



# Energeia

## Corrosion in Concrete and the Role of Fly Ash in Its Mitigation

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### INTRODUCTION

Corrosion of reinforcing steel in concrete bridges, buildings, highways, and foundations has become a considerable economic and social burden for many states and a safety issue for taxpayers. This premature deterioration has contributed to an inadequate service life for many of these infrastructures.

Our aging infrastructure is one of the most serious problems facing the U.S. Federal Highway Administration.

Therefore, the adoption of corrosion protection measures in new concrete construction has become a major focus. This includes, but is not limited to, the use of better design and construction practices, adequate concrete cover, low-permeability concrete, corrosion inhibitors, and coated reinforcing steel.

This article presents the role that fly ash can play in mitigating corrosion in steel-reinforced concrete. It considers the usefulness of current fly ash concrete technology and prevention techniques, and advances a new approach for making concrete resist the deleterious effects of corrosion.

### Economic Loss Due to Corrosion

The direct cost of repairing or replacing all deteriorated concrete structures was

estimated in 1997 to be more than \$276 billion annually or 3.1% of the nation's Gross Domestic Product (GDP). This is a dramatic increase from the 1975 benchmark study by Battelle-NBS, which calculated the cost of all corrosion to be \$70 billion per year, which was 4.2% of the nation's GDP.

A 2002 report by the U.S. Federal Highway Administration outlined the cost of corrosion. The study focused on identifying the cost of corrosion by specific industry sectors (**Figure 1**) and establishing control methods to minimize the problem. Extrapolated into 2003, the total annual estimated direct cost of corrosion damage is about \$350 billion. The report revealed that although corrosion management has improved over the past several decades, the United States still needs to research and implement better methods to control corrosion.

### Structural Distress

Of the nearly 600,000 bridges in the U.S., there are roughly 235,000 conventional reinforced concrete bridges, and about 108,000 pre-stressed concrete bridges operating in the country. They support nearly 270 million residents and 7 million business establishments. It is estimated that 15% of them are structurally deficient because of corroded steel and steel reinforcement. While there has been a decrease in the number of bridges in need of repair or replacement, the costs have continued to increase.

### Fly Ash

Currently about 720 coal-fired U.S. power plants annually produce about 76 million tons of

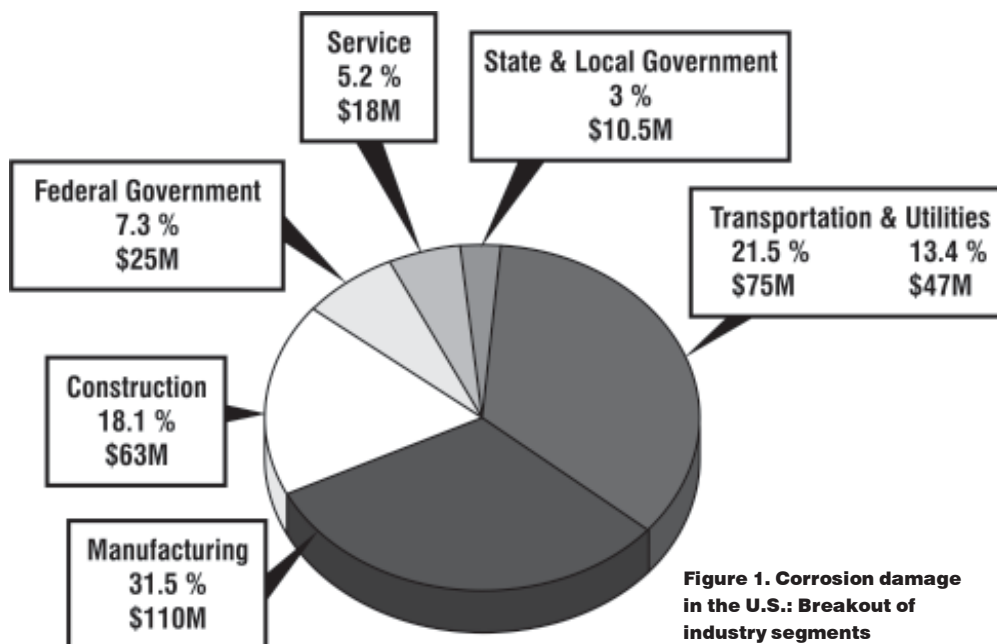


Figure 1. Corrosion damage in the U.S.: Breakout of industry segments

## Corrosion in Concrete, (cont.)

fly ash. Around 50 million tons are disposed of, either onsite or in state-regulated disposal sites. Approximately 12 million tons of fly ash are annually recycled and put to beneficial reuse in the concrete industry. Another 14 million tons are used for a range of other applications including: soil stabilization, roller compacted concrete, road-base stabilization, etc. We focus our attention on the use of fly ash as a mineral admixture for portland cement concrete.

The United States consumes more than 108 million tons of cement each year, with 75 million tons being domestically produced. Roughly 25% of all cement is imported for U.S. consumption. In the U.S., it is an accepted practice to substitute 15–35% cement in concrete with fly ash. The question that needs to be asked is: why are we only consuming 12 million tons of fly ash in concrete and allowing 50 million tons of fly ash to be disposed of every year?

The answer is that fly ash is not well understood by specifiers. The opportunity comes by promoting the features and benefits of fly ash to the specifiers, especially addressing the needs of engineers, according to a specific market segment. These market segments include architectural, chemical, civil, electrical, environmental, geotechnical, highway, industrial, mechanical, mining, sanitary, structural, surveying, and transportation.

### Reduced Carbon Dioxide Release

Concrete is second only to water as the world's most consumed product. In order to produce concrete, it is necessary to use some portland cement as a binder. The challenge is that for a ton of cement produced, about a ton of carbon dioxide ( $\text{CO}_2$ ) is released into the atmosphere. Carbon dioxide is the primary greenhouse gas attributed to the depletion of the ozone layer. By replacing one ton of cement with fly ash, an equal amount of  $\text{CO}_2$  released into the atmosphere can be prevented.

Significant economic and environmental pressures are in place on manufacturers of cement to reduce  $\text{CO}_2$  release. The cement industry is actively promoting the increased use of supplementary cementing materials to produce cement and concrete.

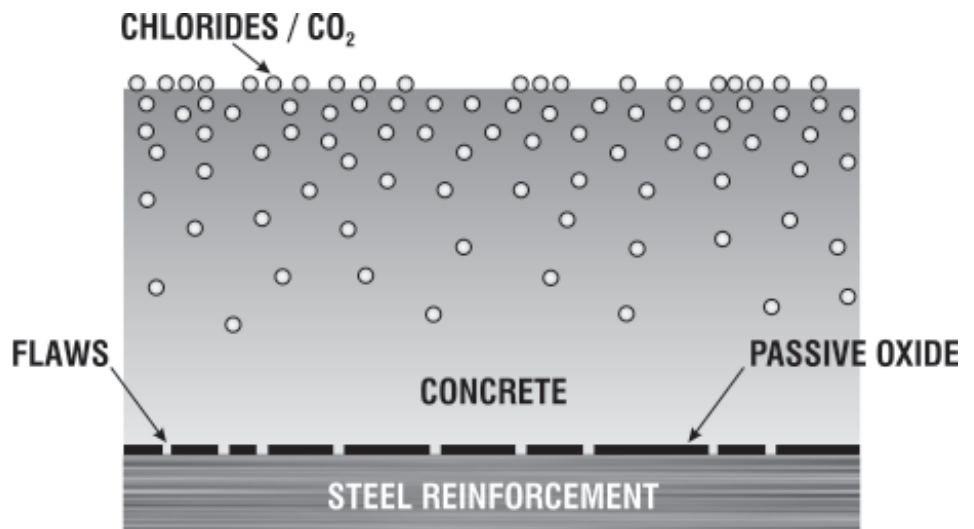


Figure 2. Corrosion model: Chlorides/ $\text{CO}_2$  penetrate concrete

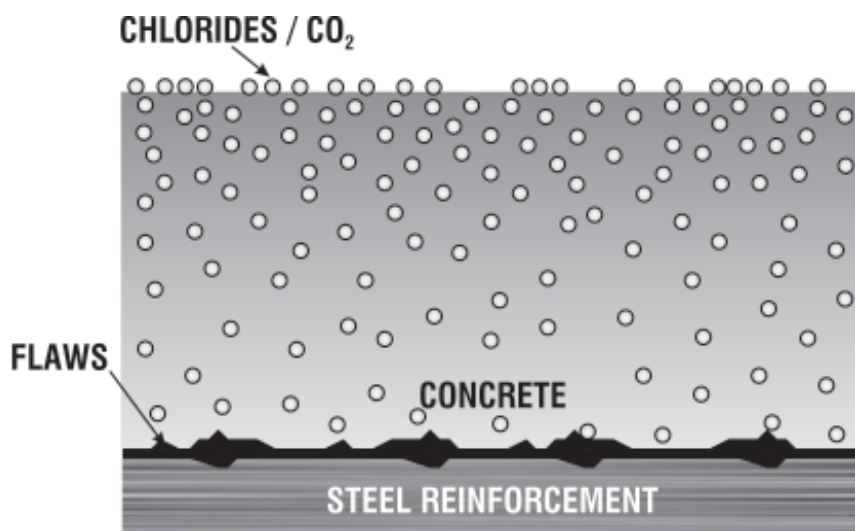


Figure 3. Corrosion model: Achievement of threshold

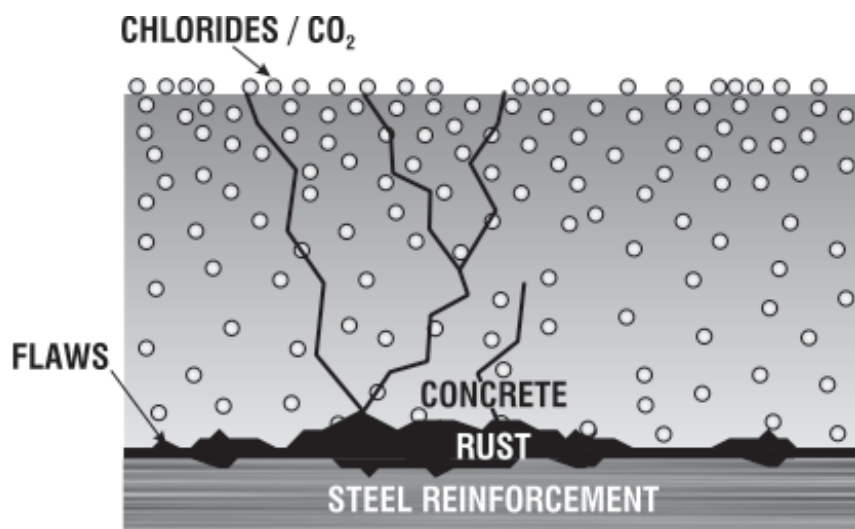


Figure 4. Corrosion model: Significant corrosion damage

### Corrosion Phenomenon

Corrosion of concrete takes place when CO<sub>2</sub> and chlorides penetrate concrete. As the chlorides and CO<sub>2</sub> penetrate concrete and dissolve in the pore solution, carbonic acid is formed. This acid reacts with the alkali in the cement to form carbonates and to lower the pH level of the concrete (Figure 2). In concrete construction, the 1.5 to 2 inches of concrete cover over the reinforcement bar acts as protective layers from the chlorides/CO<sub>2</sub> reaching the rebar.

Once the threshold is reached (Figure 3), the concrete cover is compromised and the pH of the concrete surrounding the rebar allows for corrosion. When the alkalinity begins to drop from 12-13 to about 9, the steel becomes depassivated. Corrosion begins in the presence of water and oxygen. Rust then forms on the steel (Figure 4) and expands in volume three to six times that of the original steel. This increase in volume increases the stresses in the concrete resulting in cracks, delaminations and spalls. It is well known that concrete is a brittle material that will crack with as little as one-hundredth-of-an-inch increase in the diameter of the reinforcement bar. This accelerates the corrosion process by opening larger pathways for water, oxygen, chlorides and CO<sub>2</sub> to penetrate into concrete. This weakens the concrete and reduces its service life, subsequently increasing costly maintenance until total replacement is needed.

Recent research has indicated the benefit of using fly ash in preventing corrosion damage in concrete. Reduced permeability, lower water/cement ratio, decreased drying shrinkage/cracking, and increased durability are some of the benefits of fly ash concrete.

### Fly Ash for Corrosion Mitigation

Mineral admixtures can be used to enhance the corrosion-control potential of concrete by reducing permeability. Fly ash is one of the most common admixtures used in concrete but rarely thought of to mitigate corrosion. Normally, designers focus at maintaining the alkaline pH of 12 to 13 in concrete to sustain the steel in a non-corrosive environment. Because lower pH fly ash replaces cement,

Mix (Cement / Fly Ash)	Chloride Ion Permeability (Coulombs)	Coulombs Range	Chloride Ion Penetrability	Typical of
658 / 0	4,509	> 4,000	High	W/C > 0.6 PCC
658 / 75	2,404	2,000 - 4,000	Moderate	W/C 0.4 - 0.5 PCC
530 / 130	1,497	1,000 - 2,000	Low	W/C < 0.4 PCC
530 / 260	797	100 - 1,000	Very Low	SILICA FUME
611 / 275	639	100 - 1,000	Very Low	SILICA FUME

Table 1. Chloride ion permeability for fly ash concrete mixes at 28-days of curing

	Chloride Ion Permeability (Coulombs)	
	6-Month Curing Time	1-Year Curing Time
0 % Fly Ash Mix (Control)	3,580 (Moderate)	3,410 (Moderate)
15 % Fly Ash Mix	1,160 (Low)	720 (Very Low)
30 % Fly Ash Mix	550 (Very Low)	390 (Very Low)
50 % Fly Ash Mix	530 (Very Low)	300 (Very Low)

Table 2. Chloride ion permeability for fly ash concrete mixes at 6 and 12 months of curing

the primary source of the alkalinity in concrete, many designers avoid its use. In a well-hydrated concrete mix, the portland cement may contain up to 15-40% calcium hydroxide by weight of cement. This is usually adequate to maintain the pH at 12-13. Because fly ash improves the density of concrete, it more than compensates for the slightly lower pH.

Furthermore, the unhydrated calcium hydroxide is detrimental to concrete because it aides in the premature deterioration of concrete. Chemically, calcium hydroxide will react with sulfates, alkali silica, and CO<sub>2</sub> to deteriorate concrete. Thus, the goal of the concrete mix designer is to chemically change this calcium hydroxide (CH) and maximize Calcium Silicate Hydroxide (CSH) while maintaining the pH.

The pozzolanic reaction in fly ash converts the CH into more of the CSH - thus leading to reduced permeability. With the use of fly ash, the ingress of moisture, oxygen, chlorides, and aggressive chemicals are slowed significantly - thus improving durability and serviceability.

The Ohio State University is collaborating with Headwaters Inc. in researching the use of high-volume fly ash for increased durability and lowered corrosion potential of structural concrete.

Chloride ion permeability tests were carried out on control (no fly ash) and fly ash mixes at 28 days of curing as presented in Table 1. It can be seen that the 'no fly ash' sample had the highest chloride ion permeability, while the fly ash concrete samples had much lower permeability values. As the amount of fly ash replacing cement increased, the chloride ion permeability rapidly decreased.

Longer-term chloride ion permeability tests were carried out on samples of concrete containing 0, 15, 30, and 50% Class F fly ash replacing cement. These tests, conducted at Ohio State, are summarized in Table 2. The chloride ion permeability of the fly ash mixes was significantly lower than that of the 'no fly ash' mix. The permeability was reduced with increases in

## Corrosion in Concretes, (cont.)

percent fly ash. An increase in curing time from 6 months to 1 year led to about a 4.75% reduction in the permeability of the 'no fly ash' mix, while the permeability of the fly ash mixes reduced 30-40% over the same period. Even at one year of curing, the 'no fly ash' concrete sample had moderate chloride ion penetrability while all the fly ash concrete samples had very low penetrability values. The high-volume fly ash mixes would be the most durable concrete mixes for preventing corrosion in reinforced concrete structures.

### Conclusions

Corrosion remediation and prevention in the United States continues to burden the budgets of state departments of transportation and highway administrations. Government regulations, environmentalists and society further complicate the situation by requiring lower CO<sub>2</sub> sustainable design and longer service life of its infrastructure. Fly ash through its synergies with CO<sub>2</sub>, sustainable design, and natural pozzolanic reactions with cement can provide the benefits necessary to appeal to these groups and the designers.

The pozzolanic reaction of fly ash in concrete converts calcium hydroxide into calcium silicate hydroxide, while maintaining the pH, leading to reduced permeability. With the use of fly ash, the ingress of moisture, oxygen, chlorides, carbon dioxide, and aggressive chemicals are slowed significantly.

The chloride ion permeability of the fly ash concrete mixes are significantly lower than that of no fly ash mixes. The permeability decreases with increases in fly ash. Increases in curing time from 6 month to 1 year led to a slight reduction (4.75%) in the permeability of the 'no fly ash' mix, while the permeability of the fly ash concrete mixes reduced 30-40%. Clearly, the high-volume fly ash concrete mixes, with low chloride ion permeability values, are desirable in concrete technology to prevent the deleterious effect of corrosion in reinforced concrete structures.

The increased interest in sustainable design and construction has created a renewed interest in fly ash and other coal combustion products. This trend has been accelerated by the emergence of agencies like the U.S. Green

Building Council (USGBC), Leadership in Energy and Environmental Design (LEED), and Coal Combustion Products Partnership (C<sup>2</sup>P<sup>2</sup>) of the USEPA. Their primary goal is environmentally and socially focused towards overall sustainable development.

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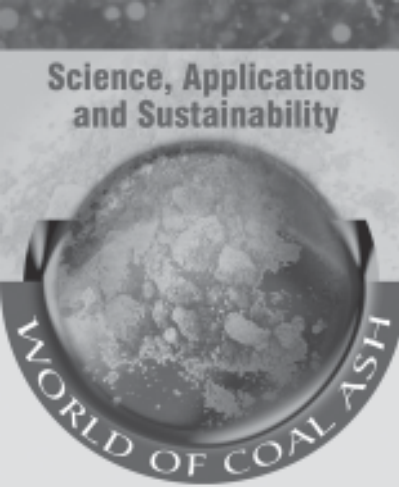
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**You No Longer Have to Choose!**

**Two coal ash organizations drop separate meetings to form new joint meeting.**

For those who have previously had to choose between attending international symposia held by the American Coal Ash Association and University of Kentucky, things have become simpler. In 2005 the two organizations are combining their previous international symposia into a combined symposium called the “World of Coal Ash (WOCA).” It will take place in Lexington, Kentucky April 11-15, 2005.

If successful, it is hoped that the groups' future biennial meetings will likewise be held together.

For more information, go to: [www.worldofcoalah.org](http://www.worldofcoalah.org) or contact Gretchen Tremoulet at: [gtremoulet@caer.uky.edu](mailto:gtremoulet@caer.uky.edu)

**Abstracts are due September 1, 2004**



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American Coal Ash Association*

It is a pleasure to address the readers of *Energieia*. This editorial speaks to change and its incumbent factors of challenge and opportunities. The ash industry continues to evolve. Remember the “good old days” when there was an abundant supply of concrete-quality fly ash? This now seems to be more memory than reality. A shortage of portland cement in many parts of the United States is prompting ash suppliers to allocate concrete-quality ash, thus creating a secondary shortage – of fly ash. As utility plants add emission-control systems to their generating stations, ash quality and characteristics change. Additives and sorbents in the ash may negatively affect its use in concrete, exacerbating the shortage. In other cases, switching from Eastern bituminous coal to Powder River Basin or other Western U.S. coals introduces another dynamic. Many states with experience using Class F fly ash may be reluctant to accept Class C fly ash without testing and verification of performance in specific applications. Again, this becomes another challenge to the marketplace.

Education, communication and outreach are the keys to addressing the above issues. There is much data available demonstrating the impact these changes have on the use of fly ash in concrete. Industry and academia have worked together for many years

## THE WORLD OF COAL ASH

to identify ways to overcome some of the obstacles. Working with producers, marketers and end-users, the university community helps identify ways to continue using fly ash, despite characteristics affected by emission control systems or fuel switching and blending.

Conjuring up supplies of concrete-quality fly ash may be difficult when none is readily available, but the distribution of technically accurate and immediately available information can help overcome end users’ questions about these changes. Additionally, it is possible to create new ways to use existing ash. For example, with new and emerging technology, it is not necessary to eliminate an ash because of high carbon content, as there are ways to overcome the detrimental effect that carbon has on fly ash in concrete. Considerable research, over the last decade, offers mitigating options to both producers and marketers.

Unfortunately, the elimination of some traditional uses of fly ash is to be expected. The creation of non-traditional uses offers opportunities in these situations. Again, research and field demonstrations enable skeptics to see that coal ash is still beneficial, despite the perception that changes have made the ash unusable. However, the most effective way to convince skeptics about overcoming negative situations is to make them aware of the research, field-testing and case studies. Again, communication is a critical element in addressing perceptions or misperceptions.

Less than four years ago the U.S. Environmental Protection Agency (EPA) seemed to be evaluating the

possibility of reclassifying coal ash as a contingent waste under Subtitle C or as a regulated waste under Subtitle D. Fortunately, industry and the EPA have worked together to address questions and challenges posed by anti-coal activists. Coal ash continues to be an under-used resource. There may be regional or local challenges to some applications, but the EPA is now fully behind an effort of outreach and the promotion of coal ash. Implementation of the EPA’s Coal Combustion Products Partnership (C<sup>2</sup>P<sup>2</sup>) is a major effort to provide information to potential users and to the public. Helping to address actual or perceived barriers to increased utilization of coal ash, C<sup>2</sup>P<sup>2</sup> is an outreach program taking the form of targeted publications, magazine articles, workshops and recognition programs. C<sup>2</sup>P<sup>2</sup> is



## *The World of Fly Ash, (cont.)*

voluntary, costs nothing and simply encourages those who believe that coal ash can help reduce greenhouse gases, conserve natural resources and cut down on the need for landfill space to sign on as program participants. Literally, anyone can join by going to the C<sup>2</sup>P<sup>2</sup> website (<http://www.epa.gov/epaoswer/osw/conserv/C2P2>) and downloading an application form.

Communicating this positive message about coal ash will continue when, in April of 2005, for the first time, the American Coal Ash Association and the Center for Applied Energy Research at the University of Kentucky will combine their previous respective bi-annual symposia into a single international event. Sponsors

for the "World of Coal Ash," (WOCA), are ACAA, CAER, the Office of Surface Mining, and potentially the Department of Energy (DOE). WOCA will take advantage of the synergies each organization offers by hosting in Lexington, Kentucky a five-day event covering many aspects of coal ash use. Supporting the theme of sustainability, science and applications, attendees from around the world will have an opportunity to receive information on new and ongoing research, emerging technologies and numerous other activities involving coal ash. More information is available on the official WOCA website (<http://www.worldofcoalash.org/>).

In closing, the ash industry remains a dynamic, ever-changing opportunity for research, business development, innovative technology and partnerships between industry, academia and government. The opportunities to work together and to share the results of these relationships will allow the coal ash industry to grow and overcome future obstacles.

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**Energieia** is published six times a year by the University of Kentucky's Center for Applied Energy Research (CAER). The publication features aspects of energy resource development and environmentally related topics. Subscriptions are free and may be requested as follows: Marybeth McAlister, Editor of **Energieia**, CAER, 2540 Research Park Drive, University of Kentucky, Lexington, KY 40511-8410, (859) 257-0224, FAX: (859)-257-0220, e-mail: [mcalister@caer.uky.edu](mailto:mcalister@caer.uky.edu). **Current and past issues of Energieia** may be viewed on the CAER Web Page at [www.caer.uky.edu](http://www.caer.uky.edu). Copyright © 2004, University of Kentucky.

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