Recycling of Refinery Effluents – Two Case Studies in India

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Abstract

In response to environmental stipulations and limited fresh water resources, the Indian Oil Corporation Ltd. Panipat and Essar Oil Ltd. Vadinar had to build water reclamation plants. The plants, which mainly treat refinery effluents, were commissioned in 2006 and 2012 respectively. Advanced multi-barrier systems (including UF and RO) were employed in order to meet the stringent quality requirements for the recycling of boiler make-up and good results with regard to all the requested standards have been achieved. The Panipat UF membranes have a lifetime of 6 years and rather than integrity, which remains quite good (fibre breakages < 0.1‰/year), the main reason for replacement is relatively low permeability (50-60 L/m^2*h*bar). The operating cost (OPEX including membrane replacement) has been calculated as 0.37 EUR/m^3 of recycled boiler make-up.

Keywords

Refinery Effluents, Operating Cost, Reverse Osmosis, Ultrafiltration, Water Recycling

INTRODUCTION

There are currently 22 refineries in operation in India and installed capacity is growing. In 2011, it amounted to 187 million metric tons per annum (MMTPA) and had reached 218 MMTPA by the end of 2013 (Verify Markets 2013). Another 50 MMTPA are to be added in the coming years through the expansion of existing refineries with a further 39 MMTPA coming from new capacity. Water recycling plays a major role in Indian industry, mainly due to limited water resources, uneven rainfall (70% during the monsoon months of July to September), increasing environmental awareness, green technology advantages and government regulations. In this paper, two water recycling case studies with regard to water recycling are presented: Panipat Refinery (Indian Oil Corporation Ltd, Haryana State, 12 MMTPA) and Essar Refinery (Essar Oil Ltd, Vadinar/Jamnagar, Gujarat State, 20 MMTPA). The reclamation plants were commissioned in 2006 and 2012 respectively.

The original Panipat refinery (6 million metric tons per annum) was commissioned in 1998 and the refinery expansion (doubling of refining capacity) in 2006. This expansion also included the petrochemical production of paraxylene (PX) and purified terephtalic acid (PTA), which form the basis for producing polyester staple fibres, polyester filament yarns and other resins. The Panipat Refinery Expansion Water Reclamation Plant (PRE-WRP), which treats both secondary refinery effluents and various refinery/petrochemical process effluents, was commissioned at the end of 2006. In 2009, refinery capacity was further enlarged to 15 MMTPA. The naphtha cracker and its downstream polymer units (naphtha cracker complex) were commissioned in 2010. The Panipat Naphtha Cracker Water Reclamation Plant went on-line in June 2010 and was presented together with the PRE-WRP in (Lahnsteiner et al 2012 and 2013). In this paper, only the most recent PRE-WRP results together with the Essar case are described and discussed.

IOCL is India's largest commercial enterprise and was ranked 125th on the Fortune Global 500 list in 2010. It owns and operates ten of India's 22 refineries with a combined refining capacity of 65.7 million metric tons per annum. Panipat is located in Haryana State, 90 km northwest of Delhi, where annual precipitation totals approx. 500 mm, but over 70 % of rainfall occurs during the monsoon months of July to September. Nevertheless, there is practically no water shortage in the Panipat region due to the availability of sufficient surface water (river water). The Panipat Refinery is located in farmland irrigated by the Yamuna Canal, which is used mainly for potable water production and agricultural irrigation and thus cannot be employed as a recipient. Therefore, rather than due to a lack of water for industrial use, reclamation plants have been installed to meet stringent governmental regulations (zero liquid discharge in the mid-term) and prevent the pollution of nearby water bodies. Water losses during the refining processes are compensated for by fresh water from the Yamuna Canal.

The Essar Oil Ltd Refinery at Vadinar/Jamnagar started commercial production (10.5 MMTPA) in 2008 and following expansion and optimisation projects, it has a capacity of 20 MMTPA. The refinery accounts for about 10 percent of India's refining capacity and is the second largest in the country. It is planned to increase current output from 20 to 40 MMTPA within the next five years. Vadinar is located in north-western India on the Gulf of Kutch (inlet of the Arabian Sea) close to the City of Jamnagar (Gujarat State). Annual precipitation is less than 500 mm and more than 80 % occurs during the monsoon months of July to September. Due to the lack of perennial rivers, declining ground water levels and seawater intrusion, this region can be considered as water-stressed. The refinery's water management is based on the use of raw water (from the Gujarat State water supply), desalinated seawater and recycled water.

METHODS

In both cases, advanced multi-barrier systems have been utilised in order to meet the strict quality requirements for recycling as boiler make-up water (and also as cooling make-up at the Essar Refiney). VA TECH WABAG India was commissioned with their construction, operation and surveillance. Figure 1 shows two operators at the Essar Refinery Water Reclamation Plant (ER-WRP) using the SCADA system to control the water reclamation process.

Figure 1 Essar Refinery - water reclamation plant control room

The following represents a description of the two cases. The different wastewater streams treated in the reclamation plants (PRE-WRP and ER-WRP) are shown in Table 1. As can be seen from this table, the PRE-WRP inlet consists of seven streams, which are blended in two equalisation tanks (3,700 m^3 each). The ER-WRP is fed by just one stream comprised of secondary effluent from the refinery effluent treatment plant (ETP), as the different partial streams (demineralisation regenerates, etc.) are already mixed upstream of the ETP.

Table 1. Panipat and Essar refineries – wastewater streams

		Reclamation Plants – Flow	
Wastewater Streams	Unit	PRE-WRP	ER-WRP
Secondary refinery effluent – ETP I	m^3/h	400	
Secondary refinery effluent – ETP II[1)]	m^3/h	300	
PX[2)]/PTA[3)] effluent including cooling tower blow-down	m^3/h	272	
Demineralisation regenerate from Panipat Refinery I	m^3/h	60	
Demineralisation regenerate from Panipat Refinery II[1)]	m^3/h	140	
Cooling tower blow-down from in-house power plant I	m^3/h	18	
Cooling tower blow-down from in-house power plant II[1)]	m^3/h	50	
Secondary refinery effluent – ETP	m^3/h		540

[1)] Expansion of refinery; [2)]PX…Para-Xylene; [3)]PTA...Purified Terephtalic Acid

The major design parameters of the water flows (inlets to the reclamation plants and reclaimed water) are shown in Table 2. As can be seen from this table, the major differences with regard to the inlet are in TDS (1,786 vs 3,000 mg/L), oil (10 vs 50 mg/L) and Q (900 vs 540 m^3/h).

Table 2. PRE-WRP and ER-WRP design basis

		Water Reclamation Plants				
		PRE-WRP		ER-WRP		
					Reclaimed Water	
Parameter	Unit	Inlet	Reclaimed Water[1)]	Inlet	to Cooling Tower[2)]	to MBIX[3)]
T	°C	15-35	15-35	25-37	25-37	25-37
TDS	mg/L	1,786	< 0.1	3,000	< 150	< 10
Silica	mg/L	98	< 0.01	50	< 2	< 0.5
COD	mg/L	150	-	150	-	-
BOD_5	mg/L	10	-	20	-	-
Oil	mg/L	10	-	50	-	-
Q	m^3/h	900	764	540[4)]	200	200

[1)]Demineralised water after the mixed bed ion exchanger; [2)]RO I permeate recycled as cooling make-up; [3)]RO II permeate, i.e. feed water for the mixed bed ion exchanger at the refinery; [4)]Phase 1; in the future, Q will be 1,350 m^3/h (phase 1 & 2: 540 + 810 m^3/h)

Panipat Refinery Expansion Water Reclamation Plant (PRE-WRP) design

Basically, the reclamation plant (design capacity = 900 m^3/h) incorporates clarification, pressure dual media filtration, ultra filtration and reverse osmosis (two passes each with low-fouling composite membranes and a brine concentrator with seawater membranes). The RO permeate is polished by mixed bed, ion exchange filters and is then mostly recycled as boiler make-up water in the refinery power plant (Figure 2).

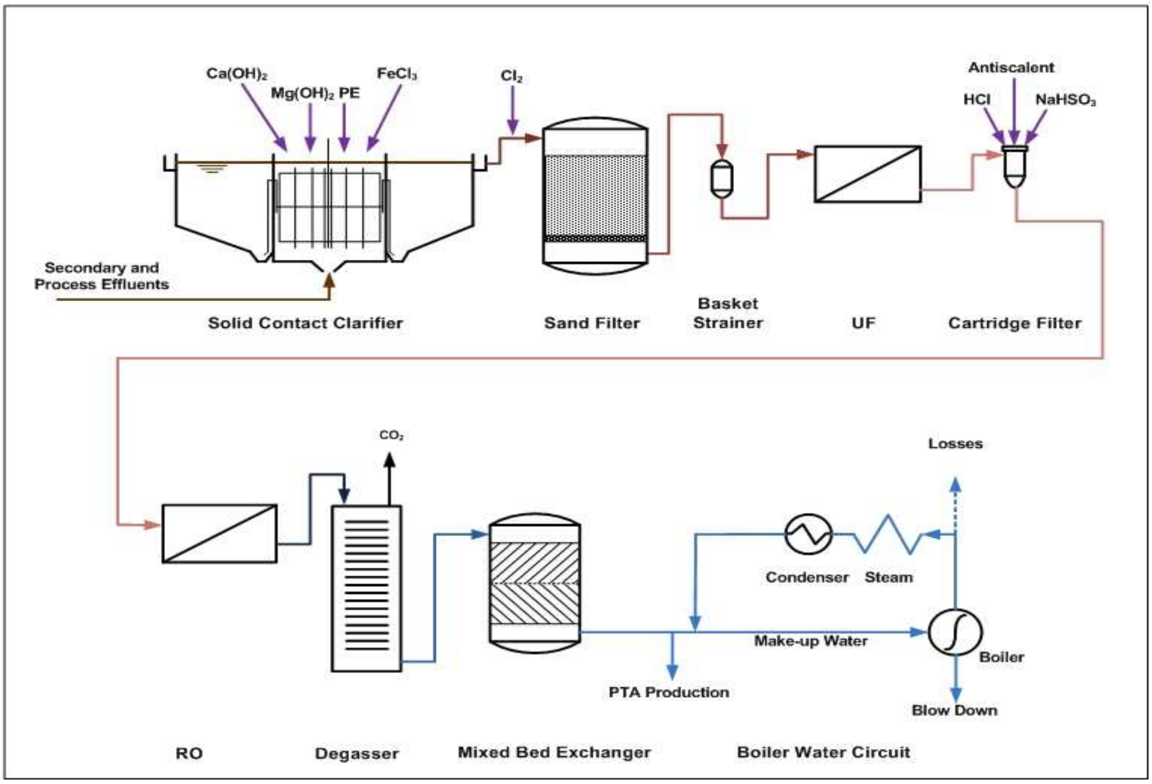

Figure 2 PRE-WRP – process flow diagram

Essar Refinery Water Reclamation Plant (ER-WRP) design

The reclamation plant (design capacity = 540 m^3/h [phase 1]; in the future: 1,350 m^3/h [phase 1 & 2]) incorporates dissolved air flotation (DAF), clarification (Figure 3), dual media filtration (DMF), ultra filtration and reverse osmosis (2 passes). Part of the RO 1 permeate (50%) is used as cooling tower make-up, while the remainder is further desalinated in RO 2. The RO 2 permeate is pumped to the refinery and polished by mixed bed ion exchange filters and then recycled as boiler make-up water in the refinery power plant. The major differences to the PRE-WRP design consist of an additional process step (the DAF unit) and a more simple reverse osmosis phase. Owing to the higher oil concentration in the inlet (PRE-WRP: 10 mg/L, ER-WRP: 50 mg/L) a DAF unit has been employed. The difference in RO design is explained in the next section.

Figure 3 ER-WRP – solid contact clarifier

Membrane process steps in both plants

Practically the same UF and RO membranes are employed in both plants. The ultrafiltration process steps consist of pressure-driven, inside-out, hollow fibre systems (X-Flow Xiga; Table 3). Both systems are operated in a dead-end mode. Ferric chloride is dosed into the feed as a coagulant (typical dosing concentration: 1 mg Fe /L). The major task of the UF is to reduce the silt density index (SDI) and remove turbidity, as well as suspended and colloidal matter, in order to minimise fouling of the downstream reverse osmosis process step. The UF membrane fouling caused by the aforementioned impurities is removed by regular backwashing with permeate. The backwash is enhanced once a day in both UF plants using chemicals (chemical enhanced backwash - CEB with caustic NaOCl and HCl). Based on the extensive experience gained from previous projects, the ER-WRP UF system was designed with a higher flux (net flux = 57 $L/m^2 \cdot h$; net flux of PRE-WRP = 46 $L/m^2 \cdot h$; Table 3). The resulting membrane areas total 16,416 m^2 in the PRE-WRP UF and 8,640 m^2 in the ER-WRP UF. The retentate of the PRE-WRP UF process step is recycled (together with the DMF backwash water and the mixed bed ion exchange regenerate) to the equalisation tanks (feed collection tanks) upstream of the pre-treatment stages of the reclamation plant. The retentate of the ER-WRP UF is recycled (together with DMF back wash water and the RO II brine) to the inlet of the clarifier.

Table 3. Ultrafiltration design

		Water Reclamation Plants	
Membrane parameters	Unit	PRE-WRP	ER-WRP
Membrane material		Hollow fibre polyether-sulfone	
Average feed flow	m^3/h	894	544
Design gross flux	$L/m^2 \cdot h$	54	63
Design permeate flow	m^3/h	760	490
Design net flux	$L/m^2 \cdot h$	46	57
Recovery	%	85	90
Skids	-	6 (+1 standby)	2 (+1 standby)
Pressure vessels/skid	-	18	27
Vessels total	-	108	54
Elements/vessel	-	4	4
Elements total	-	432	216
Membrane area/element	m^2	38	40
Membrane area	m^2	16,416	8,640

A two-pass RO system is employed in the PRE-WRP in combination with a brine concentrator. The UF permeate is fed to RO pass I (three internal stages; low fouling composite membranes, Hydranautics LFC 3). The RO I permeate is further desalinated in RO pass II (three internal stages; low fouling composite membranes, Hydranautics LFC 3) and the RO I reject is fed to the brine concentrator (two internal stages; seawater membranes, Hydranautics SWC 3). The brine concentrator permeate is recycled to RO II. This process configuration provides a recovery rate of 90 %. The RO II permeate is degassed and in order to allow the further removal of dissolved solids, polished in mixed bed ion-exchangers containing strong acid cat-ion and strong base an-ion resins mixed in a single vessel. As previously mentioned, the authorities have stipulated that the refinery has to achieve zero liquid discharge. However, it has temporary permission to dispose of the liquid waste (R.O. brine) produced in the reclamation process. At present, 100 % of the brine is used for refinery coke quenching. Other options are to blend the brine with fire-fighting water, or to use it for the irrigation (blended with low TDS water) of the free land along the refinery perimeter to create green spaces (14 km long “green belt”). Nonetheless, in the medium-term this official request will be met through the installation and operation of evaporation and crystallisation.

The RO of the RE-WRP is a two-pass system. RO I (pass I) consists of three stages: stage I and II with low fouling composite membranes (Hydranautics LFC 3), stage III with seawater membranes (Hydranautics SWC5). RO II (pass II) consists of two stages with brackish water membranes (Hydranautics CPA3). This configuration is simpler than that of the PRE-WRP as the required recovery rate is lower (80% in ER-WRP; 90% in PRE-WRP) owing to the fact that the brine of the RE-WRP RO I can be discharged (together with the brine of the seawater desalination plant) into the sea, whereas as previously mentioned, zero liquid discharge in the PRE-WRP is the (medium-term) aim. Within this context, a higher recovery rate in the RO system is advantageous for the achievement of this objective. Figure 4 shows the PRE-WRP and RE-WRP reverse osmosis process units.

Figure 4 PRE-WRP and RE-WRP - reverse osmosis systems

RESULTS AND DISCUSSION

Since the beginning of operations in November 2006, the stringent standards for recycling as boiler make-up have been met fully by the PRE-WRP. For example, silica is reduced from 13 mg/L in the plant inlet to < 0.010 mg/L in the mixed bed ion exchanger (total removal 99.94 %; VGB (2011) standard: 0.020 mg/L). Further results (e.g. UF performance from 2006 to 2011) are described in (Lahnsteiner et al 2010, 2012 and 2013).

In the following paragraphs, membrane replacement history and corresponding membrane performance and membrane integrity data are presented and discussed.

In the last quarter of 2010 and first quarter of 2011, after four and four and a half years of operation respectively, permeability remained acceptable (70 - 180 L/m^2·h bar), but nevertheless at the client’s request the skid A and B membranes were exchanged for spare membranes (rack A on November 25, 2010; skid B on April 14, 2011; Table 4). The old membranes (from rack A and B) were integrity tested. Table 5 shows that after four years of operation (3.9 and 4.3 years respectively) there was still a relatively low specific fibre breakage rate (skid A: 119 breakages in 72 membrane elements, i.e. 0.042 ‰ fibre breakages per year; skid B: 236 breakages in 72 membrane elements, i.e. 0.076 ‰ fibre breakages per year). In the second half of May 2011, the average performance of the new membranes in skid A and B (approx. 200 L/m^2·h bar) was nearly 100 per cent higher than that of the old membranes (approx. 100 L/m^2·h bar; average of skids C, D, E, F and G).

Table 4. Panipat Water Reclamation Plant - UF replacement history

Skid	Date of Replacement	Membrane Operating Time [years]	Remarks
A	Oct 10	3.9	Exchanged for spare membranes
B	Apr 11	4.3	Exchanged for spare membranes
C	Jan 12	5.1	Exchanged for new membranes
D	Jan 12	5.1	Exchanged for new membranes
G	Mar 12	5.25	Exchanged for “old“ intact A, B, C and D membranes
G	Dec 12	6.1[1)]	Exchanged for new membranes
F	Apr 12	5.3	Exchanged partly[2)] for “old“ intact A, B, C and D m.
F	Nov 12	6.0[3)]	Exchanged for new membranes
E	Nov 12	6.0	Exchanged for new membranes

[1)] 72 “old“ intact A, B, C and D membranes operated for 6.1 years
[2)] 40 of 72 elements were exchanged for “old“ intact A, B, C and D membranes (32 “old“ original membranes)
[3)] 40 “old“ intact A, B, C and D membranes and 32 “old“ original F Membranes operated for 6.0 years

At the beginning of 2012, after more than 5 years of operation, the skid C and D membranes were exchanged for new membranes (skid C on January 16, 2012, skid D on January 20, 2012; Table 4). The permeability of the old membranes was in a 50-150 L/m^2·h bar range. In the first weeks of operation, the new membranes showed permeability values in a 300 to 500 L/m^2·h bar range. The old membranes from skids C and D were integrity tested and the results (Table 5) showed that after approx. 5.1 years of operation there was still a relatively low specific fibre breakage rate (skid C: 112 breakages in 72 membrane elements, i.e. 0.031 ‰ fibre breakages per year; skid D: 138 breakages in 72 membrane elements, i.e. 0.038 ‰ fibre breakages per year).

Table 5. Integrity test results - PRE-WRP ultrafiltration

		Integrity Results		
Skid	Integrity Test Date [mm/yy]	Operating Period [years]	Number of Fibre Breakages	Fib. Breakage Rate [‰/year]
A	06/08	1.5	3	0.003
B	06/08	1.5	0	0
C	06/08	1.5	0	0
D	06/08	1.5	0	0
G	12/08	2.0	36	0.025
A	11/10	3.9	119	0.042
B	04/11	4.3	236	0.076
C	01/12	5.1	112	0.031
D	01/12	5.1	138	0.038
G	03/12	5.25	142	0.038
F	04/12	5.3	135	0.035*

* Extrapolated from 40 tested elements to 72 elements

The following membrane exchange procedure has been used in line with the investment plan of the client (IOCL). As mentioned above, the membranes of skid A and B were exchanged for spare membranes, whereas the membranes of skid C and D were exchanged for new membranes. The old “intact” membrane elements (without fibre breakages) from skids A, B, C and D were reused in skids G and F. In skid G, all 72 elements were replaced in March 2012 (Table 4) and operated until December 2012, when they were replaced by new membranes. In skid F, 40 elements were replaced in April 2012 and operated together with 32 non-integrity tested, original membranes until November 2012 when they were also replaced by new membranes.

The reason for membrane recycling was the improvement in permeate quality (i.e. the reduction in the fouling potential of downstream RO) through the reuse of intact membranes until new ones became available for an exchange. It would appear that recycling did not provide a significant cost benefit, but at least the best available membranes were employed until their replacement with new membranes.

Skid E was operated with old original membranes until November 2012 when these were replaced by new membranes. In summary, it can be stated that the membranes in skids E, F and G were in operation for a period of approx. 6 years, i.e. a relatively long lifetime for an industrial application. However, during the last 5 to 6 months before replacement, average permeability values were relatively low (50 - 60 $L/m^2{\cdot}h$ bar). Therefore, rather than membrane integrity, which was still quite good (fibre breakage rate only ca. 0.04 ‰/year; Table 5), this was the main reason for replacement. Basically, there are two criteria for membrane exchange: A.) High TMP/low permeability and B.) Membrane integrity.

Ad A) TMP and permeability are connected. TMP should not exceed 1.5 bar in order to avoid both intensified fouling and mechanical stress. At the design flux of 54 L/m^2*h a TMP value of 1.5 bar would correspond to a permeability of 36 $L/m^2{\cdot}h$ bar. For most of the time, TMPs have been below 1 bar (permeability > 54 $L/m^2{\cdot}h$ bar), i.e. this exchange criterion has not been exceeded. However, substantially increased energy consumption and CEB frequencies (and subsequently lower plant availability) already occur at lower TMP/higher permeability values. Permeability of < 100 $L/m^2{\cdot}h$ bar, which corresponds to TMP > 0.54 mbar, can be considered as a critical value with regard to such (sub-optimal) operational situations.

Ad B) In order to avoid turbidity and an increased SDI which would increase the fouling potential of downstream RO membranes, the number of fibre breakages should not be too high. Therefore, the membrane elements with fibre breakages should be exchanged (or repaired.). The aforementioned values were according to design (turbidity < 0.1 NTU [limit of detection] and SDI < 3) prior to membrane exchange (and logically also after exchange), i.e. as the fibre breakage rate was low (Table 5), no increased turbidity and SDI could be detected.

The Vadinar water reclamation plant has been in operation since mid-2012 and this plant has also met all the required standards in full, e.g. TDS was typically reduced in RO 1 from 1,188 mg/L to 74 mg/L (requirement for cooling tower make-up: 150 mg/L; Table 2) and in RO 2 from 72 mg/L to 1.6 mg/L (requirement for mixed bed ion exchange feed water: 10 mg/L; Table 2).

Table 6 shows the operating cost (OPEX) of both reclamation plants. The PRE-WRP OPEX (for the production of boiler make-up water) amounts to 0.35 EUR/m^3 (power 0.213 EUR/m^3, chemicals 0.110 EUR/m^3, manpower 0.022 EUR/m^3, maintenance 0.006 EUR/m^3). The specific power demand is 1.87 kWh/m^3 of **demineralised water** (1.37 kWh/m^3 inlet). The membrane replacement cost is 0.024 EUR/m^3 and was calculated on the basis of a membrane life of six years, an interest rate of 10% and annual production of 5.4 million m^3 demineralised water (89% utilisation ratio). The RE-WRP OPEX (for the production of cooling make-up and feed water for the mixed bed ion exchanger is 0.28 EUR/m^3 (power 0.170 EUR/m^3, chemicals 0.054 EUR/m^3, manpower 0.043 EUR/m^3, maintenance 0.013 EUR/m^3). The specific power requirement is 2.45 kWh/m^3 of **product water** (1.90 kWh/ m^3 secondary refinery effluent). This consumption is relatively high and can be explained mainly by the small plant capacity (540 m^3/h in phase 1; in the future 1,350 m^3/h), as well as both the low utilisation and recovery rates. Nonetheless, the PRE-WRP OPEX (0.35 EUR/m^3) is higher than that of the ER-WRP (0.28 EUR/m^3), due mainly to both the higher power price and higher chemicals consumption, e.g. for the operation of an additional process step (ion-exchange - regeneration chemicals).

Table 6. PRE-WRP and ER-WRP operating costs

Cost Type	Unit	Reclamation Plants PRE-WRP	ER-WRP
Power	[EUR/m^3]	0.213$^{1)}$	0.170$^{2)}$
Chemicals	[EUR/m^3]	0.110	0.054
Manpower	[EUR/m^3]	0.022	0.043
Maintenance, etc.	[EUR/m^3]	0.006	0.013
OPEX (Total Operating Cost)	[EUR/m^3]	0.351	0.280

$^{1)}$1.87 kWh/m^3 of **demineralised water**; 1.37 kWh/m^3 inlet; power price = 0.114 EUR/kWh;
$^{2)}$2.45 kWh/m^3 of **product water** (cooling make-up and MBIX feed water), 1.90 kWh/m^3 of raw water; power price = 0.0694 EUR/kWh

CONCLUSIONS

Installed refining capacity in India is growing rapidly. Related water demand is also increasing in line with this development and therefore water management is a challenging task, which apart from other sources, requires the provision of reclaimed water. The evaluation of refinery effluent recycling shows that this practice is technically and economically feasible. The specific cost depends on a wide range of factors such as raw water quality, plant capacity, utilisation and recovery rate, the type of reclaimed water (boiler make-up, cooling make-up, etc.) and the price of power, etc. In the case of Panipat, the OPEX for demineralised water amounts to 0.35 EUR/m^{3,} which is relatively inexpensive for a TDS < 0.1 mg/L and silica < 0.01 mg/L quality. In the case of Essar, the cost of 0.28 EUR/m^3 is relatively high for the production of cooling make-up (50%; TDS < 150 mg/L, silica < 2 mg/L) and feed water for demineralisation in mixed bed ion exchangers (50%; TDS < 10 mg/L, silica < 0.5 mg/L), but will be lower in future following reclamation plant extension. It can be concluded that recycling provides water at a reasonable price and water supply security is boosted due to the saving of large water volumes. This is important, as in both cases, water is also obtained from public supply, which could be endangered in future owing to the growing demand for agricultural and potable purposes, or simply due to reduced availability during droughts.

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