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A diffusive model of Pb^{2+} release by lead–ceramic glazes

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A diffusive model for the release of Pb^{2+}, both from granulates and from glazes deposed on majolica, was obtained by means of electron paramagnetic resonance (EPR) measurements on lead–ceramic glazes doped with CuO, of variable composition due to the substitution of the K^+ ion with Li^+, Na^+, Rb^+, Tl^+ or Cs^+ ions, and through the definition of empirical parameters related to composition and to ionic radii. In the case of majolica-deposed glazes, the different emission values were attributed to ionic migration across the glass–biscuit interface.

1. Introduction

In previous studies on the relationship between Pb^{2+} release and composition of ceramic glazes doped with Cu^{2+} as chromophorous ion a series of glazes characterized by a variable $[Na^+]/[K^+]$ ratio were examined by electron paramagnetic resonance (EPR).

A strict dependence of the relative population of Cu^{2+} ions in different symmetry sites (D_{4h}, C_{2h}) on the $[Na^+]/[K^+]$ ratio was observed. The amount of Pb^{2+} released by the various glazes was found to be directly proportional to the number of Cu^{2+} ions in C_{2h} sites.

Glaze composition was taken into account through the definition of a parameter ζ [1] which is a function of the ionic radii and of the cationic molar content. This parameter proved to be linearly correlated both with Pb^{2+} release and with the population of lower symmetry sites occupied by Cu^{2+}. The results obtained were in agreement with the hypothesis of Warren [2] in accordance with which alkaline and alkaline-earth ions with higher ionic radii should exert a stronger destabilizing effect on the network, causing a greater Pb^{2+} release.

In this context, the studies have been extended to include glazes doped with CuO and characterized by the partial or total substitution of the K^+ ion not only by the Na^+ ion but also by Li^+, Rb^+, Tl^+ or Cs^+ ions.

2. Experimental details

Starting from a base composition (FB1) three frits were prepared [1] for each M^+ substituent, with a ratio:

$$\eta = [M^+]/([M^+] + [K^+])$$

of $\frac{1}{3}$(FB2), $\frac{2}{3}$(FB3) and $\frac{3}{3}$(FB4), respectively. The frits of controlled composition were prepared as previously described [3] using highly purified reagents. The cationic molar contents of the different frits are reported in Table I, together with the adopted nomenclature.

High purity CuO at a 2% concentration was

TABLE I Molar cationic composition of the unfired glazes examined. M^+ indicates the cation substituting for K^+, i.e. Li^+, Na^+, Tl^+ or Cs^+.

Ion	FB1	FB2(M)	FB3(M)	FB4(M)
K^+	0.0752	0.0501	0.0251	0
M^+	0	0.0251	0.0501	0.0752
Si^{4+}	0.5937	0.5937	0.5937	0.5937
Pb^{2+}	0.0753	0.0753	0.0753	0.0753
Zn^{2+}	0.0381	0.0381	0.0381	0.0381
Ca^{2+}	0.1010	0.1010	0.1010	0.1010
B^{3+}	0.2005	0.2005	0.2005	0.2005
Al^{3+}	0.2730	0.2730	0.2730	0.2730

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TABLE II $n(C_{2h})$ relative population of C_{2h} or lower symmetry sites, lead release, values of ζ and ξ parameters for majolica-deposed glazes or granulates, respectively (see text). The errors quoted in the $n(C_{2h})$ values are the "parabolic" errors computed by the MINUIT [7] analysis.

Sample		$n(C_{2h})$ (%)	Glazes on majolica				Granulates				ζ	ξ
			m_{Pb} (ppm)	$k(M^+)$	r	μ_{Pb} (%)	m'_{Pb} (ppm)	$k'(M^+)$	r'	μ'_{Pb} (%)		
	FB1	12.4 ± 0.9	3.0 ± 0.2				95 ± 10					
Na^+	FB2	5.0 ± 0.5	1.3 ± 0.2	0.238	0.996	5.46 ± 0.8	40 ± 10	7.58	0.999	5.25 ± 1.3	0.1661	
	FB3	2.9 ± 0.8	0.6 ± 0.2			2.52 ± 0.8	25 ± 10			3.30 ± 1.3	0.1562	
	FB4	1.5 ± 0.7	0.5 ± 0.2			2.10 ± 0.8	11 ± 10			1.45 ± 1.3	0.1536	
Li^+	FB2	2.2 ± 0.6	5.7 ± 2	2.16	0.996	2.64 ± 1	190 ± 150	144	0.999	1.32 ± 1		0.1692
	FB3	1.6 ± 0.6	3.4 ± 2			1.58 ± 1	115 ± 150			0.80 ± 1		0.1544
	FB4	6.3 ± 0.8	13.9 ± 2			6.44 ± 1	788 ± 150			5.46 ± 1		0.2328
Rb^+	FB2	2.0 ± 0.4	42.5 ± 10	23.0	0.995	1.85 ± 0.4	472 ± 250	253	0.979	1.87 ± 1		0.1572
	FB3	2.5 ± 0.8	49.5 ± 10			2.15 ± 0.4	700 ± 250			2.77 ± 1		0.1629
	FB4	4.0 ± 0.4	87.0 ± 10			3.78 ± 0.4	996 ± 250			3.84 ± 1		0.1902
Tl^+	FB2	1.9 ± 0.3	43.7 ± 10	24.3	0.991	1.79 ± 0.4	192 ± 150					0.1572
	FB3	2.4 ± 0.5	49.0 ± 10			2.01 ± 0.4						0.1629
	FB4	3.9 ± 0.7	90.2 ± 10			3.70 ± 0.4	32 ± 150					0.1902
Cs^+	FB2	1.9 ± 0.3	760 ± 150	410	0.996	1.86 ± 0.4	896 ± 300	580	0.980	1.55 ± 0.5		0.1561
	FB3	2.6 ± 0.7	980 ± 150			2.39 ± 0.4	1098 ± 300			1.90 ± 0.5		0.1629
	FB4	3.7 ± 0.4	1485 ± 150			3.62 ± 0.4	1890 ± 300			3.26 ± 0.5		0.1858

then added to the frits according to the usual procedure. Lead release measurements were performed both on granulates and on glazes applied to a ceramic support of classical composition (majolica) [4] at a temperature of 1000° C. Lead release values were measured with the acid-attack method [5] and are listed in Table II.

EPR measurements in the X-band were performed at room temperature on glazes fired at various temperatures in the range between 500° C and 1100° C.

As revealed by the disappearance of the EPR Cu^{2+} signal due to undissolved CuO, at a firing temperature of 1000° C all the samples proved to be in a state of total cationic insertion. Under these conditions using computer-aided numerical methods [6–8] the best-fit values of the experimental spectra parameters were determined.

3. Results and conclusions

The EPR measurements of Cu^{2+} in FB powdered samples (granulates) were interpreted on the basis of a single-ion approximation in the crystal field [6, 9, 10]. The resonance spectrum of all the samples was interpreted as the overlapping of the following signals (see for example Fig. 1):

Signal a: a symmetric signal ($g = 2.12 \pm 0.03$, $\Delta H = (158 \pm 12) \times 10^{-4}$ T, attributable to Cu^{2+} ions in octahedral trigonally-distorted (C_{2H}), or lower, symmetry sites*;

Signal b: a non-symmetric signal with $g_{\parallel} = 2.325 \pm 0.007$, $g_{\perp} = 2.081 \pm 0.002$, $\Delta H_{\parallel} = (122 \pm 11) \times 10^{-4}$ T, $\Delta H_{\perp} = (74 \pm 4) \times 10^{-4}$ T and a partially resolved hyperfine structure with $A_{\parallel} = (132 \pm 12) \times 10^{-4}$ T, $A_{\perp} \ll A_{\parallel}$;

Signal c: a non-symmetric signal with $g_{\parallel} = 2.23 \pm 0.03$, $g_{\perp} = 2.054 \pm 0.005$, $\Delta H_{\parallel} = (296 \pm 13) \times 10^{-4}$ T and $\Delta H_{\perp} = (81 \pm 6) \times 10^{-4}$ T.

Signals resulting from Signals b and c were attributed to Cu^{2+} ions in sites with an octahedral tetragonally-distorted symmetry (D_{4h}).

The differences between the spectra of different samples were essentially accounted for by differing percentages of D_{4h} and C_{2h} sites and by poorly relevant variations ranging around the above-quoted values in the line-width of the component signals.

A discussion of the features affecting the line-widths and line-shape of Cu^{2+} in doped lead glazes by alkaline substitution is reported in [6].

The percentage of sites with either C_{2h} or lower symmetry, $n(C_{2h})$, as obtained by the numerical analysis of the EPR spectra, are reported in Table II. According to these data, for each substituent a linear dependence of the lead release, m_{Pb}, (in ppm), on the $n(C_{2h})$ can be envisaged. Such relationship holds true both for the lead release of the granulates, m'_{Pb}, as already observed in previous works [1, 6, 11], and for the lead release of majolica-deposed glazes, m_{Pb}. The best-fit coefficients were calculated by linear regression analysis. In Table II the slopes $k(M^+)$ and $k'(M^+)$ of these straight lines and the correlation coefficients r' and r are reported for the granulates and majolica-deposited glazes, respectively.

The values of the two parameters,

$$\mu_{Pb} = m_{Pb}/k(M^+) \tag{1}$$

and

$$\mu'_{Pb} = m'_{Pb}/k'(M^+), \tag{2}$$

were found to be linearly correlated in a statistically significant way ($r, r' > 0.99$) for the entire set of constituents according to the linear equation (see Fig. 2a)

$$\mu_{Pb} = 1.03n(C_{2h}) - 0.12 \tag{3}$$

with regard to the majolica-deposited samples, and according to the linear equation (see Fig. 2b)

$$\mu'_{Pb} = 1.04n(C_{2h}) - 0.41 \tag{4}$$

with regard to the granulates.

As for the substituent ion Na^+, the already established [1] linear dependence (Table II) of $n(C_{2h})$, μ_{Pb} and μ'_{Pb} on the parameter ζ according to the equations

$$n(C_{2h}) = 263\zeta - 38.5, \tag{5}$$

$$\mu_{Pb} = 263\zeta - 38.4 \tag{6}$$

and

$$\mu'_{Pb} = 262\zeta - 38.2 \tag{7}$$

was obtained.

For the Li^+, Rb^+, Tl^+ and Cs^+ substituents, our experimental data indicated an increase of m_{Pb}. m'_{Pb}, and therefore an increase of μ_{Pb} and μ'_{Pb}, with the value η of the substitution, contrary to that which is observed with the $Na^+ \rightarrow K^+$ substitution. On this basis, we attributed a stabilizing character to the Na^+ ion and a destabilizing character to the other substituents

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*g is the spectroscopic factor and ΔH is the line-width.

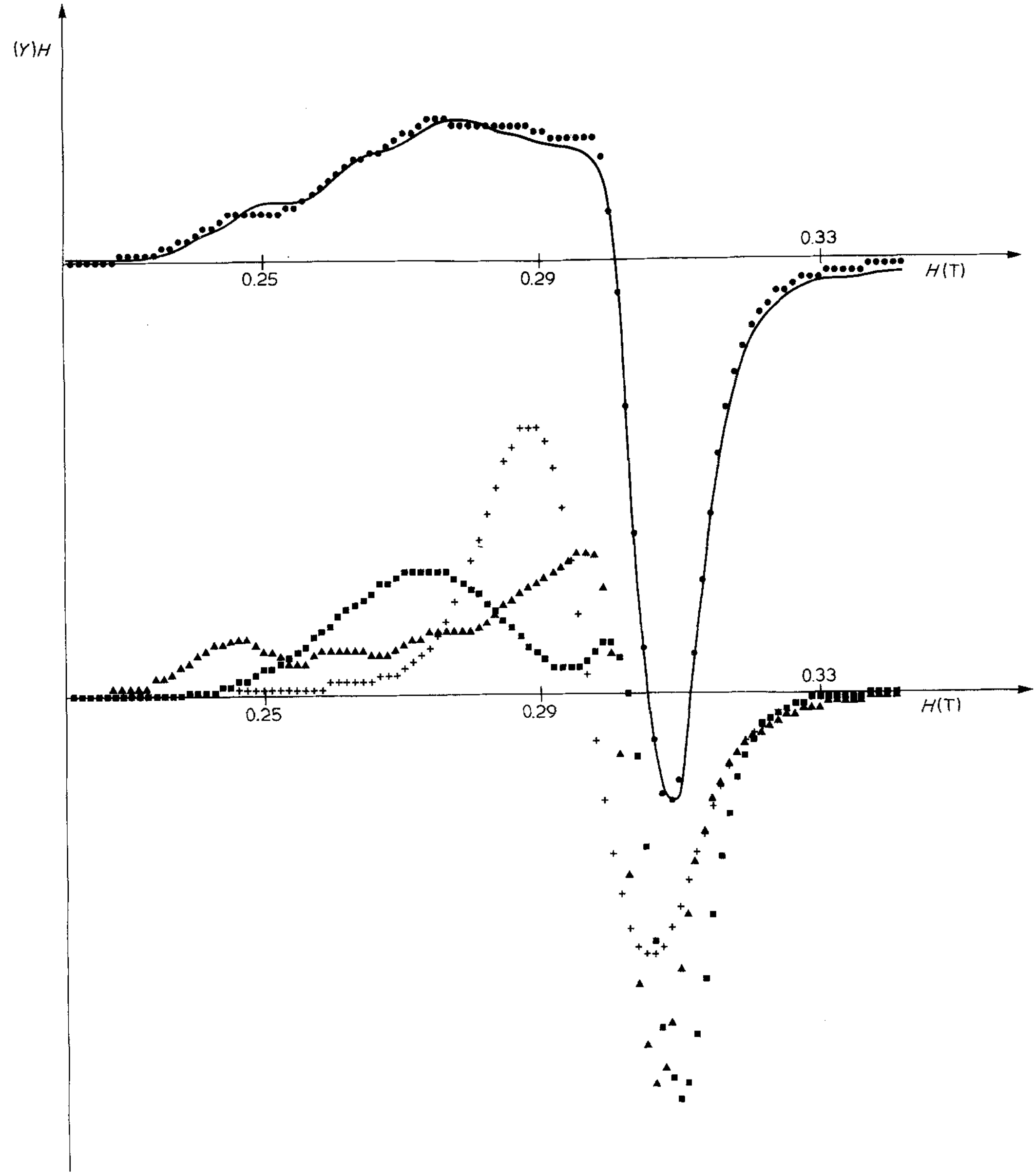

Figure 1 (a) Derivative of the electron paramagnetic resonance (EPR) experimental spectrum (continuous line) measured at room temperature for Cu^{2+} ion 2% concentrated in a $Na^{+}FB2$ glaze fired at 1000° C and its simulation (●); (b) Component signals, shown at the same amplitude, used to simulate the experimental spectra. In the case of the above-cited $Na^{+}FB2$ sample, Signal a (+), Signal b (▲) and Signal c (■) (see text) were summed by means of weights, normalized to the areas, 5%, 46% and 49% respectively.

Another parameter, ξ^{*}, (Table II) defined as

$$\xi = \frac{\left\{ \sum_{i} \frac{[M_{\mathrm{i}}^{2+}]}{r_{\mathrm{i}}^{2+}} + \frac{[M^{+}]}{r_{M^{+}}} \frac{|r_{\mathrm{K}^{+}}[\mathrm{K}^{+}] - r_{M^{+}}[M^{+}]|}{r_{\mathrm{K}^{+}}[\mathrm{K}^{+}] + r_{M^{+}}[M^{+}]} \right\}}{\sum_{j} \frac{[M_{j}^{3+}]}{r_{j}^{3+}}}_{i}, \quad (8)$$

proved to be linearly correlated with $n(C_{2h})$, μ_{Pb} and μ'_{Pb} for all the destabilizing substituents, according to the equations (see Fig. 3)

$$n(C_{2h}) = 58.0\xi - 7.15; \quad (9)$$

$$\mu_{Pb} = 60.4\xi - 7.67; \quad (10)$$

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*Σ_i, Σ_j summations are extended to all bi- and trivalent cations, respectively, listed in Table I, and r represents the ionic radius, according to Spedding and Gschneider [12].

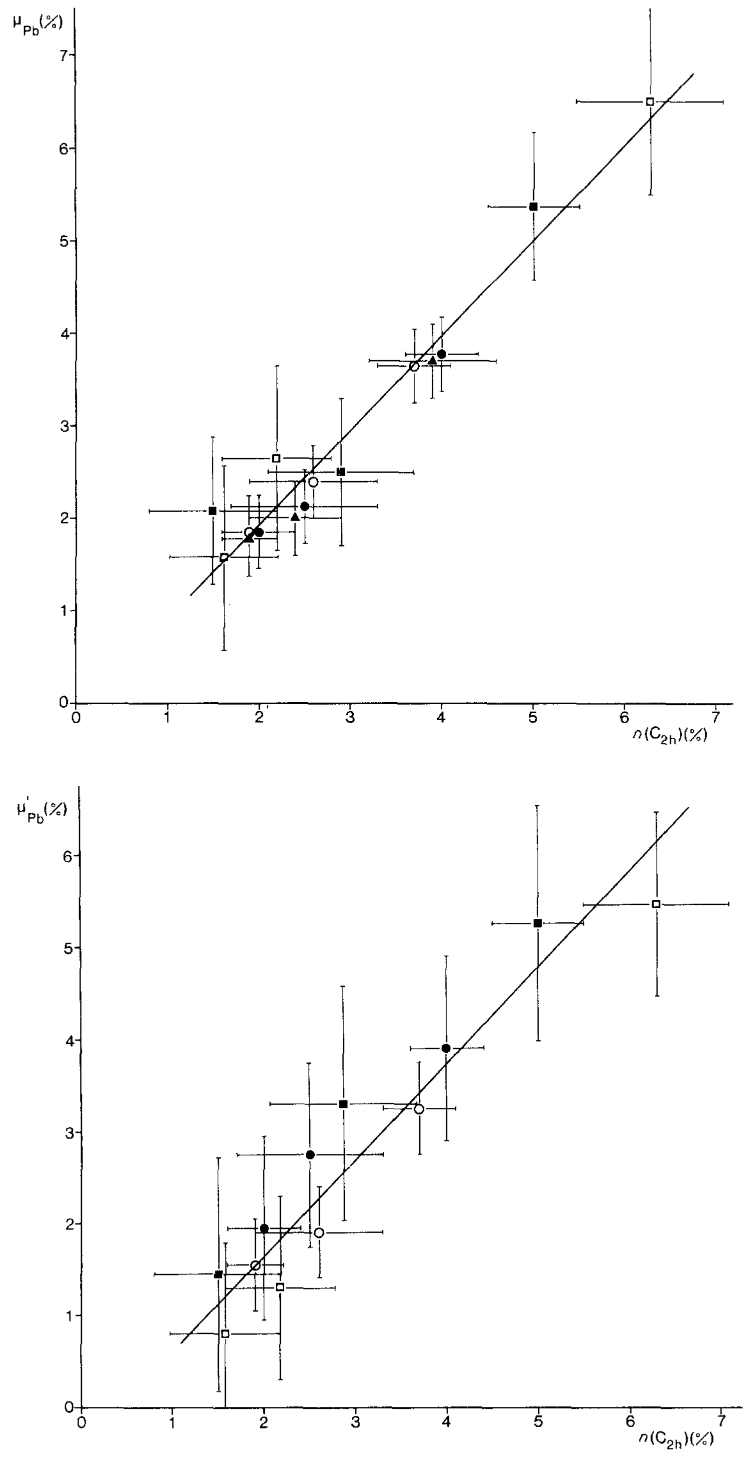

Figure 2 Linear relationship between (a) μ_{Pb} and (b) μ'_{Pb} and the relative population $n(C_{2h})$ of C_{2h} or lower symmetry sites at a 2% CuO concentration. The lines of best-fit, computed by linear regression analysis, are shown.

$$\mu'_{Pb} = 53.8\xi - 6.86. \qquad (11)$$

Moreover, our experimental data indicated that, $n(C_{2h})$ being the same, m_{Pb} and m'_{Pb} increased exponentially with $|\Delta r| = |r(M^+) - r(Na^+)|$, further proving the stabilizing character of Na^+. While, according to Warren [2], an increase of m_{Pb} and m'_{Pb} with η could be predicted only when $r(M^+) > r(K^+)$; in this work an almost identical effect was also observed for the Li^+ ion, even though $r(Li^+) < r(K^+)$.

Such dependence of lead release on $|\Delta r|$ can be explained by attributing to the destabilizing sub-

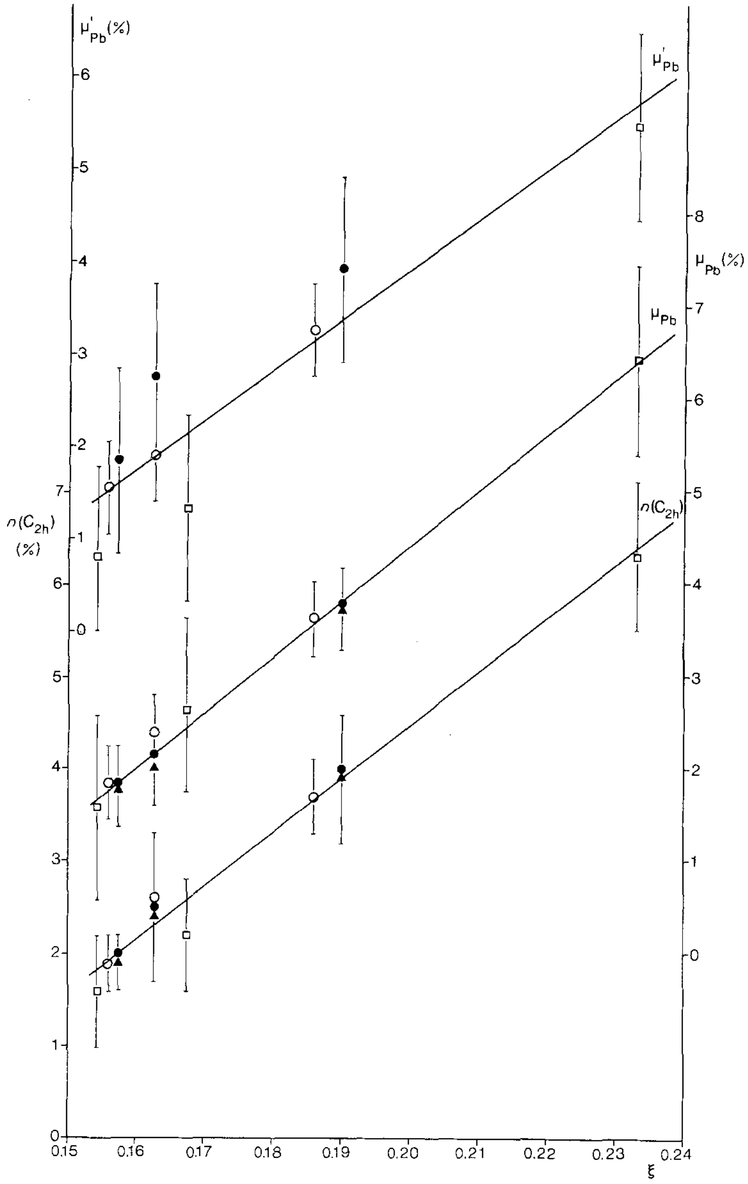

Figure 3 Linear dependence of ξ on $n(C_{2h})$, μ_{Pb}, μ'_{Pb} at a 2% CuO concentration. The lines of best-fit, computed by the method of least squares, are shown.

stituent ions the ability to create lower symmetry sites in the network with a consequent formation of interstices with dimensions (and thus total cross-sections, S) increasing with $|\Delta r|$, i.e., they favour the easy and stable insertion in the network of small ions, like Cu^{2+}, but do not favour the insertion of larger ions such as Pb^{2+}. Therefore, at higher $|\Delta r|$ values the diffusion of Pb^{2+} is favoured and, as a consequence, the $n(C_{2h})$ value being the same, a higher emission is obtained.

In fact, starting from the relations:

$$k(M^+) = \frac{dm_{Pb}}{dn(C_{2h})} \qquad (12)$$

and

$$k'(M^+) = \frac{dm'_{Pb}}{dn(C_{2h})}, \qquad (13)$$

a correspondence can be established between Equations 1 and 2 and the diffusion law at constant D, in the direction $z = \alpha n(C_{2h})$,

$$\frac{dq}{dt} = -D\frac{dc}{dz}S \qquad (14)$$

assuming

$$q = m_{Pb} \quad \text{or} \quad q = m'_{Pb}, \qquad (15)$$

$$\int_0^T \frac{dc}{dz}dt = -\frac{1}{\alpha V}\int_0^T k(t)dt \qquad (16)$$

$$D = \frac{\mu V\alpha}{ST}, \qquad (17)$$

where α represents the mean length of the intestices along the z-direction, S is the total cross-section, T is the diffusion time and V is the volume of the sample. The mean value $(1/T) \int_0^T k(t) \mathrm{d}t$ corresponds to the measured values $k(M^+)$ and $k'(M^+)$. If the meaning of a per cent ratio between the volume of interstices and V is attributed to μ and μ', the quantity $\mu V/(ST)$ is proportional to the mean diffusion rate along z; thus D, which is proportional to the product of the mean diffusion rate and the mean free path, α, has the properties of a true diffusion coefficient. For Equations 6 and 7 and Equations 10 and 11 the parameters ζ and ξ have the same meaning as μ and μ'.

On the other hand, for a given destabilizing substituent, when the value η of the substitution is increased, an increase in the value of $n(C_{2h})$ is obtained; by normalizing with Equations 1 and 2, Equations 3 and 4 are obtained, which are valid for all the substituents.

The lower emission and lower $k(M^+)$ values of the majolica-deposed glazes compared with those of the granulates, can be ascribed to glass–biscuit interactions. This fact, and the decrease of m_{Pb} and $k(M^+)$ with $|\Delta r|$, suggests a migration of the substituent cation from the glass to the biscuit with a reduction of the lower symmetry sites (and a consequent reduction of Pb^{2+} release) followed by a rearrangement of the network and a decrease of $k(M^+)$ with respect to $k'(M^+)$; the higher the $|\Delta r|$ values the more hindered are these migrations. In fact, in the case of the Cs^+ substituent, no important differences were observed between the release properties of granulates and deposed glazes.

Tl-containing granulates showed an anomalous behaviour (see Table II), probably dependent on oxidation to Tl^{3+} by reaction with atmospheric oxygen during firing. The presence in the network of even low amounts of tri-valent ions (Tl^{3+}) should cause a drastic decrease in Pb^{2+} emission, similar to that which has been observed [13] to result from the addition of small amounts of tri-valent ions together with CuO in FB glazes.

In this study, the validity of the already established relationships for the binary substitution of alkaline cations [1] has been confirmed, and their applicability was extended to other substitutions. In addition, a parameter, ξ, was defined applicable to destabilizing substituent ions, which is formally equivalent to the parameter ζ [1] applicable to stabilizing substituent ions. To both parameters, which are proportional to Pb^{2+} release, the meaning of a per cent ratio between the volume of the interstices associated with the C_{2h} sites and that of the sample was attributed; the parameters can be directly obtained from the composition of the glazes and allows their Pb^{2+} release to be predicted.

The strong glass–biscuit interaction, already hypothesized [14, 15] was interpreted to result from a migration of substituent ions. The importance of this phenomenon was directly related to the decrease of $|r(M^+) - r(Na^+)|$, the stabilizing effect of the Na^+ ion having been demonstrated.

References

1. C. B. AZZONI, G. L. DEL NERO, A. KRAJEWSKI and A. RAVAGLIOLI, *J. Mater. Sci.* **15** (1980) 646.
2. B. E. WARREN, *J. Amer. Ceram. Soc.* **21** (1938) 259.
3. A. KRAJEWSKI and R. MONGIORGI, *Chimica e Industria* **60** (1978) 303.
4. A. RAVAGLIOLI and C. FIORI, *Ceram. Inf.* **3** (1974) 146.
5. P. B. BULDINI, *Amer. Ceram. Soc. Bull.* **56** (1977) 1012.
6. C. B. AZZONI, G. L. DEL NERO, A. KRAJEWSKI and A. RAVAGLIOLI, *Lettere al Nuovo Cimento* **26** (1979) 55.
7. F. JAMES and M. ROOS, MINUIT computer program (CERN, Génève, 1974).
8. J. A. NELDER and R. MEAD, *Computer J.* **7** (1967) 308.
9. A. ABRAGAM and B. BLEANEY, "Electron Paramagnetic Resonance of Transition Ions" (Clarendon Press, Oxford, 1970).
10. H. J. ZEIGER and G. W. PRATT, "Magnetic Interactions in Solids" (Clarendon Press, Oxford, 1973).
11. C. B. AZZONI and G. L. DEL NERO, Proceedings of the XXth Congress Ampère, Tallin, 1978 (Springer-Verlag, Berlin, Heidelberg, New York, 1979) 322.
12. R. C. WEAST (ed.), "Handbook of Chemistry and Physics" (Chemical Rubber Co., Cleveland, 1972) p. F-171.
13. A. KRAJEWSKI and A. RAVAGLIOLI, *Acc. Sc. e Lett. Napoletana* (1980), in press.
14. H. KHALED, A. KRAJEWSKI and A. RAVAGLIOLI, *Ceram. Inf.* **11** (1980) 714.
15. A. KRAJEWSKI and A. RAVAGLIOLI, *Berichte der Deutch. Keram. Gesell.* **57** (1980) 76.

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