Attachment C - Recommendations to Protect Concrete from Sulfur[1] Attack

Internal- Recommended Testing and Sulfur Levels to Prevent Internal Concrete Damage from Internal Sulfur Sources.

Material Specification 522 requires petrographic[2] testing for Watershed project work only. However, for NRCS non-project work, it is recommended to do petrographic testing if the aggregate is in or near areas of concern shown on Attachment A - USGS Pyrrhotite in the U.S. Fact Sheet.

From Attachment B - NDCSMC Sulfate[1] Attack on Concrete Report; Internal sulfate attack occurs when sources of concrete aggregate are used that contain sulfate or sulfide[1] containing minerals, such as, iron sulfide or pyrrhotite[3], gypsum[4], pyrite[5], and marcasite[5]. These materials when in the presence of water can oxidize causing expansion, sulfuric acid[1] attack, sulfate attack, or both. There is currently not an American standard on the acceptable amount of sulfur, but other suggested limits are at or below 1%. Therefore, the use of any portion of the concrete aggregate that contains components known to have these properties should be avoided in all situations. NEH Part 642, Chapter 3, National Material Specification 522-Aggregates for Portland Cement Concrete currently requires petrographic examination of aggregates for NRCS project work. ASTM C 295 – Petrographic Examination of Aggregates for Concrete, Section 5.6 specifically includes the evaluation of iron sulfide minerals to be documented. This report should be made available to NRCS employees by the supplier or contractor prior to construction.

The United States Army Corps of Engineers (USACE) "Proposed Testing and Research Approach for Pyrrhotite-Induced Concrete Deterioration", October 2018, suggests taking a conservative approach that assumes pyrrhotite is present in the aggregate. The USACE recommends using a chemical test for sulfur (S) and for when S is less than 0.1 percent, accept the aggregate, when S is 0.1 to 1 percent, do further testing, and when S is greater than 1 percent, reject the aggregate. This agrees with the Concrete Society (UK) BS EN 12620:2002 Aggregates for concrete standard.

Procedure to Prevent Internal Concrete Damage from Internal Sulfur Sources;

1) For watershed project work, petrographic aggregate testing is required per MS 522.

2) For non-project work, check the map included in Attachment A - USGS Pyrrhotite in the U.S. Fact Sheet to see if concrete aggregate being used is in or near an area of concern.

3) If yes, request a petrographic report from the concrete supplier or contractor showing the percent sulfur (S) using a chemical test.

4) For the sulfur (S) test results;
    a. when S is less than 0.1 percent, it is OK to accept the aggregate.
    b. when S is 0.1 to 1 percent, do further testing to determine if iron sulfide minerals such as pyrrhotite, gypsum, pyrite, or marcasite are present.
        i) If the further testing shows pyrrhotite, gypsum, pyrite, or marcasite are present, reject the aggregate and ask the supplier to use an acceptable aggregate.
        ii) If the further testing shows pyrrhotite, gypsum, pyrite, or marcasite are not present, it is OK to accept the aggregate.
    c. when S is greater than 1 percent, reject the aggregate and ask the supplier to use an acceptable aggregate.

External - Recommendations to Prevent Damage from External Sulfur Attack Eroding the Concrete

Concrete durability is largely affected by its water/cementitious materials (w/cm) ratio. If the w/cm ratio is decreased, the porosity decreases and the concrete becomes more impermeable. The permeability of concrete is important because it controls the amount of water migration through concrete or the ability of concrete to resist penetration of aggressive chemicals. A lower w/cm ratio also increases the compressive strength of concrete, which improves its resistance to cracking. To protect against sulfate attack, ACI Committee 201 recommends the use of dense, quality concrete with a low w/cm ratio. Air entrainment is suggested because it reduces the w/cm ratio and therefore the permeability.

A stronger relationship exists between the sulfate resistance of concrete and its tricalcium aluminate (C3A) content. The higher the C3A content, the more prone the concrete is to sulfate attack. To improve the sulfate resistance of concrete, lower C3A cements are available. ASTM C 150 Type II cement (MSR) with <8% C3A, and Type V cement (HSR) with <5% C3A are typically specified in sulfate environments. This partial replacement of Portland cement with a pozzolan such as low calcium fly ash, ground granulated blast furnace slag, or silica fume equally reduce the potential for sulfate attack. These pozzolans consume the calcium in the pore water, reduce the total mass of C3A, and decrease the permeability. When deciding which pozzolan to choose, it is important to consider its CaO content. A high percentage of CaO in fly ash may accelerate the sulfate problem substantially. For instance, ASTM Class F fly ash with <10% CaO will certainly improve the resistance of concrete to sulfate attack. Similarly, silica fume, metakaolin, and natural pozzolans consume Ca to improve sulfate resistance.

The following table from ACI 201 gives recommendations for the type of cement and w/cm ratio for normal-weight concrete, which will be exposed to sulfates in soil, groundwater, or seawater.

Recommendations for Normal Weight Concrete Subject to Sulfate Attack;

Exposure	Water soluble sulfate (SO_4) in soil, percent	Sulfate (SO_4) in water, ppm	Cement	Water-cement ratio, maximum
Class 0 exposure	0.00-0.10	0-150	No special requirements	No special requirements
Class 1 exposure	0.10-0.20	150-1500	C 150 Type II IP(MS) IS(MS) Type II + Pozzolan	0.50
Class 2 exposure	0.20-2.0	1500-10,000	C 150 Type V Type II + Pozzolan	0.45
Class 3 exposure	2.0 or greater	10,000 or greater	C150 Type V + Pozzolan or slag	0.40

The contractor shall provide protection against sulfate attack on concrete structures and pavements by providing concrete manufactured according to the requirements of Table 19.3.2.1. A higher level of requirements may be used for a lower level of exposure. If the contractor provides test reports that show another class of exposure exists at a structure location, then the engineer may accept a concrete mix for that location that meets the corresponding sulfate protection requirements.

Table 19.3.2.1 - Requirements to Protect Against Damage to Concrete by Sulfate Attack from External Sources of Sulfate

Severity of Sulfate Exposure	Water-Soluble Sulfate (SO4) in Dry Soil, Percent	Sulfate (SO4) in Water, PPM	Maximum Water to Cementitious Material Ratio	Minimum f'_c, psi	Cementitious Material Requirements
Class S0	0.00 to 0.10	0 to 150	N/A	2500	Class S0
Class S1	0.11 to 0.20	151 to 1500	0.50	4000	Class S1
Class S2	0.21 to 2.00	1501 to 10,000	0.45	4500	Class S2
Class S3 Option 1	2.01 or greater	10,001 or greater	0.45	4500	Class S3 Option 1
Class S3 Option 2	2.01 or grater	10,001 or greater	0.40	5000	Class S3 Option 2

<u>Cementitious material requirements are as follows:</u>

Class S0 requirements for sulfate resistance shall be one of the following:

(1) ASTM C 150 no restrictions on Type

(2) ASTM C 595 no restrictions on Type

(3) ASTM C 1157 no restriction on Type

(4) No restrictions on use of supplemental cementitious materials.

Class S1 requirements for sulfate resistance shall be one of the following:

(1) ASTM C 150 Type II limited to maximum 8 percent C3A content; Class C fly ash shall not be substituted for cement.

(2) ASTM C 595 Blended cements with the MS designation; Class C fly ash shall not be substituted for cement.

(3) ASTM C 1157 cement with MS designation; Class C fly ash shall not be substituted for cement.

(4) When ASTM C 150 Type I or III cement is allowed, shall have no more than 8 percent C_3A content. Class C fly ash shall not be substituted for cement.

Class S2 requirements for sulfate resistance shall be one of the following:

(1) ASTM C 150 Type V; Class C fly ash shall not be substituted for cement.

(2) ASTM C 150 Type I or III with a maximum of 5 percent C_3A content; Class C fly ash shall not be substituted for cement.

(3) ASTM C 1157 cement with HS designation; Class C fly ash shall not be substituted for cement.

(4) ASTM C 595 Blended cement with HS designation; Class C fly ash shall not be substituted for cement.

Class S3 requirements for sulfate resistance shall be one of the following:

Option 1:

(1) ASTM C 150 Type V, plus pozzolan or slag cement. The amount of the specific source of the pozzolan or slag cement to be used shall be at least the amount that has been determined by service record to improve sulfate resistance when used in concrete containing Type V cement, where the blend has less than 0.10 percent expansion at 18 months when tested according to ASTM C 1012. Class C fly ash shall not be substituted for cement.

(2) ASTM C 1157 Type HS, plus pozzolan or slag cement. The amount of the specific source of the pozzolan or slag cement to be used shall be at least the amount that has been determined by service record to improve sulfate resistance when used in concrete containing Type V cement, where the blend has less than 0.10 percent expansion at 18 months when tested according to ASTM C 1012. Class C fly ash shall not be substituted for cement.

(3) ASTM C 595 Type HS, plus pozzolan or slag cement. The amount of the specific source of the pozzolan or slag cement to be used shall be at least the amount that has been determined by service record to improve sulfate resistance when used in concrete containing Type V cement, where the blend has less than 0.10 percent expansion at 18 months when tested according to ASTM C 1012. Class C fly ash shall not be substituted for cement.

When fly ash is used to enhance sulfate resistance, it shall be used in a proportion greater than or equal to the proportion tested in accordance with ASTM C 1012, shall be the same source, and it shall have a calcium oxide content no more than 2.0 percent greater than the fly ash tested according to ASTM 1012

Option 2:

(1) ASTM C 150 Type V as sole cementitious material, the optional sulfate resistance requirement of 0.04 percent maximum expansion in ASTM C 150 shall be specified.

(2) ASTM C 1157 Type HS. As tested with no additional cementitious materials.

(3) ASTM C 595 Type HS. As tested with no additional cementitious materials.

Footnotes-

[1] Sulfur (S), sulfate (SO_4^{2-}), sulfide (S^{2-})

The element sulfur is present in several chemical forms (also called "chemical species") in nature. Two species are relevant in the aggregate context: (1) sulfate (SO_4^{2-}), the oxidized form, and (2) sulfide (S^{2-}), the reduced form. Sulfide can combine with elements such as iron or copper to make different crystal structures, called minerals.

Sulfuric acid (H_2SO_4) is a very strong acid. Sulfuric acid solution in wastewater reacts with cement hydrates and slowly deteriorates the concrete surface.

[2] Petrography

Petrography is the description and classification of rock by any means, from visual observations to highly technical chemical and instrumental analyses (e.g., electron microscopy and x-ray fluorescence analysis). It is generally conducted by microscopic study. See ASTM 295.

[3] Pyrrhotite (Fe_2S)

Pyrrhotite is an iron sulfide mineral composed of the elements iron and sulfur. Pyrrhotite's chemical formula varies, as it has several crystal structures.

Pyrrhotite expands when exposed to water and oxygen, which can cause concrete containing it to crack and swell, and eventually crumble.

[4] Gypsum ($CaSO_4 \cdot 2H_2O$)

Gypsum is a soft sulfate mineral composed of calcium sulfate dihydrate. Gypsum formation during sulfate attack may cause expansion and concrete cracking.

[5] Pyrite (FeS_2) and Marcasite (FeS_2)

Pyrite is an iron sulfide that is more common but much less reactive than pyrrhotite.

Pyrite and marcasite are two forms of iron disulfide minerals. The key difference between pyrite and marcasite is that pyrite has an isometric crystal system, whereas marcasite has an orthorhombic crystal system. Moreover, pyrite has a pale brass-yellow reflective luster while marcasite has a tin-white appearance on a fresh surface.