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Effluents from copper industry: Improvised techniques

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Abstract. In India, recycling of treated effluent plays a major role in the industry. Particularly in copper industry, recycling techniques for treated effluents adopt conventional technologies which are not energy efficient and recovery of high quality process water, free flowing salts and sludge's is very low. This paper presents an overview of enhanced modern technology for treated effluents in copper industry making it more efficient with high recovery of high quality process water and free flowing salts. Life cycle cost (LCC) would be 15-20% lower than the conventional technologies. The conventional technology can be replaced with this proposed technique in the existing and upcoming copper industries.

Keywords: copper industry; life cycle; recycling; waste water; improvised techniques

1. Introduction

In Earlier days, copper industries discharged their treated effluents from effluent treatment plants (ETP) directly to storm water discharge or used within the industry as process water (Camponelli *et al*. 2010). Nowadays, copper industries are focusing on adoption of 100% recycling of treated effluent using zero liquid discharge concepts. This paper presents a clear picture about recycling of treated effluent using enhanced modern techniques and ensuring zero liquid discharge. Also this technology (Pérez-González *et al*. 2012) ensures to get high quality of permeate water which can be reused within the copper industry as process water / cooling tower make up water etc., and obtaining free flowing solids with less moisture content which is being disposed as secured landfill (Al Yaqout 2003, Zupančič *et al*. 2009, Eldredge 1986, VanGulck and Rowe 2004).

2. Site observations on effluent generation and its treatment systems

Normally in copper industries, the effluent treatment plants comprise of primary, secondary and tertiary treatments (Üstün *et al*. 2011). The treated effluents from Effluent treatment plants are further treated in Clarifier followed by filtration, UF/RO plant and Evaporation / crystallization.

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The initial separation of suspended solids from the waste water takes place in Primary treatment, the precipitation of heavy metals is carried out in Secondary treatment (Hunsom *et al.* 2005, Ahmed Basha *et al.* 2011) and pH adjustments are done in Tertiary treatment.

Different effluents generated from various sources in copper industry are collected in respective collection tanks and the collected effluents are pumped to primary treatment followed by secondary and tertiary treatments (Üstün *et al.* 2011). The final treated effluent from tertiary treatment plant which is having high Total Dissolved Solids (TDS) is being stored in treated water storage tank.

The typical block diagram for effluent treatment plants in copper industry is shown in Fig. 1.

The typical quality of treated effluent obtained from an ETP is shown in the Table 1.

Further, the effluents from Effluent treatment plant (ETP) are treated in Pre-treatment plant followed by UF/RO plant to get high quality process water which can be recycled & reused to meet process water requirements or cooling tower make up requirements in copper industry.

The typical quality of permeate water obtained from a Reverse Osmosis (RO) plant is shown in the Table 2.

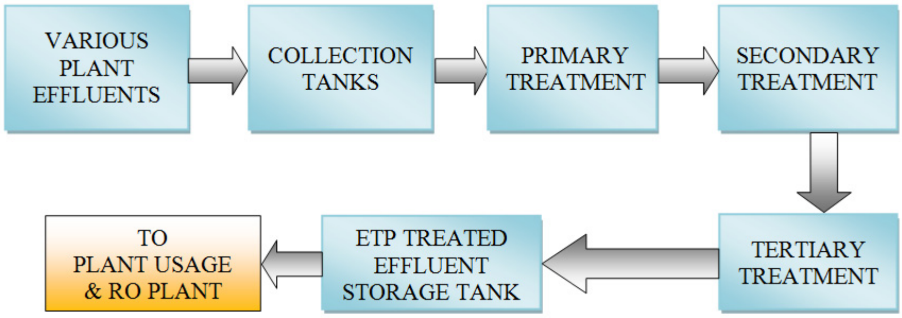

Fig. 1 Block diagram for effluent treatment plants in copper industry

Table 1 Quality of treated effluent obtained from an ETP of a copper industry in India

Sl No	Parameters	Units	Values (Average)
1	pH	---	8-10
2	Biochemical Oxygen Demand (BOD-5)	mg/l	6.5
3	Chemical Oxygen Demand (COD)	mg/l	25
4	Turbidity	NTU	35
5	Total Suspended Solids (TSS)	mg/l	900
6	M-Alkalinity as $CaCO_3$	mg/l	100
7	Sulfates as SO_4	mg/l	6800
8	Chlorides as Cl	mg/l	600
9	Arsenic (Zheng *et al.* 2013)	mg/l	25
10	Copper (Zheng *et al.* 2013, Hunsom *et al.* 2005, Meshram *et al.* 2013)	mg/l	< 10
11	Chromium (Hunsom *et al.* 2005)	mg/l	0.1
12	Nickel (Meshram *et al.* 2013)	mg/l	0.1
13	Total Dissolved Solids (TDS)	mg/l	12000

Table 2 Quality of permeate water obtained from a Reverse Osmosis (RO) plant of a copper industry in India

Sl No.	Parameters	Units	RO Output permeate water quality
1	pH	---	6.5 - 7.5
2	Biochemical Oxygen Demand (BOD-5)	mg/l	Nil
3	Chemical Oxygen Demand (COD)	mg/l	Nil
4	Turbidity	NTU	Nil
5	Total Suspended Solids (TSS)	mg/l	Nil
6	M-Alkalinity as $CaCO_3$	mg/l	< 30
7	Sulfates as SO_4	mg/l	≤ 50
8	Chlorides as Cl	mg/l	≤ 75
9	Arsenic	mg/l	≤ 0.02
10	Copper	mg/l	Nil
11	Chromium	mg/l	Nil
12	Nickel	mg/l	Nil
13	Total Dissolved Solids (TDS)	mg/l	≤ 150

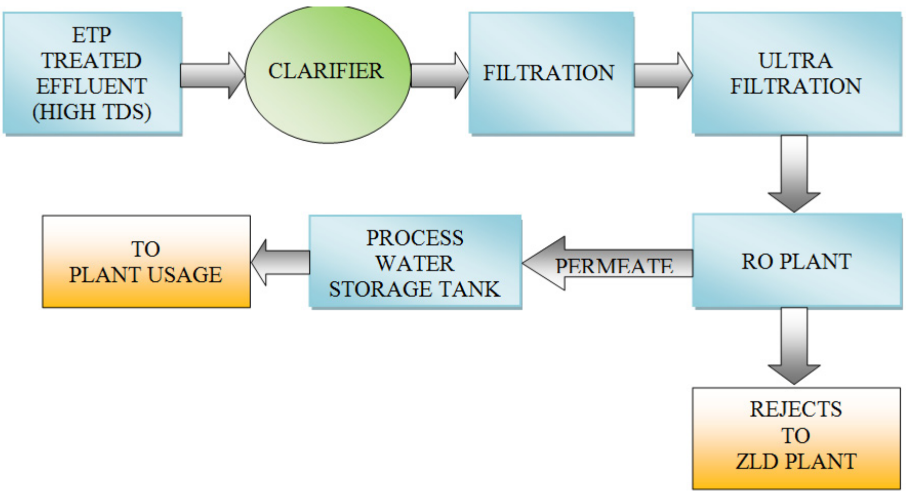

Fig. 2 Block diagram for UF/RO plant in copper industry

3. Case study analysis and discussion

3.1 Case I: (As per Site condition)

The typical block diagram (as per site condition) for UF/RO plant in copper industry is shown in Fig. 2.

The typical block diagram (as per site condition) for Zero Liquid Discharge Plant (ZLD) in copper industry is shown in Fig. 3 (News 2011, 2012).

The typical flow diagram showing “Multi Effect Evaporator using TVR (Thermal Vapor Recompression)” is given in Fig. 4.

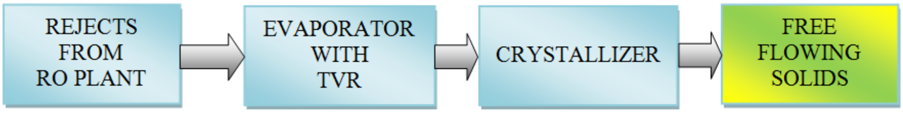

Fig. 3 Block diagram for Zero Discharge Plant (ZLD) in copper industry

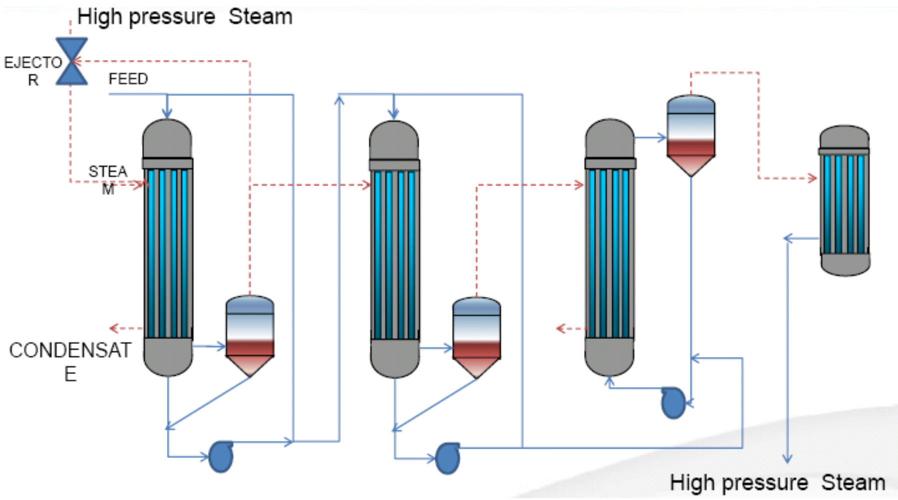

Fig. 4 Flow diagram showing "Multi Effect Evaporator using Thermal Vapor Recompression (TVR)"; Thermal Vapour Recompression, TVR

Fig. 5 Site photo showing "Multi Effect Evaporator using TVR"

Multiple effect evaporation plants save steam by repeatedly using the same quantity of heat from effect to effect. The vapours from the first effect are compressed to a higher pressure by the thermo compressor, and these compressed vapors are the heating medium for the subsequent effect. Vapors from the final effect are condensed; heat is recovered and supplemented by the cooling

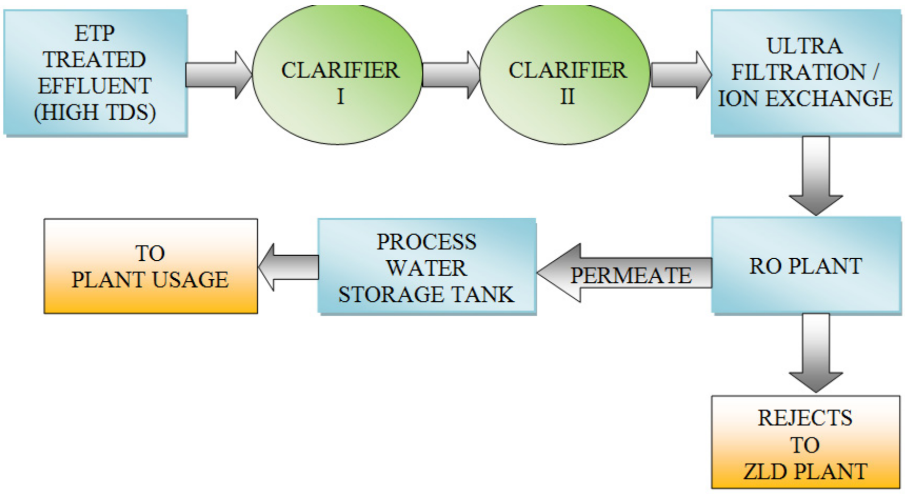

Fig. 6 Block diagram (modified) for the RO plant in copper industry

water if required.

Limitations:
Steam Condensate gets contaminated with Process Condensate

The typical site photo showing "Multi Effect Evaporator using TVR (Thermal Vapor Recompression)" is given in Fig. 5.

3.2 Case II: (Proposed modification)

3.2.1 Proposed modification in pre-treatment & RO plant

The typical block diagram (proposed modification) for the RO plant in copper industry is shown in Fig. 6.

In this proposed pre-treatment, two staged clarifier can be used against single stage clarifier to achieve better settling of heavy metals and suspended solids (Hunsom *et al*. 2005, Ahmed Basha *et al*. 2011). The merits of the proposed modification on pre-treatment are shown in Table 3.

In this proposed UF or Ion Exchange / RO plant modification,

(1) In UF section, Outside - In Polyvinylidene fluoride (PVDF) (Hsu-Hsien Chang *et al*. 2014) Submerged type Ultra filtration (Lau *et al*. 2014) (UF) is proposed against Inside Out Polyethersulfone (PES) (Basri *et al*. 2011) Pressurized type Ultra filtration (UF). The main advantage of this proposed UF system is Open tank configuration and fibers are loosely packed for easier solid removal. The other merits of proposed UF system are listed in Table 4.
(2) Ion exchange method can also be employed in place of UF system and their merits are listed in Table 4.
(3) Low fouling RO membranes are proposed against High fouling RO membranes and their merits are listed in Table 4.

3.2.2 Proposed modification in Zero Liquid Discharge (ZLD) (News 2011, 2012) plant

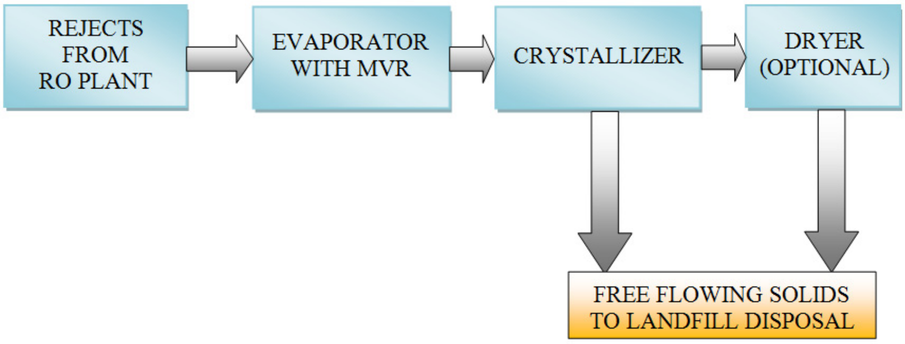

Fig. 7 Block diagram (modified) for Zero Liquid Discharge (ZLD) in copper industry

The typical block diagram (proposed modification) for Zero Liquid Discharge Plant (ZLD) in copper industry is shown in Fig. 7 (News 2011, 2012).

The typical flow diagram (proposed modification) showing "Evaporation with MVR (Mechanical Vapor Recompression)" is given in Fig. 8.

Mechanical Vapor Recompression (MVR) is an evaporation method by which a blower, compressor or jet ejector is used to compress, and as a result of the compression, increase the temperature of the vapor produced.

As a result, the vapor can serve as the heating medium for its "mother" liquid or solution being concentrated. Without the compression, the vapor would be at the same temperature as its "mother" liquid/solution, and no heat transfer could take place

The efficiency and feasibility of this process depend on the efficiency of the compressing device (e.g., blower, compressor).

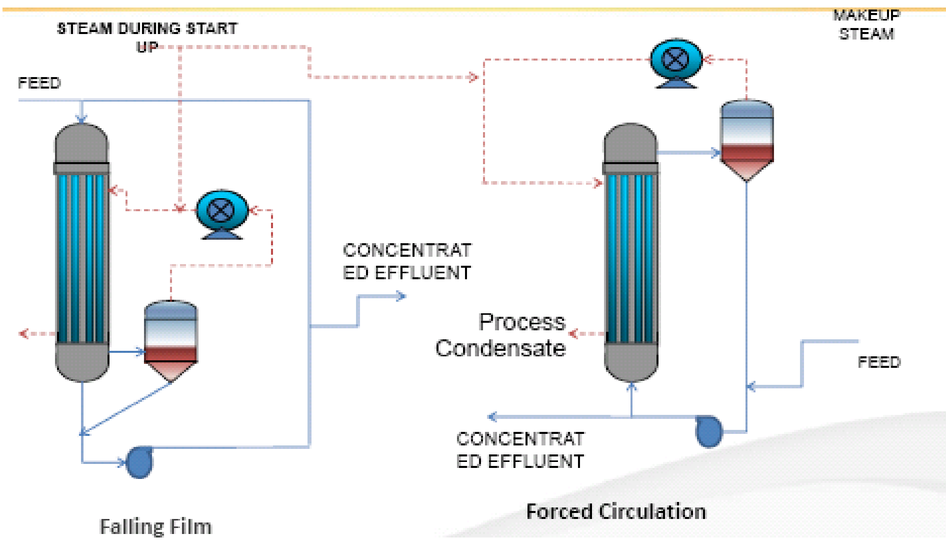

Fig. 8 Flow diagram (modified) showing "Evaporation with Mechanical Vapor Recompression (MVR)"

Table 3 Technology proposed against normal or conventional methods in pretreatment

Normal or conventional method	Technology proposed
Single stage clarifier + Commodity chemicals	Two stage clarifier + Speciality chemicals
Reliability is moderate	Dual train design gives 100% availability& reliability
Fine-tuning the consumption of chemical usage is tough as all chemicals are dosed at one location	Chemical usage shall be optimized by using speciality chemicals
Cannot take high variation in influents	Can take high variation in influents
Inconsistent water quality thereby increases the fouling of filters/ UF/RO downstream	Consistent water quality at all times reducing fouling of UF/RO downstream
Moderate residual heavy metals	Lowest residual heavy metals
Higher downtime of downstream units and lower overall recovery	Lower downtime and higher overall recovery

Table 4 Technology proposed against normal or conventional methods in UF/RO filtration

Normal or conventional method	Technology proposed
Inside Out PES (Basri *et al*. 2011) Pressurized UF Membrane Filtration	Outside in PVDF (Chang *et al*. 2014) submerged UF membrane filtration
Difficult to remove solids from confined pressure vessels because of tightly packed fibers.	Open tank configuration, loosely packed fibers for easier solid removal
Uses high pressure as membranes become fouled; high energy consumption	Low pressure, vacuum-driven operation
High cleaning frequency	Less frequent cleaning
Complex cleaning techniques to keep fibers clean inside	Cleaning technique is easier as the fibers are exteriorly located
Single train design	N-1 Configuration
Slippage in clarifier will lead to choking in membrane which results in frequent chemical flushing of membrane and thus requires high chemical consumption	Softener, Dual media filters & Hardness Removal Unit will address the slippage of heavy metals (Hunsom *et al*. 2005, Ahmed Basha *et al*. 2011) thereby limiting choking of membrane
RO membrane filtration	
Due to conventional composite polyamide membrane, fouling happens often	Low fouling composite membranes
Very high flux design operating at high pH	Low flux and high recovery, operates at low pH
Will require harsher cleaning due to heavy metal scaling at high pH	Less cleaning frequency
Flow tolerance +/– 10%	Design can accommodate 50-125% of feed flow

4. Discussion on recycling technique for treated effluents in copper industry

Although undergoing three levels of treatments Viz. primary, secondary and tertiary treatments (Üstün *et al*. 2011), the treated effluent escapes with some quantity of contaminants (Very high TDS 12000 mg/l (Average)).

Hence it is necessary to treat the High TDS effluents from ETP through recycling techniques comprising of pre-treatment, Reverse Osmosis (Pérez-González *et al*. 2012) (RO) plant and Zero Liquid Discharge (ZLD) plant (News 2011, 2012).

The pretreatment plant uses a clarifier which removes floating/solid particulates or suspended solids from liquid. At the bottom of the tank, concentrated impurities and heavy metals (Hunsom *et al*. 2005, Ahmed Basha *et al*. 2011) are settled and removed as sludge (Al Yaqout 2003).

The clarified water is stored and sent to membrane filtration/ion exchange to get high quality process water in copper industries. In pre-treatment plant of copper industry, the following technology is proposed against conventional method as given in Table 3.

Reverse osmosis (Pérez-González *et al*. 2012) (RO) filtration is a process where high pressure water is passed through a semi-permeable membrane leaving behind dissolved inorganic salts and silica called rejects which contains high TDS and the clear water from RO filtration is termed as permeate. The permeate water is recycled and reused either as process water or cooling tower makeup water in copper industry. The rejects are treated in ZLD plant (News 2011, 2012) to get clear distillate as well as free flowing solids. In UF/RO filtration, the technology proposed against normal or conventional methods in copper industry are given in Table 4.

Zero Liquid Discharge (ZLD) (News 2011, 2012): In the proposed ZLD (News 2011, 2012)

Table 5 Technology proposed against normal or conventional methods in ZLD

Zero liquid discharge ZLD (News 2011, 2012)	
Normal or conventional method	Technology proposed for new RO
Multi (3 or 4) Stage design; low flexibility, higher maintenance and downtimes	Single stage design; High Flexibility, Lower maintenance and downtimes
Thermal vapor compression	Reliable mechanical Vapor compressor
Frequent cleaning (Twice/thrice in week)	Less frequent cleaning (Once in 6 months)
Variable moisture content	Consistent Moisture content < 15%
Less variation of feed flow allowed	Design can accommodate 25-110% of feed flow
High cost of operation and downtime	Lower cost than conventional
Total Hardness (TH) (rich in $CaSO_4$) reduction in clarifier can at best be achieved up to 90%. The residual TH in feed will further concentrate in RO reject which when fed to evaporator results in precipitation of scale forming salts in the Multiple Effect Evaporator (MEE)	Maintains a very high velocity in the forced circulation heat exchanger thereby avoiding any chances of laminar flow zones within the system:; This prevents formation of scale sites and greatly reduces the scaling potential
Life cycle cost (LCC) is higher on a 15 year period, considering a power driven ZLD (News 2011, 2012) system	Power driven system will be almost 15-20% lower in Life cycle cost (LCC) over a 15 year period

plant, the Evaporator unit is integrated with MVR technology. The Forced Circulation Evaporation unit with mechanical vapor recompression (MVR) is proposed against Forced Circulation Evaporation unit with thermal vapor recompression (TVR) to provide the energy required to evaporate the water from the RO reject stream. The forced circulation crystallizer system is designed to handle the bulk precipitation of salts from the brine as evaporation occurs. The system concentrates the waste stream to salt crystal.

The brine slurry is further dewatered in a centrifuge unit to deliver a dewatered salt cake with about 10%-25% moisture content. This salt cake can be disposed to landfill (Al Yaqout 2003, Zupančič *et al*. 2009, Eldredge 1986, VanGulck and Rowe 2004) while the filtrate from the centrifuge is recycled back to the Forced Circulation evaporator system for further concentration. The System is an automatic steady state operation and thus requires little operator attention. The materials of construction have been selected to resist corrosion and ensure a long plant life. The pumps and compressor typically operate years without significant problems provided periodic maintenance is done on rotating equipment.

5. Conclusions

The following conclusions were derived based on the proposed modifications on the conventional techniques followed in the copper industry.

- Two staged clarifier achieves better settling of heavy metals and suspended solids thereby increasing overall recovery in the pre-treatment plant.
- Maintenance of Ultra Filtration (UF) system is much easier than the conventional system by using open tank configuration where fibers are loosely packed.
- Cleaning frequency reduces considerably on using low fouling RO membranes and thus reducing the cost effectively.

MVR technology yields the greatest energy efficiency for an evaporator, and requires low cooling water. Evaporation plants with mechanical vapour recompressors normally require very low live steam and shifts the necessary energy to electric energy. Cleaning frequency reduces considerably on using MVR technology and thus reduces cost effectively. Power driven system will be almost 15-20% lower in Life cycle cost (LCC) over a 15 year period.

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