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THERMAL ANNEALING OF NEUTRON-IRRADIATED CHLORINE OXYANIONS*

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Abstract—Thermal annealing of the products of the Szilard-Chalmers process in neutron irradiated alkali chlorates is similar to annealing in most salts containing oxyanions. In perchlorates and in sodium chlorite, on the other hand, an "inverse" type of annealing is observed, which means that the percentage of the activity in the chlorate + chlorite + hypochlorite fraction decreases on heating.

THERMAL annealing behaviour has been investigated in a number of neutron irradiated halogen oxyanions, like bromates,⁽¹⁾ iodates⁽²⁾ and periodates⁽³⁾ but no data have been published concerning the annealing of chlorates or perchlorates. We thought that it would be of interest to fill this gap and in the course of these experiments we observed some cases of "inverse" annealing. The general shape of the "inverse" annealing curve has been shown to be quite similar to that of a "normal" one.

EXPERIMENTAL

Materials

Potassium chlorate, sodium chlorate and potassium perchlorate were of "Merck" p.a. origin. The crystals were ground in a mortar. The powdered chlorates were oven dried at 140°C for 2 days and the potassium perchlorate was dried at 160°C for 3 days. Sodium perchlorate monohydrate $NaClO_4 \cdot H_2O$ was supplied by B.D.H. The wet crystals were washed with dry ether and dried in a vacuum desiccator for 10 hr at room temperature. Anhydrous sodium perchlorate was prepared from the monohydrate form by thermal dehydration. The compound loses its crystal water at ca. 54°.⁽⁴⁾ Our sample of anhydrous material was obtained by drying at 160° for 3 days. Cases of different thermal pretreatment are mentioned later.

Sodium chlorite was prepared from the trihydrate $NaClO_2 \cdot 3H_2O$ by thermal dehydration at 140° for 1 day. The dried sodium chlorite contained ca. 2 per cent of the chloride calculated as sodium chloride.

Neutron bombardment

The irradiations were performed with neutrons moderated in paraffin, from the Amsterdam synchrocyclotron. For irradiation salts were sealed in soft glass tubes in the presence of the air. Some of the samples of $NaClO_4 \cdot H_2O$ had cork stoppers.

Thermal annealing

For heating above 300°C we used a thermostatically controlled oven where the temperature was constant ±5°. For lower temperatures refluxing boiling liquids were used with a constant temperature of ±1°. The irradiated salts were heated in the closed glass tubes in which they had been irradiated except for annealing above 460° where the glass tubes had to be replaced by Pyrex glass after irradiation. Quick cooling of the heated samples was done by dipping the samples into liquid air.

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⁽¹⁾ J. COBBLE and G. E. BOYD, *J. Amer. Chem. Soc.* **74**, 1282 (1952); R. HENRY, C. AUBERTIN and E. de la GUERONNIERE, *J. Phys. Rad.* **18**, 320 (1957); J. JACH and G. HARBOTTLE, *Trans. Faraday Soc.* **54**, 520 (1958); A. G. MADDOCK and H. MULLER, *Trans. Faraday Soc.* **56**, 509 (1960).

⁽²⁾ R. E. CLEARY, W. H. HAMILL and R. R. WILLIAMS, *J. Amer. Chem. Soc.* **74**, 4675 (1952).

⁽³⁾ A. H. W. ATEN, G. K. KOCH, G. A. WESSELINK and A. M. de ROOS, *J. Amer. Chem. Soc.* **79**, 63 (1957).

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Analysis

One mmole of irradiated $NaClO_3$, $KClO_3$ and $NaClO_2$ respectively was dissolved in ca. 100 ml of water containing 1 mmole chloride carrier. The chloride was precipitated with nitric acid and silver nitrate (except in the case of $NaClO_2$ where nitric acid was not added) and after the addition of another portion of chloride carrier a second silver chloride precipitate was obtained. The chlorate ion and the chlorite ion were reduced in the filtrate by passing through sulphur dioxide, the excess of which was later boiled off, and the chlorine was precipitated as silver chloride.

Three to six hundred milligrams of $NaClO_4 \cdot H_2O$, $NaClO_4$ or $KClO_4$ were dissolved in water containing 1 mmole of chloride and chlorate each as carriers. The precipitation of the chloride and the chlorate as silver chloride containing ^{38}Cl was performed as described above. The excess of silver ions in the filtrate containing the perchlorate was removed by adding chloride ions and subsequent filtration. This was followed by precipitation of the perchlorate ion as tetraphenylarsonium perchlorate⁽⁵⁾ by means of tetraphenylarsonium hydrochloride.

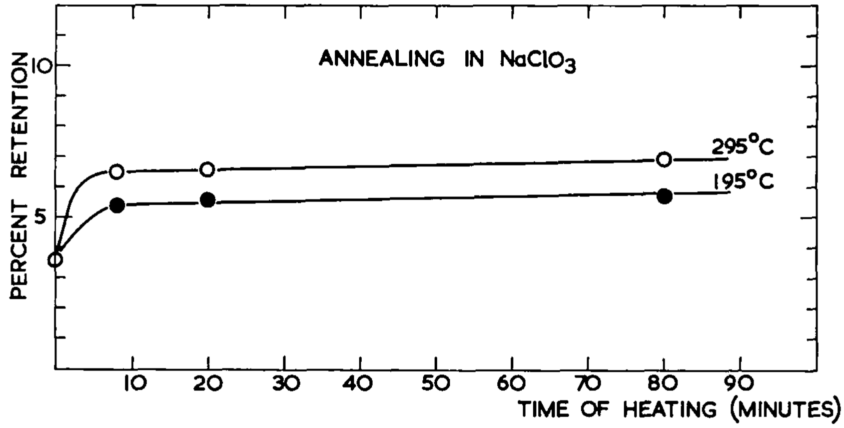

FIG. 1.—Annealing in $NaClO_3$. Per cent retention vs. time of heating (min.).

We should point out that our chemical separation was carried out under conditions in which the exchange of chlorine atoms between chloride, chlorite, chlorate and perchlorate was slow.⁽⁶⁾ All precipitates were washed with acetone and ether, dried for a few minutes at 120° and weighed for the chemical yield. Then the corrections of the activity for the incomplete recovery of the precipitates could be applied.

Counting

The precipitates were covered with cellophane tape and counted in aluminium dishes with a β-GM counter. Decay curves were drawn for all samples and the relative activities were determined from them. Half-life curves of ^{38}Cl obtained with some silver chloride samples which had been precipitated in a neutral solution showed a tail attributed to ^{32}P formed by the reaction of fast neutrons with ^{35}Cl. Although this activity was not very important a correction was made for it.

RESULTS

Thermal annealing of $NaClO_3$ *and* $KClO_3$

The heating of the neutron irradiated chlorates before analysis resulted in a slight increase in the retention. Plots of the retention against the time of annealing are shown in Figs. 1 and 2. Initial retention was found to be identical for both chlorates. Obviously the retention increases in two stages, but we did not measure with any precision the slope for the first and fast part of the reaction.

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Sodium chlorate melts at ca. 250°C so that one of the annealing curves (Fig. 1) was obtained on the melt. On heating at 295° for 80 min it was found that the salt started decomposing, which was observed by a very slight opalescence, when ca. 300 mg of the heated salt was dissolved in water and nitric acid and silver nitrate were added. Potassium chlorate is more stable to heat; it did not melt during the annealing experiment, but slight decomposition was observed on heating the irradiated salt at 350° for 80 min.

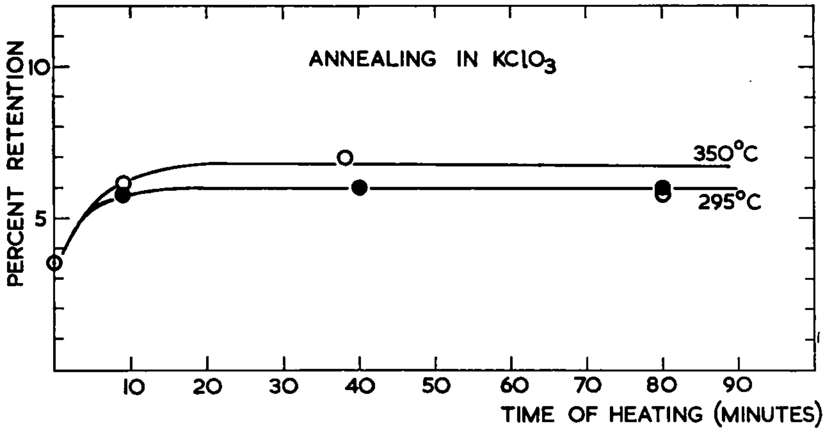

FIG. 2.—Annealing of $KClO_3$. Per cent retention vs. time of heating (min.).

Thermal annealing in $NaClO_4$ *and* $KClO_4$

No activity was found in the perchlorate fraction even after thermal annealing of the irradiated salts. The real retention was very uncertainly measured after the thermal annealing of potassium perchlorate at 490° for 80 min (ca. 2·5 per cent) and in the case of sodium perchlorate at 460° for 80 min (ca. 1·5 per cent). Most of the activity was found in the chloride fraction and the rest followed the chlorate fraction. When the percentage of activity which was found to follow chlorate is plotted against the time of annealing, we obtain curves like those in Figs. 3 and 4. In the case of sodium perchlorate heated at 295°, a small increase in the activity of the chlorate fraction was observed. When either irradiated perchlorate is heated to a higher temperature, the activity of the chlorate fraction decreases appreciably and part of the radioactivity passes into chloride. It is worth mentioning that alkali perchlorates are exceptionally stable to heat and the annealing experiments could be done without, or with very slight decomposition of the heated salts. The treatment before neutron irradiation for all samples used in these experiments was drying at 160° for 3 days. In two experiments the neutron irradiated potassium perchlorate was dissolved in the carrier solution, $NaHAsO_2$ was added and the solution was left for 20 min at room temperature. By adding acetic acid, nitric acid and silver nitrate, the silver chloride was precipitated. Further separation of the chlorate and the perchlorate was performed as was described before. By this method of analysis any existing active chlorite or hypochlorite would have been reduced and would have joined the Cl-fraction. The percentage of the active chlorate fraction did not change significantly; hence we may conclude that the "chlorate" radioactivity in general consists of ions having the actual composition ClO_3^-.

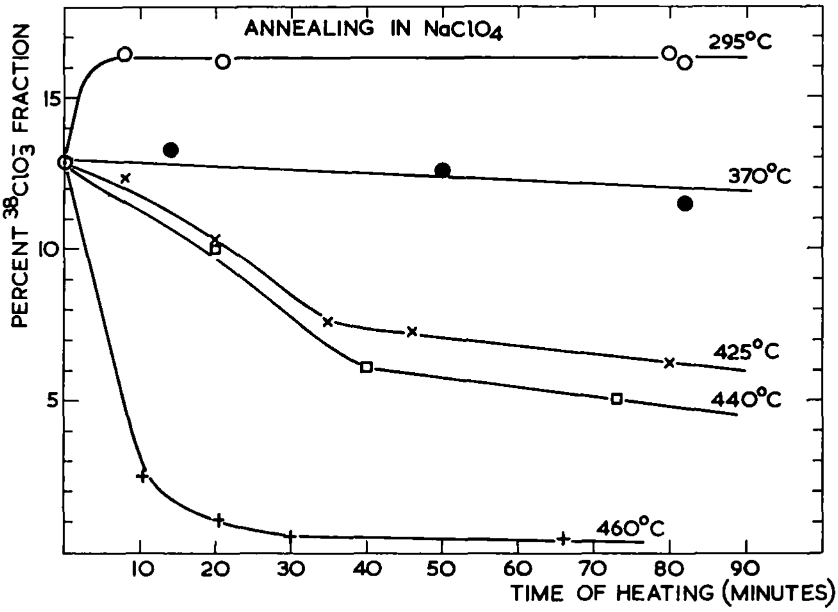

FIG. 3.—Annealing of $NaClO_4$. Per cent of ^{38}Cl in the chlorate fraction vs. time of heating (min).

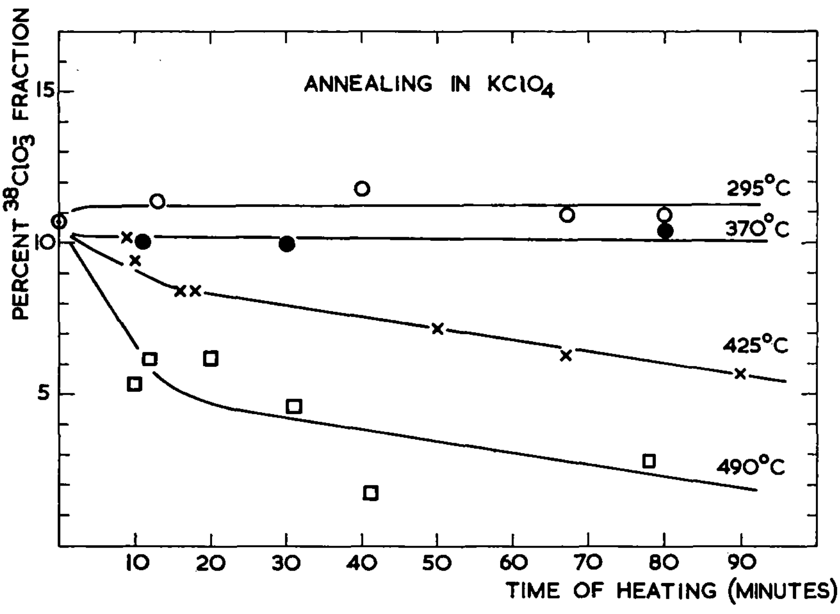

FIG. 4.—Annealing of $KClO_4$. Per cent of ^{38}Cl in the chlorate fraction vs. time of heating (min).

The influence of preirradiation treatment on the thermal annealing behaviour of $NaClO_4$

Sodium perchlorate monohydrate dehydrated at 160° for 3 days (pre-treatment a) was subsequently either dried in an oven at 370° for 12 hr (pre-treatment b) or dissolved in dry acetone; ether was added and the precipitated salt was filtered off, washed with dry ether and dried at room temperature in a vacuum dessicator for 4 hr (pre-treatment c). The salt prepared according to (c) contained about 2 per cent of moisture and acetone.

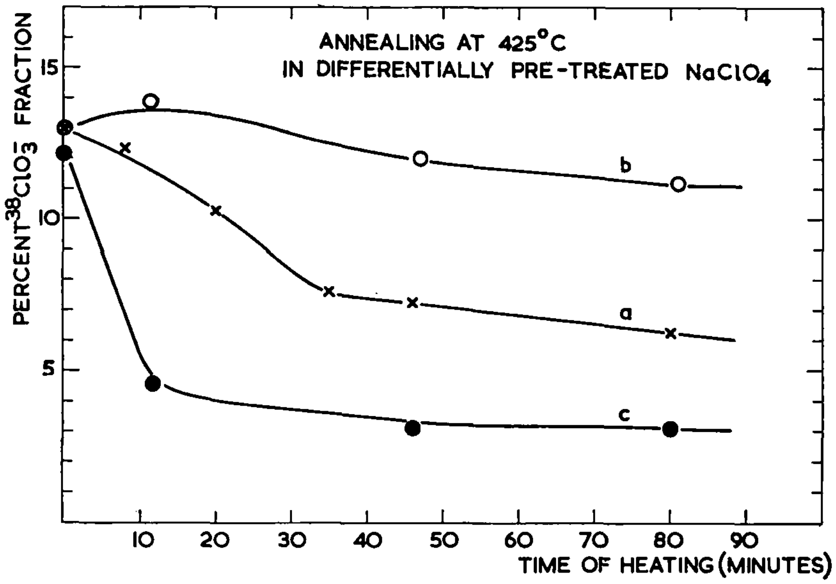

FIG. 5.—Annealing of $NaClO_4$ at 425°C. Per cent of ^{38}Cl in the chlorate fraction vs. time of heating (min). Pre-irradiation treatment of $NaClO_4$: dried 160°C, 72 hr (a) and subsequently either dried at 370°C, 12 hr (b) or recrystallized from organic solvents and dried at a vacuum (c).

Sodium perchlorate samples prepared by treatment (b) and (c) were irradiated with neutrons and annealing was carried out at 425°. The annealing curves obtained (b and c, Fig. 5) were compared with one (a) taken from Fig. 3 corresponding to the same temperature. Initial activity percentages in the chlorate fraction were almost the same in all samples, whatever the thermal pretreatment had been.

Thermal annealing of $NaClO_4 \cdot H_2O$

The percentages of the activity found in the chlorate fraction in the various experiments with sodium perchlorate monohydrate are given in the third column of Table 1. The rest of the activity was found in the chloride fraction.

Thermal annealing of $NaClO_2$

If the analysis of the irradiated sodium chlorite is performed as described above, it is possible to distinguish only between the chloride fraction and the higher oxidation states of chlorine ($ClO^- + ClO_2^- + ClO_3^-$). The relation between the percentage of radioactivity in the higher oxidation states of chlorine and the time of annealing is presented in Fig. 6. Sodium chlorite is said to decompose at 180–200°(4) but considerable decomposition was caused by keeping the salt at 154° for a period of 50 min or longer.

TABLE 1.—ACTIVITY IN THE CHLORATE FRACTION IN NEUTRON-IRRADIATED $NaClO_4 \cdot H_2O$

Group of experiments	Description of experiments	Percentage of activity in the ClO_3^- + ClO_2^- + ClO^- fraction
1	No annealing, room temperature	8·1
2	No annealing, $NaAsO_2$ was added to the solution of irradiated salt, Cl^- and ClO_3^- carriers, left 40 min. Percentage includes ClO_3^- only, without ClO^- and ClO_2^-.	7·1
3	Annealing in stream of nitrogen:	
a	at 100° for 80 min (partial dehydration occurred during annealing	8·0
b	at 154° for 40 and 83 min (partial dehydration occurred during annealing)	5·0; 3·7
c	at 292° for 40, 80 and 95 min (at the end of annealing the salt was completely dehydrated)	2·8; 2·2; 2·5
4	Annealing under vacuum:	
a	at 76° for 80 min (79% of the crystal water was lost)	8·0
b	at 100° for 80 min (at the end of annealing the salt was completely dehydrated)	8·1
5	Annealing in small glass ampoules at 292°, for 80 min, dehydration prevented (during annealing salt melted)	6·4

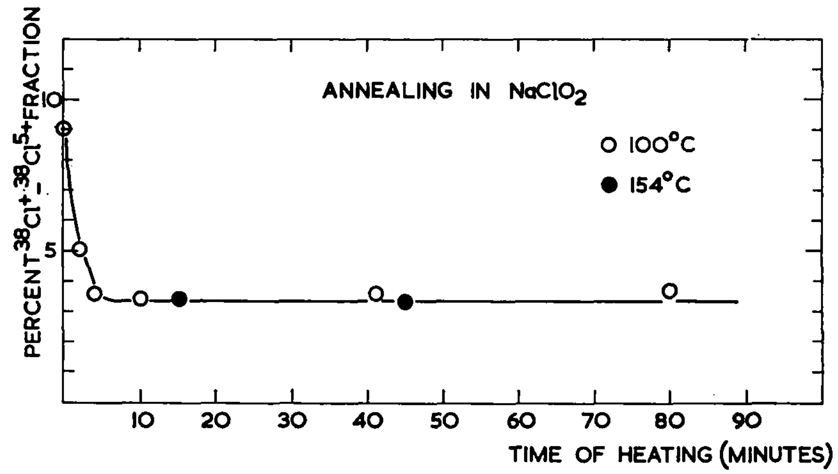

FIG. 6.—Annealing in $NaClO_2$. Per cent of ^{38}Cl in ClO^- + ClO_2^- + ClO_3^- fraction vs. time of heating (min).

DISCUSSION

The low retention amounting to 3·5 per cent found in neutron irradiated sodium chlorate and potassium chlorate supports the earlier results(7) for the $^{37}Cl(n, \gamma)^{38}Cl$ reaction in sodium chlorate where 1·5 per cent of retention was reported. The same authors, however, obtained 9 per cent retention for betatron irradiation of sodium chlorate, $^{35}Cl(\gamma, n)^{34}Cl$. This significantly higher value may well have been caused by radiation annealing when chlorate was irradiated by a betatron as is supposed in the original paper.

In the post recoil thermal annealing experiments with chlorates we obtained a slight increase of the retention; the isothermal curves (Figs. 1 and 2) show that a plateau which amounts to about double the initial retention could be reached.

An interesting feature of the neutron irradiated perchlorate is the practical absence of any retention in the strictest sense of the word (in the ClO_4-fraction) even after the annealing. This shows once more that the chemical bonds are completely ruptured by the recoil. It is of interest that in the case of a perchlorate the parent compound could not be reformed from the radioactive nucleus. This might perhaps be attributed to the fact that the formation of ClO_4^- in the crystal lattice would require a high positive charge on the chlorine atom and that sufficiently highly charge radio-chlorine atoms are not produced by the recoil process or by the internal conversion of capture γ-rays. The fact that formation of radioactive ClO_4^- is practically absent in the case of slow neutron irradiation of alkali perchlorates provides an interesting parallel to the low yield of radioactive IO_4^- in the activation of potassium periodate.(3)

Another interesting phenomenon is the decrease of the chlorate activity in the thermal annealing curves obtained (Figs. 3 and 4). These curves show fairly good reproducibility when pre-irradiation thermal treatment of the samples is identical. It is of special interest that these "inverse" annealing curves, in which the percentage activity in the oxidized fraction decreases, have the same shape as "normal" annealing curves.(8) At first we observe a fast reaction, which involves only a part of the total activity available for the reaction, followed by a second much slower process with the same general trend. The decrease in the activity of the chlorate fraction may perhaps be explained by thermal decomposition of radioactive chlorate formed in the perchlorate lattice in which the ClO_3^- ion will be less stable than the ClO_4^- ions.

The thermal decomposition of chlorate in the pure condition takes place between 400° and 500°(4) according to $4KClO_3 \rightarrow KCl + 3KClO_4$ followed by $KClO_4 \rightarrow KCl + 4O$ and the low activity of ca. 2 per cent found in the perchlorate fraction might possibly be ascribed to such a decomposition, if, at least, the latter may be assumed to take place according to the normal mechanism.(9)

There is one special feature about the "inverse" annealing, which is illustrated in Fig. 5. Although preliminary heat-treatment of the sample to be irradiated hardly affects the initial retention, the influence of heat pre-treatment on the shape of the annealing curve is most pronounced. It is quite evident that some component of the crystal participates in the annealing, which component is very sensitive to preliminary heating. The suggestion comes to mind that faults in the crystal lattice play a part in the annealing process and that these lattice faults are "ironed out" during the pre-

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liminary heat treatment. At any rate the component in question cannot be a product of the irradiation during neutron activation.

A few explanatory remarks should be made in this connection. It might be suggested that the difference between the three curves in Fig. 5 might be caused by the retention of different quantities of moisture which would mean that the "inverse" annealing would be due entirely to the action of very rare H_2O molecules left in the crystals. However a moisture content of any importance could hardly be expected to occur in the salt dried at 160° for 72 hr, and thus the difference between the two upper curves would remain unexplained. Some authors have reported the influence of pre-irradiation degassing on the initial oxidation states of ^{32}P and of ^{35}S produced in neutron irradiated alkali chlorides,(10) which seems to be due to the influence on the retention of small quantities of various gases within the crystal lattice.(11) However, in those experiments the initial retention was found to be very different in samples which had undergone different pre-irradiation treatment.

In the case of sodium perchlorate monohydrate the percentage of the total activity found initially in the oxidized fraction (8 per cent) is appreciably lower than in the anhydrous compound (Table 1). This is similar to observations made on other salts, but a rule of general validity does not seem to exist (cf. the discussions given by HARBOTTLE and SUTIN(8) and by MADDOCK and MÜLLER(1)).

As the presence of arsenite did not significantly affect the activity in the chlorate fraction we may assume that this activity goes into solution in a chemical form which is essentially ClO_3^-.

Dehydration in itself does not much influence the activity of the chlorate fraction. This is in agreement with the behaviour in the case of dehydration or hydration of other irradiated salts.(11)

The thermal annealing behaviour of the monohydrate is roughly similar to that of the anhydrous material, but there is a difference in that in the former case a lower temperature is required for "inverse" annealing than in the latter case. It should, however, be kept in mind that in the $NaClO_3 \cdot H_2O$ the annealing takes place—at least in part—during the dehydration process. It seems that the removal of water from the lattice during the annealing contributes to the lowering of the activity in the chlorate fraction.

Sodium chlorite also shows "inverse" annealing (Fig. 5). It is tempting to look for an explanation in the posibility that most of the activity in the $ClO^- + ClO_2^- + ClO_3^-$ fraction is present as ClO^- ions and that these ions in the $NaClO_2$ lattice easily decompose on heating.

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(11) L. LINDNER. Thesis, Amsterdam (1959).