

Pyrite Oxidation: Review and Prevention Practices

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Abstract

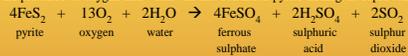
Pyrite (FeS_2) is a common mineral found in sedimentary rock and fossils, and its decay is a major problem in the conservation of fossil specimens. Pyrite oxidation, also referred to as pyrite disease or pyrite decay, is identified by a sulphuric acid odor, white crystalline powder, yellow sulphide powder, and/or gray to yellowish microcrystalline mass in and out of specimens. Its presence can be devastating to a geological collection. In the presence of oxygen, pyrite breaks down to ferrous sulphate ($FeSO_4$) and sulphur dioxide (SO_2). If water is present, sulphuric acid (H_2SO_4) is also produced and can cause damage to labeling and storage containers. The most effective method to preventing rapid pyrite oxidation decay is to store specimens within a moisture and oxygen barrier containing an oxygen scavenger. Further oxidation can be reduced or eliminated by storing specimens in an environment with a humidity level below 30%. Ammonium gas and ethanalamine thioglycollate treatments neutralize sulphuric acid and remove ferrous sulphate, and are reportedly effective in partly or completely removing oxidation reaction products. Specimens that contain large amounts of pyrite and are in danger of losing morphological information through pyrite oxidation should be molded and cast. Because latex rubber contains ammonium, its use as a molding material can have the added benefit of neutralizing sulphuric acid and ferrous sulphate. Although not tested in a controlled scientific experiment, it has been reported that this method was successful in halting the oxidation process in some specimens.

What is Pyrite Oxidation?

Pyrite (FeS_2) is one of the most widespread and persistent minerals and occurs in sedimentary, metamorphic, and igneous rocks. Pyrite grows in crystalline forms, typically cubic, octahedral, or more rarely pyritohedral (irregular dodecahedral with twelve identical pentagonal faces). The crystal can be several centimeters in diameter for well-grown cubes, or microcrystalline (0.1 to 1.0 μm for the individual microcrystals) (Birker and Kaylor, 1986, and Howie, 1992). Marcasite (FeS_2) is a polymorph of pyrite with orthorhombic form that primarily occurs in sedimentary rocks, and is not as commonly found as pyrite, but it can also be unstable and susceptible to oxidation.



Pyrite oxidation is also known as pyrite 'disease', pyrite 'rot', and pyrite 'decay', and it is caused and accelerated by the presence of oxygen and water. In this condition pyrite undergoes rapid oxidation;



Products of oxidation reactions depends on mineral composition of fossils and matrices associated with oxidizing pyrite or marcasite, but are sulphuric acid and various hydrated sulphates (e.g., ferrous sulphate ($FeSO_4$), cupiapite ($Fe^{II}_3(OH)_2(SO_4)_2(OH)_2$), fibroferite ($Fe^{II}(\text{SO}_4)_2(OH)_2 \cdot 5(H_2O)$), melanterite ($FeSO_4 \cdot 7H_2O$) (Wang et al., 1992).



Pyrite oxidation can also be caused by bacteria, *Thiobacillus ferrooxidans* and *Thiobacillus sp.* but bacterial decay typically occurs above 95% humidity, therefore it is not likely to be a problem in museum collections (Butler, 1994, and Howie, 1992).



Corrosion damage caused by *Thiobacillus ferrooxidans*.

How to recognize Pyrite Oxidation



Moisture and Oxygen Barriers Containing an Oxygen Scavenger and Desiccant

Considering that moisture and oxygen are the two most detrimental components that lead to pyrite oxidation it is advisable to create an environment devoid of these two factors. Many collections have been outfitted with humidity controlled environments. This can help in the control of pyrite deterioration of fossils if humidity is held below 50%, however, moisture and oxygen levels recommended for pyrite containing specimens are not always applicable to an entire collection. Additionally, while humidity controls in collections are common and cost effective, the ability to control oxygen is much more problematic due to the ubiquitous nature of oxygen in the atmosphere (and the need for oxygen by humans).

Solutions for this problem begin with creating a microenvironment for the specimen to live in. Introducing a barrier that surrounds the specimen and does not allow humidity or oxygen to pass through creates this environment. Once the specimen is separated from the larger environment the need to remove oxygen and humidity from an entire collections space is negated and relegated to the small, enclosed area of the microenvironment.

Types of Barriers

Coatings – Applied directly on specimens, coatings were once used to prevent air from coming in contact with its surface. Coatings are not impermeable to air and humidity. Treatment in this manner can ultimately be detrimental to further practical treatment and is *not recommended*. In the past Shellac, Bakelite, Polyvinyl Acetate and Polybutyl Methacrylate have been used (Butler, 1994).

Containers – In lieu of smearing compounds directly on specimens, the use of various types of containers impervious to moisture and oxygen are preferred. The most impermeable containers are either glass or metal (Waller, 1994) and for small specimens it is possible to store in hermetically sealed containers. Larger specimens such as those often found in vertebrate paleontological collections pose a problem both logistically and financially for this type of container. Recent advancements in the field of food storage and transport have provided alternate options for fossil specimens. Containers look and act like a typical plastic bag but consist of multilayers that prevent oxygen and humidity from being transmitted. "Consider that a single 6-mil sheet of most laminated vapor barriers will resist the transmission of water vapor (and other atmospheric gases) better than a sheet of acrylic glazing almost one-half inch thick." (Burke, 1992).

Examples of barrier film

Escal™ Ceramic Barrier Film - The outer layer of Escal™ barrier film is polypropylene. The barrier layer is a vacuum-deposited ceramic on a PVA substrate. The inner (sealing) layer is polyethylene. <http://www.keepsafe.ca/escal.html>

Marvelseal 360 (Ladlow Corp.) - The base film used in Marvelseal 360 provides a slightly stiffer and flatter product than some other pouch stocks. Dimensional stability at high percent RH is good. The outer ply is treated for printing. <http://www.jamesdawson.com>

SARAN™ polyvinylidene chloride (PVDC) films - oxygen and odor barrier; chemical and moisture resistance; temperature versatility; high tensile strength; clarity and sealability. The Dow Chemical Company (Dow). http://www.plastics.dow.com/plastics-na/prod/saran/sar_films.htm

Creating and monitoring the Anoxic Humidity Controlled Microenvironment

Relative Humidity (RH) Controls – It should be noted that controlling humidity levels is much more important than controlling oxygen. Low RH will not reverse existing pyrite oxidation, but can halt further reaction. Some Oxygen Absorbers are designed to control humidity, but it is not their main function. For pyrite containing specimens constant RH of less than 50% is recommended, however, storage at 30% RH is ideal (Howie, 1992). Humidity can be reduced with the addition of desiccant to the barrier container. A desiccant works by either absorption or adsorption of atmospheric humidity. The three most common types of desiccants are: clay, silica gel, and molecular sieve. In paleontology silica gel is most commonly used. RH can be monitored with a color-changing card also placed within the barrier.

Oxygen Absorbers/Scavengers – Technically speaking an oxygen absorber is "an oxygen-absorbing composition comprising in relatively sufficient proportions particulate annealed electrolytically reduced iron, and salt for combining with water to produce an electrolyte which combines with said iron to cause it to absorb oxygen" (McKedy, 1993).



They are packaged in small sachets and can be placed inside a container or sealed barrier with the fossil specimen. Once the barrier is sealed, the oxygen scavenger goes to work removing oxygen from the air within the barrier. As long as the barrier remains sealed the air within will remain anoxic. Absorbers come in various size packets with specifications as to how much oxygen can be absorbed by each. The size of the container/barrier will dictate the size and quantity required of the absorber.

Latex Rubber - a synergetic material?

Previous studies have shown that ammonia has the capacity to neutralize sulphuric acid, and is reportedly effective in partly or completely removing oxidation reaction products (Oddy, 1977; Shelton, 1994). Additionally, molding and casting of specimens that have been identified as containing pyrite should be considered in order to reduce the amount of information lost through decay.

Natural latex rubber contains ammonia (as a preservative) that vaporizes during curing, and has subsequently been suggested as the preferred molding material. It is thought that the ammonia contained within the latex will serve to neutralize the oxidation process and products to the benefit of the specimens. Latex molding for this purpose has not been substantiated by research or experimentation, however, it has been reported to have an effect by anecdotal observation.

Ammonium gas treatment

Ammonium gas has been successfully used to neutralize sulphuric acid in specimens affected by pyrite decay (Bannister, 1933; Bannister and Sweet, 1943; Birker and Kaylor, 1986; Howie, 1992; Rixon, 1976). Specimens are suspended above a solution of ammonium hydroxide and covered by polyethylene or glass to contain the gas created by evaporation. The RH above the solution can reach 70% but can be lowered to 30% when mixed with polyethylene glycol (PEG) in a 10% (volume to weight) solution. Because porous pyrite will absorb water vapor (resulting in further oxidation) it is important that the ammonium solution be made with a non-aqueous solvent.

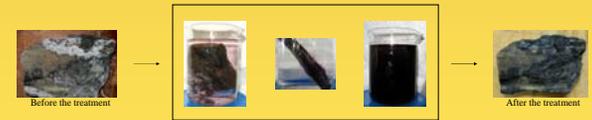
1. Make 10% volume to weight solution of ammonium hydroxide in polyethylene glycol (PEG).
2. Place a plastic coated metal rack over the solution and place specimen on top.
3. Cover the apparatus with polyethylene or glass to treat the specimen with ammonium vapor.
4. Treatment is complete when white or yellowish patches on specimen change to rust colored stains.
5. Clean the specimen with alcohol and thoroughly dry.

Ethanalamine Thioglycollate treatment

Use of ethanalamine thioglycollate is useful because it will both neutralize sulphuric acid and remove oxidation products, perhaps more effectively than ammonium gas treatment. Ethanalamine thioglycollate is an alkaline liquid that is soluble in both ethanol and isopropanol, hence the specimen will not be exposed to water during the treatment. Before treatment as much coating as possible should be removed to expose the specimen surface. Two methods are described in the literature (Cornish and Doyle, 1984 and Cornish, 1987):

Method 1: Immersion in solution

1. Make 2-5% ethanalamine thioglycollate solution in ethanol or isopropanol.
2. Immerse a specimen in solution for 1-4 hours. Change solution when it becomes dark violet color, otherwise brown insoluble precipitation will stain the specimen.
3. Wash specimen with alcohol.
4. Repeat the process until solution no longer changes its color when specimen is immersed.



Method 2: Paste application

1. Make 3-5% ethanalamine thioglycollate solution in ethanol or isopropanol.
2. Mix equal amounts (1:1 ratio) of the solution and sepiolite (magnesium silicate).
3. Apply paste to affected area and cover with polythene or aluminum foil to prevent rapid evaporation.
4. Leave specimen covered for 1-3 hours.
5. Clean and wash specimen with alcohol.

Specimens that suffered from pyrite oxidation can be treated with ammonium gas and/or ethanalamine thioglycollate solution/paste to effectively neutralize sulphuric acid and remove various sulphate products. Because sulphuric acid and sulphate will continue to cause damage to affected specimens, these treatments are widely accepted and practiced in many institutions. **Pyrite, however, will not be removed from the specimen with these treatments. Storage of specimens in low humidity and/or anoxic environments must follow afterward.**

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