

Medieval stained glass: a model for leaching of vitrified wastes

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Introduction

Silicate glasses, because of their ability to incorporate high proportions of polluting elements such as heavy metals or transition elements, represent one of the best matrices for stabilizing and storing industrial or domestic wastes. Nevertheless, these glasses are subject to atmospheric agents or pore waters during their storage or valorization, and may be deteriorated by leaching. Under natural conditions of pH, the polluting elements (Pb, Cu, Zn, Cr...) trapped in the vitreous matrix can be partly leached in aqueous fluids over several decades or several centuries. The result is potential pollution and the impossibility to valorize these vitrified wastes. Thus, a comprehension of the leaching processes of polluting elements in a vitreous matrix and the quantification of their release as a function of time, is a prerequisite for storing or valorization of vitrified wastes.

As a complement to experimental studies of leaching, we show that the evaluation of the longevity of vitrified wastes can be tackled by an analogical approach. Although basaltic glasses have already been used as natural analogues, we suggest that the stained glasses of medieval cathedrals dating from the XII to XIVth century are a much more suitable model for the study of the ageing of stabilized glasses. Indeed, these stained glasses not only have a composition very similar to that of the vitrified wastes, but have also undergone conditions of alteration which are probably similar to those envisaged for the waste glasses.

The stained glasses studied have compositions rich in silica, calcium and alkalis (see Table). They are very similar to vitrified wastes. This holds not only for major elements, but also for trace and volatile elements. Indeed, their coloration was obtained by adding heavy metals or transition elements whose concentrations are close to those measured in vitrified wastes. Moreover, stained glasses were conserved on windows or were

accidentally buried underground. Thus, they allow us to follow the alteration of glass under different conditions after 600 to 900 years exposure. These glasses show three types of alteration: 1) a meteoric alteration as deduced from a study of the outside of the windows, 2) an alteration by condensation of water as deduced from a study of the inside of the windows, and 3) an alteration by ground waters and humic acids of samples in the soil.

Methods and results

The observation of these different alterations by scanning-electron microscopy shows very different corroded zones, in terms of their area, their structure and their crystal chemistry. Stained

TABLE 1. Stained-glass compositions analyzed by electron microprobe

Composition in oxide Wt %	Marseille	Digne	Tours	Oppenheim
	Green	Violet	Pale blue	Green
SiO ₂	50.03	49.06	51.81	46.44
Al ₂ O ₃	2.47	1.82	1-35	3.54
Na ₂ O	1.60	0.83	1.76	0.25
K ₂ O	17.16	15.97	15.19	10.83
CaO	11.46	16.86	12.94	27.72
MgO	4.41	4.73	5.97	3.99
MnO	0.92	2.13	1.27	1.03
TiO ₂	0.13	0.12	0.16	0.08
Fe ₂ O ₃	0.46	0.63	0.91	0.48
CoO	0.00	0.00	0.08	0.02
NiO	0.04	0.00	*	0.03
CuO	2.84	0.06	0.26	0.02
ZnO	0.94	0.03	0.47	0.07
PbO	0.22	0.04	0.25	0.05
P ₂ O ₅	4.25	4.50	4.49	2.57
SO ₃	0.11	0.16	*	0.20
Cl	0.42	0.33	*	0.01

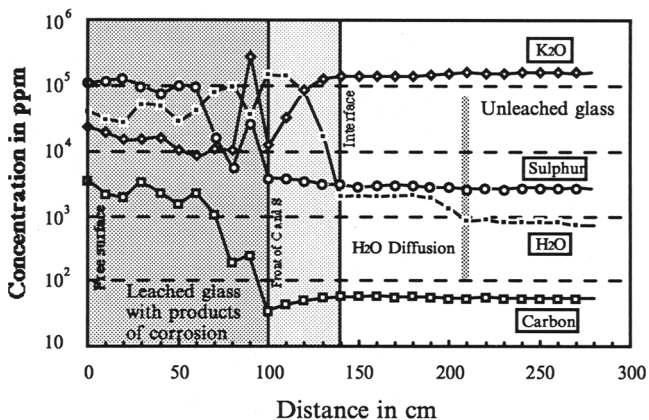


FIG. 1. K_2O , H_2O , C and S concentration in altered blue stained glass of St-Gatien de Tours, measured with ion microprobe.

glasses buried in the soil have a much thicker leached zone than stained glasses which were subject to atmospheric alteration. Moreover, the precipitated phases are different depending on the type of alteration: phases such as calcite, gypsum or syngenite are precipitated on the surface or in cracks of stained glasses submitted to meteoric alteration, whereas phases such as hydrated Caphosphates appear in the leached zone of buried stained glasses. Chemical characterization of these zones was carried out with ion and electron microprobes along appropriate sections perpendicular to the alteration front. This allows us to record the variation of major, trace and volatile elements. In particular, we can see a different behaviour between network forming (NF) and network modifying (NM) cations (Libourel et al., 1994). NF cations like silicon or aluminium have a tendency to be concentrated in the leached zone, even when NM cations like the alkalis or alkaliearths have a tendency to be leached in this same zone. Transition elements also behave differently in function of the alteration mode. For volatile elements, hydrogen behaves in a different manner to carbon and sulphur (see figure). Hydrogen is indeed concentrated near the interface between the leached and unleached

glass and decreases near the surface. In addition, hydrogen diffuses beyond the visible interface. On the contrary, carbon and sulphur are concentrated near the surface and are low at the interface, and do not show a diffusion profile inside the unleached glass. Thus, we infer that water and its ions are the principal agents of the alteration.

Conclusion

Stained glasses are a good analogue for following the ageing of vitrified wastes, not only chemically, but also structurally. Moreover, owing to the exact dating of these glasses, the chemical profiles can be interpreted in terms of diffusion. Thus, one can determine the scales and rates of leaching for each element and especially for polluting elements. This information will allow us to determine the release rate of the different pollutants. Stained glasses furnish an excellent model for understanding the ageing of vitrified wastes over times of up to a thousand years.

Reference

- Libourel, G., Barbey, P., and Chaussidon, M. (1994) *Recherche (La)*, **25**, 168–88.