

## A GENERALIZED GROUNDWATER RADIOLYSIS MODEL

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### ABSTRACT

A generalized groundwater radiolysis model which is under development at Battelle-Columbus is described. This model uses a 55 reaction basis set for the radiolysis of the solvent. The basis set of reactions was chosen from the literature after comparing several descriptions against experimental data. This basis set has been augmented with 17 additional reactions to allow the description of the radiolysis of groundwater containing iron. The mechanism is described and simulations of the radiolysis of several aqueous systems are shown.

### INTRODUCTION

Material corrosion experiments performed in a radiation field have demonstrated adverse effects which have not been observed in similar experiments performed in the absence of a radiation field. Furuya et al<sup>1</sup> have observed stress corrosion cracking of Type 304L Stainless Steel in deionized water in a radiation field (1.1E5 R/hr) at 100C but not in the absence of radiation. Chikalla and Powell<sup>2</sup> have observed increases in corrosion rates of up to an order of magnitude in irradiated brines for iron based alloys. In view of such data, it is necessary to quantitatively account for the effects of gamma radiolysis on the long term performance of nuclear waste packages. This evaluation will require a means of quantitatively assessing effects which gamma radiation has on groundwater in the vicinity of nuclear waste packages. At Battelle's Columbus Laboratories, we are developing a mechanistic description of the radiolysis of groundwaters which may exist at nuclear waste repository sites.

#### Approach

A generalized model for the description of groundwater radiolysis is being developed as part of the Battelle-Columbus program on the "Long-Term Performance of Materials Used for High-Level Waste Packaging", which is sponsored by the U.S. Nuclear Regulatory Commission. This model is being developed in a series of phases. First a mechanism for the radiolysis of pure water which might contain dissolved H<sub>2</sub> and/or O<sub>2</sub> was chosen to act as a basis for a general mechanism for aqueous groundwater systems. Gamma energy deposition rates to groundwater as a function of time and radius were also performed as part of the first phase of this work. In the second phase, this mechanism is being used as a basis for the development of a generalized model which will account for the presence of important groundwater species. The model is undergoing some benchmark calculations as part of the development process. In the third phase, tests will be performed and modifications will be made as necessary.

#### Water Radiolysis Model

The model for water radiolysis is based on a set of simultaneous differential equations which describe the time dependence of relevant aqueous species. These differential equations are a mathematical representation of a chemical reaction mechanism consisting of several elementary reactions. The

mechanism described here consists of 78 elementary reactions. The set of simultaneous differential equations are developed from the set of elementary reactions, and integrated by the computer code MAKSIMA-CHEMIST<sup>3</sup>. The set of elementary reactions is being augmented as other species are added to the model.

The basis set of elementary reactions for pure water was chosen from a mechanism in the literature following a comparison of the ability of several literature mechanisms to predict benchmark experimental data and to maintain good chemical sense. The mechanism of Rosinger and Dixon<sup>5</sup> which has 55 elementary reactions and associated rate constants has been chosen as the basis mechanism. This mechanism has been benchmarked<sup>4</sup> against data of Schwarz<sup>6</sup> and Hochenadel<sup>7</sup>. The reactions shown in Table I have been added to this set of reactions during development of the mechanism for the radiolysis of groundwater containing iron species. These reactions were developed as an iterative process. First, as described in our progress reports (Ref. 9 and 10), reactions were taken from a mechanism presented by other investigators. This mechanism worked well for ferric species but was found to be deficient when the time dependence of the hydrogen ion was calculated for a simulation of experimental data presented in the literature. Changes were made to this mechanism based on information available in the literature and some analog reactions not discussed in the literature were added for completeness. Ferric ion hydrolysis reactions were added to the mechanism as well as a qualitative description for the precipitation of ferric species. This development work and benchmark calculations for this mechanism against experimental data for the radiolysis of a ferrous sulphate system<sup>8</sup> are described in our progress reports (Ref. 9 and 10). A compilation of these reactions and associated rate constants is shown in Table I.

Ultimately, this model will be used to predict the composition of groundwater in the presence of a gamma radiation field in the vicinity of waste package barrier surfaces as well as effects of radiolysis on the water chemistry in the waste package environment.

#### Simulations of the Radiolysis of Aqueous Systems

The radiolysis model described has been used to simulate the radiolysis of a variety of aqueous systems. The gamma radiation field used in these

TABLE I

Reactions Added to the Rosinger and Dixon Mechanism

$\text{Fe}^{2+}$	+	$\text{OH}$	$\rightarrow$	$\text{FeOH}^{2+}$		$k = 3.2\text{E}08$
$\text{FeOH}^{2+}$	+	$\text{H}^+$	$\rightarrow$	$\text{Fe}^{3+}$	+ $\text{H}_2\text{O}$	$k = 1.5\text{E}09$
$\text{Fe}^{2+}$	+	$\text{e}^-$	$\rightarrow$	$\text{Fe}^+$		$k = 1.2\text{E}08$
$\text{Fe}^+$	+	$\text{OH}$	$\rightarrow$	$\text{FeOH}^+$		$k = 2.8\text{E}08$
$\text{FeOH}^+$	+	$\text{H}^+$	$\rightarrow$	$\text{Fe}^{2+}$	+ $\text{H}_2\text{O}$	$k = 1.3\text{E}09$
$\text{Fe}^+$	+	$\text{H}_2\text{O}_2$	$\rightarrow$	$\text{Fe}^{2+}$	+ $\text{OH} + \text{OH}^-$	$k = 5.29\text{E}01$
$\text{Fe}^+$	+	$\text{O}_2^-$	$\rightarrow$	$\text{Fe}^{2+}$	+ $\text{O}_2^{2-}$	$k = 3.52\text{E}08$
$\text{H}$	+	$\text{Fe}^{2+}$	$\rightarrow$	$\text{FeH}^{2+}$		$k = 1.38\text{E}06$
$\text{FeH}^{2+}$	+	$\text{H}^+$	$\rightarrow$	$\text{Fe}^{3+}$	+ $\text{H}_2$	$k = 1.06\text{E}06$
$\text{Fe}^+$	+	$\text{H}$	$\rightarrow$	$\text{FeH}^+$		$k = 1.2\text{E}06$
$\text{FeH}^+$	+	$\text{H}^+$	$\rightarrow$	$\text{Fe}^{2+}$	+ $\text{H}_2$	$k = 9.3\text{E}03$
$\text{Fe}^{2+}$	+	$\text{H}_2\text{O}_2$	$\rightarrow$	$\text{Fe}^{3+}$	+ $\text{OH} + \text{OH}^-$	$k = 6.0\text{E}01$
$\text{Fe}^{2+}$	+	$\text{O}_2^-$	$\rightarrow$	$\text{Fe}^{3+}$	+ $\text{O}_2^{2-}$	$k = 4.0\text{E}08$
$\text{Fe}^{3+}$	+	$\text{e}^-$	$\rightarrow$	$\text{Fe}^{2+}$		$k = 2.0\text{E}10$
$\text{Fe}^{3+}$	+	$\text{O}_2^-$	$\rightarrow$	$\text{Fe}^{2+}$	+ $\text{O}_2$	$k = 4.0\text{E}08$
$\text{Fe}^{3+}$	+	$\text{H}$	$\rightarrow$	$\text{Fe}^{2+}$	+ $\text{H}^+$	$k = 1.0\text{E}08$
$\text{H}$	+	$\text{OH}^-$	$\rightarrow$	$\text{e}^-$	+ $\text{H}_2\text{O}$	$k = 1.8\text{E}07$
$\text{Fe}^{3+}$			$\rightarrow$	$\text{FeOH}^{2+} + \text{H}^+$	- $\text{H}_2\text{O}$	$k = 3.0\text{E}07$
$\text{FeOH}^{2+}$	+	$\text{H}^+$	$\rightarrow$	$\text{Fe}^{3+}$	+ $\text{H}_2\text{O}$	$k = 4.7\text{E}09$
$\text{FeOH}^{2+}$			$\rightarrow$	$\text{Fe}(\text{OH})_2^+ + \text{H}^+$	- $\text{H}_2\text{O}$	$k = 6.1\text{E}04$
$\text{Fe}(\text{OH})_2^+$	+	$\text{H}^+$	$\rightarrow$	$\text{FeOH}^{2+}$	+ $\text{H}_2\text{O}$	$k = 8.0\text{E}09$
$^*\text{Fe}(\text{OH})_2^+$	+	$\text{Fe}(\text{OH})_2^+$	$\rightarrow$	$\text{FeOOH}$	+ $\text{FeOH}^{2+} + \text{H}_2\text{O}$	$k = 5.0\text{E}02$

\*  $\text{FeOOH}$  represents a range of products associated with the precipitation of ferric species.

calculations was  $1E15$  ev/l-sec which is equivalent to about 60 R/hr. This value of the energy deposition rate was chosen since it is representative of the dose rate to groundwater at the surface of the waste package overpack after about 100 years. Calculations of these dose rates have been reported elsewhere<sup>4</sup>.

Figure 1 shows a comparison of the calculated dissolved hydrogen concentration for several solutions which are initially free of dissolved gases. As can be seen in this figure, iron free waters of pH 7 and pH 4.5 behave similarly. Table II shows that the time dependence of the dissolved hydrogen and oxygen concentrations is also similar for these two solutions. Figure 1 also shows that when the solution contains an initial concentration of  $1E-5$  m/l ferrous ion at a pH of 4.5, that the calculated hydrogen concentration as a function of time is about 10X higher than for iron free water. Data in Table II also show that for this time period, most of the ferrous ion initially present is converted to other species (mostly ferric species). Figure 1 also shows that when the ferrous concentration is held constant, that the calculated long term hydrogen concentrations are about 100X higher than for iron free water. Such an effect may be relevant to aqueous systems in the vicinity of waste packages since the surrounding materials may replenish species removed from the aqueous system as a result of reactions. These reactions can include those associated with radiolysis or corrosion.

Simulations were also performed for aqueous systems containing dissolved hydrogen and oxygen. For these calculations, a dissolved oxygen concentration of  $6E-5$  m/l was chosen as a midrange value of measurements of the oxygen concentration for a simulation of a waste package environment<sup>11</sup>. Two values of the initial dissolved hydrogen concentration were chosen. The lower value was based on an expected concentration in equilibrium with air at one atmosphere at 25C. This value of  $4E-10$  m/l was calculated using a Bunsen absorption coefficient of .0175 for hydrogen in water<sup>12</sup> and a hydrogen partial pressure of  $5E-7$  atm calculated assuming a standard dry atmosphere<sup>13</sup>. The upper value of  $2E-5$  m/l was chosen based on experience with LWRs as a concentration which suppresses hydrogen generation by water radiolysis for nonboiling systems at 25C<sup>14</sup>. The initial ferrous concentration was set at  $1E-5$  m/l. The calculated time dependence of the hydrogen concentration for these two sets of reactions is shown in Fig. 2. In this figure it can be seen that the hydrogen concentration increases with time for the case where the initial hydrogen concentration is low and that the hydrogen concentration decreases with time for the case where the initial hydrogen concentration is high. Other results of these calculations, which are tabulated in Table III show that some dissolved oxygen is consumed in both cases. This table also shows that in both cases, ferrous ion is effectively converted to other forms (mostly ferric species). Radiolysis can thus affect the local water chemistry in the vicinity of waste packages.

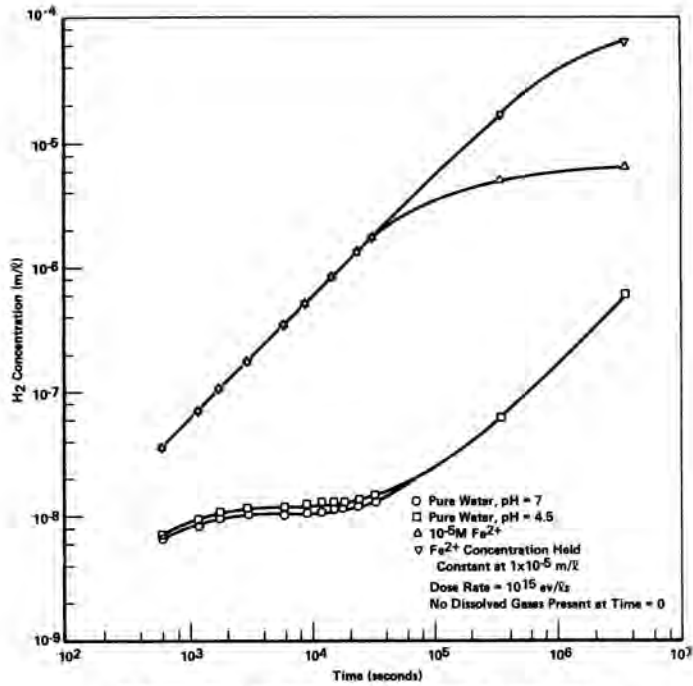
#### CONCLUSIONS

A preliminary mechanism for the radiolysis of groundwaters containing dissolved hydrogen, oxygen, ferrous ions, and ferric ions has been developed. This mechanism has undergone some benchmark tests against experimental data reported in the literature. This mechanism has been used to perform simulations of the gamma radiolysis of several aqueous systems exposed to a gamma dose rate equivalent to that at

the surface of spent fuel or high level waste package overpack at about 100 years after placement. These calculations show that the generation of radiolytic hydrogen is sensitive to the ferrous ion concentration and that dissolved oxygen can be radiolytically generated or consumed depending on the composition and conditions of the system. In all of these simulations, ferrous ion, when present, was effectively oxidized to ferric species. This may have implications on the characterization of the local water chemistry when evaluating the performance of waste package materials.

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H<sub>2</sub> Concentration vs. Time for Solutions Which are Initially Free of Dissolved Gases

Fig. 1. H<sub>2</sub> concentration versus time for solutions which are initially free of dissolved gases.

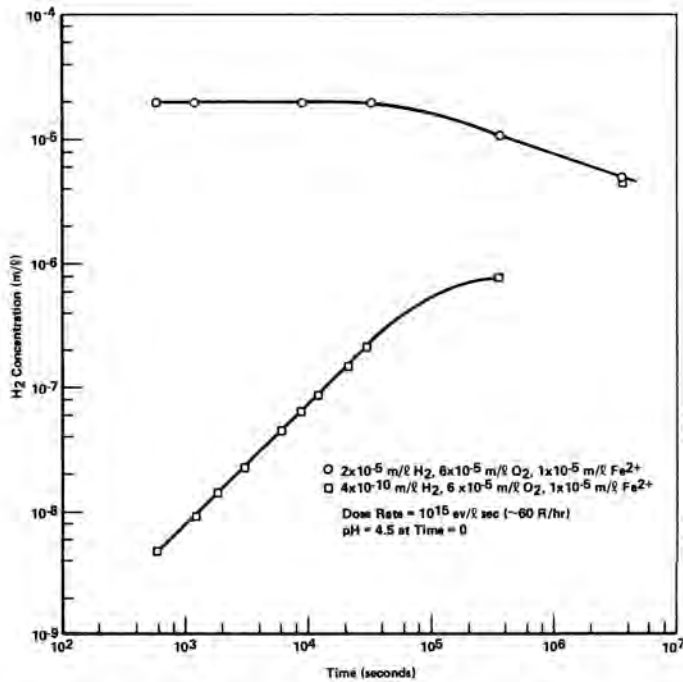


Fig. 2. Effect of the initial hydrogen concentration on the time dependence of the dissolved hydrogen concentration.