NOTES for Collectors

A RUST REMOVAL METHOD FOR MINERAL SPECIMENS

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Rust is a general term describing various hydrated ferric (Fe^{3+}) oxides and hydroxides. It is without doubt the most common disfiguring coating found on mineral specimens. The ubiquitous nature of rust is not surprising considering that iron is the fourth most common element by weight in the earth's crust and is readily dissolved as ferrous (Fe^{2+}) ions and precipitated as limonite, the natural form of rust.

Mechanical methods of rust removal such as picking, brushing, airbrasing and so on are probably the safest methods but usually do not result in completely cleaned specimens. Chemical methods, although potentially more hazardous to specimens, tend to be more effective and easier to apply.

The problem of removing rust is found in nearly every area of conservation, and in several fields of science and engineering. Consequently, numerous methods for removing rust have been proposed. The methods used by most mineral collectors are those employing acids, especially organic acids such as oxalic. The efficacy of these methods relies on the increased solubility of ferric hydroxide in low pH (acidic) solutions and the ability of the anion to sequester ferric ions. The anion is that part of an acid molecule that becomes a negative ion in solution. Sequester means that one ion combines with a different ion to prevent it from behaving normally. In the example of oxalic acid, the oxalate ions combine with ferric ions to prevent the precipitation of ferric hydroxide. Unfortunately the major reason for the success of acid, rust removal techniques, that is the low pH, is also a cause of destruction for a wide variety of minerals.

In order to avoid acid attack on minerals rust may be dissolved in neutral solutions containing sequestering anions. Examples of this type of solution include neutralized sodium oxalate and neutralized ethylenediaminetetraacetic acid sodium salt (Na_x-EDTA). Unfortunately, these solutions are too slow in action to be of much practical use in mineral specimen preparation.

Much faster and safer rust removal techniques are possible if advantage is taken of the fact that ferrous hydroxide is not only much more soluble than ferric hydroxide but is appreciably more soluble over a wider pH range. One method which utilizes this advantage is that described by Mehra and Jackson (1958) for the removal of free iron oxides from soils. An adaptation of their method is described below.

Three sodium salts are employed in this technique: sodium citrate (Na-Citrate), to sequester ferrous ions; sodium dithionite ($Na_2S_2O_4$), to reduce ferric to ferrous iron; and sodium bicarbonate ($NaHCO_3$), as a buffer to maintain pH near the optimal value of 7.3. Because $Na_2S_2O_4$ is oxidized in solution, the formulation cannot be entirely premixed and stored, but it is convenient to keep the Na-Citrate and $NaHCO_3$ as a stock solution. This is prepared by dissolving 71 g Na-Citrate and 8.5 g $NaHCO_3$ in 1 liter of water.

The specimen to be treated is placed in the smallest available beaker or jar into which it fits safely. A premeasured volume of the stock solution, enough to cover the specimen, is then poured into the beaker. Next, 1 g of $Na_2S_2O_4$ for each 50 ml of stock solution used is added. For example, if 300 ml of the stock solution is used, 6 g $Na_2S_2O_4$ should be added. 50 ml of stock solution is capable of dissolving about 0.5 g of ferric oxide (Jackson, 1956), consequently the volume of solution required to cover a specimen often exceeds that required to dissolve all rust present. It is then possible to dilute the solution by as much as 2 parts water to 1 part solution and still achieve satisfactory results. Solutions diluted more than 2:1 tend to lose their ability to buffer, therefore they should not be used to treat pH sensitive minerals.

If convenient, some automatic means of stirring may be provided but this is not strictly necessary as one minute of hand stirring every thirty minutes is usually sufficient. Using an ultrasonic cleaner to agitate the solution shortens treatment time somewhat but the bath water should be cooled regularly to prevent excessive heat build-up. Most specimens treated to date have been cleaned in 4–8 hours, although the solution will remain active for about 12 hours. After 12 hours the $Na_2S_2O_4$ will be completely oxidized and, if rust remains, the treatment must be repeated with fresh solution.

Following treatment the specimen should be set in distilled water to rinse. The amount of rinsing necessary varies considerably from one specimen to another. For most specimens, which do not contain numerous micro-fractures and are not highly porous, changing the distilled water 3 times at 12-hour intervals is usually sufficient.

When this method was first developed it was employed as a twenty-minute treatment at 80°C. Sheldrick and McKeague (1975) have since shown that the 12-hour treatment at room temperature is equally effective for soil samples. For mineral specimens the room temperature treatment is not only as effective as the 80°C treatment but also has several advantages. The most significant of these are the reduced risk of thermal shock and the reduced extent to which soluble salts are drawn into microfractures. As well, temperatures slightly above 80°C can lead to precipitation of sulfur and ferrous sulfide on the specimen (Jackson, 1956).

In addition to removing rust stains and coatings this method is useful for macerating rust-cemented matrix and dispersing many clays and soils adhering to specimens. Some of the mineral species, from which rust has previously been difficult to remove, that can be successfully treated with this method include whiteite, siderite, rhodochrosite and apatite. Species that cannot be treated with this method include all appreciably soluble minerals and calcium minerals which are slightly soluble, such as calcite and messelite. The reason for the solution of many calcium minerals is that citrate sequesters calcium as well as ferrous ions. The search for a useful sequestering agent for iron which does not affect calcium minerals is still going on in this and other laboratories (Lewin and Rock, 1976).

As with any chemical treatment there are several general rules to be followed: 1) whenever possible quality specimens should *not* be treated until trials have been made on inferior specimens from the same locality. If inferior specimens are not available, a trial can often be made with small representative fragments picked from inconspicuous places on the specimens; 2) careful examinations of treated specimens should be made one week, one month, six months and one year following treatment to ensure that specimens are stable; 3) it is most important that details of treatments be recorded and kept with other specimen information.

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