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<Original> Room Temperature Annealing Process of Recoil Fragments in Neutron Irradiated Ammonium Chromate

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Abstract

The retention of ^{51}Cr was studied as chromate after dissolution of irradiated ammonium chromate with reactor exposure time and various storage time at room temperature.

The annealing process of ammonium chromate depending on various storage time at room temperature follows first-order kinetics from zero time value to the pseudo-equilibrium value. The retention is increased with reactor irradiation time, also following first-order kinetics.

요 약

상온에서 $(NH_4)_2CrO_4$ 를 원자로에 조사하고, 조사된후 상온에서 보관된 시간과 ^{51}Cr 의 잔류값을 반응속도론적으로 연구하였다. 또한 원자로 조사시간 변화에 따르는 ^{51}Cr 의 잔류값을 반응속도론적으로 고찰하였으며 일차반응으로 표시 될 수 있었다.

1. Introduction

In the study of the Szilard-Chalmers effect, the retention is indicated as a percentage, that is the fraction of the activity retained by the irradiated species which is not extracted by the physcial or chemical methods used[1].

Maddock and Vargas[2] showed that the density and nature of the crystal defects in the irradiated material influence the retention, as well as the kinetic parameters of the subsequent thermal annealing of the recoil damage. Thermal annealing of the neutron irradiated potassium chromate has been studied by Green, Harbottle and Maddock[3]. They found that heating of the irradiated salt increased the retention and subsequent gamma irradadiation of the neutron irradiated sample resulted in a higher retention value.

Maddock and De Maine[4] postulated that the recoil fragments formed in the chromates should give Cr^*O_3, Cr^*O^{+2}, Cr^{*-4}, and Cr^{*+6} ions[3,4,5].

When the irradiated crystals are dissolved in water prior to analysis these fragments will result in the production of chromate by Cr^*O_3, $Cr^*O_2^{+2}$, since chromic anhydride and chromyl ions are known to hydrolyse to chromate under all condittions of pH. As a consequence of the nuclear process oxide ions may be ejected or lost from the original molecular ion CrO_4^{-2}. Oxide ions are brushced off during passage of the recoil fragment through the intense electrostatic fields in the crystalline matrix.

The basic annealing reaction is assumed to be

$$Cr^{*}O^{+4}+O^{-} = CrO_2^{+2},$$

and the oxide ion is assumed to be mobile.

In this work, ammonium chromates were chosen for the investigation of process associated with the Szilard-Chalmers effect. Because the half-life of ^{51}Cr is long(27.8 days) enough, lengthy experimental studies are possible. Besides, the retention of ammonium chromate is quite different from other metal chromates.

2. Experiment

2.1. Materials and Neutron Irradiation

All samples for irradiations were contained in polyethylene vials and the irradiations were performed in the pneumatic tube of TRIGA Mark Ⅱ at Atomic Energy Research Institute in Seoul. The norminal thermal neutron flux is about $3\times10^{12}n/cm^2/sec$ and the irradiation times ranged from 10 minutes to 2 hours. All reagents used in chemical procedures were of A. R. grade.

2.2. Chemical Procedures

2.2.1. Preliminary Separation Experiment

Carrying effect of carrier solutions; To investigate of carrying effect of carrier solution, various carrier solutions were prepared. Ten mg of $Al(No_3)_2\cdot9H_2O$/ml, 10 mg of $K_2Cr_2(SO_4)_4\cdot24H_2O$/ml and 10 mg of $FeCl_3\cdot6H_2O$/ml. One ml of the above carrier solution was added to separately to $(NH_4)_2CrO_4$ (200 mg of $(NH_4)_2CrO_4$/3 ml of H_2O) and 100λ of $^{51}Cr(Ⅲ)$ tracer were added. The above carrier solutions (1ml) and 100λ of$^{51}Cr(Ⅲ)$ tracer were added to inactive $(NH_4)_2CrO_4$ solution (200 mg $(NH_4)_2CrO_4$/5 ml of H_2O) in the three 50 ml centrifuge tubes. Precipitates were yielded by adding buffer solution of 1 M NH_4OH+NH_4Cl to the above mixed solutions. The precipitates were separated from filtrate and washed several times with the 1.5 ml of buffer solution.

The retention dependence on concentration of solution; 200 mg of irradiated ammonium chromate solids were dissolved in 1 ml, 2 ml, 5 ml, 20 ml of distilled water. The precipitates were obtained by the same method as mentioned before.

2.2.2. Separation of Recoil Species

Irradiated 100 mg samples which were stored various time intervals at the room temperature were dissolved in 10 ml distilled water and adjusted at pH about 9. The recoil fragments of trivalent chromium were coprecipitated with 1 ml(10 mg Al^{+3}/ml) Al^{+3} non-isotopic carrier as $Al(OH)_3$ precipitate[6]. The precipitate was filtered by a stainless filtering apparatus under slow suction and washed with small amounts of water containing trace amount of ammonia.

2.3. Counting

Precipitate and filterate phases radioactivity of ^{51}Cr was measured using NaI(Tl) scintillation counter.

Retention was computed from the ratio between precipitate and total activity of both phases. Each results consist of the average value obtained for three irradiation sets with same irradiation condistions.

3. Results and Discussion

3.1. Preliminary Separation Experiment

It is requested for the separation of micro amounts of $^{51}Cr(Ⅲ)$ from target Cr(Ⅵ) compund. The results of carrying effects of carrier solutions are as follows.

Fe(Ⅲ) carrier solution shows the highest activity recovery yield, however a good reproducibility and easiness of handling during chemical process was observed in Al(Ⅲ)

Table 1. Carrying effect of isotopic and non-isotopic carrier

Carrier	Activity in filtrate (cpm)	Activity in precipitate (cpm)	Activity recovery in precipitate(%)
Cr(Ⅲ)	64	14,212	99.5
Fe(Ⅲ)	38	15,688	99.7
Al(Ⅲ)	74	12,949	99.4

carrier solution. Therefore we have used the Al(Ⅲ) solution as a carrier solution.

3.2. The retention Dependence on Concentration of Solution

The results of concentration effects on retention are as follows;

Table 2. Retention in various concentration of $(NH_4)_2CrO_4$

Concentration	10mg/ml	40mg/ml	100mg/ml	200mg/ml
Retention	9.0	9.8	10.7	12.1

The results show that the less concentrated solutions are the less retention values. The phenomena could be explained that the trapped recoil species in the dilute medium might be less probability in recombination compared to the concentrated medium.

3.3. Kinetics Studies

The results are given as values of the retention. The retention of samples irradiated for 10 minutes -2 hours was determined at room temperature and found to increase with the increase of reactor exposure time.

Inspection of Table 3 and Fig. 1 shows that the kinetics of the process proceed by a simple first-order process.

In the each reactor irradiation, the retention increases at first rapidly and then appears of pseudo plateaus at room temperature after about 18 hours. Fig. 2 shows that the shorter the irradiation time is the smaller their retention value and the existence of various original retention values differs depend on reactor irradiation time. The retention at the end of reactor irradation was obtained by graphical extrapolation. The rate of recombination is

Table 3. Retention value(R_t) versus irradiation time(t') and storage time(t) at room temperature for ammonium chromate

**	*5	20	40	60	120	240	420	1,440
10	13.0	14.0	14.1	14.5	15.3	16.2	16.8	17.4
330	14.8	15.0	15.2	15.7	16.7	18.7	17.1	17.4
60	16.0	16.1	16.4	16.4	16.8	17.1	17.4	17.4
120	17.0	17.0	17.0	17.1	17.2	17.4	17.4	17.4

* Storage time in minutes at the room temperature
** Irradiation time in minutes

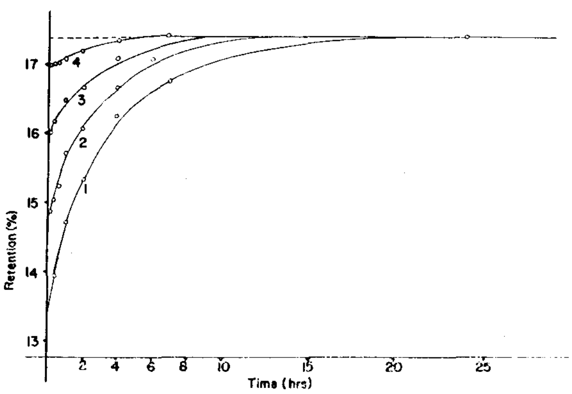

Fig. 1. Plot R_t versus storage time(t) about irradiation time.
1) 10 minutes 2) 20 minutes
3) 60 minutes 4) 120 minutes

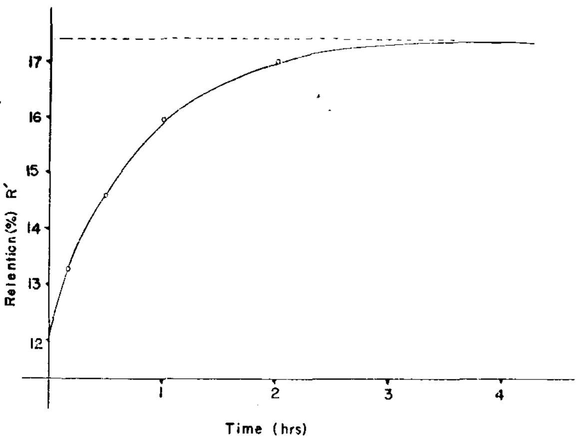

Fig. 2. Plot R_o versus irradiation time(t')

given by $by\text{-}dn/dt=kn$, where n is the number of uncombined pair and k is reaction rate constant. As an integration of the above equation, we can get simple first-order law that $n_t=n_0e^{-kt}$, in whcin n_t and n_0 are the number of uncombined pairs at times t and zero, respectively.

The above equation can be expressed in terms of retention as follows;

$$R_\infty-R_t=(R_\infty-R_0)e^{-kt}$$
$$\Delta R=(\Delta R)_\infty e^{-kt}$$

in which R_t and R_∞ are the retention at time t and at the pseudo plateau of isothermal annealing and $R_\infty-R_t$ is fraction destined to anneal at time t.

Various storage time at room temperature versus $log(\Delta R)$ plot allows for the computation of four sets of room temperature annealing kinetics curves in Fig. 3. The value of apparent rate constant k is 3.85×10^{-5} sec^{-1}.

As shown in Fig 2. the retention of ammonium chromate is proportional to irradiation time. A number of experimentals obtained similar curves in potassium chromate[3,4], antimony pentaflouoride[7], and copper oxinate[8].

Similar expression of the annealing during the reactor irradiation can be made. Reactor annealing is labbelled by single prime: R'(the

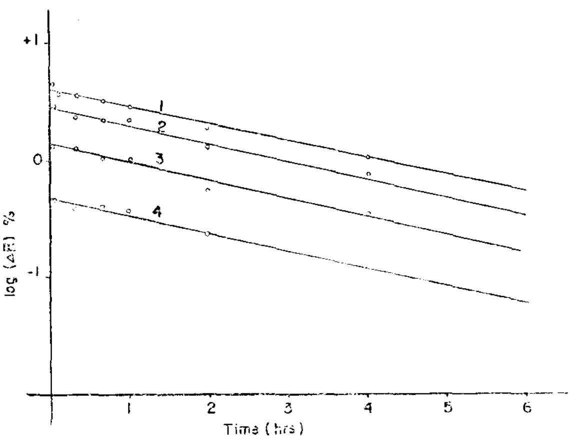

Fig. 3. Plot log(ΔR) versus storage time(t)

Table 4. Variation of the retention R_0 with the time of irradiation t' for ammonium chromate

t'(min)	10	30	60	120
R_0	13.3	14.6	16.0	17.0

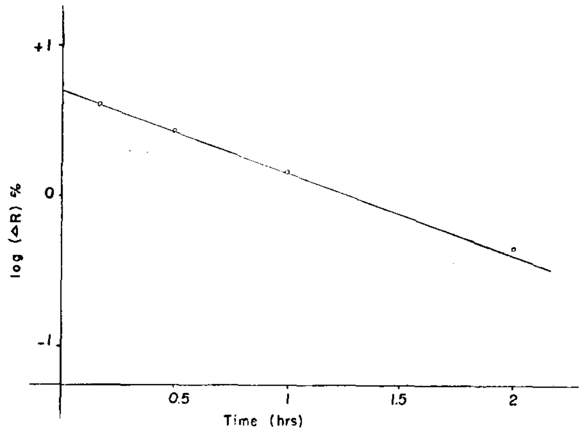

Fig. 4. Plot(ΔR) versus irradiation time(t')

retention at the end of irradiation at various irradiation time), this value virtually equals R_0, also $R'_\infty=R_\infty$ is hold, then we can use above equation directly to the reactor annealing.

The above relationships were plotted in Fig. 4 and the numberical value of $k'=1.54\times10^{-4}$ sec^{-1} was obtained by the graphical method. It also must be pointed out that elucidation the retention of chromates should give about 70%-80% of original retention from the relationship between retention and oxidation potentials[9]. But the retention of ammonium chromate is rather low than the corresponding alkali metal chromate[4].

Harboltle[4] explained this effect as a reduction of recoil fragments by the ammonium ions, Getoff[10] explained this effect that the reducing properties of the hydrazine originating from the ammonium group play an essential role in the various annealing processes. Ma dock and De Maine[5] kept the irradiated potassium chromate in air at room temperature for periods up to four months but the retention value was not altered. However in this work the significant alternation of the retention values was observed at the room temperature annealing process. Ammonium group might be responsible for the striking difference of room temperature annealing behavior in comparison with that of potassium chromate, the likely mechanism of the room temperature annealing process is migration of oxide ion to the fixed number of traps or sinks.

References

1) M. Hainssinsky, Nuclear Chemistry and its applications Addison-Wesley Publishing Company Inc. 488 (1964)

2) A.G. Maddock and J.I. Vargas, Nature, **184**, 1931 (1959)

3) J.H. Green, G. Harbottle and A.G. Maddock, Trans, Faraday Soc. **49**, 1413 (1953)

4) G. Harbottle, J. Chem. Phys. **22**. 1083 (1954)

5) A.G. Maddock and De Maine M.M., Can J. Chem. **34**, 275 (1956)

6) R.W. Cline, R.E. Simmone and W.R. Rossmassler, Anal. Chem. **30**, No. 6, 1117 (1958)

7) R.R. Williams Jr., G.H. Janks, W.B. Leslie, J.W. Richtet and Q.V. Larson, Radiochemical Studies: The fission product book 1, Edited by C.D. Coryell and N. Sugarman. McGraw-Hill Book Company, Inc. p 184, (1953)

8) I. Negoeseu and T. Costea, Can. J. Chem. **40**, 1642 (1964)

9) G. Harbottle and N. Sutin, Advances in Inorganic Chemistry and Radiochemistry, Edited by H.J. Emeleus and A.G. Sharpe, Vol. 1, Academic Press, New York, London, 1959, p 274

10) N. Getoff, Chemical Effects of Nuclear Transformations **2**, IAEA, Vienna(1965), p 290