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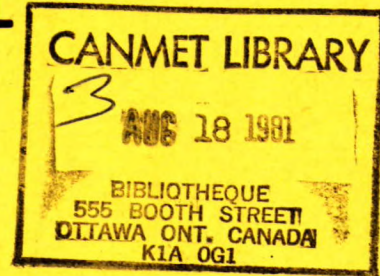
# CANMET

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Centre canadien  
de la technologie  
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et de l'énergie

### RELEASE OF LEAD FROM TYPICAL CANADIAN POTTERY GLAZES



D.H.H. QUON & K.E. BELL

MINERAL RESEARCH PROGRAM  
MINERAL SCIENCES LABORATORIES



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## RELEASE OF LEAD FROM TYPICAL CANADIAN POTTERY GLAZES

by

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

## ABSTRACT

In recent years intensive world-wide research began into the problem of release of lead and other toxic metals from glazed ceramic ware used for food and beverage service. One such study was conducted in the Mineral Sciences Laboratories, CANMET, to assess the instability of glasses melted from typical glaze compositions in contact with 4% acetic acid.

The present study was made to determine the stability of typical Canadian pottery glazes under conditions simulating domestic use and to examine the mechanisms of Pb release and stabilization as a contribution to developing stable, safe glazes.

Lead release from glazes in contact with 4% acetic acid was studied as a function of applied glaze thickness and firing temperature. It was shown that the amount of lead release was dependent not only on composition, but also on glaze thickness and firing temperature.

The reported inhibiting effect of chromate additions was examined. It was found that lead release from copper-bearing glazes can be suppressed by adding about 0.5% *m/m* BaCrO<sub>4</sub> or Cr<sub>2</sub>O<sub>3</sub>. The inhibiting effect of the chromate compounds is attributed to modification of the glaze structure.

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

## LA LIBÉRATION DU PLOMB DES GLAÇURES TYPIQUES DE POTERIE CANADIENNE

par

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

## RÉSUMÉ

Ces dernières années, des études ont été entreprises mondialement sur le problème de libération du plomb et autres métaux toxiques des pièces de poterie en céramique glacées employées pour contenir des aliments et des breuvages. Une de ces études a été effectuée aux Laboratoires des sciences minérales du CANMET pour évaluer l'instabilité des verres fusionnés à partir des compositions de glaçures typiques mis au contact de l'acide acétique à 4%.

Cette étude a été effectuée afin de déterminer la stabilité des glaçures typiques de poterie canadienne soumises à des conditions simulant l'utilisation domestique et d'examiner les mécanismes de libération et de stabilisation du Pb. Ceci constitue la contribution du CANMET à la mise au point de glaçures stables et sûres.

La libération du plomb des glaçures au contact de l'acide acétique à 4% a été étudiée en fonction de l'épaisseur de la glaçure appliquée et de la température de cuisson. On a aussi démontré que la quantité de plomb libéré dépend non seulement de la composition mais aussi de l'épaisseur de la glaçure et de la température de cuisson.

L'effet inhibiteur des additions de chromate a été examiné. On a démontré que la libération du plomb des glaçures additionnées de cuivre peut être supprimée en ajoutant environ 0.5% m/m  $\text{BaCrO}_4$  ou  $\text{Cr}_2\text{O}_3$ . Cet effet inhibiteur des composés de chromate est attribué à la modification de la structure des glaçures.

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## INTRODUCTION

The use of lead and its compounds by the ceramic industry, particularly in glazes, provides highly desirable properties that have not yet been duplicated with substitute materials. For example, lead in glazes enables a wider palette of colours, produces a brilliant gloss and promotes high molten fluidity. Several isolated cases of lead poisoning from poorly designed or applied glazes has focussed attention on developing highly acid-resistant leaded glazes. Several commercially available lead-bearing glazes developed in recent years are highly acid resistant, but this resistance may decrease when colouring oxides are added. For example, an increase in lead release was noted when copper oxide was added to the clear leaded frits. A previous study showed that the lead release was generally higher when 2% m/m copper oxide was added to typical base glaze compositions (1). It also showed that lead release is higher for the lower temperature glazes, which contain appreciably more  $B_2O_3$ . By adding chromium compounds  $BaCrO_4$  and  $Cr_2O_3$  to the copper-bearing frits, it was possible to suppress the lead release proportionally, but only up to a critical concentration.

The previous investigation, which examined the durability and leaching kinetics of crushed glasses melted from typical glaze formulations, has been extended to study the release of lead from glaze formulations applied to tableware: (a) to establish the mechanism of lead release from typical Canadian pottery glazes as a contribution to developing safe glazes for ceramic ware sold to Canadian consumers and 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.

### EFFECT OF COLOURING OXIDE ON LEAD RELEASE OF FRITTED LEAD GLAZES

Extensive research has been conducted in

various laboratories to develop sound data for formulating ceramic glazes for foodware (2,3,4). Although the use of lead and colouring agents in glazes dates back to the Assyrians, it was not until the end of the 19th century that the possibility of food extracting toxic metals from glazes was investigated.

Dubé reported that lead release from copper-bearing glazes can be suppressed by adding chromium compounds and that barium chromate inhibits lead release (5). A study by Buldini showed that copper and chromium oxides increased the release of lead;  $Fe^{3+}$  and manganese oxides had a lesser effect; and  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$  had no effect (6,7). Lehman reported the effect of colouring oxides on lead release and indicated that cobalt oxide and manganese oxide did not significantly affect the lead release of the base glaze (8). Adding 2% m/m CuO to a standard base glaze caused a lead-release increase from below 0.5 ppm to about 1.5 ppm.

Previous results showed that by adding 2% m/m CuO to leaded base glaze compositions the lead release was higher for glasses containing higher  $B_2O_3$  concentrations (1). Adding chromium compounds  $BaCrO_4$  and  $Cr_2O_3$  to the copper-bearing glasses revealed that lead release was suppressed proportionally, but only up to a critical level. It was noted that  $Cr_2O_3$  was a more effective inhibitor than  $BaCrO_4$ .

Based on the foregoing, it can be assumed that the nature of the colouring oxide in combination with the glaze composition determines its effect on release of the toxic material, and thus the mechanism of release has to be correlated with composition and concentration of the chromogenic ions, as well as firing temperature and time.

To assess the correlation between the lead release from a frit and that from a glazed body in use, a parallel conventional determination of lead release from ceramic ware decorated with glazes of the previously studied compositions was undertaken. Attempts were made to correlate the lead release with thermal history, glaze uniformity and thickness, and degree of glaze-body interaction.

## EXPERIMENTAL

As mentioned, evidence accumulated during the past years shows convincingly that the lead release of glazed ceramic ware is influenced by the following (9,10):

1. Glaze formulation, including opacifiers and colourants.
2. Thermal history of the glaze firing.
3. Thickness and uniformity of glaze application.
4. Glaze-body solution at the interface.
5. Atmospheric conditions during firing.

In this study, glaze formulation with colourant additions, thickness of glaze application, and thermal history of glaze firing were

examined. Atmospheric conditions were kept constant during firing. Factors such as glaze-body solution at the interface are closely related to the uniformity and thickness of glaze application and therefore can be grouped as a single factor influencing lead release.

## RAW MATERIALS

The raw materials for batch preparation were obtained from a commercial supplier in the form of frits. Their compositions and that of the clay used for compounding the glazes are given in Table 1. The additives subsequently used - CuO, BaCrO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> - were of certified chemical grade.

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

	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	PbO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	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			
EPK clay	0.22	0.04	0.09	0.12		38.71		45.91	0.34	0.42	14.16

## GLAZE COMPOSITIONS

Two basic glaze compositions were prepared from the individual frits or mixtures thereof 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 and 2 are typical Canadian pottery glaze formulations maturing at Cones 06 and 06-01, respectively.

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

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

Table 3 - Batch compositions of glazes in mass % and empirical formulae

	Glaze 1		Glaze 2		
	Mass %	Empirical formula	Mass %	Empirical formula	
RO	K <sub>2</sub> O	0.02	0.012	1.98	0.084
	Na <sub>2</sub> O	1.98	0.125	1.42	0.091
	CaO	3.66	0.255	4.29	0.304
	MgO	0.01	0.0004	0.01	0.0008
R <sub>2</sub> O <sub>3</sub>	PbO	34.49	0.608	29.14	0.520
	Al <sub>2</sub> O <sub>3</sub>	7.13	0.274	5.98	0.234
	B <sub>2</sub> O <sub>3</sub>	7.50	0.423	12.10	0.692
	Fe <sub>2</sub> O <sub>3</sub>	0.04	0.0002	0.04	0.001
RO <sub>2</sub>	SiO <sub>2</sub>	45.14	2.94	45.29	3.00
	TiO <sub>2</sub>	0.03	0.0002	0.03	0.001



The lead-release characteristics of these glazes applied on ceramic cups were determined with and without additives. To examine the effect of copper colourants, 2% *m/m* CuO was added to each of the basic glazes. Subsequently, further mill additions of BaCrO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> in amounts varying from 0.1 to 4.0% *m/m* were made to each of the copper-bearing glaze compositions.

#### BATCH PREPARATION

The glaze compositions were prepared in 500-g batches. The raw materials were accurately weighed on a laboratory balance capable of weighing to 0.1 g. After weighing, each batch was placed in a glass jar tightly fitted with a screw cap, and thoroughly mixed by rotation in a Turbula Mixer\* for about 1 h. After dry mixing, each mix was placed in an 850-mL porcelain jar half filled with 1.27 cm diam high-alumina cylinders. Distilled water was added to the jar at a mass ratio of 1 part water to 3 parts frit. The glaze slips were then ball milled for 3 h.

#### BISQUE-FIRED CERAMIC CUPS

The commercial ceramic ware chosen for glazing is a green clay-talc body moulded in the form of a cup. Before glazing, the green wares were bisque-fired to Cone 06-05 (991-1031°C). A chemical analysis of the major elements in the fired cup is given in Table 4.

Table 4 - Chemical composition  
of fired cup

Chemical composition	Mass %
Total Fe	0.29
CaO	7.27
SiO <sub>2</sub>	60.7
Al <sub>2</sub> O <sub>3</sub>	9.9
MgO	21.2

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

#### APPLICATION OF GLAZE TO THE BISQUE-FIRED CUPS

After milling, the glazes were stored temporarily in capped glass jars to reduce possible moisture loss before using. Two techniques were used for applying glazes on the bisque-fired cups: pouring or spraying.

In the pouring technique, the bisque-fired cups were first soaked in water, and then the glaze slip was poured into the cup, and the excess drained. Thickness was controlled by varying the drain time, and monitoring the dry and wet masses of the bisqued and glazed samples. The thickness and uniformity of coating depended largely on operator experience. Normally, if the fluidity of the glaze slips was maintained, uniform coating was readily achieved.

In the spraying technique, the glaze slip was applied to the interior of the bisque-fired cups using a manual spray gun. Spraying of the glazes was eventually abandoned owing to difficulty of inexperienced operators in controlling uniformity of glaze application over the confined interior of the cups.

#### FIRING

An electrically heated, Globar kiln of 45 x 36 x 34 cm I.D. was used for the glaze firing. The kiln was usually loaded with 12 cups for each firing. The heating rate of the furnace was kept at about 60°C/h in a static air atmosphere. After reaching the maturing temperature of the glaze, the furnace was turned off and allowed to cool naturally to room temperature before removing the glazed cups.

The maturing temperature of the glaze was established using large Orton Standard pyrometric cones and temperature and heating rate was monitored by a Pt-Pt10%Rh thermocouple.

#### PREPARATION AND PRESERVATION OF TEST SAMPLES

The glazed cups were first cleaned in a commercial detergent to remove grease and other matter. The samples were then washed at 30°C with a non-acid detergent solution, followed by rinsing in tap water and then in distilled water. After draining and drying in the drying oven, they were then ready for leaching.

### PROCEDURE FOR LEACHING EXPERIMENTS

The extraction procedure followed was essentially that recommended by the World Health Organization in 1976, currently being formalized by the International Standards Organization as ISO/DIS6480.

The samples were filled with water to 5 mm from overflowing, as measured along the surface of the cup. This volume was recorded.

The extraction was conducted at  $22 \pm 2^\circ\text{C}$  for 24 h in 4% acetic acid (1 V of glacial acetic acid diluted to 25 V with distilled water). During leaching the cups were covered by a watch glass to prevent acid loss due to evaporation.

After extraction, the leach solution was transferred to a polyethylene bottle and analyzed for lead to  $\pm 0.001$  g/L by an atomic absorption technique in the Chemical Laboratory of Mineral Sciences Laboratories, CANMET.

### DETERMINATION OF GLAZE MASS AND THICKNESS

The mass of the fired glaze was determined. Due to variation in glaze thickness between the wall and bottom of the cups, it was not possible to estimate accurately the uniform thickness of the glaze. However, the cups used for the leaching experiment had volumes between 180 and 190 mL with a bottom surface area of less than 4.5 cm diam and it may be assumed that most of the surface area subjected to extraction is at the wall of the cup. Optical microscopy was used to measure the thickness of the glaze deposited on the wall. The mass of the fired glaze was used to correlate with the thickness measurements and the results are plotted in Fig. 1. The technique of estimating thickness is rather crude, but it gives a general relationship between mass and thickness.

### RESULTS AND DISCUSSION

#### LEAD RELEASE FROM BASE GLAZES

Lead release from the base glazes was examined first. Glazes 1 and 2 were first fired to Cones 06 and 02 respectively. The mass of fired glaze and the comparable lead-release values are given in Table 5.

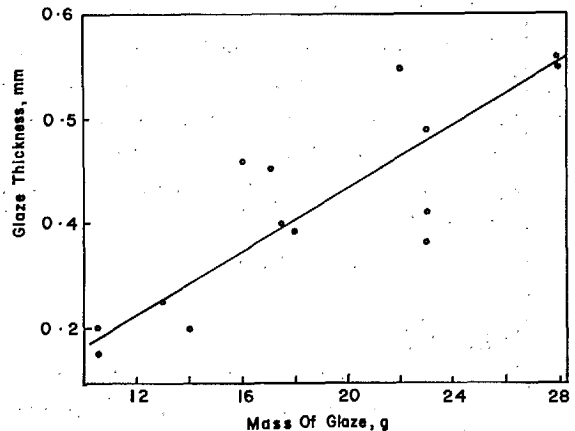


Fig. 1 - Correlation of thickness and mass of glaze applied to the bisque-fired cups

The lead-release values for glaze composition 1, with varying masses of glaze applied to the bisque-fired cups, are identical. For composition 2, there is an increase in lead extraction with increasing glaze mass. The significantly higher lead-release value for the cup coated with thicker glaze agrees with the findings of others (9,10). The lower lead-release value for the thinner glaze is attributed to glaze-body solution at the interface, altering the composition of the glaze and thus increasing the acid resistance.

Previously, it was shown that by leaching glasses of glaze compositions 1 and 2, a high lead-release value was obtained for composition 2 (1). The higher lead-release value for composition 2 is attributed to its composition. A com-

Table 5 - Mass of base glaze and lead-release values

Glaze composition	Firing temp Cone	Mass of glaze, g	Lead release, ppm
1	06*	17	0.2
	06	29	0.2
2	02*	14	0.6
	02	21	2.0

\*Cone 06 =  $991^\circ\text{C}$ , Cone 02 =  $1101^\circ\text{C}$

parison of their chemical compositions given in Table 3 shows that the glaze with lower lead release contained more  $Al_2O_3$ ,  $CaO$ , and  $SiO_2$  and less  $PbO$  and  $B_2O_3$ .

The presence of  $Al_2O_3$  in glass improves its resistance to aqueous solutions owing to the formation of  $AlO_4$  groups linked by bridging oxygens to  $SiO_4$  tetrahedra, the  $Pb^{2+}$  and alkali cations, which have donated the necessary oxygens, being held in close association with the  $AlO_4$  group for local electroneutrality. The basic cations in the  $Al_2O_3$ -containing glasses are thus much less free than they would be in the absence of alumina.

#### EFFECT ON LEAD DISSOLUTION BY ADDING COPPER OXIDE TO BASE GLAZES

After the lead-release values of the glost-fired base glazes were established, the effect of copper addition was examined. Two mass per cent cupric oxide was added to glazes 1 and 2. Lead dissolution versus mass of the copper-bearing glazes applied to the cups is given in Table 6.

The lead-release values for the copper-bearing glazes are considerably higher than those of the base glazes under identical firing conditions, apart from the minor variation in glaze thickness (Table 5). In the copper-bearing glazes, the lead-release values for composition 2 are again higher than for composition 1. The higher lead-release values for composition 2 are

ascribed to the high boron concentration in the glaze. This was explained previously and is attributed to the oxidation state of 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 (1). In high-lead glasses the  $Cu^+$  can enter the structure as a modifier resulting in loosening of the network structure (11).

Again, there is less significant change in lead extraction values for the copper-bearing glaze composition 1 with increasing mass of glaze applied to the ware.

#### EFFECT ON LEAD RELEASE BY ADDING CHROMATE COMPOUNDS TO COPPER-BEARING GLAZES

The effect of adding chromate compounds to the copper-bearing glazes as lead inhibitors was investigated for glaze compositions 1 and 2. Previous results showed that by adding chromium compounds  $BaCrO_4$  and  $Cr_2O_3$  to the 2% m/m copper-bearing glasses of these compositions, the lead release was suppressed proportionally, but only up to a critical concentration level and that  $Cr_2O_3$  was a more effective lead suppressor than  $BaCrO_4$  (1). To determine the difference in lead dissolution that may exist between the glasses and the equivalent applied glazes, the effect of adding chromate compounds to the 2% m/m copper-bearing glazes 1 and 2 was examined.

The lead release from copper-bearing glaze 2 as a function of  $BaCrO_4$  and  $Cr_2O_3$  concen-

Table 6 - Lead dissolution after 24 h leaching for various masses of copper-bearing glazes

Glaze Composition	Firing temp Cone	Mass of glaze, g	Lead release, ppm
1	06*	16	24
	06	22	27
2	02*	13	130
	02	21	160
	02	20	120
	02	7	80

\*Cone 06 = 991°C, Cone 02 = 1101°C

tration was examined in detail. The results of lead release for these glazes with varying amounts of  $BaCrO_4$  and  $Cr_2O_3$  and the mass of glaze applied to cups fired to Cone 02 are given in Table 7. Comparison of results for equivalent glazes of 10-13 g indicates that by adding  $BaCrO_4$ , lead release varied from 1 to 4 ppm and by adding  $Cr_2O_3$  it was between 3 and 5 ppm. No significant change in lead-release values is apparent with either increased or decreased chromate compound concentration. Generally, slightly lower lead-release values were obtained for samples with  $BaCrO_4$  than with  $Cr_2O_3$  additions but it is difficult to justify any significant trend due to the limited and variable data.

Also, Table 7 shows lead-release values for heavier glaze applications. A comparison of

Table 7 - Lead release from copper-bearing glaze composition 2 doped with  $BaCrO_4$  and  $Cr_2O_3$ , fired to Cone 02\*

Mass %		Mass of glaze, g	Lead release, ppm
$BaCrO_4$	$Cr_2O_3$		
0.1		8	3
		13	4
		14	4
0.5		7	1
		12	2
1.0		10	2
		15	1
2.0		11	2
		16	1
4.0		11	1
		16	2
0.5		11	3
		12	0.5
		18	2
1.0		8	11
		13	4
		18	2
2.0		13	5
		17	11
4.0		18	4
		20	13

\*Cone 02 = 1101°C

Table 8 - Lead release from copper-bearing glaze 1 with varying  $BaCrO_4$  and  $Cr_2O_3$  additions, fired to Cone 06

Mass %		Mass of glaze, g	Lead release ppm
$BaCrO_4$	$Cr_2O_3$		
0.5		10	0.8
		25	0.6
1.0		10	2.0
		15	9.0
2.0*		13	15.0
		20	14.0
4.0**		11	9.0
		20	16.0
	0.1	11	0.6
		15	1.0
	0.5	10	0.6
		28	1.0
	1.0	11	3.0
		20	12.0
	2.0	13	1.0
		15	3.0
	4.0	10	2.0
		18	9.0

\*Glaze immature at Cone 06 (991°C), good glaze obtained at Cone 02 (1101°C)

\*\*Immature glaze at Cone 02

the lead-release values for thin and thick glaze applications shows that the values for the latter are slightly higher in some cases.

Table 8 gives results from similar investigations using copper-bearing glaze 1. For comparable glaze masses from 10 to 13 g, the lead-release values range from 0.6 to 3 ppm for the various additions of  $BaCrO_4$  and  $Cr_2O_3$ . Increasing the glaze mass to above 15 g slightly increases the lead-release value.

The effectiveness of chromate compounds as lead-release inhibitors in the copper-bearing glaze compositions 1 and 2 appears to depend on the additive concentration. The results show that effective inhibition of lead release occurred with  $BaCrO_4$  and  $Cr_2O_3$  additions of less than 1% m/m. Increasing the chromate concentration in the

glaze caused a slight increase in lead-release value.

The behaviour of  $\text{Cr}_2\text{O}_3$  or  $\text{BaCrO}_4$  as lead-release inhibitors may be explained in part by the similar ionic radii of  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$ . It has been well-documented that the durability of glass strengthens with increasing  $\text{Al}_2\text{O}_3$  content up to a critical level, below which the  $\text{Al}^{+3}$  ions are in sixfold coordination and above which they enter into fourfold coordination. The Al-O bond apparently is stronger in fourfold coordination, hence less bonding power is available for sharing with Pb, rendering it more susceptible to leaching. A similar behaviour is assumed for  $\text{Cr}^{+3}$  ions, and results indicate that the critical concentration of  $\text{Cr}_2\text{O}_3$  is about 0.5% m/m.

#### EFFECT OF FIRING TEMPERATURE ON LEAD RELEASE

Glaze composition 2 was selected for examination of the effect of firing temperature on lead release. The firing range recommended by the supplier for this glaze was Cone 06-Cone 01 (991-1117°C), although the studies reported formerly had all been conducted at Cone 02 (1101°C) to ensure good glaze maturation.

The lead-release levels for the copper-bearing glaze 2 fired to Cone 06 and 02 are given in Table 9 and it shows that the lead extraction is higher for the glaze fired at the higher temperature. This was unexpected and remains unexplained, although it may be related to a change with temperature in the valency state of the copper.

The lead extractions for the copper-bearing glaze composition 2 doped with variable

Table 9 - Lead release versus firing temperature of copper-bearing glaze 2

Firing temp Cone	Copper, mass %	Mass of glaze, g	Lead release, ppm
06	2	21	32
06	2	24	41
02	2	20	120
02	2	21	160

amounts of  $\text{BaCrO}_4$  and  $\text{Cr}_2\text{O}_3$  and fired at Cone 06 are given in Table 10. A comparison with results in Table 7 for the same glazes fired at higher temperature, Cone 02, shows considerably higher lead release for the glazes fired at lower temperature.

Although both sets of glazes fired at both temperatures showed good coverage and high gloss, it is evident that their chemical maturity cannot be judged wholly on physical grounds, emphasizing the need for close firing control in concert with toxicity testing.

#### GLAZE-BODY SOLUTION AT THE INTERFACE

Marquis reported that a thin application of glaze may dissolve body constituents and thereby change the glaze composition (9). In such cases a lower lead release usually results. Data in this study indicate that the lead release is

Table 10 - Lead release from copper-bearing glaze composition 2 doped with  $\text{BaCrO}_4$  and  $\text{Cr}_2\text{O}_3$ , fired to Cone 06\*

$\text{BaCrO}_4$	Mass %		Mass of glaze, g	Lead release, ppm
	$\text{Cr}_2\text{O}_3$			
0.1			7	59
			17	130
0.5			10	15
			17	25
1.0			7	29
			28	24
2.0			11	95
			17	46
4.0			22	3
			20	4
	0.5		10	14
			17	8
	1.0		16	44
			18	31
	2.0		8	9
			17	15
	4.0		12	79
			24	44

\*Cone 06 = 991°C

invariably higher for thicker glazes and are in good agreement with Marquis. To determine the effect of glaze-body solution at the interface, four samples of copper-bearing glaze 2 with and without chromate compounds were chosen for microprobe analysis. The concentrations of CuO, BaCrO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> in these samples are given in Table 11.

The distribution of lead, copper, and chromium oxides at the boundary between the glaze and cup, as revealed by microprobe analysis, is given for the four samples in Fig. 2 to 5. Each figure includes a double scan for PbO and single scans for CuO and Cr<sub>2</sub>O<sub>3</sub>. The lead distribution for samples 1 to 3 shows lead oxide diffused into the cup from the glaze to a depth varying from 120 to 140 μm. From the cup boundary toward the glaze surface, a layer about 20 to 30 μm thick is deficient in lead, compared with the composition of the main glaze body. This indicates body solution probably occurred and Ca<sup>+2</sup>, Al<sup>+3</sup>, Si<sup>+4</sup>, Fe<sup>+3</sup> and Mg<sup>+2</sup> ions were introduced into the glaze from the cup. The copper oxide concentration shows a less pronounced effect across the glaze-body boundary, although the semi-quantitative results reveal that some copper ions were also diffused into the cup. Due to the low chromium oxide concentration in sample 2 (below the limits of detection by microprobe analysis) the extent of Cr<sub>2</sub>O<sub>3</sub> diffusion could not be established. Sample 3, containing 4% m/m BaCrO<sub>4</sub>, shows a decrease in Cr<sub>2</sub>O<sub>3</sub> concentration within the glaze toward the cup boundary, and indicates some Cr<sub>2</sub>O<sub>3</sub> apparently diffused into the cup.

Table 11 - CuO, BaCrO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> contents in glaze composition 2 samples examined by microprobe

Sample	Oxide, mass %		
	CuO	BaCrO <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>
1	2	0	0
2	2	0.1	0
3	2	4.0	0
4	2	0	4.0

The lead distribution for sample 4 is given in Fig. 5, and indicates an interfacial zone extending up to about 140 μm into the glaze and about 20 μm into the cup body. Within the glaze, the PbO content varies but is depleted well below the level in the main glaze matrix, and some has diffused into the body to a depth of more than 80 μm. Both the CuO and Cr<sub>2</sub>O<sub>3</sub> show similar distribution patterns, although no diffusion into the cup body was detected.

#### CRYSTALLIZATION OF CHROMIUM SEQUIOXIDE

It has been demonstrated that both BaCrO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> can act as lead-release inhibitors. However, there is a tendency for the BaCrO<sub>4</sub> to increase the viscosity of the glaze, observed during the experimental work for glaze composition 1. With a doping concentration of above 1% m/m BaCrO<sub>4</sub>, the glaze fired at Cone 06 had poor fluidity and as a result the surface of the glaze was blistered. The formation of these blisters is attributed to high viscosity, which traps within the glaze the oxygen being liberated during change in the valency state of the chromium oxide. To improve the fluidity and promote the release of the O<sub>2</sub> gas, it was necessary to fire the glaze to about Cone 02.

Another problem in using BaCrO<sub>4</sub> as a lead-release inhibitor is the crystallization of

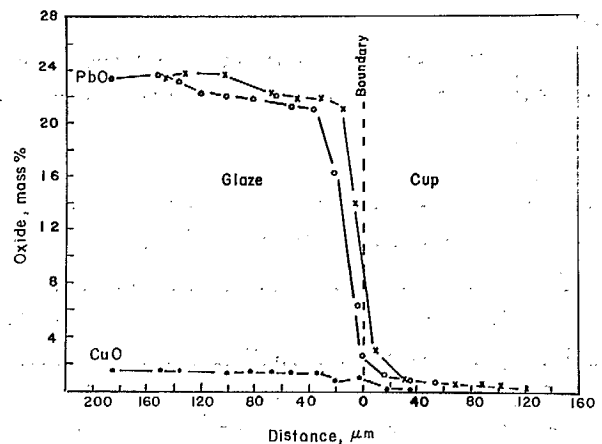


Fig. 2 - Microprobe analysis on PbO and CuO distribution for sample 1

$\text{Cr}_2\text{O}_3$ . A typical example of  $\text{Cr}_2\text{O}_3$  crystallized from the glaze is shown in Fig. 6 for glaze 2 containing 2% m/m of  $\text{BaCrO}_4$ . The crystallization of  $\text{Cr}_2\text{O}_3$  appears to be related to the dissociation of the  $\text{BaCrO}_4$  during firing, which can be represented by the following equation:

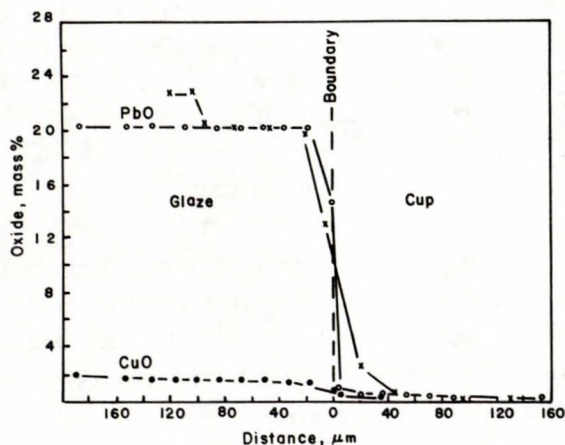
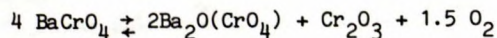


Fig. 3 - Microprobe analysis on PbO and CuO distribution for sample 2

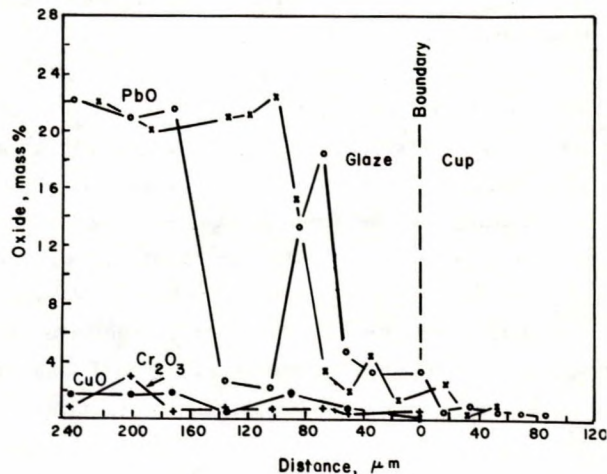


Fig. 5 - Microprobe analysis on PbO, CuO and  $\text{Cr}_2\text{O}_3$  for sample 4

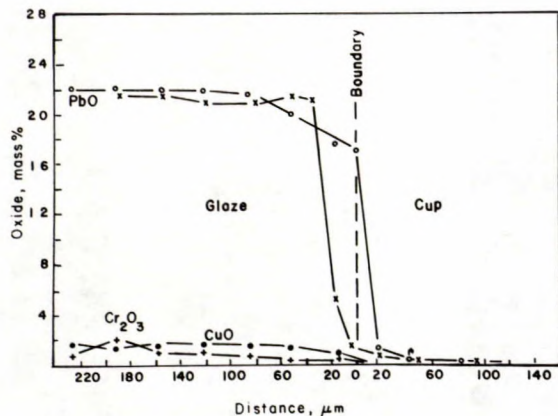


Fig. 4 - Microprobe analysis on PbO, CuO and  $\text{Cr}_2\text{O}_3$  for sample 3

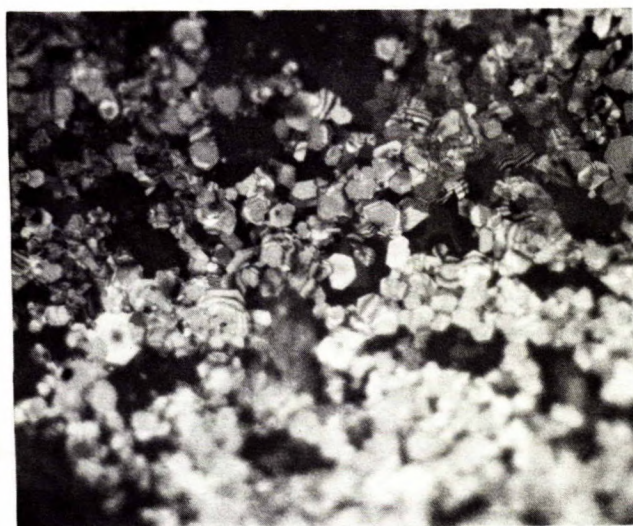


Fig. 6 - Crystallization of  $\text{Cr}_2\text{O}_3$  from  $\text{BaCrO}_4$ -doped copper-bearing glaze composition 2

## CONCLUSIONS

This study shows that lead release from glazed ceramics increases as copper oxide is added to the leaded base glazes. The decreasing durability of the glaze is explained in the  $\text{Cu}^+:\text{Cu}^{2+}$  ratio: for glazes containing higher  $\text{Cu}^+:\text{Cu}^{2+}$  ratios, the  $\text{Cu}^+$  can modify the network-forming  $\text{B}_2\text{O}_3$ , converting some of the boron from threefold to fourfold coordination with oxygen and thus loosening the network structure.

It was observed that the durability of glazes increases by adding 0.5% *m/m*  $\text{Cr}_2\text{O}_3$  or  $\text{BaCrO}_4$ . The effect of chromate compounds as a lead inhibitor has been attributed to the Cr-O bond behaving in the same way as that postulated for the Al-O bond. The critical level of  $\text{Cr}_2\text{O}_3$  concentration is estimated at about 1% *m/m*, below which the  $\text{Cr}^{3+}$  is in sixfold coordination creating more bonding power to share with the Pb ions, making them less susceptible to leaching.

It was confirmed that the firing temperature greatly influences the durability of the glaze. Low firing temperatures invariably resulted in a higher Pb release than that from glaze fired at high temperatures. The lower durability of the glaze fired at low temperature may be attributed to insufficient maturing of the glaze.

Electron microprobe analyses demonstrated that a glaze-body solution interface was formed at the glaze-body boundary. A decrease in lead-release values with decreasing thickness was explained in modification of the glaze due to the diffusion or dissolution of  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$  and  $\text{Mg}^{2+}$  into the glaze.

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