Chemical Engineering Journal 279 (2015) 1010–1022

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Review

Salt deposition problems in supercritical water oxidation

Donghai Xu *, Chuanbao Huang, Shuzhong Wang *, Guike Lin, Yang Guo

Key Laboratory of Thermo-Fluid Science & Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi Province, China

HIGHLIGHTS

- This article presents a detailed analysis of salt deposition concerning its cause, harm, and control means in SCWO.
- The current research methods for salt deposition in recent years are objectively summarized.
- The mechanisms of salt deposition are preliminarily analyzed and summarized.
- Some reactor designs and control methods are proposed to avoid salt deposition for a given wastewater in SCWO.

ARTICLE INFO

Article history:
Received 11 December 2014
Received in revised form 12 April 2015
Accepted 2 May 2015
Available online 21 May 2015

Keywords:
Supercritical water oxidation
Salt deposition
Solubility
Reactor plugging

ABSTRACT

Supercritical water oxidation (SCWO) is a promising technology that has been utilized to deal with refractory wastewater and sewage sludge at laboratory or commercial scale. However, its commercial application is postponed by corrosion and salt deposition problems in harsh SCWO environment. This work systematically and objectively reviews its current research status concerning salt deposition mainly including research methods, solubilities, deposition and separation performances, etc. and the mechanisms of salt deposition are preliminarily analyzed and summarized. Besides, several operation techniques and reactor configuration designs of either laboratory scale or commercial level used in SCWO processes are introduced to avoid reactor plugging induced by salt deposition. Finally, some subsequently alternative research ideas are proposed to reveal salt deposition mechanisms. A wise SCWO system is supposed to possess an appropriate reactor configuration and more than one control techniques to work together for a given wastewater.

Contents

1. Introduction . . . 1011
2. Salt types . . . 1011
3. Research methods . . . 1012
   3.1. Experimental methods . . . 1012
   3.2. Numerical simulation . . . 1012
   3.3. Combination of them . . . 1013
4. Solubility, deposition and separation characteristics . . . 1013
   4.1. Salt solubility . . . 1013
   4.2. Salt deposition properties . . . 1013
   4.3. Salt separation performance . . . 1014
5. Salt deposition mechanisms . . . 1014
6. Control means to salt deposition . . . 1015
   6.1. Special operation techniques . . . 1015
   6.2. Particular reactor designs . . . 1016

* Corresponding authors. Tel.: +86 29 82665749; fax: +86 29 8266 8703.
E-mail addresses: haidongxu93346423@aliyun.com (D. Xu), szwang@aliyun.com (S. Wang).

http://dx.doi.org/10.1016/j.cej.2015.05.040

7. Conclusions and outlook . . . 1020
Acknowledgments . . . 1020
References . . . 1020

1. Introduction

Above the critical point (T = 374.15 °C, P = 22.1 MPa), water exists as a single phase and has analogous transportation properties of gas and solvent properties like liquid, which is known as supercritical water (SCW) [1,2]. SCW is a non-polar solvent that can be completely miscible with organic compounds and gases such as hydrogen, nitrogen and oxygen. However, it is a poor solvent for polar materials such as inorganic salts and other ionic compounds [3,4], because the dielectric constant of SCW sharply decreases dozens or even hundreds of times than that of the water under ambient conditions, exhibiting non polarity [2,5]. In relation to viscosity, it is small enough to carry out reactions at very high velocities under supercritical conditions [6]. Therefore, SCW is an admirable medium that has been utilized in SCWO processes for the degradation of wastes such as sewage sludge, chemical weapons and other refractory organic compounds [7–9]. Meaningfully, original heavy metals such as Mn, Zn and Cu are also possible to be recovered by SCWO reactions in the form of insoluble oxides and salts [10], which exhibits practical application for the treatment of refractory waste. Besides, SCWO offers some other potential advantages such as: providing easier salts separation due to their extremely low solubilities in SCW, a very short residence time (usually less than several minutes), achieving heat self-sufficiency and energy saving with a relatively low concentration of organic matter feedstock due to exothermic reactions [11]. Therefore, SCWO technology is an effective and promising destruction method for organic wastewater and sewage sludge, or an alternative to conventional methods.

However, SCWO is seriously hindered by corrosion and plugging problems of the reactor [12,13]. Reactor materials are particularly susceptible to corrosion due to dissolved salts in water at high temperature, high density and high oxidation SCWO conditions. Methods that manage corrosion issues in SCWO systems have already been reviewed elsewhere [14]. Salt deposition is a direct consequence of poor solubilities of most salts in SCW, and its negative impacts broadly include three aspects. First of all, these precipitated salts are prone to adhere to the reactor gradually forming a salt layer there, reducing the heat transfer capability across the reactor wall [15]. Secondly, a dead microenvironment is created between the salt layer and the reactor inner wall, where considerable corrosion quite possibly occurs [14]. Thirdly, the accumulation of precipitated salts may also lead to an increased pressure drop, plugging of the reactor or associated pipelines, even the shutdown of the whole expensive SCWO equipment if it's not controlled well. These drawbacks of salt deposition seriously reduce the reliability and operational economy of the SCWO apparatus [16]. In order to overcome these unfavorable influences on commercial application of SCWO, plenty of methods and reactor configurations have been developed over the past three decades. In 2004, Hode et al. [17] and Marrone et al. [16] systematically reviewed and summarized deposition problems and solutions in commercial/full-scale applications of SCWO. However, it seems that no any method or reactor design used at the laboratory or commercial level exhibits better than all the others, or is fully successfully applied to the operation of a long-term continuous flow system.

With the remarkable development of SCWO, the research on salt deposition and its control means have been updated in the past decade. Thus, systematical summarizations of current research status concerning salt deposition problems are significant. This present article aims to review and summarize the current research status of salt deposition problems, such as research methods, salt types, solubilities, deposition properties, separation performance, deposition mechanism, and salt deposition control techniques.

2. Salt types

Salts found in SCWO mostly originate from several sources. The overall oxidation of organic wastewater containing heteroatoms such as S, P, and Cl, results in an acidic solution [17,18] and/or produces some inorganic salts in the presence of alkaline compounds. To minimize corrosion associated with the acidic solution above, neutralizing it with a base is adopted, so producing large amounts of salts [19]. It cannot be also ignored that the wastewater feedstock inherently contains some salts. Therefore, the salts in this article mainly focus on those formed from the overall oxidation process, neutralization reaction and feedstock itself.

Table 1 summarizes the classification of salts in SCWO of wastewater or sewage sludge. Salt solids carried by the feedstock commonly have very low solubility over the entire range of from subcritical to supercritical conditions. These solids exist in the form of sand, clay and rust, hardly sticking to reactor surfaces compared with nascent salt particles, so they are not responsible for scaling or plugging [16], and are defined as insoluble salts. Correspondingly, soluble salts refer to the salts that exhibit a high solubility in water at the ambient temperature, but undergo a dramatic decrease in the solubility when the temperature is heated to supercritical conditions, due to their small dielectric constants in SCW [20]. These salts seem to be much stickier, and are prone to adhere to the hot surface of the reactor. Hence, the phenomenon

Table 1
Classification of salts in SCWO of wastewater or sewage sludge.

Category	Criteria	Characteristics	Typical examples
Insoluble salts	Solubility	These salts have very low solubility from subcritical to supercritical conditions	Sand, clay and rust, etc. [16]
Soluble salts		These salts exhibit a high solubility at the ambient temperature, but undergo a dramatic decrease in solubility when the temperature is heated to supercritical conditions	Nascent salts: carbonates, sulfates, nitrates and phosphates [17,20]
Type 1 salt	Phase behavior	Type 1 salt does not exhibit critical behavior in saturated solutions, its diluted solution forms a saturated liquid and a saturated vapor phase under supercritical conditions	K_3PO_4, KCl, KNO_3, NaCl, etc. [17,22]
Type 2 salt		Type 2 salt displays critical behaviors in saturated solutions, and its diluted solution forms a supercritical fluid phase and a solid salt phase	Na_2SO_4, Na_2CO_3, etc. [23,30]