

ON THE RELATIONSHIP BETWEEN THE DEGREE OF OXIDATION OF MANGANESE OXIDE-HYDRATE PRECIPITATES AND THE CONDITIONS OF THEIR PRECIPITATION

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INTRODUCTION

One of the essential problems in the research of sedimentary manganese ore deposits is the effect of the various factors (pH, Eh, temperature, saturation of solutions, presence of foreign ions, etc.) on the composition of manganese oxide-hydrate precipitates. Since manganese can be present in the state of 2-, 3-, and 4-valency in both artificial and natural compounds, from this point of view the role of pH and Eh and the relationship between the pH and Eh conditions of the system and the oxidation degree of the resultant oxide-hydrate, respectively, are of great importance.

It seems to be obvious that the dependence of the measured oxidation degree of a manganese oxide-hydrate on the conditions of precipitation — pH and Eh, first of all — will be justified only if the possibility of any change in the oxidation degree of oxide-hydrate during post-precipitation treatment (filtering, washing, drying) is excluded. *Nota bene*, post-precipitation changes are independent of the factors of precipitation, so that such changes cannot be correlated with them.

Apart from a few exceptions, the composition of manganese oxides, manganese oxide-hydrates (their degree of oxidation) is variable and the circumstances of precipitation and the production techniques are largely responsible for these changes. As regards the technology of production of various MnO_2 modifications and various types of manganese oxides and/or manganese oxide-hydrates of higher valency, a considerable number of references are available. Various production techniques of MnO_2 modifications α , β , γ , δ , ϵ , and η as well as the results of the examination of modifications produced by different techniques were discussed in detail by O. GLEMSER, G. GATTOW, and H. MEISIEK [1961].

Numerous production techniques of MnO_2 modifications have been described in the papers of W. F. COLE, A. D. WADSLEY and A. WALKLEY [1947]; information on the means of producing various manganese oxides and/or oxide-hydrates were presented and the relevant literature reviewed by A.D. WADSLEY and A. WALKLEY [1951]; the relationships between the production techniques and characteristics of the oxidation products of manganese (II)-hydroxide — in the first place, manga-

nese(II)-manganites and δ - MnO_2 — were dealt with by W. FEITKNECHT and W. MARTI [1945a, 1945b] and by W. BUSER, P. GRAF and W. FEITKNECHT [1954], respectively.

As shown in the afore-mentioned papers, the determination of the composition and of the oxidation degree — and, consequently, the characterization of the sample — was done on filtered, washed and dried products. The experiences suggest that manganese(II)-hydroxide and the products of comparatively lower degree of oxidation, if wet, are readily oxidizable.

Avoiding of oxidation requires very thorough preparatory measures to be undertaken, as referred to by W. FEITKNECHT and W. MARTI [1945a]. These authors noted, however, that filtering in an oxygen-free nitrogen atmosphere and washing in water, alcohol and acetone, and then the expelling of the traces of acetone in a high vacuum have proved efficient measures for the samples of comparatively lower oxidation degree rather than for the more highly oxidized ones where the organic solvents induced various kinds of secondary reactions no matter how great care was taken during the treatment. In most cases the final product is filtered, washed with water acid-free and dried either above P_2O_5 , or in a vacuum at a temperature of 50° to 60° C. In manganese dioxide modifications the composition of the final product, the Mn/O ratio, is difficult to reproduce, if at all possible, or it cannot be reproduced unequivocally. This fact is readily illustrated by the 21 different powder patterns given for γ - MnO_2 by the various authors [O. BRICKER, 1965 and G. GATTOW, 1961].

In many cases, it would be important first of all to find out the relationship between the factors of precipitation (pH, Eh) and the oxidation degree, Mn/O ratio, of the resultant solid product. Since this relationship may be influenced by possible changes due to filtering, washing, and drying, it seems to be advisable to determine the Mn/O ratio in the aqueous suspension. Nota bene, such a method would permit to bring the Mn/O ratio of the fresh suspension into a direct and clear-cut correlation with the factors of precipitation. To put it frankly, what can be determined this way is the Mn/O ratio alone, even though there is a reference [O. BRICKER, 1965] suggesting that the resultant product is identifiable by means of X-ray powder pattern, if an aliquot part taken from the suspension is passed through a $0,22\text{-}\mu$ millipore filter and then carried out the X-ray investigation. In the reference quoted here the method of the treatment of the extremely low amount of solid product before the X-ray investigation has not been shown. As believed by the author of the present paper, the determination of the oxidation degree in suspension is particularly advantageous if the stability ranges of manganese oxides and/or oxide-hydrates of different oxidation degree are to be determined.

EXPERIMENTAL

For the determination of the oxidation degree of extremely small quantities of manganese oxide products, G. GATTOW [1961] has developed a method permitting to analyse each particular weighed sample (10 to 30 mg) for both manganese and active oxygen. The method is suitable for the examination of products devoid of foreign ions or at least cations which would disturb the complexometric determination of manganese or the iodometric one of oxygen.

Since the determination of the Mn/O ratio in aqueous suspension has been aimed at, the following two problems has to be settled first of all: Is the aqueous suspension properly homogenizable in order that the sampling might be made

volumetrically rather than gravimetrically, by using weighed samples and how much is the reliability of sampling influenced by the aging of the manganese hydroxide — manganese oxide-hydrate precipitate?

Various manganese(II)-hydroxide suspensions were obtained (Table 1) in such a way that 0,1 M solution of KOH or 0,1 M solution of NaOH was added to 0,05 M solution of $MnCl_2$ until precipitation took place. During this procedure the alteration of pH was measured. The suspension was homogenized for a quarter of an hour by a vibrating mixer and then six 25-ml aliquots were pipetted with a one-sign pipette. Three of these aliquots were used for the determination of Mn, three for that of active oxygen.

The suspension devoted to the determination of manganese was added to by 1—2 drops of concentrated hydrochloric acid and 1 drop of 30% hydrogen peroxide. This led to immediate dissolution of the precipitate. Peroxide was decomposed by slight boiling and the solution was diluted to 100 ml and then 0,1 g of ascorbic acid and 5 ml of NH_4Cl-NH_4OH buffer (pH = 10) were added to it. Afterwards the solution was titrated for manganese by EDTA of 0,05 M in presence of indicator Eriochromblack T (1:200 NaCl).

The determination of active oxygen in suspension can be done at an extremely swift rate and with a high accuracy, if the method developed at the Institut für Magnetische Werkstoffe, Jena, German Democratic Republic [P. KLEINERT, 1962], is applied in the following simplified form. The 25 ml aliquot is put into an Erlenmeyer flask of 200 ml capacity equipped with a Contat-Göckel attachment and containing 10 ml 15% hydrochloric acid and 15 ml of 0,05 N solution of Mohr-salt ($Fe(NH_4)_2(SO_4)_2$). To expel the air from the flask, a few tiny sodium hydrogen carbonate crystals are dropped into it. And after the weighed suspension sample is added, the flask is immediately closed by the sodium-hydrogen-carbonate-filled Contat-Göckel attachment. The solution devoted to blank test is submitted to the same procedure. The precipitate will immediately dissolve as it is put into the flask. The excess of Mohr-salt is titrated back with 0,05 N solution of Ce(IV)-sulphate. In doing so, 1 drop of 0,025 M ferroin is used as indicator. Its colour is to change from orange-red to green. It should be noted that the suspension added to the hydrochloric-acidic Mohr-salt solution will dissolve in a few moments, so there is no need in using sodium-hydrogen-carbonate stopper. If not a suspension but a solid manganese oxide sample of high solubility is to be analysed for active oxygen, the air can be expelled in the way described above, i.e. by using a Contact-Göckel attachment filled with sodium-hydrogen-carbonate solution. On the other hand, samples of low solubility require the use of a nitrogen flow for expelling the air from the device as shown in P. KLEINERT's quoted paper. In Column 1 of Table 1 the time data of aging of the precipitate have been presented in an attempt to show the time limits of reliable homogenization in dependence on aging due to coagulation, consequently — the time range of reliable sampling and determinations.

In Column 2 the mg values of the Mn found for sets of parallel samples taken from different suspensions (3 of each), in Column 3 the mg values of active oxygen of the same samples, in Column 4 the composition of the precipitate — precisely its x value (MnO_{1+x}) — have been listed.

Grain size and rate of deposition will increase and, beyond certain limits, this may influence the reliability of sampling. Parallel determination in suspension of fresh precipitates show a good agreement, but after two- or three-week aging the suspension can no longer be homogenized, as the parallel measurements will

Table 1

Time of aging of the precipitate	Mn mg	Active O mg	Composition of the precipitate (MnO_{1+x}) $x =$	
	in 25-ml aliquots			
1	2	3	4	
Mn/O ratio determined immediately after preparation of the suspensions	31,78	0,57	0,0616	
	31,73	0,57	0,0603	
	31,73	0,57	0,0603	
	29,46	3,63	0,4230	
	29,41	3,63	0,4237	
	29,41	3,63	0,4237	
	28,90	0,84	0,0998	
	28,93	0,84	0,0997	
	28,93	0,84	0,0997	
	29,41	0,34	0,0388	
	29,41	0,35	0,0399	
	29,34	0,37	0,0434	
	Determination after 1-day aging	28,05	0,93	0,1138
		27,69	0,94	0,1165
		27,75	0,94	0,1163
Determination after 2-day aging	26,27	etc.	1,1150	
	26,13	0,88	1,1183	
	26,54	0,90	1,1151	
Determination after 7-day aging	26,90	2,11	1,2705	
	27,09	2,06	1,2611	
	26,81	2,11	1,2715	

show inacceptably great divergences. It is possible, however, that acceptable results may be obtained even for long-aged precipitates, if homogenization techniques, outscoring the intensity of the vibratory mixer, are introduced. At any rate, as proven by the tabulation, volumetric sampling from homogenized suspensions permits to determine, with proper accuracy, both the Mn and active oxygen contents of the suspension and to calculate the Mn/O ratio.

Another aim of the work reported here has been to find out the differences in oxidation degree and Mn/O ratio determined in the suspension itself (as shown above), on the one hand, and in the filtered, washed and dried solid product, on the other. Therefore, on the one hand, the MnO_{1+x} composition was determined directly in manganese(II)-hydroxide suspensions precipitated

Table 2

Composition (MnO_{1+x}) found	
in suspension $x =$	in filtered, washed and dried product $x =$
0,0296	0,3700
0,0466	0,3688
0,0338	0,3667
0,0389	0,3514
0,0356	0,3768
0,0409	0,3594
0,0436	0,3580
0,0416	0,3500

from 0,05 M MnCl_2 solution by 0,1 M KOH or 0,1 N NaOH; on the other hand, other suspension aliquots were filtered, washed with ion-free water, dried at 60°C for 24 hours and then the composition of the resultant product was determined. The results are shown in Table 2.

As shown by the results, the precipitation-dependent oxidation degree, determined in the suspension itself, is much lower than the figure obtained for the filtered, washed and dried solid product which was precipitated under the same conditions and had a composition close to, and an oxidation degree somewhat higher than that of Mn_3O_4 ($\text{MnO}_{1.33}$).

So as regards the relationship between precipitation conditions and resultant product, it appears from the above that what is more logical to consider dependent on precipitation conditions is the oxidation degree of the fresh suspension rather than the figure found for the solid product after filtering and drying.

SUMMARY

An investigation into the oxidation of manganese(II)-hydroxide in aqueous solution and into relationships between the oxidation degree of precipitates and conditions of precipitation has revealed substantial differences between the Mn/O ratio in the suspension, on the one hand, and the oxidation degree of the product that resulted from the filtering, washing and drying of the precipitate, on the other. The techniques described here make it possible to determine the oxidation degree of manganese(II)-hydroxide and/or manganese oxide-hydrate directly in the fresh suspension. This fact seems to justify the view that it is the oxidation degree found in fresh suspension that depends on the conditions of precipitation rather than the composition and the Mn/O ratio determined in the filtered and dried solid product. In this latter case any change in oxidation degree is no longer dependent on the conditions of precipitation, but is provoked by post-precipitation processes such as filtering, washing, and drying.

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