

## REVERSE OSMOSIS USE FOR TREATMENT OF WASTEWATER FROM POWERPLANT ASH DISPOSAL SITE

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**Abstract:** *This work deals with treatment of leachate from powerplant ash disposal site by the means of reverse osmosis. Examined water contained high concentration of dissolved inorganic salts especially calcium sulphate. During separation, crystallization of concentrate would occur. This phenomenon is undesirable. Crystallization was delayed by addition of antiscalant, so it took place under controlled conditions. Crystallization was also affected by presence of iron ions, whose concentration in leachate fluctuated. We proposed working conditions of separation process and we found the dependence of induction time of crystallization on iron ions concentration. Quality of produced permeate is sufficient to be used in powerplant as technological water.*

**Keywords:** reverse osmosis, waste water treatment, ash disposal site leachate, crystallization

### INTRODUCTION

Reverse osmosis is an effective technique for cleaning and separation of solutions. It is used for drinking water purification, desalting sea water, production of deionized water or concentrating liquids in food industry for. In environmental protection, reverse osmosis can be used for wastewater treatment or landfill leachate treatment. In this work, reverse osmosis was used for remediation of the leachate from powerplant ash deposit, where waste products from flue-gas desulphurization are stored. Considering that leachate is produced in a big amount and need to be cleaned, a procedure for reduction of its volume was proposed. The aim of the work was to find conditions for remediation by the mean of reverse osmosis in the laboratory scale in batch system.

Examined water can be considered as an oversaturated solution of  $\text{CaSO}_4$ . In concentrate during separation saturation index grew and crystallization would take place. However, crystallization is undesirable and could lead to damage of membrane and to decrease of permeate flux. For

membrane protection a special compound which delays crystallization, an antiscalant, was added into feed.

## **METHODS**

Reverse osmosis belongs to pressure-driven membrane processes which separate feed into two different streams – permeate and concentrate. Permeate is almost pure solvent while concentrate contains all components which didn't pass through the membrane. Separation proceeds on the ionic level. For separation synthetic semi-permeable membrane is used, which holds particles and ions, only molecules of dissolvent get through membrane (Melzoch 2007; Strathmann 2005). As a driving force pressure over 2 MPa is used to exceed the osmotic pressure of the solution. The osmotic pressure depends on concentration of dissolved matter. When a solution contains high concentration of dissolved matter membrane fouling or scaling threatens, Greenlee et al. (2009). These effects are undesirable and can cause damage of membrane. To delay precipitation of any component special compound – antiscalant – is added into feed. Antiscalant is a polymere substance containing organophosphates, polycarboxylic acids and polyacrylates, which prevent nucleation and crystal growth (He et al. 2009; Bruggen et al. 2003).

## **EXPERIMENTS**

All experiments were performed on membrane separation device LAB-M20 with 34 membranes RO98pHt for reverse osmosis of overall area 0,5916 m<sup>2</sup> from producer Alfa Laval. Membranes were arranged in desk module. The apparatus works in batch system. Working pressure is provided by piston pump which can gain 6 MPa. Constant working temperature is provided by heat exchanger with tap water. The device is equipped with measuring cell for on-line monitoring of pH and conductivity in concentrate and permeate (conductivity quickly predicates about overall concentration of dissolved inorganic salts). After each experiment, membrane module was rinsed with HCl and then with tap water.

Two samples of leachate were used for experiments. Both came from ash disposal site which is used for storage of wasteproducts from flue-gas desulphurization in powerplant Prunéřov II. Therefore, in the leachate high concentration of dissolved inorganic salts occurred, especially CaSO<sub>4</sub>. These salts would cause uncontrolled crystallization in membrane module during separation process. For this reason antiscalant must had been added into each feed solution. Difference between samples was only concentration of dissolved iron; in the first sample iron had precipitated before process and the solution had zero concentration of iron, in the second sample concentration of dissolved iron was 0,786 mg/L. Presence of iron accelerated precipitation. Crystallization

was observed by measuring of conductivity of solutions, for conductivity is a parameter dependent on concentration of ions in solutions.

Chemical analysis of feed solutions, concentrates and permeates were performed.

## RESULTS AND DISCUSSION

In the first series of experiments (RUN 1 to 3) were designed and confirmed possibility of separation of this water and working conditions were set as following: working pressure 2 MPa, working temperature 20 °C, concentration factor  $c_F = 4$ ; concentration factor is defined as ratio of feed volume and concentrate volume. Concentration of antiscalant was for the first and the second stage 1 mg/L and 3 mg/L, respectively. Experiment consisted of two stages; concentrate from the first stage (RUN 1, 2) was kept in vessels to crystallize, after crystallization precipitated crystals were removed and solution continued into second stage (RUN 3).

During process conductivity and pH of concentrate and permeate and permeate flux were measured. For identifying crystallization were measured initial time from end of separation to time when first visible crystals occur and total time when crystallization stopped. Process of crystallization was monitoring by measuring of conductivity.

The aim of the first experimental series was to reduce volume of solution with high salinity. Volume of entering feed was 48 L and 12 L of concentrate were produced, from this 8 L of solutions were taken for separation in the second stage and 2 L of concentrate were produced. The volume was reduced 16-times. Quality of permeates was good with low concentration of inorganic salts. Concentration in flows and rate of removal for RUN 5 are shown in tab. 1.

**Tab. 1:** Chemical analysis for RUN 5

[mg]	Feed	Concentrate	Permeate	Removal [%]
Fe	< 0,1	0,223	< 0,1	
Mn	2,95	10,7	< 0,25	
Ca	329	1929	2,58	99,2
Mg	301	1331	1,14	99,6
K	21,9	101	1,1	95,0
Na	153	864	6,97	95,4
Zn	< 0,20	–	–	
Cl <sup>-</sup>	252	1160	10,7	95,8
NO <sub>3</sub> <sup>-</sup>	3,41	12,8	0,143	95,8
N <sub>amon</sub>	1,58	10,8	0,592	62,5
SO <sub>4</sub> <sup>2-</sup>	515	1809	6,5	98,7
PO <sub>4</sub> <sup>3-</sup>	< 0,2	< 0,2	< 0,2	
TOC	< 0,1	< 0,1	< 0,1	

For the second series (RUN 4, RUN 5) working conditions were revised as following: working pressure 3 MPa, working temperature 20 °C, concentration factor  $c_F = 5$ , concentration of antiscalant 3 mg/L. New sample was used which contained iron in concentration 0,786 mg/L. Its presence in feed solution for RUN 4 caused quick crystallization right after separation. For this reason it was decided to remove iron from solution and to observe effects of iron on crystallization of concentrate. For RUN 5, feed solution was aerated and stored in vessel until concentration value of iron was nearly zero. Then separation was performed and concentrate was divided into vessels and into each solution  $FeSO_4$  was added to get following concentration of iron: 1, 5, 20 and 100 mg/L. Process of crystallization was observed by measuring of calcium concentration. It was confirmed, that higher concentration of iron accelerated crystallization (tab. 2).

**Tab. 2:** Concentration of calcium during crystallization in dependence on concentration of iron

Time [hours]	c(Fe)[mg/L]	1	5	20	100
24	c(Ca) [mg/L]	1164	1106	1129	1160
330		661	647	620	561

In the third series effects of presence of iron in feed on crystallization of concentrate was observed.  $FeSO_4$  was added into feed solutions for RUN 6 to RUN 10, entering concentrations of iron are shown in tab. 3.

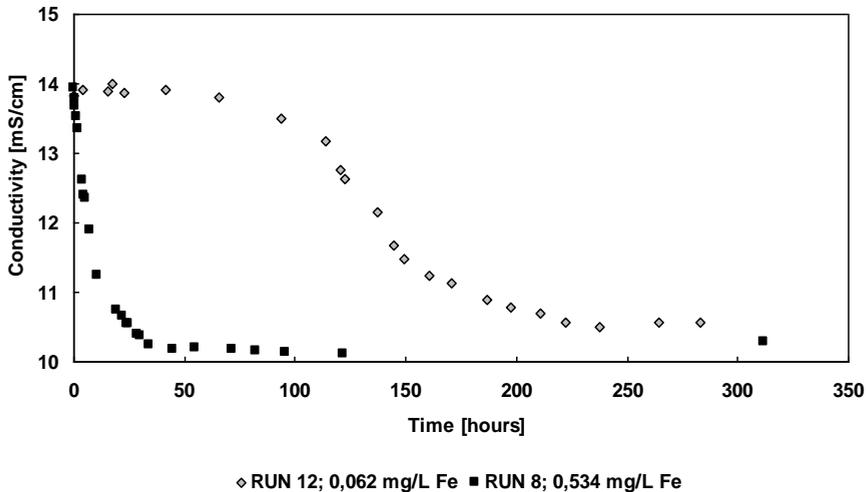
**Tab. 3:** Concentration of iron in feed solution and induction time of crystallization

RUN nr.	6	7	8	9	10	12
c(Fe) [mg/L]	8,305	0,882	0,534	0,309	0,169	0,062
Induction time [hours]	0,0	0,2	0,5	1,0	3,0	15

Feed solution for RUN 11 was not pretreated; it means no antiscalant was added. This caused quick crystallization even in the membrane module before the end of separation and necessity of antiscalant addition was confirmed. Pretreatment of feed solution for RUN 12 was only addition of antiscalant. RUN 12 represented solution with model progression of crystallization. Working conditions were the same as in the previous experiments: working pressure 3 MPa, working temperature 20 °C, concentration factor  $c_F = 5$ , concentration of antiscalant 3 mg/L.

After separation, crystallization in concentrates was observed; measured parameters were induction time and overall time of crystallization. Chemical analysis of feed solutions and concentrates were performed to find only concentration of iron, manganese and calcium – the elements which played the biggest role in crystallization. Typical progress of crystallization is shown on Fig. 1. Concentrate from RUN 12 had long induction time before crystals

formed; it is caused by presence of antiscalant which holds crystallization. Concentrate from RUN 8 contained iron in such high concentration that efficiency of antiscalant was lower and crystallization took place early after end of separation.



**Fig. 1:** Progress of crystallization of concentrates from RUN 12 (without iron) and RUN 8 (0,5 mg/L Fe in feed solution)

The dependence of crystallization kinetics is shown in Tab. 3; the higher concentration of iron in feed solution the quicker start of crystallization and also the shorter overall time period of crystallization. Critical concentration of iron was about 0,5 mg/L, higher concentration caused immediate crystallization; therefore stage for iron removal must be included before separation on membrane module if working in higher scale.

## CONCLUSION

Experiments were held to check the possibility of ash-fill leachate treatment by the means of reverse osmosis. High efficiency of dissolved matter removal was confirmed which reaches to 99 %. Volume was reduced 16-times in two stage arrangement when concentrate from the first stage is after crystallization used as a feed solution to the second stage. Crystallization was slowed by addition of antiscalant. Also iron ions presence had an effect on crystallization, its concentration in leachate fluctuated from 0 to 1 mg/L, whilst concentration under 0,5 mg/L is tolerable.

## ACKNOWLEDGEMENT

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