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ALKALI RELEASE BY VOLCANIC AGGREGATES IN CONCRETE

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ABSTRACT

Selective leaching techniques that dissolve hardened cement paste in concrete while leaving aggregate particles intact, reveal mass transfer from the aggregate to the hydrated phases during concrete hardening.

Leaching techniques based on selective cement dissolution with alkaline EDTA-TEA were applied to experimental mortars. Results are presented for two solvents whose only difference lies in the choice of cation: MET, the Li^+, NH_4^+ version, and TET, the tetramethyl-ammonium (TMA)-version. TET, which features large cations providing limited exchange capability, attacks aluminosilicates the least while dissolving clinker and paste faster. In contrast to dacite and phonolite, which reduce the level of alkali, some basalts release large amounts of alkali into the pore solution of concrete, especially when the aggregate considerable amounts of fine material and the water-cement ratio (w/c) is high. The alkali release during the first 6 months ranges from about 1%Na_2O equivalent for a rapidly cooled fresh basalt with poorly crystallised feldspars to about 0.1% for a well crystallised basalt. It follows that, despite the use of low-alkali cement, sufficient alkali can be released from some aggregates to initiate alkali-aggregate reaction.

Introduction

Although systematic measurements of the reactivity of aggregates with strongly alkaline solutions date back 50 years (1), it is only within the last decade that attempts have been made to directly analyze the pore solution present in concrete. A linear relationship between pH and alkali content of the cement has been established (2) by measurements on pore solutions expressed from experimental mortars mixed at w/c=0.5. These results showed that Portland cement at 1.4% Na_2O eq.(=%Na_2O+0.658x%K_2O) creates a pH of 14. The high pressure extraction of pore solutions requires complex equipment (3), The coring of test samples from existing structures entails addition or loss of water. In any case, such results provide a pH value for the pore solution at the time of sampling but no information about the total amount of alkali that passed through the pore solutions during the curing process. Because the source of the cement can often not be ascertained it may not be possible to derive the alkali content of the cement from works records. Goguel and St.John (4) overcame this problem by developing an identification technique for N.Z. cements. This provided proof of the usage of low-alkali cements for some concretes that were undergoing expansive alkali-aggregate reaction (AAR) accompanied by the correspondingly high alkali levels in the pore solutions. This indicated that most of the alkali had been supplied by the basalt aggregates. Preliminary information about the mass transfer from the aggregate has been presented (5). Examples of direct analysis of coressponding alteration products on a qualitative basis have been obtained by SEM , EMP (6, 7, 8) and XRD analysis (9, 10). The quantitative determination of alkali mobilised from or taken up by the aggregate requires selective dissolution of the cement, paste together with alteration products. Fresh volcanic aggregates are free of carbonates and are made up of silicate and aluminosilicate minerals. These are quite stable in slightly alkaline solutions even under complexing conditions where cements are dissolved. The EDTA-TEA complexing solvent developed for the analysis of blended cements (11) contains large concentrations of sodium to provide alkalinity. This can also be achieved by lithium or TMA thus permitting the determination of the sodium dissolved from the samples. The carbonate anion was omitted from the EDTA-TEA complexing solvent and the pH was increased from 11.6 to 12.6.

Experimental

TABLE 1: Cement composition (a) and mortar makeup (b)

a)

		(Sr/Ca)x100	*(Fe/Ca)x100*	% CaO	% SiO_2	%Al_2O_3	%K_2O	%Na_2O	*%Na_2Oeq.*
LA	Low-alkali cement	*0.09*	*3.18*	67.5	21.6	4.5	0.32	0.20	*0.41*
HA	High-alkali cement	*0.17*	*5.05*	64.3	20.0	5.8	0.66	0.81	*1.24*

b)

	a/c	w/c		size fraction (grading)					
	aggregate/cement	water/cement	relative surface	2.36-4.75 mm	1.18-2.36 mm	0.6-1.18 mm	0.3-0.6 mm	0.15-0.3 mm	<0.15 mm(Dust)
ASTM C227	2.25	0.4	1	0.1	0.25	0.25	0.25	0.15	0
Test Mortar	5.1	0.67-0.71	~3	0.35	0.2	0.15	0.1	0.05	0.15

Preparation of experimental mortars:

The aggregates were graded either to a standardized grading typical for basalt crusher dust or ASTM C 227 specifications and dry mixed with cement inside polyethylene bags before the water was added and mixed in by kneading. All aggregate samples were combined with high-alkali as well as low-alkali cement thus producing two sets of mortars. High w/c (0.67-0.71) mortars, with substantial presence of fines as shown in Table 1 were prepared for all samples. For comparison, mortars were also prepared according to ASTM C 227 which avoids the powder fraction (< 0.15 mm) of the aggregate and maintains a low w/c (0.4). The mortars hardened in heat sealed polyethylene bags in a fog room at 21 C. Half the sample was removed after 6 months and the bags with the remaining half were resealed for another 6 months hardening. The samples of hardened mortar were crushed by hand between tungsten carbide surfaces. Grinding was avoided. The crushed material was sieved. With decreasing grain size the cement content increased from about 20% in the 0.5 - 1 mm fraction to a maximum of about 40% in the 63 -125µm fraction of a mortar with a/c= 5.1. Results from alkaline leaching of crushed mortar did not significantly change when using different grain size fractions between 0.063 and 1 mm. Only a/c of the subsamples taken from the larger grain sizes (0.5-1mm fraction) varied substantially. Therefore the small grain size 0.063-0.125 mm was preferred for the leaching experiments presented here.

For the assessment of the alkaline leaching blanks , the fraction < 125 µm of unused crushed aggregate was applied in absence of cement in order to avoid the errors normally introduced by measurements based on small differences.

Leaching reagents :

(1) MET (Mixed cation EDTA-TEA solution containing 0.09M EDTA dissolved in an alkaline solution

of approximately 0.4M TEA and 0.25M NH_3 which is adjusted to pH 12.6 by LiOH addition amounting to approximately 0.4 M). It is made using reagents that are very low in sodium and potassium. Analytical reagent quality EDTA (the free acid) still contains considerable amounts of Na (e.g. 0.05%) which must be removed by recrystallisation (dissolution in purified ammonia and precipitation by acidification with redistilled hydrochloric acid). TEA (triethanolamine) is available in adequate purity (e.g. MERCK No: 8379) as is lithium hydroxide (Prolabo 25.022.232). However lithium hydroxide purity with respect to Na and K is not certified and has to be ascertained for every batch. Otherwise it may be purified by recrystallisation from alcoholic solutions (12).

(2) TET (TMA-EDTA-TEA solution containing 0.09M EDTA dissolved in an alkaline solution of approximately 0.4M TEA and 0.35M TMA which is adjusted to pH12.6 by further addition of TMA-OH.). TMA (tetramethylammonium) is available as a 25% solution of the hydroxide in outstanding purity (TAMAPURE AA-1000) shipped in Teflon (PFA) bottles by TAMA CHEMICALS in Tokyo. Most chemical supply houses still use glass bottles for this caustic solution leading to very high levels of contamination.

Procedure:
160 mg of the 500-1000μm fraction or 80 mg of the 63-125μ fraction of crushed mortar are placed in 50 ml polypropylene centrifuge tubes. 25 ml of the MET or TET solvent at 40 C are added. The screw-capped centrifuge tubes are then shaken at 40°C (2 hours with the 0.5-1 mm fraction and 1 hour with the 63-125 μm fraction). The solids are then settled by centrifugation for 10 minutes at 3000 revs/min with a swing-out rotor. The clear solution is decanted into a PTFE beaker from where it is returned to the centrifuge tube after the solids have been washed out. The solutions in the centrifuge tubes are then analyzed for Ca, Sr, Si, Al, Fe, Mn, Mg, K and Na. In order to assess the fixation of heavy alkalies the recovery of Cs added at the 1 ppm level to the leachant was added to the analytical menu.

The minerals present in the volcanic rocks were determined by XRD and are listed in Table 2.

Results and Discussion

For the presentation of the magnitude of aggregate contributions to the chemistry of the cement paste and its pore solutions it was decided to:

(1) express concentrations as percentages above the 100% due to the cement used in the mortar.

(2) to subtract the cement derived concentration values from the analysis of the leachates to present the concentration values, exclusively derived from the aggregates, rather than the relative changes of an aggregate modified cement analysis.

In order to avoid the gravimetric determination of the aggregate content of the sampled fractions of the mortars, the cement content was determined through determination of calcium using the assumption that aggregate contributions to leachable calcium are negligible. In the absence of limestone aggregate this proved to be a tenable assumption. The proposed complexing leaching methods have indicated that calcium contributions by basalt aggregate amount to a relative increase in calcium levels in the mortar leachates of less than 1%. This provides the basis for the normalisation of all analytical data relative to calcium concentration. The mobilisation of other elements from or fixation by the aggregate can thus be quantified.

The general formula is:

$$(C_{MeO}/C_{CaO} - c_{MeO}/c_{CaO}) \times \mathbf{c}_{CaO} = dMeO(\%),$$

Table 2: Results of leaching aggregate blanks *

Aggregate	Mineralogy	Cs%recvy-TET	Cs%recvy-MET	dCaO-TET	dCaO-MET	dSiO_2-TET	dSiO_2-MET	dAl_2O_3-TET	dAl_2O_3-MET	dK_2O-TET	dK_2O=MET	dNa_2O-TET	dNa_2O-MET	dCaO-HNO_3**	dSiO_2-HNO_3**	dAl_2O_3-HNO_3*	dK_2O-HNO_3**	dNa_2O-HNO_3**
Albite Al-I	pl	85	100	0.1	0.1	0.1	0.3	0.0	0.0	0.00	0.01	0.03	0.06	0.2	0.2	0.1	0.01	0.06
Albite	pl	82	98	0.4	0.4	0.1	0.8	0.0	0.5	0.00	0.03	0.03	0.30	0.5	1.9	0.9	0.02	0.52
Andesine	pl	74	90	0.0	0.1	0.1	0.6	0.1	0.2	0.00	0.02	0.00	0.04	0.2	0.5	0.4	0.03	0.04
Labradorite	pl,py	52	91	0.0	0.1	0.1	0.4	0.0	0.2	0.00	0.02	0.01	0.04	1.6	0.4	0.4	0.02	0.04
Obsidian	gl	96	102	0.0	0.0	0.1	0.4	0.0	0.1	0.00	0.01	0.01	0.05	0.0	0.0	0.0	0.01	0.01
Basalt K	gl,ol,py	78	99	0.0	0.2	0.1	0.6	0.0	0.2	0.00	0.01	0.02	0.07	1.1	1.8	1.2	0.06	0.31
Basalt B	py,pl,ne,cl,ze	1	21	0.7	1.1	0.6	1.6	0.2	0.6	0.02	0.36	0.08	0.73	5.2	22.3	19.1	2.32	9.77
Basalt ZM	pl,py,cl,an,ze	1	4	1.2	3.2	0.3	2.7	0.1	1.1	0.01	0.07	0.10	1.40	5.2	13.8	18.4	0.17	7.52
Basalt ZF	pl,py,cl,ze,qu	0	3	1.8	2.5	0.7	3.3	0.7	1.0	0.08	0.05	0.17	2.14	1.8	2.7	3.0	0.15	2.43
Basalt L	py,ol,pl,gl,ne	28	87	0.1	0.1	0.1	0.8	0.0	0.4	0.01	0.07	0.01	0.16	1.8	16.2	10.2	1.55	5.65
Basalt M	py,ol,ne,gl,pl	18	88	0.4	0.3	0.4	1.5	0.1	0.7	0.04	0.13	0.05	0.36	5.5	37.0	26.1	3.47	14.19
Basalt O	pl,py	62	98	0.0	0.1	0.1	0.4	0.0	0.2	0.00	0.02	0.00	0.03	1.0	0.8	0.3	0.03	0.09
Basalt P	py,pl,ol,ne	10	90	0.1	0.2	0.6	2.0	0.6	1.3	0.01	0.05	0.02	0.14	1.8	15.0	8.6	0.87	5.05
Basalt S	py,pl,ol,ne	4	83	0.2	0.3	0.7	2.5	0.6	1.8	0.02	0.08	0.02	0.15	2.3	19.7	12.3	0.89	7.16
Phonolite	or,pl,ne,an,ze	2	71	0.1	0.1	0.2	1.0	0.1	0.5	0.01	0.11	0.04	0.19	0.4	25.5	18.6	1.76	10.49
Dacite	pl,py,ab,qu,cr,gl	76	100	0.0	0.1	0.1	0.8	0.0	0.1	0.00	0.03	0.01	0.06	0.4	0.3	0.2	0.02	0.06
Nepheline	ne	41	97	0.1	0.2	0.2	1.4	0.1	0.9	0.01	0.11	0.05	0.47	1.8	112.5	68.0	15.40	54.47
syn.Glass	gl	95	98	0.0	0.1	0.1	0.8	0.0	0.2	0.00	0.03	0.01	0.05	0.1	0.2	0.2	0.02	0.03

ab = amphibole, an = analcime, cl = clay, cr = cristobalite, gl = glass, ne = nepheline, ol = olivine, pl = plagioclase, py = pyroxene, qu = quartz, ze = zeolite

* data have been obtained from aggregate in the absence of cement but have been calculated on the basis of an aggregate/cement ratio of 4. They are expessed as additions to the percentages of cement constituents for comparison with the mortar leaches from Tables 3 and 4

** Corresponding values for aggregate contributions, when 1 M HNO_3 is used for cement dissolution from concrete samples.

TABLE 3: MET leaches of experimental mortars

Aggregate: volcanic rocks or minerals

							a/c = 5.1 w/c = 0.67-0.71			a/c = 2.3 w/c = 0.4
a) Low-alkali cement (LA)										LA
Sample	curing(months)	Cs%recvy	100x Sr/Ca	100x Fe/Ca	$dSiO_2$	dAl_2O_3	dK_2O	dNa_2O	dNa_2Oeq.	dNa_2Oeq.
Albite	6	98	0.12	3.21	1.1	0.4	0.01	0.46	0.47	
	12	98	0.13	3.18	1.9	0.9	0.05	0.67	0.70	
Andesine	6	96	0.09	3.27	-0.3	0.0	0.00	0.08	0.08	
	12	98	0.10	3.17	0.6	0.3	0.01	0.12	0.13	
Labradorite	6	97	0.08	3.22	-0.3	-0.1	0.00	0.09	0.09	
	12	99	0.08	3.20	-0.1	0.1	0.01	0.09	0.10	
Anorthite	6	101	0.09	3.00	0.0	0.1	-0.06	0.06	0.02	
	12	100	0.09	3.06	0.7	0.5	-0.04	0.08	0.05	
Dacite	6	99	0.06	3.01	2.8	-0.1	-0.14	-0.05	-0.14	-0.16
	12	98	0.06	2.97	3.5	-0.1	-0.10	-0.02	-0.08	-0.16
Andesite T	6	97	0.08	3.32	3.6	0.6	0.00	0.07	0.07	0.03
	12	96	0.08	3.37	4.2	0.7	-0.01	0.08	0.07	0.07
Phonolite	6	75	0.07	3.92	4.1	1.5	-0.11	0.17	0.10	-0.09
	12	78	0.07	4.07	5.1	2.1	-0.11	0.21	0.14	-0.05
Basalt K	6	100	0.08	3.94	2.8	0.6	0.07	0.24	0.29	
	12	99	0.09	4.80	3.9	1.7	0.15	0.54	0.63	
Basalt O	12	98	0.08	3.25	1.2	0.2	0.08	0.10	0.15	0.06
Basalt B	6	55	0.09	4.05	4.2	1.5	-0.03	0.45	0.43	0.06
	12	50	0.10	4.20	5.0	2.0	0.00	0.59	0.59	0.11
Basalt M	6	98	0.09	3.35	5.3	3.0	0.60	0.82	1.22	0.55
	12	96	0.10	3.40	6.9	3.7	0.78	1.40	1.91	0.68
Basalt L	6	96	0.08	3.17	3.3	1.4	0.26	0.70	0.87	0.28
	12	96	0.08	3.11	4.0	1.9	0.41	0.93	1.20	0.34
Basalt S	6	97	0.08	3.40	3.0	3.3	-0.08	0.29	0.24	0.05
	12	98	0.08	3.53	3.9	3.8	-0.03	0.48	0.46	0.08
Basalt P	6	99	0.07	3.52	3.0	2.5	-0.06	0.29	0.25	0.01
	12	98	0.08	3.64	3.6	2.8	-0.04	0.42	0.39	0.05
Basalt ZF	6	7	0.08	4.53	12.0	2.8	0.71	1.62	2.08	0.80
	12	6	0.08	4.51	11.9	3.0	0.63	1.39	1.80	0.90
b) High-alkali cement (HA)										HA
Albite	12	99	0.20	4.96	1.8	0.9	0.06	0.76	0.80	
Andesine	12	99	0.17	4.98	0.5	0.0	-0.04	0.10	0.07	
Labradorite	12	100	0.17	5.01	0.0	-0.1	-0.01	0.10	0.09	
Anorthite	6	97	0.18	4.95	0.2	0.3	-0.12	-0.01	-0.08	
	12	97	0.18	4.91	1.2	0.5	-0.13	0.04	-0.04	
Dacite	12	97	0.15	5.42	2.9	0.0	-0.28	-0.26	-0.44	-0.61
Phonolite	6	80	0.17	5.76	4.5	1.4	-0.33	-0.04	-0.25	-0.33
	12	80	0.16	5.99	5.6	1.9	-0.27	0.09	-0.08	-0.30
Obsidian	6	100	0.17	5.26	7.7	0.8	0.28	0.35	0.53	0.06
Quartzite	6	100	0.17	5.16	1.5	-0.1	-0.03	-0.01	-0.02	0.02
Basalt K	6	100	0.18	5.74	3.2	0.5	0.05	0.24	0.27	
	12	100	0.18	5.88	4.2	1.1	0.05	0.37	0.40	
Basalt M	6	97	0.19	4.82	5.4	2.4	0.53	0.94	1.29	0.42
	12	96	0.19	4.85	6.6	2.8	0.66	1.13	1.56	0.58
Basalt ZF	12	8	0.15	6.00	11.1	2.4	0.76	1.01	1.51	2.20

TABLE 4: TET leaches of experimental mortars

Aggregate: volcanic rocks or minerals

a/c = 5.1, w/c = 0.67-0.71

a) Low-alkali cement (LA)

Sample	curing(months)	Cs%recvy	100x Sr/Ca	100x Fe/Ca	$dSiO_2$	dAl_2O_3	dK_2O	dNa_2O	$dNa_2Oeq.$
Obsidian,Tpo	6	105	0.09	3.27	4.8	0.6	0.29	0.35	0.54
Albite	6	98	0.14	3.22	0.2	0.5	0.02	0.30	0.31
	12	96	0.14	3.27	0.5	0.7	0.06	0.57	0.61
Anorthite	6	92	0.09	3.28	0.9	0.2	-0.06	0.06	0.02
	12	89	0.09	3.29	1.5	0.6	-0.05	0.09	0.06
Andesite T	6	100	0.08	3.47	3.1	0.6	-0.03	0.08	0.06
	12	101	0.08	3.65	4.9	0.9	-0.05	0.08	0.05
Phonolite	6	27	0.08	3.89	3.5	1.6	-0.24	0.09	-0.07
	12	9	0.08	3.81	-1.5	0.8	-0.29	0.07	-0.12
Basalt K	6	101	0.08	3.39	0.5	0.0	0.11	0.26	0.33
Basalt B	6	5	0.09	4.28	3.9	1.5	-0.28	0.17	-0.01
	12	9	0.09	4.18	1.3	1.3	-0.29	0.21	0.02
Basalt M	6	93	0.10	3.57	4.2	2.5	0.54	1.19	1.55
	12	25	0.11	3.58	-0.1	2.1	0.18	1.34	1.46
Basalt L	6	103	0.09	3.48	3.7	1.8	0.28	0.68	0.86
	12	32	0.09	3.40	0.4	1.2	0.06	0.83	0.87
Basalt S	6	72	0.09	3.83	4.6	2.9	-0.16	0.19	0.08
	12	80	0.09	3.89	5.6	3.6	-0.10	0.43	0.36
Basalt P	6	88	0.08	3.85	3.4	1.9	-0.14	0.22	0.13
	12	25	0.09	3.84	0.8	1.6	-0.21	0.32	0.18
Basalt ZF	6	4	0.06	5.32	12.5	2.6	-0.29	0.50	0.31
	12	4	0.06	4.89	5.6	1.3	-0.32	0.38	0.17

b) High-alkali cement (HA)

Anorthite	6	100	0.18	5.08	1.2	0.3	-0.09	0.04	-0.02
	12	102	0.18	5.10	1.3	0.6	-0.08	0.10	0.05
Phonolite	6	33	0.16	5.84	3.8	1.6	-0.47	-0.11	-0.42
	12	6	0.16	5.70	-3.9	0.4	-0.58	-0.15	-0.53
Obsidian,Tpo	6	94	0.18	5.26	5.8	0.6	0.29	0.34	0.53
Quartzite,Cbb.	6	103	0.17	5.33	0.7	-0.1	0.03	0.01	0.03
Basalt K	6	100	0.19	5.28	-0.4	-0.3	0.02	0.07	0.09
	12	101	0.19	5.90	1.9	0.4	0.23	0.47	0.62
Basalt M	6	97	0.18	5.53	4.7	2.5	0.42	0.77	1.05
	12	87	0.18	5.54	5.6	2.8	0.58	1.10	1.48

where the first ratio is that analytically obtained for the mortar leach and the second one that for the corresponding cement. c_{CaO} represents the CaO concentration of the cement given in %. Hence an Na_2Oeq. of the cement of, e.g. o.41% is augmented by a dNa_2Oeq. of 1.2% in the presence of basalt L after 12 months hardening producing an effective Na_2Oeq. of 1.61% in the cement.

Some aggregate leaching always takes place during the relatively brief exposure to the complexing alkaline leachant. These leaching blanks have to be determined to avoid errors in the interpretation of the analytical data obtained from leaching the hardened mortars (Tables 3 and 4). Table 2 presents the results from the leaching of fresh aggregate together with a listing of its constituents. As the table compares the leaching characteristics of TET and MET, it also confirms the usefulness of complexing alkaline leachants for selective cement dissolution relative to acid leaching. Dilute acid (1 M HNO_3) completely dissolves nepheline and most zeolites. Their common presence in basalts precludes the application of dilute acid for selective cement leaching from concrete containing them.

The stability of nepheline in the alkaline environment

Although MET at pH 12.6 leaches less than 1 % of the sodium from nepheline during 2 hours of shaking this is still an amount large enough to introduce uncertainties into the evaluation of some of the mortar leaches. The deviations from stoichiometry of nepheline leaches with MET (Table 2) (44.6% SiO_2, 34% Al_2O_3, 5.7% K_2O, and 15.3% Na_2O) are only minor. We are therefore dealing with slow congruent dissolution at the ablation rate of 2 nm/min. When ammonia was omitted from the complexing leachant and the pH of 12.6 adjusted with LiOH only, the ablation rate increased to 3 nm/min. It was therefore concluded that the cation(s) of the leachant are instrumental in the mechanism of breakdown of highly cross-linked aluminosilicate structures. The small Li ion most easily enters the lattice and exchanges against the charge balancing cations of aluminosilicates thus reducing the stability of the structures. Therefore it was assumed that a leaching solution that was free of easily exchangeable cations can provide greater protection for the aluminosilicate structures of the aggregates.

TMA is a very large cation that would not be able to enter the aluminosilicate lattices while still producing the high pH needed to keep in solution the high concentrations of silica and alumina from dissolved cement. For this reason TMA was introduced into the complexing solvent to replace the necessary cations, and indeed, aluminosilicates are much more resistant to the resulting "TET"-solution as shown in Table 2. Data in Table 2 translate into an ablation rate for nepheline of only 0.2 nm/min. On the other hand TET dissolves clinker and hardened cement paste twice as fast as MET due to the higher concentration of free EDTA and TEA resulting from the fact that EDTA, TEA complexes of TMA^+ are weaker than those of Li^+ and NH_4^+.In this context it should be mentioned that leaching experiments with a more strongly complexing solution such as CDTA, did not produce notably higher ablation rates. 50% more Na was leached from the nepheline, probably due to the formation of the more stable Na-CDTA complex. However, in the presence of TMAH, this initially faster Na-leaching can not be maintained as it is not followed by Al, when no destabilising cations enter the structure.

Although nepheline is rather reactive it is still unclear, whether in concrete it can release alkali that would appreciably increase the alkalinity of the pore solutions. Unfortunately, no mortars were prepared that contained pure nepheline as aggregate. Results of the mortar leaching shown in Tables 3 and 4 show no correlation between nepheline contents of the aggregates and alkali release during mortar hardening. For instance, the phonolite contains more nepheline than the basalts L, P, and S but does not contribute alkali to the TET and only little to the MET leach (Table 2). Lower Cs-recovery in these leaches indicates some ion exchange capacity but a virtual absence of zeolite, according to the rather high recovery of Cs from the MET leachant in contact with the fresh aggregate (Table 2). In phonolite mortar almost half of the potassium content of the cement becomes so strongly fixed to the aggregate, that after only 6 months mortar hardening, it is no longer available for dissolution or ion exchange by the MET leachant.

Consequently one of the minerals in phonolite must have slowly accessible ion exchange sites for the fixation of potassium or it acts as a substrate or nucleation site for the formation of potassium stabilised aluminosilicate structures from the pore solutions of the mortar.

Zeolites in basalt and their possible formation in the mortar

Zeolitised basalts are not used as aggregate because of their poor mechanical properties. Despite this, such a basalt (ZF) was included in the mortar samples of this work to gather information on the effects of its ion exchange capacity on the composition of MET and TET leaches. Recently it has been proposed (13) to use 30% natural zeolite in blended cements not only as a pozzolan, but also for buffering of free alkali in the pore solutions to prevent AAR. It appears that the heulandites, the low- alkali members of the heulandite-clinoptilolite group should be particularly useful for this purpose.

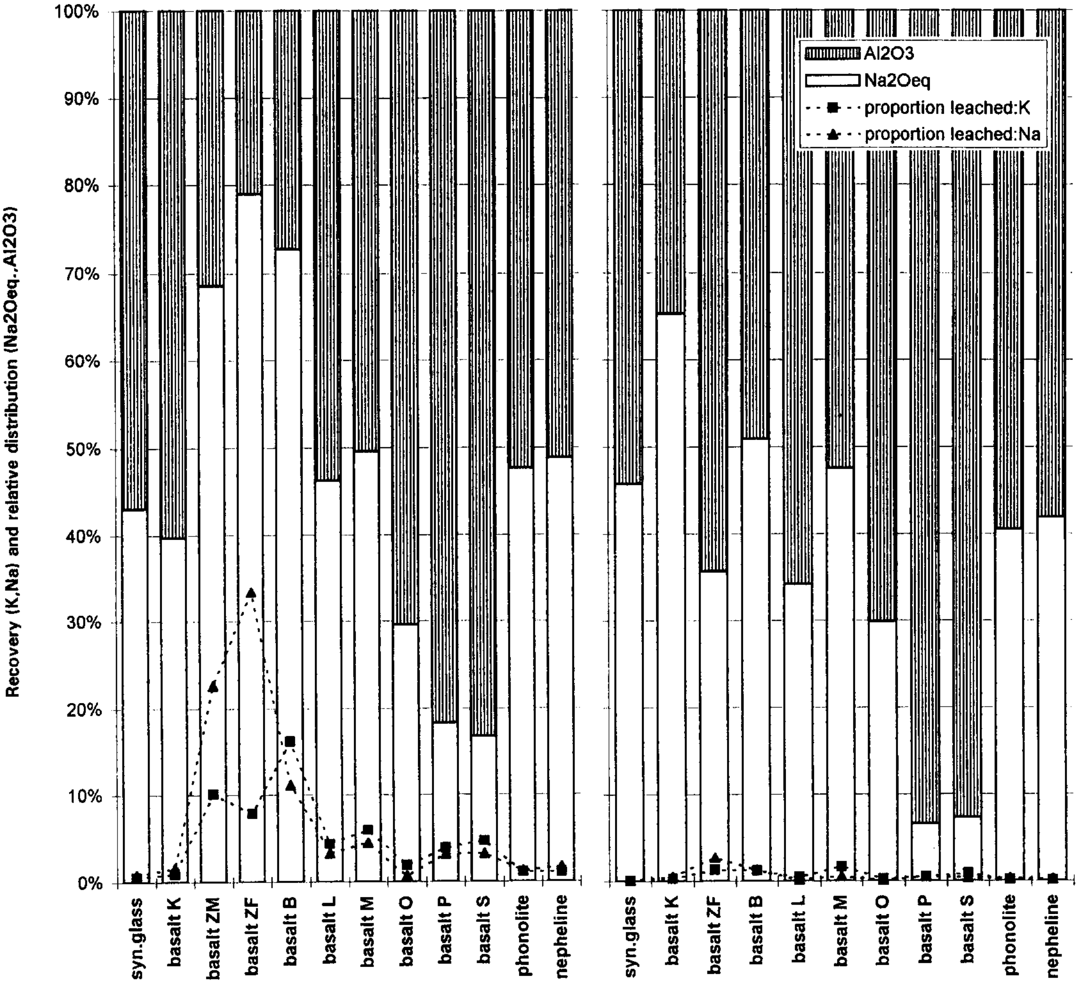
(a) MET (b) TET

FIG 1

Alkalies and aluminium in blank leaches from some volcanic aggregates and synthetic glass

On the other hand, a zeolitic phase is a likely but apparently rare reaction product from the interaction of alkaline pore solutions with aluminosilicate aggregate in concretes. Its formation would lower the levels of dissolved alkali. Zeolite formation as part of AAR has recently been reported (14) and also been predicted by thermodynamic modelling (6). An additional tool in this context is the strong sorption of cesium by zeolitic structures. Cesium is held firmly enough not to be exchanged by large concentrations of lithium and ammonium available in MET (Table 2). 1 mg Cs per litre of leaching solution was introduced for this purpose. The supply of cesium from the leachant solution at this very low level of 7.5 x10-6 molar cannot affect the ion-exchange behavior towards the other ions in the solution. Even if fully absorbed the total amount is orders of magnitude smaller than the exchange capacity of the clinoptilolite. The content of clinoptilolite in basalt ZF removed 97% of the added cesium from the lithium-ammonium based leachant (MET) (Table 2). This property is not lost by exposure of the basalt to the pore solutions of the experimental mortar for 6 and 12 months (Table 3) confirming the stability of the zeolite in portland cement paste.

Comparison of the blank leaches for basalt ZF in Table 2 and Fig 1 with the leaches of the hardened mortar shown in Tables 3 and 4, reveals the complexity introduced by ion exchange against Li^+, and NH_4^+ from MET. The large TMA cation in TET which is unable to enter the zeolite lattice, avoids this complication. From the TET leaches a small but significant release of sodium from the zeolite during 6 months mortar curing can be derived. After 12 months curing most of the mobilized silica and alumina is fixed in more slowly soluble phases that coprecipitate sodium thus diminishing alkali levels in the pore solutions. TET leaches (Table 4) obtained after 12 months curing commonly show a significant drop in silica when compared with the corresponding leaches after 6 months curing. They also show a drop in Cs-recovery but according to the MET leaches this is not indicative of zeolite formation.

Volcanic glass as a source of alkali

There is no correlation of the presence of any of the main crystalline mineral phases with alkali release of aggregates either during 6-12 months mortar curing or during a 1 hour alkaline leach. The lowest level of alkali release was observed when completely crystallised volcanic aggregate was used (basalt O, phonolite:Tables 1-3, Figures 1 and 2). Attention was therefore focused on glasses. Glasses are present in most basalts prevailingly as an intergranular filler and therefore difficult to point count in microscopy. Glasses also do not readily lend themselves to detection by selective leaching techniques as emphasised by the results presented in Table 2. Nevertheless, it is assumed that the release of alkali from glass at pH >12 can be achieved by a mechanism combining ion exchange and dissolution of the aluminosilicate lattice. Closely packed crystallized aluminosilicates, however, require the breaking down of the aluminosilicate lattice surrounding the large alkali cations before these can be released to the solution. In this case leaching should follow a stoichiometric atomic ratio near 1 for (alkalis + alkaline earths)/aluminium. The alkali/aluminium ratio derived from leaching of plagioclase should therefore be substantially lower than 1. Leached alkali/aluminium ratios substantially larger than 1 can only be obtained by the ready ion exchange with the open structures of many zeolites. Thus a tool for the assessment of the potential of basalts for alkali release in concretes may evolve from a future more thorough investigation of the alkali/aluminium ratios in alkaline leaches of basalts used as aggregate. It is observed here that the three basalts P, S, and L contain virtually equal concentrations of alkali (1.2% K_2O, 3.35-3.5% Na_2O) and produce similar blank leaches for sodium and potassium (Table 2). However, when embedded in mortar, basalt L makes a much higher MET or TET leachable alkali contribution than basalt S or P (Tables 3 and 4). When the corresponding one-hour blank leaches are compared, the only striking difference showing up in the MET and TET leaches of basalt L is an alkali /aluminium atomic ratio near 1 in contrast to the substantially lower alkali/aluminium ratios for basalts P and S (Figures 1 and 2). It may be postulated that there is much less reactive glass available in basalts P and S than in basalt L. However, point counting did not provide any evidence to support this assumption but could not disprove it either due to the presence of a very fine-grained groundmass in basalt L. Substantial amounts of glass could be concealed.

In order to gain a qualitative measure of the likely alkali contributions of volcanic glasses to the pore solutions of concrete some experiments were carried out using glass samples. The only pure natural volcanic glasses available as aggregates for the preparation of mortars were obsidian and a totally fresh, vesicular and vitreous basaltic lava (basalt K, Table 2) containing only minor olivine and pyroxene in a glass matrix. Because of its high content of magnesium and low content of alkali (2.6% Na_2O equiv.) the basaltic glass K was expected to be more resistant to alkaline attack than the more acidic (silica-rich) obsidian (6.3% Na_2O equiv.) and release an order of magnitude less alkali. According to the TET leaches in Table 4, however, the basaltic glass K yielded a level of alkali (0.33% equiv.) not too dissimilar from the obsidian (0.54 % Na_2O equiv.). The unexpectedly high level is probably due to the pronounced vesicular nature of basalt K. The highly vesicular partly vitreous basalt M, containing twice the concentration of alkali (5.3% Na_2O equiv.), adds a five times greater amount of alkali to the mortar . This corresponds to an addition of 1.6% Na_2O equiv. to the low-alkali cement. Basalt M also produces high-leaching blanks (Table 2) which indicates that its glass content might not be the principal source of added alkali in the pore solutions of this mortar.

Very low-leaching blanks are obtained from all glass samples including basalt K despite its high exposed surface area (Table 2) . The synthetic glass was prepared from a 1:1 mixture of obsidian and andesite to simulate the residual glass phase present in the mostly crystalline hard basalts from the Auckland area (basalts M, L, P, and S). All pure glasses are only negligibly attacked during the hour-long acid or alkaline leaches.

Feldspars as a source of alkali

The feldspars in basalt L are very small and poorly crystallised in contrast to the well developed feldspar crystals in basalts P and especially S. Basalt O, which shows the greatest resistance against alkaline attack and releases least alkali, has its feldspars well segregated and crystallised. These observations emphasize the importance of the cooling history of the basalt.

Experimental work (9, 15) indicates that feldspars are a major source of additional alkali in the pore solutions of concretes. The leaching data obtained here from hardened experimental mortars (e.g. basalt O) suggest that this is not necessarily so when dealing with well developed crystals free of strain. The contributions from andesine, labradorite, and anorthite to MET and TET leaches after being embedded in the experimental mortars for 6 and 12 months are rather small. According to experimental studies (6, 17, 18) albite dissolves very slowly at pH>9, e.g. 20 times slower than quartz. This contrasts with the substantial release of alkali from the albite sample in Tables 3 and 4 to the mortar after 6 months curing . The poor resistance of this albite against alkaline attack is also reflected in the high leaching blank with MET (Table 2). The higher solubilities of this sample are not surprising as its lattice is highly strained or disordered due to a high content of larger ions (0.8% K_2O, 0.18% SrO), although the structure of a low temperature albite is retained according to its XRD pattern. The albite used in earlier experimental work (8) has an even higher K_2O content (1.9%). The leaching blanks in Table 2 include a sample of true low temperature albite, low in large cations :(0.13% K_2O, 0.008% SrO). This sample, the geochemical reference standard Al-I (16), produces low aluminium and silica leaching blanks similar to those of the plagioclase samples andesine and labradorite used in the experimental mortars.

The occurrence of small poorly developed and strained feldspars in basalts used as aggregates is a sign of fast cooling of the lava. The strain is created by the inclusion of large potassium ions and provides a maximum of reactive surfaces for chemical attack by the pore solutions in concrete. Whole rock analysis shows equal alkali concentrations for basalts L, P, and S. However, electron microprobe investigation of the feldspars in basalt L revealed the presence of crystals with unusually high potassium concentrations close to 2% K_2O (e.g. crypto-antiperthite) in contrast to basalts P and S and particularly O where all plagioclases are well developed labradorites (<0.3% K_2O).

Conclusions

Selectivity of cement leaching from concretes:

It was found that leaching of aggregates of volcanic rocks during cement dissolution in alkaline EDTA-TEA solutions is reduced up to tenfold and thus to negligible levels when sodium or lithium are replaced by the large, strongly basic cation -TMA-. Specific observations are:

(1) MET leaches of the fresh aggregate-cement mixture include exchangeable alkali from zeolites and a contribution from minor nepheline dissolution.

(2) TET leaches of the fresh aggregate-cement mixture leave the aggregates practically intact. TET dissolves cement paste or clinker twice as fast as MET. It is thus most useful for cement analysis. The presence of zeolites modifies alkali contents through exchange of calcium and potassium from the cement against sodium from the zeolite. The presence of zeolites thus manifests itself by:

   (a) removal of cesium added to the MET leachant;
   (b) major differences in potassium levels between TET and MET leach.

(3) After 12 months curing some of the mass transfer from the aggregates becomes so strongly fixed that TET will not dissolve it during a one-hour leach. Especially, aluminium and silica gains from aggregate observed after 6 months hardening are appreciably reduced in the TET leaches after 12 months hardening.

The differences between TET and MET of dissolution kinetics between the various hydrated phases of cement remain to be determined, e.g. for calcium silicate phases described as alkali-aggregate reaction products (8) or synthesised (6). TET features slow dissolution of some newly formed phase(s) which contrasts with the faster dissolution of clinker and the hydrated phases of cement paste.

Mass transfer from unweathered volcanic aggregate to the cement phase:
Having produced a leachant that will selectively and quantitatively dissolve cement and its hydrates (hydrotalcite being the only exception), we are now in a position to measure mass transfer from volcanic rocks to the cement as a result of the action of pore solutions during concrete hardening. Experimental mortars made from graded, volcanic rock or mineral aggregate together with high- or low-alkali cement and high and low w/c revealed a range of major gains and minor losses of MET or TET soluble alkali. Major increases in alumina and silica after 6 and 12 months hardening were also observed. Future investigations must address the magnitude of the effect of particle size of the aggregate and of w/c of the mortar on the release of alkali.

The magnitude of release of alkali by volcanic rocks, especially basalts was not attributable to the mere presence of a particular mineral e.g. plagioclase. Particle size effects are particularly important for the glass phase and structural strain especially for the plagioclase crystals. These parameters are related to the cooling history of the basalt and could explain the differences in alkali release between basalts L, P, S, and O ranging between 1.0 and 0.3 % Na_2Oeq in the same order. Access to reactive surfaces is further enhanced by a vesicular nature of some basalts and is held responsible for the particularly high alkali release by basalt M, a glassy scoria.

The only chemical indicator for the important difference between quarry P and S on one hand and quarry L on the other is the relative distribution of alkali metals and aluminium in the blank leaches (Figs 1 and 2). Mobilised by the strongly alkaline pore solution, in concretes Al may assist in the fixation of alkali metals through crystallisation of aluminosilicates.

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