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DPST-82-231

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MEMORANDUM

TO: M. J. PLODINEC

FROM: W. N. RANKIN/P. E. O'ROURKE/P. D SOPER/M. B. COSPER/
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EVALUATION OF CORROSION AND DEPOSITION IN THE 1941 MELTER

INTRODUCTION AND SUMMARY

The 1941 melter was the first large-scale glass melter operated at the Savannah River Laboratory in an experimental program to immobilize SRP high level radioactive waste in borosilicate glass. This melter was successfully operated for 398 days and produced 74 tons of simulated waste glass. During this period the feasibility of both calcine and the slurry feeding of production-scale melters was demonstrated.

The 1941 melter was shut down and dismantled to evaluate its service life. Although the walls and throat of the melter suffered only a small amount of corrosion, an approximate 7-inch-thick layer of slag had accumulated in the bottom of the melter. An additional layer of material up to approximately 1 inch thick had formed on the wall of the melter.

This memorandum describes the results of characterization of specimens of these materials, and their impact on the 1941 melter. We conclude:

- Slag is composed of FeNiMn, FeNiMnCr spinel and sodium calcium iron silicate particles in a glass matrix.
- The material on the melter wall is primarily a viscous layer of glass containing >30 volume % FeNiMn spinel particles.
- The formation of these materials can be correlated with the temperature history of the melter.
- Formation of these materials can be prevented by controlling the temperature and the composition of the glass.
  - Keep minimum temperature above glass liquidus all the time.
  - Keep maximum temperature low enough to minimize corrosion of Monofrax K-3.

MELTER ANALYSES

The distribution of the slag and material on the wall is shown in a cross section of the 1941 melter (Figure 1). The appearance of the inside of the melter after the glass had been dumped is shown in Figure 2. Specimens of these materials were characterized by optical microscopy, scanning electron microscopy, electron microprobe analysis and x-ray diffraction.

Slag (Figure 3)

A large specimen of the entire cross section of the slag layer shows that the slag is composed of three layers (Figure 3). The results of electron microprobe analysis and x-ray diffraction analysis of specimens from each layer are given in Table 1 and discussed in the following paragraphs.

Layer 1

Layer 1 (closest to bottom) is composed of four phases:

1) FeNiMn spinel

2) FeNiMnCr spinel

3) A phase which was not identified (containing O and Si)

4) A glass matrix enriched in aluminum

Both spinel phases have a structure similar to the mineral trevorite.

Layer 2

Layer 2 (above Strata 1) is composed of 4 phases:

1) FeNiMn spinel (structure similar to the structure of the mineral trevorite)

2) Sodium calcium iron silicate (structure similar to the structure of the mineral acmite)

3) Glass matrix

4) Entrapped waste glass of normal waste glass composition

The regions containing entrapped waste glass are small near the bottom of the strata, and increase in size as the height in the strata increases.

Layer 3

Layer 3 (top of the slag) is composed of 3 phases:

1) FeNiMn spinel (structure similar to the structure of the mineral trevorite)

2) Sodium calcium iron silicate (structure similar to the structure of the mineral acmite)

3) Glass matrix

Material from the Melter Wall

A specimen from a core drilled from the wall of the melter below the melt line is shown in Figure 4. This specimen contains three different zones which are discussed below:

Monofrax K-3

Monofrax K-3 is composed of 3 phases:

1) An aluminum rich phase

2) A chromium rich phase

3) A very small amount of a glass phase

Reaction Zone between Monofrax K-3 and Glass (Figure 5)

Molten glass reacts with both the Cr rich and the Al rich phase of the Monofrax K-3. Reaction between the glass and the Cr rich phase forms a CrFeNi spinel. Reaction with the Al rich phase produces a glass that is enriched in Al. Since Al increases the viscosity of glass, this viscous glass layer remains in place on the corroding face of the Monofrax K-3. The CrFeNi spinel particles are held within the viscous glass layer. This layer remains on the Monofrax K-3 and protects it from further corrosion.

Increased temperature not only increases the corrosion rate but reduces the viscosity of the glass in this layer making it more susceptible to being swept away. Increased viscosity in the glass will remove this layer faster. This is why more corrosion occurs in melter throats and other areas when moving glass contacts the refractories. When this layer is removed glass enriched in Al and CrFeNi spinels are introduced into the glass.

This reaction zone is typical of zones found on Monofrax K-3 in the glass industry. Similar reaction zones were found on waste glass melters at PNL.[1,2]

Material from the Glass

Material from the glass that remained on the melter wall was composed of a glass matrix of the normal waste glass composition with >30 volume % FeNiMn spinel particles. This material adhered to the melter wall when the melter was drained because it was more viscous than the waste glass in the melter. Increasing the content of second phase particles in glass increases its viscosity.[3]

The composition of this material shows that it came from the glass and not from the Monofrax K-3. The FeNiMn spinel and the glass in this layer are composed primarily of elements found in waste glass (Fe, Ni, Mn, Si). This layer contains very little Cr (approximately 0.8 wt %). Chromium is one of the main constituents of Monofrax K-3. The CrFeNi spinels in the Monofrax K-3/glass reaction zone contain approximately 20 wt % Cr.

FORMATION OF SLAG AND MATERIAL ON THE WALL

The formation of these materials can be correlated with the temperature history of the melter (Figure 11). Once each strata is formed, it is not dissolved by subsequent melter operation. The formation of these materials is accumulative. Attempts to dissolve slag that formed in the small cylindrical melter by using extreme measures not possible in a remote operation were only partially successful.[4] The melter was filled with more corrosive, pure Frit 131. The velocity of the glass passing over the slag was increased by stirring with a rod and air sparging.

High Temperature

From melter startup to the beginning of CMOG-3 (approximately 3 months) melter temperature was inadvertently controlled at temperatures above 1200°C. For about 7 days during this period the temperature was about 1300°C. The temperature at the melter wall was about 50°C less than these temperatures.[6]

Most of the refractory corrosion observed in the melter probably occurred for during this period. The loss of material from Monofrax K-3 at 1150°C[7,8,9,10]) is approximately 3 mils/day. The corrosion rate doubles for each 50°C increase in temperature.[11,12] Therefore during the three months when the melter was above 1200°C and the wall was above 1150°C approximately 540 mils of corrosion would be expected. During the 7 days that the melter was about 1300°C and the wall was about 1250°C approximately 40 mils of corrosion would be expected. This accounts for 580 mils of corrosion. Only 290 mils of corrosion would have been expected during this period at 1150°C.

Measurements of the refractory show that 600 mils of Monofrax K-3 were lost at the melt line. Corrosion of Monofrax K-3 introduces Al enriched glass and CrFeNi particles into the glass as described previously.

Layer 1 of the slag was probably formed during this period of melter operation. It contains spinels which contain higher levels of Cr than were found in any other layer of the slag. The glass matrix of layer 1 contains higher levels of Al than found in any other layer in the slag. None of the material found on the wall of the melter formed during this period.

Low Temperature

The remainder of the slag and all of the material on the wall of the melter are not corrosion products of Monofrax K-3 because they contain little or no chromium. These materials formed whenever the glass temperature was low enough that a solid phase is thermodynamically stable (the liquidus temperature). This temperature for Frit 131 and TDS waste in contact with K-3 is 1081°C.[13] At temperature below 1081°C nucleation and growth of second phase particles are occurring.

These second phase particles contributed to the formation of the slag in the bottom of the melter and the material found on the melter wall. Because the particles are more dense than waste glass they would fall from the glass and accumulate at the bottom of the melter. The wall of the melter is approximately 50°C below the bulk glass temperature.[6] High concentration of particles formed in this cooler glass. As mentioned previously, concentration of particles in glass increase its viscosity. That is why this layer remained on the wall when the melter was drained.

Normal Operation (Figure 6, 7)

Temperature probes of the 1941 melter made during operation at a bulk glass temperature of 1150°C show that the temperature at the bottom of the melter was about 950°C.[5] This temperature would cause second phase particle formation in this part of the glass. Slag would result from accumulation of these particles at the bottom of the melter.

Low Temperature Idling[6]

The 1941 melter experienced two periods when the temperature was below 1081°C. During these periods second phase particles would be forming in the glass through the melter:

1. For 58 days (between CMOG 3 and CMOG 4) the melter was idled at 1050°C. After this period 7 inches of slag was discovered by probing the melter.

2. For about 1 month (after CMOG-6) the melter was shut down from 1 to 3 times a day for about a month. This period of shutdowns was necessary to convert the melter from calcine-fed to slurry-fed operation. No additional slag accumulation was observed after this period. The kinetics of slag formation may have prevented additional slag formation because the melter was thermal cycled.

CONSEQUENCES OF FORMATION

When enough slag accumulated to fill the bottom of the 1941 melter it began to come out the melter with the waste glass. This affected the waste glass quality. The presence of spinels indicates that the waste loading of the glass may have been effectively reduced, which could slightly reduce the durability of the glass product.[14,15,16]

Because slag is much more viscous than waste glass a large accumulation of slag can plug the riser and pour spout. Indications are that the riser and nozzle in the 1941 melter were almost completely plugged by slag. In order to make the last pours the temperature of the riser was increased and the melter was rocked back and forth repeatedly in order to melt a "glass" plug in the nozzle. Examination of the nozzle after the melter was dismantled showed that it was filled with slag and glass containing high concentrations of spinel particles.

PREVENTION OF FORMATION

Formation of slag and accumulation of material on the wall of the melter can be prevented by controlling the temperature and the composition of the glass in the melter.

- During normal waste glass production the temperature should be controlled so that excessive corrosion does not occur. Corrosion not only wears out the melter but contributes to slag accumulation.
- The temperature of the glass should be maintained above its liquidus temperature. Waste glass melters should be designed so that the entire melt chamber can be controlled above the glass liquidus temperature. If low temperatures are desired during idling for extended periods, the composition of the glass could be changed to prevent slag accumulations. All of the waste glass could be flushed out with a glass. A composition such as pure frit + 20 wt % Al_2O_3 which has a much lower liquidus temperature. This will result in the production of extra canisters of glass, but will prevent the problem of slag accumulations.

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Figure 1

DISTRIBUTION OF SLAG AND MATERIAL ON THE WALL

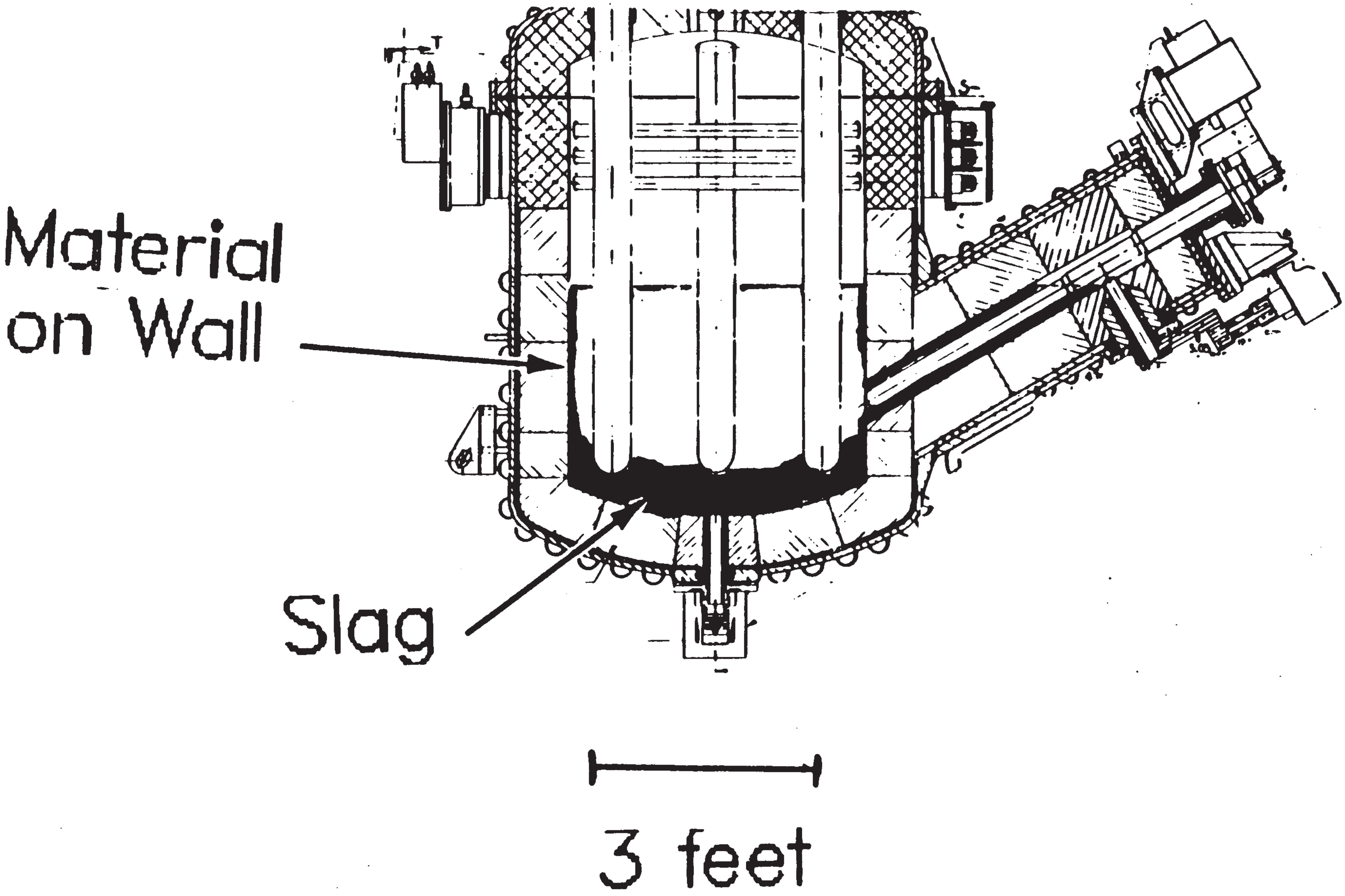
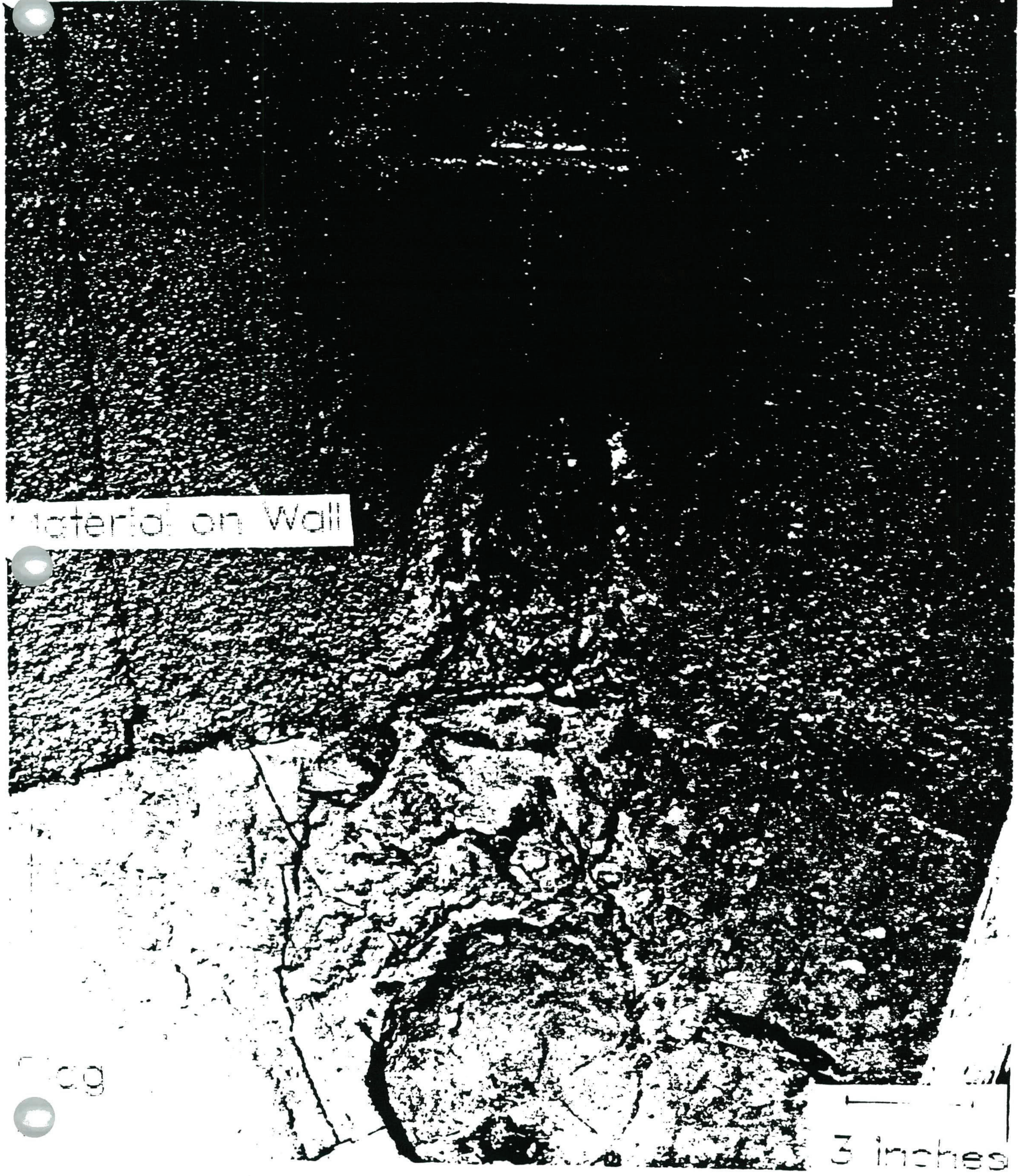


Figure 2
APPEARANCE OF INSIDE OF THE MELTER



Figure

CROSS SECTION OF SLAG

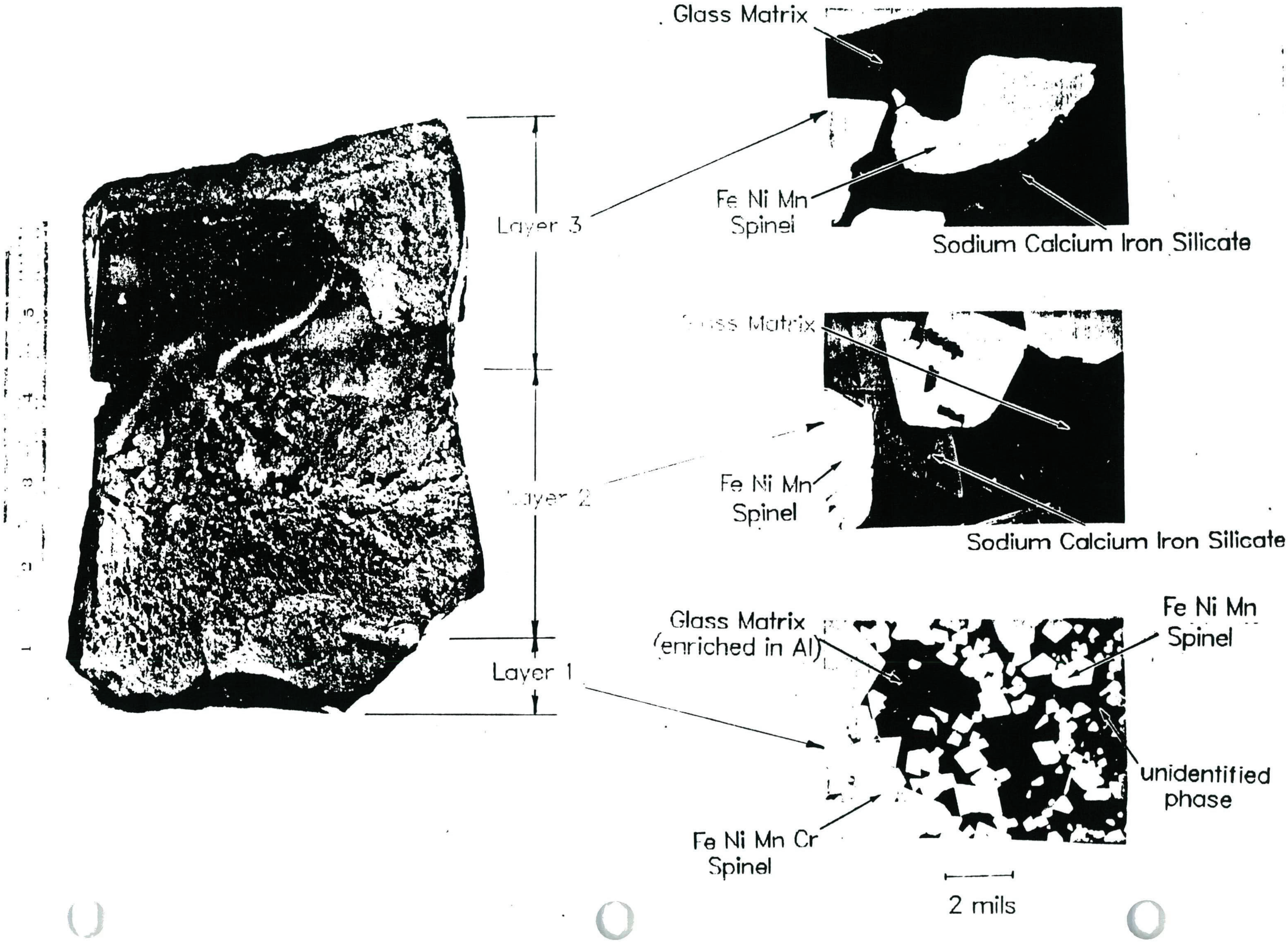


Figure 4

CROSS SECTION OF MATERIAL FROM WALL

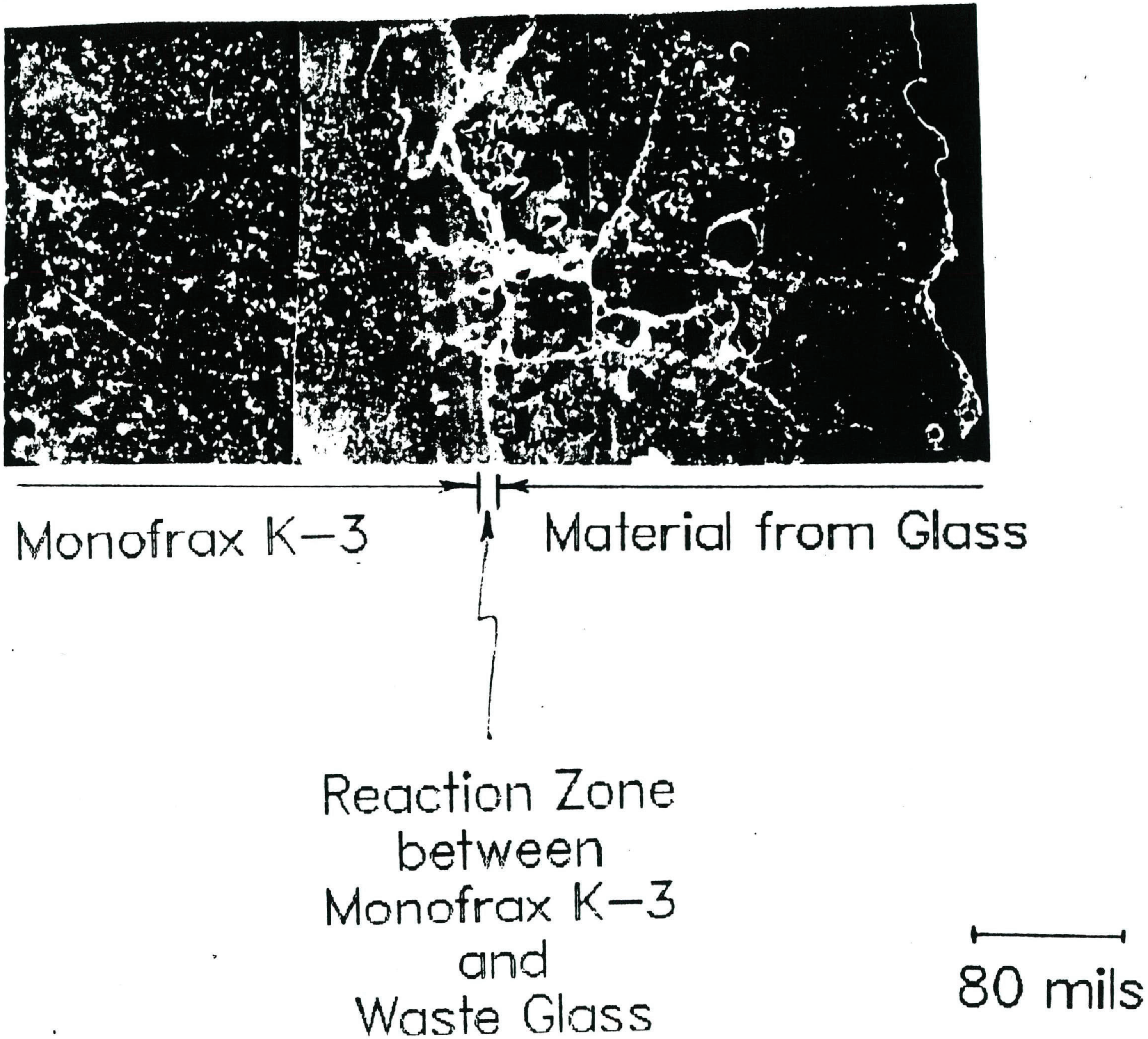


Figure 5
REACTION ZONE BETWEEN MONOFRAX K–3 AND WASTE GLASS

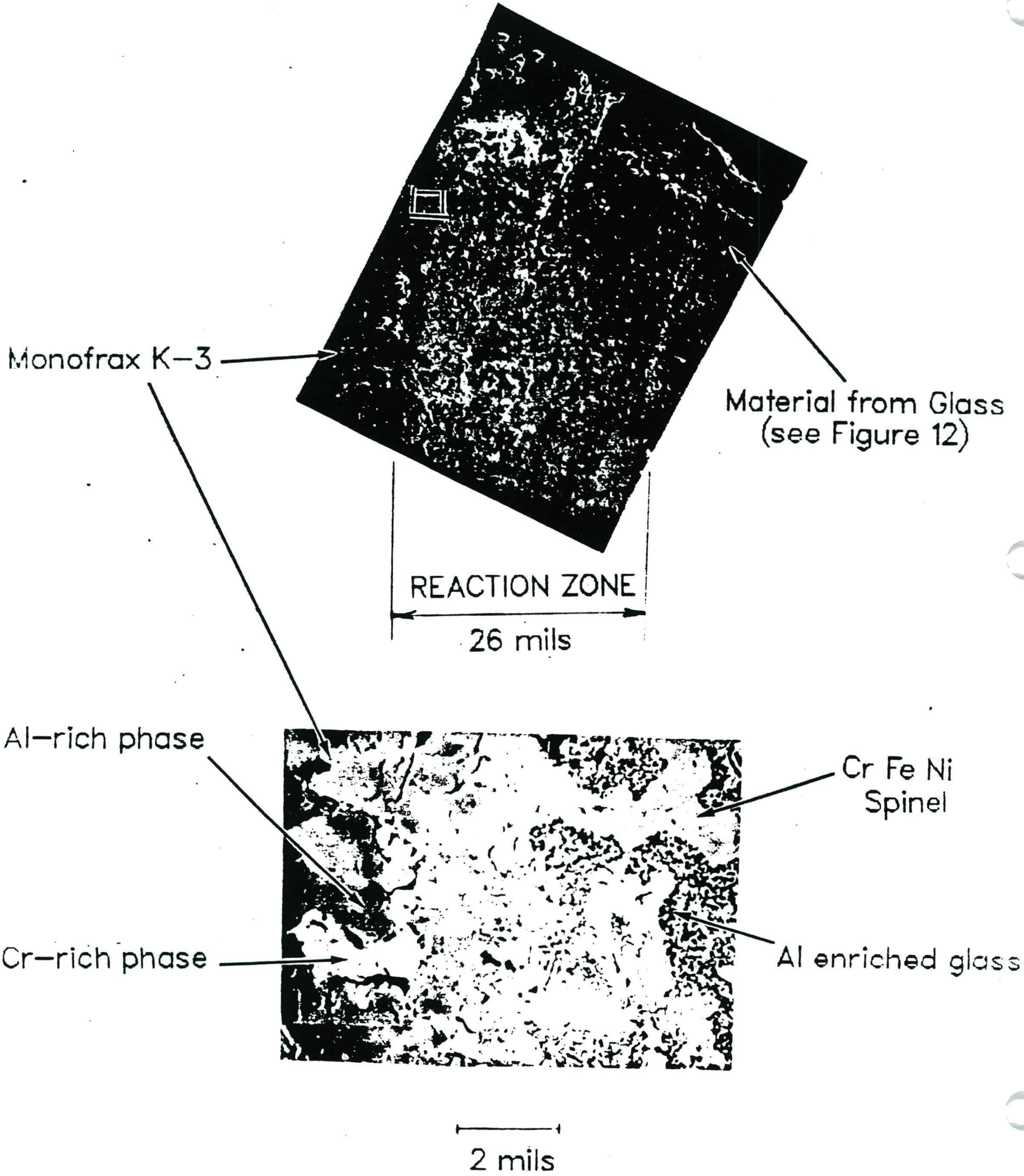


Figure 6

APPROXIMATE TEMPERATURE HISTORY OF 1941 MELTER

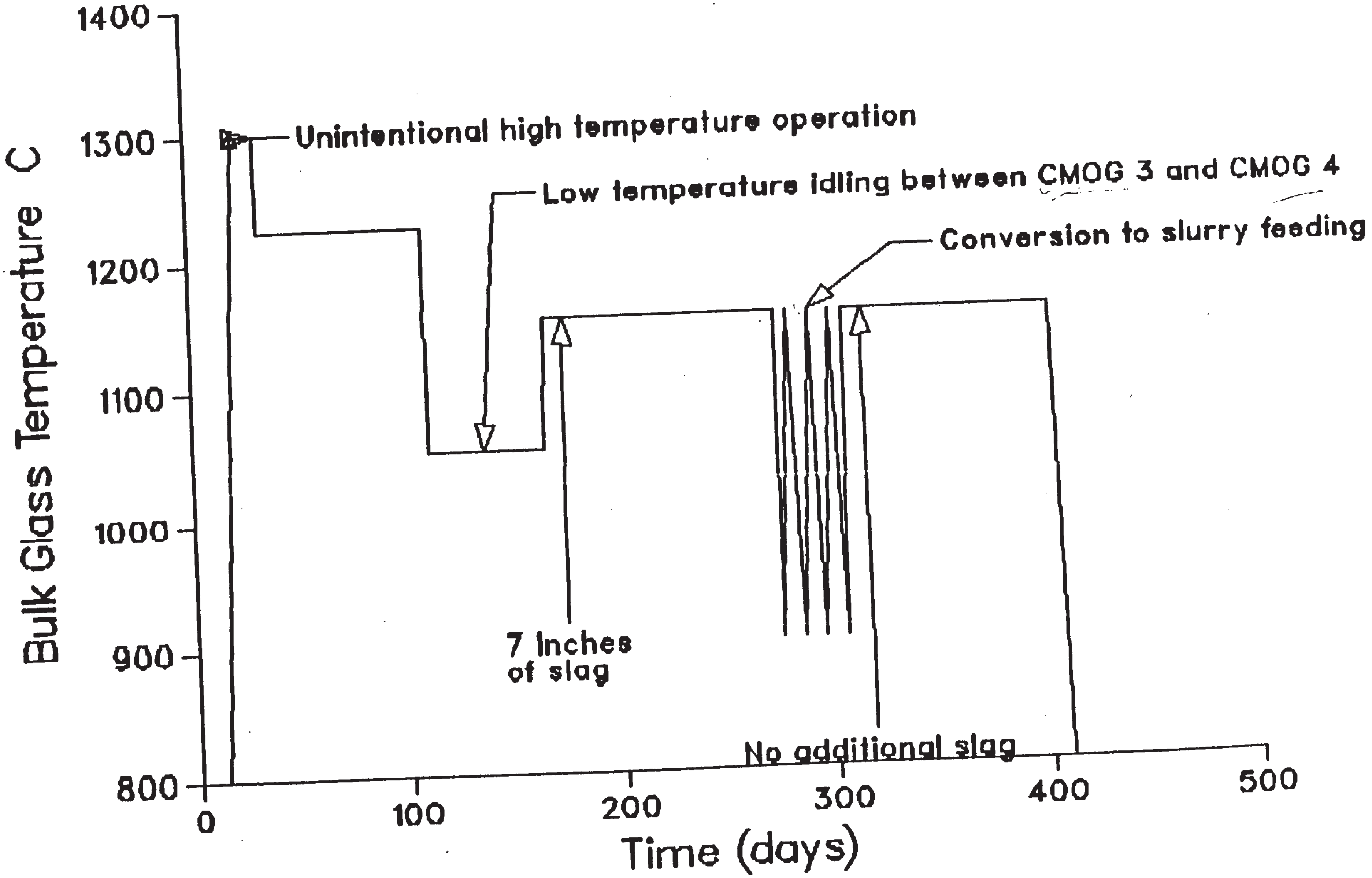
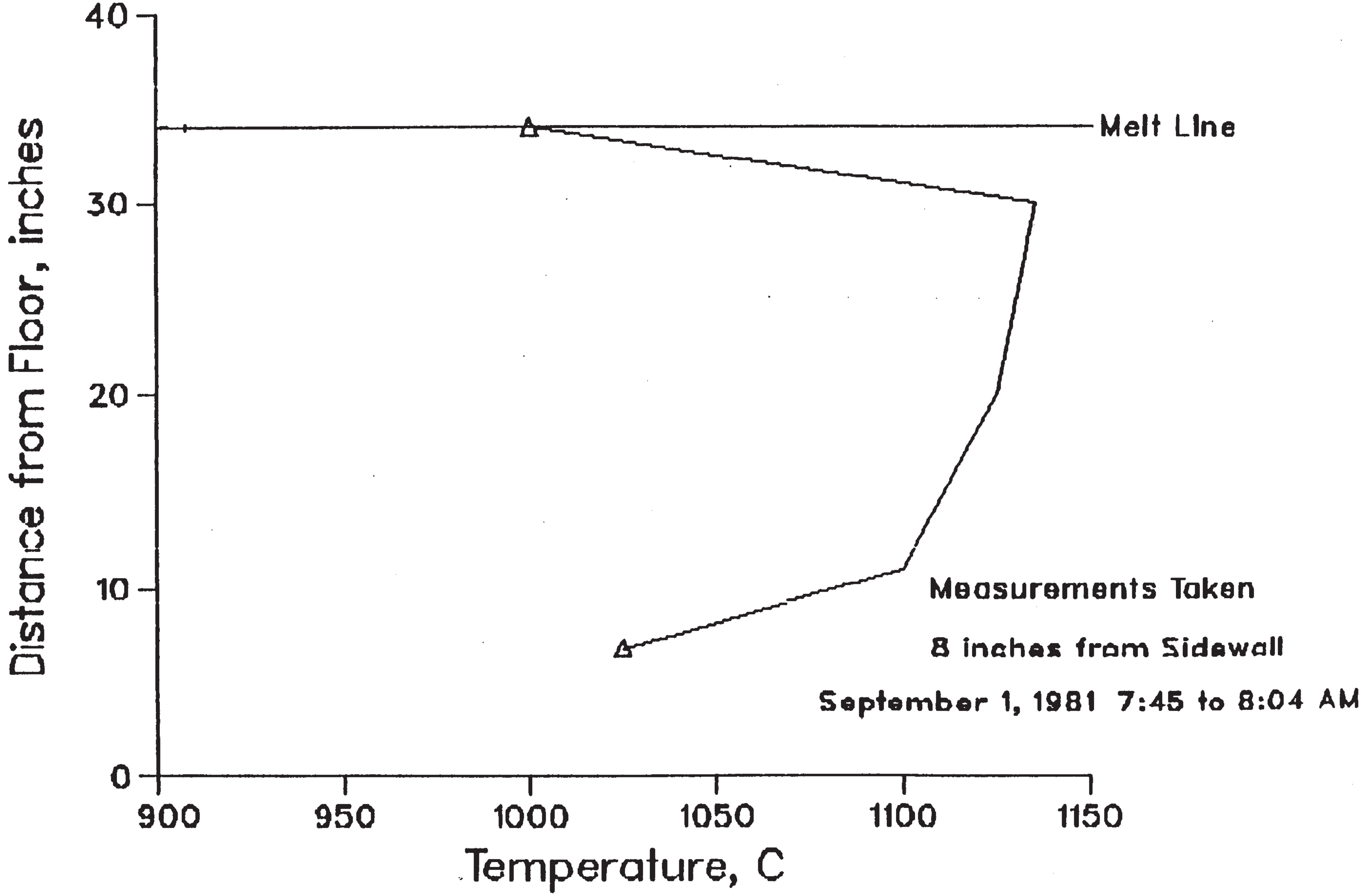


Figure 7

APPROXIMATE 1941 MELTER TEMPERATURE PROFILE



Measurements Taken

8 inches from Sidewall

September 1, 1981 7:45 to 8:04 AM