Combination of Electrodialysis and Electrodeionization for Treatment of Condensate from Ammonium Nitrate Production

Lubomir Machuca, Vit Fara

Abstract—Ammonium nitrate (AN) is produced by the reaction of ammonia and nitric acid, and a waste condensate is obtained. The condensate contains pure AN in concentration up to 10g/L. The salt content in the condensate is too high to discharge immediately into the river thus it must be treated. This study is concerned with the treatment of condensates from an industrial AN production by combination of electrodialysis (ED) and electrodeionization (EDI). The condensate concentration was in range 1.9–2.5g/L of AN. A pilot ED module with 25 membrane pairs following by a laboratory EDI module with 10 membrane pairs operated continuously during 800 hours. Results confirmed that the combination of ED and EDI is suitable for the condensate treatment.

Keywords—Desalination, electrodialysis, electrodeionization, fertilizer industry.

I. INTRODUCTION

AMMONIUM nitrate (AN) belongs to the most commonly used fertilizers in the world and it is produced by a reaction between aqueous nitric acid and gaseous ammonia. Excess water is evaporated and thereby process condensates arise. The condensates usually contain AN in the range of 1 to 10 g/l. That amount of AN is too high for direct discharge into rivers and too low for reuse in the production plant. There are several ways to treat the condensate: evaporation [1], ion exchange [2], biological treatment [3] and a membrane separation process such as reverse osmosis [4], [5].

This work presents the experience of AN condensate treatment on fertilizer producer site by a combination of electrodialysis and electrodeionization process.

II. THEORY

Electrodialysis (ED) belongs to electromembrane processes which are able to remove electrolytes. ED found a wide spectrum of applications in e.g. desalination of brackish water, production of edible salt from seawater, desalination of cheese whey, potassium tartrate removal from wine, recovery of salts of organic acids from fermentation broth [6]. An

L. Machuca is with the MemBrain s.r.o., Pod Vinici 87, Straz pod Ralskem 471 27, Czech Republic (e-mail: lubomir.machuca@membrain.cz).

V. Fara is with the MEGA a.s., Pod Vinici 87, Straz pod Ralskem 471 27, Czech Republic

The work was supported by the Ministry of Industry and Trade of the Czech Republic within the framework of the project "Research, development and application of new generation electromembrane modules" program TIP No. FR-TI4/398, using the infrastructure of the Membrane Innovation Centre (No.CZ 1.05/2.1.00/03.0084).

electrodialysis stack consists of two electrodes, an alternating order of cation exchange membranes (CM) and anion exchange membranes (AM), working and electrode spacers. The electrodes generate an electric field which drives the ionic transport inside the stack. Only cations can pass through the CM and only anions can pass through the AM. The feed solution flows inside working spacers and ions migrate through the membranes (Fig. 1). In this way, two main streams are generated: diluate, a solution with lower salt content than the feed, and concentrate, a solution with higher salt content than the feed. The electrode spacers are the closest to the electrodes and comprise the electrode chambers. In these chambers electrode reactions take place, and the electrode gasses are produced [7].

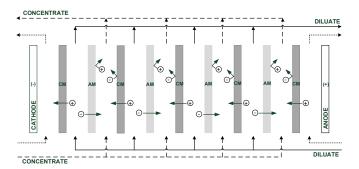


Fig. 1 Principle of electrodialysis

Electrodeionization (EDI) is an electromembrane process combining ED and ion exchange processes and it has been used to produce ultrapure water widely. CM and AM are placed between the electrodes like in an ED module. Ion exchange resins are packed between CM and AM in a diluate chamber to enhance ions removing under the driving force of direct current (Fig. 2). Water dissociation reaction during EDI operation produces hydrogen and hydroxyl ions. These ions continuously regenerate the ion exchange resins electrochemically without using chemical [8].

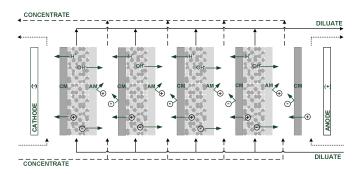


Fig. 2 Principle of electrodeionization

Both ED and EDI processes can be characterized by two parameters; salt removal and flux.

Salt removal (SR) meant an amount of salts which were removed from the treated solution in one pass through the module. SR was calculated from (1) if the water transport through the membranes is neglected.

$$SR = \frac{c_{IN} - c_{OUT}}{c_{IN}} \cdot 100\%$$
 (1)

 $c_{\rm IN}$ and $c_{\rm OUT}$ – the concentrations at the inlet and the outlet of the diluate chamber.

Flux meant an amount of salts which passed through the membrane area in defined time. Flux is expressed in (2):

$$J = \frac{\dot{V}_D \cdot (c_{IN} - c_{OUT})}{N \cdot L \cdot w}$$
 (2)

 \dot{V}_D - flow rate of dilute; N - number of membrane pairs; L - effective length of membrane; w - effective width of membrane.

III. EXPERIMENTAL

The treated condensate had temperature 70–80°C and contained mainly AN. Its composition is shown in Table I. The whole testing consisted of three parts: cooling tanks, electrodialysis and electrodeionization. The cooling of the condensates took place in three cooling tanks by air.

The ED unit consisted of three separate circuits (diluate, concentrate and electrode solution) with tank, pump, valve and flow-meter. The ED module with 25 membrane pair of CM-PES and AM-PES (MEGA, Czech Republic) membranes were installed in the unit. The total effective membrane area was $2m^2$. The operation mode was feed&bleed, the diluate and concentrate solutions were thus circulated through the ED module by 600 l/h. Applied voltage of 15 V caused desalination of diluate and missing ions were filled by the treated condensate. A diluate overflow of 60 l/h was let into the EDI unit.

The EDI unit consisted of two separate circuits (diluate and concentrate). Diluate was operated in one pass through mode and concentrate in feed&bleed mode. Diluate and concentrate flow-rates were 50 l/h and 100 l/h respectively. The EDI module contained 10 membrane pairs of CM-PP and AM-PP (MEGA, Czech Republic) membranes with the total effective area of 0.23 m². Applied voltage was 40 V.

TABLE I FEED CONDENSATE ANALYSIS

Parameter	Value	Unit
Ammonium	464 – 524	mg/l
Nitrates	1,400 - 1,500	mg/l
Chlorides	3.1 - 5.0	mg/l
Sodium	1.3 - 2.5	mg/l
Calcium	7.3 - 13.3	mg/l
Magnesium	1.7 - 2.4	mg/l

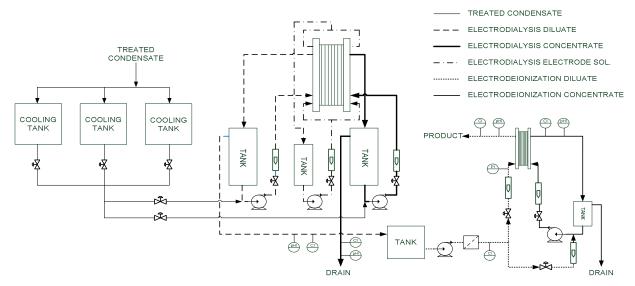


Fig. 3 Scheme of testing apparatus; CI – conductivity indicator, pHI – pH indicator, PI – pressure indicator

IV. RESULTS

The both ED and EDI processes operated continuously during 800 hours. The dependence of SR and flux on time for ED process is shown in Fig 4. Salt removal was stable in range 20–40 %. The concentrate solution was produced in the concentration up to 100 g/l. Average energy consumption for the salts transport was 0.2 kWh per 1 kg of transported salts.

Similar graph for EDI process is shown in Fig 5. SR was stable too, in this case in range 40–50 %. The higher SR and flux of EDI than ED process despite shorter length of the chamber was caused by lower inlet concentration and higher voltage in EDI. Energy consumption was average 1.8 kWh per 1kg of transported salts.

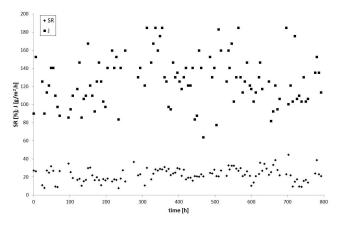


Fig. 4 Salt removal and flux of ED process

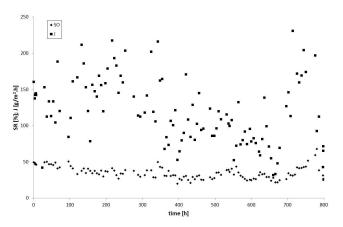


Fig 5 Salt removal and flux of EDI process

V. CONCLUSION

This study demonstrated the suitability of the combination of ED and EDI for the treatment of the condensates from AN production. Both ED and EDI processes operated continuously under the stable results during 800 hours.

REFERENCES

[1] CEAMAGwebsite:http://www.ceamag.com/index.php?option=com_content&view=article&id=35&Itemid=48&lang=en

- [2] S. Kumpović, S. Leaković, "Pretreatment of Process Condensate with Ammonia Degassing in CAN Fertilizer Production" (in Croatian), Kem. Ind., 2011, 60, 505
- [3] N. Shivaraman, A. N. Vaidya, S. V. Waghmare, W. N. Paunikar, A. Tankhiwale, K. Padoley, "A two-stage biological treatment system for ammonium-nitrate-laden wastewater," World J. Microb. Biot., 2001, 17, 447
- [4] A. Noworoty, T. Koziol, A. Trusek-Holownia, "A system for cleaning condensates containing ammonium nitrate by the reverse osmosis method." Desalination. 2003. 156, 397
- [5] P. Eriksson, "Reverse Osmosis to Concentrate Ammonium Nitrate in Condensates, from Laboratory Studies to Industrial Scale Design and Operation," Annual Meeting of The American Institute of Chemical Engineerings (AIChE), 2004, Austin, TX, USA
- [6] T. A. Davis, V. Grebenyuk, O. Grebenyuk, "Electromembrane Processes," in Membrane Technology in the Chemical Industry S.P. Nunes, K.-V. Peinemann, Eds., Wiley-VCH Verlag GmbH, Weinheim, Germany, 2001, ch. 6
- [7] H. Strathmann, "Electrodialysis, a mature technology with a multitude of new applications," Desalination, 2010, 264, 268
- [8] J. Wood, J. Gifford, J. Arba, M. Shaw, "Production of ultrapure water by continuous electrodeionization," Desalination, 2010, 250, 973.