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## **Acid Sulfate Soils in Coastal Environments**

A Review of Basic Concepts and Implications for Restoration

Christine M. VanZomeren, Jacob F. Berkowitz,  
Candice D. Piercy, and Jeffrey K. King

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# **Acid Sulfate Soils in Coastal Environments**

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## Abstract

Acid sulfate soils naturally occur in many coastal regions. However, the oxidation of acid sulfate soils can decrease soil pH to <4.0, affecting vegetation and aquatic organisms. Acid sulfate soil oxidation typically occurs where anaerobic sediments or soils were exposed to aerobic conditions (for example, extended drought, artificial drainage, or dredged material placement in upland areas). Recently, field observations documented the formation of acid sulfate materials at multiple degraded marsh restoration locations (Rhode Island, New Jersey, California) following intentional dredged sediment placement into wetland environments designed to increase marsh elevation. Unlike previous studies of acid sulfate soils, the in situ dredged material did not contain acid sulfate-bearing materials at the time of placement; instead, the interaction between the marsh substrate and the overlying dredged material appears to have caused the formation of acid sulfate soils. These findings highlight the need for additional studies of acid sulfate soil formation and fate—especially within a marsh restoration context. In response, this report provides a review of literature related to acid sulfate soils, discusses preliminary data collected to evaluate acid sulfate material formation following marsh restoration, and identifies knowledge gaps requiring additional research and technical guidance.

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## Preface

Funding for the following report was provided by the Dredging Operations Technical Support Program under Project 468907. The program manager was Dr. Burton Suedel.

The work was performed by the Wetlands and Coastal Ecology Branch of the US Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL). At the time of publication, Ms. Patricia M. Tolley was Branch Chief; Dr. Jeffrey K. King was Engineering With Nature focus area lead; Mr. Mark Farr was Chief of the Ecosystem Evaluation and Engineering Division of EL, and Dr. Todd S. Bridges was the Senior Scientist over the Dredging Operations and Environmental Research Program. The Deputy Director of EL was Dr. Jack E. Davis, and the Director was Dr. Edmond J. Russo Jr.

Colonel Teresa A. Schlosser was Commander of ERDC; and Dr. David W. Pittman was the Director.

# 1 Introduction

## 1.1 Background

Acid sulfate soils occur naturally in many coastal environments throughout the world, covering an estimated 12–15 MHa<sup>1</sup> of land area (Fanning 2002; Andriessse 2002). The formation of acid sulfate soils requires saturated and anaerobic conditions commonly found in coastal wetlands and submerged environments, where chemically reduced forms of sulfur (sulfides; S<sup>-</sup>) react with soluble cations (mostly ferrous iron; Fe<sup>2+</sup>) to form insoluble metal sulfide precipitates dominated by iron monosulfide (FeS) and pyrite (FeS<sub>2</sub>; Rabenhorst 1990).<sup>2</sup> Black iron sulfide precipitates develop and coat mineral and organic soil particle surfaces, resulting in the characteristic morphology of acid sulfate soils. Once formed, these acid sulfate soil compounds remain stable under anaerobic conditions; however, reduced iron sulfide compounds can rapidly oxidize under aerobic conditions (for example, artificial drainage, upland placement of dredged materials), potentially causing negative impacts in the surrounding terrestrial and aquatic environment (Rabenhorst, Burch, and Fanning 2002).

Recent observations document the formation of acid sulfate soils at marsh locations on the United States' East and West Coasts following dredged material placement during marsh restoration activities designed to address marsh degradation. Unlike previous observations of sulfidization, the dredged material did not contain sulfidic materials at the time of placement; instead, the interaction of the underlying marsh soil and the overlying dredge material appear to induce the formation of acid sulfate soil. The processes, conditions, and stability of acid sulfate soils formed in situ following dredged material placement is not well documented. As a result, this report documents current knowledge through a literature

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1. For a full list of the spelled-out forms of the units of measure used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 248–52, <https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf>.

2. For a full list of the spelled-out forms of the chemical elements used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 265, <https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf>.



review on acid sulfate soils as they relate to wetland restoration projects using dredged sediments.

## **1.2 Objective**

The following report reviews available literature examining acid sulfate soils, focusing on basic principles, existing methods, and implications for marsh restoration. It synthesizes preliminary field and laboratory studies to address questions and potential management implications related to the in situ formation of acid sulfate soils. This report also identifies knowledge gaps and further research opportunities related to the identification, management, and prevention of acid sulfate soil formation.

## **1.3 Approach**

Reviewed literature includes journal articles and technical publications related to acid sulfate soils, such as a 2017 special issue of the journal *Geoderma* or materials presented at the Eighth International Sulfate Soils Conference, July 2016 (Rabenhorst, Daniels, Fitzpatrick 2017; Wessel et al. 2017). Also included are several review articles outlining the history of acid sulfates, acid sulfate formation and fate, and methods to document acid sulfate soil conditions. However, data related to in situ formation of acid sulfate soils within a wetland restoration context remains limited. As a result, the following review focuses on properties and processes related to acid sulfate soil formation following wetland restoration. Specific topic areas addressed within this report include (1) an introduction to acid sulfate soils, (2) formation of acid sulfate soil in coastal marshes, (3) implications of acid sulfate soil disturbance, (4) observations of in situ formation of acid sulfate soils following wetland restoration, (5) approaches to document acid sulfate soils, and (6) identification of knowledge gaps and opportunities for additional research.

## 2 Introduction to Acid Sulfate Soils

Acid sulfate soils have long been recognized in the literature, appearing as early as the eighteenth century (Fanning, Rabenhorst, and Fitzpatrick 2017). Acid sulfate soils occur in a variety of global regions, often near coastal environments, marshes, and reclaimed agricultural lands in which dikes or artificial drainage has been implemented in support of cultivation (Andriessse and Van Mensvoort 2006). As a result, much research on the topic originates in Australia, where acid-producing parent materials are common, the Netherlands and Northern Europe, where expansive agricultural lands have been reclaimed from the sea, and the mid-Atlantic and northeastern United States, where upland placement of coastal dredged sediments is common. Acid sulfate soils have been officially recognized in the United States since the 1950s and 1960s (Fanning, Rabenhorst, and Fitzpatrick 2017). As the name suggests, acid sulfate soils have the potential to generate acidity—and negatively affect the growth of agricultural and native plant communities. Acid generation is induced when previously saturated soils are exposed to oxygen, either through natural events such as prolonged drought conditions through management activities (that is, artificial drainage; Rabenhorst and Fanning 2002). These events, whether natural or anthropogenic, alter iron and sulfur cycling rates and pathways in coastal systems. To further examine the topic of acid sulfate soils, the following sections outline common terms and definitions, formation, and development in coastal environments.

### 2.1 Acid sulfate soils terms and definitions

Throughout the scientific literature, acid sulfate soils have been described using a variety of descriptive and operational definitions as well as numerous terms related to acid sulfate soil constituents. As a result, the following section provides a brief discussion of terminology for perspective and clarity. Historical descriptions of dark, black acid sulfate soils as early as the eighteenth century included cat clays and poison earth soils (Rabenhorst and Fanning 2002). The *cat* designation was probably derived from the Dutch vernacular *kattkleigronden*, which referred to soils characterized by dark colors evoking images of cat excreta and those associated with harmful, mysterious qualities leading to crop failure (Fanning 2002). Similarly, others described acid sulfate soils using the term *Maibolt*, which is presumed to be a hybrid of German words meaning

*hay field* and *an evil ghost*, in which reclaimed agricultural lands produced low yield for unknown reasons, and *Gifterde*, which translates as *poison earth* (Prokopovich 1988).

Acid sulfate soils have been broadly defined as soil materials that are currently generating, have generated, or can potentially generate sulfuric acid at levels capable of affecting major soil characteristics (Fanning and Burch 2000). Acid sulfate soils have been operationally defined as soils that contain sulfidic materials (Soil Survey Staff 2014) which have soil pH values  $>3.5$  and contain sufficient oxidizable sulfide compounds to produce a drop in pH of  $>0.5$  units resulting in a final stable pH value  $<4.0$  following an 8- to 16-week aerobic laboratory incubation (Sullivan et al. 2009). Whether defined descriptively or operationally, the distinguishing feature of acid sulfate soils remains the presence of sulfide minerals sufficient to produce severe acidification or the severe acidification of soils resulting from sulfide mineral oxidation (Pons 1973).

Acid sulfate soils contain subcategories such as *potential* acid sulfate soils, which have the capacity to produce significant acidity if oxidized, and *active* acid sulfate soils, which are currently generating acidity (Rabenhorst, Burch, and Fanning 2002). Other distinctions, including the Australian and World Reference Base (WRB) soil classification systems, use a more inclusive description of acid sulfate soils that accounts for the magnitude of acid generating potential and results in designations of *hyposulfidic* (incubated soil pH values  $\geq 4.0$ ) and *hypersulfidic* (incubated pH  $\leq 4.0$ ; Payne and Stolt 2017).

Several publications use the term *sulfidic material* interchangeably with *acid sulfate soils*, while others refer to common sulfidic minerals (for example, pyrite:  $\text{FeS}_2$ ; iron monosulfide:  $\text{FeS}$ ) when discussing acid sulfate soils (Sullivan et al. 2010). Additionally, the taxonomy and classification of acid sulfate soils materials continues to evolve, with new recommendations currently under consideration (Wessel et al. 2017). Within the published literature, acid sulfate soils remain the most commonly applied descriptor, capturing the unique wetland soil morphologies, environmental conditions, and ecological processes associated with these soils. However, the term *acid sulfate soils* itself may cause confusion, because it encompasses both chemically reduced (that is, sulfides) and oxidized (that is, sulfates) forms of sulfur compounds,

despite the typical convention of utilizing the suffix *-ate* to identify oxidized sulfur species (for example, sulfate). Regardless, the current report applies the most common terminology, *acid sulfate soils*, throughout, except when referring to a specific chemical constituent, mineral, or process.

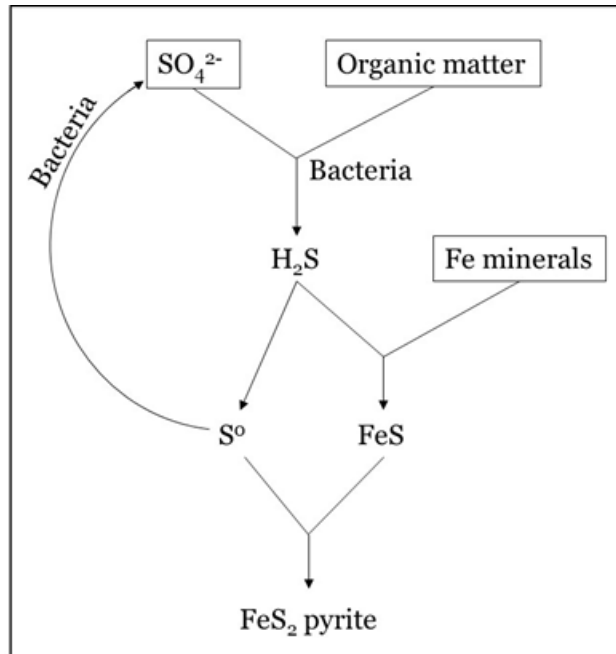
## 2.2 Formation of acid sulfate soils

Sulfidization is a process that results in the formation and accumulation of sulfide minerals in soils and sediments (Fanning 2002). Under a typical scenario, iron- and sulfur-reducing bacteria consume carbon under anaerobic conditions, resulting in the accumulation of chemically reduced forms of iron and sulfur ( $S^{2-}$ ; figure 1; Demas and Rabenhorst 1999). These reduced forms of iron ( $Fe^{2+}$ ) sulfur undergo a rapid chemical complexation, forming  $FeS_x$ .  $FeS$  and  $FeS_2$  ( $FeS_x$  herein; Rabenhorst et al. 1990) typically dominate the  $FeS_x$  precipitates. Notably, acid sulfate soil complexes are relatively unavailable and, therefore, nontoxic to vegetation and other biota (Schoepfer, Bernhardt, and Burgin 2014). However, the presence of acid sulfate soils indicates the potential presence, production, and translocation of  $S^{2-}$ , which negatively impacts plant growth and cause toxicity at high concentrations (DeLaune, Smith, and Patrick 1983). Acid sulfate soil compounds form rapidly once the dissolved constituents are available in soil solution and are easily oxidized under aerobic conditions such as those induced by drought or draining. (For more information on drought and drainage, see section 3a.) At the mineralogical level,  $FeS$  is transformed into a more stable  $FeS_2$  (that is, pyrite) complex over time and with additional sulfide inputs to the system (figure 1; Berner 1985; Schoepfer, Bernhardt, and Burgin 2014).

The essential constituents for sulfidization to occur are sulfate, iron-containing minerals, decomposable organic matter, sulfate-reducing bacteria (for example, *Desulfovibrio desulfuricans*), and anaerobic conditions, with sulfur reduction often limiting the rate of acid sulfate soil formation (Fanning, Rabenhorst, and Fitzpatrick 2017; Fitzpatrick, Shand, and Merry 2009). Another dominant control, particularly on sulfate reduction, is available carbon for microbial respiration (Westrich and Berner 1984; Berner 1985). Further, heterotrophic activity and consumption of oxygen accelerates the rate of sulfate reduction (Berner 1985). Additional research indicates that sulfides chemically reduce ferric iron to ferrous iron during the formation of iron sulfides (Fanning et al.

2010; Fanning et al. 2012; Rabenhorst, Megonigal, and Keller 2010; Rabenhorst 2013).

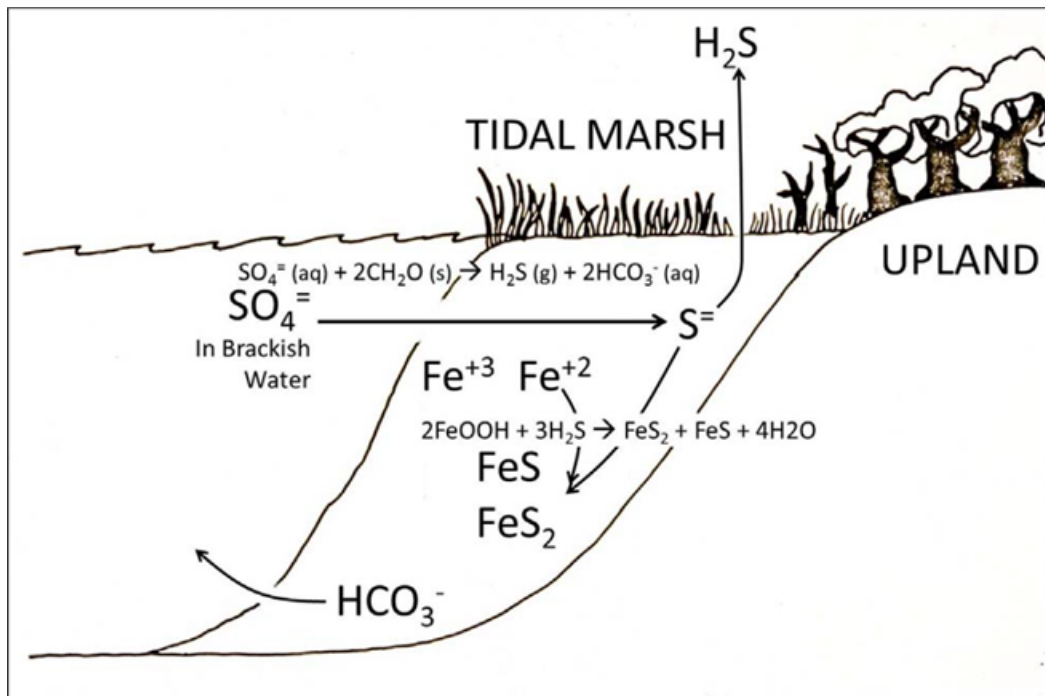
Figure 1. Schematic of sulfide compound (for example,  $\text{FeS}_x$ : pyrite) formation under anaerobic conditions (from Berner 1985).



### 2.3 Acid sulfate soil formation in coastal marshes

The constituents and environmental conditions needed for acid sulfate soil formation naturally occur in coastal environments, either in coastal sediments or marsh soils (figure 2). As such, coastal sediments and soils naturally form and contain acid sulfate materials, with brackish and some freshwater systems also displaying acid sulfate formation if sufficient sulfur sources are present (Soil Survey Staff 2014).

Figure 2. Example of the sulfidization process in a tidal marsh soil (from Fanning, Rabenhorst, and Fitzpatrick 2017).



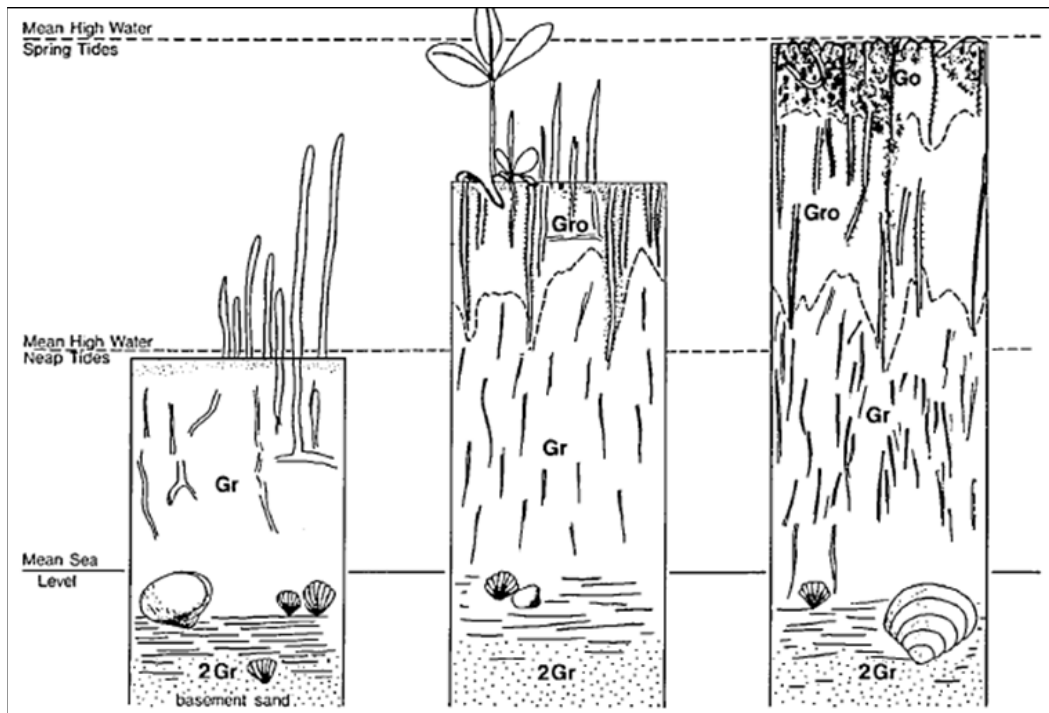
Dent (1993) identified the sequence of acid sulfate forming soil processes in coastal wetlands and developed a bottom-up model of conditions necessary for the accumulation of acid sulfides (figure 3). Conditions necessary for this soil forming process to commence include the following (adapted from Dent 1993):

1. Anaerobic conditions begin in the subsoil through prolonged soil saturation.
2. Aerobic and anaerobic conditions alternate in the surface soil through tidal cycles or hydrologic modification.
3. Soil physical processes change as water loss occurs through consolidation and evaporation.

Importantly, the unique process of sedimentation and accumulation of carbon via vegetation production in coastal wetlands results in the upwards formation of soil horizons through these accretionary processes (Dent 1993). For example, sediment is deposited on the soil surface through tidal inundation (Marriotti and Fagherazzi 2010), storm events (Turner et al. 2006), or intentional introduction of sediments at the marsh surface (that is, dredged material application; VanZomeran et al. 2018),

resulting in the burial of the surface soil. Burial of organic-rich soils initiates the acid sulfate soil development process by inducing anaerobic conditions and increasing carbon availability, thus triggering microbial respiration by iron- and sulfur-reducing bacteria (Wessel and Rabenhorst 2017). Sulfide and ferrous iron are then chemically precipitated in the form of iron sulfide minerals (Dent 1993).

Figure 3. Dent (1993) described the upwards formation of soils via accretion and subsequent formation of acid soil profile following vertical accretion (from Dent 1993).



- G Undifferentiated, unripe material deposited at the surface. Following burial by later sediments is subsequently transformed to one of the following horizons
- Gr Practically unripe or half ripe, dark grey, strong smell of  $H_2S$ , accumulating pyrite
- Gro Half ripe, grey with iron oxide pipes and coating of red iron oxide on ped faces, little or no pyrite
- Go Nearly ripe, mottled with nodules, pipes and coatings of iron oxide, no pyrite

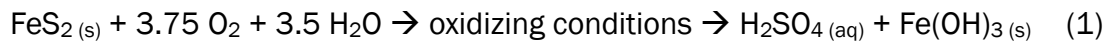
As accretionary processes continue forming soil upwards, the surface soil begins to alternate between aerobic and anaerobic conditions. Soil forming

processes are initiated at this point through the loss of water by consolidation and evaporation, resulting in intermittent oxidation of acid sulfate soils and subsequent production of sulfuric acid (Dent 1993). However, the limited vertical extent of acid sulfate soil oxidation and acid production is neutralized by intermittent tidal inundation under natural conditions (Fitzpatrick et al. 1998). As a result, the formation, subsequent oxidation, and neutralization of generated acidity approaches steady state conditions under normal sediment accretion and hydrodynamic regimes, and limited soil acidification occurs on the marsh. However, acidification and associated environmental impacts may occur if rapid oxidation of larger amounts of acid sulfate soils results from the system becoming unbalanced due to changes in hydroperiod and hydroperiod following long-term drought, disturbance, relocation of the acid sulfate soils, or other system-level alterations.



### 3 Implications of Acid Sulfate Soil Disturbance

Exposure of acid sulfate soils to aerobic conditions via artificial drainage or excavation results in the production of acid. The process of sulfuricization describes the oxidation and hydrolysis of sulfide-bearing soil materials, which results in the weathering of soil minerals by the sulfuric acid produced and the formation of new minerals derived from the dissolution products (Fanning 2002). Most commonly, observed and documented sulfuricization and associated declines in soil pH occur in cases where sediments containing oxidizable sulfidic materials were transported from stable anaerobic environments and exposed to aerobic conditions. Chemoautotrophic bacteria activity accelerates the rate of acidification: bacteria oxidize iron sulfides, resulting in the production of sulfuric acid. Oxygen exposure and hydrolysis of sulfide-bearing soil materials (that is, they produce sulfuric acid) transform *potential* acid sulfate soils into *active* acid sulfide materials (Rabenhorst, Burch, and Fanning 2002).



The resulting formation of sulfuric acid (a strong acid) rapidly reduced soil pH (on the order of weeks). Further hydrolysis of ferric ( $\text{Fe}^{3+}$ ) iron species under oxidizing conditions can produce additional acidity and soil pH values below 3.5 or 4.0.  $\text{pH} < 4$  can limit vegetation growth and establishment. Soil pH values below 2.0 have been observed in some cases (Berkowitz and VanZomeren 2020). Potential acid sulfate soils, therefore, when exposed to oxygen and hydrolysis of sulfide-bearing soil materials (that is, produce sulfuric acid,) become acid sulfide materials. The formation of sulfuric acid (a strong acid) results in a sudden—on the order of weeks—decrease in soil pH. The subsequent hydrolysis of ferric ( $\text{Fe}^{3+}$ ) species under aerobic conditions may produce additional acidity. The oxidization of iron sulfate soils often drives soil pH values below 3.5 or 4.0, severely limiting vegetative establishment and growth (Kölbl et al. 2017). In some cases soil pH values decrease below 2.0 (Berkowitz and Vanzomeren 2020).

Active sulfide soils are in a state of rapid flux, where produced acids are either neutralized or removed during tidal flushing or precipitation events (Brinkman and Pons 1973). The acidification process at the marsh scale can be rapid, on the order of several months to years, and depends on the concentration of sulfides, rate of oxidation, and rate of acid removal or neutralization (Brinkman and Pons 1973).

### **3.1 Disturbance of acid sulfate soils**

Disturbance of acid sulfate soils can result from dredging and placement of sediments in aerobic environments (that is, upland placement); artificial drainage; and droughts. Each of these scenarios exposes acid sulfate soils to oxygen, inducing sulfide oxidation and acidification.

The most extensive examples of oxidation of acid sulfate soils and soil pH declines in the United States and specifically in the North and mid-Atlantic regions, relate to the placement of dredged material into upland areas, mainly from maintenance dredging of federal waterways (United States Army Corps of Engineers 2014; Salsbury, Stolt, and Surabian 2017). Dredged sediments are transferred from anaerobic conditions to aerobic conditions, causing the oxidation of acid sulfate soils, if present, with subsequent declines in soil pH (Bramley and Rimmer 1988). Dredged material upland placement areas in Baltimore, Maryland, Somerset County, Maryland, and other locations around the Chesapeake Bay report soil pH <4 (Demas et al. 2004; Rabenhorst and Fanning 2002). Oxidation and low soil pH due to upland placement of dredged sediments is not just a problem in the United States, having occurred in a number of countries internationally (Fanning, Rabenhorst, and Fitzpatrick 2017).

Dredged material is also used for habitat development, including marsh restoration (United States Army Corps of Engineers 1978). In some cases, acid conditions may develop when previously anaerobic dredged material containing sulfidic material experiences aerobic conditions (DeLaune and Smith 1985). Lunz, Diaz, and Cole (1978) noted similarly that dredged material containing acid sulfate soils produced acidic conditions when placed in aerobic upland environments, whereas the same sediments did not produce low pH values when placed in areas with sustained anaerobic conditions. More recently, acid production was suggested as a potential cause of vegetation death at marsh restoration sites using dredged material in Poplar Island, Maryland. Staver (2015), however, did not find

enough evidence to suggest oxidation of acid sulfate soils was the main cause of vegetation die off at Poplar Island.

Water management activities, including diking and artificial drainage, can alter iron and sulfur cycling pathways in a marsh, resulting in soil acidification (Kolbl et al. 2017). For instance, drained and diked marshes along the New England coast experience oxidizing conditions and acidification to approximately pH 4.0 (Portnoy and Giblin 1997; Portnoy 1999). Drained marshes in the Netherlands displayed pH <2.5 (Edelman and Van Staveren 1958). Tidal swamps in Indonesia exhibited pH between 3.0 and 4.0 (Anda, Siswanto, and Subandiona 2008). The altered marsh soils and resulting lower water tables led to oxidation of naturally occurring acid sulfate soils, with adverse effects to estuarine fauna and agricultural productivity (Portnoy and Giblin 1997; Edelman and Van Staveren 1958).

When drought causes oxidation in acid sulfate soils, native plant communities in coastal areas also suffer (Alber et al. 2008). Examples include droughts occurring in Australia, Louisiana, and Georgia, where pHs <4.0 were observed (Elmer et al. 2013; Fitzpatrick, Shand, and Mosely 2017; Rabenhorst and Fanning 2002; McKee, Mendelssohn, and Materne 2004; Silliman et al. 2005). A drought-induced marsh dieback in Louisiana (McKee, Mendelssohn, and Materne 2004) and simulated drought conditions using marsh sediments in laboratory experiments (Mendelssohn et al. 2006; Palomo, Meile, and Joye 2013) also showed an association with acidic soil conditions. These studies demonstrate that acidic conditions can occur under natural conditions in addition to anthropogenic disturbances, with soil acidity exacerbating drought-induced water stress on marsh plants (Mendelssohn et al. 2006).

Typical marsh hydrodynamics should preclude extended periods of oxidized conditions. However, conditions such as drought or manipulation of the hydroperiod through diking, draining, or thin layer placement may produce periods of prolonged oxidation. Laboratory and field experiments have attempted to quantify the length of time for acidification to take place after oxidation occurred or the effects on marsh vegetation (Mendelssohn et al. 2006; Berkowitz and VanZomeran 2020). Field studies indicated that, while oxidizing conditions on the order of 19 hours up to 3 days resulted in oxidation of ferrous to ferric iron and likely lead to a reduction

in pore water pH, the duration of these conditions did not trigger acute marsh dieback (Hughes, Wilson, and Morris 2012).

Laboratory experiments investigating the tolerances of *Sporobolus alterniflorus* (Loisel.) P.M.Peterson & Saarela [*Spartina alterniflora* Loisel.] to alterations in pH and salinity found plants were most sensitive to lower pH conditions (pH 4 for a period of four weeks) at higher salinities (>25 ppt) (Linthurst and Blum 1981). However, exposure to lower salinities did not initiate total mortality, just signs of decreased growth and vigor. In a longer laboratory experiment examining the effects of draining and desalinizing marsh soils on biogeochemical cycling, Portnoy and Valiela (1997) observed soil pH dropped from ~6.5–7.0 to ~5.6–6.0 over the course of six months after draining and desalinization. The pH remained nearly stable until approximately 16 months after draining and desalinization, when the pH began to drop again, to ~4.5, before experiments concluded. These results indicate short periods of oxidation, on the order of weeks to months, may not result in acidification at a level to initiate marsh dieback, but prolonged periods of oxidation on the order of tens of months can lead to more severe acidification. The role of salinity on the plant response to acidification should also be noted, as acidification may affect marsh plant (specifically *S. alterniflorus*) vigor more pronouncedly at higher salinities.

### 3.2 Impacts to flora and fauna

The formation of acid sulfate soils in coastal wetlands is essential to protect vegetation from toxic effects of free sulfides (Maynard, O'Geen, and Dahlgren 2011). Sulfate enters coastal wetlands via tidal exchange of sea water and is used as an alternate electron acceptor in reduced environments (Krairapanond, DeLaune, and Patrick 1991). Sulfate is microbially reduced to sulfide; however, sulfides inhibit uptake of essential nutrients, such as ammonium, via phytotoxic effects on vegetation roots (Mendelssohn and McKee 1988). In coastal environments with prevalent iron, sulfide binds with reduced iron, thereby reducing the toxic effects of free sulfides through precipitation as acid sulfate materials (Schoepfer, Bernhardt, and Burgin 2014).

If oxidation of acid sulfate soils occurs, soils with sufficient buffering capacity (for example,  $\text{CaCO}_3$ ; Fanning 2002) or soils subject to adequate flushing from tides can neutralize the produced acid and reduce potential

environmental hazards (McKee, Mendelssohn, and Materne 2004). Oxidation of formed sulfides ensues at low tides, and generated acids are subsequently neutralized during the following high tide (Fitzpatrick et al. 1998). The reintroduction of seawater to marshes experiencing oxidizing conditions offers an opportunity to buffer active acid sulfate soils with bicarbonates, flush acidity, and induce anaerobic conditions in the soil (McKee, Mendelssohn, and Materne 2004; Portnoy and Giblin 1997).

Acid production, without neutralization, can cause adverse environmental damage. Vegetation is directly affected through acid exposure and indirectly affected by Al or Mg toxicity or smothering by oxidized Fe accumulation (South Australian Coast Protection Board 2003). The drainage of acids can also cause substantial negative impacts on nearby terrestrial and aquatic ecosystems—in particular, benthic organisms, fish, and other ecosystem components sensitive to acid exposure (Melville and White 2002). Acidic water entering the environment can result in fish kills and death to crustaceans and other organisms. For instance, acidity and Al toxicity causes fish gill damage (Demas et al. 2004). In addition, the mobilization of iron sulfide can rapidly induce anaerobic conditions in the water column as acid is produced, causing detrimental environmental conditions for fish and benthic organisms (Demas et al. 2004; Holmer, Ahrensberg, and Jorgensen 2003).

## **4 Observations of In Situ Formation of Acid Sulfate Soils Following Wetland Restoration**

Wetland creation and restoration projects use dredged materials—and have for many years (Faulkner and Poach 1996; Craft et al. 1999; Cahoon and Cowan 1988). The US Army Corps of Engineers (USACE) conducts a variety of ecosystem restoration activities, including the enhancement of wetlands, using dredged sediments. (Berkowitz and White 2013; Berkowitz, VanZomeran, and Piercy 2017). Practitioners began investigating the use and application of thin layers of dredged sediment for the benefit of degraded wetlands in the early 1970s (Reimold, Hardisky, and Adams 1978). Interest in placing dredged sediments on the marsh surface for restoration purposes is currently experiencing a resurgence (Berkowitz, VanZomeran, and Piercy 2017).

Distinct black horizons within the soil and placed dredged sediment profile formed on several recently implemented (2015–2017) marsh restoration projects using thin layer placement techniques (Berkowitz and VanZomeran 2020). These conditions were observed at two thin layer placement restoration projects: one project in the Narrow River Estuary, Rhode Island, and one project near Avalon, New Jersey (figure 4). A thin layer of sediment was strategically placed on these two degraded marshes to restore ecological function (Berkowitz et al. 2018). Researchers documented the presence of black iron sulfide materials in the field within the recently restored marsh soils (described below in more details; Fanning, Rabenhorst, and Bigham 1993; Berkowitz and VanZomeran, 2020). Laboratory incubations further verified the presence of acid sulfate soils, with pH decreases occurring in a subset of both the placed dredged material and the underlying native marsh soil. Notably, acid sulfate conditions were also observed in native marsh soils (10–20 cm below the surface) in reference areas and nonrestored marshes that received no sediment additions. This observation demonstrates that acid sulfate conditions naturally occur in the marshes; however, the extent of acid sulfate layers was more pronounced in dredged material placement locations.

Narrow River and Avalon are unique because the acid sulfate materials were not observed within the sediment sources (that is, Narrow River: upland sand; Avalon: navigation channel sediments) but rather formed in situ following sediment placement at the marsh surface. The apparent rapid (that is, 6–12 months) formation of acid sulfate materials that, prior to placement, did not contain acid sulfate soil materials, is of interest to similar marsh restoration projects under consideration in the region. For one example, Rabenhorst (1990) investigated acid sulfate soil initiation; however, no studies have documented the formation of acid sulfate soils in situ following marsh restoration activities. Reimold, Hardisky, and Adams (1978) mention that thicker applications of clay-rich sediment in a *S. alterniflorus* marsh resulted in acid sulfate soil conditions. But they collected no data to confirm in situ formation of acid sulfate soil following dredged sediment placement.

**Figure 4. Avalon, New Jersey, soil sample (left) displaying extensive acid sulfate coatings with recently placed dredged materials; Narrow River, Rhode Island, soil sample (right) displaying black acid sulfate materials at the contact point between placed upland sands and the underlying marsh soils.**



In response to these field observations, a laboratory microcosm study analyzed the potential for acid sulfate soil formation due to thin layer sediment applications (Berkowitz, VanZomeren, and Fresard 2019). A soil horizon of prominent black acid sulfate material formed after as little as 16 days from experiment initiation and formed at the interface between the marsh soil and placed dredged sediment. This observation confirms the potential for in situ acid sulfate soil formation during a restoration scenario. The rapid development of in situ acid sulfate soil formation, therefore, warrants additional investigation. Future studies should isolate additional environmental factors that may contribute to acid sulfate

formation. Other environmental factors such as hydrology (for example, water levels, inundation durations, hydraulic flushing); sediment characteristics (particle size, Fe concentration); neutralization capacity; and persistence of acid conditions require further evaluation.



## 5 Approaches to Document Acid Sulfate Soils

Acid sulfate soil formation is a naturally occurring process in coastal environments and does not pose an environmental risk if properly identified and managed. There are a number of methods available, both field and laboratory, to identify the presence of acid sulfate soils as well as the acid generating potential of these soils. Multiple methods applied in concert help to avoid false identification of potential acid sulfate conditions. The field and laboratory methods and tools are summarized below.

### 5.1 Field evaluations

There are currently five evaluation tools to identify the presence of acid sulfate soil conditions: (1) soil descriptions (Fanning and Rabenhorst 1990); (2) application of hydrogen peroxide, 3% (McVey et al. 2012); (3) exposure to hydrochloric acid, 10% (Fanning, Rabenhorst, and Bigam 1993); (4) installation of indicator of reduction in soils (IRIS) tubes (Rabenhorst, Magonigal, and Keller 2010); and (5) testing with  $\alpha$ -dipyridyl dye (Childs 1981; Berkowitz et al 2017). These tools identify the presence or absence of chemical constituents necessary to form acid sulfate soils, such as ferrous iron or sulfides. A description and figure, if applicable, of each tool can be found below (table 1; figure 5–8). Evaluation of multiple parameters is recommended to support documentation of acid sulfate soil conditions.

Additionally, pore-water equilibrators, commonly known as *peepers*, collect pore water samples in wetland soils (Hesslein 1976). Use of peepers aids in characterizing concentrations of soluble constituents (that is, sulfides and ferrous iron) required for acid sulfate soil formation (Johnston et al. 2009). The deployment of peepers into wetland soils provides a depth profile of soluble constituents (VanOplooet al. 2008; figure 9).

**Table 1. Field evaluation tools to identify the presence of acid sulfate soil conditions.**

Parameter	Diagnostic	Example
Soil descriptions	Acid sulfate soils form dark black coatings on soil particles and within soil pores (Fanning, Rabenhorst, and Bigham 1993; Fanning and Rabenhorst 1990).	Figure 5
Application of hydrogen peroxide (3%)	Acid sulfate soil materials oxidize very rapidly in the presence of strong oxidizing agents, resulting in removal of dark soil coating and revealing the underlying soil matrix color (McVey et al. 2012).	Figure 6
Application of hydrochloric acid (10%)	Acid sulfate soil materials rapidly liberate hydrogen sulfide gas in the presence of acid, resulting in formation of a strong rotten egg odor (Fanning, Rabenhorst, and Bigham 1993).	None
Installation of IRIS tubes (one hour)	When present, acid sulfate materials rapidly precipitate on the surface of IRIS tubes, resulting in the formation of a black coating (Rabenhorst, Megonigal, and Keller 2010).	Figure 7
$\alpha$ -dipyridyl dye	Diagnostic test for the presence of ferrous iron, a key component in the formation of acid sulfate soils; verifies that the soil is chemically reduced with respect to iron (Childs 1981; Berkowitz et al. 2017).	Figure 8

**Figure 5. Narrow River (left) soil sample displaying black acid sulfate materials at the contact point between placed upland sands and the underlying marsh soils; Avalon (right) soil sample displaying extensive acid sulfate coatings with recently placed dredged materials.**



Figure 6. Dark soil coatings (soil on left) from acid sulfate soil materials at Avalon, then oxidized with 3% hydrogen peroxide (soil on right) resulting in removal of dark soil coating and revealing of the underlying grey soil matrix color.



Figure 7. When present, free sulfides precipitate on the surface of IRIS tubes within one hour of installation, resulting in the formation of a black coating (left). Removal of black coating on the IRIS tube by hydrogen peroxide oxidation (right).

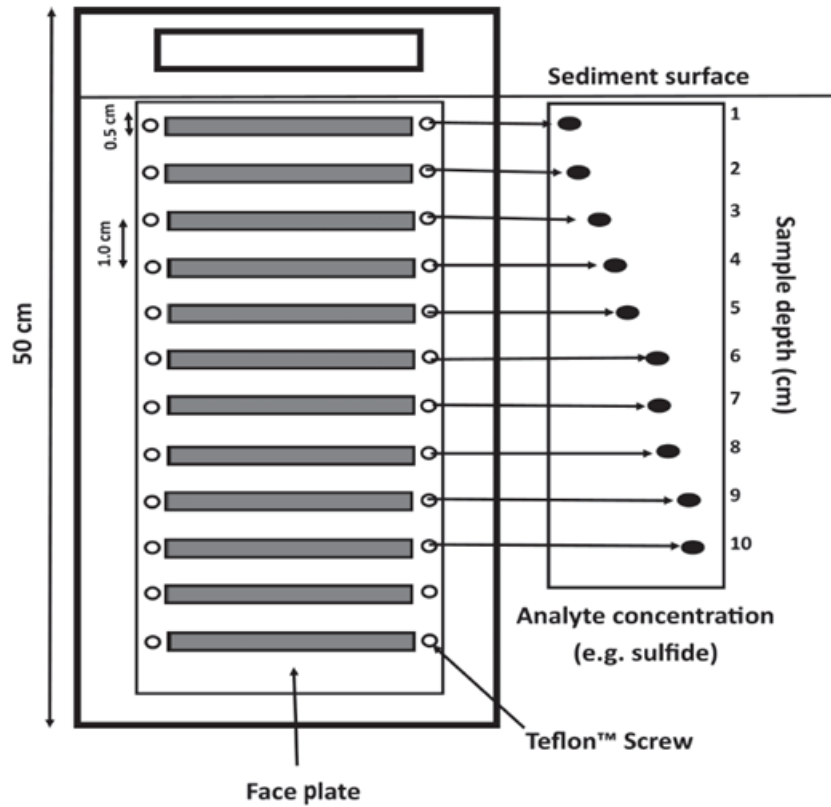




Figure 8. Reaction of reduced iron to  $\alpha$ -dipyridyl dye, seen as the development of a pink color, in the soil deposited on the marsh surface placed at Narrow River.



Figure 9. Schematic of a pore-water equilibrator (that is, peeper) for sampling dissolved constituents in soil solution (reproduced from Green and Fong 2016).



## 5.2 Laboratory evaluations

Moist aerobic incubation tests are used to determine *potential* oxidized pH in the laboratory (Wessel and Rabenhorst 2017). Field moist soils are incubated in 1 cm depths and the pH recorded once a week. The soil is remoistened to a paste each week for up to 16 weeks, or until the pH is stable (Soil Survey Staff 2014). The process of wetting and drying of the soil promotes the growth of aerobic bacteria, and in particular sulfur-oxidizing bacteria that oxidize FeS minerals, and the production of sulfuric acid (Arkesteyn 1980; Fanning and Fanning 1989). The production of sulfuric acid decreases the pH over the course of the incubation period.

## 6 Identification of Knowledge Gaps and Opportunities for Additional Research

The natural occurrence of acid sulfate soils in marshes has been studied for >100 yr, including sediment acidification following exposure of dredged materials to aerobic conditions. Notably, those studies evaluated acid production resulting from exposure and oxidation of soils and sediment that already contained acid sulfate constituents.

Observations of potential acid sulfate soils development associated with wetland restoration have been observed in passing in the 1970s and 1980s. However, no studies documented the formation and fate of acid sulfate soils following initiation of ecological restoration activities. The only mention of possible conditions resulting in acid sulfate soil development after sediment placement in a salt marsh was a study in a Georgia salt marsh, where *S. alterniflorus* smothered after placement of dredged material containing clay resulted in potential acid sulfate forming conditions (Reimold, Hardisky, and Adams 1978). However, no follow up was conducted to confirm the presence of acid sulfate conditions prior to placement, to determine if acid sulfate soils formed after placement, or if there were any long-term effects. Acid production was suggested as a cause of vegetation death at marsh restoration sites using dredged material in Poplar Island, Maryland. Again, no evidence was available to confirm that oxidation of acid sulfate soils induced or contributed to vegetation dieback (Staver 2015). Rabenhorst (1990) reported the formation of iron sulfides following the intentional burial of iron oxides in a marsh soil, suggesting iron content limited formation and accumulation of acid sulfate soils in some environments.

Several recently implemented projects, as noted in section 4.0, reported the rapid development (6–12 months) of acid sulfate compounds following dredged material placement, increasing interest in evaluating potential acidification and other impacts within restoration sites. Notably, acid sulfate materials were not observed in the dredged material prior to placement. Recent field and laboratory methods confirmed the presence of iron sulfides, indicating the formation of acid sulfate soils was occurring in situ (Berkowitz and VanZomeren, 2020; Berkowitz, VanZomeren, and Fresard 2019). Initial results suggest that iron sulfate soil formation

appears to be induced by the interaction between the marsh soil and the dredged material.

In a restoration context, there are potentially four situations where this problem is occurring: thin layer placement, thick-layer contraction of salt marsh, excavation of dredged material disposal sites to marsh elevations, and reintroduction of tidal exchange to restricted marshes. The processes, conditions, and stability of acid sulfate soils formed in situ following dredged material placement is not well documented or understood, and several restoration projects have shown negative responses to FeS (that is, vegetation die-off; no recovery). The bottom-up model outlining the progression of acid sulfate soils described by Dent (1993), as well as descriptions of iron sulfides presence in buried A horizons in Rhode Island (Wessel and Rabenhorst 2017) offer potential explanations. Current research in marsh restoration using dredged sediments has not explored these potential mechanisms directly, requiring additional research.

A combination of field and laboratory studies are necessary to document environmental conditions that favor the formation of acid sulfate materials and persistence of formed acid sulfate materials under deferring environmental conditions. Future studies will evaluate data gaps identified in this literature, to include the following: hydrology (for example, water level, frequency and duration of inundation, hydraulic flushing); sediment characteristics (that is, particle size, Fe concentration); in situ neutralization capacity; short- and long-term persistence of acid conditions; and other factors associated with potential and active acid sulfate soils in the context of marsh restoration. Additionally, development of a model to evaluate interactions of soil, dissolved constituents (for example, buffering capacity), and environmental conditions (for example, tidal prism) on FeS development and fate will provide capabilities to address management of acid sulfate materials over time.

It is important to note that the formation of iron sulfate soils in itself may not be of concern in a restoration context if proper project design, implementation, and monitoring assures limited oxidation of the formed iron sulfides, the presence of adequate neutralization capacity, and/or sufficient tidal flushing. Regardless of the origin of acid sulfate soils in marsh environments, appropriate management of the acid sulfate soils can

mitigate potential risks. Management of acid sulfate soils should consider the following:

1. Prevent or minimize oxidation of acid sulfate materials by maintaining natural tidal cycling within the marsh restoration area or avoiding extended drawdown periods (Lunz, Diaz, and Cole 1978; Melville and White 2002).
2. Neutralize acid production, if occurring, by allowing tidal exchange and buffering capacity with bicarbonate naturally present in seawater (Breemen 1976; Portnoy and Gilblin 1997).

Future research related to marsh restoration using dredged sediment should include (1) the underlying mechanisms that promote the rapid formation of acid sulfate soils, (2) development of box models to predict potential outcomes, (3) field monitoring under in situ marsh restoration conditions, and (4) potential management options. This four-pronged approach will address the cause, trajectory, and fate of acid sulfate soils associated with marsh restoration projects and will promote additional use of limited sediment resources while addressing concerns regarding the potential negative effects associated with these materials. Additional technical guidance is also likely required to ensure that restoration practitioners with a variety of backgrounds understand the basic principles, potential hazards, and best management approaches associated with acid sulfate soils.



## **7 Summary**

This report contributes to the state of the science regarding acid sulfate soils in coastal environments. A literature review summarizes studies describing the formation, disturbance, and management of acid sulfate soils. Despite the number of studies and long history of acid sulfate soils, there is a dearth of research related to the rapid formation of acid sulfate soils following marsh restoration projects using dredged sediment. This report recommends additional research to evaluate mechanisms, trajectory, and fate of acid sulfate soils associated with marsh restoration projects. Further research into the mechanisms and conditions that promote the formation of acid sulfate soils in restoration projects will aid in restoration project design, management decisions, and success of marsh restoration projects.

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<b>14. ABSTRACT</b>  Acid sulfate soils naturally occur in many coastal regions. However, the oxidation of acid sulfate soils can decrease soil pH to <4.0, affecting vegetation and aquatic organisms. Acid sulfate soil oxidation typically occurs where anaerobic sediments or soils were exposed to aerobic conditions (for example, extended drought, artificial drainage, or dredged material placement in upland areas). Recently, field observations documented the formation of acid sulfate materials at multiple degraded marsh restoration locations (Rhode Island, New Jersey, California) following intentional dredged sediment placement into wetland environments designed to increase marsh elevation. Unlike previous studies of acid sulfate soils, the in situ dredged material did not contain acid sulfate-bearing materials at the time of placement; instead, the interaction between the marsh substrate and the overlying dredged material appears to have caused the formation of acid sulfate soils. These findings highlight the need for additional studies of acid sulfate soil formation and fate—especially within a marsh restoration context. In response, this report provides a review of literature related to acid sulfate soils, discusses preliminary data collected to evaluate acid sulfate material formation following marsh restoration, and identifies knowledge gaps requiring additional research and technical guidance.					
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