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RELEASE OF LEAD FROM TYPICAL CANADIAN POTTERY GLAZE FORMULATION

D.H.H. QUON AND K.E. BELL



MINERALS RESEARCH PROGRAM
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by

D.H.H. Quon* and K.E. Bell**

ABSTRACT

The release of lead from ceramic foodware into contained foods or beverages has been known to cause lead poisoning in Canada and elsewhere and is the subject of international concern. A study has been undertaken in the Mineral Sciences Laboratories, CANMET, to assess the instability of typical Canadian pottery glazes under conditions simulating those encountered in domestic use. The objective of this study is to examine the mechanisms of Pb release and stabilization as a contribution to the development of stable, safe glazes.

Lead release from glasses melted from typical glaze compositions in contact with 4% acetic acid was studied as a function of reaction time. It was shown that the amount of Pb released was dependent on glaze composition, with high release occurring in glasses containing higher concentrations of PbO and B₂O₃ and lower concentrations of Al₂O₃ and CaO. The addition of CuO, as a colourant, was found to increase the quantity of Pb released. The reported inhibiting effect of chromate additions was examined: BaCrO₄ was found to be a less effective Pb-release suppressant than Cr₂O₃ in the Cu-bearing glazes, attributed to greater modification of the glass structure.

The kinetics for the release of Pb into solution show linear dependence with respect to the square root of leaching time, indicating that the process is diffusion-controlled and therefore sensitive to structural changes resulting from variations in glass composition.

*Research scientist and **head, Ceramic Section, Mineral Processing Laboratory, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

LA LIBERATION DU PLOMB DES PIÈCES
CANADIENNES DE POTERIE GLACÉE

par

D.H.H. Quon* et K.E. Bell**

RESUME

La libération du plomb des plats de céramique dans les aliments ou les breuvages qu'ils contiennent est à la source des empoisonnements par le plomb qui ont eu lieu au Canada et ailleurs et est un sujet d'intérêt international. Une étude a été entreprise aux Laboratoires des sciences minérales du CANMET afin d'évaluer l'instabilité des glaçures de poterie typique canadienne soumise à des usages domestiques. Le but de cette étude est d'examiner les mécanismes de libération et de stabilisation de Pb afin de contribuer à la mise au point de glaçures stables et sûres.

Le plomb libéré des verres fusionnés à partir des compositions de glaçures typiques en contact avec de l'acide acétique 4% a été étudié en fonction du temps de la réaction. Il a été démontré que la quantité de Pb libéré est fonction de la composition de la glaçure; une libération plus abondante de Pb se produit lorsque les pièces contiennent des concentrations plus élevées de PbO et B₂O₃ et des concentrations plus basses de Al₂O₃ et CaO. L'addition du CuO comme colorant est la cause d'une plus grande libération de Pb. De plus, on a examiné l'effet inhibiteur des additions de chromate; on a découvert que le BaCrO₄ est un suppresseur moins efficace de la libération du Pb que le Cr₂O₃ dans les glaçures porteuses de Cu que l'on attribue à une plus grande modification de la structure du verre.

La cinétique de la libération du Pb dans la solution démontre une dépendance linéaire en rapport avec la racine carrée du temps de lixiviation ce qui indique que le procédé est contrôlé par la diffusion et donc sujet à des modifications structurales provenant de variations de la composition du verre.

*Chercheur scientifique et **Chef, Section de la céramique, Laboratoire du traitement des minéraux, Laboratoires des sciences minérales, CANMET, Energie, Mines et Ressources Canada, Ottawa.

CONTENTS

	<u>Page</u>
ABSTRACT	i
RESUME	ii
INTRODUCTION	1
Structure of Glass	1
Relationship between Composition, Structure and Chemical Durability	2
Influence of Colouring Oxides on Toxic Materials Release	4
Formulation of Glazes for Low Lead Release	4
EXPERIMENTAL PROCEDURE	5
Raw Materials	5
Glaze Compositions	5
Batch Preparation	5
Melting	6
Lead Release Determination	6
Grinding	6
Leaching	7
RESULTS AND DISCUSSION	7
Prediction of Lead Release from Glazes	7
Lead Release from Base Glaze Compositions	7
Effect on Lead Dissolution Adding Copper Oxide to Base Glaze Compositions	8
Effect on Lead Release of Adding Chromate Compounds to Copper-Bearing Glaze Compositions	9
Leaching Mechanism	10
CONCLUSIONS	11
ACKNOWLEDGEMENT	13
REFERENCES	13
APPENDIX A - SOFTENING AND LIQUIDUS POINTS OF GLASSES	A-15

TABLES

1. Chemical compositions of frits and clay used for com- pounding of glazes	5
2. Mix proportions of frits and clay for compounding of glazes	6
3. Batch compositions of glazes in weight per cent and empirical formulae	6
4. Figure of merit for various glazes	7
5. Lead dissolution after 24 h of leaching for base and copper-bearing glazes	9

CONTENTS (cont'd)

	<u>Page</u>
FIGURES	
1. Schematic representation of crystalline lattice and corresponding glassy network	1
2. Schematic representation of sodium silicate glass	2
3. Lead release as a function of leach time for base glaze, 1 showing effect of addition of copper colourant and inhibition by BaCrO_4	8
4. Lead release as a function of leach time for base glaze 2, showing effect of addition of copper colourant and inhibition by BaCrO_4	8
5. Lead release as a function of leach time for base glaze 3, showing effect of addition of 2 wt % CuO	8
6. Lead release as a function of BaCrO_4 and Cr_2O_3 concentration for glaze 1	11
7. Lead release as a function of BaCrO_4 and Cr_2O_3 concentration for glaze 2	11
8. Lead release vs square root of leach time, glaze 1	12
9. Lead release vs square root of leach time, glaze 2	12
10. Lead release vs square root of leach time, glaze 3	12

INTRODUCTION

Lead oxide is a common ingredient in ceramic glazes because it improves the melting characteristics and their physical and chemical properties. As with any material, durability of the glazes should be adequate for the service conditions to which the product will be subjected and ceramic glazes are usually formulated to endure the most demanding of chemical and physical environments. In the event of chemical corrosion of glazes on tableware, the resulting degradation typically results in deterioration of the required properties and the release of glaze constituents. With lead-bearing glazes, the leached materials include toxic lead that can be carried into the human body via foods and beverages. Isolated instances of lead poisoning resulting from poorly glazed foodware have sharply focussed worldwide attention on this matter. Consequently, lead containing glazes on food-contact surfaces are subject by most nations to close control of permissible quantities of leachable lead. In Canada, the permissible limits of lead and cadmium release in particular, are regulated under the Hazardous Products Act.

To gain optimum durability of lead-containing glazes, it is desirable to determine the mechanisms of lead stabilization and release. This knowledge can then be exploited to develop glaze compositions having improved durability in service.

The objectives of this project are: (a) to establish the mechanism and rate of lead release from typical Canadian pottery glazes as a contribution to the development of safe glazes for application on ceramic ware sold to Canadian consumers and produced for export, and (b) to establish a basis for Canadian participation in International Standards Organization Technical Committee 166 dealing with the release of toxic materials from foodware.

This report covers studies on the effect of various compositional parameters on lead release from glasses melted from typical Canadian glaze formulations. Further work to be reported separately will deal with the effect of various

processing parameters on lead release from these glaze formulations applied to ceramic ware.

STRUCTURE OF GLASS

Glazes are special, complex types of glass, but their structures are essentially identical to those of normal glasses. The mechanical properties of glasses, particularly their strength, show that the force responsible for their coherence must be similar to that in a crystal, and that the atoms must be linked together to form an extended continuous three-dimensional network. In this network the immediate environment of each atom is the same as or similar to that in a crystal, but lacks long-range order. The distinction between a crystal and a glass has been illustrated by Zachariassen in the two-dimensional examples shown in Fig. 1 (1). Here there is seen to be no regularity in the glass, but the type of binding and coordination is the same in the two cases.

In inorganic glasses, the chemical composition of the glass may be represented by the formula A_mO_n , where A_m is the cation and O_n is the anion. According to Goldschmidt, all glass-forming oxides have ionic radii ratios, R_A/R_O , in the range of 0.2 to 0.4, because the cation:anion radius ratio determines the possible type of ionic

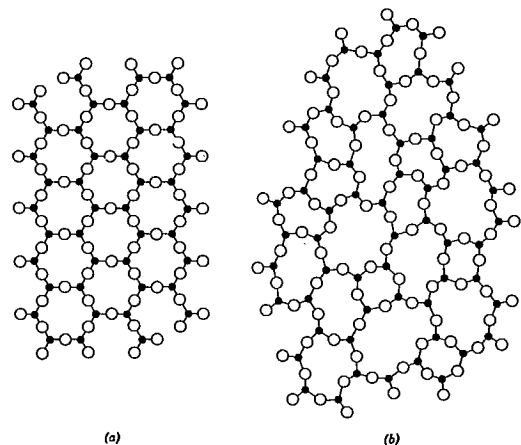


Fig. 1 - Schematic representation of (a) crystal-line lattice and (b), corresponding glassy network. After W.H. Zachariassen and B.E. Warren (3)

packing and hence determines the coordination of the cation with respect to oxygen (2). He also pointed out that the tetrahedral coordination typical of this radii ratio range was required for glass formation.

Zachariasen considered the glass-forming abilities of various oxides and concluded that, to form a glass, a substance must be capable of producing an extended three-dimensional network lacking periodicity but with an energy content similar to that of the corresponding crystal network (1). From this assumption, he derived the following requirements for glass formation:

1. an oxygen atom is linked to no more than two cations;
2. the number of oxygen atoms surrounding the cation must be small;
3. the oxygen polyhedra share corners with each other;
4. at least three corners of the polyhedra must be shared.

The oxides that readily form glass according to Zachariasen are B_2O_3 , SiO_2 , GeO_2 , P_2O_5 and As_2O_5 . The B_2O_3 glass was considered a perfect example of a structure built up from BO_3 triangles such as are formed in crystalline borates; SiO_2 , GeO_2 , P_2O_5 and As_2O_5 glasses were regarded as being built up of SiO_4 , GeO_4 , PO_4 and AsO_4 tetrahedra.

The present concept of the structure of glass is that it consists of random three-dimensional networks in which the formation of chains or sheets is not possible compared with crystalline materials. The structures of crystalline and vitreous (glassy) silica are shown in Fig. 1.

Other oxides incorporated into the glass structure are called glass modifiers. In general for multicomponent glasses, it is not essential that all constituents be glass-forming cations. A glass is formed when the composition contains a high percentage of cations surrounded by oxygen in triangular or tetrahedral coordination, when these polyhedra share corners, and when at least some oxygen atoms are bonded to two cations and do not share bonds with other cations. Thus, for

example, a sodium silicate can form a glass in which sodium ions do not contribute to the network formulation but sit in the holes in the network as illustrated in Fig. 2 (3).

RELATIONSHIP BETWEEN COMPOSITION, STRUCTURE AND CHEMICAL DURABILITY

The chemical durability of glass is dependent on composition. It is well known that pure silica glass possesses high chemical durability, compared with glass containing alkali oxides. The decrease in chemical durability with addition of a network modifier results from breaking of the continuous Si-O-Si network in the glass structure. Extensive studies of glass corrosion have been carried out in various laboratories. The complex nature of the glass composition and structure make it difficult to have a clear understanding of the corrosion process.

Glass may be subjected to chemical attack by water, acid, alkali, salt solutions, and gases, and by vapours in the atmosphere. The dependence on pH of the corrosion of glasses by aqueous solutions was investigated by El-Shamy, Douglas, and Lewin (4,5). They observed that when a soda-silica or a soda-lime-silica glass is placed in pure

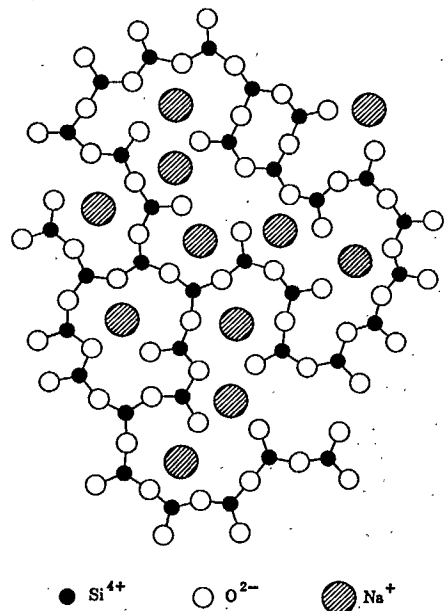


Fig. 2 - Schematic representation of sodium silicate glass. After B.E. Warren (3)

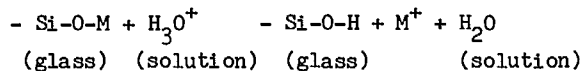
water, changes occur both in the glass and in the solution. Two main reactions take place in the glass: extraction of alkali ions with their replacement by protons from the solution, and dissolution of silica by breakdown of the siloxane bonds at the interface between the solution and the attacked glass. The removal of silica usually lags behind the alkali extraction, leading to the formation of a silica-rich leached layer on the surface of the glass. This layer plays a major role in determining the rate at which the corrosion of the glass proceeds.

In their investigations of glass powder containing 50% PbO, 43% SiO₂ and 7% K₂O leached in dilute HNO₃, Hafner and Jones reported that the corrosion process involves exchange reactions at the base of a permeable surface layer with selective adsorption characteristics for the various ions released from the glass (6). In this case, the potassium was released immediately on contact with the acid. While the alkali was being released the rate of lead release was small. As the alkali release decreased, the rate of lead release increased. Their data support the proposition that a leached-silica surface film has little power to retain K ions but is able to retain Pb ions. They postulated that the Pb ions are partially adsorbed by a silica surface layer formed by ion exchange at the base of the surface layer, or are contained in a solution in contact with the outer surface of a silica layer.

The difference in rate of corrosion is due to selective adsorption in the silica surface layer and not to the formation of two surface films of different properties as a result of the removal of both lead and potassium from the outer layer and removal of potassium only from the lower layer.

The lead release from glazes containing PbO, SiO₂, K₂O and Na₂O was studied by Yoon et al (7). The effect of different food acids was evaluated. In addition, a number of glasses with varying batch compositions and melting times was investigated to determine the kinetics of the leaching process. This showed that the amount of lead released is increased with lower pH value of the beverage, longer reaction time, and higher

reaction temperature. It also indicated that the leaching mechanism is a combination of diffusion and chemical reaction. The possible chemical reaction between glass and solution is interpreted as:



Where M = glass modifier ion

From the glass surface, glass modifier ions are released into solution due to the effect of hydronium ions in the acid solution, which in turn enter into the holes of the skeleton layer from which lead and glass modifiers were leached.

In pure silica glass, each silicon atom is surrounded by four oxygen atoms, and each oxygen atom is bonded to two silicon atoms. The number of nonbridging oxygen atoms increases with increasing quantities of glass modifiers (Na⁺, K⁺, etc).

Based on the single bond strengths given by Sun (8), Yoon et al. considered that glass modifier-oxygen bonds such as Na-O and Pb-O are easily broken, and that Na⁺, K⁺ and Pb²⁺ ions move from one nonbridging oxygen atom to another in a viscous flow process during glass melting (7). The modifier ions (K⁺, Na⁺ and Pb²⁺) on the glass surface in contact with an acid solution are released into solution due to chemical action on these weakly bonded ionic species.

Takashima and Saito examined the effects of various cations in the lead oxide-silica-metal oxide system on the extraction of Pb by 4% acetic acid (9). They observed that when alkali and alkaline earth (except Be, Mg) ions were included in the glass, the amount of Pb released was larger than that from the mother glass. They explained that the increase in Pb extraction by doping of the mother glass with glass modifier was caused by the weak bond strength of the introduced ions, their large ionic radii, and the formation of interstices in the glass structure. When Mg and Be were added to the glass, the amount of Pb ion dissolution was less than that of the mother glass. Those cations are considered to contribute to the

tight structure of the glass by binding to oxygen ions having unsaturated valency.

INFLUENCE OF COLOURING OXIDES ON TOXIC MATERIALS RELEASE

In decorative glazes and enamels, proper colours may be obtained by adding chromogenic ions, which often increase the release of toxic materials. Very little information is available on the mechanisms or the cause of the increased toxic release with these additions. In green glazes, copper oxide may be used as the colouring agent. It is incorporated into the frit as cupric carbonate, cuprous carbonate, cupric oxide or cuprous oxide. The presence of small quantities of these materials in the glazes can promote higher lead release.

Dube reported that the lead release from copper-bearing glazes can be suppressed by the addition of chromium compounds (10). He studied the effect of adding different amounts of several chromate compounds. His results showed that barium chromate decreased lead release as its concentration increased, whereas silver chromate had the reverse effect. Iron chromate passed through an effectiveness peak, suppressing lead release at low concentrations, increasing it at higher concentration.

Buldini studied the action of a 4% acetic acid solution on a ceramic glaze containing lead, zinc and chromogenic oxides (11,12). His results indicated that both copper and chromium oxides increased the release of lead and zinc; Fe^{3+} and manganese oxides had a lesser effect, and Co^{2+} , Ni^{2+} and Cd^{2+} had none.

Lehman reported the effect of colouring oxides on lead release from glazes (13). His results showed that cobalt oxide and manganese oxide did not significantly affect the lead release of the base glaze. A 2% mill addition of CuO to a standard base glaze caused a lead-release increase of from below 0.5 ppm to about 1.5 ppm.

It appears that the nature of the colouring oxide in combination with the glaze composition determines its effect on release of toxic material, but there seems to be considerable uncertainty as to the mechanism of toxic releases.

FORMULATION OF GLAZES FOR LOW LEAD RELEASE

The first attempt to correlate composition with lead release was made by Thorpe (14). Based on his studies of lead bisilicate having a $PbO:SiO_2$ molar ratio of 1:2, he proposed the following empirical ratio to compare the lead solubilities of frits:

$$\text{Solubility} = \frac{\text{Sum of moles of basic oxides} + Al_2O_3}{\text{Sum of moles of acidic oxides}} \times \frac{233}{60}$$

where 233 and 60 are the molecular weights of PbO and SiO_2 . To achieve low solubility, this ratio should be less than 2.

Mellor simplified Thorpe's expression to (15):

$$\text{Solubility} = \frac{\text{Sum of moles of basic oxides} + Al_2O_3}{\text{Sum of moles of acidic oxides}}$$

For low solubility, this ratio should be less than 0.5.

Bloor attempted to correlate several properties of glazes with two other factors based on the concepts of network formers and network modifiers (16). He treated SiO_2 and Al_2O_3 as network formers, and all other oxides as network modifiers. For each glaze the following "R" and "P" values were calculated (based on molecular formula):

$$R = \frac{\text{Sum of O in molecular formula}}{\text{Sum of Si+Al+B in molecular formula}}$$

$$P = \frac{\text{Sum of O in molecular formula}}{\text{Sum of network modifiers (Li, Na, K, Ca, Sr, Ba, Pb, Zn)}}$$

He showed that for boron-free glazes, P, R and P/R correlated well with several properties, e.g., the maturing temperature of the glaze. On the other hand, the correlation did not fit for glazes containing boron oxides. He also showed, in triaxial diagrams where the three apices of the triangle were network modifiers, $SiO_2 + Al_2O_3$ and B_2O_3 , that the lines of constant maturing temperature were perpendicular to the apex $SiO_2 + Al_2O_3$. This

indicated that the boron oxide behaved as a network modifier rather than as a network former.

It has been shown that the Pb release must take into account the effects of the entire composition of the glaze and is not related in any simple way to its Pb content. Eppler proposes a new way of predicting lead release, based on the relationship of two factors, each derived from the summation of those constituents that impart "good" and "bad" properties, respectively (17).

$$\text{Good} = 2(\text{Al}_2\text{O}_3) + \text{SiO}_2 + \text{ZrO}_2 + \text{TiO}_2 + \text{SnO}_2$$

(The factor 2 is incorporated due to two equivalents of Al in every equivalent of Al_2O_3 .)

$$\text{Bad} = 2[\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5] + \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} + \text{F} + \text{ZnO} + \text{CdO} + \text{PbO}$$

He then plotted Good/ $\sqrt{\text{Bad}}$ for every glaze versus its lead release.

Applying simple and multiple regression analysis he determined a "figure of merit" equal to Good/ $\sqrt{\text{Bad}}$:

If Good/ $\sqrt{\text{Bad}} > 2.05$, then the Pb release is less than 7 ppm.

If Good/ $\sqrt{\text{Bad}} < 1.80$ some Pb release values will most likely exceed 7 ppm.

EXPERIMENTAL PROCEDURE

RAW MATERIALS

The raw materials for batch preparation were obtained in the form of frits from a commercial supplier. Their composition and that of the clay used for compounding the glazes are given in

Table 1. The additives subsequently used - CuO , BaCrO_4 and Cr_2O_3 - were of certified chemical grade.

GLAZE COMPOSITIONS

Three basic glaze compositions were used, prepared from the individual frits or their mixtures plus the usual mill addition of 10% clay. The batch compositions are given in Table 2 and the calculated chemical compositions and empirical formulae of the glazes are given in Table 3. Glazes 1 to 3 are typical Canadian pottery glaze formulations maturing at Cones 06, 06-01, and 3 plus, respectively.

The lead release characteristics of these glaze compositions, melted as glasses, were determined without and with additives. To examine the effect of copper colourants, 2 wt % CuO was added to each of the basic glazes. Subsequently, secondary additions of BaCrO_4 and Cr_2O_3 in amounts varying from 0.1 to 4.0 wt % were made to each of the copper-bearing glaze compositions.

BATCH PREPARATION

The glaze compositions were melted in either 1000- or 500-g batches. The raw material were accurately weighed on a laboratory balance accurate to 0.1 g. After weighing, each batch was placed in a 2-L polyethylene jar tightly fitted with a screw cap, and thoroughly mixed by rotation in a Turbula Mixer* for about one hour.

*Manufactured by Willy A. Bachofen Maschinenfabrik, Basel, Switzerland.

Table 1 - Chemical compositions of frits and clay used for compounding of glazes

	K_2O	Na_2O	CaO	MgO	PbO	Al_2O_3	B_2O_3	SiO_2	TiO_2	Fe_2O_3	LOI
Frit 1					57.0			43.0			
Frit 2		6.0	11.2			12.4	23.0	47.4			
Frit 3	1.9	1.5	4.6		31.3	3.1	12.9	44.7			
Frit 4	1.6	2.7	9.6		18.7	5.6	4.9	56.9			
EPK clay	0.22	0.04	0.09	0.12		38.71		45.91	0.34	0.42	14.16

Table 2 - Mix proportions of frits and clay for compounding of glazes

Glaze 1	Glaze 2	Glaze 3
59.09 wt % Frit 1	90.91 wt % Frit 3	90.91 wt % Frit 4
31.82 wt % Frit 2	9.09 wt % EPK clay	9.09 EPK clay
9.09 wt % EPK clay		

Table 3 - Batch compositions of glazes in weight per cent and empirical formulae

		Glaze 1		Glaze 2		Glaze 3	
		Weight per cent	Empirical formula	Weight per cent	Empirical formula	Weight per cent	Empirical formula
RO	K ₂ O	0.02	0.012	1.98	0.084	1.51	0.054
	Na ₂ O	1.98	0.125	1.42	0.091	2.52	0.14
	CaO	3.66	0.255	4.29	0.304	8.95	0.54
	MgO	0.01	0.0004	0.01	0.0008	0.01	0.001
	PbO	34.49	0.608	29.14	0.520	17.40	0.265
R ₂ O ₃	Al ₂ O ₃	7.13	0.274	5.98	0.234	8.31	0.275
	B ₂ O ₃	7.50	0.423	12.10	0.692	4.56	0.22
	Fe ₂ O ₃	0.04	0.0002	0.04	0.001	0.04	0.0007
RO ₂	SiO ₂	45.14	2.94	45.29	3.00	56.68	3.19
	TiO ₂	0.03	0.0002	0.03	0.001	0.03	0.001

MELTING

To minimize volatilization of Pb from the melts, the glazes were melted at as low a temperature and for as short a time as was consistent with ensuring thorough melting and homogenization. The liquidus temperatures were first determined in a Leitz heating microscope with the results given in Appendix A (18). The batches were then melted in electrical resistance furnaces. The melting time was normally about 15 min at the liquidus temperature, which was automatically controlled to $\pm 5^\circ\text{C}$. Initially, several batches were melted in platinum dishes, but due to damage sustained by these expensive containers, subsequent batches were melted in fused-silica boats or crucibles, which have the advantage of low cost, high purity and high thermal shock resistance. At the

end of the melting period the containers were removed and the melts poured into water for quenching and disintegration. To promote homogeneity, each batch was remelted for a further 15 min at the liquidus temperature, and again quenched in water.

LEAD RELEASE DETERMINATION

Leaching of lead from the melted glazes was performed using a modified version of ASTM C225-73 standard test method for resistance of glass containers to chemical attack, in which the granulated glass is leached with 4% acetic acid at 27°C (19).

GRINDING

The quenched melt from the second melting

was oven-dried at 150°C for 3 h. The dry sample was then reduced in a jaw crusher and granulated in a micropulverizer. The ground sample was shaken through No. 20, 40 and 50 Tyler sieves. The fraction retained on the No. 50 sieve of between 300 and 425 μm particle size was retained for lead extraction. This sample was first passed through a magnetic field to remove any contaminating iron introduced by the grinding process, then washed three times to remove any adhering fines and rinsed in methyl alcohol. In each washing step a liquid:solid volume ratio of 3:1 was employed. The washed sample was oven-dried at 150°C for 3 h.

LEACHING

All leaching was conducted on duplicate samples. Ten-gram aliquots of the granulated glasses were placed in 550-mL bottles with 350 mL of 4% acetic acid (one volume of glacial acetic acid diluted with 24 volumes of distilled water). The bottles were capped and the caps attached to motor-driven shafts. The bottles were submerged in a constant-temperature bath at 27°C. During leaching, the sample and solution were constantly stirred by rotation of the motor-driven shafts.

Granulated glasses of the three basic glaze compositions were leached for 2, 4, 8, 16 and 24 h, as were the same glasses with 2 wt % CuO addition, and in turn the copper-bearing glasses with additions of from 0.1 to 4.0 wt % Cr_2O_3 and BaCrO_4 respectively.

Following leaching, 250-mL aliquots of solution were withdrawn from the bottles and analyzed for lead to ± 0.001 g/L by atomic absorption technique in the Chemical Laboratory of the Mineral Sciences Laboratories, CANMET.

RESULTS AND DISCUSSION

PREDICTION OF LEAD RELEASE FROM GLAZES

Based on the empirical formulae, the "figure of merit" for these glazes, given in Table 4, was calculated according to Eppler (17).

Each of these three glazes has a figure of merit equal to Good/Bad > 2.05 and therefore, according to Eppler, the lead release should be low. Glaze 2 has the lowest figure of merit among

these glazes, and should have the highest lead release value.

Table 4 - Figure of merit for various glazes

Glaze No.	Fig. of Merit
1	2.48
2	2.08
3	2.70

LEAD RELEASE FROM BASE GLAZE COMPOSITIONS

Lead release from base glazes was examined first. Results of the average of duplicate analyses of the lead release values versus extraction time were plotted in Fig. 3 to 5. Under identical extraction conditions, the lead release values for glaze composition 3 were significantly lower than those for compositions 1 and 2. Composition 2 gave the highest value and composition 1 had values slightly lower than glaze 2. In all cases, lead release increased with increasing extraction time. These results confirmed the prediction, based on the calculation of the figure of merit, indicating lead release from glaze 1 $<$ glaze 2 $>$ glaze 3. Comparing the chemical compositions of these glazes in Table 3, it can be seen that the glaze with the lowest release contained more Al_2O_3 , CaO, and SiO_2 and less PbO and B_2O_3 , whereas glazes with the higher release in general had less Al_2O_3 , CaO, and SiO_2 and more PbO.

The effect of MgO, CaO, ZnO, Al_2O_3 , TiO_2 and ZrO_2 in lead-borosilicate glass was examined by Cooke and Paul (20). They observed that the presence of Al_2O_3 in glass improved the resistance to attack by aqueous solutions. They ascribed this to the formation of AlO_4 groups linked by bridging oxygens to SiO_4 tetrahedra, the cations Pb^{2+} and Li^+ , which have donated the necessary oxygens, being held in close association with the AlO_4 groups for local electroneutrality. The basic cations in Al_2O_3 -containing glasses are thus much less free than they would be in the absence of alumina.

Although B_2O_3 is a network former that might be expected to improve the durability of glass, its addition to a lead-containing glaze

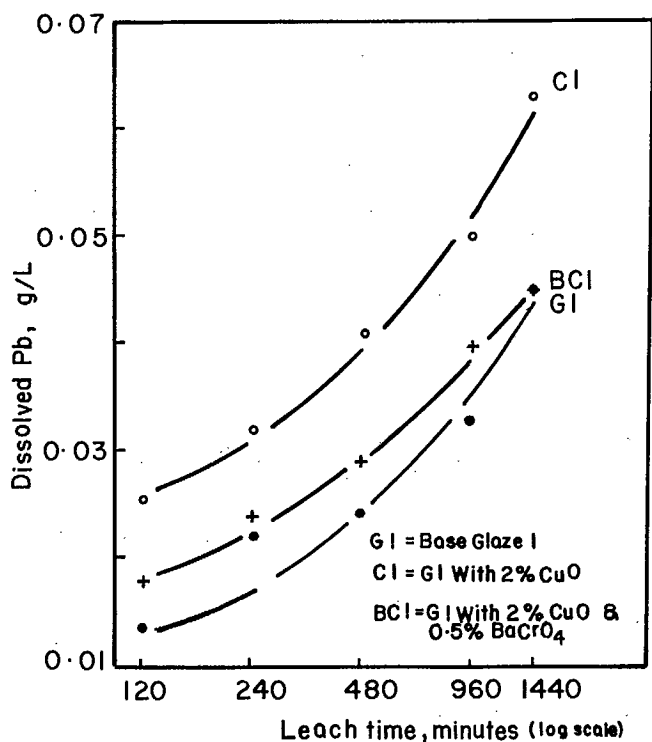


Fig. 3 - Lead release as a function of leach time for base glaze 1, showing effect of addition of copper colourant and inhibition by BaCrO₄

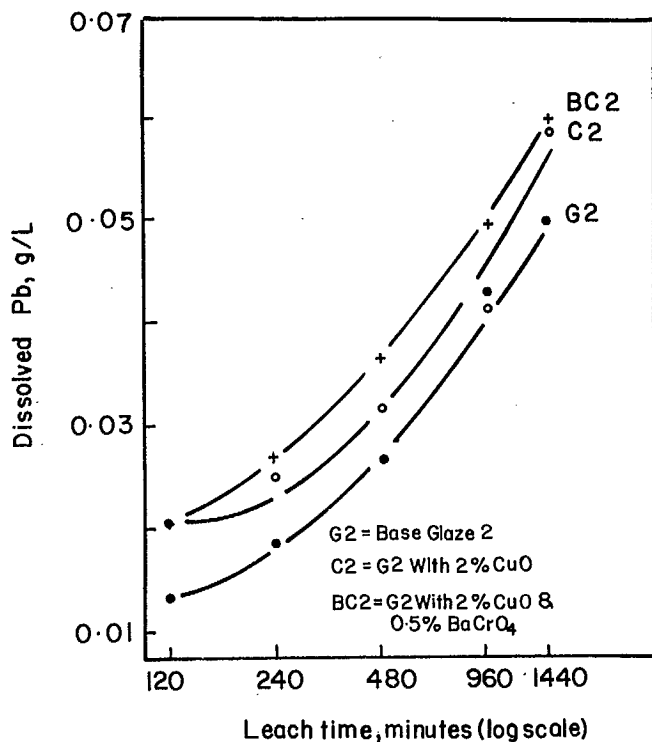


Fig. 4 - Lead release as a function of leach time for base glaze 2, showing effect of addition of copper colourant and inhibition by BaCrO₄

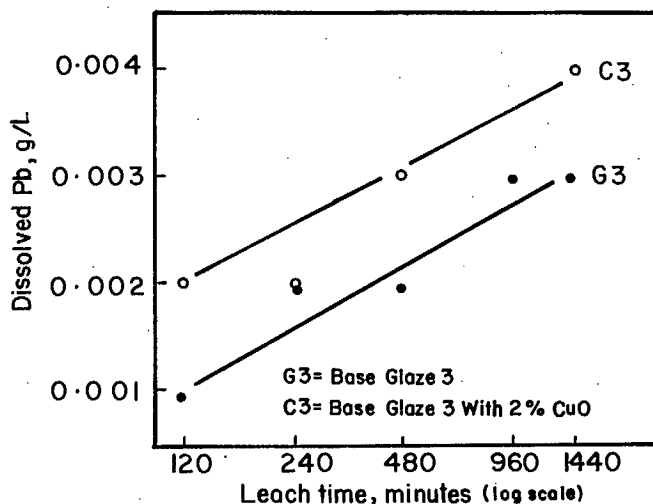


Fig. 5 - Lead release as a function of leach time for base glaze 3, showing effect of addition of 2 wt % CuO

rapidly lowers the acid resistance and increases the Pb release. According to Eppler, constituents such as Al₂O₃, SiO₂, TiO₂ and ZrO₂ improve durability of the glaze (17). Those constituents that contribute to lead release include the alkalis, the alkaline earths, ZnO, CdO, B₂O₃, F, and P₂O₅.

The higher lead release for glazes 1 and 2 appears to result from the larger amount of B₂O₃ and lesser amount of Al₂O₃ present in the structure, which is in agreement with the work reported by others (14-17).

EFFECT ON LEAD DISSOLUTION ADDING COPPER OXIDE TO BASE GLAZE COMPOSITIONS

Once the lead release values of the base glazes were established, the effect of copper addition was examined. Two wt % of cupric oxide was added to glazes 1, 2 and 3. Lead dissolution versus leach time for these copper-bearing glazes were plotted in Fig. 3 to 5. Table 5 compares the lead release values obtained for base glazes and copper-bearing glazes after leaching for 24 h.

It can be seen from the table and figures that the lead dissolution is higher for the copper-bearing glazes than for the base glazes. There is a substantial increase in lead release for glazes 1 and 2 after incorporating 2 wt % of CuO, but little difference in the values for glaze

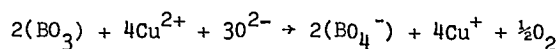
Table 5 - Lead dissolution after 24 h of leaching for base and copper-bearing glazes

No.	Base glaze	Copper-bearing glaze
	Dissolved lead, g/L	
1	0.045	0.063
2	0.049	0.054
3	0.003	0.004

3, which was also the most stable base glaze.

Cooke and Paul examined the effect of copper oxide on chemical durability of lead borosilicate glasses and showed that the lead extraction increased with increasing copper oxide concentration in the glasses (20). They observed difference in extraction of lead, silica and the colouring oxide from quenched and heat-treated glasses, the extraction increasing with heat treatment. Furthermore, heat treatment had a greater effect on extraction as the copper content of the glass increased. The low durability of the glass was due to the presence of Cu^+ and Cu^{2+} with a very small amount of Cu^0 dissolved in the glass. Under identical melting conditions the Cu^+ content increased with increasing lead oxide content of the glass. Both Cu_2O and CuO are soluble in the acid, the solubility of Cu_2O being much higher than that of CuO , and as a result the addition of copper oxide to glass decreases the corrosion resistance. In the case of the heat-treated copper-containing glasses, the marked increase in durability over that of chilled glasses was due to three-phase separation, i.e., liquid-liquid immiscibility together with a crystalline phase.

Powell and Auchmoody studied the reduction of Cu^{2+} in high-lead borate solder glasses in the temperature range of from 750 to 1300°C (21). They observed that the $\text{Cu}^+:\text{Cu}^{2+}$ ratio in the Cu-containing $\text{PbO-B}_2\text{O}_3$ glass with high lead content was found to be exponentially related to fining temperature. They concluded that the higher fining temperatures favour the participation of Cu in the Cu^+ state as a network modifier according to the equation:



The above reaction suggests that some boron is converted from threefold to fourfold coordination with oxygen. At very low and very high modifier contents, the BO_4^- tetrahedra may not play a part in strengthening the boron-oxygen network in the glass, but instead may act to break it up by forming terminal groups and complex polyions. Only at the intermediate modifier contents do the BO_4^- tetrahedra cooperate to strengthen the network. In high-lead glasses, the Cu^+ entering the structure as a modifier would result in loosening the network structure.

It has been suggested by other investigators that the ratio of $\text{Cu}^+:\text{Cu}^{2+}$ in lead-containing glasses has a great influence in controlling durability of the glass (20). In part, this may explain the increased lead release from those copper-containing glazes that developed a high $\text{Cu}^+:\text{Cu}^{2+}$ ratio.

EFFECT ON LEAD RELEASE OF ADDING CHROMATE COMPOUNDS TO COPPER-BEARING GLAZE COMPOSITIONS

It has been suggested by other investigators that the addition of small amounts of chromate compounds will suppress lead release from copper-bearing glazes (22,23). To examine this effect, 0.5 wt % BaCrO_4 was added to glazes 1 and 2 containing 2.0 wt % CuO . These glasses were leached as before, and the amounts of lead extracted were plotted as a function of leach-time in Fig. 3 to 5. With a 0.5-wt % BaCrO_4 addition to the copper-bearing glaze 1, the lead release level was about 30% lower than for the copper-bearing glaze without the addition. However, the lead release level of the copper-bearing glaze with 0.5-wt % BaCrO_4 addition was still higher than that of the base glaze.

There appeared to be no benefit from adding 0.5 wt % BaCrO_4 to copper-bearing glaze 2, as shown in Fig. 6. In this case, with the addition of barium chromate, the lead release level in the copper-bearing glaze was higher than that of the copper-bearing glaze without barium chromate addition.

The lead release from the copper-bearing glazes 1 and 2 as a function of BaCrO_4 and Cr_2O_3 concentration was examined. In this study, the

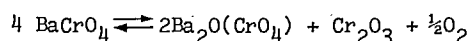
leaching time of the glazes was 24 h at 27°C. The lead release data obtained for copper-bearing glaze 1 as a function of oxide concentration are plotted in Fig. 6. It can be seen that the lead release decreased with increasing BaCrO₄ concentration up to 0.5 wt %. With further increase in BaCrO₄ concentration up to 2 wt %, the lead release reached a maximum, followed by a decrease as the BaCrO concentration reached 4 wt %. By adding Cr₂O₃ to the same glaze, the results shown in Fig. 6 indicated that the lead release was at a minimum for Cr₂O₃ at 0.5 wt %. With further additions of Cr₂O₃ to the glaze, there appeared to be no significant change in the amount of lead released.

Figure 7 shows the effect on lead extraction from copper-bearing glaze 2 by adding variable amounts of BaCrO₄ and Cr₂O₃. As can be seen from the figure, minimum lead release occurred at a BaCrO₄ concentration of 0.2 wt %, followed by a maximum at 2.0 wt %. A further addition to 4 wt % reduced the lead release to below the level of the base glaze. The effect of adding Cr₂O₃ to glaze 2 was similar to that in glaze 1, with minimum lead release at a Cr₂O₃ concentration of 0.3 wt %.

The results obtained for lead extraction from the copper-bearing glazes with various additions of BaCrO₄ and Cr₂O₃ show that Cr₂O₃ is a more effective lead-release inhibitor than BaCrO₄. The behaviour of Cr₂O₃ as a lead-release inhibitor may be explained in part by the similar size in ionic radii of Cr³⁺ and Al³⁺. It has been reported by Zamin and Murthy in their investigation into the effect of Al₂O₃ on the chemical durability of PbO-SiO₂ glass leached in dilute hydrochloric acid, that there is some relationship with the coordination of Al³⁺ in the glass (24). They explained that durability of the glass increases with increasing Al₂O₃ content up to a critical concentration below which the Al³⁺ ions are in sixfold coordination and above which they enter into fourfold coordination. Apparently the Al-O bond strength is higher in fourfold coordination, hence less bonding power is available for sharing with Pb, rendering it more susceptible to leaching. One might assume a similar behaviour for Cr³⁺ ions. The results of the present investigation would indicate that the critical concentra-

tion of Cr₂O₃, above which the coordination changes from sixfold to fourfold, is about 0.5 wt %.

Barium chromate also acted as a lead-release inhibitor, however, its effectiveness depended strongly on its concentration (Fig. 6,7). It might be assumed that on decomposition of the BaCrO₄, Cr₂O₃ would be available and thus act as a lead-release inhibitor. But Ba²⁺ would also be available, which would be expected to increase lead release due to disruption of the glass structure because of the large ionic radius of the Ba. The decomposition of BaCrO₄ is represented by the following equation:



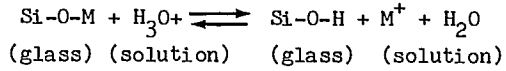
For Cr³⁺ ions to be present it must be assumed that PbCrO₄ decomposes in a similar manner, which has in fact been proposed by Mellor (25).

Another possible explanation for the reduction of lead release from the copper-bearing glazes by doping with Cr₂O₃ involves the formation of compounds such as Cu₂Cr₂O₄ and CuCr₂O₄ and the presence of ions such as Cu⁺, Cu²⁺ and Cr⁺³. Formation of the copper chromate compounds would reduce the interaction of the copper and boron ions, restricting the boron ions to threefold coordination and thus strengthening the glass structure. The foregoing assumption has yet to be verified experimentally, but X-ray diffraction analysis failed to reveal any crystalline compounds in these quenched glasses.

LEACHING MECHANISM

The lead-leaching kinetics of the glazes show a linear dependence with respect to \sqrt{t} in Fig. 8, 9 and 10, indicating that the lead release is a diffusion-controlled process and will therefore be sensitive to alterations in structure due to changes in composition. The results are in good agreement with results reported by Baranyi et al. for the leaching of cadmium from a glass frit (19).

It is the generally accepted theory that the chemical reaction between glass and a solution is:



CONCLUSIONS

where M = glass modifying ion.

From the glass surface, glass modifier ions such as alkalis, alkaline earths and Pb^{2+} are released into solution. In turn, hydronium ions enter into the holes of the skeleton layer from which the alkali and alkaline earth ions were leached.

Initial leach tests of three base glazes prepared from four commercially available frits showed that the lead release from these glasses was very sensitive to compositional variation. It has been shown that compositions containing high proportions of PbO and B_2O_3 and low proportions of CaO and Al_2O_3 result in higher lead release. Lead release was generally higher for glazes with lower "figure of merit".

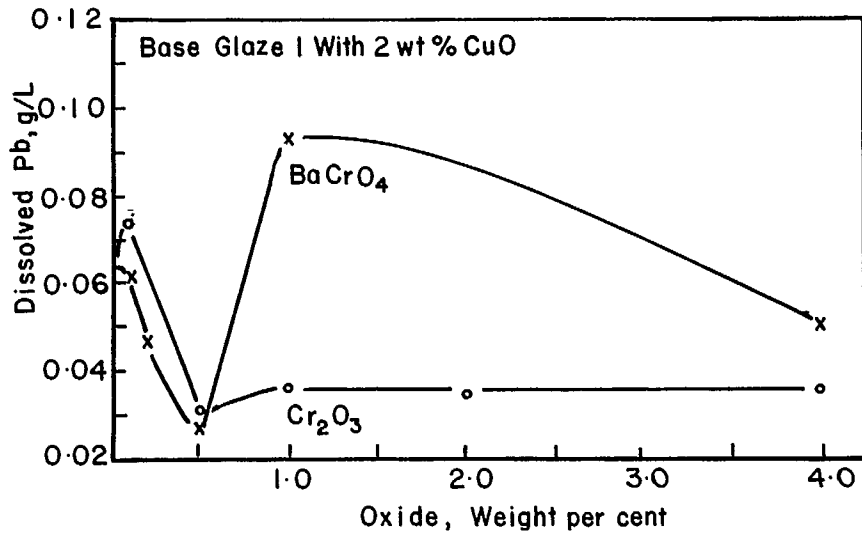


Fig. 6 - Lead release as a function of BaCrO_4 and Cr_2O_3 concentration for glaze 1

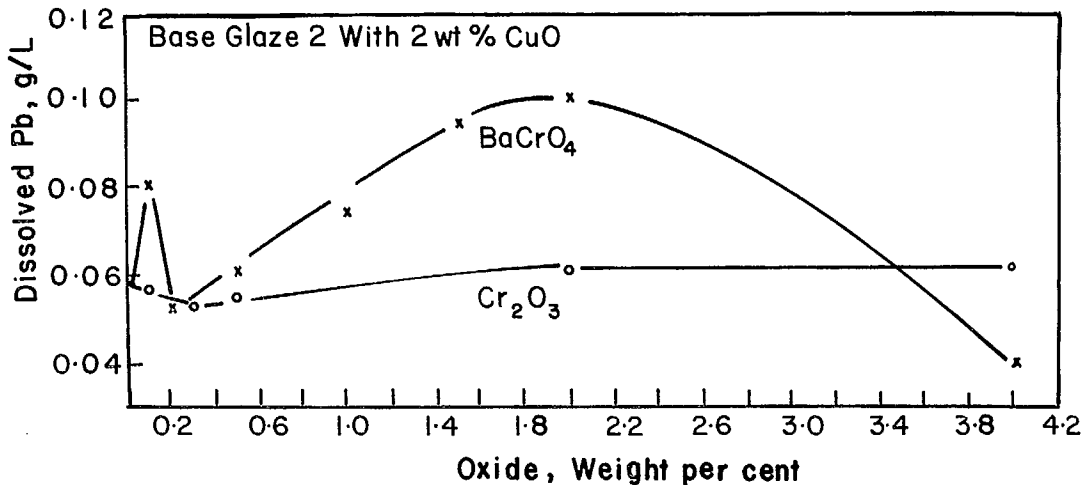


Fig. 7 - Lead release as a function of BaCrO_4 and Cr_2O_3 concentration for glaze 2

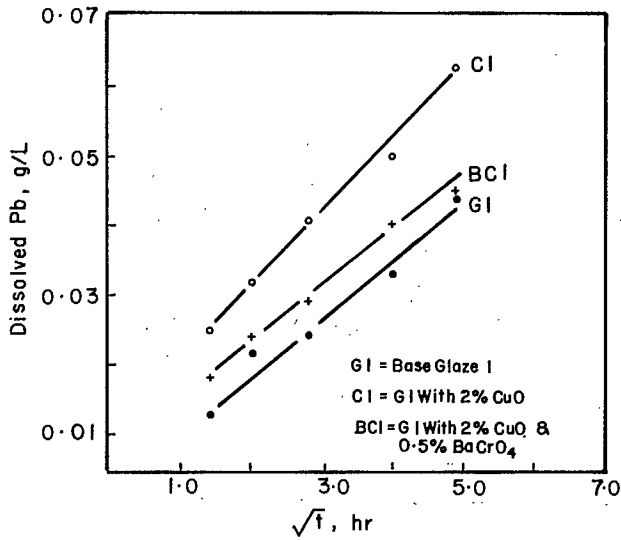


Fig. 8 - Lead release vs square root of leach time, glaze 1

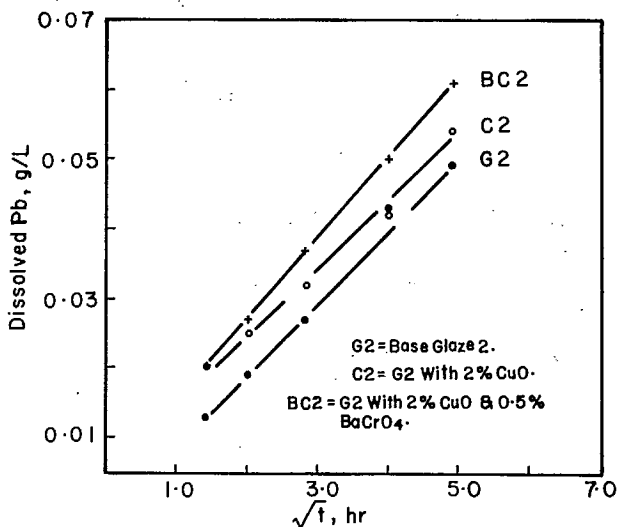


Fig. 9 - Lead release vs square root of leach time, glaze 2

On adding 2 wt % of copper oxide to the base glazes, the lead release was higher for glasses containing higher B_2O_3 concentrations. The increase in lead release for high boron oxide glasses is attributed to the oxidation state of the copper: the Cu^+ state was favoured and modified the network-forming B_2O_3 , thus converting some boron from threefold to fourfold coordination with oxygen. In high-lead glasses the Cu^+ can

enter the structure as a modifier, resulting in loosening of the network structure.

Adding chromium compounds $BaCrO_4$ and Cr_2O_3 to the copper-bearing glazes revealed that lead release was suppressed proportionally, but only up to a critical concentration. It was also demonstrated that Cr_2O_3 was a more effective lead inhibitor than $BaCrO_4$. It appeared that the lower effectiveness of $BaCrO_4$ was due to the large ionic radius of the Ba^{2+} which may cause disruption of some bonds in the glass structure and hence increase the lead release. The role of Cr_2O_3 as a lead-release inhibitor may be explained in part by the close similarity in ionic radii of Cr^{3+} and Al^{3+} . The Cr^{3+} ions can exist in either sixfold or fourfold coordination. The presence of Cr^{3+} in the fourfold coordination in effect decreases the overall bond strength in the glass structure.

The lead leaching kinetics of these glasses showed a linear dependence with respect to the square root of time and this indicated that the lead release is a diffusion-controlled process and hence is sensitive to change in structure due to compositional variation.

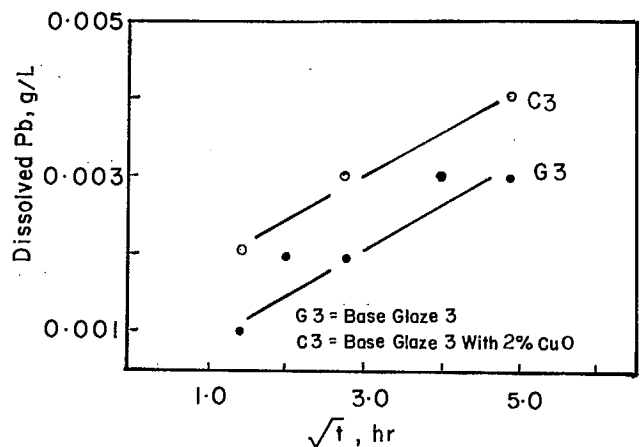


Fig. 10 - Lead release vs square root of leach time, glaze 3

ACKNOWLEDGEMENT

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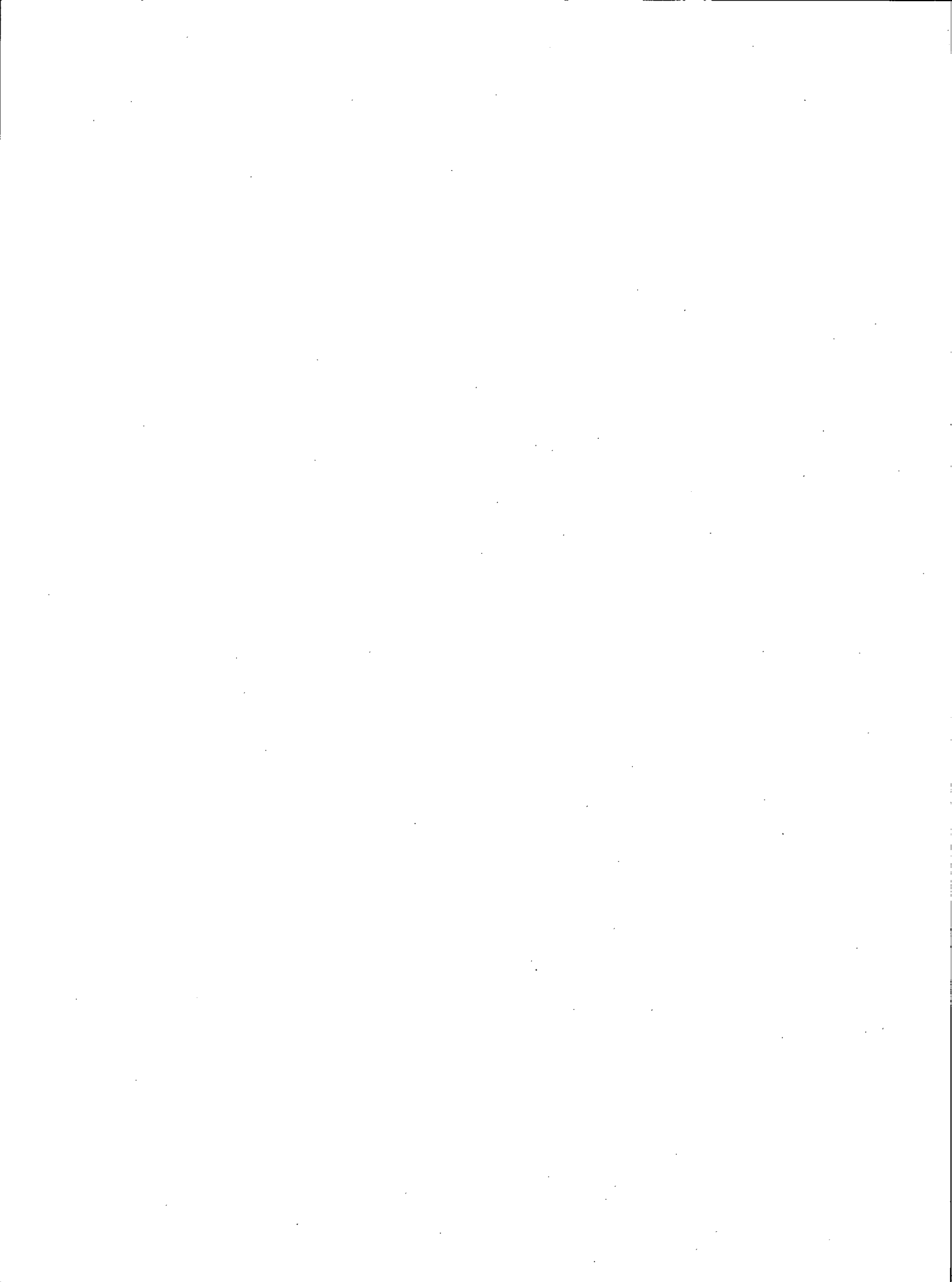
REFERENCES

1. Zachariassen, W.H. "Atomic arrangement in glass"; J Amer Chem Soc 54:10:3941-51; 1932.
2. Goldschmidt, W.M. "Geochemische verteilungsetze der elemente VIII, Vid." A. Kand, SKR Oslo, 8:137; 1926.
3. Warren, B.E. "Summary of work on atomic arrangement in glass"; J Amer Ceram Soc 24:256-261; 1941.
4. El-Shamy, T.M. and Douglas, R.W. "Kinetics of the reaction of water with glass"; Glass Tech; 13:3:77-80; 1972.
5. El-Shamy, T.M., Lewins, J. and Douglas, R.W. "The dependence of the pH on the decomposition of glasses by aqueous solution"; Glass Tech 13:3:81-87; 1972.
6. Hafner, A.C. and Jones, F.L. "Adsorption of ions by leached surface films of glass"; J Amer Ceram Soc 26:55-56; 1943.
7. Yoon, S.C., Krefft, G.B and McLaren, M.G. "Lead release from glazes and glasses in contact with acid solutions"; Bull Amer Ceram Soc 55:508-512; 1976.
8. Sun, K.H. "Fundamental condition of glass formation"; J Amer Ceram Soc 39:277-281; 1947.
9. Takashima, H. and Saito, H. "Effects of various cation additions on dissolution of Pb ion by acetic acid in lead oxide-silica-metal oxide system frits"; Yogyo Kyokai Shi 83:41-46; 1975.
10. Dube, A., "Ceramic compositions"; Canadian Patent No. 965804, April 8, 1975.
11. Buldini, P.L. "Influence of coloring oxides on heavy metals release from ceramic glazes"; Bull Amer Ceram Soc 56:1012-1014; 1977.
12. Buldini, P.L. "Influence of coloring oxides on the release of silicon and boron from ceramic glazes"; Bull Amer Ceram Soc 57:430-431; 1978.
13. Lehman, R. "Stabilization of surface layers of lead containing glasses and glazes"; Proceedings of the International Conference on Ceramic Foodware Safety, Geneva, 1979, Ed by J.F. Smith and M. McLaren; 1974
14. Thorpe, T.E. "Use of lead in the manufacture of pottery"; British Government Paper 8383-150093/1901-wt-32982 Da S-4, 1899.
15. Mellor, J.W. "The durability of pottery frits, glazes, glasses and enamels in service"; Trans Brit Ceram Soc 34:113-120; 1934.
16. Bloor, C.E. "Glaze composition, glass structural theory and its application to glazes"; Trans Brit Ceram Soc 55:631-660; 1956.
17. Eppler, R.A. "Formulation of glazes for low Pb release"; Bull Amer Ceram Soc 54:496-499, 1975.
18. Buist, D.S. "Investigation with the Leitz heating-microscope type IIA-P in the field of ceramics"; Trans Brit Ceram Soc 69:15-20; 1970.

19. Baranyi, A.C. "Study of the effect of light on cadmium release from glazes"; Final Progress Report, Ontario Research Foundation, under CANMET contract 8-9081; CANMET, Energy, Mines and Resources Canada; 1979.
20. Cooke, D. and Paul A. "Chemical durability of glass enamel containing B_2O_3 . Part I. Lead Borosilicates; Part II. Lead borosilicates containing MgO, CaO, ZnO, Al_2O_3 , TiO_2 and ZrO_2 .; Part III. Coloured lead borosilicates containing copper, cadmium and cobalt oxides."; Trans Brit Ceram Soc 77:104-125; 1978.
21. Powell, J.L. and Auchmoody, H.N. "Thermal reduction of Cu^{2+} in $PbO-B_2O_3$ solder glasses and effect of $Cu^+ : Cu^{+2}$ on the thermal properties of $PbO-B_2O_3$ glass"; Bull Amer Ceram Soc 56: 484-486; 1977.
22. Stourmaras, C.J., Zamin, M. and Murthy, M.K. "Status of toxic material release from ceramic glazes in contact with food products: a literature review and recommendations"; Ontario Research Foundation Report No. G & C-92-78-212, under CANMET Contract 7-5232; CANMET, Energy, Mines and Resources Canada; 1978.
23. "Lead Glazes for dinnerware"; ILZRO Manual No. 1 - Ceramics; (International Lead zinc Research Organization), New York; 1974.
24. Zamin, M. and Murthy, M.K. "Effect of Al_2O_3 on the chemical durability of $PbO-SiO_2$ glass in 0.5M HCl"; Bull Amer Ceram Soc 58:1199-1200; 1979.
25. Mellor, J.W. "A comprehensive treatise on inorganic and theoretical chemistry, Vol. XI"; 297; London, Longmans, Green and Co.; 1931.

APPENDIX A

SOFTENING AND LIQUIDUS POINTS OF GLASSES -



Prior to actually melting the full-size samples, the behaviour of each composition was determined by melting small samples in air using a Leitz heating microscope, type IIA-P capable of operating in air up to 1750°C. The construction and operation of this equipment has been described elsewhere (18). The samples used in the heating microscope were prepared from the batches formulated for the leaching experiments.

The small samples were heated in the microscope in a static air atmosphere at 6°C/min. The projected image of the sample was photographed at approximately 100°C intervals as the temperature was raised. In this manner, a series of photographs was obtained showing the progressive

shrinkage and deformation of the sample with increasing temperature. The softening temperature was defined as the point at which the corners of the specimen were clearly rounded, and the liquidus temperature as the point at which the melted specimen had flowed to assume an essentially flat surface. These temperatures for the three base glaze compositions were:

	Softening point °C	Liquidus point °C
Glaze 1	850	940
Glaze 2	900	960
Glaze 3	950	1100

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