The presence of ferric iron promotes calcium sulphate scaling in reverse osmosis processes

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HIGHLIGHTS

- Iron presence affects behaviour of supersaturated calcium sulphate solution.
- Even low iron concentration (1 mg/l) reduces crystallization induction time and accelerates the process.
- Significant difference between jar test and RO-system is due to solution circulation and exposure to pressure.

ARTICLE INFO

ABSTRACT

Calcium sulphate is one of the most common components responsible for inorganic scaling in industrial heat exchangers and desalination plants. Insoluble scales cause problems like material degradation and a decrease of process efficiency. This is a major challenge for wastewater containing high concentrations of calcium sulphate, e.g. power plant ash deposit site leachates. Treatment of such water by means of reverse osmosis is considered in this study. It was found that iron ions present in the solution in low concentration can affect the scaling behaviour. If present, iron shortens both induction time and overall time of calcium sulphate crystallization from its supersaturated solution.

Modelling, jar tests and RO separation tests were made to examine this phenomenon. Model solutions supersaturated by calcium sulphate were prepared in various conditions, always in two parallels: a solution containing iron ions and a solution without iron. The difference (induction time, crystal formation rate) is significant at lower supersaturation while at high supersaturation the results are very similar due to quick crystallization.

When treating such supersaturated solution (or solution close to saturation) two main possible ways offer: removing iron prior to treatment (e.g. by aeration or coagulation) or preventing scale formation by adding antiscalants.

1. Introduction

Calcium sulphate, together with calcium carbonate and silica (SiO_2) is the major compound causing membrane scaling [1,2]. In general, supersaturated solutions can be formed when undergoing a membrane process where present compounds are concentrated and their saturation index is exceeded. Hereby they form an insoluble phase covering the membrane surface [3,4,5].

Supersaturated solutions may also occur directly. This is often the case of leachates, since they tend to take up minerals in high concentrations. This was the case for a leachate from a power plant ash deposit site where flue gas desulphurization by-products and ash are stored,

located in Prunéřov in North Bohemia (Czech Republic). This fraction, containing a supersaturated solution of calcium sulphate, was purified by reverse osmosis in the past [6]. The permeate obtained in this way met the high standards to be used as a technological water in power plant. The concentrate was returned back to deposit site, where it was left to crystallize. However, what caused problems was the fluctuating concentration of iron in the leachate. There was a suspicion that its presence affects the crystallization of calcium sulphate. Crystallization may not always be a problem, if handled in the right way; influencing the rate of crystallization would raise a possibility to use the process in a beneficial way. If the crystallization takes place outside the membrane module, it could be used as a next step for treatment, however, if it takes place during the separation, severe damage on equipment would follow [1]. As permeate recovery increases the concentrations of sparingly soluble mineral salts near the membrane surface increase above their solubility

limits. This leads to surface crystallization and as a consequence flux decline and potential membrane damage [7]. Membrane scaling is affected by various factors including fluid hydrodynamics in the membrane channel, membrane surface chemistry and topography as well as the supersaturation level of the solution with respect to the mineral salts [8,9].

Supersaturation of solutions can be expressed by the saturation index SI which can be calculated by following equation:

$$SI = \log(IAP/K_{sp})$$

where IAP = ion activity product and K_{sp} = solubility product

In equilibrium SI = 0, when the saturation index is positive the solution is supersaturated and vice versa the solution is undersaturated when SI < 0 [10].

There are three main forms of calcium sulphate: calcium sulphate dihydrate or gypsum ($CaSO_4 \cdot 2H_2O$), calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), and anhydride ($CaSO_4$). All calcium sulphates have relatively low solubility and with increasing temperature the solubility of all calcium sulphate forms decreases. This is the cause of calcium sulphate scale formation on heat transfer surfaces [11,14]. While the increasing temperature decreases calcium sulphate solubility, the value of the temperature gradient at the heat transfer surface does not influence the nucleation rate. Calcium sulphate scales can be formed either by bulk crystallization, by means of direct nucleation on a surface or by means of adsorption of crystal nuclei on a surface [3,12,13]. Formation of calcium sulphate scale occurs mostly by means of direct nucleation. It takes place mostly on a heat transfer surface, on imperfection and roughness of surface by the mechanism of three-dimensional nucleation [1,14,15]. In clean supersaturated solutions (i.e., with no dispersed particles) homogeneous nucleation takes place in the fluid bulk; the metastable region and the so-called induction period for nucleation can be relatively large. On the contrary, under conditions where foreign particles or surfaces are present, heterogeneous nucleation takes place and the concentration region of meta-stability and the induction period are drastically reduced [16,17]. According to [18], in membrane technologies incipient $CaSO_4$ scaling is due to growth of membrane surface particles (from nuclei developing right on the surface and not due to deposition of crystals developing in the bulk). Surface crystallization is reported to be the dominant crystallization mechanism on desalination membranes [3,12,19].

Scale formation of sparingly soluble salts has a significant effect on flux decline in membrane systems [20]. For feedwater with calcium sulphate scaling potential, it is recommended to operate a membrane system below saturation, with a significant dosage of antiscalant [21,22]. In general, there are three main routes towards scale control: altering the system design and operating parameters, altering the nature of feed streams, and using chemical treatment methods. The latter may be the most suitable, one of the most common methods is the use of antiscalants — organic additives as scale inhibitors; they decrease the rate of scale growth by absorbing at the active growth sites on the crystal surface [23]. These scale inhibitors interfere with precipitation reactions and help to keep supersaturated solutions in a stable condition. They delay crystal growth but do not stop the supersaturated component from crystallization. The active ingredients of the antiscalant are mostly mixtures of polyphosphates, polycarboxylates and polyacrylates of various molecular weight [2,24,25]. These commercial scale inhibitors are widely used for preventing scale-deposits in heat exchangers and desalination plants [26].

The presence of iron in the water may lead to the formation of the $Fe(OH)_3$ colloid deposit on membranes. The pH of the solution plays a major role, the most intensive membrane fouling with $Fe(OH)_3$ occurs in the strongly acidic or alkaline medium. Under these conditions, iron-containing particles are responsible for the deposition rather than calcium sulphate crystals [27].

The aim of this work was to find and characterize the effect of presence of iron (in the form of Fe^{3+} ions) to crystallization of supersaturated solutions of calcium sulphate, and to understand how it affects separation of such solution by means of reverse osmosis.

2. Materials and methods

All experiments were conducted with model solutions supersaturated by calcium sulphate instead of real sample of wastewater. As a representative and relevant case, leachate from a power plant ash deposit site was used as the reference. However, due to its complexity, the not very constant composition and to lower the effect of other components, model solutions of calcium sulphate (which is the main component of the leachate) were used (Table 1). Even though the leachate contains other compounds, results from XRF confirmed that solid phase after crystallization of concentrate was formed by $CaSO_4 \cdot 2H_2O$. While composition of the leachate slightly varies over time, none of the changes had such effect on crystallization of concentrate as concentration of iron. It can come from 0 up to 10 mg/l, but still strongly affects mainly induction time of crystallization (Fig. 1).

2.1. Modelling

Prior to experiments a modelling study of all prepared solutions was made. Different conditions (oversaturation ratio, pH, concentration of iron) were simulated. Models were computed by the PHREEQC Interactive code (version 3.1.7) using the "Pitzer" database.

2.2. Experimental

For the experiments, solutions with defined supersaturation of calcium sulphate were used. Analytical grade chemicals $CaCl_2 \cdot 2H_2O$ (purchased from Chem-lab), Na_2SO_4 (Fluka Analytical) and anhydrous ferric chloride $FeCl_3$ (Chem-lab) were used for stock solutions preparation. The experimental water was prepared by rapidly mixing an equimolar stock solution of calcium chloride and sodium sulphate and in selected solutions with a small dose of ferric chloride (to obtain a concentration of iron in the working solution from 1 up to 10 mg/l). If needed, pH was adjusted by hydrochloric acid or 0.1 M sodium hydroxide.

Crystallization experiments were carried out both in jar tests and in a reverse osmosis system.

Jar tests were made in order to determine the conditions of crystallization. Crystallization experiments were carried out with two parallel solutions — with and without present iron. Iron ions in a form of diluted solution of $FeCl_3$ were added into the solution right after mixing all components. The concentration of iron in the experimental solutions was 1 mg/l (apart from the experiments focused on iron dosage). After mixing the solutions, the values of pH and conductivity were measured; conductivity was then measured in one-minute intervals, also induction time was measured as the time when a change of the solution appearance occurs (formation of first precipitates). Samples for chemical analyses were taken in different phases of the experiments: a sample of the raw solution (t = 0 min), at the beginning of the conductivity decrease (time equal to induction time), at the end of the rapid conductivity decrease (several tens of minutes), in stable conditions, (24 h and more). Solutions were stirred and kept at laboratory temperature. Chemical analyses were carried out in collected samples to determine sulphates and calcium. For sulphates, capillary electrophoresis (Capel-105 M, Lumex Instrument) was used, calcium was determined by AAS (Sensaa, GBC Scientific Equipment). These corresponded well with conductivity measurement and gave similar time curves for crystallization, thus they are not shown further in the paper.

Separation tests were carried out in a dead-end filtration unit equipped with DOW FILMTEC™ RO brackish water membrane, type XLE (expected salt rejection 99.5%) with a surface area of 22.9 cm². The working pressure in experiments was set to 7 bar. Solutions were