



Minimization of cobalt nuclide emissions in supercritical water oxidation of spent resin

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Abstract

A rapid and complete destruction of organics in the supercritical water oxidation (SCWO) of the Co-exchanged resin was found experimentally. Due to an extremely low solubility of CoSO_4 salt formed and separated effectively in the SCWO process, a minimal release of the nuclide Co would be warranted. In addition, recycling of Co nuclides is also possible by decomposition of the CoSO_4 species at elevated temperatures (>1040 K). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: SCWO; Low-level radioactive wastes; Nuclide emission

1. Introduction

Large quantities of low-level radioactive (LLR) spent resins are generated from condensate demineralizers and filters of nuclear power plants. These spent resins are difficult to process cement-solidification via existing technologies (Kinoshita et al., 1991). It has been required to expand the storage facilities or to reduce waste volume, as the years of nuclear power plant operations increase. A high volume reduction of LLR wastes effected by incineration has been recognized and the demand for practical applications is increasing. However, the LLR spent resins with basic engineering design characteristics of high water, ash and sulfur contents have made the incineration process very complicated. For better environmental considerations, one must provide a minimal release of nuclides in the gaseous emission, and a maximal possible including of radioactive species in ashes that would be solidified for final disposal.

Water above its critical point (647 K and 240 atm) becomes completely miscible with oxygen and most organic compounds, and extremely increases mass transfer rate (Shaw et al., 1991). Thus, high carbon conversion levels can be achieved with a very short residence time in the supercritical water oxidation (SCWO) process. The desired destruction and removal efficiency (DRE) may be achieved in seconds or minutes (Shaw et al., 1991; Gloyna and Li, 1993; Krajnc and Levec, 1994; Barner et al., 1992; Lin et al., 1998a,b). In addition, with increased reaction temperatures, the solubility of inorganic salts is decreased dramatically (Lin et al., 1998b; Shanableh and Gloyna 1991; Ikushima et al., 1998; Wallen et al., 1998; Cui and Harris 1995; Abdulagatov et al., 1998). Therefore, the present experimental work was directed to studies of formation of the low-solubility nuclide salt in the SCWO of resin materials (used in the nuclear power plant).

2. Experimental

The SCWO experiments were carried out in high-pressure and high-temperature batch reactors (148–150

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ml). The system pressure was controlled by a back pressure regulator (Tescom, $P_{\max} = 408$ atm) and a pressure regulator (Tescom, $P_{\text{in}} = 238$ atm; $P_{\text{out}} = 7$ atm). A safety rupture disk rated at 400 atm was installed. Hydrogen peroxide (30 wt%, Merck) was used as the oxidant (O/C ratio = 1–2) in the SCWO experiments. Fresh powder resin (Powdex) samples were provided by the Taiwan Power Company. Experiments conducted in the present work used simulated materials without radioactivity. The resin samples were ion exchanged with a cobalt (Co) nitrate solution. Concentrations of Co were measured by ICP-MS (ELAN 5000). About one gram of the Co-exchanged resin sample was oxidized in supercritical water at 673–773 K for 5–10 min. The product gas was analyzed by on-line FTIR spectroscopy and gas chromatography (Perkin Elmer, Model 5100) equipped with a TCD. A Propark-Q column was used. Infrared spectra were recorded on a Digilab FTIR spectrometer (FTS-40) with fully computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was conducted at a resolution of 4 cm^{-1} .

3. Results and discussion

The LLR resin wastes are very desirable to increase volume reduction. In the incineration process, the polymeric organics in the resin can be oxidized into water and carbon dioxide. However, as shown in Fig. 1(a), 80–90% of the ion-exchanged sites (SO_4) in the resin matrix is decomposed into SO_2 at 700–800 K in the temperature programmed oxidation of the resin. Note that CoSO_4 is not decomposed at < 1040 K (Fig. 1(b)). Oxidation of the resin organics provides the energy that enhances the decomposition rate of the SO_4 species. The

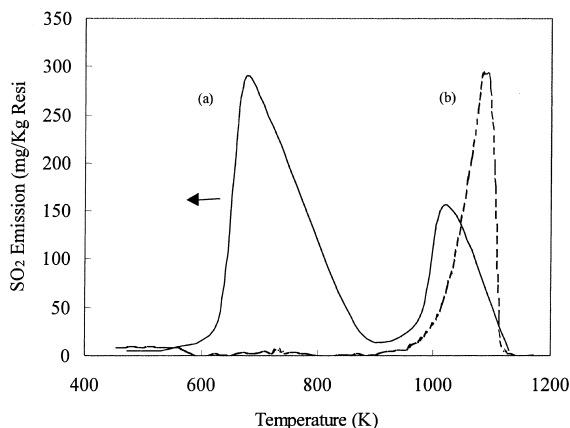


Fig. 1. SO_2 emissions in the temperature programmed oxidation of (a) the LLRA resin and (b) $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (dotted line with an arbitrary unit).

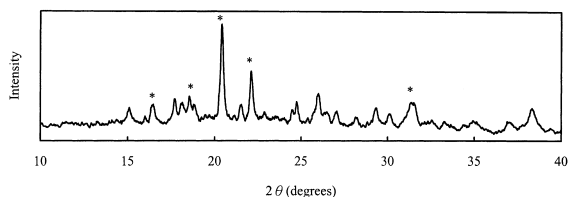


Fig. 2. X-ray diffraction pattern of the solid residue of supercritical water oxidation of the resin. * denotes the CoSO_4 species.

adiabatic temperature for oxidation of the Powdex resin might be as high as 2400 K.

Properties of supercritical water such as the complete miscibility in all proportions with oxygen, negligible surface tension, high diffusivity, low viscosity and low solubility of inorganic salts are very unique (Lin et al., 1998b; Shanableh and Gloyna, 1991; Ikushima et al., 1998; Wallen et al., 1998). Organic wastes can be completely oxidized and converted to carbon dioxide and water in a reaction time of less than a few minutes. A rapid and complete destruction of the organics in the resin with a highly enhanced reaction rate (activation energy = 7 kcal/mol) for oxidation of the resin in supercritical water was observed.

The SCWO of Co-exchanged resin samples were conducted in a batch reactor to reveal the behavior of metal salt formation. Over 95% of the cobalt salt was recovered in residual solid and brine water when separation was conducted in the supercritical water. The cobalt salt is identified as CoSO_4 species by X-ray diffraction spectroscopy (see Fig. 2). Due to the extremely and abruptly low solubility of metal salts in the supercritical water, the CoSO_4 species may be formed in the early stage of the SCWO process. As expected, the SO_2 emission (via the decomposition of the SO_4 species) in the SCWO of the resin was decreased by at least 90%, experimentally.

4. Conclusions

The extremely high DRE of the SCWO process generates a $> 99\%$ reduction in waste volume at equivalent solids concentration to the direct solidification or encapsulation process. The net volume reduction may lead to substantial cost savings for the later stages of cement encapsulation, storage, transport and disposal. In addition, the SCWO process can be totally enclosed. For LLR waste treatments, the SCWO provides little nuclides from the gaseous emission, and a maximal possible including of radioactive species in ashes, which would be solidified for final disposal. Furthermore, a minimum main reactor volume, which may account for a significant fraction of the total equipment cost, is

essential to ensure the most attractive and favorable economics for the SCWO process. In addition, recycling of the Co nuclides is also possible by simply decomposing the CoSO_4 species at elevated temperatures (>1040 K).

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