

ADSORPTION PROPERTIES OF SOME MANGANESE OXIDES

Preliminary report

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INTRODUCTION

Taken into consideration the fairly considerable number of works dealing with the general properties of natural and artificial manganese oxides as well as that of the mineralogical and geological studies on manganese ore deposits, it can be stated that the manganese oxides and oxyhydrates, respectively, belong to the minerals investigated the most frequently, from the most different viewpoints and in detail.

However, the consideration may also be arisen that presumably a problem is mansidedly investigated and discussed just when there are still several open questions, problems to be solved and hypotheses to be proved.

Although it is well known that among other factors the sorption processes play an important role in the migration and enrichment of the elements, in the literature relatively few data can be found concerning the adsorption properties of manganese oxides and oxyhydrates, respectively, based on model-experiments.

In the literature there are numerous data as regards the minor elements determined in the manganese minerals of different origin and the probability of enrichment of certain elements in oxidative environments like the manganese oxide deposits, is also known. Even the enrichment of certain minor elements in some formations and the lack of others, respectively, is assumed to be in correlation with the presence of certain MnO_2 modifications [K. H. WEDEPOHL, 1961].

Some data on the ion exchange properties of manganese oxides can also be found. According to A. D. WADSLEY [1950] the Na^+ ion of the manganese oxyhydrate $(Na, Mn)Mn_3O_7 \cdot nH_2O$ prepared by oxidation of $Mn(OH)_2$ in aqueous alkaline solution may be exchanged by other metal-ions.

The ion exchange property of MnO_2 was discussed by AKIYA KOZAWA [1959] proposing the Zn ion exchange determined experimentally as a measure for the ion exchange capacity of the different manganese oxides.

K. KRAUSKOPF [1961] dealing with the possibilities of the reduction of concentration of thirteen elements in sea water stated that among other adsorbents the

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$MnO_2 \cdot nH_2O$ plays an important role in the scavenging of some minor elements from sea water due to adsorption.

E. GOLDBERG [1954] stated that in the ferruginous sediments of the Pacific Ocean the adsorbed Ti, Co, Zr content is proportional to the iron oxide content, similarly the Cu, Ni content shows a linear correlation to the Mn content. It is very interesting that a considerable difference can be established between the amounts of Co and Ni adsorbed by manganese oxyhydrates of the deep-sea manganese nodules, though both double charged cations have similar ionic radii and both have the same geochemical character. According to E. GOLDBERG the concentration of Co shows parallelism with the iron content which fact may be interpreted so that the cobalt may be present in anionic state and thus adsorbed by the negative charged iron hydroxides.

It seems to be very reasonable that a fairly important and perhaps selective role may be attributed to the manganese oxyhydrates in the migration and distribution of certain minor elements and the results of such investigations may contribute to the detailed interpretation of genetic problems of manganese ore deposits as well as they may be useful how to solve some practical problems, too.

This fact encouraged us to start the systematic study of the adsorption properties of different natural and artificial manganese oxides and oxyhydrates, respectively, by model-experiments.

These investigations are readily carried out in two ways. 1. Introducing the minor element in known concentrations into the dilute aqueous solution of manganous salt, then precipitating the manganese oxyhydrate under well controlled conditions and determining the distribution of the minor element between the manganese oxyhydrate and the solution. In this way connections can be stated among the conditions of precipitation (pH, Eh, concentration, temperature, etc.), the composition of the solid phase and the adsorption of the ion introduced.

2. The other way in the set of experiments was as follows: starting from solid manganese oxide phases and treating them with solutions of different electrolytes of known concentration and measuring the decrease of the ion concentration of the solution owing to the adsorption.

These two ways complete each other as the first can be considered to be the model of processes taking place during the formation of manganese oxide and oxyhydrate mineral phases, the second set of experiments, however, can be taken for a model of processes occurring in manganese oxide deposits after their formation, in consequence of dilute aqueous solutions.

At present the aims and problems of the work will be merely outlined and the results obtained illustrated, however, it is not intended to give a theory on the basis of experimental data so far though it might be attractive and alluring. During these introductory experiments no effort has been taken to completeness rather a comprehension was aimed at concerning questions which may arise and be answered at least partly on the basis of experiences gained.

These questions may be outlined as follows:

a) Whether an essential adsorption may be established for the different ions on the manganese oxides investigated?

b) Whether an essential difference is revealed in the adsorption properties of different manganese oxides, that is, may a selective adsorption be established in relation to different manganese oxides as adsorbents and various ions, respectively?

c) How far is it possible to make use of the experimental data to interpret natural processes like the enrichment of certain ions and whether the data obtained

may be compared to those regarding the minor element concentration of different manganese oxide deposits.

The adsorption of Na^+ , K^+ , Ca^{2+} ions in chloride solutions and that of Cu^{2+} , Co^{2+} and Ni^{2+} ions in sulphate solutions on β -, γ -, η - MnO_2 , α - Mn_2O_3 , Mn_3O_4 , manganite and cryptomelane were studied.

EXPERIMENTAL

Preparation of the samples

The preparation of MnO_2 modifications was carried out by the methods given in the papers of G. GATTOV and O. GLEMSER [1961 a, b].

1. β - MnO_2 : $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was tempered during 24 hours at 190–200 °C, the product pulverized in an agate mortar, boiled in 2–3 N nitric acid, filtered and washed free of acid then dried at 110 °C.

2. γ - MnO_2 : A solution of 15 gramm $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1000 ml of 3 N nitric acid was mixed with 200 ml solution of 2 per cent KMnO_4 at 20–40 °C. The precipitate was filtered by decantation and washed free of acid and dried at 60 °C.

3. η - MnO_2 : α - Mn_2O_3 was boiled in 3 N nitric acid during 20 hours in a flask with reflux cooler then filtered, washed free of acid and dried at 60 °C.

The other manganese oxides were prepared as follows:

4. α - Mn_2O_3 : A saturated ammonium oxalate solution was added to the boiling suspension of manganese carbonate in water till the supernatant liquid showed acidic reaction. The manganese oxalate precipitate was filtered, washed till neutral reaction and dried. The product was ignited in a Pt-dish in open air by constant stirring till the oxalate decomposed and then ignited at 650 °C up to the total transformation into α - Mn_2O_3 .

5. Mn_3O_4 : α - Mn_2O_3 was ignited to Mn_3O_4 in an electric oven at 1050 °C.

The natural samples were as follows:

6. *Manganite*.

7. *Cryptomelane*.

Both selected samples originated from the sedimentary manganese ore deposit of Urkut, Hungary. The fraction <0,06 mm was used to the adsorption experiments.

Identification of the samples

The identification of the samples was carried out partly by X-ray powder patterns partly by differential thermal analysis. The results were confirmed by infrared adsorption spectra.

The X-ray investigations were carried out by Fe/Mn radiation with 30 kV, 10 mA. Results are summarized in Tables 1 and 2.

Of the samples only the γ - MnO_2 proved to be roentgen-amorphous. The manganite from Urkut contains some pyrolusite as shown also by the D.T.A. curve.

The D.T.A. curves give valuable information on the modification of MnO_2 as the main endothermic peak appears at 620° C in the case of the most ordered, most stable β -modification while this endothermic peak appears at a somewhat lower temperature in the case of other modifications. According to G. GATTOV and O. GLEMSER [1961 a, b] in the case of different MnO_2 modifications the temperature of this endothermic peak is as follows: γ - MnO_2 500° C, γ' - MnO_2

532° C, η -MnO₂ 543° C, η' -MnO₂ 548° C and β -MnO₂ 620° C. According to the D.T.A. curves obtained the samples used for investigation correspond to the given modifications. The same is valid for the other manganese oxides too.

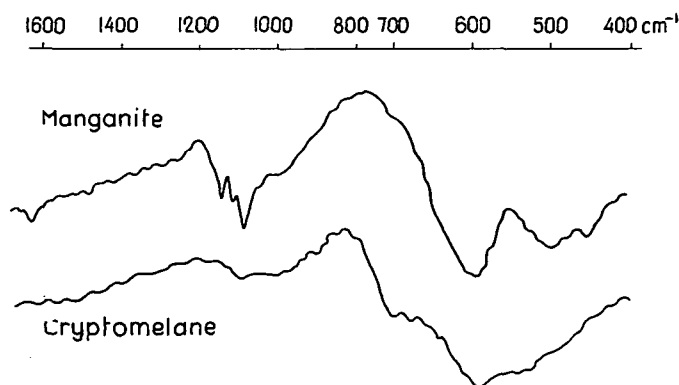


Fig. 1. Infrared absorption spectra of manganite and cryptomelane from Úrkút, Hungary

The infrared adsorption spectra can also be used to identify different manganese oxides. For the identification the absorption bands between 400—700 cm⁻¹ wave number can be used as they are characteristic for the different manganese oxides [H. MOENKE, 1962]. Infrared adsorption spectra of different manganese oxides are also published in papers by G. GATTOW and O. GLEMSER [1961 a, b]. The infrared adsorption spectra of the samples investigated are shown in Figs. 1—3.

Table 1
X-ray powder data of the natural samples
d(Å) with Fe/Mn radiation

Manganite Úrkút				Cryptomelane Úrkút			
Measured		MICHEJEV No 289		Measured		MICHEJEV No 302	
d(Å)	I	d(Å)	I	(dÅ)	I	d(Å)	I
3,418	vs	3,40	100	6,869	w	6,81	4
3,107	m			4,813	vw	4,87	4
2,623	m	2,64	60	3,098	m	3,084	10
2,513	vw			2,447	vw	2,455	2
2,413	s	2,41	80	2,397	w	2,393	4
2,269	w	2,26	60	2,151	vw	2,148	2
2,192	w	2,18	60				
2,106	vw						
1,782	m	1,77	80				
1,703	w	1,70	70				
1,673	s	1,665	80				
1,628	w	1,630	70				
1,563	vw						
1,507	w	1,495	70				
1,453	w						

vs: very strong; s: strong; m: middle; w: weak; vw: very weak

Table 2

X-ray powder data of artificial samples, d(Å) with Fe/Mn radiation

β -MnO ₂				η -MnO ₂	
Measured		MICHEJEV No 264		Measured	
d(Å)	I	d(Å)	I	d(Å)	I
3,116	vs	3,118	100	3,994	m
2,410	s	2,404	90	2,720	m
2,202	w	2,202	20	2,430	m
2,112	m	2,108	70	2,125	s
1,623	s	1,622	100	1,635	m
1,556	m	1,555	80		
1,435	m	1,434	60		

α -Mn ₂ O ₃				Mn ₃ O ₄			
Measured		A. S. T. M. 10—69		Measured		A. S. T. M. 8—17	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
3,837	m	3,84	25	4,897	m	4,86	70
2,713	vs	2,72	100	3,079	m	3,05	50
2,508	vw	2,51	3	2,868	w	2,87	20
2,350	m	2,35	11	2,760	s	2,74	90
2,097	vw	2,10	1	2,479	vs	2,47	100
2,003	m	2,01	13	2,358	m	2,34	50
1,921	vw	1,92	1	2,032	m	2,02	60
1,840	m	1,845	13	1,824	vw	1,812	10
1,715	vw	1,719	3	1,796	w	1,779	50
1,658	s	1,664	30	1,698	w	1,689	20
1,610	vw	1,615	1	1,638	vw	1,629	15
1,562	vw	1,566	1	1,572	m	1,571	60
1,526	vw	1,524	5	1,541	s	1,537	80
1,452	w	1,452	9	1,436	m	1,434	50
1,417	m	1,419	15				

vs: very strong; s: strong; m: middle; w: weak; vw: very weak

Experimental conditions

During the experiments different quantities (0,1—0,5 gramm) of the samples were weighed into polyethylene bottles and 50—50 ml solutions containing the given ions in concentration of 0,01—0,1 mmol/100 ml (in some cases up to 0,2 mmol/100 ml) were added. As the equilibrium was reached within 30 minutes the samples were shaken for 60 minutes and filtered — after or without centrifugation as needed — and the ion concentration of the solution determined. From these values the decrease of the ion concentration and the adsorbed amount of the ions, respectively, were established.

The values referred to 1 gramm of adsorbent, the specific adsorbed quantity expressed in mmol/g, was obtained. Plotting these values against the measured equilibrium concentration of the solutions (the concentration of the solutions after the adsorption equilibrium having been reached), the adsorption isotherms could be drawn.

Specific adsorption can be calculated taking into consideration the volume of the solution (V), the difference between the starting (c_0) and equilibrium concentrations (c_e) of the solution and the mass of the adsorbent (m) weighed in:

$$\alpha = \frac{V(c_0 - c_e)}{100 \cdot m}$$

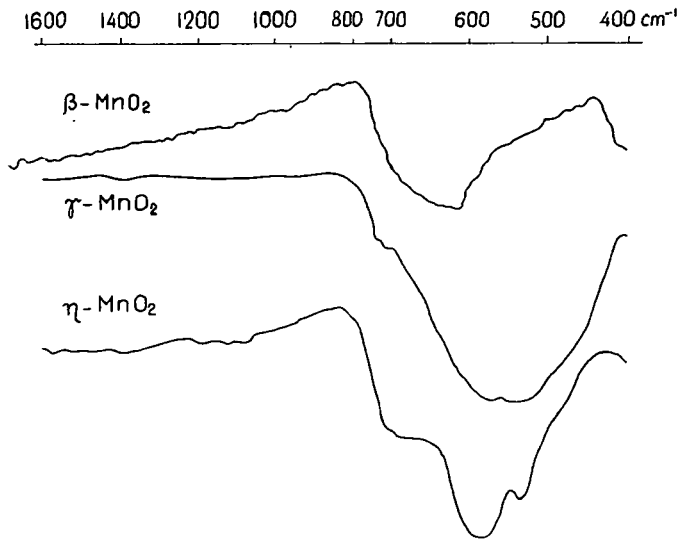


Fig. 2. Infrared absorption spectra of artificial MnO₂ modifications

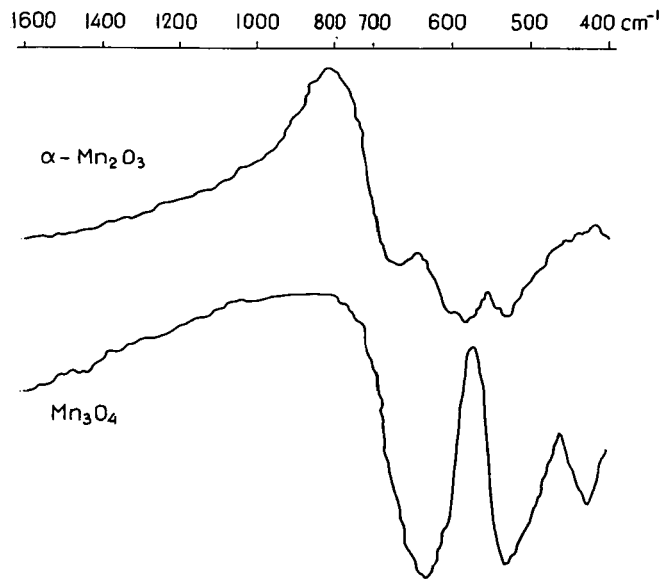


Fig. 3. Infrared absorption spectra of artificial α-Mn₂O₃ and Mn₃O₄

Determination methods applied

The concentration of Na^+ , K^+ and Ca^{2+} was determined by flame-photometry.

To determine the concentration of Cu^{2+} , Co^{2+} and Ni^{2+} spectrophotometrical methods were used as found in different textbooks [e.g. B. LANGE, 1942; F. D. SNELL and CORNELIA T. SNELL, 1951; R. PŘIBIL, 1961]. The determination of the copper is based on the reaction with potassium ferrocyanide using gelatine as protecting colloid, that of the cobalt on the reaction with potassium bichromate in presence of EDTA and finally to determine the Ni content the well known dimethyl glyoxime reaction was used.

It is to mention that the determination of the equilibrium concentration of ions in the solution and that of their adsorbed amounts on the adsorbents would have been much more elegant and accurate by radiochemical methods using labelled ions for example Co-60, Cu-64 isotopes. The spectrophotometrical methods used — especially in the field of the lowest concentrations below 0,01 mmol/100 ml — may be accompanied by errors which make the initial part of the adsorption isotherms uncertain and inaccurate.

DISCUSSION OF THE RESULTS

Adsorption isotherms are shown in *Figs. 4—19*. The adsorption isotherms for the different ions are denoted by the same number in each Fig.: Na^+ [1]; K^+ [2]; Ca^{2+} [3]; Cu^{2+} [4]; Co^{2+} [5]; Ni^{2+} [6]. The abscissa is the equilibrium concentration measured and expressed in mmol/100 ml, the ordinata is the specific adsorption calculated and given in mmol/g. For the sake of comparison the scale of ordinata and abscissa is the same in each Fig.

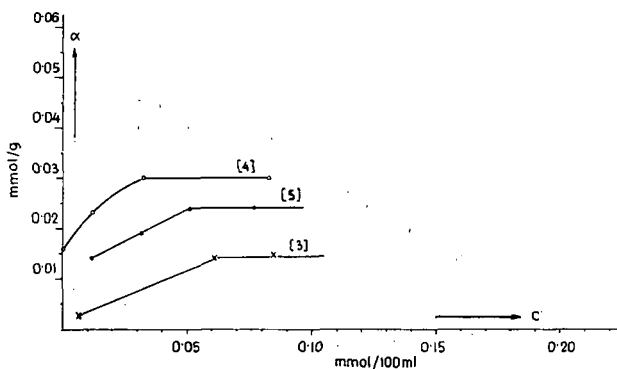


Fig. 4. Adsorption isotherms of Ca^{2+} , Cu^{2+} and Co^{2+} on natural manganite

The questions mentioned in the Introduction can be answered, at least partly, by the adsorption isotherms. According to their shape the isotherms obtained experimentally correspond either to those characteristic of electrolyte adsorption on polar adsorbent or to those of heterogeneous chemical reactions on the surface.

To use the terms unequivocally the expression „non-equivalent ion exchange adsorption” is used if the cations and anions of the electrolyte are not adsorbed at equal rate. In extreme cases only the cations of the solution are adsorbed on the surface of the adsorbent displacing the exchangeable cations from there while it is rather expedient to speak about chemo-sorption in the case of chemical reactions taking place on the surface.

Although it is hardly possible to decide surely the character of the process on the basis of the isotherms alone, some peculiar features, however, can be stated.

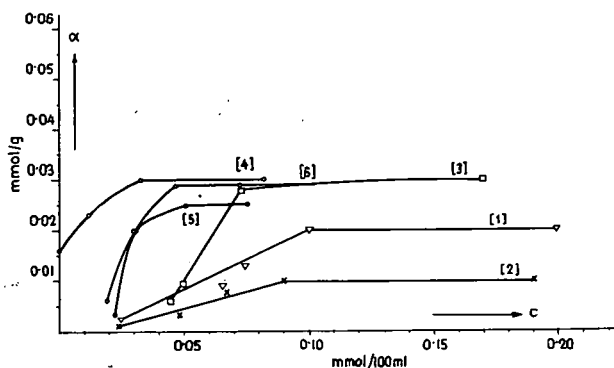


Fig. 5. Adsorption isotherms of Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} on natural cryptomelane

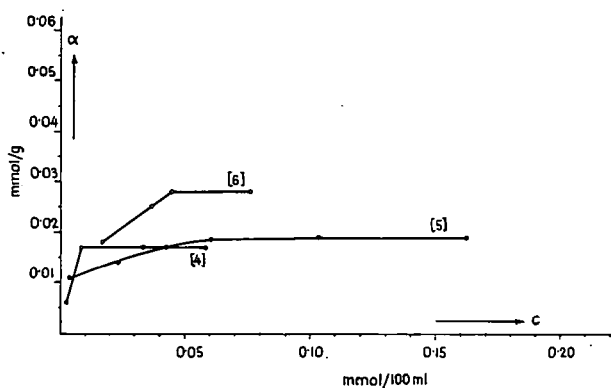


Fig. 6. Adsorption isotherms of Cu^{2+} , Co^{2+} and Ni^{2+} on artificial $\beta\text{-MnO}_2$

The steepness of isotherms gives rise to some conclusions concerning the exchange ability. The greater the exchange ability the steeper is the starting part of the isotherms. Of the samples investigated the isotherms of the ion adsorption on $\gamma\text{-MnO}_2$ are the steepest, especially in the case of Cu^{2+} , Ca^{2+} and Ni^{2+} ions. The flattest curves are those of $\beta\text{-MnO}_2$ and $\eta\text{-MnO}_2$. The adsorption was the most significant generally on $\gamma\text{-MnO}_2$ while the adsorption on Mn_3O_4 was always below 0,01 mmol/g.

The saturation was reached sometimes only at a relatively higher concentration as in the case of β -, γ -, and $\eta\text{-MnO}_2$ in respect of Co^{2+} or of $\alpha\text{-Mn}_2\text{O}_3$ in respect

of K^+ . It may be concluded that the strength of the bond of such ions is weaker than that of others reaching the saturation already at a lower concentration.

Sometimes the isotherms intersect the axis of equilibrium concentration (abscissa) as for example in the case of cryptomelane, $\gamma\text{-MnO}_2$ and $\eta\text{-MnO}_2$ in respect of Co^{2+} (Figs. 5, 6, 8, curve 5) or they intersect the axis of the specific adsorption (ordinata) e.g. the isotherms of manganite and cryptomelane in respect of Cu^{2+} (Figs. 4, 5, curve 4). It would be, however; a failure to draw conclusions from these

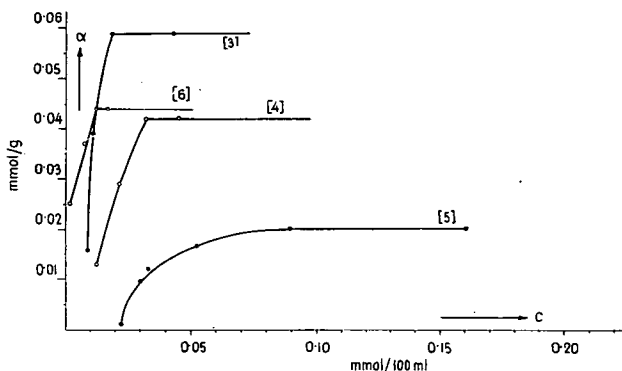


Fig. 7. Adsorption isotherms of Ca^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} on artificial $\gamma\text{-MnO}_2$

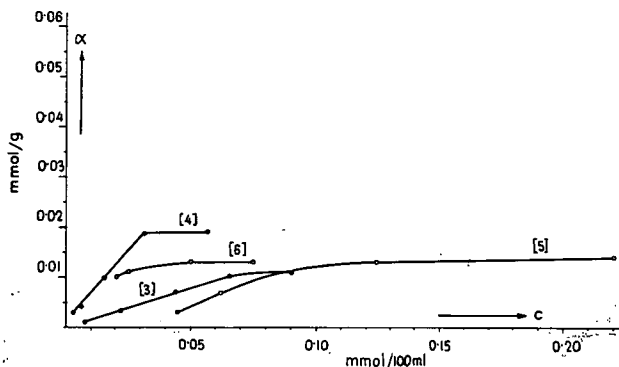


Fig. 8. Adsorption isotherms of Ca^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} on artificial $\eta\text{-MnO}_2$

facts as it was mentioned that the initial part of the isotherms is uncertain and inaccurate owing to the possible errors of the determination of fairly low concentrations. Some adsorption measurements with manganite and cryptomelane using radiochemical methods with Cu-64 and Co-60 isotopes showed that the adsorption isotherms start from the origin of the co-ordinata system. These control measurements were carried out by MR. ADAM KOVACH and MRS. HUSZTI .

How could the processes of adsorption be outlined and what supports the assumption of a non-equivalent ion exchange adsorption?

The adsorption of cations demands a net negative charge on the surface. The manganese hydroxide sol is well known for its negative charge. The crystalline

solid phase carries a net negative charge owing to substitution of cations of higher valence by cations of lower valence in the lattice. This is also possible in the lattice of manganese oxides. There are many references to such substitution. For example the quadrivalent Mn ions can be substituted in γ -MnO₂ or in other manganese oxides by trivalent or bivalent Mn ions associated with substitution of O²⁻ by OH⁻. In the case of ion exchange adsorption the cations of the solutions displace the exchangeable cations (H⁺, Na⁺ or K⁺) on the surface.

In the case of manganese oxides the non-equivalent ion exchange adsorption is rendered probable also by the fact that on treating γ -MnO₂ with a chloride-solution of calcium ions of 0,1 mmol/100 ml concentration and determining the concentration of the chloride after the equilibrium having been reached, the concentration was equal to that of the starting solution, though, at the same time 0,059 mmol/g Ca ion was adsorbed.

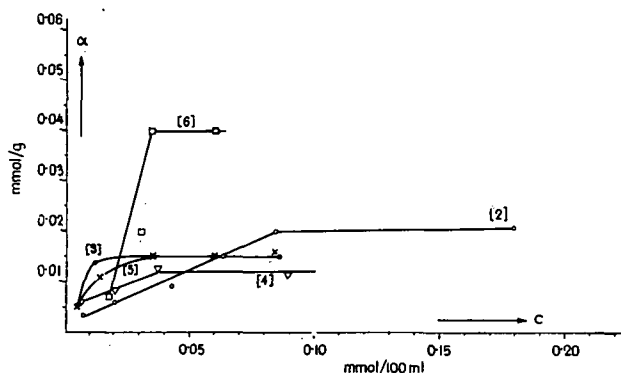


Fig. 9. Adsorption isotherms of K⁺, Ca²⁺, Cu²⁺, Co²⁺ and Ni²⁺ on artificial α -Mn₂O₃

It was very instructive to confront the behaviour of suspensions of γ -MnO₂ and cryptomelane, respectively, in 0,1 mmol/100 ml Ca-chloride solution in respect of the change of the pH value. The pH of the solution has decreased after adding γ -MnO₂ to it. The decrease in the first ten minutes amounted to nearly three pH units (pH 5,71 → pH 2,74), then a slight increase could be noted, and finally it became constant. On the contrary, the pH of the suspension of cryptomelane showed an increase only about one pH unit and reached a constant value. Treating γ -MnO₂ with distilled water a similar decrease of the pH value could be noted, however, Na⁺-desorption could not be established, though, on the surface of γ -MnO₂ beside H⁺ ions Na⁺ ions were present as exchangeable cations. The decrease of the pH on treating the adsorbent with Ca-chloride solution suggests that calcium ions of the solution first exchanged the H⁺ ions the surface resulting in a decrease of the pH and later also exchangeable Na⁺ ions (or a part of them) were displaced by the Ca²⁺ ions effecting a slight increase of the pH. Treating cryptomelane with distilled water, desorption of K⁺ ions could be established and a treatment with Ca-solution caused a K⁺—Ca²⁺ exchange from the very beginning, leading to an increase of the pH value about of one pH unit.

Comparing the amounts of various ions adsorbed by different manganese oxides (Table 3) γ -MnO₂ possesses the greatest adsorption ability, especially in respect of Ca²⁺, Cu²⁺ and Ni²⁺ ions, whereas that of β - and η -MnO₂ was much lower.

Table 3
Specific adsorption [α] in mmol/g

Adsorbent	Na ⁺	K ⁺	Ca ²⁺	Cu ²⁺	Co ²⁺	Ni ²⁺
Manganite Cryptomelane	<<0,01 0,02	<0,01 0,01	0,015 0,03	0,011 0,030	0,024 0,025	<0,01 0,029
β -MnO ₂ γ -MnO ₂ η -MnC ₂	<0i01 0,013 0,012	<0,01 0,016 0,015	<0,01 0,059 0,018	0,017 0,049 0,019	0,019 0,021 0,013	0,028 0,044 0,025
α -Mn ₂ O ₃ Mn ₃ O ₄	<<0,01 <0,01	0,02 ~0,006	0,015 ~0,008	0,01 <0,012	0,01 <0,015	0,04 <0,01

The adsorption of Na⁺ and K⁺ ions is generally low. The adsorbed quantity of Na⁺, K⁺, Ca²⁺ and even that of Cu²⁺ ion increases roughly according to the relative surface of MnO₂ modifications.

The Ni²⁺ adsorption on the oxides is higher than that of Co²⁺ ion except manganite. The manganite inclined to adsorb cobalt whereas cryptomelane adsorbed Co²⁺, Ni²⁺ and Cu²⁺ roughly in equal rate. The worst adsorption ability was shown by Mn₃O₄.

The relatively considerable adsorption on γ -MnO₂ is to be ascribed to the fact that of the three MnO₂ modifications γ -MnO₂ has the relative largest surface, further, it proved to be amorphous and such adsorbents possess generally higher adsorption ability than the crystalline modifications. On the other hand, of the crystalline modifications the stable ones have lower adsorption ability than the less stable ones. This tendency seems to be prevalent in the case of β -, and η -MnO₂, too.

Comparing the adsorbed quantities of the different ions with their concentration determined in natural manganese oxides (Tables 4 and 5) found in the literature, it may be stated that the adsorbed quantities are considerably higher than the average concentration of these ions in the Earth's crust, in the different manganese ores from India in the Hungarian manganese carbonate and oxide ores.

The adsorbed amounts fit well into the lower and upper limits of analytical data as regards the different manganese ores of the United States published by D. F. HEWETT and M. FLEISCHER [1960]. However, the adsorbed quantities are

Table 4
Specific adsorption [α] recalculated in g/t

Adsorbent	Na ⁺	K ⁺	Ca ²⁺	Cu ²⁺	Co ²⁺	Ni ²⁺
Manganite Cryptomelane	<< 230 460	< 930 390	601 1202	699 1906	1415 1474	< 587 1703
β -MnO ₂ γ -MnO ₂ η -MnO ₂	< 230 299 280	390 626 586	< 400 2365 720	1080 3113 1210	1120 1238 766	1640 2583 1467
α -Mn ₂ O ₃ Mn ₃ O ₄	< 230 < 230	785 232	601 320	763 < 635	884 590	2348 < 590

Table 5

Concentrations of Co^{2+} , Ni^{2+} and Cu^{2+} in different manganese minerals and other materials (g/t)

	Co^{2+}	Ni^{2+}	Cu^{2+}
Earth's crust, average (MASON, 1958)	23	80	45
Recent pelagic sediments: Indian Ocean (MÜLLER, 1967) Atlantic Ocean (WEDEPOHL, 1960) Pacific Ocean (WEDEPOHL, 1960)			250 130 400 soluble in 2n HCl
Indian manganese formations: [ROY, SUPRIYA, 1966] Metamorphic manganese ores Pyrolusites from colloidal dioxide ores Cryptomelanes from colloidal dioxide ores	60—160 < 100 < 100	30—1400 < 100 < 100	50—140 < 100 100—1000
Manganese oxide minerals from deposits of U. S. A. (HEWETT, D. F. and M. FLEISCHER, 1960) Supergene manganese minerals Hypogene manganese minerals	629—18 000 78—4639	150—11 942 150	79—3100 239—3515
Deep-sea manganese nodules from the Pacific Ocean (GOLDBERG, E., 1954)	120—7100	1600—11 500	1700—18 100
Manganese carbonate ores Úrkút, Hungary [NEMECZ, E., 1960]	100—500	~ 10	10—500

significantly lower than the upper limit of Co and Ni content determined in the supergene manganese minerals or the upper limit of Co in hypogene manganese minerals or than the considerable high Co, Ni, Cu content of deep-sea manganese nodules [E. GOLDBERG, 1954].

This comparison may give some information concerning the approximate quantity of ions that can be adsorbed by different minerals of manganese deposits from circulating solutions.

Naturally, it cannot be stated that the natural mineral phases corresponding to the samples studied at present will always adsorb the highest possible quantities experimentally found. It would be erroneous to assert that the amount of Co^{2+} held by adsorption on manganite always reaches the value of 1,400 g/t or that of the copper on $\gamma\text{-MnO}_2$ reaches the significant 3,113 g/t value. These values were obtained under conditions when the adsorbent was in contact with solutions containing only one electrolyte. Such conditions can hardly be supposed in natural environments.

The statement of colloid chemistry is well known that in the case of simultaneous adsorption of two or more dissolved substances the adsorption of each substance will be lower than being dissolved alone.

The experiments show that this statement is valid also for manganese oxides. Repeating some of the experiments with mixtures of different electrolytes, an essential decrease in the adsorbed quantities could be noted, even more, in some cases adsorption was not to be determined at all or at least its rate was within the error of determinations.

So, in a mixture of Na^+ -, K^+ -, Ca^{2+} -chloride solutions of 0,1 mmol/100 ml concentration, the adsorption of Ca^{2+} ions could not be detected on β - and η - MnO_2 only on γ - MnO_2 . However, the adsorption on the latter was only 1/3 of that measured in pure Ca-chloride solution. Na^+ -adsorption in the same mixture could not be measured either in the case of β - and γ - or in that of η - MnO_2 , on the contrary, Na^+ -desorption could be measured in the case of β - and η - MnO_2 . Still stronger decrease of adsorbed quantities could be determined in a mixture of Co^{2+} -, Ni^{2+} -, Cu^{2+} -sulphate solutions of the same concentrations using the three MnO_2 modifications. On the β - and η - MnO_2 adsorption of the mentioned ions could not be established, only on the γ -modification. The adsorption on the latter was, however, much lower than measured in pure solutions of the same concentration. So, the adsorbed quantity of Co^{2+} was only 1/40, that of Ni^{2+} 1/36 and that of Cu^{2+} 1/7 of the adsorbed quantities measured in solutions of single electrolytes.

Therefore, it seems not to be purposeful to attempt a conclusion that corresponding to the data obtained during the set of adsorption experiments an adequate part of the cobalt, nickel and copper content of natural manganese oxides can be considered as held by adsorption. Even more, because it is proved that in simultaneous presence of several electrolytes the adsorption does not take place on some manganese oxides.

The experiences so far may be interpreted that the adsorbed quantities from solutions containing more electrolytes may be considered as a lower limit whereas the adsorbed quantity measured in solutions containing only one electrolyte would represent the upper limit that theoretically could be reached.

SUMMARY

Summarizing it can be said that the manganese oxides in contact with dilute aqueous solutions containing different electrolytes adsorb the cations mainly by non-equivalent ion exchange adsorption, however, the possibility of equivalent adsorption and chemical reactions on the surface are presumably not out of question. The quantity of ions adsorbed by the manganese oxides is not negligible, especially taking into consideration that the processes occurring first on the surface may be extended over the whole of the adsorbent and processes like topochemical reactions may be assumed. The quantity of ions adsorbed by the different manganese oxides may be compared to that determined in the different natural manganese oxide minerals. In respect of certain ions and manganese oxides, respectively, a specific adsorption ability could be established.

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