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Apparatus for on-line measurements of iodine species concentration in aqueous and gaseous phases

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Abstract

An apparatus was constructed for on-line measurements of the concentration of iodine species in aqueous and gas phases using radioactive tracers. The apparatus and procedures for determining detector efficiencies and flow rates of both phases are described in detail. A complete description of experimental procedures is given and reactions between gaseous iodine and reactor containment construction materials such as copper, zinc and aluminium are investigated using the apparatus.

Keywords: Detectors; Iodine; Tracers; BWR

1. Introduction

This paper describes the construction and function of an apparatus for on-line measurements of the concentration of radioactive species in aqueous and gaseous phases.

Questions concerning reactions of iodine and iodine compounds both in normal operation and in the case of serious accidents in nuclear reactors have been of great concern for decades. While a great deal of research has been done in a variety of areas of iodine chemistry [1,2], many questions remain to be answered. One is how iodine reacts with some metals common in a typical boiling water reactor (BWR) [3]. Many construction details in the reactor containment are made of aluminium or exist as galvanized metal areas, i.e. covered with zinc. In case of a meltdown, much wiring below the reactor tank will melt and release copper aerosols into the containment air [4]. Aluminium, zinc and copper are all fairly reactive and will undergo reactions with iodine in the containment.

As part of the European Commission's ICHEMM (Iodine Chemistry and Mitigation Mechanisms) project, we have studied the behaviour of gaseous iodine in the presence of copper, zinc and aluminium under conditions existing in a BWR. Experiments were performed using inactive iodine with ^{131}I as a radioactive tracer. An apparatus was constructed to be able to conduct relevant experiments and is described in this paper.

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2. Design of the apparatus

The apparatus is viewed as being constructed in three parts — vessels and pipes, a temperature box and a detector system. One of the main difficulties in studying iodine chemistry in the concentration range typical for severe reactor accidents is the very high tendency of iodine compounds to stick to surfaces. All vessels and pipes are thus made of glass.

2.1. Vessels and pipes

The vessel and pipes are constructed in such a manner that experiments can be performed at conditions similar to those in a BWR, that is with high humidity and low oxygen concentration. The central part of the apparatus is a 700 cm^3 large reaction flask with a removable lid. During experiments one-third of the vessel is filled with water. The vessel has seven openings, two at the bottom below the water surface, one slightly above the water level and four in the lid. The lid itself is tightly secured to the vessel.

The lid openings have several functions. One is used as a vent for nitrogen flushing and iodine introduction, another as an inlet for metal samples and yet another for placement of a thermometer during temperature-controlled experiments.

To enable the circulation of the aqueous and gas phases, two centrifugal pumps were constructed, both handmade of glass. Gas or liquid enters through a pipe in the upper centre of the pumps and leaves through a pipe at the bottom side. The pumps are driven by two glass-enclosed magnets run by magnetic stirrers (Chiltern MS 15). The magnetic stirrers are connected to voltage regulators to secure an even voltage supply.

The metal samples are held in place in the gas phase during experiments by specially designed glass hooks. These hooks are attached to ground glass stopcocks that fit the lid openings. In the experiments, a metal sample is placed on the hook and is supported by two glass rings (Fig. 1).

The proportions of metal samples, gas volume and water volume are chosen such that they are almost proportional to those of a common BWR [5] (Table 1). The pumps have a volume of approximately 50 cm^3 each.

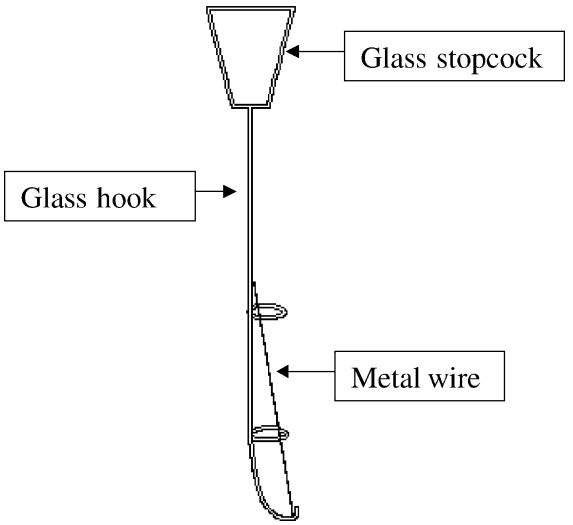

Fig. 1. Sketch of the glass hook with a metal wire attached.

Table 1
Volumes and relative proportions of the apparatus and a large BWR like Oskarshamn 3

	BWR	Apparatus
Total volume (m^3)	11870	1.01E-03
Gas volume (m^3)	8524	7.23E-04
Fraction	0.72	0.71
Water volume (m^3)	3346	2.90E-04
Fraction	0.28	0.29
Copper area (m^2)	1350[a]	9.90E-05
Surface/volume ratio	0.11	0.10
Zinc area (m^2)	6300	4.63E-04
Surface/volume ratio	0.53	0.46
Aluminium area (m^2)	11930	8.77E-04
Surface/volume ratio	1.01	0.87

[a] Assuming 10 μm Cu aerosol particles.

2.2. The detector system

The two openings at the bottom of the vessel are connected via a glass pipe loop that passes a scintillation detector. The opening at the middle of the vessel functions as an outlet for the gaseous phase, which later re-enters the vessel through one of the lid openings after having passed another

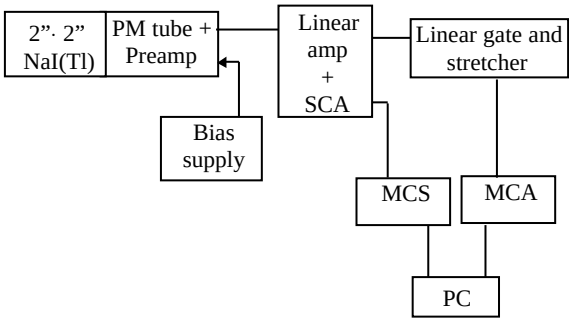

Fig. 2. The detector system. The figure shows how one of the two NaI(Tl) detectors is connected to a personal computer. The other one is connected in the same way.

scintillation detector. This construction enables activity measurements of both phases. The detectors used in this apparatus are 2 in. × 2 in. NaI(Tl) crystals for detection of the 364 keV γ-ray emitted in the decay of ^{131}I. The preamplifier is integrated with the PM tube. Each preamplifier is connected to one combined linear amplifier and single-channel analyser (SCA) (EG&G ORTEC 590). The pulses from the SCA are directed to linear gate and stretcher units (CANBERRA 1454) and then processed and stored by multi-channel analysers (MCA). The SCAs have a fixed window over the 364 keV peak and only accepts pulses within that window. A signal is also sent from each SCA to one of two multi-channel scaling cards (EG&G ORTEC MCS-Plus) that collects pulses for a set dwell time. The dwell time can be set from 5 ns to 65 535 s. A PC using software developed for the MCS-Plus follows the counted pulses during experiments (Fig. 2).

2.3. The temperature box

One of the main purposes for constructing this apparatus was to study iodine reactions with metals at elevated temperatures. The apparatus is therefore enclosed in a temperature regulation box. This box is made of wood with a Plexi-Glass front with two closable openings for easier access to the apparatus. The temperature is regulated using a heating fan connected to a temperature relay. This construction can maintain a constant temperature with a deviation of maximum ±2°C. The PM tubes work well at temperatures up to 80°C. The peaks in the energy spectrum produced by the MCA move to lower energies as the temperature increases, and the window set on the SCA must be adjusted accordingly (Figs. 3 and 4).

2.4. Detector calibration

The sodium iodide detectors are positioned in a unique geometry and must be calibrated accordingly.

The detectors are calibrated as follows. The vessel and loops are filled with a volume of water, V, holding a total activity, A. Circulation is started and the activity is measured. Since the volume of the loops surrounding the detectors, V_{loop}, the activity measured, R, the total activity and the total volume are known, a detector efficiency can be calculated according to the following equation:

$$\Psi = \frac{R}{(A/V)V_{\text{loop}}}$$

where

R is the activity measured by the detector (cps), A the total activity added to the aqueous phase (Bq), V the total aqueous volume (cm^3), and V_{loop} the loop volume (cm^3).

This detector efficiency is used to calculate the molar concentration of iodine species during experiments.

2.5. Flow rates

Since the stirring of both aqueous and gas phases is achieved using magnetic stirrers, the flow rate is adjustable. For the experiments performed within the ICHEMM project, the flow rate of the aqueous phase through the pipes was determined experimentally by adding a colour indicator to the aqueous phase and measuring the time required for the colour change to cover a certain distance. The measurement was repeated three times, and an average flow rate of 4.8 cm^3 s^{-1} was determined. The flow rate of the gaseous phase was determined in a similar way using bromine gas as a colour indicator. Six measurements gave an average flow rate of 2.10 cm^3 s^{-1} for the gaseous phase.

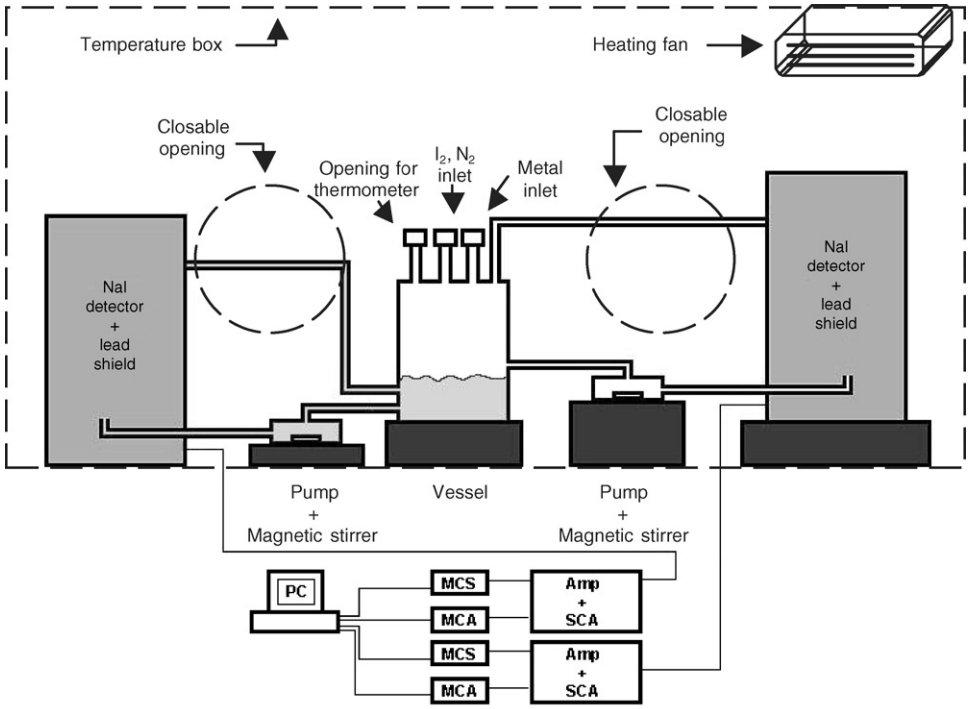

Fig. 3. Sketch of the apparatus.

Fig. 4. Picture of the apparatus. The Plexi-glass front is removed for better visibility.

3. Experimental procedures and application

Every experiment was started by filling the vessel, pump and pipes on the aqueous side with water. Air bubbles stuck in the loop around the detector were removed by pulsing the water flow with the pump. When the vessel was filled with the desired amount of water, the stirring rates of the aqueous-phase and gas-phase pumps were set. The oxygen concentration was kept low by flushing nitrogen gas through the vessel and pipes. For the introduction of gaseous iodine (I_2), a three-necked round flask was connected to the vessel through one of the lid openings. The round flask contained the iodine gas, which was flushed into the vessel by a nitrogen flow through the round flask. To release the pressure built up in the vessel, one vent in the lid was opened during iodine gas introduction. Equilibrium between the iodine concentration in the aqueous and gas phases had been established after about 1 h, after which a metal sample (copper, zinc or aluminium) was introduced using a glass stopcock. As a result of the adsorption of iodine onto the metal surface, the concentration of the iodine species in the aqueous and the gas phases decreased (Fig. 5).

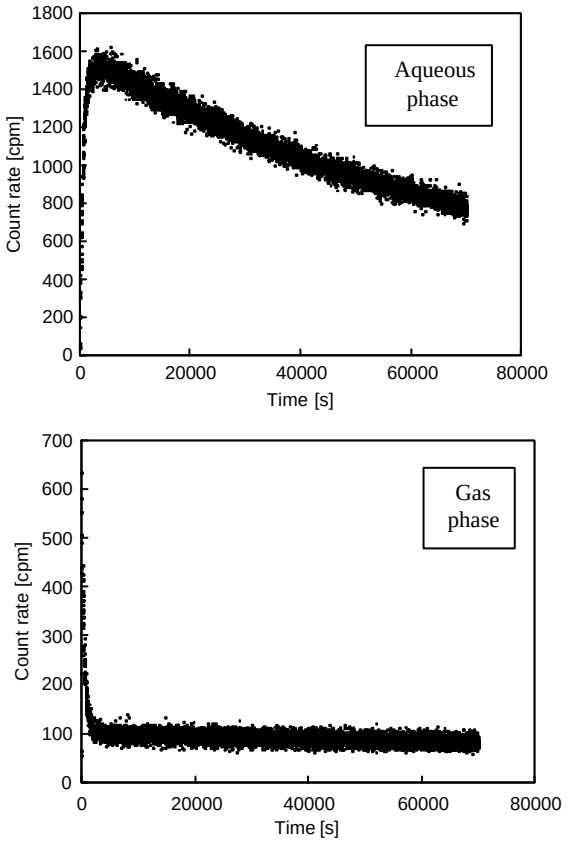

Fig. 5. Diagrams showing the aqueous-phase count rate and the gaseous-phase count rate in counts per minute (cpm) versus time. After the introduction of gaseous iodine to the gas phase at $t=0$ s, iodine is distributed between the aqueous and gas phases. As a result, the activity in the aqueous phase increases and the activity in the gas phase decreases until equilibrium is reached after approximately 1 h. At that point, a metal sample (copper) is introduced into the vessel and, as iodine reacts with the metal surface, the iodine concentration in both phases decreases.

4. Conclusions

An apparatus for measuring iodine concentration in aqueous and gas phases using radioactive tracer techniques was constructed. The apparatus is made of glass to minimize the sorption of iodine species on pipes and walls, and the dimensions are chosen such that they are proportional to those of a common boiling water reactor. The apparatus exhibits several important features:

- The atmosphere can be completely exchanged in order to be able to conduct experiments under inert conditions.
- The apparatus is enclosed in a temperature box to allow temperature-controlled experiments. The temperature can be regulated up to 80°C with a deviation ± 2°C.
- Chemical additives can easily be introduced into the apparatus, i.e. the experimental conditions can be changed during experiments.

Repeated experiments with gaseous iodine and some metals have given satisfying results, confirming the functionality and reliability of the apparatus.

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