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Attenuation of Glass Dissolution in the Presence of Natural Additives

by

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Abstract

The study described here explored the dissolution kinetics of silicate glasses in aqueous environments in systems which included a variety of natural crystalline solids in addition to the glass itself and the aqueous phase. The results demonstrated the possibility of a dramatic decrease in the rate of dissolution of silicate glass in the presence of certain varieties of olivine-based materials. This decrease in dissolution rate was shown to be due to the fact that these additives consist mostly of Mg-based material but also contain minor amounts of Al and Ca. The combined presence of Mg with these minor species affected the corrosion rate of the glass as a whole, including its most soluble components such as boron. This study has potentially important implications to the durability of glasses exposed to natural environments. The results may be relevant to the use of active backfill materials in burial sites for nuclear waste glasses, as well as to better understanding of the environmental degradation of natural and ancient glasses.

Introduction

Glass dissolution has been the subject of extensive research in recent years. One reason for this interest is the proposed use of borosilicate glass as an immobilization medium for nuclear wastes. Another reason is the increasing interest in natural and ancient glasses, such as the recently discovered K/T glasses. Characterization of the long-term corrosion kinetics of silicate glasses is complicated by the observation that the dissolution rates of such glasses can exhibit sudden increases over time as a result of pH rise,[1] nucleation of secondary phases,[2] or cracking of the exposed surface.[3-4] One aspect of the corrosion kinetics of glasses which has not yet been extensively studied is the effect of the presence of crystalline solids in contact with the same aqueous phase to which the glass is exposed. Such studies may be useful in identifying corrosion-retarding backfill materials for use in burial sites for nuclear waste glass, especially in the cases of low-level waste glasses which will not be enclosed within a metal container. Furthermore, the effect of the presence of adjacent crystalline rock materials on the interaction between silicate glasses and water may also be important in studying the degradation of natural and archaeological glasses. It is well known that the extent of corrosion of such glasses varies considerably from site to site. The study described below consisted of a preliminary investigation of the effects of crystalline solids on glass dissolution under conditions of relatively high S/V ratio and leachant exchange rate without seeking to simulate a particular geological scenario.

Several dissolved metals, including Al, Zn, Sn and Cu in neutral solutions and Be, Zn and Al in alkaline media were observed to cause retardation of glass dissolution when present in aqueous media in contact with silicate glasses.[5] In the case of Mg, conflicting findings have been reported. Under certain conditions, the presence of Mg ions resulted in significant reduction in glass dissolution rates,[6] while in other cases exposure to Mg-containing solutions was reported to have little effect or even to result in high corrosion rates of the glass due to the formation of Mg silicates.[7,8] Investigation of the effects of Mg-containing solid additives on glass dissolution can contribute to better understanding of these conflicting observations, as well as to the identification of potential active backfill materials.

The study described below concentrated on glass-water-additive systems involving rock materials and compounds of Mg and of other polyvalent metals. Only compounds and rock materials with low solubility in water were tested in order to ensure their long-term survivability.

Experimental

The glasses used in the study were experimental two borosilicate glasses developed during simulation studies of the vitrification of nuclear wastes. The principal composition used in the present study was PNL 76-68.[9] A few preliminary studies were carried out on TDS-165 glass.[10] The compositions of these two glasses are given in Table 1. The composition of PNL 76-68 glass is based on Ref. 9, with the exception of the Al_2O_3 content which was determined in the present work. The composition of the TDS-165 glass used in the present work was determined by dc plasma spectrometry. Neither one of these two glass compositions will be used in the disposal of actual nuclear waste. However, a significant data-base already exists for the leaching properties of these two glasses and therefore they were considered appropriate for the present study, which is concerned with the leach kinetics of borosilicate glasses rather than with repository applications (see above).

The rock materials used in the present studies were obtained from Ward's Natural Science Establishment (Rochester, NY). The composition of rock material additives were similarly determined. X-ray diffraction patterns of these materials were obtained using a Siemens Theta-Theta D500 diffractometer. Petrographic thin sections of these samples were subject to examination by means of an optical microscope. In the cases of the materials which appeared to have the largest effects on glass dissolution, experiments were carried out using two or three different batches of each material purchased from Ward's at different times in order to verify the consistency of the results. In addition to these rock materials, several pure oxides (analytical reagent grade) were also included used in the present studies. These oxides were obtained in powder form from Fisher Scientific (Pittsburgh, PA).

The experimental procedure outlined below was not intended to simulate repository conditions. Rather, because of the preliminary nature of the work, the experiments were intended to find out if under conditions favoring glass-additive interaction such interaction could have a significant effect on glass dissolution rates. For this reason, an excess of additive over glass was used and the surface-to-volume ratios and water exchange rates were selected to explore the effects of additive materials within a regime that is influenced, to some extent, by the kinetics of glass dissolution and does not reflect solubility control alone. Of course, the use of this experimental configuration precluded direct application of the results to repository-relevant conditions. Rock-glass interactions under such conditions require a separate study.

The standard testing configuration consisted of a combination of 1 g of SRL TDS-165 powdered glass and 2.5 g of powdered solid additive exposed to 40 mL of deionized water at 90°C. In the case of PNL 76-68 glass, 0.6 g of powdered glass and 1.5 g of powdered solid additive exposed to 20 mL of deionized water at 90°C. (In one experiment a combination of additives, consisting of 70% of olivine and 30% of anorthite, was used rather than a single additive; in another experiment, dilute aqueous solutions were used rather than deionized water.) Both the glasses and the solid additive were crushed and sieved to separate out the fraction which had a grain size of -40 +60 mesh, corresponding to a diameter of 0.25 - 0.355 mm. The test vessels were PFA Teflon 60-mL containers, Savillex Corp. #0102. The water was completely removed and replaced with fresh leachant at weekly intervals. The leachates were consistently clear and water-white and therefore they were not filtered. The leachates were analyzed using dc plasma spectroscopy, a Spectrametrics SpectraScan III spectrometer. Leachant blanks were run under the same conditions for each of experiments. The readings of Mg, Al, Ca and Si for the blanks were generally <0.02 mg/L. The pH of the leachates was determined immediately following quenching to room temperature.

Results

The results of preliminary studies on TDS-165 glass showed that the observed leachate concentrations at the end of consecutive weekly intervals became nearly independent of time after the first week. The results of uranium analysis on the leachates obtained at the end of the 6th monthly interval are given in Table 2. The concentrations of boron, silicon and lithium in the leachates, as well as the pH values, are also included in Table 2. These results showed a a decrease in dissolved uranium levels in the cases of several additives, but, except in one case, no consistent decrease in the concentration levels of all glass components, especially those which are highly soluble.

All other measurements were carried out on PNL 76-68 glass. Various rock materials, all obtained from Ward's Natural Science Establishment, were used in these studies. All of them contained magnesium except fayalite (Fe_2SiO_4), the end member of the olivine series which contains only ferrous iron and no magnesium. The two most important rock materials included in this study (see below), viz. the Kilbourne Hole (New Mexico) olivine and San Carlos (Arizona) olivine, were characterized by means of chemical analysis, X-ray diffractometry and thin section microscopy. Nominally pure olivine ($(Mg,Fe)_2SiO_4$) does not contain Al. However, chemical analysis of these two types of xenolithic olivine following dissolution in acid showed that the Kilbourne Hole material contained more Al and Ca than the San Carlos material. The major ingredients (by weight) of the Kilbourne Hole and San Carlos olivine materials are given in Table 3. X-ray diffraction of the two olivine samples used in the present study (Figure 1) showed that in both cases the major components were forsterite-rich olivine (with a large excess of forsterite, Mg_2SiO_4, over fayalite, Fe_2SiO_4) and enstatite ($Mg_2Si_2O_6$, a pyroxene group mineral with limited capacity for substitution of Fe for Mg). The main differences between the two materials were that the Kilbourne Hole material contained more enstatite than the San Carlos material, as confirmed by petrographic thin section microscopy, and, in particular, that in the case of the Kilbourne Hole material anorthite ($CaAl_2Si_2O_8$) was distinctly present as a minor component, while no anorthite has been observed in the San Carlos olivine used in the present study. (The San Carlos olivine appeared to contain trace amounts of hercynite ($FeAl_2O_4$).) In addition, more anorthite is expected to accompany the Kilbourne olivine according to the phase composition data in Ref. 14.

The results of the studies of the dissolution of PNL 76-68 glass in the presence of various additives show that the leachate concentrations obtained at the end of the weekly leaching intervals following the first week become nearly constant (Figures 2 - 5). The results of the leachate analysis at the end of the 5th week, which are typical of the leachate analysis throughout the weekly tests, are shown in Table 4. As mentioned above, the experiments involve complete exchange of the leachant at the end of each interval. Accordingly, the leach rate L_i of the i-th glass component corresponding to each interval is directly proportional to the measured concentration of this ingredient in the leachate C_i,[14,15] since

$$C_i = L_i \times f_i \times \Delta t \times S/V$$

where f_i is the weight fraction of the i-th ingredient in the glass, Δt is the length of the interval, and S/V is the ratio between the surface area of the glass and the volume of the leachant. The dependence of L_i, and hence of C_i, on the time elapsed since the beginning of the experiment represents the time dependence of the water/glass interaction. The data shown in Figures 2 -

4 are given in terms of C_i rather than L_i because concentration data represent the leachate composition whether it is determined by the leach kinetics, by solubility constrains, or by a combination of both types of constraints. In the present case, such combination is most probable, because extending the exposure interval from 7 days to 28 days causes the leachate concentrations to rise, but this rise is much smaller that the corresponding increase in the length of the interval (see Figures 2 - 5).

The results shown in Table 4 and Figures 2 -5 indicate that several additives, in particular Kilbourne Hole olivine, have very significant effects on the dissolution of PNL 76-68 glass. In an attempt to understand the difference in behavior between the Kilbourne Hole olivine and the other Mg-containing materials with respect to their effect on the dissolution rates of glass, dissolution studies were carried out on the materials listed in Table 4. The objective of these experiments was to search for an explanation of the unusually large effect of the Kilbourne Hole olivine on glass dissolution. Accordingly, it was attempted to compare the nature and concentration of the leach products of the Kilbourne olivine with those observed in the cases of other additives. In these studies, a quantity of 0.1 g of each rock material was exposed to 20 mL of water at 90°C in the absence of glass for 1 week. The results are shown in Table 5. They indicate that the most distinctive features of the interaction between Kilbourne Hole olivine (as compared with the other rock materials included in the present study) and water are relatively high levels of dissolved Al and Ca in the aqueous phase. This is probably associated with the presence of small amounts of anorthite in the Kilbourne Hole olivine.

The question remains as to whether the presence of small amounts of anorthite in the presence of olivine as a major phase can have a significant effect on the capacity of the olivine material to retard the dissolution of glass exposed to the same volume of water. In order to shed light on this problem, several additional experiments were conducted under the same conditions as those described above to identify possible synergistic effects of olivine and anorthite. Again, 0.6 g of PNL 76-68 glass was exposed to 20 mL of deionized water in the presence of 1.5 g of additive, but in the present case the additive, rather than being a single material, consisted of a 7:3 mixture of San Carlos olivine and anorthite. The results of these additional experiments are summarized in Table 6, and they show that the combined presence of olivine and anorthite indeed results in a decrease in the extent of glass dissolution.

In another experiment, the glass was leached under four different conditions, (a) in deionized water without any additive, (b) in the presence of the San Carlos olivine and a solution initially containing 10 mg/L Ca, (c) in the presence of the San Carlos olivine and 10 mg/L Al, and (d) in the presence of San Carlos olivine and a combined solution of 10 mg/L Ca and 10 mg/L Al. Again the experiment involved a combination of 0.6 glass and 1.5 g of additive exposed to 20 mL of an aqueous leachant. This experiment yielded clear evidence that olivine becomes effective in suppressing glass dissolution when leachable Al (or Al + Ca) is present in the system.

Discussion

The preliminary studies on TDS-165 glass (see Table 2) showed that the presence of several solid additives, in particular titania and magnesia, and, to a lesser extent, diopside

($CaMgSi_2O_6$), dolomite ($CaMg(CO_3)_2$) and, marginally, ceria, resulted in significant reduction of the uranium concentrations in the leachates. The introduction of magnesite ($MgCO_3$), sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$), alumina, and zirconia did not decrease the dissolved uranium concentrations. It can be seen that even those materials which caused decrease in uranium levels did not produce a decrease in the overall dissolution rate of the glass, as monitored using the concentrations of soluble elements such as B[11] and Li as indicators. The only exception was the case of diopside, in which a consistent reduction of about 20% in the extent of glass dissolution was observed, as indicated by the low concentrations of boron and lithium. In general, the specific decrease in dissolved uranium levels in the presence of the additives listed above can be attributed to sorption on the surface of the additive <u>following</u> the dissolution of the glass. It is well known that certain oxide rock materials can effectively sorb uranium from aqueous solutions.[12, 13] Furthermore, the data in Table 2 show that the presence of several Mg-containing additives (magnesite and sepiolite) can actually increase the rate of glass dissolution. This may be attributed to acceleration of the build-up of crystalline products of glass corrosion in the presence of these additives. Build-up of alteration phases has been previously shown to result in acceleration of glass corrosion.[7]

The results of the studies on the dissolution of PNL 76-68 glass in the presence of various additives (Table 4) show that only three of the materials tested here (enstatite, serpentine and one variety of olivine) exhibited significant suppression of glass dissolution, and that in the cases of two of these (enstatite and serpentine, $(Mg,Fe)_3Si_2O_5(OH)_4$) the decrease in the extent of weekly glass dissolution is only by 15-30% relative to the extent of glass dissolution in the absence of additives (line a). On the other hand, in the case of the Kilbourne Hole olivine (line

m) the observed rate of glass dissolution fell off by a factor of 30-50 relative to the rate measured in the case of the glass alone (line a). This effect is particularly dramatic upon taking into consideration the fact that none of the other olivine samples had a significant effect on glass dissolution. In particular, the San Carlos olivine, which originates in a dunite xenolith with very similar origin, morphology, composition and appearance to those of the Kilbourne Hole material,[16] had no observable effect. It should be noted that the leachate concentrations obtained in the presence of Kilbourne Hole olivine were exceptionally low at all time intervals (see Figures 2 - 4). It should also be noted that the two sets of data cited for this material (as well as for the San Carlos olivine) in Table 4 came from two separate batches, as described in the Experimental section. Preliminary, qualitative microscopic observations using SEM at a low magnification showed that in addition to its much greater effect on the leach rate of the glass as measured by solution chemistry, the presence of Kilbourne Hole olivine also resulted in the leached layer on the glass being much thinner than the leached layer produced under similar conditions in the presence of San Carlos olivine or in the absence of an additive.

It should be emphasized that the results in Table 4 indicate that the presence of Kilbourne Hole olivine (or, to a much lesser extent, of serpentine, Sample f or enstatite, Sample c) affects the glass dissolution as a whole. It is unlikely that the results can be explained in terms of re-precipitation or sorption of dissolved glass components in the presence of these additives. This conclusion is based on the fact that these additives cause a decrease in the concentration levels of boron in the solution. It is well-established that boron is a good indicator of glass dissolution because it does not tend to become re-incorporated in secondary solid phases[11]. Furthermore, in the cases that decreased boron levels are observed in the solution, similarly decreased concentrations are observed in the cases of other soluble species (Na, Li, P). Another reason for using boron as an indicator of the extent of glass corrosion, in addition to its high solubility is the fact that boron is not present as a significant component of any of the minerals which make up the rock material additives used in the present study.

The results of the experiments on the interaction of the various rock materials and water in the absence of glass (Table 5) demonstrate that the retarding effect of the pH of the Kilbourne Hole olivine leachates is quite similar to that of the leachates of other additives (e.g., those denoted by the letters g, h, j and l) which have a much smaller effect on glass dissolution (cf. Table 4).

The results in Table 5 indicate, however, that the contact between water and Kilbourne Hole olivine releases more Al into the leachate than contact with any of the other rock materials studied here. In particular, the extent of Al dissolution from the Kilbourne Hole olivine (line m) is more than 20 times the corresponding extent in the case of the San Carlos olivine (line l). The source of the Al dissolved from the Kilbourne Hole olivine is likely to be the presence of anorthite as a minor component (see above). Ca may have a small secondary effect, since serpentine (line f) and enstatite (line c), which give rise to the highest concentrations of dissolved Ca, are also the only other two additives which are observed to cause retardation of the dissolution of the glass, albeit to a much smaller extent than the Kilbourne Hole olivine. The extent of Ca dissolution from the latter material is moderate, comparable to the one observed in the case of fayalite (line k), which is not observed to affect glass dissolution. On the other hand, it does not appear that Si or Si+Mg leached out of the rock material has a major effect on glass dissolution. According to the data in Table 5, anthophyllite, $Mg,Fe)_7Si_8O_{22}(OH)_2$

(Sample a) and serpentinized forsterite (Sample g) release more Mg and Si than Kilbourne Hole olivine, but according to Table 4 they have no observable effect on glass dissolution. The same is true for fayalite (Sample k), which exhibits the highest rate of Si dissolution.

The results of the studies of the effects on glass dissolution of olivine and anorthite, individually as well as in combination with each other (Table 6), confirm the observations reported above concerning the lack of effect of the San Carlos olivine on glass dissolution. Likewise, anorthite is not observed to have any significant effect. However, when a combination of 70% San Carlos olivine and 30% anorthite is introduced, a significant drop (by about one-third) in the extent of glass dissolution is observed to take place. The results cannot be explained in terms of pH effects (see Tables 5 and 6). One possible interpretation of the data is based on the assumption that in the presence of certain combinations of minerals, which release Mg and Al (and, possibly, Ca) at favorable concentration ratios, the surface layer on the exposed glass is transformed, while still thin, into a dense form which limits further dissolution[17]. However, it is necessary to perform further experimental work, beyond the scope of the current study, in order to find out whether the effects of Mg-based additives containing smaller amounts of Al and Ca also involve factors in which solution chemistry plays an important role.

The results of the studies on the effects of adding dissolved Al or Al + Ca to the olivine/glass/water system are quite striking (Table 7). These results clearly show that the presence of the low-Ca, low-Al containing San Carlos olivine had no effect on the rate of glass dissolution even in the presence of added Ca, but upon addition of Al the dissolution rate dropped sharply, and the effect was largest in the presence of both Al and Ca in the solution to which the glass and the San Carlos olivine were exposed. (Na concentrations in the leachates obtained in all cases where the original leachant contained Al were high because Al was introduced as Na aluminate.)

Further studies are necessary in order to determine the nature and the characteristics of the surface layer formed when silicate glasses come in contact with water in the presence of Mg-based minerals when Al and Ca are also present either in the water or as minor components of the solid additive. Because of the limited scope of the current study, it is necessary to carry out further experiments in order to establish whether the striking effect of the Kilbourne Hole olivine used in the present study involve the formation of a protective surface area, an unusually large effect on solution chemistry, or both. Furthermore, the present work does not provide a full and quantitative explanation of the retardation of glass corrosion in the presence of Kilbourne Hole olivine additive, which appears to be a rather unusual phenomenon in view of the fact that most of the other Mg-based additives examined here had little or no retarding effect on glass corrosion. Further work is necessary to survey further potential additives and characterize the effects of their presence on glass dissolution.

Conclusions

The most striking conclusion of the present study is that certain solid additives, in particular Kilbourne Hole olivine, were found to have a very significant effect on the dissolution of certain silicate glasses. Thus, the extent of dissolution of PNL 76-68 borosilicate glass is reduced by a factor of 30 in the presence of this variety of olivine. It is particularly noteworthy that the suppression of glass dissolution is evident in the cases of the most soluble glass components (B, Na, Li, P) and that it persists over periods of at least 6 months without any evidence of weakening of the effect of olivine on glass dissolution. Moreover, smaller effects of rock materials in reducing the extent of glass dissolution were found with other additives (enstatite and serpentine in the case of PNL 76-68 glass, diopside in the case of TDS-165). All of these cases involve Mg-based materials. In the most prominent case, that of Kilbourne Hole olivine, there is substantial evidence to suggest that the presence of leachable Al and Ca in the rock material (apparently as a result of the occurrence of anorthite as a minor phase), in addition to Mg, is associated with the dramatic effect on silicate glass dissolution. Many questions require further study. At the present time, it is not clear whether the effect of solid additives involves the build-up of a protective layer on the glass surface or solubility constraints on the composition of the aqueous phase. It is necessary to determine whether the presence of the solid additive affects glass dissolution when it is controlled by the leach rate, by saturation of the aqueous phase, or in both cases. However, the preliminary findings presented here indicate that studies of ternary glass-additive-water systems can provide important information about the mechanisms of glass corrosion.

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Table 1

Glass Compositions, wt%

Oxide	PNL 76-68	SRL TDS-165
SiO_2	40.0	51.6
Na_2O	12.9	7.7
Fe_2O_3	11.1	10.1
B_2O_3	9.5	7.3
ZnO	5.0	0.02
CeO_2	3.9	0.04
TiO_2	3.0	0.1
MoO_3	2.4	
CaO	2.0	1.0
ZrO_2	1.9	
La_2O_3	1.9	
Nd_2O_3	1.4	0.03
Cs_2O	1.1	
NiO	0.6	2.1
BaO	0.6	
P_2O_5	0.5	0.2
SrO	0.4	0.5
Cr_2O_3	0.4	0.3
Pr_6O_{11}	0.4	
TeO_2	0.3	
Sm_2O_3	0.2	
Gd_2O_3	0.2	
K_2O	0.1	
CoO	0.1	
Eu_2O_3	0.1	
Al_2O_3	0.02	5.5
Y_2O_3	0.02	
Li_2O	0.02	4.1
MnO_2		3.4
U_3O_8		2.8
MgO		0.8
CuO		0.01

Table 2

Leach Test on TDS-165 Glass

Concentrations of Uranium and of Major Glass Components in Leachates

Additive	Additive Grain Size, mm	Concentration in Leachate (mg/L)				pH
		Uranium	Boron	Silicon	Lithium	
None	0.25 - 0.355	0.59 ± 0.06	4.5 ± 0.1	42.2 ± 0.5	4.5 ± 0.2	9.81 ± 0.13
Magnesite	0.25 - 0.355	2.18 ± 0.28	20.3 ± 0.9	9.5 ± 2.2	19.8 ± 1.1	8.78 ± 0.10
Sepiolite	0.25 - 0.355	1.17 ± 0.03	14.9 ± 0.3	86.1 ± 2.2	10.7 ± 1.0	9.89 ± 0.09
Dolomite	0.25 - 0.355	0.19 ± 0.02	4.5 ± 0.1	32.9 ± 0.3	4.3 ± 0.1	9.66 ± 0.03
Diopside	0.25 - 0.355	0.61 ± 0.03	3.3 ± 0.1	42.2 ± 0.5	3.2 ± 0.1	9.50 ± 0.09
Magnesia	< 0.075	0.02 ± 0.02	4.3 ± 0.2	0.5 ± 0.4	1.5 ± 0.4	9.83 ± 0.25
Alumina	< 0.075	0.65 ± 0.17	4.3 ± 0.1	33.5 ± 0.9	4.1 ± 0.1	9.77 ± 0.02
Zirconia	< 0.075	0.45 ± 0.08	3.8 ± 0.1	32.1 ± 0.8	3.6 ± 0.1	9.76 ± 0.03
Ceria	< 0.075	0.29 ± 0.03	4.4 ± 0.1	33.3 ± 1.0	4.3 ± 0.1	9.82 ± 0.01
Titania	< 0.075	0.00 ± 0.03	4.5 ± 0.2	24.8 ± 0.6	4.8 ± 0.3	9.76 ± 0.02

TABLE 3

Composition of Kilbourne Hole and San Carlos Olivine Materials
Weight %

Oxide	Kilbourne Hole Olivine	San Carlos Olivine
SiO_2	43.9 ± 1.2	40.0 ± 0.8
MgO	40.6 ± 1.1	47.9 ± 0.5
FeO	8.39 ± 0.07	8.94 ± 0.21
Al_2O_3	2.90 ± 0.04	0.88 ± 0.01
CaO	2.54 ± 0.03	0.81 ± 0.01
Na_2O	0.49 ± 0.01	0.08 ± 0.01
Cr_2O_3	0.31 ± 0.02	0.67 ± 0.11
NiO	0.26 ± 0.01	0.43 ± 0.04
TiO_2	0.20 ± 0.01	0.03 ± 0.01
K_2O	0.16 ± 0.01	0.03 ± 0.01
MnO	0.13 ± 0.01	0.14 ± 0.01
P_2O_5	0.11 ± 0.01	0.05 ± 0.04

Table 4

Effects of Various Additives on Dissolution of PNL 76-68 Glass
0.6 glass + 1.5 g additive in 20 mL of DI water, 90°C, 5th week

Additive	Leachate Concentrations, mg/L						pH
	B	Si	P	Li	Na	Mg	
None#	37.6±0.9	125±3	2.17±0.05	0.13±0.01	120±3	0.00±0.01	9.78±0.04
a	41.3±1.0	134±3	2.48±0.05	0.12±0.01	134±3	0.38±0.04	9.75±0.04
b	36.8±0.9	119±3	2.21±0.05	0.13±0.01	119±3	0.03±0.01	9.75±0.04
c	29.6±0.7	100±3	1.77±0.04	0.10±0.01	95±2	0.81±0.09	9.72±0.04
d	38.6±0.9	122±3	2.35±0.05	0.13±0.01	122±3	0.27±0.03	9.79±0.04
e	49.9±1.2	63±2	2.33±0.05	0.09±0.01	160±4	0.91±0.11	9.49±0.04
f	24.3±0.6	62±2	0.61±0.01	0.06±0.01	83±2	0.63±0.07	9.80±0.04
g	36.0±0.9	104±3	2.29±0.05	0.08±0.01	112±3	1.21±0.14	9.85±0.04
h	33.5±0.8	97±2	2.21±0.05	0.09±0.01	104±2	0.09±0.01	9.81±0.04
i	35.3±0.9	105±3	2.28±0.05	0.09±0.01	105±2	0.05±0.01	9.81±0.04
j	34.5±0.8	105±3	2.21±0.05	0.10±0.01	103±2	0.05±0.01	9.81±0.04
k	40.0±1.0	117±3	2.47±0.05	0.06±0.01	113±3	0.03±0.01	9.62±0.04
l##	35.9±0.9	104±3	2.18±0.05	0.11±0.01	109±2	0.02±0.01	9.81±0.04
l##	37.8±0.9	112±3	2.32±0.05	0.14±0.01	113±3	0.07±0.01	9.69±0.04
m##	1.3±0.1	18±1	0.10±0.01	0.01±0.01	8±1	0.17±0.02	9.08±0.04
m##	0.8±0.1	18±1	0.05±0.01	0.00±0.01	7±1	0.12±0.01	9.08±0.04

a = Anthophyllite, Cashiers, North Carolina (46 E 0355)
b = Cordierite, Manitowage; Ontario (46 E2210)
c = Enstatite, Lake St. John, Quebec (46 E 2885)
d = Talc, Balmat, New York State (46 E 8000)
e = Serpentinite, Roxbury, Vermont (47 E 4860)
f = Serpentine, Lancaster County, Pennsylvania (46 E 7260)
g = Serpentized Forsterite, Devil's Thumb, Washington State (49 E 1693)
h = Olivine (45 W 9224)
i = Olivine, Twin Sisters Range, Washington St. (46 E 5835)
j = Olivine, Jackson County, North Carolina (46 E 5830)
k = Fayalite, Forsythe Iron Mine, Quebec (49 E 1555)
l = Olivine Dunite Xenolith, San Carlos, Arizona (49 E 1558)
m = Olivine Dunite Xenolith, Kilbourne Hole, New Mexico (49 E 1558)
\# glass only - baseline
\## the two sets of results for each of the materials l and m are based on independent tests run on two different batches of the material under the same conditions - see text

Table 5

Dissolution of Rock Materials in Water
0.1 g solid in 20 mL of DI water, 90°C, 1 week

Additive	Leachate Concentrations, mg/L								pH
	Mg	Al	Ca	Si	K	Na	P	Fe	
a	1.90±0.22	0.21±0.01	0.08±0.01	5.77±0.15	2.75±0.43	0.22±0.01	0.06±0.01	0.48±0.06	7.22±0.04
b	0.08±0.01	0.12±0.01	0.41±0.05	2.02±0.05	0.96±0.15	0.38±0.01	0.07±0.01	0.02±0.01	6.84±0.04
c	0.45±0.05	0.06±0.01	3.08±0.39	2.68±0.07	0.62±0.10	0.32±0.01	0.02±0.01	0.01±0.01	6.85±0.04
d	0.81±0.09	0.00±0.01	0.25±0.03	1.93±0.05	0.12±0.02	0.25±0.01	0.03±0.01	0.00±0.01	6.90±0.04
e	4.32±0.50	0.01±0.01	0.71±0.09	3.05±0.08	0.03±0.01	1.57±0.03	0.06±0.01	0.14±0.02	7.06±0.04
f	2.91±0.34	0.01±0.01	4.98±0.62	0.16±0.01	0.31±0.05	0.11±0.01	0.06±0.01	0.00±0.01	8.55±0.04
g	2.17±0.25	0.00±0.01	0.71±0.09	5.24±0.13	0.02±0.01	0.10±0.01	0.08±0.01	0.28±0.03	7.89±0.04
h	2.45±0.28	0.00±0.01	0.93±0.12	0.67±0.02	0.01±0.01	0.10±0.01	0.05±0.01	0.01±0.01	7.83±0.04
i	1.52±0.18	0.00±0.01	0.29±0.04	1.00±0.03	0.00±0.01	0.09±0.01	0.09±0.01	0.00±0.01	7.69±0.04
j	1.92±0.22	0.00±0.01	0.16±0.02	0.50±0.01	0.04±0.01	0.08±0.01	0.09±0.01	0.00±0.01	7.41±0.04
j	1.92±0.22	0.00±0.01	0.22±0.03	0.52±0.01	0.00±0.01	0.03±0.01	0.08±0.01	0.00±0.01	8.01±0.04
k	2.31±0.27	0.00±0.01	1.19±0.15	15.71±0.40	0.06±0.01	0.19±0.01	0.05±0.01	0.01±0.01	6.50±0.04
n	0.16±0.02	0.10±0.01	0.76±0.10	2.68±0.07	0.04±0.01	0.42±0.01	0.02±0.01	0.00±0.01	7.75±0.04
l	0.71±0.08	0.03±0.01	0.22±0.03	1.92±0.05	0.09±0.01	0.16±0.01	0.12±0.01	0.06±0.01	7.64±0.04
l	0.57±0.07	0.03±0.01	0.14±0.02	1.62±0.04	0.05±0.01	0.12±0.01	0.06±0.01	0.02±0.01	7.87±0.04
m	0.84±0.10	0.66±0.02	0.96±0.12	4.67±0.12	0.37±0.06	0.54±0.01	0.10±0.01	0.07±0.01	8.13±0.04
m*	1.03±0.12	2.31±0.06	4.67±0.59	14.75±0.37	1.42±0.22	2.26±0.05	0.08±0.01	0.02±0.01	7.76±0.04

n = Anorthite, Grass Valley, California (46 E 0555)
All other mineral designations as in Table 4
* = 1.5 g mineral (instead of 0.1 g)

Table 6

Effects of Various Additives on Dissolution of PNL 76-68 Glass
0.6 glass + 1.5 g additive in 20 mL of DI water, 90°C, 5th week

Additive	Leachate Concentrations, mg/L						pH
	B	Si	P	Li	Na	Mg	
None#	44.5±1.1	132±3	3.12±0.07	0.15±0.01	133±3	0.01±0.01	9.86±0.04
l	42.1±1.0	125±3	3.03±0.07	0.12±0.01	123±3	0.11±0.01	9.82±0.04
n	46.4±1.1	108±3	2.31±0.05	0.02±0.01	125±3	0.09±0.01	9.68±0.04
l+n	30.9±0.7	94±2	1.98±0.04	0.02±0.01	91±2	0.20±0.01	9.84±0.04

l = Olivine Dunite Xenolith, San Carlos, Arizona (49 E 1558)
n = Anorthite, Grass Valley, California (46 E 0555)
l+n = 70% San Carlos olivine (line l) + 30% anorthite (line n)

glass only - baseline

Table 7

Effects of Aqueous Phase Composition on Dissolution of of PNL 76-68 Glass in the Presence of San Carlos Olivine

0.6 g glass + 1.5 g additive in 20 mL of leachant, 90°C, 2nd week

Leachant	**Leachate Concentrations, mg/L**						**pH**
	B	**Si**	**P**	**Li**	**Na**	**Mg**	
DI Water (no additive)	25.7±0.6	117±3	1.23±0.03	0.07±0.01	72±2	0.00±0.01	9.53±0.04
1+10mg/L Ca	28.2±0.7	88±2	1.35±0.03	0.07±0.01	86±2	3.21±0.37	9.70±0.04
1+10mg/L Al	6.4±0.2	30±1	0.53±0.01	0.01±0.01	53±1	3.55±0.41	9.86±0.04
1+10mg/L Ca +10mg/L Al	2.8±0.1	11±1	0.05±0.01	0.03±0.01	44±1	2.21±0.26	9.69±0.04

1 = Olivine Dunite Xenolith, San Carlos, Arizona (49 E 1558)

Legends to Figures:

Figure 1. X-ray diffraction patterns of Kilbourne Hole olivine and San carlos olivine.

Figure 2. Additive effects on boron concentration in PNL 76-68 glass leaching. 0.6 g glass (-40 +60 mesh) with no additive and 0.6 g glass with 1.5 g Kilbourne Hole olivine (-40 +60 mesh) in 20 mL of deionized water, 90°C.

Figure 3. Additive effects on sodium concentration in PNL 76-68 glass leaching. 0.6 g glass (-40 +60 mesh) with no additive and 0.6 g glass with 1.5 g Kilbourne Hole olivine (-40 +60 mesh) in 20 mL of deionized water, 90°C.

Figure 4. Additive effects on silicon concentration in PNL 76-68 glass leaching. 0.6 g glass (-40 +60 mesh) with no additive and 0.6 g glass with 1.5 g Kilbourne Hole olivine (-40 +60 mesh) in 20 mL of deionized water, 90°C.

Figure 5. Additive effects on the pH in PNL 76-68 glass leaching. 0.6 g glass (-40 +60 mesh) with no additive and 0.6 g glass with 1.5 g Kilbourne Hole olivine (-40 +60 mesh) in 20 mL of deionized water, 90°C.

FIGURE 1

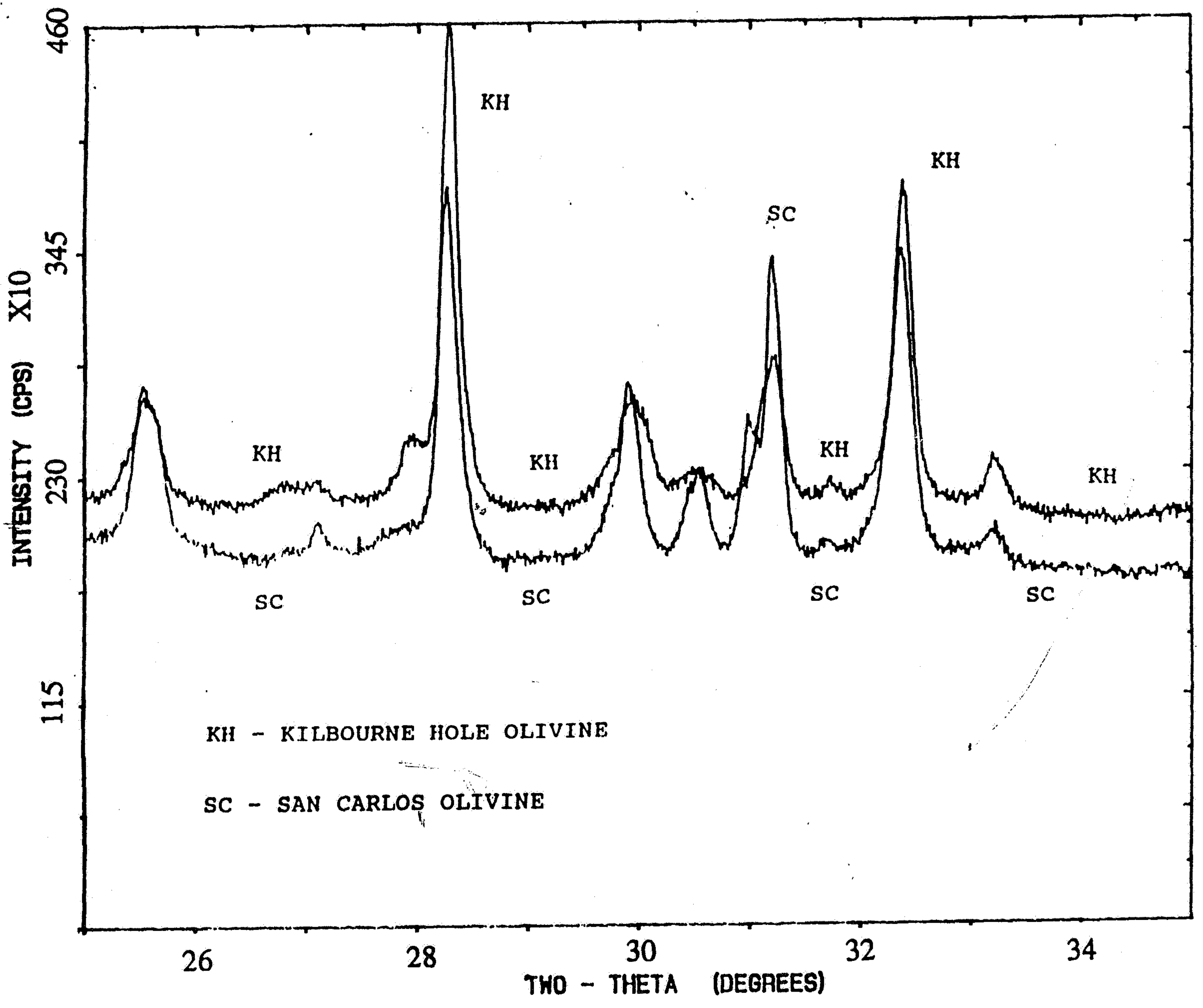
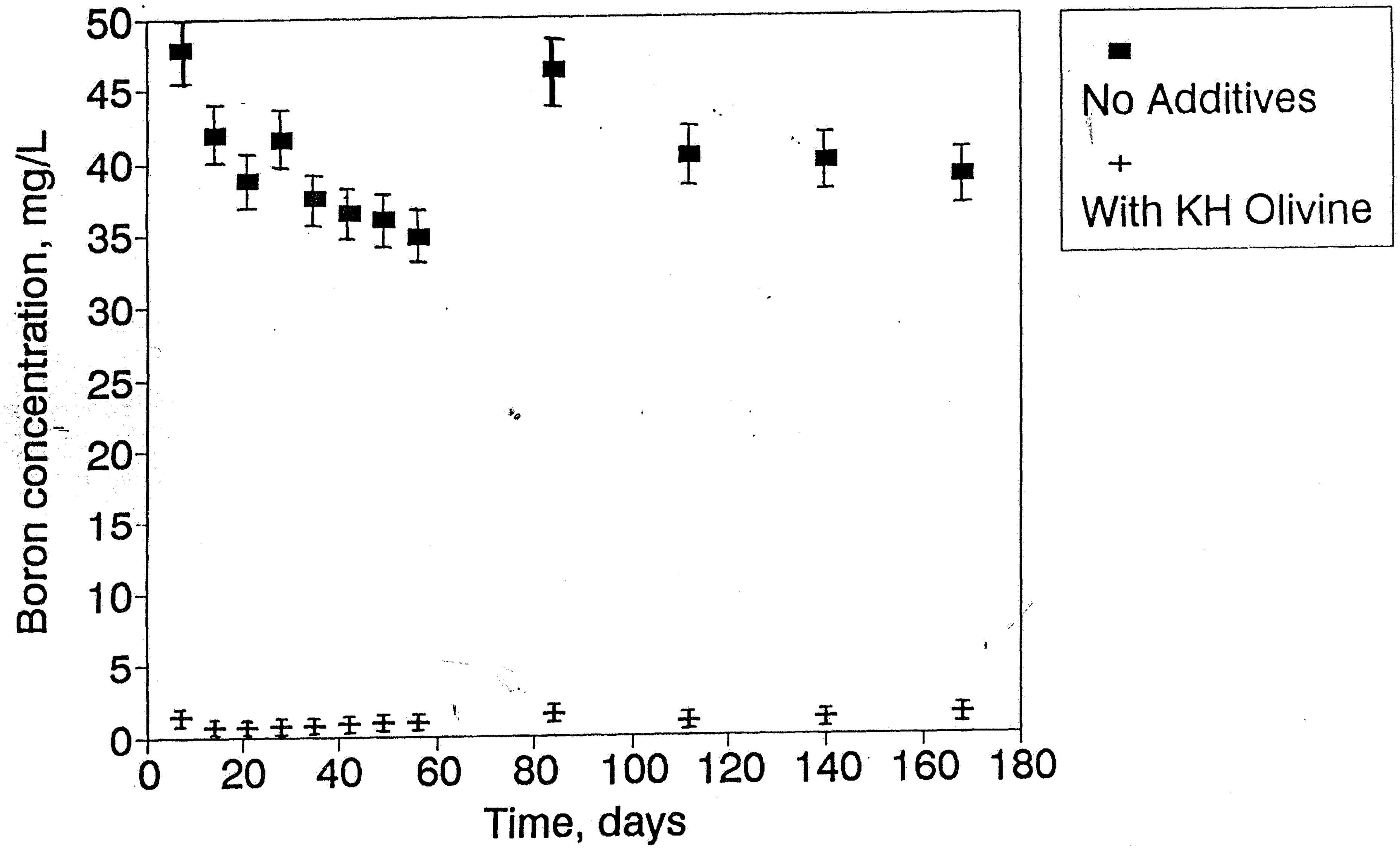

460
345
230
115
INTENSITY (CPS) X10
26
28
30
32
34
TWO - THETA (DEGREES)
KH
SC
KH
SC
KH
SC
KH
SC
KH
SC
KH
KH - KILBOURNE HOLE OLIVINE
SC - SAN CARLOS OLIVINE

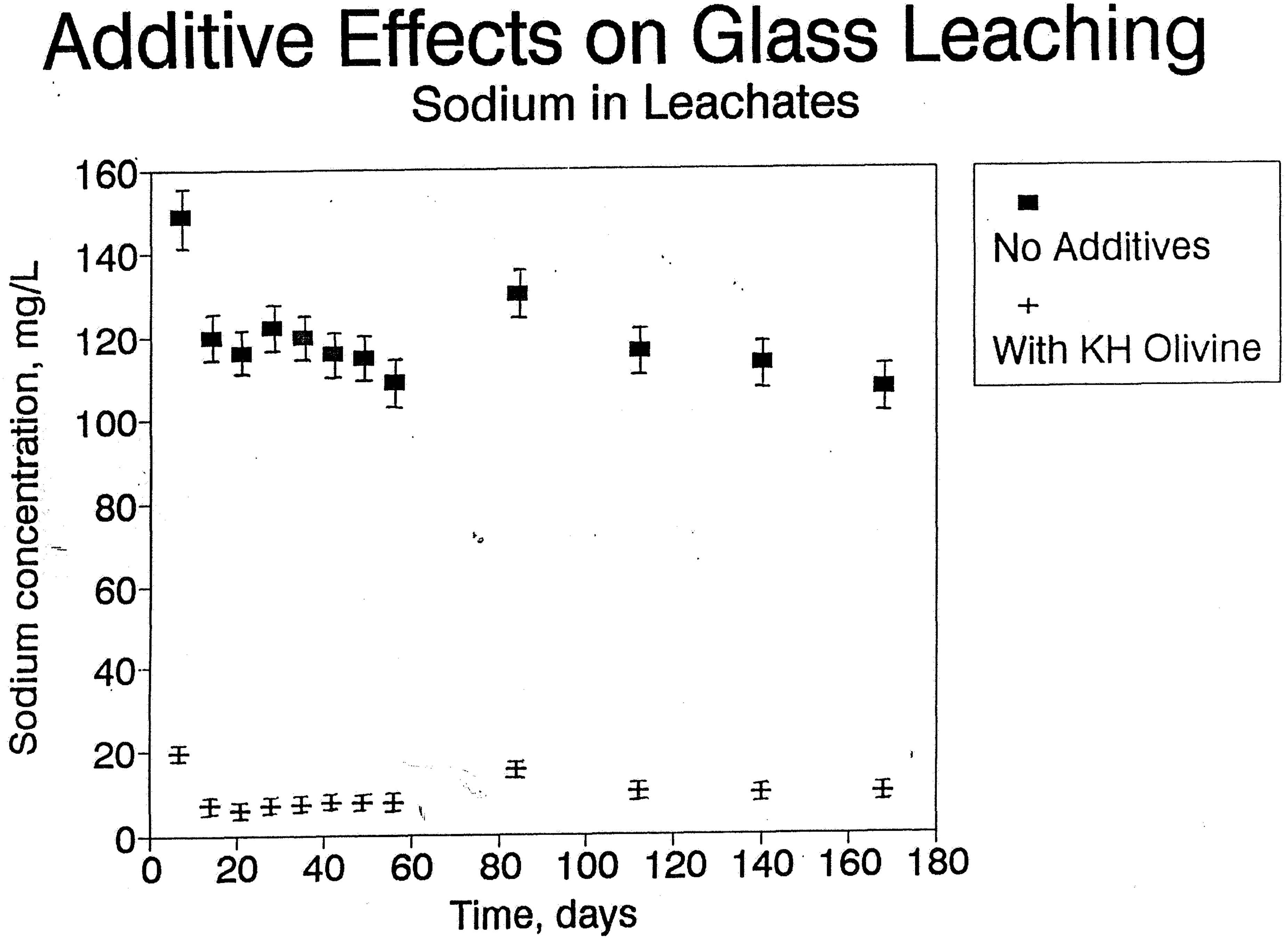
FIGURE 2



Additive Effects on Glass Leaching

Boron in Leachates

FIGURE 3



Additive Effects on Glass Leaching

Sodium in Leachates

FIGURE 4

Additive Effects on Glass Leaching

Silicon in Leachates

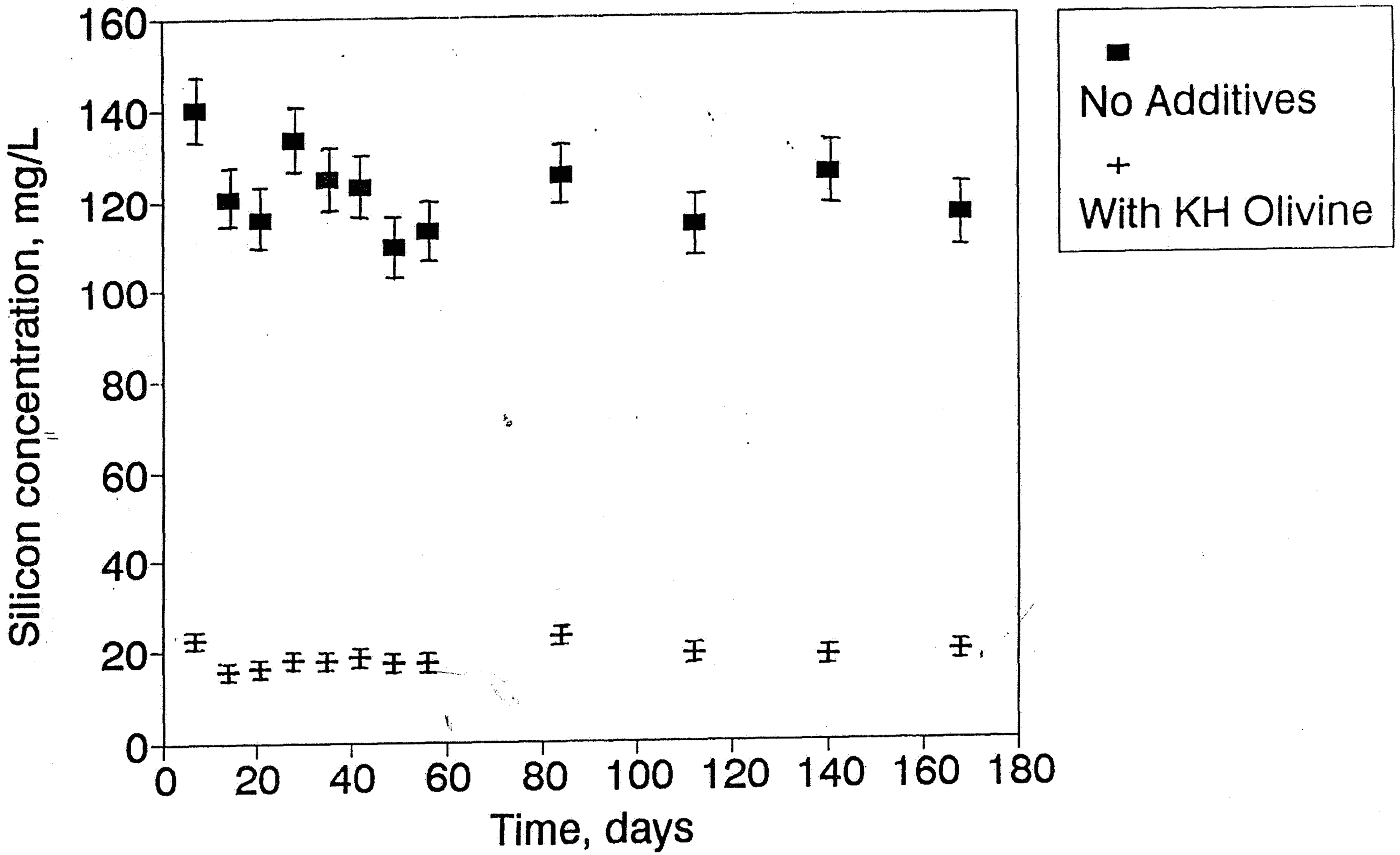
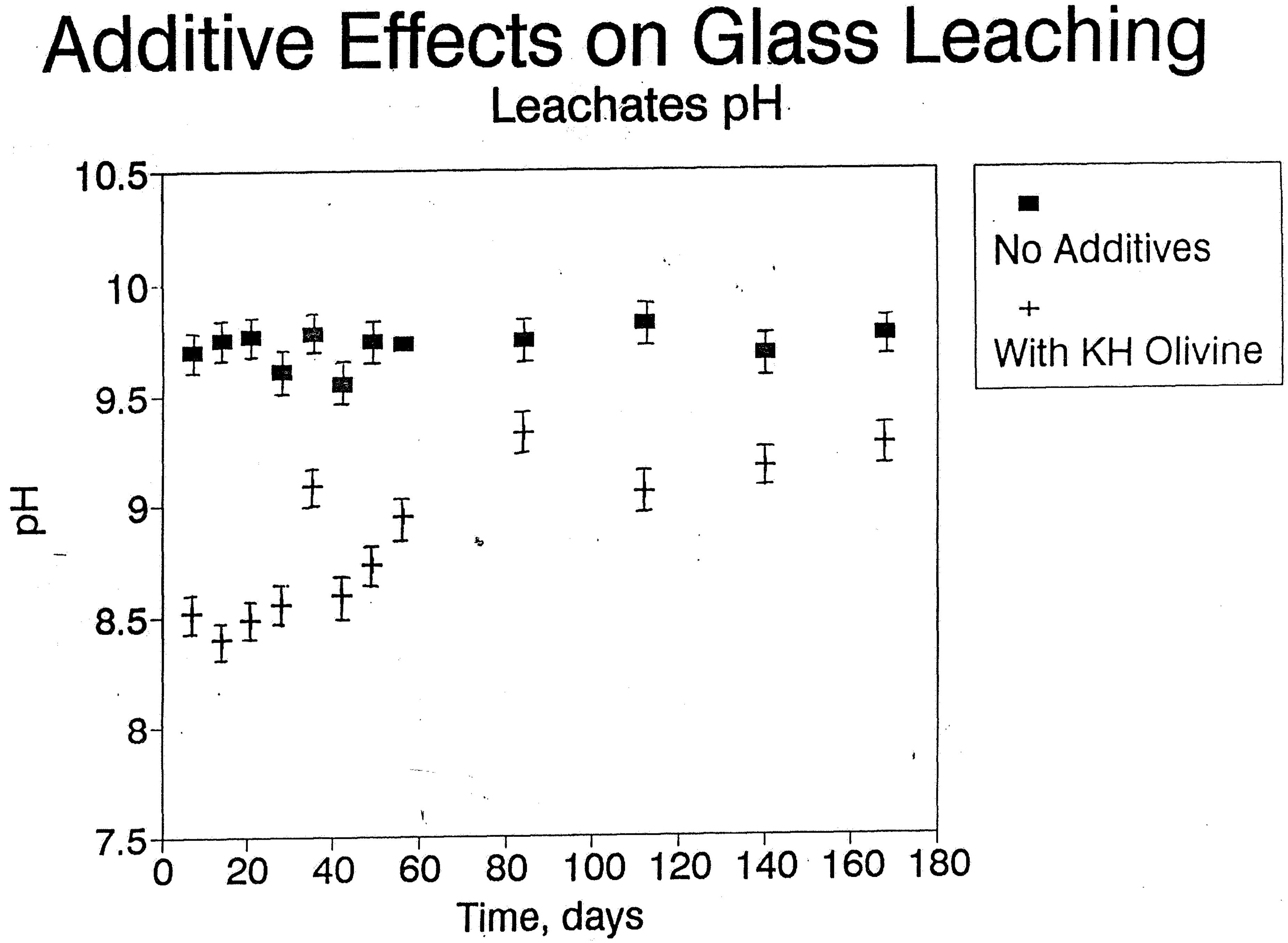


FIGURE 5


Additive Effects on Glass Leaching
Leachates pH
pH
10.5
10
9.5
9
8.5
8
7.5
0
20
40
60
80
100
120
140
160
180
Time, days
■ No Additives
+ With KH Olivine