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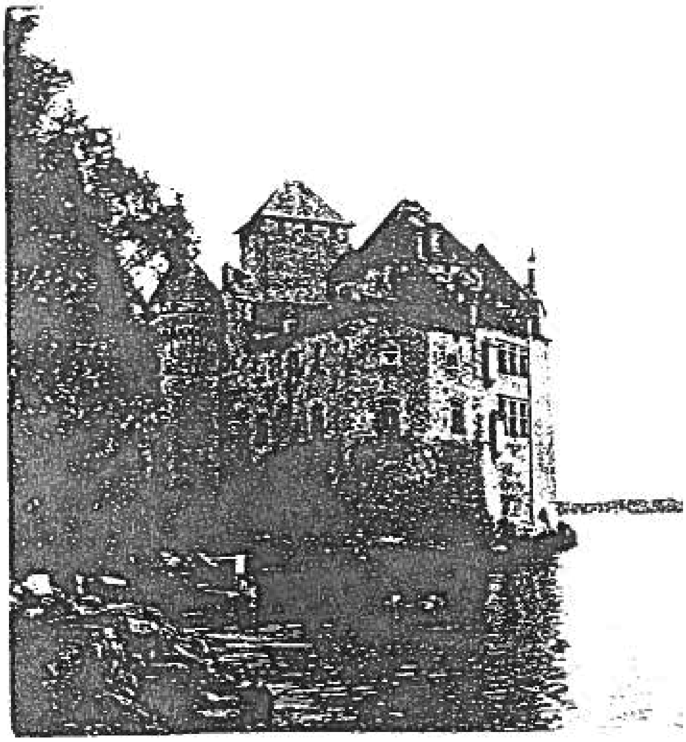
Conservation et restauration des biens culturels

Preservation and restoration of cultural heritage



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Conservation et restauration des biens culturels

Pierre
Pollution atmosphérique
Peinture murale
Etudes scientifiques et cas pratiques

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Chemical control of wall-vegetation
Neutralisation of herbicides

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Abstract

The chemical control of the limestone-growing wall vegetation has to be made carefully, to prevent damage caused by acid herbicides. The results obtained with a new methodology of herbicide neutralisation by potassium hydroxide are here presented. This neutralisation proved its efficiency both in killing the plants and decreasing the damage caused to the stone.

Introduction

The presence of higher plants growing on monuments causes visual obstruction, higher humidity retention, and mainly, physical and chemical degradation of the monuments, due mainly to the growth of their roots. All these effects cause severe damage to the monuments and, if they can not be prevented, they should, at least, be treated.

The chemical control of the wall vegetation has been stated as a suitable instrument of conservative intervention (Caneva & De Marco, 1986; Bettini, 1988, Caneva, *et al*, 1991). However, the use, and sometimes the abuse, of herbicides has not been the most adequate, endangering either the environment or the monument in question, (Caneva & De Marco, 1991).

Thus, any intervention of conservation should be made with previous, careful study of the monument, the deteriogens and the biocides. This will allow the efficiency of the treatment guaranteeing that the monument and the environment will not be affected (Caneva & De Marco, 1986; Bettini, 1988; Caneva & Tiano, 1988).

It is also important to determine potential collateral effects of the herbicides, not only for the possibility of environmental contamination (soil, air and/or water) but mainly because the oxidative degradation of the herbicides may originate products with higher acidity then the original products (Caneva & De Marco, 1986). Thus, when dealing with monuments particular attention should be given to the fate of herbicides: any interference with the stone of the monument can stain it or even worse can cause damage.

The study of the growth of higher plants in the roman town of Conímbriga, Portugal is undergoing. This town was prosperous from the 1st to the 5th Century AD and then the town was abandoned. Until a few decades ago, this area was intensely cultivated.

On the end of the 19th century excavations started. Until now only one sixth of the town has been excavated. The growth of higher plants occurs either on the non excavated locals or on the excavated monuments: walls, columns, gardens, main-wall, pools, etc. The main construction material of the buildings of Conímbriga is of Jurassic limestone. Other types of carbonate rocks were also used, but in less extent. So, the chemical control has to be made very carefully because all the carbonate rocks are particularly sensitive to the weathering action of acids.

This paper presents the results obtained through several experiments in which we took in account the weathering action of acid herbicides that could, indeed, damage the limestone.

To minimise this problem, a new methodology was followed. We have determine the efficiency of two well-known acid herbicides, after they have been neutralised (to pH=7) with potassium hydroxide (KOH). The choice of neutralising with this compound was due to its simplicity. The group OH^- reacts rapidly with hydrogen ions so abundant in acid solutions thus increasing the pH. The potassium ion may react with the herbicide, but it does not interfere with the efficiency of the herbicide.

The purpose of these experiments was to test the efficiency of the neutralised herbicides and to determine if the neutralisation diminished the damage caused by the acid herbicides.

Experimental methods

Two herbicides were selected because they were recommended as to kill plants in non agricultural areas and because they were previously used in monuments (Caneva & De Marco, 1986; Bettini, 1988; Caneva & Tiano, 1988; Caneva *et al*, 1991).

The characteristics of these herbicides are shown in Table 1.

Both these herbicides are non-selective, killing a wide range of plants. This quality is preferable for a total weed control.

Laboratory tests

The first step was to determine the proper concentrations that should be used for each herbicide, for each type of vegetation (therophytes, chamaeophytes, ...). Then the pH for each solution was determined and the exact quantity of potassium hydroxide that should be used in order to neutralise its pH. The concentration of each herbicide was determined according to the information given in the technical books.

For the herbicide Ricochet, only one concentration was given (8-12 l per hectare). It was decided to test the medium value, 10 l/ha. For the herbicide Roundup, several concentrations were recommended, depending on the type of vegetation. Thus, 4 solutions were studied. The concentrations advised and the final solutions are shown in table 2.

After the dilutions the pH for each solution was determined and the amount of potassium hydroxide (liquid) needed to reach a pH of 7. In table 3 are the results we have achieved for the neutralisation of each solution.

These five neutralised solutions, were then tested for their biocidal efficiency. The herbicides were tested on several species of plants and the results indicate that the treatment did not affect the herbicide's ability to kill the plants. Although, detailed results can not be shown in this paper for it would make it too large. These results will be published in due time.

Control of the action of the herbicides on stone

One of the main characteristics of herbicides, when used on monuments should be their chemical inactiveness with stone. Experimental tests were performed to prove that the neutralisation of the common herbicides does indeed prevent the degradation of the limestone.

The rocks used were of the same type of limestone (Jurassic limestone) of the constructions of Conimbriga. The size, shapes and weigh of the rocks were taken into consideration for great variations may be misleading when reading the results. So similar rocks were chosen. These rocks were immersed in the herbicide solution for two months. It was expected that due to the dissolution of calcium carbonate in acids there should be both an increase of calcium and of the pH in the herbicide solutions.

For the first test alterations of quantity of calcium in solution, before and after the two months' immersion, were determined. For the second test pH measurements of the solution, before and after the two months' immersion, were undertaken.

These two tests were performed on nine solutions. Only two of the Roundup solutions were tested, the ones with higher and smaller concentrations of herbicide, because the differences of concentrations are small, thus allowing to extrapolate to the intermediate solutions. Four solutions were elaborated, two neutralised and two not neutralised, for both concentrations of this herbicide. Two solutions of the herbicide Ricochet were also tested, neutralised and not neutralised. In each of these six solutions a rock was immersed.

Finally, three control solutions were elaborated corresponding to the same concentrations of the two herbicides not neutralised. The period of two months for the experiment was decided due to the persistence time of the herbicides. Both herbicides are composed by the glyphosate that has a persistence time of 60 days. The simazine, that also composes the herbicide Ricochet has a persistence time of 12 months maximum (Caneva & De Marco, 1986).Thus, the minimum interval of two months was established to allow the herbicides to interact with the stone for a certain period of time. By the end of this period both herbicides would probably diminish or stop their chemical activity.

Results

Alterations in the concentration of calcium

The weathering of calcium carbonates produces a release of calcium ions, due to the action of the hydrogen ions of the acids. Thus a greater increase of the amount of calcium is to be expected for the not neutralised herbicides then for the neutralised ones. The results obtained after two months are shown in table 4.

The results observed show a huge concentration of calcium only on the solution F, corresponding to the herbicide Ricochet, not neutralised. Comparing this value to the concentration on the solution E, of the herbicide Ricochet neutralised, the values are very distinct, being the second much smaller. The other solutions show very small differences in the concentration of calcium for neutralised and not neutralised solution.

In order to analise these results a statistical test was performed, the Student t-test, paired, two-tailed, for a confidence interval of 95%. However, when using parametric tests, we must have similar variances in the groups of data. The data were then transformed, multiplied by their $\log_{10}(x)$, to diminish the huge disparity of variances (Sokal & Rohlf, 1987).

The control solutions G, H and I, are the reference to the solutions of herbicides. Since no calcium addition was made by the neutralisation, the amounts of calcium of these three solutions represent the calcium in water plus the calcium that the herbicides may have. If the solutions with the rocks present larger amounts than these control solutions, this is due to carbonate dissolution. These solutions were thus compared with the three solutions of herbicides neutralised (A, C and E) and then compared with the solution not neutralised (B, D and F). The transformed data and their statistics are shown in table 5.

As it can be seen in tables 6 and 7 -statistical results of the two comparisons- in both cases the changes in calcium carbonate were statistically not significant, as the probability $p > 0.05$. Concomitantly we can not conclude if the neutralisation of herbicides is benefic or not, from the deterioration point of view.

Although we must refer that, for all the solutions of the herbicide Roundup, occurred the formation of a solid precipitate that, unfortunately could not be identified. This precipitate was particularly evident in the solution D corresponding to Roundup phanerophytes not neutralised. This precipitate may explain the minor alteration in the concentration of calcium observed, yet no conclusions can be drawn from this test.

pH changes

Considering that the pH changes are due to the dissolution of calcium carbonate, then larger or small changes represent bigger or smaller damage to the stone. If the neutralised solutions cause smaller dissolution of calcium carbonate, it is expected smaller increase in the pH. The measurements of pH were performed at the immersion of the rocks and after two month's immersion, when the experiments were concluded.

Results present in figure 1, show that the pH changes observed for neutralised solutions are much smaller than pH changes for the not neutralised solutions.

Again, the Student t-test was used to analise statistically the results. Tables 8 and 9 show respectively the results obtained and the statistical test for the solutions not neutralised. The probability $p < 0.05$ found means that the changes were statistically significant. Thus we may conclude that the herbicide produced a significant damage to the stone.

For the neutralised solutions the data obtained and the statistical analyses are shown in tables 10 and 11 respectively. As it can be seen, the probability is lower than 0.05, so the changes in pH are not statistically significant.

We may conclude than that, regarding pH changes, the neutralisation seems to be effective in diminishing the damage caused by the herbicides.

Conclusions

The neutralisation of herbicides does diminish the damage caused to the stone by acid herbicides. The neutralised herbicides were less damaging to the stone as a smaller increase of the pH of the solution occurred. Because pH changes are due to the degradation of the limestone, more particularly to the dissolution of calcium carbonate, the smaller the change, the smaller the degradation. The calcium quantity test did not show statistically concluding results for the solutions. However, as a precipitate was formed it may explain these results.

One must note that these experiments much amplified the harmful effects of the acid herbicides. In the field the results are not so amplified but they are, however, real.

Stone preservation is a very important issue and the need to use harmless biocides is obvious. The neutralisation with potassium hydroxide seems to be a good answer as far as the interference of herbicides with limestone. Further studies are to take place both with other herbicides and other types of stone.

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References

Bettini, C.
Il controllo della vegetazione nelle aree archeologiche: problematiche conservative, aspetti metodologici ed esperienze applicative,
Atti del convegno Le Scienze, le Istituzioni, gli Operatori alla Sogia degli anni 90, Bressassone, 1988, 207-219.

Bocharov, B.
Chemical Control of Biodeterioration with Restoration and Conservation of Historical and Architectural Memorials,
in Oxley, T. A. & Barry, S. (Eds.). Biodeterioration 5, John Wiley & Sons, Ltd, Chichester, 1983, 445-450.

Caneva, G., De Marco, G.
Il controllo della vegetazione nelle zone archeologiche e monumentali,
Atti del convegno Manutenzione e Conservazione del Costruito fra Tradizione e Innovazione, Bressassone, 1986, 553-570.

Caneva, G., Tiano, P.
La vegetazione come causa di alterazione dei monumenti esposti: metodologie di studio e di intervento,
Risveglio di un colosso - Il restauro dell'Appennino del Giambologna, Alinari, Roma, 1988, 99-102.

Caneva, G., Nugari, M. P., Salvadori, O.
Biology in the Conservation of Works of Art,
ICCROM, Rome, 1991.

Saxena, V. K., Jain, K. K., Singh , T.
Mechanisms of Biologically Induced Damage on Stone Materials,
Proceedings of the International Conference Biodeterioration of Cultural Heritage, Lucknow, 1989, 249-258.

Sokal, R. R., Rohlf, F. J.
Introduction to biostatistics,
W. H. Freeman and Company, New York, 1987.

Villa, A.
I monumenti e l'ambiente,
Ciba-Geigy, internal note, 1978, 11 pages.

Résumé

Le contrôle chimique de la végétation qui pousse sur les murs en calcaire doit être fait soigneusement de façon à prévenir la dégradation provoquée par les herbicides acides.

Dans ce but, on a suivi une nouvelle méthodologie de neutralisation des herbicides à l'aide de l'hydroxyde de potassium.

La neutralisation s'est avérée efficace puisque les plantes ravageuses ont été anéanties et l'effet corrosif des herbicides sur la pierre réduit.

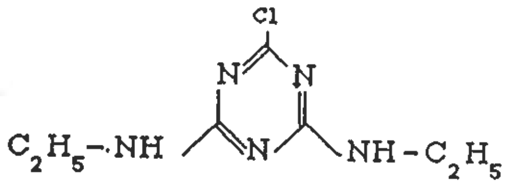
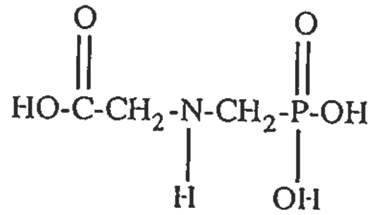
NAME	RICOCHET		ROUNDUP	
COMPOSITION	100g/l glyphosate + 280 g/l simazine		360 g/l glyphosate	
CHEMICAL GROUP	Phosphanoorganic compound and triazine		Phosphanoorganic compound	
CHEMICAL NAME (IUPAC)	Glyphosate: N-phosphane-methyl-glycin Simazine: 6 Cl- N^2,N^4-diethyl 1,3,5-triazine 2,4-diamine		N-phosphane-methyl-glycin	
CHEMICAL FORMULA	Simazine 		Glyphosate 	
WAY OF ACTION	Photosynthesis interference and inhibits the production of aromatic aminoacids		Inhibits the production of aromatic aminoacids	
ABSORPTION	Radicular and foliar		Foliar	
ACTION PERIOD	End of winter		Spring-Autumn	
SENSITIVENESS	Mainly therophytes - mono and dicotyledonous		Non-selective herbicide	
TYPE	Penetration with residual action		Systemic (penetration)	
COLOUR	White		Light yellow	
TRADE-MARK	Monsanto		Monsanto	
TOXICITY	Glyphosate: Slightly toxic; LD_{50}r-oral = 4900 mg/kg Simazine: Slightly toxic; LD_{50}r-oral = 5384 mg/kg		Slightly toxic; LD_{50}r-oral = 4900 mg/kg	
DOSE	40 ml /l H_2O	pH: 4,558	Terophytes: 8,7 ml/l H_2O Hemicript.: 18,6 ml/l H_2O Camaeoph.: 25 ml /l H_2O Phaneroph.: 34 ml /l H_2O	pH: 4,96 pH: 4,88 pH: 4,81 pH: 4,78

Table 1 : Characteristics of the herbicides tested.

	Herbicide (l/ha)	Final concentration (ml/l water)
1 - Roundup therophytes	3	0.86
2 - Roundup hemicryptophytes	6.5	1.86
3 - Roundup chamaeophytes	8	2.50
4 - Roundup phanerophytes	12	3.40
6 - Ricochet	10	4.00

Table 2 : Concentrations of herbicide adviced and final concentrations tested in laboratory.

Herbicida	N. Sol.	Conc. herb. for 100 ml H_2O	Initial pH	Final pH	KOH (liq)/100 ml herb.
ROUNDUP	1	0.86ml	4.96	6.98	1.64 ml
	2	1.86 ml	4.88	7.11	3.64 ml
	3	2.5 ml	4.81	7.01	4.48 ml
	4	3.4 ml	4.775	7.073	6.30 ml
RICOCHET	5	4 ml	4.588	7.125	2.78 ml

Table 3 : pH of the solutions tested before and after the neutralisation with KOH liquid.

Solution	Characteristcs	mg Ca/l
A	ROUNDUP neutralised phanerophyt.	8.85
B	ROUNDUP phanerophytes	5.40
C	ROUNDUP neutralised therophytes	4.04
D	ROUNDUP therophytes	7.26
E	RICOCHET neutralised	9.76
F	RICOCHET	829.70
G	Control - ROUNDUP phanerophytes	0.57
H	Control - ROUNDUP therophytes	0.68
I	Control - RICOCHET	2.98

Table 4 : Concentration of calcium in the nine solutions tested.

	Control	Neutralised	Not neutralised
ROUNDUP therophyt.	-0.167	0.606	0.861
ROUNDUP fanerophyt.	-0.244	0.947	0.732
RICOCHET	0.474	0.989	2.919
Mean	0.209	0.8476	1.5041
Std.Dv. (s)	0.3945	0.2100	0.7084
Variance(s^2)	0.1556	0.0441	1.5055

Table 5 : Calcium concentration, transformed data; means, standard deviations and variances.

DF	mean X-Y	t-value:	Probability - p
2	0.8267	4.1992	> 0.05

Table 6 : Student t-test for the changes in calcium concentration of the neutralised solutions.

DF	mean X-Y	t-value	Probability - p
2	1.4832	3.0838	> 0.05

Table 7 : Student t-test for the changes in calcium concentration of the not neutralised solutions.

	Initial pH	Final pH
ROUNDUP therophyt.	4.94	8.32
ROUNDUP phanerop.	4.64	8.27
RICOCHET	4.59	7.15
Mean	4.7233	7.9133
Std.Dv. (s)	0.1893	0.6615
Variance(s^2)	0.0358	0.4376

Table 8 : pH changes for the not neutralised solutions; means, standard deviations and variances.

DF	Mean X-Y	t-test	Probability - p
2	3.19	9.8712	< 0.05

Table 9 : Student t-test for the pH changes of the not neutralised solutions.

	Initial pH	Final pH
ROUNDUP therophyt.	6.94	9.25
ROUNDUP phanerop.	6.83	8.17
RICOCHET N.	7.12	7.69
Mean	6.9633	8.37
Std.Dv. (s)	0.1464	0.799
Variance(s^2)	0.0214	0.6384

Tabela 10 : pH changes for the neutralised solutions; means, standard deviations and variances.

DF	Mean X-Y	t-test	Probability - p
2	1.4067	2.7943	> 0.05

Table 11 : Student t-test for the pH changes of the neutralised solutions.

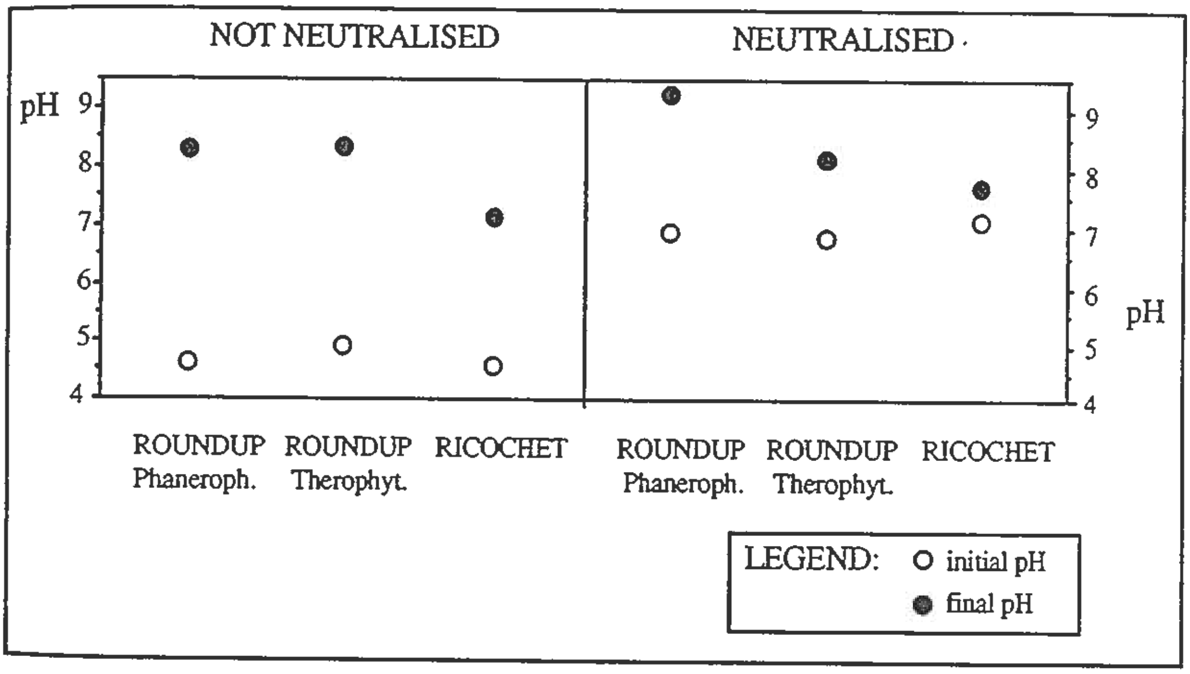


Figure 1 : pH changes suffered by the tested solutions.