Chemical Effects of Nuclear Transformations in Metal Permanganates

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=Abstract=

The chemical effects resulting from the capture of the thermal neutrons by manganese in different crystalline permanganates, that is, potassium permanganate, sodium permanganate, silver permanganate, barium permanganate and ammonium permanganate, have been investigated. The distribution of radioactive manganese formed has been determined by using different absorbents and ion-exchangers, that is, manganese dioxide, alumina, Zeolite A-3, Kaolinite and Dowex-50. The distribution of radioactive manganese in various adsorbents and ion-exchangers has almost similar result for each permanganate. The affinity for radioactive manganous ion is greatest for Dewex-50.

A significant increase of retention is shown through the thermal annealing and the retention depends on the first ionization potential of metal ion in permanganates.

1. INTRODUCTION

The most characteristic quantity associated with the chemical effects of nuclear transformation in solid compound is the retention, that is, the fraction of the total activity found after the irradiation in same chemical form as the target substance. The retention is increased in irradiated solids by very gentle heating, or by subsequent irradiation with ionizing radiation. Both these phenomena are due either to the recombination of the fragments produced by recoil or to some electronic relaxation or redistribution of charge. Adsorption phenomenon takes a significant part in the radiochemical analysis of recoil fragments. It depends upon the chemical properties of recoil species, their state in solution, the type of adsorbent and the nature of its surface.

The pH dependence of retention in permanganates has been studied by several authors[1~5] to the variations of the adsorption of manganous on solid surfaces. Libby[1] found that the retention against pH curve was flat in shape from about pH 2 to about pH 10. Apers and Harbottle[2] reinvestigated the hot-atom reactions of recoil ^{56}Mn in neutron-irradiated potassium permanganate. At pH values more alkaline than 1 the cationic activity is tightly adsorbed onto traces of MnO_2 or added Al_2O_3. The pH sensitivity of the retention in $KMnO_4$ largely disappears if the crystals are annealed before analysis. Shiokawa and Sasaki[6] studied the thermal annealing behaviour of recoil manganese atoms produced in alkali metal permanganates by

$^{55}Mn(n, 2n)$ ^{54}Mn and $^{55}Mn(n, \gamma)$ ^{56}Mn reactions. In the case of potassium permenganate, the thermal annealing of ^{54}Mn proceeded faster than that of ^{56}Mn. The retention of ^{54}Mn in the annealing curve decreased after an initial increase when it was treated at 180°C, while this irregularity was not observed in the case of ^{56}Mn. Teeling and Aten Jr. et al.[7] studied the influence of recoil energy on the retention and on the thermal annealing of radiomanganese in $KMnO_4$ and reported that the recoil energy is of no great influence. Dedgaonkar, Kulkarni and Dharmadhikari[8] studied the thermal/radiation annealing and decomposition in neutron activated $KMnO_4$, and found the activity distribution in $KMnO_4$ in the ratio of 22 : 6 : 72 in the Mn^{7+}: Mn^{4+}: Mn^{2+} states.

In this paper, the chemical effects resulting from the thermal neutron capture by manganese in different permanganates have been investigated. The distribution of radioactive manganese formed has been determined by using different adsorbents and ion exchangers.

2. EXPERIMENTAL

2.1 Materials

Ammonium permangante was prepared by the addition of ammonium chloride to a solution of potassium permanganate. The solution was filtered hot through a sintered glass funnel, to remove manganese dioxide. and cooled immediately in ice. The crystals were twice recrystallized from redistilled water. Kaolinite, Zeolite A-3 and Dowex-50 were of chromatographic grade. All the other chemicals used were of A.R. quality.

2.2 Neutron-irradiation and thermal annealing

About 3 mg each of permanganates, that is, potassium permanganate, sodium permanganate, silver permanganate, barium permanganate and ammonium permanganate, was neutron-irradiated for 3 minutes at a thermal neutron flux of $5 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ in a pneumatic tube of TRIGA mark III reactor at the Korea Advanced Energy Research Institute. After neutron-irradiation the thermal annealing treatment of permanganates was carried out by using a high temperature oven at $180 \pm 2°C$ for 2 hours, because a thermal decomposition of the sample began to occur over 190°C.

2.3 Separation procedure

The neutron-irradiated permanganates were dissolved into redistilled water at room temperature. The chemical species of radioactive manganese were separated into three fractions: MnO_4, MnO_2 and Mn^{++}. The radioactive permanganate ion was separated from the reduced species by shaking with 200 mg each of adsorbents (manganese dioxide, and alumina) and ion exchangers (Kaolinite, Zeolite A-3 and Dowex-50) for 30 minutes, followed by filtration through a sintered glass funnel. The adsorbents and the ion exchangers which contained radioactive manganese dioxide and manganous ion were washed with redistilled water until the purple colour of permanganate ion disappeared completely. The radioactive manganous ion was eluted with 10 ml of 10% manganous nitrate solution and 5 ml of concentrated nitric acid from the adsorbent or ion exchanger fraction. The fraction of adsorbent or ion exchanger was reduced into a solution by hydrochloric acid

Table 1. ^{56}Mn activity distribution(%) in neutron-irradiated $KMnO_4$

Adsorbent Ion-exchanger	MnO_4^-		MnO_2		Mn^{++}	
	Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed
MnO_2	21.7±1.5	38.4±1.1	1.4±0.1	12.8±1.2	76.9±2.5	48.8±1.8
Al_2O_3	22.8±1.7	35.6±2.1	0.9±0.5	10.8±0.9	76.3±2.2	56.3±2.1
Zeolite A-3	23.6±2.1	34.5±1.5	3.2±1.1	10.5±0.4	73.2±2.1	54.0±1.5
Kaolinite	23.4±1.9	36.8±0.9	0.7±0.2	10.8±0.7	75.9±2.7	52.4±0.9
Dowex-50	19.6±0.7	39.2±1.0	2.1±0.7	5.0±1.2	78.3±1.5	55.8±0.9

Table 2. ^{56}Mn activity distribution(%) in neutron-irradiated $MaMnO_4 \cdot H_2O$

Adsorbent Ion-exchanger	MnO_4^-		MnO_2		Mn^{++}	
	Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed
MnO_2	14.9±1.5	27.8±2.2	9.7±1.1	15.9±1.0	75.4±2.5	56.3±1.1
Al_2O_3	12.9±1.2	29.4±1.7	7.7±0.8	9.6±1.2	79.4±2.5	61.0±2.1
Zeolite A-3	11.5±0.5	28.7±1.4	9.1±1.0	13.2±1.8	80.4±1.1	58.1±1.0
Kaolinite	12.8±2.2	30.7±2.4	7.6±0.5	9.2±1.1	79.6±1.9	60.1±1.5
Dowex-50	10.3±0.4	27.9±1.1	5.4±0.7	6.2±0.9	84.3±1.5	65.9±1.5

Table 3. ^{56}Mn activity distribution (%) in neutron-irradiated $AgMnO_4$

Adsorbent Ion-exchanger	MnO_4^-		MnO_2		Mn^{++}	
	Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed
MnO_2	7.1±0.3	18.6±1.2	17.4±1.1	26.5±2.1	75.5±2.5	54.9±2.1
Al_2O_3	4.5±0.3	15.6±1.3	12.8±1.4	19.8±1.1	82.7±2.1	64.6±1.8
Zeolite A-3	5.1±0.9	19.2±0.8	8.6±0.5	19.5±1.1	84.3±1.7	61.3±1.2
Kaolinite	6.1±1.1	17.5±1.5	11.0±0.8	29.4±1.2	82.9±1.5	53.1±1.1
Dowex-50	4.8±0.5	15.1±0.7	5.7±1.1	10.3±0.8	89.5±1.1	74.6±1.2

containing a small amount of hydrogen peroxide.

2.4 Paper-electrophoresis

The paper-electrophoretic separation of radioactive manganese was carried out with a specially designed paper-electrophoresis apparatus[9]. A strip of Whatman No. 1 filter paper, 40 cm long and 1.5 cm wide, was wetted with 0.1 M-HNO$_3$ supporting electrode solution and the excess solution was soaked with filter paper. The strip was set on the migration plate and its both ends were dipped into the electrode cells containing 300 ml each of 0.1 M-HNO$_3$ electrolyte. About 0.01 ml of neutron-irradiated permanganates dissolved in 0.5 H-HNO$_3$ was applied at the fiducial point of the paper strip. The electrodes were connected to the D.C. power supply, Toyo Model BA-8, Osaka, Japan, and a potential of 1,000 volts was applied for 20 minutes. After the electrophoresis run was over, the strip was removed from the migration apparatus, dried and cut into pieces of 1 cm length.

Table 4. ^{56}Mn activity distribution(%) in neutron-irradiated Ba(MnO$_4$)$_2$

Adsorbent on-exchanger	MnO$_4^-$		MnO$_2$		Mn^{++}	
	Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed
MnO$_2$	12.8±2.4	27.1±1.7	9.0±0.5	19.3±0.8	78.2±2.1	53.6±1.8
Al$_2$O$_3$	13.5±1.2	28.2±1.8	2.6±1.0	16.5±1.2	83.9±2.5	55.3±2.1
Zeolite A-3	14.6±1.1	29.2±1.4	5.5±0.2	15.2±1.5	80.4±1.7	55.6±2.5
Kaolinite	12.5±0.4	26.1±1.1	5.4±0.8	13.1±0.7	82.1±2.8	60.8±3.1
Dowex-50	10.5±1.1	26.5±0.9	4.7±1.1	6.1±1.0	84.8±1.5	67.4±2.5

Table 5. ^{56}Mn activity distribution(%) in neutron-irradiated NH$_4$MnO$_4$

Adsorbent Ion-exchanger	MnO$_4^-$		MnO$_2$		Mn^{++}	
	Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed
MnO$_2$	16.4±1.8	33.1±1.4	7.7±0.5	18.5±1.2	75.9±2.5	48.4±1.0
Al$_2$O$_3$	16.9±1.1	35.1±3.1	11.6±1.1	20.0±1.5	70.5±2.4	44.9±2.4
Zeolite A-3	17.4±0.9	36.4±1.5	12.2±0.4	21.3±1.4	70.4±1.1	42.3±1.4
Kaolinite	18.2±1.1	33.2±2.4	15.1±1.1	20.5±1.0	66.7±0.4	46.3±4.1
Dowex-50	16.7±1.7	38.9±1.5	10.1±1.0	12.1±1.1	73.2±1.2	49.0±2.1

The radiaoctivity was measured by means of Baired model 810 poly-spec research spectrometer, connected with a well type NaI (Tl) gamma scintillation detector. The intensity of 0.847 MeV gamma-ray was measured for ^{56}Mn.

3. RESULTS

3.1 Separation by adsorption and elution

The optimal shaking time for the separation by adsorption and elution was determined using Dewex-50 with permanganates for 15 minutes, 30 minutes, 45 minutes and 1hour period, and found 30 minutes. Table 1~5 indicate the radioactivity distribution of ^{56}Mn in the MnO$_4^-$ MnO$_2$ and Mn^{++} forms observed following neutron-irradiation of permanganates, that is, potassium permanganate, sodium permanganate, silver permanganate, barium permanganate and ammonium perma-

nganate, while using manganese dioxide, alumina, Zeolite A-3, Kaolinite and Dowex-50 for separation. The distribution of radioactive manganesen in various adsorbents and ion-exchangers has almost similar result for each permanganate, that is, in KMnO$_4$ approximately in the ratio of 22 : 2 : 76 in the MnO$_4$: MnO$_2$: Mn^{++} states, in MaMnO$_4$·H$_2$O in the ratio of 12 : 8 : 80, in AgMnO$_4$ in the ratio of 6 : 11 : 83, in Ba(MnO$_4$)$_2$ in the ratio of 13 : 5 : 82 and in NH$_4$MnO$_4$ in the ratio of 17 : 11 : 72.

3.2 Annealing treatment

The results of thermal annealing are shown in Table 1~5. The retention values of annealed permanganates are higher than those of unannealed permanganates in each adsorbent and ion exchanger.

3.3 Separation by paper-electrophoresis

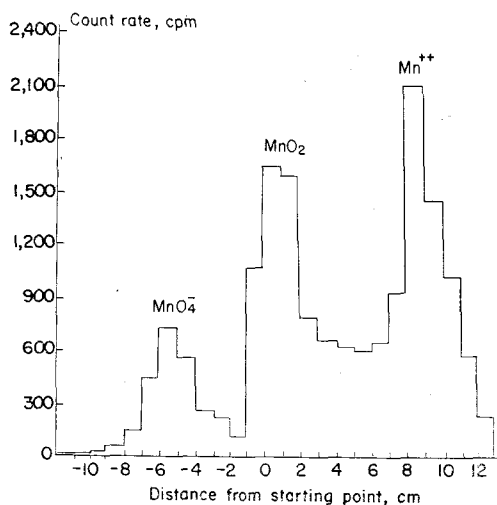A typical paper-electrophoresis histogram

Fig. 1. Paper-electrophoresis histogram of neut-
ron-irradiated sodium permanganate.

of neutron-irradiated permanganates is shown
in Fig. 1. A considerable amount of the ra-
dioactivity remains almost at the starting
point, due to the formation of MnO_2. The
peaks at -6 cm and $+9$cm are represented
anionic MnO_4^- and cationic Mn^{++}, respectively.

4. DISCUSSION

4.1 Nature of the fragments

The fragments, Mn^{++} and MnO_2, produced
following neutron-irradiation of permangana-
tes are characterized by the following assu-
mptions.

An atom does not lose or gain any electrons
on modest recoil. When such an atom is bo-
und in a covalent molecule, it leaves its site
without further ionization. In this case, the
effective charge of the manganese in a per-
manganate ion is close to zero or less than
unity. After neutron capture, molecular oxy-
gen is left as is observed in radiolytic deco-
mposition and the manganese atom recoils in
its original charge state. If there is any po-
ssibility for the recoil atom to remain tra-

pped in the crystal lattice, or if it loses one
or two electrons, the possibility of recove-
ring it on solution in a highly reduced state
is not excluded. The reduced manganese is
converted into manganese dioxide by the
reaction:

$$3\,Mn^{++}+2\,MnO_4^-+2\,H_2O \rightarrow 5\,MnO_2+4\,H^+$$
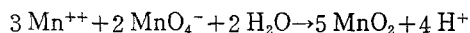
But this reaction is slow at room tempera-
ture and in the absence of catalyst, so their
survival of the reduced state is possible.
Some reduced species, Mn^{++} and Mn^{+++}, sur-
vive and are adsorbed on the surface of any
adsorbent or ion-exchanger, and some of re-
coil manganese is recovered as the mangan-
ese dioxide. Therefore, the radioactive man-
ganous ion fraction obtained after dissolution
is already present in the solid state following
neutron-irradiation, not the result of extran-
eous reaction of the recoil fragments with
water.

The activity presented as MnO_2 is not ori-
ginally formed in solid. It is explained that,
based on the assumption that the recoiling
atom retains its oxidation state unchanged
even when it has become thermalized, some
bond breaking occurs leaving the recoil atom
linked to a reduced number of oxyanions and
trapped in the crystal lattice, from which it
is released only on solution. The possible
fragments are as follows: MnO_3^+, MnO_2^{3+},
MnO^{5+}, Mn^{7+}. As oxygen ions are available,
the MnO_3^+ species are present in the largest
proportien. The $^{56}MnO_2$ activity is originated
from $^{56}MnO_3^+$, which is reduced to $^{56}MnO_2$ in
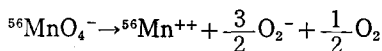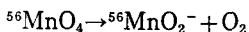neutral aqueous medium:

$$2^{56}MnO_3^+ + H_2O \rightarrow 2^{56}MnO_2 + 2H^+ + \frac{3}{2}\,{}^3O_2$$
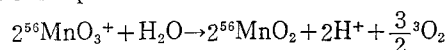
Also the MnO_2 activity is not due to the in-
complete desorption of Mn^{++} and/or its oxi-
dation during the chemical separation.

The lowest value of $^{56}MnO_2$ in Dowex-50
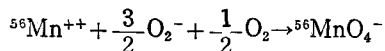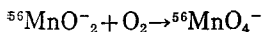is due to the difference of general properties,

that is, ion-exchange capacity or cationic affinity of organicion-exchanger for $^{56}Mn^{++}$ is greater than that of inorganic ionexchanger or alumina and MnO_2. After the thermal annealing, the increase of $^{56}MnO_2$ is due to the presence of colloidal manganese dioxide which is formed during the dissolution of decomposed permanganate in neutral water.

4.2 Retention

The observed retention values of unannealed and annealed permanganates can be explained by the hot zone model[10], in which chemical reaction, returning into parent form, in the quenched hot zone of solid proceeds further by receiving the energy through thermal annealing. The annealing mechanism is as follows:

$$^{56}MnO_4 \rightarrow ^{56}MnO_2^- + O_2$$

$$^{56}MnO_4^- \rightarrow ^{56}Mn^{++} + \frac{3}{2}O_2^- + \frac{1}{2}O_2$$

$$: \text{due to recoil}$$

$$^{56}MnO_2^- + O_2 \rightarrow ^{56}MnO_4^-$$

$$^{56}Mn^{++} + \frac{3}{2}O_2^- + \frac{1}{2}O_2 \rightarrow ^{56}MnO_4^-$$

$$:\text{during annealing[5]}.$$

$^{56}MnO_2^-$ and $^{56}Mn^{++}$ are to be formed during activation and they remain trapped at the recoil site. These species oxidize to $^{56}MnO_4^-$ by second reaction on heating.

In Fig. 2, the retention values after the thermal annealing depend on the first ionization potential of metal ion in permanganates, that is, the large retention is obtained with the decrease of ionization potential. This effect suggests that the process might be

$$^{56}Mn^{++} \rightarrow ^{56}MnO_4^- + 5e^-$$
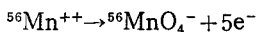
through an electron-transfer exchange reaction between the permanganate ion and the reduced species of those manganese recoil
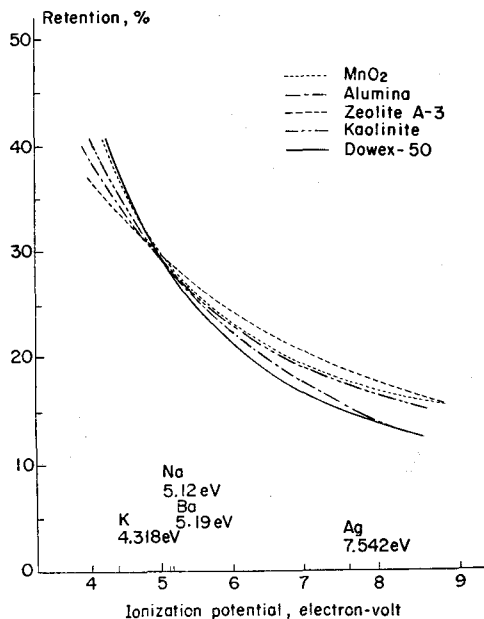

Fig. 2. The relationship between retention and the ionization potential of metal ion in permanganates with adsorbents and ionexchangers.

which are positively-charged.

The retention of hydrated permanganate, $NaMnO_4 \cdot H_2O$, is a little low and this is due to the reducing action by the water of hydration[11]. In ammonium permanganate, a hot atom reaction, which the recoil fragment strikes and reacts with an ammonium ion, decomposes NH_4 to produce NH_3 and H^+ [11]. NH_3 molecule is coordinated to the ^{56}Mn recoil species forming a complex and decreasing the possibility of its reformation to obtain the parent state.

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금속 과망간산염의 핵변환에 의한 화학적 효과

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=요   약=

금속 과망간산염 즉 과망간산칼륨, 과망간산나트륨, 과망간산은, 과망간산바륨, 과망간산암모늄에서 망간의 중성자 포획으로 야기되는 화학적 효과를 고찰하였다. 생성된 방사성 망간의 분포는 각종 흡착제 및 이온교환체 즉 이산화망간, 알루미나, 제올라이트 A-3, 카울리나이트, 도엑스 -50을 사용하여 결정하였다.

각종 흡착제 및 이온교환체에 대한 방사성 망간의 분포는 각 과망간산염에 대하여 거의 유사한 결과를 갖는다.

방사성 망간의 친화력은 도엑스 -50이 가장 크다.

잔류율의 현저한 증가가 열—어니일링을 통하여 나타나며 잔류율은 각 과망간산염의 금속이온의 제1차 이온화 전위에 의존한다.