Journal of the European Ceramic Society **19** (1999) 2647–2657
© 1999 Published by Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(99)00041-2
0955-2219/99/$ - see front matter

Environmental Optimisation of Blue Vanadium Zircon Ceramic Pigment

M. Llusar,* J. B. Vicent, J. Badenes, M. A. Tena and G. Monrós

Departament Química Inorgànica i Orgànica, Universitat Jaume I, Ap. Correos 224, 12080 Castelló, Spain

(Received 6 August 1998; accepted 6 February 1999)

Abstract

*Thermal treatment and the addition of V_2O_5 and of different mineralising agents (NaF, NaCl and borax) have been optimised in terms of colour yield (*L*a*b**) and of environmental considerations (atmospheric emissions and vanadium leachates). The formation of different reaction intermediates depending on mineralising agent (ZrV_2O_7 for no mineraliser, $NaVO_3$ and/or sodium–vanadium bronzes for added sodium halides, and a borosilicate vitreous phase for added borax) proves be important for the pigment synthesis, leading to different zircon yields and to different colour performance in the fired pigments. The composition $(ZrSiO_4)(V_2O_5)_{0\cdot19}$ $(NaF)_{0\cdot05}(NaCl)_{0\cdot10}$ has been found to be the optimal environmentally (firing loss = 5·8%, vanadium leached = 284 ppm and *b* $= -16\cdot4$*), though the non-mineralised composition (with 0·19 mol of V_2O_5 per zircon formula weight) also performs well. © 1999 Published by Elsevier Science Limited. All rights reserved*

Keywords: powders-solid state reaction, colour, halides, SiO_2, ZrO_2.

1 Introduction

The blue vanadium zircon ceramic pigment is accepted to be a solid solution of tetravalent vanadium in the zircon lattice,[1–4] V^{4+}–$ZrSiO_4$. In this system, vanadium acts not only as chromophore, but also as mineraliser for the synthesis of zircon[2,5] allowing this phase to be formed at lower temperatures and within a narrower temperature range. Similarly, alkaline fluorides are widely used as mineralisers in the synthesis of the pigment, basically because F^- ions can substitute for O^{2-} ions in the zircon lattice,[4,6,7] easing the entrance of vanadium in the solid solution.

Structural studies[4] indicate that V^{4+} enters at low temperatures in the tetrahedral sites substituting for Si^{4+}, but thermal activation promotes V^{4+} migration to dodecahedral sites substituting for Zr^{4+} at higher temperatures.

Considering the studies reported first by Matkovitch and Corbett[8] which were conducted in the absence of mineralisers, a zirconium pirovanadate (ZrV_2O_7) forms as reaction intermediate around 690°C, decomposing around 760°C prior to zircon formation. The pigments obtained without mineralisers are usually green, but a blue pigmentation can also be obtained without fluorides depending on the vanadium content and on the firing temperature (the colour is blue with vanadium amounts lower than 0·03 mol per formula weight).[4,9] In this respect, it is assumed that the relative amount of V^{4+}:V^{5+} incorporated in the zircon lattice determines the pigment colour:[9,10] it becomes greener as the V^{5+} content increases and as the solid solution V^{4+},V^{5+}-$ZrSiO_4$ forms. Fluoride addition is believed to stabilise V^{4+} and to substitute for O^{2-} in the zircon lattice forming the turkish blue F^-,V^{4+}-$ZrSiO_4$ solid solution. However, fluoride addition does not guarantee the blue colour, since the firing temperature and the preparation method are also decisive.[11]

On the other hand, the use of vanadium and mineralisers brings environmental problems due to the emission of V_2O_5 vapour and HF, as well as the leaching of vanadium and fluorides when washing the fired pigments. These environmental problems must be treated by appropriate optimisation of vanadium and mineraliser additions, as well as by appropriate thermal treatment.

2 Aims

In the present work, the thermal treatment as well as the addition of V_2O_5 and of different mineralising agents (NaF, NaCl and borax) have been optimised

---

*To whom correspondence should be addressed. Fax: +34-964-728214; e-mail: mllusar@qio.uji.es

in terms of product (zircon yield, presence of unreacted phases), the colour yield accomplished (*L*a*b** parameters), and the environmental compatibility (atmospheric emissions on firing and vanadium leaching). The employment of mineralisers such as NaF, NaCl and borax in the synthesis of ceramic pigments has been previously reported by Booth and Peel.[1] All these compounds give rise to flux phases during the thermal treatment: borax can be considered as a low-melting point mineraliser (~741°C), NaCl melts at intermediate temperatures (~800·4°C), while NaF is a relatively high-temperature mineraliser (~992°C). Therefore, the effect of these mineralisers can be different depending on the stage of the solid state reaction at which the flux phases are provided. Moreover, halides are assumed to have an important mechanistic and structural role in the pigment synthesis.

Na_2O -- 0.188		
K_2O -- 0.123		
CaO -- 0.448	Al_2O_3 -- 0.532	SiO_2 -- 5.193
BaO -- 0.050		ZrO_2 -- 0.352
ZnO -- 0.096		
PbO -- 0.094		

Fig. 1. Seger formula of the opaque commercial glaze employed.

The specific aims of this work can be summarised as follows:

1. to analyse the effect of V_2O_5 on colour synthesis, determining the optimal amount of chromophore-mineraliser agent to be used;
2. to study the effect of firing temperature and mineraliser addition (NaF, NaCl and borax) on the V_2O_5-optimised composition, determining the optimal single mineraliser addition and firing temperature;
3. to analyse and optimise the addition of a binary mineraliser system;
4. to characterise the final optimised composition.

3 Experimental Procedure

With these aims, different blue-vanadium zircon compositions were prepared by using traditional

Table 1. Evolution of powder colour and crystalline phases with V_2O_5 molar content in non-mineralised samples $(ZrO_2)(SiO_2)(V_2O_5)_x$

x	*0·05*	*0·10*	*0·15*	*0·20*	*0·25*	*0·30*
Powder colour	Green–yellow	Green	Green	Green–yellow	Green–yellow	Green–yellow
Crystalline phases (XRD)	Z[a] (m),[b] B (m) Q (w)	Z (vs), B (w) Q (w)	Z (vs), B (vw) Q (vw)	Z (vs), B (vw) V (vw)	Z (vs), V (vw)	Z (s), V (vw)

[a] Crystalline phases: Z = zircon ($ZrSiO_4$), B = baddeleyite (monoclinic ZrO_2), Q = quartz (SiO_2), V = vanadium pentoxide (V_2O_5).
[b] XRD peak intensity: vs = very strong, s = strong, m = medium, w = weak and vw = very weak.

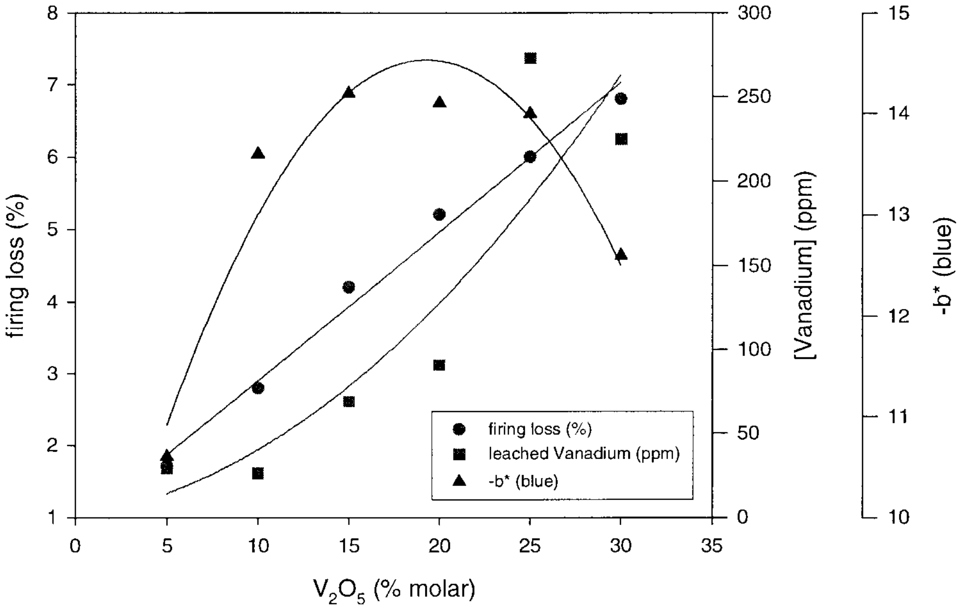

Fig. 2. Evolution of firing loss (%), vanadium leached (ppm) and blue colour (*−b** values of samples enamelled with an opaque glaze) with vanadium content.

Table 2. Evolution of powder colour and crystalline phases with firing temperature in non-mineralised and single-mineralised samples $(ZrO_2)(SiO_2)(V_2O_5)_{0\cdot19}(M)_{0\cdot62}$

Without mineraliser	*650°C*	*700°C*	*750°C*	*800°C*	*850°C*	*900°C*
Powder colour	Light brown	Yellowish brown	yellowish brown	Green	Green	Green
Crystalline phases (XRD)	B[a] (vs)[b], Q (s) V (w)	B (s), Q (s) P (w–m)	B (s), Q (s) P (w)	Z (s), V (vw)	Z (s), V (vw)	Z (vs), V (vw) Q (vw)
*With NaF addition (*M*=F)*	*650°C*	*700°C*	*750°C*	*800°C*	*850°C*	*900°C*
Powder colour	White	White–yellow–blue	Blue	Blue	Blue	Blue
Crystalline phases (XRD)	B (s), Q (m) N (vw)	B (s), Q (s) N (vw)	Z (m), B (w) Q (vw), N (vw)	Z (s–vs) B (vw), N (vw)	Z (s) B (vw), N (vw)	Z (s) B (vw), N (vw)
*With NaCl addition (*M*=Cl)*	*650°C*	*700°C*	*750°C*	*800°C*	*850°C*	*900°C*
Powder colour	Light brown	Light brown	Yellowish white	Blue	Blue	Blue
Crystalline phase (XRD)	B (s), Q (m) N (vw)	B (s), Q (s) N (vw)	B (vs), Q (s) N (vw)	Z (s), B (vw) N (vw)	Z (vs), B (vw) N (vw)	Z (vs), B (vw) N (vw)
*With borax addition (*M*=B)*	*650°C*	*700°C*	750°C	800°C	850°C	900°C
Powder colour	Brown	Brown	Brown	Brown	Brown	Brown–orange
Crystalline phases (XRD)	B (vs), Q (s) V* (vw)	B (s), Q (m) V* (vw)	B (vs), Q (m) V* (vw)	B (m–s) Q (w), V* (vw)	Z (w), B (m) Q (w)	Z (s) B (vw)

[a] Crystalline phases: Z = zircon ($ZrSiO_4$), B = baddeleyite (monoclinic ZrO_2), P = zirconium pirovanadate (ZrV_2O_7), Q = quartz (SiO_2), V = vanadium pentoxide (V_2O_5), N = sodium vanadium oxide $NaVO_3$, V* = sodium vanadium bronzes ($5Na_2O\cdot xV_2O_4\cdot(12-x)V_2O_5$).

[b] XRD peak intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

Table 3. Zircon unit cell parameters and volume in 800°C-fired samples

$(ZrSiO_4)\ (V_2O_5)_{0\cdot19}(M)_{0\cdot62}$	a = b(Å)	c(Å)	V(Å^3)
Without mineraliser	6·6212 (±0·0005)	6·0136 (±0·0008)	263·64 (±0·07)
M = F (NaF)	6·6078 (±0·0006)	5·9899 (±0·0008)	261·54 (±0·08)
M = Cl (NaCl)	6·611 (±0·002)	5·991 (±0·002)	261·8 (±0·2)

ceramic methods. Commercial silica (SiO_2 content = 95·5%, D_{50} = 3·9 μm), zirconia (ZrO_2 content = 95·0%, D_{50} = 5·6 μm) and ammonium metavanadate (NH_4VO_3 content ≈100%), all of them of industrial quality and supplied by J. J. Navarro, were used as SiO_2, ZrO_2 and V_2O_5 precursors, respectively. In the mineralised compositions, different halides (commercial NaF and NaCl supplied by J. J. Navarro, Castellón, Spain) and borax (Panreac) were used as mineralisers.

The appropriate amounts of precursors and mineralisers were ball-milled in acetone. Residual acetone was removed by evaporation and the dried powders were finally homogenised in an agate mortar. To allow the ceramic pigment to be formed by solid-state reaction, the dried powders were fired in an electrical furnace with heating to the selected temperature in 2 h 45 min, and with a soaking time of 1 h 25 min.

To quantify the atmospheric emissions during the thermal treatment, the firing loss (wt%) of the samples during calcination was determined gravimetrically (previously calcined crucibles were used).

X-ray diffraction (XRD) patterns of the calcined pigments were obtained using conventional powder techniques in a Siemens diffractometer with Ni filtered CuK_α radiation (0·05°2θ s^{-1} and 1 s of counting time per step). To analyse the structural effect of halide and vanadium additions, the zircon unit cell parameters and size in representative fired samples were also measured using the POWCAL (powder-calculation) and LSQC (least-squares-calculation) programs from the Department of Chemistry of the University of Aberdeen (UK). The former refines the *d* values of tested polycrystals using an internal standard mixed with the sample; the latter calculates the crystallographic unit cell parameters by comparing the refined *d* values with standard values.[12] With this aim α-Al_2O_3 (40%) was used as internal standard in the XRD run between 15 and 70°2θ at low goniometer speed (0·01°2θ s^{-1}).

Fired pigments were washed before being enamelled, both to eliminate undesirable soluble salts that can have negative effects during the enamel firing and to measure the vanadium concentration leached from the pigment in the washing solution. For this purpose, 1 g of calcined powder in each case was washed with 0·3 M HNO_3, until 250 ml of washing acid were obtained. To determine the concentration of washed-off vanadium, 5 ml of 0·5 M H_2SO_4 were added to an aliquot of 10 ml of washing acid. The vanadium was reduced to its tetravalent state with 0·05 g of $FeSO_4\cdot7H_2O$ and finally 10 ml of 0·1 M H_2O_2 were added to form a brown complex with V^{4+}. Vanadium was then

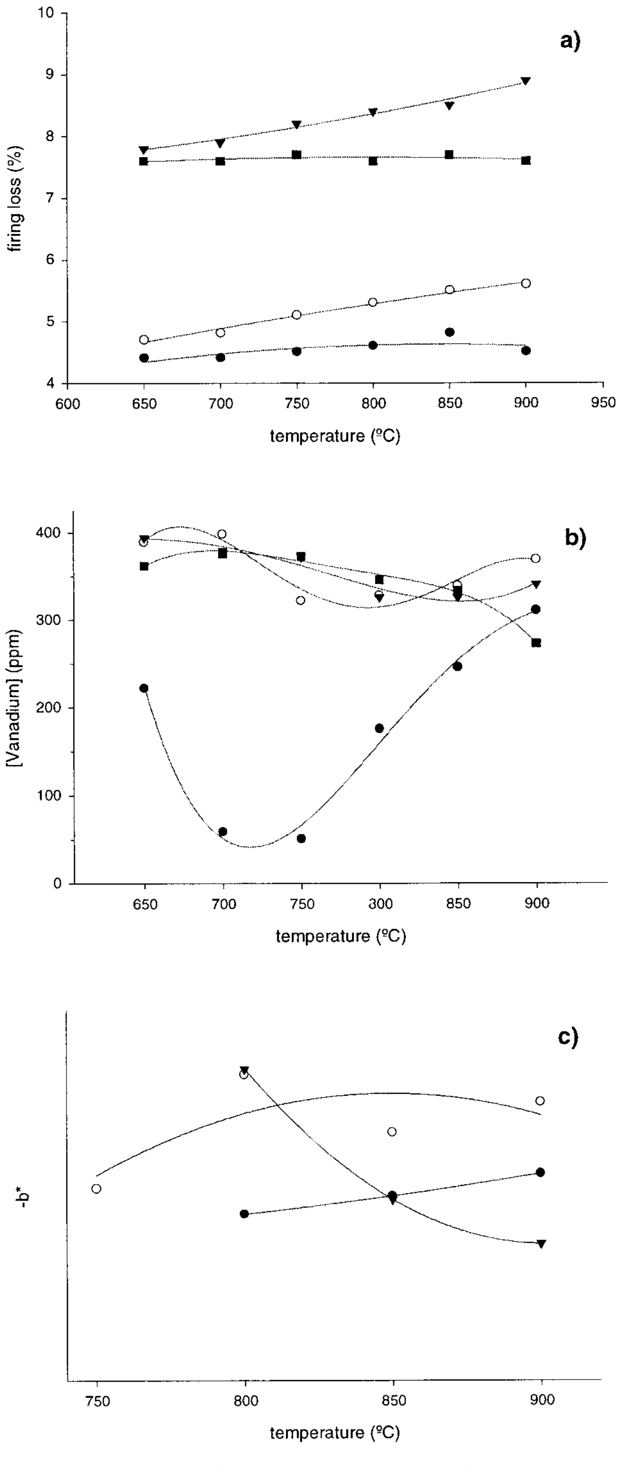

Fig. 3. Evolution with firing temperature of: (a) firing loss (%), (b) vanadium leached (ppm) and (c) blue colour ($-b^*$) of samples enamelled with an opaque glaze, using different mineralisers. (●: without mineraliser, ○: with NaF, ▼: with NaCl, and ■: with borax)

determined colourimetrically at 470 nm with a Perkin–Elmer spectrophotometer.

Washed pigments were also enamelled with an opaque glaze. For this purpose, each colour was mixed with the glaze (a 5 wt% of colour was used) and slip-coated onto commercial ceramic biscuits, being then fired up to 1000°C in an electrical furnace following a fast firing shedule (5 min of soaking time at 1000°C and 90 min for the whole firing–cooling cycle). The oxide composition of the opaque glaze can be seen in Fig. 1 expressed as Seger formula. $L^*a^*b^*$ colour parameters of enamelled samples (or representative fired powders) were measured with a Perkin–Elmer spectrophotometer using standard lighting C, following the CIE-$L^*a^*b^*$ colourimetric method recommended by the CIE (Commission Internationale de l'Eclairage).[13] On this method, L^* is the lightness axis [black (0) → white (100)], b^* is the blue (–) → yellow (+) axis and a^* is the green (–) (red (+) axis.

Information about the oxidation state and coordination environment of the chromophore (vanadium) in some optimised powder and enamelled samples was also obtained by means of UV–V–NIR spectroscopy (diffuse reflectance) performed with a Perkin–Elmer spectrophotometer at a range between 200 and 2000 nm. The final optimised composition was also characterised by Scanning Electron Microscopy (SEM), using a Leo-440i Leyca electron microscope equipped with an Energy Dispersion X-ray (EDAX) attachment by Oxford University.

4 Results and Discussion

4.1 Effect of V_2O_5 on colour synthesis: optimisation of V_2O_5 addition

As a preliminary study, the effect of V_2O_5 addition on colour synthesis (without mineralisers) was analysed. With this aim, different compositions responding to the overall stoichiometry $(ZrO_2)(SiO_2)(V_2O_5)_x$ (where x took the values 0·05, 0·10, 0·15, 0·20, 0·25 and 0·30) were prepared. The mixed powders were then fired up to a temperature of 800°C. In Table 1 the evolution of crystalline phases and the colour of fired powders with different V_2O_5 contents are shown.

All the fired powders presented a green or yellowish-green colour instead of a blue colour. The yellow colour is observed to be stronger in compositions with considerable unreacted ZrO_2 (composition $x = 0{\cdot}05$), or with unreacted, residual V_2O_5 (compositions with $x \geq 0{\cdot}20$).

XRD showed that fired samples doped with less than 15% molar V_2O_5 ($x = < 0{\cdot}15$) still present an important amount of unreacted baddeleyite and quartz. Moreover, very weak XRD peaks assigned to unreacted V_2O_5 can be observed in compositions with a V_2O_5 content equal to or higher than 20% molar ($x \geq 0{\cdot}20$), suggesting the limit to solid solution.

Figure 2 shows the evolution of the firing loss (wt%), vanadium leached (ppm or mg/l of vanadium in the washing acid) and the blue colour, $-b^*$ (of samples 5%-enamelled with an opaque glaze), with V_2O_5 content. The firing loss is observed to rise linearly (from 1·7 to 6·8%) as a consequence of

Table 4. Evolution of powder colour and crystalline phases with single mineraliser addition (NaF or NaCl) at optimised firing temperatures

$(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaF)_x$ $T = 750°C$	x = *0·1*	x = *0·3*	x = *0·5*	x = *0·8*	x = *1·0*
Powder colour	Dark green	Green	Strong blue	Light blue	Light blue
Crystalline phases (XRD)	Z[a] (vs),[b] V (vw) V* (vw), B (w) Q (vw)	Z (s), V*/ N (vw) B (s), Q (m)	Z (m), N (vw) B (m), Q (vw)	Z, (vw), N (vw) B (w), Q (vw)	Z (vw), B (vw) Q (vw)
$(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaCl)_x$ $T = 800°C$	x = *0·1*	x = *0·2*	x = *0·3*	x = *0·4*	x = *0·5*
Powder colour	Dark green	Light green	Green	Blue	Strong blue
Crystalline phases (XRD)	Z (vs), V* (vw) Q (m)	Z (vs), V* (vw) B (vw), Q (m)	Z (vs), V*/N (vw) B (vw), Q (m)	Z (s–vs), N (vw), B (m–s), Q (vw)	Z (s–vs), N (vw) B (m–s), Q (vw)

[a] Crystalline phases: Z = ziron ($ZrSiO_4$) B = baddeleyite (monoclinic ZrO_2), Q = quartz (SiO_2), V = vanadium pentoxide (V_2O_5), N = sodium vanadium oxide ($NaVO_3$), V* = sodium vanadium bronzes $(5Na_2)\cdot xV_2O_4\cdot(12\text{–}x)V_2O_5$).

[b] XRD peak intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

the partial volatilisation of V_2O_5 during calcination, while the vanadium concentration in the washing acid rises almost asymptotically. Samples doped with a 25 or 30% molar of V_2O_5 present very high values of vanadium leached (273 and 225 ppm) and must therefore be discarded. As a result of washing with 0·3 M HNO_3, the fired powders became slightly bluer. Despite the green colour of the fired powders, all the samples developed a bluish colour once enamelled. As observed in Fig. 2(c), b^* values present a maximum at about 15–20% molar of V_2O_5.

Since the XRD pattern of the 20% V_2O_5 composition shows the presence of a small amount of unreacted V_2O_5, a slightly lower V_2O_5 content (19% molar) has been used for the further optimisation studies.

4.2 Effect of mineralisers addition: optimisation of firing temperature

Compositions with the overall stoichiometry $(ZrO_2)(SiO_2)(V_2O_5)_{0\cdot19}$ and $(ZrO_2)(SiO_2)(V_2O_5)_{0\cdot19}(M)_{0\cdot62}$ were prepared by the ceramic method (where M represents the F, Cl or B introduced with the mineralisers: NaF, NaCl or borax) and calcined up to different temperatures (650, 700, 750, 800, 850 and 900°C) following the same thermal shedule. The colour of the fired powders and the crystalline phases detected by XRD are summarised in Table 2.

In non-mineralised compositions, the zircon phase is first observed at 800°C. At lower temperatures (between 750 and 800°C), a zirconium pirovanadate phase (ZrV_2O_7) occurs together with unreacted quartz and zirconia, in accordance with the reaction mechanism proposed by Matkovitch[8] and Cini.[14] The formation of this phase as a reaction intermediate and its decomposition at about 760°C to form a liquid phase account for the self-mineralising effect of vanadium in colour synthesis. In this respect, unreacted, residual V_2O_5 is also detected by XRD between 800 and 900°C, contributing to the green colour of this samples. Despite this, enamelled samples develop an acceptable bluish colour ($-b^*$ around 14–15), which is also relatively dark (L^* around 70) in comparison with mineralised samples (L^* higher than 75).

With NaF addition, the zircon phase is observed at lower temperature (it is first observed at 750°C and reaches a maximum yield at 800°C). With NaCl, zircon is formed from 800°C.

Compositions mineralised with NaF and NaCl develop the blue-turquoise coloured powder characteristic of the V^{4+}–$ZrSiO_4$ solid solution, in contrast to the green colour of non-mineralised powders. Furthermore, XRD peaks about 29–30 °2θ are observed over the whole firing temperature range corresponding to $NaVO_3$, while free V_2O_5 is not detected.

Compositions doped with borax do not fully stabilise zircon up to 900°C (at 850°C only weak zircon peaks are detected), producing brown powders. Together with the formation of sodium–vanadium oxides or bronzes, borax addition generates a borosilicate vitreous phase, confirmed by greatly reduced quartz peaks and by a vitreous halo centered at 7°2θ. At 850°C, the borosilicate phase starts reacting with ZrO_2 to give $ZrSiO_4$, but the brown colour of the fired powders obtained indicates that vanadium does not enter the zircon lattice.

Therefore, three different intermediate phases have been observed: zirconium pirovanadate (ZrV_2O_7) in the absence of mineralisers, sodium metavanadate ($NaVO_3$) when sodium halides are added, and sodium–vanadium bronzes and a borosilicate vitreous phase in the case of borax mineralised samples.

To analyse the structural effect of halide additions, the zircon unit-cell parameters and volume in 800°C-calcined samples were determined (Table 3)

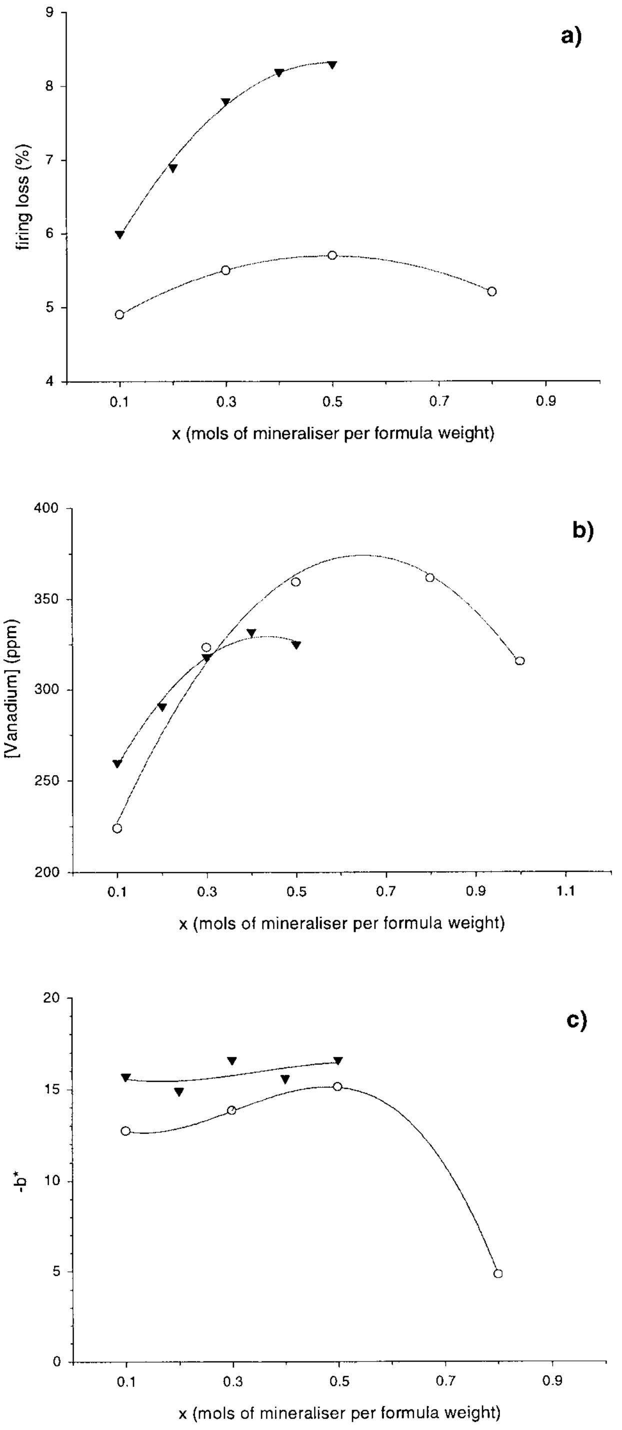

Fig. 4. Evolution of (a) firing loss, (b) vanadium leached and (c) blue colour ($-b^*$) of samples enamelled with an opaque glaze with mineraliser addition (○: with NaF, ▼: with NaCl).

using the POWCAL and LSQC programmes. In accordance with the literature,[4] the entrance of both F^- and V^{4+} in the zircon lattice, substituting for O^{2-} and Zr^{4+}, respectively, involves a decrease in the zircon unit cell volume [Shanon–Prewitt ionic radii:[15] $r_{F^-} = 1{\cdot}16$ Å (threefold)-1·19 Å (sixfold), $r_{O^{2-}} = 1{\cdot}22$ (threefold)-1·26 Å (sixfold), $r_{V^{4+}} = 0{\cdot}86$ Å (eightfold), $r_{Si^{4+}} = 0{\cdot}40$ Å (fourfold) and $r_{Zr^{4+}} = 0{\cdot}94$ Å (eightfold)]. As can be observed in Table 3, the zircon unit cell parameters and volume become smaller with NaF and NaCl additions. In the NaCl mineralised sample, the bigger chloride ion [$r_{Cl^-} = 1{\cdot}67$ Å (sixfold)][15] does not seem to substitute for the oxide ion, since this would involve an increase in unit cell volume.

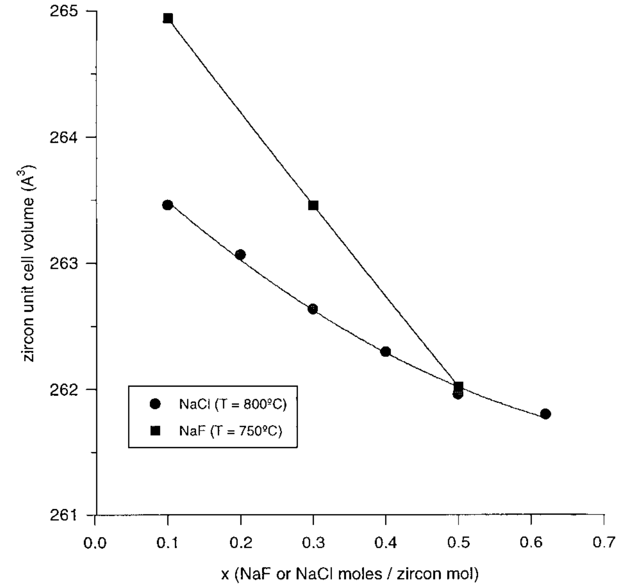

Fig. 5. Evolution of zircon unit cell volume with the NaCl or NaF addition.

Regarding the environmental parameters studied (Fig. 3), the firing loss rises slightly with the firing temperature and with mineraliser addition. Vanadium leached is observed to increase substantially in mineralised samples for temperatures where zircon is still being formed and vanadium is not accommodated in the zircon-lattice. The lowest values of vanadium leached are obtained at 750°C in NaF and at 800°C when using NaCl.

With regard to the blue colour of samples enamelled with the opaque glaze, compositions mineralised with NaF and NaCl become bluer at 800°C ($-b^* = 18{\cdot}4$), though an acceptable blue colour is also obtained with the NaF-mineralised sample fired at 750°C. Borax-mineralised samples did not develop green or blue colouration.

While borax addition must be discarded for blue vanadium zircon synthesis, NaF and NaCl prove to have a positive effect, producing bluer colours, but also raising the vanadium concentration in the washing acid. The optimal firing temperatures appear to be 750°C using NaF (firing loss = 5·1%, vanadium leached = 322 ppm, $b^* = -15{\cdot}2$) and 800°C when using chlorides (firing loss = 8·4%, vanadium leached = 326 ppm, $b^* = -18{\cdot}4$). In the case of NaF addition, though firing at 800°C yields a bluer colour, from an environmental and energy-saving point of view, firing at 750°C is preferred. The composition without mineralisers fired at 800°C is environmentally attractive (firing loss = 4·6%, vanadium leached = 176 ppm, $b^* = -14{\cdot}5$), confirming the importance of vanadium addition optimisation.

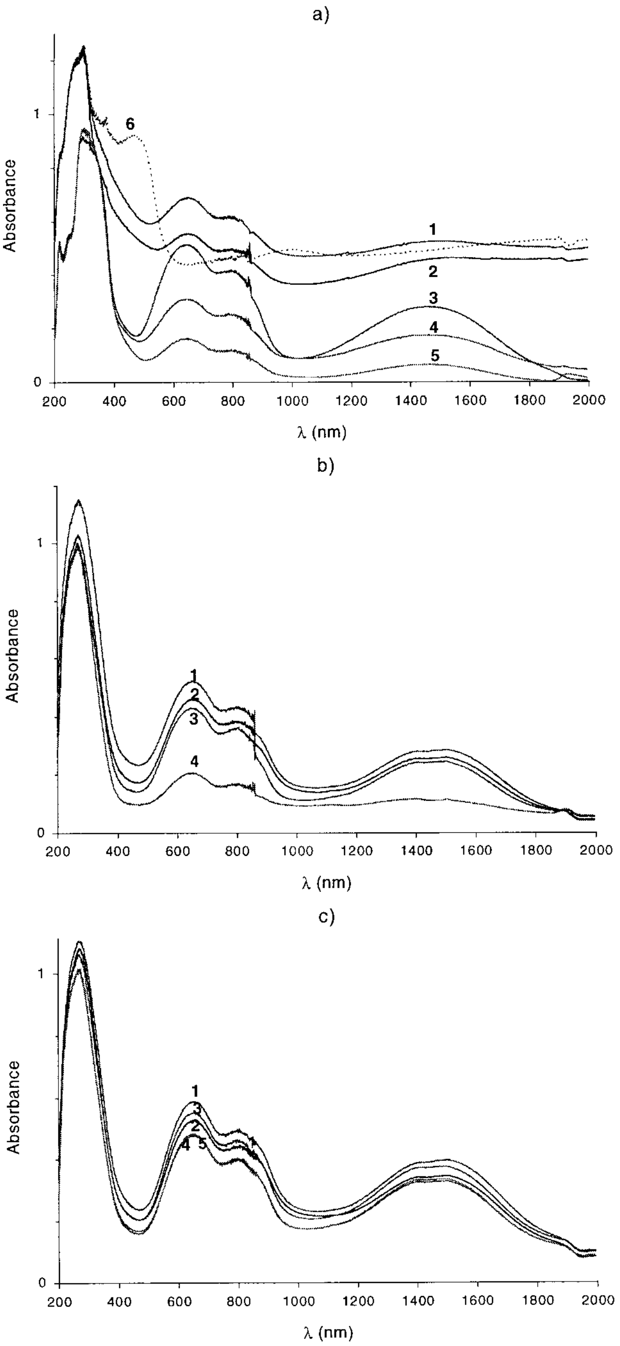

Fig. 6. UV–VIS–NIR spectra of: (a) unwashed powders, 750°C-fired and mineralised with NaF (1: 10% NaF, 2: 30% NaF, 3: 50% NaF, 4: 80% NaF, 5: 100% NaF and 6: commercial V_2O_5 of Fluka); (b) washed, NaF-mineralised compositions enamelled with an opaque glaze (1: 10% NaF, 2: 30% NaF, 3: 50% NaF and 4: 80% NaF); (c) washed, NaCl-mineralised compositions enamelled with an opaque glaze (1: 10% NaCl, 2: 20% NaCl, 3: 30% NaCl, 4: 40% NaCl and 5: 50% NaF)

4.3 Optimisation of single mineraliser addition

Different compositions with the overall stoichiometry $(ZrO_2)(SiO_2)(V_2O_5)_{0\cdot19}(M)_x$ were prepared by the ceramic method; the moles (x) of mineraliser M (expressed as F or Cl) added per zircon formula weight were 0·1, 0·3, 0·5, 0·8 and 1·0 in compositions mineralised with NaF (M = F), and 0·1, 0·2, 0·3, 0·4 and 0·5 in NaCl-mineralised compositions (M = Cl). The former compositions were fired at 750°C, while the later were fired at 800°C. The evolution of fired powder colour and crystalline phases with the mineraliser addition is summarised in Table 4. Similarly, in Fig. 4 the evolution of firing loss, vanadium leaching and blue colour ($-b^*$ value obtained with enamelled samples) with the mineraliser addition is presented.

Addition of NaF and NaCl in molar ratios equal or lower than 30% ($x \leq 0\cdot3$) gives rise to green powders instead of blue pigments. Nevertheless, washed and enamelled samples develop acceptable bluish colours. Higher NaF or NaCl additions ($x \geq 0\cdot4$) produce blue–turquoise powders, which become lighter as the mineraliser content increases. In addition, XRD patterns of mineralised samples show the presence of residual phases: sodium and vanadium bronzes ($5Na_2O{\cdot}xV_2O_4(12-x)V_2O_5$) are observed (main peak around 27·5–27·8°2θ) in powders with $x \leq 0\cdot3$, while the sodium metavanadate ($NaVO_3$) is observed when $x \geq 0\cdot3$. Furthermore, although the powder colour changes from green to blue, the addition of higher amounts of mineraliser (NaF or NaCl) is accompanied by a lower zircon yield, resulting in higher firing losses and higher vanadium concentrations in the washing acid (see Fig. 4). The highest zircon yield and the lowest firing losses and vanadium leaching are obtained in compositions mineralised with 10% molar of NaF or NaCl ($x = 0\cdot1$). Therefore, though enamelled samples exhibit a slightly bluer colour with a NaF or NaCl addition around 50% molar, compositions with only 10% of NaF or NaCl are optimal environmentally.

The reduction of the unit cell volume with NaF or NaCl addition can be seen in Fig. 5. The employment of higher amounts of NaF or NaCl seems to facilitate vanadium accommodation in dodecahedral sites substituting for Zr^{4+} ions, in agreement with the literature.[4] The bigger chloride ions do not seem to enter into the zircon lattice, since the zircon unit cell is also observed to diminish in NaCl-mineralised samples.

UV–V–NIR spectroscopy of NaF and NaCl mineralised samples has been carried out to reveal the coordination sites occupied by tetravalent vanadium, as well as to confirm the presence of pentavalent vanadium in the samples and explain the colour changes observed. The assignment of the absorption bands of V^{4+} ions in tetrahedral and dodecahedral coordination can be found in the literature.[16] Although the coordination of V^{+5} cannot be determined by optic spectroscopy due to its closed electron shell, its presence can be confirmed by a broad charge transfer band around 400 nm.[14]

In Fig. 6, the UV–V–NIR spectra of unwashed NaF-mineralised powders [Fig. 6(a)] can be seen,

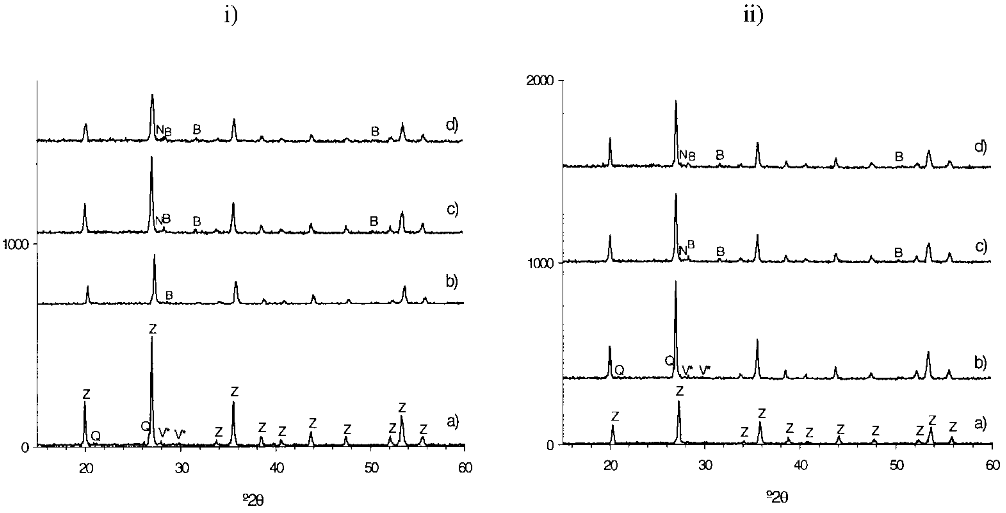

Fig. 7. XRD patterns of 800°C-fired powders corresponding to both binary series: (i) series $(ZrO_2)(SiO_2)$ $(V_2O_5)_{0{\cdot}19}(NaF)_{0.10}$ $(NaCl)_x$, and (ii) series $(ZrO_2)(SiO_2)(V_2O_5)_{0{\cdot}19}(NaF)_x(NaCl)_{0{\cdot}10}$ (a) $x=0{\cdot}00$, (b) $x=0{\cdot}05$, (c) $x=0{\cdot}10$ and (d) $x=0{\cdot}15$. Crystalline phases: Z = zircon ($ZrSiO_4$), B = baddeleyite (ZrO_2), Q = quartz (SiO_2), V* = sodium–vanadium bronzes ($5Na_2O{\cdot}xV_2O_4{\cdot}(12-x)V_2O_5$) and N = sodium vanadium oxide ($NaVO_3$).

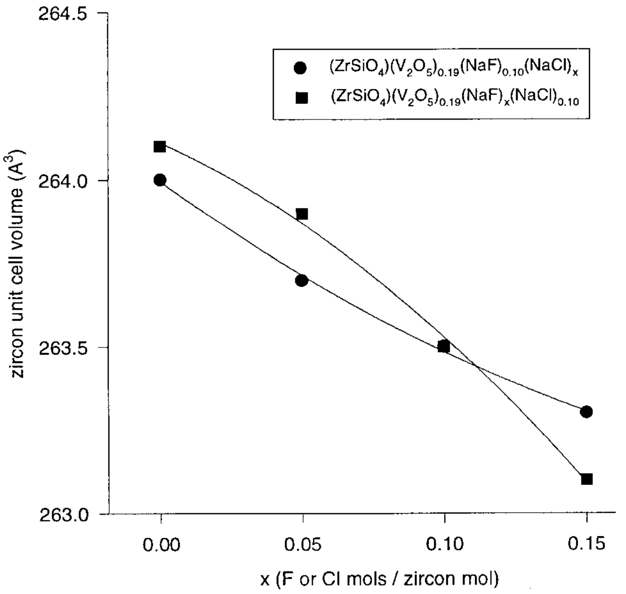

Fig. 8. Evolution of zircon unit cell volume with NaCl and NaF addition in samples with a binary NaF–NaCl mineraliser system.

together with the spectra of enamelled samples mineralised with NaF and NaCl [Fig. 6(b) and (c)]. The unwashed fired powders with green colour (10 and 30% molar NaF) present a much higher absorbance around 400 nm as well as a steadily high absorbance between 1000 and 2000 nm, very similar the V_2O_5 spectrum. These features of V^{5+} are not observed in blue powders (%NaF≥50%) and enamelled samples [see Fig. 6(b) and (c)], which present the typical bands of V^{4+}.

Analysing the spectra of enamelled samples (mineralised with NaF and NaCl), the band exclusively attributed to vanadium in dodecahedral sites (290–297 nm)[14] does not change substantially, while the band assigned to vanadium in tetrahedral environment (1381–1405 nm)[14] becomes smaller with NaF or NaCl addition. This result suggests that vanadium preferentially occupies dodecahedral sites as the amount of NaF or NaCl increases, confirming the literature data.[4]

Therefore, 10% molar additions are optimal, despite the green colour of fired powders, since these compositions with NaF or NaCl give a higher zircon yield, minimise the firing loss and vanadium leaching and develop an acceptable blue colour once enamelled.

4.4 Optimisation of the addition of a binary NaF–NaCl mineraliser system

Two binary series, $(ZrO_2)(SiO_2)(V_2O_5)_{0{\cdot}19}(NaF)_{0{\cdot}10}$ $(NaCl)_x$ and $(ZrO_2)(SiO_2)(V_2O_5)_{0{\cdot}19}(NaCl)_{0{\cdot}10}$ $(NaF)_x$, with $x = 0{\cdot}00$, $0{\cdot}05$, $0{\cdot}10$, $0{\cdot}15$, were prepared in order to optimise the binary NaF–NaCl mineraliser system. The powders were calcined up to 800°C following the same thermal shedule as in previous studies.

Samples mineralised with 10% NaF (Fig. 7) did not improve the zircon yield with NaCl addition. In contrast, compositions with 10% of NaCl, presented a higher zircon yield when NaF was added. The highest zircon yield was obtained in the sample doped with 10% NaCl and 5% NaF and in the sample with only 10% NaF. Very weak XRD peaks corresponding to sodium-vanadium bronzes (for $x < 0{\cdot}10$) or sodium metavanadate (for $x \geq 0{\cdot}10$) were also detected.

In Fig. 8 the reduction of zircon unit cell parameters and volume with the addition of the second mineraliser (NaCl or NaF) can be seen.

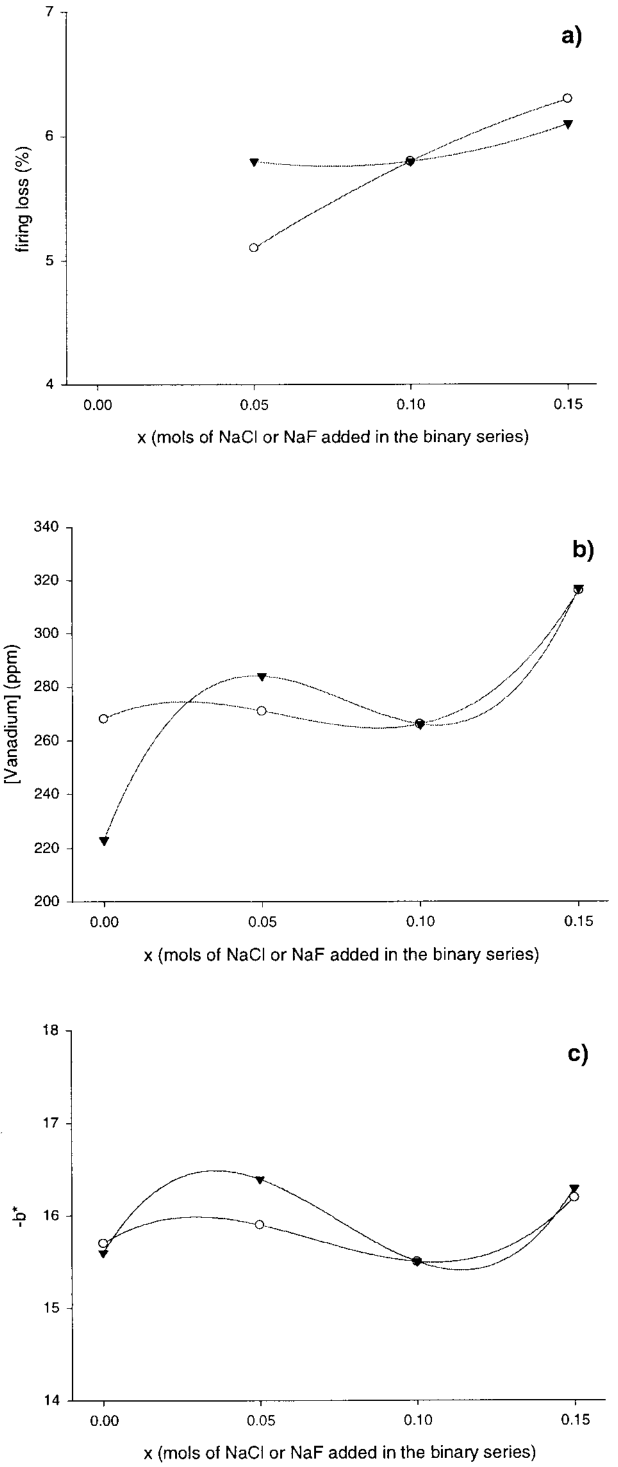

Fig. 9. Evolution of (a) firing loss, (b) vanadium leached and (c) blue colour (−*b**) of samples enamelled with an opaque glaze with the addition of the second mineraliser in both binary series; ○: $(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaF)_{0\cdot10}(NaCl)_x$, and ▼: $(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaF)_x(NaCl)_{0\cdot10}$.

Analysing the environmental performance (Fig. 9), the firing loss is observed to rise with halide additions. On the other hand, vanadium leaching is observed to rise with the amount of second mineraliser (NaF or NaCl) up to 5%, then to diminish slightly and finally to reach the highest values with additions of 15%. Vanadium leaching is slightly higher in binary-mineralised samples than in samples with a single NaCl addition. Enamelled samples developed a bluish colour. The blue component (−*b**) present a similar behaviour to that of vanadium leaching.

Accordingly, despite the slight increase in vanadium leached, a binary NaF–NaCl mineraliser system gives a higher zircon yield and a better blue colour; the composition doped with 10% NaCl and 5% NaF (firing loss = 5·8, vanadium leached = 284 ppm, *b** = −16·4) is the optimal binary mineralised sample.

In Table 5 the environmental and colour (*b**) parameters obtained in the different optimisation studies are summarised. The use of mineralisers gives better blue colours, but also higher emisions to the atmosphere and higher vanadium leaching.

4.5 Characterisation of the final optimised composition

Finally, the optimal binary mineralised composition, $(ZrO_2)(SiO_2)(V_2O_5)_{0\cdot19}(NaCl)_{0\cdot10}(NaF)_{0\cdot05}$,

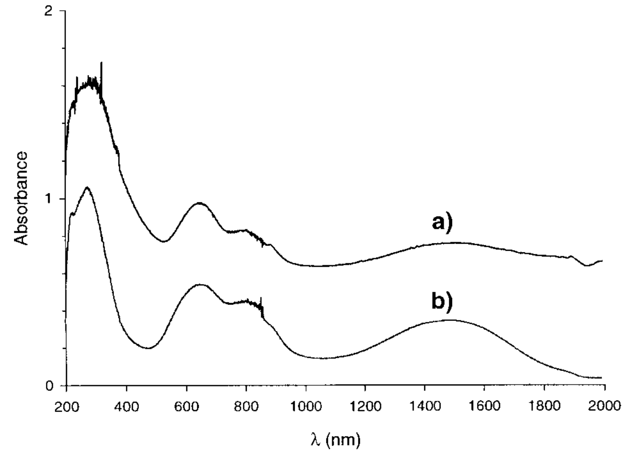

Fig. 10. UV–V–NIR spectra of the optimal binary mineralized sample (with 0·10 mol of NaCl and 0·05 mol of NaF per zircon formula weight) fired at 800°C (a) spectrum of the unwashed, fired powder, and (b) spectrum of the sample enamelled with an opaque glaze.

Table 5. Environmental and colour (*L***a***b**) parameters[a] obtained with different optimised samples

Optimisation	*Composition*	*Firing loss (%)*	*Vanadium leached (ppm)*	*L**	a*	*b**
V_2O_5 content	$(ZrSiO_4)(V_2O_5)_{0\cdot19}$/800°C	4·6	176	70·1	−13·1	−14·5
NaF content/***T***	$(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaF)_{0\cdot10}$/750°C	4·9	224	74·0	−11·7	−12·7
NaCl content/***T***	$(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaCl)_{0\cdot10}$/800°C	6·0	260	71·8	−13·3	−15·7
NaF-NaCl content	$(ZrSiO_4)(V_2O_5)_{0\cdot19}(NaF)_{0\cdot05}(NaCl)_{0\cdot10}$/800°C	5·8	284	71·3	−13·2	−16·4

[a] Colour parameters measured on samples enamelled (5% colour) with an opaque commercial glaze.

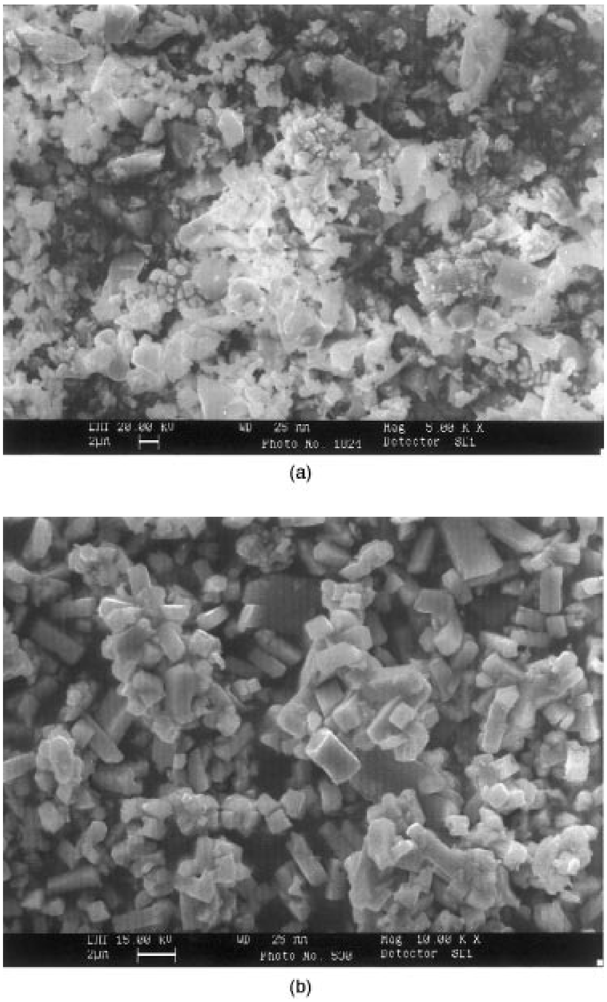

Fig. 11. SEM details (secondary emission images) of the optimal binary mineralised composition $(ZrSiO_4)(V_2O_5)(NaF)_{0\cdot 05}(NaCl)_{0\cdot 10}$: (a) raw, (b) fired at 800°C.

has been characterised by UV–V–NIR spectroscopy and by SEM/EDX.

In Fig. 10 the optic spectra corresponding to the 800°C-fired, unwashed powder and to the washed and enamelled sample are shown. Signals for the V^{5+} charge transfer band[14] and for tetravalent vanadium[16] are clearly present, similarly to the spectra shown in Fig. 6 (Section 4.3).

The microstructure of raw and 800°C-fired powders of this optimal mineralised composition have been characterised by scanning electron microscopy (Fig. 11) Coarse particles of different morphologies and sizes (ranging from 1 to 10 μm), corresponding to the different precursors, are present in the raw powder.

In the 800°C-fired powder, zircon particles with tetragonal symmetry (~1–2 μm) form aggregates (~5–10 μm). Together with these zircon aggregates, bigger (5–10 μm), coarse particles can also be observed. EDAX-mapping (not shown) indicates that these coarse particles correspond to unreacted, residual quartz, in agreement with XRD characterisation. Likewise, EDAX analysis confirms the presence of vanadium enriched zones, mainly associated with sodium and forming large, prism-shaped crystalls (~5 μm), in accordance with the observation of sodium–vanadium bronzes by XRD.

5 Conclusions

1. The formation of different reaction intermediates for different mineralising agents (ZrV_2O_7 with no mineralisers, $NaVO_3$ and/or sodium–vanadium bronzes with sodium halides, and a borosilicate vitreous phase with borax) proves to have an important effect on pigment synthesis, leading to different zircon yields and to a different colour performance in the fired pigments.
2. The composition $(ZrSiO_4)(V_2O_5)_{0\cdot 19}(NaF)_{0\cdot 05}(NaCl)_{0\cdot 10}$ has been found to be optimal environmentally (firing loss = 5·8%, vanadium leached = 284 ppm and $b^* = -16\cdot 4$), though the non-mineralised composition (with 0·19 mol of V_2O_5 per zircon formula weight) also presents good behaviour.

Acknowledgements

M. L. is grateful to the Consellería de Cultura, Educació i Ciència de la Generalitat Valenciana for his research grant.

References

1. Booth, F. T. and Peel, G. N. *Trans. Brit. Ceram. Soc.*, 1959, **58**, 532.
2. Matkovitch, V. I. and Corbett, P. M., Formation of zircon from zirconium dioxide and silicon dioxide in the presence of vanadium pentoxide. *J. Am. Ceram. Soc.*, 1961, **443**, 128.
3. Monrós, G., Carda, J., Escribano, P. and Alarcón, J., Synthesis of V–$ZrSiO_4$ solid solutions. *J. Mater. Sci. Lett.*, 1990, **9**, 184.
4. Monrós, G., Carda, J., Tena, M. A., Escribano, P., Sales, M. and Alarcón, J., Different kinds of solid solutions in the V_2O_5–$ZrSiO_4$-NaF system by sol–gel processes and their characterization. *J. Eur. Ceram. Soc.*, 1993, **11**, 77.
5. Tena, M. A., Monrós, G., Carda, J., Escribano, P. and Alarcón, J., Efecto mineralizador del V_2O_5 en las transiciones de fase de pigmentos cerámicos. *Bol. Soc. Esp. Ceram. Vidr.*, 1990, **29**(3), 177.
6. Marchesini, L. and Ramous, E., Sulla struttura dei pigmenti verdi e bleu turchese contenenti vanadio. *Vetro Silic.*, 1964, **45**, 5.
7. Demiray, T., Nath, D. K. and Hummel, F. A., Zircon–vanadium blue pigment. *J. Am. Ceram. Soc.*, 1970, **53**, 1.
8. Matkovitch, V. I. and Corbett, P. M., Formation of zircon from zirconium dioxide and silicon dioxide in the presence of vanadium pentoxide. *J. Am. Ceram. Soc.*, 1961, **44**(3), 128–130.

9. Monrós, G., Martí, M. C., Carda, J., Tena, M. A. and Escribano, P., *J. Mat. Sci.*, 1993, **28**, 5852.
10. Monrós, G., Carda, J., Tena, M. A., Escribano, P., Cantavella, V. and Alarcón, J., *Mat. Res. Bull.*, 1992, **27**, 753.
11. Vicent, J. B., Badenes, J., Llusar, M., Tena, M. A. and Monrós, G., Microstructural differentiation between the green and turkish blue solid solutions of V in a zircon lattice obtained by the sol–gel process. *J. Sol–Gel Sci. Tech.*, 1998, **13**, 347–352.
12. ASTM card, Zircon, 6-0266.
13. CIE, *Recommendations on Uniform Colour Spaces, Colour Difference Equations*. Psychometrics Colour Terms. Suplement no. 2 of CIE Publ. No. 715 (E1-1.31) 1971. Bureau Central de la CIE, Paris, 1978.
14. Cini, L., Reactions between SiO_2–ZrO_2–V_2O_5; their relations to the formation of Pigments. *Ceramica (Florence)*, 1963, **16**(3), 345–346.
15. Shannon, R. D., *Acta Crystallogr.*, 1976, **A32**, 751–767.
16. Hong Xiayou, Bai Gui-Ku and Zhao Ming-Guang , The study of the optical and the EPR spectra od V^{+4} in zircon-type crystals. *J. Phys. Chem. Solids*, 1985, **46**, 719.