Production and Dissolution of Glazed Tiles Containing Cement-Dust

[1]F.M. Ezz-Eldin, [1]H.H. Mahmoud, [2]Y.K. Abd Elmonem and [3]M.R. Zakariya

[1]National Center for Radiation Research and Technology, Nasr-City, Cairo, Egypt.
[2]Menufya Univ., Faculty of Sci., Chem. Dept., Menufya, Egypt.
[3]Color Preparation Dept., Ceramica-Marselia Factory, Cairo, Egypt.

Abstract: Acidic and basic corrosion behavior of industrial ceramic-glaze with different cement-kiln-dust (CKD) contents (10, 20, 30 & 50wt. %) was investigated. Aqueous solutions containing 0.1, 0.5, 1 and 2N HC1 beside 1N of either H_2SO_4 or NaOH were used to measure the chemical corrosion of the prepared ceramic-glazes. SEM, EDX, pH and hardness measurements were used to evaluate the morphological and compositional changes of the corroded glaze sample by the action of aqueous solutions. The results indicate that when CKD content exceeds 30%, the chemical durability of the glazes is deteriorated by accelerating the hydrolysis of the basic glaze network. The corrosion weight loss is observed to vary with the nature of leaching solution and shows the highest corrosion with H_2SO_4 and the lowest with NaOH. CKD additions are observed to decrease the melting temperature from 1450 to 1200°C. Also, the FTIR results are observed to be affected by corrosion and CKD%. The FTIR spectra are in agreement and support the suggested corrosion behavior. Moreover, the prepared samples were further studied by soaking in a weakly alkaline cleaning agent solution (detergent solution) with pH value 9, in order to imitate the influence of normal household detergents on the surface properties of ceramic glazes.

Key words: CKD waste, Glazes, Corrosion, Surface analysis, Hardness.

INTRODUCTION

The bulk of cement-kiln-dust, mostly with high alkali contents, is land filled with a significant financial loss to the local cement industry in terms of the value of raw materials, processing, and energy consumption during pyroprocessing, dust collection, and disposal. This fine dust is emitted from cement kilns to prevent the build up of excessive salts in the cement products. Various methods for utilizing CKD in industrial applications, including existing or proposed methods for alkali removal, are reported in the literature (Bathy 1995, Nicholson 1978, Miller *et al.,* 1980). Because of the generally high lime content of CKD and subsequent ability to harden upon exposure to moisture, CKD has been used as a binder in soil stabilization suitable for a sub-base in streets and high way construction. It is commonly used as a mixture with different solid-waste materials such as waste glass, fly ash, waste water sludge with the addition of cement or other admixture if necessary (Nicholson, 1978; Bathy, 1983).

It is acceptable that (Sinton and LaCourse, 2001), the chemical durability of a glaze refers to its ability to withstand corrosion in a given environment (usually aqueous). Although glaze chemical durability is an important factor to be considered in waste vitrification, it is also a concern in the glaze-ceramics industry. High chemical durability is desired because even minor surface dissolution can lead to surface roughness and reflection of the glaze.

In general, glazes have an acceptable chemical durability in aqueous environments except in strong acids and bases. The high alumina as well as low alkali oxide content makes commercial glazes superior to other materials such as conventional soda-lime type of glasses. Immersion time, temperature and pH of the attacking medium are the most important factors for characterizing aqueous corrosion of ceramic coating (Eppler, 1992).

However, in several applications, the glazed surface also contains crystalline components. Predicting the chemical durability of glazes cannot thus be based on the simple additive principles used for homogeneous glasses. The typical crystals in glazes are mullite, anorthite and wollastonite, i.e. different crystalline silicates (Kingery *et al*., 1967), Literature of the behavior of these crystals in environments where glazes are typically used, is sparse. Recently, wollastonite and anorthite phases in glazes were reported to be attacked in acidic and neutral environments (Escardino *et al*., 2002, Kronberg *et al*., 2004, Bolelli *et al*., 2005).

Dissolution kinetics of silicates have been thoroughly studied at conditions typical for geochemistry or mineral processing (Kundu *et al*., Ezz-Eldin *et al*., 2010). For most silicate crystals, the dissolution is linear and show strong pH dependence. The reactions are reported to initiate at grain boundaries and other imperfections in crystal structure or at impurities attached to the grain surfaces. Dissolution of wollastonite was reported to be incongruent, i.e. to have different velocities for the dissolution of calcium and silicon ions, and thus lead to a formation of a silica gel in the surface. The dissolution studies on diopside crystals did not, however, show differences in the mutual solubility of the different components. Corrosion of crystalline albite in a glassy phase

---

Corresponding Author: Y.K. Abd Elmonem, Menufya Univ., Faculty of Sci., Chem. Dept., Menufya, Egypt.

174

with corresponding composition indicated that albite is dissolved congruently, as sodium ion dissolution from the glassy phase was much higher than of the other components, i.e. corresponding to a typical ion exchange reaction of glasses. Studies on the corrosion of fine-grained polycrystalline glass-ceramics indicate that the chemical durability cannot be solely deduced from the durability of the separate phases (Golubev *et al.*, 2005).

In the present study, it is aimed to clarify the following points from the corrosion studies of some prepared ceramic-glazes with addition of cement kiln dust: (1) The pH dependence of incongruent dissolution, if any, of the glaze constituents (2) The possible existence of leached layers and hillocks on the surfaces of corroded glazes (3) The changes of mechanical properties versus composition of ceramic-glazes.

Experimental Details:
2.1. Glaze-CKD Composite Preparation:

The detailed compositions of both CKD waste together with the industrial glaze are given in Tables 1 and 2, respectively. CKD used in the experiments was sampled from local Beni-Suef Cement-Company, while glaze was from local Sheeni Company. The chemical compositions for both CKD and industrial glaze were analyzed with a combination of inductively coupled plasma (ICP) and X-ray fluorescence spectroscopy (XRF) techniques. The prepared glaze batches were formulated as shown in Table 3. The cement dust was added with increasingly amounts in the different batches from 10% to 50%. The batches were melted individually in platinum crucibles 2%Rd for a dwelling time (4-5 hours) and at temperatures of~ 1200-1450°C, depending on the CKD%. The melts were stirred frequently for complete homogeneity until reasonably free from air bubbles. Slabs with dimensions 1 x 1 x 0.4 cm, were shaped in a stainless steel mold and selected on the basis of uniformity of dimensions and freedom from bubbles. The prepared specimens were annealed in an electric furnace at 500°C and after soaking for 1 hr, the specimens were left to cool slowly over-night at a rate of 20°C/hr inside the furnace.

Table 1: Analysis of Portland cement and CKD (Wt.%).

Constituents	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	CI	I.L.
Portl. Cem.	63.77	20.36	5.33	3.97	2.1	0.14	0.48	2.72	0.03	19.10
CKD	45.14	11.45	3.22	1.88	0.53	3.73	2.72	5.14	2.59	23.60
I.L.: ignition	loss									

Table 2: Frit composition for the industrial glaze (Wt.%).

Borax	B_2O_3	Albite	ZnO	Dolomite	$CaCO_3$	Zircon	Sand	$Na_2(CO_3)$
11.418	27.71	12.026	0.78	3.634	8.992	13.929	18.788	2.722

Table 3: Cement-dust-glaze (CDG) compositions (Wt.%).

Glaze notation	Frit	B_2O_3	CKD
Gl	90	10	0
G2	80	10	10
G3	70	10	20
G4	60	10	30
G5	40	10	50

2.2. Chemical Dissolution Test:

A series of glaze coupons (1x1x0.2 cm) were placed horizontally in 50 ml polyethylene BD Falcon™ 50 ml Conical Tube with Flip Top Cap which allows the leachant solution (50ml) to completely cover the whole glass surfaces of the specimen, and then the tube is tightly closed. The inlet solutions (0.1, 0.5, 1 and 2N HCl) used in this study were prepared from deionized water plus reagent grade of HCl acid. Also, the prepared glazes were immersed in 1N solution from either H_2SO_4 or NaOH.

The test duration ranged from 1 up to 25 days at room temperature (~25°C) and, from 2 up to 30 hours at 100°C± 2°C. After complete specified immersion times in each acid solution, samples were cleaned in de-ionized water and left to dry completely in air in a desiccator and then accurately weighed. As the corrosion is affected by surface area, so the relationship between the geometric area of the glaze samples and the volume of the solutions was maintained constant as S/V= 0.056 cm^2/ml.

Chemical wearing of the surfaces was achieved by soaking the glaze samples surfaces in a weakly alkaline detergent solution (pH 9) corresponding to a typical household detergent. The detergent consisted of soap (5%), non-ionic surfactant C 13-oxoalcohol ethoxylate (10%) and tetrapotassium pyrophosphate (5%). Samples of 2cm x 2cm x 0.4cm with 20ml of detergent solutions were put in covered container and kept at 37°C for 40 days. The solution was replaced with fresh solution every 2 days. After soaking, the samples were rinsed carefully with distilled water and ethanol before examination.

2.3. Solutions Analysis:

For quantitative determination of the concentrations of cations (sodium and calcium), about 10 ml of the leachant solution after being immersed in different HCl solutions with variable concentrations were sampled and analyzed by using atomic absorption spectroscopy (Perkin Elmer, Zeeman 5000). The experiment for each sample

was repeated twice to confirm the results.

Outlet fluid pH was measured immediately after corrosion tests using an Orion Research (601 A) at 25°C. Initial (before experiments) solutions were used as standards to minimize matrix defect.

Superficial deterioration of samples was directly observed by scanning electron microscopy (SEM) (Philips XL30) which was used to undertake a detailed study of the surface morphology of the attacked samples. Likewise, microanalyses were performed by energy dispersive X-ray spectrometry (EDX) with a DX4i analyzator attached to the former microscope. EDX was used to follow chemical compositional changes in the corroded glass surface. EDX enables rapid analysis of area < 1 um^2.

2.5. Infrared Absorption Spectral Measurements:

The infrared absorption spectra of the glazes were measured at room temperature (≈25°C) in the range (4000-400 cm^{-1}) by an IR spectrometer (type; Jasco, FTIR 6100, Japan) using, the KBr technique. The investigated samples were ground to fine particles to avoid errors caused by scattering, and then mixed with KBr in the ratio; 0.001 to 0.2 glass to KBr, respectively. The weighed mixture was then subjected to a pressure of 5 tons/cm^2 to obtain the required discs just before infrared measurements.

2.6. Hardness Test (Mohs Scratch Test):

Mohs scale of mineral hardness is measured to characterize the scratch resistance of the material in this case the glazed surface. The Mohs scale is based on ten minerals that are all readily available except the last one, diamond (Table. 4). The hardness of a material is measured against the scale by finding the softest/hardest mineral that can scratch the material. On the Mohs scale, values between 1-5 are considered soft surface while those values above 5 up to 10 are considered hard surface.

The studied glaze test pieces (1x1x0.2cm) were cleaned and completely dried prior to testing. The prepared test pieces were subjected to scratch using the mineral found in the Mohs Scratch Test kit. The scratch while using as minimal pressure as possible was done starting with the mineral of lowest hardness value, which is 1 on the Mohs scale and subsequently changed to the next mineral that could inflict or cause scratch to the glaze surface.

Table 4: Hardness of minerals based on Mohs scale.

Mohs Hardness	Minerals	Absolute Hardness
1	Talc (Mg$_3$Si$_4$Oio(OH)2)	1
2	Gypsum (CaS0$_4$.2H$_2$0)	3
3	Calcite (CaC0$_3$)	9
4	Fluorite (CaF$_2$)	21
5	Apatite (Ca$_5$(P0$_4$)$_3$(OH\ C1\F))	48
6	Orthoclase Feldspar (KAlSi$_3$0$_8$)	72
7	Quartz (Si0$_2$)	100
8	Topaz (Al$_2$Si0$_4$(OH\ F")$_2$)	200
9	Corundum (A1$_2$0$_3$)	400
10	Diamond (C)	1500

RESULTS AND DISCUSSION

Figure 1. presents the effects of introducing different amounts of CKD% into the base glaze (Gl) on the corrosion weight loss (gm/cm^2) after immersion in 2N HC1 for 25 days at room temperature (R.T.) ~25°C. Obviously, two regions may be distinguished in this graph: (i) faster and aggressive leaching (1-10 days), and (ii) slower and slightly leaching (10-25 days). But, for glaze G5 there is a third region (incubating region) between the two mentioned regions (3-15 days). Moreover, the amount of leaching weight loss increases slightly with increasing the CKD content, and shows an obvious increase when the CKD concentration exceeds 30%.
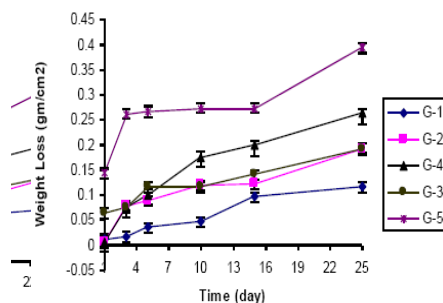

Fig. l: The weight loss (gm/cm^2) vs. time (days) for the studied glazes after been immersed in 2N HC1 for 25 days at R.T.

The effects of different HC1 concentrations (0.1, 0.5, 1 and 2N) on the prepared glaze (G3) after been immersed for 25 days at (R.T.) are shown in Figure 2. It can be observed that, the chemical durability decreases when the HC1 concentration exceeds 0.5N. Also, when the temperature of the leachant solution (2N HC1) was elevated up to ~100°C (Fig.3), the weight loss (gm/cm^2) data for all the studied glazes are observed to increase when the samples were immersed for 30 hours, especially for glazes G4 and G5

Figures 4 and 5 depict the measured released Ca^{++} and Na$^+$ ions from glazes G2, G3 and G4 after been immersed in 0.5, 1 and 2N HC1 for 25 days at R.T.. It obvious from these figures, a remarkable jump in calcium concentration (Fig.4), while a dramatic drop in sodium concentration (Fig.5) when the HC1 concentration exceeds 1N. Moreover, the extraction level of Ca^{++} or Na$^+$ increases when CKD% is increased. The pH values for the leachant solutions are plotted against different introduced CKD% (Fig.6). This figure indicates that the change in pH values is relatively dependant on either the CKD% or the corrosion reactions, i.e. the pH values increase when the CKD% or the weight loss is increased.
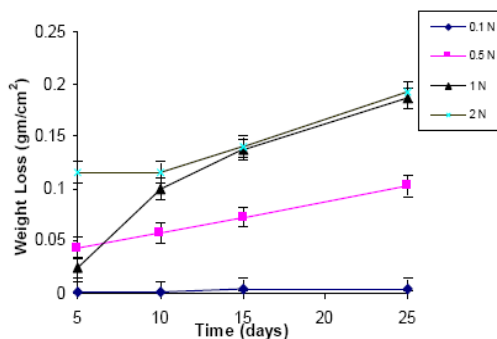

Fig. 2: The weight loss (gm/cm^2) vs. time (days) for the glaze G3 after been immersed in different HC1 concentrations for 25 days at R.T.
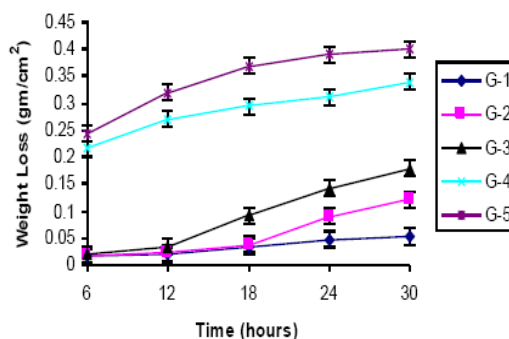

Fig. 3: The weight loss (gm/cm^2) vs. time (hours) for the studied glazes after been immersed in 2N HC1 for 30 hours at ~100°C.

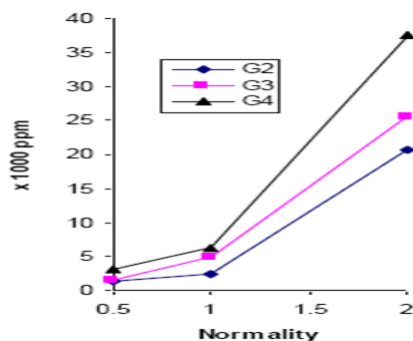**Fig. 4:** The calcium released (x1000 ppm) from G2, G3 and G4 vs. different HC1 concentrations (0.5, 1 &2N) after been soaked for 25 days at R.T.
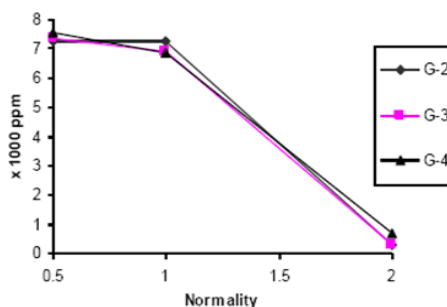
Fig. 5: The sodium released (x1000 ppm) from G2, G3 and G4 vs. different HC1 concentrations (0.5, 1 &2N) after been soaked for 25 days at R.T.
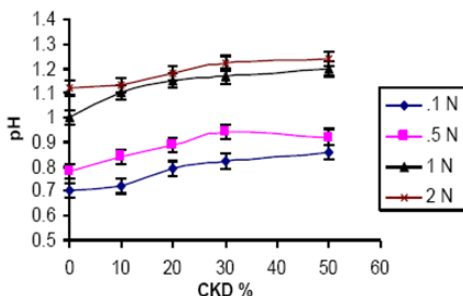

Fig. 6: The pH values vs. CKD% for the glaze G3 after been immersed in different HC1 concentrations for 25 days at R.T.

The EDX-SEM was used to determine the surface microanalysis for the studied glazes after the same leaching conditions (2N HC1, 25 days, R.T.) and the data are given in Table 5 and Figures (7&8), respectively. Because the EDX could not analyze the elements which have small atomic weights, the analyzed elemental contents were normalized to 100% as shown in Table 5. The Ca, Al, Mg, Na, and Zn were almost enriched, whereas other elements (Si, K and Zr) are seemed to decrease. Figure 7 shows the EDX microanalyses performed on the surface of the glaze G3 once submitted to different HC1 acid concentrations (0.5, 1 and 2N) and after been immersed for 25 days at room temperature. No obvious composition differences on the glaze surface could be found, except slight difference in Mg, Na and K. The changes in the topography of the corroded glaze surface (Gl, G3 and G5) at the same leaching conditions (2N HC1, 25 days, R.T.) are shown in figure 8. where the spaces between the micro phases are observed to increase relatively according to the CKD%.

Figure 9 reveals the effect of different kinds of immersion solutions 1N (HC1, H_2SO_4 or NaOH) on the glaze (G3) after been immersed for 25 days at R.T. From this figure it is evident that, the high deterioration is caused when the glaze specimen was immersed in H_2SO_4 solution, while NaOH solution causes a slight change in the glaze durability. Moreover, the effect of commercial detergent on the durability of the prepared glazes shows a very slight weight loss with increasing CKD% when it immersed for 40 days at 37°C. (Fig.10).

The spectral infrared absorption curves extending from 4000-400 cm^{-1} region for the corroded glaze samples (G1&G3) after been immersed in 2N HC1 for 25 days at R.T. are shown in (figure 11). The two spectra exhibit most intense bands in the 3785-2370 cm^{-1} (~3785, 3695, 3515, 3197, 2740 and 2370 cm^{-1}) region. Two small broad bands at ~1120 and 1020 cm^{-1} beside three other bands at~ 1542, 729 and 555 cm^{-1} without sharp features.

Table 5: EDX microanalysis performed on the glazes (G1-G5) after been soaked in 2N HC1 for 25 days at R.T.

Element	Gl	G2	G3	G4	G5
Si	76.43	52.31	51.7	41.71	37.65
Ca	8.72	25.41	22.3	36.15	41.79
Mg	0.17	1.25	0.88	1.09	0.87
Na	0.57	1.07	1.77	1.82	1.29
K	2.51	2.01	2.06	1.46	1.50
Al	3.17	7.64	6.4	5.66	8.06
Fe	0.13	0.60	0.57	1.16	1.92
Zn	7.10	9.01	13.56	10.98	6.71
Zr	1.2	0.71	0.76	0.20	0.22

The mechanical data of glaze hardness either after immersing the studied glazes in 2N HC1 for 25 days or after immersing the glaze G3 in different strengths of HC1 (0.5, 1 and 2N) are plotted in Figs. 12 and 13, respectively. Generally, it is obvious that increasing either HC1 solution concentrations or CKD%, lead to a decrease in the Mohs hardness of the corroded samples.
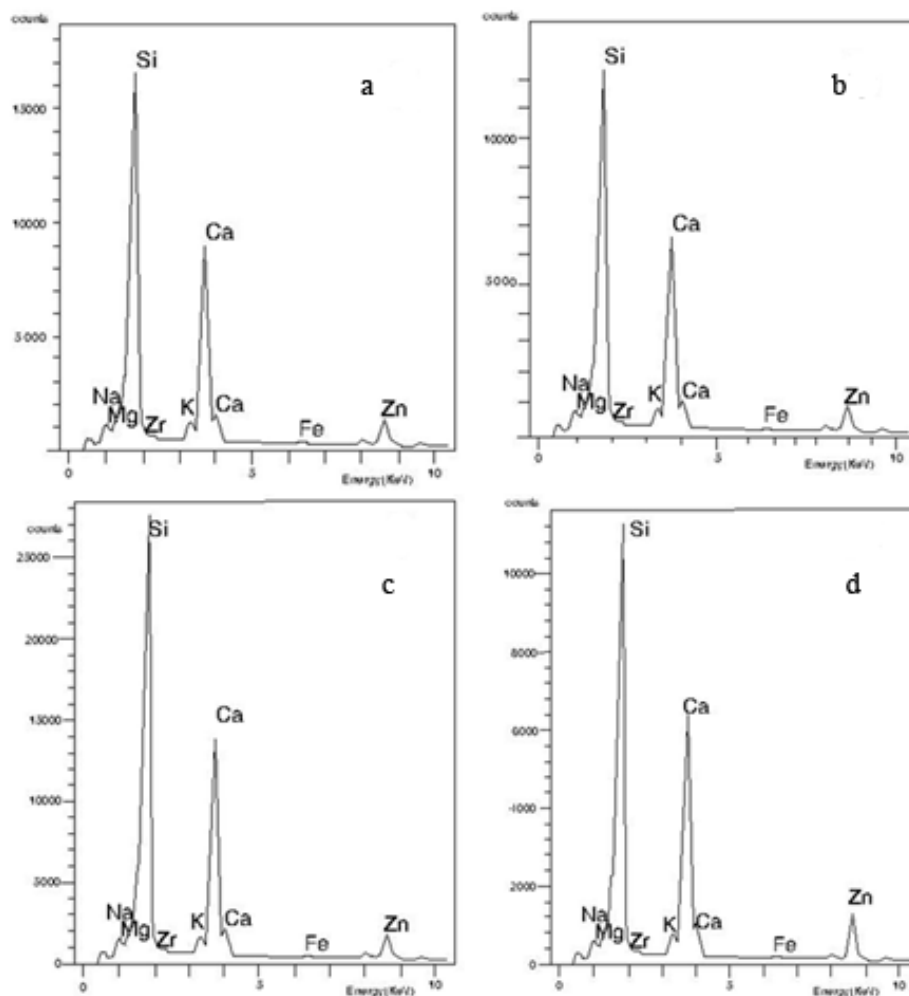
Fig. 7: EDX spectra for the glaze G3 after been immersed in different HC1 concentrations, 0.5N (a), 1N(b), 2N (c) for 25 days at R.T. and 2N for 30 hours at 100°C(d).
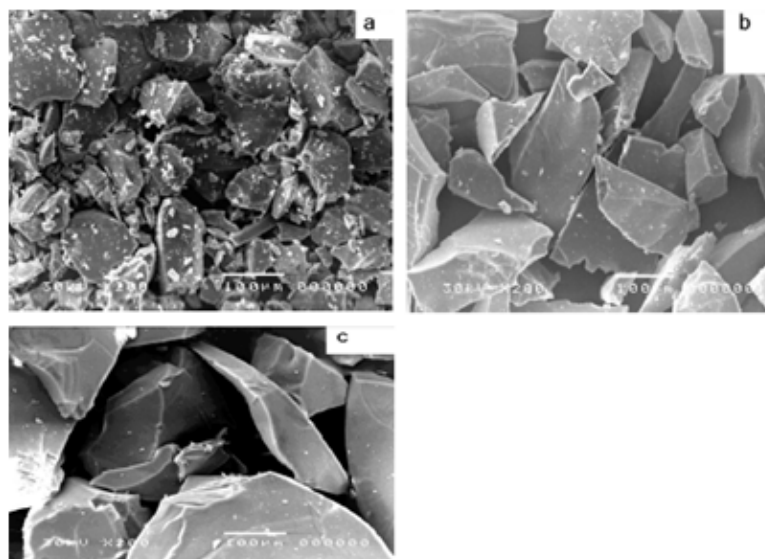

Fig. 8: SEM for the glazes after been immersed in 2N HC1 for 25 days at R.T.G1 (a), G3 (b) and G5 (c).
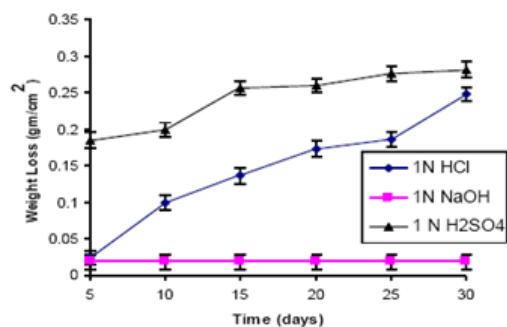
Fig. 9: The weight loss (gm/cm^2) vs. time (days) for the glaze G3 after been immersed in different (IN) leaching solutions (H$_2$S0$_4$, HCl and NaOH) for 25 days at R.T.
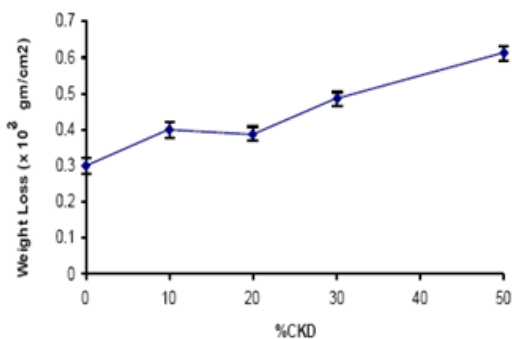

Fig.10. The weight loss (gm/cm^2) vs. CKD% for the studied glazes after been immersed in commercial detergent for 40 days at 37°C.
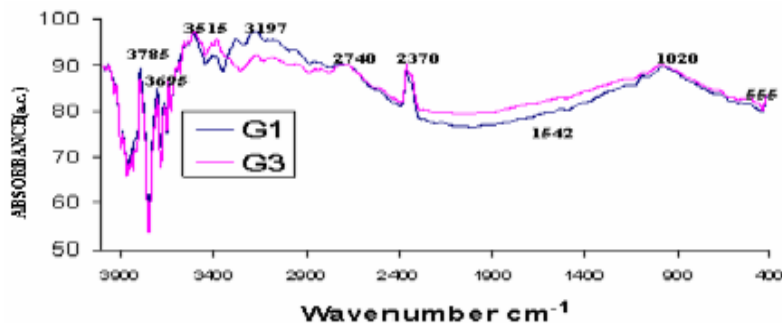

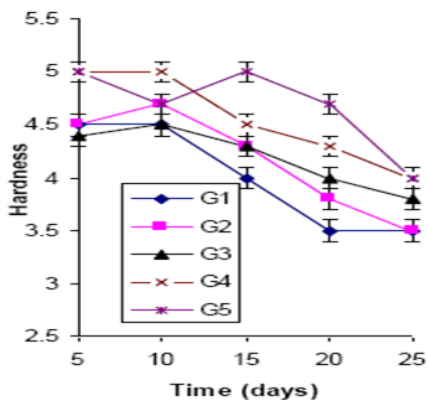**Fig. 11:** IR spectra for the glazes Gl and G3 after been immersed in 2N HCl for 25 days at R.T.

Fig. 12: The hardness values vs. time (days) for the studied glazes after been immersed in 2N HCl for 25 days at R.T.
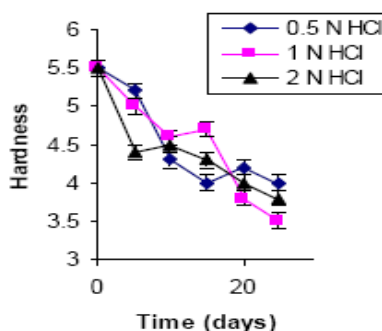
Fig. 13: The hardness values vs. time (days) for the glaze G3 after been immersed in different HCl concentrations for 25 days at R.T.

Discussion:

Chemical durability of glazes in aqueous environment is often studied by referring to the durability of the glassy phase within the matrix of the glaze. The glassy phase is assumed to react similarly to conventional glasses, i.e. with ion-exchange of alkali and other modifier ions in acidic environments. In the case of preparing glazes containing boron components beside the silicate matrix, the sequences of corrosion behavior are expected to be somewhat similar to that with borosilicate, silicate and borate glasses (Ezz-Eldin &Wagdi, 2001).

Clustering of MO polyhedra (M=cation) into larger structural units is well known method of improvement. It has been well established that in borosilicate glasses containing SiO_2 and B_2O_3 form tetrahedral networks of SiO_4, BO_4 beside BO_3 rather than discrete clusters (Brawer, 1986), but the roles of added metal cations and resultant structures are complicated. For example, cations in some oxide glasses may form clusters and hence affect viscous flow.

A detailed model of the chemical interaction between the adsorbed H_2O and the Si-O bond was proposed by (Michalske and Freiman, 1983) explaining why water is so efficient in the stress-activated corrosion of glass whereas the chemical durability of pure silica glass in pure water is so good. They showed that any molecule able to donate a proton on one side, and with a lone pair of electrons on the other side, is able to react with the strained Si-0 bond at the tip of a crack, provided that it is small enough to be transported to the tip (Michalske &Bunker 1983). The fact that constrained Si-0 bonds have their chemical reactivity with water and enhanced according to the strain was directly shown in hydrolysis experiments for different siloxane ring structures (cyclosiloxane) (Michalske & Bunker, 1987).

Effect of HCI Solutions:

In all the tested glazes, hydrolytic attack is assumed to take place. It begins by the ion exchange of H+ ions from the leachant solution (HC1) with the alkaline-ions (R= Na+, K+...) from the glaze surface. Although a priori it would be expected that glaze G5 will show good hydrolytic resistance due to its higher content of CaO ions (which behaves as stabilizing oxide to alkali oxide) in comparison with other studied glazes. So, the higher deterioration observed in glaze G5 (Fig. 1) can be explained on the basis of its alkaline oxide content (Table. 5) which is higher with K2O content. In the glazes studied, the alkaline hydroxide (KOH or NaOH) formed, as a consequence of the ion-exchange process, interacts with the siloxane bonds (=Si-O-Si=) of the glaze and destroys the silicate network itself according to equation (1):

$$\equiv Si\text{-}O\text{-}Si\equiv\ +\ M^+OH^- \quad \rightarrow \quad \equiv Si\text{-}OH\ +\ \equiv Si\text{-}O^-M^+ \tag{1}$$

This deals with the glaze depolymerization, especially in the case of KOH formation which is relatively stronger basic hydroxide than NaOH. Once the glaze network is broken down, Ca^{2+} ions leaching as $Ca(OH)_2$ is enhanced forming a considerable amounts of calcium silicate and calcium carbonate which deposit on the glaze surface and associate in the formation of surface corrosion crust. Then the higher is the CaO content, the higher is the corrosion crusts formed. The formation of $CaCO_3$ was realized by (**Ojovan *et al.*, 2001**) who have assumed that HCO_3^- ions as a leachant intermediate product of glasses used for nuclear waste immobilization, which indirectly support our results. Thus, $CaCO_3$ is firstly formed and thereafter displacement of carbonate-ions by chlorine-ions takes place.

Moreover, due to the high content of CKD (50%), the dissolution process is assumed to depend on the formation of a thin interfacial glassy layer with low chemical resistance than the main glassy phase in glaze G5. Thus the corrosion in this case is obviously due to corrosion of glassy phase, not their crystals. These suggested interpretations described before can clarify the incubating period (3-15 days) showed in figure 1, and, the obvious jumping in weight loss when the immersion time exceeds 15 day which is assumed to be due to the weakness of this detached layer.

On the other hand, the relatively high durability exhibited by glaze Gl (Fig. 1) is due to its high content of ZrO_2 (Table 2). The explanation for this lies in; a- The formation of zirconium hydroxide or hydrated zirconia layer which is relatively an insoluble species, may probably offer a very high activation barrier for the diffusion of the other ionic species through it. This layer must be dense to have a protective effect. The reaction of zirconium oxide in acidic medium may be represented as follows:

$$ZrO_2 \; + \; 4H^+ \quad \rightarrow \quad Zr^{4+} \; + \; 2H_2O \tag{2}$$

b- Beside the role of zirconium oxide, we cannot ignore the presence of the low percent of Zn^{2+} which is assumed as a divalent cation to interfere or retard the passage of the alkali ions from the glaze into the solution which are liberated only after the breaking of silica network (Brawer, 1986). This may be due to the ability of zinc oxide to form network forming groups and the alkali ions are bound to these groups to achieve electrical neutrality (Bunker *et al.,* 1988).

c- Also, in glaze Gl which is CKD free, the presence of alumina from albite, silica from sand, and the stoichiometrc combination of magnesia, lime and silicate from diopside, all these oxides cause no obvious interfacial attack leading to the improvement of the durability of glassy phase.

Effect of Different Hcl Concentrations:

The influence of different concentrations of HC1 acid solutions on the glass durability is well understood (Bunker *et al.*, 1988). With increasing HC1 concentrations (Fig.2), the concentration of the anion (C1⁻) increases to a level which is sufficient to interact with cations. Furthermore, elevating the strength of the acidic range increases the extent of leaching of alkali components in glazes and decreases the dissolution of hydrated layer. This is the result of increasing hydrogen ion concentrations in solution, which increases the ion exchange flux between proton $(H)^+$, or hydronium ion $(H_3O)^+$ and alkali ions. It is well known that (Froberg *et al*., 2009), the phase boundary attack was assumed to be due to stresses or minor compositional gradients at the interface, then further dissolution or growth of glaze crystals is likely to form interfacial layer around them affecting the durability of the surface. Thus, when the glaze G3 was immersed in high concentrated HC1 solutions (1 and 2N) the crystals started to be corroded after a short exposure time (5 days).In addition, at such high concentration the glassy layer covering the crystals just underneath the surface, was severely attacked, and the previous silica rich layer was peeled.

Effect of Temperature:

The high dissolution weight loss observed with high temperature as represented in figure 3 can be explained as follows. At such high temperature (~100°C), the convection currents promote ease ionic contacts, diffusion and more continuous dissolution and further continuous ionization of protons from the dissociated acid replacing the consumed ones which leads to the observed continuous increase in corrosion weight loss data. In addition, the reaction temperature does not only alter the kinetic reaction but also dictates the rate controlling mechanism of corrosion. At ~100°C, the corrosion rate is controlled by total dissolution, while at ~25°C selective leaching is the rate controlling.

Leachant Solution Analysis:

Figure. 4 shows the high extraction level of Ca ions from the glazes G2, G3 and G4 as a function of HC1 concentrations at R.T. It is well known that (Steel *et al*., 2001), the solubility of Ca bearing minerals is carried out almost completely in aqueous HC1 solutions at R.T. The high extractions of Ca ions are due to the obvious reactivity and solubility of Ca bearing minerals (dolomite and anorthite) in the mineral matter toward HC1 solution. However, the drop in Na ions extraction level observed (Fig.5) at such high concentration (2N), could be related to the increase in Na_2O concentration in the glaze surface giving an Na-depleted layer; then, the rate of extraction could be decreased with increasing diffusion distances. Alternatively, the accumulation of the released products either as soluble compounds or in the form of a protective thin layer may diminish the extraction level of Na. Moreover, we can't ignore the overall low content of Na in the prepared glaze compared to calcium content.

Ph Measurements:

The changes in the pH values are seen in Figure 6. The pH value appears to behave in the same manner to that described for the dissolution process. In other words, the higher acidity of the solutions the greater the pH values after corrosion (i.e. becomes more basic). Thus, increasing the HC1 strength is assumed to cause a severe attack of HC1 solution leading to high running and dissolution of alkalies from glazes to the leachant which form hydroxides causing the increase in pH values. Subsequently, from this figure the pH values increase when the CKD% exceeds 30% and this is due to the presence of large amount of K_2O which form KOH and leads to a respective high pH value of the leachate minor microcracks due to the reformation of silicate grouping and transformation from Si-O Na → Si-OH → Si-O-Si, through successive different reactions. Sample G5, exhibits large spaces between the glass

matrix indicating that the glaze microphases were easily leached by HC1 compared to Gl and G3 (Figure 8). It is postulated that this can be related to more severe microphase separation occurring in high percentage of CKD. In addition leaching is also suggested to produce hillocks and showing a sub-microphase separation. This indicates that, the increase in micro-roughness caused by selective dissolution of the surface is the main reason for the observed differences in surface texture degree. Poor chemical resistance of the interfacial layer appears to initiate the corrosion reactions and thus revealing the crystal surface for direct attack of the aqueous solution.

Effect of H_2SO_4 Solution:

The almost observed similar behavior of H_2SO_4 solution with HC1 solution (Fig.9) on the corrosion of glazes studied may be explained as follows. The dissociation or ionization of the two mentioned acids is high enough to supply the leaching solution with sufficient (H^+) or hydronium (H_3^+O) to precede the attack or the hydrolysis of the glaze. The continued solubility of both cationic and anionic constituents of the glaze initiates further and complete dissolution due to the ease of solubility of the released alkali ions. Some of the sulphates are less soluble than the chloride analogues and thus the results may show some variations.

Effect of Naoh Solution:

It is obvious from inspection of the corrosion data (Fig. 9) that, the sodium hydroxide (1N) gives the least corrosion in contrast to the known fact that NaOH solution easily corrodes ordinary soda-lime-silica glass because it attacks both network modifiers and also the silica network itself. It is known that almost all sodium compounds are easily soluble and therefore the released sodium ions from the glass are continuously replaced by protons or hydronium (H_3O^+) ions from contact solution. The obvious presence of high lime content in the studied glazes produces a screening or controlling factor for the continuation of ion exchange reaction through the formation of gelatinous $Ca(OH)_2$ precipitates. Also, Ca^{2+} ions exchange much more slowly with H^+ or H_3O^+ than Na^+ when glass is exposed to aqueous solution.

Some authors (Khedr & El-Batal, 1996; Paul, 1990; ElShamy, 1966) believed that the pronounced effect of lime (up to 10%) in increasing the durability of glass is not extended if the lime content is present with high percent (e.g. 24.5 wt.%). However, extensive studies (Hench, 1991) indicate that the presence of such fair amounts of lime beside soda leads to a desirable corrosion extent to be able to produce the chemically firm bond through the sequence of 12 successive reactions. (Clark *et al*., 1976) studied the corrosion of binary soda-silica and ternary soda-lime-silica glasses and found that the corrosion proceeds at a much slower rate in ternary glasses than in the binary glasses. They attributed this difference to the development of a Ca enriched zone ~ 1500 A thick within the Na depleted layer. Moreover, (Budd & Frackiewiez, 1962) have assumed that this behavior associated with high CaO content may be either due to microphase separation and/or the activity of CaO in silicate glasses which may be disproportionately higher than in other glasses.

Effect of Detergent:

The commercial and prepared glaze-ceramics have a relatively good chemical resistance as indicated by weight loss (gm/cm^2) data after soaking in commercial detergent solution (Fig.10). However, the soaking slightly increased the corrosion, thus implying selective corrosion of either the glassy or crystalline phase. The glaze with diopside crystals is reported to have a good chemical resistance in alkaline solutions (Budd & Frackiewiez, 1962). The change in corrosion values was assumed to depend mainly on cracks in the glaze surface. The cracks were assumed to form due to variation in the roughness of the glaze surface and difference in the composition of the samples. Nevertheless, crack formation can be avoided by a careful optimization of the parameter during the melting and sintering.

FTIR:

The FTIR was employed in order to have better understanding about the structure of the studied glazes. The lack of sharp features is indicative of the general disorder in the silicate network mainly due to a wide distribution of on (polymerization in the glass structure, where *n* denotes the number of bridging oxygens) units occurring in these glazes. The FTIR spectra for the glazes Gl &G3 (Fig.l 1) reveal several bands: A weaker intensity band at~ $555 cm^{-1}$ which is characteristic of the metal-oxygen vibrations (possibly Ca-O, Zn-O, Zr-O) in the glaze samples (Lelechkaite, 2005), while the least intensive band at~ $730 cm^{-1}$ is related to the stretching vibration of the Al-O bonds with Al^{3+} ions in 4-fold coordination (Kansal et al., 2009). The bands at~ 1105 and $1020 cm^{-1}$ can be attributable to SiO_4 and the vibration of bridging oxygen normal to the Si-O-Si plane (Hunt et al., 1988). The small absorbance band at ~ $1542 cm^{-1}$ corresponds to B-O vibrations in (BO_3) triangle (Kansal et al., 2009). In addition the infrared spectra include 5 bands at about; 3787, 3694, 3520, 3420, 3210, 2730 and 2370 $cm^{"1}$ which are generally correlated to the stretching and deforming modes for (OH) groups, molecular water or silanol groups (Chen &James, 1988). The observed decrease in the intensity of the bands (~3335-2370 cm^{-1}) was assumed to the high solubility of the constituent of glaze G3 and it seems that the action of HC1 solution is obviously severe. Also, this could be associated with stimulate adsorption of water from the HC1 leachant solution. Generally, the

experimental 1R spectra indicate that the main structural grouping of the glazes after corrosion remain unchanged as revealed by the maintenance of the original features of the glazes. This indicates the persistence of the silicate network after corrosion to a large extent.

Hardness:

It has been assumed that, ion exchange during dissolution may cause the formation of M-OH and hence afterward to promote cracking of a leached layer (Casey *et al.,* 1993, Bunker *et al.*, 1983). Alternatively, the residual stress of the glaze due to devitrification and/or cooling may account for the cracking of a leached layer during dissolution and leading to the formation of weakened surface.

Thus, the degradation in hardness with increasing immersion times or HC1 concentrations is attributed to the progressive attack of solution on the whole surface, and particularly within the microcracks, rendering them curved at both ends and consequently reduce the hardness. Moreover, it should be mentioned that according to Ezz-Eldin *et al.*, 2010, Ezz-Eldin, 2001, the surface energy of glass substances likewise can lead to an earlier fracture. However, the reaction with acid can also leads to the opposite effect in glaze, that is, in the situation where a flaw is so corroded that its radius is increased at the crack tip. This corresponds to a shortening of the crack and thus has the effect of increasing the strength. It explains the observation that glazes can be broken more easily right after being scratched than it can after some time has elapsed. Also, we can assume that some stress relaxation may occur after the penetration of the Na^+ ions.

The unexpected damage in the hardness of Gl and G2 (Fig. 12.) may be due to large release of calcium ions from the surface according to the EDX data (Table 4.). Furthermore, the formation of alkali depleted layer which is rich in silica and poor in calcium and aluminum contents enhance the formation of relatively soft surface. However, the observed increase in absolute hardness for the glazes G3 after 20 days in Fig. 13 and G5 in Fig. 12 can be attributed to the formation of corrosion crust which is composed mainly from Al, Ca and Mg ions. This detached crust layer is to assumed be dissolved either when increasing immersion time or acid concentration, and, then the hardness restricts its uniform behavior.

Conclusions:

The prepared glazes have the advantage of easy processing as conventional waste composite glazes and their dissolution resistant can be improved by devitrification treatments to form zirconia and zirconolite which are dissolution-inert as in SYNROC materials.

Corrosion studies were carried out by using various solutions including (HC1, H_2SO_4, NaOH and detergent). The results show that the prepared glazes are more stable in basic medium compared to acidic medium. This behavior is assumed to be related to the possible interference of the divalent and relatively large Ca^{2+} with the passage of the mobile and easily soluble Na^+ ions in the percolation pathway channels during the ion exchange process. The leaching data indicate that, there is a remarkable weight loss for glaze G5 compared to other prepared glazes. Such damage is exclusively attributed to a dealkalinizations process as a consequence of the ion-exchange enhanced by the hydrolytic attack. According to the present data, it could be concluded that there is an optimum amount of CKD (20-30%) which could give the best prepared ceramic-glaze (G3 and G4). Moreover, the network molecular structure of the glaze after immersion is relic of the original glaze before immersion and the ion exchange process on the surface of the glaze has no profound effect on the structure, but only FTIR was affected by CKD%.

Since the CKD wastes contain a high level of AI_2O_3 and alkaline earth oxides MO (M= Ca, Mg) which seem to be good candidates for practical purposes and to enhance good durability in glaze manufacture. In addition, the CKD has been seen to decrease glazes melting temperature. These positive effects suggested that CKD waste can easily be used in the glazes manufacture alternative to frit. Moreover, the dissolution, especially with acidic and basic leaching of metal cations, is of concern in the use of these prepared compositions as ceramic-glaze and nuclear waste immobilizing materials. By doing so, glaze cost will be reduced and a waste material will be effectively utilized for safer environment.

REFERENCES

Bhatty, J.I., 1995. Alternative Uses of Cement Kiln Dust, RP 327, Portland Cement Association,Skokie, Illinois, U.S.A.

Bhatty, M.S.Y., 1983. Use of Kiln Dust in Blended Cements, PCA R&D Serial No. 1717, PortlandCement Association, Skokie, Illinois, U.S.A.

Bolelli, G., V. Cannilo, L. Lusvarghi, T. Manfredini, C. Siligardi, C. Bartuli, A. Loreto and T. Valente, 2005. J.Eur.Cer. Soc., 25: 1835.

Brawer, S., 1986. Mat.Res.Soc. Symp.Proc., 61: 21.

Budd, S.M., 1962. Frackiewiez, J., Phys. Chem. Glasses, 3(4): 116.

Bunker, B.C., G.W. Arnold, E.K. Beauchamp and D.E. Day, 1983. J.Non-Cryst. Solids, 58: 295.

Bunker, B.C., D.R. Tallant, T.J. Headley, G.L. Turner and R.J. Kirkpatrik, 1988. Phys.Chem.Glasses, 29: 106.

Casey, W.H., H.R. Westrich, J.F. Banfield, G. Ferruzi and G.W. Arnold, 1993. J.Non-Cryst. Solids, 366: 253.

Chen, A. and P.F. James, 1988. J.Non-Cryst.Solids, 100: 353.

Clark, D.E., O.E. Dilmore, E.C. Ethridge and L.L. Hench, 1976. J. Am. Ceram.Soc., 59(1-2): 62.

El-Shamy, T.M., 1966. Corrosion of silicate glasses by aqueous solutions, Ph.D. Thesis,Univ.of Sheffield, UK.

Eppler, R.A., 1992. Corrosion of glaze and enamels. In Corrosion of glass, ceramics and ceramic superconductors, ed. D.E.Clark & B.K.Zoitos, Noyes Publications, Park Ridge, NJ.

Escardino, A., J.L. Amoros and A. Gozalbo, 2002. Oris, M.J., Lucas, F. and Belda, A., Qualier, in Proc. of VII World Congress on Ceramic Tile Quality, Castellon, Spain, 201: 2002.

Ezz-Eldin, F.M. and W.N. Wagdi, 2001. Ind. J. Pure &Appl.Phys., 39: 514.

Ezz-Eldin, F.M., T.M. Abd-Elaziz and N.A. Elalaily, 2010. J.Mat. Sci., 45: 5937.

Ezz-Eldin, F.M., 2001. J.Nucl.Inst.& Methods Phys.Res. B, 183: 285.

Froberg, L, L. Hupa and M. Hupa, 2009. J.Eur.Cer.Soc, 29(1): 7.

Golubev, S.V. and O.S. Porkovsky, 2005. Schott, J. Chem. Geol., 217: 227.

Hench, L.L., 1991. J. Am. Ceram.Soc., 74: 1487.

Hunt, J.M., M.P. Wishered, L.C. Bonham, 1988. J.Non-Cryst.Solids, 128: 310.

Kansal, I., A. Goel, D.U. Tulyaganov, J.M.F. Ferreira, 2009. Ceram.Int.J., 35: 3221.

Khedr, A. and H.A. El-Batal, 1996. J. Am. Ceram.Soc., 79(3): 733.

Kronberg, T., L. Hupa and K. Froberg, 2004. Key Eng.Mater., 1565: 264.

Kingery, W.D., H.K. Bowen and D.R. Uhlmann, 1976. Introduction to ceramics, John Wiley Sons, New York.

Kundu, T.K., K. Hanumantha Rao and S.C. Parker, 2003. Int. J.Miner. Process, 72: 111.

Leleckaite, A., A. Kareiva, H. Bettentrup, T. Justel, H.J.Meyer and Z. Anorg, 2005. JAllg. Chem., 631: 2987.

Michalske, T.A. and B.C. Bunker, 1987. J. Am. Ceram. Soc., 76(10): 2613.

Michalske, T.A. and S.W. Freiman, 1983. J.Am. Ceram.Soc., 66(4): 284.

Michalske, T.A. and B.C. Bunker, 1983. J. Am. Ceram. Soc., 70: 780.

Miller, C.T., D.G. Bensch and D.C. Colony, 1980. Use of Cement Kiln Dust and Fly Ash in Pozzolanic Concrete Base Courses, Emulsion Mix Design, Stabilization and Compaction, Transportation Research Record 754, TRB, Washington D.C., U.S.A., 36-41.

Nicholson, J.P., 1978. Stabilized Mixtures, U.S. Patent, 4: 101,332.

Ojovan, M.I., N.V. Ojovan, I.V. Starteeva, G.N. Chuikova, Z.I. Golubeva and A.S. Barinov, 2001. J.Nucl.Mat., 298: 174.

Paul, A., 1990. Chemistry of glasses, 2nd Edition, Chapman & Hall, New York.

Sinton, C.W. and W.C. LaCourse, 2001. Mat.Res.Bullet., 36: 2471.

Steel, K.M., J. Besida, A.Thomas, O. Donnell and D.G. Wood, 2001. J. Fuel Processing Techn., 70: 171.