Article 600
Standard for Pozzolan Enhanced Grouts
Used in Annular Seals & Well Destruction

BACKGROUND

General

In 2012 the water well drilling industry became aware of the substitution of pozzolan, commonly known as fly ash, for cement in batches of cement slurries ordered from “ready mix” cement companies for water well annular seals and destructions. While the addition of fly ash pozzolan had been commonly accepted in the construction industry, it had not been specifically endorsed in the regulations governing water well construction and destruction. California county and state regulators immediately questioned its appropriateness as the addition of fly ash to the cement batch ticket was not part of the traditional water, sand, and/or cement mixtures utilized in the water well industry under California Department of Water Resources Bulletins 74-81 and 74-90. Therefore, it has become necessary to consider the use of pozzolan enhanced grouts in water well sealing material formulations.

The use of pozzolan in water well grouts triggers the following questions:

1. Should fly ash be considered as an admixture or a component of the cement in slurries used for seals?
2. Which ASTM specification(s) should be considered the appropriate one(s) for regulating fly ash and sealing slurries?
3. What size sand should be used in cement seal slurries?
4. What ratio of fly ash (pozzolan) to cement should be used in the cement portion of any slurry?
5. What is the correct ratio of sand and cement, where the cement portion of the mix is a sand/fly ash combination?
6. Is the use of fly ash where it will come in contact with potable water safe? Is there any known pathology associated with fly ash?
DISCUSSION

The American Society for Testing and Materials (ASTM) C125 defines a pozzolan as "a siliceous and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." This definition, not only takes into account fly ash, but also naturally occurring pozzolans that have been utilized in construction activities since the Roman Empire. However, common usage almost universally equates pozzolan with fly ash.

Fly ash is a byproduct of the coal fired electricity generating industry and is defined in Cement and Concrete Terminology (ACI Committee 116) as “the finely divided residue resulting from the combustion of ground powdered coal, which is transported from the fire box through the boiler by flue gases.” These flue gases are collected in baghouses or electrostatically, and then stored for either shipment to a disposal facility or further use. ASTM C618, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, creates two categories of fly ash based on their chemical composition with a general distinction being made upon the type of coal being burned. Class C fly ash is generally produced by burning lignite or subbituminous coal; coals which produce an ash with higher lime content. Class F is normally produced by burning anthracite and bituminous coal; producing an ash that is lower in lime content but higher in silica, alumina, and iron than Class C fly ash. Class F fly ash is generally more prevalent on the west coast of the United States due to the type of coal being burned. Natural pozzolans are also defined as Class N in ASTM C618, which is beyond the scope of this standard.

Fly ash is recognized as one of two types of “Cementitious Materials” under Section 5.2 of ASTM C94, Standard Specification for Ready-Mixed Concrete. Section 5.2.2 defines “Supplementary Cementitious Materials” as coal fly ash or natural pozzolans that conform to Specification C618; silica fume; or slag cement. The other cementitious material, section 5.1.1, is “hydraulic cement” defined under C150, 595, or 1157. Therefore, under the ASTM guidelines, if fly ash is in accordance with C618, it is an acceptable component of cement mixtures.

For purposes of water well cement mixtures, “cement” refers to Portland cement type I-V as set out in ASTM C150, Standard Specification for Portland Cement. Bulletin 74-90 requires that cementitious materials used as or in annular sealing material be as defined in ASTM C150. Bulletins 74-81 and 74-90 also permit the use of setting accelerants and retardants and other additives as long as the field additives meet the requirement of ASTM C494, Standard Specification for Chemical Admixtures for Concrete. ASTM C494 section 1.2 also recognizes the use of pozzolan as a component of cement mixtures.
The use of sand or aggregate in concretes mixtures for water well annular seals or well destruction is well accepted under Bulletins 74-81 and 74-90, although their definitions are not detailed. This has led to some misunderstandings between the water well industry and the concrete ready mix plants supplying ready mix well seals. For water well purposes, “sand or aggregate” refers to sand or aggregate as defined by ASTM C144, ASTM C33 or the Standard CALTRAN’s gradation specification defining aggregate. CGA Standard Practice Series article 210 provides a “good working practical definition of ‘sand’ as used in sand-cement mixtures, is that (the sand) is classed as “fine aggregate”; (and that) all particles should be 3/8 inch or smaller, and nearly 100 percent of the particles should be 3/16 inch in diameter or smaller.” Bulletins 74-81 and 74-90 further clarify that in concrete mixes the maximum “size of the aggregate (shall) be no more than 1/5 the radial thickness of the annular seal.” (Bulletin 74-90, page 19).

Common concrete construction industry practice permits up to 50% fly ash substitution for cement in concrete mixtures. However, this maximum percentage may vary if the design engineer or architect specifies a lesser ratio dependent upon the application, anticipated cure time or other factors. Likewise, the type of fly ash to be used is commonly specified given the two types have different chemical compositions and preferred uses in concrete applications. Given the higher lime content in Class C fly ash, it may have self-cementing properties when water is added. Therefore, Class C is used in “performance” mixes where early strengths are important and in soil stabilization projects. Class F moderates heat gain during concrete curing and also provides sulfide and sulfate resistance, making it suited for applications where exposure to sulfate ions in soil and groundwater is a possibility. Therefore Class F fly ash is preferred in water well seals.

One of the concerns with the use of fly ash in cement mixtures for water well annular seals and destructions has been the possibility that heavy metal constituents from the cement/pozzolan grout would leach into the surrounding water. This concern is a result of negative public perception of fly ash due to media publication of mass failures of large fly ash surface impoundments into surrounding water courses. In 2012, the United States Environmental Protection Agency (USEPA) released a report entitled “The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on the Leaching Constituents from Cements and Concretes.” The conclusion was that “the available data suggests that the use of coal combustion fly ash in cement materials, for different combinations of fly ash source and usage rates, will not increase leaching of some constituents to levels greater than typical ranges for cement materials not containing fly ash…. Based on available data…results indicate that some (and likely a large portion) of coal fly ashes can be used in cement and concrete formulations without causing a greater range in leaching of COPCs [Contaminants of Potential Concern] than observed from analogous cement materials not containing fly ash and without causing adverse
environmental and health impacts.” (The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material of the Leaching Constituents from Cements and Concretes, page 22.)

Since DWR Bulletin 74-90 recognizes sealing materials containing Portland cement as defined in ASTM C150 as acceptable and ASTM C94 recognizes pozzolan as a legitimate supplement to cement, a look at the comparative advantages of mixing pozzolan with cement is relevant.

Advantages of fly ash in cement grouts:

Commonly recognized advantages gained by using fly ash in cement grout or sand/cement grout used in annular seals or well destructions include:

- Reduced permeability
- Reduced heat of hydration when using Class F fly
- Possibly reduced mix water
- Reduced shrinkage and reduced possibility of a micro annulus between casing and hardened sealing material
- Reduced bulk density as less dense fly ash is substituted for cement
- Reduced leaching of free lime
- Enhanced workability and flowability due to the spherical nature of the fly ash particles
- Increased resistance to corrosion from salt water or seawater when using Class F fly ash
- Increased long-term strength
- Better economics for cement grouting as fly ash is a recycled product whereas cement is mined raw material
- Reduces the amount of fly ash placed in landfills thereby decreasing the amount of land impacted by new landfills

Disadvantages of fly ash in cement grouts:

- Negative public perception of fly ash as it is a byproduct of coal fired power plants
- Lack of clear regulatory guidelines in the current specifications governing the California water well industry
- Uncertainty on the use and mixture of pozzolan enhanced grouts in the water well industry

RECOMMENDATIONS

The California Groundwater Association recommends that the following practices when using fly ash in water well sealing materials.
Ready-Mix Formulations

1. Fly ash shall conform to all applicable ASTM standards regarding the use of fly ash as a “supplementary cementitious material.”

2. The batch plant or supplier of fly ash enhanced cementing material shall supply documentation that the pozzolan/fly ash used meets ASTM 618 Class F.

3. The ratio of pozzolan to cement in any grout batch used for sealing should not exceed 50%. The pozzolan cement combination together constitutes the cement requirement called out in Bulletin 74-81 and its amendments. Ratios are by weight.

4. The combined weight of cement and fly ash in a cubic yard of 10.3 sack sand cement slurry should be 968.2 lbs.

5. Mix water for sand cement/fly ash and cement/fly ash slurries shall range between 5 to 8 gallons of water per 94 lb bag of cement bag or combination of cement and fly ash. Variation of the amount of the water used shall be adjusted for ambient temperature, delivery time of the batch, the tremie pipe diameter and pumping equipment. Slurry batches may need to be retarded or accelerated with additives that meet the ASTM C494.

6. Sand or aggregate used in cement grouts, with or without fly ash, should conform to the above referenced specifications in the discussion section which are standard California water well industry practice. Also relevant is that mechanically crushed sand may result in reduced flowability and pumpability compared with naturally occurring sand due to its angularity. (See CGA Standard Practice Series, Article 210). Data on sand properties should be available from the material supplier on request.

7. Mechanical screening devices at the pump inlet may be used to prevent oversized aggregate and cementitious lumps from entering the pumping apparatus and tremie pipe. It may also be used to gauge the flowability of the mix.

8. The batch plant supplying the fly ash mixture should be able to state what the permeability of the batch is. This permeability should not be less than 2.0 x 10⁻⁶ cm/sec. after a 28 day cure time. (For testing procedures see ASTM C 5084.)

Factory Manufactured Pre-Mixed Sealing Materials
1. Fly ash used in factory manufactured pre-mixed sealing materials shall conform to all applicable ASTM standards regarding the use of fly ash as a supplementary cementitious material.

2. The manufacturer is responsible for the design of the well seal grout so that it meets all applicable California water well industry standards, as well as the flow ability and permeability requirements of the industry.

3. The ratio of fly ash, cement and sand shall be proprietary to the manufacturer. However, the ratio for a fly ash/cement grout mix can be 10% fly ash/90% cement and up to 50% fly ash/50% cement. These ratios are by weight. The amount of mix water shall be in the mixing instructions written on the bag.

4. Sand size remains proprietary to the manufacturer. Sand or aggregate used in cement grouts, with or without fly ash, shall conform to the above referenced industry specifications in the discussion section which are standard water well industry practice. Additionally, sand must conform to all paragraphs of ASTM C144 except those dealing with sieve or particle size.

5. Bag labeling must reference ASTM C150 Portland Cement and ASTM 618 Class Fly Ash. The bag label also must contain a Manufacturer’s Certificate of Compliance that the Fly Ash meets ASTM 618 Class F. The bag label must contain a manufacturer’s certification that the product after 28 day cure time, will meet 2.0 x 10^{-8} \text{cm/sec.} permeability when tested per ASTM D5084.

**SELECTED REFERENCES**

- ASTM C33: Standard Specification for Concrete Aggregate
- ASTM C94: Standard Specification for Ready-Mixed Concrete
- ASTM C125: Standard Terminology Relating to Concrete and Concrete Aggregates
- ASTM C144: Standard Specification for Aggregate for Masonry Mortar
- ASTM C494: Standard Specification for Chemical Admixtures for Concrete, Type B: Retarding Admixture
- ASTM C618: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for use in Cement


