



Temperature dependent volatilisation behaviour of Cs from two commercial adsorbents used at Fukushima measured using novel experimental apparatus

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ABSTRACT

Results from a custom-built experimental volatilisation apparatus are presented. The apparatus consists of a tubular furnace to volatilise and then entrain the volatilised species into a cooled segment to reprecipitate for collection. This design allows for meticulous collection of the volatilised species, which are then analysed with atomic absorption spectroscopy. This paper includes an evaluation of the apparatus and a comparative study of the temperature dependence of Cs volatilisation from two commercial adsorbents. The Cs volatilisation from A-51 JHP and IE-96 was examined from 600 °C to 1000 °C. At 1000 °C the relative volatilisation was found to be 1.67% for A-51 JHP and 0.097% for IE-96. As the adsorbents requiring immobilisation contain volatile Cs species, the temperature dependence of this behaviour is important as it will affect Cs retention during the immobilisation process. Evaluation of the volatilisation apparatus showed it to be a reliable method to measure volatilisation behaviour from adsorbents.

1. Introduction

Many options exist for the disposal of nuclear waste, however many of them are high temperature processes (Lee et al., 2006). These options are suitable for many types of waste, mainly those requiring a highly durable final waste form. One of the problems of high temperature immobilisation is that volatile species are often released and need to be dealt with appropriately (Wilds, 1978; Spalding and Jacobs, 1989; Spalding et al., 1992; Parkinson et al., 2005; Parkinson, 2007; Ghiloufi and Girold, 2011). Many melter configurations incorporate off-gas treatment to capture released volatiles (Darab and Smith, 1996a). Off-gas treatment usually uses standard particulate scrubbers, both wet and dry, and High Efficiency Particulate Air (HEPA) filters. Often specific steps are included to trap specific species (Zamecnik and Choi, 2010), however this adds an extra waste stream to be treated, adding to the complexity of the immobilisation process (Yoon et al., 2012). To this end, accurate data on the volatilisation behaviour of radionuclides is required to be able to effectively design immobilisation processes for volatile wastes. Here we present the working of a custom-built

experimental apparatus that can be used to determine temperature dependent volatilisation behaviour and this tool was used to determine the volatilisation behaviour of Cs from two commercial ion exchange adsorbents, IE-96 and A-51 JHP.

The remediation of the Fukushima site has required extensive use of water treatment and, due to the use of sea water as an emergency coolant during the early stages of the Fukushima response, there is high NaCl content in the system (Kani et al., 2013). Many of the fuel elements in the cores were exposed to sea water at temperatures above 1000 °C, which formed chloride species in the coolant loop. The cooling water was treated by the various Advanced Liquid Processing System (ALPS) and this led to high concentrations of chlorides in the spent adsorbents (Baba, 2013). The spent adsorbents from the ALPS are stored on-site, while an immobilisation solution is developed (Pletser, 2017). These spent adsorbents are heat-generating and highly contaminated with volatile Cs and Sr halides. The temperature dependence of the Cs volatilisation behaviour, presented here, has served to set the temperature boundary for the processing conditions of waste form development (Pletser, 2017; Pletser et al., 2017).

Abbreviations: A-51JHP, A zeolitic ion exchange adsorbent; AAS, Atomic Absorption Spectroscopy; ALPS, Advanced Liquid Processing System; HEPA, High Efficiency Particulate Air; IE-96, A zeolitic ion exchange adsorbent; LTA Linde Type A, a type of zeolite; MFC, Mass Flow Controller; NPP, Nuclear Power Plant; ppb, Parts-per-billion; a measure of concentration, equal to µg/kg; ppm, Parts-per-million; a measure of concentration, equal to mg/kg; SDS, Submerged Demineralizer System

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Many nuclides can be volatile, mainly in the form of metal halides, but some form these volatile halide compounds more readily than others. Both Cs and Sr are well-known for forming such species (Parkinson et al., 2005; Parkinson, 2007; Sill, 1988; Roki et al., 2008; Mallampati et al., 2015). Other well known volatile species include, iodine, rhenium and technetium (Evans, 1996; Langowski et al., 1996; Xu et al., 2015; Darab and Smith, 1996b; Lee et al., 2016).

Halide retention during immobilisation has been studied by other authors (Hrma, 2010) and both CsCl and SrCl species are highly volatile and form volatile fractions (Spalding, 1994) and work from Kamizono et al., 1986, 1987, 1989 showed that volatilisation of Cs does occur from vitreous waste forms.

The body of literature concerning volatilisation from adsorbents is comparatively sparse. Volatilisation of adsorbed nuclides from adsorbents used for radionuclide adsorption has been carried out by Ames and Knoll (1962) and by Mimura and Kanno (1978). In the work of Mimura and Kanno Cs was volatilised from various commercially available adsorbents using an experimental set-up that heated the adsorbents to between 600 °C and 1200 °C after which the volatilised Cs was recovered from the apparatus and analysed (Mimura and Kanno, 1978). However there is no recent, publically available, literature concerning volatilisation from modern commercial adsorbents.

We present the working of a custom-built experimental apparatus, of modular design, consisting of a tubular furnace through which Ar is flowed to entrain volatilised species, which are then reprecipitated in a cooling trap for collection and analysis. The design of the apparatus was inspired by the work of Mimura and Kanno (1978) and was used to assess the Cs volatilisation behaviour from two modern, optimised, ion exchange adsorbents, IE-96 and A-51 JHP, at temperatures up to 1000 °C.

2. Materials and methods

An experimental apparatus was used to assess the temperature dependence of the volatilisation behaviour of Cs from commercial adsorbents. Two different commercial adsorbents were tested using the volatilisation rig, A-51 JHP and IE-96. Both of these adsorbents have been used in the remediation of the Fukushima site and are commercially available from Union Showa (8–40, Konan 1-chome, Minato-ku, Tokyo 108-0075, Japan).

2.1. Materials

2.1.1. A-51 JHP

A-51 JHP is a zeolite and is a modified version of the A-51 beads available from the Honeywell UOP A-50 range. The A-50 range is a synthetic Linde Type A (LTA) zeolite, with the A-51 designating the bead form of the adsorbent (Ikarashi et al., 2014). LTA are a class of zeolites with known Cs adsorption capacity (Munthali et al., 2015). LTA has previously been used as an ion exchange adsorbent for many commercial applications. A-51 is optimised for Sr removal from wastewater, but is able to adsorb Cs and has been used in the Submerged Demineralizer System (SDS) at Three Mile Island (Collins et al., 1982; Nagaishi et al., 2014). It has a reported selectivity series of Sr > Ca > Na, Mg > K > Rb > Li > Cs (Mimura et al., 2014).

2.1.2. IE-96

IE-96 is a zeolitic adsorbent with a large capacity for the sorption of Cs (Munthali et al., 2015). It is a modified zeolite which was developed from naturally occurring chabazite, which has a large cation exchange capacity (Inglezakis, 2005). IE-96 was engineered and developed for the cleanup of the Three Mile Island NPP (Honeywell, 2012). It is a Na-Chabazite (Mimura et al., 1995) which is delivered in 1 mm granule form. It is used for the primary bulk removal of caesium at Fukushima, with a distribution coefficient (K_d) of approximately 2000 relative to seawater. It is widely used for wastewater remediation as it has a high

selectivity for Cs and has a reported selectivity series of Cs > K > Na > Li, Ba > Sr > Ca > Mg (Honeywell, 2012, 2013).

2.2. Experimental rig

Volatilisation studies were performed at Hitachi Research Laboratories (7-1-1, Omika-cho, Hitachi-shi, Ibaraki-ken 319-1292, Japan). Fig. 1 shows the configuration of the rig, including gas lines, manifolds, regulators and wet traps.

The experimental set-up was a custom built tubular furnace. It consisted of a thermocoupled fused quartz tube furnace, with argon carrier gas, a volumetric flow controlled by a Mass Flow Controller (MFC), a cooling system designed to condense volatilised Cs and two bubble traps designed to scrub the effluent carrier gas of Cs. The constructed set-up consisted of a fused quartz tube of 13 mm in diameter and 50 cm long. This tube was enclosed on either end with stainless steel flanges sealed with a pair of rubber O-rings. The flange on the entry side has an opening for inflow of carrier gas and a thermocouple which was protected by a fused quartz tip. The exit side of the furnace has a cooling loop, through which cooling water was pumped, around which fused quartz wool was folded to catch entrained Cs and an exhaust for the effluent carrier gas. The exhaust side of the tube was wrapped externally with flexible cooling tube through which cooling water was pumped and all exposed parts of the fused quartz tube are wrapped in insulating fused quartz wool wrap to avoid heat loss and unintended temperature gradients. This tube was placed in a heating mantle, which was a thermocoupled furnace. The sample was loaded on a fused quartz boat and placed in the middle of the tube. Argon carrier gas was flowed through the furnace to ensure that volatilised Cs was entrained to the cooling loop. The flow of argon gas was controlled by an MFC. The effluent gas was passed through two bubblers filled with 0.1M HNO₃, to ensure maximum Cs retention in the experimental set-up, as seen in Fig. 2.

Fig. 2A is a photograph of the set-up while it was in operation, illustrating clearly the fused quartz wool thermal insulating wraps covering the ends of the fused quartz tube. Fig. 2B shows the heating mantle opened to show the inside of the tube, containing a fused quartz boat with sample and the thermocouple with a fused quartz tip.

The fused quartz boat and protective thermocouple tip can be seen in more detail in Fig. 2C. The fused quartz tube can be completely removed from the wraps and the heating mantle while still keeping the stainless steel flanges on either end as seen in Fig. 3. The flange consists of six components, which can be seen disassembled next to it. The six components, from left to right, are: the threaded bottom part of the flange, orange rubber O-ring, stainless steel spacer, rubber O-ring, stainless steel O-ring and threaded top of the flange. These parts assemble in that order onto the fused quartz tube and are screwed tight, with the two O-rings, separated by the stainless steel spacers, providing an impermeable seal. Once the flange was assembled and properly sealed, the end caps can be assembled, as in the top left hand of Fig. 3 showing the exhaust side cap, complete with cooling loop and fused quartz wool collector. This end cap was secured with an O-ring and a screw-top clamp. The apparatus further consists of a cooling water and an MFC to ensure a consistent carrier gas flow. Three separate temperature controllers, one for the sample thermocouple, one for the furnace heating mantle and one emergency cut-off temperature controller ensure accurate measuring of the temperature. After furnace operations have been completed, a fan was used to ensure rapid cooling to room temperature, so that the shut down procedure can be performed as quickly as possible.

2.3. Experimental procedures

2.3.1. Furnace operation

The furnace was meticulously stripped after every use, with each component washed in a 0.5M HNO₃ solution to ensure complete Cs

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