Table 4. Overview of the various	mortar
bars contents of alkalies (eqv Na2	C)

Silica Fume	Contents of eqv Na ₂ O		
% mass binder	kg/m ³ mortar	% mass binder	
0.0	3.00	0.49	
	6.00	0.98	
4.0	2.88	0.48	
	5.88	0.98	
8.0	2.77	0.47	
	5.77	0.98	

 Table 5. Various measures describing the binder of the mortar bars

Silica Fume % mass binder	W/B* by mass	W/C by mass	eqv W/C** by mass
0.0	0.400	0.400	0.400
4.0	0.407	0.424	0.392
8.0	0.414	0.450	0.384

* B = binder = cement + silica fume = C + S** $eav W/C = W/(C + 2 \times S)$ according to DS 411





Fig 2. Variation of the flow of mortar. The target flow was 130 mm

Fig 3. Expansion versus time. Mortar bars with: chert 0-4 % by volume of aggregate, quartz as inert aggregate, alkalies 6 kg/m³ of mortar and no silica fume. Notice that the rate of expansion is large from start and vanishes after appx. 40 weeks of exposure.



Fig 5. Expansion versus time. Mortar bars with: chert 0-4 % by volume of aggregate, feldspar as inert aggregate, no silica fume and alkalies 6 kg/m³ of mortar. Notice that the rate of expansion is slower from start than that shown in Fig 3. Rate of expansion vanishes after appx. 40 weeks of exposure.

Fig 6. Expansion versus time. Mortar bars with: chert 5-10 % by volume of aggregate, feldspar as inert aggregate, no silica fume and alkalies 6 kg/m³ of mortar. Notice that the rate of expansion rises after appx. 25 weeks of exposure and does not vanish on the whole even after 7 years of exposure.





Fig 8. Expansion versus time. Mortar bars with: chert 0-6 % by volume of aggregate, quartz as inert aggregate, no silica fume and alkalies 3 kg/m³ of mortar. No expansion occurs as expected, since the alkalies of the mortar are 3 kg/m³ of mortar which corresponds to 1.8 kg/m³ of normal concrete.

Fig 9. Expansion versus time. Mortar bars with: chert 0-6 % by volume of aggregate, quartz as inert aggregate, silica fume 4 % by mass and alkalies 6 kg/m³ of mortar. As it is seen the influence of 4 % added silica fume does not change the expansion behaviour significantly, cf. Fig 3 and 4 (the critical expansion is 0,1 %).

Fig 10. Expansion versus time. Mortar bars with: chert 0-6 % by volume of aggregate, quartz as inert aggregate, silica fume 8 % by mass and alkalies 6 kg/m³ of mortar. The graph (shown shaded) is the expansion of mortar bars with 4 % chert and no silica fume. Notice that 8 % silica fume will cause delay and decrease of expansion.









Fig 11. Expansion of mortar bars at 60 weeks of exposure versus chert in aggregates. The mortar contains: 6 kg eqv Na₂O per m³ of mortar, no silica fume and quartz as the inert aggregate. Notice, that the pessimum proportion increases from 4 % to 5 % by volume by changing from quartz to feldspar.

Fig 12. Expansion of mortar bars at 364 weeks of exposure versus chert in aggregates. The mortar contains: 6 kg eqv Na₂O per m³ of mortar, no silica fume and quartz as the inert aggregate, cf. Fig 10. Notice that the pessimum proportion has now increased to 6 % by volume by changing from quartz to feldspar.





Fig 13. Expansion of the mortar bars versus the increase in their masses. During expansion the mortar bars absorb water and thus its mass increases. The diagram shows the relation of the expansion versus the mass increase for 0 to 60 weeks of exposure. The mortar contains: chert 0 to 10 % by volume, alkalies 6 kg/m^3 of mortar, quartz as inert aggregate and no silica fume added.

Fig 14. Diagram similar as shown in Fig 13, but feldspar is used instead of quartz as the inert aggregate. Notice that while expansion and the mass increase seem correlated when using quartz there is a change of correlation when replacing quartz with feldspar. There seems to be two separate relations, one having a larger slope and one having a smaller slope than found in Fig 13.



Fig 15. Release of alkalies from crushed granite in a saturated solution of calcium hydroxide at 38 °C (100 °F) versus time of exposure and particle size, cf. [6]. From the top and down: \circ granite crushed down to 0.1 mm; • granite crushed down to 1 mm and \Box granite crushed down to 10 mm.



Fig 16. Release of alkalies from different types of sand (fine aggregates) in a saturated calcium hydroxide at 38 °C (100 °F), cf. [6]. From the top and down: \Box a potassium rich feldspar crushed down to 0.1 mm; \blacksquare a sodium rich feldspar crushed down to 0.1 mm; \bigcirc a natural sand (fine aggregates) crushed down to 0.1 mm and \bullet the same natural sand in its natural occurrence, i.e. not crushed.

Durability of Concrete 823



Photo 1. Thin section micrograph of mortar bar No. 33-2 after 365 weeks of exposure. Clear signs of alkali-silica reaction are observed. The expansion of the mortar has attained a value of 0.22 % by length. Several cracks radiate from the chert particle to the right (C). Colourless, clear alkali-silica gel is seen in the cracks (\rightarrow). Other abbreviations used: Quartz aggregates (S), cement paste (P). Depicted area 2.3 × 3.4 mm. Mixture proportions, cf. Photo 3.



Photo 2. Thin section micrograph of mortar bar No. 33-2 after 365 weeks of exposure. Alkali-silica gel is seen in air voids close to the chert particle (C). Note that the alkali-silica is oriented horizontally in relation to the original orientation of the bar during exposure. Only a thin crack running from the chert particle to the gel-filled air void is seen (\rightarrow) . Depicted area: 0.8×1.1 mm.

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Photo 3. Thin section micrograph of mortar bar No. 37-2 after 365 weeks of exposure. No cracking is observed. Chert particles are labelled (C). Other abbreviations used: Quartz aggregates (S), cement paste (P) and air void (A). Depicted area 2.3×3.4 mm.

Mixture proportions

Mixture proportions	Mortar bar No. 33-2	Mortar bar No. 37-2	Unit
Alkali-reactive chert:	3.0	6.0	% by volume
Equivalent Na ₂ O:	6.0	3.0	kg per m ³ of mortar
Silica fume:	4.0	8.0	% by mass

<u>SP 192–50</u>

Relation between Pozzolanic Reactivity of Fly Ash and its Effect in Controlling Alkali-Silica Reaction

by T. Yamamoto and T. Kanazu

ABSTRACT

Forty fly ash samples obtained from twenty four different thermal power stations were used in the pozzolanic reactivity test, and twenty four fly ashes, original ashes, and air stream classified ones from a single boiler were used in the ASR (Alkali-Silica Reaction) controlling tests. The present work evaluates the pozzolanic reactivity of fly ash by estimating consumption ratio of Ca^{2+} in the cement and fly ash mixed suspension while considering interactions of other alkali ions released from the cement particle. The index derived from the acceleration test was named as Assessed Pozzolanic-reactivity Index (API), estimating the consumed Ca^{2+} ratio in the suspension. There was a linear correlation between the API and activity indices obtained from mortar tests (JIS A 6201-1999). On the other hand, the API also showed a linear correlation with expansion ratio, the control effect of fly ash on ASR, obtained from mortar tests (ASTM C 441). The API can stand for the ASR-controlling efficiency. The pozzolanic reactivity of fly ash significantly influences the control effect on ASR, the higher the pozzolanic reactivity, the higher the control effect on ASR.

<u>Keywords</u>: accelerated tests; alkali-silica reactions; fly ash; portland cement; pozzolans

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INTRODUCTION

Fly ash is the finely divided residue that results from the combustion of pulverized coal and is collected from the flue gas by electrostatic precipitators. Fly ash has pozzolanic properties in the presence of hydrating cement system to form compounds possessing cementitious properties (1). It is generally accepted that pozzolanic reactivity is greater, the finer the fly ash (by Blaine (2,3) or by 45 μ m sieve (2,4), and the percentage of fine particles (4-7)), but this does not mean that all fine fly ashes are necessarily chemically reactive.

The chemically reactive part of fly ash, the pozzolanic material, is thought to be amorphous material (glass), the higher the proportion of amorphous material (determined by using XRD), the higher the pozzolanic reactivity (8). By applying other methods, the amount of chemically reactive phase of fly ash was estimated by measuring the rate of dissolved silica in hydrofluoric acid (HF) (9, 10). The thermogravimetric analysis was used as a direct method to estimate pozzolanic reactivity of fly ash by assessing the amount of lime consumed at different curing times in wet mixture of 50% Ca(OH)₂ and 50% fly ash exposed to 60°C in a 100% R.H. environment (11). The most rapid method for the evaluation of pozzolanic reactivity was proposed by applying conductivity measurements to pozzolan-Ca(OH)₂ or NaOH solutions. The literature suggested that the results can be obtained in a minimum time of two minutes (12).

Many references suggest a significant effect of free $Ca(OH)_2$ on ASR in concrete (13). The presence of free $Ca(OH)_2$ in concrete was thought to be a necessary condition for the development of destructive ASR, so it was suggested that the depletion of $Ca(OH)_2$ due to pozzolanic reaction would play a major role in controlling ASR expansion (14). Calcium oxide content of fly ash showed a correlation to the ASR expansion. Some references suggested that the calcium oxide content may be useful in predicting the effectiveness of an ash to control ASR (15, 16). On the other hand, many references concluded that the control effect of pozzolans on ASR were due to its reactivity with Na⁺ and K⁺ and lowering pH in pore solution (17, 18).

The objective of this study was to determine the relation between pozzolanic reactivity of fly ash and its control effect on ASR, and to propose an accelerated chemical test to assess pozzolanic reactivity of fly ash and its control effect on ASR.

SCOPE

Forty fly ash samples obtained from twenty-four thermal power stations in

Japan were used in the pozzolanic reactivity tests. mortar and accelerated chemical tests. The proposed chemical tests are to determine the consumption ratio of Ca^{2+} in a fly ash-cement suspension. The point of the test is to operate a chemical reaction among Ca^{2+} , Na^+ , K^+ , and fly ash particles simultaneously. Those ions are released not only from cement but also from fly ash particles. The authors aimed to take into account the roles of Na^+ and K^+ during pozzolanic reaction. The surface of fly ash glass is an amorphous phase. The amorphous phase is easily to corroded firstly by Na^+ and K^+ to deform Si-O-Si system into Si-O-Na(K) + H-O-Si, then secondarily forming relatively long chained gel, Si-O-Ca-O-Si with the charge of Ca^{2+} (19).

Twenty-four fly ash samples were used in ASR controlling tests, mortar and accelerated chemical tests. Six original ashes were divided into three grades, fine, medium, and coarse, by using an air stream classifier. Almost of those samples (five original ashes, totally twenty samples) were obtained from the same boiler at a power station, so this experiment enabled us to estimate the effect of two major properties of fly ash, fineness and the difference in source of coal.

MATERIALS

Portland Cement

A normal portland cement was used. Its physical properties and chemical analysis are given in Table 1.

Fly Ashes

Forty samples obtained from twenty-four different thermal power stations were used in Test-1, the tests for pozzolanic reactivity. The physical properties and chemical analysis are given in Table 2. Figure 1 shows the quality of fly ashes that were classified according to JIS A 6201-1999. The number of fly ashes belonging to class-I, II, III, and IV were one, twenty-eight, five, and three, respectively. Three fly ashes did not meet the requirements of JIS A 6201-1999.

Twenty-four samples including air stream classified ashes were used in Test-2, the tests for ASR controlling. The original ashes Lb, MS, U, B, and Mo, were all collected from the same boiler (T) at a power station. These characters stand for the source of coals. WA-S, WA-A, WA-B were collected at each electrostatic precipitator (EP) of the boiler T, downstream, middle, and upstream, respectively. The sample N was collected at another power station. The physical properties and chemical analysis are given in Table 3. Figure 2 shows the quality of fly ashes that were classified according to JIS A 6201-1999. The particle size distributions, derived from laser diffraction and scattering method analyzer (SLAD 3000J, refractive index: 1.80-0.0i), are shown in Figure 3 and Figure 4.