ATTACK ON REFRACTORY CLAY POTS BY OPTICAL GLASSES

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ABSTRACT

Examinations were made of the walls and bottoms of approximately 200 refractory clay pots of lined and unlined types to determine the extent of penetration of optical glasses into refractory material. Examinations made with a petrographic microscope of samples of unused pot bottom indicated the structure of the heat-treated refractory. Similar examinations of selected samples from the bottoms of 62 used pots revealed the manner of attack by corrosive glasses and identified the crystalline and glassy reaction products formed. These reaction products were found at the interface between refractory and glass and within pot bottoms penetrated by glass. The pots were used in the manufacture of barium crown, barium flint, light crown, borosilicate crown, and several different flint optical glasses.

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I. INTRODUCTION

In the manufacture of optical glasses in refractory clay pots, reactions occur along the pot-glass interface at high temperatures. When such reactions attain considerable magnitude, not only the quality of the glass may be affected in regard to its optical properties,

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striae, or seed content, but also the pot is damaged. In some instances, failure of the pot to hold the melt may result.

The purpose of the present investigation was to determine the manner and extent of attack on the refractory by optical glasses of different compositions and to identify the accompanying reaction products.

Examinations were made visually of the walls and bottoms of pots after the production of glass to reveal the extent of penetration of glass into the refractory. Samples for detailed microscopic study were collected showing both corroded and noncorroded regions of the pot bottom. The pots were used in the manufacture of barium crown, barium flint, light crown, borosilicate crown, and several different flint optical glasses.

II. REFRACTORY CLAY POTS

The clay pots investigated were made, cured, and used in the production of optical glass at this Bureau. Details on the manufacture and the physical properties of the pots are given by Heindl, Massengael, and Cossette [1].[1] The batch composition and the chemical analysis of most of the pots are given in table 1. Four semisiliceous pots contained powdered flint, in addition to the batch materials listed in table 1, in quantity sufficient to bring the SiO_2 content of the heat-treated pots to approximately 68 percent [1]. One semisiliceous pot contained quartz sand in place of powdered flint.

Examinations were made of two types of pots, lined and unlined. The two were alike, except that the walls and bottoms of the lined pots had a coating, about ⅛ in. thick, of relatively fine-grained material with a composition similar to that given in table 1. Two pots contained alumina-rich linings whose raw batch materials included alumina, prepared mullite, ball clay, and kaolin [1].

TABLE 1.—*Composition of refractory clay pots used in the production of optical glass*

Raw batch composition [a]		Chemical analysis of heated refractory [b]	
Material	Amount	Oxide	Amount
	Percent		*Percent*
Maine feldspar	6.0	SiO_2	59.5
Tennessee ball clay	10.0	Al_2O_3[c]	35.6
Kentucky ball clay	10.0	Fe_2O_3	0.76
North Carolina kaolin	12.5	TiO_2, ZrO_2, etc	.8
Delaware kaolin	4.5	CaO	(d)
Georgia kaolin	4.5	MgO	.3
Pot shell grog	52.5	Na_2O	.68
		K_2O	2.2
	100.0	Ignition loss	0.18
			100.02

[a] From Heindl, Massengale, and Cossette [1].
[b] Analyst: I. Mockrin, National Bureau of Standards.
[c] Determined as R_2O_3 minus Fe_2O_3 and TiO_2, ZrO_2, etc.
[d] Less than 0.1 percent.

The pots were preheated in furnaces for about 60 hours, during which time the temperature was raised gradually from near 100° to 1,350° or 1,400° C. The pots were then transferred to glass-melting

[1] Figures in brackets indicate literature references at the end of this paper.

furnaces where they remained for 19 to 26 hours during the melting and fining of the different optical glasses. The temperatures within the furnaces ranged from 1,350° to 1,450° C,[2] depending on the schedule for the type of glass being produced. These temperatures were maintained for 8 to 20 hours, after which they were lowered gradually to pot-exit temperatures between 950° and 1,100° C.

III. PROCEDURE

The walls and especially the bottoms of about 200 pots were inspected when the pot body was separated from the glass. For the present investigation, a selection was made of pots that in most instances had leaked in the furnaces or were cracked and penetrated by glass. Such pots probably best showed the effects of glass attack on the refractory. Samples, for detailed microscopic examinations, were collected from the bottoms of 62 pots. These samples included the pot-glass interface as well as refractory penetrated by the melt. Additional samples were obtained from a few pot bottoms not penetrated by glass. Unless otherwise stated, all references to the refractory apply to samples from the bottoms of pots. All samples were examined in thin section and some also in powdered form with a petrographic microscope. Preston [2] has suggested a similar microscopic procedure for the examination of pots.

IV. VISUAL EXAMINATIONS OF USED POTS

Visual examinations revealed that the more porous refractory of unlined pots was deeply penetrated by barium crown and barium flint glasses (fig. 1). Glass not only filled and enlarged existing pores, but also formed continuous channels, with a maximum diameter of ½ in., which sometimes continued entirely through the bottom. The glass that penetrated into the pores and small channels was colored a pale yellow, but the glass filling the larger channels was essentially colorless. The walls were not penetrated except within 4 to 5 in. of the bottom.

The extremely reactive or corrosive nature of the ingredients of barium glasses under certain conditions was illustrated during the manufacture of a barium crown glass in which the batch materials were added in two lots: first, the least corrosive and later, the more corrosive (boron, zinc, lead, arsenic, antimony, and that part of the barium added as nitrate). Just after the second lot of batch material was added, the melt bubbled up and spilled over. The molten material that ran down the outside of the pot corroded channels, or grooves, ¼ to ⅜ in. deep in the walls.

Borosilicate crown and most of the flint glasses usually did not penetrate the unlined pots. Sometimes pores just below the pot-glass interface were filled or partly filled with glass, but penetration rarely occurred to a depth of more than ½ in. An exception was a flint glass with 62 percent of PbO, which sometimes penetrated as much as 2 in. Any flint glass that did penetrate into the pores and small channels was colored a deep yellow, although the glass in large channels or cracks was essentially colorless.

The lined pots revealed no evidence of attack by any type of glass

[2] The maximum temperature for one special melt of barium crown was only 1,200° C.

on the typical [3] lining. Despite this resistance to glass attack, the lining did not always protect the main part of the pot bottom. Cracks and voids in the lining permitted glass to make contact with the underlying more porous refractory (fig. 2). When such flaws occurred, barium glasses spread laterally beneath the lining as much as 6 in. Borosilicate crown and flint glasses filled cracks in the lining, but did not penetrate or spread over ½ in. into the main refractory material with the occasional exception of the flint glass containing 62 percent of PbO. Cracks in the walls, except in the lower 3 or 4 in., did not result in glass penetration. Two alumina-rich linings, however, showed visual evidence of moderate reactivity with molten glass by a change in color and luster of the lining material.

Many seeds of various sizes were observed in glass-filled pores, channels, and cracks in both lined and unlined pots. Examinations were made visually and with the aid of a binocular microscope (magnification about 12 times) of samples from 25 pots in an effort to determine the origin of these seeds. In areas penetrated by glass, all pores in the refractory were not completely filled. Some pores were coated by a thin layer of glass (fig. 3, A). Others were considerably enlarged and contained numerous small seeds (fig. 3, B).

The seed rating of the glass was compared with the extent of cracking of the pot bottom for 137 barium melts. Some 111 of the melts were produced in uncracked or only slightly to moderately cracked pots. Of these melts, 35 percent were very seedy. The remaining 26 melts were produced in pots with badly cracked bottoms, and 61 percent were very seedy.

V. MICROSCOPIC EXAMINATIONS OF SPECIMENS FROM POT BOTTOMS

1. STRUCTURE OF UNUSED POTS

Heat-treated unlined pots in which no glass was melted contained a relatively large number of pores, as illustrated by figure 4. The pores were of two kinds: large (1 to 3 mm in average diameter), spherical pores (fig. 1) and numerous, narrow, channel-shaped openings (figs. 2 and 4). A majority of the larger of these channels were oriented with their long dimensions essentially vertical. The linings were only about one-sixth as porous as the main refractory materials [1]. The pores in the lining were small (0.1 mm in maximum diameter) and more or less spherical in shape (fig. 5).

The pot bodies were composed largely of a glassy bond containing numerous needlelike crystals of mullite. The mullite needles in the more porous refractory were relatively long (maximum 30 microns) and narrow (1 to 2 microns). They were often spaced irregularly, but were arranged sometimes in 60° networks. In the lining the mullite needles were similar but smaller. Grog grains contained a higher proportion of mullite and were often darker in color than the surrounding material (fig. 5). Infrequent, small, irregular, isotropic grains (5 to 10 microns in diameter) of glassy or amorphous material showed no evidence of mullite growth. Occasional small quartz grains with visible solution rims were also present.

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[3] Where necessary for clarity, linings or pots of the composition given in table 1 are referred to as typical linings or pots.
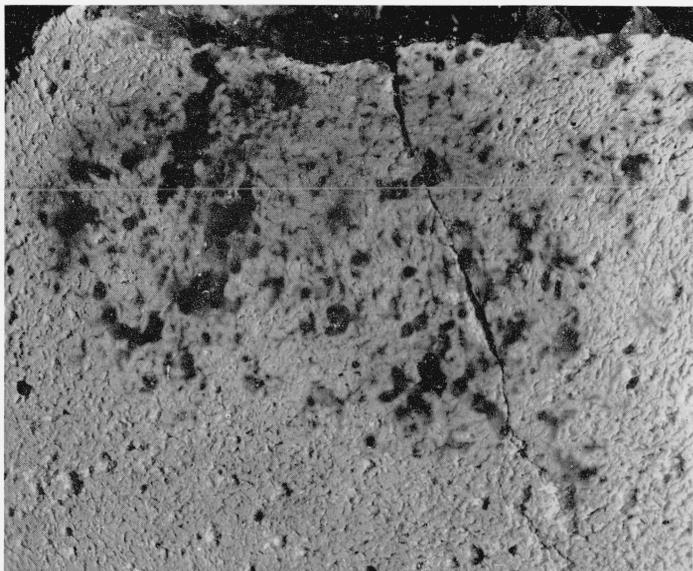
FIGURE 1.—*Bottom of unlined pot penetrated by glass.*

Refractory-glass interface at top.   Dark areas are glass.   Glass-filled pores are greatly enlarged and connected as compared with unpenetrated pores in lower part of photograph.   (Crack formed during cutting of specimen.)   Magnification, × 1⅓.
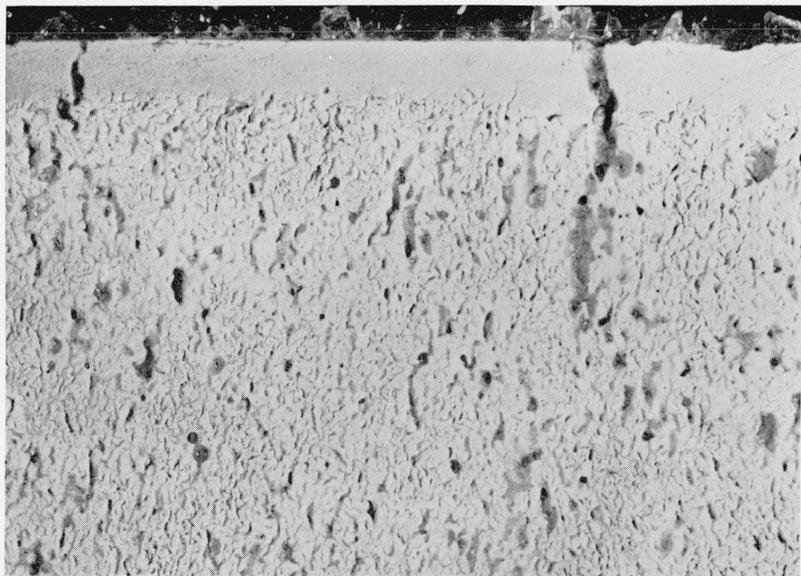

FIGURE 2.—*Bottom of lined pot penetrated by glass through cracks in lining.*

Lining-glass interface at top.   Gray areas are glass; black areas, open spaces.   The glass has spread in the more porous refractory after passing through the lining along two small cracks.   Observe elongated shape and vertical orientation of pores.   Magnification, × 2⅓.
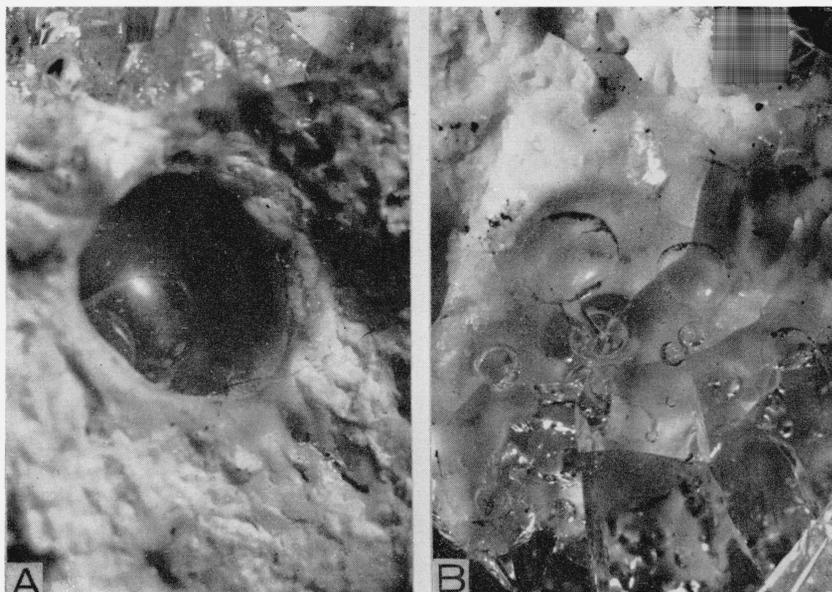
FIGURE 3.—*Seeds in pot bottom penetrated by glass.*

A, Gas bubble in refractory coated on inside with glass forming a large stationary seed. Magnification, × 7.   B, Several small seeds in a glass-filled channel in the refractory.   Magnification, × 12.
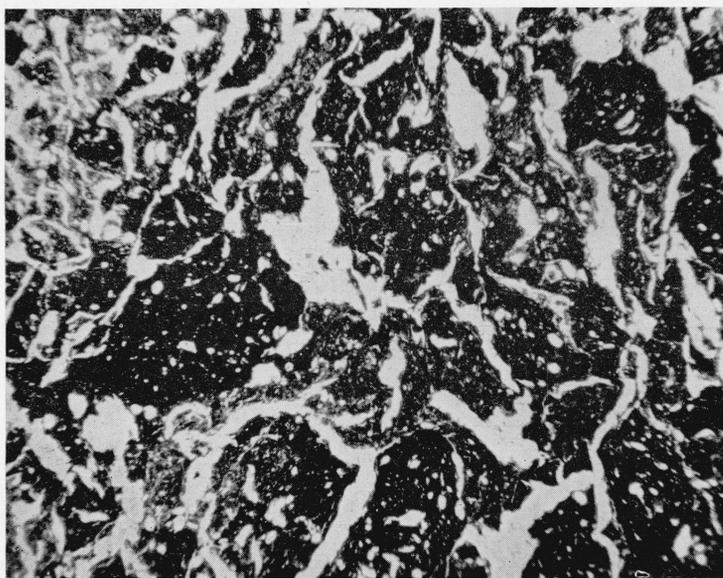

FIGURE 4.—*Bottom of heat-treated unlined pot before production of glass.*

Note channel-like character and essentially vertical orientation of pores (white).   Ordinary light.   Magnification, × 24.
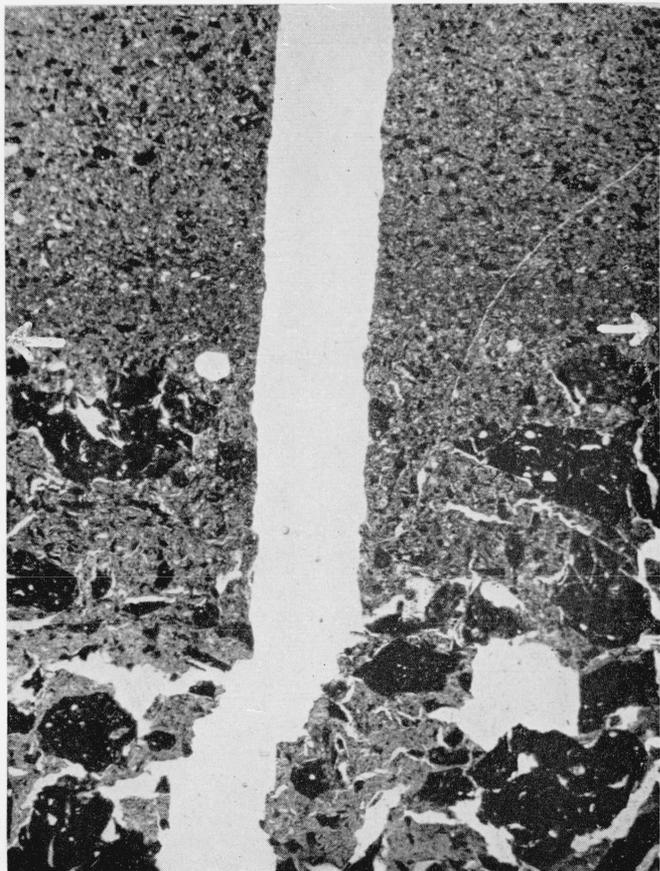
FIGURE 5.—*Glass-filled crack in bottom of lined pot.*

Observe structure of lining and contact (arrows) of lining (above) with the more porous refractory (below). Opposite walls of the crack match each other.   Black areas are grog grains; white area of the crack and of pores connected to it (lower left) is glass; white of the other pores is open space.   Ordinary light.   Magnification, × 18.
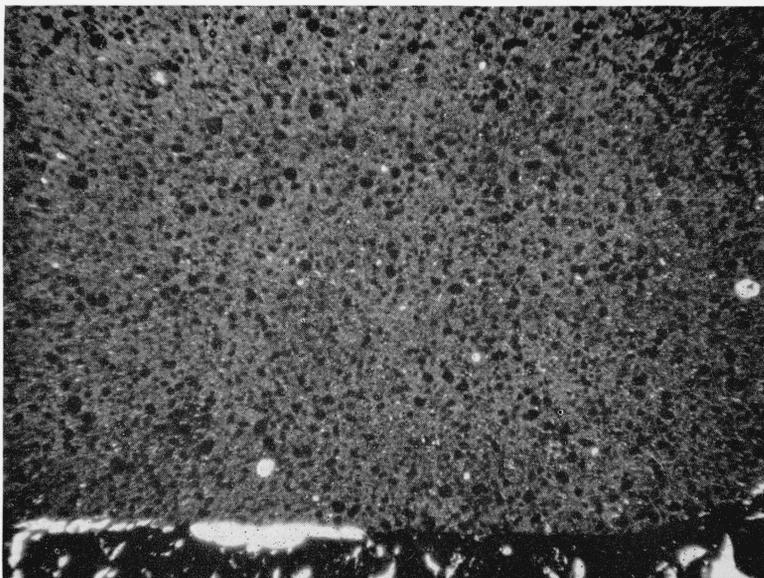
FIGURE 6.—*Heat-treated alumina-rich lining before production of glass.*

More porous refractory at bottom. Dark spots are aggregates of corundum crystals; gray areas are a mixture of mullite and glassy bond; white specks and areas are pores. Ordinary light. Magnification, × 24.
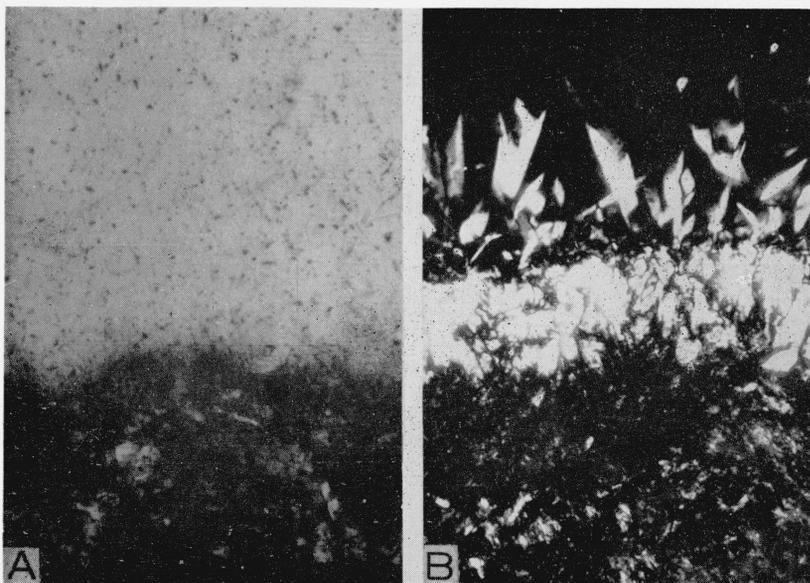

FIGURE 7.—*Lining-glass interface of a BaC 6109 melt.*

A, Glass above, lining below. Reaction crystals are invisible because they have a refractive index near that of the glass. Ordinary light. B, Same field as A but with crossed nicols. Double layer of barium-feldspar crystals visible (white). White grains in the lining are mullite crystals. Magnification, × 210.

The semisiliceous pots were similar to the typical pots in appearance and mineral composition with the addition of numerous well dispersed, sharply angular quartz grains. The quartz grains averaged from 10 to 40 microns in diameter, with a few up to 70 microns, in the pots made with powdered flint and about 200 to 300 microns (0.2 to 0.3 mm) in the pot made with quartz sand. Many grains had a narrow reaction rim (1 to 2 microns wide) of a dense isotropic material, possibly cristobalite.

The alumina-rich linings, which had a tendency to crumble when examined, consisted of many minute aggregates (30 to 80 microns in diameter) of fine-grained corundum crystals surrounded by mullite and a glassy bond (fig. 6). The mullite occurred in two different textures: prismatic crystals (5 by 15 microns in average dimensions), which corresponded in grain size and appearance to the prepared mullite in the batch, and needles (about 10 microns long by 1 micron or less in thickness) in glass.

2. STRUCTURE AND REACTION PRODUCTS OF USED POTS

The results of the microscopic examinations of pots attacked by 16 different optical glasses are summarized in table 2. The observations are described in further detail in this order: first, the reaction rim at the pot-glass interface and, second, refractory penetrated by glass. The individual optical glasses are designated by numbers which correspond to that portion of the value for the index of refraction which lies to the right of the decimal point plus these abbreviations: BaC=barium crown, BF=barium flint, LC=light crown, BSC= borosilicate crown, and F=flint.

(a) BARIUM GLASSES

(1) *BaC 6109 and BaC 617.*—A reaction rim 0.15 to 0.2 mm in thickness at the interface on both lined and unlined pots consisted of closely spaced barium feldspar (celsian, $BaAl_2Si_2O_8$) crystals without good external form. An upper layer was observed in two pots, which consist of well-developed, bladed crystals extending into the glass (fig. 7).

Below the pot-glass interface, many of the very small channels contained numerous long mullite ($Al_6Si_2O_{13}$) needles. Barium feldspar and barium disilicate (sanbornite, $BaSi_2O_5$) in prismatic crystals and zinc spinel [4] (gahnite, $ZnAl_2O_4$) in well-formed, colorless, octahedral crystals occurred along the walls of other channels (figs. 8 and 9). Zinc spinel was not observed when the melts contained less than 2.5 percent of ZnO (table 2). The crystals were in a glass with a variable index of refraction as low as 1.54 but averaging 1.57. Glass in very large channels or cracks contained no crystals and had an index of refraction about 1.61, approximately that of the original glass.

The indices of refraction of both the barium feldspar and the barium disilicate were slightly lower than those of the pure com-

[4] The optical identification was checked experimentally as follows: 4-g samples of four individual glasses (BF 584, BaC 5725 without ZnO, a glass with 20 percent of BaO and no ZnO, and a glass with 20 percent of ZnO and no BaO) were powdered and mixed thoroughly with equal weights of powdered pot shell. Each mixture was heat-treated separately to approximately 1,400° C for 2 hours and then cooled slowly. Octahedral crystals were found in the two preparations containing ZnO and not in the other two. An X-ray diffraction pattern of these crystals showed them to be zinc spinel.

TABLE 2.—*Reaction products between refractory clay pots and optical glasses of various compositions*

Number of pots examined	Type of glass [a]	Approximate partial glass composition [b]						Maximum melting temperature	Reaction products at the pot-glass interface (in approximate order of abundance)	Reaction products within glass-penetrated pot bottom (in approximate order of abundance)	Approximate lowest index of refraction of glass which has penetrated the pot bottom [e]
		BaO	ZnO	PbO	SiO_2	K_2O	Na_2O				
		BARIUM GLASSES									
		%	%	%	%	%	%	°C			
2	BF 584	13	8	19	50	8	2	1,400	Traces of nephelite-kaliophilite S. S.[j] and cristobalite.	Barium feldspar, zinc spinel, cristobalite, mullite, trace of corundum.	1.51
4	BF 604	14	8	23	46	8	0	1,410 to 1,425	Cristobalite, trace of kaliophilite	Mullite, barium feldspar, barium disilicate, cristobalite, zinc spinel, trace of corundum.	1.52
3	BaC 5725 [d]	17	0	4	52	0	8	1,350 to 1,390	Barium feldspar	Barium feldspar, mullite, barium disilicate.	1.51
1	BaC 541	20	4	0	59	10	3	1,410	Nephelite-kaliophilite S. S., cristobalite	No penetration of lined pot bottom	
2	BF 588	28	8	6	46	6	2	1,400	Barium feldspar, cristobalite	Mullite, barium feldspar, barium disilicate, zinc spinel, cristobalite, corundum.	1.51
15	BaC 5725	30	7	0	48	7	1	1,400 to 1,445	Cristobalite (two layers), barium feldspar.	Barium feldspar, mullite, barium disilicate, zinc spinel, corundum, trace of cristobalite.	1.51
10	BaC 6109 [e]	43	[h] 4	tr	39	0	0	[i] 1,350 to 1,425	Barium feldspar (two layers in some pots).	Barium feldspar, mullite, barium disilicate, zinc spinel.[k]	1.54
1	BaC 617 [f]	45	6	1	37	0	tr	1,400	Barium feldspar	Barium feldspar, mullite, barium disilicate, trace of zinc spinel.	

2	LC 523 ᵍ	0	0	0	71	2	15	1,450	Trace of corundum	Mullite, corundum	1.50
1	BSC 511	0	0	0	69	15	8	1,400	Nephelite-kaliophilite S. S. (with oriented inclusions), carnegieite S. S.	do	
7	BSC 517	0	tr	0	66	12	8	1,400	Nephelite-kaliophilite S. S. (with oriented inclusions in some pots), carnegieite S. S., trace of corundum.	do	1.495
2	F 5795	1	0	36	53	10	tr	1,400	Trace of cristobalite	No penetration of lined pot bottom	
1	F 605	0	0	41	48	9	2	1,390	do	do	
4	F 617	0	0	43	46	5	6	1,350 to 1,390	Nephelite-kaliophilite S. S. (with oriented inclusions in some pots), carnegieite S. S., cristobalite, trace of corundum.	Mullite, corundum	1.55
2	F 620	0	0	45	46	5	4	1,390	Nephelite-kaliophilite S. S. (with oriented inclusions), carnegieite S. S., cristobalite, trace of corundum.	do	1.60
3	F 649	0	0	51	41	6	1	1,400	α KAlSiO$_4$ S. S. or KAlSiO$_4$ glass, nephelite-kaliophilite S. S. (with inclusions), traces of cristobalite and corundum.	do	1.60
2	F 720	0	0	62	34	4	0	1,400	KAlSiO$_4$ glass and kaliophilite (with various inclusions).	One or more lead aluminum silicates of undetermined composition, mullite, corundum, cristobalite, trace of metallic lead.	1.60

[a] Optical glasses are designated by numbers which correspond to that portion of the value for the index of refraction which lies to the right of the decimal point plus these abbreviations: BF=barium flint, BaC=barium crown, LC=light crown, BSC=borosilicate crown, and F=flint.
[b] Included here are only those oxides which sometimes enter into the crystalline pot-glass reaction products.
[c] Numbers to the right of the decimal are comparable with those given under "type of glass."
[d] An experimental composition. Also contains 8 percent of CaO.
[e] Also contains 4 percent of Al$_2$O$_3$.
[f] Also contains 5 percent of Al$_2$O$_3$.
[g] Also contains 9 percent of CaO.
[h] ZnO content variable: 4 percent in 6 melts; 0 percent, ½ percent, 2½ percent, and 8 percent, respectively, in the other 4 melts.
[i] Maximum temperature of 1 special melt was 1,200° C.
[j] S. S.=solid solution or mixed crystals.
[k] Present in those melts with 2½ percent or more of ZnO.

pounds, possibly because of a small amount of $KAlSi_3O_8$ and of alkaline disilicate, respectively, in solid solution [3].

(2) *BaC 5725.*—A multiple reaction rim about 0.1 mm in thickness was present in typical lined and unlined and semisiliceous unlined pots. This rim was more uniform in width on the lined pots. An upper layer of "pine-tree," or skeletal, crystals of cristobalite (SiO_2) extended into the glass (fig. 10), next below was a dense, isotropic layer of the same compound, and finally a lower uneven zone of barium feldspar and partially dissolved refractory material. Only one layer, the barium feldspar zone, was found in pots containing an experimental composition BaC 5725 glass (17 percent of BaO, see table 2).

Reaction zones were not formed along the walls of cracks in the typical linings. In alumina-rich linings, however, barium feldspar laths (fig. 11) and small octahedrons of zinc spinel replaced the mullite and glassy bond but not the corundum of the refractory.

The crystalline reaction products in glass-filled channels in the more porous refractory were the same as those formed by BaC 6109 glass plus occasional traces of very thin corundum (Al_2O_3) plates and cristobalite. The same reaction products occurred in about the same quantity in semisiliceous pots. No zinc spinel was formed by BaC 5725 glass of the experimental composition. Two glasses were present in some large channels. Glass next to the channel walls contained reaction crystals and numerous seeds and had a variable index of refraction (minimum about 1.51). Glass in the middle of the channels was free of crystals, contained only a few seeds, and had an index of refraction about 1.57.

(3) *BaC 541.*—A reaction rim about 0.1 mm in thickness consisted of two parts. Cristobalite crystals with typical pine-tree forms extended into the glass. The lower layer, yellowish brown in color, consisted of nephelite-kaliophilite solid solution ($\beta NaAlSiO_4$-$\beta KAlSiO_4$) with a possible trace of carnegieite solid solution($\alpha NaAlSiO_4$-$\alpha KAlSiO_4$) [4]. No glass penetrated below the lining-glass interface.

(4) *BF 584, BF 604, and BF 588.*—Single reaction rims, which were thin and irregular in width, occurred with BF 584 and BF 604 glasses. These rims were composed of isotropic cristobalite containing partly dissolved refractory constituents and traces of nephelite-kaliophilite solid solution crystals. A double rim, thicker (about 0.1 mm) and more uniform in width, occurred with BF 588 glass. This rim had an upper layer of pine-tree cristobalite crystals and a lower layer of bladed barium feldspar extending into the refractory.

Below the interface, barium feldspar and barium disilicate (figs. 12 and 13), mullite (fig. 14), zinc spinel (fig. 15), and cristobalite (fig. 16) were in abundance and corundum in small amounts. Two glasses were present with a sharp line of demarcation (fig. 15) or a zone of cristobalite crystals (fig. 16) between them. One glass had indices of refraction below 1.53 and contained the reaction crystals and numerous seeds. The other glass resembled the melt in refractive index and was free from crystals.

The following observations apply to all barium glasses that penetrated below the interfaces or through cracks in the linings. The original elongated pores of the refractory were filled by glass, and most of them were considerably enlarged into continuous, winding channels with many branches and interconnections (figs. 8 and 17). The re-
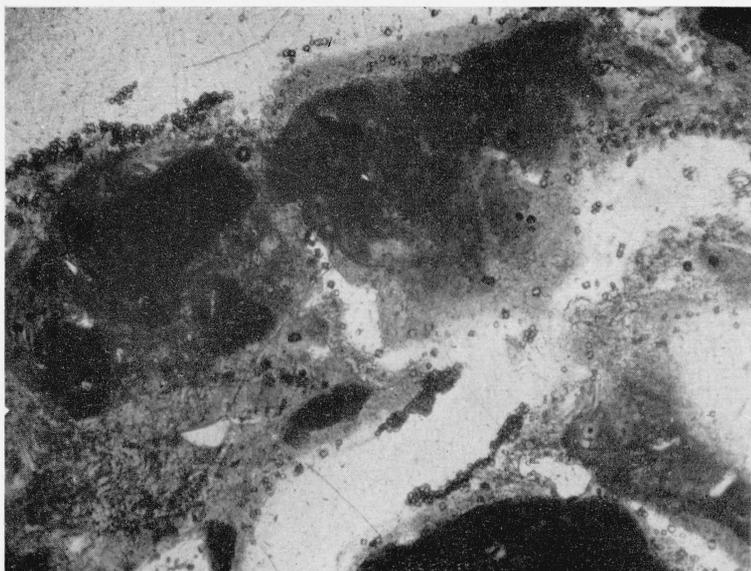
FIGURE 8.—*Reaction products in pot bottom penetrated by BaC 6109 glass.*

Small octahedral crystals of zinc spinel (dark grains with light centers) are within and at borders of glass-filled channels. The grog grains appear less corroded than the rest of the refractory. White areas are glass; black, grog; gray, remainder of refractory and reaction products. Ordinary light. Magnification, × 115.
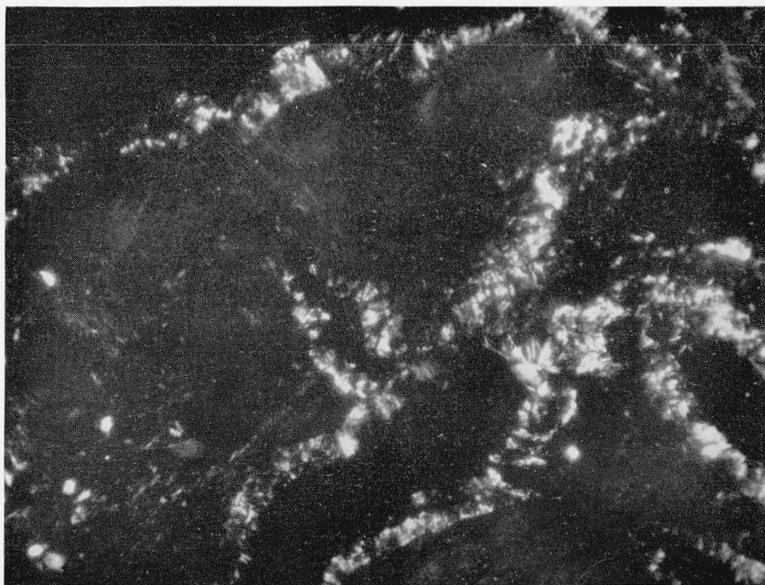

FIGURE 9.—*Same field as figure 8 but with crossed nicols.*

Doubly refracting barium feldspar crystals (white) are at borders of glass-filled channels (black). Cloudy areas are refractory; the cloudiness is due to masses of fine needles of mullite, which are most numerous in the grog grains. Magnification, × 115.
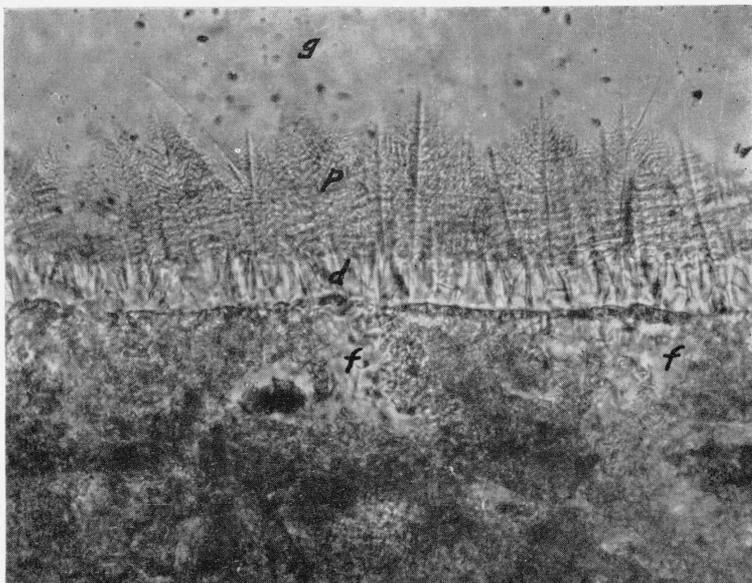
FIGURE 10.—*Lining-glass interface of a BaC 5725 melt.*

g, Glass; p, layer of "pine-tree" cristobalite crystals; d, layer of dense cristobalite; f, masses of barium feldspar filling penetrated regions in the refractory.   Ordinary light.   Magnification, × 520.
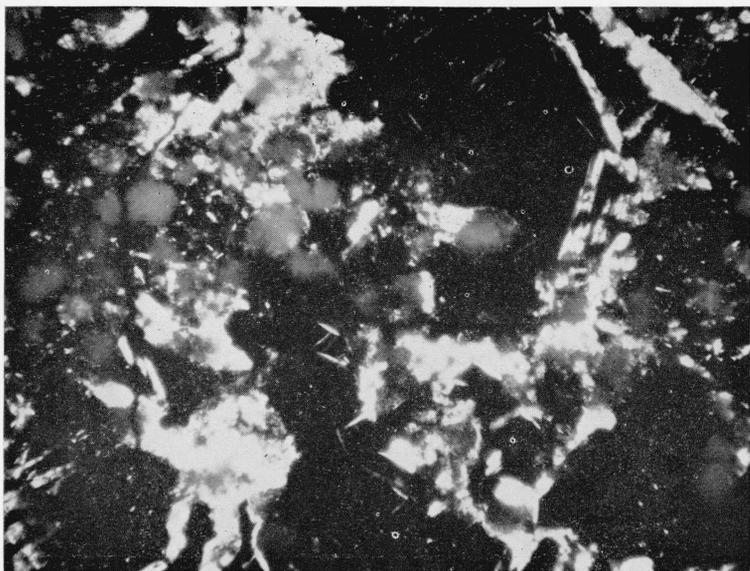

FIGURE 11.—*Alumina-rich lining penetrated by BaC 5725 glass.*

White areas are doubly refracting crystals of barium feldspar; black, glass; gray, aggregates of corundum of the original lining (see fig. 6).   Crossed nicols.   Magnification, × 100.
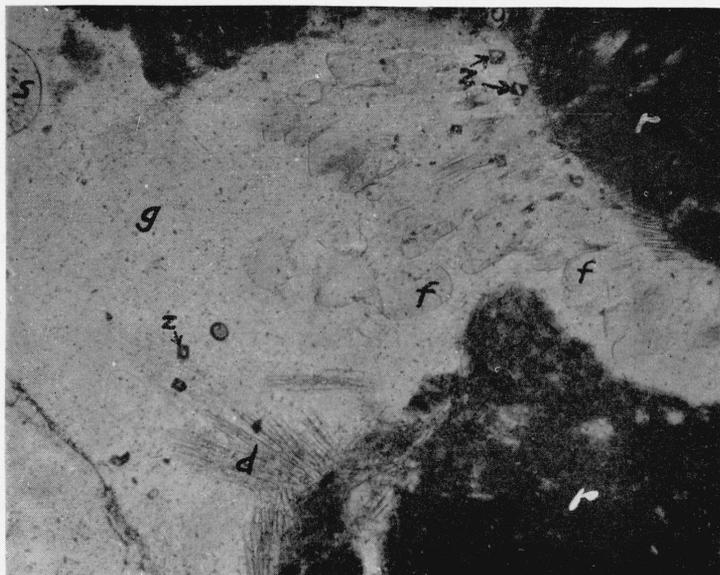
FIGURE 12.—*Reaction products in pot bottom penetrated by BF 604 glass.*

d, Prismatic barium disilicate crystals; f, barium feldspar crystals; z, octahedral zinc spinel crystals; r, refractory material; g, glass; s, seed in glass. Ordinary light. Magnification, $\times$ 115.
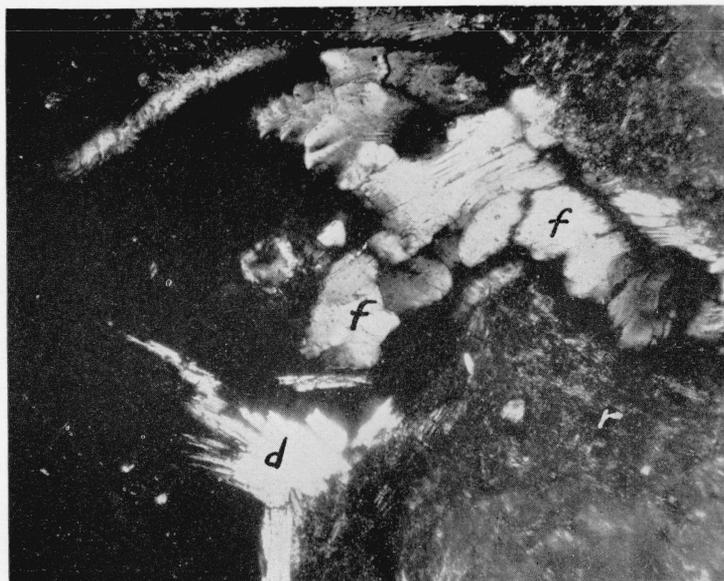

FIGURE 13.—*Same field as figure 12 but with crossed nicols.*

d, Barium disilicate; f, barium feldspar; r, refractory material. Black areas are glass. White specks in the refractory are mullite needles. Magnification, $\times$ 115.
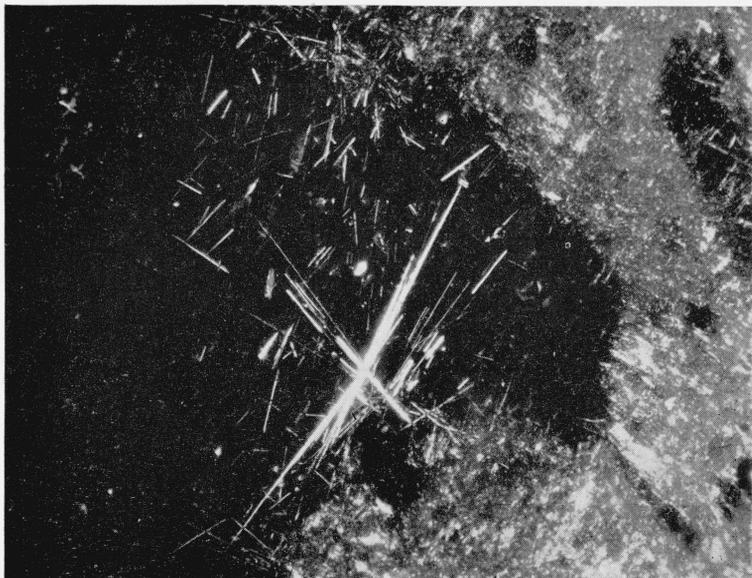
FIGURE 14.—*Mullite needles in pot bottom penetrated by BF 604 glass.*

Dark areas are glass; white lines are mullite needles; light areas are refractory in which the white specks are mullite. Crossed nicols. Magnification, $\times$ 115.
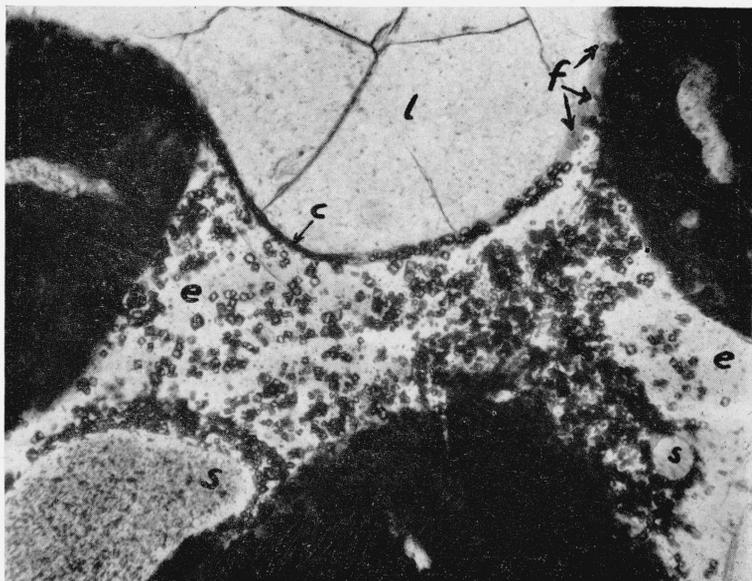

FIGURE 15.—*Contact of two glasses in pot bottom penetrated by BF 604 glass.*

e, Earlier glass containing octahedral crystals of zinc spinel; l, later glass; c, contact of the two glasses; f, film of earlier glass along refactory material (dark areas); s, seeds. Curve of the contact of the two glasses suggests that the later glass pushed against the earlier glass. Ordinary light. Magnification, $\times$ 115.
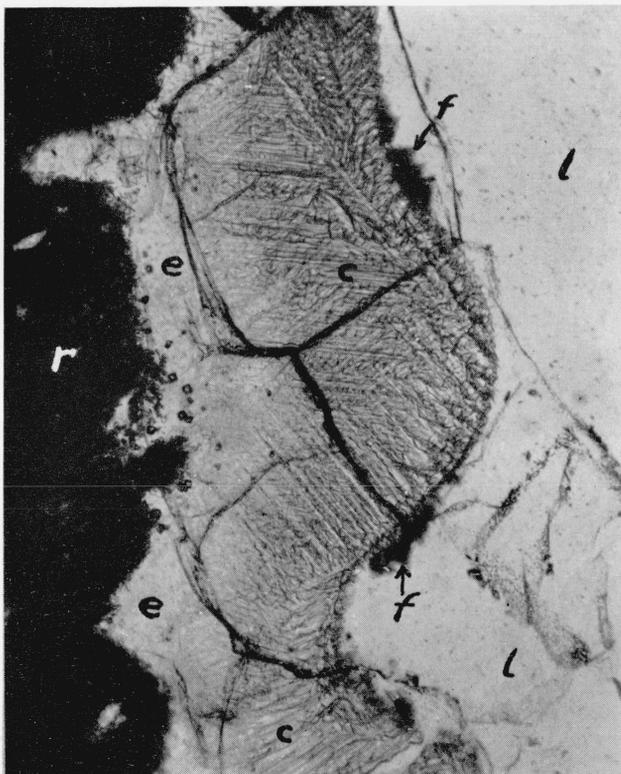
FIGURE 16.—*Cristobalite at two-glass contact along wall of large glass-filled channel in pot bottom penetrated by BF 604 glass.*

r, Refractory; e, earlier glass containing a few zinc spinel crystals; c, coarse-grained cristobalite crystals; f, fine-grained "pine-trees" of cristobalite; l, later glass. Ordinary light. Magnification × 115.
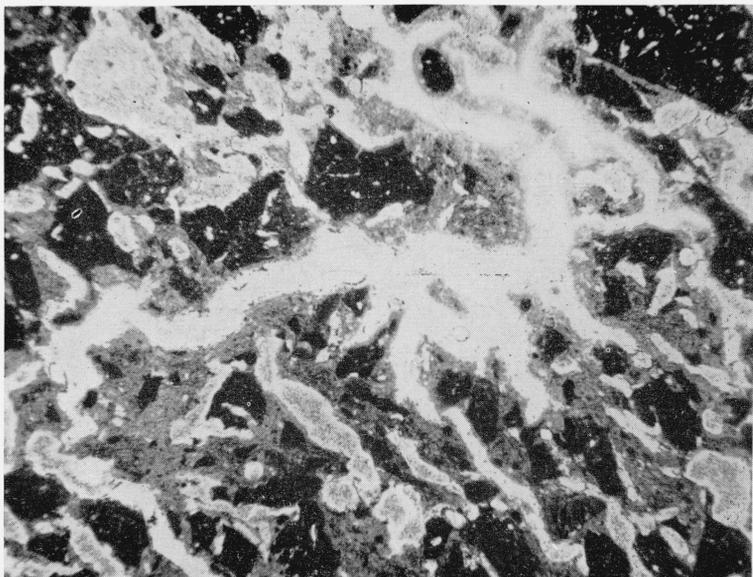
FIGURE 17.—*Pot bottom penetrated by barium glass.*

Branching channels were formed by corrosion of walls of original elongated pore spaces (compare with fig. 4). Grog grains appear less attacked than the rest of the refractory. White areas are glass; black, grog; gray, remainder of refractory. Ordinary light. Magnification × 24.
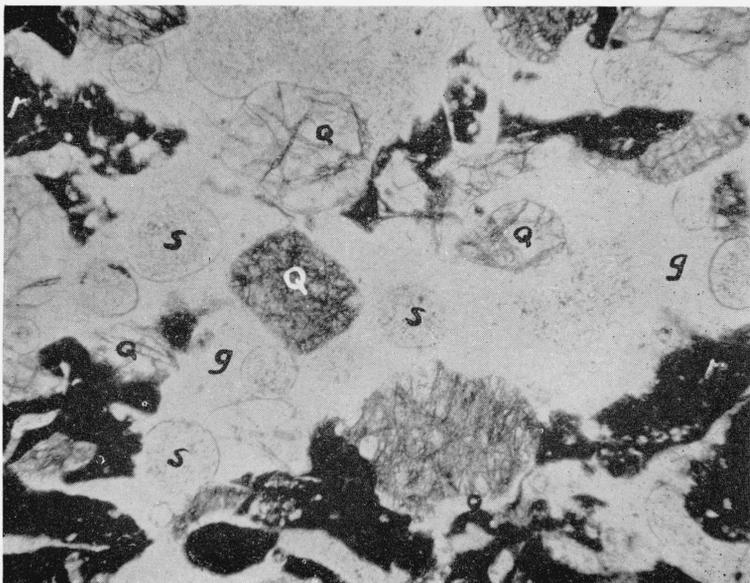

FIGURE 18.—*Bottom of semisiliceous pot penetrated by barium glass.*

The aluminous portion of the refractory has been dissolved by glass leaving quartz grains. Observe numerous seeds in the glass. r, Aluminous part of refractory; q, quartz of refractory; g, glass; s, seeds. Ordinary light. Magnification, × 50.

fractory material along the walls of these channels was partly corroded and filled with reaction crystals, chiefly mullite. The walls between channels were sometimes entirely dissolved to form the large glass-filled spaces seen previously by visual examination (fig. 1).

The grog grains in the refractory were less corroded than the bond and often appeared in thin section as islands in the larger channels (fig. 17). Small channels were observed between grog particles, but not through such particles (fig. 8). The quartz grains of the semisiliceous pots presented a similar appearance (fig. 18).

Cracks through the lining were mechanical in origin, as indicated by complimentary irregularities in the opposite sides (fig. 5).

No apparent relation existed between the maximum melting temperature or its duration and the character of the channels and reaction products. For example, the maximum temperatures of the 10 BaC 6109 melts ranged from 1,200° to 1,425° C. The pot in which glass was melted at 1,200° C contained numerous channels and the same reaction products as the pots heated at higher temperatures.

(b) CROWN GLASSES

(1) *LC 523.*—No well-defined reaction rim occurred. A few small corundum plates were scattered along the interface.

Pores in the refractory which were filled with glass were neither noticeably enlarged nor connected into continuous channels. A few reaction crystals of mullite and corundum gave the only evidence of pot attack. The maximum scheduled melting temperature, 1,450° C, was the highest of that for any glass.

(2) *BSC 511 and BSC 517.*—A double reaction rim was about 0.1 mm in maximum thickness (fig. 19). An upper layer consisted of intricately twinned crystals of carnegieite $\alpha KAlSiO_4$ solid solution, and a lower layer contained nephelite-kaliophilite solid solution. Some of the nephelite solid solution contained fine, oriented inclusions (fig. 20) which might be TiO_2, Fe_2O_3, or both. These inclusions were derived probably from the constituents of the refractory and imparted a brownish or yellowish color to the interface. A few, small corundum plates were also associated with or oriented in the nephelite layer. A similar but slightly thinner and less uniform reaction rim was formed on semisiliceous pots.

Mullite needles and thin corundum plates occurred sparingly in glass-filled pores below the interface. The corundum plates were sometimes colored pale blue or violet-blue and were then pleochroic.

(c) FLINT GLASSES

(1) *F 5795 and F 605.*—A very thin, intermittent reaction rim consisted of isotropic cristobalite. No glass penetrated below the lining-glass interface.

(2) *F 617 and F 620.*—A double reaction rim was 0.1 to 0.2 mm in thickness on both lined and unlined pots. An irregular upper layer of skeletal cristobalite crystals (fig. 21) was partially intermixed with the lower layer of nephelite-kaliophilite solid solution and carnegieite-$\alpha KAlSiO_4$ solid-solution crystals (fig. 22). The lower layer usually contained traces of corundum and tiny inclusions of TiO_2, Fe_2O_3, or both oriented in the nephelite.

The alumina-rich lining was less resistant to attack by F 617 glass than the typical lining. Not only was a reaction rim, 0.1 to 0.2 mm

in thickness, formed at the interface, but penetration into and replacement of the lining occurred to a depth of 0.3 mm, especially along the walls of cracks. The reaction rim (fig. 23,A) had two parts: an upper layer of pine-tree cristobalite crystals and a lower layer of carnegieite-αKAlSiO$_4$ solid-solution crystals. The penetration zone (fig. 23,B) also had two parts. Just below the reaction rim was a zone of nephelite-kaliophilite solid-solution crystals and numerous large corundum plates, which completely replaced the mullite and glassy bond of the refractory, but only partially replaced the aggregates of original corundum. Deepest within the lining was a zone of large corundum plates in glass which had replaced the mullite and glassy bond of the refractory but not the fine-grained corundum aggregates.

Pores in typical refractory penetrated by glass were slightly enlarged and a few continuous channels formed by corrosion. A small amount of mullite and corundum (fig. 24) occurred in deep yellow-colored glasses. These yellow glasses had indices of refraction (table 2) somewhat lower than those of the original glasses, while colorless glasses, which filled large cracks, had the approximate indices of refraction of the melts.

(3) *F 649.*—An even reaction rim was about 0.05 mm in width. This rim was a fine-grained mixture of isotropic αKAlSiO$_4$ solid solution or KAlSiO$_4$ glass, nephelite-kaliophilite solid solution with minute inclusions, traces of skeletal cristobalite extending into the glass, and a few corundum plates at the base of the rim.

Mullite and corundum crystals and two glasses occurred below the interface as with F 617 and F 620 glasses.

(4) *F 720.*—The reaction rim, 0.1 to 0.15 mm in thickness, was a fine-grained mixture of isotropic and anisotropic grains and partly dissolved refractory material (fig. 25). The isotropic grains were, apparently, KAlSiO$_4$ glass. The anisotropic grains were of two kinds: crystals of kaliophilite and yellowish, irregular-shaped grains, some of which were TiO$_2$ or Fe$_2$O$_3$ inclusions, and others were, possibly, lead compounds.

Where glass penetrated below the interface, through cracks in the lining, pores were enlarged and some channels formed by corrosion. The bulk of the crystalline reaction material consisted of one or more lead-aluminum silicates (figs. 26, 27, and 28) of undetermined composition. Other reaction products included mullite needles, corundum plates, skeletal crystals of cristobalite, and tiny globules of metallic lead (fig. 27). The glass filling the small channels and containing the reaction crystals was deep yellow in color and had a low index of refraction (average about 1.64, minimum near 1.60). Large channels and cracks contained clear glass with the refractive index (1.720) of the original glass.

Abundant feathery (figs. 27 and 28) and prismatic (fig. 26) crystals had an average index of refraction of 1.61, moderate birefringence, and a large extinction angle. The X-ray diffraction pattern was similar to that of the crystals in preparation 128 [5] in the system PbO–Al$_2$O$_3$–SiO$_2$ [5]. This fact, together with lack of agreement of optical properties, suggests a new lead-aluminum silicate of undetermined composition. Some of the thicker, more tabular crystals had slightly

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[5] The X-ray diffraction pattern of the present crystals contained all the lines of medium or greater intensity, except the first two, found in the pattern of preparation 128 [5].
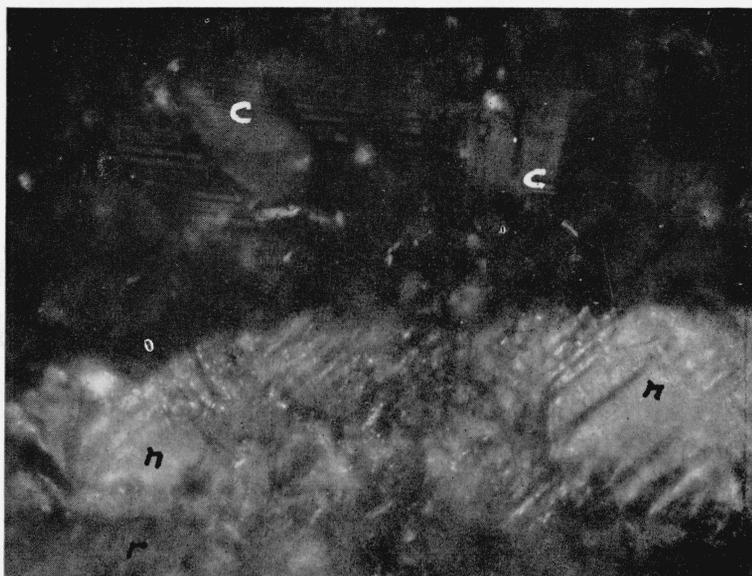
FIGURE 19.—*Refractory-glass interface of a BSC 517 melt.*

c, Intricately twinned carnegieite—αKAlSiO$_4$ solid solution crystals; n, layer of twinned nephelite-kali ophilite solid solution crystals; r, refractory.   Crossed nicols.   Magnification $\times$ 520.
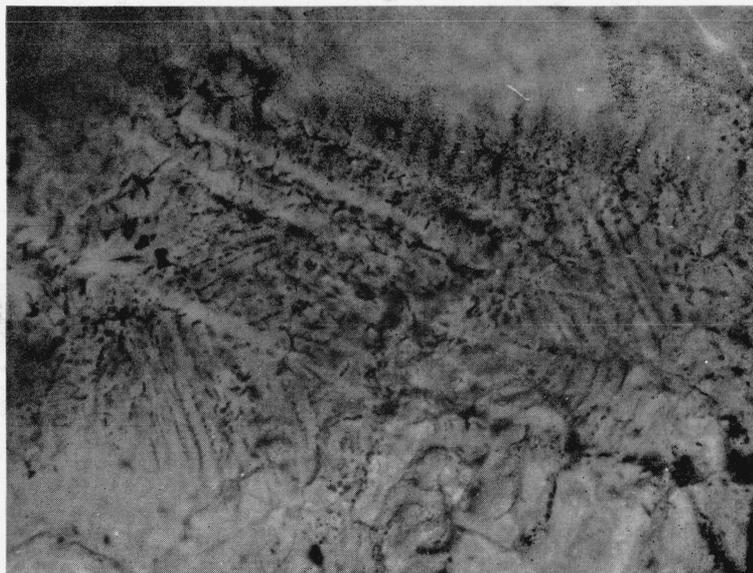

FIGURE 20.—*Oriented inclusions in nephelite-kaliophilite crystals at the refractory-glass interface of a BSC 511 melt.*

The small dark crystals and specks, apparently composed of TiO$_2$ or Fe$_2$O$_3$, or both, are arranged along twinning bands in the nephelite-kaliophilite solid solution crystals.   Ordinary light.   Magnification, $\times$ 520.
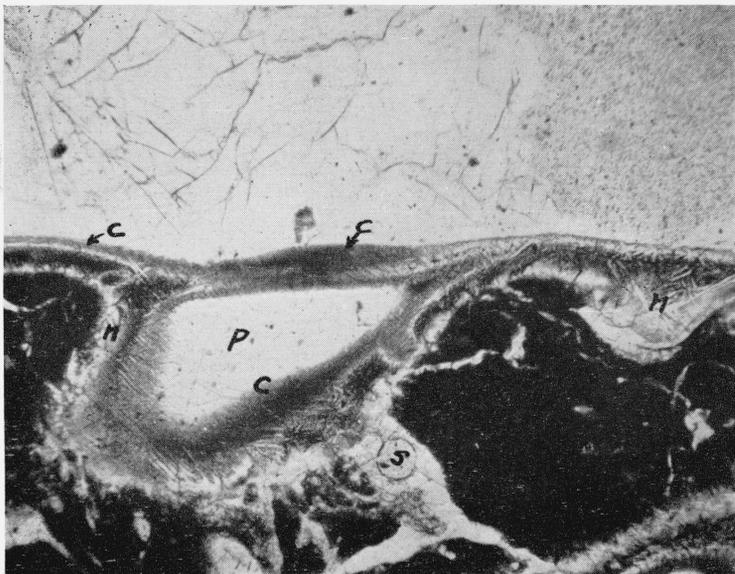
FIGURE 21.—*Refractory-glass interface of a F 617 melt.*

n, Layer of nephelite-kaliophilite and carnegieite—αKAlSiO₄ solid solution crystals; c, cristobalite; p, a
large pore in the refractory open to the melt except for a layer of reaction crystals; s, a small seed in glass.
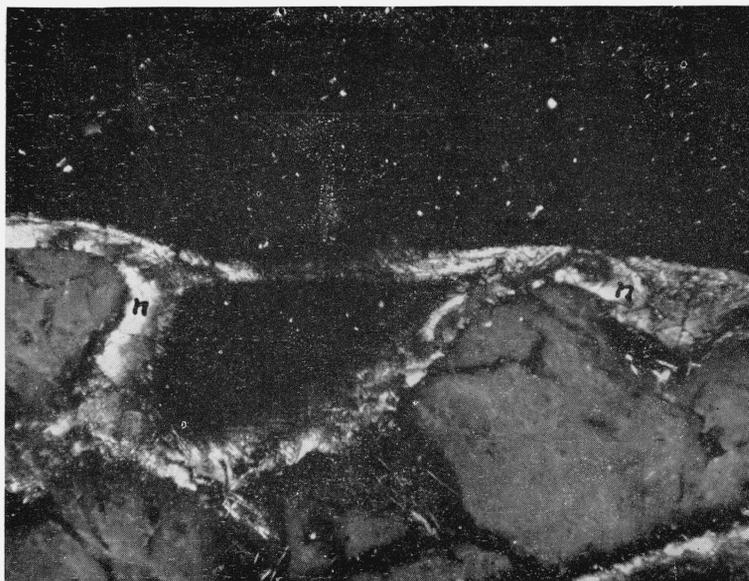Black areas are refractory.   Ordinary light.   Magnification, × 46.

FIGURE 22.—*Same field as figure 21 but with crossed nicols.*

n, Doubly refracting nephelite-kaliophilite solid-solution crystals.   Black areas are glass; cloudy, refractory
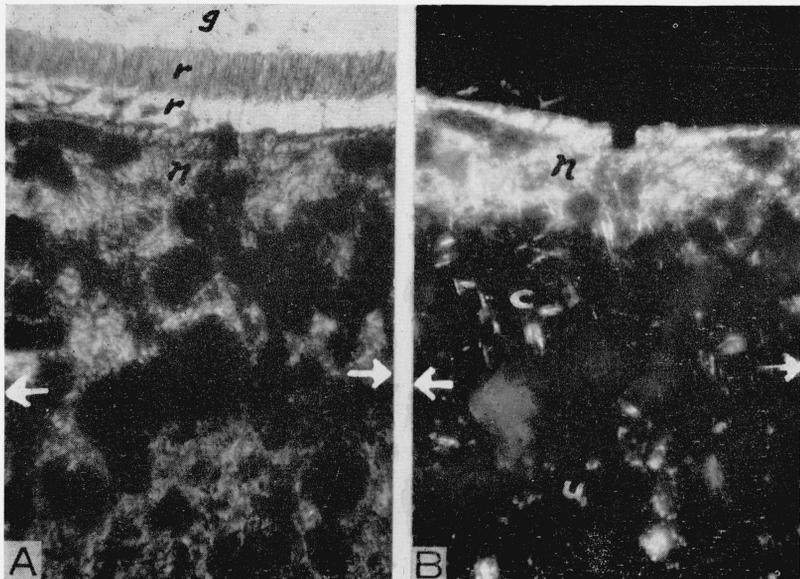material.   Cristobalite is invisible.   Magnification, × 46.

FIGURE 23.—*Alumina-rich lining penetrated by F 617 glass and lining-glass interface.*

A, Ordinary light; B, same field as A but with crossed nicols. Arrows indicate depth of glass attack. Black areas in A and gray clouded areas in B are the aggregates of corundum of the original lining (see fig. 6). g, Glass; r, reaction rim (invisible in B) at interface with cristobalite layer above and carnegieite–αKAlSiO$_4$ layer below; n, nephelite-kaliophilite (light areas) partly replacing refractory; c, corundum plates (white lines) and glass (black) partly replacing refractory; u, unattacked refractory showing mullite (white areas) glassy bond (black), and corundum aggregates (gray). Magnification, $\times$ 180.
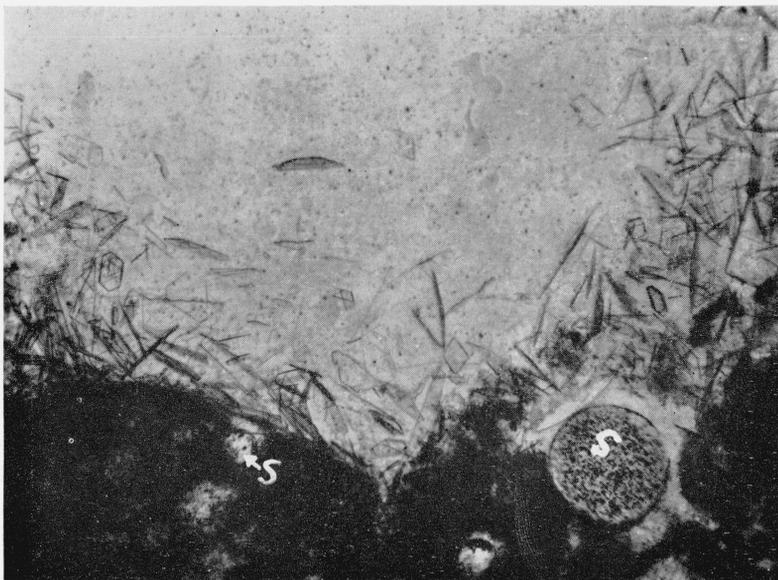

FIGURE 24.—*Corundum in pot bottom penetrated by F 617 glass.*

Corundum occurs in thin plates, many of which are standing on edge and look like needles or laths. Lightest areas are glass; darkest, refractory; s, seeds. Ordinary light. Magnification, $\times$ 120.
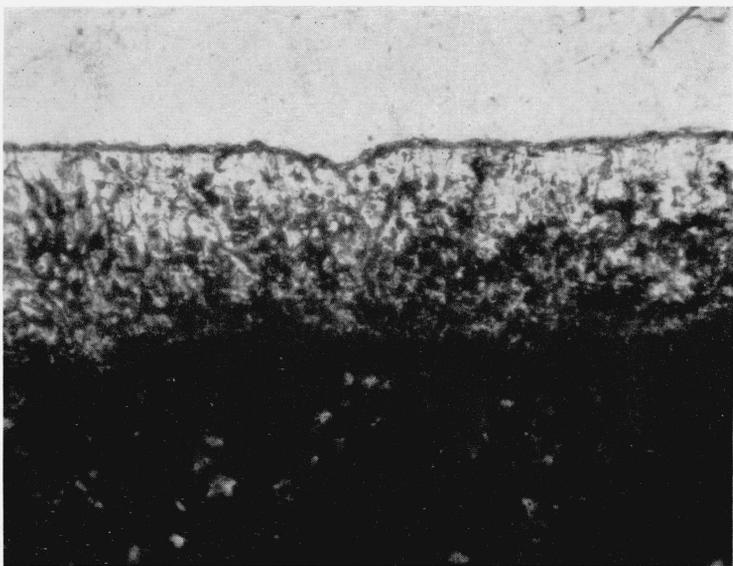
FIGURE 25.—*Lining-glass interface of a F 720 melt.*

Reaction zone (middle) of fine-grained $KAlSiO_4$ glass and nephelite (white grains) and various inclusions and undissolved remnants of the refractory (black grains). Melt above and unattacked refractory (black) below. Black line between melt and reaction zone is a refraction phenomenon. Ordinary light. Magnification, $\times$ 210.
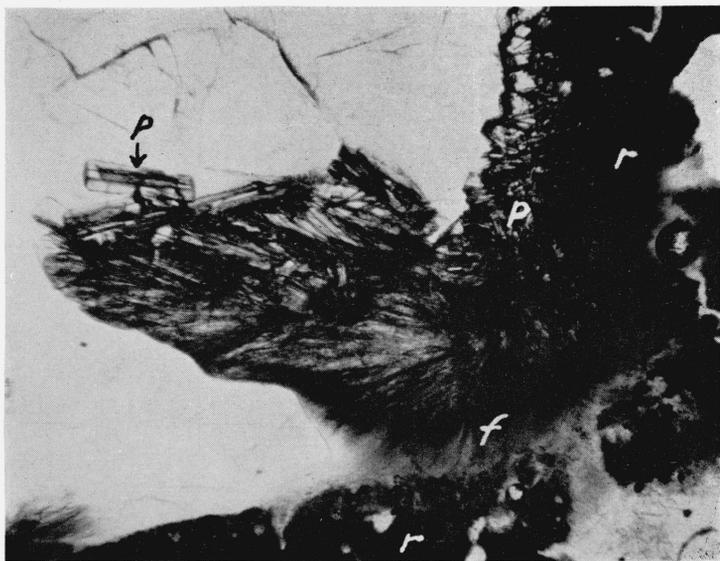
FIGURE 26.—*Lead aluminum silicate in pot bottom penetrated by F 720 glass.*

p, Prismatic type of crystals; f, feathery type; r, refractory. Clear areas are glass. Ordinary light. Magnification, $\times$ 50.
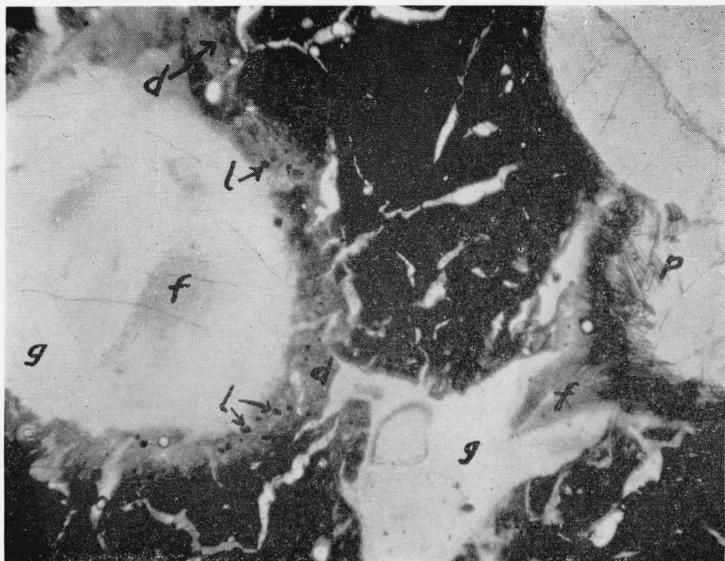
FIGURE 27.—*Reaction products in pot bottom penetrated by F 720 glass.*

p, Prismatic crystals of lead aluminum silicate; f, feathery crystals of lead aluminum silicate; l, globules of metallic lead; g, glass; d, partly dissolved refractory. Black areas are unattacked refractory. Ordinary light. Magnification, × 24.
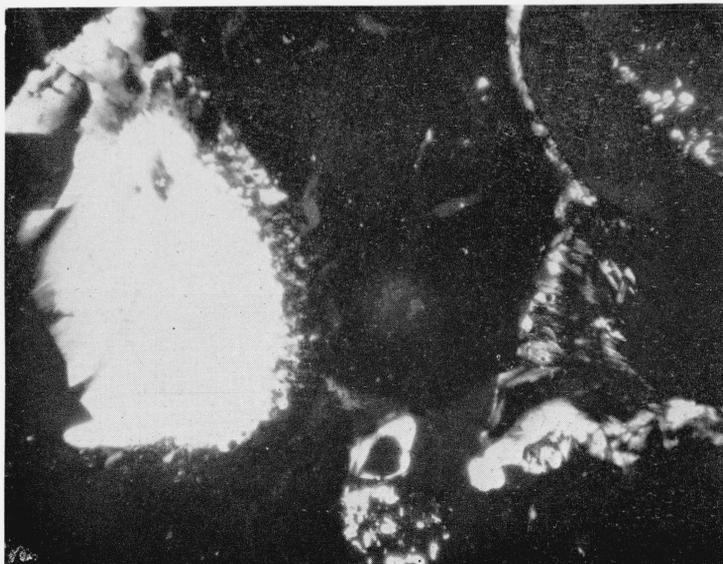
FIGURE 28.—*Same field as figure 27 but with crossed nicols.*

White areas are doubly refracting crystals of lead aluminum silicate. Magnification, × 24.

lower birefringence and a higher index of refraction than the feathery crystals, suggesting the presence of more than one new lead-aluminum silicate.

VI. DISCUSSION

Layers of crystalline material (reaction rims) at the interface between both lined and unlined pots and any type of optical glass indicated that the refractory was attacked by the glasses. An approximate correlation was apparent between thickness and character of the rims and extent of corrosion and penetration of the pot bottoms by the glasses. For example, very thin or intermittent rims were found with glasses (LC 523, F 5795, and F 605) which did not corrode the pot, whereas thicker (0.1 to 0.2 mm) and sometimes multiple rims occurred with glasses which were moderately to extremely reactive.

The crystalline phases in the rims depended on the amount of refractory dissolved and the composition of the individual glasses. As indicated later, alumina and silica were the chief constituents dissolved from all types of refractory. Poorly defined rims of single oxides (corundum or cristobalite) were associated with glasses containing alkalies alone (17 percent in LC 523) or alkalies and a moderate amount of PbO (36 and 41 percent, respectively, in F 5795 and F 605) as the principal corrosive constituents. Thicker rims, composed largely of alkali-aluminum silicates (such as nephelite-kaliophilite solid solution) and cristobalite, occurred when the corrosive constituents included 8 to 12 percent of B_2O_3, 43 to 62 percent of PbO, or 13 to 20 percent of BaO, in addition to 4 to 23 percent of alkalies, as exemplified in the borosilicate crown and some flint and barium glasses. Rims of barium aluminum silicate (barium feldspar) and sometimes cristobalite, however, were associated with glasses containing 25 to 45 percent of BaO or BaO plus CaO. Lime, present in only one barium glass, apparently acted with BaO as a corrosive constituent and possibly formed a solid solution in the barium feldspar.

Multiple rims were indicative of considerable variation in composition in a very narrow zone (0.1 to 0.2 mm in thickness) at the pot-glass interface. In this zone the content of alumina increased on approaching the refractory, as shown by the order of the phases. For example, with many barium and lead glasses the phases were arranged (1) a layer of cristobalite, (2) an underlying layer of alkali or barium-aluminum silicates, and (3) an occasional concentration of corundum crystals with the lead glasses only. The corundum, however, was more often associated with nephelite, as described by Insley [6].

Glasses were classed as noncorrosive or corrosive, depending on the depth of penetration by the glass and the formation of enlarged pores and channels in the pot bottom. The crown and the flint glasses with 36 to 41 percent of PbO were classed noncorrosive because penetration, other than along cracks, was less than ½ in. and pores were not enlarged. Flint glasses with 43 to 51 percent of PbO were considered slightly corrosive because glass-filled pores were somewhat enlarged although penetration rarely extended more than ½ in. below the interface. A flint with 62 percent of PbO was a moderately corrosive glass, as indicated by occasional penetration to a depth of approximately 2 in., enlargement of pores, and formation of some channels by the glass. Most of the barium glasses were extremely corrosive, as shown by deep penetration, considerable enlargement of pores,

formation of extensive interconnecting channels, and occasional leakage in the melting furnace. Peddle [7 and 8] pointed out similar pot attack, indicated by corrosion extending nearly through the pot or by small holes in the center of the pot bottom, caused by glass with a BaO content of more than 40 percent and by glass with a high content of PbO.

The extent to which optical glass penetrated the pot bottom depended on many factors. Variations of the maximum temperature during the melting and fining operations of different glasses might be expected to have an effect on the extent of penetration [9 and 10]. No relation was apparent, however, partly because the actual temperature variations were not very great (1,350° to 1,450° C, with one exception at 1,200° C) and partly because any existing relations were masked by the effects of other factors.

The porosity of the refractory was one of the more important factors [11 and 12]. Penetration of glass into the bottoms of unlined pots was facilitated considerably by the elongated shape and vertical elongation of many pores. The linings, however, were not penetrated because the pores were fewer in number, much smaller, and essentially spherical in shape. Thus the underlying more porous refractory in the bottoms of lined pots was protected completely from penetration except when cracks or other flaws occurred in the lining.

In alumina-rich linings some of the batch constituents did not react, at the temperatures encountered in the preheating furances, to form a cohesive refractory with low porosity. Consequently, these linings were penetrated slightly by glass.

The viscosity of the molten glass was apparently sufficient to prevent penetration of the openings in the walls of the pot, especially toward the top, where the hydrostatic pressure of the melt was low. On the other hand, glass was sometimes forced into the pores in the bottom of the pot and the lower part of the walls, in spite of the viscosity, partly because of the increase in hydrostatic pressure. This would be especially true for the heavier glasses. For example, the flint glass (F 720) with the highest density penetrated the deepest of any flint. Unfortunately, the heavier glasses, F 720 and most barium glasses, were also extremely corrosive. These glasses were not only forced deep into the pot bottom but readily dissolved the refractory constituents exposed in the pore walls, enlarging and connecting the openings in the refractory to form winding and branching channels.

A wide variation in the resistance to glass attack of the different constituents of the refractory was apparent with the more corrosive glasses, although all glasses were at least mildly reactive. The crystalline phases were more resistant than the glassy bond. The portions of the refractory where mullite needles were most numerous, that is, the grains of potshell grog, were less subject to attack by the glass than regions in which glassy bond predominated. Hyslop [13] noted that between two otherwise similar pots the one with the higher mullite content was the more resistant to corrosion. The quartz and corundum in the special refractories, furthermore, were by far the most resistant of the constituents.

An explanation of the origin of the two types of glasses occurring in the refractory was suggested as a result of petrographic observations on the corroded regions of the refractory. When the walls of pores and channels were dissolved by molten barium or lead glasses,

the content of Al_2O_3 and SiO_2 in the attacking glass was increased. Thus, the resulting lowering of the refractive index of the altered glass can be accounted for because both vitreous silica and alumina have index factors below 1.46. Although the content of Fe_2O_3 and TiO_2 in the refractory was low, sufficient amounts of these oxides may have been dissolved to impart a yellow color to the relatively small amounts of altered glass in the openings of the refractory. By continued corrosion of the refractory, the altered glass gained access to additional pores and small channels. Unaltered glass from the melt was subsequently forced into some of the enlarged pores and channels pressing the altered glass against the channel walls and also deeper into the refractory. In this way a sharp division line was produced at the contact between the two glasses. Furthermore, the later unaltered glass apparently protected the melt from contamination with altered glass by isolating the latter in the pot bottom.

Crystalline reaction products in the altered glass depended on the amount and composition of the refractory dissolved as well as the composition of the melt [14 and 15]. Because SiO_2 and Al_2O_3 were the chief oxides dissolved from the refractory, the appearance of cristobalite, mullite, corundum, or some aluminate or silicate whose additional oxide constituent was derived from the glass was not surprising. In fact, the widespread formation of numerous needles of mullite, even with the noncorrosive glasses, was to be expected. Cristobalite, as suggested by its occurrence at the two glass contact, generally appeared where the content of dissolved Al_2O_3 was relatively low. Insley [6] has suggested that corundum, at the contact of clay refractories and soda-lime glass, was formed by the dissociation of aluminum silicates.

The occurrence of the aluminates and silicates was in accordance with known phase equilibrium relations. For example, zinc spinel ($ZnO.Al_2O_3$), which is the primary crystalline phase over a major part of the system SiO_2-ZnO-Al_2O_3 [16], was formed with all glasses that contained more than 2.5 percent of ZnO. Conversely, lead-aluminum silicates appeared only with the flint glass having the highest content of PbO (62 percent). Such silicates, however, should not be expected as reaction products except with glasses containing considerably more than 50 percent of PbO because the primary phase fields of the various known and suspected lead-aluminum silicates are limited to a small part of the entire field in the system PbO-Al_2O_3-SiO_2 [5]. That barium feldspar ($BaO.Al_2O_3.2SiO_2$) and barium disilicate were formed by glasses with a BaO content ranging from 13 to 45 percent suggested that these compounds have extensive fields in the system BaO-Al_2O_3-SiO_2.

The fact that seeds in the glass-filled channels in the pot bottom were largely associated with the altered glass throws some light on the origin and possible migration of the seeds. The formation of some of these seeds by molten glass entrapping the gas in the original pores was demonstrated by the great differences in the extent to which pores were filled with glass (section IV, p. 34). Other seeds probably were formed by the liberation of gases in the unfined molten glass. Seeds formed in either of the above ways would be more plentiful in the altered glass because the latter was not only the first glass to enter the pores of the refractory but entered, presumably, at an early stage in the fining period. That the altered glass was

isolated from the melt and that glass continued to move downward into the pot bottom apparently were arguments against migration of the seeds into the melt. The occurrence of very seedy glass in pots with badly cracked bottoms, however, suggested that some of these seeds possibly did migrate into the melt. Jebsen-Marwedel [17] believed that seeds he found originating in the refractory were released into the melt and suggested that the gas forming these seeds was a reaction product of pot attack.

VII. SUMMARY

Examinations were made visually and with a petrographic microscope of samples of pot bottom before and after the production of optical glass to determine the manner and extent of attack by the glass on the refractory and to identify the reaction products formed. In most instances, samples were selected that were cracked and penetrated by glass.

The refractory was composed of mullite needles in a glassy bond, both of which were attacked by the more corrosive glasses. Semisiliceous pots contained quartz grains and alumina-rich linings contained corundum crystals in addition to mullite and glass. The quartz and corundum were only slightly attacked, if at all, by molten glass.

The bottoms of unlined clay pots were penetrated sometimes by optical glasses, in large part because of the size, shape, and orientation of the pore spaces in the refractory. Lined pots, however, were not penetrated by any type of glass except when the relatively dense lining was cracked.

The corrosive action of barium glasses not only greatly enlarged but connected the pores in the refractory, forming a system of branching channels that sometimes continued entirely through the bottom. Crystalline reaction products identified at the interface between pot and glass (reaction rims) were barium feldspar, nephelite-kaliophilite solid solution and cristobalite. When glass penetrated the refractory barium feldspar, barium disilicate, zinc spinel, mullite and, occasionally, cristobalite and corundum were formed.

Borosilicate crown and most flint glasses were only slightly corrosive and did not noticeably enlarge the pore spaces nor form channel systems. The penetration of glass did not exceed about ½ in. A flint glass with 62 percent of PbO, however, was moderately corrosive. Nephelite-kaliophilite solid solution and related materials, cristobalite and corundum were found at the pot-glass interfaces. Mullite and corundum were the only reaction crystals in pot bottoms penetrated by these glasses, with the exception of the flint glass (F 720) with 62 percent of PbO. One or more new lead-aluminum silicates of undetermined composition and a trace of metallic lead occurred with this glass.

Variations of the maximum temperatures (1,350° to 1,450° C) in the glass-melting furnaces apparently did not affect the extent of penetration or the type or amount of reaction products formed.

The presence of two types of glasses was characteristic of refractory penetrated by barium and some lead glasses. One type was a glass altered in composition and certain physical properties by the attack on the pot constituents. This glass contained numerous seeds formed

by the entrapment of the gas in the original refractory and probably, also by the liberation of gas in the glass batch. The second type of glass resembled closely the melt.

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