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Using reverse osmosis technology for recycling wastewater from a coal-fired power plant

Marek Šír*, Zuzana Honzajková, Martin Podhola, Tomáš Patočka, Pavel Kocurek, Martin Bystrianský, Radek Vurm, Martin Kubal, Mečislav Kuraš

Department of Environmental Chemistry, Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague, Czech Republic
Tel. +420 220 444 077; Fax: +420 220 445 029; email: sirm@vscht.cz

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ABSTRACT

Use of reverse osmosis for treatment of water with high scaling potential was investigated in this study. Treated water comes from a disposal site of ash and desulfurization products and its saturation index of calcium sulfate dihydrate (gypsum) ~0.94. Among other components of the leachate are other dissolved solids (~800 mg/L) with significant content of iron ions (~2.7 mg/L). A series of experiments were performed to study the gypsum bulk crystallization in the presence of antiscalant and iron ions followed by pilot plant testing at the locality with raw leachate and leachate pretreated by coagulation/flocculation to investigate membrane scaling. The results showed that the presence of iron ions significantly reduced the induction time of gypsum crystallization, thereby reducing antiscalant effectiveness for its crystallization suppression. Severe membrane scaling confirmed by permeate flux measurement and pressure drop measurement was found, when raw leachate was treated. Removal of most of iron by pretreatment caused that no undesirable precipitation of solution components and an abrupt decrease in permeate flux was detected during separation process. Average rejection of total dissolved solids was 99.5% in this case. Produced permeate could be reuse as source water for the power plant, thus 80% of wastewater could be recycled by means of reverse osmosis.

Keywords: Reverse osmosis; Calcium sulfate; Induction time; Antiscalant

1. Introduction

1.1. Background

Crystallization of calcium sulfate from aqueous media can lead to three of main forms: calcium sulfate dihydrate ($CaSO_4.2H_2O$), calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$), and anhydride ($CaSO_4$). Under the conditions of a pressure membrane separation only the form of $CaSO_4.2H_2O$ occurs. Experimental research on the crystallization kinetics of calcium sulfate usually uses supersaturated solutions prepared by mixing sodium sulfate (or sodium bicarbonate) and calcium chloride (or calcium nitrate) [1–6]. A number of studies providing valuable information on the determination of induction time of gypsum crystallization at different supersaturation levels have been done. Various methods such as conductivity measurement [1,3,7] or

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*Corresponding author.

Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain light scattering through transmittance and absorbance studies [4,8,9] were described in previous studies. Induction time is the time between the generation of a supersaturated state and the first observed change in calcium concentration or turbidity. Induction time preceding precipitation depends strongly on both the degree of supersaturation and the temperature. Antiscalants that are used to inhibit the crystallization of calcium sulfate and prolong the induction time, which consist mainly of substances from the group of polyacrylates, polymetacrylates, polyphosphates and aminophosphates, organophosphates, polycarboxylates, and derivatives of polysulfonate acid and polymaleic acid [1,6]. The effect of commercial antiscalant for suppression of gypsum crystallization or to mitigate membrane scaling was investigated in previous studies [5,9–11]. The effect on the extend of induction time by antiscalant dosage varies greatly depending on the type of antiscalant [12]. The join effect of presence of metal ions and antiscalant on the rate of gypsum crystallization is poorly understood. Presence of some metal ions can lead to inhibition of gypsum crystal growth. The mechanism of inhibition has not been fully explained yet. Growth inhibitors are able to retard or block the growth process, which can be described by their preferential adsorption at active growth sites on the crystal surface. The degree of inhibition may depend on the concentration of metal ions and degree of supersaturation [7]. On the other hand, some metal ions such as Al^{3+} can reduce antiscalant effectiveness for suppression of gypsum crystallization [8].

1.2. Investigated locality

The study site belongs to the coal-fired power plant complex, which is situated on the western edge of the North Bohemian brown coal basin. The sludge bed receives the products of wet limestone scrubbing and flue gas desulphurization, cinder and a portion of the fly ash. Studied leachate from this site is collected through a drainage system into the pits located around the perimeter of the sludge bed and then moved into the repump station. Currently the production of the leachate is approximately $100\,m^3/h$. Its main component is calcium sulfate dihydrate, due to the high proportion of wastewater from the SO_2 absorbers.

2. Materials and methods

Membrane unit LAB M-20 was used for induction time studies. This unit is equipped with a plate and frame module and is designed for the testing of separations on a small scale. Basic technical data: membrane modul—LabStack M20 (DSS), membrane—RO98pHt (Alfa Laval), thin-film composite on polypropylene, active membrane area—0,625 m^2, standard permeate flux—30 L/h, and maximum operating pressure—6.0 MPa.

Membrane unit LAB M-30 was used for pilot plant testing. The unit is equipped with a container for RO/NF elements of the standard size "4040" (i.e. diameter 4", length 40"). The module is equipped with an integrated Clean-in-Place system and can be used to test the effectiveness of different methods of membrane cleaning. Basic technical data: membrane element—FILMTEC SW30–4040 (Dow), active membrane area—7.4 m^2, standard permeate flux—300 L/h, and maximum operating pressure—6.9 MPa.

Conductivity and pH values were measured using devices GMH 3430, GMH 3530, respectively (Greisinger Electronic). Metals were measured with atomic absorption and emission spectrophotometer SensAA (GBC Scientific Equipment). Anions were measured with capillary electrophoresis system Capel 105 M (Lumex Ltd). The total organic carbon (TOC) and total inorganic carbon (TIC) values of samples were measured with TOC/TNb analyzer liquiTOC II (Elementar Analysensysteme GmbH). Total dissolved solids (TDS) were determined by gravimetric method at the temperature 105˚C. Working pressure and pressure drop were measured using digital pressure gauges A-10 (Greisinger Electronic).

Commercial antiscalant PermaTreat 504 (Nalco) for high-sulfate waters was obtained from its supplier. Reported active ingredients are phosphonates. The content of "residual solids" (i.e. nonvolatile material) was determined by low-temperature evaporation (50˚C) of 1 g of antiscalant solution until no weight loss was observed.

The degree of supersaturation with respect to gypsum was quantified in terms of saturation index of gypsum (I_{sg}) [13] defined as:

$$I_{sg} = \log \frac{a_{Ca^{2+}} a_{SO_4^{2-}}}{K_{S_{CaSO_4 2H_2O}}} \tag{1}$$

where a is activities of ions. The solubility product of $CaSO_4{\cdot}2H_2O$ $K_{Sgypsum}$ (Eq. (2)) was determined from the equation of solubility s (g/L) (Eq. (3)) established by Linke and Seidel [14] and verified by Dutrizac [15]:

$$K_{S_{gypsum}} = [Ca^{2+}][SO_4^{2-}]\gamma_{Ca^{2+}}\gamma_{SO_4^{2-}} \tag{2}$$

$$s = 2,091 + 0,003173T - 8,19,310^{-5}T^2 \tag{3}$$

where T is temperature in ℃ and γ_i is the activity coefficient of ion i. It was calculated using the ionic strength I by the following equation (Eq. (4)):

$$\log(\gamma_i) = -Az_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0,3I\right) \tag{4}$$

where $A = 1,82 \cdot 10^6(\varepsilon T)^{-1,5}$, ε is the dielectric constant of water and T is the temperature in K.

Inductions time of gypsum crystallization were determined by the conductivity measurement at 20.0 ± 0.2°C following the method of Lioliou et al. [1] The formation of calcium sulfate crystals was detected by a decrease of the solution conductivity due to the reduction of calcium concentration. The time lapse between reaching the supersaturation state that corresponds to $c_F = 5$ and the appearance of the inflection point in the conductivity-time profile was defined as the induction time, T_{ind}.

3. Experimental

A series of laboratory experiments were performed to determine the antiscalant effectiveness for suppression of gypsum bulk crystallization followed by the investigation of gypsum crystallization in the presence of antiscalant and iron ions. Experiments were carried out with leachate pretreated by coagulation with ferric sulfate at neutral pH followed by flocculation with auxiliary polymer flocculant. A stock solution containing 1 g/L of antiscalant (PermaTreat 504, Nalco) was prepared and stored at 4℃ in the dark. It was determined that content of residual solids in delivered antiscalant was 39.2% wt. A stock solution containing 1 g/L of Fe was prepared from $FeSO_4.7H_2O$ and stored at 4℃ in the dark. Working solutions were prepared by mixing the pretreated leachate and corresponding stock solutions. Dilution of working solution was negligible in this case and was not calculated further. Conditions for the conduct of experiments were as follows: experiments were carried out in batch mode. Input volume of treated water was 20 L. Concentration factor $c_F = 5$ was achieved. All experiments were performed at the pressure of 2.0 MPa. The operating temperature was set to 20℃. Induction time of gypsum crystallization was determined in the presence of different amount of antiscalant and iron ions in remaining concentrate.

Pilot experiments at the locality were performed with raw leachate and leachate pretreated by coagulation with ferric sulfate at neutral pH followed by flocculation with auxiliary polymer flocculant to remove iron. The reverse osmosis process had been set with regard to previous laboratory tests as follows: experiments were performed in batch mode; the operating temperature was set to 20℃. The concentration factor was $c_F = 5$. All experiments were performed at the pressure of 1.5 MPa. The dose of the antiscalant (PermaTreat PC-504) was 3.0 mg/L. Experiments were performed with the initial volume of the batch of 500 L followed by longer experiments with the initial

Table 1
Composition of solution used for reverse osmosis treatment and studies of gypsum crystallization in the presence of antiscalant and iron ions

Parameter	Pretreated leachate mg/L (mM)	Concentrate used in gypsum crystallization studies mg/L (mM)
Na^+	175 (7.61 mM)	832 (36.18 mM)
K^+	27.6 (0.71 mM)	123 (3.15 mM)
Ca^{2+}	605 (15.09 mM)	2,730 (68.11 mM)
Mg^{2+}	294 (12.09 mM)	1,406 (57.84 mM)
B	20.3 (1.88 mM)	49.9 (4.62 mM)
SO_4^{2-}	2,680 (27.90 mM)	12,100 (125.90 mM)
Cl^-	134 (3.78 mM)	580 (16.36 mM)
TIC	10.1	41.1
TOC	1.5	2.8
TDS (mg/L)	4,030	16,300
Conductivity (mS/cm)	4.53	15.15
pH	7.2	7.3
I_{sg}	0.94	2.06

volume of 2000 L at the same operating conditions. Conductivity of technological streams, permeate flux, and pressure drop was measured during experiments. Table 1.

4. Results and discussion

4.1. Induction time measurement

Fig. 1 shows the dependence of induction time of antiscalant dosage in concentrate obtained from pretreated leachate. Concentration of residual iron in the solution was $c(\mathrm{Fe}) = 0.18\,\mathrm{mg/L}$. The join effect of iron ions and antiscalant dosage on the gypsum bulk crystallization is illustrated in Fig. 2. The effectiveness of antiscalant is suppressed by the iron ions significantly even in the trace amounts.

4.2. Pilot plant experiments

Crystallization of gypsum was suppressed by the addition of 3 mg/L of antiscalant. Fig. 3 shows the difference between the permeate flux characterization of the separation process with raw leachate and pretreated leachate. No abrupt decrease in the permeate flux was detected during pretreated leachate separation. Permeate flux decreased due to increasing salt concentration in solution. In the case of raw leachate, severe membrane fouling started, when concentration factor $c_F = 3.2$ was reached, which corresponds to the saturation index of gypsum $I_{sg} = 1.86$. The experiment was discontinued because of this event (see Fig. 4).

Average rejection remained almost the same level of 99.5% during the separation experiment with pretreated leached. Fig. 5 shows a rapid decline of rejection in the case of raw leachate treatment. Rejection started to decrease, when concentration factor $c_F = 3.2$ was reached, which corresponds to the beginning of membrane scaling. Permeate was produced for subsequent analysis only from pretreated leachate. The concentrations, in mg/L, of ions present in permeate are: $[\mathrm{Na}^+] = 3.0$; $[\mathrm{K}^+] \leqslant 0.5$; $[\mathrm{Ca}^{2+}] = 0.5$, $[\mathrm{Mg}^{2+}] = 1.0$, $[\mathrm{Cl}^-] = 4.0$, $[\mathrm{SO}_4^{2-}] = 8.0$. The content of total dissolved solid is 25 mg/L. For comparison, currently used river water for production of demineralized water for power plant has the following composition, in mg/L: $[\mathrm{Na}^+] = 10.1$; $[\mathrm{K}^+] = 5.3$; $[\mathrm{Ca}^{2+}] = 21.3$, $[\mathrm{Mg}^{2+}] = 13.6$, $[\mathrm{Cl}^-] = 17.2$, $[\mathrm{SO}_4^{2-}] = 87.7$; content of total dissolved solid is 170 mg/L. Produced permeate can be used instead of

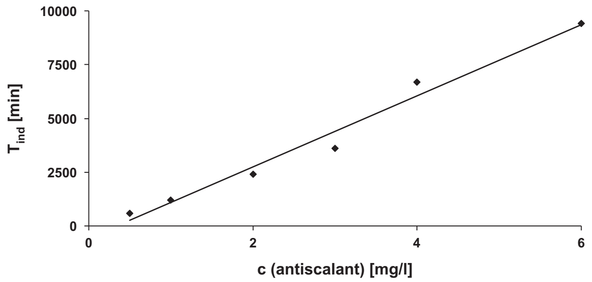

Fig. 1. Dependence of induction time of gypsum crystallization on antiscalant dosage, $I_{sg} = 2.06$ and $c(\mathrm{Fe}) = 0.18\,\mathrm{mg/L}$.

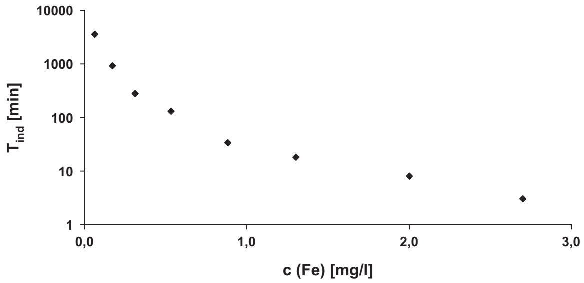

Fig. 2. Dependence of induction time of gypsum crystallization on concentration of iron ions, $I_{sg} = 2.06$, antiscalant dosage = 3 mg/L (content of residual solids in antiscalant was 39.2% wt.).

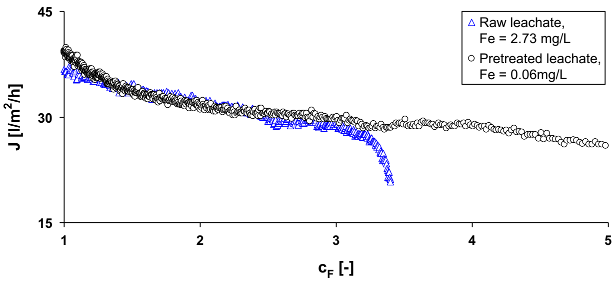

Fig. 3. Dependence of permeate flux on concentration factor for pilot plant experiments, the effect of pretreatment on membrane scaling.

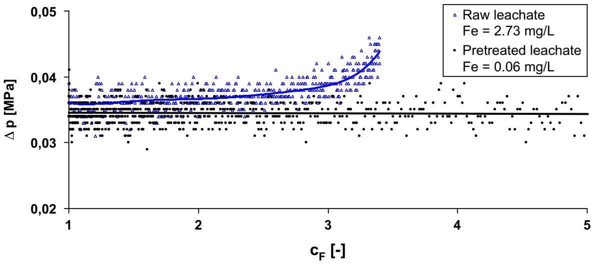

Fig. 4. Dependence of pressure drop on concentration factor for pilot plant experiments, the effect of pretreatment on membrane scaling.

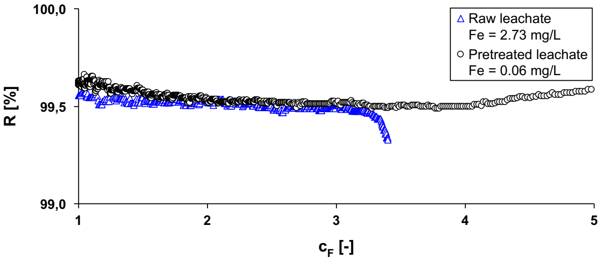

Fig. 5. Dependence of average rejection on concentration factor during separation process for pilot plant experiments.

provided river water. Its demineralization process in the line may results in lower comsumption of chemicals and energy saving.

5. Conclusions

This paper dealt with reverse osmosis treatment of leachate with high scaling potential. Studies focused bulk crystallization and membrane fouling caused by calcium sulfate dihydrate in the presence of antiscalant and iron ions.

The main conclusion is that iron ions reduced antiscalant effectiveness for suppression of calcium sulfate crystallization. The degree of reduction strongly depended on the iron concentration even in trace amounts. The presence of iron in treated raw leachate caused severe membrane scaling confirmed by permeate flux measurement and pressure drop measurement. Removal of most part of iron by pretreatment by coagulation/flocculation caused that no undesirable precipitation of solution components and an abrupt decrease in permeate flux was detected during sepration process. Average rejection of total dissolved solids was 99.5% in this case. Produced permeate could be reused as source water for the production of demineralized water instead of currently used river water. The pilot experiments showed that 80% of produced wastewater can be recycled using reverse osmosis technology.

Acknowledgments

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