Nuclear Engineering and Design 300 (2016) 536–540

Contents lists available at ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes

A new dissolved gas sampling method from primary water of the Paks Nuclear Power Plant, Hungary

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HIGHLIGHTS

- We constructed and applied a lightweight portable dissolved gas sampling device.
- A membrane contactor has been used to sample the dissolved gases from the water.
- Gas compound and gamma spectrometric measurements were done from the samples.

ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form 2 December 2015
Accepted 20 February 2016
Available online 7 March 2016

JEL classification:
S. Waste management

ABSTRACT

This article describes a novel sampling method for dissolved gases from radioactive waters. The major aim was to build a portable, lightweight sampling device in which the gas sample container is not in contact with the water itself. Therefore, a membrane contactor was used to take representative dissolved gas samples from the water of spent fuel pools. Quadrupole mass spectrometric and gamma spectrometric measurements were made from the samples to determine the gas composition and to detect any radioactive gas of fission origin. The paper describes (i) the construction of the sampler in general, (ii) the operation of the sampling unit and (iii) the measurement results of the first samples and the interpretation of the data. Both small and large fluctuations were able to be detected when the freshly spent fuel rods were put into the spent fuel pool or when the head valves of the toques of the fuel rods were replaced. In the investigated period (2013–2014), the main gas composition did not show large fluctuations, it was close to the composition of dissolved air. However, the activity concentration of ^{85}Kr varied in a broad range (0.001–100 kBq/l).

1. Introduction

By investigating the dissolved gases in fluids in a radioactive or toxic environment, information can be obtained about the conditions and on-going processes in the liquid media (Miter et al., 2009). From the 2003 incident of Paks NPP (Hózer et al., 2009; Aszódi et al., 2010), the dissolved gases of the water in Unit 2 were sampled by the vacuum degassing method until 2013 (Molnár et al., 2010). In this latter sampling process, the water is released into an evacuated glass bulb where the dissolved gases get into the headspace. The headspace gas is then admitted to an evacuated glass ampoule for further analysis. We wanted to modify this method to increase the amount of the gas sample and to improve reproducibility. The basic idea was to build a portable dissolved gas sampler specially designed for the sampling of dissolved gases in radioactive water. The device had to comply with the following major criteria. It must be lightweight and quite small. Furthermore, it is very important that the sample container must not get in contact with the water. This is necessary as radioactive particles and compounds in the water can be absorbed in the walls of the sample container in which the gas sample is taken for further analysis. The dissolved gases have to be extracted from the water. The unit was developed specifically for the sampling of only the dissolved gases in the water of different water reservoirs of nuclear power plants, for example the spent fuel pool.

The main components of the air (N_2, O_2, Ar, CO_2) are usually in solubility equilibrium with the water of open surface. However, if there is some continuous gas production in the spent fuel pool, the concentration of this gas in the water will first increase and then

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http://dx.doi.org/10.1016/j.nucengdes.2016.02.024
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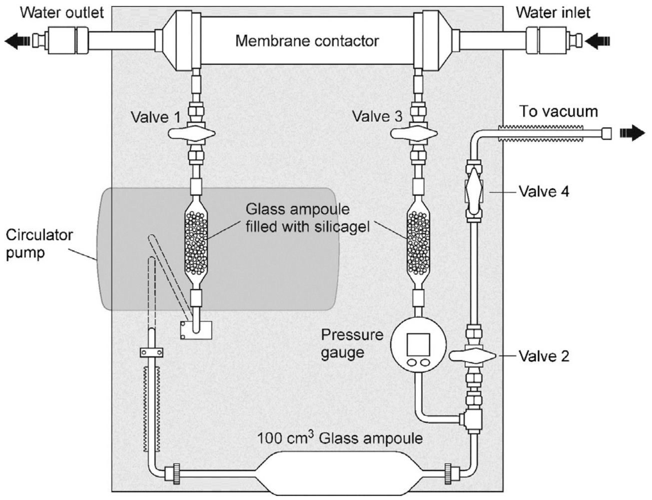

Fig. 1. Schematic drawing of the dissolved gas sampling unit.

tend to equilibrate with the ambient air. Biological processes can be revealed by an increased CO_2 concentration and decreased O_2 concentration or a lower O_2/N_2 ratio. On the other hand, a high H_2 concentration refers to radiolysis (Takiguchi et al., 2004), either of water or hydrazine (N_2H_4).

There are containers in the spent fuel pool, which contain broken fuel elements from the 2003 incident (Aszódi et al., 2010). Therefore, the ^{85}Kr content of the water is worth investigating to check the gas release from these vessels. Moreover, if short-lived volatile radionuclei (for example ^{133}Xe) cannot be detected, fission processes within the broken fuel elements can be excluded.

This paper aims to describe how our sampling unit works and the first results are also presented.

2. Method

2.1. General description of the dissolved gas sampling unit

The sampling device was built to extract the dissolved gases from the water (Fig. 1). Recently, extraction of dissolved gases from fluids is performed by membrane contactors (Mächler et al., 2012). The sampling unit consists of five main components: a membrane contactor, a circulator pump, a glass ampoule, a pressure gauge and silicagel gas driers. The mass of the device is less than 5 kg. Our system is based on that of Matsumoto et al. (2011) with small modifications. The idea of the sampling is that the system is evacuated by an external vacuum unit, the dissolved gases extracted by the membrane contactor fill the glass ampoule and the pressure can be read in the pressure gauge. The representative gas composition is maintained by circulating the extracted gas with a pump. The major part of the device is a membrane contactor (size: 1.7″ × 8.75″, type: MiniModule®, homepage: www.Liqui-Cel.com) which provides an interface between the water and gas phases. The diameter of the water inlet side is 0.5 in. Within the membrane contactor, the water flows through 7400 tiny polyurethane tubes and is discharged in the outlet side back to a tube. The inner diameter of the tiny polyurethane tubes is 220 μm, while their outer diameter is 300 μm. The volume of the lumen side and the shell side of the contactor is 73 and 132 ml, respectively. The total inner active surface area is 1 m^2 and the outer surface area is 1.4 m^2. The maximum flow rate of the water in the membrane contactor is 3000 ml/min at a maximum temperature of 40 °C.

The gas volume of the membrane contactor is attached to the gas pathway by gastight silicon tubes (Tygon R3603). Two Swagelok (SS-42GS4-1466) valves (Valve 1 and Valve 3) can separate the gas volume of the membrane contactor from the gas space of the sampling unit. Behind the valves, 10 cm^3 glass ampoules filled with silicagel were installed to trap water vapour. Hence, dry gas can be collected. To circulate the gases in the system, a circulator pump was integrated. Behind the output of the circulator pump a 100 cm^3 glass ampoule was installed via a stainless steel membrane tube. This ampoule is the sample container. Both ends of the glass ampoule are attached to the line via O-ring connections (Swagelok, ULTA-TORR-316). From this point, there are two pathways: one is the part of the closed circuit while the other one is a pathway to the vacuum system. In the closed circuit, a precise pressure gauge (Keller LEO 1) measures the internal gas pressure. The overall uncertainty of the pressure gauge is better than 6 mbar (<0.2% FS between 0 and 3000 mbar). The device measures the pressure 5000 times a second and displays it twice a second. Via the other valve, the gas circuit is connected to the shell side of the membrane contactor. An external vacuum system can be connected to the sampling unit via two valves (Valve 2 and Valve 4).

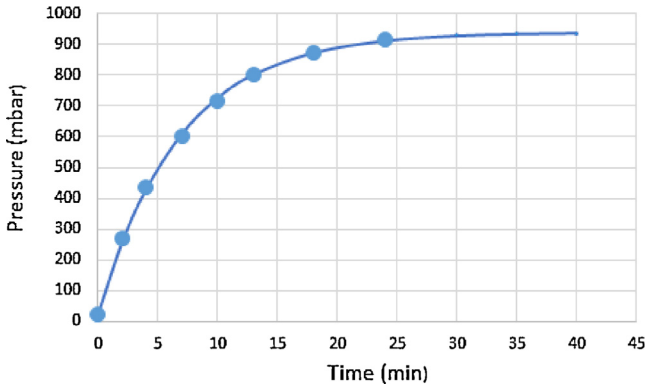

Fig. 2. The internal gas pressure as a function of time during sampling.

2.2. Operation of the sampling unit

Prior to sampling, the gas sampling unit has to be evacuated until the vacuum gauge in the rough vacuum pumping unit reaches 1×10^{-3} mbar. Valves 1 and 3 are opened for 1–2 min to pump away the remaining air from the gas contactor while the water is flowing in the lumen side. If the sufficient vacuum is reached, valve 2 shall be closed and valves 1 and 3 shall be opened. From this time, the inner gas pressure increases exponentially (Fig. 2). As soon as the inner gas pressure is close to 1000 mbar, the 100 cm^3 glass ampoule is flame sealed at both ends. This occurs when the pressure and the composition of the gas are very close to solubility equilibrium with the sampled water. This ampoule contains the gas sample. It is possible to decrease the internal gas pressure by opening and closing valve 2 and valve 4 separately.

To obtain the exact concentration of the various dissolved gases in the water, three parameters have to be known: the total dissolved gas pressure (p_{TDG}), the mixing ratio of each gas component and the water temperature. The total dissolved gas pressure can be calculated from the pressure data using the

$$p(t) = p_{TDC}(1 - \exp(-\lambda * t))$$

equation, where $p(t)$ is the measured pressure, t is the time elapsed and λ is the parameter of the exponential function. When looking for p_{TDG}, an exponential function is searched for, varying p_{TDG} and λ until the best fit is found according to a chi-square test. For Fig. 2, the p_{TDG} equation is

$$p(t) = 938 * (1 - \exp(-1.15 * t))$$