

《Original》 Evolution of Iodine from NaI-Na₂O₂ System

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Abstract

The evolution of radioiodine ¹³¹I from a sodium peroxide system as a function of time, temperature, and carrier gas (nitrogen) flow rate was studied. Virtually no iodine was volatilized at 250°C and a very small amount, of the order of 10⁻³% per hour, at 630°C. Substantially greater amounts of iodine were volatilized at 725°C and 830°C. The data are consistent with the hypothesis that the mechanism of transfer is distillation of sodium iodide, and that elemental iodine is not produced in this system.

요 약

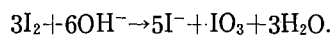
Sodium 을 冷却劑로 使用하는 增殖原子爐系(LMFBR)에서 原子爐의 正常, 非正常 稼動下에서 Sodium 또는 Sodium 化合物과 核分裂物質의 하나인 氣體狀 I¹³¹의 役割은 障害度評價에 重要한 要因이 된다. 본 實驗에서는 Sodium peroxide 系에서 時間, 溫度, flow rate 에 따른 I¹³¹의 放出課程을 규명하였음.

1. Introduction

Knowledge of the behavior of fission product iodine in a sodium or sodium compound environment is important in evaluating the potential hazards associated with liquid metal fast breeder reactor (LMFBR) operations under both normal and accident conditions. Consideration of the chemistry of iodine leads to the expectations that (1) sodium iodide in the coolant will remain nonvolatile even under conditions of a sodium fire, and that (2) any iodine leakage from fuel elements, presumably as molecular iodine will be converted to sodium iodide.

The possible oxidation of iodide to volatile

forms is of concern in reactor safety. Iodide is readily oxidized to I₂ by oxygen or by peroxide. In alkaline systems such as are commonly present in an LMFBR environment, however, I₂ disproportionates to iodide and iodate according to the following reaction:



For these reasons, an investigation was undertaken of the volatility of iodine, originally present as iodide, in oxidizing systems.

Investigations of the release of iodine from sodium iodide when heated under alkaline oxidizing conditions included these parameters:

- temperature;
- mass of iodide in the mixture;
- gas flow rate over the heated NaI;
- duration of heating.

2. Generation of Iodine Stream, Sampling, and Analysis

a. Generation of Iodine Stream

A nitrogen stream containing a low concentration of iodine was required for testing the samplers. It was prepared by passing nitrogen through a bed of elemental iodine. The saturated vapor pressure of iodine at 0°C corresponds to about 40 ppm (by volume); at 25°C it corresponds to about 430 ppm. At a nitrogen flow rate of 120 ml/min for 4 hours, a total of 120 mg of I₂ would be evaporated for saturation at 0°C, and a total of 130 mg for saturation at 25°C.

The iodine was prepared by oxidation of sodium iodide with nitrous acid. To minimize transfer problems of the radioactive iodine, the reaction was carried out in the funnel of a filter apparatus consisting of a fritted support disk with a 20-ml chimney. It was supported in a 125-ml filter flask. A fine (0.45 μ m) glass fiber filter disc was placed on the support and a few ml of water placed in the chimney. The required amounts of stable NaI and of radioactive NaI¹³¹ were then added to the chimney with a little water and mixed by blowing air into the filter flask so that it bubbled up through the filter. After mixing, an excess of NaNO₂ solution was added and finally HCl was added dropwise. The addition of HCl initiated the oxidation. After two minutes, suction was applied to the flask, drawing the excess reagents and soluble reaction products through the filter and leaving the I₂ precipitate on the filter. The precipitate was washed with a small amount of water.

b. Sampling

The iodine samplers were bubblers about one inch in diameter with a total available volume of 30 ml. They were fitted with extra-coarse (170-220 μ m) fritted glass tubes. Two bubblers were used in series, each containing

twenty ml of 0.1 M NaOH-0.1 M Na₂S₂O₃ solution. The efficiencies of the bubblers were measured by determining the ratio of the counting rates in each bubbler after passage of I₂¹³¹ (about 400 ppm in N₂) through two bubblers in series. It is clear that the two bubblers in series absorbed I₂ quantitatively.

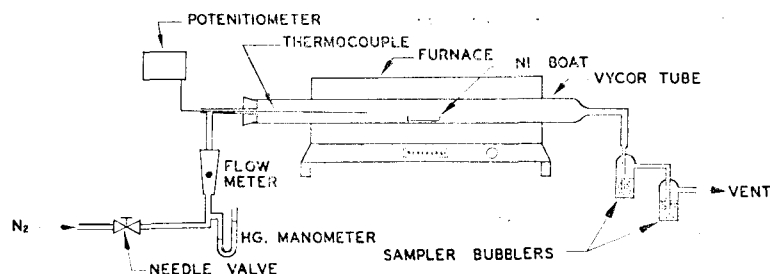
c. Analytical

The analytical method chosen was gamma counting of iodine-131 tracer. To permit measurement of iodine-131 in the sampler in the presence of much larger quantities of iodine-131 in the system, single channel counting in the iodine peak region was selected. This enabled the counting system to reject scattered gamma radiation, which would be reduced in photon energy. The counting configuration chosen was 20 ml of aqueous sample, which was dictated by the sampling system. The energy region selected was 335-385 keV, approximately centered on the 364 keV I¹³¹ gamma radiation. The spectrometer system consisted of a 1-3/4 x 2 NaI(Tl) well crystal connected to a linear amplifier and a single-channel analyzer.

These bubblers were calibrated by counting various volumes of radioactive sodium iodide solution. Since all measurements in the experiment could be relative, the supplier's value for the activity of the radioiodine was used. Table 1 gives the results of these measurements.

Table 1. Calibration of I¹³¹ counting system

Vol. (ml)	Activity (μ Ci)	Counting rate (net cpm)	Counting Yield (cpm/ μ Ci)
5	0.0835	6569	7.87 $\times 10^4$
10	0.167	9771	5.85 $\times 10^4$
15	0.2505	11040	4.41 $\times 10^4$
20	0.334	11709	3.50 $\times 10^4$
25	0.4175	12597	3.02 $\times 10^4$

Fig. 1. Apparatus for volatilization of iodine from NaI-Na₂O₂Table 2. Volatilization of ¹³¹I from NaI-Na₂O₂ mixtures summary

Run No	Flow Rate ml/min	Duration hrs	Av Temp °C	Iodide mg	¹³¹ I volatilized		
					In bubbler %	In tube %	Total %
1V ^a	66	4.25	630	2.0	0.009	0.023	0.032
2V	120	5.25	630	2.0	0.006	0.059	0.065
3V	66	5.0	250	2.0	0.002	0.004(est.)	0.006(est.)
4V	120	2.67	630 ^c	0.2	0.037	6.12	6.15
5V ^b	120	3.3	632	0.2	0.041	—	—
6SS ^a	120	5.0	632	0.2	0.058	—	—
7V	120	1.5	628	2.0	7.09	8.04	15.13
8V	120	1.0	800 ^d	2.0	4.21	9.69	13.90
9V	120	1.8	735 ^d	2.0	1.76	6.37	8.13
10SS	120	4.0	735	0.2	0.62	7.06	7.68
11SS	120	4.0	737 ^e	2.0	1.12	7.91	9.03
12SS	120	4.0	736 ^e	0.02	1.30	6.9(est.)	8.2(est.)
13SS ^f	120	1.25	740	2.0	0.05	2.52	2.57

a: V Vycor tube; SS Stainless steel tube

b: The Vycor tube cracked during run 5

c: No Na₂O₂ was used in run 7; 2 grams were used in all other runs

d: Thermocouple difficulties were encountered in runs 8 and 9. The temperature may have gone higher than indicated

e: Higher temperatures were reached early in these runs 800 in run 4, 773 in run 11, 747 in run 12

f: Carrier gas was N₂ until temperature reached, then air (start of air flow is time zero)

The data of Table 1 show that, in the vicinity of 20 ml, there is an increase in counting yield of about 5.2% per ml decrease in volume, and a decrease in counting yield of about 2.7% per ml increase in volume. As the volume could easily be maintained within ± 0.5 ml, no corrections for volume were needed.

3. Experimental and Results

The system investigated were NaI-Na₂O₂. Varied quantities of NaI in 2 grams of Na₂O₂ were heated in a stream of nitrogen, and the stream was then passed through NaOH-Na₂S₂O₃

absorbers to detect any volatilized iodine. A diagram of the apparatus used is shown in Figure 1. The reaction mixtures were prepared by gently drying appropriate volumes of NaI and NaI¹³¹ solutions in a nickel boat under an infra-red lamp, and adding 2 grams of Na₂O₂. The two chemicals were thoroughly mixed with a spatula. Tests showed that more than 90% of the radioactivity accompanied the Na₂O₂ when this was removed from the boat.

A total of 13 runs were made at varying temperatures, flow rates, and ratios of NaI to Na₂O₂. These are summarized in Table 2.

In the early runs, a Vycor tube was used. However, it soon became apparent that this tube was badly attacked and eventually (run 5) the tube failed completely. The point of attack was almost exactly above the boat, and the corrosion is attributed to alkali distilled out of the boat. Most of the volatilized iodine was in the tube as a white deposit just beyond the downstream end of the furnace. This was clearly volatilized material depositing on a cooler surface. From its ready solubility in water, both from Vycor and from stainless steel, this was believed to be sodium iodide, rather than iodine. Other oxidized forms such as sodium iodate and periodate would be expected to decompose at the elevated temperature. Even if they did not decompose, they would be expected to react with the stainless steel in a manner such that the iodine would be rather firmly attached to the metal. Inspection of the remainder of the system with the survey meter showed that there was no large deposition of radioiodine except in this zone just beyond the furnace.

To test the variation of iodine release with temperature, experiments were made in which the NaI-Na₂O₂ mixture was maintained at 250°, 630°, 735°, and 800°C.

There is a marked influence of temperature.

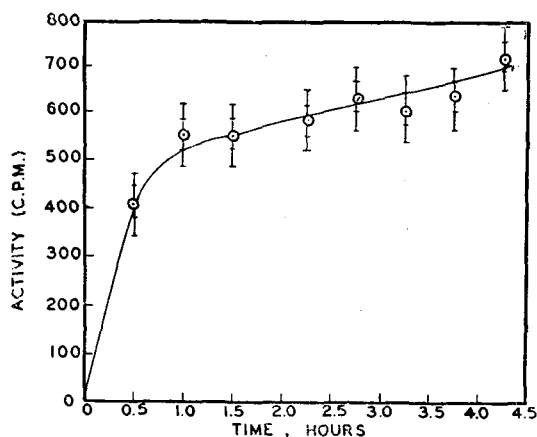


Fig. 2. Time course of radioactivity in bubbler, run No. 1

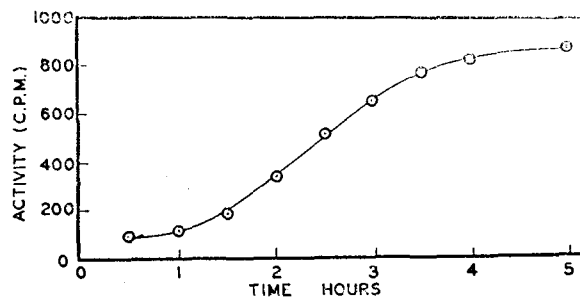


Fig. 3. Time course of radioactivity in bubbler, run No. 6

Very little iodine is volatile at 250°C (Run 3V).

The amount in the tube is indicated as being estimated in Table 2 because approximately half of the tube washings were spilled. Even if the amount spilled was as much as 3/4, which is most unlikely, the total amount volatilized would be only 0.01%. At 635°C at the same flow rate (Run IV), the amount of iodine volatilized is greater, but still quite small 0.032%. The volatilization at 735°C may be best compared to that at 630°C in Run 10 SS vs Run 6SS, in each of which smaller quantities of iodide used. The amount of iodine reaching the bubbler at 735°C is approximately ten times as much as at 630°C. The tube washings were not counted in Run 6SS, but external reading of the tube with the survey meter were also in the 10:1 ratio, 24,400 counts per minute vs 2400. In the other runs at 735°C (9V, 11SS, and 12SS), somewhat larger quantities of iodine were volatilized. The early overheating apparently evaporated the iodide before the temperature was reduced to 735°C. This is confirmed by the single experiment at 800°C, in which almost 14% of the iodine became volatile in only one hour. This experiment cannot be taken as conclusive of conditions at 800°C since there was some question as to the validity of the temperature reading. It may have been somewhat higher than 800°C. In several experiments, the ratio of NaI to Na₂O₂ was changed. The highest ratio was

2 mg of NaI to 2 g of Na₂O₂. In other experiments, 0.2 and 0.02 mg of NaI were used, again with 2 g of Na₂O₂. The best test of the effect of the iodide: peroxide ratio is given by Runs 12, 11, and 10, which were operated under essentially the same conditions except for the amount of iodide used, which was 0.02, 0.2 and 2.0 mg in the three runs. The total amount of iodine evaporated was 8.2, 7.7, and 9.0% in the three cases. Obviously there is no marked dependence on the amount of iodide used, and the higher values in runs 11 and 12 are probably attributable to the early overheating. In run 7V, sodium peroxide was used. This run may be compared with Run 2V, in which all other conditions were the same. The amount of iodine volatilized in Run 7V was 233 times the amount in Run 2V, and the duration of the run was less by a factor of 3.5. The rate of evaporation was then about 820 times as great in the absence of Na₂O₂. Only two of the experiments, IV and 2V, give any measure of the effect of flow rate, the amount volatilized at the high flow rate, corrected for the duration of the experiment, is 1.6 times the amount volatilized at the low flow rate. The ratio of the flow rates is 1.8. This strongly suggests that the amount of evaporation is proportional to the flow rate.

It proved impossible to follow the course of evolution of iodine with time, since only the iodine in the bubblers could be counted periodically during the experiments and this was usually much less than the amount which collected on the tube wall. In run I, the activity in the bubbler increased sharply in the first hour (Figure 2), but in most of the other runs below 735°C, there was a slow increase in the first 1 to 2 hours, then a sharp increase, and finally a levelling off after 3 to 4 hours (Figure 3). At higher temperatures,

more iodine was released early. This is particularly evident in those runs where early overheating occurred. As an example, Run 11 may be compared with Run 10.

In one investigation (No. 13) an attempt was made to simulate more closely the situation in an LMFBR accident by passing oxygen over the NaI-Na₂O₂ mixture rather than nitrogen. In effect, atmospheric oxygen, which would be the major oxidizing material in the LMFBR, was added to supplement the oxidizing power of the sodium peroxide. In this experiment, nitrogen was passed through the tube until the operating temperature of 785°C was reached and then oxygen was passed through. This was done to avoid the possibility that oxygen might attack unmixed NaI before the entire mixture was properly heated. This experiment should be compared with the others carried out at 734°C. A very small amount of radioiodine, 0.05%, reached the bubblers, and the amount recovered from tube washings, 2.52%, was also smaller than that found in the other 735°C runs. This experiment was somewhat marred by the fact that a considerable quantity of moisture from the atmosphere had entered the combustion tube before heating was started and some of the Na₂O₂ had reached to form NaOH. Even with this fact taken into account, it is clear that the atmospheric oxygen did not produce significantly more volatile iodine than the peroxide alone.

4. Discussion

In the reactor system, the sodium iodide in the aerosol will be intimately mixed with a great excess of Na₂O, Na₂O₂, NaOH and Na₂CO₃. The relative proportions of these four compounds will depend on the circumstances of the release and the nature of the atmosphere into which the sodium is released. Heating with Na₂O₂ was selected as the most severe

oxidizing condition possible for a sodium aerosol. It is somewhat more severe, in addition, because the sodium iodide is not in the same crystal as the sodium peroxide. This less intimate mixing makes possible, or at least conceivable, the oxidation of sodium iodide not in contact with the strongly alkaline sodium peroxide. Intimate mixing, as from solution, would have been desirable, but was not possible because of the reaction of sodium peroxide with water.

It has been suggested (2) that the volatilization of radioiodine from sodium iodide-sodium peroxide mixtures is due to the evaporation of sodium iodide, rather than to its oxidation to some more volatile compound. The nature of the radioactive deposit in the combustion tube has already been cited in support of this. The vapor pressure of NaI is described, (3) over the temperature 1063-1307°C, by the expressions:

$$\log_{10} P(\text{mm}) = \frac{-(52.23)(165.1)}{T(^{\circ}\text{K})} + 8.171$$

If extrapolated to 630°C, the equation gives a calculated vapor pressure of 0.067 mmHg. A 66-ml/min, stream, if saturated, would evaporate 2.1mg/hr. In Run 1, only 0.032% of 2mg was evaporated in 4.25 hours. The observed evaporation was less than the calculated by a factor of 1.4×10^4 . If the 2mg of NaI dissolved in the 2g of Na_2O_2 , its mole fraction was 6.1×10^{-4} , and if its vapor pressure was depressed proportionately, following Henry's Law, this would account for a factor of about 2×10^3 . The remaining factor of 7 can be readily accounted for by the non-applicability of the vapor pressure equation at this temperature, and to possible non-saturation of the gas stream. If the equation is extrapolated to the other temperatures, it predicts that the vapor pressure at 735°C should be 10 times that at 630 and at 800°C about 5 times that at 735°C.

The amount of radioiodine volatilized at

250°C is far greater than would be predicted, but is so low that it may be attributed to dust carryover. The effect of varying the ratio of sodium iodide to sodium peroxide is further confirmation of the hypothesis that sodium iodide is being evaporated. The highest ratio of sodium peroxide was 2mg to 2g, corresponding to a mole fraction of 0.000661. The other ratios used were 1/10 and 1/100 of this value. At these low concentrations, Henry's law can be expected to apply, and the vapor pressure of sodium iodide should be proportional to its mole fraction. The percentage of iodine evaporated should, therefore, be the same in all cases. The close agreement between Runs 12, 11, and 10 has already been noted. The much higher rate of volatilization of iodine from sodium iodide in the absence of sodium peroxide, about a factor of 820, is about half of what would be predicted from Henry's Law alone. This is close enough, considering the approximation involved, to be a rough verification.

5. Summary

The evolution of iodine from mixture of sodium iodide-sodium peroxide has been studied. The rate of evolution at 250°C and 635°C is not greater than 0.03% over several hours. The mechanism appears to be evaporation of sodium iodide, rather than oxidation to a more volatile form. The evaporated sodium iodide deposits rapidly on cooler surfaces.

Acknowledgements

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