

MANGANESE STAINING: PREVENTION AND CONTROL

Introduction

Manganese stain is a brown or tan-colored deposit that remains on the surface of clay masonry after being dissolved by an acid and transported through the brick pores. Such deposits appear on the face of the brick (as shown in Photo 1) or in the mortar joints (as shown in Photo 2). Manganese stains on brick masonry primarily occur when an unbuffered acid such as hydrochloric (muriatic) acid is used to clean the brick, an incorrect cleaning agent is applied, or the cleaning manufacturer's instructions are not followed. These stains can be prevented by adhering to proper brick cleaning methods and are usually removed through the use of a proprietary cleaning product.



Photo 1: Manganese Stain on Brick



Photo 2: Manganese Stain in Mortar Joints

Formation of Manganese Stains

Manganese coloring agents are often added to clay brick units during the manufacturing process to darken the color. When fired, the coloring agents will undergo several chemical changes that produce various shades of brown or black in brick units.

For most manganese stains, there are three simultaneous conditions that must exist for them to occur:

- A soluble material/compound
- A solvent/liquid to dissolve the soluble material into solution
- A pathway/pore structure for the solution to reach the brick surface

In most cases, stains that appear on brick consist of water-soluble compounds. However, manganese stains consist of compounds that are soluble in acid, not water.

In a recent study conducted at the National Brick Research Center (NBRC), brick were partially submerged in either distilled water or unbuffered hydrochloric (muriatic) acid (Photo 3). After exposure, the amount of soluble material in solution was determined for each brick unit (Figure 1), and their appearance was observed (Photo 4). For the brick exposed to distilled water, minor efflorescence was observed, as shown on the right in Photo 4. None of the manganese in the brick dissolved when exposed to distilled water, and no manganese staining was observed. However, brick that were exposed to unbuffered hydrochloric (muriatic) acid dissolved the manganese and iron and took it into solution. The manganese and iron then migrated to the surface and left a dark-colored stain, as shown on the left in Photo 4. While it was found that the solubility of the different unfired manganese compounds varied, the study concluded that for certain types of fired brick, exposure to hydrochloric (muriatic) acid, not water, consistently dissolves manganese and iron. As a result, removing or reducing the acid solvent can be an effective method to reduce or prevent stains in brickwork.

Staining is not the only consequence of exposure to unbuffered acids. The resulting leaching of manganese and iron can also erode or etch the surface of the brick and alter or remove any finishes or sheen, causing



Photo 3: Brick Units Partially Submerged in Water (top left) and Hydrochloric Acid (top right)

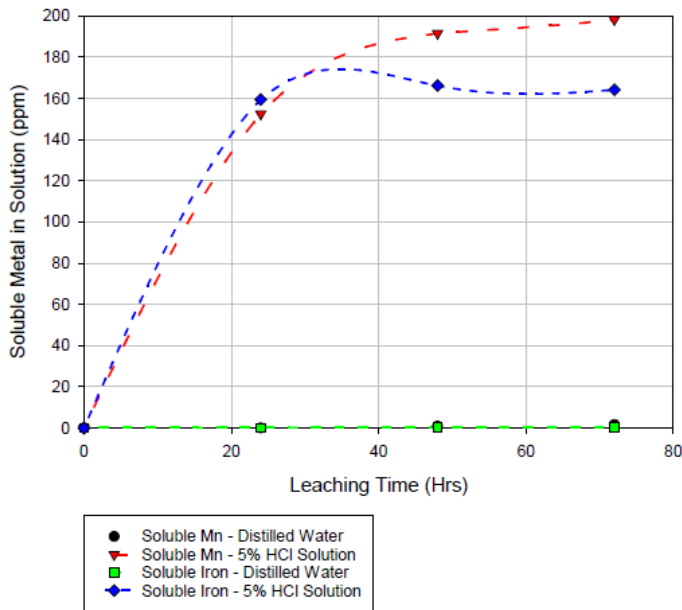


Figure 1: Amount of Soluble Manganese and Iron in Solution

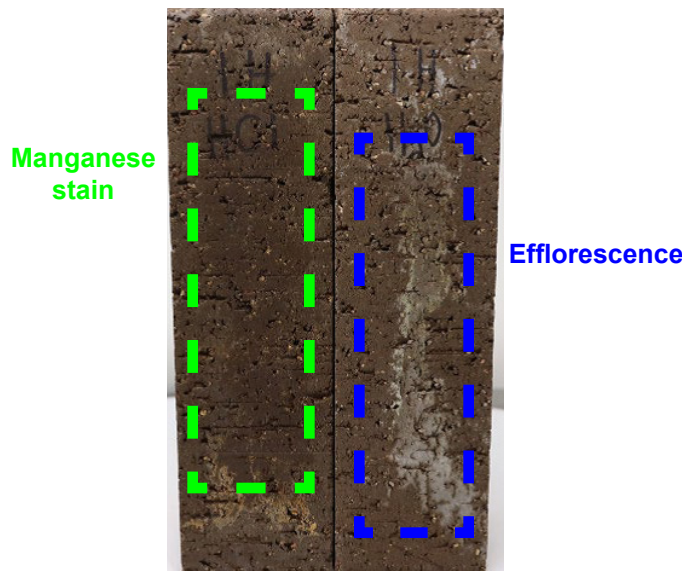


Photo 4: Manganese Stain vs. Efflorescence

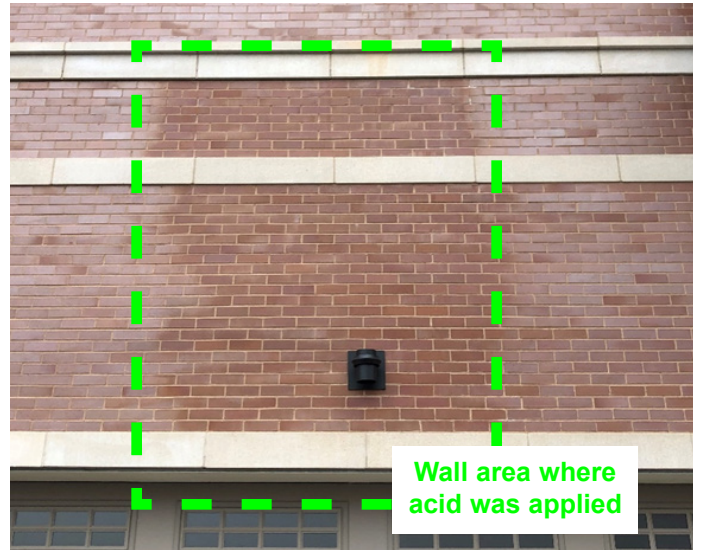


Photo 5: Acid Etched Brick and Removal of Sheen

permanent damage to the brick or the mortar joints (Photo 5).

Sources of Acid that Lead to Stains or Damage

Exposure to acid occurs via a variety of situations:

- Cleaning
 - Using unbuffered acids or other improper cleaning products
 - Not following brick manufacturer and/or cleaning product manufacturer recommendations for cleaning products and procedures
- Architectural precast concrete panel fabrication
- Exposure to corrosive environmental conditions such as acid rain

Cleaning. The most likely exposure to unbuffered acid occurs during the cleaning of brickwork, which is why it is critical to strictly follow the recommendations provided by the brick manufacturer and the cleaning product manufacturer. Others outside the masonry industry recommend using diluted hydrochloric (muriatic) acid for cleaning, with which BIA strongly disagrees, due to the potential for staining and damage as described herein. Contemporary cleaning products intended for use on masonry may contain acids, but they are formulated with other chemicals (buffers) to make them safer for use on brick. Be aware that some cleaning products contain compounds that will convert to a strong acid when combined with water. Review the cleaning product safety data sheet, and avoid using products that contain these compounds.

Even if the correct cleaning product is selected, not following proper cleaning procedures can also lead to damage and staining. BIA *Technical Note 20* includes specific information on proper cleaning methods and procedures for brickwork and should be consulted in combination with available brick manufacturer and

cleaning product manufacturer recommendations. Prior to cleaning, the brickwork should be thoroughly saturated with water to keep it from absorbing the cleaning product. After cleaning, the wall should be thoroughly rinsed to ensure that all the cleaning product was removed; otherwise residue remaining in the pores of the brick can lead to staining and damage.

Architectural Precast Concrete Fabrication. Brick embedded in precast concrete panels could be exposed to unbuffered acids as part of the precast concrete fabrication process, as shown in Photo 6. Precast concrete panel manufacturers will often use an unbuffered acid or diluted acid solution on a concrete panel to clean form liner leakage on embedded brick, to create a consistent look for the joints, or to create a “sugar cube” or “sparkle” finish surface effect.

It is important to note that concrete and brick behave very differently when hydrochloric acid is applied. For concrete, the acid dissolves the calcium-rich cement paste, which allows for the removal of any unwanted material. This is an acid–base chemical reaction, which results in neutralizing the acid, leaving only a soluble calcium salt and water. This neutralization does not occur when acid contacts brick. Consequently, the acid can etch the surface and/or absorb into the pores of the brick, causing permanent degradation of the appearance of the brick in some situations. In cases where the acid has been absorbed deeply into the pores of the brick, usually due to the lack of proper pre-wetting, the reaction of the acid can continue to cause damage to the brick for a long period of time.

Another potential source of stains in the process may occur when the concrete panels include a colorant or pigment. When cleaning the panel with an unbuffered acid, the colored concrete paste can be dissolved and become a residue that is deposited in the mortar joints or on the brick surface, resulting in stains.

To mitigate the potential damage caused by acid etching, some precast manufacturers will saturate the panel with water before and after applying the acid. However, this may only limit the amount of acid absorbed by the brick in the panel, and staining could still occur. Therefore, it may be necessary to test different dilution ratios of the acid solution on a sample panel prior to full-scale application to ensure that staining or damage to the brick do not occur.

Corrosive Environmental Conditions. Because the amount of acid needed to dissolve manganese and iron varies, in some cases moisture sources such as acid rain, wastewater or proximity to industrial facilities are sufficient to cause staining.



Photo 6: Applying Acid to Brick Embedded in a Precast Concrete Panel

Prevention

When cleaning brick masonry, do not use an unbuffered acid. Improper cleaning with an unbuffered acid, like unbuffered muriatic acid, will result in staining of and damage to the brick units and mortar joints. To ensure that proper cleaning methods are being implemented, strictly follow the cleaning recommendations provided by the brick manufacturer. In addition, explicitly follow any cleaning instructions provided by the cleaning product manufacturer. Table 1 provides a select list of proper and improper practices to implement when cleaning brick that contain manganese compounds. Please refer to BIA *Technical Note 20*, “Cleaning Brickwork,” for additional recommendations for cleaning brick masonry.

Removal or Correction of Manganese Stains

In all cases, attempt to remove manganese stains only after all residue that caused the stain has been removed from the brickwork. If the residue is not fully removed, the stain will likely reoccur when it is brought to the surface of the brickwork. If the staining is not widespread, spot cleaning is acceptable and cleaning the entire wall is not required.

TABLE 1:
Cleaning Do's and Don'ts for Brick That Contain Manganese

DO: Strictly follow cleaning recommendations from the brick manufacturer, when provided. Explicitly follow cleaning instructions provided by the cleaning product manufacturer.	DON'T: Use unbuffered acids, including hydrochloric (muriatic) and hydrofluoric.
DO: If the brick are tan, brown, black or gray (colors most likely to contain manganese), use proprietary cleaning products intended for brick of that type.	DON'T: Use generic cleaning products.
DO: Thoroughly pre-wet the wall before cleaning.	DON'T: Allow cleaning product to be absorbed by the brick.
DO: Thoroughly rinse the wall after cleaning.	DON'T: Allow runoff to be absorbed by brick under the area being cleaned.

In certain conditions, it may be possible to remove mild cases of manganese staining when the affected brickwork is flooded with water or exposed to weather over a long period of time. However, in most cases, a proprietary masonry cleaning product specifically formulated to remove metallic stains is required to remove discoloration from manganese compounds. To determine which cleaning product or method is acceptable, refer to the brick manufacturer and the cleaning product manufacturer for their recommendations.

Where manganese staining occurs on brick masonry that has been painted, the stain is usually trapped behind the paint film on the surface of the brick. When this occurs, removal of the paint may be required to clean the stain. Proprietary paint removers formulated for application to brick masonry are the most effective at softening or dissolving paint for removal with a stiff bristle brush and water. For more information on removing paint, please refer to the BIA *Technical Note* 20, "Cleaning Brickwork."

In cases where contact with an unbuffered acid etches the brick and removes the finish or sheen from the face of the brick, professional brick staining will be required to restore the appearance of the brick. Brick staining is an accepted industry practice that involves applying ceramic stains and pigments that are absorbed into the brick, resulting in a colorfast, durable finish. For more information on staining, please refer to the BIA Brick Brief "Modifying the Color of Brickwork with Brick Stain."

Removal and replacement of brick combined with repointing of adjacent mortar joints can also be an option to correct conditions with etching and other finish damage, as well as severe stains that are resistant to additional cleaning.

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