Articles

Thermodynamic Calculation in Elimination of Water Pollutants at Hydro-geo-chemical Barriers

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Thermodynamic saturation coefficients (K_s) and transformation indices (I_t) can be used to evaluate the possibility of forming hydro-geo-chemical precipitation barriers and assess the solid phase (rock) stability in aquifers. Calculations are made on the basis of data on water pH, E_h, conductivity (χ) and some relevant ion concentrations. The dependencies of K_s and I_t on water pH and E_h values can be expressed graphically to estimate the barriers parameters. Barrier generation leads to a decrease in concentrations of pollutants due mainly to precipitation, co-precipitation and/or sorption processes. Using the diagram K_s, $I_t = f$ (pH, E_h), supplemented with representative data on concentrations of pollutants before and after the barrier, the elimination and migration of pollutants can be roughly evaluated (predicted) only on the basis of determining pH and E_h values of water and concentrations of ions participating in the barrier formation. The proposed method is applied to assess the migration and elimination of pollutants (U, ^{226}Ra, β-emitters, SO_4^{2-}) in Bulgarian uranium mine surroundings.

Introduction

The knowledge of the possibility for pollutants migration and elimination in aquifers can help in taking important decisions, such as: (a) whether a given industry is dangerous for the environment and especially for the surrounding soil and groundwater? (b) what are the possibilities for natural retention of pollutants and for making them harmless outside industrial regions? (c) what steps are to be taken in order to restrict pollution and/or restore the water quality? Is it indispensable to halt oper-

ations at the mine enterprise?

The main hydro-chemical processes decisive for forming the composition of ground (and surface) waters affected by mining operations are: (a) hydrolysis (most often, protolysis) and incongruent dissolution (leaching) of the basic rock- and ore-forming minerals, (b) complexation of ions, (c) precipitation of secondary minerals, which in most cases are not only a sedimentation way of eliminating preliminarily leached ingredients, but also a suitable matrix for their sorption retention. The so-called hydro-geo-chemical precipitation-sorption barriers are thus formed.

The aim of the present paper is to describe a method developed for evaluating 1) the possibility for hydro-geo-chemical barrier formation; 2) the barrier parameters; 3) possibilities for pollutants elimination (to a certain degree).

Experimental

The possibility for a solid phase precipitation can be evaluated by means of the saturation coefficient K_s. For a generalized reaction (in equilibrium):

$$A_m^{n+} B_n^{m-} = m A^{n+} + n B^{m-} \tag{A}$$
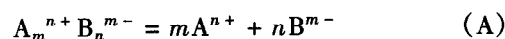
K_s is expressed by the following equation:

$$K_s = a_A^{m_{n+}} a_B^{n_{m-}} / P_{A_m B_n} \tag{1}$$

where $A_m B_n$ is low soluble compound (mineral);

$P_{A_mB_n}$—solubility product of the compound; $a_{A^{n+}}$, $a_{B^{m-}}$—thermodynamic activities of ions and m, n—stoichiometric coefficients.

The thermodynamic stability of a given solid phase can be evaluated by means of the irreversibility (transformation) index I_t.[1] For a generalized reaction:

$$A_m B_n + u H_2O = m A^{n+} + n(BO_p)^{\nu-} + 2u H^+ + q e^- + D_d S_s,$$ (B)
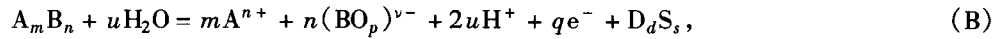
I_t is expressed by the following equation:

$$I_t = m \lg a_{A^{n+}} + n \lg a_{BO_p^{\nu-}} - 2u pH + f(t, E_h)$$ (2)

where: d, ν, u, m, n, p, q, s—stoichiometric coefficients; a_A^{n+}, $a_{BO_p^{\nu-}}$—the activities of ions A^{n+} and $BO_p^{\nu-}$; $f(t, E_h)$ is empirical function, which depends on the temperature and oxidation-reduction potential of the medium ($f(E_h)$ is related to the number of electrons, exchanged during the reaction, if any); $D_d S_s$—another (secondary) low soluble mineral.

When $K_s > 1$, reactions of type (A) are directed to the left, i.e. under specific hydro-geo-chemical conditions (and at given pH and E_h values, as summarized parameters) thermodynamically stable solid phases-precipitates are formed. The elimination of the polluting ions can take place by (a) participation in the precipitate formation, (b) co-precipitation, and (c) (most often) adsorption on the formed precipitate. Reactions of type (B) are shifted to the left, when $I_t > 0$.

To calculate K_s and I_t, taking into account also the complexation of ions and electro-kinetic phenomena at the mineral/solution interface, computer programs can be used such as WATROCK[2] (Fig. 1) to which additional thermodynamic data[1,3] are needed. Concentrations of ions entering the solid phases, pH, E_h and conductivity of groundwater are the main parameters (in the program) needed for a quick estimation of thermodynamic activities. The expressions of the activity coefficients necessary to calculate the thermodynamic activities are as follows:

$$- \lg f_i = \frac{A z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} (\text{if } \mu < 0.2 \text{ mol/L});$$

$$- \lg f_i = A z_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.25\mu \right)$$
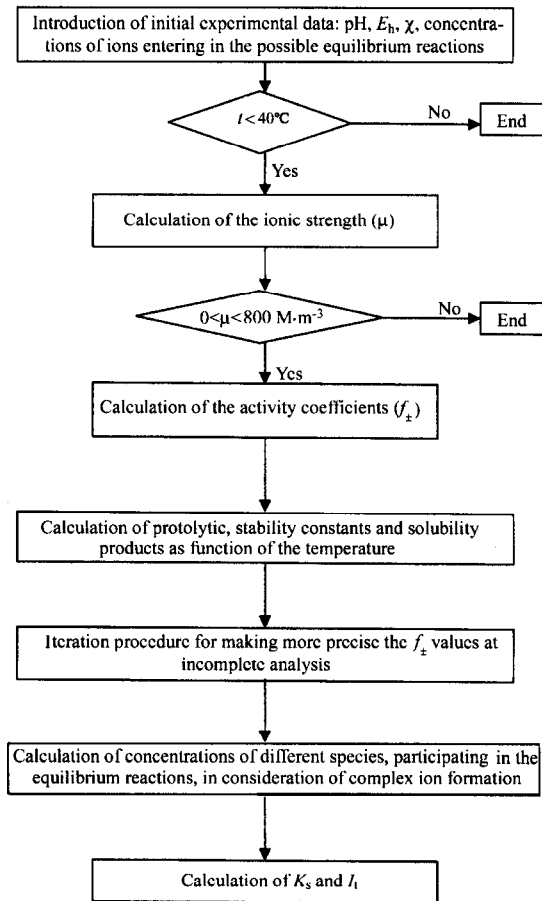
$$(\text{if } 0.2 < \mu < 0.8 \text{ mol/L}),$$ (3)

Fig. 1   Algorithm of WATROCK program for a quantitative thermodynamic assessment of water-rock interactions.

where z_i is the valency of ion i, μ is the ionic strength, A is the temperature dependent constant and within the range from 0 to $40\,^{\circ}\mathrm{C}$, A is given by the following expression:[2]

$$A = 0.000845(T - 273.15) + 0.488$$ (4)

The ionic strength μ (mol/L) can be found using the formula:

$$\mu = 0.5 \, \delta \sum_{i=1}^{n} c_i \cdot z_i^2$$ (5)

where δ is a factor, that takes into consideration the complexation (but predominantly with inorganic ligands) of the ions. It is calculated by use of the following equation:[4]

$$\delta = -0.09627\ln M + 1.4212 \qquad (6)$$

where M is the mineralization of the groundwater in mg/L. To evaluate quickly water mineralization and/or ionic strength at incomplete analysis, the dependencies on the conductivity χ are used:[2,5]

$$M = \alpha \cdot \chi^p \qquad (7)$$

where α and p are constants with values depending on the water conductivity as given in Table 1, and:

$$\mu = 0.01835 \cdot \chi_{20C} \qquad (8)$$

where μ is expressed in mmol/L and χ is in $\mu S/cm$. The exact analytical relation between μ and χ has to be predetermined for the particular investigated region.

The proposed method for thermodynamic evaluation has been applied to estimate the possible migration of different pollutants (U, ^{226}Ra, β-emitters, and SO_4^{2-}) in the area of a uranium mine in South Bulgaria. In this case uranium is extracted by means of underground sulfuric acid leaching through boreholes. 29 samples of groundwater have been taken for examination. Values of pH, E_h and χ of the investigated waters have been measured "*in situ*". Concentrations of ions, such as Na^+, K^+, Fe^{2+}, Al^{3+}, UO_2^{2+} and SO_4^{2-}, and of H_4SiO_4 have been determined with Bulgarian State standard or internationally approved methods.[6,7]

Table 1 Coefficients for calculation of water mineralization by use of conductivity

Type of water	Conductivity, χ ($\mu S \cdot cm^{-1}$)	α	p
Low mineralized	$\chi < 250$	0.37	1.17
Hydrocarbonate-calcium	$250 < \chi < 800$	1.04	1
Sulfate-calcium	$500 < \chi < 3000$	1.07	1

Results and discussion

Bearing in mind the composition of the groundwa-

ter, as well as the type of rocks in the region, reactions given in Table 2 have been chosen for our thermodynamic calculation. Data on the equilibrium constants, solubility products, stability constants and their temperature dependencies have been taken from the literature.[1,4,8,9] The following species have been considered in the thermodynamic calculations for the $UO_2^{2+} - H_2SO_4$ system (reaction 7, Table 2):[10] UO_2^{2+}, UO_2SO_4, [UO_2-$(SO)_4$]$^{2-}$ and $UO_2(OH)_2 \cdot 2H_2O$. Reactions 4 and 5 (Table 2) have been mainly used to obtain K_s values for $Fe(OH)_3$ and $Al(OH)_3$, presented in Fig. 2. Most probable complexes of Fe^{3+} and Al^{3+} with OH^- (water) and HSO_4^- (H_2SO_4) as ligands have been considered.[11] Table 3 presents formulas used to calculate K_s and I_t (as function of the temperature and E_h) for reactions 8—16 described in Table 2.

The values obtained for K_s and I_t show that (a) kaolinite is the most stable solid phase (under the existing hydro-chemical conditions), (b) solid phases from $Fe(OH)_3$ and $Al(OH)_3$ may be formed, (c) the elimination of U in the form of $UO_2(OH)_2 \cdot 2H_2O$ is possible only if pH > 6 and $C_{SO_4^{2-}} < 100$ mg/L.

Direction estimation for reaction 9, and from 12 to 15 is indicative of the way, in which rocks in the region neutralize huge quantities of H_2SO_4 (about 200000 t), introduced in the geological stratum during the uranium extraction.

Except for the above-mentioned hydrolysis, reactions 4, 5, 6 and 11 are also pH-dependent. Reactions 4 and 5 are also E_h-dependent (in terms of the relationship between pH and E_h), and practically the total conversion of Fe^{2+} into Fe^{3+} for reaction 4 is due to the highly oxidizing conditions.

K_s values, calculated for $Fe(OH)_3$ and $Al(OH)_3$ at different pH and E_h values of the groundwater are shown in Fig. 2. Parameters of the precipitation-sorption barrier formed can be read from the graph. In the case being described they are pH values above 3.65 and E_h values below 402 mV for the iron hydroxide barrier and pH values above 4.52 and E_h values below 346 mV for the gibbside one. Experimental concentrations of some pollutants (UO_2^{2+}, ^{226}Ra, β-activity and SO_4^{2-}) and of barrier forming ions (Fe^{3+} and Al^{3+}) are also pictured in Fig. 2.

Table 2　Chemical equilibria used in thermodynamic calculation

Investigated reaction	K_s	I_t
1. $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	$\ll 1$	
2. $CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	$\ll 1$	
3. $CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$	< 1	
4. $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$	generally $\geqslant 1$	
5. $Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$	generally $\geqslant 1$	
6. $Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2OH^-$	$\ll 1$	
7. $UO_2(OH)_2 \cdot 2H_2O \rightleftharpoons UO_2^{2+} + 2OH^- + 2H_2O$	$< 1^a, > 1^b$	
8. $FeS_2 + 8H_2O \rightleftharpoons Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$		$\ll 0$
9. $NaAlSi_3O_8 + 4H_2O + 4H^+ \rightleftharpoons Na^+ + Al^{3+} + 3H_4SiO_4$		< 0
10. $Al_2Si_2O_5(OH)_4 + 6H^+ \rightleftharpoons 2Al^{3+} + 2H_4SiO_4 + H_2O$		Generally $> 0^c$
11. $SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4$		Generally > 0
12. $NaAlSi_3O_8 + H^+ + 4.5H_2O \rightleftharpoons 0.5Al_2Si_2O_5(OH)_4 + Na^+ + 2H_4SiO_4$		< 0
13. $KAlSi_3O_8 + H^+ + 4.5H_2O \rightleftharpoons 0.5Al_2Si_2O_5(OH)_4 + K^+ + 2H_4SiO_4$		< 0
14. $CaAl_2Si_2O_8 + 2H^+ + H_2O \rightleftharpoons Al_2Si_2O_5(OH)_4 + Ca^{2+}$		$\ll 0$
15. $[6Ca_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 2H^+ + 23H_2O \rightleftharpoons 7Al_2Si_2O_5(OH)_4 + Ca^{2+} + 8H_4SiO_4]/6$		< 0
16. $Al_2Si_2O_5(OH)_4 + 5H_2O \rightleftharpoons 2Al(OH)_3 + 2H_4SiO_4$		> 0

^{a} at pH < 6 and $[SO_4^{2-}] \sim 100$ mg/L;　^{b} at pH > 6 and $[SO_4^{2-}] < 100$ mg/L;　^{c} except for samples with pH $\leqslant 3.35$.
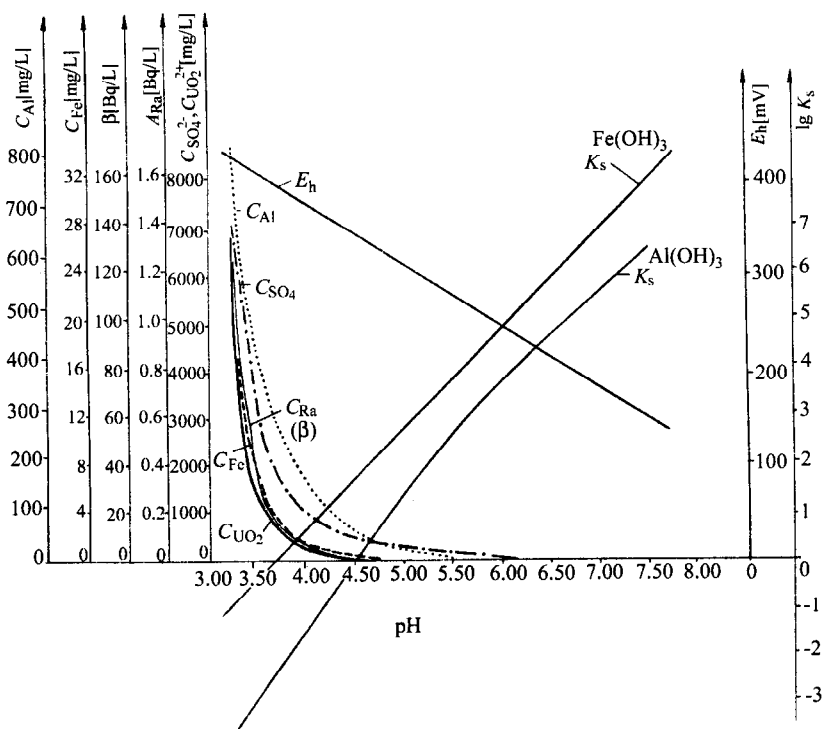

Fig. 2　Dependence of K_s and concentrations of pollutants on pH and E_h values of groundwater.

Having in mind (a) the clearly pronounced decrease in concentrations of pollutants in the thermodynamically determined pH-E_h region, where precipitates from $Fe(OH)_3$ and $Al(OH)_3$ may be formed (as proved by the thermodynamic calculations), (b) the thermodynamic impossibility for precipitation of $UO_2(OH)_2 \cdot 2H_2O$ and the possibility for uranium migration in the form of complexes $UO_2SO_4^\circ$ (under the investigated conditions),

(c) the sorption capabilities of $Fe(OH)_3$ and $Al(OH)_3$, a conclusion could be drawn that the elimination of the polluting ions (of U and other radio-nuclides, and SO_4^{2-}) is due mainly to their sorption on the hydroxides formed and on the stable alumosilicates. The observed "delay" in SO_4^{2-} elimination (compared to the elimina-

tion of U, [226]Ra and some β-emitters) could be assigned to the higher sorption (ion exchange) capacity of alumosilicates and colloidal H_4SiO_4 with respect to radionuclides, as compared to the capacity with respect to SO_4^{2-}.[11]

Table 3   Expressions used to calculate K_s and I_t for reactions presented in Table 2

Reaction No. according to Table 2	Formula
8	$I_t = \lg[Fe^{2+}] + 2\lg[SO_4^{2-}] - 16pH - 11.6 - (70449.5\ E_h - 29295.38)/T$
9	$I_t = \lg[Na^+] + \lg[Al^{3+}] + 3\lg[H_4SiO_4] + 4pH - 3.94 + 0.038(T - 298.15)$
10	$I_t = 2\lg[Al^{3+}] + 2\lg[H_4SiO_4] + 6pH - 7.63 + 0.0823(T - 298.15)$
11	$I_t = \lg[H_4SiO_4] + 0.09 + 779/T$
12	$I_t = \lg[Na^+] + 2\lg[H_4SiO_4] + pH - 0.046 - 0.00323(T - 273.15)$
13	$I_t = \lg[K^+] + 2\lg[H_4SiO_4] + pH - 0.01629(T - 273.15) + 2.931$
14	$I_t = \lg[Ca^+] + 2pH - 18.84 + 0.07114(T - 273.15)$
15	$I_t = \{\lg[Ca^+] + 2pH + 8\lg[H_4SiO_4] - 0.01143(T - 273.15) + 16.6\}/6$
16	$I_t = 2\lg[H_4SiO_4] - 0.02(T - 273.15) + 8.79$

[ion] is the activity of an ion.

The formation of a hydro-geo-chemical precipitation barrier from $Fe(OH)_3$ and $Al(OH)_3$ can also cause elimination (by sorption) of other heavy metal ions. According to some authors[12] $Fe(OH)_3$ and $Al(OH)_3$ have a good sorption capacity with respect to ions of Cd, Cu, Pb, Se, Zn, and As.

As a result of long-term and representative measurements of pH, E_h, χ, C_{Al}, C_{Fe} and concentrations of pollutants, graphs similar to these shown in Fig. 2 can be drawn. Using these graphs, only on the basis of data on pH, E_h, C_{Al} and C_{Fe} values, an express evaluation can be made of (a) possibility for formation of hydro-geo-chemical precipitation barriers, (b) barrier parameters: pH and E_h values at which it is formed, its width, concentrations of pollutants beyond the barrier, (c) probability for sorption elimination of different pollutants.

Conclusion

The hydro-geo-chemical barrier formation and the elimination of different pollutants by these barriers can be shown by graphs drawn with the aid of thermodynamic calculations based on a representative set of data. Parameters of the barrier and the extent of elimination of possible pollutants can be predicted by use of these diagrams and only on the basis of pH, E_h data values of

the water and concentrations of ions participating in the precipitates, forming the barriers in the aquifer.

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(E200003060   SONG, J.P.; LING, J.)