

CHANGES IN THE MACRO-MICROCOMPONENT COMPOSITION OF WATER IN THE ROCK-WATER SYSTEM AT INCREASING TEMPERATURE AND PRESSURE

¹Khasanova G.I.* and ²Bakiev S.A., ²Kudratov A.M. ²Ibragimov A.S.

¹*Institute of Seismology of the Academy of Sciences of the Republic of Uzbekistan*

²*SE "Institute HYDROINGEO" Tashkent Architecture and Construction Institute*

ABSTRACT

Experimental research into leaching of rare and rare-earth elements (REE) (limestone, carbonaceous argillite and sandstone) from rocks by distilled water at increasing temperature and pressure is carried out. The groups of rare and REE have been analyzed separately.

Keywords: *Water, Core, Rare and REE, pH, Mineralization, Temperature, Pressure, Leaching*

INTRODUCTION

The chemical composition of groundwater and REE content are indicators of seismic and environmental conditions of groundwater and can be used for monitoring water bodies. Actuality of the problem is determined by the poor study of the mechanism and the nature of the behavior of rare and REE in groundwater. To solve this problem, we have conducted experimental studies on leaching of REE heavy metals in the rock-water system in the autoclave at increasing temperature and pressure.

Purpose: To reveal changes in REE and heavy metals concentrations at different temperatures and pressures in the rock system ↔ water (at 20, 50, 100, 150, 170 and 225°C).

Objects: For experimental studies, we have selected core material from the field Chordorboza at various intervals (from 2485 to 2862) represented by limestone, coal mudstone and sandstone.

MATERIALS AND METHODS

The concentration of REE and heavy metals (64 elements in total) was determined by mass spectrometric method with inductively coupled plasma in the central chemical laboratory of the State Committee of Geology. REE or lanthanides are divided into two groups: light (LREE) - La, Ce, Pr, Nd, Sm and heavy (HREE) - Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, sometimes into three: light (La-Pr), medium (Nd-Gd), heavy (Tb-Lu) (Patra *et al.*, 2012). The determination of REEs was possible with the help of new methods of mass spectrometric analysis (ICP-MS), high resolution (HR-ICP-MS) (Safronova *et al.*, 2017).

Interest in the study of REE in water is due to the fact that the nature of their distribution in water generally follows the nature of the distribution of these elements in water-bearing rocks (Sholkovitz, 1995; Shand *et al.*, 2005; and Shannon, Wood, 2005).

The similarity of REE behavior in natural processes represents a huge opportunity to study the sources of matter and the nature of the ongoing geochemical processes, and the redox properties of cerium and europium make a group of REE sensitive to changes in the hydrogeochemical environment in natural processes (Sholkovitz, 1995; Shand *et al.*, 2005; and Shannon, Wood, 2005).

In this regard, a comprehensive study of the behavior of the chemical composition of water and REE in water and their leaching from rocks under the influence of high temperatures and pressures in the autoclave becomes particularly relevant. Complex study and monitoring of changes in the chemical composition of groundwater, including the concentration of rare and rare-earth elements in time, can be additional indicators in the forecast of earthquakes, taking into account the already existing forecast indicators used since the discovery № 129 (change in the concentration of groundwater gas composition and the content of uranium and fluorine).

In our case, thermobaric experiments were carried out at temperatures up to 600°C and 25 (kgf/cm²) pressures.

Research Article

Table 1. The content of microcomponents in distilled water is shown.

Name of elements	Content, mcg/l
Sodium (Na)	2800
Potassium (K)	1700
Calcium (Ca)	240
Magnesium (Mg)	34.0
Bromine (Br)	28.0
Rubidium (Rb)	7.3
Phosphorus (P)	7.10
Bohr (B)	6.8
Iodine (I)	3.2
Copper (Cu)	2.8
Strontium(Sr)	2.8
Iron(Fe)	1.70
mercury (Hg)	0.004

The result of the analysis determines the geochemical series: Na → K → Ca → Mg → Br → Rb → P → I, Br → Sr → Cu → Fe, Hg → U.

As a result of the increase in pressure and temperature in water samples, an increase in elemental REEE concentrations was detected (Table 2). In addition, during the experiments in solutions it was found that the concentration of silicon increased from 12 to 36 mg/l, while its hardness reached 8.70 mg-equiv/l.

Table 2: Distilled water measurement results

Cations	Contents in litres			Other determination	
	mg/l	mg-equiv/l	% eq	Total hardness (mg-equiv/l)	0.1
Na ⁺ , K ⁺	22.08	0.96	90.5	Removable	-
				Permanent	-
NH ⁺	no	-	-	Carbonate	0.2
Ca ²⁺	2.0	0.1	9.5	Noncarbonate	-
Mg ²⁺	no	-	-	pH	6.65
Fe ³⁺	no	-	-	Oxidizability (mg/l)	-
Total	24.08	1.06	100	Dry residue at t(mg/l)	64.8
Anions	Contents in liters			Calculated (mg/l)	60.4
	mg/l	mg-equiv/l	% eqv	Weightedparticles (mg/l)	-
Cl ⁻	17.75	0.5	47	Physical properties	
SO ₄ ²⁻	17.2	0.36	34.4	Turbidity (mg/l)	-
NO ₃ ⁻	Her	-	-	SiO ₂	no
NO ₂ ⁻	Her	-	-	Colour	Without colour
CO ₃ ²⁻	Her	-	-	Smell	No odor
HCO ₃ ⁻	12.2	0.2	18.6	Sediment	Without sedimentation
Total	47.15	1.06	100	Change in condition	
The formula of salt water composition: $\frac{0.06 \text{ Cl}^{47} \text{ SO}_4^{34} \text{ HCO}_3^{18}}{(\text{Na K})^{90.5}}$				Notes:	

Research Article

REE study in water samples is carried out to identify and evaluate the general geochemical background of concentrations of dissolved forms of REE as well as to determine the main regularities of changes in concentrations and distribution of REE. The rapidly changing pH and Eh values (acid-alkaline and redox properties) were measured. These parameters were measured using portable analysers. The content of rare-earth elements was determined using the mass spectral method with inductively coupled plasma in the accredited laboratory of the State Enterprise Uzbekhydrogeology, chemical laboratory of the State Enterprise "Institute HYDROINGEO", the work related to core leaching was carried out in the autoclave, laboratory of chemistry and chemical technology of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan.

RESULTS AND DISCUSSION

Experience conditions: the experiments were first conducted in an open glass under normal room conditions using distilled water and crushed steam, to a fraction of 0.1 mm ratio 50g : 500ml, for 24 hours. The obtained solution was analyzed for complete chemical analysis, with determination of heavy metal ion concentrations. Then the experiments were continued in a glass, that the crushed sample and distilled water were heated up to 100°C (excluding pressure). Then the experiments continued in a special autoclave (in the rock system ↔ distilled water) with a gradual increase in temperature and pressure (100°C, 175°C, and 226°C), (the pressure increased from 1.4 and 8.0 atm. to 24.5 atm. respectively). As a result of the experiments, the following changes in element concentrations and mineralization were obtained:

1) *Increased element concentration (µg/l):*

1 to 2 times Al, Cr, Fe, Co, Br, Cd, Sn, La, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Ta, Tl, Th;

2 to 3 times Ti, Zn, Rb, In, Cs, Ce, Pr, Er, Pt;

3 to 5 times Be, Na, Mg, P, Sc, Se, Sr, Nb, Re, Au;

5 to 10 times B, K, Mn, Te, I, W;

10 to 100 or more times Li, Ca, Cu, Bi, U.

2) *Decrease in element concentration:*

from 1 to 2 times -Pb;

from 7 to 9 Times-As, Sb. Apparently, the reduction is due to the formation of hydroxyl complexes.

3) *Increase in mineralization (initial mineralization to distilled water 0.06 g/l):*

at 100°C, pressure 1.4 atm. -0.2 g/l;

at 150°C, 4.5 atm. pressure: 1.4 atm -0.2 g/l. -0.3 g/l.: at 100°C, pressure of 1.4 atm -0.2 g/l; at 150°C, pressure of 4.5 atm;

at 170°C, pressure 8 atm. -0.4 g/l;

at 225°C with a pressure of 24.5 atm. -0.5-0.6 g/l.

4) *Increase in silicon oxide (SiO₂), mg/l:*

at 100°C and a pressure of 1.4 atm. is -6;

at 150°C and a pressure of 4.5 atm. is -12;

at 170°C and 8 atm. pressure is -18;

at 225°C and 24.5 atm. pressure is -36.

5) *Variation (pH):*

At 100°C and a pressure of 1.4 bar it is -8.15 bar;

at 150°C and a pressure of 4.5 bar is -8.25;

at 170°C and 8 atm. pressure is -8.50;

at 225°C and a pressure of 24.5 bar is -8.7.

6) *Rigidity change, mg-eqv/l:*

at 100°C and a pressure of 1.4 bar is -1.0;

at 150°C and a pressure of 4.5 bar is -1.5 bar;

at 170°C and 8 atm. pressure is -1.7;

Research Article

at 225°C and a pressure of 24.5 bar is -2.7 bar

Analyses show that as temperature and pressure rise, mineralization and rigidity of water increase. The content of lithium and other elements also increases.

CONCLUSION

As a result of experimental studies in the rock-water system, regularities of changes in the concentration of rare and rare-earth elements under various thermobaric conditions have been established.

The increase in water mineralization (from 0.06 to 0.6 mg/l) and hardness (from 1 to 2.7 mg/l), i.e. the increase was about 10 times.

The most sensitive elements that pass into the aqueous solution when the temperature and pressure increase are detected (Na → K → Ca → Mg → Br → Rb → P → I → Br → Sr → Cu → Fe → Hg → U). Detailed study of chemical and macro-micro-component composition of groundwater during monitoring studies can be additional indicators that increase the reliability of earthquake prediction [Radomskaya *et al.*, 2016; Abdullabekov, 1992, Khasanova *et al.*, (no date)].

REFERENCES

Abdullabekov K (1992). Can an earthquake be prevented? Tashkent "Uzbekistan".

Khasanova GI, Khudaiberdieva NS, Narkhadzhaeva DD (No Date). Changes in the chemical composition of groundwater during earthquakes. *Respiration Scientific-practical conf. of the XXI century Intelligent Youth*. 212.

Patra S, Liu CQ, Wang FS, Li SL, Wang BL (2012). Behavior of major and minor elements in a temperate river estuary to the coastal sea. *International Journal of Environmental Science and Technology*. 9 647–654.

Radomskaya VI, Radomsky SM, Kulik EN, Rogulina LI, Shumilova LP, Pavlova LM (2016). (in Russian) Geochemical specificity of the rare-earth elements in the surface and underground waters of the field of Albyn gold ore deposit (Amur region). *Water resources*. T 43(6) 648–660.

Safronova NS, Grishantseva ES, Garanin VG, Fedorova LP (2017). Atomic emission determination of the rare-earth and rare-earth elements in the ecological and geological objects using the MAES analyser (in Russian). *Diagnostics of materials* T. 83(1) 57–63.

Shand P, Johannesson KH, Chudaev O, Chudaeva V, Edmunds Rare WM (2005). Earth contents of high pCO₂ groundwaters of Primorye, Russia: mineral stability and complexation controls. *In: Rare earth elements in groundwater flow system*. Ed.K. Johan-nesson. Netherlands: Springer, Ch. 1. 161–186.

Shannon WM and Wood SA (2005). The analysis of pictogram quantities of rare earth elements in natural waters. *Rare earth elements in groundwater flow system*. Ed. K. Johannesson. – Netherlands: Springer. Ch. 1. 1–37.

Sholkovitz ER (1995). The aquatic geochemistry of rare earth elements in rivers and estuaries. *Aquatic Geochemistry*. V. 1. P. 1–34.