






## Solubility study of aerosols and vinyl paint on stone surfaces

## Estudio de solubilidad de aerosoles y pintura vinílica en superficies pétreas

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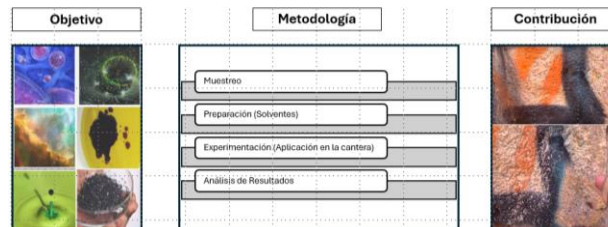
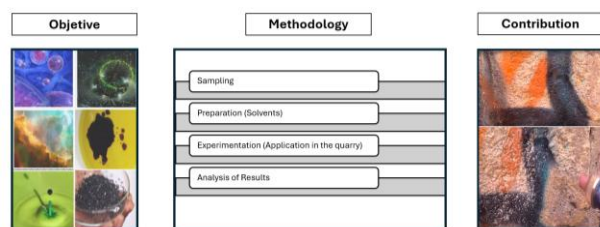


## Abstract

Due to the existing needs, presented by the current state of conservation of the stone surfaces in ashlars of historic buildings in the city of Zacatecas, the conservation area of the INAH Zacatecas center will receive trained personnel to carry out the study of elements used in the removal of paint on stone surfaces, specifically pink quarry. This analysis seeks to provide solutions that allow the safeguarding of materials in conservation processes, facilitating the work to compensate for damages that are generated after anthropogenic activities of any kind. In the study, solutions were found that facilitate the elimination of products manufactured from alkenyl functional groups and acrylic functional groups, establishing the elimination parameters from pure substances and the elimination from specific colloidal systems.

## Resumen

Debido a las necesidades existentes, que presenta el estado actual de conservación de las superficies pétreas en sillares de inmuebles históricos de la ciudad de Zacatecas, el área de conservación del centro INAH Zacatecas destino personal capacitado para llevar a cabo el estudio de elementos empleados en la eliminación de pinturas en superficies pétreas, específicamente cantera rosa. Se busca con este análisis se puedan dar soluciones, que permitan la salvaguarda de los materiales en los procesos de conservación, facilitando los trabajos de resarcimiento de daños que se generan tras actividades antropogénicas de cualquier índole. En el estudio se encontraron soluciones que facilitan la eliminación de productos fabricados a partir de los grupos funcionales alquénicos y los grupos funcionales acrílico, estableciendo los parámetros de eliminación a partir de sustancias puras y la eliminación a partir de sistemas coloidales específicos.



## Quarry, Solvent, Cleaning

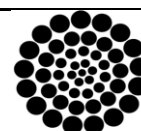
## Cantera, Solvent, Limpieza

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## Introduction

In this work, the use of colloidal systems was proposed for cleaning slogans and insignia after anthropogenic activities on the surfaces of historical buildings. An important part of this research consisted of the capacity of the gelling agents available in the laboratory for the preparation of gels. of the reagents used in cleaning. We sought to define the efficiency of the gels and their performance, in order to reduce costs in conservation processes. At the same time, carry out experimental processes of commercial gelling agents in the compatibility of the thinner, since, according to analyzes carried out, it is the most used solvent in the graffiti removal process, as well as the most economical solvent on the list of solvents. tested in the solubility triangles.

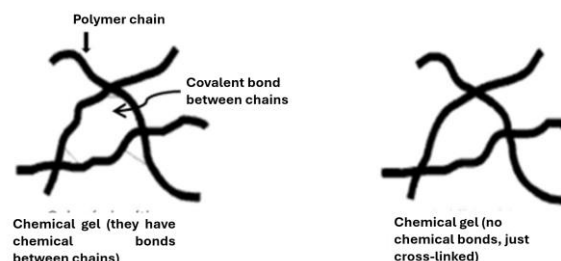
Polymeric solids are especially suitable for forming gels thanks to their long chain structure. The flexibility of these chains makes it possible for them to deform to allow the entry of solvent molecules into their three-dimensional structure.

Gels can be classified into two types, depending on the nature of the connections of the three-dimensional network that constitute them.

**Chemical gels:** are those in which the network is formed through covalent bonds. This type of bond is very strong and its breakdown leads to degradation of the gel. For this reason, it is said that chemical gels are not reversible with temperature; once the bonds are broken, they cannot be re-formed. This type of bonds gives rise to a gelation process.

**Physical gels:** present a three-dimensional network formed by joints that are not completely stable, but are associated with a bond  $\leftrightarrow$  non-bond reaction, which can occur in both directions. Generally, the bonds are of the Van der Waals type, much weaker than covalent bonds.

## Box 1



**Figure 1**

Physical and chemical colloidal systems

With regard to swelling, the essential difference between cross-linked and non-cross-linked polymers is that, in the former, the entry of solvent is not capable of separating the macromolecular chains that form the gel because they are covalently linked, while in the In physical gels the solvation mechanism can unravel and separate from each other as solvent entry into the macromolecular network progresses. This entry reaches a limit or maximum degree of swelling since the covalent structure cannot deform indefinitely. (UNISON, s/f)

A physicochemical system composed of two phases: one continuous, normally fluid, and another dispersed in the form of particles; usually solid, microscopic in size. Gels are semi-solid forms formed by a solvent thickened by the addition of substances of a colloidal nature.

Although the colloid par excellence is one in which the continuous phase is a liquid and the dispersed phase is composed of solid particles, colloids can be found whose components are in other states of aggregation:

## Box 2

**Table 1**

Types of colloids according to the state of their continuous and dispersed phases

Continuous phase	Dispersed phase		
	Gas	Liquid	Solid
Gas	It is not possible since all gases are soluble in each other.	Liquid aerosol Example: Fog, mist	Solid aerosol Example: Smoke, suspended dust
Liquid	Foam Example: Shaving foam	Emulsion Example: Milk, sauce, mayonnaise, blood, hand cream	Colloidal Dispersion Example: Paints, Chinese ink
Solid	Colloidal Dispersion Example: Solid foam, pumice stone, Aerogels	Gel Example: Gelatin, jelly beans, cheese	Solid sol Example: Ruby Crystal

The use of gels, packs or dressings implies the use of a supporting material that reduces subsequent mechanical action.

It allows you to control the amount of the selected cleaning agent and prolong contact times with the wall. Thickeners such as cellulose ethers, agar-agar, carbogel or carbopol are macromolecular substances that, when mixed with organic solvents or water, generate highly viscous solutions. For their part, the supports or supports do not form true gels, but rather pastes or emulsions.

The supports are inert and among the most used is cellulose pulp, it is composed of pure cellulose fibers of different lengths. Among the absorbent clays used, there is sepiolite and attapulgite.

Colloidal or micronized silica also stands out as a support. In addition to the wax that can be used to generate stearic emulsions called pappina, there is Japanese paper that, on many occasions, is also used as an intermediate layer between another support and the work to avoid residues of the second.

Gels are formulations that consist of a solvent or mixture of solvents and a thickener that gels the solution. Thanks to the high viscosity of the system, the penetration of the components into the pictorial layer is limited and controlled, allowing controlled contact for a certain time.

Carbopol produces carboxylate ions (COO-) that can complex certain bivalent and trivalent ions such as calcium or magnesium present in wall paint. If this reaction occurs, Carbopol becomes insoluble in water and can present a clear rinsing problem. It is established that due to this ionic character, it should not be used on surfaces that contain humidity or high pH such as wall paints.

In their study, Carlon and Petersen (2019) carried out artificial aging tests on seven different surfactants. The result is that Ethomeen C12 breaks down over time into small volatile molecules and after 36 hours of artificial aging, no traces or damage to the paint are detected. As for Ethomeen C25, its presence is reduced by 60% during the first 48 hours. Being, together with Agar, the best gelling agent for use in cleaning stone supports.

### Pink quarry

The understanding of the intervention processes requires material knowledge of its elements, compounds and the understanding of the physical, chemical and mechanical phenomena that are required for the task, in the case of this series of characterization of materials for the removal of paint from spray graffiti and vinyl paint is based on knowledge of the material you want to clean, pink quarry.

Rocks are divided into three different groups: igneous, sedimentary and metamorphic.

- **Igneous Rocks:** They are formed by the cooling and crystallization of magma, forming hard and firm rocks. Within igneous rocks there are extrusive and intrusive rocks.
- **Extrusive:** They are formed when lava cools on the outside of the Earth's mantle or when pyroclastic material is also expelled, such as; glass, ashes and slag consolidate and cool outside.
- **Intrusive:** They are formed when magma solidifies within the Earth's crust, leaving the rocks buried.
- **Sedimentary Rocks:** They are formed by the fragmentation or erosion of igneous rocks. The fragmentation of these rocks is known as sediments, these are continuously deposited in a single place where they are compacted and carry out lithification processes, forming sedimentary rocks.
- **Metamorphic Rocks:** They are formed by the burial of sedimentary rocks in the Earth's crust, being affected by agents of metamorphism, transforming into metamorphic rocks. Extrusive igneous rocks of pyroclastic material form rocks with a microcrystalline texture, which are called tuffs.

The pink volcanic tuff, cantera ignimbrite, is a stone abundant in pumice, quartz and sanidine phenocrysts, it is pinkish in color and is very abundant in the geographical area of San Luis Potosí, Zacatecas, Guanajuato and Morelia.

The abundance of pink quarry allowed it to be one of the main construction materials, it is present in historical monuments, colonial centers, and in artistic manifestations. However, tuffs are very susceptible to deterioration or alteration of their physical-chemical properties, if are exposed to the elements. Some of the main causes of damage to stone material are strong wind currents, natural light, high temperatures, in conjunction with relative humidity. (Pedroza, 2019)

Moisture, whose presence may be due to rain, condensation or capillary rise, plays a key role in the degradation of porous materials, being directly or indirectly responsible for various decomposition processes, such as freeze-thaw cycles, salts soluble substances, crystallization cycles, biological growth, chemical attack by acid from rain and wind erosion.

Atmospheric movement and humidity have negative effects on conservation. Wind can cause extensive damage to soft rock due to the particles it carries, while changes in temperature and frost can cause fragmentation and splintering in wet environments creating internal stresses. While the polluted atmosphere causes deterioration of the rock in the form of chemical dissolution with the effect of water and organisms (lichens, fungi, bacteria and moss), thin layers of dust that cover the rock generally accumulate and form layers that affect to the entire rock structure.

## Background

Molina (2016) studied Intelligent and non-invasive methodologies using nanotechnology for the maintenance, conservation and restoration of heritage buildings. concluded that the treatment of heritage buildings with nanocomposites allows for more efficient maintenance of them and contributes to their conservation.

Morales (2024) evaluated three types of surface coatings applied to quarry stone samples: a coating based on calcium hydroxide, and two commercial coatings based on organosilicon. Surface color of the quarry, water absorption by capillarity and contact angle monitoring were analyzed before, during and after exposure to chemical and natural deterioration.

Di Napoli et al. (2024), carried out a conservative restoration intervention, the structural consolidation and security of the monumental staircase on the Po River side, the restoration of the plaster and the review of the architectural finishes of the castle façade. The methodology chosen based on historical research, physicochemical analyzes of materials and sampling, helped define the most appropriate restoration techniques to guarantee the authenticity and historicity of the monument. The criteria followed were “minimal intervention”, “reversibility” and “physicochemical compatibility” of the materials used.

Barrios (2024), presents the contribution of Paolo Marconi by pointing out the importance of recovering the use of traditional techniques and materials in restoration. He left evidence in his books and articles, also in collective works such as the manuali del recupero of Rome and Palermo, which constitute a commitment to recover and transmit the constructive knowledge peculiar to each region or city of Italy.

## Methodology

Based on the information collected and the resources delimited by the scope of the conservation laboratory of the INAH Zacatecas center, in relation to the material and equipment, it was determined that:

- The focus of the tests will be based on the elimination of acrylic paint (lacquers) and the elimination of water-soluble vinyl paint, on pink quarry surfaces obtained from pink quarry deposits in the metropolitan area of Guadalupe Zacatecas, samples with diverse physical characteristics.
- The solvents to be used will be determined by the results obtained after solubility calculations using tools such as the Teas solubility triangle, Cemoneci solubility values, as well as the data provided by theoretical values of London dispersion forces, dipole and hydrogen bond.

- The conservation conditions of the specimens will be equalized in relation to the current deterioration on the stone surfaces, using the use of cleaning techniques observed in graffiti removal processes, using physicochemical cleaning with brushes of different hardness, brushes, swab cleaning.
- Agar and gelatin will be used as a gelling substance for the colloidal systems and the degree of effectiveness in the removal of acrylic paint (lacquers), vinyl paint with different degrees of solubility in water will be verified, the effect of waste generated will be determined. and the degree of penetration into the pores.

The solubility values were determined according to the triangle of firebrands based on the main characteristics of the Alkenyl (ethylene; vinyl) functional groups and the Acryl functional group. The values of permanent dipole force, values of hydrogen bond force, values of Van der Waals forces in the literature.

The spaces were delimited in relation to the real conditions of the stone surfaces of the historic buildings in the city of Zacatecas, testing the colors pink, purple, blue, white, red, of acrylic paint (lacquer) on surfaces where the stone had the porous surface, smooth surface, sanded surface, surface with the presence of salts. At the same time, the areas where the pure vinyl paint would be tested and diluted to 50% of the main colors obtained by the sample, which are green, pink, purple.

In the experimental process, information on the effect of citric acid nanoparticles, colloidal silver, xylol, and citric acid essential oil on test tubes of vinyl paint and acrylic paint (lacquers) was incorporated directly. In order to identify the physical behaviors of the paint when directly exposed to solvents.

Solubility tests were carried out on samples of acrylic paint and vinyl paint, testing the dissolution phenomenon of the solvents characterized in table 3, using as samples the color pink, purple and blue in the acrylic paint (lacquers), and the color green, black, pink and purple in undissolved and 50% vinyl paint.

Prior to the preparation of gels, the behavior of the paints in pure state in the case of vinyl paint and in a 50% solution in water was carried out, and the behavior of acrylic paint (lacquers) in aerosol was studied. Using the thinner as a solution for making gels.

## Results

All the solvents established in the theory were tested, of which those that obtained the best results were those that were carried out with the use of benzene and cyclohexanone, since it does not generate migration of the paint, nor the presence of halos on the stone surface.

The use of benzene, although it generates optimal results, the best for this test, has important implications regarding its use due to the damage to health it generates, however, its management requires special conditions found in the standard. STP 014 of Mexican standards. As well as the safety data of the product technical sheet. The effect of the colloidal system for benzene requires special handling due to its poorly soluble characteristics in water, the handling of a gel of a different nature is required, the use of sol gel for the colloidal system is proposed. Or identify the stability of the gel based on gelatin and agar in a solution with a mixture of alcohol in the solvent.

Cyclohexanone has more stable characteristics in terms of pH for agar or gelatin gels, at the same time it presents fewer implications for health risks to human personnel, and it is soluble in water.

Similarly, optimal results were obtained with the use of thinner, with the characteristics that the thinner generates discoloration on the stone surface, generating a whitish mark if applied directly; however, in all cases it was carried out. a reaction and a paint dispersion phenomenon. That is why the results obtained with the colloidal system reduced the discoloration effect on the stone surface, obtaining good results in the removal of vinyl and acrylic paint, since the paint migrates to the plastic film generated by the colloidal system (gel).

It does not generate a residue, since the plastic film migrates the paint. However, the use of water as a washing effect could generate penetration of dispersed particles inside the pores; the real effect of the absorption phenomenon will be tested by means of stratigraphy in the specimens.

Regarding the effectiveness of the gels, those that presented the best results in dissolving acrylic and vinyl paint were the 20% 30% gelatin gels and the 40% agar gel.

The effect of colloidal silver on the surface of vinyl paint and acrylic paint in the stone material generates inconclusive results regarding its effectiveness in dissolving vinyl and acrylic paint, since a reaction is generated with the surface, it is unknown. this stage of the project if the reaction is generated by the minerals of the stone material or by the functional groups of the acrylic and vinyl paint.

In the case of acid, an effect similar to that of thinner is generated, in the same way the biggest problem lies in the fact that the dissolution of vinyl and acrylic paint generates discoloration of the surface of the stone material. And the problem with the colloidal system is the degree of acids that generates problems for the system.

## Conclusions

In relation to the scope established in this work, it is recognized that the result obtained in terms of information is part of a stage that requires the analysis of the behavior of the reactants over time, where their effect is evaluated in real environmental conditions. in order to determine the safety of the processes used in its use as a cleaning methodology for work of this nature.

At the same time, data analysis information is required with specialized equipment that is not available in the area laboratory. The information collected allows us to provide a solution in terms of intervention, since solutions were found for the elimination of graffiti and vinyl paint on volcanic tuff, data that is proven by theoretical information and information, generating optimal safeguard solutions with relation to existing ones carried out by untrained personnel.

It was found that the use of the gels tested with a thinner solution generates benefits over the methods tested so far, since no residue or plastic film is generated that persists on the surface, generating problems of buffering or waterproofing of the stone material, In turn, the search for buffer reagents that do not modify the degree of acidity over time and the search for agents that allow high concentrations of solvent without the expansion of the system inside it are promoted. As an analysis of the phenomenon, it is suggested for intervention to try the dissolution of paint molecules on the surface and the absorption of systems that generate force contrary to the displacement movement on the surface.

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