Pergamon

Cement and Concrete Research, Vol. 28, No. 7, pp.1037–1048, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00067-2

AGGREGATE-CEMENT CHEMICAL INTERACTIONS

W.A. Tasong,[1] J.C. Cripps, and C.J. Lynsdale[2]
Centre for Cement & Concrete, Dept. of Civil & Structural Engineering,
The University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

(Received December 7, 1995; in final form April 27, 1998)

ABSTRACT

This paper highlights the role played by aggregate with respect to the chemical interactions that take place within the interfacial transition zone between aggregates and cement paste matrix. Four commonly used aggregates with different chemical properties, basalt, limestone, silica sand, and quartzite, were investigated. It was observed that ions are both absorbed and released by the aggregates in all the aggregate-cement solution systems, with basalt being the most active in this respect. The findings reveal that aggregates are more chemically active than has been supposed and that a wide range of chemical interactions between the aggregates and cement should be anticipated. *© 1998 Elsevier Science Ltd*

Introduction

The aggregate-cement paste interfacial transition zone (ITZ) is known to be the weakest region in concrete, influencing both mechanical properties and durability performance. Many investigations (1–3) have shown that the amount and nature of the hydration products at the ITZ influence these properties of concrete. The processes responsible for the formation of the microstructure of the ITZ are not well understood. Some studies (4–8) postulate that the mechanisms responsible for the formation of the ITZ are related to differential ion diffusion caused by the zone's high porosity, resulting from the arrangement of the cement grains in contact with the aggregate. The precipitation of calcium hydroxide (CH) on the aggregate surface has been attributed to the heterogeneous nucleation and subsequent growth of CH on the aggregate surface from an oversaturated solution to form a duplex film.

The influence of aggregate chemistry on the properties of the ITZ have been given very little attention compared with the numerous studies on the influence of the cementitious matrix properties (e.g., water/cement ratio, use of admixtures, etc.). It is often assumed that most rock aggregates used in concrete making are chemically inert and that their interaction with the cementitious matrix is mostly physical. Thus, while some understanding of the ITZ's microstructure has been developed from the viewpoint of the cementitious matrix properties,

---

[1] Current address: Centre for Research in the Built Environment, University of Glamorgan, Pontypridd CF37 1DL, UK

[2] To whom correspondence should be addressed.

considerable work is still needed to provide a complete understanding of the importance of aggregate chemical properties on the development of the ITZ microstructure.

The reactions between aggregate and pore fluid can cause problems, especially when the reaction causes a volume change after the concrete has set; an example would be the alkali-silica reaction. However, in some aggregates these reactions, which take place at the interfaces, are helpful, as they increase cement paste-aggregate bond strength, making it possible to obtain high-strength concrete and improve its chemical resistance. For example, in studying cement paste-marble or limestone aggregate interfaces, it has been found (9,10) that a chemical reaction between calcite, the main rock constituent, and tricalcium aluminate of the cement takes place, yielding calcium carboaluminate phases that improve bond strength. On the limestone aggregate side, the evidence of etching of calcite grains by the cement paste has been observed in scanning electron micrographs (11). Similarly, selective leaching techniques that dissolve hardened cement paste in concrete while leaving aggregates particles intact reveal mass transfer from the aggregate to the hydrated phases during concrete hardening (12). It has also been found (13–17) that the concentration of the pore fluid in mortar or concrete can be affected by aggregate type. Other studies have shown that the use of reactive aggregates significantly affects the amount and the degree of orientation of $Ca(OH)_2$ crystals in the ITZ (18,19).

Compared with crushed sandstone aggregate, approximately a 15% increase in compressive strength was observed in 56-day-old concrete when crushed limestone of the same maximum size was used as coarse aggregate in a given concrete mixture (20). In addition, significantly higher compressive strengths, in the range 200–220 MPa, were reported when calcined bauxite (21) and tabular alumina (22) aggregates were used, probably due to chemical interaction between these aggregates and the cementitious matrix. Similarly, in the case of lightweight aggregate, it has been proposed that the reaction between calcium hydroxide and the aggregate surface is responsible for the high strength of the ITZ (23).

In this paper, an attempt is made to provide evidence elucidating the role played by aggregates in influencing ionic chemical interactions at the interface. Evidence suggesting that aggregates are more chemically active than has been supposed is presented. This investigation forms part of a large project investigating the bonding properties of natural rock aggregates used for concrete making and the influence of aggregate chemical properties on the development of the microstructure within the ITZ. The overall aim is to enrich our understanding of the role played by aggregate in influencing the nucleation and growth of mineral phases at the ITZ to enable advances in the field of high performance concrete to be made.

Experimental Procedures

Materials

Four concrete aggregates with different chemical properties, namely basalt, limestone, silica sand, and quartzite, were chosen for the study as examples of rocks typically used as concrete aggregates. They were selected to have potentially contrasting chemical interaction with the cement paste. The mineralogy of the rocks was determined using optical microscopy and X-ray diffraction (XRD). The petrography of the rocks used was as follows:

TABLE 1
Chemical composition obtained by XRF of OPC and rocks.

	Percentage Composition by Mass				
Composition	OPC	Basalt	Silica Sand	Limestone	Quartzite
SiO_2	20.78	50.14	97.36	2.10	96.28
Fe_2O_3	3.74	10.56	0.04	0.03	0.26
Al_2O_3	4.52	14.64	0.56	0.05	0.65
CaO	63.53	8.60	0.03	54.07	0.05
MgO	1.19	7.49	0.05	0.33	0.05
SO_3	2.81	0.05	0.05	0.58	0.06
Na_2O	0.47	2.92	0.23	0.24	0.16
K_2O	0.78	0.47	0.02	0.02	0.19
P_2O_5	0.13	0.16	0.02	0.01	0.02
TiO_2	0.21	1.71	0.10	0.01	0.10
MnO	0.10	0.15	0.01	0.01	0.01
LOI at 800°C	1.13	2.16	0.17	42.22	1.04
Total	99.39	99.11	98.60	99.14	98.86

Note: LOI is loss on ignition.

Basalt. The basalt aggregate samples were obtained from a quarry working a basaltic intrusion into carboniferous limestone at Water Swallows in Derbyshire, UK. It consisted of plagioclase (albite & anorthite), potash feldspar (sanidine) and pyroxene (augite) with some quartz, brucite, and clays.

Limestone. The limestone aggregate samples were obtained from a Carboniferous Limestone quarry at Stoney Middleton in Derbyshire, UK. It consisted of calcite with very minor quantities of quartz.

Silica Sand. Silica sand was supplied by David Ball Ltd, UK. It consisted only of quartz.

Quartzite. The quartzite aggregate samples were collected from alluvial workings in terrace gravel/cobbles from the Trent Valley at Rampton in Nottinghamshire, UK. It consisted of quartz with minor quantities of microcline feldspar.

The cement used was ordinary Portland cement (OPC). The chemical compositions of the cement and the rocks in terms of major element oxides, as determined by X-ray fluorescence (XRF), are given in Table 1 and the mineralogy of the rocks, as revealed by X-ray diffraction analysis, are given in Table 2.

Specimen Preparation

The experimental procedure consisted of suspending a known amount of finely crushed aggregate particles in a cement solution extract and in deionised water under temperature-controlled conditions for various time periods. Extracts were taken from the suspensions and analysed for metal ions, sulphur, and hydroxyl ions. Comparison of the results with those for

TABLE 2
Summary of the results of XRD analysis showing original rock and residue mineralogy.

State	Basalt	Limestone	Silica Sand	Quartzite
Original Rock	feldspar (*sanidine*), plagioclase (*albite and anorthite*), pyroxene (*augite*), quartz, olivine, calcite, and clays (*hydrobiotite-vermiculite, illite, kaolinite, montmorilonite, calcium-mordenite, and chlorite*)	calcite and quartz	quartz	quartz and feldspar (*microcline*)
Residue in deionised water	albite, anorthite, sanidine, quartz, augite, olivine, calcite, clays (*illite, kaolinite, montmorilonite, calcium mordenite and chlorite*), CSH, and αC_2AH_8	calcite and quartz	quartz	quartz and microcline
Residue in cement solution	albite, anorthite, sanidine, quartz, augite, olivine, calcite, gibbsite, clays (*illite, kaolinite, montmorilonite, calcium mordenite and chlorite*), CSH, αC_2AH_8, C_4AH_{13}, and ettringite	calcite and quartz	quartz and CSH	quartz, microcline and CSH

the original cement solution (which serves as the control) may indicate a potential aggregate-cement chemical interaction.

The aggregates were crushed into fine powder, with particle size distribution as given in Figure 1, in a Tema mill with great precautions taken to ensure that there was no contamination. The grinding compartment was thoroughly washed, and dried in an oven at 105°C, between testing of different aggregates; the powders were stored in sealed glass bottles.

A method similar to that described by Lawrence (24) was used to obtain the cement solution. Cement-deionised water suspensions (1 part of OPC in 4 parts of deionised water by weight) were mixed in 500 mL polythene bottles, which contained metal balls, using a mechanical tumbler. The suspensions were left in this state for about 3–4 h, after which the solid phases were filtered off through a 0.45-μm membrane filter. The filtrate obtained was sealed in polythene bottles and before use stored overnight in a refrigerator kept at 4°C. This gave a cement solution containing Ca^{2+}, K^{+}, Na^{+}, Al^{3+}, Si^{4+}, OH^{-} and other minor ions.

To prepare the test specimens, 25 g of aggregate powder was suspended in (a) 150 mL of cement solution, and (b) 150 mL of deionised water in 250 mL conical flasks. Each flask was

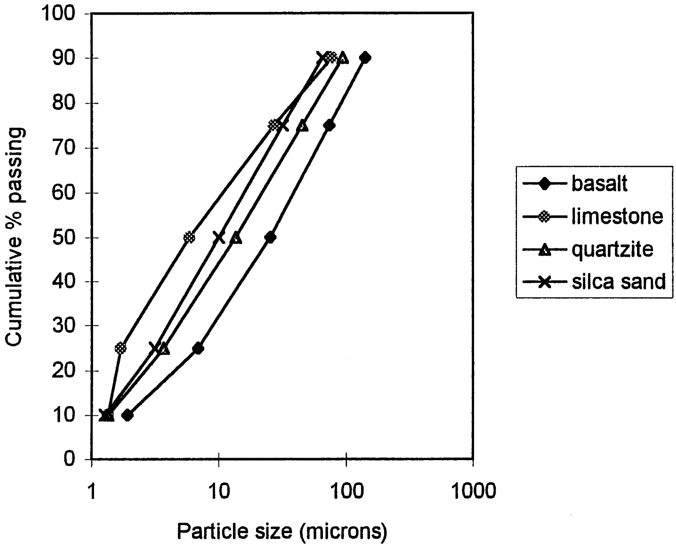

FIG. 1.
Particle size distribution of aggregate powders obtained by Coulter Counter LS 130.

shaken gently to mix its contents before it was securely stoppered to prevent loss of moisture through evaporation, and then was stored at constant 70°C. This temperature, which was used to accelerate the reaction, corresponds approximately with the maximum elevated curing temperature for precast concrete in the UK. As such it might be expected in mass concrete.

Chemical Analysis of Filtrate and Residue

After different lengths of time (i.e., 1, 3, 7, and 28 days) the suspensions were cooled and the filtrate for analysis obtained, using disposable 2.5 mL syringes equipped with 0.45 μm membrane filters.

The filtrate was analysed for Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, Na^{+}, K^{+}, Si^{4+}, and SO_4^{2-} using Inductive Coupled Plasma (ICP)-Atomic Emission Spectrometric (AES) methods (25) for element analysis. The basis of the method is the measurement of atomic emission by an optical plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductive coupled plasma (ICP). Many wavelengths of varied sensitivity are available for the determination of any one element, so that ICP-AES is suitable for all concentrations, from ultratrace levels to major components. The use of ICP in conjunction with a spectrometer enables the simultaneous determination of a large number of elements to be accomplished. A complete multielement analysis can be undertaken in a period as short as 30 s and with the consumption of only 0.5 mL of sample solution. The hydroxyl (OH^{-}) ion concentration of the filtrate was measured by titration against a 0.054 M HCl solution using phenolphthalein as the indicator.

After extracting the 28-day-old filtrates, the residues were analysed for mineral phases present using XRD. The results obtained were compared with those of the original aggregates in order to identify any changes due to chemical reactions.

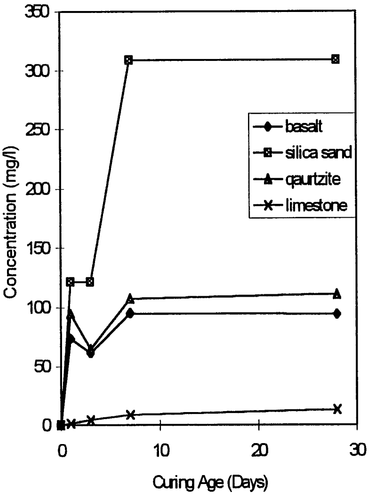

FIG. 2a.

Changes in concentration of Si^{4+} in deionised water-aggregate filtrates with curing age.

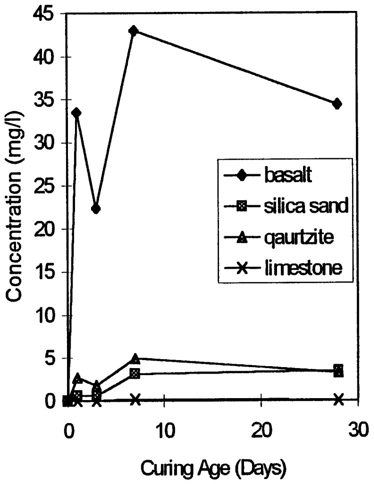

FIG. 2b.

Changes in concentration of Fe^{2+} in deionised water-aggregate filtrates with curing age.

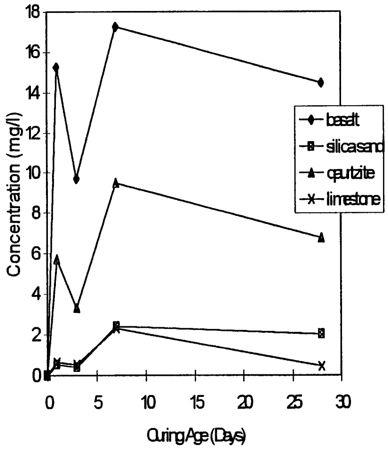

FIG 2c.

Changes in concentration of Al^{3+} in deionised water-aggregate filtrates with curing age.

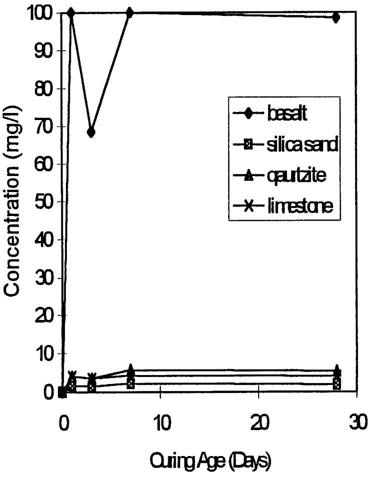

FIG. 2d.

Changes in concentration of Mg^{2+} in deionised water-aggregate filtrates with curing age.

Results and Discussion

All the aggregates studied showed significant chemical activity, but this varied according to aggregate type and the type of solution in which the aggregate is suspended. This chemical activity increased during the first seven days for the aggregate suspensions in cement solution and deionised water.

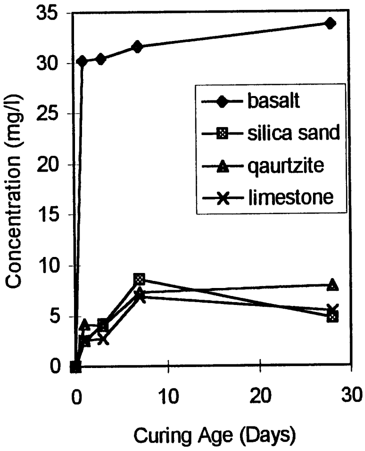

FIG. 2e.
Changes in concentration of Na^+ in deionised water-aggregate filtrates with curing age.

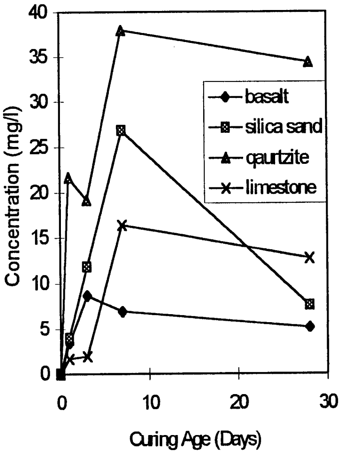

FIG. 2f.
Changes in concentration of K^+ in deionised water-aggregate filtrates with curing age.

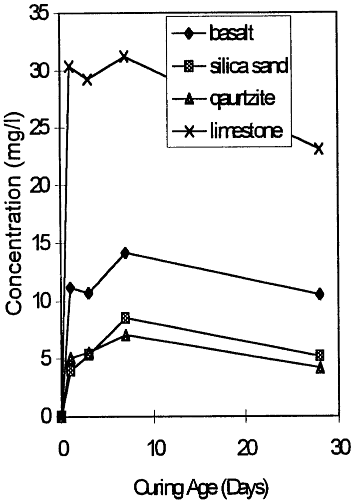

FIG. 2g.
Changes in concentration of Ca^{2+} in deionised water-aggregate filtrates with curing age.

Aggregate Suspension in Deionised Water

The graphs shown in Figures 2a to 2g are typical results for the aggregate suspensions in deionised water. Two specimens were tested for each result, and the average presented.

Basalt. Basalt released very significant amounts of Si^{4+}, Al^{3+}, Fe^{2+}, Mg^{2+}, and Na^+; significant amounts of Ca^{2+}; and minor amounts of K^+ and SO_4^{2-} to the deionised water.

These results are consistent with hydration of surface layers in a manner possibly similar to that proposed for weathering processes (26).

Limestone. Limestone released very significant amounts of Ca^{2+} and minor amounts of SO_4^{2-}, Al^{3+}, Mg^{2+}, Fe^{2+}, Na^{+}, Si^{4+}, and K^{+} into the deionised water. The results indicate that significant dissolution of calcite took place, releasing Ca^{2+} ions into the deionised water.

Silica Sand. Silica sand released very significant amounts of Si^{4+} and minor amounts of Al^{3+}, Mg^{2+}, Fe^{2+}, Na^{+}, and K^{+} into the deionised water, as might be expected. The results indicate that silica was leached out of the sand into the deionised water.

Quartzite. Quartzite aggregate released significant amounts of K^{+}, Si^{4+}, Al^{3+}, Mg^{2+}, Fe^{2+}, and minor amounts of Ca^{2+} into the deionised water. The results indicate that hydration of the surface layer had taken place. The likely source of K^{+}, Si^{4+}, and Al^{3+} is the chemical alteration to clay minerals of microcline (feldspar) present in the original aggregate.

In general, the results showed an increase in concentration of elements released into the deionised water during the first 1 or 2 days, followed by a fall at 3 days before again increasing to the 7th day, after which the concentrations stayed fairly constant right up to 28 days. The drop in concentrations of the elements released into the deionised water at 3 days could possibly indicated a flash point or the growth of a secondary mineral, which later dissociated and released the elements back into the deionised water. There were great similarities in behaviour between the Fe^{2+} and Mg^{2+} ions.

Aggregate Suspension in Cement Solution

The graphs shown in Figures 3a to 3e are typical results for aggregate suspensions in cement solution. Two specimens were tested for each result presented.

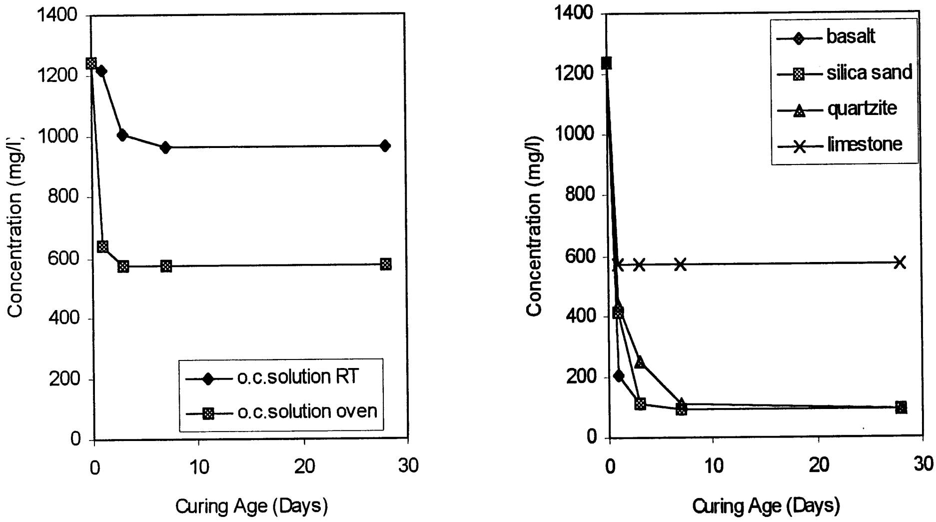

FIG. 3a.

Changes in concentration of OH^{-} in the original cement solution (o.c. solution) and aggregate-cement solution filtrate with curing age, (RT, room temperature).

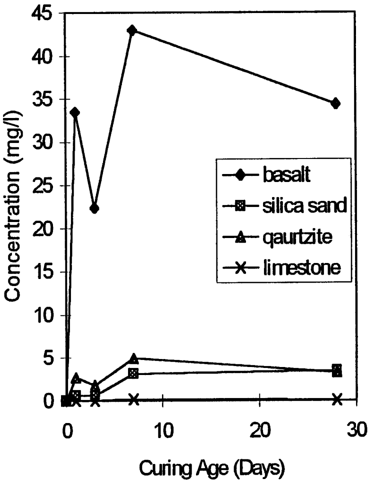

FIG 3b.

Changes in concentration of Si^{4+} in aggregate-cement solution filtrates with curing age.

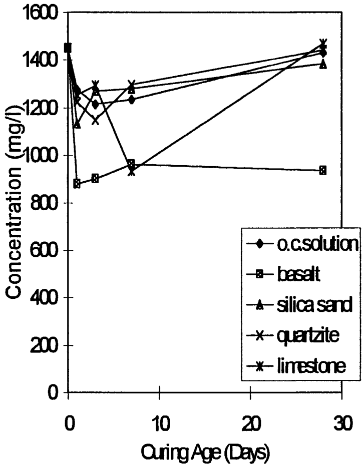

FIG. 3c.

Changes in concentration of K^{+} in aggregate-cement solution filtrates with curing age.

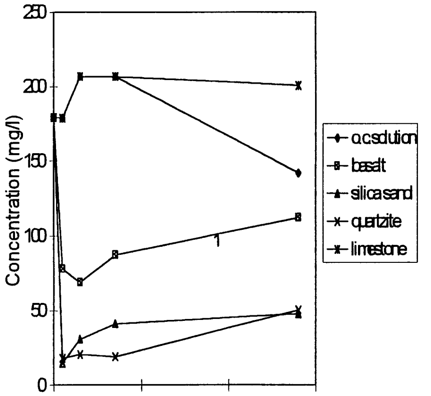

FIG. 3d.

Change in concentration of Ca^{2+} in aggregate-cement solution filtrates with curing age.

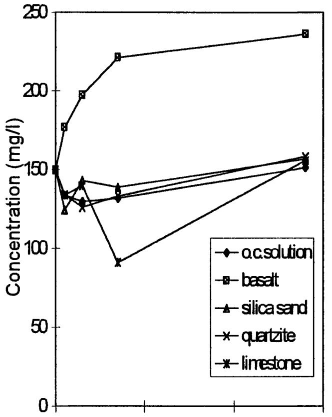

FIG. 3e.

Changes in concentration of Na^{+} in aggregate-cement solution filtrates with curing age.

Basalt. Basalt absorbed very significant amounts of OH^{-}, SO_4^{2-}, Ca^{2+}, and K^{+} and released significant amounts of Si^{4+}, Na^{+}, Mg^{2+} and Al^{3+} to the cement solution. This indicates that significant chemical interaction at the surface layer of the aggregate particles had taken place. The mechanism by which elements are released into the solution is similar to that discussed for aggregate in deionised water. The absorption of Ca^{2+}, OH^{-} and SO_4^{2-}

by basalt aggregate probably indicates the formation of hydrated calcium silicates as well as sulphates on the hydrating surface layer of the aggregate particles. The difference in behaviour between Na^+ and K^+ is presumably either due to K^+ being absorbed into the hydrating surface layer or because feldspars, which are the main sources of Na^+ and K^+ (27,28), are predominantly albite (Na-feldspar).

Limestone. Limestone absorbed significant amounts of Na^+ and $SO_4{}^{2-}$ from the cement solution, and had little effect on the concentration of the remaining elements. The loss of $SO_4{}^{2-}$ from the cement solution probably indicates the formation of sulphates (sulfoaluminates). As perhaps to be expected (29), the hydroxyl ion concentration of the cement solution was not affected by this aggregate.

Quartzite. Quartzite absorbed significant amounts of OH^- and Ca^{2+}, and released very significant amounts of Si^{4+} to the cement solution. This observation possibly indicates the formation of hydrated calcium silicates on the surface layer of the aggregate particles.

Silica Sand. Silica sand absorbed very significant amounts of OH^- and Ca^{2+} from the cement solution; and released very significant amounts of Si^{4+} into the cement solution and had little effect on the concentration of remaining elements. The absorption of Ca^{2+} and OH^- by the silica sand probably indicates the formation of hydrated silicates, as observed for the quartzite aggregate.

The data show a falloff in the hydroxyl ion concentration with time (before 7 days) for the original cement solution at both room temperature (RT) and 70°C (oven). This presumably suggests that the sample preparation procedure used had resulted in the occurrence of carbonation of the solution, or else a reaction with the glass flask resulted in reducing the alkalinity of the solution. Carbonation could have this effect because it reduces the alkali metal ion concentration in concrete pore fluid (17).

Differences in results between cement solution and deionised water probably reflect the formation of insoluble calcium compounds on the surface of the aggregate particles in the cement solution. In this case Si, Fe, and Al would occur as hydrated anions in the high pH cement solution. In the case of Mg^{2+}, the formation of insoluble $Mg(OH)_2$ in the high pH cement solution would account for the low Mg^{2+} levels in the cement solution extracts.

It should be borne in mind that the term “cement solution” does not imply a definite solution composition. Different cements produce cement solutions with different compositions, and the water/cement ratio used will also affect the concentrations produced in the cement solution, in particular the alkali metal ion concentration. The cement solution used in this investigation is lower in concentration than that expected in cement paste pore fluid. This however, should not alter the main conclusion of the investigation.

Residues

Mineralogical analysis of the residues by XRD showed significant mineralogical changes occurred to the aggregates. As shown in Table 2, these varied according to the aggregate type and the type of solution in which they were suspended.

The results show that basalt aggregate underwent significant chemical changes with calcium silicate hydrate (CSH) and aluminate hydrates being formed. The formation of tetracalcium aluminate hydrate (C_4AH_{13}) could be a result of a chemical reaction between the feldspars in this rock and the calcium hydroxide of the cement solution.

As may be expected, some new mineral phases in amorphous form may not show any peaks on the XRD trace. For instance some hydrated aluminates and silicates may occur in the form of gels.

Limestone aggregate residue appeared to show no chemical change in either deionised water or cement solution. The results revealed only minor chemical changes to the quartzite and silica sand aggregate residues. Calcium silicate hydrate was formed as a result of chemical interaction between these aggregates and the cement solution.

Conclusions

The results show that basalt is by far the most reactive of the aggregates studied. Ions were both released and absorbed by this aggregate, possibly indicating that hydration of the surface layer had taken place. The release of alumina by this aggregate could have wider implications. For example, alumina leaching out from concrete containing this type of aggregate in concrete storage tanks for drinking water could present a health hazard.

Quartzite, silica sand, and limestone show less chemical activity in both the cement solution and the deionised water. The hydroxyl ion concentration of the cement solution is not affected by limestone aggregate.

The results reveal that the aggregates are more chemically active than has been previously supposed, and that a wide range of chemical interactions between the aggregates and the cement solution (or cement pore fluid) should be anticipated. Such processes would be expected to have significant effects on the structure of the interfacial zone in concrete.

Acknowledgments

Financial support by Centre for Cement and Concrete (CCC) of the University of Sheffield is gratefully acknowledged. The authors thank Dr. C.D. Lawrence for his comments on the experimental results.

References

1. C.Z. Yuan and W.J. Guo, Mat. Res. Soc. Symp. Proc. 114, 41 (1988).
2. W. Kern and Z. Jianhua, Mat. Res. Soc. Symp. Proc. 114, 29 (1988).
3. A. Bentur, A. Goldman, and M.D. Cohen, Mat. Res. Symp. Proc. 114, 97 (1988).
4. P.J.M. Monteiro, J.C. Maso, and J.P. Ollivier, Cem. Concr. Res. 15, 953–958 (1985).
5. J.C. Maso, Proc. 7th Intl. Cong. Chem. Cem., Paris, 1, Vii-1/3 to Vii-1/5, 1980.
6. B.D. Barnes, S. Diamond, and W.L. Dolch, Cem. Concr. Res. 8, 233 (1978).
7. D. Breton, A. Carles-Gibergues, and J. Grandet, Cem. Concr. Res. 23, 335–346 (1993).
8. L. Struble, Mat. Res. Soc. Sym. Proc. 114, 11–20 (1988).
9. C.Z. Yuan and I. Odler, Cem. Concr. Res. 17, 784 (1987).
10. P.J.M. Monteiro and P.K. Mehta, Proc. 8th Intl. Cong. on the Chem. of Cem., Rio de Janeiro, III, 433, 1986.
11. P.K. Mehta and P.J.M. Monteiro, Mat. Res. Soc. Sym. Proc. 114, 65–75 (1988).
12. R. Goguel, Cem. Concr. Res. 25, 841–852 (1995).
13. S. Diamond, R.S. Barneyback, and L.J. Struble, Paper 22, Alkali-Aggregate Reaction in Concrete, Cape Town, 1981.

14. S. Diamond and S. Ong, 9th Intl. Conf. on Alkali-Aggregate Reaction in Concrete, 1, 269–278, London, 1992.
15. P.J. Nixon and C.L. Page, Katherine and Bryant Mather Intl. Conf., Atlanta, 1987.
16. J.J. Kollek, S.P. Varma, and C. Zaris, 8th Intl. Cong. on the Chem. of Cem., IV, 263–275, Rio de Janeiro, 1986.
17. M. Kawamura, M. Koike, and K. Ishikawa, ICAAR 8th Intl. Conf. on Alkali-Aggregate Reaction, Kyoto, 271–278, 1989.
18. M. Saito and M. Kawamura, Proc. of the RILEM Intl. Conf., 1993.
19. W. Yuji, Mat. Res. Soc. Symp. Proc. 114, 49 (1988).
20. P.K. Mehta, Concrete: Struct. Prop. and Mat., 2nd ed., pp. 57, Prentice Hall, 1986.
21. ACI Committee 226, ACI Journal, Mar-Apr, 158–166 (1987).
22. E. Dingsoyr and J.F. Young, Mat. Res. Soc. Symp. Proc. 42, 211–218 (1985).
23. T.A. Holm, ACI Publication No. SP-65, p. 589, 1980.
24. C.D. Lawrence, Highway Research Board, Special Report 90, pp. 378–391, 1966.
25. M. Thompson and J.N. Walsh, Handbook of Inductively Coupled Plasma Spectrometry, 2nd ed., Chapman and Hall, New York, 1989.
26. F.C. Loughnan, Weathering of the Silicate Minerals, American Elsevier Publishing Company, Inc., New York, 1969.
27. J.H.P. Van Aardt and S. Visser, BRR 574–1982, National Building Res. Inst. CSIR, Pretoria, 1982.
28. O.R. Batic, J.D. Sota, and R. Iasi, Petrography Applied to Concrete and Concrete Aggregates, ASTM, STP 1061, pp. 159, Am. Soc. for Testing of Mat., Philadelphia, 1990.
29. M. Thomas, Report for BRE 11, 1994.