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The Use Of Electrolytic Reduction For The Removal Of Chlorides From Iron-Nickel Meteorites

W. Brett Whitenack

ABSTRACT

Iron-nickel meteorites are susceptible to rusting, at times to the point of completely destroying the specimen. Early preservationists attempted to halt corrosion by coating specimens with various sealants to keep out moisture and met with limited success. The issue of chloride removal was not addressed and was later found to be the source of the corrosion problem. Chlorides can accumulate in meteorite specimens from chloride containing groundwater. The chlorides facilitate the oxidation of the nickel poor mineral kamacite which is converted to the mineral akaganéite. High humidity and heat can liberate the chloride from the akaganéite structure, allowing it to move on to other chemical sites and continue the corrosion process. Inside the meteorite, an electrochemical cell is formed with chlorides acting as a salt bridge in the electrolyte solution and facilitating the process of oxidation. The removal of these chlorides is the key to halting this corrosion. Electrolytic reduction cleaning, a process used in the marine archeology conservation field, was adapted and used to remove the chlorides from four different iron-nickel meteorite specimens. This method was shown not only to successfully remove chlorides from each specimen, but also to remove traces of corrosion from the outer surface of the meteorite specimen. This process has proved it can be a reliable and cost effective means to preserve iron-nickel meteorites in both museum and private collections.

Keywords: *akaganéite, chlorides, electrolytic reduction cleaning, iron-nickel meteorites, lawrencite, Widmanstätten patterns.*

INTRODUCTION

As soon as an iron-nickel meteorite lands on the earth, corrosive processes begin to attack the metallic minerals contained within the specimen. These processes will continue to act upon the meteorite until all the iron has been oxidized and converted into iron oxides making the meteorite almost indistinguishable from terrestrial rocks.

Corrosion of iron-nickel meteorites has been the bane of the collector and museum curator. Many fine specimens of iron-nickel meteorites have been lost due to their rusting away. Various techniques including; sealants, oils, and storage under nitrogen, have been employed to reduce or eliminate the problem. All have met with limited success as the issue of chloride removal was not addressed (Buchwald, Clarke, 1988).

It was established that chloride ions are responsible for creating an electrochemical environment for a corrosion reaction to take place (Farrington, O.C., 1915). Originally, it was thought that the mineral lawrencite ($FeCl_2$) was an indigenous mineral in meteorites and the source of these chloride ions (Jackson, Hayes, 1844). However, it was later proven that lawrencite was, in fact, not found within meteorites and that the chloride ions were acquired through the exposure to chloride containing groundwater (Buchwald, 1977).

Buchwald proposes a corrosion mechanism whereby the mineral akaganéite [ß-FeO(OH)] is produced and incorporates chlorides into its structure. Interfaces between the nickel-rich mineral taenite ?-(Fe,Ni) and the nickel-poor mineral kamacite a-(Fe,Ni), generate different electrochemical potentials. Oxidation primarily takes place for kamacite. At the interfaces between the two minerals, as well as cracks within the specimen, occur sites were oxygen and electrolytes invade the meteoritic metal. Anodic kamacite is moved into solution with electrons passing through metal to the cathodic site. At this site oxygen is reduced to form hydroxide (OH^-) ions. Iron ions from oxidized kamacite then precipitate forming akaganéite. This reaction can be expressed as

$$\underset{\text{(kamacite)}}{30Fe^0} + 2Ni^0 + 47O + 19H_2O + 4H^+ + 4Cl^-$$

$$\xrightarrow[\textit{irreversible}]{} \underset{\text{(akaganéite)}}{2[Fe_{15}Ni][O_{12}(OH)_{20}]Cl_2\,(OH).}$$

If the meteorite experiences warming and an increase in humidity, hydroxide (OH^-) ions can exchange with chloride (Cl^-) ions, liberating the chloride ions which are then released back into solution to travel to other sites on the corrosion front or are flushed out of the meteorite structure (Buchwald, Clarke, 1988, 1989).

Because the mineral phases in iron-nickel meteorites allow water containing chloride (electrolyte) to intercalate into the specimen, oxidation is then not limited to the exposed surfaces. Iron oxidation occurs by establishing an electrochemical cell; with the iron as a conductor, the electrolyte solution as a salt bridge, and any exposed surfaces allowing electrons to move onto oxygen.

Finally, as the akaganéite loses its chloride, it becomes unstable and decomposes to the iron oxide minerals maghemite and goethite.

Electrolytic reduction cleaning, a process used in the marine archeology conservation field, is a way to eliminate chloride ions in iron specimens, stabilizing the iron, and thus preserving the specimen (Hamilton, D.L., 1988). In this process, the object is placed in an electrolytic solution such as sodium hydroxide (NaOH). The iron specimen is wired as the cathode and mild steel mesh, placed around the specimen, is wired as the anode. A current is passed through the system by means of a regulated DC power supply causing oxidation and reduction (Figure 1).

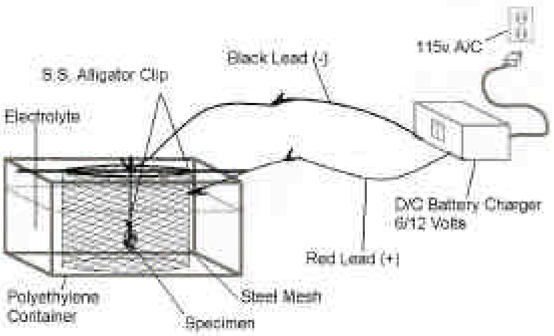

Figure1. Electrolytic reduction cleaning arrangement.

As the process takes place, positively charged metal ions are reduced to a metallic state and chlorides are drawn from the specimen by electrolytic attraction. The length of the electrolytic reduction process depends on the size of the specimen and the amount of chlorides present within it and can last from a few days for small objects to as long as a year for a specimens as large as a cannon.

By adapting this process, a low cost, simple, and effective means of cleaning and stabilizing iron-nickel meteorites has been achieved and hopefully will benefit museums and collectors alike.

MATERIALS AND METHODS

Four specimens of iron-nickel meteorites (Brenham, Campo del Cielo, Elyria, and Nantan) were obtained. Each specimen was weighed, measured, and photographed so comparisons could be made before and after electrolytic reduction.

Electrolytic reduction cleaning containers are made using polyethylene containers ranging in size from three to six liters. Each meteorite specimen is placed into a separate container and surrounded by an anode made of 16-gauge expanded mild steel mesh with 12.5 mm openings to allow for circulation of electrolyte. Cathodic terminal wires are fabricated from U.S. National Electric Code Standard 16 AWG, Separation 2, 300V maximum rating insulated copper wire and terminated with No. 25 steel Mueller clips. Anodic wires are terminated with 36mm steel alligator clips. These supplies can easily be obtained at most local hardware stores. All the clips are dipped in dilute hydrochloric acid for a short time to remove the zinc plating so that the zinc does not go into anodic dissolution and plate onto the specimen.

The specimen is suspended so that it does not touch the anode by securing the cathode wire to a dowel placed across the container. Only the steel Mueller clip of the cathodic wire is immersed in the electrolytic solution. This assures that the electrolytic solution will be free to circulate around the specimen and also keeps the copper wire out of the solution so that copper does not go into anodic dissolution and plate onto the specimen.

Various means were tested to keep the copper wire from coming into contact with the electrolyte. These included coating the wire with silicone sealant or petroleum jelly. Both attempts were found to be unsatisfactory and the simplest solution was to keep the wire out of the electrolyte. The electrolyte solution should cover the specimen and the steel clip up to the point just below where it attaches to the wire (Figure 2).

Figure 2. Close up of electrolytic reduction. A meteorite specimen is suspended in with only the Mueller clip of the cathode wire immersed in electrolyte. Note: Foam is normal and comes from H_2 and O_2 gas formed from the electrolysis of NaOH solution.

The electrolytic solution level is monitored closely and deionized water is added to replace any volume lost due to evaporation and electrolysis.

The terminal wires are connected to a DC power supply, in this case a battery charger, to provide the necessary current for chloride removal. Current is adjusted by the means of a ten amp 19.5 ohm variable resistor with a meter wired inline to monitor amperage. If the battery charger has a built in meter, it can be used in place of a separate amp meter. An electrolyte solution of 5% Rooto® Household Lye

Drain Opener (pure sodium hydroxide) is then added to the container, totally immersing the specimen (Figure 3). Purity of the lye was verified by the manufacturer and confirmed that it was 100% sodium hydroxide (*Caution*: many drain openers contain aluminum).

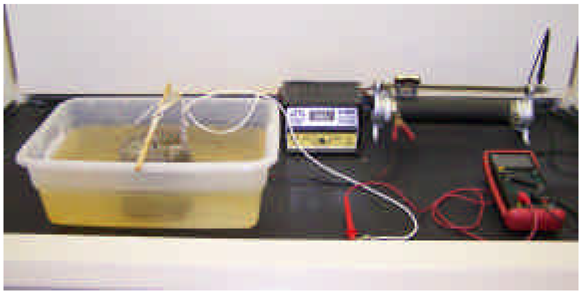

Figure 3. Electrolytic reduction set up. Battery charger provides DC power supply. Charger is wired to a variable resistor to control current and monitored by a volt/amp meter.

The surface area of the specimen is estimated from height, width, and length measurements and then current densities of 0.05 amp/cm^2 are used to provide optimum conditions for chloride removal without excessive development of hydrogen. High current densities (0.1 amp/cm^2) should be avoided as they encourage the vigorous evolution of hydrogen which can cause the corrosion to flake off and alter the shape of the specimen (Hamilton, D.L., 1988). High current densities also carry the risk of sealing off the object by depositing reclaimed metal to the specimen's surface, preventing the removal of deeply seated chlorides.

Chloride concentration monitoring of the electrolyte is accomplished by means of the potentiometric titration test using silver nitrate ($AgNO_3$). A 20 mL sample is taken from the electrolyte solution and placed in a 50 mL beaker with a stir bar. Using a pH/mV meter, the pH of the solution is reduced to 2.0 using 9M sulfuric acid. A silver electrode is placed in the electrolyte solution and the meter is set to read millivolts. The initial voltage is recorded and then 0.005M silver nitrate is titrated 0.5 mL at a time with the volume and voltage recorded at each aliquot until two clear potentiometric end points can be discerned.

The electrolyte is monitored with the chloride level calculated in parts per million (ppm). This is recorded and a graph is made showing the progress of chloride removal from the specimen. This allows for determination of when all detectable soluble chlorides have been removed from the specimen and also serves as a guide on when to change chloride-contaminated electrolyte.

After chloride concentrations level off, the specimen is removed from the container and washed several times with alternating rinses of boiling and cold deionized water. It is then placed in a final rinse bath of deionized water with the addition of sodium glucoheptonate to prevent rusting. The specimen should stay in this final rinse for a minimum of 24 hours. After this time, the rinse water is given a final qualitative test for chlorides. A 10 to 20 mL sample is placed in a clean test tube and acidified with several drops of 10 percent nitric acid. After mixing, five drops of 0.2 N silver nitrate ($AgNO_3$) are added and the test tube is held up to a black background with good side lighting. A white, milky cloud will be apparent if chlorides are present. If chlorides are detected, the specimen is returned for electrolysis or rinsed further until chlorides are removed and a qualitative test gives negative results.

The specimens are dried by placing them in ethanol for a minimum of 24 hours to ensure that all the water is removed from the specimen. The final step in preparation for specimens that have been cut is to etch the specimens. They are initially polished by sanding them with progressive grades of wet-dry sandpaper starting with 220 grit and finishing with 1500 grit. A solution of nitol (5% nitric acid and 95% ethanol) is brushed on the specimens until the Widmanstätten patterns showing the taenite and kamacite crystals appear. The specimens are subjected to a final rinse with deionized water and allowed to soak in ethanol for another one-two hours to dehydrate all traces of water. Drying is completed by placing the specimens in a low-temperature oven (110°C) for 24 hours and then allowing them to cool.

A protective coating of CMS 180W microcrystalline wax (Viachem, Ltd. Plano, Texas), is applied as a sealant. The wax is melted to approximately 175° C and the specimen is placed in the wax and allowed to remain until it no longer evolves bubbles indicating that the wax has penetrated the specimen. The wax is allowed to cool to 93-107° C before the specimen is removed. Cooling insures that the wax does not immediately run off the hot metal. Excess wax is wiped off with a rag. Steps can be taken to prevent further corrosion by placing desiccants with the specimen in a sealed container to remove humidity.

RESULTS

The concentration in parts per million (ppm) of chloride was monitored for each specimen with samples being drawn and tested every two days. When the chloride concentration leveled, and the electrolyte solution became excessively dirty, the electrolyte was changed and the process continued. As expected, chlorides leveled off at lower concentrations in the new electrolyte indicating chloride removal from the specimen was complete.

After electrolytic reduction was finished, each specimen was covered with a black residue which was easily removed by washing in deionized water and gently using a small wire bristle brush to reveal the metal underneath. Each specimen was then weighed a final time to determine mass lost during the electrolytic reduction process. The specimens were etched with nitol to reveal the Widmanstätten patterns and then sealed in microcrystalline wax.

Brenham Specimen

The Brenham (Kiowa County, Kansas) specimen weight before electrolytic reduction was 170.1 grams and heavily oxidized. Surface area was determined to be approximately 86 cm^2. Amperage was calculated at 4.3 amps and was held at this setting ± 0.5 amps for the whole run. Chlorides rose until peaking at 84 ppm on day 12 and remained constant until day 14 when the electrolyte was changed due to excessive contamination by corrosion that had come off the specimen. Starting with day 16, and all subsequent tests through day 22, chlorides leveled off at 13 ppm and remained there (Figure 4). Electrolytic reduction was stopped and a qualitative test using 0.2 N silver nitrate indicated an absence of chlorides.

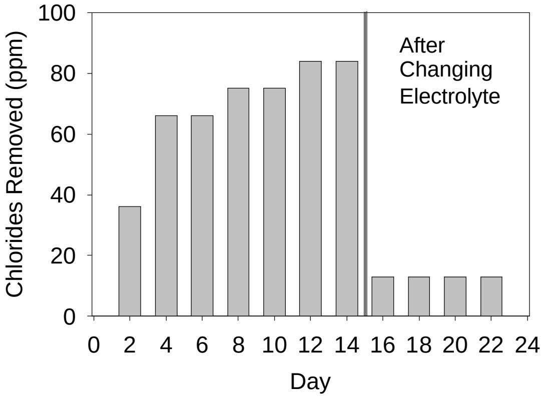

Figure 4. Chloride removal. Chlorides removed from the Brenham specimen measured in parts per million (ppm). Samples were tested every two days. After day 14, electrolyte was changed. Similar graphs were generated for each specimen.

Final weight of the specimen was 139.4 grams with 30.7 grams of oxidation removed during the electrolytic process for a loss of 18% of the initial weight of the specimen. Total time for the electrolytic reduction process was 22 days. However, chlorides were apparently removed within 14 days.

Campo del Cielo Specimen

A slice of the Campo del Cielo (Gran Chaco Gualamba, Argentina) specimen was cut from a larger specimen. The weight of the slice before the electrolytic reduction process began was 74.0 grams. Surface area was estimated at 43 cm^2. Amperage needed for optimum chloride removal was calculated at 2.2 amps and was maintained at this level ± 0.5 amps during the process. Chlorides leveled off at 22 ppm on day two and remained constant for 6 days. The specimen was removed from the electrolytic reduction, rinsed, and a qualitative test was conducted with 0.2 N silver nitrate. A milky opalescence indicated the presence of chlorides so the specimen was reintroduced to the electrolytic reduction process with new electrolyte solution. Chlorides leveled off at 16 ppm on day eight and did not rise again throughout the rest of the run. The electrolytic reduction process was stopped on day 14. A qualitative test was again conducted using 0.2 N silver nitrate and it indicated an absence of chlorides.

Final weight of the specimen was 70.5 grams with 3.5 grams of oxidation removed for a loss of 4.7% of the initial weight of the specimen. Total time in electrolytic reduction was 14 days.

Elyria Specimen

The Elyria meteorite (McPherson County, Kansas), weighed 423.1 grams before electrolytic reduction began. Surface area was determined to be approximately 142 cm^2. Optimum amperage was calculated at 7.1 amps. There was some initial confusion as the amp meter would blow a fuse when the optimum amperage was attempted to be maintained. It was soon discovered that the amp meter was set for alternating current instead of direct current. This was quickly remedied and the optimum amperage was adjusted and maintained at ± 0.5 amps during the rest of the process. Chlorides rose to a peak of 86 ppm by day six before the electrolyte was changed. The chlorides then rose slightly from 18 ppm by day ten, to 22 ppm by day 12 were it remained constant through day 20. A qualitative test using 0.2 N silver nitrate indicated an absence of chlorides.

Final weight of the Elyria specimen was 411.6 grams with 11.5 grams of oxidation removed for a loss of 2.7% of the initial weight of the specimen. Total time in electrolytic reduction was 20 days.

Nantan Specimen

A slice of the Nantan (Nandan County, Guangxi, China) specimen was cut from a larger specimen. Weight of the slice before electrolytic reduction began was 145.3 grams. Surface area was estimated to be 128 cm^2. Optimum amperage was estimated to be 5.3 amps and was maintained at ± 0.5 amps during the electrolytic reduction process. Chloride levels rose sharply to 124 ppm by day six and then remained constant until day 12 when the contaminated electrolyte was replaced. Chlorides rose to 9 ppm on day 14 and remaining constant until day 20 when the electrolytic process was stopped. A qualitative test using 0.2 N silver nitrate indicated an absence of chlorides.

Final weight of the Nantan specimen was 79.0

grams with a total of 66.3 grams of corrosion removed from the specimen. This amounts to a 45.6% decrease of the initial weight of the specimen. Total electrolytic reduction time was 20 days.

DISCUSSION

Both the Brenham and the Nantan specimens had considerable amounts of corrosion surrounding them before the electrolytic reduction process began. The Brenham specimen had a coating of corrosion approximately 1mm thick which was fully removed during the process leaving bare metal (Figures 5a and 5b).

Figure 5a. Severely oxidized Brenham specimen. Specimen was surrounded with approximately 1 mm of oxidation.

Figure 5b. Brenham specimen after electrolytic reduction. Notice oxidation has been removed in the process.

With the removal of oxidation, the crystalline structure of the taenite and kamacite can be observed in three dimensions.

The Nantan specimen had an outer layer of approximately 7-8 mm of corrosion that completely dropped off during the process with additional corrosion being removed from deep cracks within the specimen (Figure 6).

Figure 6. Nantan specimen after electrolytic reduction. Meteorite has been etched with nitol to reveal the coarse Widmanstätten lines.

The Elyria meteorite specimen had previously been cut and polished but over time had developed severe oxidized areas between the Widmanstätten lines (Figure 7). In addition, there was a coating of corrosion of 0.7 mm surrounding the exterior portions of the specimen (Figure 8).

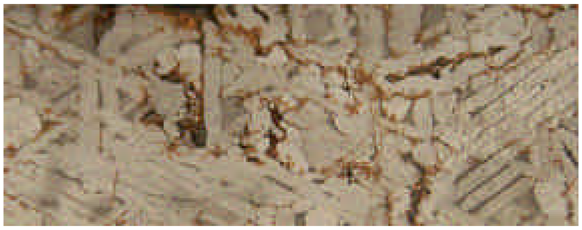

Figure 7. Close up of Elyria meteorite. Notice oxidation between Widmanstätten lines.

Figure 8. Oxidized Elyria specimen. Oxidation surrounds the edges of the meteorite and also infiltrates the Widmanstätten lines.

The corrosion on both the outer surface and the polished surfaces was removed in the reduction process leaving behind bare metal (Figure 9).

Figure 9. Elyria specimen after electrolytic reduction. Notice oxidation has been removed and no longer infiltrates between the Widmanstätten lines.

The Campo del Cielo specimen had the least amount oxidation surrounding it. During the process a coating of less than 0.2 mm was removed (Figure 10).

Chlorides were successfully removed from all four of the meteorite specimens as indicated by the qualitative tests using silver nitrate. The lengths of time needed to remove chlorides appeared to depend on the amount of chlorides present within the specimen and also the overall volume versus surface area of the specimen. In this research, it was observed that the specimens with higher amounts of visible oxidation correlated to a higher amount of chlorides present within them. These specimens took the longest time to reach stable chloride levels in the electrolyte.

Figure 10. Campo del Cielo specimen. Meteorite has been etched with nitol and reveals the coarse Widmanstätten lines.

Whole meteorite specimens, having a smaller surface area and a larger volume, will likely take a longer time for the chlorides to be removed (since they have to be pulled from deep within the specimen.) Additionally, those meteorites that have been in contact with chloride containing groundwater for long periods of time, as well as those that have been in groundwater that is highly concentrated in chlorides, will have accumulated more chlorides in them and it will take longer for the chlorides to be removed by electrolytic reduction.

As shown by this study, electrolytic reduction seems to be a low-cost and effective means to remove chlorides from iron-nickel meteorites, helping to stop and prevent further oxidation and can be of use to the museum curator and advanced collector to preserve specimens in their collections.

The materials used to set up an electrolytic reduction process can generally be obtained for less than $250.00 and found in most hardware and electrical supply stores. Larger meteorite specimens may require a regulated D.C. power source that can provide more amperage, resulting in a larger investment. However, after the initial cost input, the only required investment would be for consumables such as lye and expanded metal to fabricate the anode. With the cost of meteoritic specimens increasing, this is a small price to pay to preserve meteorite specimens in collections.

Additional work should be carried out on the effects of electrolytic reduction with pallasite (stony-iron) meteorites, especially the Admire and Brenham specimens from Kansas as they have the reputation of being notorious for rusting away.

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