

REACTION OF LOW CONCENTRATION GASEOUS IODINE WITH CESIUM CARBONATE

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ABSTRACTS

The reaction mechanism of iodine with cesium carbonate is of great importance in nuclear reactors, particularly in the event of an accident. Since the iodine concentrations in such cases are very low, any laboratory scale experiments should be carried out at same concentration level to obtain representative results. In this study, an experimental system was designed to measure the reaction of low concentration gaseous iodine with cesium carbonate powder using an on-line UV-VIS spectrometer system. Iodine gas that was not reacted in the reaction chamber was trapped in a solution containing 0.1 N aqueous NaOH that is a very efficient molecular iodine absorber. The solution was circulated through a flow-through cell of the spectrometer using a peristaltic pump. An absorption peak of iodine trapped in 0.1 N NaOH solution was noted at 220-230 nm ranges. The reaction of the gaseous iodine with cesium carbonate was performed with setting the spectrometer at 228 nm. Both qualitative and quantitative measurements of iodine were possible with this arrangement.

Introduction

Radioiodine aerosols can be released to the atmosphere during the operation of reactor and more importantly at the time of severe nuclear reactor accidents, especially in LWR (Light Water Reactor).¹ This might have many adverse health effects to reactor operators and the general public, who live in the vicinity of the reactor. Therefore, the reaction of radioiodine with materials in the reactor containment building has been studied extensively. A number of iodine isotopes are produced in considerable quantities in nuclear reactors as a result of nuclear fissions. The long lived isotope I-129 (1.57×10^7 half-life) is generally present in very small quantities in the off-gas stream.^{2,3} However, the I-131 is of primary concern in the reactor safety, because of its relatively shorter half-life (8 days) and a high fission yield. The magnitude of iodine gas released from the reactor containment to the environment depends on the amount of the iodine that becomes airborne, and is usually very difficult to estimate the quantity accurately.^{3,4}

All of the iodine produced in the reactor may not get released to the atmosphere. Since radioiodine can react with other aerosols within the reactor, it can change its physical and chemical forms very rapidly and readily in the presence of moisture. It can be deposited

on the walls, other surfaces, and in the water pool in the form of iodide (I^-).⁵ The most dominant form of iodine is the CsI compound, and the largest fraction of iodine in forms other than CsI is HI and I, which is about 3 % together. The volatility of iodide into iodine gas depends strongly on its chemistry, such as pH. In water pool where the pH is controlled to less than 7, it might be assumed that a large amount of iodine gas can be produced. However, if the pH is controlled above 7, small amounts of iodine gas may be released to the containment atmosphere.^{1,4} The maximum gaseous iodine concentration that may be released in the event of an accident is estimated to be in the range of 5×10^{-6} mol/L to 5×10^{-5} mol/L.⁶ Hence, the investigation of the reaction of iodine with aerosols should be performed in the same concentration range.

The objective of this research is to study the reaction of iodine gas with cesium carbonate aerosols using an on-line UV-VIS spectrometer system to analyze the time evolved chemical reaction. As a result of the reaction, cesium iodide and cesium iodate will be produced. The chemical reaction of this event is given by,



A large body of research on the safe management of airborne radioactive materials have been published in the literatures.¹⁻⁶ However, in these studies, the $I_2 - Cs_2CO_3$ reaction was not investigated adequately. In most of these studies, the resultant products were analyzed at a certain time interval followed by the reaction. The measurement systems were not employed to follow the progress of the reaction in real time. It was possible to track the time evolved temperature dependent chemical reaction of gaseous iodine with the organic aerosols with our experimental setup.

Beahm et al. at Oak Ridge National Laboratory studied the reaction of I_2 and various organic iodine compounds with a number of aerosols.⁶ Fraction of total iodine (I_2) that deposited on the cesium carbonate samples were from ~60 % to ~99 % using a moisturized air flow, depending upon the gas flow rate, sample mass, and the reaction duration. The authors concluded that the reactions between iodine gas and aerosols were very rapid.

Experimental System

The experimental system consists of an iodine gas generation system, a reaction chamber, and an on-line UV-VIS spectrometer system. The gas delivery system was made of Teflon and Viton tubes, and brass valves to prevent the reaction of I_2 with other system components. Dry air from a cylinder was used as a carrier gas. The flow rate of the carrier gas was controlled by a flow meters and controllers at 20 ± 1 SCCM (cm^3/min) during the experiment. A schematic diagram of the experimental system is shown in Figure 1. Iodine gas was generated using a standard and high emission tubular permeation device (VICI Metronics Inc.). According to the manufacturer's instructions, the permeation rate of the standard tubular device is 370 ng/cm/min with 15 % error.⁸ The active length of the permeation device used in the experiment is 19 cm and permeation rate, therefore, is 7000 ± 1000 ng/min. The iodine gas concentration of the system was estimated using an equation, $C = P K_m / F$, where C is the iodine gas concentration, P is the permeation rate in ng/min, F is the flow rate, and K_m is the molar constant which is given by 22.4/mol.wt. This gives the iodine gas concentration of 31 ppm (volume), which is equivalent to 1.385×10^{-6} gmol/L or 0.352 mg/L. The concentration generated by this method is the same level generally encountered in the reactor containment as mentioned earlier.

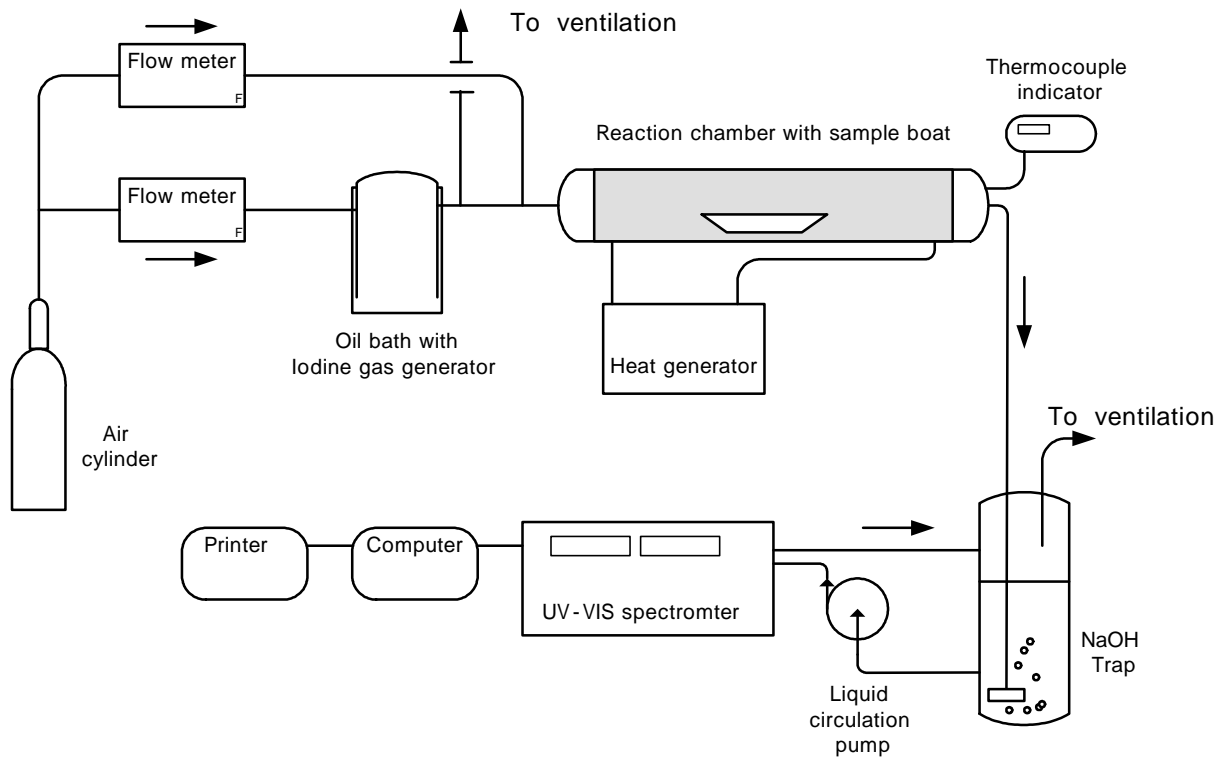


Figure 1. A Schematic Diagram of the Experimental System

The permeation device was placed inside a U-tube heat exchanger, which was submerged in the oil bath. Figure 2 shows the permeation tubular device and U-tube heat exchanger. The temperature of U-tube was maintained at the 100 ± 0.1 °C using a constant temperature oil bath. A dry air enters the inlet of the U-tube and flows through a column of glass beads, which provide a large surface area for heating the air. With this arrangement, carrier gas could reach the desired temperature before it flow out of the permeation tube on the other side of the U-tube as shown in Fig. 2.

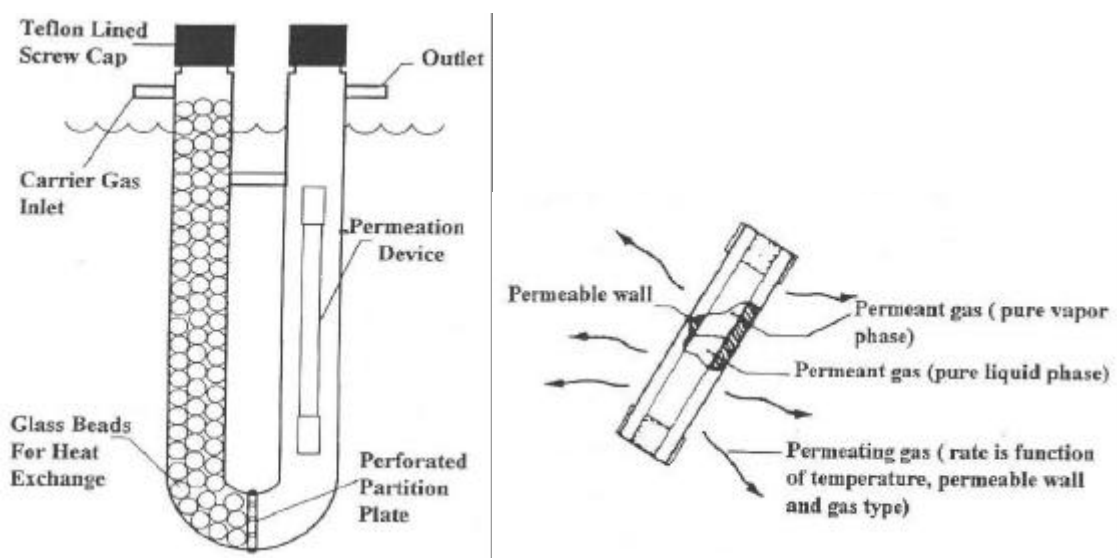


Figure 2. Heat Exchanger U-Tube with Standard Iodine Permeation Tube

The reaction chamber was made of the 5 cm diameter Pyrex glass with the length of 58 cm. Temperature of the chamber was controlled and maintained by a heating tape and insulation wrapped around the reaction chamber. A thermocouple was placed at the center of the chamber where the ceramic sample boat containing cesium Cs_2CO_3 powder was located. Surface area of the exposed portion of the sample boat was 7.2 cm^2 and could hold approximately 6.0 g of Cs_2CO_3 (99.9 % of purity, Johnson Matthey). The iodine gas flowing out of the reaction chamber was trapped in a 0.1 N NaOH solution in a cylindrical polyethylene trap as shown in Figure 1. It was checked that there were no reactions between polyethylene trap and iodine gas and the series of trap was tested to check the trap reliability if a single trap is enough for capturing all iodine released from the reaction chamber. Since pH value of trap solution is 13, captured I in NaOH solution is not volatile forming I_2 gas again.

Iodine quantity in the form of iodide (I) in NaOH solution was estimated by the Beer-Lambert law. Using a linear relationship between variables in the Beer-Lambert equation, absorptivity coefficient could be determined by measuring the absorbance of known concentration of iodine. A known quantity of iodine crystal was dissolved in a known amount of 0.1 N NaOH solution. Absorbance of the sample solutions was scanned at 228 nm where the highest peak in the spectrum is located, and the solution was further diluted with known volume of NaOH solution and was scanned at the same position.

During the experiment, NaOH solution trapped the iodine that was not reacted with cesium carbonate in the reaction chamber, and was circulated by a pump (Master Flex) through a quartz flow-through cell placed inside the UV-VIS spectrometer (Lambda 2 Perkin Elmer accompanying PECSS software). Absorbance of iodine in the trap solution was scanned at 228nm simultaneously. By comparing these measurements with the cases when no sample boat was placed in the reaction chamber, it was possible to estimate the fraction of iodine reacted with cesium carbonate at each experimental condition. Also, the experiments were conducted in time drive mode with the temperatures of reaction chamber at $30 \text{ }^\circ\text{C}$, $60 \text{ }^\circ\text{C}$, $100 \text{ }^\circ\text{C}$, and $130 \text{ }^\circ\text{C}$ during 15min and 60 min. Both gas and solution delivery systems were flushed using an air and distilled water, respectively, to clean the system after each run. The UV-cells were also cleaned by distilled water prior to each run.

Experimental Results

A maximum absorption peak of the iodide (I) in the solution was observed at 228 nm in the spectrum. A small shift of the peak towards to the lower energy region was observed at very low concentrations and also noise was observed in the region of less than 210 nm. Based on the Beer-Lambert equation, which is given by equation, $A = \epsilon cl$, where ϵ is the absorptivity coefficient, c is the concentration of the solution, and l is the path length of the light beam (cell width), a plot of absorbance versus concentration should be a straight line.^{9,10} Figure 3 shows the linear relationship between the iodine concentration and the absorbance as suggested by the Beer-Lambert law. At high concentrations, a small increase in the absorption coefficients as well as shifting of the maximum in the peak was observed. Estimated absorptivity coefficient from the experiment was $72.9 \pm 4.5 \text{ L/g/cm}$ at 228nm. Estimated amounts of iodine that can be produced from the permeation device are $0.427 \pm 0.064 \text{ mg}$ and $0.211 \pm 0.032 \text{ mg}$ during 60 minutes and 30 minutes from the given permeation rate, respectively. Hence, iodine concentrations in 600 ml 0.1 N NaOH trap solutions would be $0.712 \pm 0.107 \text{ mg/L}$ and $0.352 \pm 0.053 \text{ mg/L}$, respectively. Absorbance of these concentrations at 228 nm were calculated using previously determined absorptivity coefficient and are compared with the absorbance measured after 60 minutes and 30 minutes of trapping

of iodine gas without the sample boat in the reaction chamber. The measured absorbance is well agreed with the estimated absorbance as shown in Table 1. Hence, it is assumed that the NaOH trap solution can collect all the iodine gas released from the system. And also, the experimental system is reliable for the qualitative and quantitative analyses of iodine reaction with cesium carbonate.

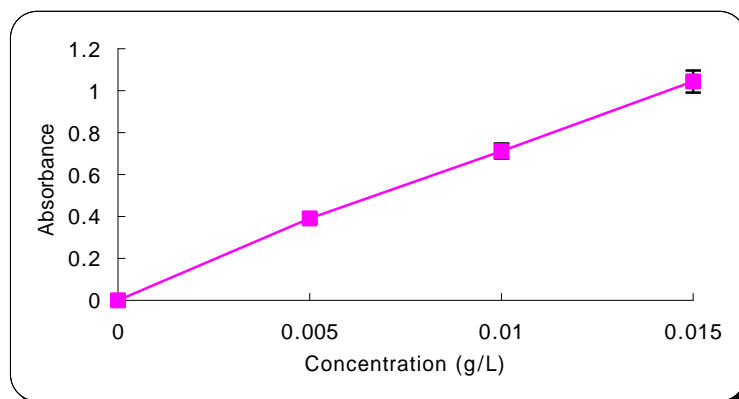


Figure 3. A Plot of Iodide (I⁻) Concentrations in NaOH Solution vs. the Absorbance at 228nm

Figure 4 and Figure 5 show the variations of iodine concentration in NaOH trap solution following the reaction of iodine with cesium carbonate for 900 sec (= 15 min) and 3600 sec (= 60 min), respectively. Absorbance at 228 nm was measured at several reaction temperatures. Increase of absorbance as the reaction time elapses is due to trapping of iodine continuously during the experiment. However, it is clear that total amounts of iodine absorbed in the solution during an iodine reaction were less compared to when no reaction occurs. The difference between these amounts is the quantity of iodine reacted with the cesium carbonate. It is also clear that the reaction is strongly dependent on the reaction temperature. However, it was observed that the effect of the temperature on the reaction in the range of 30 °C to 60 °C was minimal. At reaction temperature 100 °C and 130 °C, which is the similar conditions in reactor steam system, reaction of iodine with cesium carbonate is more rapid and active. Quantities of iodine reacted with cesium carbonate are estimated in Table 2 and Table 3. Fraction of reacted iodine from total generated iodine for 15 min period is higher than those for 60 min period. This is due to limited sample boat surface area, since amounts of cesium carbonate on the boat surface decreases as the reaction time elapses.

Table 1. Comparison between Measured and Estimated Absorbance of I₂ Collected for 30 min and 60 min Without Reaction with Cs₂CO₃ in the Reaction Chamber

Collection Time	Measured Absorbance	Estimated Absorbance
30 min	0.025	0.026
60min	0.053	0.052

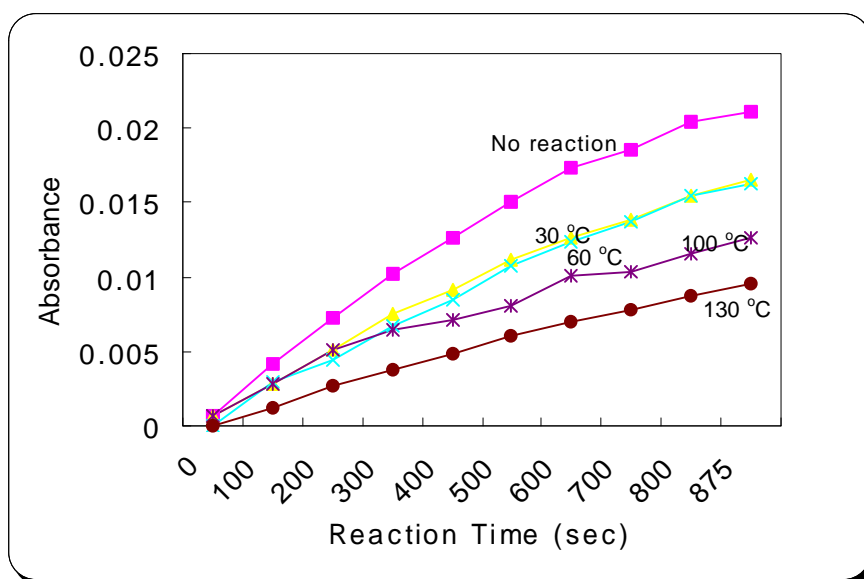


Figure 4. Variation of Iodine Absorption in the Trap Solution Measured at 228 nm at Various Temperatures following Reaction with Cesium Carbonate during 900 sec

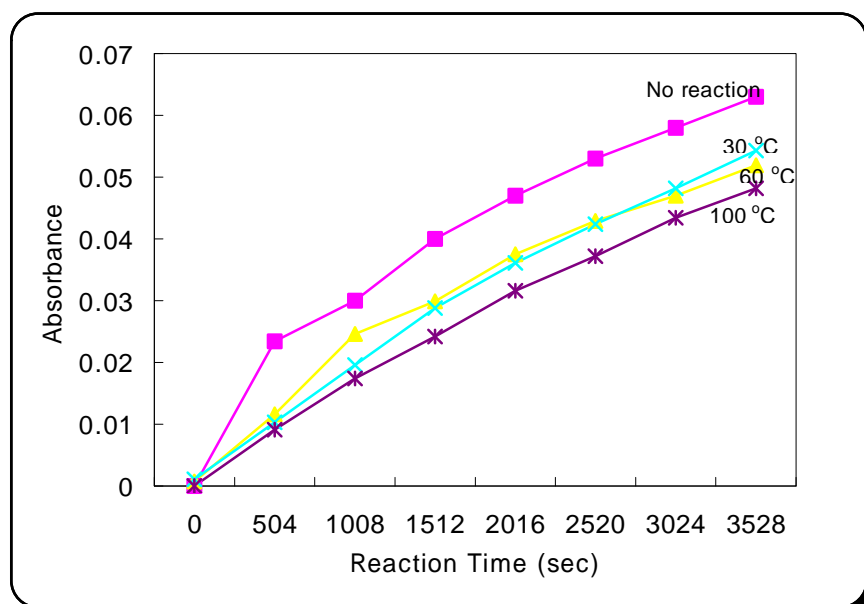


Figure 5. Variation of Iodine Absorption in the Trap Solution Measured at 228 nm at Various Temperatures following Reaction with Cesium Carbonate during 3600 sec

Table 2. Amounts of Iodine Trapped in the 0.1 N NaOH Solution and Fraction of Iodine Deposited on Cesium Carbonate for 15 min.

Reaction Temperature	No Reaction	30 °C	60 °C	100 °C	130 °C
Iodine Trapped in NaOH Solution (mg)	0.1418	0.1100	0.1088	0.0856	0.0636
Fraction of Deposited on the Cs ₂ CO ₃ (%)	0.0	22.4	23.4	39.4	55.1

Table 3. Amounts of Iodine Trapped in the 0.1 N NaOH Solution and Fraction of Iodine Deposited on Cesium Carbonate for 60 min.

Reaction Temperature	No Reaction	30 °C	60 °C	100 °C
Iodine Trapped in NaOH Solution (mg)	0.4218	0.3472	0.3631	0.3228
Fraction of Deposited on the Cs ₂ CO ₃ (%)	0.0	17.7	13.9	23.5

Conclusions and Discussions

The reaction of low concentration iodine gas with cesium carbonate forming particulate iodide and organic iodide in the similar reactor situation was investigated using an on-line UV-VIS spectrometer system. The iodine concentration and the absorbance in NaOH solution showed linear relationship as assumed by the Beer Lambert law. For quantitative analyses of the reaction, the absorptivity coefficient (72.9 ± 4.5 L/g/cm) of iodide in solution at 228 nm was determined experimentally. No difference in the reaction between 30 °C and 60 °C was observed. However, the reaction was found to have strong temperature dependency above 60 °C. At 100 °C and 130 °C, more than 40 % of iodine was reacted with cesium carbonate within 15 minutes. These fractions are smaller than those reported by the other investigators (>60%), since dry air was used in our experiment while humidified air was used in their experiment.⁶ As mentioned earlier, radioiodine release from the reactor accidents strongly depends on the degree of formation of organic iodide or particulate iodide in the reactor containment or RCS (Reactor Cooling System). Hence, it is clear that the effect of moisture in iodine reaction is significant and the formation of airborne iodine under actual operating condition is more severe.

In this investigation, it was shown that the formation of particulate iodide and organic iodine using cesium carbonate aerosol, which is one of the existing materials in the reactor containment, is significant at the temperature above 60 °C and is also moisture sensitive. It is recommended to investigate several other reactor materials such as CsO, CsNO₃, MnO, and CsOH, etc. in a similar manner to simulate the production of iodine aerosols that released in the severe reactor accident. In reality, however, many other important factors are involved in this process such as pressure in the system, total amount of produced molecular iodine, radiation dose in the reactor system, pH level of the coolant determining reproduction of volatile molecular iodine from iodide in solution, and reaction of iodine with containment surface, etc.

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