

# Zld Evaporation Crystallization Plant In The Hydrometallurgical Industry

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Environmental considerations along with economical benefits of the water re-use have triggered the interest of the industry to develop a new zero-liquid-discharge (ZLD) technology for the treatment of liquid effluents.

A hybrid ZLD process was developed for an effluent from a Molybdenum production facility containing among others ammonium sulphate, sodium chloride, as well as magnesium and potassium sulphates. The process is foreseen for a waste water capacity of up to 110m<sup>3</sup>/h. The process consists of a pre-treatment section with brine purification, followed by a reverse osmosis pre-concentration and further concentration in a falling film mechanical vapour recompression evaporator. A crystallizer and a solid separation complete this process, which produces pure water for the re-use in the production facility under ZLD conditions.

While traditional technologies are rather sensitive to incrustations, the present process is specifically designed to remove hardeners and fouling components in front of the concentrations units, so allowing the use of reverse osmosis (RO) in pre-concentration, with a significant energy saving and improving of the process economics.

In order to proof the new process, laboratory and pilot tests were carried out, initially in the premises of the plant constructor and later on factory's site at a larger scale. Major focus was on the full precipitation of the Calcium being the essential pre-condition for the economic use of the subsequently following concentration steps (membrane, evaporation, and crystallization), in the way that even the falling film evaporator could be operated un-seeded, thereby simplifying the overall process design.

The process was tested successfully and showed excellent results. The critical compounds, i. e. fouling and incrustation forming components, like e.g. colloidal SiO<sub>2</sub>, Mn and Fe, could be reduced below any critical concentrations. The start-up of the industrial plant took place in the last quarter of 2006.

## 1. Introduction

Molybdenum production facilities are typically complex water households with high water consumptions. In the actual case the waste water capacities are ranging between 80 m<sup>3</sup>/h – 100 m<sup>3</sup>/h. Moreover, the facilities under question are located in an arid environment, i.e. the availability of water is limited and the discharge of used water is regulated by environmental laws, not allowing any further liquid purge from the factory to the environment.

## 1.2 Composition of the waste water

The average composition of the respective waste water can be taken from Tab. 1 below:

Tab. 1: Capacity and composition of the waste water

Compound		Remarks
Flow	80 m <sup>3</sup> /h – 110 m <sup>3</sup> /h	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1,09 wt-%	
CaSO <sub>4</sub>	0,28 wt-%	Saturated
Others	0,13 wt-%	(Mg, K, Na, Cl, etc.)
H <sub>2</sub> O	98,5 wt-%	

Ammonium sulphate and most of the other compounds are highly soluble substances and must be concentrated strongly before solids can be formed by crystallization. Calcium Sulphate instead, with its small solubility, even inverse with temperature, complicates any pre-concentration process by formation of incrustations at an early pre-concentration stage. RO membranes and evaporators, which can be used for this purpose, require intense pre-cautions or, respectively, appropriate pre-treatment steps.

## 1.3 Targets for the ZLD process concept

The internal re-use of the recovered water can be a self-understanding process target in a ZLD concept. This is even more valid in arid environments and was one of the driving forces for this process development. In this special application the recycled water could still hold up to 0.2 wt.-% of TDS without affecting the local production line. The separated solids must be of disposable quality.

Another main target was a minimization of the plant energy consumption. Available on site were steam and electrical power.

## 2. Developing the process

With reference to these targets three process alternatives were drafted and their specific costs compared. These process alternatives were:

- i) Single-effect MVR evaporation with a final crystallization stage
- ii) Multiple-effect evaporation crystallization plant
- iii) Hybrid process with brine purification and pre-concentration by RO and a subsequent MVR driven falling film evaporator. The final concentration by TVR evaporation to solids is performed in a forced circulation crystallizer followed by a belt filtration. Fig. 1 shows the respective block flow diagram.

### 2.1 Energy consumptions of the process alternates

The specific operation costs of each process alternative were estimated as follows:

- i) An energy consumption of the MVR in the range of 1,900 kWh/h; the steam consumption of the final crystallization plant amounted to 3,500 kWh/h.
- ii) In order to avoid rapid CaSO<sub>4</sub> incrustations in a multiple-effect evaporation crystallization the system must be fed parallel. Such a system has a remarkable consumption of heating steam in the magnitude of 12 GWh/h.

iii) In opposite to that the hybrid process offers a much lower energy consumption. For the first 56 m<sup>3</sup>/h of water recovered by the reverse osmosis only 300 kWh/h of electrical energy are needed. For the next 23 m<sup>3</sup>/h recovered in the MVR evaporation step the consumption reaches 560 kWh/h of electrical power, whereas the last process step, driven by TVR, consumes only 1.9 GWh/h of steam.

Due to these advantageous figures the hybrid process was selected.

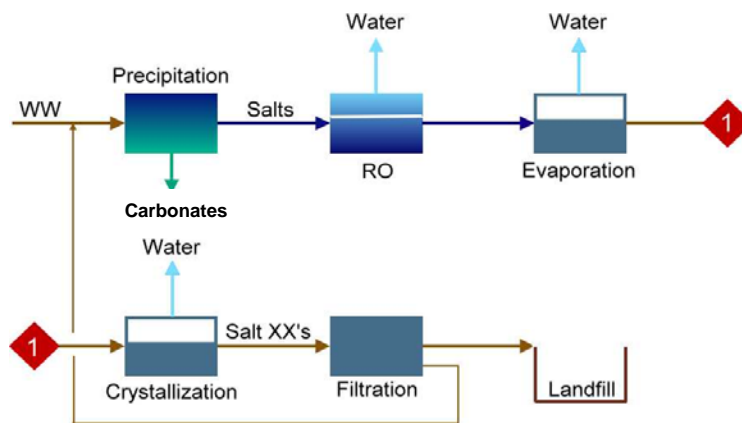


Figure. 1 Block Flow Diagram of Alternative iii)

### 3. The Hybrid Process

#### 3.1 The brine purification

A brine purification by addition of Sodium carbonate was tested to reduce the concentration of the hardener Calcium. This was done to avoid scale formation by CaSO<sub>4</sub> hydrates in the Reverse Osmosis and in the subsequently following falling film evaporation step. The presence of Ammonium sulphate avoided the precipitation of Magnesium as Magnesium hydroxide completely (and will also during the further concentration of the solution), whereas the Calcium could be reduced to a concentration lower than 20 ppm.

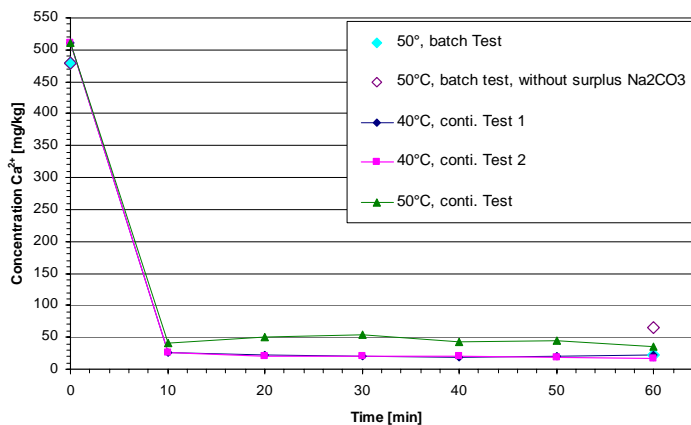


Figure 2: Brine purification: Reduction of Ca<sup>2+</sup> in the feed solution

Tab. 2: Composition of the purified brine

Compound	Feed	after purification
Calcium	400 – 500 mg/kg	< 20 mg/kg
Magnesium	max. 300mg/kg	max. 300 mg/kg
Iron	max. 10 mg/kg	< 5 mg/kg
Manganese	max. 20 mg/kg	< 2 mg/kg
Silicon	max. 10 mg/kg	< 5 mg/kg

A second focus was placed on the precipitation of various scaling compounds, e.g. Mn, Fe, Si, as well as Sr and Ba, which are known as severe scalants of membrane surfaces. The Tab. 2 above shows the concentrations of these scalants before and after the brine purification.

### 3.2 The Reverse Osmosis

The Brine Purification and the Reverse Osmosis steps (RO was tested using 1:1 module sizes) were tested in a pilot plant operation before the set up of the industrial plant. Concentration factors of higher than  $CF = 3.5$  were tested successfully. The worst rejection among all the dissolved species was 99.7%. The industrial RO plant meanwhile shows the identical efficiency in pre-concentration and rejection. The TDS-concentration obtained in the Permeate is 0.02 wt-% up to 0.2 wt-%, so reaching the expected performances as water recovery.

### 3.3 Evaporation and crystallization

In accordance to the process design the RO concentrate was foreseen to be fed to the falling film evaporator, where the solution shall be concentrated to 23 wt.-% TDS, i. e. short before reaching the saturation of  $\text{CaSO}_4$  again. Due to the low boiling point elevation, measured in laboratory trials, this evaporator was designed to be operated by means of an energy saving double-stage mechanical vapour recompression system (blower type) operating at atmospheric pressure. All these assumptions, based on laboratory data, had been perfectly met by the large-scale unit now in operation.

The concentrate from the FF evaporator is sent to the final FC-type crystallizer which is crystallizing the salt mixture under vacuum conditions. In order to save energy, this system is heated by a thermocompression system (TVR).

The final salt is a mixture of mainly Ammonium Sulphate with Sodium sulphate. Some other compounds and double salts appear from time to time depending on the ratio of the various compounds in the feed solution. For the average salt composition see Tab. 3 below.

Despite the continuously shifting ratio of these salts the crystallizer reaches operation cycles of one week, before a washout, which can be organized within one shift. Improvements are possible by consequent polishing of the crystallizer surfaces and expected with increasing recirculation rates.

$(\text{NH}_4)_2\text{SO}_4$	68 – 70 wt-%
$\text{Na}_2\text{SO}_4$	15 – 20 wt-%
$\text{K}_2\text{SO}_4$	1 – 2 wt-%
Others	1,5 – 3,5 wt-%

The separation of the suspension formed is performed by means of a belt filter. This separation type was selected to produce dry filter cakes but also to control the liquid purge rate in form of adherent mother liquor. This way operated the crystallizer does only reach those mother liquor compositions which are still predictable, and the crystallizer remains continuously under controllable operation conditions.

The large-scale unit meanwhile could prove also the filtration system properly. The moisture of the filter cake could be controlled easily by filtration rate and belt speed. Moreover, further solidification takes place, when the adherent mother liquor is cooled and hydrates are formed before disposal.

The selected materials of construction are stainless steels of different alloyed qualities, dependent on the concentration factor, for all solution-sided exposures. Plastic materials had been used as far as possible. All materials of construction were found to be completely resistant.

### 3.4 The large-scale plant

The working principle of the installed plant is shown in Fig.4.

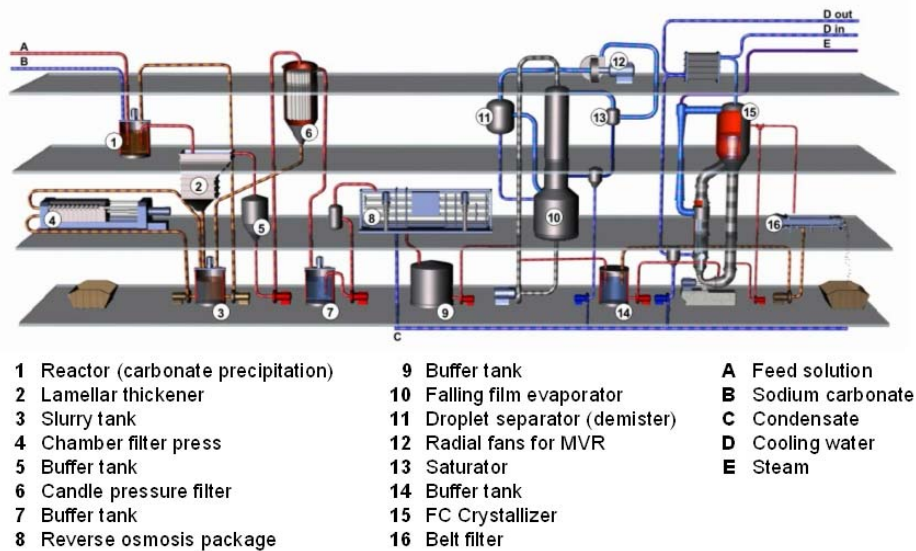


Fig. 4: The final plant

The Soda ash precipitation is performed in the reactor (1). By means of a lamellar thickener the precipitated solids are separated and the nearly solid-free and purified solution overflows to the buffer tank (5). The underflow of the lamellar thickener is

pumped to the chamber filter press (4), which finally separates the solids from the suspension. The filtrate is sent back to the lamellar thickener. From the buffer tank (5) the clear liquor is sent to a candle pressure filter (6) for the final polishing filtration.

The subsequently following Reverse osmosis package (8) can now concentrate the solution to around 8 % TDS and recover a permeate for re-use (stream C). The concentrate is sent to the falling film evaporator, operated by two radial fans in series (12).

The still undersaturated solution from the falling film evaporator is sent to the mother liquor buffer tank (14) from where it is fed to the forced circulation crystallizer (15). The FC crystallizer is heated by the thermocompression (TVR) principle.

The final step is the separation of the solids on the belt filter (16) in a quality suitable for disposal in a landfill. The filtrate is sent back to the feed tank (14) to the FC-crystallizer.

Process condensate from the falling film evaporator, as well as from the crystallizer, is made available for water re-use, together with permeate from RO.

The photo of the plant in Fig. 5 was taken during the late erection phase and shows the falling film evaporator and the FC-type crystallizer from the right to the left.



Fig. 5: Industrial plant in the late erection phase