Water allocation between coal mines and chemical plants based on zero liquid discharge technology

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\textbf{abstract}

Water shortage is one of the main bottlenecks in the development of coal chemical industry in China, and one solution is to allocate water resources between colmunes and coal chemical plants in a systematic perspective. In this paper, the zero liquid discharge technology is proposed and tested in field on a coalmine in Mengshan Area, northwest of China, and the water recovered is allocated to a local coal chemical plant. After in operation for more than 4 y, this project has solved the problem of mine water drainage on one hand, and on the other hand, provided chemical production water, residential water and ecological water for the surrounding areas, which greatly alleviated the impact of water intake on the ecological environment of the Yellow River. As this project continues in operation, the socio-economic benefits of relevant surroundings will gradually become apparent.

\textbf{Keywords:} Mine water; Mining/chemical integration; Desalinization; Zero liquid discharge

\section{1. Introduction}

As one of the major energy resources, coal accounts for 62\% of China's primary energy consumption [1], and achieving sustainable development has become first priority for coal resource utilization [2,3]. In recent years, new chemical plants are built around the coal mining area, and the liquefied gas/oil or high-added-value intermediates are produced and transported globally, whereas pollutants, greenhouse gases or wastewater are under centralized processing before disposing [4,5]. Geographically, the region with abundant coal resources is in the north-western part of China, where the natural conditions are fragile with limited rainfalls. Therefore, conflicts between industrial water demand and the local water supply capacity has become increasingly prominent [6-8], and water resources have become a major constraint for sustainable development of coal chemical industry in this region [9,10].

When taking coal chemical industry and coal mining together, the problem of water shortage in coal chemical plants may find new ways out [11]. During the coal mining process, part of the surface water, groundwater and coal seam seeps into the roadway through the cracks to form mine water, and fail to find outbound channels for drainage would seriously affect the normal operation of the mine [12]. In view of the depletion of surface water and the increasing demand for industrial water on one hand, and on the other hand, the huge amount of groundwater discharged from colmunes becomes a good resource for chemical production and ecological supplement. In this paper, coal mining and coal chemical processes are collaborated to form water network between both industries, so as to alleviate the
pressure on industrial water scarcity, and to eliminate the
danger of water inrush during the mining process.

To build a “water bridge” between both industries, com-
prehensive treatment and utilization methods are obligatory
because mine water contains impurities such as suspended
solids (SS), total dissolved solids (TDS), silicates, chemical
oxygen demand (COD) and salts, and cannot be directly sup-
plied to the chemical plants [13]. In addition, after reverse
osmosis (RO) and nanofiltration (NF), the concentrate con-
tent is complex and with high salinity, which has become
the main technical constraint for the utilization of mine
water [14,15]. Failure to dispose these concentrate streams
properly would cause disastrous environmental impacts,
such as soil compaction [16] and eutrophication [17,18].

In face of water scarcity and ever-stringent regulations
[19], discussion on wastewater-free production has gained
considerable momentum in coal-to-chemicals industry in
China, and zero liquid discharge (ZLD) becomes a serious
possibility, to realize product recovery and the energy-
saving treatment of concentration.

The last decade has witnessed a tremendous develop-
ment of ZLD technology. To decrease the energy demand,
sets of pre-concentration membranes are applied to reduce
subsequent thermal processing volume, which includes
RO, electrolysis (ED) or electrolysis reversal (EDR),
forward osmosis (FO) and membrane distillation (MD), etc.
[22,23]. In addition, before all membrane-based processes,
pre-treatments to reduce organic components or soften
the effluent are mandatory to alleviate the impact of mem-
brane fouling [24]. These pre-treatment processes include
a wide range of methods/technologies, that is, precipita-
tion, coagulation, biodegradation [25,26], ion exchange
[27], adsorption and advanced oxidation. Usually, evapo-
ration and cooling are frequently adopted for salts recov-
ery from the brine concentrate. Since thermal processing
is energy intensive, studies also focus on multi-stage flash
(MSF) [28], multi-effect distillation (MED), heat pumps [29]
or mechanical vapor recompression (MVR) [30] to recover
energy of the secondary steam.

Obviously, mine water reuse involves an innovative and
synergistic establishment to achieve ZLD, which not only
focuses on volume minimization, but also takes account
the recovery of recyclable materials. Recovery of a mixture
containing Na\textsuperscript{+}–Cl\textsuperscript{−}–SO\textsubscript{4}\textsuperscript{2−} is challenging because the mixed
salts generated by conventional ZLD necessitates further
solid waste disposal procedures, which may cause nega-
tive environmental impacts [31]. Therefore, obtaining high
purity salts separately is becoming increasingly popular.
Different from slats recovery from brackish water or seawa-
ter, organic substances in mine water should be eliminated
before crystallization [32]. For this reason, NF is frequently
applied [33–35].

The process of mine water innocent disposal and utili-
ization requires comprehensive use of the above-mentioned
methods. ZLD is an ambitious wastewater management
strategy that eliminates any liquid waste leaving the facility,
with the majority of water being recovered for reuse, which
obviates the risk of pollution associated with wastewater
discharge and maximizes water usage efficiency, thereby
striking a balance between exploitation of freshwater
resources and preservation of aquatic environments. In this
paper, a ZLD establishment is proposed and tested in field
on a coalmine in the Mengshan Area, northwest of China;
production water recovered is allocated to a local coal chem-
ical plant. After in operation for more than 4 y, this project
has solved the problem of mine water drainage, plus, pro-
vided industrial, residential and ecological water for the sur-
rounding area, which greatly alleviated the impact of water
intake on the ecological environment of the Yellow River.

2. Materials and methods

Fig. 1 is an overview of the water allocation strategy
between coalmines and chemical processes based on ZLD
technology. The aim of this research is to develop a holis-
tic solution for brine concentrates arising from mine water
reuse while taking into account the various technical poss-
sibilities, to realize product recovery and the energy-
saving treatment of concentration.

2.1. Sampling

Mine water from coalmines is pumped to an artificial
lake for adjusting and blending. During operation days,
random samples are taken twice throughout the day.
After sampling, indexes were analyzed immediately, and
composition analysis of a typical sample is provided in
Table 1. The treated water is supplied to the coal chemi-
cal plant as a substitution to the Yellow River water, and
comparison against the sampling water reveals that
contaminants of concern are mainly SS, TDS, silicates,
COD and sulfates, and the following ZLD technology is
developed based on elimination of these contaminants.

2.2. Demonstration plant

The demonstration plant developed by China Coal
Group was piloted at a few industrial production sites.
For illustration purpose, a mine water treatment project is
detailed in this paper, which is tested in field on a coalmine
at Mengshan Area, northwest of China, and the water recov-
ered is allocated to a local coal chemical plant. Originally,
the water resource comes from Yellow River, which needs
to transport and purified before utilization. Since the oper-
ation of the mine water ZLD project, about 3,000.0 m\textsuperscript{3}/h
industrial water is provided by the treatment site.

![Fig. 1. Scheme of mine plant wastewater treatment.](image-url)
Also focuses on water allocation between coalmines and chemical plants.

3. Mine water ZLD technology

This section details mine water ZLD technology that bridges the mining and chemical production industry, where RO membrane is used to produce industrial water, seawater desalination RO and MVR are adopted for brine volume minimizing purpose, and NF and Evap. & Cryst. are implemented for separative recovery of high purity NaCl and Na₂SO₄ salts.

3.1. RO for water production

RO is a membrane separation technology that relies on pressure drop inside and outside of the membrane to produce pure water, and it is widely-used for water treatment. As is shown in Fig. 3, after being piped to the regulate tank, the mine water passes through sedimentation tank and V-shaped filter to remove SS to less than 10 and 1 mg/L, consecutively. Sterilant and lime are added to prohibit the growth of algae, to prevent the coagulating of filter solids, and to reduce hardness. Then, it passes through ultrafiltration-reverse osmosis (UF-RO) dual membrane to produce pure water.

By mixing with the coagulant (polyacrylamide, PAM), sediments from the sedimentation tank and V-shaped filter are dehydrated to a moisture content <80% by through screw pump. Dried sludge (mainly SS and COD by precipitation) combined with the chemical waste residues, are send to landfill for unified disposal.

Because the water from V-shaped filter still contains solid particles (SS < 3 mg/L), it needs to be heated and then, enters the self-filter to further remove SS, and to prevent damage of UF membrane. UF can further remove 99% colloid, E. coli; bacteria and pathogen in the water, and ensure RO inlet quality, that is, SDI ≤ 3, turbidity ≤0.1 NTU. Note that secondary steam from Evap. & Cryst. can be used to preheat the water to about 20°C in winter, before it enters the UF-RO devices. The RO membrane retains partials larger than 0.0001 μm, meaning that all dissolved salts and organics with molecular weight larger than 100 could be retained. Since the RO membrane needs no acid or alkali regeneration, it can work in continuous mode. After RO,
75 wt.% mine water is recovered as fresh water, and the desalination rate reaches 98%.

3.2. Volume minimization

After UF RO dual membrane, the permeate decreases to about 25% its original volume, which goes through seawater desalination membrane and MVR to obtain near saturation brine, for liquid volume minimization purpose.

Because the seawater desalination membrane has high specificity for inlet requirements, pretreatments are more complicated than those of the UF-RO dual membrane. As is shown in Fig. 4, the RO concentration accompanied with AlCl3 enters the clarification tank. Lime, soda, NaCLO and anionic flocculants are added for SS coagulation and flocculation. After the clarifier, 95% hardness is removed and the SS content in the effluent is ≤5 mg/L.

About 10 t/h mud cake is produced in the clarification tank, and the components are mainly precipitated products such as CaCO3, Mg(OH)2, and CaSO4 (in small amount), which can be treated as conventional chemical wastes for unified landfill disposal. Then, the effluent goes through multi-filtering to reduce SS ≤ 1 mg/L. Ca2+ and Mg2+ can be replaced by Na+ ion exchange membrane, and acetic exchange membrane is employed to soften the brine and to achieve 99% hardness removal. At last, after the decarburizer, the brine enters seawater desalination membrane.

Seawater desalination operating under high pH (10–12) could assist saponification of the fatty acids and prevent membrane fouling. High pH also promises silicates in a dissolved state (solubility >2,000 mg/L), which eliminates the possibility of membrane obstruction. By combining UF-RO and seawater desalination, a total 80% mine water is recovered, and the residual water is highly saline with a TDS content of about 57,000 mg/L, as well as high CODCr (about 500 mg/L) and silicates (about 300 mg/L) content.

When pH is adjusted to about 8.3, the soluble silicates are precipitated in the form of colloid (with the additives NaAlO2 and polymerized ferrous sulfate). Then, it passes through 10, 1, and 0.1 um precision folding-type filters in series to remove silicates to ≤100 mg/L, and SS can be further reduced to 1 mg/L through the security filter.

In order to reduce organics (introduced not only from mine water but also through water treatment, that is, coagulants, flocculants, anticipants, etc.) and ensure purity and whiteness of the salts, a three-stage O3 oxidation process, pre-oxidation, 1st-stage oxidation and 2nd-stage oxidation, is arranged, and operational details are provided as follows, which is based on experiments analysis given in section 4.2.

Totally 2 × 40.0 kg/h O3 is produced and aerated into the residual water: at the pre-oxidation stage, 30 kg/h is consumed to maintain 230 g dissolved O3 per ton water, and the feed ratio is designed as O3: COD = 1: 0.7, which promises COD content of the wastewater ≤320 mg/L; at 1st-stage, 30 kg/h is consumed to maintain 230 g dissolved ozone per ton water, and the feed ratio is set as O3: COD = 1: 0.7, which promises the COD content ≤159 mg/L; at 2nd-stage, O3 and wastewater are mixed again by the dissolved gas pump, and 6 kg/h O3 is consumed to maintain 45 g dissolved O3 in per ton water; ideally, the produced water contain no more than 100 mg/L COD and the designing feed radio is O3:COD = 1.5. Exhaust gas from the oxidation/release tank is defogged and then sucked into the exhaust gas destruction tower. After heating and catalytic processing, the residual O3 in the exhaust gas is removed, and the treated exhaust gas meets the standard discharge.

3.3. Salts recovery by NF and Evap. & Cryst.

The concentration treated by O3 oxidation is sent to MVR to obtain near saturation brine, and the MVR outlet content is shown in Table 2. Since Na2SO4: NaCl = 7: 1, when the brine enters double effect evaporator (DEE) for Evap. & Cryst., Na2SO4 emerges as salt first and partial crystallization can obtain high purity Na2SO4. Therefore, the slurry from the bottom is circulated in the first effect heating chamber and Na2SO4 is separated out, where MVR outlet is used to wash salts. Part of the supernatant is discharged to the second evaporation chamber, and circulated between both chambers.

After DEE, part of the liquid-solid mixture enters the cyclone, and the rest keeps the second crystallizer at equilibrium state. The mixture washed by saturated solution ensures salt purity. Dense slurry is extracted from the cyclone and sent for centrifugal separation and dehydration, where
Na$_2$SO$_4$ (moisture content ≤ 4%) is produced as by-product; while, the overflow is sent back to the second crystallizer. Total recovery of Na$_2$SO$_4$ as pure salt is impossible, and it is examined that the residual brine approaching Na$_2$SO$_4$: NaCl ≈ 1:1.5 promises maximum Na$_2$SO$_4$ recovery as well as guaranteed salt purity (≥99 wt.%). While, separation of Na$_2$SO$_4$ and NaCl from the residual brine is one of the main technical bottlenecks for the success of mine water ZLD. As is provided in Fig. 5, temperature variance (say, between 10°C and 25°C) leads Na$_2$SO$_4$ solubility to change significantly, which could be applied to separate Na$_2$SO$_4$ out. However, the energy cost is substantial, contaminants like silicates, COD or organic compounds also affect salt quality, and the worst aspect of this method is about 1.02 t/h useless mix salt being generated, which might cause risk of secondary pollution. Therefore, UF-NF is adopted for SO$_4^{2–}$ and Cl$–$ separation.

As is shown in Fig. 6, SS is removed by pretreatment, but the high salinity brine (TDS = 362,632 mg/L, COD = 2,304 mg/L) needs to be diluted 4 times of its original quantity before entering any membrane. Then, UF is implemented to remove about 80% silicates, ≥30% COD or organic compounds as well as contaminants like silicate, COD or organic compounds. Through UF, 0.47 m$^3$/h concentrated water goes to desiccation, and the rest 13.57 m$^3$/h enters a two-stage NF system. The 1st-stage can retain most SO$_4^{2–}$ while allow Cl$–$ passing through, but high TDS content in the solution causes massive SO$_4^{2–}$ penetrating through the membrane; hence, a 2nd-stage NF is set up, where the remaining SO$_4^{2–}$ is intercepted to allow most of the Cl$–$ to pass through. To increase water recovery and salt separation, 1.2 m$^3$/h of dialysis water is added, and the concentrated water from second-stage NF membrane returns before the 3rd-group. At last, over 80% NaCl is recovered by this two-stage NF, and the 1.2 t/h concentrated water (contain all SO$_4^{2–}$) from 1st-stage NF is returned for catalytic oxidation.

Similar to crystallization of Na$_2$SO$_4$, 13.57 t/h brine from NF enters a DDE device for Evap. & Cryst. To ensure salt purity, solution from NF is used to wash the solid. Then, dense slurry is extracted from the cyclone and sent for centrifugal separation and dehydration, where NaCl is produced as by-product; while, part of the overflow is sent back to the second crystallizer, and the rest is sent to desiccation according the quality of NaCl product.

### 4. Results and discussion

Treatment of RO concentration is the key for the mine water ZLD technology, and removal of the main influencing contaminants, that is, silicates, COD and TDS are focused in this section.

#### 4.1. Silicates removal by pH adjustment

Here, silicates are mainly 1–0.001 μm well-dispersed colloids formed by aggregate silica or SiO$_2$, which need to be removed before Evap. & Cryst.; otherwise, these impurities would adhere to the surface of the evaporator, deteriorating...
heat transfer or even blocking the tube. Typical silicates removal technology introduces Mg(OH)$_2$ or Al(OH)$_3$ precipitation into the solution, which adsorbs colloid and forms particles that could be removed by filtration.

MgO is frequently used as the source for the formation of Mg(OH)$_2$, but it needs to acidize (pH 8.05–9.0) first to obtain enough Mg$^{2+}$ for silicate removal, which consumes HCl on one hand, and on the other, to guarantee outlet Mg$^{2+}$ content low, Ca(OH)$_2$/NaOH is subsequently added (pH ≥ 11.3), which generates excessive Mg(OH)$_2$. Therefore, one should find an agent that is dissoluble to the solution first, and then, precipitation is formed by pH adjustment. Therefore, NaAlO$_2$ is provided as the source for Al(OH)$_3$ precipitation.

The brine after seawater desalination membrane contains about 165 mg/L silicates, and the sample pH is 8.61, experiments are set to evaluate silicates removal by NaAlO$_2$, where polymeric ferric sulfate (PFS) and PAM are used as additives. When PFS content is kept 80 mg/L, and PAM content is 1 mg/L, increasing NaAlO$_2$ concentration promises well silicates removal, as well as slight increase of pH value. However, when NaAlO$_2$ content is beyond 600 mg/L, adding NaAlO$_2$ input slows silicates removal efficiency significantly (Fig. 7). Therefore, silicates removal conditions are lists as follows: NaAlO$_2$ content is 600 mg/L, PFS is 80 mg/L, PAM is 1 mg/L and pH is kept 8.3–8.75, the effluent silicates can decrease to ≤30 mg/L.

4.2. COD removal by O$_3$ catalysts oxidation

To ensure salts purity and whiteness, the high COD (COD$_c$ = 500 mg/L) content also need to be removed previous to Evap. & Cryst. Hence, O$_3$/catalysts oxidation is inserted, which could intensify generation of [•OH] through –O$_2$ as well as reducing the interference of Cl$^–$. A total 3-stage oxidation process is arranged, where pre-oxidation uses only O$_3$ to activate the brine, and 1st- and 2nd-stage oxidation add catalysts. Experiments are set where water samples are collected and Cl$^–$ is precipitated by AgNO$_3$ first, then, the COD content is tested based on GB11914-89 protocol.

Influence of pH on COD degradation is shown in Fig. 8, where the aeration time is sufficient. COD content does not change significantly at the pre-oxidation stage, but both 1st- and 2nd-stage exhibit a COD declining trend as pH increase, and obtains the best degradation at pH = 10, continuing to increase pH will not decrease COD further. The reason might be that when pH ≤ 9, dual effects of direct O$_3$ oxidation and [•OH] are functional, while pH > 9, indirect oxidation by [•OH] becomes dominant, and the optimal operation condition hence is set as pH = 10. Similarly, influence of O$_3$ concentration on COD degradation is shown in Fig. 9, and the trends indicate that the dissolved O$_3$ reaching 150 mg/L is optimal, which is used to calculate the total O$_3$ demand. Residence time of each stage also influences COD degra-
dation, when pH = 10.0, O$_3$ reaches 150 mg/L and the input brine COD content is between 350 and 390 mg/L, influence of residence time for pre-oxidation, 1st- and 2nd-stage oxidation.
catalysts oxidation are shown in Fig. 10, and the optimal design parameters are pre-oxidation, 1st- and 2nd-stage catalysts oxidation are 20, 30 and 30 min, respectively.

4.3. Brine volume minimization and Na$_2$SO$_4$ crystallization

To further downsize brine quantity, the best Evap. & Cryst. inlet state is being saturated. MVR is a self-heating evaporation system that increases temperature and pressure of the evaporated steam (secondary steam) by mechanical recompression, then, the compressed steam vaporizes the inlet brine through a falling-film evaporator, and near saturated brine is obtained after the brine volume decreased to 1/4.

As is shown in Fig. 11, at the start up stage, fresh steam is introduced to the heating chamber, and the brine is vaporized by a falling-film evaporator. Dried gas is separated from the secondary steam by a high-speed rotating separator (removing micro-droplets by centrifugation), and then, enters the centrifugal compressor to lift temperature. As supplement of the heated secondary steam increase, the amount of fresh steam is gradually reduced till zero, forming a self-heating system. To make sure the heat source being saturated steam, a small flow of condensed water (about 107°C) is re-circulated to the evaporator, for eliminating superheat purpose. After the secondary steam is condensed, it is forced to flow through a circulation pump, and sensitive heat is recovered by heat exchange with the inlet flow, while the concentrated liquid enters the next step for crystallization.

Computer-aided Aspen Plus (version 7.2) simulation can be implemented to assist MVR design. Note that when the brine approaches saturation, its boiling point would raise rapidly (Fig. 12), meaning that vaporizing the brine needs more mechanic work exerted to the secondary steam, and design heat transfer temperature deviation by 5°C–9°C is plausible in engineering. Since phase change occurs in a H$_2$O-Na$_2$SO$_4$-NaCl ternary system, ENRTL-RK model (electrolytes are calculated by the electrolyte NRTL model, and gas phase uses the Redlich–Kwong model) is employed to model the phase equilibrium.
equation of state, assuming that the solute follows Henry’s law) is adopted. Through simulation, a flow of 30°C, 2 × 68,060 kg/h brine recovers sensitive heat of the condensate water to achieve an inlet temperature 80°C, and enters MVR alone the falling-film evaporator (94,301 Pa), where 73.6 wt.% liquid is vaporized at 100.1°C. The remaining liquid is sent to DEE to produce salts. Through MVR, 2 × 1,238 kW electricity is consumed to obtain 98.74 t/h condensed water. Since no steam is discharged, MVR maximizes utilization of the secondary steam, and the coefficient of performance (COP) for MVR is calculated as follows,

\[
\text{COP} = \frac{\text{evaporative heat}}{\text{work}}
\]  

In this case, the COP reaches 25.8, that is, for 1 kWh electricity consumed, the MVR system generates 25.8 kWh heat for brine evaporation; it is an energy-saving heat pump technology.

Through Aspen simulation, process information is provided to the vendor (Howden) for compressor selection. 63,000 kg/h of 98°C, 94,301 Pa steam is boosted by the compressor to 35,108 Pa, with a multi-stage efficiency of 0.797. 63,000 kg/h of 98°C, 94,301 Pa steam is boosted by the compressor to 35,108 Pa, with a multi-stage efficiency of 0.797.

Prior to this mine water ZLD project, water source for water blending from desalination unit, which accounts for about 75% of all the mine water. RO membrane can retain substances larger than 0.0001 μm, and it is the finest membrane separation product. It can effectively retain all dissolved salts and organic matters with a molecular weight greater than 100. However, chemical production does not need such high purity water, SS < 600 mg/L and sulfates <250 mg/L satisfy chemical utilization. Therefore, the desalinated water and raw mine water need to be blended to achieve best economic outcome.

5. Allocation and dispatch of production water

The goal of this process is to build a “water bridge” between coal mining and coal chemical industry. Mine water is a good resource for chemical production, but SS, sulfates, silicates, DS and COD need to be eliminated first. Hence, ZLD of mine water is discussed above. The following is the detailed scheme of how to use the product water, and the allocation procedure is conducted based on analysis of Yellow River water (original water source of chemical plant), as well as standards like GB/T 50050 and SH3099, where GB/T 50050 is frequently applied by chemical plants, and SH3099 is executed in petrochemical industry.

5.1. Water blending from desalination unit

Most product water is generated by the RO unit, which accounts for about 75% of all the mine water. RO membrane can retain substances larger than 0.0001 μm, and it is the finest membrane separation product. It can effectively retain all dissolved salts and organic matters with a molecular weight greater than 100. However, chemical production does not need such high purity water, SS < 600 mg/L and sulfates <250 mg/L satisfy chemical utilization. Therefore, the desalinated water and raw mine water need to be blended to achieve best economic outcome.

Prior to this mine water ZLD project, water source for chemical production comes from the Yellow River. After the Yellow River water was pre-treated (coagulated, precipitated, and filtered), it was pumped to the chemical plant as replenishment for the chemical water workshop. The desalinated water can be blended with the front-end UF water, only that the mixed water needs to meet the water quality requirements shown in Table 3, so that the chemical production water source can be switched seamlessly from the Yellow River water to the blended water.

Combined with the original water treatment system in the chemical production area, according to the quality requirements of the circulating and desalinated water by the chemical plant, and taking account of the existed water treatment conditions, only 62,000 m³/d (or 2,583 m³/h) enters the...
ZLD process for desalination treatment, and the remaining 10,000 m³/d (or 416 m³/h) is supplied for blending, the following water supply methods can be achieved:

- 46,500 m³/d pure water (product water) after desalination (i.e., 1,937.0 m³/h, TDS < 56.7 mg/L) and 10,000 m³/d (i.e., 416.0 m³/h, TDS < 2,800 mg/L) UF product water are blended, and the total water volume is 56,500 m³/d (2,353.0 m³/h, TDS = 541.7 mg/L), which can replace the demand for Yellow River water, and be supplied to the purification workshop;
- 40,800 m³/d (1,700 m³/h, TDS < 56.7 mg/L) pure water after desalination can be supplied to desalination station as product water;
- The remaining pure water after desalination is 5700 m³/d (216.0 m³/h, TDS < 2,800 mg/L) and the ultra-filtered product water is 10,000 m³/d (653.0 m³/h, TDS < 1,804.3 mg/L). The blending is 15,700 m³/d (653.0 m³/h, TDS < 1,804.3 mg/L), which can be supplied to the water purification station. Since the amount of water stored in the purified water tank is much larger than the blended one, overall water quality will not deviate sensibly.

### 5.2. Water blending from secondary enrichment unit

The desalination section has a water production rate of 75% with desalination rate 98.0%, so the remaining water after RO is 15,500 m³/d (646 m³/h). Considering aging and pollution of the RO membrane, water production rate will reduce with time. Hence, the processing scale of secondary enrichment is enlarged to 18,000 m³/d (750 m³/h) at the designing stage. After passing through anti-pollution seawater desalination membrane, 12,432 m³/d (518.0 m³/h, TDS = 300 mg/L) pure water is produced. The following water supply methods can be achieved:

- The product water mixing with all RO and UF production water obtains blended water with TDS = 498.1 mg/L, then supplied to water purification station of the chemical plant as product;
- It is partially blended with the mixed RO and UF water to produce a TDS of about 1,138.86 mg/L, and is delivered to the water purification station front as an supplement of Yellow River water, which by mingling with the circulation water, can satisfy industrial standards.

### 5.3. Water Blending from evaporative crystallization unit

The water source of this section comes from secondary enrichment and post UF/NF residual. Amongst, the secondary enrichment residual is 130 m³/h, with a COD content of about 470 mg/L and TDS of 55,233 mg/L; the filtration residual is 1.56 m³/h, with COD content of about 3,148 mg/L and TDS of 131,325 mg/L. The evaporative crystallization process is complicated, and the following water supply strategy can be achieved:

- The condensate water from MVR is about 28.16 t/h, and the main impurities are TDS and COD, which could mix with NaCl crystallization residual and send back to the regulating tank or purification tank, in accordance with the TDS content.
- The condensate after Na$_2$SO$_4$ crystallization is about 3.51 t/h. Due to the high salinity, it cannot pass through the membrane directly, and it is diluted to 14.04 t/h, by

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### Table 3

Industrial water quality standard

<table>
<thead>
<tr>
<th>Testing items</th>
<th>Yellow River water After pre-treatment</th>
<th>GB/T 50050 Circulating cooling water (open)</th>
<th>SH3099 Water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.61</td>
<td>7.0~8.5</td>
<td>6.5~9.5</td>
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<tr>
<td>Suspended solids, mg/L</td>
<td>&lt;1.0</td>
<td>≤10</td>
<td>–</td>
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<tr>
<td>Turbidity, NTU</td>
<td>≤1</td>
<td>≤5</td>
<td>–</td>
</tr>
<tr>
<td>Dissolved solids, mg/L</td>
<td>≤100</td>
<td>≤1,000</td>
<td>–</td>
</tr>
<tr>
<td>Total hardness, mg/L</td>
<td>≤373.8</td>
<td>≤250</td>
<td>–</td>
</tr>
<tr>
<td>Total alkalinity, mg/L</td>
<td>≤226.8</td>
<td>≤200</td>
<td>–</td>
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<td>Petroleum, mg/L</td>
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<td>≤5</td>
<td>–</td>
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<tr>
<td>Ca$^{2+}$, mg/L</td>
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<td>–</td>
<td>≤175</td>
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<tr>
<td>Ammonia/nitrogen, mg/L</td>
<td>2.57</td>
<td>≤5</td>
<td>–</td>
</tr>
<tr>
<td>Fe, mg/L</td>
<td>≤0.2</td>
<td>≤0.5</td>
<td>≤0.3</td>
</tr>
<tr>
<td>Mn, mg/L</td>
<td>≤0.034</td>
<td>≤0.2</td>
<td>–</td>
</tr>
<tr>
<td>Cl$^-$, mg/L</td>
<td>132.3</td>
<td>≤250</td>
<td>–</td>
</tr>
<tr>
<td>SO$_4^{2-}$, mg/L</td>
<td>175.35</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>COD$_{cr}$, mg/L</td>
<td>16</td>
<td>≤30</td>
<td>–</td>
</tr>
<tr>
<td>BOD$_5$, mg/L</td>
<td>≤4</td>
<td>≤5</td>
<td>–</td>
</tr>
<tr>
<td>PO$_4^{3-}$, mg/L</td>
<td>0.53</td>
<td>≤1</td>
<td>–</td>
</tr>
<tr>
<td>Free chlorine, mg/L</td>
<td>–</td>
<td>0.1~0.2</td>
<td>–</td>
</tr>
<tr>
<td>Total bacteria</td>
<td>–</td>
<td>&lt;1,000 mL</td>
<td>–</td>
</tr>
</tbody>
</table>
adding production water from RO unit. The diluted solution is subjected to pretreatment and UF membrane to remove about 80% of total silicon, more than 30% of COD and big organic matters. Then, 0.47 m³/h of high-salinity concentrated water goes for desiccation.

• After UF, 13.57 m³/h product water enters NF unit, and 1.2 m³/h dialysis water is added to this unit for better Na₂SO₄/NaCl separation purpose. The 1st-stage NF produces about 1.2 m³/h (mainly containing Na₂SO₄) and is refluxed to the Na₂SO₄ crystallization unit.

• After NF, 13.57 t/h product water goes to the NaCl crystallization unit, and condensate goes to the regulation tank or purification station, by blending with the secondary enrichment condensate.

6. Conclusion

To realize mine water ZLD and resources reuse, this paper focuses on selecting and arranging existing, mature and industrially available units in a cost-effective and economic friendly manner, which requires the designer to have professional literacy in various separation technologies, engineers being experienced in water treatment engineering, and R&D personnel to integrate different devices through a systematic perspective, and apply them ingeniously.

By this work, severer objectives are achieved: (1) coal mining waterways are dredged to ensure safe operation of the mine, and the cleansed water is allocated to the chemical plant to alleviate coal chemical-water shortage, (2) ZLD technology is developed to avoid potential environment risk of secondary pollution; (3) Salt separation technology is developed to make this project economically reasonable. Note that the environmental and social effects of this project are prominent, but systematic design of the process in an economically acceptable manner, easy to operate and maintain are also the objectives.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References


