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Modeling the leaching behavior of simulated HLW-glass using PHREEQC

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Abstract PHREEQC is a geochemical model to study aqueous ion reaction equilibrium in water systems. In this paper, PHREEQC was used to calculate concentrations of main elements (Si, Na, B, Al, Sr, Cs, Fe and Nd) leached from simulated HLW-glass in solution. The experiments were preformed in deionized-water or simulated underground water at 90℃ or 150℃ under low oxygen atmosphere. The calculated results agreed well with the experimental results.

Key words PHREEQC program, Aqueous ion, Reaction equilibrium, Simulated HLW glass

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1 Introduction

Deep geological disposal of solidified radioactive waste in HLW (High Level Waste)-glass is a recommended method in the world. HLW-glass has been studied in a number of laboratories. However, leaching behavior of HLW- glass in deep geological disposals in tens of thousands of years is not definitely clear. Proper numeric models can be used to evaluate corrosion behavior of HLW-glass and check reliability of the experimental data.

Some geochemistry models, such as PHREEQC,[1] PHREEQE[2] and EQ3/6[3] have been used to study the problem. In this paper, PHREEQC (version2.7) was used to calculate leaching behavior of HLW-glass under low oxygen environment, and the results were compared with the experimental data. The calculation and experiment were performed on the leachate compositions (oxides of Si, Na, B, Al, Sr, Cs, Fe and Nd).

Based on an ion-associated aqueous model, PHREEQC is capable of calculating speciation and saturation-index. It performs also batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions in liquids, minerals, gases, solid-solutions, surface-complexation, and ion-exchange equilibria, and irreversible reactions, such as specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes. It provides inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits.

PHREEQC Version 2 has some new features. It is capable of simulating dispersion (or diffusion) and stagnant zones in 1D-transport calculations. It models kinetic reactions with user-defined rate expressions, and formation or dissolution of ideal, multi-component or non-ideal, binary solid solutions. It also models fixed-volume gas phases and fixed-pressure gas phases. It allows the number of surface or exchange sites to vary with the dissolution or precipitation of minerals or kinetic reactants. It includes isotope mole balances in inverse modeling calculations. It uses multiple convergence parameters. It prints user-defined quantities to the primary output file and/or a file suitable for importation into a spreadsheet, and defines solution compositions in a format more compatible with spreadsheet programs.

However, some limitations of PHREEQC are related to its use of ion-association and Debye Hückel expressions to account for the non-ideality of aqueous

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solutions. The other limitation of the aqueous model is lack of internal consistency in the data of the databases. The ion-exchange model assumes that the thermodynamic activity of an exchange species is equal to its equivalent fraction. In inverse modeling, the numerical method has shown some inconsistencies in results due to the way by which the solver handles small numbers.

Curti[4], Lolivier[5] and Van Iseghem[6] have done some study on glass leaching experiments and simulated with PHREEQC, and gained some referenced results.

2 Model and assumption

Assumptions for the calculation are as follows:

(1) The leaching behavior of the ion in HLW-glass complies with stoichiometry;

(2) Following the mass equilibrium;

(3) Every particle is not electrified. The surface adsorption and gel formation are not taken into account;

(4) The oxygen concentration is lower than 20 μmol/mol, and effects of CO_2 and O_2 can be neglected;

(5) As boron is in the whole process of glass dissolution,it is regarded as a standard element in the dissolution process to study other elemental dissolution in water;

(6) The sediment phases are selected with relative program.

According to concentration equilibrium of aqueous ions, the concentration of element *m* is the sum of the concentrations in mineral and in aqueous systems:

$$n_m = \sum_{p}^{N_p} b_{m,p} n_p + \sum_{i}^{N_{aq}} b_{m,i} n_i \qquad (1)$$

$$n_i = m_i \times W_{aq}\ , \quad a_i = \gamma_i \times m_i$$

where n_m is the moles of element *m* in solution; $b_{m,i}$ is the n_m over moles of aqueous ion *i*; $b_{m,p}$ is n_m over moles of mineral *p*; n_p is the moles of mineral in solution; N_p is the number of mineral in solution; N_{aq} is the number of aqueous ion; a_i is the activity of aqueous ion *i*; m_i is the molality of aqueous ion *i*; n_i is the moles of aqueous ion *i* in solution; W_{aq} is the mass of solvent water in solution; γ_i is the activity coefficient.

Mass action can be expressed as:

$$K_i = a_i \prod_{m}^{M_{aq}} a_m^{-c_{m,i}} \qquad (2)$$

$$\log K_i = \log a_i - \sum_{m}^{M_{aq}} c_{m,i} \log a_m \qquad (3)$$

where K_i is the equilibrium constant; a_i is the activity of aqueous ion *i* in solution; a_m is the activity of element *m* contained by aqueous ion *i*; M_{aq} is the total number of main ions in solution; $c_{m,i}$ is the stoichiometric coefficient of element *m* in ion *i*.

Mineral equilibrium expression is as follows:

$$K_p = \prod_{m}^{M_{aq}} a_m^{c_{m,p}} \qquad (4)$$

where $c_{m,p}$ is the stoichiometric coefficient in the reactions; M_{aq} is the total number of element *m* in solution; K_p is the equilibrium constant.

With regard to the concentration of mineral reached the saturation in solution, the following expression is applied:

$$SI_p = \log \prod_{m}^{M_{aq}} a_m^{c_{m,p}} \qquad (5)$$

where SI_p is the mineral saturation index. When $SI_p>0$, the mineral is saturated; and when $SI_p<0$, the mineral is under saturation.

The following expression shows the reaction path of glass dissolution:

$$\mathrm{d}n_m = \sum_{p}^{N_p} b_{m,p} \mathrm{d}n_p + \sum_{i}^{N_{aq}} b_{m,i} \mathrm{d}n_i \qquad (6)$$

where $\mathrm{d}n_m$ is the variational moles of element *m*; $\mathrm{d}n_p$ is the variational moles of mineral phases *p* in solution; $\mathrm{d}n_i$ is the variational moles of aqueous ion *i*. Because element boron is completely depleted during the dissolution process, the variational moles of element boron are used for indicating the dissolution process.

3 Experimental

Static leaching tests[7] (MCC-1) of simulated

HLW-glass under low oxygen condition were carried out at 150℃ and 90℃, respectively, for 546 days. The contents of main composition of the glass in deionized water or simulated under ground water are given in Table 1.[8]

Table 1 The main composition of simulated HLW-glass in deionized water or simulated underground water

Oxide	Weight fraction /%	Stoichiometric factor v_i /10^{-3}	Deionized water n_i /μg•g^{-1}	Simulated underground water n_i /μg•g^{-1}
SiO_2	50.23	8.36	1.02	2.38
Na_2O	11.21	3.62	0.02	2.97
B_2O_3	18.48	5.31	0.01	0.05
Al_2O_3	4.39	0.86	0.2	0.12
SrO	0.037	0.0036	0.012*	0.052*
Cs_2O	0.12	0.0085	0.75*	1.06*
Fe_2O_3	3.24	0.41	0.020	0.040
Nd_2O	2.03	0.12	0.012*	0.032*

*unit: ng•g^{-1}

4 Results and discussion

The calculated and experimental results are listed in Table 2[8] and Table 3 [8], respectively.

The calculated results agreed well with the experimental results. This indicates that the leachate composition obtained with the PHREEQC calculation is credible. There are some differences between the results of theoretical calculation and experiment, such as Al at 90℃ in underground water, and Sr at 90℃ in deionized water. These may be caused by the sediment phases. In the assumptions, dissolution of the main elements in the glass was considered as stoichiometric. Although some different phenomena appeared in the experiment, the theoretical calculation did not show obvious defects. So, the assumption could be accepted. Neither surface adsorption nor gel formation was considered in the assumption, which did not show obvious disadvantage.

Table 2 The calculating results compared with experimental results in deionized water (mol•L^{-1})

Element	150℃		90℃	
	Experiment	Theory	Experiment	Theory
Si	(1.47±0.09)×10^{-4}	1.42×10^{-4}	(4.58±0.02) ×10^{-5}	4.73×10^{-5}
Na	(2.33±0.08) ×10^{-4}	2.63×10^{-4}	(9.94±0.01) ×10^{-5}	8.65×10^{-5}
B	(3.09±0.04) ×10^{-4}	3.09×10^{-4}	(1.27±0.01) ×10^{-5}	1.27×10^{-4}
Al	(1.53±0.03) ×10^{-6}	1.39×10^{-6}	(2.17±0.07) ×10^{-6}	2.52×10^{-6}
Sr	(2.06±0.09) ×10^{-11}	2.68×10^{-11}	(1.19±0.03) ×10^{-11}	8.66×10^{-12}
Cs	(3.05±0.05) ×10^{-8}	4.14×10^{-8}	(1.41±0.03) ×10^{-8}	1.44×10^{-8}
Fe	(1.89±0.09) ×10^{-8}	1.95×10^{-8}	(1.37±0.08) ×10^{-8}	1.34×10^{-8}
Nd	(1.69±0.03) ×10^{-11}	1.58×10^{-11}	(1.75±0.07) ×10^{-11}	1.81×10^{-11}

Table 3 The calculating results compared with experimental results in underground water (mol•L^{-1})

Element	150℃		90℃	
	Experiment	Theory	Experiment	Theory
Si	(1.57±0.08) ×10^{-4}	1.33×10^{-4}	(3.98±0.09) ×10^{-5}	4.42×10^{-5}
Na	(2.61±0.09) ×10^{-4}	3.03×10^{-4}	(8.61±0.08) ×10^{-5}	5.68×10^{-5}
B	(3.59±0.04) ×10^{-4}	3.59×10^{-4}	(1.10±0.09) ×10^{-4}	1.10×10^{-4}
Al	(1.58±0.02) ×10^{-6}	1.25×10^{-6}	(7.78±0.09) ×10^{-7}	1.21×10^{-6}
Sr	(5.83±0.09) ×10^{-12}	8.09×10^{-12}	(6.47±0.05) ×10^{-12}	2.69×10^{-12}
Cs	(3.47±0.04) ×10^{-8}	4.43×10^{-8}	(1.73±0.03) ×10^{-8}	1.17×10^{-8}
Fe	(3.29±0.09) ×10^{-8}	2.98×10^{-8}	(1.17±0.07) ×10^{-8}	1.06×10^{-8}
Nd	(2.23±0.05) ×10^{-11}	1.79×10^{-11}	(2.65±0.04) ×10^{-11}	2.98×10^{-11}

5 Conclusion

In view of aqueous ion equilibrium, PHREEQC model could be used for calculating the concentration of leachate elements in solution under low oxygen atmosphere. The theoretical calculation results well agreed with the experimental results.

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