

## **SYNTHESIS OF Mn, Fe, Ni, Co OXIDE-HYDROXIDE PHASES ON MANGANESE OXIDES: ON A MODEL FOR TRANSITION METAL ORE FORMATION IN RECENT BASINS**

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### **ABSTRACT**

Experimental data are presented on the sorption dynamics of the dissolved forms of Ni, Co, Mn, Fe from seawater by manganese oxides ( $Mn_3O_4$ ). The study of the initial sorbent and final products by scanning microscopy, X-ray photoelectron spectroscopy, X-ray analysis has revealed that these components accumulate in the form of a newly-formed sorbed layer. The process is of a multistage nature. The initial stages are characterized by the development of ion-exchange and hydrolytic reactions, and the later ones by the interface autocatalytic oxidation of the components accumulated. The composition of the newly-formed compounds is controlled by the kinetics of the two basic stages, viz.: a) sorption proper; b) interface catalytic oxidation.

The highest oxidized forms of the metals accumulated are observed at the relatively lower sorption rates, when the blocking effect of the first stage does not inhibit the development of the second stage. For instance, during the final experimental runs, at the relatively lower sorption rates, the external parts of the newly-formed layer show fairly large amounts of oxidized forms (%):  $Mn^{4+} = 60$ ,  $Ni^{3+} = 30$ ,  $Co^{3+} = 30$ . Iron, as evidenced by MÖSSBAUER spectroscopy, is present within the sorbed layer as  $FeOOH \cdot H_2O$ .

The specific feature of the sorption of metals by hydrous manganese oxides is a partial interaction of Ni and Co with structural  $Mn^{2+}$  and  $Mn^{3+}$ . As a result of this interaction, Mn is displaced from the substrate into the solution in an amount equivalent to 16.14% of the sorbed Co or 17.96% of the sorbed Ni.

The results presented together with a survey of the existing situation in the experimental field relating to the problem under study support the validity of an earlier model describing formation of the transition metal ore accumulations in recent basins. According to this model, the process is a multistage chemisorption interaction in which the main role is the interface autocatalytic oxidation of the sorbed metals.

### **INTRODUCTION**

There are two principal and widely occurring types of ores in the World Ocean, viz. ferromanganese nodules and metalliferous sediments. The ferromanganese nodules of certain oceanic regions are presently regarded as high-grade ores of Mn, Ni, Co, Cu and other metals.

Notwithstanding the sharply differing views as to the genesis of Fe—Mn nodules, the data available enable the majority of investigators to believe that their formation is associated with the process of the extraction of metals from the component-bearing solutions [ANDRUSCHENKO and SKORNYAKOVA, 1967; BEZRUKOV *et al.*, 1976; VARENTSOV, 1972, 1976; VARENTSOV *et al.*, 1978; VERNADSKY, 1954; PRONINA and VARENTSOV, 1973; PRONINA *et al.*, 1973; SKORNYAKOVA, ANDRUSCHENKO, 1970; STRAKHOV, 1976; BURNS, 1976; BURNS, BURNS, 1975, 1977; GLASBY, 1974; GOLDBERG, 1954, 1961; GOLDBERG, ARRHENIUS, 1958; LALOU *et al.*, 1973, 1976; MICHARD,

1969; MURRAY, 1974, 1975 *a, b*; RENARD *et al.*, 1976; VAN DER WEIJDEN, 1976 *a, b*; VARENTSOV and PRONINA, 1973, 1976].

For the large deposits of Fe—Mn nodules, such a metal-bearing solution is seawater, usually bottom water, where the trace amounts of transition metals are present in a solute form [ROBERTSON, 1968, 1970; SCHUTZ and TUREKIAN, 1965; BREWER, SPENCER, 1974; MURRAY and BREWER, 1977; SLOWEY and HOOD, 1971; SPENCER and BREWER, 1969; SPENCER *et al.*, 1970].

J. MURRAY [1887] and F. CLARKE [1924], (both cited by VERNADSKY, 1954), and V. I. VERNADSKY [1954] paid attention to the fact that concentration of Mn, Fe and other transition metals in the World Ocean does not show any increase, despite their uninterrupted supply from the endogenous and exogenous sources. Considering these facts, V. M. GOLDSCHMIDT [1937] assumed that sorption is the main process responsible for the removal of these metals from seawater. Later, at the beginning of extensive geochemical studies of the Ocean, GOLDSCHMIDT's ideas were advanced by GOLDBERG [1954] and KRAUSKOPF [1956, 1957]. Emphasizing a high sorption activity of hydrous ferric oxides, GOLDBERG and ARRHENIUS [1958] suggested that the sorption of heavy metals from seawater by this sorbent is an autocatalytic process. However, no evidence for the nature of this process has been suggested by the authors.

The processes of the extraction of microamounts of transition metals from seawater by hydrous ferric and manganese oxides is characterized by extremely low rates of reactions [LALOU *et al.*, 1973, 1976; KU, 1977]. Investigations into the individual components of the nodule formation in the Oceans (nodules seawater; associated sediments; specificity of the metal sources, etc.) permit only a rough assessment of the processes and indirect judgement on its mechanism to be made.

Investigations under way during the last two decades by researchers in the various branches of chemistry and geochemistry into the sorption of transition metals from the solutions of complex electrolytes by the hydrous oxides of Fe, Mn and other metals have significantly advanced the ideas of the intrinsic aspects of these processes. The principal results of these investigations are summarized as follows.

### 1. Sorbed metal concentration and composition in solution

Investigations into the processes of heavy metal sorption by hydrous ferric oxides in the ocean basins demonstrate that they occur in a wide range of concentrations the lower boundary being defined by the solubility products of the final products.

It is not uncommon, however, that determination of the lower concentration limit does not give reliable results because of the complex-formation phenomena.

Of particular importance to these investigations is the problem of sorption specificity in the region of relatively low ( $10^{-1}$  to  $10^{-2}$   $\mu\text{g/l}$ ) and relatively high (over  $10^3$   $\mu\text{g/l}$ ) concentrations. It is shown in a number of works [CHUYKO *et al.*, 1974; KURBATOV *et al.*, 1951; TEWARI *et al.*, 1972; VARENTSOV and PRONINA, 1973] that in the region of relatively low concentrations, the ion-exchange nature of the sorption of heavy metals by hydrous ferric and manganese oxides is not so important as at higher concentrations.

At relatively low concentrations (under  $10^{-4}$   $\mu\text{M}$ ), the sorption of Co and Zn is not described by the LANGMUIR equation, whereas K and Na follow this equation over a wide concentration range.

## 2. Composition and concentration of the background electrolyte components

Natural environments where the sorption of heavy metals by hydrous manganese and ferric oxides takes place represent complex solutions of electrolytes with a considerable content of alkaline, alkaline-earth cations and also chloride, sulphate and hydrocarbonate anions. Seawater is a vivid example of such a natural electrolyte. BEEVERS [1966], IDZIKOWSKI [1971, 1972 *a, b*, 1973], NOVIKOV [1972] NOVIKOV and GONCHAROVA [1972, 1977 *a, b*] have indicated that the sorption of some heavy metals (Zn(II), Pb(II), Co(II), Cd(II), Cu(II), Ag(II) and others) by hydrous ferric oxides shows a significant increase with the content of the background electrolyte components. In the case of Na, K, Mg sulphate solutions sorption proceeds at a rate several times (by a factor of about 3) as great as compared with nitrate and chloride solutions of equivalent ionic strength. This effect is interpreted by NOVIKOV [1972] as being due to the ionic hydration of "neutral" salts, being present in solution in significant concentrations, and to the associated increase in the effective concentration of the sorbed component, increase in its polymerization (a salting-out effect), which results in higher sorption at the same pH's. In acidic medium the increase in the background salt concentration leads to lower sorption.

In the case of the transition metal sorption by manganese oxid-hydroxide no significant effect of the background salt components in the pH interval 6—8 has been observed [TEWARI *et al.*, 1972]. The competitive influence of Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, manifesting itself in a substantially lower sorption as exemplified by Co, has been observed for the concentrations of these elements corresponding to their amounts in seawater at a Co content of  $1 \cdot 10^{-7}$  M in a wide range of pH's: 2—10 [MURRAY, 1975 *b*].

## 3. Special features of phase composition, structural and surface characteristics of hydrous ferric and manganese oxides

Investigations by SIPALO-ŽULJEVIĆ and WOLF [1973] have revealed that La(III) and Co(II) are equally sorbed both by a newly-formed oxide hydroxide in the solution of these components and by a substantially crystallized variety. The only differences are sorption rates. The authors not only point to a surface nature of the process but also stress an important role of the sorbed cation penetration into the sorbent structure.

Results obtained by ANDERSON *et al.* [1973] suggest that sharp differences in the crystallinity of the two MnO<sub>2</sub> modifications (birnessite,  $\delta$ -MnO<sub>2</sub>, and pyrolusite,  $\beta$ -MnO<sub>2</sub>) used as sorbents affect only the time of reaching silver equilibrium concentration and not the sorption capacity.

## 4. Special features of heavy metal sorption by hydrous ferric and manganese oxides in various pH, Eh intervals and dissolved O<sub>2</sub> concentrations

Considering the role of such parameters as pH, Eh and dissolved O<sub>2</sub> concentration, in studying the processes of heavy metal sorption by hydrous manganese and ferric oxides, it is significant that conditions in the interface zone differ most significantly from those taking place in a solution mass.

GABANO *et al.* [1965] suggested a model of heavy metal sorption on MnO<sub>2</sub>. The authors believe that the surface charge of MnO<sub>2</sub> is governed by the pH of the solution. In the pH interval characteristic of natural waters (pH 5—11) the hydrated manganese dioxide is negatively charged. These ideas are shared by POSSELT *et al.*

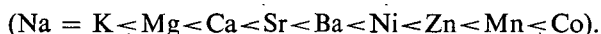
[1968]. However, POSSELT *et al.* admit the possibility of the contact oxidation  $\text{Mn(II)} \rightarrow \text{Mn(III)}$  to account for a high sorptive capacity of  $\text{Mn(II)}$  as compared with some other ions:  $\text{Ag(I)}$ ,  $\text{Ba(II)}$ ,  $\text{Ca(II)}$ ,  $\text{Mg(II)}$ ,  $\text{Nd(III)}$ ,  $\text{Sr(II)}$ .

It has been found by some investigators [BALZANOVA *et al.*, 1977; CHUYKO *et al.*, 1974; DUSHINA, ALESKOVSKY, 1976; SIPALO-ŽULJEVIĆ; WOLF, 1973; DUVAL, KURBATOV, 1952; TEWARI *et al.*, 1972; ANDERSON *et al.*, 1973] that the sorption of heavy metals, particularly those subjected to hydrolysis, increases markedly with increasing pH up to a certain value. At relatively low pH's the phenomena of sorption are regarded as ion exchange between  $\text{H}^+$  from the sorbent OH-group and sorbed ion. At alkaline pH's the authors consider hydrolysis to be the main sorption factor. However, as a result of studying Ag sorption by various  $\text{MnO}_2$  modifications, ANDERSON *et al.* [1973] emphasize particularly that these phenomena cannot be explained in terms of "surface sorption". The sorption of Ag involves exchange with  $\text{H}^+$ , foreign ions of the sorbent structure and structural  $\text{Mn(II)}$  proper.

5. *Relationships between molecular sorption and ion exchange; interaction with the structural ions of oxide hydroxides; chemical reactions within the interface zone in the process of heavy metal sorption by hydrous oxides.*

It was noted in the preceding Section that the observed behaviour of heavy metal sorption by hydrous oxides can only partially be described by ion-exchange or molecular sorption models.

MURRAY and BREWER [1977] evaluated the relationship between specific (chemical) adsorption, electrochemical adsorption (Coulombic type) and solvation adsorption. Experimental determination of the separate influence of each of these adsorption types presents great problems. Evaluation of the relative contribution of each sorption type is largely performed by calculations using a number of theoretical models. The simplest case is that of ion adsorption in which the number of the ions adsorbed cannot exceed a value equivalent to a surface charge. It is shown experimentally [MURRAY, 1975 *a, b*] that alkaline metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ) interact with a hydrous surface oxide only electrostatically. Transition metal ions are sorbed by manganese dioxide more intensively as compared with alkaline and alkaline-earth ions



The ions whose sorption intensity increases markedly with pH are only partly and with differently desorbed with decreasing pH. Such a prominent sorption selectivity on hydrous metal oxides is attributed to their specific (chemical) sorption.

STUMM *et al.* [1976] reviewed the existing models describing the interaction of metals with the surface of oxide-hydroxides. Considering the dependence of the sorption of monomeric metal forms by oxide-hydroxides on pH, these authors did not think it necessary to resort to hydrolysis phenomena. They believed that such a dependence may be interpreted in terms of variation in the basicity of the surface  $\text{MeO}^-$ -groups and chemical affinity of these groups for the sorbed metal ion.

It is shown by NOVIKOV [1972] and NOVIKOV, GONCHAROVA [1972; 1977*a, b*] that the existing numerous ideas of the chemical nature of sorption and coprecipitation of transition and other metal microamounts by hydrous oxide-hydroxides can not provide adequate explanation of the experimentally observed results. These authors propose a model of "coordination coprecipitation and sorption", relying on the formation of various bonds in the system "hydrous oxide-sorbed component".

JAMES *et al.* [1975] considered the various models of metal ion sorption at the hydrous oxide/solution interface and concluded that none of the models reported

is completely satisfactory. The authors note that the observed increase in metal sorption from 0 to 100% in the narrow pH interval can be explained by the formation of hydroxo-complexes. But it is not uncommon that the sorption of metals takes place from solutions with such pH's that only a small proportion of the total amount of metal aquo-compounds is available in the form of soluble hydroxo-complexes. Clarification of the true mechanism of the process is most difficult because of experimental problems and assumptions in the writing down of the reaction schemes. The authors place particular emphasis on the fact that their model of the formation of aquo-hydroxo-complexes [JAMES and HEALY, 1972 *a, b, c*; JAMES *et al.*, 1975] does not make it possible to reveal unequivocally the significance of the participating mechanisms (ion exchange, surface hydrolysis, hydrolysis and specific adsorption of hydrolysis products).

EGOROV [1975] introduced the idea of peptizing, oxy-acidic, hydroxo-complex sorption mechanisms. Ion exchange does not exclude chemisorption interaction which forms the basis of the author's model. Ju. V. EGOROV stressed that "primary sorption" implies the effect of completing the solid phase by the sorbed ion and its structural incorporation into the sorbent.

MCKENZIE [1970, 1972] has significantly broadened the ideas of heavy metal sorption by hydrous manganese oxides. This author shows that in the sorption of Co, Cu, Ni by hydrous manganese oxides from chloride solutions at pH 5 the process runs in two stages: 1) rapid sorption of metal ions ( $\text{Cu} > \text{Co} > \text{Ni}$ ) accompanied by the displacement of the exchange ions  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{Mn}^{2+}$  from the surface; 2) Co(II), upon sorption, interacts with structural Mn(III): In this case redox reactions take place:  $\text{Co(II)} \rightarrow \text{Co(III)}$ ;  $\text{Mn(III)} \rightarrow \text{Mn(II)}$ , accompanied by the release of Mn into solution. The possibility of these reactions is attributed to the differences in the magnitudes of the Crystal Field Stabilization Energy for these elements.

LOGANATHAN and BURAU [1973] have further advanced the ideas of MCKENZIE. Their works have been refined by MURRAY [1975 *a, b*] showing that no more than 10% of the sorbed Co can be associated with Mn released into the solution from a manganese dioxide as the sorbent. MCKENZIE's ideas [1970, 1972] have been advocated by RENARD and MICHARD [1973] for Pacific manganese nodules.

GIOVANOLI *et al.* [1969, 1976 *a, b*] [GIOVANOLI and STÄHLI, 1970; GIOVANOLI, 1976] have studied a number of transition metal sorption problems by using hydrous oxides to study natural processes. It has been established that the ions of divalent transition metals can enter into the structure of the 10 Å-modification of  $\text{MnO}_2$ , i.e. buserite (todorokite), promoting the enhancement of crystalline lattice stability of this compound.

A number of geochemical works [GOLDBERG, 1961; HEM, 1963, 1977; MORGAN and STUMM, 1965; STUMM and MORGAN, 1970; MURRAY *et al.*, 1968; MICHARD, 1969; MCKENZIE, 1975; BURNS, 1965, 1976; BURNS and BURNS *et al.*, 1975] have shown that the sorption of Mn, Co and other transition metals by hydrous oxides occurs over a wide concentration range typical of seawater and involves the interface oxidation of the sorbed metals. No experimentally supported model describing the interaction mechanism has been presented by these workers.

It can be concluded from the brief survey of the above studies that most authors note inadequacy of existing models for the explanation of the observed phenomena of sorption interaction between microamounts of metals and hydrous oxides. The reason for such an inadequacy lies in a fragmentation of the studies conducted, inconsistency of the assumptions adopted, problems encountered in the identification of

the system component, starting with a form of the sorbed component, through hydrated metal monomers and polymers of low and high molecular weight compounds up to the colloidal-crystalline hydrous oxides and oxides.

Our studies [PRONINA and VARENTSOV, 1973; PRONINA, VARENTSOV *et al.*, 1973; VARENTSOV, DIKOV *et al.*, 1978; VARENTSOV and PRONINA, 1973, 1976] on the sorption of Mn, Fe, Ni, Co and synthesis of the hydroxide phases of these metals on hydrous ferric and manganese oxides have permitted some of the special features of the process mechanism to be evaluated. High selectivity of the sorption of these metals from seawater has been established. The initial stages of the process are of an ion exchange nature, largely for Ni, and to a lesser extent for Co, Mn, Fe. At the later stages one can observe the development of nonexchangeable forms of these metals represented by hydroxide phases. The study of the compounds formed on the hydrous ferric oxides ( $\gamma$ -FeOOH) using X-ray diffraction analysis and X-ray photoelectron spectroscopy has made it possible to identify the composition of the newly-formed compounds and to evaluate the accumulated metal valencies. It has been found that in this complex multistage interaction the major role is played by a chemisorption, involving autocatalytic oxidation, of these transition metals. The composition of the resulting phases is to a large extent controlled by the quantitative relationships of the accumulated components in solution and kinetic parameters.

It is the purpose of the present paper, based on experimental studies, to show the principal parameters of the sorption of Mn, Fe, Ni and Co from seawater solution by hydrous manganese oxides, to identify the composition of the newlyformed compounds, to assess the relative role of the factors controlling these processes and possibilities of the extrapolation of the results obtained to develop a model of ore formation in recent basins.

## MATERIALS AND METHODS

We used in our experiments as the oxide phase a synthetically obtained hausmannite —  $Mn_3O_4$  as the oxide phase. This sorbent was synthesized in laboratory conditions using the method of MCKENZIE [1971]. The sorbent obtained was identified by X-ray powder diffraction and electron diffraction methods supported the existence of a homogeneous hausmannite phase (see Fig. 7). The role of hausmannite in

### *Dynamics of the sorption synthesis of Fe, Mn, Ni, Co compounds under*

No. of runs	Initial concentrations in solution ( $\mu\text{g/l}$ )				Final concentrations in solution ( $\mu\text{g/l}$ )				Amount of element sorbed from solution ( $\mu\text{g/l}$ )			
	Ni	Co	Fe	Mn	Ni	Co	Fe	Mn	Ni	Co	Fe	Mn
1	1640	1580	1320	700	910	938	864	552	730	642	546	148
2	1500	1540	1000	600	995	927	492	396	505	613	508	104
3	1420	1600	1360	400	980	857	805	342	440	743	555	58
4	1280	1360	960	500	811	894	665	624	469	466	295	-124
5	1060	1320	1540	620	885	935	7	703	175	385	1533	-83
6	1140	1260	1000	630	847	934	575	790	293	326	425	-160
7	1000	1000	940	565	600	850	0	1015	400	150	940	-450

\* Volume of the solution = 5 l, time of interaction = 72 hours, weighed amount of the sorbent =  

$$\% \text{ Me}_{s. ph.} = \frac{\text{Me}}{0.3 + \text{Ni} + \text{Co} + \text{Fe}} 100\%.$$
 Me = amount of the sorbed metal (Ni, Co, Fe, in g).

the geochemistry of the processes within recent basins is shown in previous works [GIOVANOLI, 1976; GIOVANOLI *et al.*, 1976; STUMM, GIOVANOLI, 1976 *b*]. Similar experiments were performed with synthetic birnessite. Their results were very similar to those reported below. This paper presents information on the runs in which hausmannite was used as the sorbent.

A synthetic seawater was prepared as described by BRUEVICH [1946]. A deionized water was used for this purpose. The seawater had the following characteristics:  $\text{Cl}^- = 19\%$ ,  $\text{S} = 35\%$ ,  $\text{pH} 8.10-8.15$ .

The metals under study, in order to avoid hydrolytic effects, were introduced with the addition of a complex-forming agent, i.e. citric acid, in a 10-fold excess with respect to the molar amounts of the metals. Iron was introduced in the form of ferric ammonium alum, analytical pure grade; manganese — as  $\text{MnSO}_4$ , analytical pure grade; cobalt — as  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ , analytical pure of "nickel-free" grade; nickel — as  $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ , analytical pure "cobalt-free" grade. The initial concentrations of the metals are presented in Table 1.

The sorption experiment was conducted in 5-litre polyethylene bottles containing 0.3 g of sorbent. The bottles were agitated for 72 hours, and the sorbent was separated centrifugally from the solution. To account for the sorption by the bottle walls and the possible hydrolytic precipitation, blank experiments were carried out. In the final solution the content of Ni and Co was determined by a polarographic method according to the hydrogen catalytic wave in the presence of dimethylglyoxime [VINOGRADOVA *et al.*, 1968], (the sensitivity of the method in parallel determinations of the content of Ni and Co being not lower than  $0.3 \mu\text{g/l}$ , determination reproducibility  $\pm 2.35\%$  — (coefficient of variation), — at the content of the elements equal to  $2.9 \mu\text{g/l}$ ); the content of Fe — by photometric reaction with 1.10-phenanthroline [MARCHENKO, 1971], (the molar extinction coefficient equal to  $11.8 \cdot 10^3$ , the sensitivity of the method being  $20 \mu\text{g/l}$ ); the content of Mn — photometrically by a permanganate method [MARCHENKO, 1971], (the molar extinction coefficient being equal to  $2.4 \cdot 10^3$ ). The centrifugally separated sorbent was added to a new portion of the starting solution. Accumulation of the sufficient amounts of metals in the experiment required seven successive interaction cycles to be made, which made it possible to accumulate reasonable amounts of Ni, Co, Mn, Fe (Table 1). The precipitate obtained was washed from the residual impurities of seawater components using deionized water.

TABLE 1

*static conditions from seawater solution on a manganese hydroxide substrate\**

Total amount of element sorbed from 5 l solution			Element sorption rate ( $\mu\text{g/h}$ )				Total element sorption rate ( $\mu\text{g/h}$ )			% of sorption		
Ni	Co	Fe	Mn	Ni	Co	Fe	Ni	Co	Fe	Mn		
3,650	3,210	2,280	740	50.69	44.58	31.67	126.94	44.21	40.06	34.54	21.14	
6,175	6,275	4,820	1260	35.07	42.57	35.28	112.92	33.33	39.63	50.80	17.33	
8,375	9,990	7,595	1550	37.50	51.59	48.54	127.63	30.98	43.12	40.84	14.50	
10,720	12,320	9,070	930	32.57	32.36	20.49	85.42	36.61	34.18	30.07	-24.80	
11,595	14,245	16,735	515	12.15	26.74	106.46	145.35	16.50	28.22	99.00	-11.16	
13,060	15,875	18,860	-285	20.35	22.64	29.51	62.50	25.73	25.91	42.50	-25.39	
15,060	16,625	23,560	-2535	27.78	10.41	65.28	103.47	40.00	15.50	100.00	-79.65	

0.300 g. Content of the sorbed metals in the solid phase (%): Ni=17.67, Co=19.50, Fe=27.64.

The composition of the starting sorbent and final product was studied by X-ray analysis (Guinier camera, Fe — anticathode), and in a powder camera (57.3 mm, Cr — anticathode, V — filter, G. V. SOKOLOVA, Geological Institute, USSR Acad. Sci.).

The structure of the starting and final products was studied by using a scanning electron microscope (Hitachi, Akashi, Model MS, M-2, Japan) and a high-resolution electron microscope (JEOL, Japan; N. D. SEREBRENNIKOVA, Geological Institute, USSR Acad. Sci.).

The composition and valency state of the metals accumulated were studied by X-ray photoelectron spectroscopy (spectrometer model VIEE—15). Photoelectrons were excited with the aid of Mg  $K\alpha$ -radiation whose photon energy was equal to 1253.6 eV. The binding energy for the narrow lines was determined to an accuracy of  $\pm 0.1$  eV, the resolution being as high as 1.2 eV. The spectrometer was evacuated to  $3 \cdot 10^{-7}$  Torr. Spectra calibration was made by the carbon  $1_{s}$  line for which the value of the electron binding energy ( $E_{\text{bind}}$ ) was taken to be 285.0 eV. Intact samples were applied to a finely corrugated aluminium cylinder in such a way that its surface was covered completely.

The valency state of Fe in the product was determined by MÖSSBAUER spectroscopy. The spectra were taken by using an electrodynamic MÖSSBAUER spectrometer. Used as the  $\gamma$ -quanta source was  $\text{Co}^{57}$  in a Pd-lattice. Recording was performed by using a NaJ(Tl)-crystal scintillation counter. The procedure took place at room and liquid-nitrogen temperatures.

## EXPERIMENTAL RESULTS

Data analysis for the sorption dynamics of the components under study (Table 1) reveals the following features:

(a) The amount of the sorbed Co decreases progressively to the final experimental stages, from 40.06 to 15.50%.

(b) For Ni this trend toward the decrease of the sorbed amount is less pronounced.

(c) For Fe, a gradual and substantial increase in the sorbed amount is observed at the final stages (after stage 5) and reaches 100%.

(d) For Mn, there is a gradual decrease of the sorbed amount (from 21.14 to 14.50%) up to stage 3. Later on (stages 4—7) the desorption of Mn takes place. The amount of Mn released into the solution at the final stages markedly exceeds its amount in the starting solution.

As result of the 7-time changes of the starting solutions the following relative amounts of metals (%) on the sorbent were accumulated: Ni=17.67, Co=19.50, Fe=27.64. From the data on sorption dynamics (Table 1) there is observed, as a whole, no accumulation of manganese under the experimental conditions. The amounts of manganese released into the solution at the final stages exceed the content of this metal in the starting solution by 2535  $\mu\text{g}$ . These data suggest that the amount of Mn equivalent to 16.14% of the sorbed Co or 17.96% of the sorbed Ni was removed from the substrate structure ( $\text{Mn}_3\text{O}_4$ ) in the interaction with the Ni and Co in solution.

Study of the sorbent starting phase, made with the use of a scanning electron microscope (*Fig. 1*) demonstrates that synthetic hausmannite is represented by microglobular aggregates on whose surface there are well developed extremely small needle-like crystallites. It can be seen in the micrographs taken under a transmission



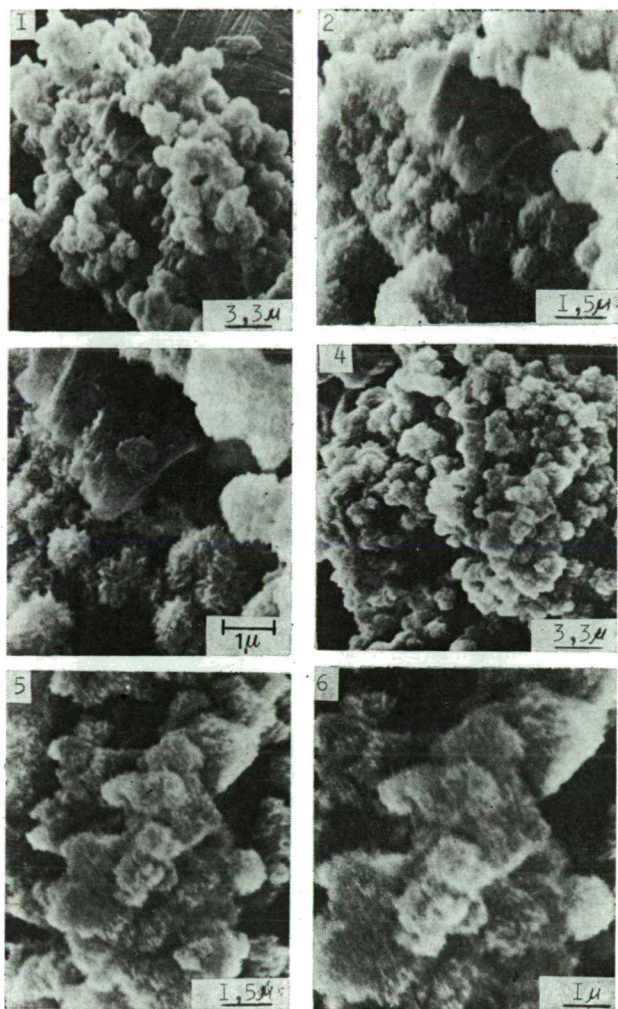


Fig. 1. Micrographs of the initial manganese oxide ( $Mn_3O_4$ ), taken under a scanning electron microscope. Photos 1—3 and 4—6 are a successive series taken at increasing magnification. The photos show clearly a microglobular structure of the aggregates with the development of fine needle-like crystallites on the surface

electron microscope with a higher resolution ( $4 \cdot 10^3 \times$  magnification) that the surfaces of the globular aggregates contain the developed, extremely small bipyramidal-octahedral crystals typical of hausmannite (Fig. 3, photo 1).

In the micrographs of the newly-formed product (Fig. 2), a significant enlargement of the aggregates, disappearance of the pronounced globularity and development of microlaminated stepped forms of epitaxial outgrowths of the newly-formed phases (Fig. 3, photos 2, 3) can clearly be seen.

X-ray photoelectron spectroscopy enables one to study the parameters of the atom valency state and their crystallochemical behaviour. The potentialities of this method have been widely discussed recently [MINACHEV *et al.*, 1975; NEMOSHKALENKO,

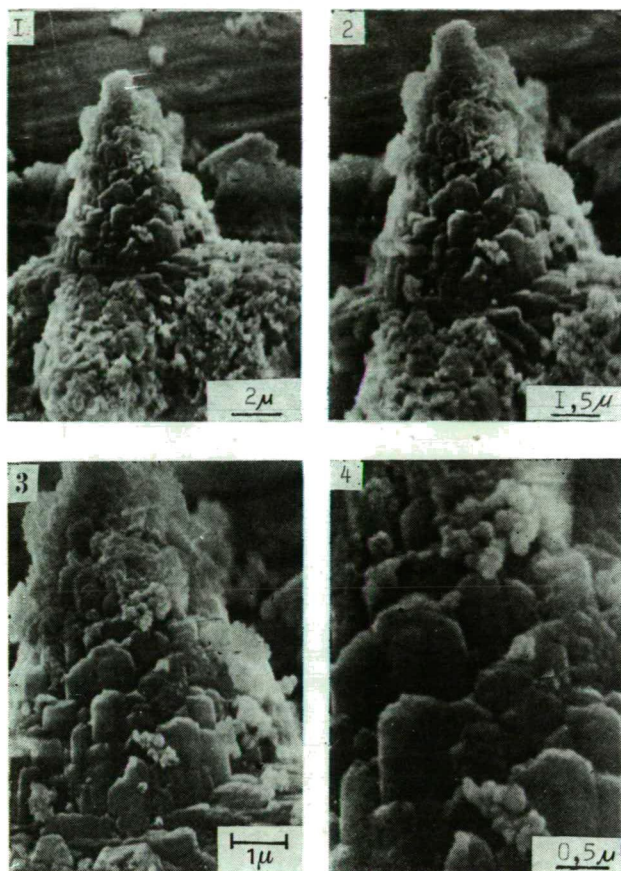
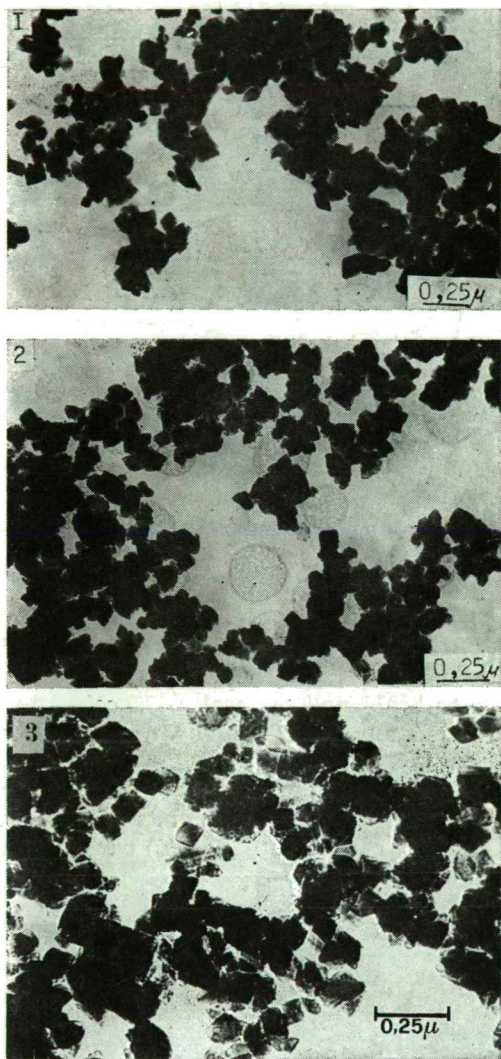


Fig. 2. Micrographs of the product obtained as a result of the sorption of the dissolved forms of Ni, Co, Fe, Mn from seawater by  $Mn_3O_4$  taken under a scanning electron microscope. Photos 1—4 are a successive series taken at increasing magnification. The photos show clearly a substantial enlargement of the aggregates, disappearance of a prominent globularity, development of microlaminated stepped epitaxial outgrowths of the newly-formed phases

*et al.*, 1976; FROST *et al.*, 1972; MATIENZO *et al.*, 1973; TEWARI and LEE, 1975, 1977; BRIGGS and BOSWORTH, 1977]. A characteristic of this technique is that reliable information on the valency of the ions of interest can be obtained only for the sample surface: the penetration ability of photoelectrons averages 50—70 Å. Therefore, study of the deeper zones of the sample required etching of the sample with argon ions at an energy of 0.7 keV and a current of 6 mA (argon pressure in the sample conditioning chamber being 0.14 Torr). The samples under study were subjected to double and triple etching by steps of 3400—6000 Å. Determination of the structural-chemical behaviour of the sorbed layer was made by the (2p<sub>3/2</sub>) spectra of Ni, Mn and Co, shown in Figs. 4a, 5a, 6a.

**Manganese.** The Mn (2p<sub>3/2</sub>) spectrum in the external part of the sorbed layer is characterized by a structure with a clear-cut separation of the low-energy group of peaks (binding energy region 640—644 eV). This low-energy spectrum is dis-





*Fig. 3.* Micrographs of the sorbent ( $Mn_3O_4$ ) and products obtained as a result of the sorption of the dissolved forms of Ni, Co, Fe, Mn from seawater by ( $Mn_3O_4$ ), taken under an electron microscope. *Photo 1.* The initial phase is ( $Mn_3O_4$ ). Shown clearly are bipyramidal, octahedral crystalline forms of individual grains ( $40 \cdot 10^3 \times$  magnification). *Photos 2—3.* The sorbent ( $Mn_3O_4$ ) after interaction with seawater containing Ni, Co, Fe, Mn (products of parallel experiments). Shown clearly is aggregation of the grains, their less distinct crystalline faces, with indications of the corrosion of the primary grains and development upon them of newly-formed sorption outgrowths: relatively brighter rims and areas around comparatively dark primary grains ( $40 \cdot 10^3 \cdot$  magnification)

tinguished by a considerable breadth and an asymmetry suggesting a superposition of several charge states of Mn. This is supported by a non-uniform, stepped configuration of the spectrum top portion in the given binding energy region. From correlation of the spectrum obtained with those known for various manganese oxides

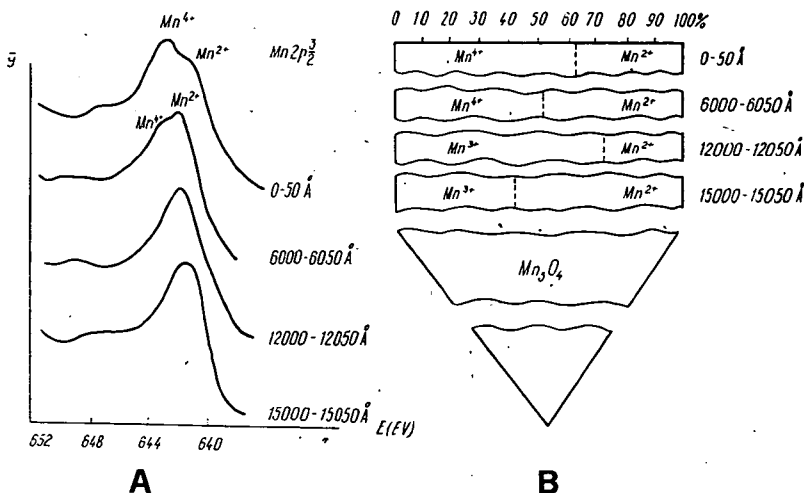


Fig. 4. *A*) Mn X-ray photoelectron ( $2p_{3/2}$ ) spectra for the external and internal parts of the newly-formed layer  
*B*) Relationships (%) between the Mn valency states in the external and internal parts of the newly-formed layer

[MINACHEV *et al.*, 1975; ROSENCWAIG *et al.*, 1971; FROST *et al.*, 1972; NEMOSHKALENKO and ALESHIN, 1976] it can be concluded that the peak corresponding to the binding energy 641.6 eV relates to  $Mn^{2+}$  and the peak 642.7 eV — to  $Mn^{4+}$ . These peaks suggest that the relative amounts of  $Mn^{4+}$  and  $Mn^{2+}$  are 60 and 40%, respectively (see Figs. 4a, b).

At a depth of 6000 Å, a variation in the relationships between the peaks responsible for  $Mn^{4+}$  and  $Mn^{2+}$  and the relative amounts of these valency forms of Mn being approximately equal to each other (50:50%) can be observed in the sorbed layer.

For the deeper levels of the sorbed layer (12,000 and 15,000 Å) disappearance of the peak characteristic of  $Mn^{4+}$  and appearance of a clear-cut peak (641.4 eV) corresponding to  $Mn^{3+}$  are observed. For the depth interval 12,000—12,050 Å the relative amounts of  $Mn^{3+}$  and  $Mn^{2+}$  are 70 and 30%, respectively. For the levels deeper than 15,000—15,050 Å this ratio decreases substantially:  $Mn^{3+}=40$ ,  $Mn^{2+}=60\%$ .

*Nickel.* The Ni ( $2p_{3/2}$ ) spectra in the external part of the sorbed layer are also distinguished by a considerable breadth, i.e. 3 eV (Fig. 5a). In addition, in the high-energy spectrum portion at a distance of 6—7 eV, there are observed satellite lines. These lines can be readily subdivided into two narrow components with a binding energy of 862.5 and 863.0 eV, respectively. Transition to the intermediate part of the sorbed layer (a depth of 6000 Å) leads to a prominent narrowing of the main line of the Ni ( $2p_{3/2}$ ) spectrum and its shift to the low-energy side down to 855.5 eV as compared with the binding energy of the Ni main peak in the external part of the layer (856.3 eV). The value 855.5 eV is characteristic of divalent nickel [MINACHEV *et al.*, 1975; NEMOSHKALENKO, ALESHIN, 1976; ROSENCWAIG *et al.*, 1971; FROST *et al.*, 1972], the Ni satellite line has a binding energy of 861.5 eV. The spectrum of Ni in the external part of the layer, as evidenced by its appreciable breadth and the double structure of the satellite line therefore suggests that it represents a superposition of

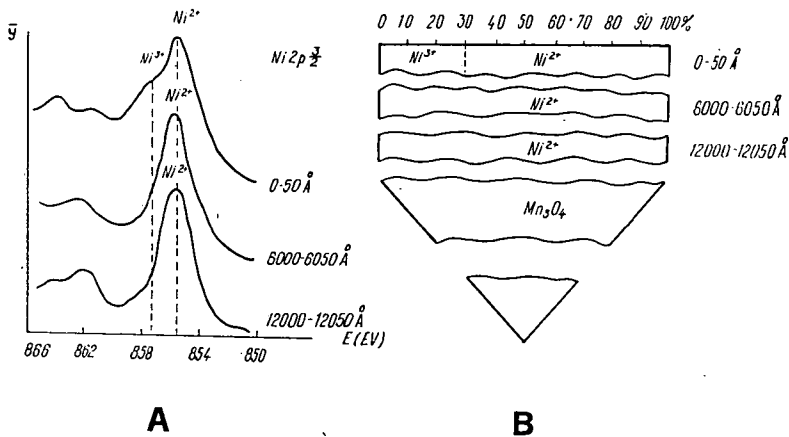


Fig. 5. A) Ni X-ray photoelectron (2p<sub>3/2</sub>) spectra for the external and internal parts of the newly-formed layer  
 B) Relationships (%) between the Ni valency states in the external and internal parts of the newly-formed layer

two valency states of Ni, i.e. Ni<sup>2+</sup> and Ni<sup>3+</sup> with their relative amounts 70 and 30%, respectively (see Fig. 5b).

In two deeper levels of the sorbed layer, Ni is found largely in a divalent state. In this case the corresponding redistribution of intensity on the satellite lines as well is also observed. The Ni (2p<sub>3/2</sub>) spectrum in the lower part of the layer (12,000 Å) does not differ from that of the intermediate part of the layer.

**Cobalt.** The structure of the Co (2p<sub>3/2</sub>) spectrum is very much the same as that of Ni (Fig. 6a, cf. Fig. 5a). The Co spectrum for the external part of the layer is

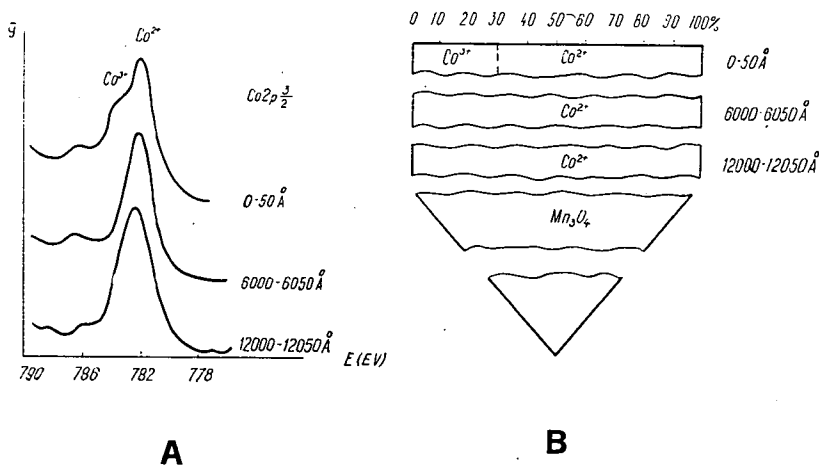


Fig. 6. A) Co X-ray photoelectron (2p<sub>3/2</sub>) spectra for the external and internal parts of the newly-formed layer. B) Relationships (%) between the Co valency states in the external and internal parts of the newly-formed layer

MÖSSBAUER spectra parameters of hydrous ferric oxides synthesized on the substrate represented by hydrohausmannite

TABLE 2

Sample	$T_{meas}$ (°K)	Isomeric shift $\delta E$ (mm/s) $\pm 0.02$ mm/s	Quadrupole splitting E (mm/s) $\pm 0.03$ mm/s	Half-width of lines (mm/s) $\pm 0.02$ mm/s	Effective magnetic field intensity (kOe)	$\pm 0.05$	
a	300	0.18	0.68	0.61	—	1.00	0.55
	80	0.17	0.66	0.48; 0.42	—	1.80	
b	300	0.18	0.71	0.61	—	0.53	
	80	0.17	0.69	0.45; 0.60	—	1.50	0.34
c	300	0.18	0.66	0.65	—	0.20	
	80	0.17	0.69	0.54; 0.39	—	1.16	0.15
Fe(OH) <sub>3</sub> , synthesized	300	0.18	0.66	0.62	—	2.50	
	80	0.17	—	0.54; 0.60	—	3.80	0.66
Goethite from the Red Sea (X-ray amorphous)	300	0.15	0.57	0.46	—	7.70	—
	80	0.15	0.69	0.45	454	—	—
Goethite ( $\alpha$ -FeOOH) fine-grained 200 Å	300	0.20	0.55	0.44	—	—	—
	80	0.08	0.58	—	—	—	—

characterized by a significant breadth and shifts to the high-energy side as compared with the internal part of the sorbed layer. As in the case of Ni, this spectrum corresponds to the superposition of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  in the ratio (%):  $\text{Co}^{3+}:\text{Co}^{2+}=30:70$  (Figs. 6a, b).

It should be noted that the Co spectrum has a satellite structure in the external part of the newly-formed layer. There are serious reasons to believe that the given satellite in the binding energy region 785.2 eV is due to the discrete losses which are associated with the secondary  $3d-4s$  electrons transition on the  $\text{Co}^{3+}$  ion. The Co spectrum at depths of 6000 and 12,000 Å are identical and characterized by fairly symmetrical lines. The peak of the Co main line for these levels has binding energy in the range 780.5—781.5 eV, which corresponds to the presence of  $\text{Co}^{2+}$  [MINACHEV *et al.*, 1975; NEMOSHKALENKO, ALESHIN, 1976; ROSENCWAIG *et al.*, 1971; FROST *et al.*, 1972]; the presence of a satellite in the Co spectrum for the external part of the sorbed layer is due to the special features of the nearest surrounding of  $\text{Co}^{2+}$  and not  $\text{Co}^{3+}$ , since it follows from studies by ROSENCWAIG *et al.*, [1971] that  $\text{Co}^{3+}$  has no satellite structure; moreover, this is also suggested by a relatively small distance satellite —  $\text{Co}^{3+}(2p_{3/2})$ , i.e. 3.3 eV instead of normally observed 4.5 eV.

It is known from experimental studies by MINACHEV *et al.* [1975]; NEMOSHKALENKO, ALESHIN [1976]; FROST *et al.* [1972] that satellites are largely typical of the octahedral configuration Co-ligand, and their absence implies the transition of Co into the tetrahedral surrounding. In the internal part of the sorbed layer,  $\text{Co}^{2+}$  is therefore distributed largely in tetrahedral voids.

MÖSSBAUER spectroscopy was used to study the crystallochemical features of Fe compounds in the newly-formed layer sorbed on the hausmannite substrate. The study was made on a set of samples (a, b, c) obtained in parallel experiments (see Table 2, Fig. 7).

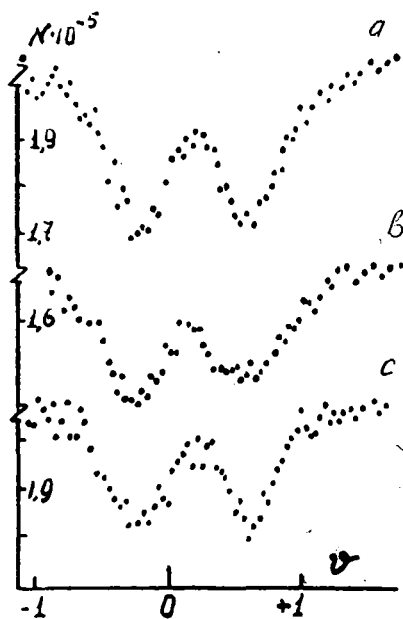


Fig. 7. Mössbauer spectra of the product obtained as a result of the sorption of the dissolved forms of Ni, Co, Fe, Mn from the solution of seawater by  $\text{Mn}_2\text{O}_4$ . The spectra were taken at a temperature of liquid nitrogen. The samples a, b, c are the products of parallel experiments. The parameters of these spectra correspond to  $\text{FeOOH} \cdot \text{H}_2\text{O}$ . The samples of the a—b—c series show a decrease of crystallinity of  $\text{FeOOH} \cdot \text{H}_2\text{O}$



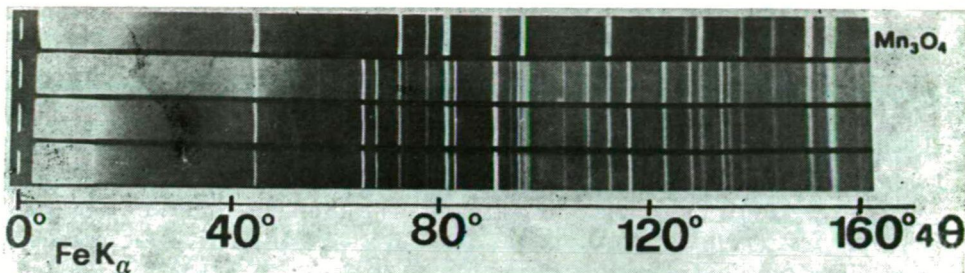


Fig. 8. X-ray powder pattern of varieties of final products (Guinier camera,  $\text{FeK}_\alpha$ -radiation). Note the distinctive new lines of the newly-formed phases. *Sample 1* is the sorbent represented by  $\text{Mn}_2\text{O}_4$ . *Samples 2–4* are the products obtained as a result of the sorption of the dissolved forms of Ni, Co, Fe, Mn from seawater by hausmannite (parallel experiments)

1. *Sample a*. The spectrum represents a quadrupole doublet with an isomeric shift of 0.17 mm/s and a quadrupole splitting  $\Delta E = 0.66$  mm/s, these parameters being characteristic of ferri-compounds. The line width is 0.48 mm/s, which is 1.5 times more than the instrumental line width. The magnitude of the effect is of the order of 1.8%.

2. *Sample b*. The spectrum also represents a quadrupole doublet with the same magnitude of isomeric shift and a somewhat larger magnitude of quadrupole splitting,  $\Delta E = 0.69$  mm/s. The lines are slightly asymmetrical, their widths being equal to 0.45 mm/s and 0.60 mm/s for the left and the right component respectively (the line widths exceed the instrumental line width by a factor of 1.40 and 1.87, respectively). The magnitude of the effect is 1.5%.

3. *Sample c*. The spectrum has a quadrupole doublet similar to the previous case with reverse asymmetry and the magnitude of the effect equal to 1.16.

The constancy of isomeric shift, of the order of 1.17 mm/s, as well as the magnitude of quadrupole splitting, in the range 0.66 to 0.69 mm/s, suggest that in all three cases trivalent iron occurs. As a whole, these parameters are characteristic of ferric oxides, which corresponds most closely to the compound  $\text{Fe}(\text{OH})_3$ . At the same time, the differences observed in the spectra, relate to the magnitude of the effect, that varies, on passing from *sample a* to *sample c*, from 1.80 to 1.16, and also to the line width. It is obvious that this corresponds to variation in a degree of amorphism. In the successive series *a–c* one can observe a decrease in crystallinity, which is represented by the line broadening and variation in the above parameters.

The parameters listed above were obtained for the spectra taken at a temperature of liquid nitrogen. There is practically no parametric variations when passing from room temperature to a temperature of liquid nitrogen, except for a prominent increase of the effect, which characterizes a degree of amorphism. At the same time, for a fine-dispersed goethite and synthesized ferrihydrite at a temperature of liquid nitrogen, one can observe the effect of splitting. The data presented have suggest the availability of the compound type  $\text{Fe}(\text{OH})_3$  within the newly-formed layer.

The sorbent as starting material and newly-formed phases were identified by using various methods of X-ray analysis (Table 3, Fig. 8). It can be concluded from a comparison study of the X-ray patterns by their direct (side-by-side) application that the sorbed layer on the hausmannite substrate is characterized by a number of new reflections (3.39–3.26–2.69–1.97–1.88–1.74 and others) typical of this



layer only. Attempts to refer these reflections to the published tabulated data (ASTM and others) suggest the occurrence within the sorbed layer of the following phases:  $\gamma$ -MnOOH (manganite), CoOOH (heterogenite),  $\text{Co}_2\text{O}_3$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ . These phases are not inconsistent with the X-ray photoelectron spectroscopy data.

TABLE 3

*X-ray powder patterns of the starting material and final product, experiments on the chemisorption autocatalytic oxidation interaction of hydrous manganese oxides with the dissolved forms of Fe, Mn, Ni, Co (Guinier camera,  $\text{FeK}_\alpha$ )*

Starting hydroxide		Newly-formed phase		Hausmannite $\text{Mn}_3\text{O}_4$ ASTM 16—154		Starting hydroxide		Newly-formed phase		Hausmannite, $\text{Mn}_3\text{O}_4$ ASTM 16—154	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
4.91	20	—	—	4.94	30	—	—	2.35	0.5	—	—
—	—	4.37	0.5	—	—	—	—	2.33	1.0	—	—
—	—	3.93	0.5	—	—	—	—	2.32	1.0	—	—
3.56	0.5	3.56	0.5	—	—	—	—	2.18	1.0	—	—
—	—	3.43	0.5	—	—	—	—	2.11	0.5	—	—
—	—	3.39	10.0	—	—	2.04	5.0	2.10	2.0	2.04	40
—	—	3.33	0.5	—	—	—	—	1.97	6.0	—	—
—	—	3.30	0.5	—	—	—	—	1.88	5.0	—	—
—	—	3.26	8.0	—	—	—	—	1.81	4.0	1.82	20
3.06	0.6	3.02	0.5	3.09	50	1.782	5.0	—	—	1.795	50
2.87	1.0	2.82	0.5	2.89	30	—	—	1.75	0.5	—	—
2.76	10.0	2.72	0.5	2.77	90	—	—	1.74	4.0	—	—
—	—	2.69	7.0	—	—	1.696	5.0	1.72	2.0	1.706	30
2.48	9.0	2.45	0.5	2.49	100	1.634	2.0	1.64	0.5	1.642	20
—	—	2.40	1.0	—	—	1.579	7.0	—	—	1.575	80
2.31	2.0	2.37	3.0	2.36	40	1.541	10.0	1.55	0.5	—	—
—	—	—	—	—	—	1.44	6.0	1.49	0.5	1.468	10

A precision analysis of the studied sample using a Guinier camera with a subsequent side-by-side comparison together with the reference samples and a direct correlation of the X-ray patterns obtained in the same conditions revealed that MnOOH and CoOOH can be discarded. A purely numerical coincidence of the values of the reflections was not supported by the availability of a complete set of the corresponding lines needed for the identification of these compounds. The possibility of the presence of  $\text{Co}_2\text{O}_3$  and  $\text{Ni}_2\text{O}_3$  is improbable since the conditions for the synthesis of these compounds, as indicated for the ASTM reference samples and the experimentally obtained phases, are different. Experimental results reported by R. AMMANN and H. GÜDEL at the Bern University also indicate a small probability for the formation of  $\text{Co}_2\text{O}_3$  and  $\text{Ni}_2\text{O}_3$  under the conditions of the experiment conducted. The availability of  $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$  is somewhat doubtful as in the given conditions this compound is more likely to be present in the form of tetrahydrate. Despite the conclusive evidence for the presence of newly-formed phases within the sorbed layer therefore the problem of their exact identification is still to be solved.

## RESULTS AND DISCUSSION

Experiments on the accumulation of Ni, Co, Mn, Fe from seawater by hausmannite required a thorough maintenance of identical conditions throughout the entire 7 cycles (stages). However, the behaviour of each of the four sorbed components is

characterized by markedly specific features. Data on the sorption dynamics (Table 1) suggest the following conclusions:

1. The amount of the sorbed Co decreases progressively toward the final experimental stages, from 40.06% down to 15.50%.
2. For Ni, this trend is less marked than for Co.
3. For Fe, there is a less pronounced but gradual increase in the sorbed amount of this metal, which is especially evident during the final (after the fifth) stage, up to 100%.
4. For Mn the initial stages (before the third one) are characterized by a gradual decrease in the sorbed amount, of this metal (from 21.14% down to 14.50%). At the later stages (between the fourth and the seventh ones) one can observe a prominent desorption of Mn. The amount of Mn released into the solution at the final stages exceeds noticeably the content of this metal in the starting solution.

It would be possible to conclude from the data on the sorption dynamics that Mn does not accumulate under experimental conditions as the amounts of this metal released into the solution during the final stages exceed its initial amount by 2535  $\mu\text{g}$ . These data therefore suggest that the amount of Mn equivalent to 16.14% of the sorbed Co or 17.96% of the sorbed Ni was removed from the substrate structure ( $\text{Mn}_3\text{O}_4$ ) in the interaction with the solution-contained Ni and Co.

Studying the micrographs of the starting sorbent ( $\text{Mn}_3\text{O}_4$ ) and the newly-formed products, taken under a scanning microscope, permits the following features to be noted:

(a) The starting sorbent (*Fig. 1*) is characterized by small-globular forms in whose surface there developed very fine needle-like crystallites representing tetragonal bipyramids of  $\text{Mn}_3\text{O}_4$ .

(b) The final product (*Fig. 2*) is represented by large globular aggregates with the distinct patterns of the newly-formed sorbed layer featuring stepped-laminated epitaxial outgrowths.

The process of accumulation of the sorbed components involves aggregation, growth of the sorbent grains and perhaps even formation of epitaxial outgrowths on their surface where previously needle-like crystallites were present. This reduces the active surface of the sorbent substantially during the runs, which, in turn, affects the sorbed amounts of Co and Ni. Similar relations were observed in studies of the dynamics of the sorption synthesis of Ni, Co, Fe, Mn oxide phases on hydrous ferric oxides [VARENTSOV *et al.*, 1978].

X-ray photoelectron spectra of Co, Ni, Mn and MÖSSBAUER spectra of Fe reveal that, for the newly-formed layer there is a distinct trend toward accumulation of these components on the state of relatively high valencies. However, the intensity of oxidation processes at the solution/sorbent ( $\text{Mn}_3\text{O}_4$ ) interface is relatively lower than for hydrous ferric oxides ( $\text{FeOOH}$ ), [VARENTSOV *et al.*, 1978]. The most prominent feature in this case is the absence of higher states of Mn oxidation ( $\text{Mn}^{7+}$  and  $\text{Mn}^{5+}$ ). For the present case, the above pattern of Mn distribution shows up in a relative enrichment of the newly-formed layer with divalent Mn (*Fig. 4*). At the same time, the Ni and Co spectra of the newly-formed layer retain similarity with the spectra of the compounds synthesized on lepidocrocite. However, in this case the distribution of the Ni and Co valency forms is close to that which was observed not in the surface part of the layer formed on the lepidocrocite substrate but rather at a certain depth, i.e. of the order of 3400 to 3450 Å.

Attention is drawn to a relative general weakening of the processes of Co, Ni, Mn accumulation on hausmannite as compared with lepidocrocite (Table 4). It can be concluded from the data of Table 4 that the process of the component accumulation proceeds in a nonuniform way, i.e. accumulation is highest at the initial stages and, as the newly-formed layer develops, the relative amount of the sorbed components decreases. This conclusion agrees with the data on the sorption dynamics (Table 1). As stated above, the decrease in the sorption rates is associated with a substantial reduction of the sorbent surface.

TABLE 4

*Relationships between the intensities of the (2p 3/2) lines of Co, Ni, Mn for the phases newly-formed on the substrates represented by hydrous manganese oxides (hydrohausmannite) and hydrous ferric oxides (lepidocrocite) — [VARENTSOV et al., 1978]*

Depth from the surface of the newly-formed layer (Å)	Co	Ni	Mn
	I(2p3/2) hausmannite I(2p3/2) lepidocrocite		
0—50	0.74	0.68	0.44
6000—6050 (6800—6850)	1.27	1.58	0.93

It is interesting to note that for this case the decrease of the relative share of Ni<sup>3+</sup> and Co<sup>3+</sup> with depth occurs more noticeably than in experiments with lepidocrocite, which fact is likely to be due to a specific effect of the substrate and higher rates of the accumulation of these metals.

By and large, the observed relationships between the valency forms of Ni, Co and Mn confirm an earlier conclusion [VARENTSOV et al., 1978] to the effect that the development of the highly oxidized metal forms in the external part of the newly-formed layer is attributable to the lower accumulation rates of the metals sorbed. It is obvious that the composition of the definite zones of the newly-formed layer is governed by the relationship between the rates of the two processes, i.e. that of the initial sorption of an ion-exchange and hydrolytic nature and a later process of autocatalytic contact oxidation.

A special place is occupied by the solid-phase redox reactions in the diffusion of the sorbed ions into the sorbent structure. It is these reactions to which it is possible to relate an apparent inconsistency of the data on the Mn sorption dynamics (Table 1) and distribution of the valency states of this metal within the newly-formed layer. The results of the experiments conducted and particularly X-ray photoelectron spectra permit a more definite interpretation of the phenomenon consisting in the displacement of Mn<sup>2+</sup> and Mn<sup>3+</sup> out of the structure of hydrous manganese oxides in the sorption of Ni and Co [MCKENZIE, 1970, 1972; LOGANATHAN and BURAU, 1973; MURRAY, 1975a, b]. The data obtained suggest that along with the sorption of Mn and formation of the phases of this metal within the newly-formed layer (see Fig. 4), there is an exchange displacement of Mn<sup>2+</sup> under the action of Ni and Co ions, and of Mn<sup>3+</sup> under the action of Co ions from the hausmannite lattice, primarily from the zones of the defect structure. This process is not stoichiometric in that amount of Mn equivalent to 16.14% of the sorbed Co or 17.96% of the sorbed Ni releases into the solution over 82% of Co and Ni therefore accumulate in the sorbed layer.

It is important to note that Fe as the most intensively sorbed component (see Table 1) is present in the newly-formed layer, as evidenced by MÖSSBAUER spectroscopy, nearly in full, in a higher degree of oxidation, i.e. as  $\text{Fe}^{3+}$  (compound type  $\text{FeOOH} \cdot \text{H}_2\text{O}$ ).

## GEOCHEMICAL INTERPRETATION

The criterion of the validity of a genetic model developed by analyzing the observations of a natural process and experimental simulation of some of its elements is conditioned by an adequacy to which this model describes the known facts and new information relating to this process.

Considering recent basins (first of all those of the World Ocean) as ore formation systems, it is possible to distinguish among them the following three categories: (a) sources; (b) transportation medium; (c) ore formation process proper [GREENSLATE *et al.*, 1973; VARENTSOV, 1976]. The above experiments were directed at studying the process of the formation of Mn, Ni, Fe, Co hydrous oxide compounds in the interaction of a component-bearing solution (seawater) with hydrous manganese oxides. The work conducted was based on earlier studies [MICHARD, 1969; MORGAN and STUMM, 1965; STUMM and MORGAN, 1970; PRONINA, *et al.*, 1973; PRONINA and VARENTSOV, 1973; VARENTSOV and PRONINA, 1973, 1976, and others]. These experiments suggest that the hydroxide phases of Mn, Fe, Ni, Co form as a result of a multistage, involving autocatalytic oxidation, interaction of active surfaces with component-bearing solutions. The initial stages of this process involve sorption and ion-exchange reactions proper with a prominent selective sorption of transition metals. The main reasons for such a high selectivity are the chemical (crystallochemical) affinity of the sorbent and sorbed metal ions, as well as hydrolytic reactions in the interface zone. The later stages involve the reactions of the interface catalytic oxidation of the metals sorbed and their interaction with the sorbed structural ions (hydrous oxides of Fe, Mn and sometimes other transition metals). At the subsequent stages the phases appeared undergo various postsedimentation transformations. Such individual cycles are likely to be multiplied repeatedly in the course of geological time. Experimental laboratory conditions favour the simulation of only separate parts of a natural process taking place at extremely low rates measured by geochronological intervals. The experiments conducted here demonstrate that the composition of the hydroxide compounds of transition metals, appearing as a result of such an autocatalytic process, are governed by a number of critical parameters. The process is most vigorous in the range of weak alkaline pH's (8) and the prominent oxidative values of Eh in the presence of a free soluble  $\text{O}_2$ . The composition of the newly-formed phases is governed by both the concentrations of the transition metals and their relationship in the component-bearing solution. Such a solution is represented by bottom seawater to which the dissolved metals can be supplied by the currents and in some instances by diffusion from the underlying sediments and other ways.

It has been revealed experimentally that the mineral composition of the compounds results from optimal relationships between the rates of the two basic stages of the process: (a) sorption and (b) catalytic oxidation. It should be noted that the latter stage controls the entire process. The relatively high rates of the first stage leads to the blocking of the second stage, namely interface oxidation. To evaluate how consistently this genetic model explains the known natural phenomena, it is

appropriate to consider, by way of example, the formation of the World Ocean's nodules containing the greatest amounts of transition metals, viz. the equatorial North Pacific [GREENSLATE *et al.*, 1973; ARRHENIUS, 1963; FRAZER, 1977; MENARD and FRAZER, 1978; PIPER, 1977; HORN *et al.*, 1974]. This zone belongs to a sub-equatorial region of a high biological productivity, relatively low sedimentation rates (under 1 mm/10<sup>3</sup> years), a pronounced erosion activity of underwater currents. The consolidated sediments represented largely by Late Tertiary radiolarian oozes contain, in a scattered form, the considerable amounts of the fragments of altered basic volcanites — palagonites acting as cores for most nodules [HORN *et al.*, 1974]. It is important to note that this nodule zone is adjacent to the western flank of the East Pacific Rise characterized by large-scale hydrothermal activity.

Analysis of the foregoing factors permits the following interpretation to be made. Metals accumulated in the nodules (Mn, Ni, Cu, Co) are present in seawater in solution as the products of biological planktonic transformation occurring in the zone of photosynthesis. The nodule growth is favoured by the presence of the fragments of the altered basic volcanites acting as cores. The presence of hydrous ferric and manganese oxides within the altered basic volcanites makes it possible to regard them as more active sorbents as compared with siliceous radiolarian oozes. The low accumulation rates of the associated sediments favour the process of nodule formation since sedimentary particles produce little or no blocking effect on the active surfaces where transition metals are sorbed. A similar function is performed by bottom currents which, along with the removal of sedimentary material, supply fresh portions of metal-bearing solutions to the zone of natural chromatography. It is obvious that the favourable action of the bottom currents on the nodule formation in this part of the Ocean has been taking place for a long period, presumably since Late Miocene. It is likely that the content of the components in natural water and Eh conditions had a controlling effect on the accumulation rates and composition of Fe—Mn hydroxide phases; for example, the sequence of minerals reflects the growth of oxidative conditions: todorokite — birnessite— $\delta$ -MnO<sub>2</sub> (2.4-Å phase), — [CHUKHROV *et al.*, 1976, 1978]. It is interesting to note that characteristic feature of the successive catalytic accumulation of the transition metal hydroxide phases shows up distinctly in the presence of microlaminated epitaxial outgrowths observed under an optical and a scanning microscope. Comparison of the synthetic hydroxide compounds (Figs. 1, 2) with the naturally occurring nodules [FEWKES, 1973; MARGOLIS and GLASBY, 1973; SOREM and FOSTER, 1972; WOO 1973; VARENTSOV *et al.*, 1978] points to their having most similar texture features.

A definite role of microorganisms has been assigned to the processes of oxide ferromanganese ore formation in recent basins [DUBININA, 1976; ERHLICH, 1972, 1975; SCHWEISFURTH *et al.*, 1978, and others]. EHRlich and coworkers [EHRlich, 1972, 1975] show that the process of microbacterial oxidation is based on the phenomenon of enzymatic (biological) catalysis. Two stages are distinguished in this process [EHRlich, 1972, p. 66]: (a) sorption; (b) catalytic oxidation proper. In the first stage, the sorption accumulation of transition metals takes place on the active surface. In the second stage, there is catalytic oxidation of the sorbed metals, involving specific enzymes. The intensity or the rate of such an oxidation depends on enzyme concentration. SCHWEISFURTH *et al.* [1978] have found that for a number of microorganisms (*Pseudomonas manganooxidans*) the oxidation of Mn(II) is likely to occur in that case only when the concentration of this metal in solution is under 3.10<sup>-5</sup> M. Moreover, it is important to note that biocatalytic oxidation of Mn is favoured by the introduction of complexing agents into solution, decreasing the

ionic activity of this metal [SCHWEISFURTH *et al.*, 1978, p. 926]. It has been shown by EHRLICH [1972, p. 67] that the enzymatic oxidation of Mn(II) can take place in a range of relatively not high (for the Ocean) pressures, i.e. up to 567 atm. Thus, the reactions of microbacterial oxidation of transition metals, however, involved they may be, occur in complete agreement with the principal laws of chemical transformations [JENCKS, 1969; BRUCE, BENKOVICH, 1970; THOMAS, THOMAS, 1967]. For the phenomena of microbacterial oxidation of Mn, the mechanism of chemical transformations is likely to be based on the above reactions of catalytic oxidation. However, it can be suggested that these reactions suffer relatively lesser limitations in the basins. Moreover, autocatalytic oxidation is the main process in the formation of oxides of metalliferous sediments [VARENTSOV, 1976; MORGAN, STUMM, 1965].

Among the investigators studying the formation of Fe—Mn nodules, there are those who advocate an exclusively alternative biogenic or abiogenic origin of such ores. The existing situation is similar to that in biological chemistry when in the 1870's there was a lively discussion between J. LIEBIG and L. PASTEUR on the nature of enzymes. Later on, based on the achievements of chemistry and chemical kinetics, it was shown that enzymatic processes (biocatalysis) represent a variety of chemical reactions, without any principal differences.

Thus, taking into consideration all the limitations that are typical of the experiments simulating natural processes, the data obtained may be useful for the fairly satisfactory explanation of the phenomenon of ore formation in recent basins, thereby permitting better understanding of the genetic nature of these processes.

## CONCLUSIONS

Results of the experiments conducted and diagnostic data for the compounds synthesized on a substrate represented by manganese oxides ( $Mn_3O_4$ ) permit the following conclusions to be made:

1. As a result of the data analysis for the sorption dynamics of the dissolved forms of Ni, Co, Mn, Fe from seawater by manganese oxide, study of the starting sorbent and final products under a scanning microscope and by using X-ray photoelectron spectroscopy, MÖSSBAUER spectroscopy, and X-ray identification, it has been established that these components accumulate as a newly-formed sorbed layer.

2. The process is of a complex, multistage nature. The initial stages are characterized by the development of ion-exchange and hydrolytic reactions. In the later stages, the interface autocatalytic oxidation of the components accumulated is observed.

3. The composition of the newly-formed compounds is controlled by the kinetic parameters of the following two main stages of the process: a) the component sorption proper; b) interface catalytic oxidation. Data on the sorption kinetics and X-ray photoelectron spectra of the various levels of the newly-formed layer suggest that the highest oxidized forms of the metals accumulate at the lower sorption rates, when the blocking effect of the first stage does not inhibit the second one. For example, at the final experimental stages at an appreciable decrease of the sorption rates in the external part of the newly-formed layer there are relatively large amounts of the oxidized forms of metals (%):  $Mn^{4+} = 60$ ,  $Co^{3+} = 30$ ,  $Ni^{3+} = 30$ . Iron, as evidenced by MÖSSBAUER spectroscopy, is present in the sorbed layer in the form: amorphous  $FeOOH \cdot H_2O$ .

4. The specific feature of the sorption of transition metals by hydrous manganese oxides consists of a partial interaction of Ni and Co with structural  $Mn^{2+}$  and

Mn<sup>3+</sup>. It has been established that, as a result of such an interaction, the amount of Mn equivalent to 16.14% of the sorbed Co or 17.96% of the sorbed Ni is displaced from the substrate into the solution. The main part of Ni and Co accumulates in the sorbed layer.

5. The results presented and survey of the existing situation in the experimental field concerning the problem under consideration enable one to use the above model of the formation of transition metal ore accumulations in recent basins. According to this model, the process is a multistage chemisorption phenomenon in which the principal role is played by interface autocatalytic oxidation of the metals accumulated.

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