

## Article

# Principal Component Analysis (PCA) Combined with Naturally Occurring Crystallization Inhibitors: An Integrated Strategy for a more Sustainable Control of Salt Decay in Built Heritage

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**Abstract:** Salt inhibitors have been receiving increasing attention as potential innovative systems to counteract salt damage by preventing crystallisation of the salts within the natural stone structure—and related disruptive action—of built heritage. Especially, we focus on biomass-derived inhibitor systems featuring complete solubility in water or alcohol and intrinsic non-toxicity. Moving from the promising results obtained, the present study aims to develop research concerning the possibility of rationalizing the collected data sets and making them amenable to statistical analysis. This paper reports on an exploratory application of one of the most powerful methods in chemometrics, i.e., principal component analysis (PCA), in this area. It will be seen that this method is a promising tool to extract information from a series of tests to optimize them and to reduce the level of “noise” present in the data collected, i.e., unnecessary information or experimental errors, and to suggest new directions.

**Keywords:** bio-based inhibitors; weathering; statistics; natural stone; conservation



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## 1. Introduction

Multidisciplinary research to address major challenges related to the conservation of the Built Heritage is gaining ever growing importance. Indeed, considering the diversity of the phenomena of degradation pertaining to heritage sites, the different behavior of the constituting materials, and the possible environmental effects, the involvement of different scientific disciplines is essential to improve conservation practices. Salt decay, in particular, is a harmful and complex widespread process. It is generally understood as a temperature/humidity dependent weathering process arising from: (1) the presence of salt crystals on the surface of porous materials, which generally results in an aesthetic rather than mechanical damage (i.e., efflorescence), or (2) mechanical stresses introduced by salt crystals deposited within the material pores (i.e., sub-florescence or crypto-florescence), which may undermine the structural safety of the materials as well as cause widespread loss of (sometimes precious) surface. Despite having acquired significant knowledge of the decay mechanisms, several relative fundamental issues have not yet been fully understood [1–3].

Accordingly, adequate prevention or mitigation strategies are often lacking. Classical desalination techniques usually involve washing with water and application of poulticing using highly absorbent materials; other approaches include chemical cleaning, salt extraction by barium compounds, electromigration, the creation of chemical barriers, and the employment of a variety of consolidants and surface coatings, such as water repellents. However, the classical desalination approaches are sometimes ineffective or too expensive, therefore justifying the need to find new approaches [1–3].

In the last two decades, there has been an ever growing attention to the development of organic crystallization inhibition chemicals as an innovative strategy for controlling salt crystallization in porous materials, which, ultimately, may provide a means of conserving modern/historical buildings, and protecting heritage sites in a sustainable manner [1–20]. It is commonly understood that inhibitors act through two different mechanisms [1], i.e., preventing or delaying the formation of stable nuclei, and so causing salt precipitation delay or modifying crystal behavior by adsorption on specific faces of a growing crystal, which decreases its growth rate.

In this context, relatively recently, the authors' research group has introduced for the first time [11–20] the use of naturally occurring (i.e., biomass-derived) inhibitors, namely hydroxy-carboxylates (i.e., maleate, citrate, tartrate), [21] and their phosphorylated derivatives, to control salt crystallization in porous media, in order to develop a sound methodology suitable for addressing the conservation needs of different salt-weathered sites. The rationale behind the choice of the families of inhibitors relies on the fact that the inhibitory efficiency depends on the presence of ionizable groups, which are able to form a given number of coordinative bonds with salt cations when in aqueous solution and/or on the salt crystal surface [9].

On this basis, compounds possessing up to five possible dissociation groups appeared worthy of consideration. Notably, the above inhibitors are without risk, and exhibit complete solubility in water and/or alcohol, thereby avoiding the use of harmful solvents in their formulation process. These characteristics enable the use of inhibitors while complying with the relevant legislative and regulatory requirements in Europe, North America and Asia, in developed countries, on chemical substances and mixtures [22–25].

Thus, in a series of papers [11–20] it has been demonstrated that phospho-citrate, when applied to porous media as aqueous solution (1–100 ppm), was one of the most promising and versatile inhibitors, because of its effectiveness in controlling the crystallization of different salts typically found in efflorescences (e.g., sodium sulphate, sodium chloride, sodium nitrate, calcium carbonate and their binary/ternary mixtures) in a wide range of materials (natural stones—tuff, different types of limestones—and bricks), and at various relative humidity/temperature conditions. Notably, negligible sub-florescence occurred in most cases, since almost all crystallization took place on the porous material surface as efflorescence, limiting markedly the material structural damage, as exemplified in Figure 1 in the case of a phospho-citrate/brick/sodium sulphate system.



**Figure 1.** Brick sample showing surface deteriorations due to sub-florescence, induced by  $\text{Na}_2\text{SO}_4$  in the presence of phospho-citrate inhibitor. The inset shows the effect of structural damage occurring in the absence of inhibitor.

As a step forward, here a demonstration case using one of the most important and powerful methods in chemometrics, i.e., principal component analysis (PCA), is reported as a promising tool to describe and interpret the experimental data, with the ultimate aim of identifying the most significant factors influencing the performance of the proposed

conservation treatment. Despite their potential, to date there are only a handful of studies in the literature [26–28] which employ chemometric tools in Cultural Heritage science to obtain a comparative basis for a set of results, and none of them deals the subject of salt weathering.

It will be seen that this method promotes an inductive approach for the research process, with the aim of generating meanings from the collected data sets in order to identify patterns and relationships to achieve a standardization of processes.

An optimization of tests to extract as much information as possible is recommended in the field of Cultural Heritage, where the scientist is an essential element for describing materials, environment, and their interactions.

## 2. Materials and Methods

### 2.1. Materials

The porous material samples used in the crystallization tests that were considered for this chemometric study are tuff, brick, and three different types of limestone, namely Noto and Palazzolo limestone (Italy, South Eastern Sicily area), and Globigerina limestone (Maltese Islands). For Globigerina limestone, the more weatherable *soll* as well as the more durable *franka* (*bajda* and *safra*) types were included. The groups of samples differ essentially in chemical and physical properties, e.g., chemical composition, porosity, pore size distribution. Details concerning the materials' characteristics have been reported elsewhere [12–17,20].

The salts used were the single salts sodium chloride (NaCl), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), calcium sulphate (CaSO<sub>4</sub>), and the binary mixtures 3:1 NaCl:Na<sub>2</sub>SO<sub>4</sub>, 1:3 NaCl:Na<sub>2</sub>SO<sub>4</sub>, 1:1 NaCl:Na<sub>2</sub>SO<sub>4</sub>.

The type of inhibitors used for the selected crystallization tests are phospho-citrate, citrate, maleate, and tartrate. Their concentration in water is from 1 ppm to 10 ppm to 100 ppm.

### 2.2. Methods

**Crystallization tests.** The basic method adopted to perform the crystallization tests was the following. Material slabs (typically 2.5 × 2.5 × 12.5 cm) were cleaned and dried to constant weight. Next, they were treated with the aqueous solution of the inhibitor, using brush application, followed by drying to constant weight, and subsequent contamination with the salt solution through capillarity, in a controlled environment [12–17,20].

Following the above basic procedure, a set up as described in the literature [12–17,20] was used, with sealed containers to promote capillary rise through the material samples. The weight loss ( $\Delta W$ , g) by water evaporation was measured per unit of exposed surface area ( $S$ , cm<sup>2</sup>), at different time intervals. The  $\Delta W/S$  ratio is the key parameter to assess the treatment efficiency [12–17,20]. In all tests, at least three samples were used per treatment type, with the equivalent blank samples.

**Principal component analysis.** The basic idea of principal component analysis (PCA) [29] is to extract the maximum information from the collected data, removing the unnecessary; more specifically, the data set is transformed in a  $N \times P$  matrix, where  $N$  is the number of objects,  $i$  (i.e., the samples) and  $P$  the number of variables,  $k$  (i.e., the parameters quantified during an experiment). Every object can be represented as a point in a  $P$ -dimensional space. This means that there will be  $N$  objects in a space with  $P$  dimensions.

Operating in this multi-dimensional space, the aim of PCA is to find the directions along which most of information is displayed, i.e., the principal components, PCs. This method follows a similarity parameter [29], generating a statistic model able to describe all the available data by using the method of least square. In this case, the most common multiple linear regression techniques cannot be used because they do not evaluate connections among variables or properties involved in a chemical process, since they only find cause-effect relationships [29].

Once the number of PCs,  $A$ , has been found, the evaluation of coefficients to solve the matrix is a math problem [29]. Results are shown graphically for ease of understanding:

- Number of PCs: identify the number of latent variables effective in defining the data structure.
- Loadings plot: shows the correlation among variables used.
- Scores plot: shows eventual clustering and can be used as pattern recognition method for classification problems.
- Information included in the residues: these values describe the non-systematic part of the data series, i.e., the part not explained by the model.

To realize this chemometric study, a data set from 41 crystallization tests was considered, obtaining 140 objects, each one associated with a single stone sample.

To each object has been assigned a code of four letters, one for each peculiarity selected, that is stone variety, salt type, inhibitor type, and inhibitor concentration (Table 1).

**Table 1.** Identification of objects.

Peculiarities Selected	Codes
<b>Stone</b>	T: tuff R: brick N: Noto Limestone (Sicily) P: Palazzolo Limestone (Sicily) A: Malta Globigerina Limestone, Soll B: Malta Globigerina Limestone, Bajda C: Malta Globigerina Limestone, Safra
<b>Salt type</b>	C: NaCl S: Na <sub>2</sub> SO <sub>4</sub> K: 3:1 NaCl:Na <sub>2</sub> SO <sub>4</sub> Z: 1:3 NaCl:Na <sub>2</sub> SO <sub>4</sub> X: 1:1 NaCl:Na <sub>2</sub> SO <sub>4</sub> O: CaSO <sub>4</sub> H: NaCl (1): NaHCO <sub>3</sub> (1)
<b>Inhibitor type</b>	F: phosphocitrate C: citrate L: maleate T: tartrate N: not treated
<b>Inhibitor concentration</b>	6: 1 ppm 5: 10 ppm 4: 100 ppm 0: not treated

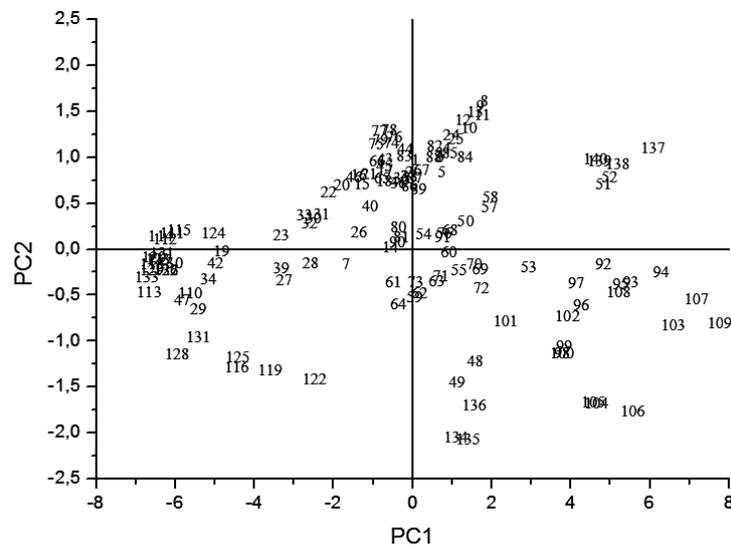
Each object has been characterized by nine independent variables, that is the values of water loss for exposed surface unit ( $\Delta W/S$  in g/cm<sup>2</sup>, data not shown) at nine different time (t) intervals. The intervals were chosen to give a representative picture of the beginning, the middle, and the end phases of each test.

PCA analysis has been performed using SIMCA software [30] by entering a matrix of data (Table 2) whose rows constitute the single stone samples and whose columns represents  $\Delta W/S$  at the different time intervals. A specific program code has been used to indicate eventually missing values.

**Table 2.** Matrix of data per Principal Component Analysis (PCA).

			Variables, k								
			$\Delta W/S$ (t <sub>1</sub> )	$\Delta W/S$ (t <sub>2</sub> )	$\Delta W/S$ (t <sub>3</sub> )	$\Delta W/S$ (t <sub>4</sub> )	$\Delta W/S$ (t <sub>5</sub> )	$\Delta W/S$ (t <sub>6</sub> )	$\Delta W/S$ (t <sub>7</sub> )	$\Delta W/S$ (t <sub>8</sub> )	$\Delta W/S$ (t <sub>9</sub> )
Objects, i	1	TKF4	$x_{i,k}$								
	2	RSL6									
	...	...									
	140	CSF6									

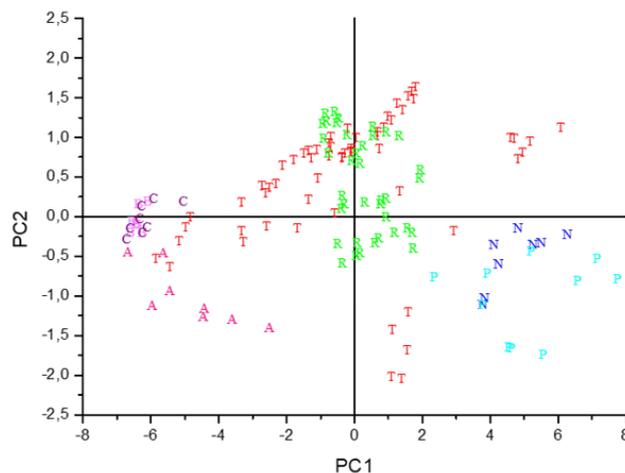
The construction of the predictive model gave the number of Principal Components, A, which was two; SIMCA software, indeed, returned a two-dimensional layout (scores plot, Figure 2), which is parametrized by coordinates (cartesian axes) and in which is identified the position, in the multivariate space, where most of the data are located [29].



**Figure 2.** Scores plot.

**3. Results and Discussion**

The scores plot reported in Figure 3 shows the distribution of 140 objects selected for this study, where the different types of stone have been highlighted. Note that in the scores plot, the proximity of the objects is the key parameter; specifically, the greater the distance between the objects, the more their diversity [29].



**Figure 3.** Scores Plot: stone varieties highlighted.

At first glance, the data are grouped by stone varieties. In particular, tuff and brick (i.e., silicate materials) are centered in the graph area, while the Globigerina limestone and the limestone from South Eastern Sicily are displayed to the left and right of the graph, respectively.

Further, in each of these two latter cases, sub-groups can be distinguished. For stones from Malta, a different grouping for soll (A) and franka (i.e., bajda, B, and safra, C) varieties can be seen. This reflects the different physical characteristics of the two types of Globigerina limestone, particularly in terms of porosity and pore structure. Porosimetry measurements indicate in fact that soll exhibits lower overall porosity compared to bajda and safra (29.8% vs. 30.4% and 35.6%, respectively). For the soll, the maximum concentration of distribution of pores is in the ranges 1–0.6  $\mu\text{m}$  and 1–2  $\mu\text{m}$ , whereas franka has a higher percentage of large pores (2–4  $\mu\text{m}$ ) [1,13,20]. Similarly, within the group of limestones from South Eastern Sicily, the somewhat different grouping for Noto and Palazzolo varieties (N and P, respectively) reflects small differences in terms of chemical composition (P limestone has a larger silicate component compared to N counterpart, i.e., 5.4% vs. 3.5%) and porous structure (P limestone exhibits a higher percentage (32.5%) of large pores (2–4  $\mu\text{m}$ ) relative to N (20.1%)) [14].

Note that, in the case of tuff, we can also distinguish two sub-groups (i.e., upper center and lower center of graph); however, this has been attributed to small variations in the chemical composition of the samples belonging to each sub-group, which came from different sources [15–17].

There is no detectable grouping based either on salt types, inhibitor type, or inhibitor concentration, as shown in Figures 4–6, respectively. This suggests that such parameters do not contribute to the classification of the tests, since they do not influence the distribution of objects.

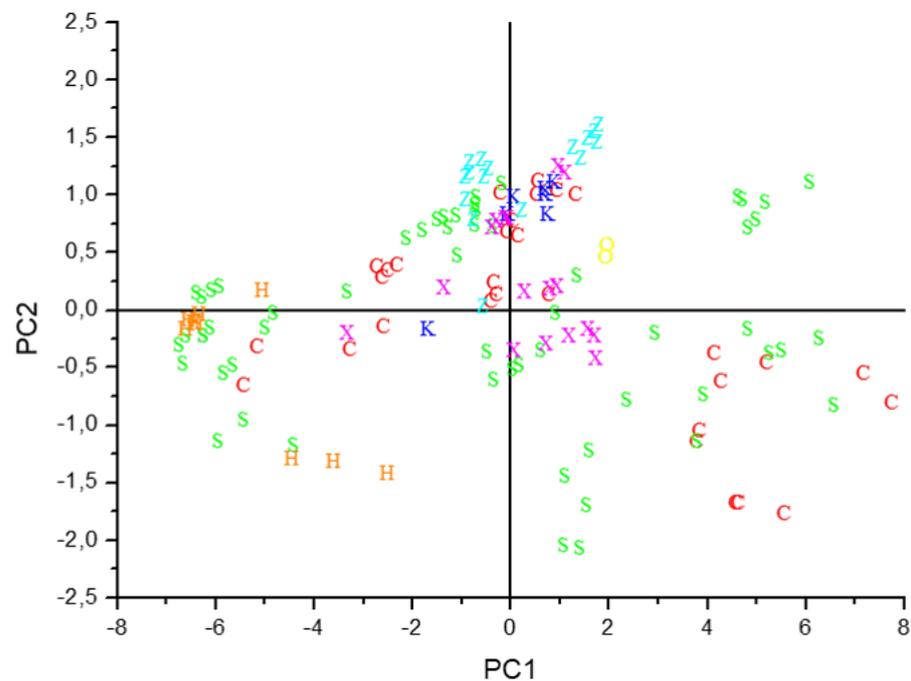


Figure 4. Scores Plot: salt types highlighted.

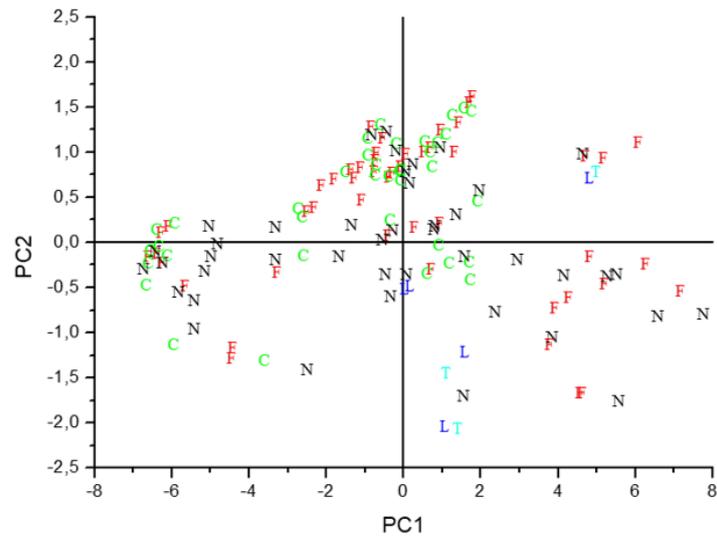


Figure 5. Scores Plot: inhibitor types highlighted.

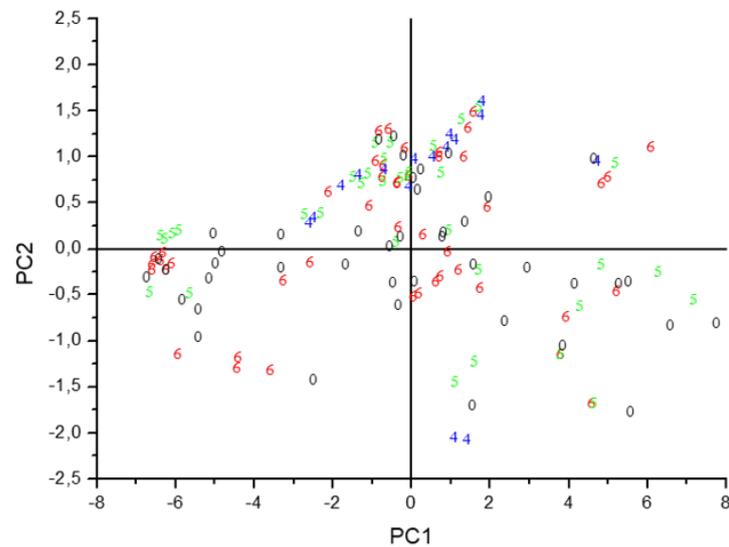
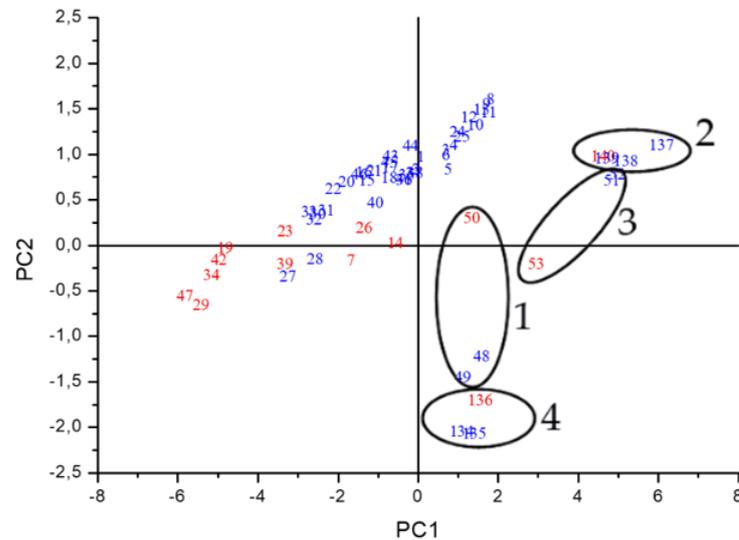


Figure 6. Scores Plot: inhibitor concentrations highlighted.

Furthermore, in the scores plot it is possible to observe that the objects extracted from a given crystallization test typically tend to cluster. Bearing in mind that the proximity of the points translates into their similarity (*vide supra*), this helped to rationalize the efficiency of an inhibitor treatment within each experiment.

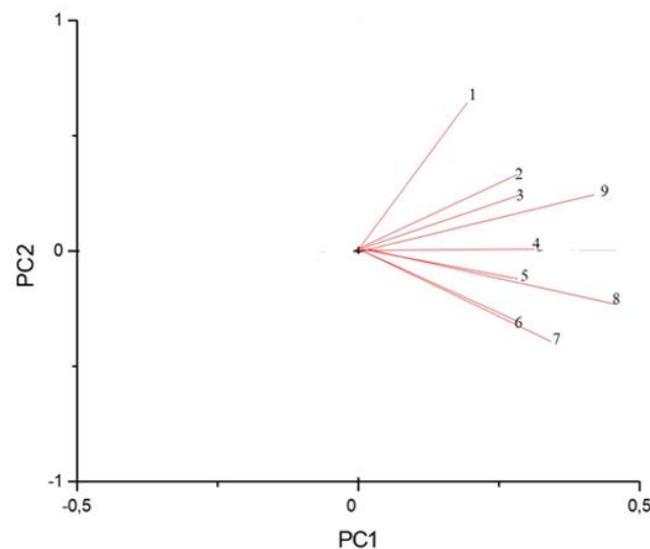
This is exemplified in Figure 7. For clarity, the scores plot, here, shows only the objects associated with crystallization tests involving tuff. The blue color has been used to identify the objects associated with the treated tuff sample, while the red-numbered objects identify the non-treated objects. Here, in most of cases the significant distance between treated and untreated samples suggests a pronounced effect of the conservation treatment. For example, the reader is referred to the circled four sets of objects (areas 1–4) in Figure 6. These sets correspond to the four crystallization experiments where the samples were treated, respectively, with an aqueous solution of: (1) maleate or tartrate at 1 ppm concentration; (2) phospho-citrate at 1 ppm, 10 ppm or 100 ppm concentration; (3) maleate or tartrate at 10 ppm concentration; and (4) maleate or tartrate at 100 ppm concentration [12–17,20].



**Figure 7.** Scores Plot of the objects associated with tuff samples. Blue numbers: treated samples; red numbers: untreated samples.

By comparing the distances between the blue and red objects within each of the areas 1, 3 and 4, it can also be concluded that different types of inhibitors (i.e., maleate or tartrate) produce comparable effects on the tuff samples, keeping the other experimental conditions constant. On the other hand, the proximity of the objects in area 2 gives information on the effect of concentration for phospho-citrate. All these findings correlate well with the experimental results [12–17,20].

Besides, the loading plot (Figure 8) has also been generated through SIMCA. The loading plot is complementary to the scores plot and graphs the weights (“loadings”) of each independent variable on the PCs [29]. The distribution of the loadings enables us to identify which variables have the largest effect on each principal component. Note that loadings close to 1 or  $-1$  indicate that the variable strongly influences the PC, while loadings close to zero indicate that the variable influences the PC weakly.



**Figure 8.** Loading Plot of the independent variables.

In this loading plot, variables 8 and 9 have the largest loadings on component 1, so this component primarily measures the final phase of the crystallization experiments, i.e., a long-term trend of water loss. On the other hand, variable 1 has the largest loading on component 2, so this component primarily measures the initial phase of the experiments. It

can also be observed that variables 3–5 (mid-phase) give similar information, since they contribute nearly equally to the PCs.

Moreover, it can be stated that since variable 1 is “sparse” relatively to variables 8 and 9, they contain complementary information [29]. Upon comparison of the scores plot with the loading plot, it is possible to suppose that for the objects in the upper part of the scores plot the inhibitor effect is more pronounced in the initial phase of the experiment. On the other hand, the objects in the lower part of the scores plot are more affected from the presence of inhibitors over longer times. This nicely supports the experimental findings [12–17,20].

#### 4. Conclusions

Chemometrics, with reference to the PCA method, was revealed to be an interesting tool to extract information from a series of salt crystallization tests aiming to assess the efficiency of inhibitor-based treatments, and to optimize such information. An increase in the number of parameters under consideration is expected to enhance the amount of information extracted from the tests. Studies along this line are currently in progress.

The use of the chemometric approach in the field of conservation is envisaged, since it may help to look at the associated issues from a different point of view, especially in view of the many variables involved.

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