

SORPTION MECHANISM AS MEANS FOR FORMING OF THE CHEMICAL COMPOSITION OF OCEANIC FERROMANGANESE ORE DEPOSITS

Novikov G.V. (IO RAS), Sirotkina I.V. (RCTU)

The geological lengthy growth process of ferromanganese ore deposits (FOD), i.e. nodules, crusts and crusted nodulous deposits ones of which being dated by hundreds of million years is worth assuming that the chemical composition of those might have been forming due to sorption nature of manganese oxyhydroxides and iron hydroxides. There are some accumulations of heavy, rare and dispersed elements occurring in FOD according to sorption mechanism being postulated by a great deal of foreign and domestic publications. However, it is well to point out that there have extremely been few experimental data confirmed the hypothesis involved so far.

For it is approving, it was rewarding to carry out a number of experiments dealt with sorption of heavy metals cations on the typical for oceanic medium samples of diagenetic nodules and sedimental crusts extracted out from the Clarion-Clipperton ore field and the Magellan Seamounts of the Pacific Ocean respectively. It is appropriate to note Mn-minerals, i.e. buserite-1 and asbolane-buserite, Fe-vernadite and Mn-feroxyhite association to be the overwhelming minerals of nodules and crusts accordingly (see table 1).

Table 1.

FOD types	Main ore minerals	Chemical composition, %							
		Mn	Fe	Cu	Co	Ni	Zn	Sr	Cd
ferromanganese nodules (FMN)	Buserite-1, asbolane-buserite	28,21	4,31	1,04	0,22	1,12	0,15	0,02	$6,4 \cdot 10^{-4}$
Cobaltmanganese crusts (CMC)	Fe-vernadite, Mn-feroxyhite	20,15	12,52	0,11	0,47	0,33	0,06	0,08	$3,8 \cdot 10^{-4}$
Crusted nodulous deposits (CND)	Fe-vernadite, Mn-feroxyhite, buserite-1	19,32	12,43	0,12	0,45	0,37	0,04	0,06	$4,1 \cdot 10^{-4}$

As a result of interaction between FOD and the NaCl solution there was received Na-form followed by various cation derivatives contained the cations of heavy metals such as – Cu^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} and Sr^{2+} property. While forming the cation mentioned above it would be observing the full extracting of the Na^+ , K^+ , Ca^{2+} cations and the partial extracting of the Mg^{2+} and Mn^{2+} ones. High capacity values of FOD make it possible to consider the metals cations sorption proceeding throughout the crystal chemical volume of ore Mn-minerals. Should be noted that for the FOD types studied one can see the certain dependence of sorption capacity degree from nature of metal ions adsorbed. Capacity increases from alkaline to heavy metals, as it is shown from the following series (mg-eqw/g):

FMN $\text{Na} < \text{Cd} < \text{Sr} < \text{Co} < \text{Ni} < \text{Zn} < \text{Cu};$
 0,95 1,15 1,46 1,91 2,06 2,07 2,21

CMC $\text{Na} < \text{Cd} < \text{Sr} < \text{Ni} < \text{Zn} < \text{Co} < \text{Cu};$
 0,82 1,31 1,63 2,06 2,32 2,41 2,47

CND $\text{Na} < \text{Cd} < \text{Sr} < \text{Ni} < \text{Co} < \text{Zn} < \text{Cu}.$
 0,78 1,31 1,72 2,09 2,49 2,52 2,68

Thus, in spite of the different genetic character all the samples of the ferromanganese ore deposits have shown sorption properties. There is some deviation in their sorption degrees that might be caused by mineral contents, crystallochemical and physic-chemical properties of minerals.

To study metal cation affinity degree in accordance with the ferromanganese ore deposits there have been carried on some investigations applied to Cu^{2+} cations sorption from 1n CuCl_2 solution for Ni, Cd and Sr forms of FOD. While performing experiments the various extraction degrees of the Ni^{2+} , Cd^{2+} and Sr^{2+} from the appropriate forms could be marked, i.e. from 24,96 up to 95,77% (see table 2).

Table 2.

Cation form	FOD type	Sorption capacity for Cu^{2+} , mg-eqw/g	Extraction degree of Ni^{2+} , Cd^{2+} and Sr^{2+} cations respectively, %
Ni-form	FMN	1,43	24,96
	CMC	2,56	66,72
	CND	2,36	69,59
Cd-form	FMN	2,19	73,11
	CMC	2,99	95,77
	CND	3,03	94,99
Sr-form	FMN	2,46	47,35
	CMC	2,69	64,94
	CND	2,32	56,95

Sorption capacity degree at the experiments carried out for Cu^{2+} cations was to be 1,43 – 2,69 mg-eqw/g. It was founded that the tendency of increasing of Cu^{2+} extraction degree from solution while increasing cations extraction degree of heavy metals out from the appropriate forms maintains that can be seen on fig.1 on an example of exchange reaction between Cu^{2+} and Ni^{2+} where upper curve is a Cu^{2+} extraction cations degree from solution and lower curve is a Ni^{2+} extraction degree from solid phase.

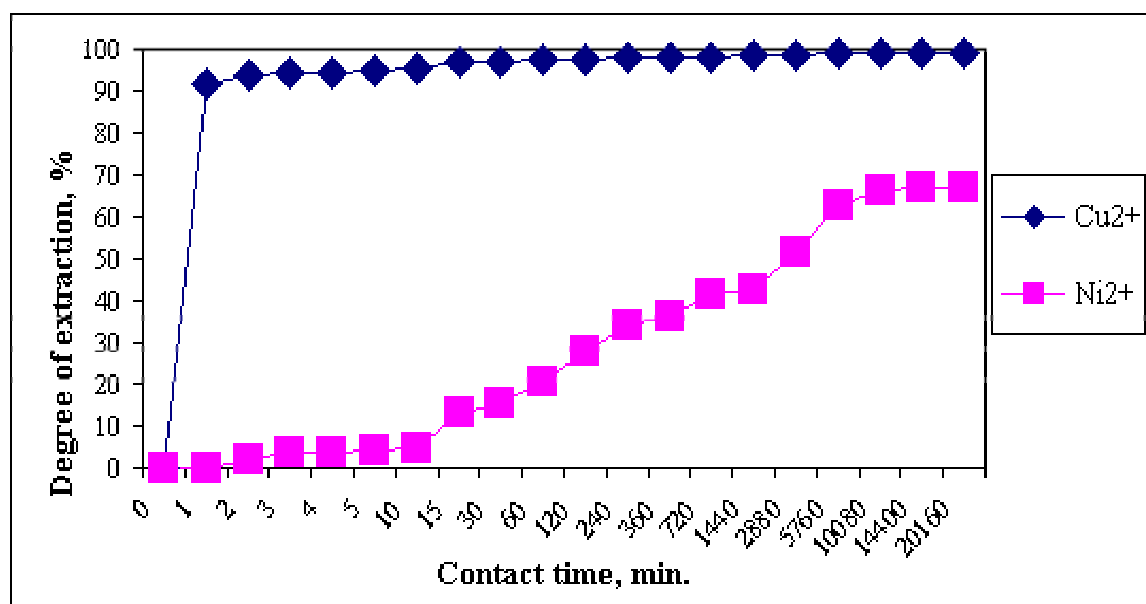


Fig. 1. Cu^{2+} cations sorption on the Ni-form of CMC

Heavy metals cations sorption out from multicomponent solutions in static as well as in dynamic conditions, have been studied concentrations of those solutions are as follows.

Solution I, g/l (Cu²⁺- 0,1; Ni²⁺- 0,15; Zn²⁺- 0,15; Cd²⁺- 0,13);
 Solution II, g/l (Cu²⁺- 0,2; Ni²⁺- 0,004; Sr²⁺- 0,1145);
 Solution III, mg/l (Cu²⁺- 0,4; Ni²⁺- 4,1; Cd²⁺- 130).

The heavy metals cations sorption process in both conditions does proceed on the following stages; on the one hand there occurs sorption of some groups during the first 30 minutes while on the other hand there can be marked the selective type of sorption (see fig. 2, 3).

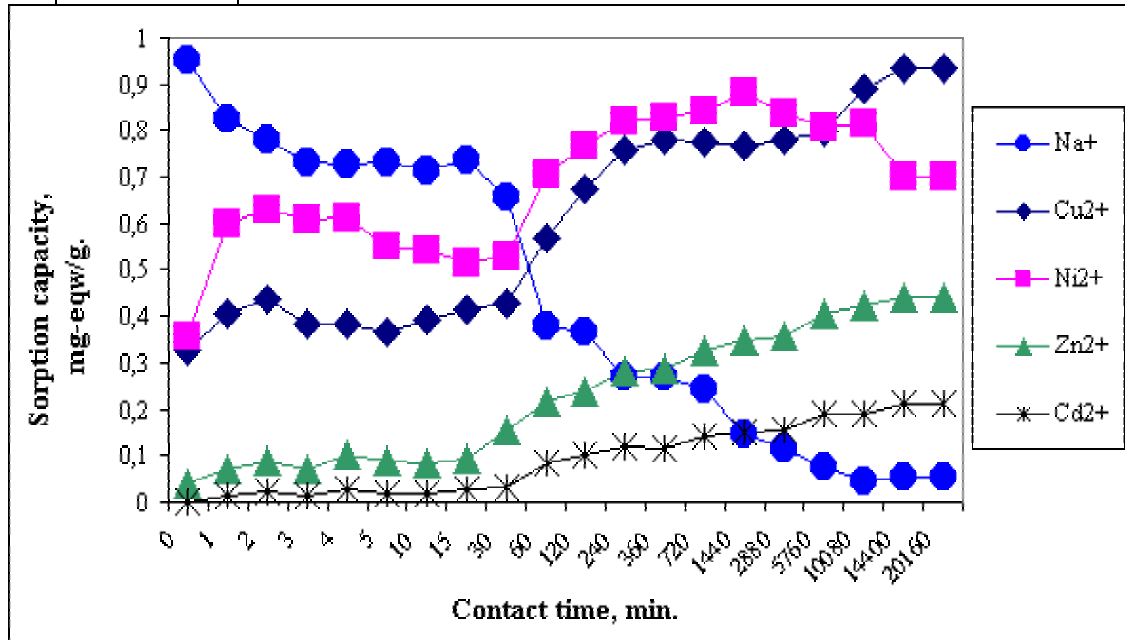


Fig. 2. Metals cations sorption out from multicomponent solution I on the Na-form of FMN in static conditions

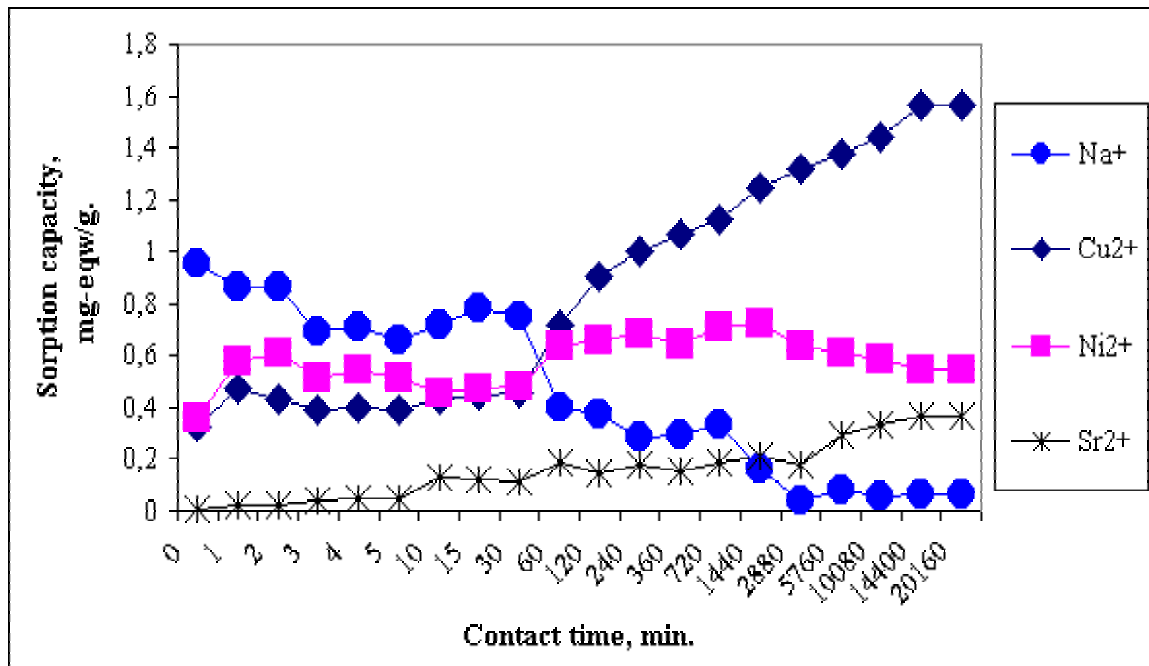


Fig. 3. Metals cations sorption out from multicomponent solution II on the Na- form of FMN in static conditions

Due to the results of experimental data obtained, the metals cations affinity applied to FOD can be represented by the following way:

Solution I $\text{Na} < \text{Sr} < \text{Cd} < \text{Ni} < \text{Zn} < \text{Cu}$;

Solution II $\text{Na} < \text{Sr} < \text{Ni} < \text{Cu}$;

Solution III $\text{Na} < \text{Cd} < \text{Cu} < \text{Ni}$.

The data, given for heavy metals cations sorption on the dynamic conditions are in accordance with the results of experiments carried on the static conditions. The sum total of the data obtained has confirmed the high selectivity of ferromanganese deposits in relation with heavy metals cations.

Thus, the given experimental investigations have testified without any doubt to the fact that ferromanganese deposits of different mineral contents and genesis are an effective natural sorbent for heavy metals, sorption processes being these of the main ones to differentiate chemical elements on the barrier of the separating the oceanic water – nodules/crusts phases.

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