

Characterisation of an intermediate decay phenomenon of historical glasses

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In the present work the degree of deterioration of different historical glasses from the Cathedral of León (Spain) has been studied. The glass samples were removed from their original position during the restoration carried out in 19th. Century. Chemical analyses of the bulk glasses, as well as different areas on their surfaces have been characterised by several techniques (optical microscopy, scanning electron microscopy and X-ray diffraction). This study on the degradation of the original glass samples was essential for the knowledge of the successive steps that occur during the whole corrosion phenomenon of glasses conserved outdoors. Likewise, the study allowed the statement of the most adequate criteria for restoration and further protection of such historical glasses. The results obtained were consistent with an intermediate degree of deterioration not described previously in the scientific literature about historical glasses of similar composition. The reaction mechanism involved in the formation of corrosion crusts based on insoluble salts (sulphates) was envisioned as further precipitation from the early formed salts (carbonates). © 2006 Springer Science + Business Media, Inc.

1. Introduction

The León Cathedral gathers one of the most important ensembles of stained glass windows in Spain. Stained glass windows from the Middle Ages, the Renaissance and the 19th. Century constitute that heritage. During the actual restoration tasks the study of the behaviour of the different materials present in the stained glass windows was essential to understanding the corrosion process of the pieces maintained outdoors for long periods of time [1]. There are numerous case studies of historical stained glass windows in which chemical analyses were performed, and the degree of corrosion characterised [2–8]. These previous studies have been valuable for the understanding of both the chemical attack submitted by the glasses and the best methods to be applied for a correct restoration, warranting their further conservation [9]. The two main causes

that originate glass degradation are: i) the long weathering effect due to the atmospheric pollution during the last century, and ii) the chemical composition of historical glasses [10–14]. Moreover, related studies tried to find relationships between the chemical composition and the degradation processes to which they were submitted [15–19]. Researches on model glasses subjected to artificially accelerated ageing processes with controlled environmental parameters have also been carried out [20]. However, due to the great number of external factors affecting the different corrosion processes (temperature, relative humidity, pollutants, microorganisms, etc.) [21], it has not been possible clarify the relationships governing the entire degradation path. Up to now only approximations about the degree of corrosion and the chemical composition of the historical glasses is available.

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TABLE I Bulk chemical composition of some selected glass samples. Analyses performed by EDX (wt. %)

Oxides	Glass sample no																
	1	2	8	9	10	11	12	16	17	18	19	21	22	25	26	27	28
P ₂ O ₅	0.9	5.5	2.8	6.5	4.2	4.9	1.7	1.2	1.5	3.1	4.6	4.5	2.5	3.5	3.0	1.8	2.2
SiO ₂	45.8	54.4	54.1	50.3	53.5	49.9	45.4	45.1	44.0	45.0	51.6	55.1	44.3	57.7	54.2	64.1	71.4
Al ₂ O ₃	1.4	1.7	2.9	1.6	1.4	1.3	1.4	1.3	1.5	1.9	1.6	3.8	2.1	4.0	4.1	4.0	1.8
Fe ₂ O ₃	–	1.2	1.5	1.4	0.9	1.0	0.7	1.8	2.3	2.3	1.1	0.7	1.0	1.2	1.5	1.2	1.3
MgO	1.9	2.6	1.5	4.2	4.3	4.1	1.6	1.8	1.9	2.0	3.2	1.8	2.5	1.5	2.0	1.9	0.9
CaO	24.9	14.8	29.2	14.3	15.7	15.6	21.0	22.9	22.7	21.2	16.4	26.0	22.7	23.4	25.6	12.0	15.6
PbO	–	–	–	–	0.2	–	–	1.3	0.7	0.4	0.7	–	–	–	–	–	0.8
ZnO	–	–	–	–	–	–	–	0.8	–	–	–	–	–	–	–	–	–
MnO	1.0	1.6	1.2	2.1	1.1	2.5	0.9	0.7	1.2	0.4	1.4	1.2	1.1	1.1	1.0	1.2	–
CuO	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Na ₂ O	0.4	1.4	0.6	0.8	1.0	0.9	0.5	–	0.8	0.7	1.0	0.4	0.8	0.3	–	3.3	4.3
K ₂ O	23.7	16.8	6.2	18.8	17.7	19.8	23.3	24.5	23.7	22.7	18.4	6.5	23.0	7.3	8.6	10.5	1.7
BaO	–	–	–	–	–	–	1.4	–	–	–	–	–	–	–	–	–	–

In the present work the analytical characterisation and the deterioration state of 30 historical glass samples from the Cathedral of León is performed. The major part of the pieces was removed from its original position in the stained glass panels during the restoration carried out in the middle of the 19th. Century. The glass pieces were conserved outdoors in “*glassman boxes*”. These are boxes in which glass pieces from the stained glass windows are conserved. Restorers and people working at cathedrals and churches use these pieces in order to replace them during restoration works and likewise they keep those unallocated, unidentified, broken, etc. This fact suggests that the samples studied are a special case, whose description and scientific study lack in the literature available. They have an intermediate deterioration degree, since that glass pieces were remove in the 19th. Century and saved in those *glassman boxes* preserved from the high concentration of pollutants (SO₂) emitted to the atmosphere during 20th. Century.

2. Experimental

2.1. Glass samples

All the samples used in this research were original historical glasses from the stained glass windows of the Cathedral of León (Spain). This Cathedral gathers stained glass windows from different historical periods: Middle Age, Renaissance and 19th. Century. Most of glass pieces were removed from the stained glass panels during the 19th. Century restoration and they were kept in *glassman boxes* up to the beginning of the present research. It was also possible to characterise some pieces from stained glass windows destroyed in recent vandalism actions. All the samples were studied as they were received from the Cathedral of León Restoration Workshop, once they were softly cleaned with cotton pieces soaked in an ethanol-water solution (50% vol.).

2.2. Analytical techniques

Physical characterization of the glass surface was carried out with a binocular stereo lupe Nikon mod. SMZ-2T, and

by optical polarisation microscopy (OM) with a Nikon microscope mod. Optiphot2-POL, provided with an accessory to obtain microphotographs. Chemical characterization of bulk glasses and superficial crusts was performed with a scanning electron microscope (SEM) Philips XL30, connected with an EDX DX4i analyser. In order to coat the samples with a gold conducting thin film, a Sputter Coater SC502 was used. Likewise, the corrosion crusts were characterised by means of an X-ray diffractometer Siemens mod. D5000, equipped with a Kristaloflex 710 generator. The radiation K α 1 ($\lambda = 0.15405$ nm) of Cu with a Ni filter, a 0.1 mm collimator under working conditions of 50 kV–30 mA, were used. Diffraction spectra were recorded directly from the corresponding glass piece with crusts placed in the sample holder.

3. Results and discussion

3.1. The glass chemical composition

As noted above, one of the main factors affecting the glass deterioration process is its chemical composition [12]. In the glass samples studied here, three EDX chemical analyses from bulk glasses from three different areas were recorded. Average values of the results obtained for selected samples are collected in Table I. Among those results, the exclusive presence of potash-lime silicate glasses is a noticeable fact. Na₂O contents higher than 4.5% wt. were not found; confirming that the glasses studied could be from the Middle Ages. In such a period the raw materials used as melting compounds were plant ashes rich in K₂O, while before and after the Middle Ages raw materials that were Na₂O-rich were used as the batch melting component. On the other hand, among the studied glass samples, lead oxide has not been almost detected. This is a difference in chemical composition when compared with other historical glasses previously analysed [18].

The percentages of K₂O, CaO and SiO₂ were found to be the ones with highest variations in the analysed samples. The glass samples were classified following the criterion most frequently used [17]. Such a classification

TABLE II Appearance of the selected glass samples

Glass no	Period	Colour	Glass type ^a	Real appearance i. s	o. s
1	Medieval 13th century	Ochre + violet	3	Unaltered	Thick crust
2	Medieval 13th century	Red + colourless	2	Thin crust	With craters
8	Medieval 13th century	Dark blue	1	Thin crust	With craters
9	Medieval 13th century	Dark blue	2	Thin crust	With craters
10	Medieval 13th century	Colourless	2	Unaltered	With craters
11	Medieval 13th century	Violet	2	Unaltered	With craters
12	Medieval 13th century	Red + colourless	3	Pitted	Thick crust
16	Medieval 13th century	Green	3	Pitted	Thin crust
17	Medieval 13th century	Green	3	Unaltered	Pitted
18	Medieval 13th century	Green	3	Unaltered	Pitted
19	Late medieval	Yellow	2	Unaltered	Thin crust
21	Renaissance	Colourless	1	Unaltered	Unaltered
22	Renaissance (1565)	Violet + colourless	3	Thin crust	Thick crust
25	Renaissance (1565)	Green	1	Thin crust	Thick crust
26	Renaissance (1565)	Green-yellowish	1	Thin crust	Thin crust
27	19th century	Blue	1	Unaltered	Thin crust
28	19th century	Green	1	Unaltered	Unaltered

i s.—indoor side.

o. s.—outdoor side.

^aJ.M. Bettembourg's classification [17].

divides the glass types into three categories: 1) durable glasses (DG) that do not show deterioration, with SiO₂ content between 54–61% wt., K₂O content between 15–28%. 2) crater altered glasses (CAG), with SiO₂ content between 48–57% wt., K₂O content between 15.5–17.5% wt. and CaO content between 12–20% wt. 3) uniformly altered glasses (UAG), with superficial corrosion crusts, SiO₂ content between 46–52% wt., K₂O content between 17–27% wt. and CaO content between 11.5–20.0% wt.

As this classification indicates the degree of alteration that the present glass samples should show, based on their chemical composition, is consistent with the real deterioration observed (Table II). Some exceptions are samples 8 and 25 with corrosion crusts, even though they are included the most chemically resistant glass group (group 1). These crusts could be due to residual putty from the lead profile network or from general contamination, instead to the corrosion or deterioration of the glassy surface of samples. The medieval glasses 17 and 18 are included in group 3 and they should show thick corrosion crusts. However, for both samples the sides placed indoors appear unaltered and the sides placed outdoors show small pits.

Sample 22, firstly considered as a Renaissance glass piece, should be classified as a typical medieval glass, taking into account the analysis results. It is possible that this medieval glass piece was further re-used. In some cases the chemical analysis performed on historical samples have clarified and corrected typological datings.

3.2. Deterioration process

The initial chemical attack of a glass is possible if it is submitted to a humid environment. The presence of atmospheric pollutants such as sulphur and nitrogen oxides, increase the environmental acidity, thus raising the aggressiveness of the atmosphere. At the early stages of glass corrosion, isolated pits appear that further grow and con-

nect with each other forming craters that become deeper and more abundant. In turns, the craters grow and become interconnected in such a way they form a continuous altered layer or corrosion crust. The chemical species most frequently formed in higher proportions are hydrated silica, gypsum and calcium-potassium sulphate [6–8].

The characterisation of the different superficial corrosion stages found in glass samples from a determined stained glass window is essential and necessary. The reason is that, frequently, different deterioration types and degrees have been found in glasses from the same panel (Fig. 1).

Likewise, the environment to which the stained glass windows were submitted has affected the degradation of glass pieces of the same group, with similar chemical compositions (DG, CAG or UAG). This is probably due to the influence of different external factors (humidity, environmental pollution, microorganisms, etc.) on the glass surface. As a consequence of the influence of the environmental factors in the deterioration process of the same glass, in all samples the side placed indoors is always less deteriorated than the side placed outdoors, which suffered the most intense weathering process (Table II). Samples 17 and 18 are two glass samples from group 3 (uniformly altered glasses). However, they are lightly deteriorated.

3.2.1. Pits

In some glass sides placed indoors (sample glass 12 and 16 of group 3, very sensitive to degradation) pits were observed. In addition, pits were also observed on some glass sides placed outdoors (sample glasses 17 and 18 also of group 3). As a general rule, the morphology of glasses with superficial pits is similar for all the cases studied. The indoor side of sample 12 was lightly altered by small shallow isolated pits, located at the central part of



Figure 1 General appearance of the outdoor side of a stained glass window in the cathedral of León.

the sample (Figs 2a and b). Chemical analyses performed on the glass surface (light grey area, S12CA1, Table III) and on the inner part of the pit (deep grey area) (S12CA2, Table III), respectively, show a diminished K_2O content and a moderate decrease of the CaO percentage, while a relative increasing of the SiO_2 content in the glass surface occurs. In addition, both potassium and calcium oxides practically disappear in the inner part of the pits, which were composed almost exclusively by SiO_2 .

In the outdoor side of sample 17 (Fig. 2c), the glass surface just in the pit border shows cracks and small crystals of calcium sulphate inside the pit (S17CA1, Table III). The borders of the glass sample that were initially protected by the lead profile network supporting the stained glass

pieces (*lead comes*) also show similar pits. Perhaps this glass piece was removed from its original place during the whole restoration carried out in the 19th. Century and then removed to another site under more aggressive weathering conditions, which favoured pit formation throughout the glass surface. That is why it is assumed that corrosion took place under a polluted environment usual during the 20th. Century. This could explain the difference between the degree of deterioration of sample 17 (pits with $CaSO_4$ deposits) and all the other pieces stored in the “Glassman boxes” (without $CaSO_4$).

3.2.2. Craters

The samples showing craters on their outdoor side (samples 2, 8, 9, 10 and 11) were classified into several groups, in terms of their morphology. Chemical composition of the inner part in all these samples are very similar and can be included in the group of glasses altered by craters, following Bettembourg’s classification [17]. Thus, the degree of deterioration of such glasses should be similar. However, the surface appearance is different; some glasses, for instance samples 2 and 11 (Fig. 3a) show brown-white craters in concentric rings irregularly distributed upon the surface and filled by crystals formed as a result of the corrosion process. Figs 3b and c show a transverse section of glass 11, where the area corresponding to the inner non-altered part of the glass (light grey colour) is observed (glass 11, Table I); and, on the other hand, the dark area shows the penetration paths of the chemical attack (S11CA1, Table III). In this latter area the intense leaching of K_2O from the glass is confirmed, at the expense of a relative enrichment of SiO_2 . The X-ray diffractogram of the outdoor side surface of this sample (Fig. 4) indicates the presence of calcium oxalate (weddelite, $CaC_2O_4 \cdot 2H_2O$). Formation of this salt can be attributed to the vital processes of microorganisms (fungi, lichen and bacteria) [22, 23]. Former literature describes how the oxalic acid segregated by such microorganisms transform the calcite into calcium oxalate [24]. This could explain the different appearance

TABLE III Chemical composition of corrosion crusts on the outdoor side of the selected glass samples. Analyses performed by EDX (% wt.)

Sample and position	Oxides										
	P_2O_5	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	PbO	MnO	Na_2O	K_2O	SO_2
S12-CA1 Sample 12. Glass surface	2.3	63.2	1.7	0.8	1.3	13.2	3.9	0.9	0.1	10.8	1.8
S12-CA2 Sample 12. In the pit	3.1	82.7	2.1	1.1	0.9	1.5	2.3	0.8	–	2.6	2.9
S17-CA1 Sample 12. Needles in the pit	2.3	3.3	0.4	0.7	0.4	44.3	–	0.7	0.8	0.8	46.3
S11-CA1 Sample 11. In the crater	4.8	71.6	2.7	1.2	0.9	13.9	–	2.0	–	1.6	1.3
S10-CA1 Sample 10. In the crater, outdoor side	7.3	32.4	8.0	6.2	–	38.1	–	–	–	3.7	4.3
S9-CA1 Sample 9. Thin crust, indoor side	7.6	34.8	6.6	4.3	–	30.1	10.1	0.7	–	5.8	–
S22-CA1 Sample 22. Needles in the outdoor side	2.4	5.4	1.1	0.3	–	43.9	–	–	–	1.0	45.9
S25-CA1 Sample 25. Corrosion crust, outdoor side	3.0	21.4	5.0	10.3	1.3	26.6	–	0.6	1.8	1.5	28.5

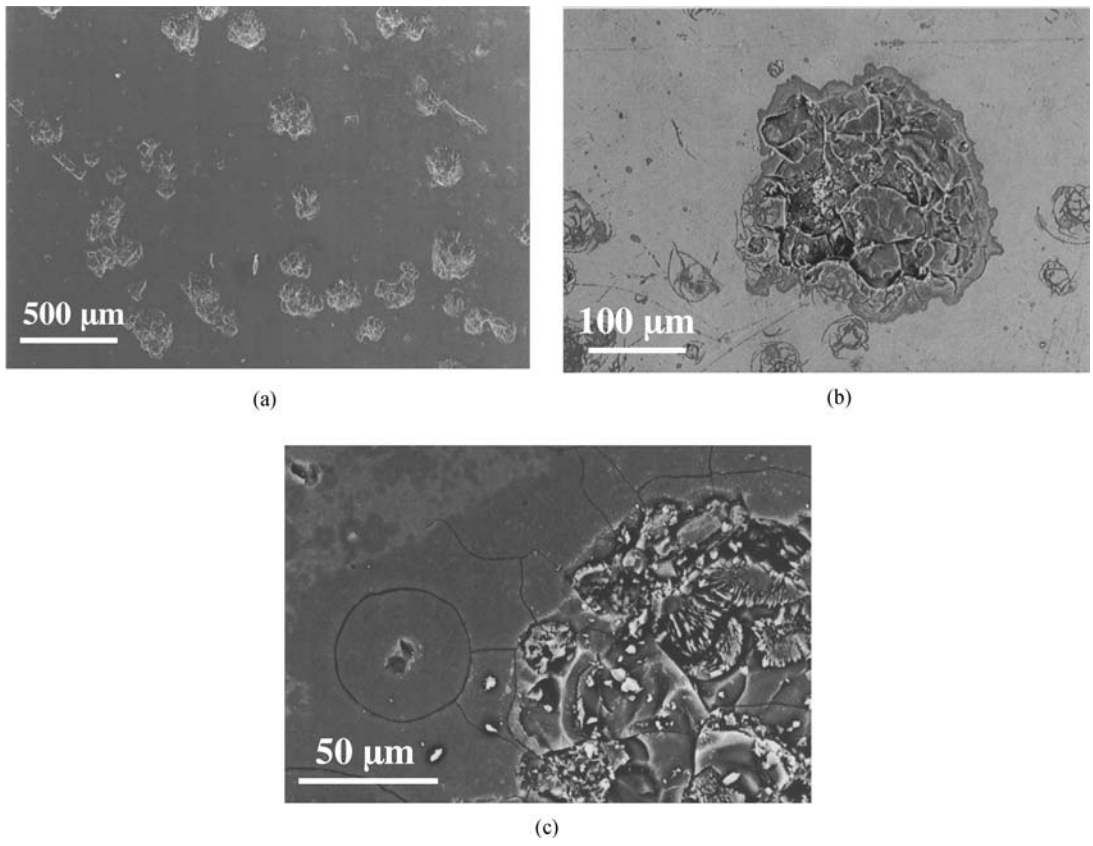


Figure 2 Micrographs of: (a) pits on the indoor side of glass sample 12; (b) a pit detail of glass sample 12, and (c) pit detail of glass sample 17, where the cracked glass sample surface and crystals inside a pit can be observed.

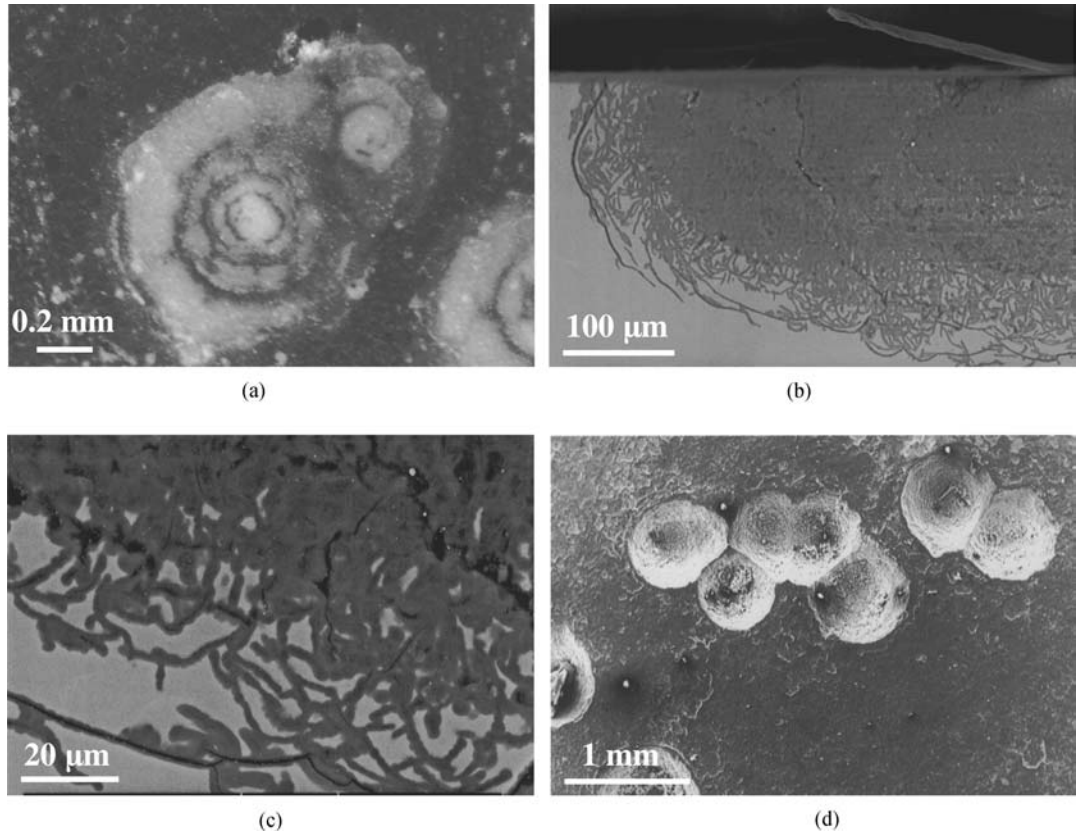


Figure 3 (a) Optical microscopy image from a crater on the outdoor side of sample 11; (b) and (c) Transversal sections of sample 11, near the border of the outdoor side in which attack penetration lines are observed; (d) craters on the outdoor side of sample 10.

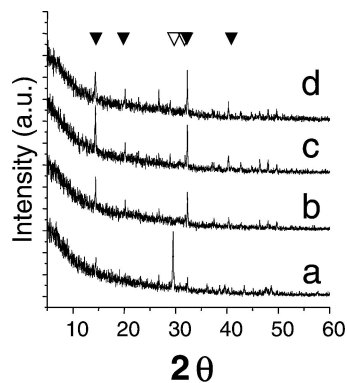


Figure 4 X-ray diffraction patterns of corrosion crusts of samples: (a) 1; (b) 11; (c) 12 and (d) 19 (▽: calcite; ▼: weddellite).

between the several kinds of craters found under visual observation. The craters observed in samples 2, 8, 9 and 10 (Fig. 3d) are deep and open with a semicircular shape, while they are not filled with corrosion products. The chemical analysis performed in the inner part of one of the craters in sample 10 (S10CA1, Table III) shows SiO_2 and CaO as major components. Probably, CaO is present as a carbonate, formed as a consequence of the chemical attack induced by humidity and environmental CO_2 .

3.2.3. Corrosion crusts

The crusts formed on the glass surfaces are a consequence of the chemical composition of the glasses and of the high degree of alteration produced by the atmospheric agents, with which the glasses interacted for long periods of time. In most of the analysed crusts, the presence of carbonates has been detected, while very few sulphates were found. On the contrary, in the available literature, sulphates were commonly detected [1, 19]. The major part of samples from group 3, following the Bettembourg classification [17], show corrosion crusts on their outdoor side. The crusts are thinner than 1 mm in glasses samples 19, 26 and 27; and thicker than 1 mm (up to several millimetres) for the other samples (glasses 1, 12 and 22).

The crusts formed due to the chemical attack are composed by carbonates in those samples removed during the restoration carried out during the middle years of the 19th. Century. As an example, the diffraction pattern of the external corrosion crust of sample 1 (Fig. 4a) is shown, in which calcite (CaCO_3) was detected. In some other cases calcium carbonate has been found as a deposit on the indoor side of the stained glass windows. It is assumed that in such cases calcium carbonate could appear due to the lead profile network filled with putty rather than to a chemical attack process (sample 9, S9CA1 in Table III). Calcium carbonate can produce calcium oxalate after reaction with the oxalic acid generated by some microorganisms. Dehydrated calcium oxalate (weddellite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were also found in the X-ray diffraction patterns carried out on some external crusts (sample glasses 11 (on the borders), 12 and 19; Fig. 4b, c and d, respectively). In

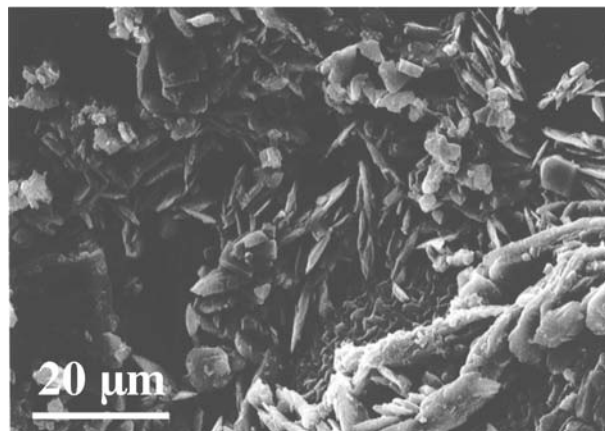


Figure 5 SEM micrograph of the outdoor side of glass sample 22.

these areas near the glass borders a high degree of deterioration has been recorded. This is undoubtedly due to cementing materials (e.g. putty) which contain nutritive compounds for microorganisms. In this way a synergic mechanism between the microorganisms appearing and growth and the increased crust thickness takes place [22].

In glasses placed in the stained glass windows up to recent years (sample 22 and 25) corrosion crusts mainly composed of sulphates have been found. The micrograph of Fig. 5 shows the appearance of the outdoor side of glass 22. Chemical analyses carried out on laminar crystals observed in the former figure, demonstrated the presence of calcium sulphate (S22 CA1 and S25-CA1, Table III). Moreover, X-ray diffraction patterns performed in those crystals also indicated the formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

3.2.4. Attack mechanisms

During the last century the highest SO_2 concentrations have been recorded and they are responsible for the intensive acid attack encountered by the glasses from stained glass windows. Fortunately, nowadays SO_2 emissions to the atmosphere are controlled. The attack mechanisms formerly described in the literature have been confirmed in the glass samples studied in the present work. Such mechanisms begin with the ion exchange of alkaline ions (Na^+ and K^+) from the glass surface by H^+ ions from environmental water (reaction 1, Fig. 6). The *in situ* formed K_2O increases the pH on the outdoor side surface, thus favouring depolymerisation of the glassy network as well as the leaching of calcium ions to form the corresponding hydroxide (reactions 2 and 3, Fig. 6). The $\text{Ca}(\text{OH})_2$ formed is progressively carbonated (reaction 4) by the action of environmental CO_2 . When the environment is polluted by SO_2 , carbonate ions are displaced by sulphate ions, which finally form crusts of hydrated or anhydrous sulphates (reaction 5, Fig. 6). The intermediate formation of calcium carbonate explains the fact that corrosion crusts of the glass pieces removed from stained glass

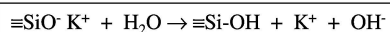
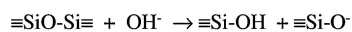
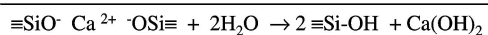
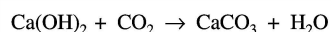
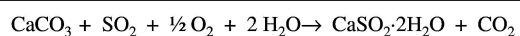
STEP 1**STEP 2****STEP 3****STEP 4****STEP 5**

Figure 6 Chemical degradation mechanism of glasses.

windows during the restoration carried out in the 19th century, only present deposits of carbonates and oxalates (Fig. 4b, c and d). This result is consistent since those samples have not been exposed to the extreme pollutant conditions of the atmosphere during the last 100 years. Great amounts of calcium sulphate have been only detected in samples recently removed (22 and 25). In those samples a noticeable calcium sulphate amount has been identified (S22 CA1 and S25 CA1, in Table III). In addition, sample 17 constitutes a special case, since it showed pits and CaSO_4 crystals, even though it was found in the *Glassman box* together with the other Medieval and Renaissance pieces of glass that only showed CaCO_3 deposits. That is why a kind of replacement was assumed for sample 17 during 20th. Century. This confirms that sulphate crusts have been formed during the last century, when SO_2 emissions were abundant and concentrated, and it is assumed that the formation of carbonates as an intermediate step took place. The former mechanism was also confirmed by means of accelerated ageing tests carried out with model glass samples prepared at the laboratory [20].

4. Conclusions

Chemical composition of glasses is the most important factor affecting their degree of deterioration. SiO_2 contents higher than 55% wt. provide glasses with higher resistance against chemical attacks. Samples with potassium oxide at about 15% wt. show pits. When the percentage of potassium oxide increases, deep craters and even thick corrosion crusts are formed.

In most of the alteration crusts analysed the presence of calcium carbonate instead of calcium sulphate, as is described in the literature, is due to the samples provenance (they were removed during the restoration carried out in 19th. Century). Noticeable amounts Calcium sulphate were only found on samples recently removed. Oxalate deposits found were probably due to the synergic activity of microorganisms.

This study has allowed the identification of corrosion crusts formed by carbonates and oxalates upon the surface of historical glass samples for the first time. The historical glass deterioration in stained glass windows pass through an intermediate stage, in which carbonates are formed, then sulphate ions displace carbonate ions, when environmental SO_2 concentration has been high enough. The last step is the corrosion mechanism that only occurs if the environmental SO_2 concentration is high enough to displace carbonate ions from the insoluble salts deposited on the crusts. These were the real environmental conditions to which the glasses from stained glass windows were submitted during the last century.

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