Non-Spec Fly Ash Remediation

Jeffrey Whidden\textsuperscript{1} and Joseph E. Thomas\textsuperscript{2}

\textsuperscript{1}CR Minerals, US 84/285 RD #19147, Espanola, NM 87532; \textsuperscript{2}Magmatics Inc., 100 East 155 South, Malad City, ID 83252

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EXECUTIVE SUMMARY

It has been determined through extensive testing that a natural pozzolan may be used to effectively remediate a non-spec fly ash by enhancing both the chemical composition and the physical qualities of the fly ash. The remediated fly ash (RFA) meets or exceeds all specifications related to ASTM C618. Testing has further determined that not only does RFA exceed the specifications of C618, but it also effectively mitigates against chemical attack such as alkali silica reaction - ASR (ASTM C1567/1260) and sulfate induced degradation (ASTM C1012). Rapid chloride permeation testing (ASTM C1202) has determined the RFA also significantly reduces concrete permeability. This fly ash remediation technology allows for the potential beneficiation and use of millions of tons of fly ash that otherwise are destined to be wasted. Land-filling non-spec fly ash is a major cost to both power-plants and to society as a whole. Removing this non-spec material from the waste stream and re-directing it to a beneficial use in the concrete industry will help to alleviate fly ash shortages and reduce the burden on existing landfills and waste ponds. This technology has been field verified and the first fly ash remediation plant is scheduled to be online later this year (2017).

BACKGROUND

Fly ash, also known as flue-ash, is one of the residues generated in coal combustion and comprises the fine particles that rise with the flue gases. In an industrial context, fly ash usually refers to ash produced during the combustion of coal to generate electricity in a coal-fired power generation plant. In the past, fly ash was generally released into the atmosphere, but pollution controls mandated in recent decades now require that the fly ash be captured prior to release. Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plants. All fly ash includes substantial amounts of silica (silicon dioxide, SiO\textsubscript{2}), alumina (aluminum oxide, Al\textsubscript{2}O\textsubscript{3}), and calcium oxide (CaO) – the percentages of each dependent upon the type of coal being burned.
Fly ash, as well as natural pozzolans, can be used as a replacement for a portion of the Portland cement content in a concrete mix design. Fly ash has historically been available at a lower cost than natural pozzolans as fly ash is a waste material, or a by-product of the power generation process, with associated disposal costs.

Two classes of fly ash are defined by ASTM C618: Class F fly ash and Class C fly ash. The primary difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned. Class F fly ash is generally used when chemical attack, such as alkali-silica reaction (ASR), or sulfate attack is expected. Class C fly ash is generally used as a Supplementary Cementitious Material (SCM) to reduce the cost of the concrete mix design and enhance the physical properties of the concrete.

Prior to the widespread use of fly ash, natural pozzolans were used on various infrastructure projects in the first half of the 20th century to enhance the chemical resistance of the concrete and to increase durability. Natural pozzolans were first used in concrete - in mass quantities - by the engineers of the Roman Empire. Modern engineers incorporated natural pozzolans into dams, tunnels, aqueducts and other mass concrete structures in the western US beginning in the early 1900s.

Molten lava, flash frozen upon explosive expulsion from a volcanic vent, instantly became what the Romans called "pozzolana"—or pumice pozzolan, the key ingredient, along with lime, in Roman concrete. Roman structures such as the Pantheon, the Coliseum and other massive structures used this volcanic ash as pozzolan in their concrete. The natural pumice pozzolan combined with lime to form Calcium Silicate Hydrate (C-S-H), the same binder found in modern concrete. Concretes using natural (pumice) pozzolan have proven to last thousands of years.

Pozzolans, both natural and artificial, fortify concrete, providing protection by mitigating various forms of chemical attack such as ASR, sulfate induced expansion, efflorescence, as well as rebar oxidation and debondment caused by the ingress of chlorides. Pozzolans densify concrete, reducing porosity and permeability, thereby reducing chemical ingress and increasing long-term compressive strength and durability. In the modern era, natural pozzolans are still available for use in concrete mixes, however, artificial pozzolan, particularly coal combustion residuals (CCR), or fly ash, is widely used due to a combination of its widespread availability, low cost, and performance.

**FLY ASH PRODUCTION, HANDLING, AND USE**

The burning of harder, older anthracite and bituminous coal (and some lignites) typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 20% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or
hydrated lime, with the presence of water in order to react and produce cementitious compounds. Calcium hydroxide, \( \text{Ca(OH)}_2 \), the major byproduct of the hydraulic reaction between cement and water, is the key chemical with which pozzolan reacts to form additional Calcium Silicate Hydrate (C--S--H), the binder in all Portland cement-based concretes.

Fly ash produced from the burning of younger lignite or subbituminous coal yields Class C fly ash. In addition to having limited pozzolanic properties, it also has some self-cementing properties due to lime (calcium hydroxide) content usually in excess of 20%. In the presence of water, Class C fly ash will harden and gain strength over time. Unlike Class F fly ash, self-cementing Class C fly ash does not require an activator.

For the coal-fired power industry, concrete has been a convenient market for fly ash. For concrete companies, fly ash has been a low-cost source of pozzolans and SCMs which has also been beneficial to the engineering and design community seeking concrete with greater durability properties. Recently, however, a supply shortage has started to emerge caused in part by the increase in construction but also due to expanding environmental regulations and the increased availability and economic viability of natural gas as the energy of choice for thermal power plants. This has resulted in a decrease in the availability and sometimes, even the quality of fly ash that is used in concrete. As coal fired power plants close, switch to natural gas, or add additional pollution control equipment, there has been a general decline in the availability of high quality fly ash, particularly Class F fly ash, in several regions of the country. This situation will likely worsen in the coming years as coal fired plants are closed or converted to natural gas, and other renewable energy sources such as wind and solar achieve increased economies of scale and efficiency.

Contemporaneously with the above, we are experiencing an increasing need for pozzolans to protect the nations’ concrete infrastructure. Regions of the nation that were not particularly concerned with ASR or sulfate attack have since determined that even lower levels of chemical attack cause significant long term damage to infrastructure and are now requiring mitigation efforts in all new concrete mix designs. State DOTs and other regulatory agencies are more often mandating the use of pozzolans in concrete to protect against chemical attack and to increase durability – life span – for costly infrastructure projects. The result is the demand for Class F pozzolan increasing at the same time that supply is decreasing.

Whereas half or more of the fly ash produced in the USA is ponded or land-filled (ACAA, 2016), there is sufficient supply to meet the current needs of the concrete industry, in terms of shear tonnage. Unfortunately, much of this fly ash is not of an acceptable quality in that it cannot meet the requisite standards for use in concrete and/or cement, particularly ASTM C618 and AASHTO M295.
BENEFICIATION OF NON-SPEC FLY ASH

In view of the challenges facing these two industries (coal-fired electrical power generation and concrete production), a method to upgrade the quality of fly ash is needed for material which is otherwise destined for disposal. This could take the form of a remediation or beneficiation agent and/or process whereby non-certifiable, poor-quality fly ash, often referred to as non-spec fly ash or off-spec fly ash, may be upgraded in quality in order to meet the standards and specifications of ASTM C618 for either Class F or Class C.

There are current remediation/beneficiation projects along the eastern seaboard of the country which process fly ash containing high carbon content (out of spec LOI per C618) (Fedorka et al, 2013) These plants essentially burn the carbon out of the fly ash which permits the ash to then meet the C618 standard and be utilized in concrete mix designs. This process can remediate a certain, limited portion of the non-spec fly ash that is wasted around the country. However, additional remediation processes are needed in order to recover otherwise useful fly ash that cannot be used due to failure to meet specifications. Examples of such off-spec or non-spec fly ash include materials which do not comply with standards relating to chemical composition such as Silica-Alumina-Iron content, Calcium Oxide content, moisture content, and LOI. Other examples of non-spec fly ash include materials which retain more than 34% on the 325-mesh screen, or do not meet Strength-Against-Index (SAI) requirements of at least 75% of index (a 100% cement mix).

There are many people in the concrete industry who assume that as fly ash availability fades, particularly Class F fly ash, either natural pozzolans will step in and fill the gap, or the industry will have to require all cements to meet low-alkali specifications. Both of these solutions have challenges that must be overcome before they can be fully implemented to meet the needs of the concrete industry. For example, even if all cement production was able to switch to 100% low alkali cement, ongoing research has clearly indicated that concretes which uses only low alkali cements to mitigate against chemical attack are only partially successful. Pozzolan is still required in many cases in order to achieve sufficient mitigation to protect the concrete infrastructure investment. In any case, a wholesale change to low alkali cements is not a feasible alternative.

In the case of natural pozzolans, regional availability of volcanic raw materials will be mostly limited to the Western USA and Canada. Furthermore, in the event of a rapid decline in the availability of Class F fly ash, the development of a natural pozzolan manufacturing base, while already started to some degree, will take time in terms of permitting new mines and building the necessary processing plants. This is in addition to educating the users in the appropriate use of this relatively, “newer” pozzolan material and the differences it may have in terms of plastic properties and usage.

In both cases, as it relates to either low alkali cements or natural pozzolan, the solutions are not immediate, nor will they fill the entire spectrum of needs as it concerns cost, availability, and the desired physical properties of the concrete.
With all of that said, a new remediation method has been discovered that can provide fly ash an extended run in the concrete world for many years to come, even as the number of coal fired power plants decrease or fly ash quality decreases. This method uses natural pozzolans as a beneficiation agent, rather than using them as an immediate replacement of fly ash. Those very same materials that the Romans and 20th century dam builders used so effectively can be used to beneficiate non-spec fly ash in order to achieve complete compliance with C618, and to create a remediated fly ash that is actually performance enhanced. Research has indicated that this remediated fly ash product is more effective as a pozzolan, and an SCM, than the remediation agent (the natural pozzolan) and the fly ash are, individually. There is, in other words, a synergistic effect created by remediating the fly ash with a high quality natural pozzolan (for the purposes of this paper, a high quality natural pozzolan is defined as one that has a silica, alumina, and iron content of 85% or more). Given the right particle size distribution, physical properties, and chemistry, a natural pozzolan can be used to beneficiate, remediate, enhance and convert a non-spec or off-spec ash into a high-performance fly ash.

**PERFORMANCE DATA**

Over the past four years, extensive testing has been conducted that led to this discovery. This testing has encompassed a variety of different fly ashes including many non-spec ashes as well as C6 Class ashes. In addition, testing was conducted on a variety of different natural pozzolans. Selected results over this period of testing are shown below.

**ASTM C618:** In pozzolanic certification tests, all of the tested remediated fly ashes (RFAs) met or exceeded all chemical and performance standards and specifications as detailed in Table 1.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>RFA-CO</th>
<th>RFA-TX1</th>
<th>RFA-TX2</th>
<th>RFA-OK</th>
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<td>ASTM C618 Certified</td>
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<td>Yes</td>
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<td>Water Requirement % of control</td>
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Table 1 – Results of C618 testing of various remediated fly ashes.
ASTM C1012: The RFA-CO sample provided complete sulfate resistance for the full 12 and 18-month duration of the test as depicted in Figures 1a and 1b below (testing and data provided by CTL-Thompson, Denver, CO). Over the 12-month period, the expansion of the RFA-CO was 0.027% vs nearly 0.200% for the Type I/II control specimen. Over the 18-month period, the expansion of the RFA-CO was 0.038% vs nearly 0.300% for the control.

![Figure 1a and 1b – 12 and 18-month results of C1012 testing.](image)

ASTM C1567/1260: The RFA-CO, at a 25% cement replacement level, completely mitigated the most reactive aggregate in Colorado at both 14 and 28 days (testing and data provided by CTL-Thompson, Denver, CO). The remediated fly ash exhibited expansion of 0.02% at 14 days and 0.07% at 28 days whereas the control, which consisted of Type I/II OPC had expansion of 0.67% at 14 days. See detailed data in Table 2 and Figures 2a and 2b below.
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<th>Age</th>
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Table 2 – Expansion results of C1567 ASR testing.

Figures 2a and 2b – Results of control (2a) and RFA-CO (2b) testing for ASR.

**ASTM C1202 (RCP):** The RFA-CO, at a 25% cement replacement, provided significant reduction in conductivity versus the control, achieving less than 1,000 coulombs (penetrability class – very low) versus over 3,000 coulombs for the 100% OPC (testing and data provided by CTL-Thompson, Denver, CO). Additionally, as part of the C1202 testing, Strength Against Index (SAI) tests indicated RFA-CO had 110% versus index at 28 days (7320 vs 6670 psi).

**University of Texas at Austin Evaluation Program**

In addition to the testing at independent labs described previously, the University of Texas at Austin has used several of the RFA materials in a comprehensive testing program that is being sponsored by the Texas DOT. This work is being conducted by the Civil, Architectural, and Environmental Engineering Department and is led by Professor Maria Juenger, PhD and Assistant Professor Raissa Ferron, PhD as well as Saif Al-Shmaisani (Masters Candidate), and Ryan Kalina (PhD Candidate).

The following figures (Figures 3, 4a and 4b) depict strength testing (C109) as well as sulfate (C1012) and ASR (C1567) test results. Materials testing were as follows: OPC - 100% cement Control; FA - Class F Fly Ash Control (20% replacement); Q - Inert Quartz Filler; RM-C - Remediated Fly Ash (RFA-CO); RM-L - Remediated Fly Ash
(RFA-TX1); RM-S - Remediated Fly Ash (RFA-OK). In each case the remediated fly ashes performed very well and in some cases superior to all the other materials.

**Figure 3 – C109 testing results conducted by UT-A.**

**Figures 4a and 4b – Results of ASR (4a) and sulfate (4b) testing of RFAs versus OPC and fly ash controls.**

**COMMERCIALIZATION OF TECHNOLOGY**

The commercialization of this remediation technology, under US Patents 9561983 and 9611174, is poised for operation later this year in the form of a new remediation plant that is under construction in Pueblo, CO. This plant will initially be able to produce over 200,000 tons of beneficiated fly ash for a strained pozzolan/SCM market on the Colorado front-range and surrounding region. This location will be the first of CR
Minerals’ beneficiation plants. Plans exist to construct additional plants in other geographies across the country, particularly where fly ash demand is exceeding capacity. Each location will intercept non-spec fly ash, otherwise destined for the landfill, and turn it into a high-performance Class F (or Class C) fly ash to be utilized in the concrete market. The technology has been under study for the last four years and has demonstrated time and again that it can produce high performance fly ash products which meet all pozzolan standards and specifications, and mitigate chemical attack as well as, or better, than any pozzolan, artificial or natural, on the market.

The Pueblo beneficiation plant will produce a Class F specification remediated fly ash (RFA) pozzolan. As the test data above indicated (all tests were conducted by CTL-Thompson concrete lab in Denver, CO, or Braun Intertec Labs in Minneapolis, MN, or by the University of Texas-Austin), this new RFA Class F pozzolan will yield superior performance to currently available pozzolan materials. The RFA provides a product to the industry that not only mitigates extremely well against chemical attack, but provides the end user a concrete having relatively higher early-strengths as well as increased 28 day strengths when compared to most any other fly ash pozzolan or raw natural pozzolan available in the local market area.

CONCLUSIONS

Based on years of research, including standards testing conducted at industry certified labs and the Civil, Architectural, & Environmental Engineering School at the University of Texas-Austin, there is conclusive evidence that a properly engineered natural pozzolan can be used as a remediation agent to beneficiate a non-spec ash in order to meet and exceed the specifications of ASTM C618. The necessary characteristics of the natural pozzolan remediation agent are dependent upon the inherent limitations of the non-spec fly ash that is to be remediated, i.e., non-conformance based on: insufficient fineness, or strength against index (SAI), or excessive SO₃ content, or excessive LOI, etc. Except for the most extreme cases of non-compliance, most non-spec fly ashes can be beneficiated using this technology. Most importantly, the RFA has proven to be a very effective mitigation agent in the battle against ASR and sulfate attack. All of the remediated fly ashes tested to date have also provided desirable workability and impressive compressive strength in the concrete. This technology can extend the era of fly ash SCMs and pozzolans in the concrete marketplace, as materials that were once destined for disposal will now strengthen and protect concrete across the country. This new process is a win for the fly ash industry and a win for the construction industry.

REFERENCES