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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

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MEMORANDUM

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June 5, 1981

TO: L. M. PAPOUCHADO/M. L. HYDER

FROM: G. G. WICKS/W. C. MOSLEY/P. G. WHITKOP/K. A. SATURDAY

DURABILITY OF SRP WASTE GLASS - EFFECTS
OF PRESSURE AND FORMATION OF SURFACE LAYERS

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DURABILITY OF SRP WASTE GLASS - EFFECTS
OF PRESSURE AND FORMATION OF SURFACE LAYERS

INTRODUCTION AND SUMMARY

During repository storage, waste glass products will experience lithostatic pressure (salt, shale) or hydrostatic pressure (shale, granite, basalt and tuff). The exact pressure exerted on the waste glass will depend on the depth of storage and geology involved. As part of the SRP Durability Program[1], the effect of pressure at anticipated storage temperatures on the chemical durability of SRP waste glass was assessed. In addition, surface interactions were examined and corrosion mechanisms discussed. Conclusions from this study are as follows:

- There is no significant effect of pressure up to 1500 psi at 90°C on leachability of simulated SRP waste glass, studied in deionized water.

- The leachability of SRP waste glass at 90°C for one month at pressures of 14.7-1500 psi are in the 5×10^{-5} to 5×10^{-6} g/cm^2-day range, based on silica extraction.

- Leached glass surfaces have surface layers rich in Fe, Mn and Mg. These layers are thought to form primarily as a result of the insolubility of these constituents in the leachate. The presence of these layers indicates (a) minor constituents of waste glass are important during corrosion, (b) surface layer formation should be expected during long-term storage, and (c) layers would be expected to have a beneficial effect on retarding subsequent glass corrosion by inhibiting dissolution processes.

- Under the surface layers, the glass surface was slightly enriched in Fe and Si and slightly depleted in Na. This was a result of primarily diffusion controlled processes which extract modifiers from the network structure of the glass. A modifier deficient or silica rich interface is known to retard additional corrosion.[2]

- Using sample surface area to volume of leachant ratios (SA/V) of 10:1 cm^{-1} and 1:10 cm^{-1}, leachate pH values rose from an initial pH value of about 5 to over 11 and 9, respectively. This shows that a pH increase does occur for simulated waste glass systems studied in distilled water. With an increase in pH, solubility of constituents extracted from the glass could increase significantly and the corrosion mechanisms involved could change from diffusion controlled processes to primarily network dissolution. These effects would increase leachability of waste glass and emphasize the importance and the possible use of buffering materials in controlling these features.

EXPERIMENTAL PROCEDURE

Two sets of tests were completed. All experiments involved leaching waste glass in deionized water for one month using a waste glass composition designated TDS/131, as shown in Tables 1 and 2. The first set of tests, TP-3, studied the corrosion of TDS/131 waste glass at 90°C/14.7 psi and 90°C/1000 psi. A relatively high glass surface area to volume of leachant (SA/V) of 10:1 cm^{-1} was used. In order to accomplish this ratio and accelerate reactions, both glass powder and as-cut slices were used with distilled water in each test.

The second set of tests, TP-4, was conducted at 90°C/14.7 psi and 90°C/1500 psi. These experiments reflected improvements over TP-3 including (a) use of acid washed Teflon® vessels, (b) ultrapure water, (c) slices mounted on edge with no powders involved, (d) individually prepared 600 grit surfaces, and (e) a SA/V ratio of 1:10 cm^{-1}. An oven was used for the 90°C/14.7 psi samples while an autoclave was used in all high pressure experiments. The experimental units and conditions of TP-3 and TP-4 are depicted in Figure 1. Intercomparisons were made of leachability data within TP-3 and also TP-4 as a function of pressure. However, because of the different conditions used in the two sets of tests, direct comparisons between data from TP-3 and TP-4 were not attempted.

ANALYSES

An integrated approach to studying the corrosion process was used. This included combining leachate solution analyses with both bulk and surface studies. Analytical techniques for studying leached glass surfaces have been pioneered by L. L. Hench and coworkers at the University of Florida. These techniques have been further developed at Savannah River for studying waste glass systems. Used in the bulk and surface analyses were optical microscopy, scanning electron microscopy (SEM), x-ray energy spectroscopy (XES), wide angle x-ray diffraction (WAXD), electron microprobe analysis (SEMQ), infrared reflectance spectroscopy (IRRS), electron spectroscopy for chemical analysis (ESCA), and Auger electron spectroscopy (AES). Raman spectroscopy was not successful due to the opaque nature of the waste glasses. Also, profiles of key elements were obtained by three approaches: 1) cross-sectioning the specimens and analyzing the layers by SEMQ, 2) mechanical polishing to various depths and investigating newly formed surfaces by IRRS, and 3) argon ion milling in conjunction with AES. The importance of these techniques to studying glass corrosion is depicted schematically in Figure 2. Following is a brief summary of the advantages and disadvantages of each technique.[3]

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A. Solution Analyses

Silica content of the leachate was determined by colorimetry while sodium, iron, manganese and magnesium were assessed by atomic absorption (AA). Other studies are under way which use inductively coupled plasma spectroscopy (ICP) to analyze the leaching solution. ICP provides a new capability at SRL which will allow routine simultaneous monitoring of many different minor as well as major elements in the leachate. An additional technique, neutron activation analysis (NAA), will also be investigated for possible use on future samples. This method allows analysis of small quantities of glass constituents in the leached solids as well as leached solutions.

B. Bulk and Surface Analyses

● **Optical and Scanning Electron Microscopy** (SEM)

Macroscopic and microscopic features on leached surface layers of glasses were characterized by optical and scanning electron microscopy. Topographical structure on the scale of microns was investigated by optical microscopy. Smaller structural details and better depth of resolution were achieved by scanning electron microscopy (SEM). Future studies will also utilize a new piece of equipment at SRL, the scanning/transmission electron microscope (STEM). This will allow direct correlation of structural features with chemical composition on leached glass surfaces.

● **WAXD**

Wide angle x-ray diffraction (WAXD) was used to study possible structural changes on leached glass surfaces. While amorphous gels do not produce any reflections in the x-ray spectra, reflections can be produced from accumulation of crystals on the surface. If the crystals produced are greater than 1000Å and the crystalline layer formed is a few microns thick, the crystalline interface can be indexed.

● **SEMQ**

The scanning electron microprobe quantometer (SEMQ) produced quantitative elemental analyses of glass surfaces to a depth of 1 to 3μ. Chemical analyses were then determined as a function of depth into the leached layer by obtaining x-ray line profiles from sample cross-sections. This technique was especially useful for glasses with a significant degree of corrosion and containing deep corrosion layers. Since SEMQ can only detect elements heavier than Be, Li in SRL compositions could not be measured by this technique. Also, the amount of B present was below the SEMQ detection limit of 5 weight percent.

● <u>IRRS</u>

Infrared reflectance spectroscopy (IRRS) studied chemical
and structural changes in the leached layer to a depth of
about 0.5μ. Additional information was achieved by
mechanically polishing into the leached layer and obtaining
compositional profiles as a function of depth. Layer thick-
ness could be measured with a precision of ±0.1μm. The IRRS
spectra provides valuable information on cation species
which are bound to the silica network structure.

IRRS was also used as a quality control tool for defining
surface finishes and obtaining a reproducible glass surface
prior to leaching experiments. The IRRS spectra of both
polished surfaces on all specimens used in the TP-4 tests
were recorded prior to leaching. The average peak reflect-
ivity, which is a function of surface quality, was 27.2%
with a standard deviation of 1.4%. All samples outside the
±2 σ region were rejected.

● <u>AES/ESCA</u>

Auger electron spectroscopy (AES) and electron spectroscopy
for chemical analysis (ESCA) were used to study the surfaces
of the leached layers. These techniques are sensitive to a
depth of approximately 50Å, which is the maximum escape
depth of inelastically scattered electrons. Chemical pro-
files of important glass constituents were obtained to a
depth of about 20,000Å into the glass by argon ion milling
coupled with AES. AES was used to identify chemical elements
on the surface, while ESCA provided information on chemical
bonding and oxidation states of selected species. The pro-
blem of ion migration in glass subjected to electron beam
bombardment was addressed. Most ions were depleted by the
electron beam during AES analysis. Sodium was depleted
most rapidly (within two minutes) while most other ions
of importance were depleted at much slower rates (half lives
were on the order of 6-10 minutes). Although absolute
surface concentrations could not be ascertained because of
this phenomenon, relative relationships are still valid,
since care was taken to ensure reproducibility of experi-
mental conditions. Sodium concentrations were determined
by plotting the natural log of the peak height versus
analysis time and extrapolating back to zero time.

GLASS CORROSION MECHANISMS

Two basic corrosion modes are important for SRP waste glasses.[2]
First, alkali or alkaline earth ions can be extracted from the
glass matrix by ion exchange with either hydrogen or hydronium
ions from the solution leaving an alkali-depleted surface layer
behind. This surface layer probably controls the long-term
durability of waste glasses. Ideally, this process is diffusion

controlled and the amount of alkali or alkaline earth ions extracted is proportional to the square root of time in a neutral pH regime. This corrosion mode dominates the initial leaching process and would be expected to be the dominant mechanism for release of Sr and Cs from SRP glass.

The second corrosion mechanism, network dissolution, is a more severe corrosion process in which the Si-O bonds forming the glass network are attacked. This is perhaps the major release mechanism for plutonium ions and the most important corrosion mode for long term storage. Network dissolution can occur to a bulk glass containing no protective layer as well as to a silica rich layer if the silica concentration is not large enough to provide adequate protection. The resulting total dissolution involves equal losses of alkali and silica as the corrosion inter-face moves into the glass. This destructive mechanism has been observed in glass systems immersed in alkali media where the OH⁻ ions attack the Si-O bonds. This is the most important corrosion mode in waste glass systems for pH values greater than 8.5 at 90°C.[4] In addition, accelerated corrosion, by selective etching and/or network dissolution, can also occur for pH values less than about 6.

The two basic corrosion modes of ion-exchange and network dis-solution can be significantly affected by leachant conditions and formation of protective layers on glass surfaces.

RESULTS

A. TP-3 (90°C/14.7 psi, 90°C/1000 psi, SA/V = 10/1 cm⁻¹)

- Leachability and pH Effects

    The leachabilities of samples studied at 14.7 psi and 1000 psi were in the 10^{-5} and 10^{-6} g/cm²-day range. This is a relatively low leachability considering the time and tempera-ture involved and the fact that solution pH values for the oven and autoclave samples rose to 11.68 and 11.14, respect-ively. The pH measurements were made after the solutions cooled to room temperature. At these high leachate pH values, network dissolution, the most detrimental corrosion mode for the glass would be expected.

    Leachabilities were calculated using surface areas deter-mined by BET for powders and geometric surface areas for slices. The presence of the powder, used to achieve a high SA/V ratio, was found to complicate analyses.

    The corrosion of the glass was limited because the leachate became partially saturated in important glass constituents such as silica. This is a result of the high ratio of sample surface area to volume of leachant used and the solubility of silica at the pH value of the leachant. Glass

corrosion was also influenced by thick gel surface layers that formed on each specimen. These layers remained on the glass surfaces even though the glass leachant became very alkaline. Leachability and pH results for TP-3 are summarized in Table 3.

● Surface Analyses

The top surface of the waste glass slices was covered with a thick brown deposit that consisted of glass particles embedded in a gel layer. This deposit is pictured schematically in Figure 3 and shown in more detail in Figure 4. The deposit was composed primarily of glass particles up to 100μ in size which resulted mainly from the glass powder used in the experiment adhering to the top sample surface. The bottom surface of the specimens also contained a gel layer but without the glass powder deposit. SEMQ analyses of both the top and bottom surfaces (Table 4) showed a general enrichment in Mg, Fe, Mn and Ni and a deficiency in Na compared to the bulk glass. Analysis by Auger electron spectroscopy showed that the outermost surface of the deposit on the top of the glass was very rich in silicon (Table 5). This may have resulted in precipitation of silica out of solution due to the localized saturation of silica in the vicinity of the glass powder. The interaction zone was defined by IRRS using mechanical milling techniques to be about 71μm and 63μm deep for the 14.7 and 1000 psi samples, respectively. This zone included the brown deposit and leached glass layers. SEMQ examinations showed that the leached layers on the top and bottom of the glass slices consisted of surface and subsurface layers 2 to 6μ in depth.

IRRS spectra of the surface layers of the glass showed a general depletion of bound cation species, Si-O-X, where X can be cations such as Ca, Mn or Na. The depletion was larger for the high pressure sample. IRRS analysis does not preclude the existence of compounds of elements such as Mg, Fe, or Mn but indicates that if these constituents do concentrate on the surface they are bound to the random network structure of the glass.

SEMQ analyses showed the surfaces to be composed of two distinct layers. Surface layers were depleted in Na and enriched in Mg, Fe, Mn and Ni relative to the bulk glass. Subsurface layers were depleted in Mg and Na and enriched in Ca, Fe, Mn, Ni, Ti, Al and Si relative to the bulk glass. Cracks extended through these surface layers into the glass.

Elemental x-ray intensity profiles of cross sections of the deposited film and bottom surfaces of the 14.7 and 1000 psi samples are shown in Figure 5 through 7. Wide angle x-ray diffraction of the surfaces of the leached glasses revealed no crystalline phases.

B. **TP-4 (90°C/14.7 psi, 90°C/1500 psi, SA/V = 1/10 cm^{-1})**

- **Leachability and pH Effects**

  The leachabilities of samples studied at 14.7 psi and 1500 psi were in the 10^{-4} to 10^{-5} g/cm^2-day range based on silica extraction. The leachability of the high pressure sample was actually slightly less than that of the sample studied at atmospheric pressure. The corrosion of the glass was again influenced by partial saturation of silica in solution at the pH value of the leachant and by surface layers that formed. The pH of leachate solution for the 14.7 and 1000 psi samples rose from 4.68 to 9.6 and 9.4, respectively, for the 30 day tests. The results of TP-4 are summarized with TP-3 in Table 3.

- **Surface Analyses**

  The surfaces of the 14.7 and 1500 psi waste glass slices contained thinner leached zones than in the previous experiments. IRRS spectroscopy defined a corrosion or leached zone of about 5.6μ for the 14.7 psi sample and only 1.8μ for the 1500 psi specimen. SEMQ analyses showed the leached glass surfaces had only single surface layers but these layers were composed of at least two distinct phases. No brown deposit was observed. (No glass powders were used in TP-4 experiments.) A significant difference existed in the morphologies of the surfaces of the two specimens. The surface layer of the 14.7 psi sample was hard and very brittle and flaked off easily. There was extensive cracking between this layer and the glass beneath. In contrast, the surface layer of the 1500 psi sample was a gold colored film that appeared to be very adherent to the glass but could be scraped off. These surface layers and the glass surfaces below the layers are shown in Figure 8.

  IRRS spectra of the leached layer again indicate a general depletion of bound cations and oxide species in the surface layer. Consistent with TP-3, TP-4 experiments indicate that the depletion is greater on the surface of the high pressure sample.

  The leached layer was examined in more detail by SEMQ. Consistent with the previous experiments, the surface layer was again very depleted in Na and slightly depleted in Si. Also noted was a greater than 200% increase in Fe content in the surface layer compared to the bulk glass. The surface layers of both the 14.7 and 1500 psi samples were also generally enriched in Ca, Ti, La, Mn, Ni, Mg and Zr (Table 7). Glass surfaces exposed where the surface flaked off of the 14.7 psi sample and where the surface layer was scraped off of the 1500 psi sample were slightly enriched in Fe and Si and slightly depleted in Na relative to the bulk glass. Elemental x-ray intensity profiles

of the surfaces of the 14.7 and 1500 psi samples are
shown in Figures 9 and 10.

Auger spectroscopy was used to examine the outermost portion
of the surface layer and to obtain depth profiles of major
elements within the leached surface of the glass.   At 15$\overset{\circ}{A}$
into the surface, the approximate escape depth of electrons
in glass, a general depletion of Si and Na was observed
compared to the bulk glass. Within this outermost region,
most of the other minor constituents within the glass were
found in relatively large quantities compared to the bulk
material (Table 8). The data suggest that minor constituents
may be absorbed onto the glass surface during the leaching
operation.

About 1300$\overset{\circ}{A}$ (0.13μm) into the surface, maxima in Fe, Al,
Mn and O concentrations were observed. Also noted at this
position was a corresponding minimum in Si concentration.
The Mg concentration was largest on the outermost surface
of the sample and continually decreased into the surface
layer. Depth profiles of major elements show in general a
constant concentration between 0.5μ and 2.0μ as shown in
Figure 6. Near 2μm, which would begin the subsurface glass
region, the Si concentration starts to increase and con-
centrations of Fe, Al and O show a decreasing trend. With-
in this 2μ surface layer, a large depletion in Si and Na
was observed and a large excess of Fe, Mg and Mn was also
noted along with increased quantities of Al and Ni, when
compared to the composition of the bulk glass. These data
were consistent with SEMQ analyses of this layer.

ESCA spectra were obtained for the high pressure TP-4 sample.
Prominent peaks in the spectrum showed oxygen, carbon and
silicon. A smaller peak indicated the presence of iron.
The effect of surface charging was assessed by comparing
experimental binding energies to literature values. The
bulk of the iron on the glass surface was indexed as Fe^{3+}.
The Fe^{3+}/Fe^{2+} ratio could not be quantitatively determined
due to the small peak height and low signal to noise ratio.

INTERPRETATIONS AND CONCLUSIONS

A. Effects of Temperature and Pressure

The effect of temperature on dissolution of silica within the
glass is shown in Figure 7.[4] In general, within the neutral
range of pH values, silica dissolution increases less than a
factor of ten for leaching at room temperature compared to
leaching performed at 90°C. However, for solutions containing
either very high pH values or very low values, dissolution
can be significantly increased.

As temperature is increased, the region of diffusion controlled dissolution becomes narrower (see Figure 7). For very high temperatures (over 300°C), the dissolution curve should be very narrow and network dissolution would be expected to be the dominant corrosion mode. Hence, different corrosion mechanisms are applicable for high temperature leaching studies. These data indicate that one cannot realistically simulate leaching of waste glasses in long term storage at lower temperatures by accelerated tests performed at high temperatures, unless the pH is carefully controlled.

There were no significant effects of pressure up to 1500 psi at 90°C on leaching of SRP waste glass. This observation was made for leaching in distilled water for one month using both high and low SA/V ratios. However, there was a difference in morphology of the glass surface layers. The high pressure glass contained a more adherent surface layer.

B. Surface Layer Formation

In general, the formation of surface layers would be expected to retard subsequent glass corrosion. On samples of TP-3 (SA/V = 10/1 cm), a dual surface layer was observed. The surface consisted of an adsorbed film over an alkali depleted subsurface. For samples of TP-4 (SA/V = 1/10 cm^{-1}), the subsurface region was much less defined and SEMQ and Auger data only suggest silicon enrichment. The outermost surface layer on the glass was an adsorbed film that resulted primarily from saturation effects and precipitation of minor elements out of solution onto the glass surface. It is interesting to note that these layers remain intact even in relatively alkaline solutions.

The importance of silica saturation would be expected to increase as solution pH increases. However, in the neutral pH range, silica solubility does not change appreciably, but for high pH values, solubility changes can be very significant (Table 9). The leachant solution used in TP-3 was saturated with silica quickly due to the high SA/V used. For TP-4, a much lower SA/V was used and hence, the solution was relatively dilute. While the importance of partial or total saturation of silica is generally recognized, saturation effects due to minor constituents are not always fully considered. This is a feature that distinguishes the more familiar simple glass systems from waste glasses.

An element found in very large quantities on the leached glass surface, even in dilute solutions, was iron. Qualitative calculations of the solubility of hydroxides of Fe^{2+} and Fe^{3+} show large differences due to oxidation state.[5] For example, Fe^{3+} has a solubility of only 10^{-23} while Fe^{2+} has a solubility of 10^{-5} moles/ℓ for a solution pH of 9. The solubility of silica has been reported to be in the 10^{-3} moles/ℓ range.[6] This suggests that Fe^{2+} may be less soluble than silica but

Fe^{3+} is very much less soluble (twenty orders of magnitude difference). Therefore, if iron exists and is present as Fe^{3+}, it could precipitate out of solution and adhere to the glass surface. This may include iron in the form of compounds such as ferric hydroxides (FeOOH or $Fe(OH)_3$ or complexes such as acmite ($NaFeSi_2O_6$). The presence of Fe^{3+} suggests oxidizing conditions. ESCA further suggests that the bulk of the iron on the surface of the leached layer of the glass is in the +3 state.

The adsorbed surface layer appeared inhomogeneous. The chemical composition and morphology of this layer would indicate that as a protective film, it would be less effective than the alkali depleted subsurface layer in retarding diffusion controlled corrosion of the glass. However, the data also suggest that the film may protect the silica enriched subsurface and hence, retard glass corrosion via network dissolution. If this can be substantiated, film formation would have a beneficial effect by retarding release of actinides during long term storage. In addition, the high pressure sample in TP-4 contained a very adherent film compared to the cracked, brittle flaky layer of the 14.7 psi specimens. The difference in morphology may be due to the different redox conditions of the tests and subsequent oxidation states and complexes found on the surface of the glasses. The 14.7 psi samples were tested in an oven (open system) and the high pressure samples in an autoclave with helium environment (closed system).

C. Corrosion Kinetics Due to Solution pH and SA/V

One of the most important parameters defining glass corrosion is the pH of the leachant solution. In an earlier study, a parabolic relationship was found between glass corrosion and solution pH.[4] For SRP waste glass studied at $90^{\circ}C$, glass corrosion was minimum for solution pH values between 6 and 8.5. Above pH 8.5 and below pH 6, corrosion increased significantly as shown in Figure 12. These data suggest a diffusion controlled process ($t^{\frac{1}{2}}$ kinetics) between pH 6 and pH 8.5 and primarily network dissolution (t kinetics) above pH 8.5. Below pH 6 accelerated corrosion by selective etching and perhaps some network dissolution also occurs. Initially, the pH value of leachants used in experiments TP-3 and TP-4 was about 5. This pH value dropped to even lower values in the first stages of the experiments due to extraction of fluorine from the Teflon® containers and production of HF in solution. However, very quickly the pH value will rise to the 6 to 8.5 range as the glass begins to corrode in deionized water. This is a result of the ion exchange processes in which the alkali and alkaline earth ions of the glass immediately exchange with either hydrogen or hydronium ions of the water leachant. This results in an increased OH^- content of the solution and accompanying increase in solution pH. Also resulting from this process is a silica enriched surface and other possible protective surface films that

may be produced by dealkalization, surface reactions or pre-cipitation from solution. As long as these barriers exist, the kinetics of the corrosion process will be retarded. When the solution pH exceeds the critical pH value for SRP waste glass of 8.5 at 90°C,[4] a transition from the diffusion con-trolled reactions and $t^{\frac{1}{2}}$ kinetics to network dissolution and t kinetics occurs. This mode of corrosion can destroy surface layers and greatly accelerate corrosion. Therefore, it is very desirable to retain solution pH values in the 6 to 8.5 range for SRP waste glass at 90°C.

The pH of the leachant solution is affected by many factors including the ratio of sample surface area to leachant volume, SA/V. For the TP-3 tests which used a relatively high SA/V of 10:1 cm^{-1}, the change from $t^{\frac{1}{2}}$ kinetics below 8.5 to t kinetics about 8.5 occurred quickly. This is reflected in the high final leachate pH values of over 11. In contrast to this experiment, TP-4 had a SA/V of 1:10 cm^{-1} and hence, took longer to reach the critical pH value of 8.5. This is consistent with the lower final pH values of the leachate of over 9.

In general, it would be anticipated that the larger the pH value over 8.5, the greater would be glass corrosion in the network dissolution mode. However, for large SA/V, partial and total saturation of important minor and major ions, such as silicon, can occur which will retard subsequent corrosion. The resulting supersaturated solutions could result in pre-cipitation products and other reactions which could produce adsorbed layers on the surface of the glass. Therefore, there are two competing effects associated with SA/V that affect glass corrosion: changes in pH and saturation of the solution.

D. Relevence to Repository Storage

The most important potential leachants in a repository are ground waters. The ground water composition, which will vary even for a specific geologic site, could affect the chemical durability of the product. Depending on the characteristics and composition of the ground water, the pH of the solution could decrease or increase during leaching. In addition, saturation conditions could also be affected. These changes would, therefore, determine the degree of glass corrosion by affecting the corrosion mechanisms involved as well as form-ation of layers on the surface of the glass. For example, the presence of sodium ions in a brine solution would increase the pH of the leachant and hence, could accelerate corrosion of the glass, unless the solution is buffered by other con-stituents within the ground water. In the case of silicate ground waters, the leachant will tend to saturate more quickly with silicon during leaching. Therefore, this would have a beneficial effect on retarding subsequent glass corrosion.

In a practical sense, the use of buffer materials and other elements of the multibarrier system could control the pH of the potential leachant and the subsequent long term durability of the product.

Repository temperatures will depend on waste loading, age and heat content of the waste, canister spacings, multiple barriers that are used and the geology of the site. With acceptable canister spacing, the temperatures generated for SRP defense waste will be less than 100°C. This is a very advantageous range of temperatures. For example, for SRP Stage 1 glass containing 15 year old waste, the canister surface temperature will be about 90°C in either a salt or granite repository. This temperature would exist for a loading of 226 watts per canister and canisters spaced edge to edge about four feet apart.[7] Temperatures in other geologic media could be slightly higher.

The hydrostatic and lithostatic pressures are a function of the depth of burial and geology involved. Realistic pressures within a repository may range from less than 10MPa to 33MPa (1450 psi to 4786 psi) depending on these conditions. The pressure used in the present study of 1500 psi, approximates the hydrostatic pressure exerted on the product at a depth of about 100 meters. This pressure also represents the upper limit of pressure possible with existing equipment and facilities. At 1500 psi, no significant changes in leachability were observed and no new potentially detrimental mechanisms were noted. Therefore, this suggests that even higher pressures would not be expected to adversely affect the chemical durability of the waste glass.

As suggested in laboratory-scale tests, the oxidation-reduction potential of the solution may affect the chemical and mechanical properties of surface layers and the subsequent protective nature of the outermost glass region. More studies are needed in this area to determine the general importance of solution pH on glass dissolution.

The surface area to leachant volume ratio (SA/V) could be influenced by the properties of the multiple barriers in retarding or preventing water from contacting waste glass, especially during the thermal period. The SA/V ratio will also depend on the geology involved. For example, a salt repository will be very dry while other potential geologic sites, such as basalt, granite, tuff or shale will eventually contain water after the repository is sealed. Even in the relatively dry salt site, the canister temperatures will cause any limited amount of water present to seek the heat source, i.e., canister of waste glass. A final consideration which could affect SA/V is the possibility of flooding in the repository geology that is finally selected.

The flow of ground waters can also have an important effect on glass corrosion. Ground water flow will affect the pH of the leachate in contact with the glass as well as the solubility of glass waste constituents. In addition, the dynamic flow of waters, including velocity and any cyclic effects, could mechanically affect the growth and retention of surface layers. A repository site containing fast moving, dilute ground waters which allows an increase in pH around the glass but prevents saturation from occurring, might be considered a worst case with respect to glass leaching.

GGW/WCM/PGW/KAS:lmn

REFERENCES

1. G. G. Wicks and M. D. Dukes, "Durability of SRP Waste Glasses - Program Document," DOE Report DPST-80-542, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, September 1980.

2. D. E. Clark, C. G. Pantano and L. L. Hench, Corrosion of Glass, Magazines for Industry (1979).

3. M. D. Dukes, W. C. Mosley and K. A. Saturday, "Joint CTD-ACD Program to Determine Mechanisms of Glass Leaching," DOE Report DPST-79-485, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, October 1979.

4. G. G. Wicks, "Durability of SRP Waste Glasses - Effect of Ground Water pH," DOE Report DPST-80-675, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, November 1980.

5. R. M. Wallace, personal communications.

6. P. B. Macedo, personal communications.

7. N. E. Bibler, personal communications.

Table 1

TDS/131 WASTE GLASS COMPOSITION*

A.   131 Glass Frit

SiO_2	57.9 Wt %
Na_2O	17.7
B_2O_3	14.7
TiO_2	1.0
Li_2O	5.7
MgO	2.0
ZrO_2	0.5
La_2O_3	0.5

B.   TDS Simulated SRP Waste

Fe_2O_3	43.2 Wt %
Al_2O_3	3.9
MnO_2	12.2
U_3O_8	4.1
CaO	3.2
NiO	5.4
SiO_2	3.9
Na_2O	8.8
Na_2SO_4	1.2
Ion-Siv IE 95	9.1

*Starting composition consisted of
 72% 131 Frit and 28% TDS waste.

Table 2

SEMQ ANALYSIS OF IMPORTANT ELEMENTS IN TDS/131 WASTE GLASS*

Component	Content w/o
Ca	0.5
Ti	0.4
La	0.3
Fe	0.1
Mn	2.5
Fe	9.1
Ni	0.7
Zr	0.2
Na	13.1
K	0.1
Mg	0.7
Al	2.4
Si	22.2
S	0.1

*Chemical composition of solidified product, Li and B not detected by SEMQ analysis. Calculated standard deviation for all elements is < 0.1 w/o.

Table 3

LEACHABILITY AND pH DATA

Sample	SA/V (cm^{-1})	T(°C)	P(psi)	Leachant	Initial pH	Final pH	Leachability g/cm^2-day* Silica	Sodium
TP3-1**	10:1	90	14.7	Deionized Water	5.10	11.68	6.8×10^{-6}	2.97×10^{-5}
TP3-2			1000			11.14	9.7×10^{-6}	4.25×10^{-5}
TP4-1	1:10	90	14.7	Ultra Pure Water	4.68	9.66	7.5×10^{-5}	12.59×10^{-5}
TP4-2						9.65	7.6×10^{-5}	12.96×10^{-5}
TP4-3			1500			9.34	4.5×10^{-5}	6.79×10^{-5}
TP4-4						9.44	4.3×10^{-5}	6.26×10^{-5}

*Leachability tests conducted for 30 days.
**TP-3 sample surfaces were as-cut, TP-4 samples surfaces were polished.

Table 4

TP-3

SEMQ ANALYSES* OF SURFACES OF TDS/131
WASTE GLASS LEACHED FOR 30 DAYS AT 90°C

Component	Bulk Glass	14.7 psi		Bottom Surface	1000 psi		Bottom Surface
		Top Surface			Top Surface		
		Rough	Smooth		Rough	Smooth	
Ca	0.5	0.5	0.4	0.7	0.3	0.4	0.5
Na	13.1	4.5	4.0	2.9	2.4	2.2	2.5
Mg	0.7	1.4	1.2	1.8	**	**	2.1
Fe	9.1	12.3	12.6	14.1	12.0	12.2	12.8
Mn	2.5	3.3	3.2	3.9	3.6	3.6	3.8
Ni	0.7	0.9	0.9	1.0	1.0	1.0	1.3
Ti	0.4	0.5	0.5	0.5	0.5	0.5	0.6
Al	2.4	2.6	2.6	2.5	1.7	2.1	2.2
Si	22.2	23.0	21.9	23.1	19.4	21.1	20.6

*Compositions in weight percent.
**Not measured.

Table 5

TP-3

AUGER ANALYSES* OF TDS/131
LEACHED IN DISTILLED WATER FOR
30 DAYS AT 90°C

Element	Bulk Glass	Leached at 14.7 psi Analyses of Particle Surfaces Adhered to Glass	Leached at 1000 psi Analyses of Particle Surfaces Adhered to Glass
Fe**	2.3***	4.2	2.6
Ni	0.4	Trace	Trace
Mg	0.7	2.8	6.1
Al	3.1	5.4	5.0
Si	59.9	65.0	65.7
Na	1.1	2.6	Trace
Mn	Trace	Trace	0.9
B	Trace	Trace	Trace
Ca	0.7	0.7	Trace

---

*Sensitivity factors used to determine composition were calculated for pure elements—factors for waste glass not now available. Hence, only relative differences in composition important. Absolute values of composition must still be normalized.

**Only the important elements with respect to glass corrosion mechanisms have been listed. Other constituents, such as carbon and oxygen omitted.

***Composition in atomic percent. Peak heights measured with a relative standard deviation of three percent.

Table 6

TP-3

SEMQ ANALYSES OF TDS/131 LEACHED
IN DISTILLED WATER FOR 30 DAYS AT 90°C
BOTTOM OF SAMPLE*

| Component | Bulk Glass | Leached at 14.7 psi | | Leached at 1000 psi | |
		Surface Layer (Max-Min)**	Subsurface Layer (Max-Min)**	Surface Layer (Max-Min)**	Subsurface Layer (Max-Min)**
Ca	0.5	0.8-0.3	0.9-0.5	0.7-0.0	1.0-0.5
Na	13.1	4.4-2.9	16.5-4.4	4.5-3.8	3.8-2.9
Mg	0.7	2.2-0.7	0.7-0.3	3.7-3.3	0.5-0.1
Fe	9.1	12.9-6.8	12.9-9.1	5.1-5.1	12.0-11.3
Mn	2.5	3.4-3.3	3.4-2.2	3.5-1.9	3.5-2.9
Ni	0.7	1.1-0.9	0.9-0.7	1.4-0.5	1.3-0.7
Ti	0.4	0.4-0.1	0.7-0.4	0.6-0.1	0.7-0.4
Al	2.4	2.5-1.5	3.0-2.5	3.6-1.9	3.9-3.1
Si	22.0	22.0-20.2	22.9-22.7	30.5-14.0	25.3-23.4

*Bottom of sample did not contain adherent glass particles.
**Composition in weight percent relative to bulk glass as determined from x-ray intensity line profiles.

Table 7

TP-4

SEMQ ANALYSES* OF TDS-131 LEACHED IN DISTILLED WATER FOR 30 DAYS AT 90°C

Element	Bulk Glass	Leached at 14.7 psi		Leached at 1500 psi	
		Surface Layer	Glass Under Surface Layer**	Surface Layer	Glass Under Surface Layer**
Ca	0.4*	1.1	0.6	1.0	0.5
Cs	0.0	0.0	0.0	0.0	0.0
Ti	0.4	1.0	0:5	0.9	0.4
La	0.3	0.6	0.4	0.6	0.4
Ce	0.1	0.1	0.1	0.1	0.1
Nd	0.1	0.1	0.1	0.2	0.1
Mn	2.2	7.0	2.3	5.4	2.4
Fe	8.9	25.6	9.6	20.9	9.6
Ni	0.3	1.2	0.3	0.9	0.3
Zn	0.0	0.0	0.0	0.0	0.0
P	0.1	0.1	0.0	0.0	0.0
Zr	0.3	0.4	0.3	0.5	0.4
S	0.1	0.0	0.1	0.1	0.2
Cl	0.0	0.0	0.0	0.0	0.0
F	0.0	0.0	0.0	0.0	0.0
Na	12.8	0.8	10.8	1.9	11.5
Mg	0.9	3.1	0.8	2.1	0.9
Al	2.3	3.0	2.3	2.4	2.1
Si	15.9	9.6	16.4	10.1	16.4
Sr	0.0	0.0	0.0	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0
K	0.0	0.0	0.0	0.0	0.0

*Composition in weight percent.
**Analysis of area where surface layer flaked off.
***Analysis of area where surface layer was scraped off. Areas under surface layer show slightly higher Fe and Si content and slightly lower Na content than bulk glass.

Table 8

TP-4

AUGER ANALYSES OF TDS/131
LEACHED IN DISTILLED WATER FOR 30 DAYS AT 90°C

Element	Bulk Glass	Leached at 14.7 psi Outermost Surface Layer (15A)	Leached at 1500 psi Outermost Surface Layer (15A)
Fe	2.3*	6.1	3.2
Ni	0.4	0.8	2.5
Mg	0.7	5.0	10.7
Al	3.1	12.9	0.5
Si	59.9	40.7	37.8
Na	1.1	Trace	Trace
Mn	Trace**	Trace	1.1
B	Trace	Trace	Trace
Ca	Trace	Trace	Trace

*Composition in relative atom percent. Peak heights measured with 3% standard deviation.
**Trace denotes less than 0.1 atom percent.

Table 9

SOLUBILITY EFFECTS

A. Solubility of Amorphous Silica as a Function of Solution pH

pH	SiO_2 Solubility[5] $(X10^{-3})$ moles/ℓ
5	1.8
6	1.8
7	1.8
8	1.8
9	2.1
10	4.4
11	31
12	666

B. Silica Concentrations in TP-3 and TP-4

	SA/V	Pressure	pH	Conc.
TP-3	$10/1cm^{-1}$	14.7 psi	11.7	9.65×10^{-3} moles/ℓ
		1000 psi	11.1	13.68×10^{-3} ($\sim$43% Saturation)
TP-4	$1/10cm^{-1}$	1.47 psi	9.7	0.92×10^{-3}
		1500 psi	9.4	1.60×10^{-3} ($\sim$53% Saturation)

Retardation in leachability has been observed at 30% of silica saturation.[6]

FIGURE 1
EXPERIMENTAL UNITS

TP-3

SA/V = 10/1 cm⁻¹

TEFLON® CONTAINER

DEIONIZED
WATER LEACHANT

GLASS SLICES

GLASS POWDER
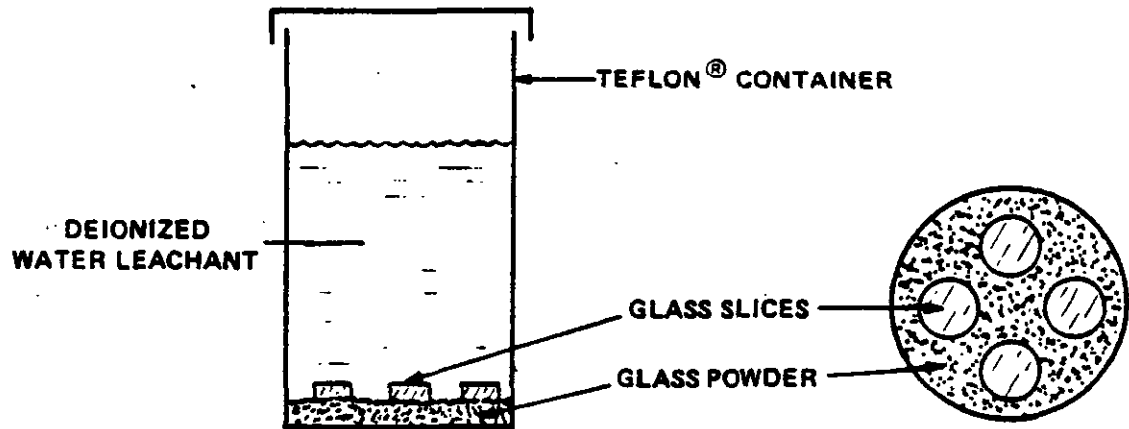
Samples at 90°C/14.7 psi & 90°C/1000 psi

TP-4

SA/V = 1/10 cm⁻¹

TEFLON® CONTAINER

ULTRA PURE
WATER LEACHANT

GLASS SLICES

TEFLON MESH
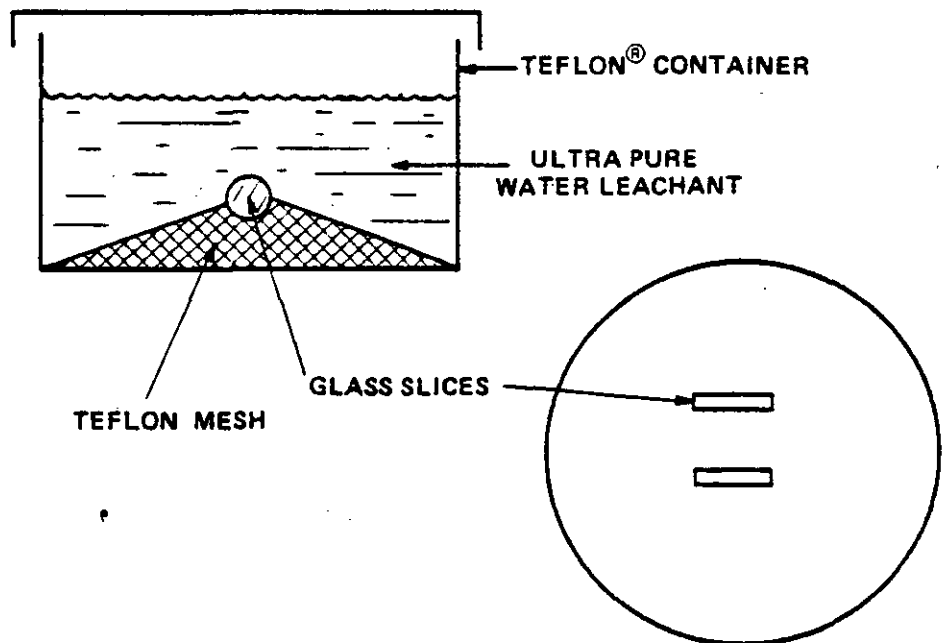
Samples at 90°C/14.7 psi & 90°C/1500 psi

®Teflon is a registered trademark of DuPont

FIGURE 2

ANALYSES OF CORROSION LAYERS*

WAXD

SEMQ

SEM/XES

IRRS

AES/ESCA

SOLUTION
ANALYSES
(AA, ICP)

SURFACE
FILM

5-50Å

0.5μ

SURFACE
LAYER

CORROSION
LAYERS

1.5μ

1-3μ

SUBSURFACE
LAYER

10μ
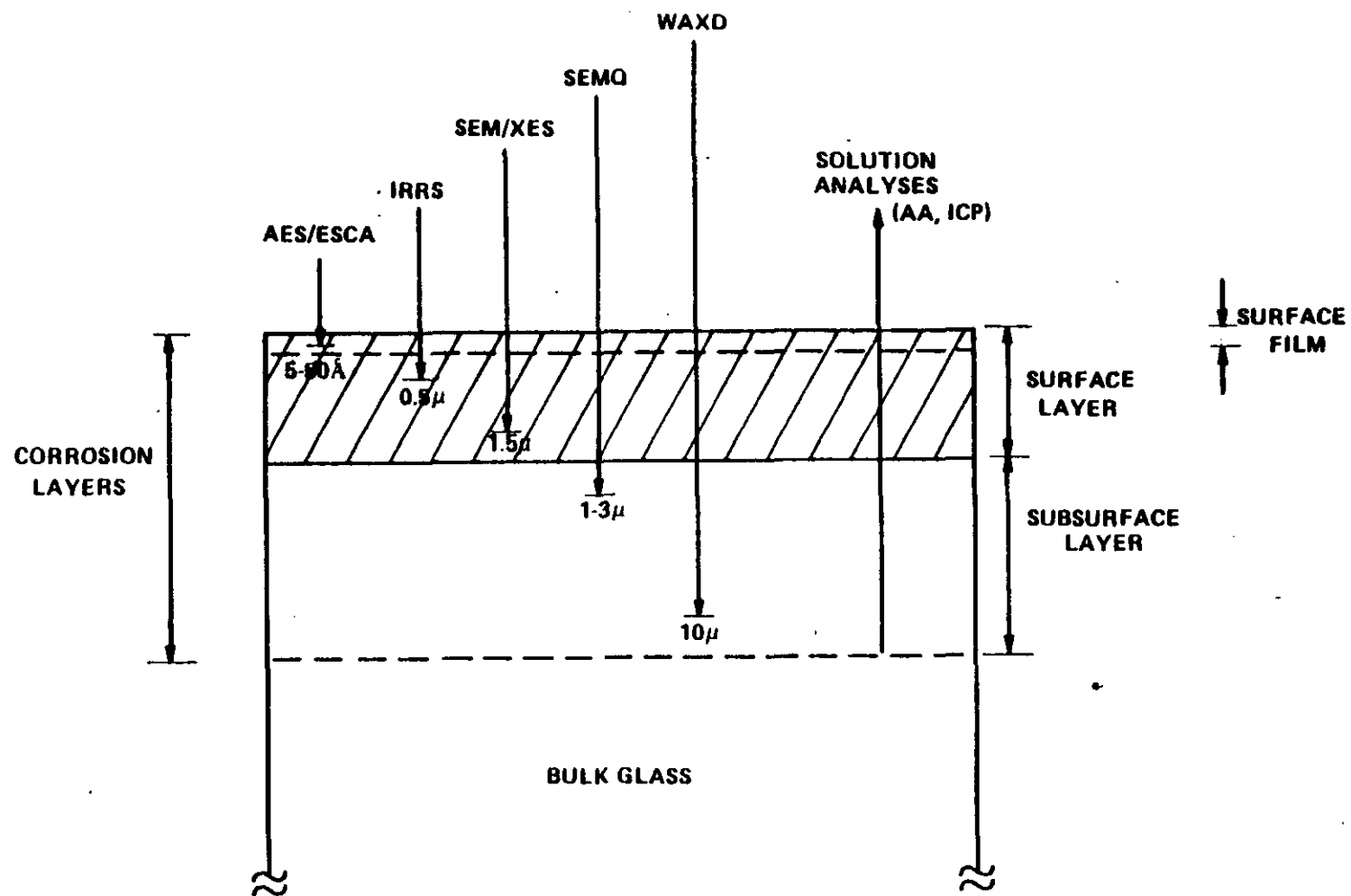
BULK GLASS

*Beam penetration generally increases with voltage (kV) and decreases with increasing sample density (ρ) and average atomic number (Z). The surface layer most likely has different Z and ρ than the bulk glass so the estimated range of penetration given is approximate.

FIGURE 3

SCHEMATIC REPRESENTATION ON SURFACE LAYERS

TP-3 SA/V = (10/1)cm^{-1}

VERY ROUGH GEL SURFACE
SURFACE LAYER
SUBSURFACE REGION
CRACKS
BULK GLASS
14.7 psi/90°C
1000 psi/90°C
63μ
1·5μ
2·3μ
71μ
3·5μ
0·5μ
2·3μ
2·3μ

TP-4 SA/V = (1/10)cm^{-1}

HARD SURFACE LAYERS
BRITTLE
ADHERENT
SUBSURFACE REGION
CRACK
14.7 psi/90°C
1500 psi/90°C
(NO CRACKS)
2·4μ
3·5μ
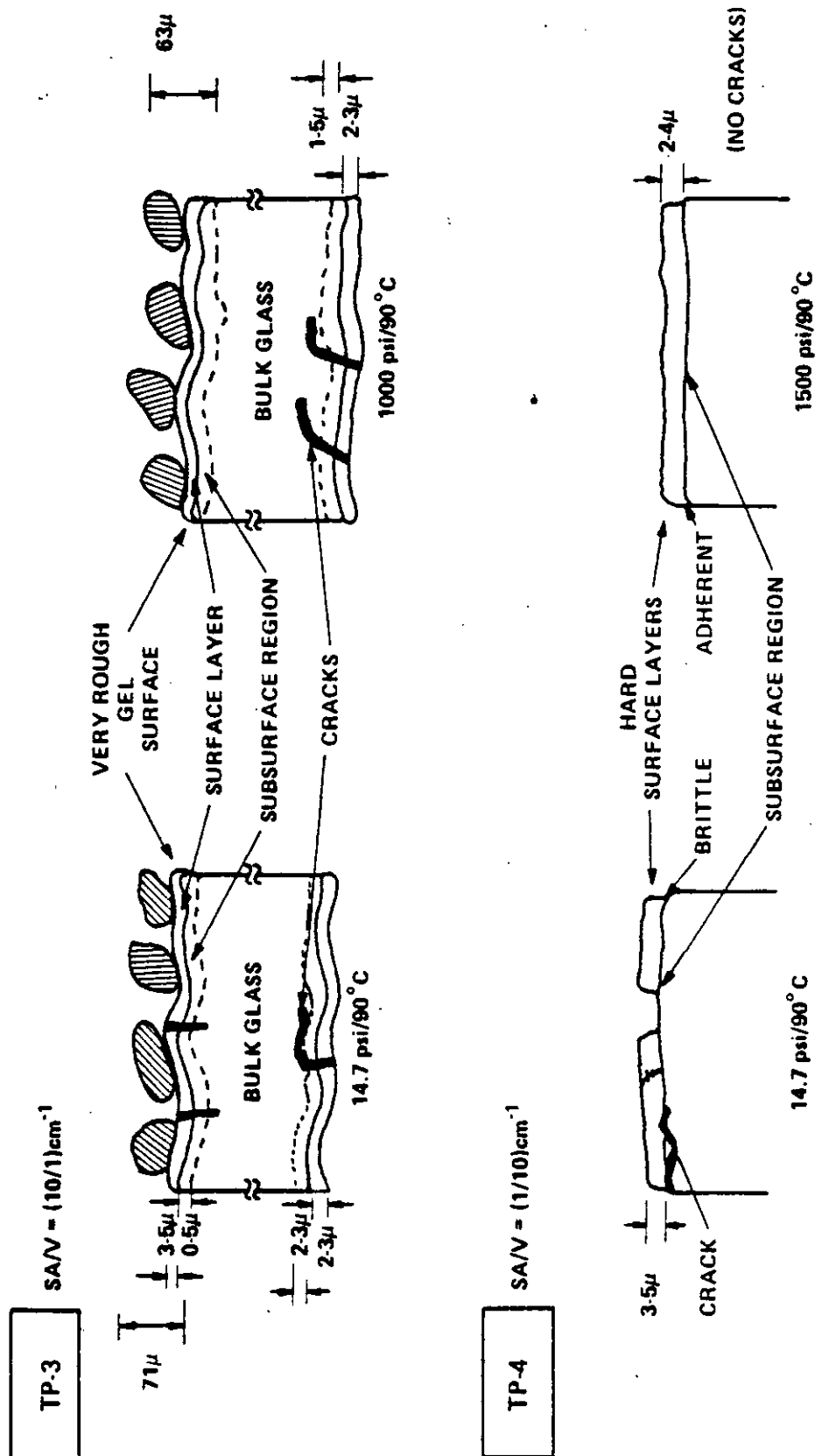
FIGURE 4.   Glass Surface Layers at TP-3
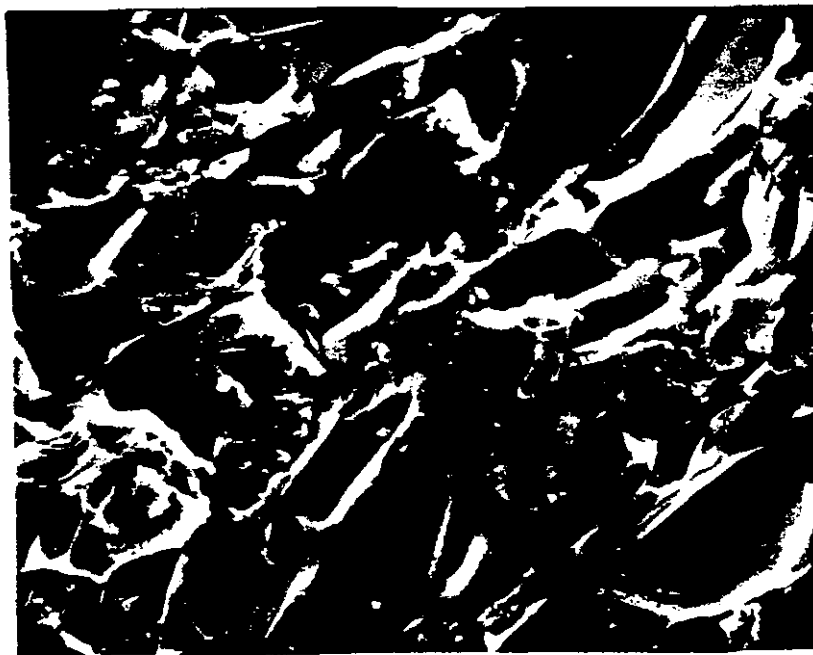
90°C/14.7 psi   1600X   As-cut   1600X   90°C/1000 psi   1600X
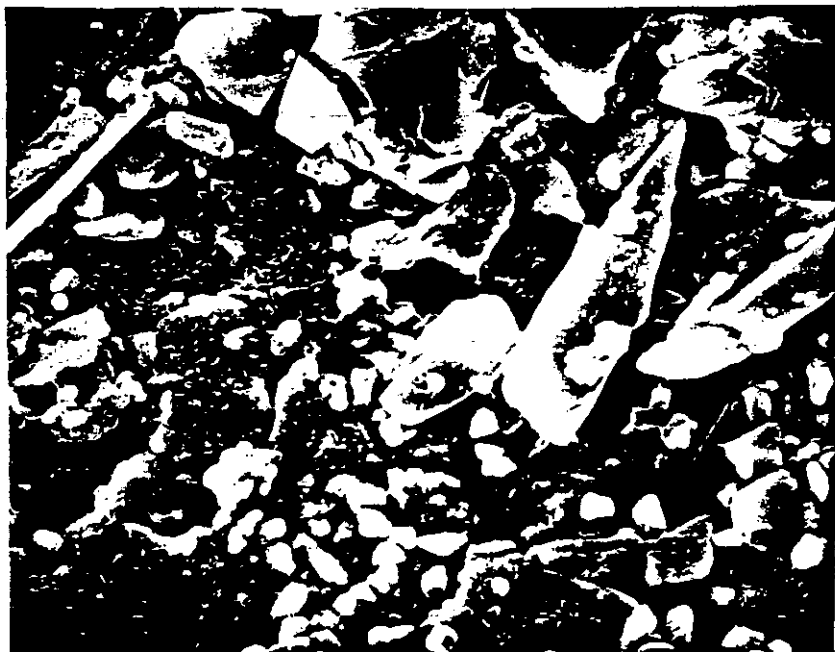
FIGURE 5. Cross Section of Top Surface, 90°C/14.7 psi
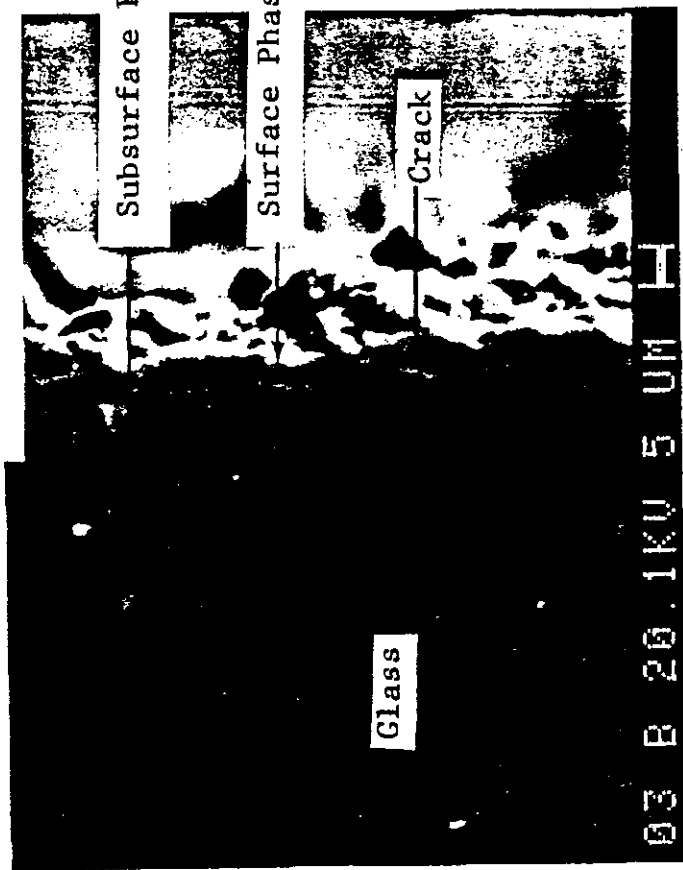
Subsurface Phase

Surface Phase

Crack

Glass

Leached Surface Layers

Na Profile

Ca Profile

Mg Profile

FIGURE 5 (Continued)

Ni Profile

Ti Profile

Fe Profile

Mn Profile

FIGURE 5 (Continued)

Si Profile

Al Profile

FIGURE 6.   TP-3 – Cross Section of Bottom Surface, 90°C/14.7 psi
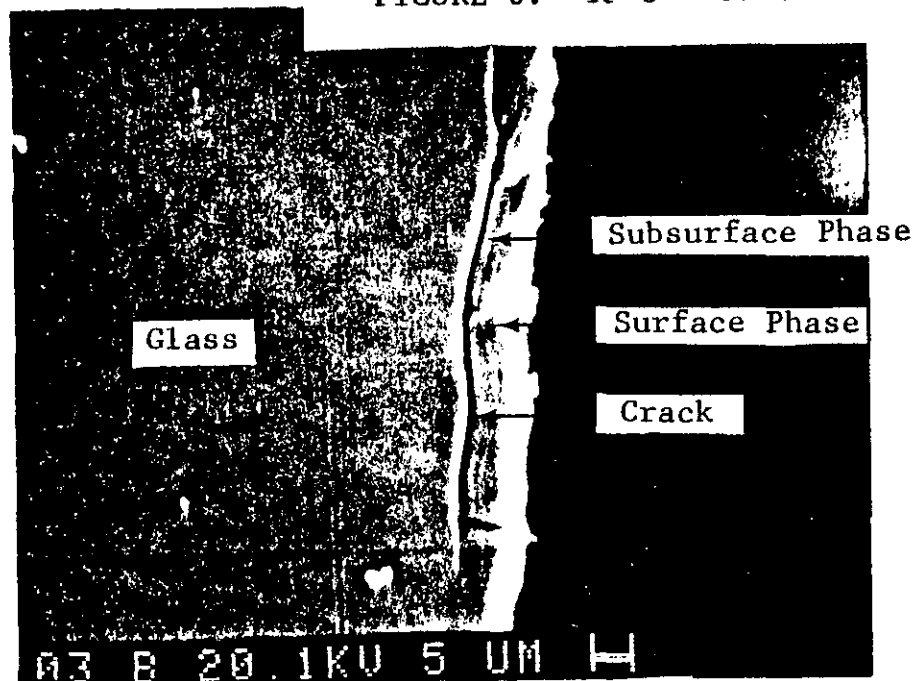
Leached Surface Layers
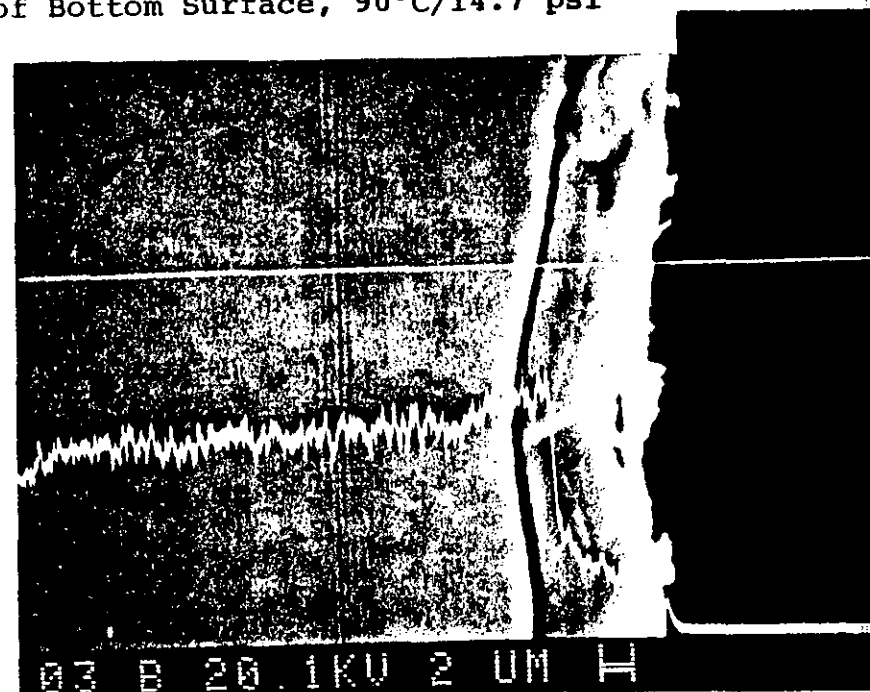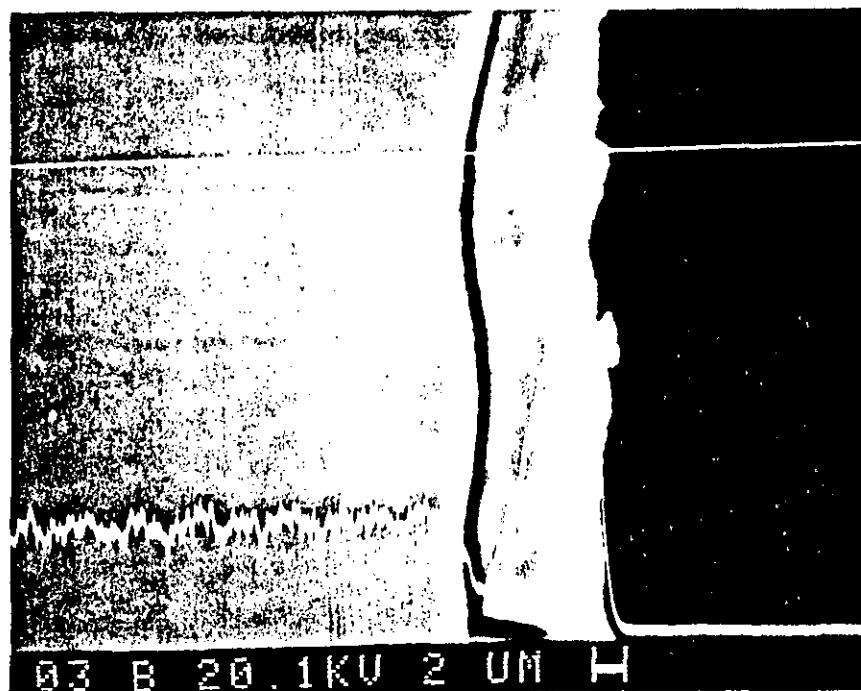
Na Profile

Mg Profile

Ca Profile

FIGURE 6 (Continued)

03 B 20.1KV 2 UM

Fe Profile

03 B 20.1KV 2 UM

Ni Profile

03 B 20.1KV 2 UM

Mn Profile

03 B 20.1KV 2 UM
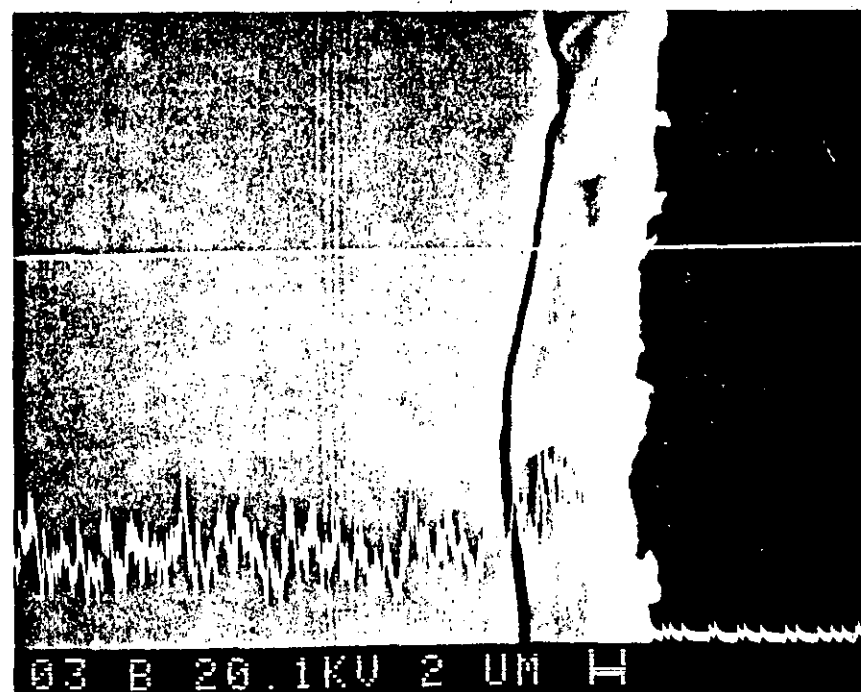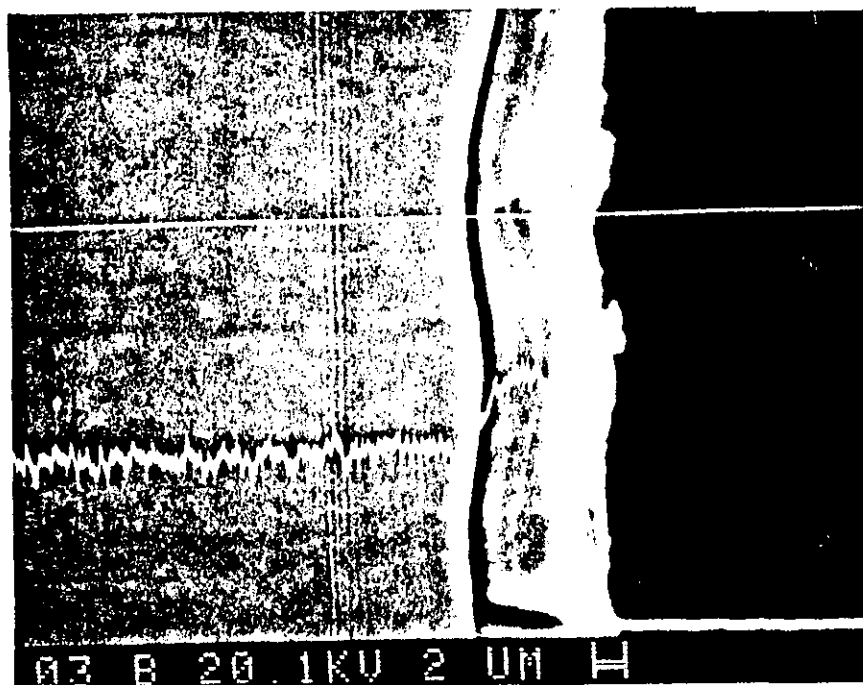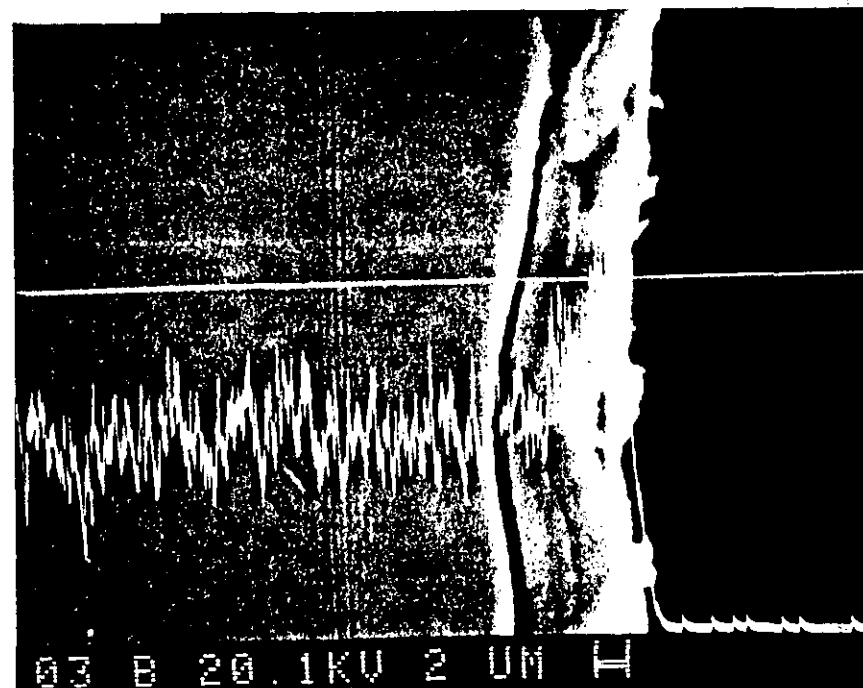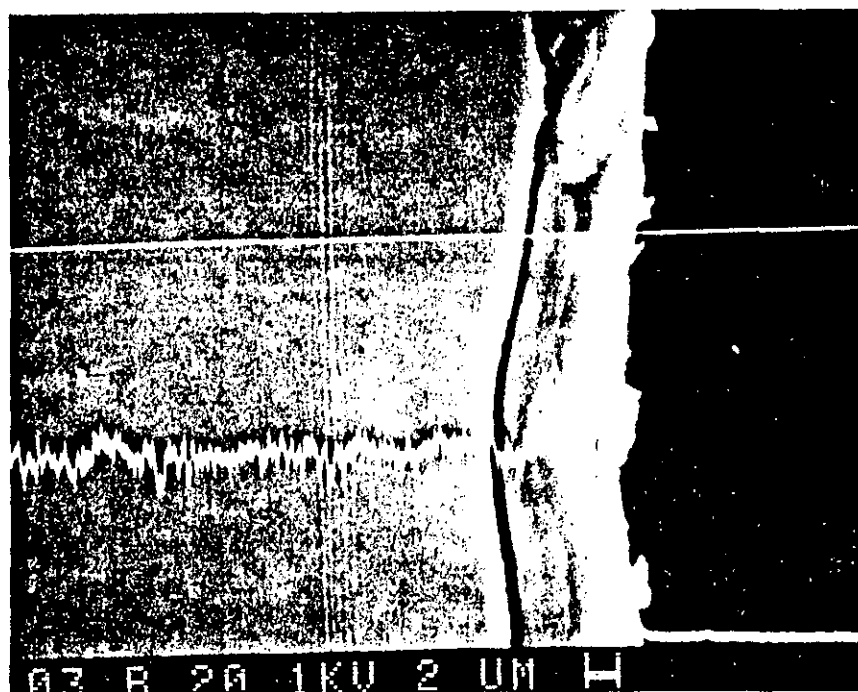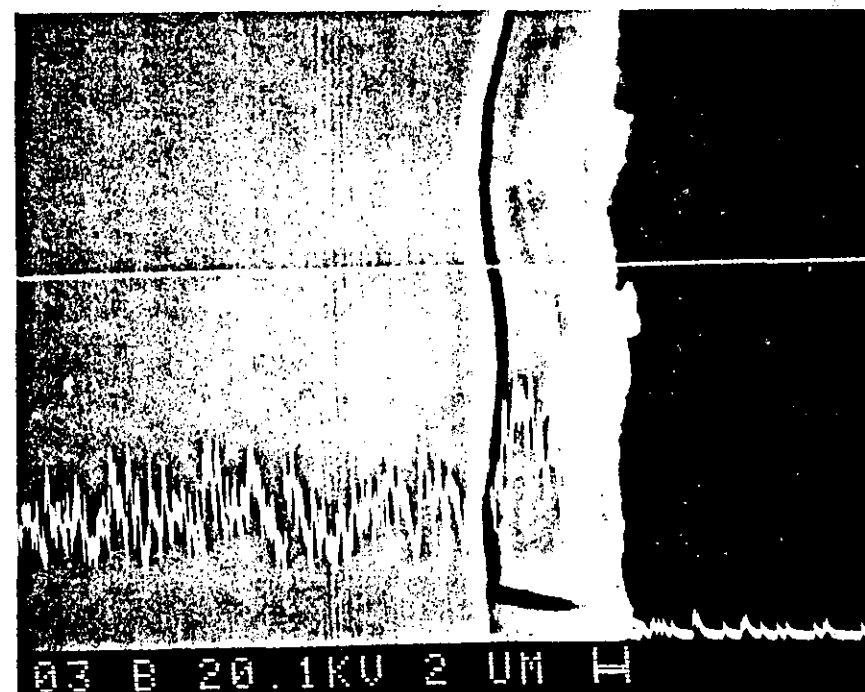
Ti Profile
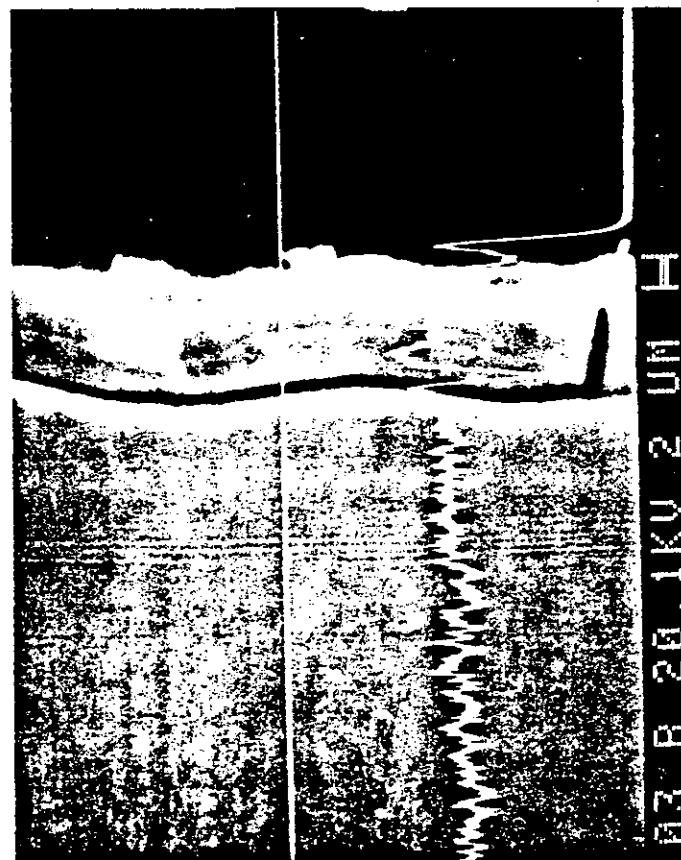
FIGURE 6 (Continued)
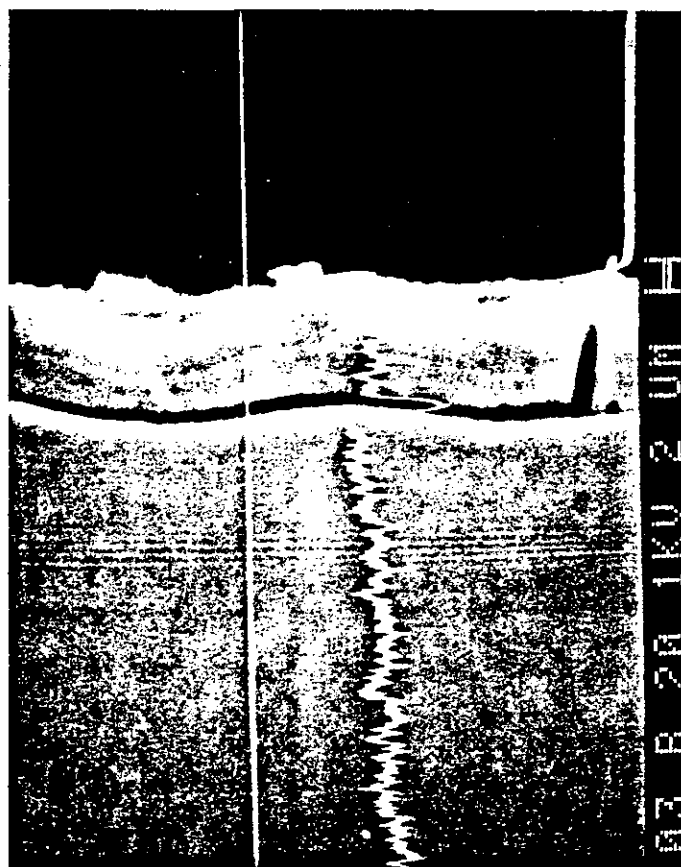
Si Profile

Al Profile

FIGURE 7.   TP-3 – Cross Section of Bottom Surface, 90°C/1000 psi

Crack
Subsurface Phase
Surface Phase
Glass

02 B 20.1KV 5 UM ⊢
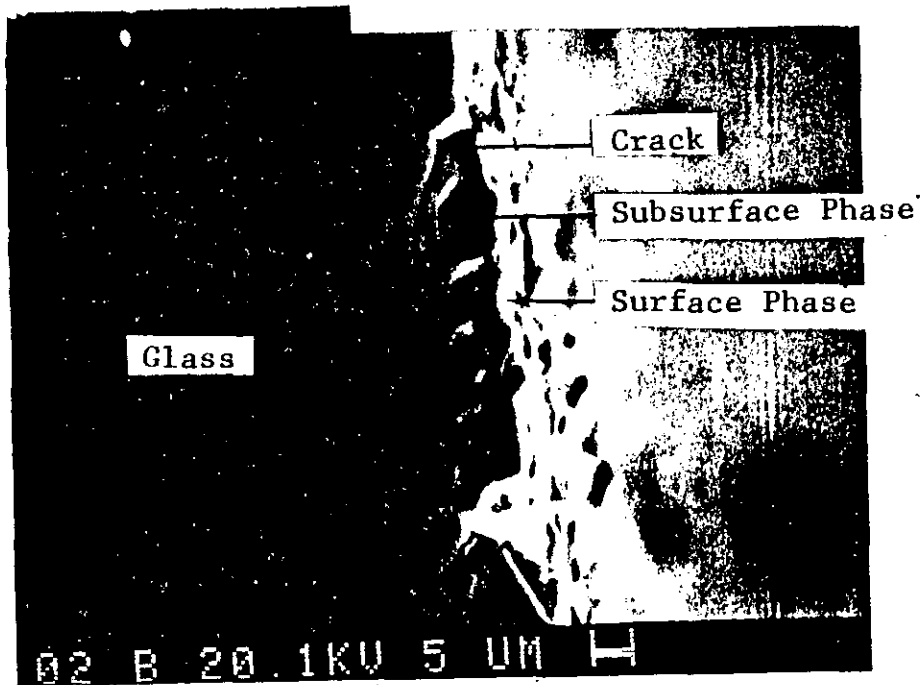
Leached Surface Layers
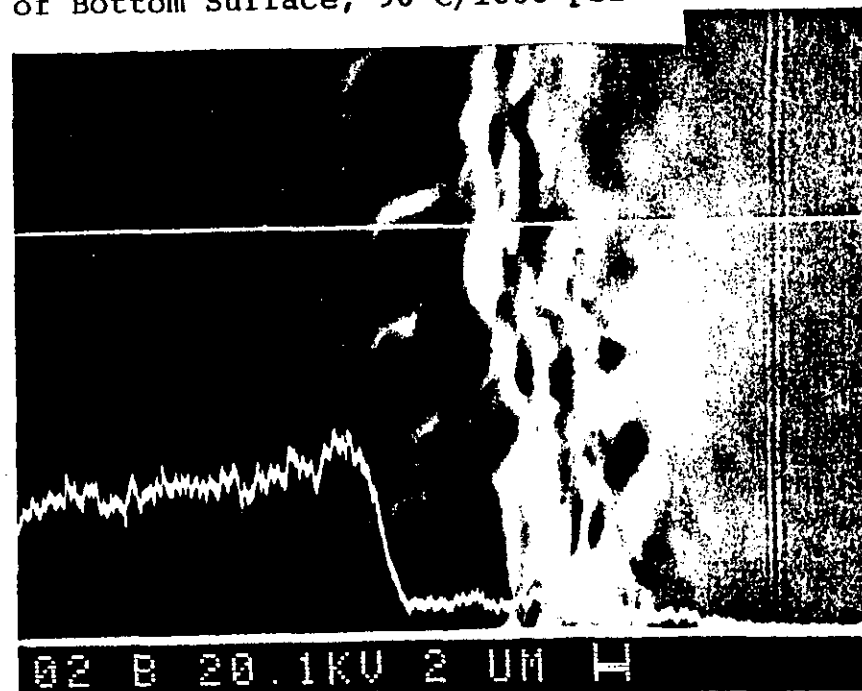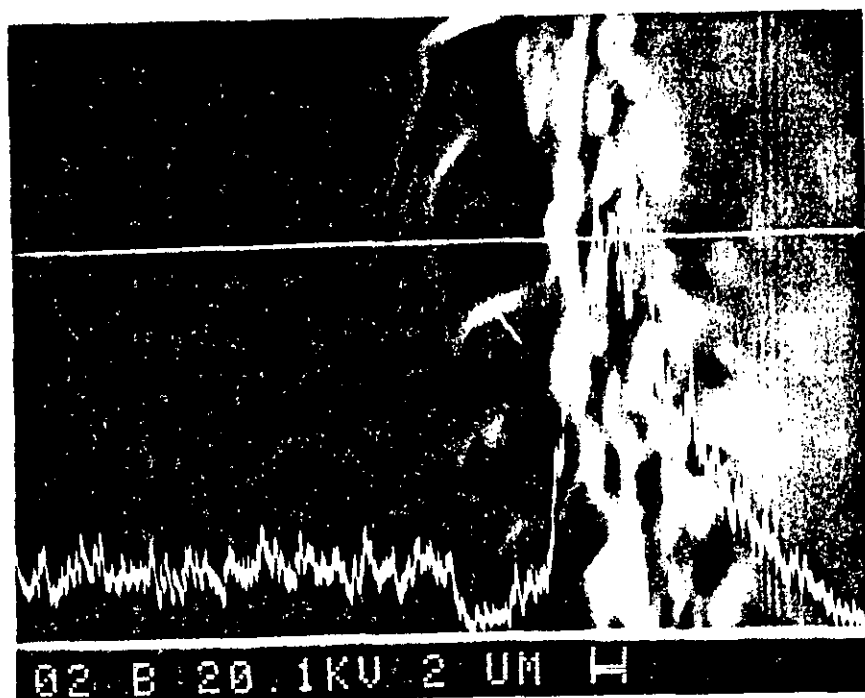
Na Profile
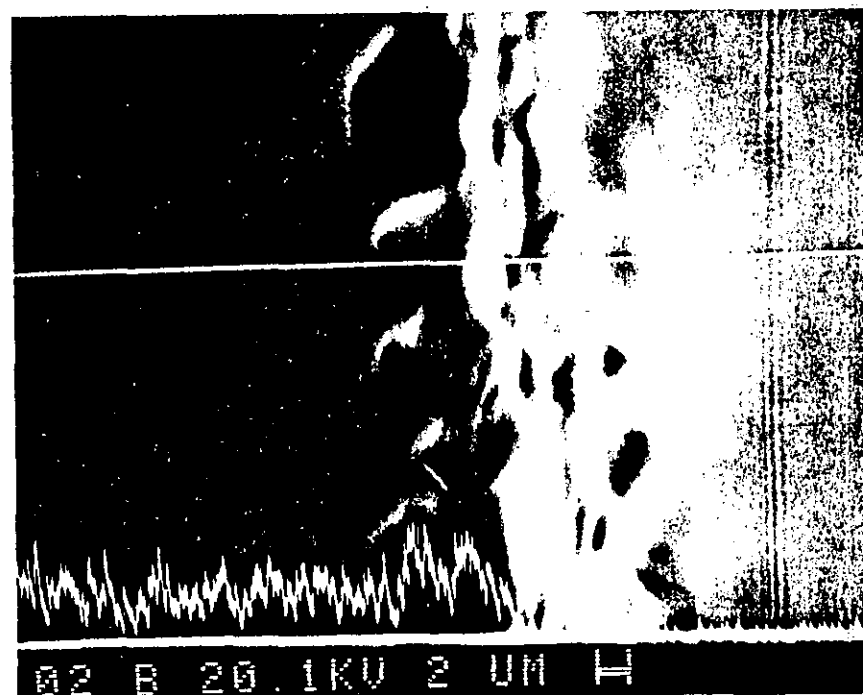
Mg Profile

Ca Profile

FIGURE 7 . (Continued)

Ni Profile

Ti Profile

Fe Profile

Mn Profile

FIGURE 7 (Continued)
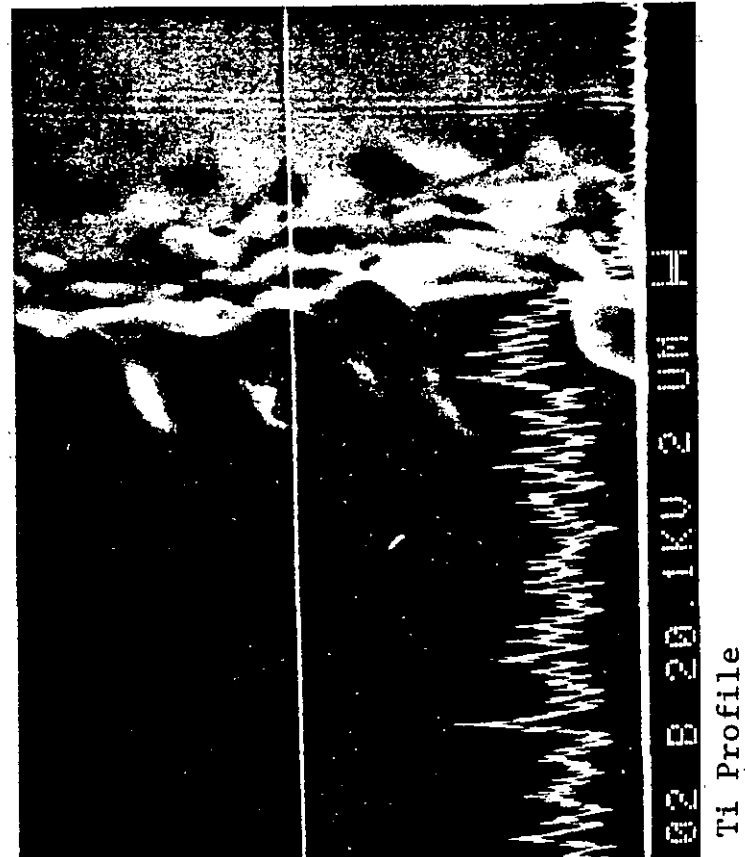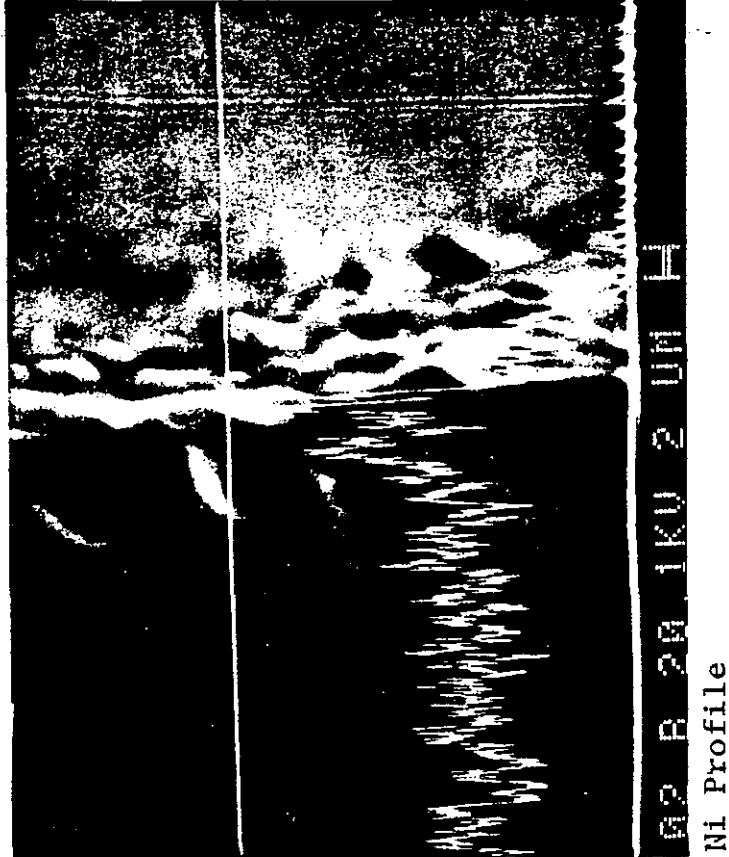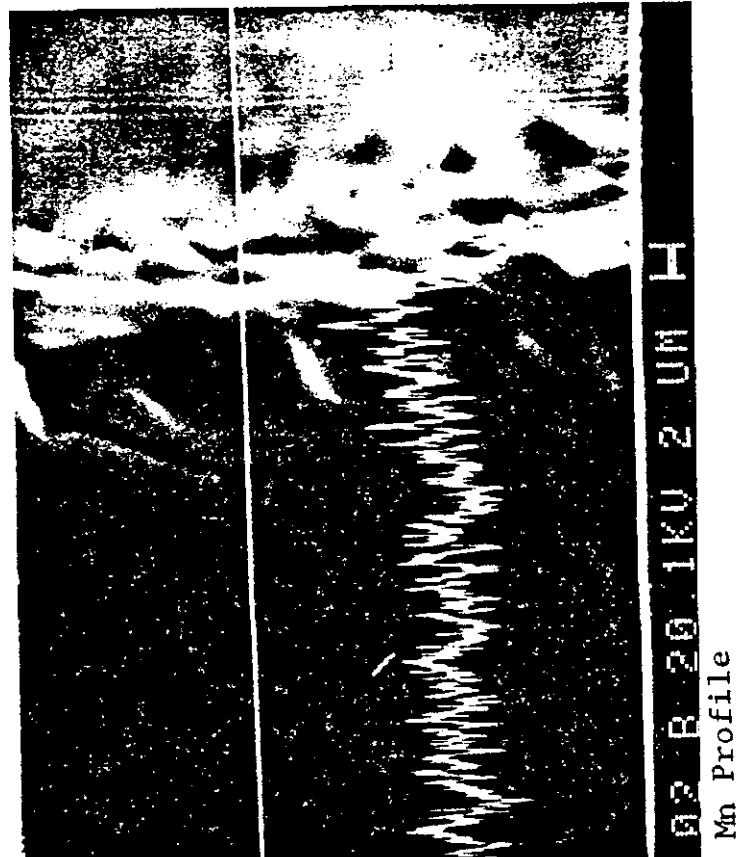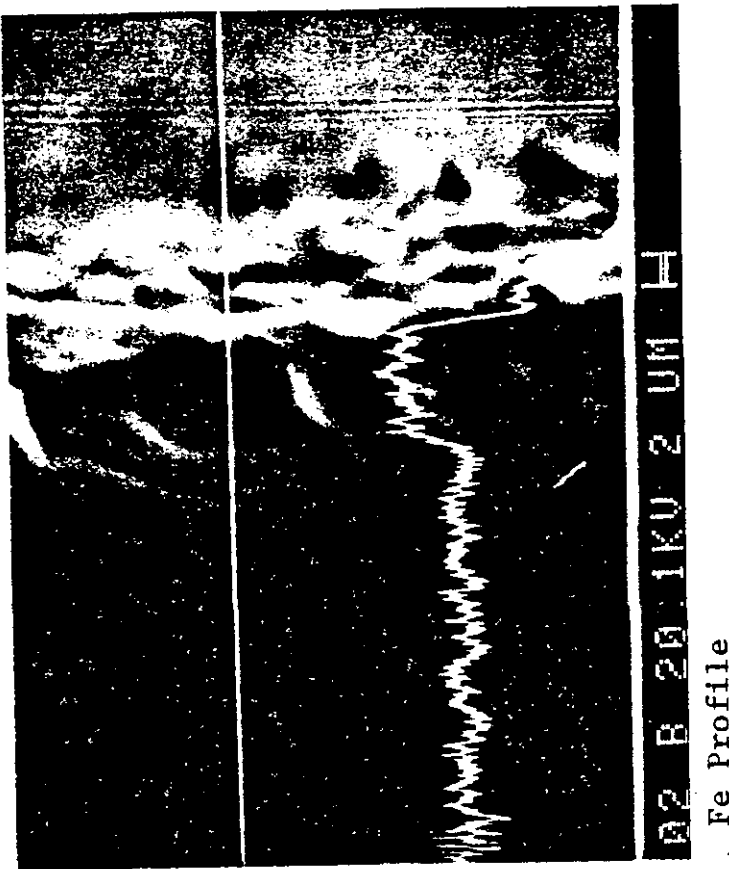
Si Profile
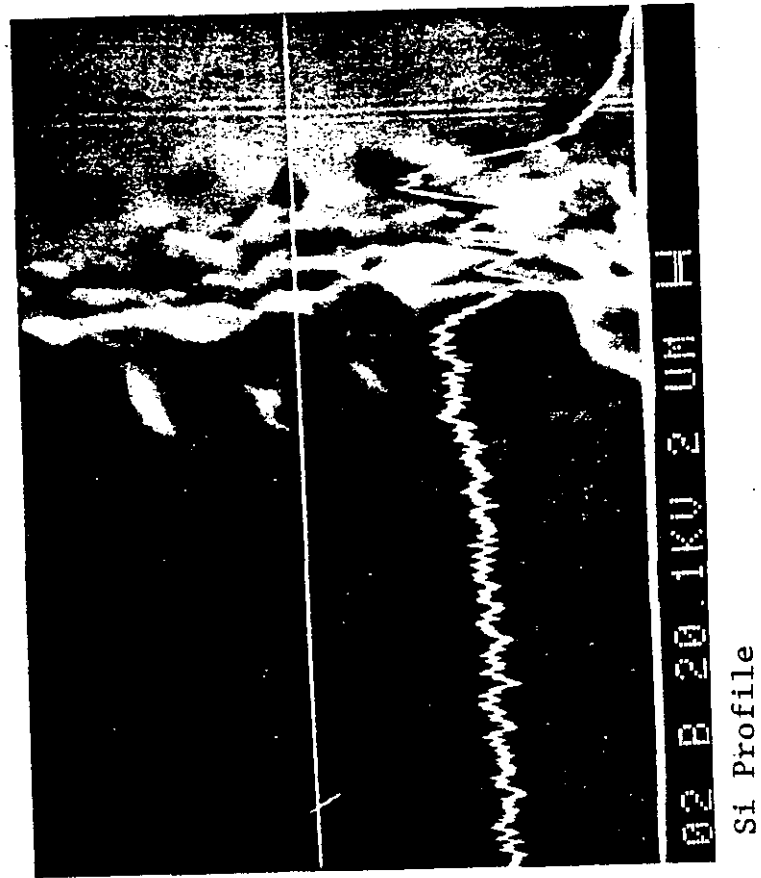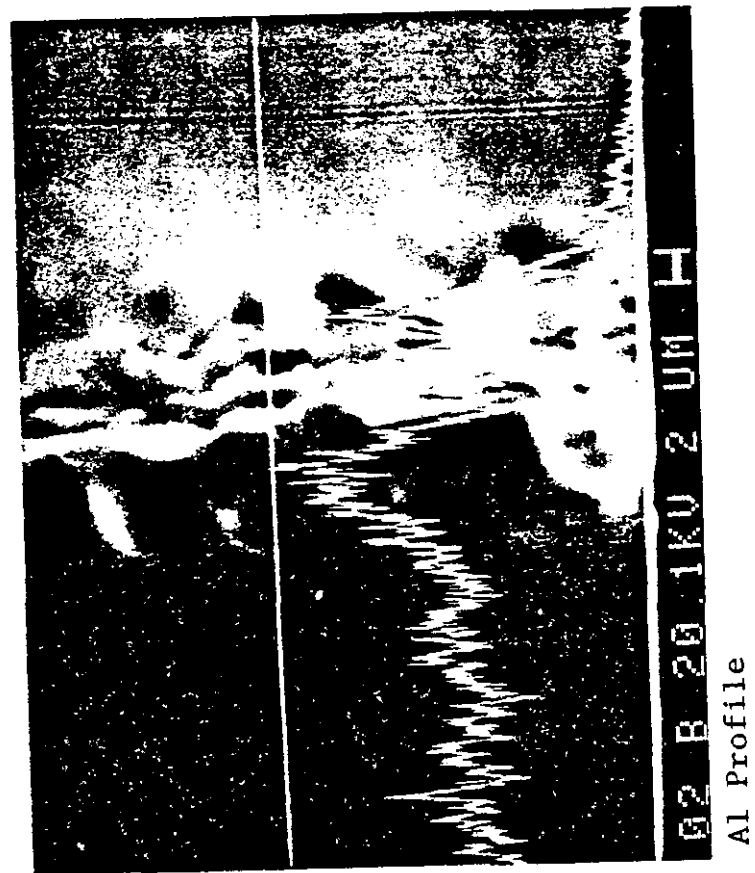
Al Profile

FIGURE 8.   Glass Surface Layers of TP-4
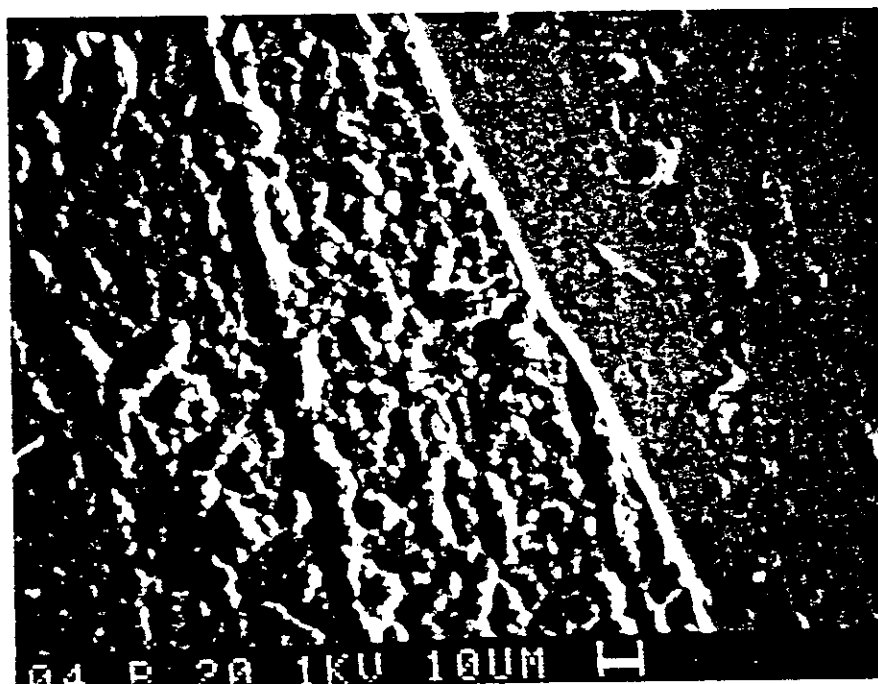
Surface
Film

Glass
Under Film

90°C/14.7 psi
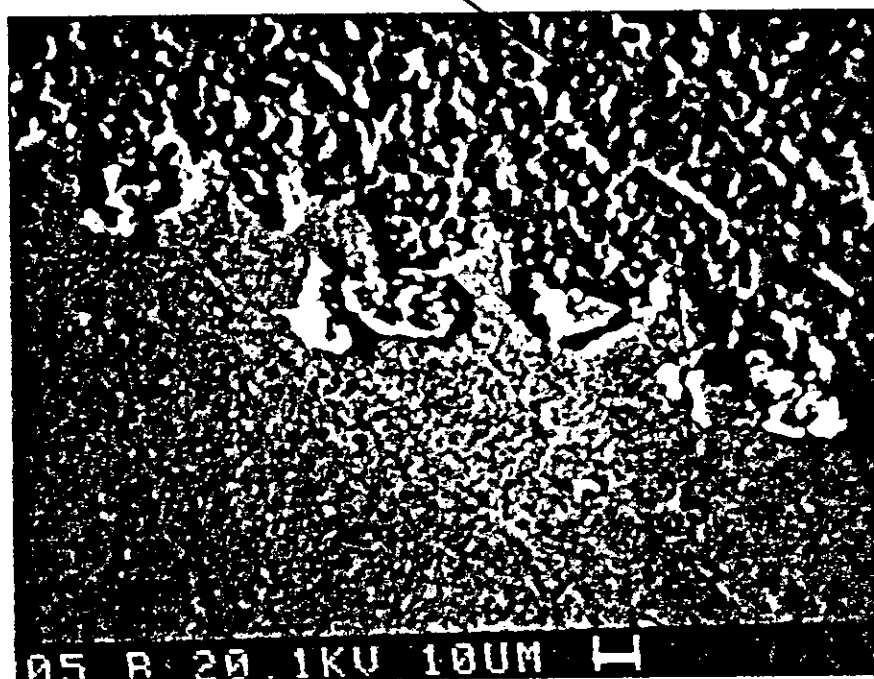
90°C/1500 psi

FIGURE 9. TP-4 – Cross Section 131/TDS, 90°C/14.7 psi
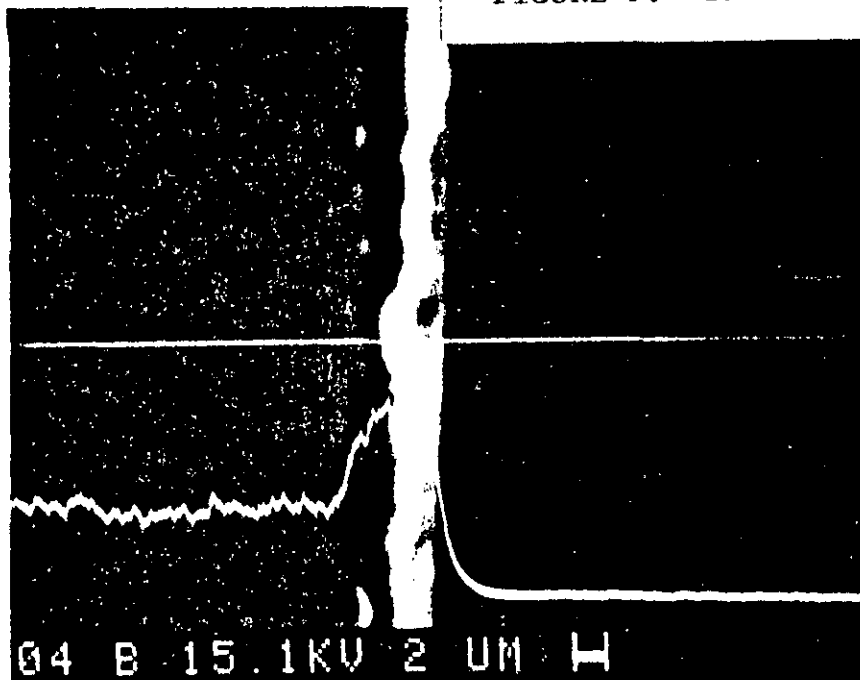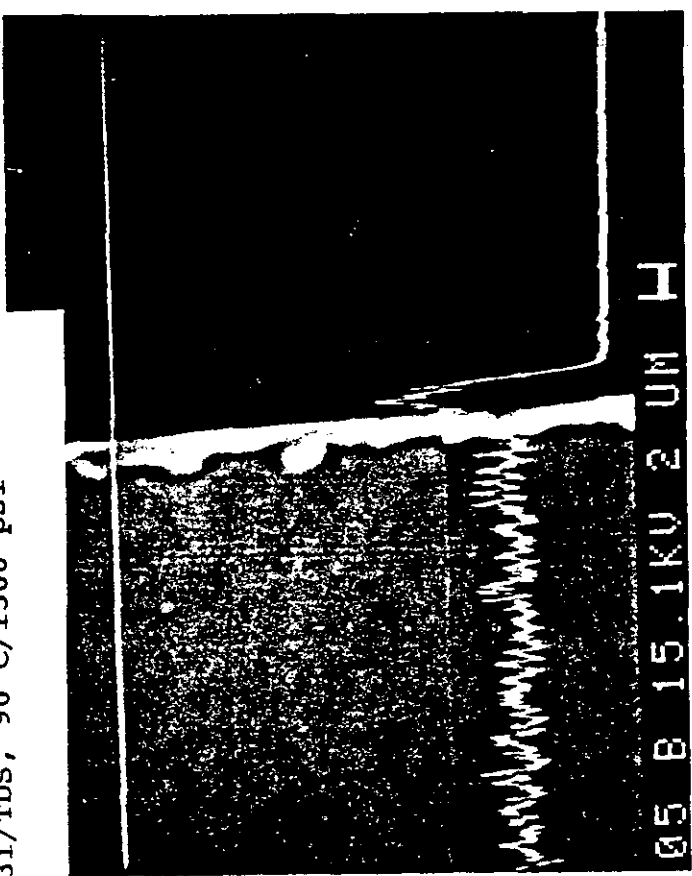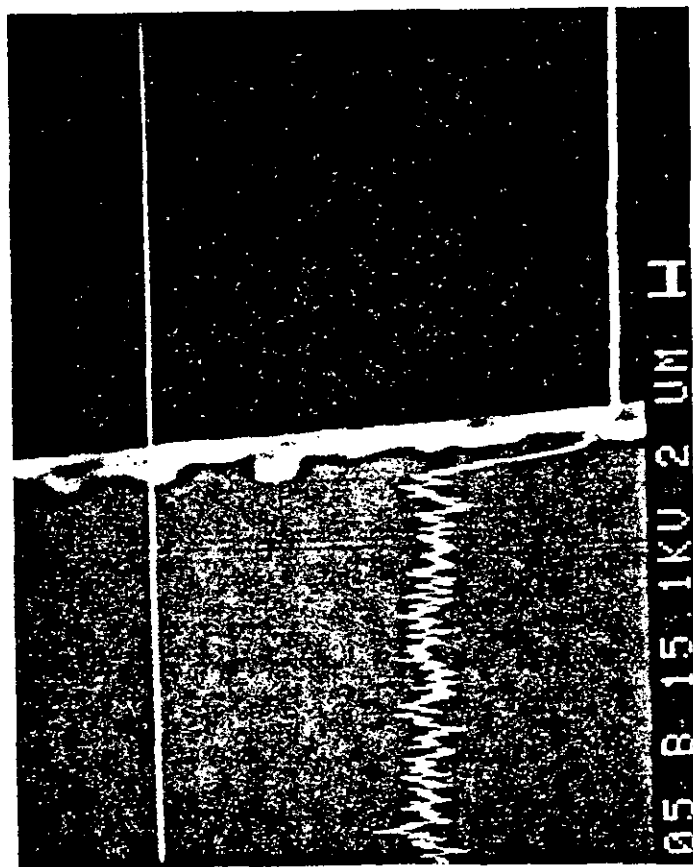

Fe Profile

Mg Profile

Na Profile

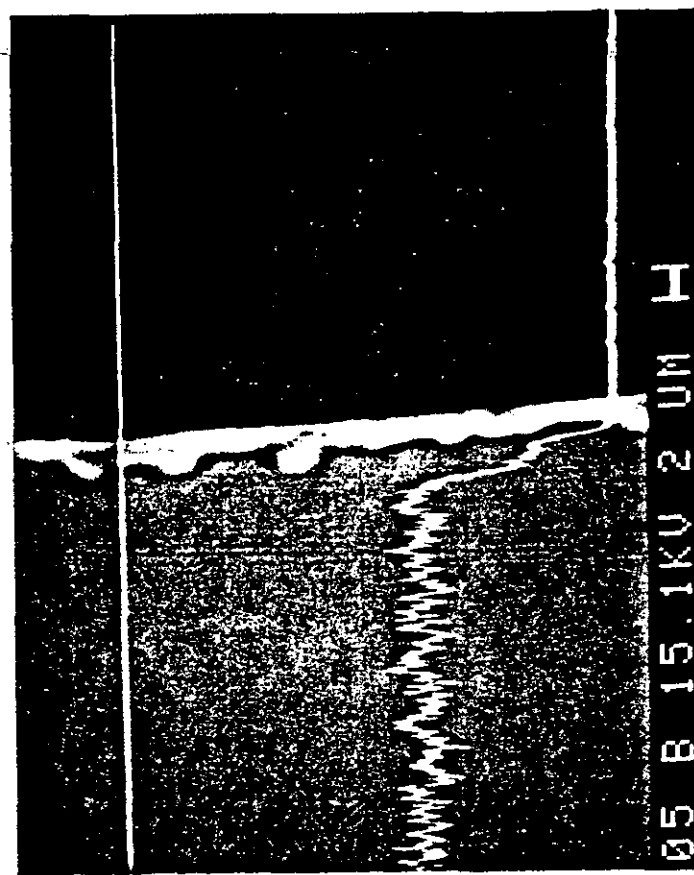Si Profile

FIGURE 10. Cross Section 131/TDS, 90°C/1500 psi

Mg Profile

Si Profile

Fe Profile

Na Profile

FIGURE 11

DEPTH PROFILE OF SURFACE LAYER OF WASTE GLASS
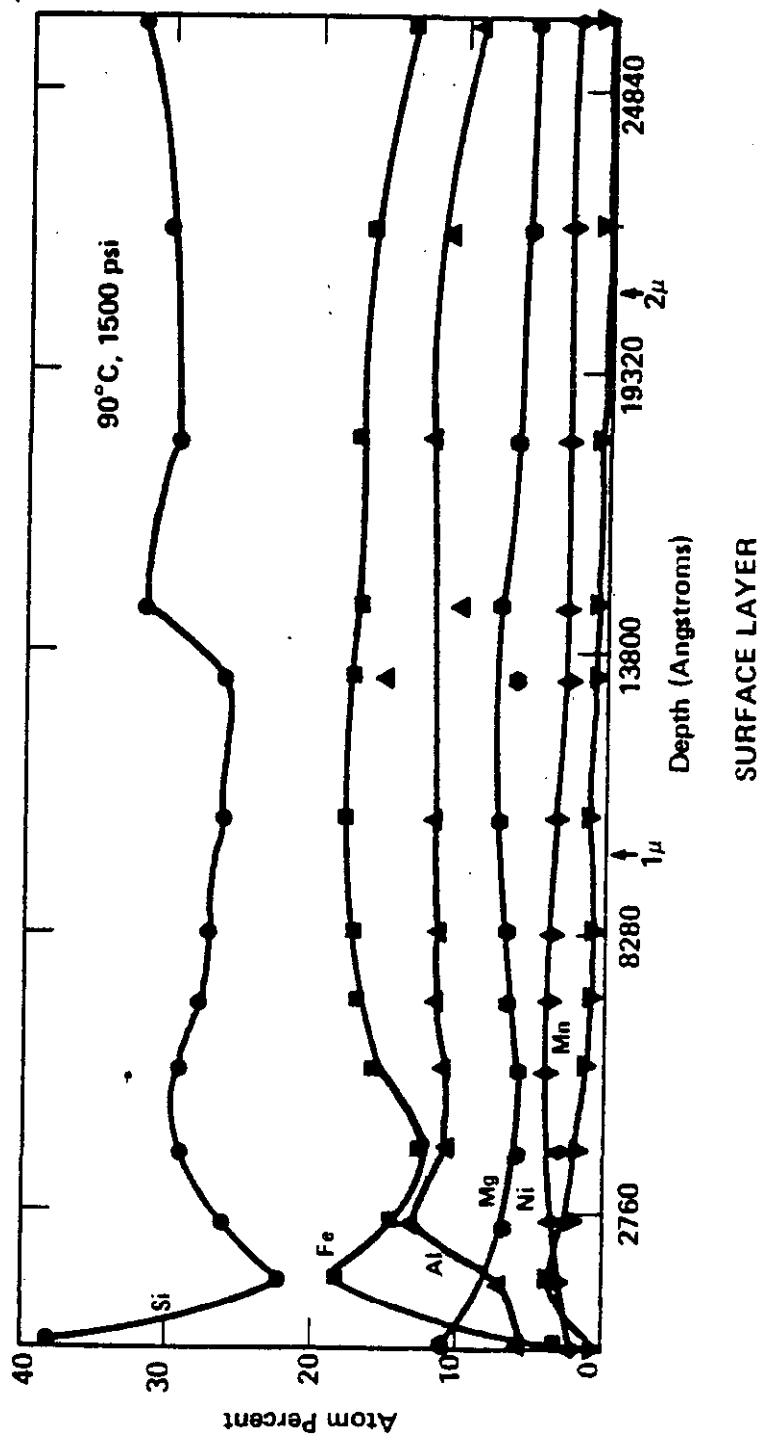AT 90°C/1500 psi USING AUGER ANALYSES, TP-4

FIGURE 12

EFFECT OF pH ON LEACHING OF SRP WASTE GLASS

SILICA DISSOLUTION