May 1983 corresponds to a tail length of over 12×10^6 km, and the other lengths range from 2×10^6 to 8.5×10^6 km.

In order for Venus to be in the center of a magnetotail rooted in the Oljato orbit, the solar wind would have to flow at an angle to the ecliptic plane equal to at least 15° on the days on which events were detected. Deviations in the solar wind flow of up to 15° can occur but are extremely rare (*7*). Thus, we interpret our observations as occurring at the edge of a disturbed region, about 1.3×10^6 to 2×10^6 km from the center line of the sun-asteroid interactions. This gives us lower limits on two dimensions, the length of the tail and its width. In order to estimate its thickness, we use the duration of the field enhancement and assume a velocity. Using the relative velocities of Venus and Oljato across the Venus sun line, we obtain the values in column 3 of Table 1. Assuming that the wake is passing Venus at 30 km/sec (or 1 standard deviation of the flow velocity about the radial direction) (*7*), we obtain the thickness in column 4. This wide but thin field enhancement resembles the plasma density enhancement found in the recent magnetohydrodynamic simulation of a comet (*8*). At a distance of only 2×10^6 km behind the comet the simulated plasma disturbance is 0.15×10^6 km thick and 1.7×10^6 km wide. We expect the field disturbance that is rooted in this mass-loaded plasma to have similar dimensions.

For a wake cross section of 0.3×10^{12} km^2 in a solar wind flowing at 400 km/sec, 3×10^{29} solar protons per second are affected. However, when the wake has spread to this size, we see no perceptible perturbation in the velocity of the plasma. Assuming therefore that the velocity effect is thus less than 1 percent, we calculate that only the equivalent of 2×10^{26} oxygen ions per second are being added to the flow. This amounts to about 5 kg of gas per second. This process could occur for 10^5 years or longer for an Oljato-sized object [the expected dynamical lifetime for Apollo asteroids is a few tens of millions of years (*9*)].

The estimated outgassing for Oljato is much less than the outgassing rates associated with visible comets. For example, estimates of the mass loss of comet West at 0.4 AU are close to 2×10^{31} proton masses per second (*10, 11*). Comet-like properties for an Apollo asteroid are thus not totally unexpected. Apollo asteroids have been postulated to be extinct cometary nuclei because of the weakness of the asteroidal source in this region and because of their size (*12*). The comet Encke seems to be well on its way to becoming an Apollo asteroid (*13*). Oljato itself has been postulated on the basis of meteoric evidence to be a defunct comet (*14*) and even to be undergoing outgassing on the basis of ultraviolet reflectivities (*5*). We would like to encourage further ground-based observation of this interesting object to search for further signs of its activity.

C. T. RUSSELL
Department of Earth and Space Sciences and *Institute of Geophysics and Planetary Physics, University of California, Los Angeles 90024*
R. AROIAN
Jet Propulsion Laboratory, California Institute of Technology, Pasadena 91125
M. ARGHAVANI
Department of Earth and Space Sciences and *Institute of Geophysics and Planetary Physics*
K. NOCK
Jet Propulsion Laboratory

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Lead-Iron Phosphate Glass: A Stable Storage Medium for High-Level Nuclear Waste

Abstract. *Results are presented which show that lead-iron phosphate glasses are a promising new waste form for the safe immobilization of both high-level defense and high-level commercial radioactive waste. Relative to the borosilicate nuclear waste glasses that are currently the "reference" waste form for the long-term disposal of nuclear waste, lead-iron phosphate glasses have several distinct advantages: (i) an aqueous corrosion rate that is about 1000 times lower, (ii) a processing temperature that is 100° to 250°C lower, and (iii) a much lower melt viscosity in the temperature range from 800° to 1000°C. Most significantly, the lead-iron phosphate waste form can be processed using a technology similar to that developed for borosilicate nuclear waste glasses.*

A new lead-iron phosphate glass nuclear waste form has been developed that appears to be unusually well suited to the safe immobilization and permanent disposal of various types of high-level radioactive waste. By melting lead-iron phosphate glass together with simulated nuclear waste, it is possible to form at a relatively low temperature a homogeneous stable glass in which the radioactive nuclei are chemically incorporated in the glass structure. The idea of creating a nuclear waste form by dissolving radioactive waste in a glass is, of course, not new; variations of this idea have been intensively investigated during the past 30 years. Most of this research, however, has focused on the use of different forms of borosilicate glass with compositions similar to Pyrex. Phosphate glasses were eliminated from serious consideration during the formative stages of nuclear waste host development. The lack of attention given to phosphate glasses as a nuclear waste form can be traced, in part, to an early study of a particular phosphate glass process developed at Brookhaven National Laboratory (*1*). The results of this study were not encouraging. Subsequently, with the exception of work carried out in West Germany during the development of the PAMELA process (*2*) (a waste disposal scheme in which alkali phosphate glass beads were incorporated in a metal matrix), research into essentially all phosphate glass waste forms was curtailed. In addition, the familiarity of researchers in the glass industry with the engineering and processing technology associated with the production of silicate or borosilicate glass has undoubtedly provided some impetus to the development of silicate-based nuclear waste forms.

Recent work on synthetic analogs of natural phosphate minerals such as monazite as possible storage media for high-level nuclear waste has rekindled interest in the development of phosphate glasses (*3*). Indeed, the highly stable lead-iron phosphate glass described in this report was discovered while working with synthetic polycrystalline monazite ceramics.

Lead-iron phosphate glasses with several different compositions have been investigated as potential hosts for radioactive wastes. The lead-iron phosphate glass frit that is combined with the nuclear waste and melted to form radioactive waste monoliths can be prepared by two simple processes. In one process, appropriate amounts of PbO and Fe_2O_3 are combined with $NH_4H_2PO_4$ and the glass is formed when the mixture is heated to ~850°C. In the second procedure PbO and Fe_2O_3 are mixed with the appropriate amount of P_2O_5. The formation of the lead-iron phosphate glass frit can be accomplished in standard chemical processing facilities, since radioactive material is not involved at this stage of the production of a nuclear glass waste form. For the purposes of discussing the formation of the frit and its characteristics, we will limit our discussion to a consideration of the second process. In this case, the practical concentration limits for the three oxide constituents of the host glass are as follows (in percentage by weight): PbO, 40 to 66; P_2O_5, 30 to 55; and Fe_2O_3, 0 to 10 (the amount depending on the type of high-level nuclear waste).

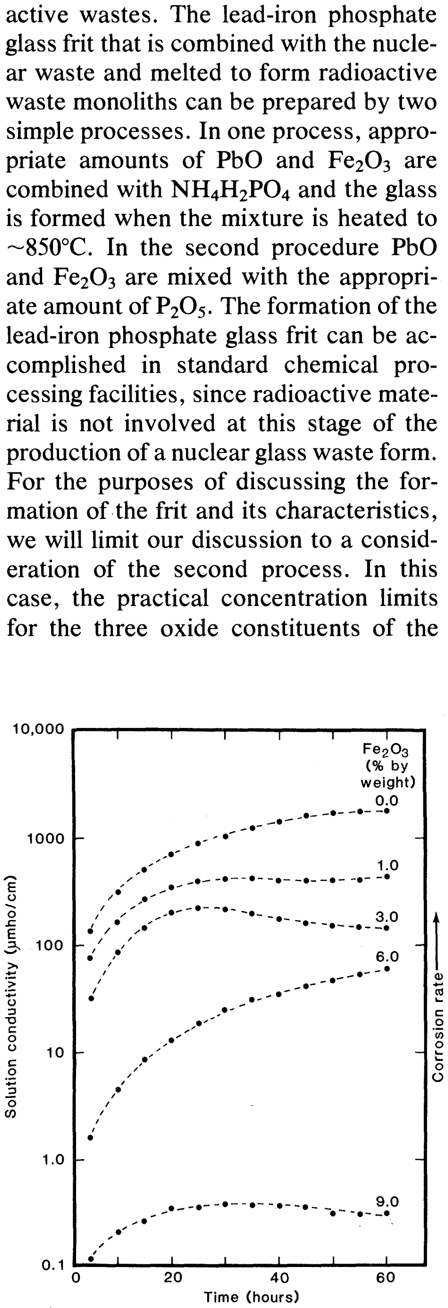

Fig. 1. Leachate conductivity versus time for a lead metaphosphate glass [$Pb(PO_3)_2$] doped with 0.0, 1.0, 3.0, 6.0, and 9.0 percent Fe_2O_3. The leachate conductivity is proportional to the total ionic concentration released by the glass into solution. A change in the leachate conductivity of 1 μmho/cm corresponds roughly to a total change in the ionic concentration of 0.5 ppm. The addition of 9.0 percent Fe_2O_3 to lead metaphosphate glass reduces the corrosion rate (at 90°C in distilled water) by a factor of about 10,000 relative to that for the undoped glass.

One can prepare pure lead phosphate glass (that is, a glass that does not contain either iron or nuclear waste) by fusing PbO with P_2O_5 between 800° and 900°C. One can vary the composition of the resulting glass frit by adjusting the ratio of PbO to P_2O_5. If the percentage of PbO exceeds about 66 percent (by weight), however, a crystalline form of lead phosphate and not a glass is formed. Hence, 66 percent PbO represents a critical limit for glass formation. The lower limit on the amount of PbO that can be melted with P_2O_5 to form a suitable host glass for nuclear waste is not as well defined. A composition consisting of ~45 percent PbO and 55 percent P_2O_5 was taken to represent the practical lower limit for the amount of PbO, since the viscosity of the molten glass increased rapidly as the PbO content was reduced below 45 percent. The higher the melt viscosity, the harder it is to pour the glass and the higher the processing temperature becomes. High processing temperatures for nuclear waste are undesirable since volatile radioactive species may be lost through vaporization. The amount of Fe_2O_3 that must be added to form the lead-iron phosphate waste glass depends on the iron concentration already present in the nuclear waste. High-level defense waste typically contains about 50 percent Fe_2O_3 (*4*), and, for this type of nuclear waste, no additional iron is added to the pure lead phosphate frit for the formation of a very stable nuclear waste glass. For most high-level commercial waste of the type generated by light-water nuclear power reactors (*5*), however, additional Fe_2O_3 must be added to the pure lead phosphate glass in order to form a sufficiently stable, corrosion-resistant nuclear waste glass.

The effects of Fe_2O_3 on the properties of pure lead phosphate glasses are quite remarkable. These glasses are relatively susceptible to aqueous corrosion (*6*) and tend to devitrify (crystallize) at temperatures as low as 300°C (*7*). The addition of Fe_2O_3 improves the corrosion resistance by a factor of more than 10,000 (see Fig. 1) and results in the formation of glasses that do not exhibit any evidence of devitrification after being heated in air at 575°C for 100 hours. Perhaps most significantly, extremely stable lead-iron phosphate glasses can be prepared and poured easily at temperatures between 800° and 900°C. The results illustrated in Fig. 1 can be used in tailoring the composition of the lead-iron phosphate glass frit, depending on the iron concentration of a given type of nuclear waste. The highly stable waste form is realized when the iron concentration is adjusted to a content of about 9.0 percent Fe_2O_3 relative to pure lead phosphate.

We prepared test specimens of several lead-iron phosphate nuclear waste glasses by mixing appropriate amounts of PbO, $NH_4H_2PO_4$, and Fe_2O_3 with a powdered form of the simulated nuclear waste and melting the resulting powder in an alumina crucible at temperatures between 800° and 1050°C. The molten glass was then poured into a graphite crucible and allowed to solidify. Lead-iron phosphate nuclear waste glasses loaded with both classes of high-level nuclear waste [defense (*4*) and commercial (*5*)] were prepared and evaluated. All components of the simulated nuclear waste readily dissolved in the lead-iron phosphate glass at 1000°C, and all components except Al_2O_3 and ZrO_2 were dissolved at temperatures between 800°

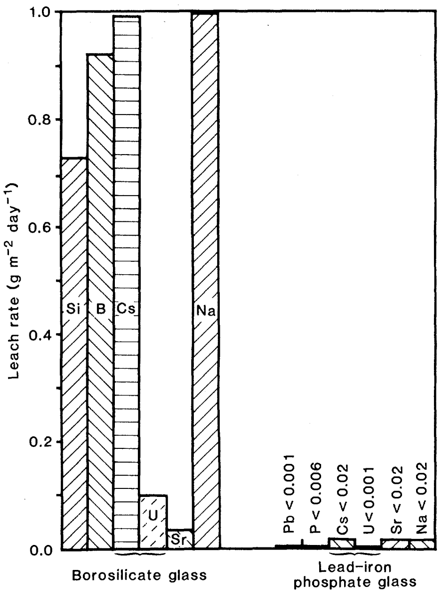

Fig. 2. The 30-day corrosion rates (at 90°C in distilled water) for lead-iron phosphate [$Pb(PO_3)_2$ + 15 percent simulated high-level defense waste] and borosilicate (frit 131 + 29 percent simulated high-level defense waste) nuclear waste glasses. The compositions of the borosilicate glass frit and the simulated high-level defense waste are given by Baxter (*4*). The composite composition of the simulated high-level defense waste (*4*) was used in preparing both the lead-iron phosphate and borosilicate glass nuclear waste forms. The concentrations of all elements present in the lead-iron phosphate leachate were below the detectability limits of standard analytical chemical techniques, and, accordingly, the limiting values shown for lead-iron phosphate represent the analytical detectability limits for each element indicated. Lead-iron phosphate and borosilicate nuclear waste glasses had the same waste-per-volume loading.

and 900°C. The lead-iron phosphate glasses prepared at 800° to 900°C in which the Al_2O_3 and ZrO_2 were not completely dissolved, however, were as corrosion-resistant as those prepared at 1000°C. Both the commercial and the defense-loaded lead-iron phosphate nuclear waste glasses were black, were reflective, were very homogeneous, and had a density of about 5 g/cm^3. The maximum amount of simulated nuclear waste that could be completely dissolved in the lead-iron phosphate host glass was approximately 15 to 20 percent. Because of the high density of the lead-iron phosphate waste form, this corresponds to the same waste-per-volume loading obtained in a typical borosilicate glass loaded with 30 to 40 percent waste.

One of the most important characteristics of any potential nuclear waste glass is the ability to retain hazardous radioactive nuclei in the event of prolonged or repeated contact with ground water. Leaching of radioactive nuclei from the glass into ground water is generally regarded as the most likely mechanism by which radioactive waste could be reintroduced into the biosphere. Corrosion tests of the type developed by the Materials Characterization Center (*8*) were used to make comparisons between the corrosion behavior of lead-iron phosphate nuclear waste glasses and identically loaded borosilicate nuclear waste glasses. Nuclear waste glasses loaded with either simulated U.S. defense waste or simulated reprocessed nuclear power reactor waste were investigated.

Each glass waste form was exposed to distilled water at 90°C for 1 month. We then analyzed the leachate solutions for all major elements present in a given glass type by using standard quantitative analytical techniques (inductively coupled plasma-emission analysis, atomic absorption, and fluorometry). The results of these experiments show that, under the specified corrosion conditions, the net release of all elements from lead-iron phosphate nuclear waste glasses containing either defense or power reactor waste was less by at least 100 to 1000 times than the corresponding release from a comparable borosilicate nuclear waste glass. A comparison of the typical leaching data for defense waste–loaded lead-iron phosphate glass with that for defense waste–loaded borosilicate nuclear waste glass is shown in Fig. 2. The concentrations of all elements present in the lead-iron phosphate leachates were below the detectability limits of the analytical chemical techniques used. Under these corrosion conditions, the lead-iron phosphate waste form successfully immobilizes cesium, sodium, and molybdenum, elements that are notoriously difficult to retain in borosilicate waste glasses exposed to aqueous conditions (*8*).

The effects of the corroding solution *p*H on the corrosion rate of a defense waste–loaded lead-iron phosphate nuclear waste glass were also investigated and compared to the corrosion behavior of a defense waste–loaded borosilicate nuclear waste glass. The results of these investigations are illustrated in Fig. 3. For solution *p*H values between 5 and 9, which encompass the *p*H range of almost all natural ground waters (*9*), the corrosion rates of the lead-iron phosphate glass were smaller by at least 100 to 1000 times than the corrosion rates of the borosilicate glass. At the *p*H extremes of 2 and 12 (Fig. 3), the corrosion rate of the lead-iron nuclear waste glass approaches but does not exceed that of the borosilicate glass.

A nuclear waste form, after it is placed in a deep geologic repository, will be subjected to large doses of gamma radiation during the first several hundred years of storage. In addition, the potential leachate will be ground water whose chemistry reflects the chemical nature of the interaction between water and surrounding rock formations. Moreover, during the early "thermal" period of waste disposal, the waste form could conceivably experience hydrothermal conditions (that is, exposure to ground water at temperatures above 100°C). In order to study the behavior of defense waste–loaded lead-iron phosphate glass under simulated operating conditions of this type, samples were simultaneously exposed to J-13 well water at 115°C in a gamma radiation field of 10^6 R/hour [J-13 well water is the reference water type for waste disposal in a tuff formation (*10*)]. This dose rate is about 100 to 1000 times that experienced by a U.S. defense waste form during the initial storage period. No measurable weight loss in the glass was found after this high-temperature corrosion test, an indication that the corrosion behavior of lead-iron phosphate glass is not significantly affected by the combination of large doses of gamma radiation and tuff ground water corrosion at 115°C.

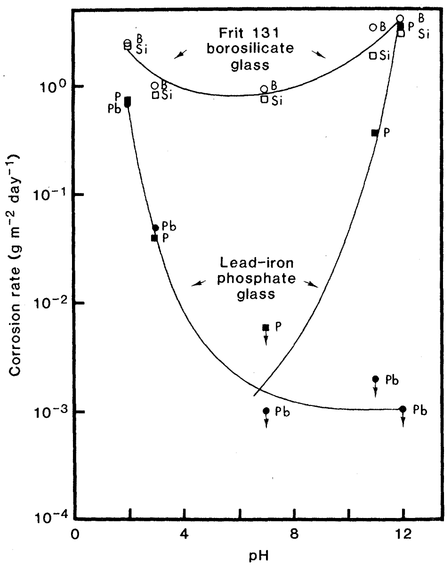

Fig. 3. The 30-day corrosion rates of lead-iron phosphate and borosilicate nuclear waste glasses at 90°C as a function of the solution *p*H. The compositions of both nuclear waste glasses are the same as those described in the legend to Fig. 2. For clarity, the corrosion rates of only the major constituents of each glass are shown; however, for each glass type the corrosion rates of the other elements including the waste constituents follow the same general trend as the solution *p*H is varied.

In the temperature range from 800° to 1050°C, the viscosity of molten lead-iron phosphate glass is much lower than that of a comparably loaded borosilicate glass waste form, as evidenced by the fact that lead-iron phosphate glass can be easily poured at 800°C. In spite of the low viscosity of the molten lead-iron phosphate glass between 800° and 1050°C, the defense waste–loaded lead-iron phosphate glass waste form did not soften until a temperature of 600°C was reached. This softening point is about 15°C higher than that of a comparably loaded borosilicate nuclear waste glass. This observation is consistent with the large activation energy for viscous flow reported for pure lead-phosphate glass by Furdanowicz and Klein (*11*). A defense waste–loaded lead-iron phosphate glass was exposed to air at 575°C for 100 hours in order to determine if the material exhibited any rapid tendency toward devitrification. X-ray diffraction analysis indicated no devitrification of the waste form, and a subsequent corrosion test on the sample showed no degradation in corrosion resistance. An identical test of defense waste–loaded borosilicate glass revealed that there was some crystallite formation and that the corrosion rate was approximately 40 percent higher after the heat treatment.

These results indicate that lead-iron phosphate nuclear waste glasses represent a new, very stable, and easily prepared medium for the disposal of some important classes of nuclear waste. Relative to borosilicate nuclear waste glass, the lead-iron phosphate nuclear waste glass has several distinct advantages, including the following: (i) a corrosion rate at 90°C that is generally about 1000 times less than that of comparable borosilicate glass; (ii) a formation temperature that is 100° to 250°C lower than the temperature (~1150°C) required for a comparable borosilicate glass; (iii) a relatively good capacity of the molten glass for dissolving the elements found in both defense and commercial power reactor wastes; (iv) a melt viscosity and processing (that is, pouring) temperature in the range from 800° to 1000°C, significantly lower than the pouring temperature (~1150°C) of borosilicate glass; and (v) suitability for use for both commercial and defense-related nuclear waste disposal. Of greatest significance, it appears that the lead-iron phosphate glass waste form can be processed using a technology similar to that developed for borosilicate glass nuclear waste forms.

B. C. Sales
L. A. Boatner

Solid State Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831

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X-ray Absorption Spectroscopic Investigation of Sulfur Sites in Coal: Organic Sulfur Identification

Abstract. *High-resolution x-ray absorption spectroscopy was used to probe the chemical and structural environments of sulfur in coal. Measurement of the sulfur K-edge spectra down to 2472.0 electron volts under nonvacuum conditions was made possible in an all-helium path, and a Stern-Heald type ion chamber was used for fluorescence detection. For a number of selected sulfur-containing minerals and organic model compounds, results show that near-edge spectral features are diagnostic for sulfur in specific organic moieties such as thiols, disulfides, and various heterocyclics, as well as in mineral sulfide and sulfate phases. The spectrum of a model system containing 35 percent iron pyrite and 65 percent benzothiophene was found to match the observed spectral features of a bituminous coal from the eastern United States.*

Sulfur takes on several forms in coal including elemental, mineral, and organic (*1*). Further classification is possible. Mineral sulfur forms include pyrite or sulfate groups; organic sulfur may occur in heterocyclic species, thiol moieties, or thioether units, among others (*2*). Because of the heterogeneity and opacity of coal, it has not been possible to determine directly the sulfur forms in coal by conventional techniques. Knowledge of the sulfur forms is indirect, based primarily on spectroscopic studies of pyrolytic or chemically degraded fragments of coal and model compounds. Even the simple quantification of organic versus inorganic sulfur in coal is usually indirect, because it relies upon sequential leaching of sulfate, then pyritic compounds, with organic sulfur presumed to comprise the residue. This assumption is subject to error since the occlusion of nanometer-sized mineral fragments in the organic matrix has been commonly observed (*3*).

Sulfur is one of the most pernicious elements in coal. When released into the atmosphere through combustion, it may produce so-called acid rain (*4*). Because of this possibility, several countries now limit sulfur emissions from coal-burning power plants. Some alkali sulfates have low-melting eutectics and may cause fouling and corrosion when in contact with hot metal surfaces (*5*). Sulfur-containing compounds may have deleterious environmental, health, and safety effects (*6*). Sulfur may poison catalysts during processing (*7*). It may also inhibit prolonged storage of coal by catalyzing spontaneous ignition (*8*). Acid mine drainage results from microbial degradation of metal sulfides in the coal (*6*).

For these reasons, several processes for the removal of sulfur in coal have been recently developed (*9*). Certainly, a better understanding of the nature and distribution of sulfur-bearing minerals and organic sulfur–containing functional groups and their concomitant chemistry will have a desirable impact on advanced coal preparation processes and the environmental acceptability of coal-derived energy.

The K-edge spectra of sulfur in coal have been measured by Hussain *et al.* (*10*), who used a total electron yield technique under ultrahigh vacuum conditions. In that study, the sulfur species in coal were not identified since organic compounds of sulfur, which are usually vacuum-incompatible, were not measured. The ability to obtain soft x-ray absorption spectra down to 2.4 keV under nonvacuum conditions with the use of a fluorescent ion-chamber detector arrangement has recently been shown by Lytle *et al.* (*11*). This nonvacuum procedure (*11*) may be summarized as follows. Spectra were obtained on beam line VII-3 wiggler side station at the Stanford Synchrotron Radiation Laboratory during a dedicated run of the Stanford positron electron accelerator ring (SPEAR) at an electron energy of 3.0 GeV and an injection current of ~75 mA. The synchrotron x-ray beam from SPEAR was monochromatized with double Si(111) crystals and a 1-mm entrance slit, which yielded a resolution of ~0.5 eV (*11*) at the sulfur K-edge of 2472.0 eV (*12*). Spectra of sulfur in coal and model compounds were measured by the fluorescence extended x-ray absorption fine structure (EXAFS) technique (*13*). This technique monitors the sulfur K_α fluorescence intensity, which is proportional to the degree of absorption of the incident beam, and hence monitors the x-ray absorption spectrum. A Stern-Heald type fluorescence detector (*13*) was used, the construction of which has been described (*11*). Helium and nitrogen were used as detector gases in the incident ion chamber and fluorescence detector, respectively. The incident beam was detuned up to 90 percent to minimize harmonic contents at the sulfur K-edge energy. An