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ALKALI-SILICA REACTION MITIGATION: STATE-OF-THE-ART AND RECOMMENDATIONS

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ABSTRACT

Alkali silica reaction (ASR) mitigation techniques from various states in the United States, and from various countries and international organizations, were assessed and summarized. A set of recommended mitigation procedures was developed, which requires the not only the use of low alkali cement, but replacement of part of it by Class F fly ash (or Class N pozzolan) (25% to 40% by weight), or ground granulated blast furnace slag (GGBFS) Grade 100 or 120 (40% to 50% by weight), or a combination of both. The Class F fly ash (or Class N pozzolan) should also have a maximum of 1.5% available alkali, a maximum 6% loss on ignition, and a maximum of 8% CaO (lime). A modified ASTM C 1260 using the actual mix is recommended for ASR testing. In addition to mitigating ASR, these recommendations are expected to: (1) reduce concrete costs, (2) enhance the durability of concrete, (3) increase fly ash and GGBFS recycling, and (4) support the 1997 Kyoto protocol by significantly reducing CO_2 production. If 25% of all cement were to be replaced, total savings to the United States economy could be in excess of $1 billion every year.

Keywords: alkali silica reaction, ASR, concrete, durability, slag, fly ash, silica fume, lithium.

RESEARCH SIGNIFICANCE

In 2001, Congress passed Military Authorization Bill - Public Law 106-398 (HR 4205) (Section 389), and Military Construction Appropriations Bill - Conference Report 106-710 for Public Law 106-246. The Conference Report directs the Under Secretary of Defense for Acquisition, Technology, and Logistics to assess the overall condition of Department of Defense (DOD) facilities and infrastructure with respect to Alkali-Silica Reaction (ASR). Public Law 106-398 directs the Secretary of Defense to assess the damage caused to aviation facilities by ASR, and explore available technologies capable of preventing, treating, or mitigating ASR. To date 23 Air Force, 3 Army, and 6 Navy and Marine Corps airfields have reported ASR problems (Malvar et al., 2001). ASR is often only apparent after 5 to 15 years and can affect any concrete structure (e.g. NRC, 2000; Spencer and Blaylock, 1997; Lead States, 2000b).

There are some problems with current practice in ASR mitigation. For example, the Environmental Protection Agency (EPA) encourages the use of recycled materials such as fly

ash and ground granulated blast furnace slag (GGBFS). Their use in concrete cannot be prevented, but since no minimum usage is set, often the concrete does not include these materials. When fly ash is used, the current practice is to use cement replacements around 15%. Even with Class F fly ash, this low volume replacement can actually worsen the ASR problem. The objective of this paper is to address these problems and derive an optimum set of ASR mitigation techniques.

BACKGROUND

ASR and AAR

Alkali silica reaction (ASR) is the reaction between the alkali hydroxide in Portland cement and certain siliceous rocks and minerals present in the aggregates, such as opal, chert, chalcedony, tridymite, cristobalite, strained quartz, etc. The products of this reaction often result in significant concrete expansion and cracking, and ultimately failure of the concrete structure, including significant potential for foreign object damage to aircraft (see Helmuth et al., 1993, or Thomas, 1996, for details on the chemical reactions). Alkali aggregate reaction (AAR) is the reaction between the cement hydroxides and mineral phases in the aggregates, which are usually of siliceous origin. In this paper no distinction is made between AAR and ASR. The ASR reaction needs several components to take place: alkali (supplied by the cement, although external sources can exist), water (or high moisture content), and a reactive aggregate.

CALTRANS

The California Department of Transportation (CALTRANS) recently studied the use of mineral admixtures to mitigate ASR (Glauz et al., 1996). Some conclusions were:

- ASR will increase proportionally to the cement alkali content.
- The ASTM C 150 limit of 0.6% alkali content (Na_2O equivalent) in Portland cement may be too high to mitigate ASR deleterious expansion.
- High calcium oxide (CaO, or lime) content in admixtures seems to promote ASR.
- Class F fly ash (and Class N pozzolan) (ASTM C 618) are effective against ASR when replacing up to 30% of the Portland cement (by mass).
- Fly ash with more than 10% CaO is unsuitable for mitigating ASR.
- Natural pozzolans with low lime content (<2%) and low total alkali content (<3%) are very effective against ASR when replacing 15% of the Portland cement (by mass).
- Small amounts of silica fume are effective in inhibiting ASR expansion.
- Alkali ions from outside sources will contribute to ASR expansion.

Recommendations include using either a 15% fly ash replacement if the fly ash has less than 2% CaO, or 30% fly ash replacement if the CaO content is less than 10% (and total alkali content is less than 3%). These recommendations were implemented in CALTRANS standard specifications Section 90-4.08, "Required Use of Mineral Admixtures."

AASHTO, Lead States, and FHWA

From 1995 to 2000, the Lead States Team for ASR (New Mexico, North Carolina, Pennsylvania, South Dakota, Virginia, and partners from universities, industry, and the Federal Highway Administration – FHWA) established by the American Association of State Highway and Transportation Officials (AASHTO) developed guidelines and technologies for treating and

preventing ASR. They prepared a draft guide specification (Lead States, 2000a) to be published in the Guide Specifications for Highway Construction (AASHTO, 2001). The Team prepared a Transition Plan (http://leadstates.tamu.edu/asr/transition/) (Lead States, 2000b), which included:

- A survey of State Highway Agencies to assess the extent of ASR.
- An updated "Handbook for the Identification of ASR in Highway Structures," SHRP-C-315 (http://leadstates.tamu.edu/asr/library/C315/).
- A draft AASHTO Guide Specification on ASR-Resistant Concrete (http://leadstates.tamu.edu/ASR/library/gspec.stm).
- An aggregates database and a list of resources.
- A list of ASR Lead State contacts, and a bulletin board for technical assistance.

The draft Guide Specification on ASR-Resistant Concrete proposes the following tests for aggregates: AASHTO T 303 (which limits a mortar bar expansion at 14 days to 0.08% for metamorphic aggregates, 0.1% for all others), and ASTM C 1293 (which limits a concrete prism expansion at 1 year to 0.04%). Methods to prevent ASR in new concrete include the use of: (1) low alkali and/or blended cements, (2) minimum 15% Class F fly ash or 25% GGBFS cement replacement, and (3) lithium admixtures.

AASHTO M 295 (similar to ASTM C 618) used to require a 5% MgO limit in the fly ash (ACAA, 1995) but this requirement has been dropped. For Class F fly ash, this does not seem to be a problem since the MgO content is typically very low (e.g. see Malhotra et al., 1994).

New Mexico State Highway and Transportation Department

The State of New Mexico has some of the most reactive aggregates in the U.S., and its specifications are of special importance. Section 510 on Portland Cement Concrete from the New Mexico State Highway and Transportation Department (NMSHTD) requires aggregates to be tested via AASHTO T 303 or ASTM C 1293, with expansion limits of 0.1% and 0.04%, respectively. Aggregates with less expansion are assumed innocuous (non-reactive). Class F fly ash is required if either fine or coarse aggregate shows reactivity, otherwise Class C fly ash is permitted. Both fly ashes are required to have less than 10% CaO, less than 1.5% available alkalis, and a loss on ignition (LOI) of less than 3%. If the aggregate is potentially reactive, the following minimum admixtures (among others) are to be incorporated: either (1) 20% of Class F fly ash by weight of cement, (2) 25% to 50% GGBFS, or (3) lithium nitrate – 4.6 L/m^3 (0.55 gal/yard^3) of solution per kg (pound) of cement sodium equivalent. Admixture effectiveness is determined using AASHTO T 303 with a 14-day expansion limit of 0.1%.

A recent NMSHTD-sponsored study (McKeen et al., 1998) concluded that 25% to 27% Class F fly ash replacement was sufficient for most of the reactive aggregates studied. Class C fly ash and blends of Class F and C did not provide enough expansion reduction. The City of Albuquerque Specification for Portland Cement Concrete requires 20% Class F fly ash whether or not the aggregates are reactive.

Washington State Department of Transportation

In the State of Washington ASTM C 1260 (or AASHTO T 303) is recommended to test for ASR. Mitigation procedures include using low-alkali cement, fly ash, and lithium. However, the aggregate is considered non-reactive if either ASTM C 1293 or C 295 are satisfied, with an expansion limit of 0.04% in C 1293, and deleterious material limits in C 295 as follows: (1) optically strained, microfractured, or microcrystalline quartz – 5% max, (2) chert or chalcedony – 3% max, (3) tridymite or cristobalite – 1% max, (4) opal – 0.5% max, (5) natural volcanic glass

– 3% max. In this state it appears that only a single test out of the three needs to be satisfied for the aggregate to be accepted without any mitigating measure.

Portland Cement Association

The Portland Cement Association (PCA) has a guide specification for concrete subject to ASR (PCA IS415, 1998) where it requires ASTM C 1260 (limit 0.1%) and ASTM C 295 (same limits as Washington State). Potentially reactive aggregates can be further evaluated using ASTM C 1293 (limit 0.04%). Aggregates having shown reactivity in service are considered reactive regardless of test results. Potentially reactive aggregates can be used in concrete in one of three ways: (1) with a combination of pozzolan or slag with Portland or blended cement shown to be effective, (2) with a blended cement shown to be effective, or (3) with the alkali content in the cement and other concrete ingredients limited to levels proven to limit reactivity in field conditions. Effectiveness can be proven either via: (1) ASTM C 1260 (limit 0.1%), or (2) ASTM C 441 if the test mix with the admixture results in less expansion than a control mix made with low-alkali cement with total Na_2O equivalent alkali content between 0.5% and 0.6%.

Federal Aviation Administration

The Federal Aviation Administration (FAA) addresses concrete pavements in Item P-501 (FAA, 1999). Aggregates are tested using either ASTM C 1260 or a set of tests that includes ASTM C 295, C 289, and C 227. It also mentions that C 289 test results may not be correct, and that C 227 should be conducted for at least 6 months, or preferably 1 year. Item P-501 indicates that total cementitious materials (slag and fly ash) can replace cement in the proportion of 25% to 55%. However, for fly ash alone, they recommend 10% to 20% replacement only.

American Concrete Institute

ACI Committee 221 completed a state-of-the-art report (ACI 221.1R, 1998) that states:

- Although a maximum of 0.6% Na_2O equivalent alkali is often used for cement, a limit of 0.4% is preferable.
- A low calcium oxide (CaO) content is desirable for fly ash, and Class F fly ash generally contains less than 5% CaO.
- GGBFS grades 100 and 120 are recommended for ASR mitigation.
- If densified pellets of silica fume are not well dispersed while mixing, they may act like reactive aggregate and cause ASR.
- An expansion limit of 0.08% is suggested for ASTM C 1260.
- Aggregates with lower particle size produce less expansion.

ACI Committee 232 completed a guide on the use of fly ash in concrete (ACI 232.2R, 1996). Some highlights:

- 50 million tons of fly ash were produced in the United States in 1991 and only 10% to 12% of that total was used in concrete.
- Increases in the dosage rate for air-entraining admixtures are often necessary to insure that the required percentage of entrained air will be obtained.

ACI Committee 233 completed a guide on the use of GGBFS in concrete (ACI 233R, 1995). Some highlights:

- 13 million tons of GGBFS were produced in 1991 in the United States.
- A 40% to 50% GGBFS cement replacement provides high strength gain at 28 days.
- Small increases in the dosage rate for air-entraining admixtures are often necessary.

- Grade 120 slag cement replacements result in lower strengths in the first 3 days, but greater strengths after 7 days (compared to mix without replacement).
- Grade 100 slag gives lower strengths in the first 21 days, greater strengths after that.
- Grade 80 slag gives lower strengths at all ages.
- Stable long-term strength gain beyond 20 years has been documented.
- A minimum 40% GGBFS cement replacement is needed to mitigate ASR.
- Precast mixes with Grade 120 slag cement replacement can get 1-day compressive strengths higher than without replacement.

International Center for Aggregate Research

The International Center for Aggregate Research (ICAR) at the University of Texas at Austin, has recently produced a very comprehensive state-of-the-art report (Touma et al., 2001) (http://www.ce.utexas.edu/org/icar/). For slowly reactive aggregates, or for highly reactive aggregates with low alkali cement, the report recommends using at least either: (1) 17% calcined clay, (2) 55% slag, (3) 25% Class F fly ash, (4) 35% Class C fly ash, (5) 10% silica fume, (6) 4.6L $LiNO_3$ per Kg of Na_2O. ASTM C 1260 or C 1293 using the actual mix are used to assess the effectiveness of the mitigation. Based on cost comparisons, the report concludes: "the use of Class F fly ash appears to be the best alternative for the mitigation of ASR."

Canadian Standards Association

The Canadian Standards Association (CSA) developed CSA A23.2-25A and CSA A23.2-14A, similar to ASTM C 1260 and C 1293, respectively. However, the limit expansion in CSA A23.2-25A is 0.15% (CSA A23.2-27A, 2000; Fournier et al., 2000b), greater than the 0.1% allowed by ASTM C 1260, although Appendix B of CSA A23.1 recommends using the 0.1% limit as well. For the fly ash used, CSA A23.2-27A indicates that low lime (CaO) contents below 8% are preferred. For highly reactive aggregates, CSA A23.2-27A recommends at least 25% to 30% low lime fly ash, or at least 50% GGBF slag cement replacement.

RILEM

RILEM (International Association for Building Materials and Structures) Technical Committee TC 106-AAR on Alkali Aggregate Reaction has published two recommendations for detection of aggregate reactivity: RILEM TC 106-2 (2000) (ultra accelerated mortar-bar test) and RILEM TC 106-3 (2000) (method for aggregate combinations using concrete prisms). RILEM TC 106-2 is similar to ASTM C 1260 and AASHTO T 303 (all are based on the South African National Building Research Institute, accelerated test method). Aggregates with more than 2% by mass of porous chert and flint are not recommended (they can give misleading results). RILEM TC 106-3 is similar to ASTM C 1293 but the specimens are wrapped in cotton cloth and sealed inside polythene lay-flat tubing. In RILEM TC 106-2 aggregates are considered non-expansive for expansion less than 0.1% at 14 days, potentially expansive if between 0.1% and 0.2%, and expansive otherwise. In RILEM TC 106-3 aggregates are considered non-expansive for expansion less than 0.04% to 0.05% at 14 days, potentially expansive if less than 0.15%, and expansive otherwise (Nixon and Sims, 2000).

Other Countries

The British Research Establishment (BRE) recommends the use of low-alkali cement. Test method BS 812-123, 1999 (formerly DD 218) from the British Standards Institution, is used

to categorize the expected reaction as: (1) expansive if more than 0.2% expansion after 12 months, (2) possibly expansive if between 0.1% and 0.2%, (3) probably non-expansive if between 0.05% and 0.1%, and (4) non-expansive if less than 0.05%.

In the Netherlands, CUR-Recommendation 38 indicates that if cement replacement in the amount of at least 25% by mass of fly ash, or 50% by mass of GGBFS is implemented, then the potential reactivity of the aggregates is of no concern (Heijnen and Larbi, 1999).

In Australia, the Queensland Department of Main Roads (1999) requires 20% fly ash cement replacement in all prestressed roadway concrete. All other concrete meeting the minimum 20% requirement is exempt of additional testing for reactivity. Fly ash with a maximum total alkali content of 2%, and a maximum available alkali content of 0.5%, is required. For GGBF slag the corresponding contents are 1%, and 0.5%, respectively.

Additional ASR work in Denmark, France, Korea, Portugal, New Zealand, Hong Kong, Taiwan, Italy, and Iceland is summarized by Touma et al. (2001). In Norway, ASTM C 1293 is not considered reliable (Jensen and Fournier, 2000; Touma et al., 2001).

TEST METHODS

Accelerated Mortar Bar Test (ASTM C 1260 / AASHTO T 303 / CSA A23.2-25A)

ASTM C 1260 (or its equivalents AASHTO T 303 and CSA A23.2-25A) – the accelerated mortar bar test (AMBT) – is perhaps the most widely used test method. The accepted maximum expansion for innocuous aggregates is 0.1% (14 days after the zero reading, or 16 days after casting) for both United States methods, or 0.15% for CSA A23.2-27A (although 0.1% is recommended in Appendix B of CSA A23.1). These limits have been lowered to 0.08% for metamorphic aggregates (Lead States, 2000b). This is consistent with Note X1.1 of ASTM C 1260 that indicates "some granitic gneisses and metabasalts have been found to be deleteriously expansive in field performance even though their expansion in this test was less than 0.1% at 16 days after casting". ACI 221.1R (1998) and Stark et al. (1993) also suggests using a 0.08% limit. Grosbois and Fontaine (2000) suggested 0.08% or even 0.06%. ASTM C 1260 is somewhat conservative in that it provides excess NaOH in the 1N solution in which the specimen is immersed, and high temperature (80ºC or 176ºF). In reality no external NaOH source may exist, and the reaction may terminate earlier. On the other hand, ASTM C 1260 is useful for identifying slowly reacting aggregates (PCA IS413, 1997). Aggregates found innocuous with ASTM C 1260 are likely to perform well in the field, although some reactive granites and gneisses may not be detected (Touma et al., 2001). In this test, the solution is supposed to provide a sufficient source of alkali to complete any reaction, and the alkali content of the cement is supposed to have little or no influence. However, different cements have sometimes yielded different results (Simon and Wathne, 2000), and a modified ASTM C 1260 is often completed where the actual concrete composition is used (PCA IS415, 1988; Appendix B of CSA A23.1, 2000; Shayan, 1992). In the modified test, an expansion limit of 0.1% has been recommended (Appendix B of CSA A23.1, 2000; Shayan, 1992).

Concrete Prism Test (ASTM C 1293 / CSA A23.2-14A)

In ASTM C 1293 (and its Canadian equivalent CSA A23.2-14A) – the concrete prism test (CPT) – concrete prism samples are kept in a moist (100% relative humidity) environment at a temperature of 38ºC (100.4ºF) for 1 year. Maximum expansions are limited to 0.04%. This

method may appear more realistic than ASTM C 1260, but it has two drawbacks: samples are tested only for 1 year in a non-accelerated environment, and it may be difficult to ascertain that the aggregates used for the samples 1 year ago are representative of the ones used today. This method is less conservative than the AMBT and more likely to allow slow reacting aggregates.

Comparison between ASTM C 1260 and ASTM C 1293

Grosbois and Fontaine (2000) show comparisons of the two methods for various aggregate types. For carbonate aggregates, C 1260 did not appear conservative enough, and a 0.08% (or 0.06%) threshold would have been more appropriate. For sandstones, both methods predicted similar reactivity. For igneous and metamorphic rock, in two cases C 1260 seemed too conservative. Thomas and Innis (1999) data show the same results between the two tests in 73% of the cases. Fournier et al. (2000a) use the CPT as the reference test but indicate the AMBT is a good screening test. In New Brunswick, Canada, a study showed the AMBT to conservatively indicate reactivity while the CPT did not in 46% of the cases tested (Strang, 2000), however, given that about 70% of the structures built between 1930 and 1950 show reactivity, it is difficult to assess which test was more accurate. Although some of the previous works indicate that the CPT will give more realistic results, there is evidence that aggregates that appeared innocuous with the CPT actually showed field reactivity (Jensen and Fournier, 2000). In Norway, the CPT method is not used (Jensen and Fournier, 2000; Touma et al., 2001).

Mortar Bar Method ASTM C 227

This method is similar to ASTM C 1293 in terms of specimen exposure (100% relative humidity and 38ºC). However, unless specifically required at later dates, the expansion is reported at 14 days, which is too short of a time. Appendix XI of ASTM C 33 indicates that the expansion is considered excessive if it exceeds 0.05% at 3 months, or 0.10% at 6 months. The FAA requires running it for at least 6 months, and preferably 1 year (FAA, 1999). In general, this test method may not produce significant expansion, especially for carbonate aggregate (PCA IS413, 1997), and has been deemed unreliable (Wigum et al., 1997; Touma et al., 2001).

Petrographic Examination ASTM C 295

This analysis can detect reactive constituents, such as opal, cristobalite, tridymite, siliceous and intermediate volcanic glass, argillites, phyllites, metamorphic graywackes and quartz, etc. Problems with this examination are: (1) its list of potentially reactive aggregates may be incomplete, (2) it is very dependent on the reliability of the operator, and (3) it may not clearly identify some microcrystalline, strained, or microfractured quartz (Touma et al. 2001).

Chemical Method ASTM C 289

In this method, samples of crushed and sieved aggregates are reacted with an alkaline solution at 80ºC (176ºF), measuring the dissolved silica. This method may not be reliable for many aggregates (PCA IS413, 1997; FAA, 1999; ACI 221.1R, 1998; Wigum et al., 1997; Touma et al., 2001), although it may serve as a good indicator for other aggregates (Freitag et al., 2000).

BENEFICIAL ADMIXTURES

Advantages of Class F Fly Ash

Class F (low calcium, ASTM C 618) fly ash in replacement amounts around 25% has been shown to significantly mitigate ASR, even in marine environments (for water/cement ratios below 0.5) (Malhotra et al., 1994; Bérubé et al., 2000; McKenn et al., 1998). In a study by Touma et al. (2000) on several reactive aggregates, 25% Class F fly ash cement replacement reduced the ASTM C 1260 expansion from more than 0.9% to 0.12% in one case, and less than 0.1% in all other cases. This 25% Class F fly ash cement replacement also resulted in less expansion than 35% Class C fly ash cement replacement in all cases (while Class C fly ash has some similar advantages, it has often shown to not reduce or even aggravate the ASR problem, see PCA IS413, 1997; Touma et al., 2001; Dunstan, 1982). Similar expansion reductions were found by Barringer (2000) and McKeen et al. (1998) using 24% to 27% Class F fly ash and reactive New Mexico aggregates. Several other reports confirm the effectiveness of Class F fly ash in ASR mitigation at replacement levels usually between 15% and 45% (ACI 232.2R, 1996; Rogers et al., 2000; Fournier, 1999), although levels below 25% may not be effective unless low-lime fly ash is used with 10% or less CaO (Malhotra et al., 1994; Rogers et al., 2000; Glauz et al., 1996; Thomas and Innis, 1999; Touma et al., 2001).

The lime content changes the effectiveness of Class F fly ash to mitigate ASR (Dunstan, 1982; Thomas, 1996). CALTRANS requires a maximum CaO content of 10%, and lowers the required fly ash if the CaO content is below 2% (Glauz et al., 1996). In Canada, CSA A23.2-27A (2000) supports a maximum CaO content of 8%. Generally, Class F fly ash contains less than 5% CaO by mass (ACI 221.1R, 1998). A maximum CaO content of 8% is recommended here (Class C fly ash is not recommended). Class F fly ash has also been reported to mitigate expansion caused by delayed ettringite formation in steam-cured concrete (Zacarias et al., 1999).

Besides mitigating ASR, Class F fly ash has the following advantages (many apply to GGBFS as well):

Reduced construction costs. Cement is the most expensive constituent of concrete. A cubic yard of 5000-psi ready-mix concrete costs $68.25 (for Los Angeles, ENR 5 Oct 98). Up to $21, or 30%, of the cost is due to the cement itself. Replacement of 25% of the cement by fly ash can result in total concrete savings around 4% (see also Touma et al., 2001).

Savings in Portland cement production. The global cement production in 1995 was 1.4 billion tons (Malhotra 1999). A significant reduction in cement production could be accomplished if all projects incorporated 25% fly ash (or 50% GGBFS) cement replacement. In the United States, 87 million tons of cement were produced in 1999 (http://www.global-cement.dk/files/facts.htm). Since cement costs $81.83 per ton (http://www.enr.com/cost/cost2.asp), and fly ash for use in concrete costs from $20 to $45 per ton (at the site, source: American Coal Ash Association), total savings to the United States economy could be in excess of $1 billion every year.

Reduced heat of hydration, reduced permeability, and enhanced durability. Class F fly ash reduces concrete permeability (Class C fly ash provides less reduction – Ellis, 1992), reduces the heat of hydration (and shrinkage cracking), and slows down the ingress of chloride ions, increasing durability (reducing maintenance costs). Class F fly ash also increases the sulfate resistance of concrete (Class C decreases it) (Ellis, 1992).

Concrete strength. Long-term strengths are usually higher with fly ash (or GGBFS) cement replacement. For Class F fly ash replacement, the early strength is usually lower. This can be compensated by reducing the water-cement ratio, or by using partial (modified) replacement (i.e. where the amount of fly ash added exceeds the amount of cement replaced) (Malhotra et al., 1994; Naik et al., 1989; Illinois, 2001).

Reduction in CO_2 generation. Experts on global warming link 7% of the world's carbon dioxide emissions to the production of Portland cement (Malhotra, 1999). Each ton of cement that is not produced reduces carbon dioxide emissions by about 1 ton (Malhotra, 1999; Mehta, 1998). If all projects worldwide were to incorporate 25% to 30% fly ash replacement, total world CO_2 emissions could decrease by 2%. This would be a significant contribution towards meeting the 1997 Kyoto Protocol to the United Nations, where nations intend to reduce their CO_2 emissions by at least 5% below 1990 levels in the commitment period 2008 to 2012 (http://www.cnn.com/SPECIALS/1997/global.warming/stories/treaty/index.html).

Higher recycling. Recycling fly ash and slag, both by-products, will reduce the need for their disposal into landfills. Today only 10 percent of the 60 million tons of fly ash annually produced in the United States is used in concrete (Rosenbaum, 1998). If 25% of all cement produced in the United States were replaced, 22 million tons of fly ash would be reused.

Environmental Benefits. RCRA Section 6002 directs federal agencies to establish affirmative procurement programs for procuring items containing recovered materials to the maximum practical extent. Items listed by the EPA in 40 CFR 247.12(c) include cement and concrete with fly ash or GGBFS (http://www.epa.gov/epaoswer/non-hw/procure/rman1.htm#technical). Increasing the fly ash content in concrete would enhance conformity to these environmental requirements, and others such as Executive Order 13101 and Navy EQ recommendation 3.1.13.a. Reuse/Recycling of Hazardous/Polluting Materials.

Energy Savings. Because it takes 4 GJ of energy to produce 1 ton of cement, a 25% fly ash cement replacement would provide energy savings of 88 million GJ or 83,000 BBtu per year.

Resistance to jet exhaust. A benefit for airfield pavements is that fly ash and slag have been shown to increase pavement resistance to high thermal gradients and temperatures from jet exhaust (Robins et al., 1995).

In current practice 15% to 25% fly ash cement replacements are common, and previously recommended. The Navy, Army, and Air Force already allow for up to 25% or 30% cement replacement with Class F fly ash. However, while this use is allowed, no minimum cement replacement is usually required, and consequently no fly ash is usually included. It is recommended here that a minimum Class F fly ash cement replacement of 25% be required, with a maximum CaO content of 8%.

Strength Gain Rate with Class F Fly Ash

Mixes incorporating fly ash typically show higher long-term strengths (e.g. at 90 days), however, their strength gain rate is initially lower than for regular mixes without replacement.

The Naval Facilities Engineering Service Center completed a laboratory investigation where several mixes were tested with 0% to 40% Class F fly ash cement replacement for Pier D, Naval Station Bremerton, Washington (Tables 1 and 2). This fly ash had a 10% CaO content and actually showed a pessimum (worse ASR expansion) at a 15% replacement level (Table 2). These and other mixes showed that the compressive strength at 28 days with Class F fly ash cement replacement is between 80% and 95% of the strength without replacement. Replacement appeared to have an even lesser effect on the flexural strength at 28 days (Malhotra et al., 1994; Galeota et al., 1995). To maintain the initial strength gain rate the water cement ratio can be lowered. Alternatively, some DOTs use replacement ratios, e.g. replacing each bag of cement with 1.5 bags of Class F fly ash (Illinois, 2001). In summary, either direct or partial substitution can allow for similar compressive and flexural strengths at 28 days.

Advantages of Class N Natural Pozzolans

Although Class N raw natural pozzolans (ASTM C 618) have been less used, a comprehensive study by CALTRANS (Glauz et al., 1996) shows that these pozzolans, with the same limitations in composition as for Class F fly ash, can provide the same advantages as Class F fly ash. That study also shows that some good Class N raw pozzolans exist with a CaO content below 2%, almost no alkalies, and an LOI of less than 4%.

Calcined clay (or metakaolin) can mitigate ASR expansion at replacement levels of 10% to 20% for moderately reactive aggregate (Sibbick et al., 2000; Touma et al., 2001; Detwiler et al., 2001; Barger et al., 2001), or 25% for highly reactive ones (Touma et al., 2001). It is recommended here that Class N pozzolans be allowed, with the same restrictions as for Class F fly ash.

Advantages of GGBFS

GGBFS (ASTM C 989) offers similar advantages to Class F fly ash, but only when used in higher quantities (Malhotra et al., 1994; Rogers et al., 2000; Ramachandran, 1998; Thomas, 1996). For example, in blended cements, while typical replacements for fly ash are around 15% to 40%, for GGBFS they are around 25% to 70%. A 40% GGBFS cement replacement can provide benefits similar to a 25% fly ash replacement (BRE, 1999). In the Netherlands, 25% fly ash is considered equivalent to 50% GGBFS (Heijnen and Larbi, 1999). GGBFS has been successful in mitigating ASR (Hooton et al., 2000; Malhotra et al., 1994), although a minimum 40% GGBFS cement replacement may be needed (Appendix X3 of ASTM C 989, 1997; ACI 233R, 1995). GGBFS Grades 100 or 120 are preferred to Grade 80 (ACI 221.1R, 1998; ACI 233R, 1995; Brewer, 2000), and are the ones recommended for ASR mitigation (ACI 221.1R, 1998). Low alkali levels in GGBFS are preferable (Thomas, 1996). Also, pavements with GGBFS exhibit a lighter color, which can reduce energy absorption, increase pavement life, reduce temperature levels, and lighting requirements (http://eetd.lbl.gov/HeatIsland/Pavements). Finally, the cost of slag is about 3/4 the cost of cement (source: slag cement association), resulting in up to 4% savings in concrete costs.

Strength Gain Rate with GGBFS

GGBFS is not a pozzolan, rather it is a hydraulic cement. For Grades 100 and 120, GGBFS will result in higher strengths at 28 days (and later). ACI 232.2R (1996) reports that: (1) Grade 120 slag cement replacements result in lower strengths in the first 3 days, but greater strengths after 7 days, (2) Grade 100 slag cement replacements result in lower strengths in the

first 21 days, but greater strengths after that, and (3) Grade 80 slag gives lower strengths at all ages (Grade 80 is not recommended here).

Pessimum Effects and Minimum Replacements

For fly ash, a pessimum effect (i.e. more expansion instead of less) can be observed which gets worse as the CaO content increases (Malhotra et al., 1994; Rogers et al., 2000; Dunstan, 1982). This pessimum effect is very pronounced for Class C fly ash (with typical CaO contents between 10% and 30%), and is also present with Class F fly ash (with typical CaO contents between 0% and 10%). For Class F fly ash with 10% CaO, the pessimum effect often occurs for replacements around 10% to 15%, and the minimum replacement to reduce the expansion to an acceptable level is at least 30% (e.g. Table 2; Touma et al., 2001; Chen et al., 1993). This indicates that standard practice replacements of 15% may have resulted in concretes with worse expansion. This pessimum effect is also reflected in the CALTRANS specification, which allows for 15% replacement only if the Class F fly ash CaO content is less than 2%, and requires 25% replacement for CaO contents between 2% and 10%. It is recommended here that a Class F fly ash (or Class N pozzolan) with 8% CaO or less be used, and that a minimum replacement of 25% be used. If the fly ash has a CaO content between 8% and 10%, it could be allowed if the minimum replacement is increased to 30%. For GGBFS, minimum replacements of 35% (Cheung and Foo, 1999) and 40% (ASTM C 989, Appendix X3) have been suggested to mitigate ASR, but pessimums were reported near 35% (Chen et al., 1993) – a minimum replacement of 40% is recommended.

Advantages of Lithium Salts

Lithium salts can be added to the concrete mix to counter aggregate reactivity (Durand, 2000; Stokes et al., 2000a; Thomas et al., 2000; Thompson, 2000; McKeen et al., 1998; Touma et al., 2001; Lead States, 2000b). However, lithium hydroxide (LiOH) and lithium carbonate (Li_2CO_3) have been found to increase the expansion of alkali-carbonate reactive rock, and some lithium compounds in insufficient quantities can actually have a pessimum effect (Lead States, 2000a; Appendix B of CSA A23.1, 2000). Lithium hydroxide is also a hazardous material. Lithium nitrate ($LiNO_3$) does not exhibit a pessimum effect, is safe to handle, and is recommended (Lead States, 2000a; Appendix B of CSA A23.1, 2000; Touma et al., 2001). For moderately reactive aggregates, 4.6L of $LiNO_3$ per Kg of Na_2O equivalent (replacing a volume of mix water equal to 85% the $LiNO_3$ volume) appears effective (Lead States, 2000a; Touma et al., 2001), although the use of fly ash or slag would be cheaper. For very reactive aggregates, Class F fly ash replacement may not be sufficient, and use of lithium in addition to fly ash may be necessary (Stokes, 2001). Lithium salts can also be applied topically to existing concrete experiencing ASR and slow down or complete the reaction (Stokes et al., 2000b; Johnston et al., 2000). In practice, the lithium may not penetrate sufficiently into the structure and may not be able to mitigate the reaction below the surface, resulting in continuing decay. Methods of driving lithium ions using electrical fields are being studied to improve penetration (Whitmore and Abbott, 2000). If the concrete is cracked enough, the salts may penetrate deeply, but the concrete may be already too decayed.

Advantages and Disadvantages of Silica Fume

Silica fume has also been proven to mitigate ASR, for example 10% silica fume cement replacement has been reported to reduce expansion to a level close to 20% Class F fly ash

(Touma et al., 2000). Silica fume can also increase the concrete strength and lower its permeability. However, as indicated by Diamond (1998): "silica fume can induce ASR rather than mitigating it" (see also Pettersson, 1992; ACI 221.1R, 1998; Marusin et al., 2000; Escadeillas et al., 2000). Silica fume is prone to lumping (ACI 234R, 1996) and undispersed grains in lump sizes from 40 μm to 800 μm (and up to 3000 μm) can react with the cement alkalis just like reactive aggregates. Other difficulties in using silica fume have been reported elsewhere (ACI 234R, 1996; Al-Amoudi et al., 2001). Silica fume is also much more expensive than cement, fly ash, or slag (Touma et al., 2001). In summary, care should be taken when using silica fume, or it should be avoided in favor of fly ash or slag. If silica fume is used, the following precautions should be taken (see also ACI 234R, 1996): (1) it should be used in slurry form to facilitate dispersion (note that silica fume in a water suspension is prone to settling), (2) shreddable bags should be avoided, (3) extra mixing is recommended, and (4) proper curing must be followed. A 10% silica fume cement replacement seems to be effective for moderately reactive aggregates (Touma et al., 2001; Glauz et al., 1996).

Air Entrainment and Problems with Deicing Salts

Air entrainment can also somewhat mitigate the deleterious ASR expansion (ACI 221.1R, 1998; Ramachandran, 1998; Touma et al., 2001). The generated expanding gel can fill air voids, reducing the internal pressures created. However, this could reduce the freeze-thaw resistance, and a level of air entrainment higher than initially planned may be desirable to address both issues. Many Class F fly ashes, in particular those with LOI above 3%, may require higher dosages of air-entraining admixtures to obtain specified air contents, due to the interference of carbon solids with the surfactant action of the air entraining agents (Gao et al., 1997; Whiting and Nagi, 1998). In freeze-thaw areas where deicing salts are used, a related potential problem with more than 25% fly ash or 50% GGBFS is that the salt scaling resistance could decrease (Malhotra et al., 1994; Table 4.2.3 of ACI 318, 1999; ACI 232.2R, 1996), requiring conducting a salt scaling test (ASTM C 672).

RECOMMENDED MITIGATION PROCEDURES

Low alkali cement (ASTM C 150) with less than 0.6% alkali content (equivalent sodium oxide) should be required. For potentially reactive aggregates, a maximum cement alkali content of 0.4% is recommended, if available (ACI 221.1R, 1998; Lead States, 2000a). However, use of low alkali cement is not, by itself, sufficient to control ASR (PCA IS413, 1997).

It is recommended that either Class F fly ash (or Class N pozzolan) (ASTM C 618), or GGBFS (ASTM C 989) be used as cement replacement in all concrete. For Class F fly ash and Class N pozzolan, minimum replacements of 25% are recommended. A practical upper limit for the replacement could be around 40% due to increased difficulties with concrete finishing and lower strength gain rates at higher volume replacements. The fly ash (and the natural pozzolan) should also have a maximum 1.5% available alkali, a maximum 6% loss on ignition (3% would be preferable), and a maximum 8% CaO (2% would be preferable). Contents of CaO between 8% and 10% could be allowed if the minimum replacement is 30% (by weight). Class C fly ash is not recommended. For GGBFS, Grade 120 or 100 should be used (Grade 120 is preferred), and replacements between 40% and 50% are recommended.

Lithium admixtures have shown potential to mitigate ASR, however, only lithium nitrate is recommended since it is safe to handle and does not show a pessimum effect.

The best way to prevent ASR is to use non-reactive aggregates. This can be done by using aggregate that has historically performed well, or aggregate shown to be non-reactive by either ASTM C 1260, C 1293, or C 295. Historical performance may be very difficult to demonstrate since in many cases deterioration only occurs after 15 years or more (Lead States, 2000b) and knowledge of the actual mix used would be necessary. Whether or not the aggregates are reactive, the previous fly ash or slag minimum replacements are recommended.

DOD IMPLEMENTATION

The Naval Facilities Engineering Command (NAVFAC) is responsible for maintaining building materials guide specifications for the U.S. Navy. Navy, Army and Air Force specifications are currently being integrated into Tri-Service Unified Facilities Guide Specifications (UFGS). There are 36 UFGS targeted for implementation of these ASR mitigation guidelines (Malvar et al., 2001). The U.S. Army, Cold Regions Research and Engineering Laboratory, is also implementing these recommendations into an Air Force Engineering Technical Letter.

CONCLUSIONS AND RECOMMENDATIONS

To prevent ASR, it is recommended to use low alkali cement and include a cement replacement of 25% to 40% Class F fly ash (or Class N pozzolan), or 40% to 50% GGBF slag (Grade 100 or 120), or a combination thereof. The Class F fly ash (or Class N pozzolan) should have a maximum 1.5% available alkali, a maximum 6% loss on ignition (3% would be better), and a maximum 8% CaO (up to 10% CaO if a minimum replacement of 30% is used). Fly ash and GGBFS will, in general, improve the concrete quality and make it cheaper, and they should be considered for all new concrete, whether the aggregates are reactive or not. In addition to mitigating ASR, the recommended cement replacements with Class F fly ash or slag are expected to: (1) reduce concrete costs, (2) significantly enhance the durability of concrete, (3) increase fly ash and GGBFS recycling, and (4) support the 1997 Kyoto protocol by significantly reducing CO_2 production. If 25% of all cement were to be replaced, total savings to the United States economy could be in excess of $1 billion every year.

In addition it was also determined that:

1) Current practices using 15% fly ash cement replacement may worsen the ASR expansion, even with Class F fly ash.
2) For very reactive aggregates, lithium nitrate may be needed in addition to Class F fly ash.
3) If used, silica fume should be added only in slurry form and well mixed. A 10% replacement has shown to mitigate moderate reactivity.
4) Mitigation using lithium nitrate, silica fume, or calcined clay will increase the cost of concrete, whereas using Class F fly ash, Class N raw pozzolan, or GGBF slag will generally reduce it by about 4%.
5) Class C fly ash, lithium carbonate, and lithium hydroxide are not recommended for ASR mitigation.

6) A modified ASTM C 1260 is recommended for testing for ASR.
7) Additional research is needed to further refine these recommendations and to address the mitigation of ASR in existing structures.

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Table 1. Laboratory Investigation, Pier D, Concrete Strength.

FLY ASH	COMPRESSIVE STRENGTH psi (MPa)				FLEXURAL STRENGTH psi (MPa)		
(%)	1-day	7-day	28-day	180-day	7-day	28-day	180-day
0	2787 (19.2)	4490 (31.0)	5580 (38.5)	5885 (40.6)	575 (4.0)	565 (3.9)	615 (4.2)
10	1993 (13.7)	3933 (27.1)	4860 (33.5)	5440 (37.5)	550 (3.8)	610 (4.2)	640 (4.4)
15	2183 (15.1)	4583 (31.6)	5603 (38.6)	6250 (43.1)	605 (4.2)	650 (4.5)	705 (4.9)
20	2137 (14.7)	4240 (29.2)	5070 (35.0)	5730 (39.5)	570 (3.9)	590 (4.1)	640 (4.4)
25	1590 (11.0)	3603 (24.9)	4580 (31.6)	5180 (35.7)	540 (3.7)	510 (3.5)	610 (4.2)
30	1477 (10.2)	3680 (25.4)	4267 (29.4)	4640 (32.0)	495 (3.4)	590 (4.1)	605 (4.2)
35	1590 (11.0)	3603 (24.9)	4580 (31.6)	4713 (32.5)	440 (3.0)	560 (3.9)	610 (4.2)
40	1477 (10.2)	3680 (25.4)	4267 (29.4)	4467 (30.8)	440 (3.0)	520 (3.6)	560 (3.9)

Table 2. Laboratory Investigation, Pier D, Concrete Properties.

FLY ASH	SET (minutes)		28-DAY EXPANSION*	RAPID CHLORIDE PERMEABILITY ASTM C 1202 (Qs, Coulombs)	
(%)+	Initial	Final	ASTM C 1260 (%)	60-day	180-day
0	252	333	+ 0.128	7939	8561
10	227	274	+ 0.168	8305	3445
15	217	269	+ 0.221	6150	4219
20	209	259	+ 0.138	6879	3537
25	207	256	+ 0.111	7250	4405
30	220	279	+ 0.070	7744	3078
35	233	294	+ 0.088	6241	3091
40	250	318	+ 0.042	5906	3870

+ This fly ash had a 10% CaO content and shows a pessimum around 15% replacement.
* Readings were taken beyond the standard 14 days.