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METHODS OF SIMULATING LOW REDOX POTENTIAL (Eh) FOR A BASALT REPOSITORY

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ABSTRACT

In the selection of a repository for burying vitrified nuclear waste, the leach rate of the waste form in groundwater is of concern. Basaltic groundwaters have inherently low redox potentials which may affect the waste form leach rate. Laboratory simulation of the Eh-pH conditions to be found in a basalt repository can be achieved when crushed basalt is added to deoxygenated deionized water. The effects of other redox-active waste package components, such as iron, were found to stabilize solution redox potential at different valves under oxic and anoxic conditions. When iron was present, different waste form leach rates were observed with and without oxygen.

INTRODUCTION

Radioactive waste glasses contain many elements which are redox active, i.e. can occur in more than one redox state. The valence state of an ion, in particular technetium and the actinide elements, can be important in determining its equilibrium solubility and its rate of release from the waste form. Moreover, the adsorption and migration of multivalent elements in geologic media are highly dependent upon the distribution of the redox states in the groundwater. This is particularly important for repositories in which the groundwaters are expected to be anoxic.

The geologic formations being examined as potential high-level waste repositories in the United States are tuff, salt, and basalt. In the tuff and salt repositories, the groundwater is expected to be mildly anoxic with a redox potential of 0.0 to -0.1 V [1]. Basalt groundwater is expected to be strongly anoxic with a redox potential of -0.45 ± 0.05 V [1,2]. Redox potential (Eh) is the relative measure of the electron transfer potential in a solution.

Waste form leach tests have to date, not addressed leaching under anoxic repository conditions [3,4]. Since technetium and actinide solubilities are strong functions of temperature, Eh, pH, and water chemistry, the effects of these variables must be measured in order to determine defensible limits of radionuclide release rates.

Interactions between waste form and waste package components must also be considered as a function of groundwater chemistry. This is of particular concern when one or more of the waste package components is redox active and may affect or control the Eh. Two pertinent examples are the potential use of crushed basalt as a packing material and the use of iron (or low carbon steel) as a canister/overpack material in a basalt repository [5]. Dissolution of the intergranular glassy phase in basalt is believed to control the

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Eh-pH relations in solution because it is a reactive phase that contains a redox-active component, e.g. ferrous silicate [2]. The leaching of waste glass under oxic conditions in the presence of basalt may, therefore, be different than under anoxic conditions. Likewise, iron [6] or any metallic species [7] in a laboratory waste form leach test may have very different interactions with the waste form under oxic or anoxic conditions.

A systematic examination of the effect of various waste package components (e.g. metal canister materials, basalt packing, and waste glass) on solution Eh was undertaken [8] as a first step toward the assessment of the interactions between waste form and waste package components under repository conditions. Eh was measured [8] as a function of residence time of the solid in an aqueous media and as a function of the ratio of the surface area of the solid to the volume of solution. It was shown that the concentration of redox-active species released by the solid is a function of the reactivity parameters, time, and surface area. Iron and crushed basalt are components of the Basalt Waste Isolation Project (BWIP) waste package design [9]. Therefore, the present study examines the interactions of basalt in solution under anoxic conditions. Interactions of SRP waste glass with solutions in the presence of ductile iron were also studied. Anoxic leaching was examined to simulate repository conditions at the time of groundwater ingress. Oxic leaching experiments were made for comparison.

Eh MEASUREMENT WITH PLATINUM ELECTRODES

Oxidation-reduction reactions can be thought of as reactions which involve the transfer of oxygen or the transfer of electrons. Since many redox reactions do not involve molecular oxygen directly, it is more convenient to consider redox reactions as electron transfers [10]. Even if molecular oxygen were involved, kinetic problems complicate the use of oxygen activity as a thermodynamic variable at low temperatures [11]. Because the absolute potential cannot be measured, a platinum measuring electrode is used to provide an inert means of transferring electrons to or from solution [10] and the potential difference is measured relative to a reference electrode [11].

Platinum electrodes can be used under the following conditions:

1) when anoxic conditions below the platinum oxygen couple are achieved
2) when sulfur is absent and
3) when the redox couple being measured is known.

All of these conditions can be achieved in simulated laboratory experiments [8]. Since many redox processes are very slow in reaching equilibrium and a meaningful Eh cannot be defined for non-equilibrium systems, known singular redox couples were investigated [8] with Pt electrodes and the results were compared to calculated equilibrium Eh-pH diagrams [12]. In this study this technique is applied to more complex systems.

Eh STABILIZATION WITH REDOX ACTIVE SOLIDS

Many recent attempts at laboratory stabilization of low Eh have not fully addressed possible experimentally induced interactions. The use of hydrazine [13] or a redox-active metal [6,7] in an oxygenated system may cause interactions that will not occur in the repository, e.g. when no hydrazine or oxygen are present. The presence of iron precludes the use of a potentiostat for Eh stabilization [14,15]. Hydrothermal experiments can achieve low Eh but often use temperatures higher than those expected [16] for defense waste glass. Moreover, higher temperature interactions may not be representative of the reactions occurring at lower temperatures. An Ar-4%H_2 gas mixture in the presence of a palladium catalyst can be used to lower solution redox potentials. Measurements of only -0.12V have been reported [17].

The use of redox-active solids in deoxygenated solutions to stabilize low redox potentials was, therefore, examined. The iron-bearing species such as basalt and ductile iron yield redox-active species in solution which give stable Eh measurements. Moreover, they are integral components of the BWIP waste package design.

EXPERIMENTAL

The experimental detail is given elsewhere [8]. The deoxygenated experiments were contained in a glove box continually purged with argon. The Eh and pH were continuously monitored in situ. Deionized water and basaltic groundwater (GR-3) were used as leachants. Ductile iron bars and crushed Hanford Umtanum basalt were used as redox-active solids. MCC-1 tests without continuous monitoring were run for comparison. The surface area-volume ratio SA/V of the glass and ductile iron were kept the same as previously described by McVay and Pederson [7].

The leachates were acidified but not filtered unless indicated. Solution analyses were done by inductively coupled plasma (ICP), ion chromatography (IC) and atomic absorption (AA). The monolithic samples and filtered precipitates were dried at 90°C for 1 hour. The surfaces and precipitates were examined by x-ray diffraction. In addition, the monolith surfaces were examined by electron microprobe.

RESULTS

INTERACTIONS BETWEEN UMTANUM BASALT AND DEIONIZED WATER

Crushed Umtanum basalt was found [8] to be the most reactive material to set or control the Eh at negative anoxic values. Eh values of -0.42V at a pH of 8.44 can be reached with deoxygenated deionized water and crushed basalt in 20 to 120 hours depending upon the SA/V of the basalt in the leachant. Duplicate and triplicate experiments with deionized deoxygenated water and crushed Umtanum basalt confirmed the results shown in Figure 1. These values compare favorably to the -0.40V at pH 9.1 ± 0.5 calculated [2] for a basalt repository at 70°C, but never measured in-situ due to sampling difficulties associated with field measurements [11,18]. The calculated Eh and pH values for the BWIP repository groundwater are shown by the cross on Figure 1. The vertical bar shows the range of Eh values actually measured [19].

Basalt SA/V ratios of <10 cm^{-1} have little effect on Eh equilibration in deionized water but larger ratios affect the Eh dramatically, and make it a strong function of rock residence time in solution [8]. Because the Fe^{2+}/Fe^{3+} redox couple dominates the controlled laboratory experiment, it was assumed that the electrode measurements were controlled by this redox couple.

Crushed Umtanum basalt interactions with deionized water produce a colloidal suspended material. Chemical analysis showed the colloid to be iron rich (12.2 mg/L total iron). A portion of the solution was filtered through a 0.45 μm filter and the filtered solution was reanalyzed. The difference in composition of the filtered and unfiltered solutions suggested that the precipitate had the general formula $Fe_{0.47}Mg_{0.53}SiO_3$ and $Na_{0.33}Ca_{0.66}Al_{1.8}Si_{2.2}O_8$. The precipitate was dried for 1 hour and an x-ray pattern revealed a crystalline oligoclase-plagioclase phase

($0.83NaAlSi_3O_8$-$0.16CaAl_2Si_2O_8$; JCPDS 9-457) and an amorphous material assumed to be the $(Fe,Mg)SiO_3$ component. This amorphous iron silicate is the reactive component proposed [2] to control the redox potential in basalt. Preferential leaching of the intergranular amorphorous phase of many glass-ceramics, such as basalt, is well documented [20].

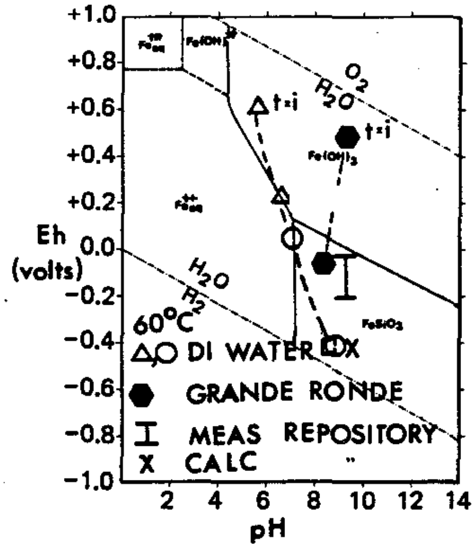

FIG. 1. Eh-pH changes measured (±0.5V) for deoxygenated deionized water and Umtanum basalt (open symbols) and the Eh-pH changes measured for deoxygenated GR-3 simulated basaltic groundwater (solid symbols). The X represents the calculated Eh and pH values for the basalt repository groundwater (Ref. 2) and the vertical bar represents the range of Eh values actually measured for the BWIP groundwaters (Ref. 19). SA/V = 5 to 28 cm^{-1} (<100 mesh).

INTERACTIONS BETWEEN UMTANUM BASALT AND GROUNDWATER

Since crushed basalt in deoxygenated deionized water achieved the calculated Eh and pH of the Basalt Waste Isolation Project repository [2], a similar experiment was attempted with deoxygenated Grande Ronde groundwater (GR-3) [21]. Even with SA/V ratios as high as 28 cm^{-1} and residence times as long as 144 hours at 60°C, the calculated Eh and pH values achieved with deionized water could not be achieved (Figure 1).

The simulated Grande Ronde groundwater is pH-adjusted in air-saturated conditions, as suggested by Jones [21]. As the crushed basalt is added, the pH decreases from 9.2 to 8.6 while the Eh decreases as shown by the solid symbols in Figure 1. The open symbols on Figure 1 show the Eh-pH trends delineated from the crushed rock-deionized water experiments. Difficulty in the laboratory measurement may be due to the presence of sulfate in the GR-3 groundwater composition and/or nonequilibrium between the simulated groundwater composition and the basalt. There is independent data that the latter may be the responsible mechanism [22].

INTERACTIONS BETWEEN DEFENSE WASTE GLASS, DUCTILE IRON, AND SOLUTION

Interactions between defense waste glass, iron (low carbon steel), and solution are different under oxic and anoxic conditions. SRL 165 waste glass and ductile iron bars placed in aerated deionized water at 70°C with continuous Eh monitoring demonstrated that oxidation of the iron creates aqueous

Fe^{++}. The Eh-pH relations of the solution then follow the calculated Fe^{++} (aq)/$Fe(OH)_3$ equilibrium boundary (Figure 2a). In Figure 2 the equilibrium boundaries are shown for 10^{-6} and 10^{-4} M concentration of iron since solution analysis revealed 10^{-4} M total iron after the solutions were acidified. After an initial 100 hours, the pH continued to increase and the Eh of the solution followed the calculated* equilibrium boundary for the reaction:

$$FeSiO_3 + 2H_2O \rightarrow Fe(OH)_3 + SiO_2(am) + H^+ + 1e^-$$

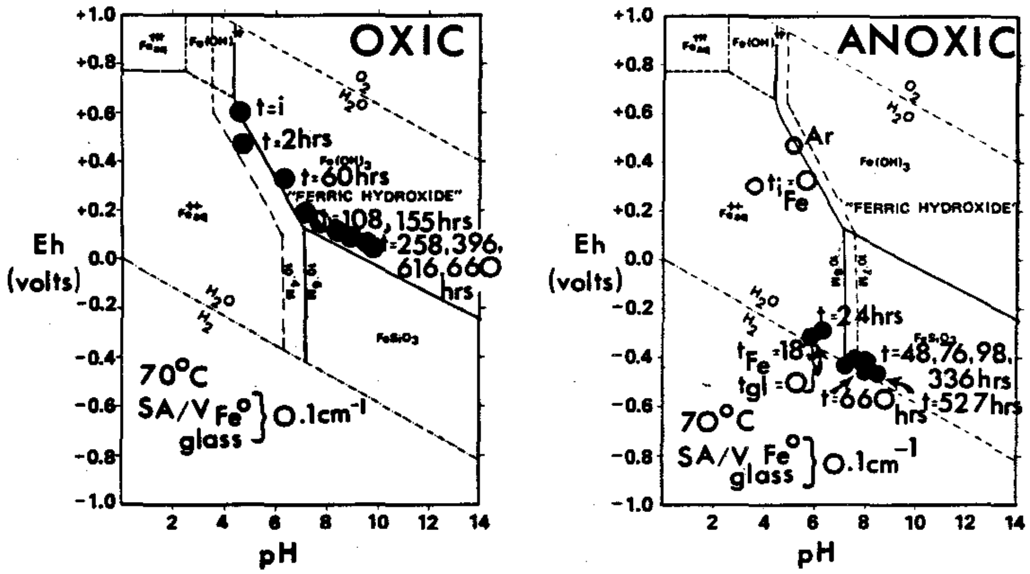

FIG. 2. Eh-pH relations measured when SRL 165 waste glass and ductile iron are present in deionized water under oxic and anoxic conditions. Boundaries which are dependent on the amount of iron in solution are calculated for the actual iron concentrations found in the solutions.

The observed enhancement of waste glass dissolution in the presence of metallic iron [6] is related to the changes in Eh caused by the presence of metallic iron in an open, aerated, system (Figure 2). The iron acts as a source for Fe^{++} (aq) in the presence of oxygen and drives the Eh into the region of stability of ferrous iron silicate. The aqueous ferrous iron, therefore, scavenges silica from the solution forming a stable iron silicate precipitate. When the leachant is undersaturated with respect to silica it acts as the driving force for further dissolution of the glass. Note that in Figure 3 enhanced silica concentration is accompanied by enhanced iron in solution.

The presence of iron silicate and iron oxide precipitates was confirmed by drying the 28-day leachant at 90°C and analyzing the solids by x-ray diffraction. The presence of $Fe(OH)_3$ (JCPDS 22-346), $\gamma Fe_2O_3 \cdot H_2O$ (lepidocrocite, JCPDS 8-98) and greenalite, $3FeO \cdot 2SiO_2 \cdot 2H_2O$ (JCPDS 2-1012 11-265) were confirmed. X-ray diffraction analysis of the upper glass surface also revealed $Fe(OH)_3$ and lepidocrocite while x-ray analysis of the corrosion products on the iron bars revealed $Fe(OH)_2$, $Fe(OH)_3$, and greenalite.

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* Using the data of Garrels and Christ [12] Eh = 0.585 - 0.059 pH

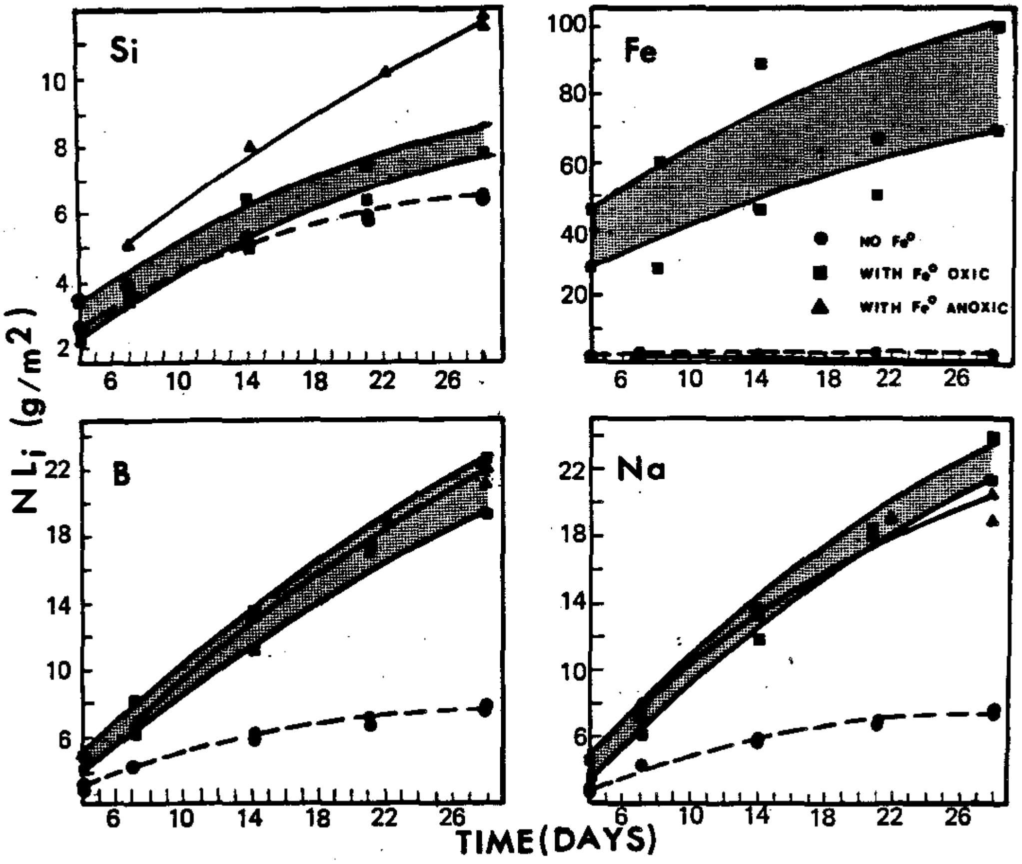

FIG. 3. Concentrations of Si, Fe, B, and Na leached from SRL 165 waste glass under oxic conditions with ductile iron present (squares), under oxic conditions with no ductile iron present (circles) and under anoxic conditions with ductile iron present (triangles). All samples in deionized water at 70°C. The shaded area indicates the poor reproducibility of the solution analyses when colloids are present even though the solutions are acidified. All solution analyses were run in duplicate.

SRL 165 waste glass and ductile iron placed in deaerated deionized water at 70 to 80°C with continuous Eh monitoring demonstrated that the iron drove the Eh to the lower stability limit of water in 24 hours (Figure 2b). This is predicted for a closed system in the absence of oxygen because the thermodynamically calculated Eh-pH couple for iron lies below the lower stability boundary of water [12]. After 24 hours of iron reaction in water, the SRL waste glass was added (Figure 2b). The SA/V of the iron and the glass was 0.01 cm^{-1}. The pH increased slightly and the Eh value followed the lower stability boundary for water. After 660 hours (28 days) leaching, the Eh was at -0.42V and the pH was 7.93. The solution concentration of iron was between 10^{-6} and 10^{-7} M. Filtration through a 0.45 μm filter did not change the solution analysis and no colloids were observed on the filter paper. The iron bars were free of brown corrosion products and portions of the glass did not have a reaction layer. Drying of the glass monolith surface for 1 hour at 90°C gave a poorly crystallized x-ray diffraction spectra for Y-SiO_2 (JCPDS 31-1233). Part of the layer was scraped off and crystallized at 500°C for 1 hour. This yielded a poorly crystallized x-ray spectra for (Fe,Mg)SiO_3 (JCPDS 31-635).

The solution analyses for oxic and anoxic leaching of waste glass in the presence of ductile iron show that the release of boron and sodium is the same. The silica release rate is greater under anoxic conditions than oxic while the opposite is true for the release of iron (Figure 3). Note that the enhanced silica release is not concomitant with enhanced iron as in the oxygenated case. Therefore, it is likely that the mechanism by which colloidal iron silicate precipitates when oxygen is present is not the same mechanism causing enhanced silica dissolution under anoxic conditions.

The monolithic samples of glass had been removed from the leach vessel and referenced as to which surfaces were exposed to the gravity settling of agglomerated colloids (top surface) and which surfaces were not (bottom). These surfaces were examined by electron microprobe. In the oxygenated experiment, the altered upper surfaces were composed of loosely agglomerated particles. Quantitative analysis given in wt % showed this layer to be 87 Fe as iron oxide or iron hydroxide. This confirmed the results of the x-ray diffraction analyses. The quantitative electron microprobe analysis of the bottom surface showed that the surface layer was continuous, and composed of 63 Fe, 3 Ni and 20 Mn and 10 Si as is usually found on SRL glasses leached in the absence of ductile iron [23]. Quantitative analysis of the surface of the iron bars revealed only Fe, present as iron oxide or iron hydroxide.

In the anoxic experiment containing SRL 165 waste glass and ductile iron in deionized water, the upper altered surface of the glass was discontinuous. Quantitative analysis showed the layer to be iron silica rich as confirmed by the x-ray diffraction analysis. The bottom surface had a thinner discontinuous surface layer similar in composition to the upper surface. The ductile iron was coated with a thick layer of iron silicate with no Ni or Mn, e.g. 34 wt % Si and 55 wt % Fe. The surface layer composition and hence the reactions of the waste glass and iron in solution are different under anoxic conditions.

CONCLUSIONS

Redox-active solids can be used to control the oxidation potential of waste glass leachants. Materials in which iron is present in the ferrous and ferric state appear to be most active and readily give stable and reproducible Eh readings when measured with platinum electrodes. The redox species must be present in sufficient concentrations to be measured reliably. Concentration, in turn, is a function of SA/V of the redox-active solid leachant system and the residence time of the redox-active solid leachant interaction.

Crushed basalt was found to be the most reactive material to maintain the Eh at negative anoxic values. Eh values of -0.42V at a pH of 8.44 can be reached with deoxygenated deionized water and crushed basalt in 20 to 120 hours depending on the SA/V of the basalt in the leachant. These values compare favorably to the -0.4V at pH 9.1 calculated for a basalt repository but never measured in situ. The reactive species in basalt was found to be amorphous $(Fe_{0.47}Mg_{0.53})SiO_3$, preferentially leached from the basalt mesostasis.

The presence of a metallic component in a laboratory waste form durability test open to air was shown to cause experimentally-induced interactions. Basalt repositories are anticipated to be mildly to strongly anoxic and the presence of free oxygen will be limited. In the case of the interactions between ductile iron and waste glass, these are truly synergistic, i.e. the iron enhances glass leaching and the glass enhances iron corrosion. It is the oxygen which acts as the driving force for supplying aqueous ferrous iron to the solution. The iron drives the Eh into a known Eh-pH stability field for ferrous iron silicate. The aqueous ferrous iron then scavenges silica from the solution and precipitates ferrous iron silicate causing undersaturation of silica in the leachant. This in turn acts as the driving force for further dissolution of the glass. Thus, oxygen is necessary to continually oxidize metallic iron to aqueous ferrous iron. The interrelation of iron with silica is a function of the the low temperature stability of aqueous iron silicate and not a function of leaching under anoxic conditions.

The presence of a metallic component in a laboratory waste form durability test in the absence of oxygen did not form iron silica colloids in solution. However, anoxic conditions retard the formation of surface layers, which may be passivating. Leach rates for B and Na under oxic and anoxic conditions are similar. Leach rates for Si are actually enhanced under anoxic conditions but there is no concomitant increase in the leach rate of iron from either the glass or the ductile iron bars. When the component oxygen is absent from the system, the surfaces of the glass and the ductile iron are covered by discontinuous surface layers of iron silicate. Since no colloids were observed when the solution was filtered (0.45 μm) and the solution analyses were identical before and after filtration, the iron silicate layers must be forming by reaction at the solid-solution interface, e.g. counterion adsorption. This mechanism would be self-limiting once surface layer formation is complete.

Although the anoxic Eh-pH relations predict the formation of iron silicate as in the oxygenated case, the solution is depleted in both iron and oxygen and it is silica that is mobile. Since the component oxygen is absent, one degree of freedom is lost from the system. In the oxygenated case, the constant supply of oxygen and $Fe^{++}(aq)$ from the ductile iron is only limited by the source of either component. Agglomeration of colloidal iron silicate or adsorption of colloids on the glass surface can continually deplete the solution of silica and iron.

Potential waste package component interactions in oxygenated leachants can be predetermined based on the thermodynamics of known reactions for metal silica systems at low temperatures. If synergistic interactions are predicted for oxygenated systems, then the experiments must be conducted under the anoxic conditions predicted for the repository.

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