

## STUDY OF PRECIPITATION PROCESSES OF HEAVY METALS ON NATURAL MINERALS

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The pollution of ground water reservoir results in necessity of use for the drinkable purposes. It is known, the underground water are described by the high contents of heavy metal compounds [1]. Now one of significant problems for water purification technology is the working of effective extraction sorbition methods of dissoluble impurities of high metals.

There is a large class of natural sorbents - minerals, which one because of poor study for wide technical application have not found [2-4]. By the way the high sorbition characteristics, cheapness and wide application in a nature do by theirs economically rational raw for a water purification technology [5,6].

For study of physical-chemical properties, including sorbition characteristics the natural calcium-magnesium minerals of carbonate and silicate rocks were selected for this papers. The chemical properties of these minerals allow to esteem these natural minerals as future sorbents-ion-exchangers.

### Experimental part

The minerals for studies were prepared definitely procedures, for what the cutting exposed to crushing. Then the selected fraction (1÷3 mm) was washed by distilled water from dust and was dried at 100°C (±5°C).

The series of independent analysis methods were applied to the determination of structural, mechanical and sorbition characteristics of studied minerals. The phase composition of rocks was identified by X-rays analysis, which one was carried out by DRON-3M (CuKα-radiation).

The determination of the microstructure characteristics of minerals surface were tested by scanning electronic microscope JSM-840 of the "Jeol" corporation (Japan) (magnification 200, 1000 and 5000 times), furnished by the x-ray microanalyser LINK, on which one determined an element composition of surface layer fragments.

For the rate of minerals mechanical strength the abrasability was determined. The sample of mass 10 g (fraction 1,0÷3,0 mm) was located in a bulb with 100 ml of distilled water and was shaken up (oscillation frequency - 50 hertz) during 10 minutes. Then minerals were dried at 100°C up to a constant weight, the fraction with the size of fragments less than 0,5 mm - abrasability was chosen.

For account of minerals water absorbition the prepared samples were weighed, were boiled in distilled water during one hour. After one day samples were taken out from water, were dried during 5 minutes for removal of a surface moisture and were weighed.

Solidphase transformation of rocks were studied by differential thermal analysis by derivatograph Q-1500D (heating rate was 10°C/min, recording sensitivity of a DTA-curve was 1/10) in an interval 20°C-1000°C. The preliminary analysis of results of thermogravimetric investigation and literary dates has shown rational to carry out treating minerals burning of samples in air atmosphere at 500, 600, 700 and 800 °C during 2 hours.

For study experiment about adsorbition properties study was carried out at room temperature. Exchange capacity of minerals (N) valued on sorbition of iron (II) and manganese (II) ions from sulfate solutions. 0,5 g of the prepared granulated minerals was added in 100 ml of sulfate solution and, is periodic mixing, held out of two day (time of equilibrium approach), then water sample was chosen. The contents of iron and manganese in water by photocolorimetry as coloured complexes was determined.

Magnitude of specific sorbition capacitance N (mg/g) was calculated by the equation:

$$N = \frac{C_1 - C_2}{V \cdot m} \quad (1)$$

$C_1$  – starting concentration of metal in solution, mg/l;  $C_2$  – concentration of metal in solution in equilibrium state, mg/l; V – solution volume, ml; m – sorbent mass, g.

## Discussion

In the table 1 some characteristics of studied minerals are reduced.

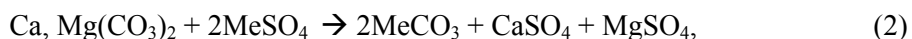
It is established, that the sorption process begins to take place effectively at following values water pH: for Fe - pH=6,5-7,5 on silicate rocks, pH=2,5-3,0 on carbonate rocks and for Mn - pH > 6 - on silicates, pH > 7 - on carbonates. Such dependence is explained to that than less value pH, the more substance surface layer passes to solution (there is a dissolution of mineral). The process of washout on silicate rocks opposes to ion exchange, and on carbonaceous - the moderate dissolution is accompanied by bonding of heavy metals ions on a surface.

**Table 1.**

Composition and physical-chemical characteristics of studied minerals

Mineral	Main phase (admixture)	Composition of minerals surface by heat treating	Absorption of water, %	Abradability, %
Quartz	SiO <sub>2</sub>	SiO <sub>2</sub>	1,37	0,06
Wollastonite	CaO·SiO <sub>2</sub> (SiO <sub>2</sub> )	CaSiO <sub>3</sub> , SiO <sub>2</sub>	1,39	0,58
Diopside	CaO·MgO·2SiO <sub>2</sub> (SiO <sub>2</sub> )	CaSiO <sub>3</sub> , MgSiO <sub>3</sub> , SiO <sub>2</sub>	1,60	0,24
Tremolite	2CaO·5MgO·8SiO <sub>2</sub> ·H <sub>2</sub> O (CaCO <sub>3</sub> )	CaSiO <sub>3</sub> , CaCO <sub>3</sub> , CaO	5,44	1,02
Dolomite	CaCO <sub>3</sub> ·MgCO <sub>3</sub> (Mg(OH) <sub>2</sub> )	CaCO <sub>3</sub> , MgO	2,79	0,83
Marble	CaCO <sub>3</sub>	CaCO <sub>3</sub> , CaO	1,07	0,30

The results of the held experiments about sorption on untreated samples demonstrate, that all minerals sorb impurities of iron and manganese, but different degree. The differences are explained by different composition and structure of minerals. On dates of microanalysis on a surface of the washed samples of all minerals there is an element Fe and Mn, and on dolomite and wollastonite the decrease of Ca part in surface layer is observed. These dates allow to suspect, that the sorption flows past partly under the schema of ion exchange:



Me: Fe, Mn.

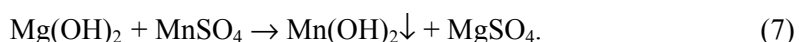
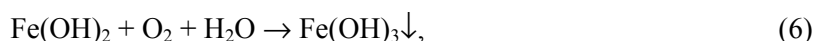
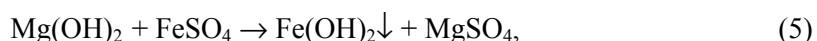
The precipitation of Fe and Mn hydroxides takes place on marble surface because of increase; pH: for iron - 3,0-3,5, for manganese - 8,5-9,1 [7].

The precipitation of metals on a quartz and diopside surface takes place because of coagulation on surface active centers, since the precipitating impurities are not keep on a surface at washing. The process flows past under the schema: the impurity is precipitated on an earlier precipitating impurity, i.e. the surface of quartz and diopside works, as a mechanical filter, accumulating precipitate.

The similar schema to quartz on tremolite is observed, but the presence in phase composition CaCO<sub>3</sub> determines the large extent of extraction from solution.

It is visible (table 2), that sorption properties depend on mineral pretreatment. The change of capacitance values is explained by chemical transformations occurring in surface layer during treating. The heat treating promotes increase of capacitance of carbonate rocks.

Heat treating of carbonates figure promotes loosening of samples with formation of patterns with the greater porosity and specific surface area (fig.1-2). According to dates of differential - thermal and x-ray analysis there are also chemical transformations during heat treating, which result in formation amorphous calcium carbonate and magnesia. Therefore, process of ion exchange is accompanied to precipitation of hydroxides of metals:

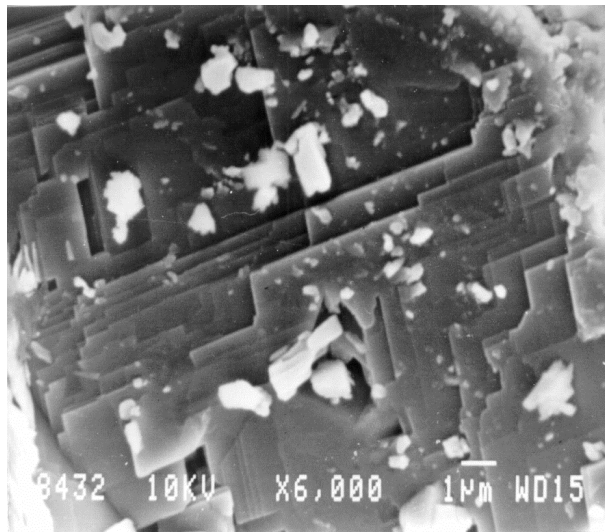
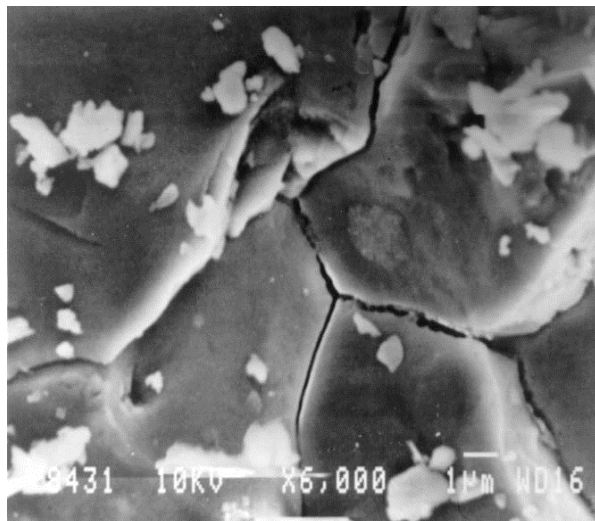


**Table 2.**

The volume of statical exchange capacitance sorbents on Fe и Mn

Mineral		Statical exchange capacitance, <i>mg/g</i> N <sub>Fe</sub> – capacitance of ions Fe; N <sub>Mn</sub> – capacitance of ions Mn.				
		Sours samples	Samples, treated on temperature, °C			
			500	600	700	800
Dolomite	N <sub>Fe</sub>	1,13	1,30	1,57	2,50	4,00
	N <sub>Mn</sub>	2,21	2,60	2,65	3,00	3,50
Diopside	N <sub>Fe</sub>	0,95	1,12	0,65	0,18	0,03
	N <sub>Mn</sub>	0,18	0,08	0,00	0,00	0,01
Wollastonite	N <sub>Fe</sub>	0,34	0,65	0,50	0,20	0,05
	N <sub>Mn</sub>	0,00	0,00	0,01	0,00	0,07
Marble	N <sub>Fe</sub>	1,00	1,30	1,54	2,56	2,72
	N <sub>Mn</sub>	1,20	1,25	1,27	1,80	2,03
Tremolite	N <sub>Fe</sub>	0,53	0,58	1,06	0,59	2,50
	N <sub>Mn</sub>	0,00	0,06	0,20	1,83	3,00
Quartz	N <sub>Fe</sub>	0,20	0,25	0,04	0,04	0,02
	N <sub>Mn</sub>	0,06	0,07	0,03	0,01	0,01

The decrease of extraction extent on silicate rocks is connected both to an decrease of value of specific surface area, and with heat release on a surface of silicon dioxide fragments (x-ray dates) after heat treating, which one opposes to ion exchange. The Tremolite is exception: it the surface contains basically an impurity of calcite after treating.

**Fig.1.** The surface of source dolomite**Fig.2.** The dolomite surface, pretreated at 800°C

### Resume / Summary

Thus, from six studied natural minerals the dolomite is the most perspective for clearing underground waters from divalent iron and manganese ions.

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