

## **USING OF MINERAL RESOURCES FOR WATER PURIFICATION**

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### **Abstract**

Pollution of surface waters results in necessity of underground waters using for drinking. Underground waters are characterized by the high quantity of heavy metals salts. This led to development of methods reducing the concentration of the metal salts in water. Wide spread occurrence, cheapness and high sorption properties of nature minerals allow to consider them as perspective sorbents for different impurities extraction, including dissoluble compounds of heavy metals. Reachable purification efficiency with mineral resources use for the moment satisfies sanitary indexes and standards presenting to portable water in Russia. In given material there are presented the results of research of artificial sorbent and certain minerals sorption characteristics, which are typical for West Siberia. For purification quality improvement from Fe and Mn ions there are suggested to use the method of boiling bed.

**Keywords:** *nature minerals, sorbent, boiling bed, purification of water.*

### **INTRODUCTION**

The great reserve of fresh water on earth available for use and its ability to renew permanently generate strong people's assurance about its inexhaustibility. In the process of population increasing and enhancement of human activity on nature transformation this assurance was destroyed. To the middle of the XX century this let people to strict accounting of all fresh waters on Earth and also to reconsideration of meaning of water in our life, like one of the most important resources. For the moment drinking water is social, political, medical, geographic, and also engineering and economic problem [1].

Pollution of the majority of surface waters let to impossibility of their use for drinking [1]. Transitions to use of underground waters generate the number of new problems. For an example, water-bearing horizon in Tomsk region is characterized by high concentration of nature toxic substances, and it is noted higher rates of anthropogenic pollution of underground waters by impurities of heavy metals, such as Fe and Mn. According to medical statistic occurrence of heavy metal impurities tend to reduce of immunity and increase of number of "stone" diseases [2-3].

At present, the one of the most effective methods of heavy metal extraction is sorption on non-organic materials [4]. Among the materials of nature origin, which are actively applied in great scale on modern water purifying stations, segregate silica sand, albitophir, and "burnt rock", which are used as mechanical filters for disperse impurities separation. Silica has low sorption characteristics against to heavy metals, and the others are

characterized by very difficult and rather unsteady content. That is lead to necessity of more effective sorbents search.

### AIM OF INVESTIGATION

There is a big class of nature sorbent-minerals, which does not have a wide industrial use because of their insufficient research. Meanwhile, these nature sorbent-minerals have high sorption characteristics, they chip and widespread. These features make them expedient primary in the water preparation technologies from the economic point of view [5]. In this work is considered the content investigation and data about structure and characteristics of nature minerals surface which are presented in Table 1.

**Table 1.** Characteristics of investigated minerals

Mineral (Deposit)	Main phase	Impurities (phase)	Apparent density, kg/m <sup>3</sup> (d=1÷3 mm)
Silica (Volgogradskoe Volgograd region)	SiO <sub>2</sub>	---	1350
Wollastonit (Sinyuhinskoe Altai)	CaSiO <sub>3</sub>	SiO <sub>2</sub>	1410
Diopside (Sludjanskoe Irkutsk region)	CaSiO <sub>3</sub> ·MgSiO <sub>3</sub>	SiO <sub>2</sub>	1370
Tremolite (Alguyskoe Kemerovo region)	2CaSiO <sub>3</sub> ·5MgSiO <sub>3</sub> · SiO <sub>2</sub> ·H <sub>2</sub> O	CaCO <sub>3</sub>	1260
Dolomite (Sovetskoe Altai)	CaCO <sub>3</sub> ·MgCO <sub>3</sub>	---	1460
Marble (Sayanogorsk)	CaCO <sub>3</sub>	CaCO <sub>3</sub> ·MgCO <sub>3</sub>	1340

### EXPERIMENTAL TECHNIQUE

There were chosen nature calcium and silicate minerals of Siberian deposits for investigation: silica, wollastonit, dolomite, diopside, tremolite and marble. The reasons for such choice are formation of sparingly soluble compositions of heavy metal cations at ion exchange with soluble carbonates and silicates, and low hydrolysis rate of formed compounds. Also, it is known that fresh water of nature sources which contact with carbonate and silicate rock, almost not containing impurities of heavy metals. Thereby, wide spread of chosen minerals in nature and their high chemical affinity to cations of heavy metals let make an assumption about possibility of their use as sorbent-ionexchangers for water purification, specifically from Fe and Mn impurities.

Norms and standards operating on the territory of Russian Federation, as it's known from experience, will become tougher and step-by-step be equal to West Europe standards. According to such tendency the use of nature minerals will become complicated with the fact that minerals of nature origin have non steady content. This fact have to make a conclusion

about the necessity of development of such sorbent content, the use of which in the processes of water purification wont let to a bigger water pollution.

The investigation of the content and surface structure of the given sorbent and also some characteristics of sorbent surface were made with help of roentgen phase analysis, differential thermal analysis, electronic microscopy and others.

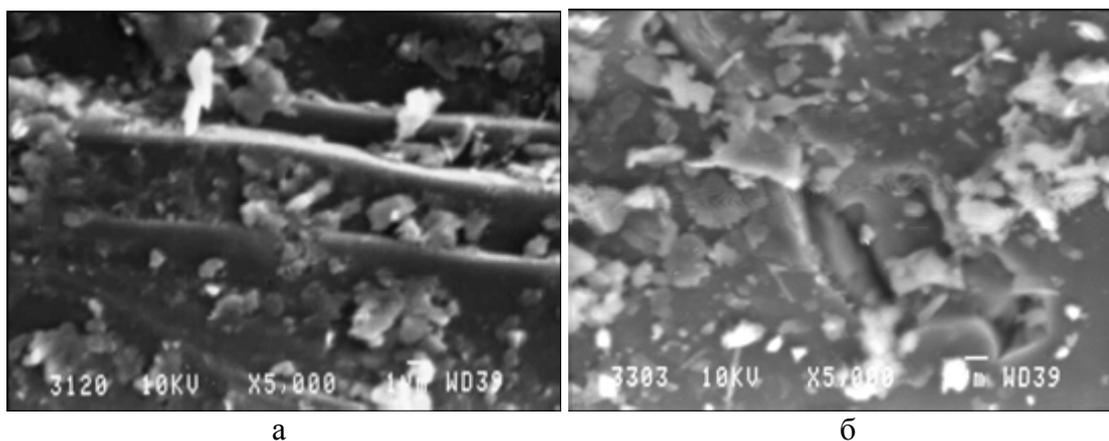
## EXPERIMENTAL RESULTS AND DISCUSSIONS

As a consequence of the investigation it is determined that by heating (10<sup>0</sup>/min) of pure silicate content minerals in the interval 20-1000<sup>0</sup>C for diopside and wollastonit it observed consistency of phase and chemical content, for silica it is typifying reversible phase conversion  $\beta$ -silica  $\leftrightarrow$   $\alpha$ - silica on 575<sup>0</sup>C. At the same time for all of three minerals it is typically imperfection of primary surface structure and ambiguous change of relative surface area (Table 2)

**Table 2.** Values of sorbents relative surface area

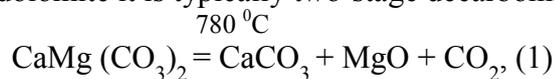
Sorbent		S <sub>relative</sub> , m <sup>2</sup> /kg*	
Virgin sample	Sample calcined at 600 <sup>0</sup> C	Sample calcined at 800 <sup>0</sup> C	
Silica	51	240	180
Wollastonit	72	85	99
Diopside	130	91	110
Tremolite	100	57	69
Dolomite	170	290	7500
Marble	110	150	790

\* - error of measurement of S<sub>relative</sub> is 10%.



**Figure 1.** Microfoto of surface ( $\times 5000$ ):  
a) initial silica; б) silica calcined at 500 C.

It is occurred the thermal decomposition of carbonate comprising minerals at their calcinations. For samples of dolomite it is typically two-stage decarbonization:



870<sup>0</sup>C



Calcite in a composition of marble dissociate at 880<sup>0</sup>C, in a composition of tremolite impurity of calcite (~ 25% mass.) dissociate totally at 830<sup>0</sup>C.

Calcinations of samples of marble and dolomite at 600-800<sup>0</sup>C goes with intensification of processes of destruction and recrystallization of surface layers, increasing of relative surface area (figure 1).

Calcinations of samples of tremolite in general lead to preservation of acicular surface structure which is typical for tremolite, but with increasing of treatment temperature it is observed the fragmentation of needles.

It has been found experimentally that calcination of investigated minerals at 500<sup>0</sup>C lead to re-allocation of impurity components between surface and near-surface layers. It is typically beneficating of surface layers with silicon for diopside containing  $\beta$ -SiO<sub>2</sub> impurity, for tremolite containing CaCO<sub>3</sub> - with calcium. It is observed depletion of content of micro-impurities (iron, manganese, phosphorus, potassium and others) in surface layers of samples for marble, as far as for tremolite.

**Table 3.** Sorption characteristics of minerals and their wearability while operating in “boiling bed”

Mineral	Amount of extraction, %		Abradability, %	
	on iron (II)	on manganese (II)	pH=6÷7	pH=2÷3
Marble	1,58	22,55	0,03	0,05
Tremolite	15,75	69,61	1,02	2,39
Dolomite	25,20	99,99	0,81	0,83

As a result of investigation of the processes it is determined that effectivity and lifetime of sorbent in the conditions of “boiling bed” depend on its sorption as far as on mechanical characteristics. The most important from them is abradability of sorbent determined as mass of sample which has been removed from the surface by particles collision, %mass.

The experimental data let to determine that in the content of sediments, which were formed after sorption in the “boiling bed” of manganese cations, is MnO<sub>2</sub>, after sorption of iron cations - FeOOH (Fe<sub>2</sub>O<sub>3</sub>). The results of roentgen phase analysis and infrared spectroscopy let to assume that the process of Fe<sup>2+</sup> and Mn<sup>2+</sup> cations extraction by the surface of heat-treated samples of dolomite, marble and tremolite goes with coprecipitation of Ca(Fe)SO<sub>4</sub> and Ca(Mn)SO<sub>4</sub> sulfates.

There was investigated the microstructure of crystallizable impurities of manganese, which were hold by the sorbent surface. It was determined that crystallizing of impurities in the “boiling bed”, instead of static conditions, goes almost on the whole surface of samples. These data let to conclude that surface characteristics of sorbents seemingly change in the process of sorbent operating. Thus, the value of relative surface area on the part of acicular crystal formation exceed the value of S<sub>relative</sub> of the same part of initial sorbent in 9-10 times. And this appropriately should enable the sorption process intensification.

Thereby, according to the investigations, milled nature minerals are efficient sorbents for water purification from the iron (II) and manganese (II) cations. Such nature minerals as

diopside, dolomite and marble have the best sorption characteristics in static conditions of sorption.

On the basis of the investigation results it was offered to develop a sorbent, which can be used for soluble heavy metals impurities extraction in the future. It is offered to prepare the sorbent by mixing of chemically pure reagents, granulate and thermally treat at 600<sup>0</sup>C (Table 4).

**Table 4.** Content of artificial sorbent for water purification

№ п/п	Component	Content, %mass
1.	CaCO <sub>3</sub>	35-45
2.	MgCO <sub>3</sub>	25-28
3.	Na <sub>2</sub> CO <sub>3</sub>	7-5
4.	NaCl	3-2
5.	MgO	the rest

There were prepared 3 compounds in the interval of the given components correlation for more detailed investigation of the processes of heavy metal impurities extraction, specifically, extraction of iron and manganese compounds from the water solution (Table 5). Each composition was mixed, granulated and thermally treated at 400<sup>0</sup>C

**Table 5.** Content of artificial sorbents

Component	Content of component, % mass		
	Compound I	Compound II	Compound III
CaCO <sub>3</sub>	35	40	45
MgCO <sub>3</sub>	25	26,5	28
Na <sub>2</sub> CO <sub>3</sub>	7	6	5
NaCl	3	2,5	2
MgO	30	25	20

The experiments on investigation of sorbent sorption characteristics in static conditions showed that on all of the 3 samples the processes of iron and manganese extraction goes effectively (Table 6). But methodic, which was adopted for capacity determination on nature minerals is not appropriate for investigated sorbent. Firstly, the time of balance in case of the process of Mn<sup>2+</sup> ions extraction is considerably exceed the time calculated for methodic. Secondly, it is impossible to determine the capacity on the sorbent because the extraction will continue till the whole sorbent is not used.

The process of Fe<sup>2+</sup> ion extraction goes faster than Mn<sup>2+</sup> ion extraction as it can be seen from the table data. It can be explained by such a fact that pH of Fe<sup>2+</sup> transferring to Fe<sup>3+</sup> is lower (3-3,5) than Mn<sup>2+</sup> ions sedimentation (8-8,5). But formed compositions of iron easily wash away from the sorbent surface and manganese impurities withholds by surface to a certain extent.

**Table 6.** Experimental data in static conditions

Sorbent	Index	Time of sorbent reacting with impurity, h						
		0	20	30	50	60	70	90
I	pH	2-3	2-3	2-3	2-3	6	7	7
	C <sub>Fe</sub>	15	6	0	-	-	-	-
II	pH	2-3	2-3	2-3	3-4	6	7	7
	C <sub>Fe</sub>	15	6	0	-	-	-	-
III	pH	2-3	2-3	2-3	4-5	6	7	7
	C <sub>Fe</sub>	15	6	0	-	-	-	-
I	pH	2-3	4-5	7	7	7	8-9	9
	C <sub>Mn</sub>	15	15	15	5	0	-	-
II	pH	2-3	5-6	7	7	7	8-9	9
	C <sub>Mn</sub>	15	15	15	5	0	-	-
III	pH	2-3	6-7	7	7	7-8	8-9	9
	C <sub>Mn</sub>	15	15	15	5	0	-	-

The process of Fe<sup>2+</sup> ion extraction goes faster than Mn<sup>2+</sup> ion extraction as it can be seen from the table data. It can be explained by such a fact that pH of Fe<sup>2+</sup> transferring to Fe<sup>3+</sup> is lower (3-3,5) than Mn<sup>2+</sup> ions sedimentation (8-8,5). But formed compositions of iron easily wash away from the sorbent surface and manganese impurities withholds by surface to a certain extent. Such results indicate that the process of manganese ions sedimentation goes with the process of adsorption of impurity by surface, as in case of marble, tremolite and dolomite treated at 700-800<sup>0</sup>C.

The control of pH indexes in sorbent-solution system showed that pH indexes in the volume 1-4 points higher than pH indexes fixed on the interface of liquid and solid phases. Such results indicate that the process of coprecipitation of metal ions goes in thin layer on the sorbent surface. [6]

## CONCLUSIONS

In the work there are presented the investigations of sorption characteristics of nature minerals relative to Fe and Mn ions. The results of the investigations showed expediency of thermal treat of minerals samples (size of particles is 1÷3 mm) in air atmosphere at 500, 600, 700 and 800<sup>0</sup>C during 2 hours. Investigation of sorption characteristics of samples which were calcined at higher temperatures is difficult because of chemical and mechanical instability of carbonate minerals and wastage of sorption effect on silicate minerals.

The use of minerals in “boiling bed” leads to intensification of water purification. As a result of continuous mineral particles collision the compounds, which were formed in the process of sorption and containing iron (II) and manganese (II) ions, are withdrawn from the particles surface in the form of suspension, and renewed surface actively participate in the process of impurities extraction from the water. Such mechanical activation of the surface can substitute the sorbent regeneration during the whole period of exploitation.

Thus, creation of the “boiling bed” leads to considerable enhancement of sorption effect, which is connected with mechanical activation and surface activity change because of crystallizable impurities morphology.

The sorption capacity of the minerals containing carbonate become higher for dolomite and marble in 1,5-3,0 times, for tremolite in 1,5-18,0 times in static conditions after thermal treat. In the conditions of “boiling bed” the highest speeds of water purification from

the iron (II) and manganese (II) cations were achieved for sorbents obtained by calcinations of dolomite and tremolite at 700<sup>0</sup>C.

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