Journal of the European Ceramic Society 21 (2001) 1131–1138

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The effect of albite wastes on glaze properties and microstructure of soft porcelain zinc crystal glazes

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Received 12 July 2000; received in revised form 6 October 2000; accepted 10 October 2000

Abstract

The efficient utilisation of waste materials arising from diverse industrial branches is of technological importance. As a replacement material for feldspar in some soft porcelain zinc crystal glazes, albite triage wastes which contain high levels of titania have been investigated. It has been seen that this material decreases glaze maturing temperature and that during slow cooling it promotes crystallisation resulting in very attractive natural crystal growth. These positive effects suggest that albite triage wastes can easily be used in zinc crystal glazes as an alternative to feldspar. By doing so, glaze cost will be decreased and a waste material will be effectively utilised. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Albite wastes; Glazes; Microstructure-final; TiO_2; Waste materials; Zinc crystal glazes

1. Introduction

Living standard is dependant upon continuously improved technological development. However, to prepare high quality materials and to use them effectively in daily life requires that many industrial branches continue to consume natural sources. This can disturb the ecological conditions, vital and necessary for living creatures, and can eventually threaten our future. Therefore, in the 21st century as well reaping the profits of high technology, it is important to respect environmental issues; recycling attempts of waste materials are, therefore, of importance for the sake of present and future generations.

In conventional ceramic industry, beside several technical properties such as strength, durability etc. decorations and attractiveness of final products are also desired.[1] Amongst other ceramics especially porcelain items have preserved their valuable and comforting place in daily life. Their attractiveness is brought by several glazes. Crystalline glazes are only one of those. They can be either raw or fritted. For their development on the surface of the substrates suitable nucleation agents must be present in the glaze receipe and precise firing cycles have to be employed. Pure TiO_2 is valuable due to supplying acid resistance in the frit and in glazes and owing to the easiness of its solubility in the glaze and of the re-crystallisation causing matte appearances during cooling.[2,3] It has been also reported as an effective nucleating agent for the development of some specific crystal phases such as willemite.[4]

In nearly all glaze compositions feldspar is one of the main constituents to facilitate glaze maturing. Many of feldspar mines have been exhausted or have become uneconomical. Therefore, alternative sources are required. There are vast deposits of pegmatite which are being utilised to supply feldspar, produced by froth flotation.[1]

The Aydın Çine region of Turkey is rich in albite ores and several studies of triage and flotation wastes in glazes have already been made.[5,6] Since the albite triage wastes contain a high level of titania they seem to be good candidates for fluxing purposes and to promise good crystallisation in soft porcelain zinc containing crystalline glazes.

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PII: S0955-2219(00)00296-X

Table 1
The chemical composition of albite triage waste

	Wt.%		Wt.%
SiO_2	57.0	P_2O_5	2.0
Al_2O_3	19.3	Fe_2O_3	0.1
Na_2O	10.3	K_2O	0.1
TiO_2	8.5	Ignition loss	0.2
CaO	2.5		

Table 2
Seger formula of starting glaze

0.097 Na_2O		
0.005 K_2O		
0.048 CaO	0.240 Al_2O_3	1.910 SiO_2
0.039 MgO	0.003 Fe_2O_3	0.011 TiO_2
0.763 ZnO		
0.048 BaO		

2. Experimental procedure

2.1. Glaze preparation

Albite triage waste with the bulk dimension of about 15 cm was firstly crashed to decrease the particle size below to 1 mm. To start the investigation with an homogeneous waste material samples were taken from different part of the crashed waste.

Table 3
Heat treatment cycles applied[a]

	Heat treatment cycles (HTC)			HTC no.
Gloss firing temperature (°C)	Holding time (h)	Crystal growth temperature (°C)	Holding time (h)	
1280	3	1180	5	1
1250	3	–	–	2

[a] Heating rate 5°C/min and cooling rate 2°C/ min.

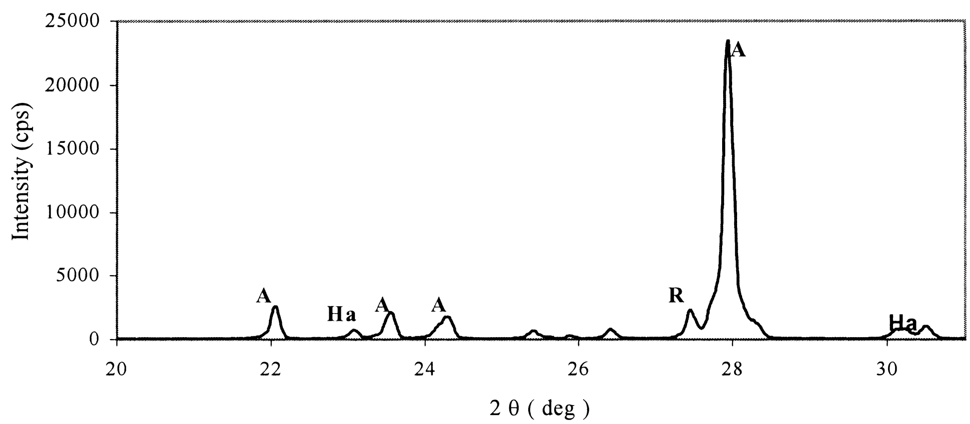


Fig. 1. XRD pattern of albite triage waste material (A, albite; R, rutile; Ha, hydroxyl apatite).

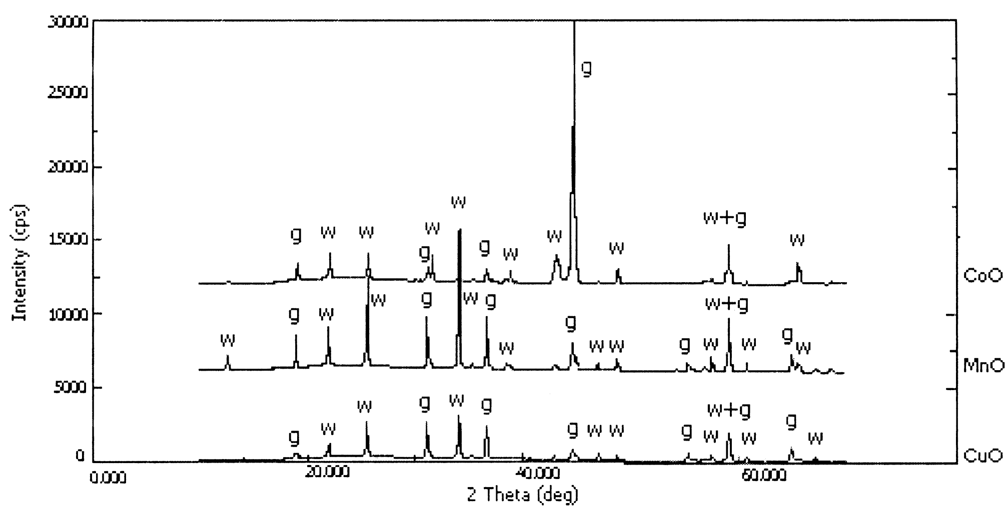
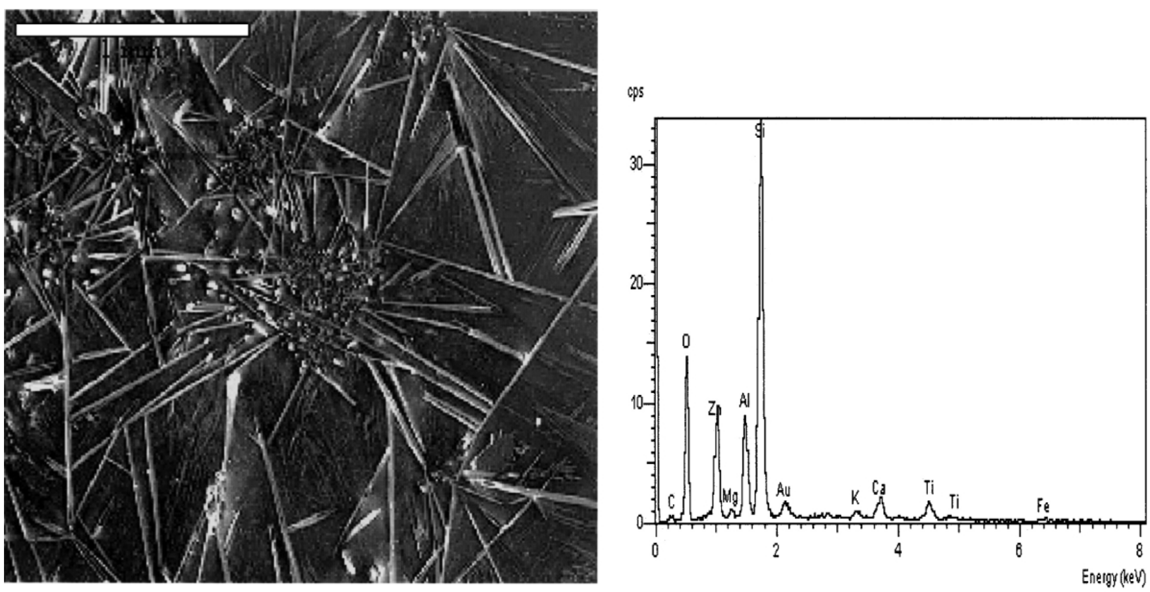


Fig. 2. XRD results of fired glazes with the replacement of albite triage waste for feldspar and the addition of CoO, MnO and CuO, respectively (w, willemite; g, gahnite).

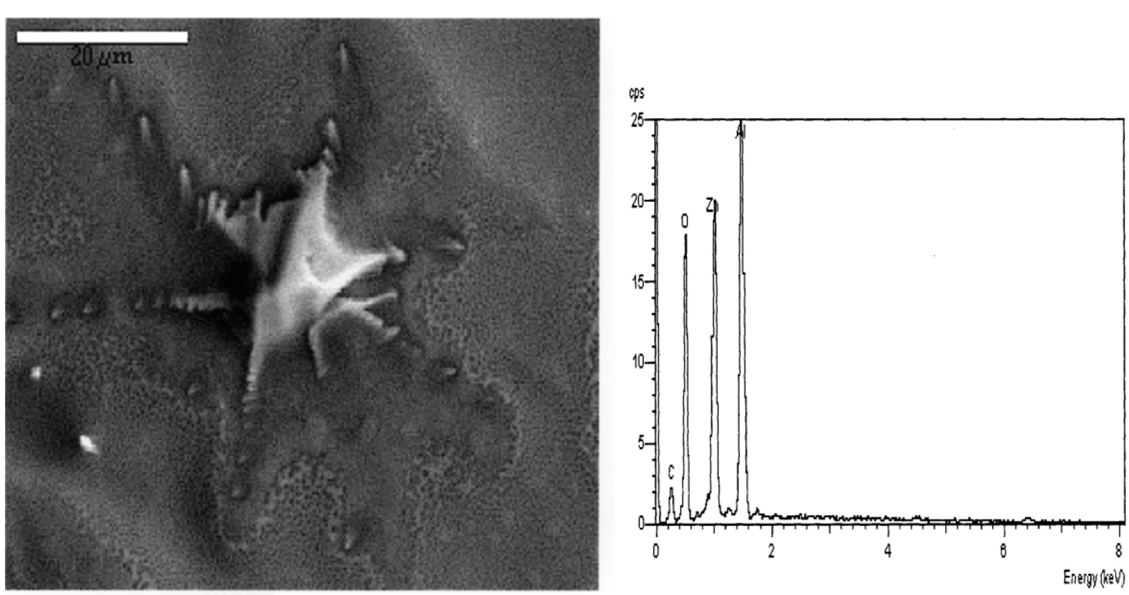
At the beginning of this study one specific zinc crystal glaze composition was selected as a base. Sodium feldspar was replaced by albite triage waste in this standard glaze. At the same time some colouring agent like CoO (at the level of 0.3 and 3%) MnO and CuO (at the level of 0.3 and 0.6%) in the form of pure oxide and limonite based pigments (as 1%) were added into newly synthesised glaze compositions.

After precise weighing of raw materials glaze batches were put into ball mills and ground 1 hour 15 min. Then colouring agents were incorporated into some of glaze slips and they are ground 45 min more. When milling operations were over, prepared glaze slips were put through 100 mesh sieves and under sieve was taken for glaze applications. Prepared glazes were applied onto soft porcelain bodies with the dimensions of 60×60×15 mm, which were prepared by an industrially used soft porcelain plastic slip (Kütahya Güral Porselen of Turkey) hand pressed into Plaster of Paris moulds and after drying biscuit fired at 1000°C for an hour, by pouring. Glazed samples were gloss fired at 1200–1280°C in oxidising atmosphere. After confirming nicely distributed



(a) (b)

Fig. 3. Willemite (rods) and gahnite (starlets) crystals in the starting glaze treated by HTC 1: (a) SEM and (b) EDX results of willemite.



(a) (b)

Fig. 4. Gahnite (starlets) crystals in the starting glaze treated by HTC 1: (a) SEM and (b) EDX results of gahnite.

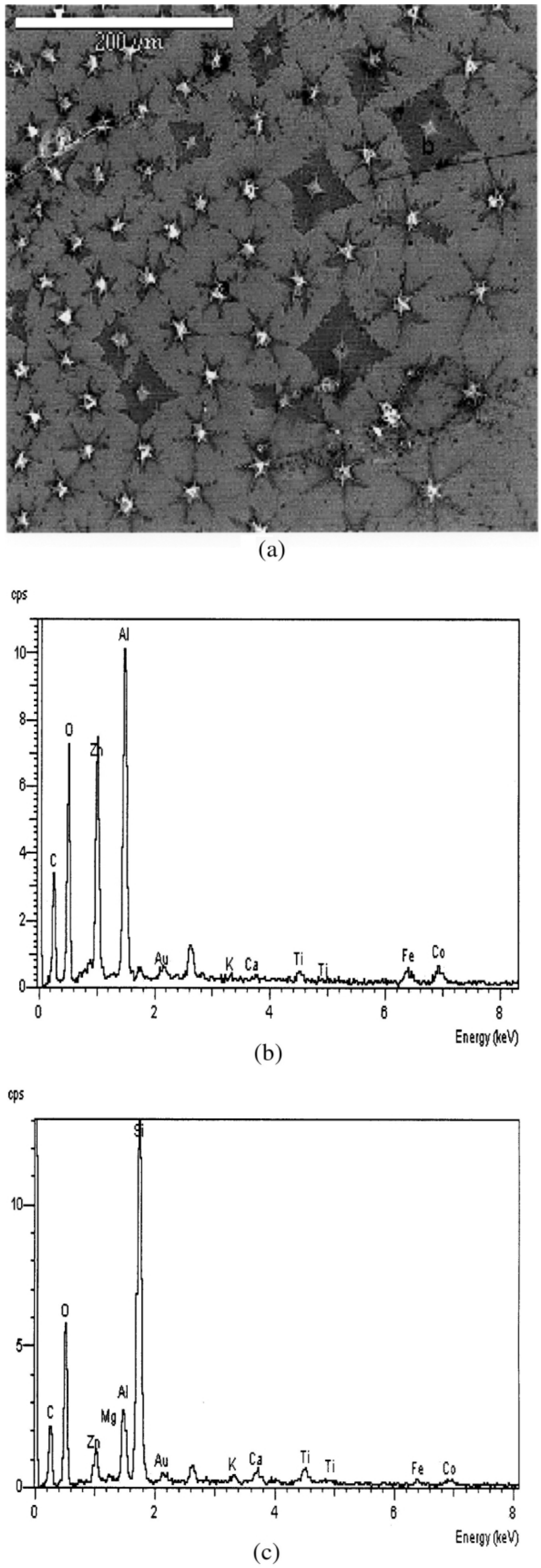


Fig. 5. (a) SEM picture showing overall crystals distribution of the glaze containing triage waste and 3% CoO treated by HTC 2; (b) EDX results of gahnite [starlet shown with letter a in (a)]; (c) EDX results of glassy phase [shown with letter b in (a)].

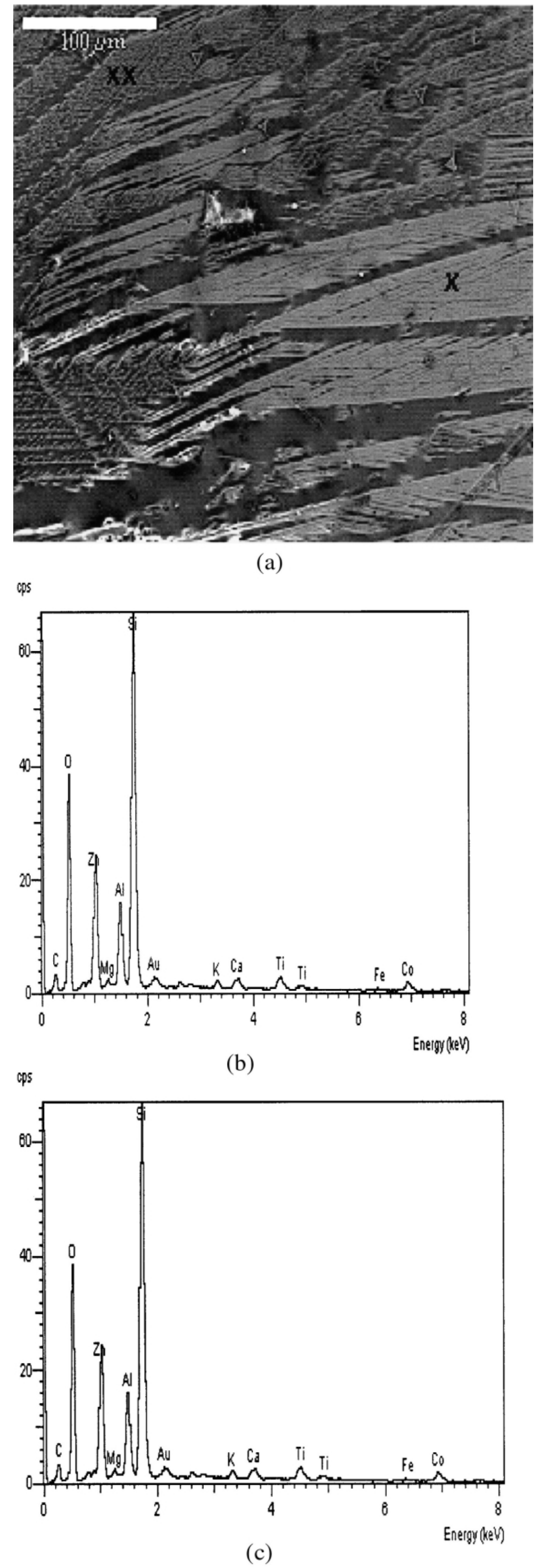


Fig. 6. (a) SEM picture showing willemite formation of the glaze containing triage waste and 3% CoO treated by HTC 2; (b) EDX results of the region shown with letter x in (a); (c) EDX results of the region shown with letters xx in (a).

crystal formation on plate shape samples, glazes with triage waste and CoO (0.3 and 3%, respectively) have also been applied on actual hollow wares industrially produced too.

2.2. Characterisation

The crystalline phases in the bulk materials were identified by X-ray diffraction (XRD) (Rigaku Rint 2000 Series) using CuK_α radiation. After that, same samples were investigated using scanning electron microscopy (SEM). The samples were coated with a thin film of gold-palladium or carbon and examined using a CamScan S4 at 20 kV. An ultra thin window energy dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to SEM was also used for chemical analysis.

3. Results and discussion

The triage and post flotation wastes of albite which is mined in Aydın Çine region of Turkey have recently been studied as a replacement for feldspar in some stoneware and soft porcelain glazes.[5,6] Their positive effect on glaze maturing has been reported. Table 1 shows the chemical composition of albite triage waste. Since it contains reasonable amount of both rutile and hydroxyl apatite (Fig. 1), its possible use in zinc containing crystalline glazes as a nucleation promoting material has been investigated in the present study.

Zinc oxide (ZnO) is not classified as a crystallisation agent but known to improve crystallisation in soft porcelain crystalline glazes producing its own phases; willemite (zinc silicate — Zn_2SiO_4) and gahnite (zinc aluminate —

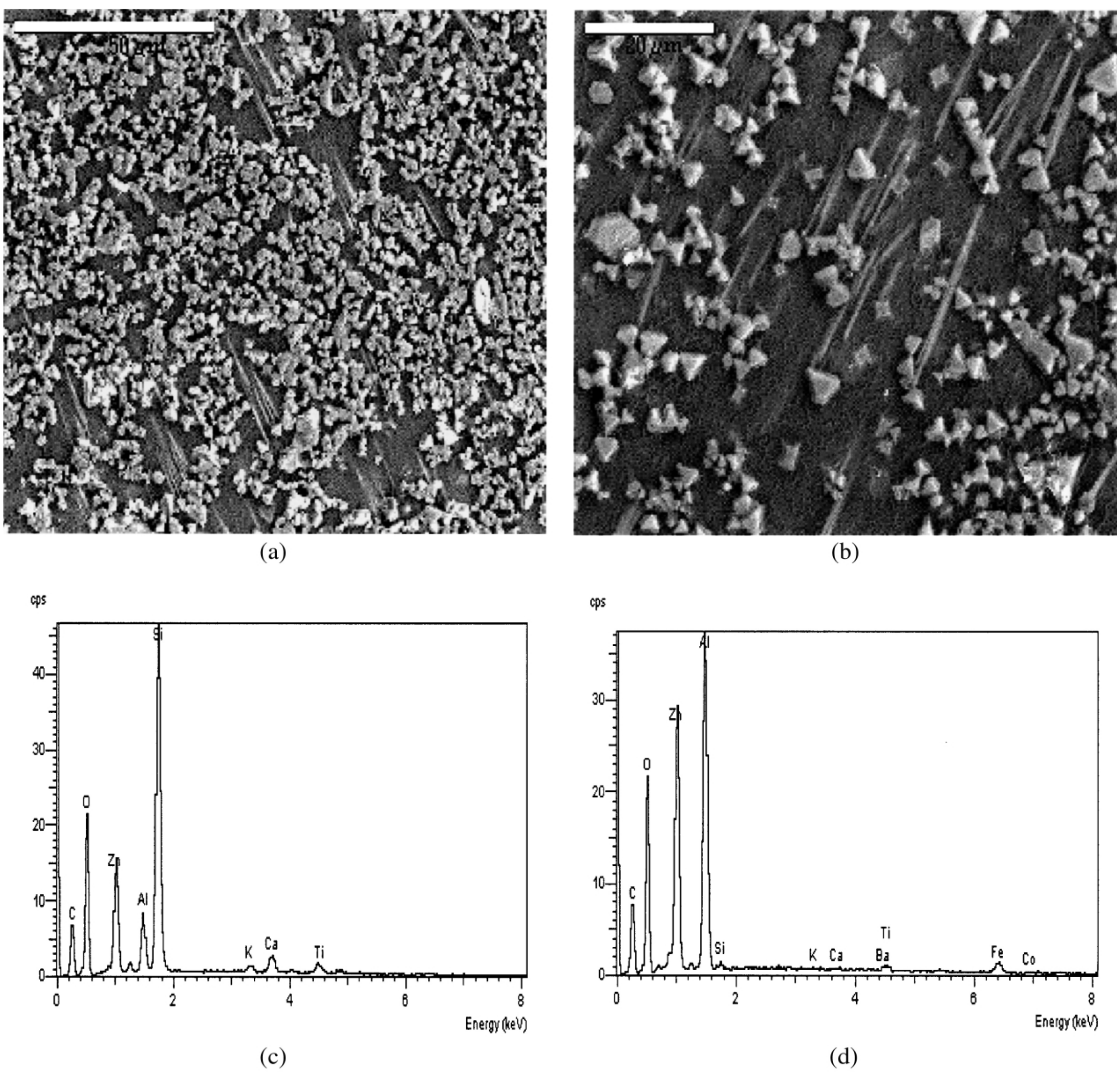


Fig. 7. (a) and (b) SEM picture of the glaze, consisting of albite triage waste and 1% Fe_2O_3 equivalent raw limonite, treated by HTC 2; (c) EDX results of the willemite rods in (a) and (b); (d) EDX results of gahnite (starlets) in (a) and (b).

$ZnAl_2O_4$) in the presence of enough amount of alumina and silica.[7–10] It is also reported that with those crystal phases ZnO can be used to produce opaque and matte glazes.[11–13] In some of previously done studies[7–10] although the relevant glaze systems did not contain titania which is known to produce nuclei for the development of zinc-based crystals[4] it was shown that even in the absence of TiO_2, ZnO is still capable of forming its own crystals.

In the current study a reference Zn-containing soft porcelain glaze (Table 2) was taken as a starting composition, which was originally studied before by applying HTC 1 (Table 3), and feldspar content of the glaze has been replaced by triage waste in order to see the overall effect in glaze maturing behaviour and the final microstructure. At the same time, CoO, MnO and CuO were incorporated into the glaze recipes with triage waste. Fig. 2 shows XRD results of fired glazes with these colouring agents. Colouring agent change the shape of willemite crystals from needle-like to leaves-like ones (Figs. 3, 5 and 6). Hereby only such effect of CoO is given.

With the use of albite waste in glaze batch actual glaze maturing temperature decreased from 1280 to 1250°C and for the crystal formation only one step heat treatment became sufficient in such case (Table 3).

Microstructural studies confirmed that whether Zn-containing glazes consist of waste material or not main crystal phases did not changed and remained as willemite and gahnite as reported before[7–10] (Figs. 3–7 and

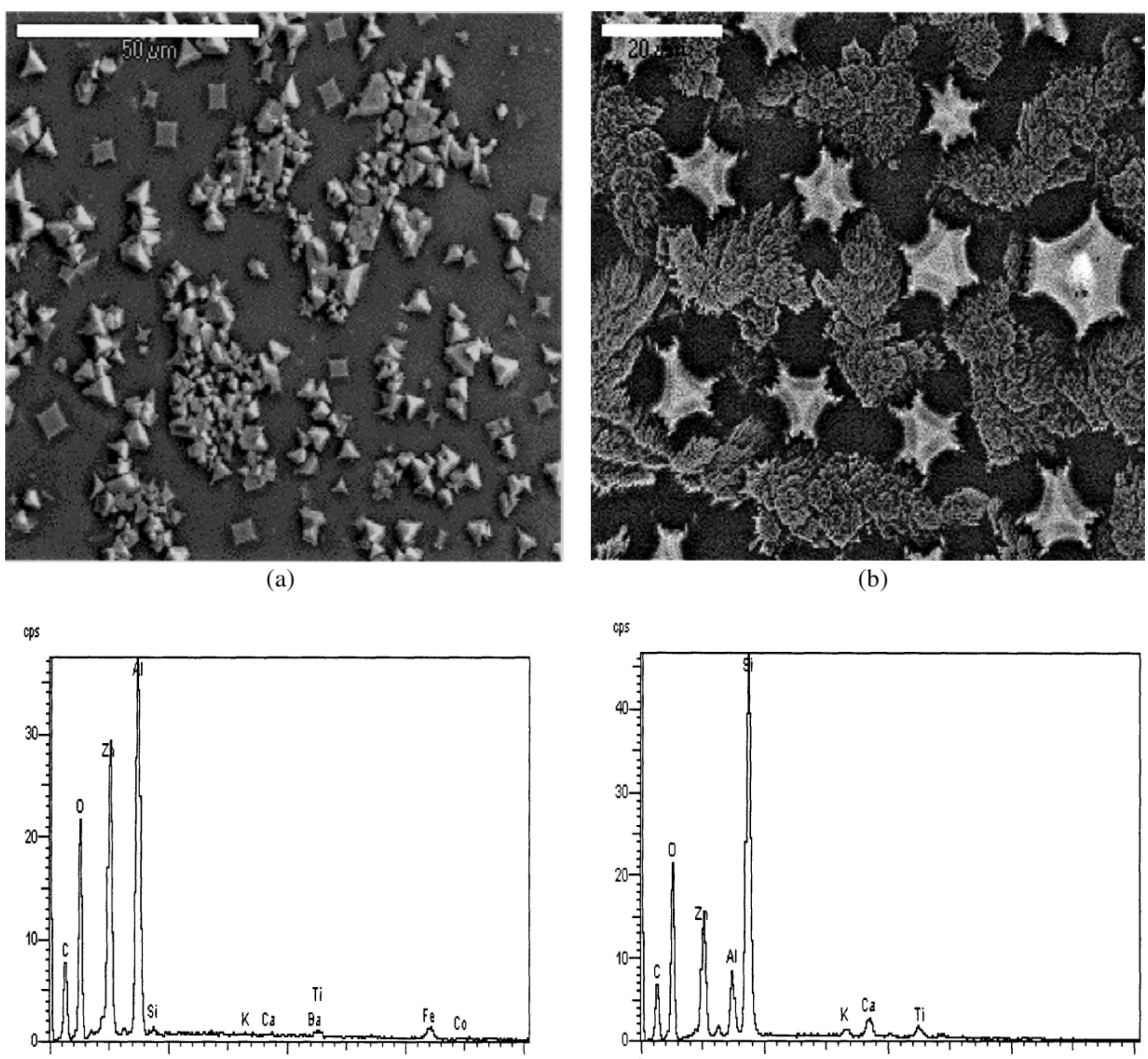


Fig. 8. (a) and (b) SEM picture of the glaze, consisting of albite triage waste and 1% limonite based pigment calcined at 1000°C, treated by HTC 2; (c) EDX results of star-like gahnite crystals in (a) and (b); (d) EDX results of leaf-like willemite crystals in (b).

(a)

(b)

Fig. 9. (a) Front view of a hollow ware glazed with albite and 0.3% CoO containing glaze heat treated by HTC 2; (b) top view of the same item.

Fig. 10. A vase glazed with albite and 3% CoO containing glaze heat treated by HTC 2.

8). Although it has been expected to see titania crystals playing a role for forming nucleous centres of willemite crystals there was no sign of its presence in crystal form suggesting that in these systems titania remains in glassy phase.

Additionally, limonite ore mined in Eskişehir Mihalıççık region of Turkey has also been previously studied in many different kind of ceramic glazes in order to determine its usage capacity as a colouring agent.[14–16] In this study, both raw limonite and calcined one at 1000°C have been put into glaze batches with albite triage waste separately at the level of 1 wt.% and the effect of such change on crystal formation, size and distribution under the same HTC (HTC 2 — Table 3) was examined. As can be seen from Figs. 7 and 8 again only willemite and gahnite formations take place noteworthy the shape of willemite crystals is again changed from needle-like shape to leaves-like ones.

Figs. 9 and 10 nicely confirm that the glazes with albite triage waste and a colouring agent can easily be utilised on industrially produced soft porcelain items.

4. Conclusions

1. For the development of zinc crystals, only one step HTC is sufficient enough by the use of albite triage waste.
2. The use of triage waste does not cause titania to play a nucleation promoting role in these systems.
3. Both the use of triage waste, limonite either raw or calcined and different kind of colouring agents result in change of willemite crystal shape but not in the type of crystal. In any case, only willemite and gahnite formations are observed.
4. Albite triage waste can easily and efficiently replaces feldspar in soft porcelain crystalline glazes decreasing maturing temperature from 1280 to 1250°C.

Acknowledgements

The authors would sincerely like to thank Mr. Gürsoy Arslan for XRD and Mr. Emrah Dölekçekiç and Mr. Güray Kaya for SEM and EDX measurements.

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