Characteristics of metal cations sorption from aqueous solutions on ferrimanganese nodules of the Gulf of Finland compared to ferrimanganese sediment of various deposits

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Abstract
This article provides thermodynamic characteristics of non-ferrous metals cations ion-exchange sorption on ferrimanganese nodules (FMN). Lyotropic series of cation sorption on ferrimanganese nodules from the Gulf of Finland was compared with cation sorption on ferrimanganese nodules from other deposits.

Keywords: Ion-exchange sorption, ferrimanganese nodules, sorbed cations radii, ion-exchange Gibbs energy, lyotropic series of cation sorption.

Metallurgical enterprises wastewater treatment from non-ferrous and heavy metals cations is an important ecological problem. Metals inflow into natural waters occurs in various ways: from natural leaching of rocks via industrial processing stage to natural water bodies and watercourses discharge. The most large-scale and significant way is via industrial enterprises waste waters: as a result of technological processes of metallurgical and mining and processing industry, electrochemical industry (electrolysis, plating, etching, deep etching, etc.), as well as various kinds of solid wastes leachates. Waste and natural water composition most commonly includes copper, nickel, chromium, cadmium and cobalt. Some waste waters have high lead content [1-3]. Industrial enterprises in large cities most commonly have local water treatment plants, which do not ensure complete treatment. Partially treated water is then diluted and discharged. Metals inflow to hydrosphere may have different degree, seasonal nature and depend on various factors. E. g. enterprise and municipal storm collectors are discharged directly to water bodies, very occasionally via intermediate settling basins or containment ponds and oil removers [4]. Depending on waste waters inorganic impurities concentration and composition, the following methods of treatment are employed: reversed osmosis, biological purification, thermal, reagent, ion-exchange, electrochemical (electrodialysis), ultrafiltration and other methods. In these latter days waste water sorption treatment and extraction of valuable components from waste and process solutions become more and more widespread due to high efficiency of this method. Artificial and natural mineral and organic sorbents are used for waste water treatment [5].

One of the main sorbent characteristic is its exchange capacity. Full sorbent capacity is the amount of ions (in gram-equivalents) in water that 1 m$^3$ of sorbent can adsorb before total saturation. Sorbent working capacity is the amount of ions (in gram-equivalents) in water that 1 m$^3$ of sorbent can adsorb in the filter when processing water before adsorbed ions start slipping into filtrate. Moreover, when determining sorbent capacity in static and dynamic conditions, static (equilibrium) and dynamic exchange capacity of ion exchangers are recognized [6]. The capacity depends on both cations affinity to ionite and on geometric factors: cation "landing field", ionite specific area and ion-exchange groups’ concentration. Cations displacement ability, which causes sorption selectivity, is determined by chemical affinity and quantitatively characterized Gibbs energy of ion-exchange.

The usage of different ion-exchange resins permits achieving high degree of treatment, but the cost of this method is high due to high heavy spending on synthetic sorbents. High sorptive properties of ferriferrous manganese ore and metals affinity permit using it as the material for obtaining sorbents with optimal capacitive and economic characteristics. Ferriferrous manganese ore is perspective and renewable type of manganese ore raw material. At the present time ferriferrous manganese ore underwater deposits of Baltic Sea and Russian part of Clarion-Clipperton zone of the Pacific Ocean are involved into processing [7].

In ferriferrous manganese ore manganese minerals are represented by the following: birnessite, braunite, vernadite, hydrohausmannite. Among iron minerals akatene, hematite, maghemite, magnetite, ferroxygite and lepidocrocite are mentioned. Ferriferrous manganese ore composition also includes: pyroxene, apatites, mica, quartz, feldspar, olivine and other minerals [8, 9].

Formation process (ferriferrous manganese ore: nodules, crust and crusted concentration fillings) is carried out at the expense of sorption nature of manganese and ferrous minerals being part of ferriferrous manganese ore, which speaks for their high capacitive characteristics [10;11].
To obtain comparative capacitive characteristics the studies of non-ferrous metals sorption on FMN of the Gulf of Finland were conducted and the specific area of FMN of the Gulf of Finland was determined. The obtained results were compared with literature. In Table 1 ferriferrous manganese ore chemical compositions were quoted over the main components.

Table 1.

<table>
<thead>
<tr>
<th>Types of ferriferrous manganese ore</th>
<th>Main minerals in the composition</th>
<th>Chemical composition %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FMN of the Gulf of Finland</td>
<td>Vernadite, buserite</td>
<td>Mn 30.84  Fe 14.02  Co 0.034  Ni 0.067  Zn 0.0134  Sr 0.057</td>
</tr>
<tr>
<td>FMN of Clarion-Clipperton zone</td>
<td>Buserite, asbolan-buserite</td>
<td>Fe 28.20  Mn 4.31  Co 1.04  Ni 0.22  Zn 1.12  Sr 0.15</td>
</tr>
<tr>
<td>Cobalt-manganese crusts CMC</td>
<td>Fe-vernadite, ferroxygite</td>
<td>Fe 20.15  Mn 12.52  Cd 0.11  Co 0.47  Ni 0.33  Zn 0.06  Sr 0.08</td>
</tr>
<tr>
<td>Crust-nodule deposits</td>
<td>Fe-vernadite, ferroxygite, buserite</td>
<td>Fe 19.32  Mn 12.43  Cd 0.12  Co 0.45  Ni 0.37  Zn 0.04  Sr 0.06</td>
</tr>
</tbody>
</table>

The study of specific area of FMN of the Gulf of Finland was conducted by two methods. First, when using methylene blue sorption from the solution, FMN specific area was 43.81 m²/g [12]. Second, when using N₂ desorption at 770 K (NOVA 1000e, Quantachrome instrument), FMN specific area was 36.8 m²/g. The obtained results vary, which is explained by FMN natural samples mineral composition heterogeneity. Ferriferrous manganese ore natural samples have various exchangeable cations, therefore before starting the experiment the samples were converted into sodium form, because sodium ions are most easily displaced by other cations.

The experiment

Ion-exchange was studied on FMN of the Gulf of Finland from metal salts standard test solution: CuSO₄ with concentration of 0.01-0.8 mol·kg⁻¹, Co(NO₃)₂ 0.05-1.26 mol·kg⁻¹, Pb(NO₃)₂ 0.05-0.50 mol·kg⁻¹, Hg(NO₃)₂ 0.006-0.025 mol·kg⁻¹ at the temperature of 298 K. Cations sorption value Γ (mol·kg⁻¹) was studied in static conditions at liquid phase volume to solid phase mass ratio V/n=10 dm³·kg⁻¹ and FMN sample mass 5 g by concentration difference between the initial C₀ and equilibrium Cₚ solution by using the following formula:

\[ \Gamma = (C_0 - C_p) \cdot V \cdot \rho / m, \]

where \( \rho \) - solution density in kg·dm⁻³.

Metal salts solutions were mixed with FMN samples until equilibrium condition at the constant temperature of 298 K. Equilibrium time, meeting solution concentration constancy, is 5-6 hrs. During the experiments phase contact time was set for not less than 10 hrs.

On Fig. 1 experimental data on studying isotherms of metals and sodium cations ion-exchange sorption on FMN of the Gulf of Finland are quoted.

As Fig. 1 shows, by limiting sorption value \( \Gamma \) mol·kg⁻¹ cations are arranged in the following series of sorption abilities:

\[ \text{Na}^+ < \text{Sr}^{2+} < \text{Co}^{2+} < \text{Hg}^{2+} < \text{Pb}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} \]

When comparing this series of sorption abilities with the series, which was arranged in paper [13], by increasing the capacity (Table 2), slight disagreement is observed.

Table 2

<table>
<thead>
<tr>
<th>FMN mgEq/g</th>
<th>Na  0.95  &lt;Sr  1.15  &lt;Co  1.91  &lt;Ni  2.06  &lt;Zn  2.07  &lt;Cu  2.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt-manganese crusts mgEq/g</td>
<td>Na  0.82  &lt;Sr  1.31  &lt;Ni  1.63  &lt;Zn  2.06  &lt;Co  2.41  &lt;Cu  2.47</td>
</tr>
<tr>
<td>Crust-nodule deposits mgEq/g</td>
<td>Na  0.78  &lt;Sr  1.31  &lt;Ni  1.72  &lt;Zn  2.49  &lt;Co  2.52  &lt;Cu  2.68</td>
</tr>
</tbody>
</table>

However cations displacement ability which causes sorption selectivity is determined by chemical affinity and quantitatively characterized Gibbs energy of ion-exchange. And the capacity depends on both cations affinity to ionite and on geometric factors: cation "landing field", sorbent specific area and ion-exchange groups’ concentration. In Table 3 there’re shown cation radii acc. to Bokiy, radii of aquated ions, calculated acc. to Stokes equation, and radii of sorbed cations, calculated from experimental data.
As Table 3 shows, the obtained values of radii of cations, sorbed on FMN surface, are intermediate between cations crystallographic radii acc. to Bokiy and aquated cations radii acc. to Stokes; therefore they can be studied as mean effective radii of partially dehydrated ions.

Dehydration degree can be estimated acc. to the following formula:

$$\alpha = \frac{r_{aq} - r_{sorb}}{r_{aq} - r_{cr}}$$

The value of dehydration degree varies from 0 at \( r_{sorb} = r_{aq} \) to 1 at \( r_{sorb} = r_{cr} \). It's logical to explain dehydration degree by the increase of electrostatic interaction strength of cations in the Stern-Helmholtz layer with negatively charged active centers at the FMN surface. The latter forms polianite at hydrozolized surface as a result of ≡Mn – OH group dissociation. According to data from [14], pH value of isoelectric condition of manganese ores comprising FMN is 1.5-3. Consequently, in the conditions of conducted tests FMN surface was negatively charged. The strength of Coulombic interactions in double electrical layer has to correlate with the increase of cations ionic potential in sorbed state and the decrease of ion-exchange sorption Gibbs energy. This is confirmed by cations displacement ability series, which was made up on the basis the obtained results, as shown in table 4. The major criterion of cations sorption capacity when making lyotropic series was the decrease of ion-exchange sorption Gibbs energy, therefore they differ from similar series that were made by capacity increase.

### Table 3

<table>
<thead>
<tr>
<th>Cation</th>
<th>( r_{cr} ) acc. to Bokii, pm</th>
<th>( r_{aq} ) acc. to Stokes, pm</th>
<th>( r_{sorb} ) (sorbed cations radii), pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>80</td>
<td>324</td>
<td>127</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>74</td>
<td>340</td>
<td>136</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>112</td>
<td>289</td>
<td>160</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>125</td>
<td>262</td>
<td>163</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>78</td>
<td>340</td>
<td>186</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>120</td>
<td>309</td>
<td>219</td>
</tr>
</tbody>
</table>

Along cations sorption capacity series or lyotropic series, according to terminology proposed by academician K. K. Gedroite, with the decrease of ion-exchange sorption Gibbs energy, cations displacement ability increases. At a first approximation the correlation with the increase of cations ionic potential and dehydration degree is observed.

In literature there are data on non-ferrous and heavy metals cations sorption from multicomponent solutions having Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Sr\(^{2+}\) cations in various ratios. The series look the following:

1. Na < Sr < Cd < Ni < Zn < Cu
2. Na < Sr < Ni < Cu
3. Na < Cd < Cu < Ni

The authors showed the execution of group sorption process at zero time and selective sorption after passing the first stage [13]. The shown series match the lyotropic series which was made up based on Gibbs energy decrease for FMN.

### Conclusion

Data analysis on non-ferrous and heavy metals cations sorption on ferriferrous manganese ore with variable mineral composition and genesis indicate that ferriferrous manganese ore is an effective natural sorbent with developed surface, high capacity and sorption selectivity, which is related to the affinity of cations and sorbent.

### Resume

1. Isotherms of non-ferrous and heavy metals sorption on FMN of the Gulf of Finland were obtained. The values of capacity for these cations for FMN of the Gulf of Finland were found. Lyotropic series was made up.
2. The major criterion of cations sorption capacity when making lyotropic series was the decrease of ion-exchange sorption Gibbs energy, therefore they differ from similar series that were made by capacity increase.
3. The cumulative data shows prospectivity of ferriferrous manganese ore as the material for making sorbents with high capacity and sorption selectivity.

### References


