CHEMICAL INTERACTIONS ASSOCIATED WITH BUREAL OF LIQUID TECHNOLOGICAL WASTE IN SAND BEDS.
RESULTS OF KINETIC-THERMODYNAMIC MODELING

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Acid liquid waste (LW) of Siberian Chemical Industrial Complex were pumped into Carbon water-bearing horizons, consisted of polymineral sands. The horizons are isolated by clay waterproof layers. Pumping of LW took place periodically, every three month. Chemical compositions of LW and a press back solution are shown in tab.1.

Table 1

Chemical composition of LW and a press-back solution

Component	units.	Press-back solution	LW
HNO_3	g/l	6.26	-
$NaNO_3$	g/l	-	140.39
Hac	g/l	-	20.54
Fe	g/l	-	0.34
Cr	g/l	-	0.37
Al	g/l	-	0.09
Ni	g/l	-	0.37
Mn	g/l	-	0.61
SiO_2	g/l	-	0.15
P	g/l	-	0.06
pH		*1.25*	*2.5*
Actinides			
		-	U, Pu, Np
Short-living isotopes			
		-	90Sr, 137Cs

Table 2

Mineral composition of sands

Mineral	Formula	Average content, %	Grain size, mm	F_s (exposure)
Quartz	SiO_2	53.77	0.1	0.01
Albite	$NaAlSi_3O_8$	4.13	0.1	0.01
Microcline	$KAlSi_3O_8$	10.14	0.1	0.01
Biotite	$K(Mg_{0.9}Fe_{2.1})AlSi_3O_{12}H_2$	0.45	0.1	0.01
Muskovite	$KAl_3Si_3O_{12}H_2$	2.85	0.1	0.01
Chlorite	$(Fe_{2.5}Mg_{2.5})Al(AlSi_3)O_{10}(OH)_8$	0.17	0.005	0.01
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	7.82	0.005	0.01
Montmorillonite	$Si_4(Al_{1.67}Mg_{0.33})O_{10}(OH)_2Ca_{0.117}K_{0.066}Na_{0.033}$	10.51	0.005	0.01
Kaolinite	$Al_2Si_2O_9H_4$	5.26	0.005	0.01
Syderite	$FeCO_3$	1.04	0.1	0.001
Rodochrosite	$MnCO_3$	0.06	0.1	0.001
Calcite	$CaCO_3$	0.77	0.1	0.001
Goetite	$FeOOH$	0.48	0.005	0.01
Rutile	TiO_2	0.33	0.1	0.01
Pyrolusite	MnO_2	0.02	0.01	0.01
Pyrite	FeS_2	0.06	0.1	0.01
Titanite	$CaTiSiO_5$	0.21	0.1	0.01
Clinozoisite	$Ca_2Al_3Si_3O_{13}H$	0.42	0.01	0.01

Because of radioactive decay of ^{90}Sr and ^{137}Cs, temperature in the sand bed increased up to 150°C [1].
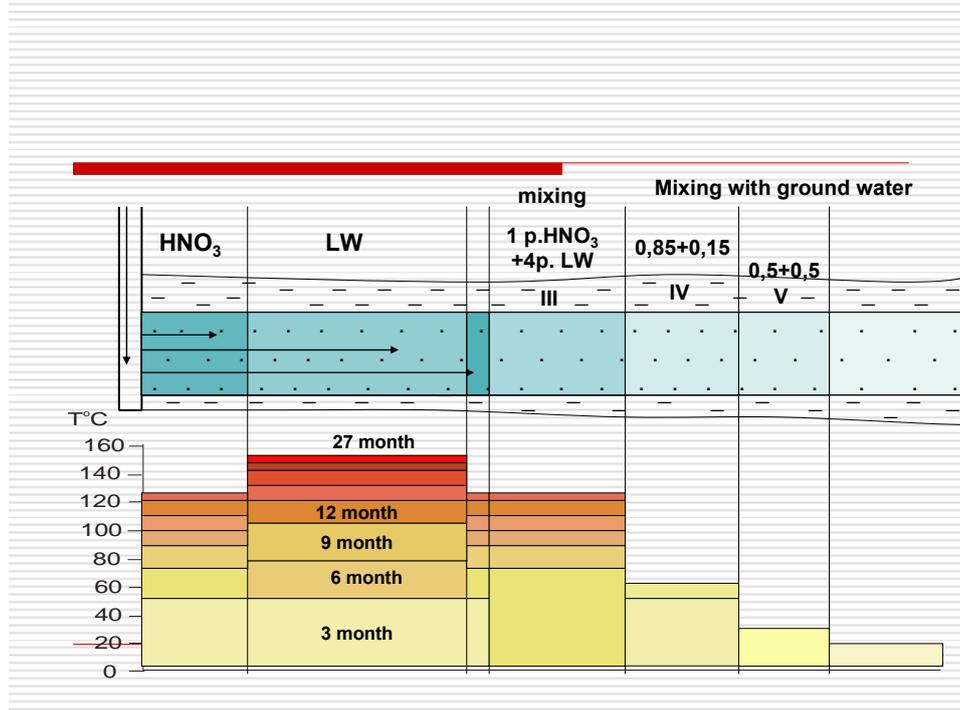
Fig.1. Scheme of pumping LW and temperature increase in the sand bed in time according to [1]

The goal of the study is a computer modeling of passing of chemical interactions of LW with rock-forming minerals to estimate expansion of contaminants and zonality of mineral alteration in sand beds. We applied a kinetic-thermodynamic model, which combines a consequent calculation of chemical equilibria with accounting rates of congruent mineral dissolution depending on temperature, pH, and a degree of mineral undersaturation. Rates of mineral dissolution were calculated using the following equation

$$r_i = \left[k_{0H+}(a_{H^+})^n + k_{0H2O} + k_{0OH-}(K_W a_{OH^-})^m \right] \times \exp[\frac{Ea}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)] \times \left\{1 - \exp\left[p(\frac{\Delta G}{RT})^q \right] \right\},$$

which is a combination of Laidler's equation for pH-dependence of dissolution rates [2], Arrhenius's equation for temperature dependence, and Lasaga's equation of transition state theory [3].

Bulk chemical compositions of systems at every time step t were calculated based on current solution composition and masses of dissolved minerals during time Δt. Change in mineral surface aria due to dissolution or precipitation was taken into account. More detailed description of the model is in [4].

We considered 18-component system *O-H-K-Mg-Ca-Al-C-Si-Ti-N-P-S-Cr-Na-Mn-Fe-Ni-Act*. In order to block a fast oxidation of nitrate by acetate, we introduce a new "component" acetate (Act). Calculations were performed for temperatures 25-150° C and pressure of 5 bar, 43 minerals, 64 aqueous species, and 5 gas species ($CO_2, H_2O, N_2, O_2, H_2$) were taken into account. Water/rock mass ratio was equal to 0.076, which corresponds to full filling of pore space of the sand. Kinetic constants of mineral dissolution were taken from [5-12].

In fig. 2 the calculated mineral transformations in LW zone in time are shown. One can note dissolution of carbonates, pyrite, micas, chlorite, and deposition of hematite, appatite, and albite. Solution pH increases very fast in contact with the rock

The calculated zonality of mineral transformation of sands after 2.5 years of pumping is shown in fig. 3. In the near-well zone, which was filled by press-back solution of HNO$_3$, dissolution of carbonates, pyrite, microcline, and chlorite took place. Kaolinite was formed.
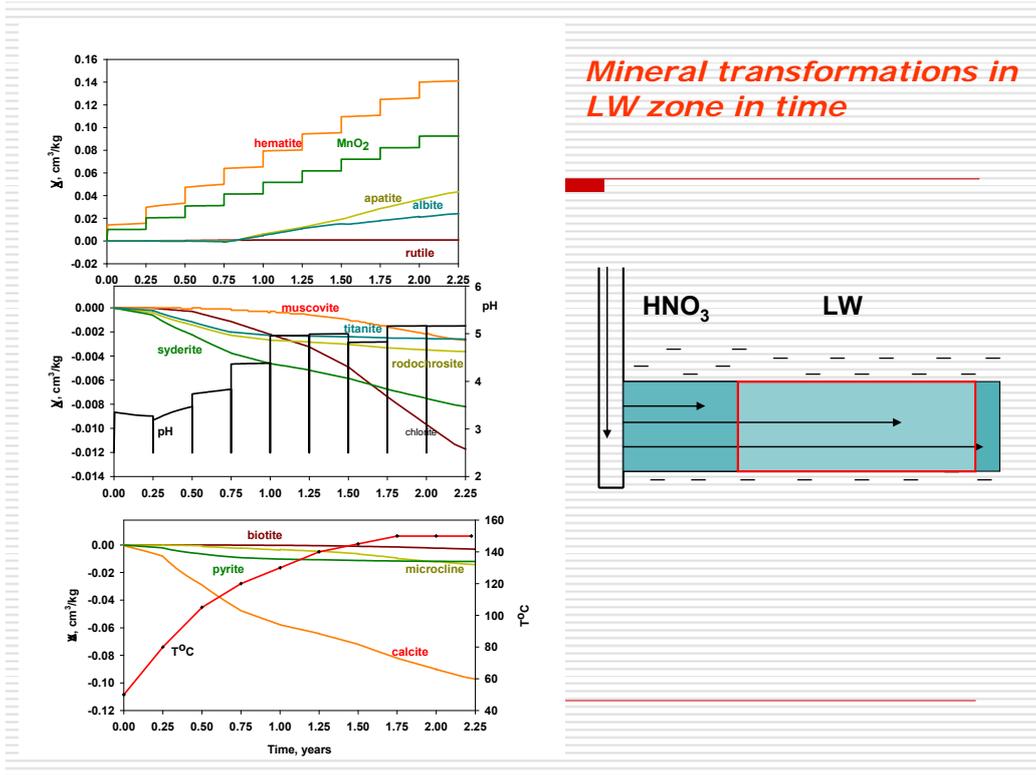
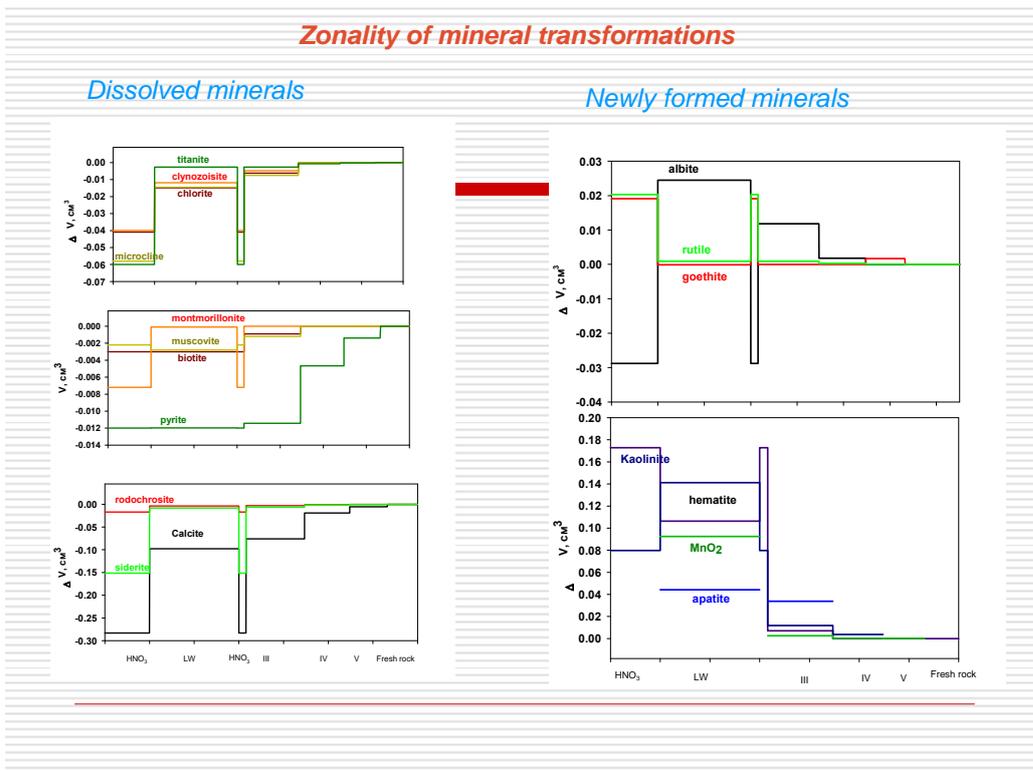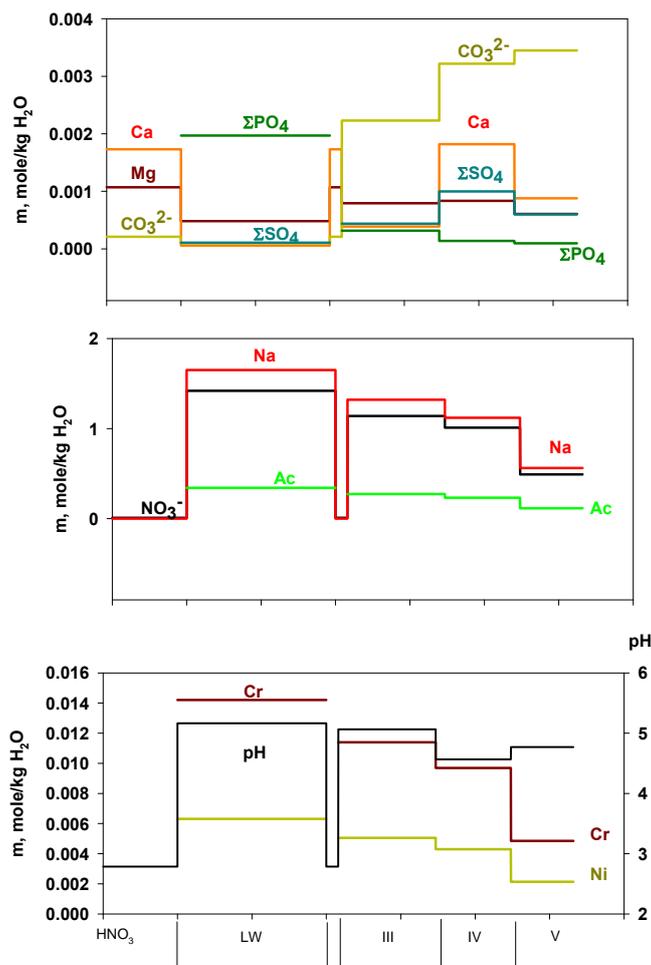**Fig.2.** Alteration of the sand in LW zone in time. Results of modeling

Fig.3. Zonality of alteration of sands. Results of calculations

The evolution of chemical composition of solution during it's moving is shown in fig. 4. The changes are due both to solution-rock chemical interactions and a gradual mixing with natural underground water.

Fig.4. Change of a chemical composition of LW during it's moving in sand bed

Based on results of model experiments of E. Zakharova [1], we can suppose that ^{137}Cs и ^{90}Sr were almost completely sorbed by clay minerals, and uranium, plutonium, and neptunium coprecipitated with ferric oxides.

Because of uncertainty of a number of kinetic parameters, especially degrees of exposure of mineral grains to aqueous solution, and thermodynamic data on montmorillonites, the results should be supposed as very preliminary.

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