TREATMENT USING REVERSE OSMOSIS OF AN EFFLUENT FROM STAINLESS STEEL MANUFACTURE

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Abstract—Reverse osmosis (RO) and physical/chemical technology were evaluated for treatment of neutralized spent acid effluent (seepage) containing high concentration levels of TDS (7500 mg/l), Ca (400 mg/l), Cr^{VI} (42 mg/l), nitrate-nitrogen (827 mg/l), ammonia-nitrogen (33 mg/l), fluoride (13 mg/l), phenolics (45 mg/l) and COD (620 mg/l). The calcium concentration level in the seepage could be reduced from approximately 400 to 5 mg/l with soda ash softening. Initial permeate flux (feed and bleed system, 85% water recovery) was 278 l/m²·d. Permeate flux, however, dropped rapidly in the beginning of the run and then remained approximately constant to the end of the run. However, chemical cleaning of the membranes was necessary to maintain flux. The TDS of the RO feed could be reduced in one case from 34,253 to 1560 mg/l (95.5% removal) at 85% water recovery. Nitrate and ammonia nitrogen were reduced from 2691 and 103 mg/l to 414 (84.6% removal) and 15 mg/l (85.3% removal), respectively. Chromium^{VI} and fluoride were reduced from 183 and 90 mg/l to 0.38 (99.8% removal) and 2.8 mg/l (96.9% removal), respectively. COD removals varied between 60 and 80%. No phenolics, however, could be removed from the feed (approximately 32 mg/l) with the cellulose acetate RO membranes. Phenolics, however, could be effectively removed (<0.2 mg/l) from the RO permeate with hydrogen peroxide oxidation or ion-exchange treatment. Preliminary test work has shown that it should be possible to treat the seepage effectively with RO for pollution control, effluent volume reduction and water recovery. Capital costs for a 600 kl/d plant for lime softening, RO and oxidation equipment are estimated at U.S. $58,000, U.S. $350,000 and U.S. $87,500, respectively. Copyright © 1996 Elsevier Science Ltd

Key words—neutralized spent acid, reverse osmosis, pollution control, permeate flux, chemical cleaning, nitrate-nitrogen removal, ammonia-nitrogen removal, chromium^{VI} removal, phenolics removal, COD removal

INTRODUCTION

Hazardous effluent is produced by a stainless steel manufacturer in South Africa. Effluent originates as a result of metal pickling with nitric, sulphuric and hydrofluoric acids and coal gasification. The spent acid effluent is neutralized with lime and disposed of together with coal gasification liquor to evaporation ponds. This effluent has the potential to pollute ground water sources in the vicinity of the factory. The effluent contains high concentration levels of organics (including phenols) and other hazardous inorganics (F, NO_3-N, NH_3-N, Cr) and is also almost saturated with calcium sulphate. Seepage of the effluent is taking place through the walls of the evaporation ponds which is intercepted in infiltration trenches below the ponds and returned to the ponds.

Reverse osmosis (RO) technology has been investigated (Krug and McDougall, 1989; Chian and de Walle, 1976; Slater *et al.*, 1983; Whittaker *et al.*, 1988; Weber and Holz, 1991) and is applied (Weber

and Holz, 1991; Peters, 1994) for treatment of municipal leachate. Reverse osmosis has also been evaluated for treatment of coal gasification liquors (Williams, 1991). Tubular (Weber and Holz, 1991) and disc tube RO (Peters, 1994) are successfully applied for the treatment of municipal leachate for TDS, COD and ammonia-nitrogen removals. It appears from the literature that tubular RO can be successfully applied for treatment of coal gasification liquors for TDS, COD and ammonia-nitrogen removals (Williams, 1991). The hazardous effluent produced by the stainless steel manufacturer has similar characteristics (high TDS, COD and ammonia-nitrogen levels) as municipal leachate. Consequently, it was decided to evaluate RO for treatment of the industrial leachate.

Preliminary studies in the laboratory have indicated that it should be possible to treat the effluent successfully with soda ash softening followed by RO desalination. However, membrane fouling by organics in the effluent may lead to process failure. Poor rejection of organics by RO membranes may also make the process unsuitable for pollution control. Consequently, it was necessary to evaluate physical/

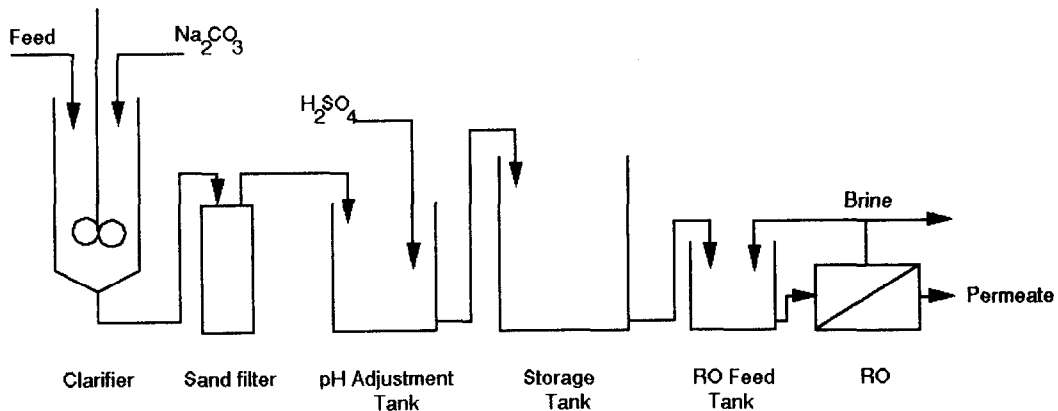*Author to whom all correspondence should be addressed [Fax: (27) 12 841 4785].

Fig. 1. Pilot plant setup.

chemical and membrane technologies for effluent treatment through pilot studies to develop process design criteria for a full-scale application.

The objectives of the study were to: (1) evaluate physical/chemical and membrane technology for treatment of the effluent; (2) develop process design criteria for a full-scale plant; and (3) determine the economics of the process.

EXPERIMENTAL

Process description

The pilot plant set-up is shown in Fig. 1. Seepage from the infiltration trenches was pumped into a 1.7 m³ clarifier/thickener. Soda ash (2.6 kg) was used for water softening. The partial clarified softened effluent was sandfiltered and stored in a 1 kilolitre storage tank where the pH of the effluent (approximately 10) was reduced to approximately 6.5 with concentrated sulphuric acid (150 to 450 ml concentrated acid per kl effluent). The pH adjusted effluent was pumped into a 5 kl storage tank and this water was used as feed to the RO unit.

The RO unit contained two tubular cellulose acetate membrane modules (3.5 m² area). Sponge ball cleaning with flow reversal was applied every 60 min. The level of the feedwater (approximately 200 l) in the RO tank was kept constant with a level controller. Brine was circulated back to the feed tank and runs were conducted at approximately 50 and 85% water recovery to study the fouling potential of the effluent for the RO membranes. Feed pressure was kept at 4000 kPa. Permeate flux (corrected to 25°C), brine flow rate, pressures, pH, conductivities of the RO feed, permeate and brine, were measured at regular intervals. The chemical composition of the effluent, softened effluent, pH adjusted effluent, RO feed, permeate and brine, were also determined at regular intervals.

Membrane cleaning

Biotext (0.5%), citric acid (2%; pH 4.5), EDTA (0.5%; pH 10) and P3 Ultrasil 50 (0.5%) were evaluated for membrane cleaning. Cleaning agent was circulated through the membrane modules at reduced pressure for one hour followed by a tap water rinse for 30 min. Clean water fluxes were measured before and after cleaning.

Treatment of RO permeate with ion-exchange

Reverse osmosis permeate was treated with Amberlite XAD-4 resin in a glass column (16.5 mm diameter, one bed volume (BV) equal to 85 cm³). Loading was conducted at 5 BV/h. Phenol in the column effluent was determined colorimetrically and with high-pressure liquid chromatog-

raphy. The resin was regenerated with 5 BVs methanol at a flow rate of 8 BV/h.

Phenol oxidation with hydrogen peroxide

The pH of 11 RO permeate was reduced to 4 with sulphuric acid. 10 mg/l ferrous iron was added to the samples and different molar ratios of H_2O_2 (30%) to phenol were added to the samples which were stirred for 30 min. The samples were filtered and phenol and COD analyses were conducted.

RESULTS AND DISCUSSION

Chemical composition of effluent and pretreated effluent

A typical composition of the leachate, leachate after softening with soda ash and pH-adjusted effluent is shown in Table 1.

The electrical conductivity of the leachate is high. The leachate is also approximately saturated with calcium sulphate. The leachate also contains high concentration levels of hazardous chemicals like phenolics, chromium^{VI}, fluoride, nitrate and ammonia-nitrogen.

Table 1. Chemical composition of leachate, softened and pH adjusted effluent

| Constituents (mg/l)	Leachate	Softened effluent	pH adjusted effluent
COD	620	600	520
TKN	66.9	48.4	41
Ammonia-nitrogen	32.9	39.1	41.6
Nitrate-nitrogen	826.5	815.1	860.1
Alkalinity	145	907	207
Iron	0.15	0.06	0.07
Chromium	43.8	40.40	34.30
Sodium	1223	1543	1719
Potassium	906	827	771
Calcium	400	5	12
Magnesium	6	2	9
Sulphate (total)	1327	1324	1706
Chloride	717	671	671
Phenolics	44.89	42.2	37.95
Manganese	0.040	<0.025	<0.025
Nickel	0.060	0.040	0.040
Chromium^{VI}	42	40	34
Fluoride	12.6	11.6	11.9
Conductivity (mS/m)	602	617	634
TDS	7421	7865	7192
pH	11.3	11.27	6.62
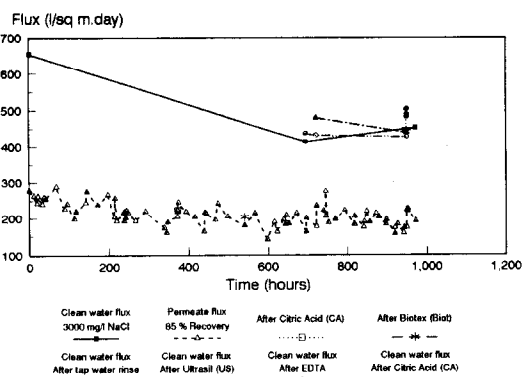
Fig. 2. Permeate flux as a function of time at 85% water recovery.

Calcium could be removed effectively from the effluent with soda ash softening. However, the sodium and alkalinity levels of the softened water were significantly increased with soda ash addition. The sulphate concentration level of the pH-adjusted effluent was also significantly increased after sulphuric acid addition to lower the pH to less than 7 prior to RO treatment.

Permeate flux as a function of time

Permeate flux as a function of time at 85% water recovery is shown in Fig. 2. Permeate flux declined fairly rapidly at the beginning of the run and then appeared to remain approximately constant at the end of the run. However, some decline in permeate flux was observed. Permeate flux was determined at 278 l/m²·d when the run was commenced. Permeate flux, however, dropped to 243 l/m²·d after 5 h of operation. This drop in permeate flux could be ascribed to surface fouling of the membranes. Permeate flux declined further and was measured at 205 l/m²·d after 372 h of operation. The membranes were now for the first time cleaned and cleaning with citric acid increased permeate flux to 224 l/m²·d. Flux again decreased and was determined at 180 l/m²·d after 540 h of operation. Cleaning of the membranes with a Biotex solution increased permeate flux to 203 l/m²·d. Permeate flux again decreased and was determined at 176 l/m²·d after 722 h of operation. The membranes were cleaned with P3 Ultrasil 50 cleaning agent and permeate flux was measured at 235 l/m²·d after 722 h of operation. Permeate flux again decreased and was determined at 173 l/m²·d after 950 h of operation. The membranes were then cleaned with Ultrasil, citric acid and EDTA (2×, pH 10). Permeate flux was determined at 225 l/m²·d when the run was commenced. Permeate flux was measured at 191 l/m²·d when the run was terminated after 972 h of operation.

Clean water flux (3000 mg/l NaCl) was measured at 650 l/m²·d when the run was commenced. Clean water flux (3000 mg/l NaCl) was determined at 414

(after 695.5 h) and 454 l/m²·d when the run was terminated after 972 h of operation. This showed that a certain degree of irreversible membrane fouling had taken place or that the membranes were not completely cleaned with chemical cleaning. More frequent cleaning, however, should give better results.

Clean water flux with tap water was determined at 437 l/m²·d after 695.5 h of operation. Clean water flux decreased slightly to 433 l/m²·d after 722 h of operation. However, clean water flux increased significantly to 480 l/m²·d after the membranes were cleaned with Ultrasil cleaning agent. Clean water flux, however, decreased to 428 l/m²·d after 950 h of operation. Cleaning of the membranes with Ultrasil cleaning agent increased the clean water flux to 441 l/m²·d. Therefore, it appeared that the clean water flux could not be restored to the level of 480 l/m²·d that was obtained after the previous cleaning with Ultrasil cleaning agent. Cleaning of the membranes with citric acid increased the clean water flux to 450 l/m²·d. This increase in permeate flux, however, was not very significant. Further cleaning of the membranes with EDTA (2×, pH 10) increased the clean water flux to 483 and 504 l/m²·d. Therefore, it appeared that it should be possible to control membrane fouling with regular chemical cleanings.

It is further interesting to note that permeate flux has increased significantly after tap water rinses. Tap water rinses were conducted every day for 30 min at reduced pressure. Permeate flux, for example, increased from 162 to 201 l/m²·d after a water rinse (696 h of operation).

Conductivity of the RO feed, permeate and brine as a function of time

Conductivity of the RO feed, permeate and brine as a function of time is shown in Fig. 3. The conductivity of the RO feed varied between 1500 and 2600 mS/m over the test period. Brine conductivity was only slightly higher than that of the feed because brine was recirculated back to the feed tank. Permeate conductivity varied between 55 and 245 mS/m over the test period.
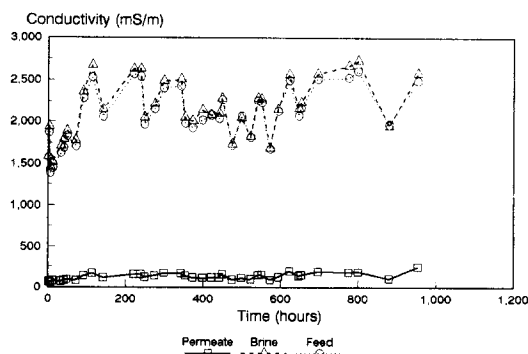

Fig. 3. Conductivity of RO feed, permeate and brine as a function of time at 85% water recovery.
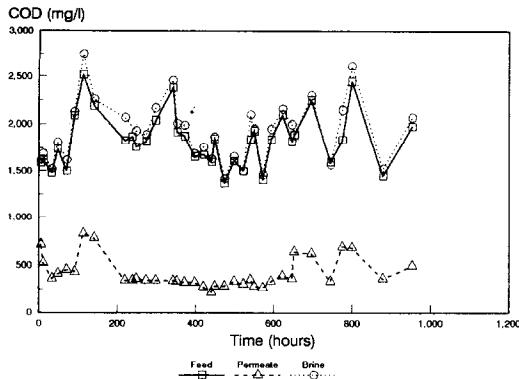
COD (mg/l)

Fig. 4. COD of RO feed, permeate and brine as a function
of time at 85% water recovery.

Chemical oxygen demand (COD) of the RO feed, permeate and brine as a function of time

The chemical oxygen demand of the RO feed, permeate and brine as a function of time is shown in Fig. 4. The COD of the RO feed varied between 1500 and 2500 mg/l. The COD of the brine was also only slightly higher than that of the RO feed. COD of the RO permeate varied between approximately 800 and 250 mg/l over the test period. This showed that a significant amount of organics in the RO feed were not removed by the cellulose acetate RO membranes.

Conductivity, COD rejection and percentage water recovery as a function of time

The conductivity, COD rejection and percentage water recovery as a function of time are shown in Fig. 5. Water recovery was kept at approximately 85% for the entire run. Conductivity rejection varied between 90 and 95%. Conductivity rejection remained approximately constant for more than 800 h of operation. This showed that serious membrane fouling was not experienced. COD rejection varied between approximately 60 and 80%. Therefore, relatively poor organic removals were obtained.
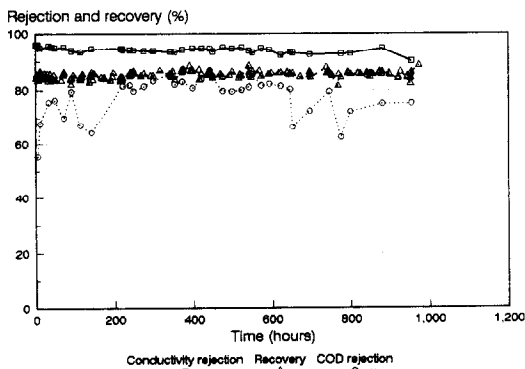
Rejection and recovery (%)

Fig. 5. Conductivity, COD rejection and percentage water
recovery.

Chemical composition of RO feed, permeate and brine

An example of the chemical composition of the RO feed, permeate and brine is shown in Table 2. Excellent conductivity (93.5%) and TDS (95.5%) removals were obtained. Chromium^{VI} could be reduced from 183 to 0.38 mg/l (99.8% removal). Fluoride could be removed from 90 to 2.8 mg/l (96.9% removal). COD was removed from 1840 to 350 mg/l (81.0% removal). However, poor phenolics removal was obtained. It appeared that no phenolics removal was obtained with RO.

Phenolics removal with ion exchange

Removal of phenolics from the RO permeate with ion exchange is shown in Table 3. Phenolics in the RO permeate (68 mg/l) could be reduced to approximately 0.01 mg/l. Approximately 80 BVs water with a low concentration level of phenolics could be obtained.

Phenolics removal with hydrogen peroxide

Removal of phenolics from the RO permeate with hydrogen peroxide oxidation is shown in Table 4. Phenolics could be effectively removed from the RO permeate with hydrogen peroxide oxidation. A 99.7% removal of phenolics could be obtained with a hydrogen peroxide dosage of 285 mg/l. Phenolics were removed from 52.3 mg/l in the RO permeate to 0.16 mg/l in the treated water. However, it appears that it will not be possible to reduce the phenolics concentration to much lower levels.

Organics could also be effectively removed with hydrogen peroxide. COD was removed from 420 to 72 mg/l (82.8% removal) at a hydrogen peroxide dosage of 648 mg/l.

Economics

A preliminary estimate of capital and operational cost to treat 600 kl/d effluent is shown in Table 5.

The capital and operational costs shown in Table 5 are a preliminary estimate of the cost that will be involved to treat 600 kl/d effluent. A more accurate estimate of cost involved can be obtained from a detailed design of the process to treat the effluent.

CONCLUSIONS

It appears that industrial seepage produced by a stainless steel manufacturer can be effectively treated with RO, oxidation (H$_2$O$_2$) or ion exchange for pollution control, effluent volume reduction and water recovery. Oxidation or ion-exchange treatment of the RO permeate will be necessary to reduce phenolics in the effluent (approximately 50 mg/l) to low concentration levels (< 0.2 mg/l). Water recovery of 85% should be possible. A steady decline in RO

Table 2. Chemical composition of RO feed, permeate and brine (85% recovery)

Constituents (mg/l)	Feed	Brine	Permeate	Rejection (%)
COD*	1840	2100	350	80.98
TKN†	111.8	137.2	26.6	76.21
Ammonia-nitrogen	102.6	104.2	15.1	85.28
Nitrate-nitrogen	2691.1	2772.4	413.8	84.62
Alkalinity	886	994	116	86.91
Iron	0.72	0.73	<0.03	95.83
Chromium (total)	183	184	0.58	99.68
Sodium	8314	8490	309	96.28
Potassium	3646	3915	185	94.93
Calcium	75	81	2	97.33
Magnesium	38	43	1	97.37
Sulphate (total)	4402	6696	557	87.35
Chloride	3366	3473	82	97.56
Phenolics	32.17	32.17	48.63	
Manganese	0.09	0.09	<0.025	72.22
Nickel	0.31	0.32	<0.025	91.94
Chromium^{VI}	183	184	0.38	99.79
Fluoride	90	92.5	2.8	96.89
Conductivity (mS/m)	2260	2290	146	93.54
TDS	34,253	35,352	1560	95.45
pH	7.37	7.38	6.28	

*COD = chemical oxygen demand, †TKN = total Kjeldahl nitrogen.

permeate flux, however, was observed as a function of time. However, it appears that it should be possible to control membrane fouling with chemical cleaning. A preliminary estimate has shown that a membrane lifetime of approximately 3 yr can be expected.

Excellent conductivity removals were obtained at 85% water recovery. Conductivity of the RO feed varied between 1500 and 2600 mS/m. Permeate conductivity varied between 55 and 245 mS/m. Conductivity rejection between 90 and 95% was obtained.

Relatively good COD removals were obtained at 85% water recovery. COD of the RO feed varied between 1500 and 2500 mg/l. COD of the RO permeate varied between 250 and 800 mg/l. COD rejection between 60 and 80% was obtained.

Excellent calcium removals were obtained with soda ash softening. Calcium was removed in one case from 400 mg/l in the feed to 5 mg/l in the treated water.

Excellent chromium, fluoride, manganese, nitrate and ammonium nitrogen removals were obtained at 85% water recovery. Chromium^{VI} was in one case removed from 183 mg/l in the RO feed to 0.38 mg/l in the RO permeate (>99% removal). Fluoride and

manganese were removed from 90 to 2.8 mg/l (96.9% removal) and 0.09 to <0.025 mg/l, respectively. Nitrate-nitrogen and ammonia-nitrogen were removed from 2691 to 414 mg/l (84.6% removal) and 103 to 15 mg/l (85.3% removal), respectively. Phenolics, however, were poorly rejected by the cellulose acetate RO membranes.

Phenolics could be effectively removed from the RO permeate with ion exchange. Phenolics could be removed from 68 mg/l to less than 0.1 mg/l.

Phenolics could also be effectively removed from the RO permeate with hydrogen peroxide oxidation. Phenolics were removed from 52 mg/l in the RO permeate to approximately 0.1 mg/l in the treated water. COD in the RO permeate could also be significantly reduced with hydrogen peroxide oxidation (from 420 to 72 mg/l).

Capital costs for lime softening, RO and oxidation equipment are estimated at U.S. $58,000, U.S. $350,000 and U.S. $87,500, respectively. The operational cost for softening is estimated at U.S. $0.47/kl. Reverse osmosis and hydrogen peroxide oxidation operational costs are estimated at U.S. $0.47/kl and U.S. $0.50/kl, respectively.

Table 3. Phenolics concentration in ion-exchange product water as a function of bed-volumes of RO permeate passed through the column (1 BV = 85 ml)

BVs	Phenolics concentration (mg/l)
0	68.0
20	0.03
40	0.01
60	0.01
80	0.01
100	
120	1.47
140	24.7

Table 4. Phenolics and COD removal with hydrogen peroxide oxidation

Mol H$_2$O$_2$ Mol Phenol	H$_2$O$_2$ (mg/l)	Phenolics* (mg/l)	% Removal	COD* (mg/l)	% Removal
4	81	29.41	43.8	340	19
8	162	15.48	70.4	360	14.3
10	201	2.22	95.7	191	54.5
12	243	0.36	99.3	164	60.1
14	285	0.16	99.7	168	60
16	324	0.16	99.7	142	66.2
18	363	0.11	99.8	112	73.3
20	402	0.10	99.8	112	73.3
22	441	0.12	99.8	85	79.8
32	648	0.15	99.7	72	82.8

*Initial phenolics and COD concentrations were 52.3 and 420 mg/l, respectively.

Table 5. Capital and operational cost (preliminary estimate) to treat 600 kl/d effluent

Item	Capital cost (U.S.$)	Operational cost (U.S.$)
Clarifier/thickener (softening)	58,300	0.47
RO unit	350,000	0.47
Oxidation	87,500	0.50

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