Condensate reuse in the chemical industry – pilot scale experience

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Abstract:

Water reuse in industry is a hot topic in times of droughts and water shortages. In boiler systems, quality requirements for feed water are high. That is why adequate treatment of the return condensate is needed before it can be reused. In the IMPROVED project, a mobile testing installation was developed that can test different treatment technologies on site on a relevant scale, to give an indication of the most suitable treatment, both technologically and economically. At Yara, RO proved to be the most economically interesting technology, but the water quality was not sufficient so an additional mixed bed treatment would be necessary. Membrane distillation on the other hand produced the right water quality, but turned out to be too expensive for application.

Keywords: Condensate reuse, boiler, pilot, RO, ED, MD

Introduction

Increasing fresh water shortages (caused for example by groundwater salinization) are pushing major industries to look for alternative water sources. However, alternative water sources bring uncertainties related to quality, quantity and their effect on the existing (pre-)treatments and processes themselves with them.

One of the processes most sensitive to water quality is the boiler in steam-water cycles. Impurities in the feed water can results in the formation of corrosive products, such as organic acids, under the influence of the high pressure and temperature (hydrothermolysis). In this research, the re-use of two process condensates, contaminated with NH_4^+, NO_3^- and organics, is investigated. Different technologies, traditional and cutting-edge, were investigated, both on lab-scale and in an innovative mobile pilot-scale testing facility, to compare their technical and economic potential for full-scale application. The resulting water was subjected to boiler conditions and the formation of corrosive products was investigated.

The IMPROVED project

This research is conducted as part of the Interreg IMPROVED project (Integral Mobile PROcesswaterproduction For an Economic Delta), which entails the design, build and exploitation of a mobile testing infrastructure containing several water treatment installations to be put on site of three large chemical companies. This allows flexible on-site testing of several technologies under realistic conditions.

The technologies available in the mobile installation are (in no particular order), the one used in this research are indicated in bold:

- Ion-exchange (WAC-SAC-degasser-WBA-SBA-MB)
- Granular activated carbon
- Ultrafiltration
- **Electrodialysis**
- **Reverse osmosis**
- **Membrane distillation**
- Advanced oxidation (UV, ozone and peroxide)

A virtual visit to this facility is available at www.virtualtourimproved.ugent.be.

Material and Methods

Water treatment

Electrodialysis (ED), reverse osmosis (RO) and membrane distillation (MD) were tested short-term on lab-scale and for 6 months in total in the mobile installation to treat the condensates and obtain a reusable water stream. A short description of all set-ups will be given here.

Lab-scale:

- ED: PCCell ED 64004, 5 cell-pairs (64 cm^2), FujiFilm Type I membranes, batch operation
- RO: 110 cm^2 flat-sheet BW30HR-440i, batch operation
- MS: 110 cm^2 flat-sheet Aquastill, batch operation, feed pH 9, permeate pH 2

Pilot-scale:

- ED: PCCell ED 1000A, 25 cell-pairs (95 cm^2), PCA membranes, feed-and-bleed mode.
- RO: LC HR4040 module, 20-25 lmh.
- MD/MS: 7.2 m^2 Aquastill module, temperature difference: 55-35°C (feed-condensate) in MD, pH difference: 10-4 (feed-condensate).

Boiler experiments

Boiler conditions (380°C and 40 bar in this case) were simulated in a mini-boiler set-up in the laboratory. The boiler has a volume of approximately 5 mL and was operated at a residence time of 1.24 seconds. 0.1 ppm carbohydrazide was added to the feed solution to keep the oxygen level in the feed vessel below 20 ppb. An overview of this set-up is given in Figure 1.

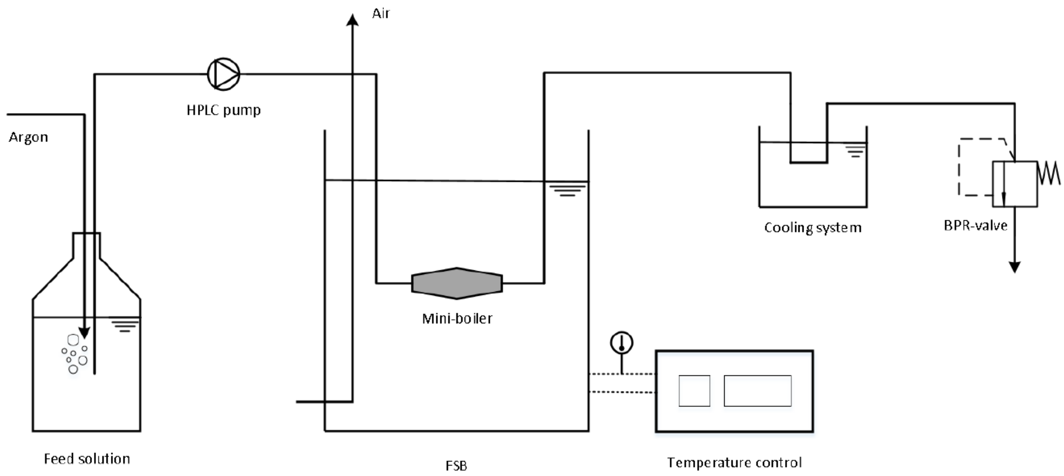

Figure 1 Schematic overview of the mini-boiler set-up.

Feed water

Two different condensates were investigated. The average composition of these condensate, from now on referred to as C1 and C2, is given in Table 1.

Table 1 Composition of the two condensates

	C1 (mg/L)	C2 (mg/L)
NH_4^+	10-15	130-400
NO_3^-	35-50	-
Fe(tot)	1.8	-
TOC	0.2-4	230-700
Formate	-	1-10
Acetate	-	10-15
Ethanol	-	20
Urea	-	0.2

Results and Discussion

Lab-scale tests

The efficiency of the techniques tested on lab-scale were compared based on produced water quality, to give an indication for their potential on larger scale. The variability of the composition on the different condensates caused a difference in starting concentrations between the different experiments. The ammonia removal and final concentration for the different techniques after treatment of C1 and C2 is shown in **Table *2***.

Table 2 Ammonia removal and final concentration after treatment of both condensates by ED, RO and MD.

	C1		**C2**	
	Removal (%)	Product (mg/L)	Removal (%)	Product (mg/L)
ED	97	0.32	94	24.88
RO	93	1.10	95	11.36
MS	55*	1.17	99	0.15

* Due to technical issues, removal was limited to 55%

Based on these preliminary lab experiments, ED is most capable of removing the ammonia from the feed stream for C1, but MS performs the best for C2. This can be attributed to the pH of the streams, influencing the volatility of the ammonia in the MD system. The same is expected for the C1 stream, but could not be reached due to technical issues.

All resulting water streams (after treatment) were also subjected to boiler conditions in the lab, after which the formation of organic acids was analyzed (propionic and acetic acid) and compared to that of the untreated condensate. The results are also compared to those after an additional mixed bed (MB) treatment, further polishing the treated water to reach the required quality. Results are shown in Figure 2.

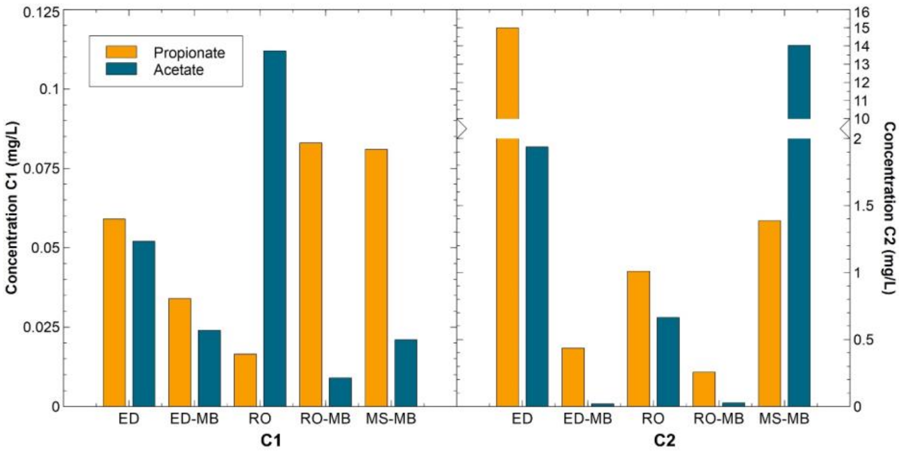

Figure 2 Propionate and acetate content of the treated condensate after the boiler and of the original condensate (without boiler treatment). Please not the different scales of the y-axes.

Organic acids are believed to be one of the main causes of corrosion in boiler feed systems, because of the local pH drop they induce when formed. Although initial concentrations in the condensates are low for C1, decomposition of the residual TOC after treatment results in higher concentrations of organic acids both in ED and RO treatment, with or without a mixed bed (MB) as a polishing step. For C2, with a high initial TOC and organic acid concentration, the treatment steps are able to the decrease the amount of organic acids formed in the boiler significantly. However, in ED and MS (the latter even after MB), the amount of organic acids formed is relatively high, causing concern regarding the application of these technologies for boiler feed water production.

Pilot scale tests

Based on the lab-scale testing, it was decided to run ED and RO for both streams on pilot-scale. For C1, MD was selected as a suitable technique, while for C2 (because of the higher initial ammonia concentration), MS was selected. The general results and estimated costs for all of these tests can be found in Table 3.

Table 3 Comparison of different treatment efficiency for the treatment of C1 and C2.

	C1			C2		
	ED	**RO**	**MD**	**ED**	**RO**	**MS**
Product conductivity (µS/cm)	39.3	140.9	BDL[1]	29.3[2]	469	28600[3]
Water recovery (%)	85-95	75-85	68-75	Max.80	70-85	50[4]
Energy requirement (kWh/m³)	0.10-0.26	0.58	0.29	2.7-4.1	0.87	2.85
CapEx (kEUR)	759	189	1 604	266	97.6	387
OpEx (EUR/m³)	0.26	0.06	0.74	2.74	0.22	1.46

[1]BDL = below detection limit.
[2]minimum conductivity reached in feed and bleed mode, in continuous mode, the minimum conductivity was 1839 µS/cm.
[3]A flux of 30 mg/m²/h of ammonia was reached. Methanol and ethanol also moved through the membrane until a concentration equilibrium was reached.
[4] in membrane stripping, water transport is minimal and flow rates are equal on the feed and condensate sides.

Although generally speaking, the quality attained is lowest when using RO, the costs is also lowest. Both ED and RO would need additional polishing before reuse of the water is possible, so an additional MB treatment is suggested. For C1, water quality is great after MD, but the costs render this technology unfeasible at this moment. For C2, ammonia can efficiently be captured in the product water, but methanol (up to 1499 ppm) and ethanol (up to 26 ppm) are also found in the product water. An additional IEX step before MS could solve this problem, as the resins would retain the alcohols.

Conclusions

By reusing condensates from the steam-water cycle, enormous amounts of water can be saved and the wastewater treatment plant can be downsized. At Yara Sluiskil B.V., two condensate streams were investigated on pilot scale. Although MD clearly resulted in the best product quality, RO and ED were more economically interesting. The latter technologies performed similar but would both need a polishing step for the water to be reused in the boiler system. MS offered interesting perspectives for the reuse of the ammonia in the water, but would also require an additional treatment step.

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