Thermodynamic model of Ak-Tuz deposit surface water formation

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Abstract. In Ak-Tuz deposit surface water macro and micro components concentrations are measured. Thermodynamic model is developed for aqueous composition prognosis at variation of water exchange. The concentration of n×10⁻⁸ mg Th / kg H₂O and more testifies about Th containing colloid species in aqueous solution.

1. Introduction
Ak-Tuz ore field (Kirgiz Republic) is located in the west part of Munkumo-Naratskogo median massif of the Zailisky Alatau Mountains and it is composed of amphibolite shists and Archean-Proterozoic gneises. Deposits of Y, REE, Th, Zr, Mo, Be, Pb and other metals are related to Early Permian biotite granite and alaskite granophyre of Keminsky massif. The exposed part of the granite massif, 24 km in length and 1-4 km in width, is like fracture intrusion, subducted (160°) under rock mass of amphibolite shists and gneises. The basic body of Keminsky massif is formed by meso and leucobiotite granites, their ore-bearing cupolas are leuco and alaskite granites [8, 12, 9].

Up to 90-th years of the last century Ak-Tuz deposit was the main source of rare earth elements and yttrium in the former USSR. The yttrium ore-bearings themselves are confined to upper horizons of deposit low zone with Y mineralization and lanthanide of yttrium group. From 1960 to 1995 years the deposit was exploited for rare earth elements extraction by open-cut quarry. Rear earth, yttrium oxide, plumb, tin, copper, niobium, tantalum, thorium and iron are the main products of mining. Rear ores are high radioactive due to content of thorium minerals (monazite, thorite, zircone and others). Total volume of tailing ponds and storages is 4.17 million m³, their square is 51 Ga. Beside ponds and storages, there are three large heaps of rock, their volume are 50 million m³.

It is necessary to evaluate and forecast possible environmental disasters. The area under consideration is influenced by various factors. It means that beside traditional methods of investigation (chemical analysis, statistics etc) computer simulation of water-rock-gas system should be used [2, 3].

2. Materials and methods
Ak-Tuz surface waters chemical composition (Ca, Mg, Na, K, Cl, SO₄, HCO₃, NO₃, NO₂, NH₄ and microelements) has been determined in 40 samples taken across the area. To determine
macrocomponent content a balance between cations and anions was checked as shown in (Figure 1) as discord of their equivalents and the simple statistics was carried out (table 1).

![Figure 1. Discord of balance between cation and anion equivalents according to samples collected in 2014 (dotted line is ± 10 %).](image)

It is seen the discord increases with salinity decrease. Taken 10% balance and less as boundary the aqueous analytical determinations of 100 mg/L and more (sum of cations and anions < 3 mg-eq/L) may be considered as good enough.

| Parameter | pH | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ | Cl | SO$_4^{2-}$ | HCO$_3^-$ | NO$_3^-$ | Salinity, mg/L | Sum of cations and anions, mg-eq/L |
|-----------|----|-----------|-----------|--------|----|-------------|----------|----------|----------------|----------------------------------|
| Max.      | 8.9 | 88 | 29 | 26 | 13 | 189 | 299 | 9.8 | 502 | 14.2 |
| Min.      | 7.3 | 24 | 4.0 | 0.8 | 4.0 | 3.7 | 67 | 0.7 | 120 | 3.2 |
| Average   | 8.1 | 41 | 11 | 7.0 | 6.1 | 24.4 | 145 | 2.5 | 234 | 6.2 |

Factor analysis is also used to identify geochemical processes responsible for surface water composition formation. The values of pH, Ca, Mg, Cl, SO$_4^{2-}$, HCO$_3^-$ determined for all samples are used. The results of factor analysis show four significant processes responsible (97.6%) for the composition formed (table 2). Please pay attention that Factor 2 depends on chloride content. It is not obvious due to low accuracy of chloride determination.

| Parameter | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|-----------|----------|----------|----------|----------|
| pH        | -0.178   | 0.087    | **-0.961** | -0.193   |
| Ca        | 0.595    | 0.007    | 0.172    | **0.746** |
| Mg        | **0.744** | -0.242   | 0.193    | 0.533    |
| Cl        | 0.025    | **-0.978** | 0.082    | 0.172    |
| SO$_4^{2-}$ | **0.987** | 0.043    | 0.132    | -0.003   |
| HCO$_3^-$ | -0.002   | -0.243   | 0.178    | **0.949** |

Surface water sample analysis (macro and micro components) was considered in terms of mineral equilibriums. The sample aqueous solutions were saturated with respect to BaSO$_4$ (barite), CaCO$_3$ (calcite), CaMgC$_2$O$_6$ (dolomite), HFeO$_2$ (goethite), TiO$_2$ (rutile) and SrCO$_3$ (strotianite). The solution samples are unsaturated with respect to ore minerals of Ag, Zn, Pb, Ni, Sb, Cr. Aqueous species are
regular: they are simple cations for alkaline and alkaline-earth elements, they are hydroxides, sulfates and carbonates for two charged cations of color metals, for Sb and Fe – hydrospecies, for chromium – CrO$_4^{2-}$; for nitrogen mostly NO$_3^-$ and probably NO$_2^-$. Such aqueous species are explained by low concentration of the elements (mkg/L): Ag 0.n, Ni 0.n, Pb 0.n, Cr n, Cu n, Zn n×10, Ti n×10, Ba u Sr 0.n; concentration of Sb, which equals to n×100, is probably wrong. The results described above allow us to consider environmental state as satisfactory with respect to all studied elements but Sb (pmc 5 mkg/L).

Thermodynamic model of water-rock-gas system shows equilibrium concentrations of the elements in aqueous phase which contacts the rock (the rock of basic composition in this study) as [3] proves, equilibrium concentrations depend on four main factors: (a) rock composition of the sites of water-rock contact and interaction, (b) water exchange (rain, dry weather, etc.) and inflax and outflax, (c) temperature, (d) partial pressure of atmosphere gases.

For simulation of water-rock-gas system the model containing 26 chemical elements (Al-Ag-As-Ba-Ca-Cl-Cr-Cu-Fe-H-K-La-Mg-Mn-Mo-N-Na-O-Pb-Sb-Si-Sr-Th-Ti-U-Y-Zn), 110 solids (minerals and phases) and 120 simple and complex aqueous species was developed. Sorption of thorium which is of special interest of study was considered as ideal solid solution of sorbent (iron hydroxide, humic substance) and thorium adsorbed aqueous species (Th(OH)$_4^{3-}$) using experimental value of sorption constant. Comparison of the simulation results with chemical composition of surface water samples was done.

Ak-Tuz site temperature was taken as summer average (10°C). Total pressure was taken according site position at 2 km. Chemical and mineral compositions are taken as basic rock features according to Ak-Tuz ore field description [4, 10]. Gibbs Free energy values of solids and gases, aqueous species are taken from [6, 13] and from improved base UNITHERM [2]. In some cases, BR model was used to calculate constants of unstudied steps of aqueous complex ionization [7].

The water-rock-gas system is considered as open with respect to atmosphere gases with CO$_2$ partial pressure equal to 0.001 bar and with oxygen partial pressure corresponding NO$_3^-$ predominance in surface water samples of Ak-Tuz site.

Simulation results of water-solid-gases interaction show the following: micro component concentrations correspond to active water exchange (mass ratio rock to water R/W≈0.0001-0.004) and to positive redox potential Eh≈+750-800 mV and pH≈8.0 (see table 3). Comparison of simulation and analytical data of macro and micro components of aqueous phase shows that the water exchange when sampling corresponds to R/W≈0.004 (bold shift) and with such water exchange the element concentrations do not exceed pmc. Significant decrease (more than 10 times) in water exchange will lead to pmc excess (at R/W>0.06 only). Model concentrations of micro and macro components might be more accurate if Ak-Tuz rock and tailings compositions are known.

Model concentration of SO$_4^{2-}$ is significantly lower than analytical one. It supports the opinion about oxidation sulfides. Surplus of sulfate decreases barium concentration in equilibrium to barite BaSO$_4$. Simulation permits us to say that concentrations of As, Se, Hg with low pmc might be overcome at passive water exchange only.

Table 3. Comparison of results of simulation of water-rock-gas system at R/W=0.0001-0.2 (various water exchange) and results of analytical determination of the same chemical elements (mg/L) of Ak-Tuz surface water samples.

| Elements | Concentrations at various water exchange (R/W model) | Analysis |
|----------|---------------------------------------------------|----------|
|          | 0.0001 | 0.0007 | 0.004 | 0.03 | 0.06 | 0.2 | min | max |
| Ca       | 7.6    | 35     | 36    | 57   | 97   | 205 | 24  | 88  |
| Mg       | 0.5    | 2.9    | 5.4   | 8.5  | 14.5 | 30.1| 4   | 29  |
| Na       | 0.3    | 1.8    | 11.1  | 68.8 | 171  | 426 | <0.1| 26  |
| K        | 0.04   | 0.2    | 1.4   | 8.6  | 21.3 | 49.2| <0.1| 0.7 |
| HCO$_3^-$| 28.4   | 121    | 122   | 108  | 90.5 | 73.6| 31  | 256 |
Table 4. Simulated concentrations of Th aqueous species in surface waters of Ak-Tuz 2014-sampling.

| Sample | Th(OH)$_4$ (mg/L) | Th(OH)$_3$(OH) | Th(OH)$_2$(CO$_2$)$_3$ | Sum (mg/L) | Th(OH)$_4$ (%) | Th(OH)$_3$(OH) (%) | Th(OH)$_2$(CO$_2$)$_3$ (%) |
|--------|------------------|-----------------|------------------------|------------|----------------|-------------------|------------------------|
| Ak-1   | 2.54E-10         | 6.98E-08        | 1.51E-08               | 8.51E-08   | 0.3            | 81.93             | 17.77                  |
| Ak-2   | 2.54E-10         | 7.77E-08        | 1.60E-08               | 9.39E-08   | 0.27           | 82.71             | 17.02                  |
| Ak-3   | 2.54E-10         | 3.05E-08        | 2.68E-08               | 5.75E-08   | 0.44           | 53.06             | 46.5                   |
| Ak-4   | 2.54E-10         | 7.26E-08        | 1.84E-08               | 9.13E-08   | 0.28           | 79.54             | 20.18                  |
| Ak-5   | 2.54E-10         | 1.25E-07        | 1.39E-08               | 1.39E-07   | 0.18           | 89.78             | 10.04                  |
| Ak-6   | 2.54E-10         | 4.98E-08        | 2.27E-08               | 7.28E-08   | 0.35           | 68.4              | 31.25                  |
| Ak-7   | 2.56E-10         | 6.50E-08        | 1.01E-08               | 6.54E-08   | 0.39           | 99.45             | 0.15                   |
| Ak-8   | 2.54E-10         | 6.28E-08        | 2.00E-08               | 8.30E-08   | 0.31           | 75.61             | 24.09                  |
| Ak-9   | 2.54E-10         | 5.68E-08        | 2.29E-08               | 7.99E-08   | 0.32           | 71.01             | 28.67                  |
| Ak-10  | 2.54E-10         | 2.68E-08        | 3.18E-08               | 5.89E-08   | 0.43           | 45.53             | 54.04                  |
| Ak-11  | 2.54E-10         | 4.66E-08        | 2.22E-08               | 6.91E-08   | 0.37           | 67.49             | 32.14                  |
| Ak-12  | 2.54E-10         | 2.03E-07        | 1.00E-08               | 2.14E-07   | 0.12           | 95.19             | 4.69                   |
| Ak-13  | 2.54E-10         | 2.43E-07        | 9.16E-09               | 2.52E-07   | 0.1            | 96.26             | 3.64                   |
| Ak-14  | 2.54E-10         | 1.39E-08        | 4.49E-08               | 5.91E-08   | 0.43           | 23.55             | 76.02                  |
| Ak-15  | 2.54E-10         | 5.87E-08        | 2.01E-08               | 7.90E-08   | 0.32           | 74.27             | 25.41                  |
| Ak-16  | 2.54E-10         | 2.37E-08        | 3.32E-08               | 5.72E-08   | 0.45           | 41.48             | 58.08                  |

Simulation allows us to evaluate pMC of Th in 40 samples of surface waters. Simulation was done assuming the presence of chloride, sulfate, hydroxo and carbonate Th-complexes formation. Thermodynamic properties of the complexes were taken from [11]. Simulation shows the predominance of hydroxo and hydroxo-carbonate species with total concentration less than \(n \times 10^8\) mg/kg H$_2$O (table 4) in most aqueous phase samples.
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3. Thermodynamic model is created and simulation of water-rock-gas system is done. Comparison of waters is calculated (n×10^{-8} small variations of isotopic composition of water samples proves identical precipitate income.

3. Summary
1. Statistics of macro and micro component chemical analysis of Ak-Tuz surface waters samples collected in 2014 is done. The results of statistics lead to following conclusions:
   - water exchange time of several months proves atmosphere precipitates as main source of Ak-Tuz surface waters;
   - sulfides oxidation in ore tailings is estimated,
   - small variations of isotopic composition of water samples proves identical precipitate income.
2. The various competing Th-complexes are calculated. The thorium aqueous concentration in surface waters is calculated (n×10^8 mg/kg H2O). The surpass of this thorium concentration means the presence of colloids and dispersed species of thorium in Ak-Tuz surface waters.
3. Thermodynamic model is created and simulation of water-rock-gas system is done. Comparison of simulation results and analytical determination of macro and micro component aqueous concentrations proves the model to be efficient to predict surface waters composition at other water exchanges.

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