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SCWO of salt containing artificial wastewater using a transpiring-wall reactor: Experimental results

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Abstract

Experimental results using a transpiring-wall reactor (TWR) for supercritical water oxidation (SCWO) containing a hydrothermal flame as an internal heat source are presented. Our reactor set-up is aimed at overcoming the problem of reactor fouling and plugging due to precipitation of salts. Two types of transpiring-wall elements with different porosity were investigated. Experiments with artificial wastewater containing methanol and sodium sulfate in concentrations up to 6 and 3 wt.%, respectively, were used for a maximum operation time of 3 h. The salt deposition in the reactor was determined by electric conductivity and ionic chromatography measurements of the reactor effluent. About 65 % of the salt introduced to the reactor was detected in the effluent. No plugging of the reactor and equipment was observed during the experiments and methanol conversion ratios higher than 99.99 % were measured.

Keywords: Supercritical water oxidation (SCWO); Hydrothermal oxidation; Hydrothermal flame; Transpiring-wall reactor; Salt precipitation

1. Introduction

Supercritical water oxidation (SCWO) is a high-pressure high-temperature process for the destruction of toxic, hazardous or non-biodegradable aqueous organic waste. SCWO is carried out at conditions above the critical point of pure water ($T_c = 374\,°C$ and $p_c = 221$ bar). As a result of the complete miscibility of organic compounds and gases in supercritical water (SCW), high reaction rates and conversions close to unity can be achieved.

The thermophysical properties of water near and above its critical point change significantly compared to ambient conditions. Water, which is polar in the liquid state, is much less polar in its critical state and becomes a good solvent for non-polar compounds and gases such as oxygen, nitrogen or carbon dioxide [1–3]. The lack of interfacial mass transfer resistances in such a single-phase mixture (under salt-free conditions) combined with high reaction temperatures, leads to short residence times and small reactor volumes (i.e., high space–time yields).

Corrosion of reaction vessels and process equipment with SCW combined with reactive ions such as Cl^-, F^-, H_3O^+ and oxygen is one of the major challenges [4–9]. Furthermore, equipment fouling and plugging due to precipitation of salt particles in SCW is the most severe problem that SCWO processes face nowadays [6]. The solubility of inorganic salts in SCW decreases sharply when exceeding the critical point of water [10–12]. Agglomerates of precipitated salts formed during operation adhere to reactor walls and thus change the flow field and the heat transfer conditions across the reactor walls. Generally, industrial liquid waste contains inorganic matter in significant amounts, e.g. salt concentrations up to 3 wt.% can be found in paper mill sludge or pharmaceutical wastewater [13].

Examples of solubility and deposition studies of various mixtures can readily be found in the literature. Armellini and Tester [14] and Armellini et al. [15] used sodium chloride and sodium sulfate for investigations of the rapid or so called "shock like" precipitation in binary salt–water systems. Rogak and Teshima [16] performed solubility and deposition studies of sodium sulfate in a fully turbulent tube flow and developed a heat-transfer model, similar to the one described in the work of Chan et al. [17] at Sandia National Laboratories. Furthermore, the solubility

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of sodium sulfate, sodium carbonate and their mixtures in SCW was investigated by Khan and Rogak [18]. Hodes et al. [19] provided solubility and deposition experiments on a hot finger using sodium sulfate and potassium sulfate water mixtures at pressures and temperatures typical for SCWO conditions and compared the results to a deposition rate model [20,21]. A comprehensive review of fundamental aspects and research of the precipitation of salts in SCWO is given in Ref. [22]. In addition, Marrone et al. [23] described commercial technologies and approaches aimed to control salt precipitation and formation of solids in SCWO systems.

Different reactor concepts to handle the salt accumulation and corrosion during SCWO had been proposed in literature, e.g. double-tube reactors [24–27]. In our study, we focused on the promising concept of the transpiring-wall reactor (TWR) [28–48].

Foster Wheeler Corp., Sandia National Labs. and Aerojet GenCorp Inc. reported experiments with transpiring-wall reactors using the platelet liner technology. Experiments with salts (sodium sulfate) in the waste stream were performed. The transpiring-wall nearly eliminated the salt deposition on most of the reactor surface. The salt deposition was restricted to the heating section of the top of the reactor [37]. Conductivity measurements detected, that about 70% of salt came trough the system [38]. Recently, results from an U.S. Army program for the destruction of chemical weapons were presented [40]. Two reactor designs equipped with a solid wall system (design by General Atomics) and a transpiring-wall system (design by Foster Wheeler Development Corp.) were investigated. No salt plugs occurred during operation with different feeds.

Abeln et al. [41] at the Forschungszentrum in Karlsruhe performed experiments with salt containing wastewater using a TWR. Electric conductivity and inductively coupled plasma (ICP) measurements indicated, that about 50 wt.% of the salt remained in the reactor.

Fauvel et al. [45] recently reported results using a TWR equipped with an porous ceramic α-alumina tube. No corrosion damage was observed even if aggressive compounds were treated. However, oxidation of aqueous mixtures containing sodium sulfate (up to 5 wt.%) and ethanol led to reactor plugging.

The effect of the transpiring-wall designs on the SCWO process was presented by Bermejo et al. [46]. Three transpiring-wall designs were tested using fully and partially porous transpiring-walls. Pore sizes greater than 24 μm were found to be recommendable to avoid pore blocking in the transpiring-wall. In experiments using sodium sulfate concentrations up to 4.74 wt.%, no plugging of the reactor was observed. The recovery of salts varied between 55 and 5%. Influence of the introduced salt on the temperature profile and the TOC removal was reported. This behavior was explained by changes in the phase equilibria, when salt is introduced to the reaction mixture. An overview of transpiring-wall reactors tested by various research groups was presented.

At the Swiss Federal Institute of Technology (ETH) a TWR [49–54] containing a hydrothermal flame was investigated using various analyzing methods. The so-called "hydrothermal flames" have been observed in semi-batch reactors [55–60] and also successfully investigated in continuously operated reactors [61–64].

The hydrothermal flame provides desired reaction temperatures operating at low inlet temperatures, which reduces corrosion and avoids plugging (when introducing salt containing waste streams) of the reactor inlet lines and allows a cold feed of the wastewater into the reactor. Furthermore, a permanent radial water flow through the transpiring-wall prevents any wall contact of the hot, corrosive and/or particle containing reaction mixture by fluid dynamical means. Precipitated salt is either redissolved or flushed away by the water film formed on the inner surface of the transpiring-wall.

The actual study investigates the feasibility of the transpiring-wall reactor containing a hydrothermal flame to prevent salt deposition and corrosion of the reactor and/or its components during SCWO.

2. Experimental

2.1. Reactor design and pilot plant

Fig. 1 shows the sectional drawing of the transpiring-wall reactor. The vertical reactor vessel made of nickel-based Alloy 625 has an inner diameter of 34 mm and a transpiration zone length of 375 mm. The vessel was designed to sustain burst pressures up to 600 bar and temperatures up to 600 °C. The coaxial burner setup in the upper zone of the reactor consists of a burner tube, combustion chamber and an outer insert made of Alloy 625 and separates the fuel, oxygen and wastewater inlet stream (see Fig. 8). The burner tube is an air-gap-insulated double-tube system, where the inner tube and the burner nozzle were made of Alloy 230.

High-porous cylindrical elements (sintered Alloy 625 GKN Sinter Metals Filters, Radervormwald, Germany) with an inner diameter of 22 mm and a thickness of 3.75 mm form the transpiring-wall. The transpiration zone has an active length of 313 mm and is divided into four separate sections. In the first three sections (TW1, TW2, TW3) the transpiring water was introduced, while in the last section (CW) cooling water was supplied. The advantage of this setup is the possibility to control the mass flow rates of the transpiring water flows and temperatures for each section separately. The elements are easy to replace and different tube porosities can be employed. We used sinter tube elements with a porosity of 17% (equivalent laminar diameter of 3 μm) and 21% (equivalent laminar diameter of 5 μm) in our experiments. Furthermore, three intermediate rings made of Alloy 625 allowed a lead-through of thermocouples into the transpiration zone. Radial temperature profiles at three different heights (planes P2–P4; plane P1 was not used in this study) were measured. At each plane temperatures at four positions over the radius $r = 0$ (centerline), 3, 6 and 9 mm were measured. Further measuring points are shown in Fig. 1.

Four conveyor units are used for pressurizing the reactor. The system pressure is measured with a pressure transducer and controlled using a PI controller. Mass flow rates of the fuel (F_{f}), oxygen (F_{ox1}, F_{ox2}), wastewater (F_{ww}), transpiring (F_{tw1}, F_{tw2},