

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

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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 coalmines 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.

Keywords: Mine water; Mining/chemical integration; Desalinization; Zero liquid discharge

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 coalmines 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

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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, comprehensive 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 supplied to the chemical plants [13]. In addition, after reverse osmosis (RO) and nanofiltration (NF), the concentrate content 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 alternative [20,21]. However, applying a series of thermal processes to realize ZLD is not recommendatory, because the associated energy consumption and capital cost are substantial and failure to dispose the concentrated brine or solid waste properly might cause risk of secondary pollution.

The last decade has witnessed a tremendous development of ZLD technology. To decrease the energy demand, sets of pre-concentration membranes are applied to reduce subsequent thermal processing volume, which includes RO, electrodialysis (ED) or electrodialysis 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 membrane fouling [24]. These pre-treatment processes include a wide range of methods/technologies, that is, precipitation, coagulation, biodegradation [25,26], ion exchange [27], adsorption and advanced oxidation. Usually, evaporation and cooling are frequently adopted for salts recovery 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 $\text{Na}^+\text{-Cl}^-\text{-SO}_4^{2-}$ is challenging because the mixed salts generated by conventional ZLD necessitates further solid waste disposal procedures, which may cause negative environmental impacts [31]. Therefore, obtaining high purity salts separately is becoming increasingly popular. Different from slats recovery from brackish water or seawater, 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 utilization 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 chemical plant. After in operation for more than 4 y, this project has solved the problem of mine water drainage, plus, provided industrial, residential and ecological water for the surrounding 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 holistic solution for brine concentrates arising from mine water reuse while taking into account the various technical possibilities, 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 chemical 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 recovered 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 operation of the mine water ZLD project, about 3,000.0 m³/h industrial water is provided by the treatment site.

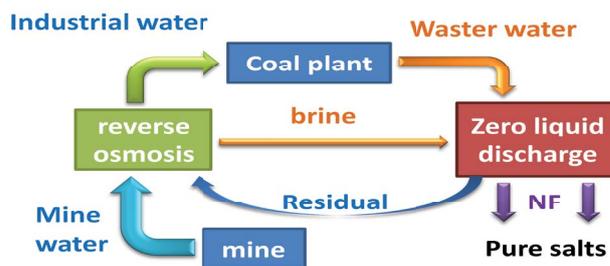


Fig. 1. Scheme of mine plant wastewater treatment.

Table 1
Mine water composition analysis

Testing items	Value
pH	6.5–9.5
Na ⁺ , mg/L	814.99
Ca ²⁺ , mg/L	86.94
Mg ²⁺ , mg/L	10.07
NH ₄ ⁺ , mg/L	1.32
Fe, mg/L	0.14
Al ³⁺ , mg/L	0.15
Sr ²⁺ , mg/L	4.27
SO ₄ ²⁻ , mg/L	1,550.16
HCO ₃ ⁻ , mg/L	264.56
Cl ⁻ , mg/L	152.45
Dissolved solids, mg/L	2,800
Hardness, mmol/L	5.17
Suspended solids, mg/L	30.0
Total solids, mg/L	2,817.43
SiO ₂ , mg/L	17.85
NO ₃ ⁻ , mg/L	2.34
COD _{Cr} , mg/L	30.00
TOC, mg/L	3.65
BOD ₅ , mg/L	3.23
Turbidity, NTU	4.46
Conductivity, μS/cm	3,987.54

Note that prior to our demonstration plants, many mine water treatment units in operation adopts RO separation, where even 80% water is recovered for industrial usage. However, dealing with the 20% high salinity (200,000 ppm) residual is a challenging task. For this purpose, ZLD technology is developed.

As is shown in Fig. 2, three consecutive steps are adopted to accomplish mine water ZLD and salt recovery. The RO permeate goes through high efficiency RO (adopting seawater desalination membrane) and MVR for concentrating purpose, subsequent technologies include catalytic oxidation, NF and Evap. & Cryst. Besides the investigation of the overall process combination, this paper

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% colloids, *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,

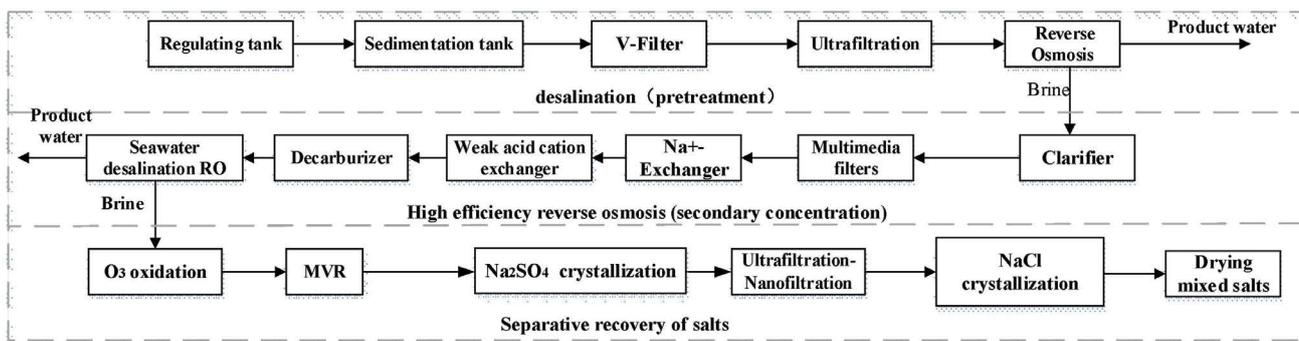


Fig. 2. Overview of the ZLD process.

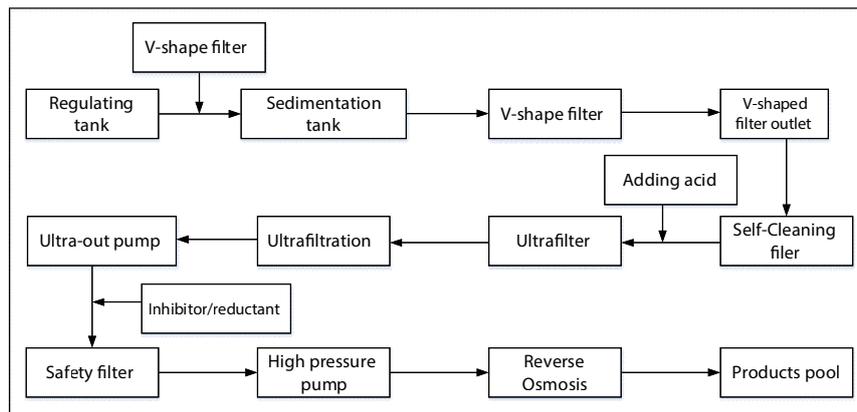


Fig. 3. Flowsheet for the UF-RO process.

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 AlCl_3 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 CaCO_3 , $\text{Mg}(\text{OH})_2$ and CaSO_4 (in small amount), which can be treated as conventional chemical wastes for unified landfill disposal. Then, the effluent goes through multi-filtering to reduce $\text{SS} \leq 1$ mg/L. Ca^{2+} and Mg^{2+} 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 COD_c (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 NaAlO_2 and polymerized ferrous sulfate). Then, it passes through 10, 1, and 0.1 μm 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, antipants, etc.) and ensure purity and whiteness of the salts, a three-stage O_3 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 O_3 is produced and aerated into the residual water: at the pre-oxidation stage, 30 kg/h is consumed to maintain 230 g dissolved O_3 per ton water, and the feed ratio is designed as O_3 : COD = 1: 0.8, 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 O_3 : COD = 1: 0.7, which promises the COD content ≤ 159 mg/L; at 2nd-stage, O_3 and wastewater are mixed again by the dissolved gas pump, and 6 kg/h O_3 is consumed to maintain 45 g dissolved O_3 in per ton water, ideally, the produced water contain no more than 100 mg/L COD and the designing feed ratio is O_3 :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 O_3 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 O_3 oxidation is sent to MVR to obtain near saturation brine, and the MVR outlet content is shown in Table 2. Since Na_2SO_4 : $\text{NaCl} \approx 7$: 1, when the brine enters double effect evaporator (DEE) for Evap. & Cryst., Na_2SO_4 emerges as salt first and partial crystallization can obtain high purity Na_2SO_4 . Therefore, the slurry from the bottom is circulated in the first effect heating chamber and Na_2SO_4 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

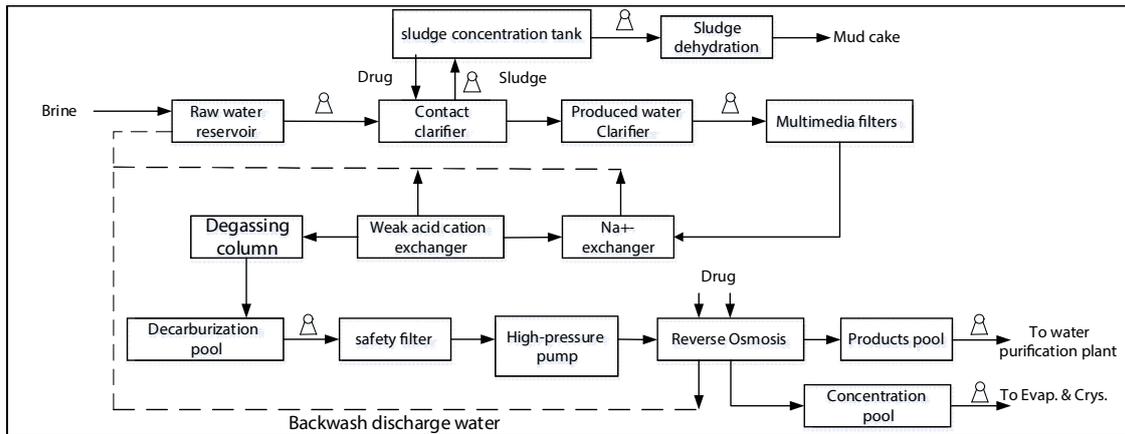


Fig. 4. Flowsheet for the seawater desalination process.

Table 2
MVR concentration outlet quality

Index	Value
COD _{Cr} , mg/L	≤600
Cl ⁻ , mg/L	16,697
SO ₄ ²⁻ , mg/L	131,003
NaCl, mg/L	27,515
Na ₂ SO ₄ , mg/L	193,775

Na₂SO₄ (moisture content ≤ 4%) is produced as by-product; while, the overflow is sent back to the second crystallizer.

Total recovery of Na₂SO₄ as pure salt is impossible, and it is examined that the residual brine approaching Na₂SO₄: NaCl ≈ 1:1.5 promises maximum Na₂SO₄ recovery as well as guaranteed salt purity (≥99 wt.%). While, separation of Na₂SO₄ 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 Na₂SO₄ solubility to change significantly, which could be applied to separate Na₂SO₄ 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 SO₄²⁻ 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 and most organic matters. Through UF, 0.47 m³/h concentrated water goes to desiccation, and the rest 13.57 m³/h enters a two-stage NF system. The 1st-stage can retain most SO₄²⁻ while allow Cl⁻ passing through, but high TDS content in the solution causes massive SO₄²⁻ penetrating through the membrane; hence, a 2nd-stage NF is set up, where the remaining SO₄²⁻ is intercepted to allow most of the Cl⁻ to pass through. To increase water recovery and salt separation, 1.2 m³/h of dialysis water is added, and the concentrated

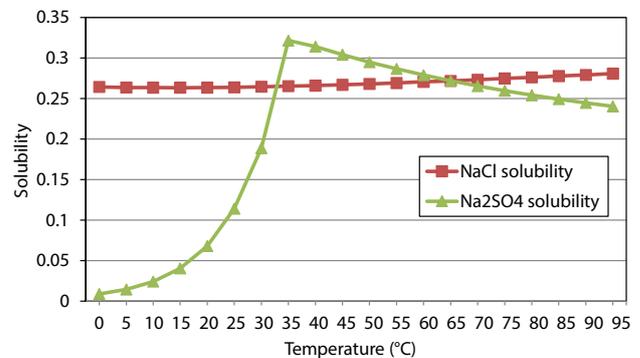


Fig. 5. Na₂SO₄ and NaCl solubility with varying temperature at 1 atm.

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 SO₄²⁻) from 1st-stage NF is returned for catalytic oxidation.

Similar to crystallization of Na₂SO₄, 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 to 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 SiO₂, which need to be removed before Evap. & Cryst.; otherwise, these impurities would adhere to the surface of the evaporator, deteriorating

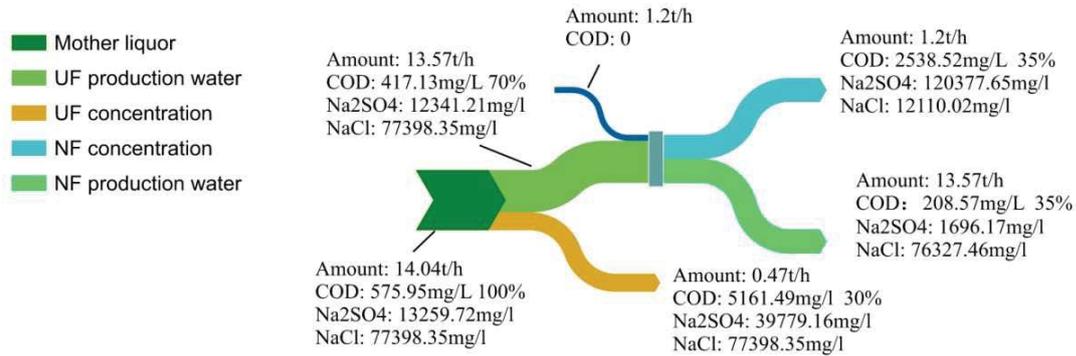


Fig. 6. Water balance diagram for $\text{Na}_2\text{SO}_4/\text{NaCl}$ membrane separation.

heat transfer or even blocking the tube. Typical silicates removal technology introduces $\text{Mg}(\text{OH})_2$ or $\text{Al}(\text{OH})_3$ 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 $\text{Mg}(\text{OH})_2$, 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, $\text{Ca}(\text{OH})_2/\text{NaOH}$ is subsequently added (pH ≥ 11.3), which generates excessive $\text{Mg}(\text{OH})_2$. Therefore, one should find an agent that is dissolvable to the solution first, and then, precipitation is formed by pH adjustment. Therefore, NaAlO_2 is provided as the source for $\text{Al}(\text{OH})_3$ 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.

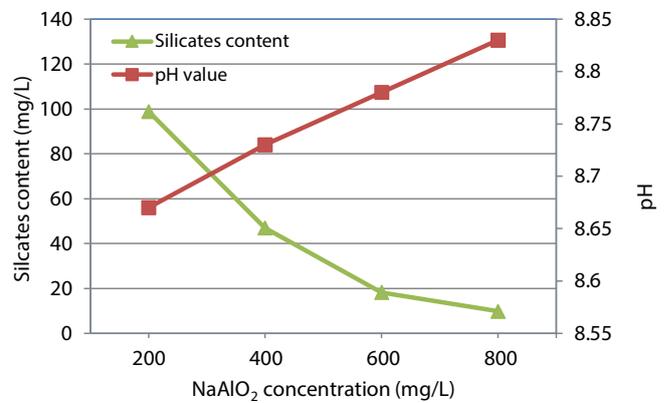


Fig. 7. Silicates concentration with varying NaAlO_2 inputs.

4.2. COD removal by O_3 catalysts oxidation

To ensure salts purity and whiteness, the high COD ($\text{COD}_{\text{Cr}} \approx 500$ mg/L) content also need to be removed previous to Evap. & Cryst. Hence, O_3 /catalysts oxidation is inserted, which could intensify generation of $[\cdot\text{OH}]$ through $-\text{O}_2$, 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

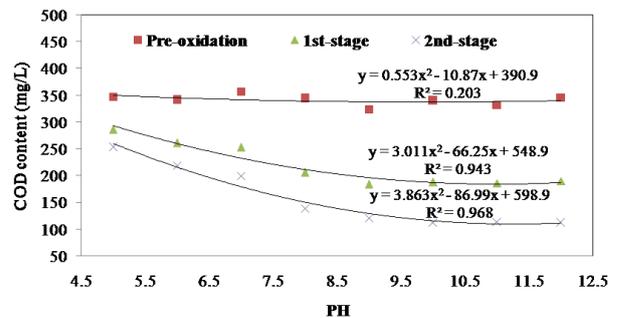


Fig. 8. Influence of pH on COD degradation for pre-, 1st- and 2nd-stage oxidation.

COD further. The reason might be that when $\text{pH} \leq 9$, dual effects of direct O_3 oxidation and $[\cdot\text{OH}]$ are functional, while $\text{pH} > 9$, indirect oxidation by $[\cdot\text{OH}]$ becomes dominant, and the optimal operation condition hence is set as $\text{pH} = 10$. 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 degradation, when $\text{pH} = 10.0$, 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

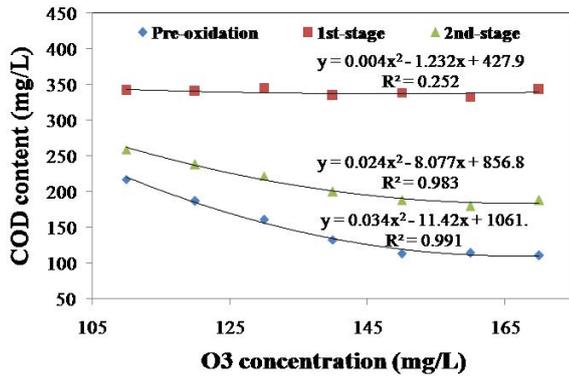


Fig. 9. Influence of O₃ on COD degradation for pre-, 1st- and 2nd-stage oxidation.

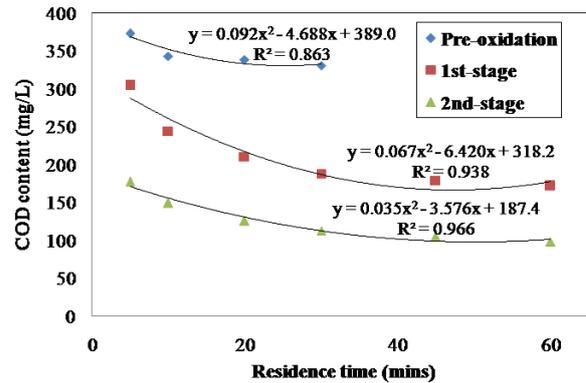


Fig. 10. Residence time on COD degradation for pre-, 1st- and 2nd-stage oxidation.

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 Na₂SO₄ 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 H₂O-Na₂SO₄-NaCl ternary system, ENRTL-RK model (electrolytes are calculated by the electrolyte NRTL model, and gas phase uses the Redlich-Kwong

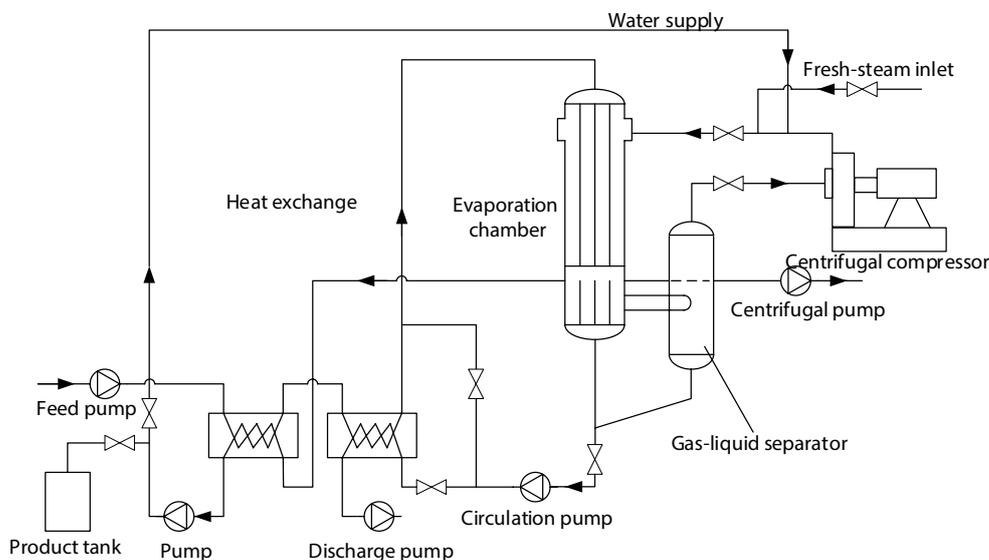


Fig. 11. Schematic of the MVR process.

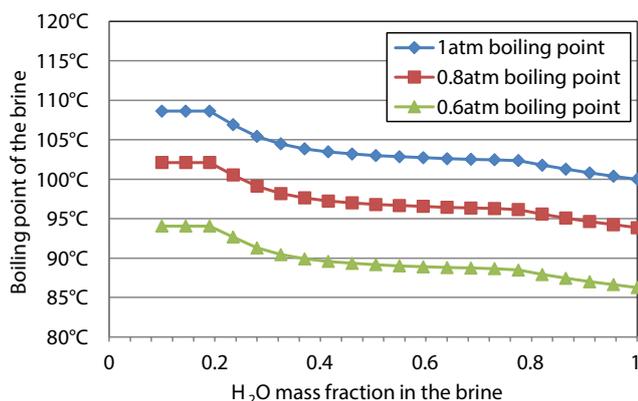


Fig. 12. Boiling points for the NaCl-Na₂SO₄ mixture.

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,

$$\text{COP} = \frac{\text{evaporative heat}}{\text{work}} \quad (1)$$

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 and a mechanical efficiency of 1.0 (1,242.9/1,244 ≈ 1.0), and temperature increase to 135.7°C. The overheat is eliminated by mixing 1,490 kg/h of saturated water at 107°C; the average heat transfer coefficient is 878.92 kcal/(hm²°C) and heat transfer temperature difference is 9.01°C. The evaporator heat exchange area is 4397 m², designing falling-film area as 5,000 m² (a margin of 13.7%) provides a heat exchange amount of 40,519.6 kW.

Since Na₂SO₄:NaCl = 7.1: 1, Na₂SO₄ is crystallized first. The high COD content (about 600 mg/L) affects salt's whiteness and purity, hence, after DEE, salt slurry from the bottom is back to the inlet for re-crystallization, and the MVR outlet is used to wash this slurry, whereas the supernatant from the top, which contains most COD, is sent to subsequent NF processing. In addition, by controlling the vacuum degree in the mixed salt crystallization tank, the crystallization temperature of the mixed salt can be well controlled, so as to control Na₂SO₄:NaCl = 1:5 in the supernatant, which helps to stabilize the subsequent NF system.

The draft tube bubbled crystallizer is adopted in this project, and experiments are set to study crystal formation

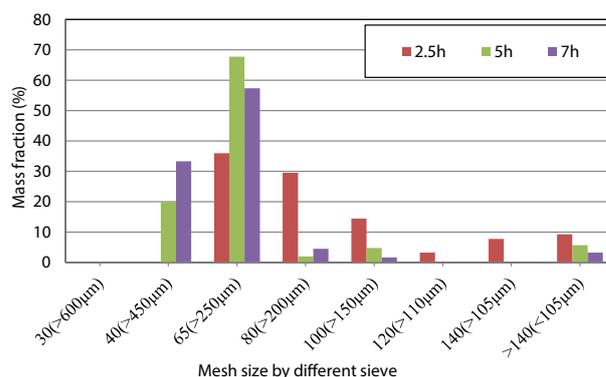


Fig. 13. Crystal size distributions by different residence time.

vs. the residence time. As is shown in Fig. 13, even at 2.5 h residence time, about 80% particles achieve over 100 mesh size, which is acceptable in industry.

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

Table 3
Industrial water quality standard

Testing items	Yellow River water After pre-treatment	GB/T 50050 Circulating cooling water (open)	SH3099 Water quality
pH	8.61	7.0~8.5	6.5~9.5
Suspended solids, mg/L	<1.0	≤10	–
Turbidity, NTU	≤1	≤5	–
Dissolved solids, mg/L	600.0	≤1,000	–
Total hardness, mg/L	373.80	≤250	–
Total alkalinity, mg/L	226.80	≤200	–
Petroleum, mg/L	<0.85	≤5	–
Ca ²⁺ , mg/L	77.60	–	≤175
Ammonia/nitrogen, mg/L	2.57	≤5	–
Fe, mg/L	<0.20	≤0.5	≤0.3
Mn, mg/L	<0.034	≤0.2	–
Cl ⁻ , mg/L	132.3	≤250	–
SO ₄ ²⁻ , mg/L	175.35	–	–
COD _{Cr} , mg/L	16	≤30	–
BOD ₅ , mg/L	<4	≤5	–
PO ₄ ³⁻ , mg/L	0.53	≤1	–
Free chlorine, mg/L	–	0.1~0.2	–
Total bacteria	–	<1,000 mL	–

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 (416.0 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 supplementary 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 Na₂SO₄ 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

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.

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