When an object made from silver or copper is buried shallowly in land or water many different types of corrosion can occur. Using the type of corrosion that has occurred, it is possible to determine the exact composition of the metal and what conservational issues it might be facing. Stability diagrams are used to interpret the information, especially when small organisms are involved. These organisms are often difficult to distinguish and the stability diagrams aid in the determination of the condition of the object.

Stability diagrams are used to study and interpret the chemicals the object may have come into contact with. They look at the chemicals that have influenced the deterioration of the object and determine what kind of damage has been done at a fixed temperature and single chemical condition. It examines the Eh in comparison to the pH of the environment. Eh measures the oxidation or reduction potential. A low Eh means reductive conditions while a high Eh indicates oxidizing. However, pH looks at the acidity and alkalinity of the environment. It looks for the presence of hydrogen ions and the concentration of these ions.

Figure 1 is an example of a stability diagram. It examines the damage to silver in seawater compared with different concentrations of sulfur. Line a is the oxygen line where oxygen generation in the water will become unstable. Line b represents the hydrogen line. Any point below this is where hydrogen evolution in the water becomes unstable. These points are exclusive to shallow land and sea environments. Line c is where cerargyrite (AgCl) and metallic silver become unstable. The hatched area below line d is the reduction-oxidation behavior of shallow land or sea where the reaction and reverse reaction are performed at the same rate. Line e is representative of the reduction and oxidation conditions for water sampled from an industrialized area of Scandinavia. This was a stagnant pool with high oxygen content near the surface and high levels of Hydrogen Sulfide and decomposing organic substances at the bottom. The upper and lower Eh limits were determined by pond conditions at a pH near 7. The highest and lowest pH values commonly found in the biosphere are what bind the parallelograms. The first or upper parallelogram refers to water less than 10 meters from the surface. The lower represents water more than 10 meters from the surface and are not found near archaeological evidence but are still achievable in the biosphere. If a biofilm were present it would cause conditions not represented in this diagram and different conditions on the surface of the artifact. This diagram exhibits the stable conditions for silver with several different sulfur arrangements within the salt water. This graph is only true if the sulfur is in equilibrium and just as much is being produced as is being broken down. The area above line c presents the stable conditions for cerargyrite and below line c is stable for metallic silver, excluding the area pointing right and downward which is for monoclinic acanthite.
Stability diagrams measure corrosion by examining the mineral coating on an object to understand the thermodynamically stable corrosion process. By determining the mineral it is possible to understand the conditions in which the artifact corroded and discern some important conservational information. For example, copper coated with azurite instead of malachite indicates the water had higher carbonate activity. This often means that organic material is being decomposed by microbiological means. Another example is when chalcocite (Cu2S) is formed instead of covellite (CuS). This means the chalcocite was formed in an environment in which it would be stable.

Sometimes a two-dimensional diagram is not enough to capture the complexities in corrosion. Often copper corrosion deals with more than just Eh and pH. Cuprite and nantokite that forms under cuprite can often indicate bronze disease and type 2 pitting. In this case a more comprehensive, four-planed graph would be necessary, with axes of pH, Eh, chloride and copper activity.

Corrosion can also be caused by small life forms. Bacteria can attach to metals and when they colonize, they produce a film across the surface. This is called a biofilm. These organisms cause a different type of corrosion than the rest of the artifact is suffering from. Biofilms maintain their own environment with different pH and dissolved oxygen. Depending on the environment, different organisms are found. An example would be obligate anaerobic SRB, which grows in anaerobic conditions, would be found in soil, sediment, or seawater that is oxygenated. They can cause negative Eh values, which in turn creates more SRB growth. SRB is commonly found with metal-depositing bacteria and produces sulfide and higher pH values. Knowing the type of microbiological damage is essential in determining the conservation needs of an object due to the different kinds of damage being done to the artifact.

As silver corrodes, it often gets converted into cerargyrite (AgCl). This conversion is primarily due to oxidation of the silver near the surface of the water or when buried shallowly in land that is near heavy rain or groundwater deposits. Cerargyrite becomes stable in seawater and land rich in chloride. Silver also corrodes when reduced with sulfur. Sulfur in the air can come from degradation of other materials that will produce monoclinic acanthite and damage the artifact. When in salt water, silver often comes in contact with SRB and converts into acanthite and cerargyrite. Sulfides that come in contact with silver can also produce acanthite and argentite.

Argentite has not been reported as naturally occurring, so argentite present in soil or water often indicates an artifact is underneath. These silver objects will have been buried in sediment for long periods. If a chlorine ion is present, it will form argentite or acanthite and cerargyrite.

Laboratory databases have hypothesized the reactions of silver and sulfides. First, the silver is corroded by the sulfide by reduction and produces acanthite. Second, carbon disulfide does not corrode. Third, the corrosion caused by organic sulfides is easily controlled by transport mechanisms and vapor pressures. Fourth, how quickly sulfidation occurs is affected by ammonia and silver in water with no life forms, but with reduced sulfur can produce acanthite.
SRB is essential to converting silver into a sulfide because of the content of reduced sulfide in water with a pH more acidic than 9 is very rare. If SRB is not present, sulfates that are present in most waters take a great deal of time to convert to sulfides.

It can be argued that argentite formation only occurs when silver is precipitated, copper ions are present, and they are reduced by a type of sulfur. When argentite is formed using pure silver, it remains unstable at room temperature; however it can bond with copper to form a more stable molecule. That is the main reason argentite is not naturally occurring and only forms when artifacts are in the perfect conditions to deteriorate. The presence of this mineral indicates that the artifact originally contained some copper.

When copper corrodes in the presence of oxygen or water it forms cuprite. The cuprite often dissolves the copper ions and in saltwater will re-precipitate them as botallackite. The botallackite can convert to several other minerals depending on the different elements and minerals found in the water. When copper is mixed with nickel, however, it corrodes much more slowly. The addition of nickel changes the mass transport characteristics of the oxide, meaning the formation of different minerals causes oxygen to affect it differently. Depending on what is added to the copper, such as zinc or tin, there are different chemical reactions in water and land burials.

The exact composition of an object is incredibly important knowledge for a conservator to have in order to make the best decisions to preserve that object. Having this information allows an expert to determine the conditions in which the artifact was decomposing and the original composition. Before preserving an object, knowing exactly what was done to it will allow the conservator to better discover any possible damage that is not as easily seen. The stability diagrams give conservators a great deal of information concerning the possible environment of the object.

Work Cited