290g A Nucleation Theory Based Approach for Understanding Nanofiltration/Reverse Osmosis Membranes Scaling Limits

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Both, thermal and membrane desalination efficiencies are strongly limited due to the scaling phenomenon. In the case of saline waters desalination, i. e. seawater or saline minewater, calcium carbonate and calcium sulfate are commonly shown as major scale deposits. Since $CaCO_3$ deposition can be easily avoided by adjusting the feedwater pH, the calcium sulfate precipitation in desalination systems constitutes the major obstacle for long term operation. Therefore, significant amount of research to elucidate the mechanism of calcium sulfate scaling phenomenon in nanofiltration and reverse osmosis systems has been recently conducted. It was shown that in the case of most commonly used spiral-wound membrane modules, pure gypsum ($CaSO_4 \times 2H_2O$) deposits are created rather by the bulk crystallization than the surface crystallization process. It was also proven that $CaSO_4$ scaling occurs at relatively high calcium sulfate supersaturation level due to the existence of a wide metastable zone under these conditions. Concerning the above, Hasson et al. proposed the method for reverse osmosis (RO) membranes gypsum scaling limits determination based on the so-called upper and lower water recovery bound (threshold limits). The former parameter is defined by the process parameter at which immediate permeate flux decline can be observed while the latter occurs when the inorganic scaling is prevented or at least delayed for a sufficient period of time and is mainly governed by the gypsum nucleation induction time. These authors found that both abovementioned parameters might be suitable for understanding the scaling limits better and consequently increase the desalted or softened water recovery. A great deal of literature data dealing with gypsum induction time at different temperatures and saline waters compositions is available, facilitating lower water scaling limits determination. However, there is a lack of knowledge concerning upper water scaling threshold due to the laborious and expensive laboratory tests. Considering that, the authors, proposed the nucleation based approach for the determination of upper water scaling limits. Based on the literature data mentioned above, the bulk (mass) crystallization mechanism was assumed and primary heterogeneous nucleation mechanism was set as a base for the presented approach. At first, the gypsum nucleation kinetic parameters, namely heterogeneous nucleation constant and heterogeneous nucleation factor were measured in laboratory. Subsequently the upper water limit threshold corresponding, maximum permissible calcium sulfate supersaturation levels (Smax) were measured in laboratory nanofiltration (NF) stand, applying spiral-wound module, under different operational conditions. Finally the primary heterogeneous nucleation kinetic expression based calculated Smax values were compared with experimentally measured ones. It was found that predicted based on the proposed approach Smax values were somehow lower than measured during laboratory NF stand operation. This was identified as the result of the complexity of the membrane scaling mechanism that takes place in the following steps: primary heterogeneous nucleation, crystal grow together with secondary nucleation and finally bulk precipitate sedimentation on the membrane surface. Based on the strongly required absence of the solids inside the spiral wound modules retentate chamber, even in the micrometer size, it was concluded that the gypsum nucleation should be set as the limiting step while the others steps led to large crystals formation. Thus the applicability of the proposed approach for NF membranes gypsum scaling limit determination was proven. Due to the similarities between these processes, the presented approach was found to be more useful for NF and RO desalination systems Smax prediction than laboratory measurements. The authors believe that the above presented results will let them better understand gypsum nanofiltration/reverse osmosis membranes scaling phenomenon and consequently let the plant operators to increase softened or desalted water recovery.