 microns are also very common in the concretes with high flint/chert contents which have not cracked or expanded. The cracks divide the paste into small blocks forming a reticulated pattern on a very much finer scale and quite different in appearance to anything seen in the paste of concrete with pessimum flint/chert contents. There is very little sign of attack on the aggregate particles and only very small amounts of discrete gel are found in voids near to aggregates.

The majority of the cement is darkened and has a milky appearance under crossed polars. It appears therefore that the majority of the cement paste is impregnated with gel. The only unaffected areas are zones bordering the micro cracks; the reverse of the situation in the 'pessimum' concretes.

3.4 Extent of attack on the siliceous aggregate

The amount of attack on the siliceous aggregate was monitored by measuring the increase in the soluble silica content of concrete using the method for cement content determination in BS 1881: part 124. This method consists of attacking the sample with dilute hydrochloric acid and then with sodium carbonate solution so that any silica from the cement and any siliceous gel formed from the aggregate is taken into solution, evaporating and coagulating the silica from the solution and then determining gravimetrically. Concretes with three alkali levels and either 15 or 85% flint in the aggregate combination were investigated. The concretes were stored in moist conditions at either 20°C or at 38°C after 1 month at 20°C.

The results up to 10 months, expressed as percentage soluble silica in the concrete sample, are given in Table 1. It can be seen that there is a progressive increase with time for all the samples. The differences between the concretes with different alkali levels are small and inconsistent. However, in most cases, there is a greater increase in the soluble silica in the mix containing 85% flint compared with the mix with 15% flint. Also there is a greater increase in the concretes stored at 38°C than those stored at 20°C.

3.5 Effect of flint content on hydroxyl ion concentration of pore solution during reaction

For this part of the study 100 mm concrete cubes containing 400 kg/m³ of cement (equivalent to 3.7 kg Na₂O_e/m³) were cast with combinations of the Thames Valley and limestone aggregates such that the flint contents were 5, 35 or 8%. In order to express pore solutions from the concretes a free water/cement ratio of 0.55 was used. After demoulding at 24 hours the specimens were wrapped first in absorbent paper and then in a double layer of polythene. Before sealing the polythene 100 ml of deionised water was added. The wrapped specimens were

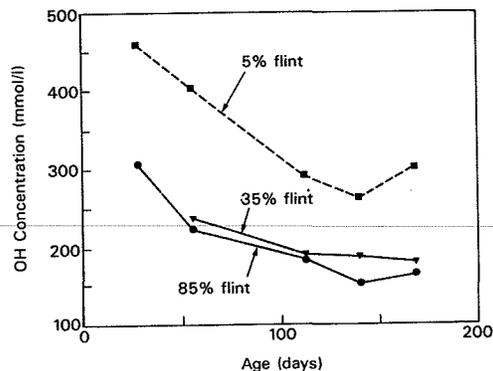


Figure 3. Change in OH in pore solution of concrete with three flint contents.

stored at 38°C until testing. Before testing the cubes were crushed and sieved through 1.18 mm. The crushed sieved material was pressed as described by Page and Vennessland[3]. The expressed fluid was collected in a plastic syringe and analysed for OH⁻ by titration with HNO₃ using phenol-phthalein indicator.

The change in hydroxyl ion concentration with age of specimens for concrete with the three flint contents is shown in Figure 3. It can be seen that in each case there is a decrease in hydroxyl ion concentration and that the decrease is most marked for the highest flint content mix. It is also apparent that by the time of the first measurement at 28 days there has been a considerable drop in hydroxyl ion concentration especially in the high flint content mixes. Similar results have been obtained for other aggregates at higher alkali levels in the concrete.

4. DISCUSSION

The measurements of expansion in high alkali concretes confirm earlier studies and field experience in showing that the greatest expansions are produced when the content of flint or chert is relatively small and that at high flint/chert contents the expansion is not significant. In this particular aggregate the pessimum flint content was found to be about 10% by volume of the aggregate. However, this cannot be assumed for other aggregates as there may well be differences in reactivity between flints or cherts from different sources.

It is apparent however that there has been a considerable amount of reaction in the high flint/chert content concretes. The total amount of silica dissolved is greater and the hydroxyl ion concentration is reduced to a greater extent the higher the flint/chert content. The optical examination also shows that there has been reaction in the high flint concretes producing cracking on a fine scale and much impregnation of the paste by gel.

These observations have implications for the diagnosis of alkali silica reaction and for the determination of cement contents. It is to be expected that there will be evidence of reaction even in concrete which has not expanded or cracked. However, it should be possible using the criteria described above to differentiate by microscopic examination between reaction producing damage and non-expansive reaction. Such extensive reaction in concretes made with a variety of contents of siliceous aggregate could also lead to serious overestimate of cement contents by the soluble silica method whether or not there is evidence of damage.

The results suggest the following reasons for the lack of expansion in the high flint concretes. The gel produced appears to be able to dissipate itself into the cement paste without causing excessive stress in the concrete. The widely distributed sites of reaction may help this both by altering the composition of the gel so that it is more fluid and by distributing the gel throughout the concrete so that it has as much paste as possible to dissipate into. Such stresses as are produced seem to be absorbed by the fine cracks spread throughout the cement paste.

Damaging expansion and cracking seems to occur when the reaction occurs at a relatively small number of sites producing local concentrations of gel. The total amount of reaction between silica and alkali is low but the gel produced has the composition and is present locally in sufficient amounts to produce an expansive stress to which the concrete cannot accommodate itself without cracking.

5. CONCLUSIONS

1. Concrete made with this sand and gravel expanded to the greatest amount when the flint content in the aggregates was low and expansion was insignificant at high flint contents.

2. The amount of silica dissolved from the aggregate and the reduction in the hydroxyl ion content of the pore solution both increased as the flint content increased, showing more reaction at high flint contents.

3. At high flint/chert contents any gel produced seems to be able to dissipate itself into the cement paste without causing sufficient stress to damage the concrete.

6. REFERENCES

- [1] Hobbs, D W. 'Influence of mix proportions and cement alkali content upon expansion due to the alkali silica reaction'. C & CA Technical Report No 534, June 1980.
- [2] Nixon, P J and Bollinghaus, R. 'Testing for alkali reactive aggregates in the UK'. Proceedings 6th International Conference, Alkalis in Concrete, Copenhagen, 1983, pp 329 - 336.
- [3] Page, C L and Vennesland, D. 'Pore solution composition and chloride ion binding capacity of silica fume cement pastes'. Materials and Construction, Vol 16, No 91, 1983, p 19.

TABLE 1. % SOLUBLE SILICA IN CONCRETE

Aggregate	Thames Valley sand/ limestone coarse (15% flint)			Thames Valley sand and gravel (85% flint)		
	3.7	5	7	3.7	5	7
Alkali in concrete (kg Na ₂ O _e /m ³)	3.7	5	7	3.7	5	7
<u>20°C</u>						
24 hours	2.98	3.02	3.02	3.33	3.49	3.25
1 month	3.12	3.17	3.12	3.41	3.60	3.35
2 months						
3 months	3.35	3.30	3.19	3.68	3.84	3.72
4 months						
6 months	3.61	3.43	3.22	3.90	4.03	3.9
<u>38°C</u>						
24 hours	2.98	3.02	3.02	3.33	3.49	3.25
1 month	3.12	3.17	3.12	3.41	3.60	3.35
2 months	3.25	3.31	3.29	3.71	3.56	3.63
3 months						
4 months	3.40	3.38	3.45	4.00	3.97	3.99
6 months						
7 months	3.49	3.58	3.64	4.48	4.10	4.15
10 months	3.61	3.77	3.85	4.68	4.27	4.33