



# Limestone



**Restoration  
Graffiti Removal  
New Construction**

SAFE, SIMPLE AND <sup>HIGHLY</sup> PROFITABLE



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# Limestone Restoration

The restoration cleaning of limestone has traditionally been a hunt and peck type of search for the appropriate products. Standard HF restoration technology has not been functional because the fluoride ion has such an affinity for calcium that it can never be removed and it initiates a cycle of degradation that is virtually impossible to halt. Even the safer “fluoride salt” products have this residual problem. Further complicating this issue is the porosity of the stone and its tendency to develop deep stains of two distinctly different natures. The first is environmental staining relating principally to urban pollution and its reaction to the calcium. This usually results in black streaks or black crust. The second problematic set of stains is from humidity and heat which results in mold or mildew related shadows deep in the stone. We have developed two easy-to-use products that are almost one hundred percent effective. The only situation where this chemistry has not proven effective is when abrasive blasting has damaged the limestone. This process seems to open the stone in such a fashion that the chemical cleaning process has no chance to be successful. We strongly advise against abrasive blasting of any kind of stone or brick.

## SafeRestore on Limestone

*Application:* Apply the product to the surface by brush or spray. Lightly prewet the surface before application. In difficult staining situations we have seen greatly improved release of deep staining both biological and pollutant with a double application of the product without rinsing in between. This allows a penetration of the stain followed by a release.



Limestone restoration at the Monroe County Historical Society's building in the heart of Indiana's limestone country. The area of black in the arch is not yet rinsed, but has been treated with SafeRestore.



Professionally restored century and a half old imported French Limestone fireplace surround.



The same surround cleaned with SafeRestore by mason's apprentice. The job was done by hand and rinsed with a damp cloth.

*Dilutions:* Dilutions will vary from a straight on straight without a rinse in between to a 10-1 dilution for light clay staining or light urban dirt.

*Removal:* Rinse with high or low-pressure taking care not to etch the surface with the pressure. It is recommended that you use a nozzle of 25° or greater at all times.

## Stripper Cream on Limestone

*Application:* Apply the product to the environmental pollution stains

by roller or spray. Spraying should be confined to areas with limited

danger of damage from the caustic. Prewet the surface lightly before application. Do not apply the product too thin. There must be adequate thickness of the stripper to allow total soaking with the caustic.

*Dilutions:* Generally the product is applied undiluted to the staining on the black crust and may be diluted up to 4-1 on mineral stains that are not dimensional on the surface.

*Removal:* Rinse with a pressure washer, being careful not to harm the surface.



Black crust that was 1/4" thick removed from the Cathedral of Learning at the University of Pittsburgh with one application of Stripper Cream in one hour.

## Graffiti on Limestone

A very common problem on limestone is the removal of graffiti shadows from limestone. While we have specific graffiti removal products, we prefer the use of Stripper Cream in this application. One reason is the cream has proven it will not change the color of the stone or damage the structural quality of the stone. A second is that Stripper Cream has proven effective at removing shadows of almost all paints from porous surfaces such as limestone, concrete block, mortar joints, or concrete.



Before and after of graffiti removed from porous concrete block wall leaving no shadow.



Limestone at Ohio State University's Administration building cleaned with Stripper Cream after a graffiti attack.

*Application:* First, adequately prewet the wall and then roll in the Stripper Cream. Prewetting can be done best with a pressure washer. This done to create a reaction medium for the caustic in the stripper. The stripper will create heat. Rolling or brushing the stripper on helps push it into the interstitial pores of the stone and begins the reaction with the water to increase the speed of removal.

The stripper may be sprayed on and this would prove beneficial if there was a very large area to be covered and very little protection required.

*Dilution:* At higher temperatures, higher dilutions of Stripper Cream may be appropriate. The contractor should rely on either experience or test patches to determine how far the product can be diluted and still be effective. Always bear in mind that it is much more expensive to redo work because of not allowing adequate dwell time or over-diluting product than it is to do the job right once.

*Removal:* Before actual removing, low pressure water should be sprayed on the area and color run should be observed. If the shadow does not release with low pressure, do not proceed. Reapply in this rinsed area and allow longer dwell time. If adequate color run is observed, begin pressure wash rinsing. Pressure from 700 to 3000 PSI is appropriate, but never use a nozzle of less than 25° and *care must be taken to not apply too much pressure if the shadow is not released.* Repeat the chemical application or switch to Graf-Ex or Stripsol, whichever is best to remove any paint that Stripper Cream does not remove.

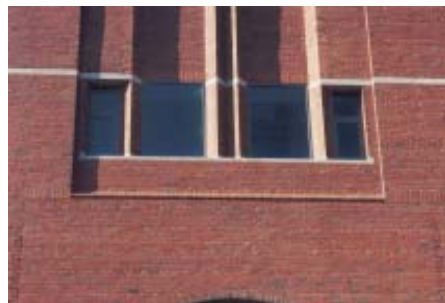
## New Construction

The general problems associated with limestone in new construction clean-up have all been solved just by the use of NMD80. Mortar smears, clay stains, rust, tannic acid stains and biological stains are all generally removed easily by the “80”. SafeRestore quickly removes any subsequent discoloration that occurs because of bad water or minerals in the limestone.

*Application:* We recommend a complete but lightweight prewetting of the stone followed by a spray on application of NMD 80.

*Dilution:* We have exposed historic register limestone buildings to up to four repeat straight applications of NMD 80 with no detrimental effect, so dilution is not critical. Recommended dilution is between 4-1 to 7-1 depending how much mortar smear is on the stone.

*Removal:* Care should be taken to apply the product on the surface evenly and rinse evenly. Nozzle degree should not be less than 25° and care should be taken to not get close enough to etch the surface with the pressure.



NMD80 used on Federal Courthouse in Boston. No limestone or granite had to be covered



One of the buildings at the newly constructed Federal Fish & Wildlife Management College in Shepherdstown, WV. The building's many different stones, bricks, blocks and limestone were cleaned with NMD80.

# Myth and Facts concerning use of Hydrochloric Acid on Limestone

The following article will be presented in paragraph form. The purpose is to try to clear up some common misconceptions concerning the use of Hydrochloric Acid. The Indiana Limestone Institute literature states that “special consideration and protection shall be provided when brickwork is cleaned above the limestone. Strong acid compounds used for cleaning brick *will* burn and discolor limestone. Use of sandblasting, wire brushes or acids will only be permitted under special circumstances, approved by an architect.”

This is a common misconception that any product that lists Hydrochloric Acid (HCl) as one of its ingredients should automatically be banned for use on Limestone because it should be interpreted as a strong acid and would do the type of damage indicated in the statement issued by the Indiana Limestone Institute. This statement would be true if using the HCl in its raw state. Modern limestone cleaner formulations have been blended and compounded to successfully incorporate HCl without these adverse effects on the limestone. EaCo Chem’s product SafeRestore is a product which falls under this classification. Throughout the country, SafeRestore has successfully been used to clean historic limestone as well as buildings that have limestone on their windowsills or as one of their components. Partial lists of these buildings along with photos have been prepared and are enclosed. Our new masonry detergent, NMD 80, which contains four times the amount of hydrochloric acid as SafeRestore, has been used to clean new and historic buildings that also contain limestone as a component of their windowsills. A second look at these buildings shows no apparent etch or discoloration to the limestone which would be apparent if raw HCl had been used instead of our blended product. Typically limestone will etch when it comes in contact with hydrochloric acid. This “etch” is apparent by the reaction on the surface of the limestone listed below.



*Note: CaCO<sub>3</sub> is Calcium Carbonate, one of the main components of limestone.*

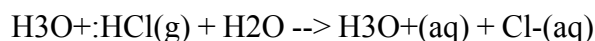
*Quick Chemistry lesson concerning this reaction:*

*Acid - base reactions are always proton transfers between conjugate pairs. Under the classical Arrhenius definitions, reactions of acids with bases always form water because  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ .*

*The proton transfer reactions of aqueous acids and bases are generally rapid and take the place stoichiometrically whenever possible. In all cases, the reaction proceeds from strength to weakness, in that the resultant acid and base is always weaker than the species from which it originated. A strong acid reacts with a weak base to yield the weak acid, which is the conjugate acid of the weak base.*

SafeRestore lists hydrochloric acid on its MSDS because it is the only hazardous ingredient added to the blend. It does not exist in its raw state once the product has been completely blended. We have provided an explanation to what happens specifically to HCl when placed in a solution where the main ingredient is water. The water will be listed as a solvent at this point to fully explain the nature of this basic reaction. Keep in mind that the product SafeRestore contains many other ingredients that will produce a molecule at the end of the reaction that will depict what is listed here. The purpose of this discussion is to prove chemically that HCl is not in its raw state when combined successfully with other ingredients and our compounded product which has undergone a leveling effect will not produce the type of adverse reactions listed initially by the Indiana Limestone Institute.

In any solution the solvent is always the substance present in the largest amount. If the solvent contains ionizable protons it is said to be protonic, and if it is protonic, it will engage in acid-base reactions. Many solvents are protonic, including water, liquid ammonia and glacial acetic acid. A protonic solvent is often amphiprotic, like water, and engages in acid-base reactions. When an acid which is stronger than the conjugate acid of water, such as hydrochloric acid, is added to water the stronger acid will react with water to give the weaker acid which is the aquatic proton or hydronium ion.



All acids which are stronger than the hydronium ion will react with the essentially limitless supply of water to quantitatively produce hydronium ion, and so their strength will be leveled to that of the hydronium ion. This **leveling effect** is the reason why, in aqueous solution, the strongest acid which can exist is the hydronium ion. All others will be leveled to the hydronium by reaction. In aqueous solution hydrochloric acid, sulfuric acid, perchloric acid, and nitric acid are all equally strong.

The leveling effect operates in any protonic solvent. In liquid ammonia, for example, all acids are leveled to the strength of the ammonium ion,  $\text{NH}_4^+$ , and all bases are leveled to the strength of the amide ion,  $\text{NH}_2^-$ . Many of the acids which are weak in water act as strong acids in liquid ammonia because they are stronger than ammonium ion.

Glacial acetic acid is another protonic solvent in which the leveling effect takes place. Glacial acetic acid can be used to show that hydrogen chloride is weaker acid than perchloric acid, since hydrogen chloride behaves as a weak acid in glacial acetic acid. Methanol is also a protonic solvent in which some of the acids are strong (completely dissociated) in water are found partially in molecular form. The end reaction indicates what components are left in their raw (or unreacted) state.

SafeRestore does not cause discoloration or etch on limestone when used properly. EaCo Chem is providing a blended product that contains hydrochloric acid without the adverse effects that are typical of the raw material when used. It is just one of the many components of this product and this is why we feel it is appropriate to evaluate this product on performance and safety issues not on one of its raw materials because in the product's finished state, the problems associated with its use do not exist.

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