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Reactions between reactive metals and iodine in aqueous solutions

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Abstract

Volatile I_2 is likely to be released from the core and primary system to the reactor containment in the event of a severe nuclear reactor accident. Within the containment, I_2 will be distributed between the aqueous and gas phases which makes it very important to study how I_2 will interact with containment surfaces in order to determine which processes might reduce the concentration of volatile I_2. This study focused on the reactions of I_2 with some reactive metals available in the aqueous phase of the containment. The experiments were done under conditions similar to those in the containment of a boiling water reactor in a severe accident situation. Copper, zinc and aluminium are all capable of reducing the concentration of I_2 in the aqueous phase either by adsorption or by conversion of I_2 to I^-. Copper binds I_2 on the surface as CuI, while zinc and aluminium converts I_2 to I^-. Rate constants were determined for the adsorption of I_2 on Cu in the temperature range of 25–85 °C and for the conversion of I_2 to I^- on Zn and Al in the temperature range of 25–140 °C. The rates of adsorption and conversion increased with temperature.

1. Introduction

A severe nuclear reactor accident would cause the release of a large number of volatile fission products from the molten core. Among those, iodine is considered one of the most hazardous owing to its high volatility and biological activity in the thyroid gland with a subsequent increase in cancer risk and/or acute injury (loss of thyroid gland function).

Due to the very high temperatures during a severe accident, iodine will initially be released from the fuel as atomic iodine, I^0. Iodine, together with other volatile fission products will then be transported through the primary system where they will react with each other, with steam and structural surfaces. Iodine was long believed to react with caesium in the primary system to form caesium iodide, which dissolves in water when entering the containment. Modern research has shown that this might not be the case, and that iodine could enter the containment as molecular iodine (I_2) and different metal iodides [1,2]. I_2 present in the containment of the nuclear reactor can then be released to the

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environment and significantly contribute to the source term. Not all iodine would escape however, since interactions will take place with materials inside the containment building, such as large metal surfaces. Studying the deposition on various materials inside the containment will help us to gain a better understanding of the mechanisms available for mitigating the iodine release from the containment. Research has mainly concerned adsorption of I_2 on steel surfaces [3], but this study focuses on other metal surfaces in boiling water reactors. For example, many construction details in the reactor containment are made of aluminium or galvanized steel, i.e. they are covered with zinc. In the case of a meltdown, much wiring below the reactor vessel will also melt and release copper aerosols into the containment air [4]. Aluminium, zinc and copper are all fairly reactive metals and would undergo reactions with iodine in the containment. Data on the reactions of I_2 with these metals in a humid atmosphere have been reported elsewhere [5]. This study concerns the reactions of I_2 with metals in water.

2. Experimental

Two separate experimental series were done. The first studied the conversion of molecular iodine (I_2) to iodide ions (I^-) on zinc and aluminium surfaces in water and the second the adsorption of I_2 on copper surfaces in water. Both experimental series also studied the influence of temperature on the reactions. The experimental apparatus differed both between the two experimental series and in the first experimental series, as experiments above 100 °C in water required special equipment. The containment building of a boiling water reactor will withstand a pressure of up to 7 bars in case of an accident, and the water temperature may thus rise above 100 °C.

All solutions were adjusted to pH 2.2 using sulphuric acid to ensure that iodine initially existed only as I_2 [6]. This might not be solutions with chemical compositions relevant for an accident scenario, but the aim of these experiments was to study the reactions between I_2 and metal surfaces, not to do laboratory scale experiments on aqueous phase chemistry in the containment. The I_2 solution used in all experiments was analyzed using ion chromatograph methods. No iodate and only very low concentrations (micro molar) of iodide ions were present in the solution. The pH value was checked before and after experiments and was found to remain constant.

2.1. Zinc and aluminium experiments at 25, 50 and 90 °C

A 668 cm^3 cylindrical glass beaker with a removable lid was filled with 215 cm^3 of dilute sulphuric acid (pH 2.2). The metal sample (a 3.5 cm long zinc wire with a 0.185 cm diameter or a 15 cm long aluminium wire with a 0.3 cm diameter) was placed in the water phase using a specially designed glass hook attached to the lid of the beaker [7]. A magnet was placed at the bottom of the beaker and a combined magnetic stirrer and heater was adjusted to a slow speed in order to mix the solution. Mixing was achieved using a glass encapsulated magnet placed at the bottom of the beaker. The apparatus is schematically described in Fig. 1. Blind tests were done to determine whether iodine–iodide conversion took place on the glass surface of the beaker. The blind tests were done without any metal in the solution.

The heater was used during the experiments at elevated temperatures and the temperature was adjusted by reading a thermometer with a tip encapsulated in glass that was lowered into the solution. This procedure ensured that the temperature did not deviate more than two degrees from the preferred value. As the preferred temperature was reached and stabilized, 215 cm^3 of an I_2 solution (pH 2.2) was added to the water to achieve an I_2 concentration of approximately 0.25 mM in the experimental beaker. The experiment was started as the I_2 solution was added to the beaker.

The progress of the reaction was followed by measuring the concentration of iodide ions and molecular iodine in aqueous samples removed from the experimental beaker several times during each experiment.

The concentration of iodide ions in each sample was measured using an ion selective electrode that was sensitive to iodide ions. The electrode was calibrated in the concentration range of 5×10^{-7}–5×10^{-3} mol dm^{-3} × 5 cm^3 samples from the experimental beaker were mixed with 5 cm^3 0.2 M KNO_3 solution (pH 2.2) to achieve a constant ionic strength of 0.1 M NO_3^- during each measurement. After reading the iodide ion concentration, ascorbic acid was added to the solution to reduce all I_2 to I^-. The iodide concentration was then measured again. The I_2 concentration of each sample was thus calcu-

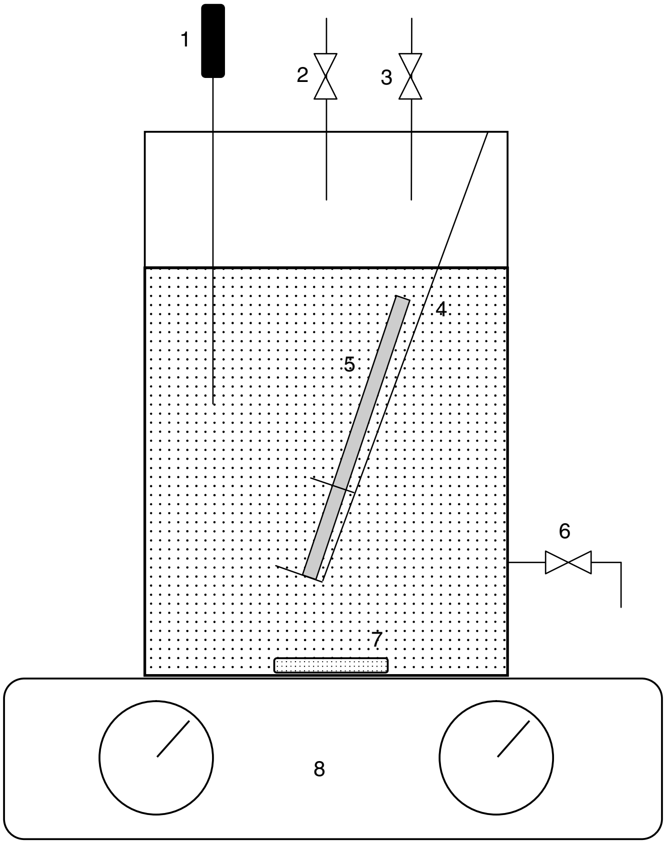

Fig. 1. Apparatus used for the experiments with I_2 and Al or Zn in water at 25, 50 and 90 °C: (1) thermometer with tip encapsulated in glass, (2) valve for addition of I_2 solution, (3) pressure relief valve, (4) glass hook, (5) metal sample, (6) sampling valve, (7) magnet encapsulated in glass and (8) combined heater/stirrer.

lated by subtracting the iodide concentration before and after the addition of ascorbic acid.

2.2. Zinc and aluminium experiments at 140 °C

A 45 cm^3 cylindrical stainless steel pressure vessel with an inner lining of PEEK (Poly Ether Ether Ketone) was used for these experiments. The metal sample (a 1 cm long zinc wire with a 0.185 cm diameter or a 1 cm long aluminium wire with a 0.3 cm diameter) was placed inside the vessel. The lid was then tightly secured with screws and the vessel was placed in a furnace, where it was heated to 140 °C. The temperature deviation was estimated not to be more than four degrees from the preferred value. When the desired temperature was reached, 29 cm^3 0.5 mM I_2 solution (pH 2.2) was injected into the vessel through a valve in the lid. The experiment was started as the I_2 solution was added to the vessel.

Samples of the aqueous solution were taken at regular intervals and rapidly cooled to room temperature. The concentration of iodide ions and molecular iodine in each sample was measured using the same procedure as described above, apart from different sample volumes; 2.5 cm^3 samples were mixed with 2.5 cm^3 dilute sulphuric acid (pH 2.2) and 5 cm^3 of the 0.2 M KNO_3 (pH 2.2) solution to achieve a constant ionic strength of 0.1 M NO_3^- during each measurement.

2.3. Copper experiments

These experiments were done using an apparatus described in detail elsewhere [7] and schematically shown in Fig. 2. The central part of the apparatus is a 668 cm^3 cylindrical glass beaker with a removable lid. There are two outlets on opposite sides of the beaker connected to separate piping, one for circulating a gaseous phase and the other for

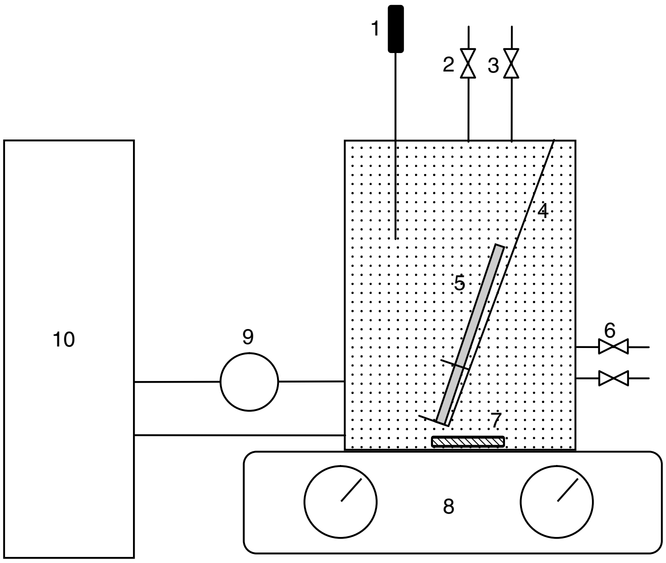

Fig. 2. Apparatus used for the experiments with I_2 and Cu in water: (1) thermometer with tip encapsulated in glass, (2) valve for addition of I_2 solution, (3) pressure relief valve, (4) glass hook, (5) metal sample, (6) closed valves (intended for circulation of a gas phase), (7) magnet encapsulated in glass, (8) combined heater/stirrer, (9) pump for circulation of aqueous phase and (10) gamma detector (NaI).

circulating an aqueous phase. Each pipe is wrapped around a scintillation detector (NaI(Tl)) for measurement of the radioactivity of the aqueous and gaseous phases respectively. During all experiments described in this paper the pipe circulating the gaseous phase was sealed off, as the glass beaker contained only aqueous phase.

A thermometer with a tip encapsulated in glass was attached to the lid of the beaker for measurement of the temperature in the aqueous phase. This procedure ensured that the temperature did not deviate more than two degrees from the preferred value.

The beaker was placed on a combined heater/magnetic stirrer in order to mix and heat the solution. Mixing was achieved using a glass encapsulated magnet placed at the bottom of the beaker.

The beaker was filled with dilute sulphuric acid (pH 2.2) and an I_2 solution (pH 2.2) spiked with I-131. The initial I_2 concentration varied between experiments. When the radioactivity was equally distributed in the aqueous phase, the copper sample (a 7 cm long copper wire with a 0.1 cm diameter) was placed in the aqueous phase using a specially designed glass hook attached to the lid of the beaker. The adsorption of iodine on copper was then monitored by measuring the decrease in iodine concentration in the aqueous phase.

3. Results

3.1. Zinc and aluminium experiments at 25, 50, 90 and 140 °C

In contrast to experiments by Funke [3] and Deane and Marsh [8], no iodine–iodide conversion on the glass surfaces of the experimental beaker could be observed in the blind tests. At pH 2.2 the reaction between iodine and quartz glass (represented as $\equiv$SiOH below) would be of very little importance because of the high concentration of hydrogen ions:

$$I_2 + \equiv SiOH = SiOI + I^- + H^+ \tag{1}$$

Reaction (1) might be of greater importance at higher pH values.

Neither was any iodine–iodide conversion observed on the PEEK surfaces of the pressure vessel used for the high temperature experiments. The theoretical background and the analysis of experimental data were therefore the same as in the experiments at lower temperatures. The experimental set-up and sampling procedures were however much more complicated in the high temperature experiments. In combination with a greater temperature deviation (as mentioned in Section 2.2) this resulted in larger uncertainties in the experimental data as compared to the experiments done at lower temperatures.

Earlier experiments have shown that adsorption of molecular iodine on zinc and aluminium is negligible [5]. Thus, we can conclude from the discussion above that the only reaction that takes place in the experimental system is:

$$I_2(aq) \rightarrow 2I^-(aq) \quad k_{conv} \tag{2}$$

with k_{conv} as a first-order reaction rate constant. The I_2 concentration decreases according to

$$d[I_2]/dt = k_\Sigma \cdot [I_2], \tag{3}$$

where $[I_2]$ is the aqueous I_2 concentration, t is the time and k_Σ is the overall reaction rate constant. Since there are no other reactions than (2), k_Σ will be equal to $k_{conv} \cdot (A/V)$, where A is the metal surface area and V is the volume of the aqueous phase. Integration of (3) then gives

$$[I_2] = [I_2]_0 \cdot \exp(-k_{conv} \cdot A/V \cdot t), \tag{4}$$

where $[I_2]_0$ is the aqueous iodine concentration at the start of the experiment. In this study, k_{conv} was directly evaluated from (4), using plots as are shown in Fig. 3.

In addition to a few pre-tests to develop the necessary experimental procedures, at least three separate experiments were carried out for each metal at each temperature. The use of triplet samples showed that the experiments were repeatable within an acceptable range of uncertainty. The uncertainty in k_{conv} was calculated using a least square method that fitted the logarithmic form of (4) to experimental data. The least square method assumed that all measurements within one experimental series had the same fractional error and returned k_{conv} together with its standard deviation, $s(k_{conv})$. The rate constants derived from these experiments are shown in Fig. 4.

Another least square method was used to fit the logarithmic form of the Arrhenius equation to pairs of $\ln(k_{conv})$ and the reciprocal temperature, $1/T$. The values of $\ln(k_{conv})$ were then weighted with $s(k_{conv})/k_{conv}$ in accordance with standard treatment of chemical data [9]. A linear curve could only be fitted to experimental data between 25 and 90 °C. From the fitted linear curve, the activation energy for the iodine–iodide conversion reaction could be determined to be 46.3 kJ/mol for Zn and 35.6 kJ/mol for Al. At $T > 90$ °C values of $\ln(k_{conv})$ were below the fitted linear curve.

3.2. Copper experiments

Gaseous iodine dissolved in the aqueous phase was adsorbed on the copper surface. The following reaction takes place:

$$2Cu(s) + I_2(aq) \rightarrow 2CuI(s) \tag{5}$$

A mass balance for the system shows that the decrease in molecular iodine in the aqueous phase can be described by an exponential function

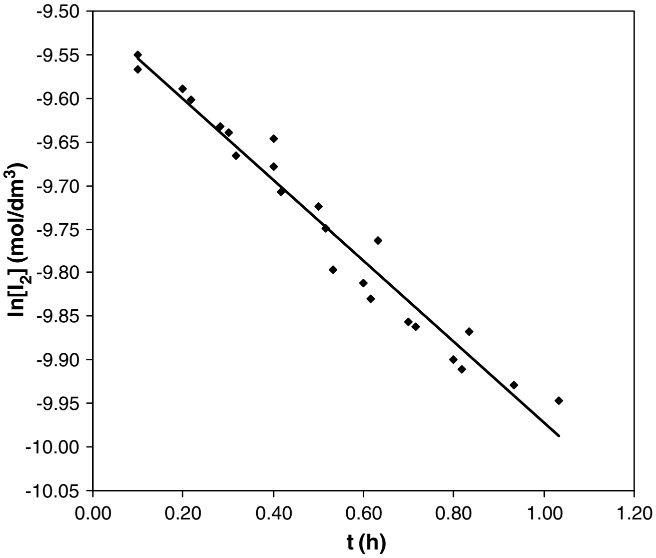

Fig. 3. I_2 concentration plotted against time. k_{conv} and $[I_2]_0$ are determined from the fitted line.

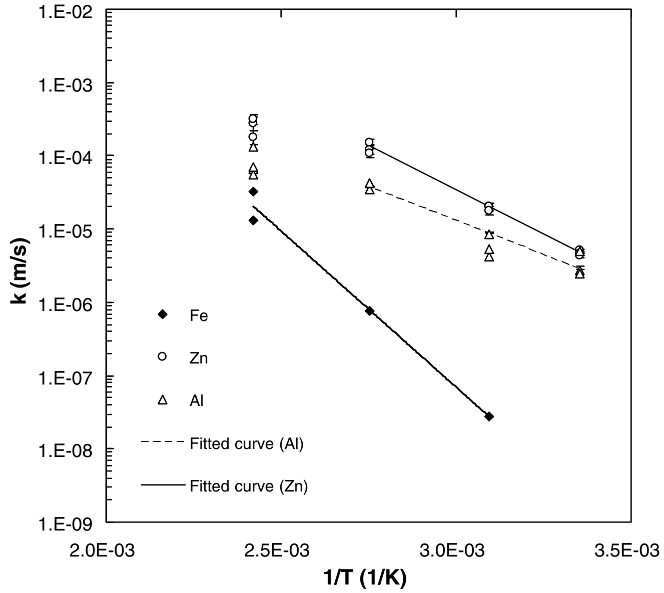

Fig. 4. Rate constants for the conversion of I_2 to I^- on Al and Zn plotted against the reciprocal temperature. Values measured for steel by Funke et al. [3] are added for comparison.

$$[I_2] = [I_2]_0 \cdot \exp(k_{ad} \cdot 2 \cdot A/V \cdot t), \quad (6)$$

where k_{ad} is the rate constant (m/s) for the adsorption reaction, A is the copper surface area and V is the solution volume.

Experimental data showed that the decrease in molecular iodine in the aqueous phase was exponential with time. Krausmann et al. [10] studied adsorption of iodine on silver surfaces and confirmed the constant adsorption rate for the adsorption of molecular iodine on silver. They also studied the adsorption of iodide ions on the silver surface and treated that as a two-step process. As expected, no such behaviour could be noted in this study because of the very low content of iodide ions in the experimental solution.

Three separate experiments were done at each temperature. To study the influence of I_2 concentration on the adsorption rate, different initial concentrations were used at each temperature. No dependence of concentration on the adsorption rate could be found within the concentration range covered in this study (2×10^{-4} mol/dm^3–2×10^{-6} mol/dm^3). The adsorption rate increased with temperature and was found to be $(2.45 \pm 0.02) \times 10^{-6}$ m/s at 25 °C, $(11.95 \pm 0.01) \times 10^{-6}$ m/s at 50 °C and $(17.92 \pm 0.02) \times 10^{-6}$ m/s at 85 °C. No linear dependence was seen between $\ln(k_{ad})$ and $1/T$, however, and as a result no activation energy for the adsorption process could be determined.

4. Discussion and conclusions

4.1. Zinc and aluminium experiments

Zinc and aluminium surfaces do not adsorb molecular iodine since the solubility of zinc iodide and aluminium iodide is too large to allow any accumulation of iodine on these surfaces. Instead, molecular iodine is converted to iodide ions.

The rate of the conversion reaction is temperature dependent and increases exponentially up to 90 °C. Above that temperature, the rate does not follow an exponential curve. There could be several reasons for this. First, the experimental set-up producing data above 90 °C was different from the set-up at lower temperatures and experimental uncertainties were thus greater, as mentioned earlier. There might also be a competing surface reaction that becomes more important at elevated temperatures. Microscope pictures of zinc and aluminium wires placed in water at 140 °C for 24 h indicated an oxidized surface layer. The build-up of such an oxide layer would likely slow down the iodine–iodide conversion process on the surfaces.

The conversion reaction can be an important factor for mitigating volatile iodine inside a nuclear power plant after a core meltdown. Depending on the surface-to-volume ratio (A/V), the reaction will be of varying importance, with a large surface-to-volume ratio favouring the reaction. The mitigating effect can be described by calculating the half-life of the initial I_2 concentration

$$t_{1/2} = -\ln(1/2)/(k_{\mathrm{conv}} \cdot A/V). \tag{7}$$

For very high surface-to-volume ratios such as a thin liquid film covering a large surface area, the half-life is in a timescale of minutes and seconds. Smaller surface-to-volume ratios representing for instance a large sump or a pressure suppression pool will result in longer half-lives in a timescale of hours and days.

4.2. Copper experiments

Copper areas bind molecular iodine on the surface. The reaction rate increases with increasing temperature. The temperature dependence of the reaction rate did not follow the Arrhenius law. As with zinc and aluminium, an oxidized surface layer could be observed on copper wires placed in water at 140 °C for 24 h. The oxide layer would be likely to retard the iodine adsorption process on the copper surface.

The adsorption of I_2 on copper surfaces in water is another important mechanism in decreasing the concentration of volatile iodine species inside the containment. The half-life of the initial I_2 concentration in this case is

$$t_{1/2} = -\ln(1/2)/(k_{\mathrm{ad}} \cdot 2 \cdot A/V). \tag{8}$$

The I_2 concentration in the aqueous phase will be reduced to half within minutes at large surface-to-volume ratios. Smaller surface-to-volume ratios result in longer half-lives in the range of days and months.

Acknowledgement

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