THE INFLUENCE OF PENETRATING GAMMA RADIATION ON THE REACTION OF SIMULATED NUCLEAR WASTE GLASS IN TUFF GROUNDWATER*

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ABSTRACT

Static leaching experiments have been performed to determine the influence of penetrating gamma radiation on the reaction of simulated nuclear waste glass in tuff groundwater at 90°C. Both the leachates and the reacted glass monoliths were analyzed to characterize the reaction. Radiation was seen to acidify the leachates, but the high bicarbonate content of the groundwater prevented the pH values from dropping below 6.4. The glass reaction tended to raise the pH. Glasses based on SRL 165 black frit and PNL 76-68 glass compositions were leached. The SRL 165 type glasses were quite durable (as measured by the elemental mass loss after constant reaction times) and were unaffected by radiation. The PNL 76-68 glasses were much less durable, with the durability decreasing (after constant reaction times) as the exposure rate was increased. The primary effect of radiation is a lowering of the leachate pH which then affects the glass leaching rate.

INTRODUCTION

An extensive series of experiments has been performed to determine the influence of penetrating gamma radiation on the reaction of simulated nuclear waste glass in tuff groundwater. The Yucca Mountain Project (YMP) is studying the suitability of the volcanic tuff beds at Yucca Mountain, Nevada, as a repository site for the isolation of nuclear waste. While the horizon under study has been characterized as hydrologically unsaturated [1], the waste package performance must be understood under the unlikely but possible condition of liquid water intrusion into the repository. The high post-closure temperature will prevent liquid water

from entering the repository for several hundred years, though water vapor may exist. Water which may eventually enter the repository will be subjected to weak gamma radiation fields generated by the waste. The air in the repository will have been irradiated at high doses for many years and will also affect the groundwater chemistry. See [2] and references therein for a detailed discussion of the effect of radiation on the waste package environment for an unsaturated repository. The behavior of the waste in such groundwater must be understood to project the long-term performance of the repository.

Experiments have been performed over a four-year period to measure the effect of radiation on the leaching behavior of simulated nuclear waste glass in a saturated environment relevant to the tuff repository [3-6]. In this report we provide a comparison of the results and discuss the influence of radiation dose on glass reaction.

EXPERIMENTAL

The experiments were similar to the MCC-1 static leach tests [7] and were performed at 90°C under gamma exposures of 2 x 10^5 R/h, 1 x 10^4 R/h, 1 x 10^3 R/h, or without radiation for up to 278 days. The exposure rate was determined by dosimetry performed prior to the experiments. SRL 165 black frit doped with uranium, referred to as SRL U glass, or with uranium, neptunium, plutonium, and americium, referred to as SRL A glass, and PNL 76-68 based glasses ATM-1c and ATM-8, which contains uranium, neptunium, and plutonium, were reacted. While these glasses do not represent actual compositions that will be used to encapsulate waste, they provide a diverse range of glass reactivities which are useful in understanding the effects of radiation on leaching. Repository reference groundwater from well J-13 was prereacted with pulverized tuff rock at 90°C to produce the leachant, which is referred to as the EJ-13 solution. The glass and leachant compositions have been presented elsewhere [3-6]. The experiments were performed in 304L stainless steel vessels having a volume near 22 mL. An amount of leachant was added to attain a glass surface area/leachant volume ratio (SA/V) near 0.3 cm^{-1} and an air/leachant volume ratio near 0.3. Polished tuff wafers were added to some vessels as well.

The final leachates were analyzed for pH, anions (ion chromatography), cations (ICP, AA), and transuranics (α-counting). The reacted glass samples were measured for weight loss and the surfaces analyzed using SEM with EDS and SIMS. Some of the results are presented below, with an emphasis on the affects of radiation on the glass reaction.

RESULTS

The final leachate pH values are plotted vs. the reaction time for experiments with SRL A and ATM-8 glasses at the various exposure rates in Figure 1. The pH values of experiments with SRL U glass were identical to those with SRL A glass, within experimental error. The pH values of the nonirradiated experiments are higher than that of the initial leachant for both glass types. This is due to the production of hydroxide ions accompanying the alkali release from the glass. Irradiated experiments are acidified relative to the nonirradiated experiments due to the radiolytic production of nitric acid in moist air [8]. This was evidenced by a decrease in the pH and an increase in the concentration of fixed nitrogen. Burns et al. have proposed an expression for the nitric acid production in a similar two phase vapor/liquid system in which the amount of acid produced is proportional to the exposure [9]. Thus, more acid is expected to be produced at higher exposure rates for the same reaction time. This is observed in Figure 1 where the rate of acidification decreases as 2×10^5 R/h > 1×10^4 R/h > 1×10^3 R/h for both glass types.

Blank experiments (without glass) were acidified to pHs below 7 at all exposure rates, though the pH was prevented from dropping below 6.4 by the high bicarbonate concentration in the groundwater (~120 ppm). The presence of glass results in slightly higher pH values as the glass reaction produces sufficient hydroxide to partially neutralize the acid. The pH, therefore, reflects the balance between acidification due to radiolysis and basification due to the glass reaction. At long reaction times, the pH appears to approach a common value for all exposure rates, near 7 for SRL A glass and 7.5 for ATM-8 glass. The higher "final" pH of the experiments with ATM-8 glass indicates a greater extent of glass reaction, since the nitric acid production is the same in experiments with both glass types.

The release of various species from the glass into the leachate is indicative of the extent of reaction. The normalized elemental mass losses of boron, silicon, and sodium are shown plotted vs. the reaction time for SRL A and ATM-8 glasses in Figures 2a-2f at the various exposure rates. The release of these species from SRL A glass is not affected by irradiation, with NL(Na) > NL(B) $\cong$ NL(Si). Analysis of the reacted SRL U glasses showed the altered surfaces to be depleted in alkalis relative to the bulk glass, while the silicon concentration remained nearly constant [6].

The normalized elemental mass loss of all elements is greater from ATM-8 glass than from SRL A glass, and the mass loss after a given reaction time is influenced by irradiation. The release rate of all elements increases with the exposure rate as nonirradiated $< 1 \times 10^3$ R/h $< 2 \times 10^5$ R/h; and the elemental releases decrease as NL(Na) > NL(B) > NL(Si) at all exposures.

The release of transuranic elements was measured for SRL A (Am, Np, Pu) and ATM-8 (Np, Pu) glass in unfiltered and filtered (50 Å filter) leachate samples, and an acid strip fraction of the vessel. Neptunium was found in both the filtered and unfiltered fractions, but no neptunium was plated onto the stainless steel. The concentration of neptunium measured to be in the leachate is plotted against the reaction time for different exposure rates in Figures 3a and 3b for SRL A and ATM-8 glasses. The neptunium concentration is low in experiments with SRL A glass and the results of duplicate experiments show relatively large deviations. Nevertheless, the neptunium release rate does not vary significantly with the exposure rate for SRL A glass. ATM-8 glass, on the other hand, showed marked differences in the neptunium concentration at different exposure rates at constant reaction time, with the concentration increasing with the exposure rate. The plutonium concentration in the filtered fraction is shown in Figures 4a and 4b for SRL A and ATM-8 glasses. The plutonium solubility limit is sensitive to the pH, and only experiments irradiated at 2×10^5 R/h, which reached the lowest pH values, have a significant concentration of plutonium in the aqueous phase. Plutonium is preferentially plated onto the stainless steel vessel surface in other experiments with both glass types.

DISCUSSION

The primary effect of gamma radiation in these experiments is through acidification of the leachate by the radiolytic production of nitric acid. An equation describing the production of nitric acid in a moist air/liquid water system has been given by Burns et al. [9], which takes the following form at low exposures:

$$N = 2.9E\text{-}5 \bullet C_o\ R\ G\ Dt \qquad (1)$$

where N is the molar concentration of nitric acid produced, C_o is the initial concentration of nitrogen, R is the air/liquid volume ratio, G is the radiolytic yield, D is the dose rate, in Mrad d^{-1}, and t is the exposure time, in days. Using the results of the experiments irradiated at

2×10^5 R/h, a G value for the production of HNO_3 of 2.4 molecules/100 eV was obtained. Substituting the experimental values C_o = 3.6E-2M , R = 0.3, and G = 2.4, Eq. (1) is reduced to

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$$N(M) = 5.95E\text{-}7\ Dt \qquad (2)$$

The nitric acid production is therefore predicted to occur at 2.86 μM day^{-1} at an exposure rate of 2×10^5 R/h, 0.14 μM day^{-1} at 1×10^4 R/h, and 0.01 μM day^{-1} at 1×10^3 R/h. The amount of nitric acid formed is not limited by the available gases. For example, after 100 days at 2×10^5 R/h, which is about twice the maximum exposure attained, only about 0.3 mM of N_2 and O_2, or about 1% of the initial N_2 and 3% of the initial O_2 are consumed. (At greater exposures, the HNO_3 yield may decrease as the oxygen partial pressure decreases [8].) Bicarbonate in the tuff groundwater inhibits acidification below about 6.4 (which is the pK_a of the bicarbonate/carbonic acid equilibrium at 90°C [2]), and so the pH difference between irradiated and nonirradiated experiments is limited to about 2 pH units (the difference between the pH of the starting water and 6.4). This small pH difference may be sufficient to alter the solubility limit of some species and so perhaps alter the reaction rate. The leachates are predicted to be acidified to pH 6.4 after less than 1 day, about 3 days, or after 29 days at exposure rates of 2×10^5 R/h, 1×10^4 R/h, or 1×10^3 R/h, respectively. Figure 1a shows the experiments with SRL A glass to be acidified to near pH 6.5 after 28 days at 2×10^5 R/h. Experiments with ATM-8 glass are acidified to a pH near 6.6 after only seven days at 2×10^5 R/h, but are acidified less at longer reaction times, probably because of the glass reaction.

The final pH is less acidic than predicted by the nitric acid production also because the glass reaction raises the pH. This is seen in the nonirradiated experiments which reach pH values above 9 for both SRL A and ATM-8 glass. The glass reaction partially neutralizes the nitric acid produced in the irradiated experiments. Hydroxide is produced with the release of alkalis but may be consumed by network dissolution reactions. The glass reaction appears to proceed at a maximum rate early and slow with time while the radiolytic production of nitric acid proceeds at a nearly constant rate over the duration of these experiments. Early in the reaction, the glass reaction may overwhelm the nitric acid production and raise the pH. This is seen to occur in the ATM-8 experiments irradiated at 1×10^3 R/h after 28 days. At longer times the glass reaction slows and the pH drops. Eventually the two rates may become similar and the pH attain an apparent steady-state value. This appears to happen in experiments with SRL A glass near a pH of 7 and with ATM-8

glass at a pH near 7.5 over the reaction times tested. Nonirradiated experiments are expected to show increasing pH values until either the reaction stops or the pH becomes buffered by secondary phase formation.

The rate of the SRL A reaction is not influenced by irradiation or by the resulting changes in the leachate pH, as measured by elemental release rates. This reflects the high durability of this glass composition in tuff groundwater at a near-neutral pH. Acidification of the leachate below about 7 is prevented by the bicarbonate buffer. The rate of nitric acid production (that is, the exposure rate) does not influence the rate of the glass reaction. The rate of release of species from ATM-8 glass is increased upon irradiation. These results show the leachate pH to only drop to about 7.5 upon irradiation at all exposure rates. Because more acid is produced at higher exposure rates, more glass must react to maintain the pH near 7.5. The higher exposure rates require greater glass reaction rates to maintain a pH value near 7.5, and so the glass reaction is accelerated by radiation through the pH drop. The glass appears to buffer the leachate to a pH value near 7.5. It is generally found that silica glasses are more reactive at higher pH values than at near neutral pHs due to the greater solubility of silica above pH $\sim$ 9.5. However, the glass reactions may also be inhibited by the formation of surface layers which may be more soluble in neutral or acidic solutions. The SRL A and ATM-8 samples are undergoing further characterization using analytical electron microscopy to determine how the secondary phases that make up the reacted layer are affected by the different irradiation conditions. The present results imply that a clear difference in secondary phase formation will exist for the two glass types.

Irradiation was also seen to produce nitrite ions in the solution at all exposure rates [3,5,6] which indicates the solution Eh is reduced from that of the starting leachant. Experiments irradiated at 2 x 10^5 R/h generated both nitrate and nitrite ions, but experiments irradiated at the lower exposure rates showed a decrease in the nitrate concentration with a corresponding increase in the nitrite concentration. Equation (2) predicts an amount of nitrate near the detection limit ($\sim$0.1 ppm) will be produced in experiments irradiated at 1 x 10^4 R/h or 1 x 10^3 R/h over the duration of these experiments, which is negligible compared to the initial leachant nitrate concentration of about 7.6 ppm. Figure 5 shows the nitrite/nitrate concentration ratio plotted vs. the total exposure for experiments without glass. The presence of glass increases the ratio slightly. The solution is seen to be reduced at low total exposures but to approach the Eh of the starting leachant (which corresponds to a ratio of zero) at higher exposures. This may indicate a transient (or nonequilibrium) nature of the reduction or an influence of the solution pH on the ratio.

The lack of effect of radiation on the SRL 165 glass reaction in the present experimental conditions may be due to the low reactivity of the SRL 165 type glasses, or may be the result of different processes controlling the reaction compared to the ATM-8 glass. Further studies are in progress to assess the effect of radiation on glass reaction at more repository-relevant R values (smaller volumes of water).

CONCLUSIONS

Static leach experiments using simulated nuclear waste glasses based on the composition of SRL 165 black frit and PNL 76-68 were performed under gamma radiation fields of 2 x 10^5 R/h, 1 x 10^4 R/h, and 1 x 10^3 R/h, and in the absence of radiation. The SRL 165 type glasses reacted similarly under all radiation fields while the PNL 76-68 type glasses reacted to a greater extent in the high radiation fields. Radiolysis of the moist air produced nitric and nitrous acids which acidified the leachates relative to the nonirradiated experiments. The leachate pHs remained between 7 and 9 for the SRL glasses and between 7.5 and 9.5 for the PNL glasses. The high bicarbonate ion concentration buffered the pH in experiments without glass and in experiments with SRL glasses. Experiments with the PNL 76-68 glasses were apparently buffered to a pH near 7.5 by the glass reaction. A greater extent of glass reaction was required to maintain a pH of 7.5 at higher exposure rates because of the increased nitric acid production. The behavior of the PNL 76-68 type glasses is contrary to that expected from the silica solubility as a function of leachate pH, and may point towards a secondary influence of radiation.

ACKNOWLEDGMENTS

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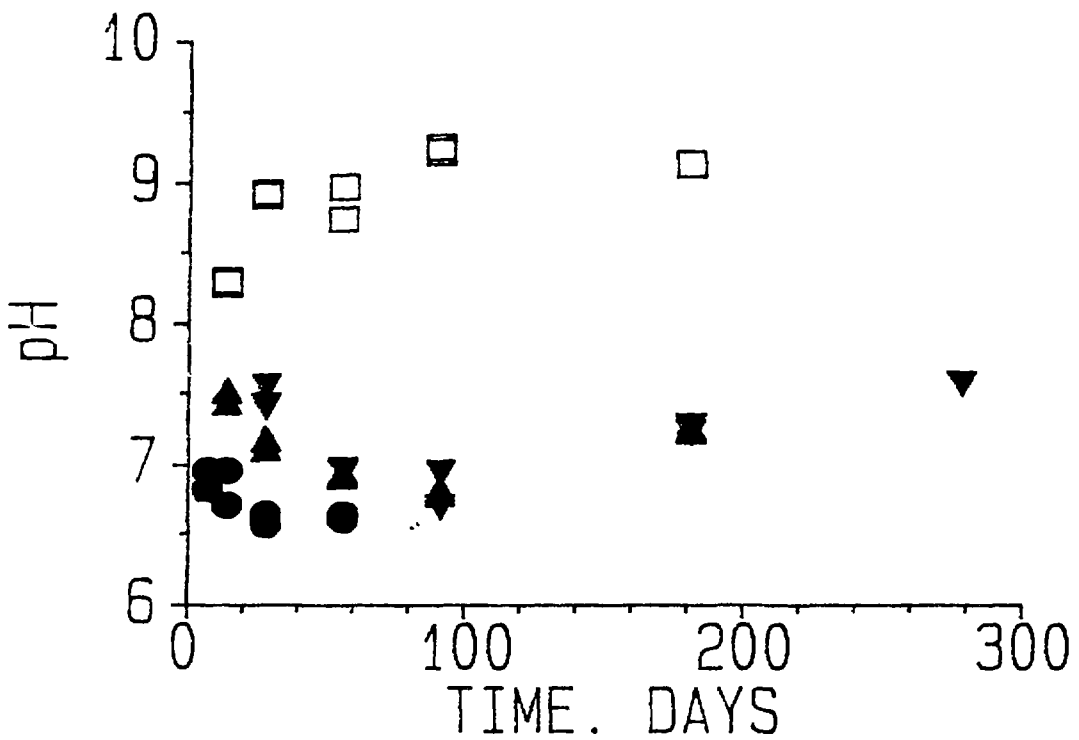
Figure 1. Final Leachate pH for Experiments with (a) SRL A Glass, or (b) ATM-8 Glass Irradiated at (●) 2 x 10^5 R/h, (▲) 1 x 10^4 R/h, (▼) 1 x 10^3 R/h, or (□) Nonirradiated vs. the Reaction Time.

Figure 2. Normalized Elemental Mass Loss for Experiments Irradiated at (●) 2 x 10^5 R/h, (▲) 1 x 10^4 R/h, (▼) 1 x 10^3 R/h, or (□) Nonirradiated vs. the Reaction Time: (a) Boron from SRL A, (b) Boron from ATM-8, (c) Silicon from SRL A, (d) Silicon from ATM-8, (e) Sodium from SRL A, and (f) Sodium from ATM-8.

Figure 3. Concentration of Neptunium-237 in the Leachate vs. Reaction Time for (a) SRL A Glass, or (b) ATM-8 Glass in Experiments Irradiated at (●) 2 x 10^5 R/h, (▲) 1 x 10^4 R/h, (▼) 1 x 10^3 R/h, or (□) Nonirradiated.

Figure 4. Concentration of Plutonium-239 in the Leachate vs. Reaction Time for (a) SRL A Glass, or (b) ATM-8 Glass in Experiments Irradiated at (●) 2 x 10^5 R/h, (▲) 1 x 10^4 R/h, (▼) 1 x 10^3 R/h, or (□) Nonirradiated.

Figure 5. Nitrite/Nitrate Concentration Ratio in Leachate for Experiments Without Glass, Irradiated at (●) 2 x 10^5 R/h, (▲) 1 x 10^4 R/h, and (▼) 1 x 10^3 R/h vs. Reaction Time.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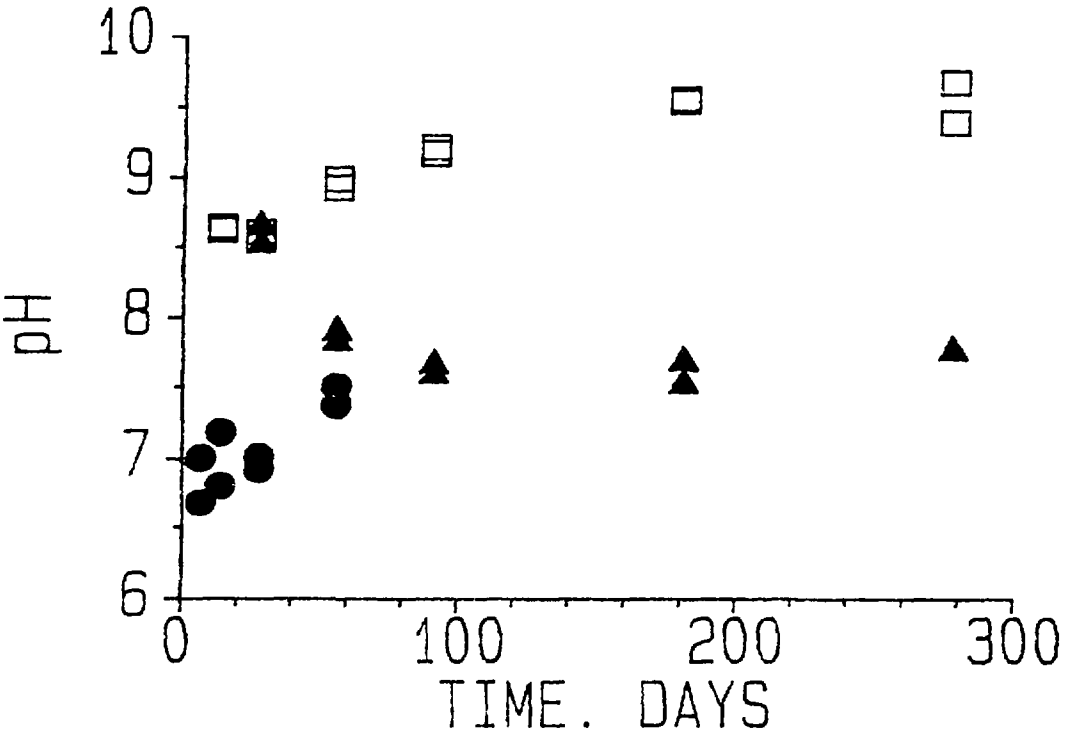
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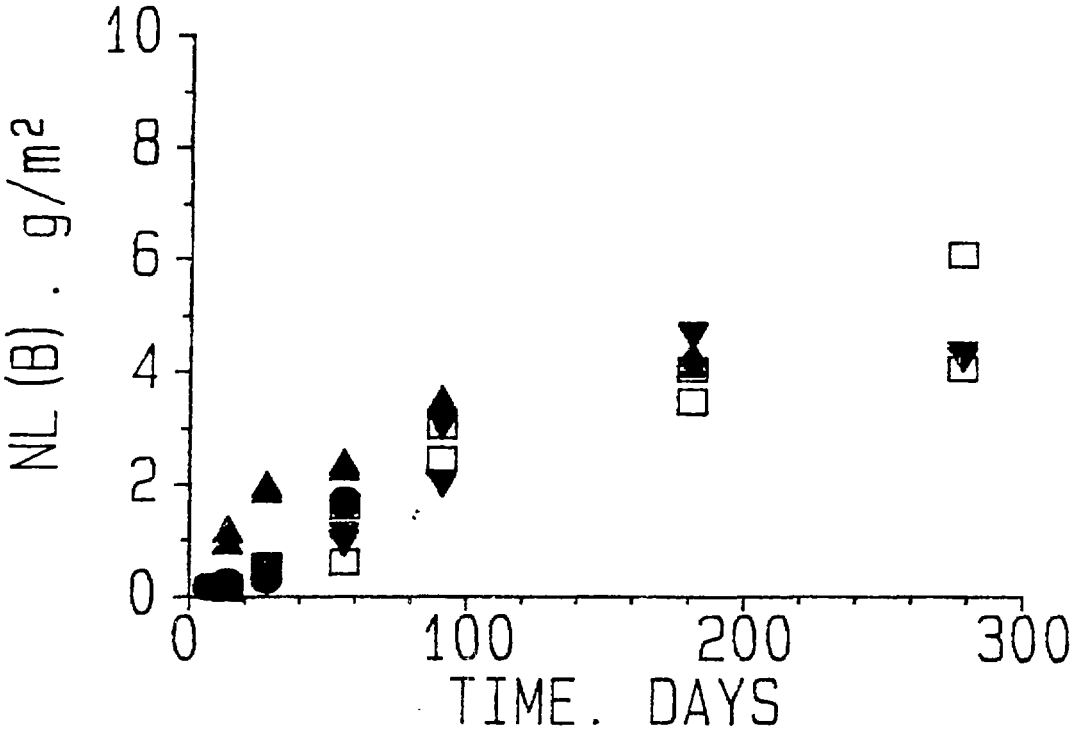
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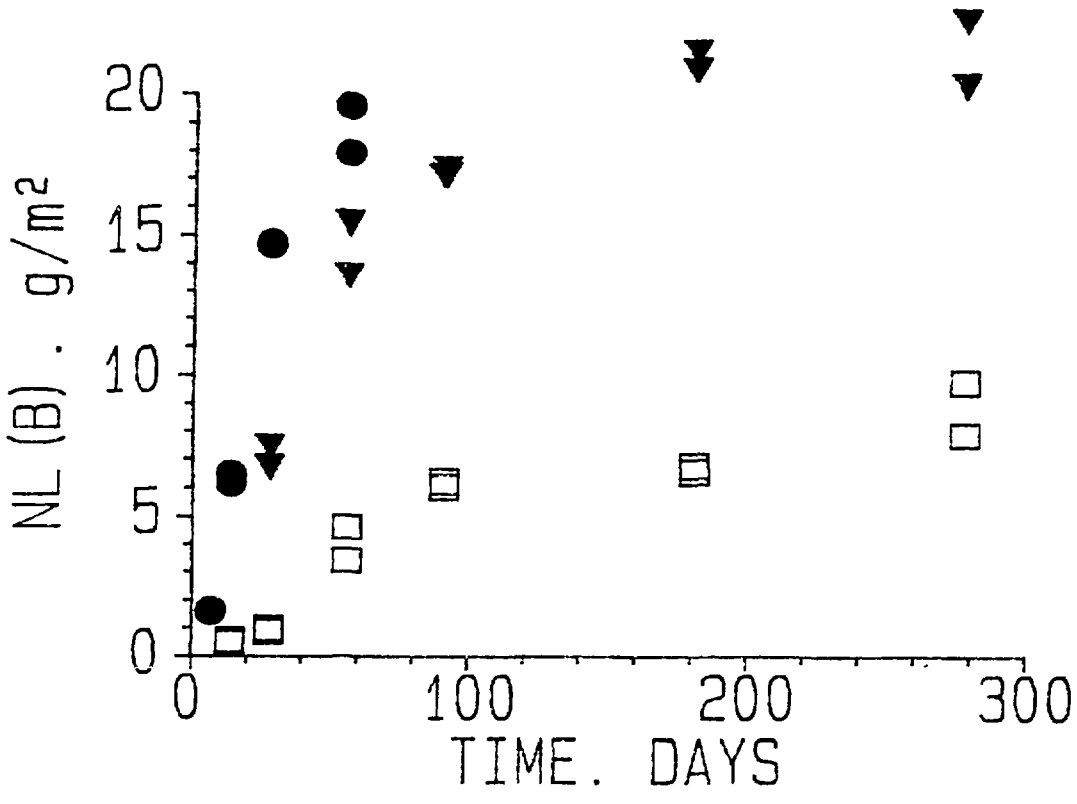
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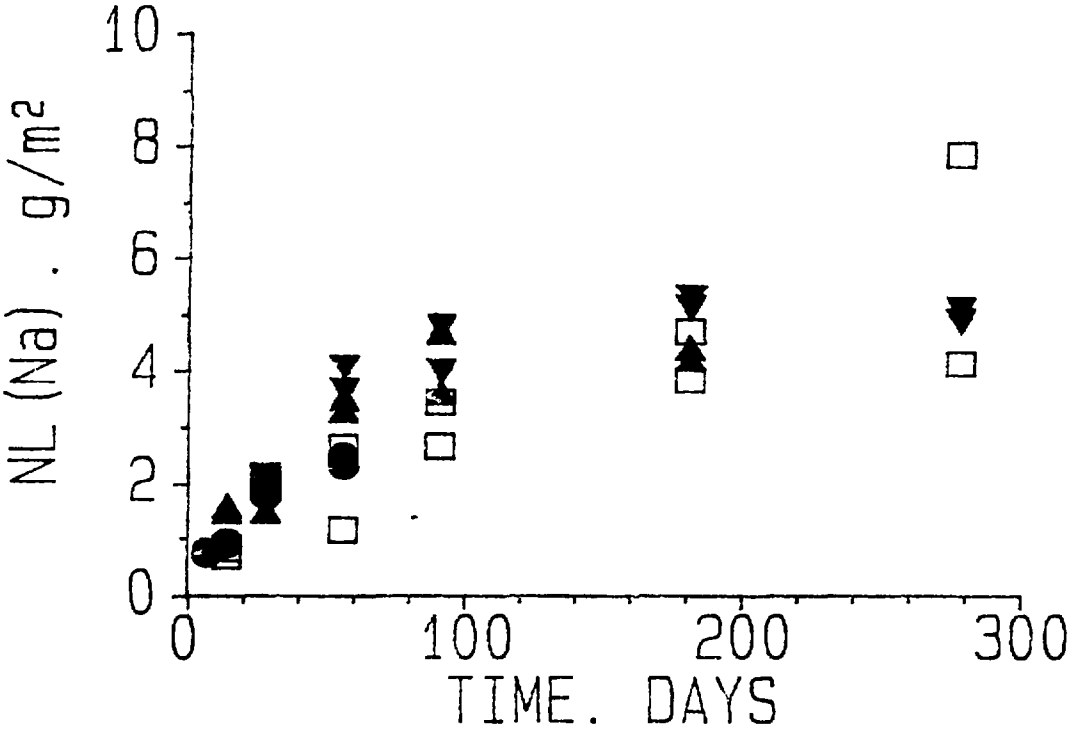
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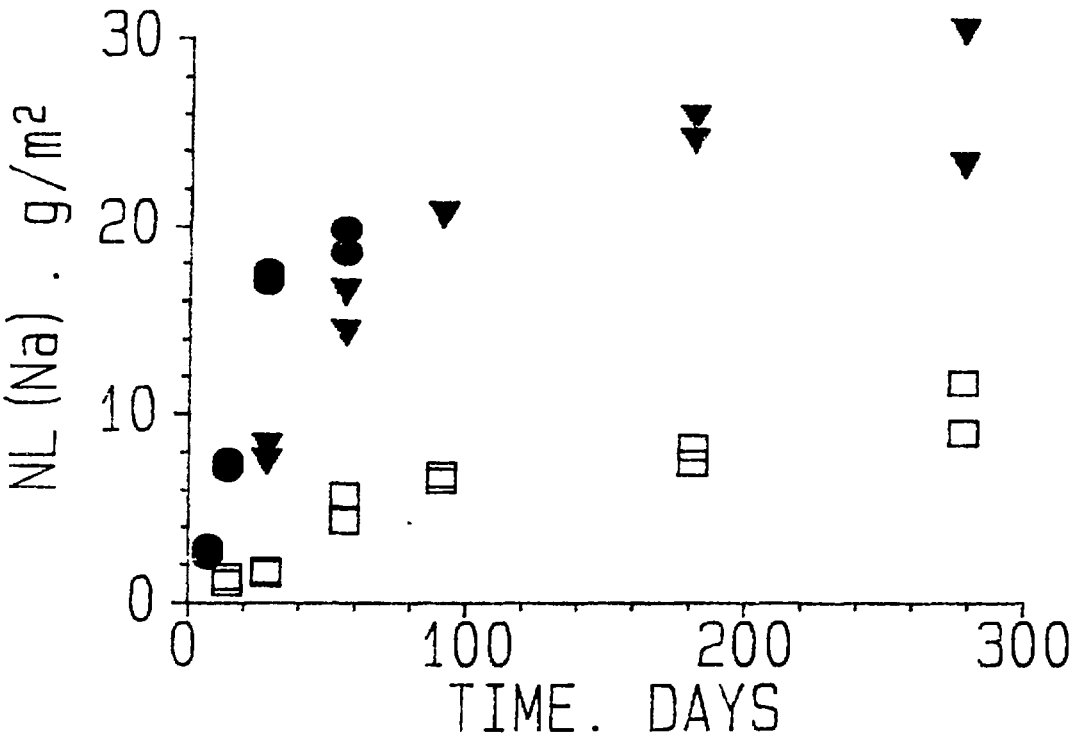
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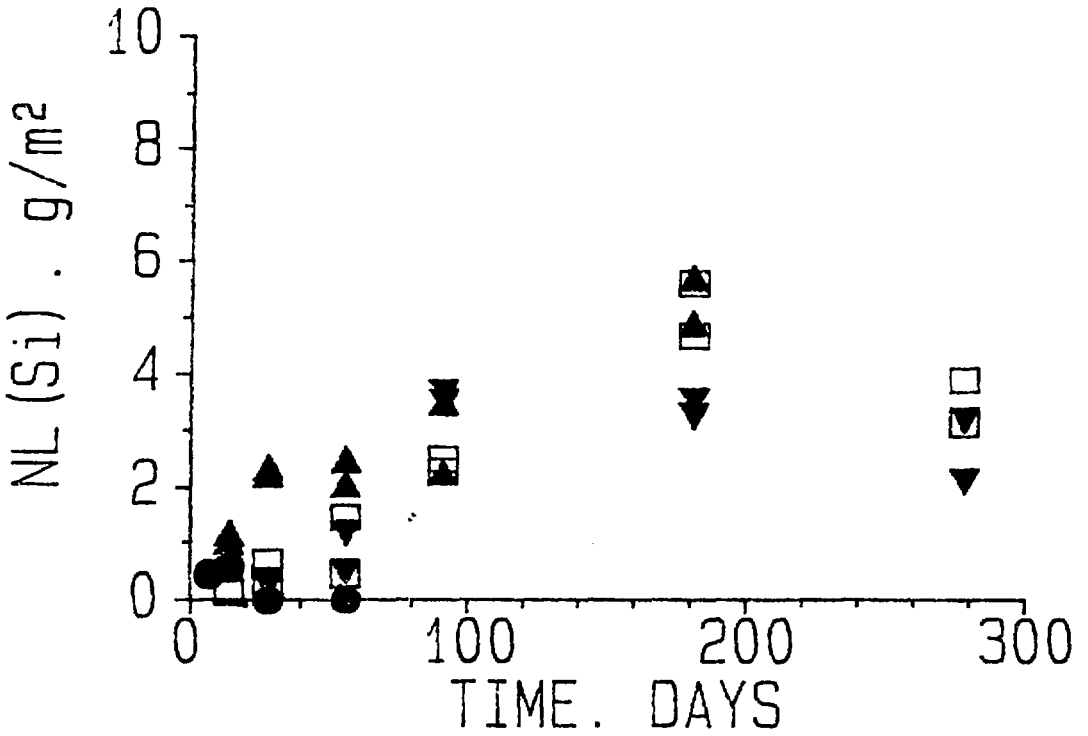
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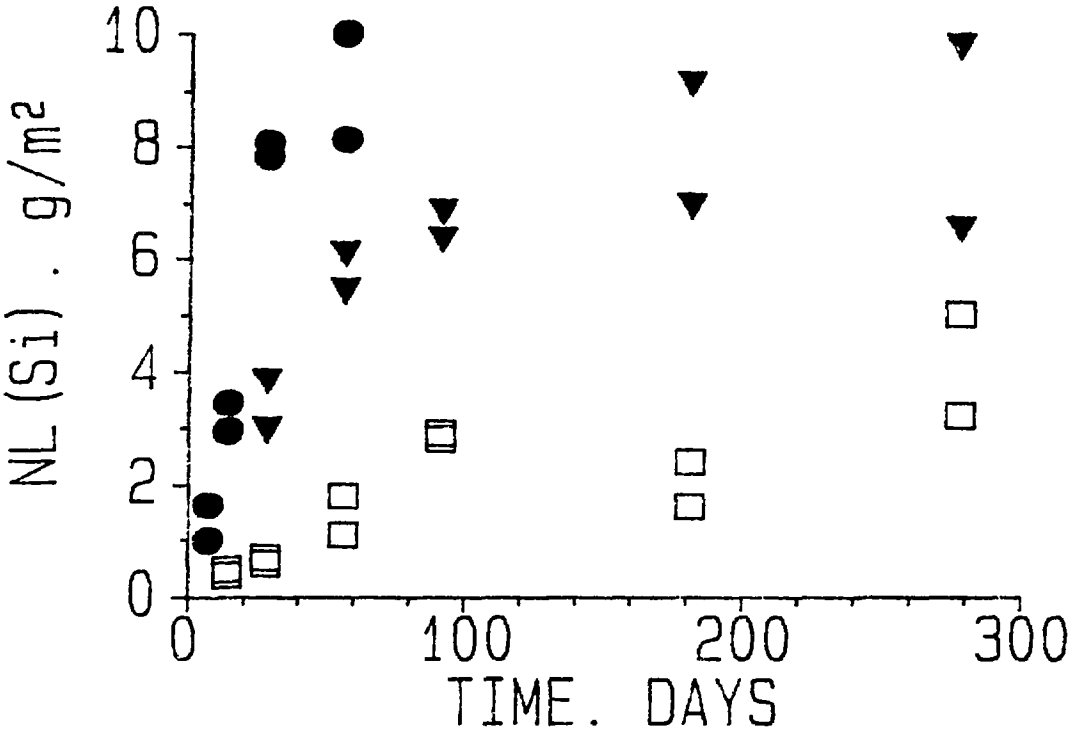
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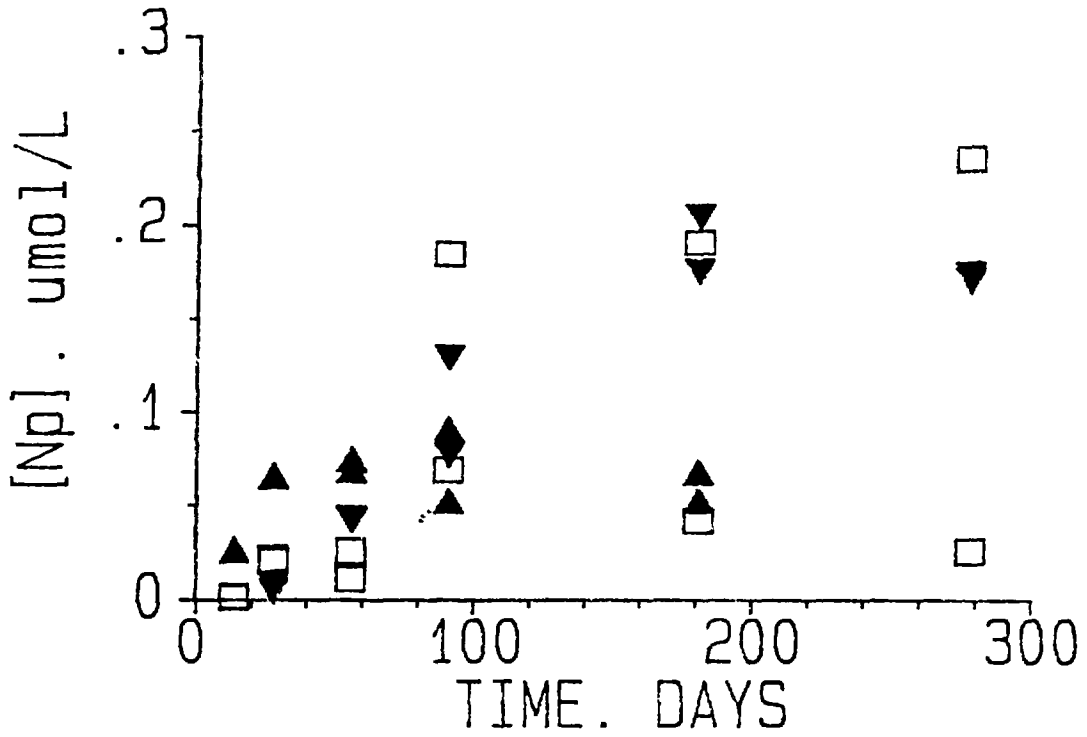
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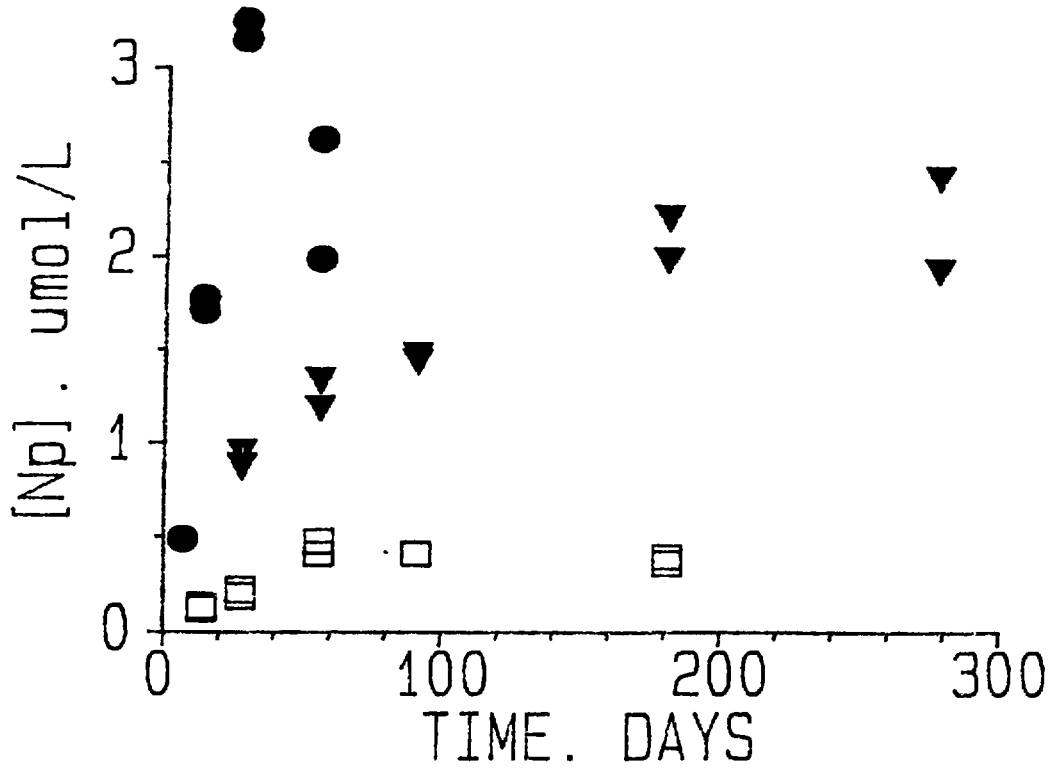
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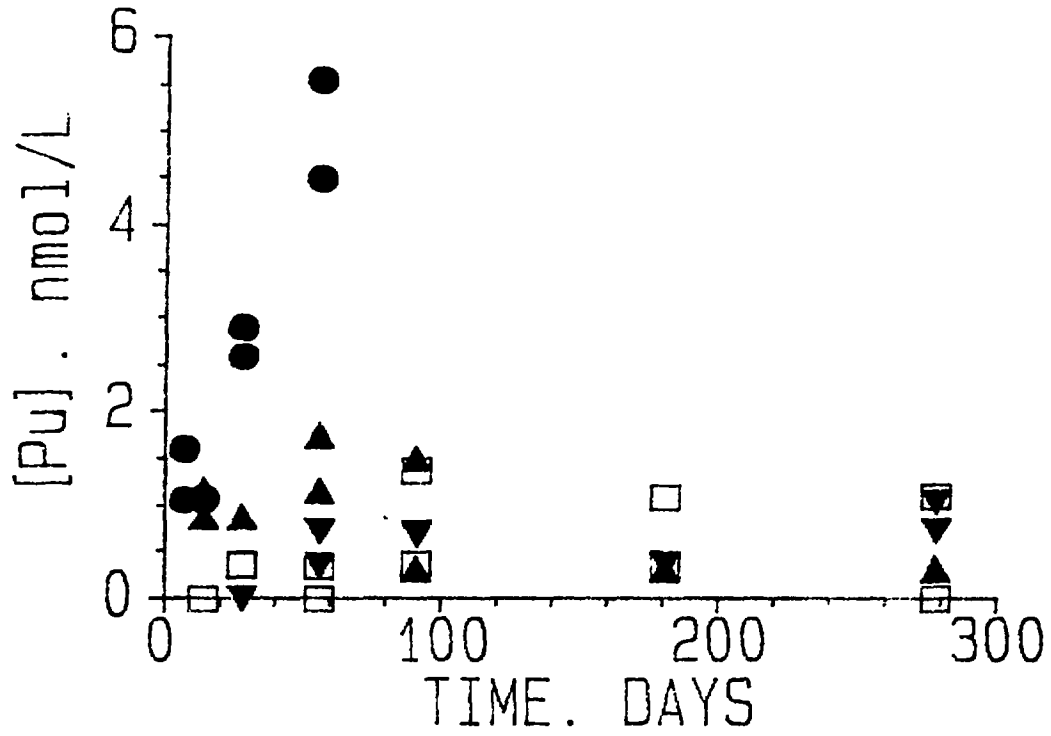
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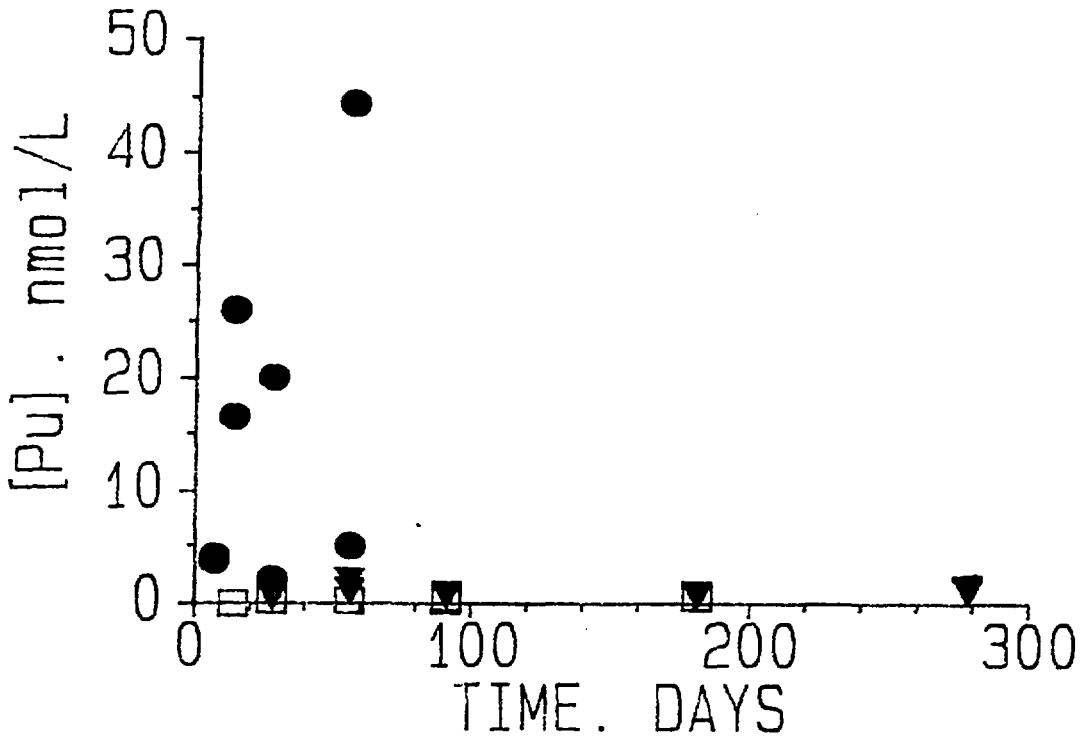
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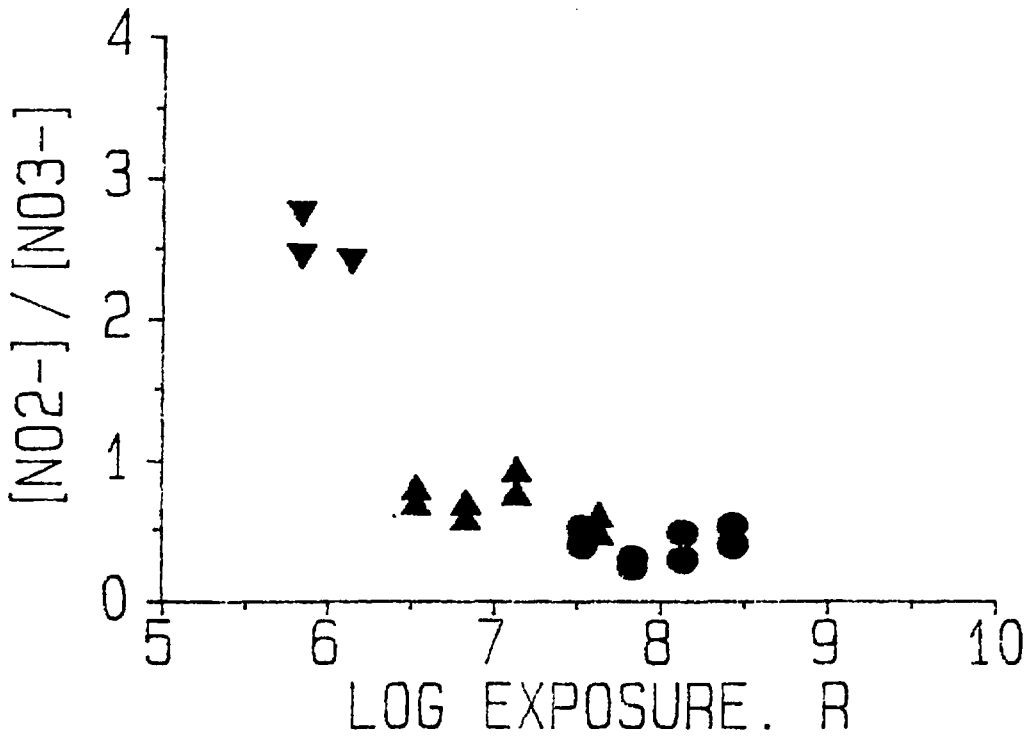
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LOG EXPOSURE. R