Applied Thermal Engineering 75 (2015) 779–788

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research paper

Influence of non-thermal plasma pre-treatment on the scaling characteristics of viscous oil wastewater during evaporation

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HIGHLIGHTS

- Using non-thermal plasma (NTP) pre-treatment reduced the pH, silicon content and hardness in the viscous oil wastewater.
- NTP pre-treatment inhibited scale formation.
- The scale became irregular and loose after NTP pre-treatment.

ARTICLE INFO

Article history:
Received 1 July 2014
Accepted 20 October 2014
Available online 27 October 2014

Keywords:
Viscous oil wastewater
Non-thermal plasma
Evaporation
Scale
Heat transfer resistance

ABSTRACT

Evaporation is one of the most important measures in the recovery of viscous oil from wastewater in steam injection boilers at oil fields, whereas the formation of silicate and carbonate scales inhibits the heat transfer process. To avoid scale formation without the addition of chemicals, a non-thermal plasma (NTP) reactor was adopted to pre-treat viscous oil wastewater before evaporation. The wastewater samples from two different oil fields were first atomised and sprayed into the NTP reactor tube to mix with ions and free radicals generated from high-voltage direct current (DC) pulsed discharge, and the treated water was subsequently sent to the evaporator. The influence of the DC pulse discharge frequency was also analysed. NTP pre-treatment reduced the silicon dioxide content, hardness, metal content and salinity in the wastewater. Additionally, during the evaporation process, scale formation on the evaporator surface was inhibited, and subsequently, the heat transfer resistance of the scale was reduced. A morphological analysis determined that the scale tended to be loose and irregular in shape after NTP pre-treatment, and the silicon content in the scale decreased. Pre-treatment with NTP was demonstrated to be an effective scaling prevention technique for evaporation which could be applied to wastewater recovery from different oil fields.

1. Introduction

Steam assisted gravity drainage (SAGD) is one of the most important methods in viscous crude oil extraction. During the SAGD extraction process, a large amount of high-quality and high-pressure steam is consumed in the underground well to melt the viscous crude oil. This process also generates a significant amount of viscous crude oil wastewater as a result of steam condensation and underground water carry-over. Usually, the wastewater is recycled as boiler feed water after treatment. However, the wastewater generally contains a high sodium chloride concentration, high silica concentration and high alkalinity. The costs for viscous oil wastewater treatment and steam generation comprise a considerable proportion of the total cost in viscous oil extraction [1–4]. Evaporation is a practical and facility-available method to recover wastewater as boiler feed water due to the availability of residual heat from the SAGD extraction process and the fact that viscous oil wastewater is typically at high temperatures. However, scaling prevention becomes necessary with evaporation. Chemicals, such as scale inhibitors, are typically added into the wastewater for this purpose; however, scale inhibitors have limitations, including high price and the resultant final discharge by products in oil fields. In addition, wastewaters from the SAGD extraction process have high silica content. Scale inhibitors are seldom effective against the combined presence of calcium, magnesium carbonates and silicate scale [5]. Special attention should be paid to silicate scale during SAGD wastewater evaporation.

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http://dx.doi.org/10.1016/j.applthermaleng.2014.10.070
1359-4311/

Nomenclature

$\dot{m}$	evaporation rate per m^2 of evaporation surface, kg (m^2 s)$^{-1}$
q_f	heat flux of the evaporator, W m^{-2}
R	latent heat of evaporation of wastewater at its boiling point, kJ kg^{-1}
R_s	heat resistance of the scale, (m^2 K) W^{-1}
T_{lf}	mainstream temperature of the fluid, °C
T_w	inner wall temperature, °C
U_s	heat transfer coefficient of the scale, W (m^2 K)$^{-1}$

Subscripts and superscripts

Aq	aqueous
F	flux
Lf	liquid fluid
S	scale
w	wall

Numerous techniques have been suggested to remove silicon from wastewater, of which precipitation and coagulation are practical at a moderate cost [6–8]. However, the application of these methods can only reduce silica concentration from several hundred mg L^{-1} to several dozen mg L^{-1}. For example, Luo et al. reported that the silica from heavy oil wastewater can be reduced from 250 to 300 mg L^{-1} to 50–100 mg L^{-1} using lime softening agents at the expense of approximately 50 cents (RMB) m^{-3}. Silica removal comprised more than half of the SAGD-produced wastewater treatment costs [9]. Other desiliconisation technologies, such as membrane separation, are prohibitively expensive for the treatment of SAGD wastewater. In addition to scale prevention, the recovery of distilled water to feed the boiler also requires strict limitations on the silicon content in the vapour. To improve the viscous oil extraction, a drum boiler producing over-heated steam should replace a boiler used for steam injection. This approach would require the reduction of the feed water silica concentration limitation from 50 mg L^{-1} [10] to 0.02 mg L^{-1} [11]. Therefore, measures should be taken to further decrease the silica content in wastewater undergoing evaporation to prevent scaling and silica carry-over by vapour.

Recently, non-thermal plasma (NTP) processes have attracted attention because of their ability to promote oxidation, enhance molecular dissociation, and produce free radicals that stimulate chemical reactions. Plasma treatment appears to be a promising alternative for the oxidation of aqueous organic pollutants [12]. The pulsed high-voltage direct current (DC) discharge reactor generates NTP through narrow pulsed corona discharges. Additionally, the ascendant edge climbs sharply, and the trailing edge drops steeply within a limited time duration; therefore, the discharge energy is primarily consumed to accelerating electrons, imparting enough energy to the electrons to collide with H_2O or other gas molecules to form active free radicals. This process achieves a high efficiency in converting input energy to free radicals. Therefore, a high-voltage DC pulsed discharge reactor is often adopted to generate NTP for wastewater treatment, and the reactors are typically designed to have needle-cylinder electrodes, with the stainless-steel needle serving as the high-voltage discharge electrode. As discharge occurs simultaneously along the needle length, the discharge zone is large enough to treat a considerable amount of wastewater [13,14].

Electrical discharges that directly contact the air-liquid spray initiate a variety of physical and chemical effects in water, including a high electric field, intense ultraviolet radiation, an overpressure shock wave, and the formation of various reactive chemical species, such as radicals ($H\cdot$, $O\cdot$, and $HO\cdot$) and molecular species (H_2O_2, H_2, O_2, and O_3) [15–17]. In turn, these reactive species and physical conditions have been shown to degrade many organic compounds rapidly and efficiently. In addition, the oxidation of several inorganic ions in water has been studied with various electrical discharge processes [18,19].

If an identical NTP treatment process is used to treat wastewater that will go to the evaporator, the salt crystallisation process will also change. Therefore, the behaviour of scale formation during wastewater evaporation process would also change; however, this has been seldom reported [20,21].

In this study, the NTP pre-treatment of viscous oil wastewater was performed in a high-voltage DC pulsed discharge NTP reactor before evaporation. The scale formation process was studied to determine the effects of NTP pre-treatment on the evaporation process, and the mechanisms involved in this process were investigated and discussed.

2. Materials and methods

2.1. *Characteristics of viscous oil wastewater*

Viscous oil wastewater was sampled from two different viscous oil fields. These samples were labelled Sample A and B. The properties of the two samples are shown in Table 1.

As shown in Fig. 1, Sample A was reddish brown in colour (in web version), and the colour of Sample B was a little lighter appearing as clear water without obvious impurities. Both samples had an oily odour and contained high silicate content with high electrical conductivity. The two samples had similar oil contents. Additionally, both samples had high concentrations of calcium and magnesium ions, suggesting the potential for scale formation during evaporation.

During experiments, the viscous oil wastewater was first pre-treated in the high-voltage DC pulsed discharge NTP reactor. The wastewater samples were then collected for evaporation, and the vapour was condensed to obtain distilled water. A small amount of residual concentrated liquid remained after evaporation. The properties of the distilled water and concentrated liquid were analysed.

2.2. *The NTP and evaporation reactor and experimental methods*

The schematic diagram of the experimental set-up is shown in Fig. 2. The set-up comprised an NTP reactor and an evaporation-condensation apparatus. The NTP pre-treatment process is shown in Fig. 2(a). The power to generate the plasma originated from a pulsed DC power with a 30 kV voltage, and the DC narrow discharge frequency had a peak value of 1000 pulses per second (pps). Additionally, the corona zone consisted of a group of needle-

Table 1
Properties and metal concentrations of the viscous oil wastewater samples.

Parameters	Sample A	Sample B
pH	8.79 ± 0.01	7.82 ± 0.01
Electrical conductivity (μS cm^{-1})	2840 ± 10	3010 ± 10
SiO_2 (mg L^{-1})	103.29 ± 0.01	134.86 ± 0.01
Hardness (mg L^{-1})	75.80 ± 1.80	36.15 ± 1.02
Ca (mg L^{-1})	20.90 ± 0.63	27.10 ± 0.79
Mg (mg L^{-1})	2.18 ± 0.09	1.15 ± 0.05
Fe (mgL^{-1})	1.08 ± 0.05	0.52 ± 0.01
Cu (mg L^{-1})	0.30 ± 0.01	0.14 ± 0.00
Al (mg L^{-1})	0.31 ± 0.00	0.43 ± 0.01
Na (mg L^{-1})	109.74 ± 2.52	123.12 ± 2.43