ELSEVIER

Desalination 221 (2008) 238–243

DESALINATION

www.elsevier.com/locate/desal

Salt production from coal-mine brine in NF — evaporation — crystallization system

Marian Turek[a]*, Piotr Dydo[a], Romuald Klimek[b]

[a]*Silesian University of Technology, Faculty of Chemistry, B. Krzywoustego 6, 44–100 Gliwice, Poland*
Tel. +48 32 2372735; email: Marian.Turek@polsl.pl
[b]*"Debiensko" Desalination Plant, ul. Mlynska 24, 44–230 Czerwionka-Leszczyny, Poland*

Received 24 December 2006; accepted 3 January 2007

Abstract

At "Debiensko" Desalination Plant salt crystallizer is supplied with untreated brine concentrated by RCC evaporation method that results in high energy consumption and huge amount of post-crystallization lye. Nanofiltration pre-treatment of coal-mine brine was then considered to improve plant outcome.

Desal-5L (Osmonics) nanofiltration membrane was found to be suitable for the above purpose. The rejection coefficients were found as follows (%): Ca^{2+} – 68.8, Mg^{2+} – 71.6, SO_4^{2-} – 98.0, Cl^- – 11.9, that lets us to estimate the composition of NF permeate at 85% recovery to be as follows (g/L): Ca^{2+} – 0.242, Mg^{2+} – 0.188, SO_4^{2-} – 0.064, Cl^- – 32.2. The performance of crystallization step was then estimated based on chemical composition of NF permeate and compared with operational data from "Debiensko" Desalination Plant. The energetic efficiency of the presently operated coal mine brine treatment system was compared with the one involving NF softening as the pretreatment for low energy VC thermal desalination in place of seeded VC (RCC presently applied). This comparison shows that unit energy consumption decreases from ca 970 kWh per 1 t of evaporated salt for untreated brine concentrated by RCC method to ca 450 kWh/t when low energy VC evaporation is applied. At the same time the amount of salt in post-crystallization lye decreases from approx. 110 kg per 1 t of evaporated salt produced to ca 50 kg.

Keywords: Desalination; Brine concentration; NF; Evaporation

1. Introduction

The objective of this paper is the Debiensko and Budryk high salinity coal-mine brines utilization efficiency enhancement by rearrangement of the presently applied technology.

Presently the brine of ca 60 g NaCl/L content is been concentrated up to the saturation level by the thermal method, namely vapor compression. Since the considerable amounts of calcium and sulfate ions are present in the treated brine, the seeded falling films evaporators were applied. The presence of gypsum or hemihydrate seeds into the evaporators prevents $CaSO_4 \times nH_2O$

*Corresponding author.

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

doi:10.1016/j.desal.0000.00.000

deposition on the heat exchange surface and inhibits scaling to the great extent. Then the resulting brine containing calcium sulfate crystals is roughly clarified from solid and the supernatant solution feeds the crystallizer after the pH correction with caustic soda. The crystallizer was described in more details elsewhere [1,2]. The above utilization technology, being in operation since 1994, is however considered to be cost consuming. This results in the utilized mine water energy consumption by seeded VC (731 kWh/1 t of salt produced) being three-fourth of the total energy consumption (962 kWh/1 t of salt produced), because all the efforts addressed to avoid $CaSO_4$ scaling increase utilization cost to a great extent since energy consuming seeded falling film evaporator have to be applied in place of energy saving low-energy consuming thermal concentration methods. We concluded that the cost consuming seeded VC may be, however, replaced with the cost efficient one only when softened, low calcium sulfate containing, brine is to be concentrated. This may be achieved by applying membrane softening pretreatment, such as electrodialysis with univalent permselective membranes or nanofiltration.

In our previous research the profitability of low salinity mine water utilization in the electrodialysis evaporation system was proved [3]. Also the advantages of electrodialytic seawater desalination [4] and dual purpose desalination-salt production electrodialysis [5] were also demonstrated.

Recently [6] we discussed the influence of electrodialytic (ED and EDR) softening on the coal-mine brine utilization cost. There we showed that replacement of the existing seeded VC with ED – EDR – low energy evaporator system may result in approx. 50% reduction in the total energy consumption.

Since the nanofiltration is another, and more likely [7,8], softening method, in the present work the economic feasibility of the nanofiltration — low energy evaporator — crystallization system

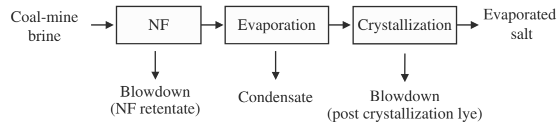

Fig. 1. The system proposed to replace the one existing at Debiensko coal-mine brine treatment facility.

(Fig. 1) for the mine waters in question was discussed and compared with the energetic efficiency of the present system. The deliberations present in this paper were based on the existing desalination plant operational data and data provided by the evaporators suppliers while the efficiency of NF softening for the mine water in question was examined in our laboratory.

2. Nanofiltration of the Debiensko coal-mine brine

The nanofiltration experiments were conducted in a lab-scale flat sheet NF module of active membrane area of $1.47 \cdot 10^{-3}$ m^2. The cross-sectional flow velocity was set at 0.7 m/s. NF-200 (Filmtec), MPS-34 (KOCH), N-50 (Separem) and Desal-5L (Osmonics) membranes were tested. Every experiment was conducted at 15 atm excess pressure. The observed rejection coefficients of calcium, magnesium, sulfate and chloride ions are tabulated in Table 1.

It can be clearly seen in Table 1 that of all the membranes tested, Desal-5L membrane is the

Table 1
The results of "Dębieńsko" coal-mine brine nanofiltration

Membrane, manufacturer	Flux, L/m^2 h	Rejection coeff. (%)			
		Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-
NF-200, Filmtec	51.3	74.1	82.5	92.5	25.9
MPS-34, KOCH	19	21.3	22.0	27.6	5.2
N-50, Separem	118	18.9	26.3	31.5	7.0
Desal-5L, Osmonics	102.4	68.8	71.6	98.4	11.9

applicable since it efficiently rejects sulfates and Ca^{2+} as well Mg^{2+} while Cl^- are rejected only slightly. This enables maximum NaCl permeation at the highest possible absolute $CaSO_4$ rejection. MPS-34 and N-50 membranes, of the lowest NaCl rejection are not applicable since they do not enable efficient softening of the brine in question. NF-200 membrane seems applicable, however, two times higher NaCl rejection than for Desal-5L membrane suggest drastic increase in the amount of salt produced and an increase in salt production cost. Moreover when applying NF-200 the salinity of NF wastewater (retentate) should be approx. two times higher than using Desal-5L, as well as its (retentate) utilization cost.

The possibility of nanofiltration softening of the Debiensko mine water applying Desal-5L membrane was further investigated to identify optimum softened water recovery. In the examined case the optimum water recovery is determined by the maximum permissible, without scaling risk, calcium sulfate supersaturation level. According to the data presented in [9] inside spiral wound modules scaling does not occur up to the relative supersaturation level of 2 (calculated as calcium and sulfate activity product divided by the gypsum solubility product). In the case of Desal-5L the above condition corresponds to the NF recovery level of 0.85. The permeate and retentate composition under these condition are presented in Table 2.

Table 2
Composition of NF process streams at 85% recovery

Concentration (g/L)		
Ion	Permeate	Retentate
Ca^{2+}	0.242	1.70[a]
Mg^{2+}	0.188	1.49
Cl^-	32.2	42.3
SO_4^{2-}	0.064	11.77[a]

[a]Relative supersaturation level of 1.94 (calculated as in [9]).

Since permeate Ca^{2+} and SO_4^{2-} ion product (of $4.03 \cdot 10^{-6}$) is much lower then the value provided in [7] to determine the thermal desalination method scaling limit ($4.54 \cdot 10^{-5}$), the NF permeate of the composition as in Table 2 may be thermally concentrated up to the saturation without calcium sulfate scaling risk. Thus a cheap, low-energy consuming, evaporation method may be considered in place of energy consuming seeded vapor compression presently applied.

3. The effectiveness of NF — evaporation — crystallization system for the examined coal-mine brine utilization

In the crystallization step, because of the optimum crystallization effectiveness, the magnesium content should vary in the 1800–2110 kg/m^3 range. Therefore two separate cases were considered: one of lower magnesium content in the post-crystallization lyes and its related higher amount of salt into the waste and second of higher magnesium content, lower amount of salt in the wastes and slightly lower energy consumption. The present and predicted Debiensko desalination plant performance indices are tabulated in Tables 3 and 4.

The process energetic efficiency, namely the energy consumption per 1 t of salt produced was calculated assuming: 44 kWh/m^3 of seeded VC distillate and 66 kWh/m^3 of distillate from the crystallizer. Following the data presented by Magdziorz and others [10] from the demonstration NF plant for coal-mine brine softening, the NF treatment energy consumption was set as 2.3 kWh/m^3 of permeate, while the low-energy evaporator energy consumption was set to 11 kWh/m^3 of the distillate, following the manufacturer (Alfa Laval) data. In both, present and proposed systems (Tables 3 and 4), the energy consumption differ slightly with post-crystallization lyes magnesium content. At higher magnesium content lower energy consumption is observed since less salt remains in post-crystallization

Table 3
The present “Debiensko” plant performance

Item		Inlet brine	Seeded VC	Crystallizer	Salt, t per 1 m^3 of inlet brine	Salt in lye, kg/t salt produced	Total energy consumption, kWh
1	Volume, L	1000	186.4	14.93			
	Mg^{2+}, meq/L	31.5	169	2110			
	Cl^-, meq/L	925	4962.4	5800	0.049	103.6	
	Volume, m^3/t salt produced	20.409	3.804	0.305			
	Energy consumption, kWh/t salt		730.6	231.0			961.6
2	Volume, L	1000	186.4	17.5			
	Mg^{2+}, meq/L	31.5	169	1800			
	Cl^-, meq/L	925	4962.4	5800	0.048	123.6	
	Volume, m^3/t salt produced	20.779	3.873	0.364			
	Energy consumption, kWh/t salt		743.9	231.6			975.5

Table 4
The predicted “Debiensko” plant performance

Item		Inlet brine	Nanofiltration	Low energy evaporator	Crystallizer	Salt, t per 1 m^3 of inlet brine	Salt in lye, kg/t salt produced	Total energy consumption, kWh
1	Volume, L	1000	850	155.5	6.22			
	Mg^{2+}, meq/L	31.5	15.45	84	2110			
	Cl^-, meq/L	925	908	4962.4	5800	0.043	49.2	
	Volume, m^3/t salt produced	23.259	19.77	3.617	0.145			
	Energy consumption, kWh/t salt		45.5	177.7	229.2			452.3
2	Volume, L	1000	850	155.5	7.296			
	Mg^{2+}, meq/L	31.5	15.45	84	1800			
	Cl^-, meq/L	925	908	4962.4	5800	0.043	58.2	
	Volume, m^3/t salt produced	23.459	19.94	3.65	0.171			
	Energy consumption, kWh/t salt		45.9	179.2	229.5			454.5

lyes and higher crystallization efficiency is observed.

By comparing data in Tables 3 and 4 it can be clearly seen that, unlike magnesium ion content, the rearrangement of the coal mine brine treatment system affects the treatment energetic effect. In fact the energy consumption decreased to less than half of the presently reported (from ca 962 to ca 450 kWh/t of salt produced) when nanofiltration softening of the treated coal-mine brine coupled with low energy evaporation was applied in place of seeded VC. This is the result of application of low-energy consuming treatment methods (NF of 2.3 kWh/m^3 and low energy VC of 11 kWh/m^3) in place of energy consuming seeded VC unit of 44 kWh/m^3 energy consumption. So high decrease in energy consumption suggest the proposed system to be economically privileged, however, since the NF step recovery is equal to 85%, the remaining 15% constitutes waste of high salinity and high calcium sulfate content that have to be utilized. One of the ways to mitigate this is the chemical softening and recirculation to the NF feedwater. This is going to compensate somehow the advantage of the proposed system application, namely the great decrease in unit energy consumption, however, we believe that since the amount of the wastes to be treated is small, as related to the mine brine, its utilization will not increase the overall process cost much. This, however, have to be considered separately.

4. Conclusions

At "Debiensko" Desalination Plant salt crystallizer is supplied with untreated brine concentrated by RCC evaporation method that results in high energy consumption and huge amount of post-crystallization lye. In this paper the nanofiltration pre-treatment of coal-mine brine prior to thermal concentration and further salt crystallization was considered to improve plant economics. Desal-5L (Osmonics) nanofiltration membrane was found to be applicable. The rejection coefficients were found as follows (%): Ca^{2+} – 68.8, Mg^{2+} – 71.6, SO_4^{2-} – 98.0, Cl^- – 11.9, that lets us to estimate the composition of NF permeate at 85% recovery to be as follows (g/L): Ca^{2+} – 0.242, Mg^{2+} – 0.188, SO_4^{2-} – 0.064, Cl^- – 32.2. The performance of crystallization step was then estimated based on chemical composition of NF permeate and compared with operational data from "Debiensko" Desalination Plant. The energetic efficiency of the presently operated coal mine brine treatment system was compared with the one involving NF softening as the pretreatment for low energy VC thermal desalination in place of seeded VC (RCC presently applied). This comparison shows that unit energy consumption decreases from ca 970 kWh per 1 t of evaporated salt for untreated brine concentrated by RCC method to ca 450 kWh/t when low energy VC evaporation is applied. At the same time the amount of salt in post-crystallization lye decreases from approx. 110 kg per 1 t of evaporated salt produced to ca 50 kg.

Acknowledgement

These studies were supported by the following projects: Polish Ministry of Science and Higher Education, grant No. 3 T09D 085 28 during 2005–2008 period, and SUT project (BK-222/RCh-01/2006).

References

[1] J. Masarczyk, C.H. Hansson, R.L. Soloman and B. Hallmans, Desalination plant at KWK Debiensko, Poland: advanced drainage water treatment engineering for zero discharge, Desalination, 75 (1989) 259–288.

[2] B. Ericsson and B. Hallmans, Treatment of saline wastewater for zero discharge at the Debiensko coal mines in Poland, Desalination, 105 (1996) 115–123.

[3] M. Turek, Recovery of NaCl from saline mine water in an electrodialysis-evaporation system, Chem. Pap., 1 (2003) 50–52.

[4] M. Turek, Cost effective electrodialytic seawater desalination, Desalination, 152 (2002) 371–376.
[5] M. Turek, Dual-purpose desalination-salt production electrodialysis, Desalination, 153 (2002) 377–381.
[6] M. Turek, P. Dydo and R. Klimek, Salt production from coal mine brine in ED — evaporation — crystallization system, Desalination, 184 (2005) 439–446.
[7] T. Turek and M. Gonet, Nanofiltration in the utilization of coal-mine brines, Desalination, 108 (1996) 171–177.
[8] A.I. Schafer, A.G. Fane and T.D. Waite, Nanofiltration — Principles and Applications, Elsevier, 2005.
[9] S. Lee, J. Kim and C.-H. Lee, Analysis of $CaSO_4$ scale formation mechanism in various nanofiltration modules, J. Membr. Sci., 163 (1999) 63–74.
[10] A. Magdziorz and T. Thorsen, Nanofiltration pretreatment of coal-mine brine, Presented at Conference on Membranes and Membrane Processes in Environment Protection, Wisla 1995, p. 39–43 (in Polish).