How to Improve FGD Economics with Chloride Removal Using Selective EDR

Key Takeaways:

- As regulations on FGD wastewater tighten, additional treatment is required. Often, this is chemically intense, and high cost. The best means to lower treatment costs is to reduce the volume of wastewater generated, usually by increasing internal recycle.
- Internal recycle of FGD wastewater is limited by high chloride concentrations that inhibit sulfur dioxide absorption and can cause corrosion issues as chlorides are cycled up – this can be solved by the solution below:
- Chlorides can be selectively removed from FGD wastewater by industrially available electrodialysis reversal (EDR) with monovalent selective membranes

(mEDR). mEDR selectively transports chlorides under an electric field through monovalent anion exchange membranes while blocking sulfates. This reduces the chloride load to enable internal FGD recycle while producing a non-scaling brine of sodium/calcium chloride at greater than 90% recovery (or 10% brine waste volume).

- 100% recycle of the low chloride treated water will not be possible due to cycling up of organics not removed by mEDR, however even partial recycle will reduce the cost of expensive FGD wastewater treatment infrastructure.
- Highly robust monovalent ion exchange membranes with >98% selectivity should be used, such as Saltworks' Ionflux, which prevent scaling by blocking almost all sulfates and can be cleaned with strong oxidants such as bleach.
- mEDR can be integrated into existing FGD wastewater treatment trains, and eliminates the need for costly soda ash softening while producing a brine concentration almost equivalent to evaporators.
- Although chlorides can be removed to less than 200 mg/L, reducing them to between 1,200 and 1,500 mg/L chlorides is more economical. Lower chloride levels can be attained at the expense of higher capital and higher energy due to reduced membrane flux below 1,200 – 1,500 mg/L Cl.

Background: FGD Wastewater

Coal fired power plant flue gas desulfurization (FGD) systems are used to remove sulfur dioxide (SO_2) air emissions. They create wastewater often saturated with calcium sulfate while containing both metals and chlorides. FGD water is recycled internally and then purged out of the system when chloride concentrations exceed a set level. High chloride concentrations inhibit SO_2 absorption from the flue gas and create corrosion concerns with wetted equipment. Chloride blowdown levels range with operations from 10,000 mg/L to as high as 30,000 mg/L.

Most FGD installations already include some wastewater treatment, typically referred to as "triple box", wherein heavy metals and fluorides are removed via moderate pH (~pH 9) precipitation combined with polymer and coagulation, followed by a filter press. Historically the filtrate is released, however chloride, selenium, and other constituents that make up total dissolved solids (TDS) are not removed. The industry is facing new regulations that force TDS removal. The authors of this work reviewed and tested multiple options to inform an appropriate path for future development. The top three contending options are summarized herein with their economics compared. The results show that monovalent electrodialysis reversal (mEDR) holds the greatest promise to provide a step change in FGD wastewater treatment cost reduction.

The top three contending options are all based on industrially practiced technology, however leading innovation is applied to options (1) and (3).

- **UHP RO:** Chemical Softening –> Seawater 80 bar Reverse Osmosis (SWRO) –>Ultra High-Pressure 120 bar Reverse Osmosis (UHPRO)

- **EVAP:** Chemical Softening –> Seawater Reverse Osmosis (SWRO) –> Evaporator
- **mEDR:** Monovalent Electrodialysis (mEDR), without Chemical Softening
    1. Desalt down to 1,500 mg/L chlorides
    2. Desalt down to 500 mg/L chlorides

All options assume an upstream "triple box" treatment step is already in place. All options produce a final brine reject that is either combined with fly ash for solidification and landfill disposal or sent to a ZLD system. The recovery and brine reject volume for each option is included in the analysis, however the final disposal costs of said brine is excluded and assumed to be roughly equivalent, or at least not impact the final conclusions drawn for next steps.

FGD Wastewater Treatment Options

Option 1 (UHP RO) and 2 (EVAP):

FGD wastewater treatment options 1 and 2 simplified process flow diagram is shown in Figure 1 and Figure ***2*** below. They differ in their final concentration step: (1) includes ultra-high pressure reverse osmosis (UHP RO), which can produce a brine reject at 130,000 mg/L TDS and (2) includes an evaporator, which produces a more concentrated brine reject at 180,000 mg/L TDS, but at a higher cost than UHP RO.

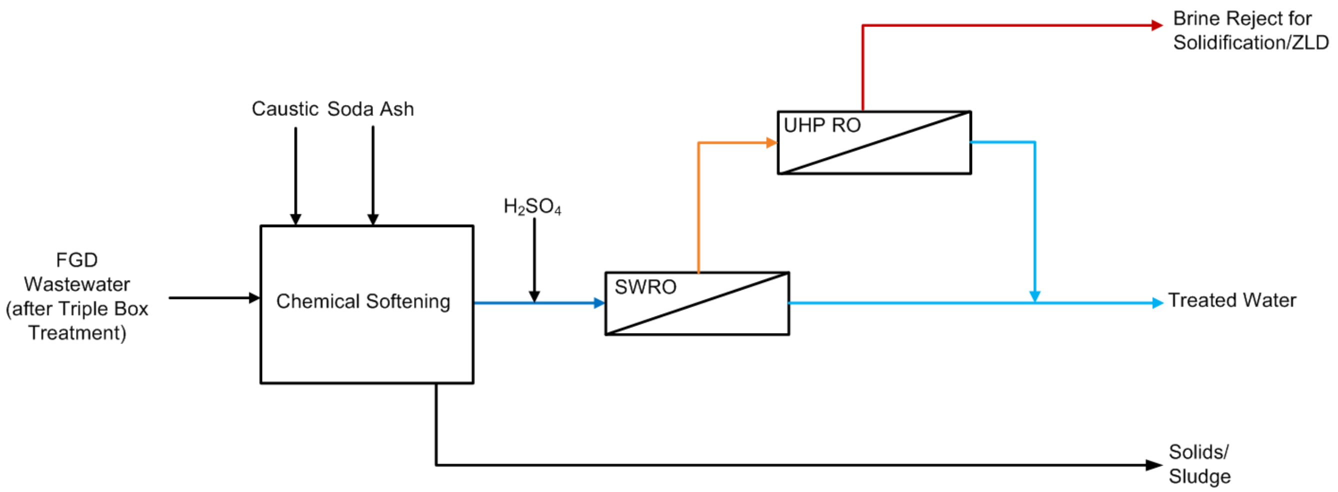


Figure 1. Option 1 Simplified process flow diagram: Chemical softening – SWRO – UHPRO

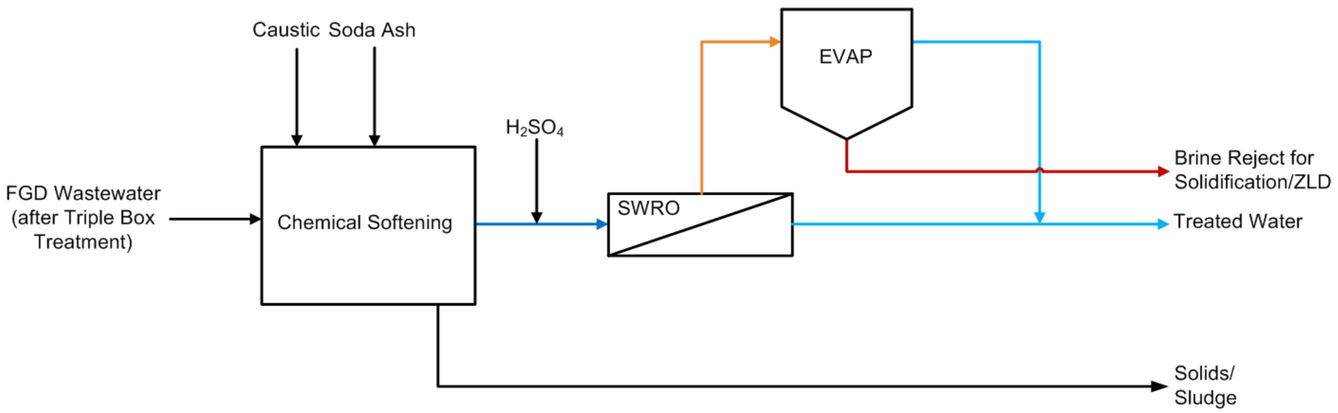


Figure 2. Option 2 Simplified process flow diagram: Chemical softening – SWRO – Evap

Both options produce treated water that is suitable for environmental discharge and leverage an upstream seawater reverse osmosis (SWRO) step, which is low cost and widely available. Based on the FGD waters tested by the authors, the chemical softening soda ash must be employed with RO and evaporators. Its cost accounts for almost 50% of the treatment total cost of ownership (capital plus operating cost; see Table 2 below).

Option 3 (mEDR):

Monovalent electrodialysis (mEDR) selectively pulls out chlorides to increase internal recycle rate and decrease wastewater volume. See Figure 3 for simplified process flow diagram.

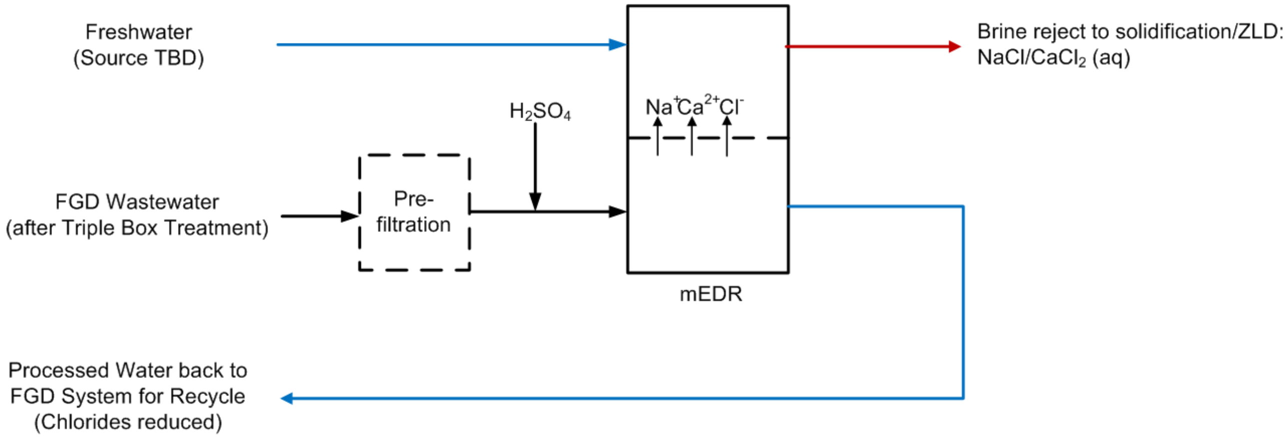


Figure 3. Simplified process flow diagram: mEDR

mEDR builds upon traditional electrodialysis technology, the world's second most practiced membrane desalination technology, and is enabled by recent advances in monovalent ion exchange membranes. These are manufactured from a ductile and highly conductive ion exchange polymer. Under an electrical field, these membranes selectively allow monovalent anions, such as chloride, to pass through the membrane and concentrate up in the brine reject stream while blocking multivalent ions, such as sulfate (see Figure 4). Similar to how kidneys remove waste from human body, mEDR removes chloride in the wastewater and recycles the low chloride water back to the FGD system for reuse.

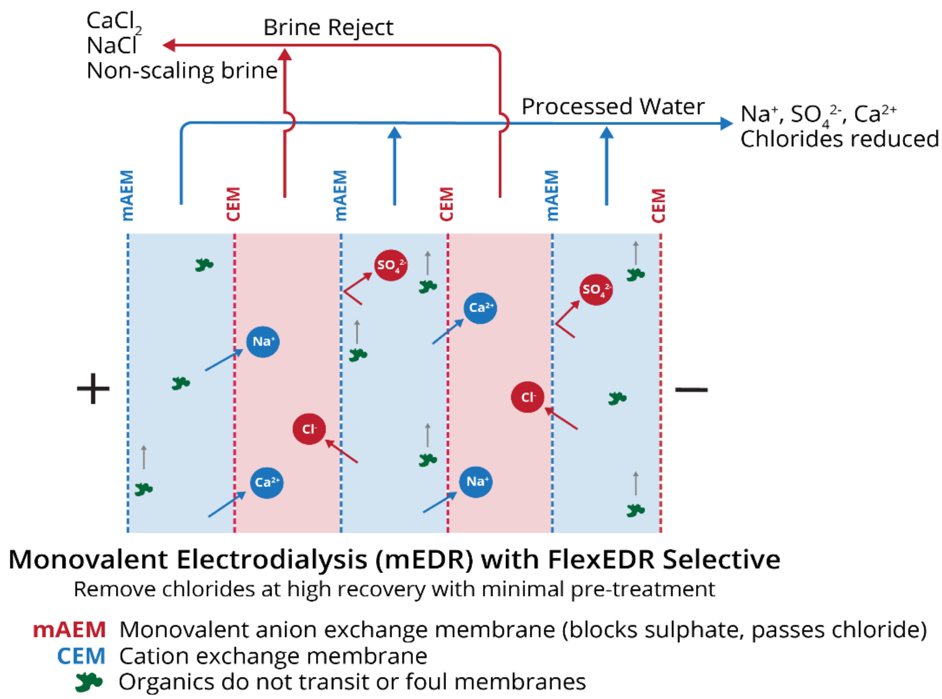


Figure 4. Monovalent electrodialysis stack

Since mEDR only moves chlorides and calcium to the brine reject, it produces a non-scaling brine composing of primarily sodium and calcium chloride. Since sulfates are prevented from entering the brine, scaling products do not form and high membrane system brine concentrations can be achieved without the need for expensive soda ash softening.

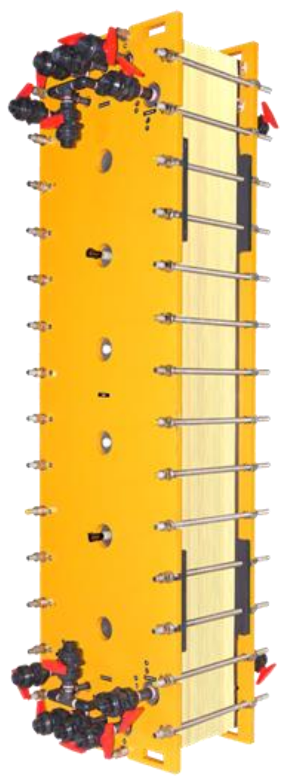
mEDR Tests on Real FGD Wastewater

The mEDR process has been tested on a micro-pilot (see Figure 5) and Saltworks' micro-stack with real power plant FGD wastewater to prove feasibility and provide initial performance data. Full scale stacks are available in two sizes also shown in Figure 5 and results scale-up linearly based on a series of past projects.

Micro-pilot – fully automated and complete process

Micro-stack

E100 Stack: 100 m^3/day



E200 Stack: 200 m^3/day

Figure 5. EDR Micro-pilot and full-scale stacks

The tests show that mEDR can achieve over 90% recovery and remove more than 90% of the chlorides. The brine reject produced consisted mainly of calcium, magnesium, and sodium chloride, and greater than 150,000 mg/L TDS. The analytical results of the inlet

FGD wastewater, processed water and brine reject are shown in Table 1 below. Figure 6 shows the relative removal of various ions, including the extremely high rate of chloride removal vs sulfate.

Parameter	Raw FGD waste water	Processed water	Brine Reject
Units:	mg/L	mg/L	mg/L
pH	3	4.13	2.03
Total Dissolved Solids	20,800	4,100	185,000
Total Hardness (as CaCO3)	16,970	3,060	161,000
Alkalinity (as CaCO3)	<1	<1	<1
Aluminum	0.3	0.73	0.99
Ammonia (as N)	0.19	0.06	-
Antimony	<0.010	<0.010	<0.025
Arsenic	0.002	<0.002	<0.005
Barium	0.18	0.062	1.97
Beryllium	<0.0010	<0.0010	<0.0025
Bicarbonate (as CaCO3)	<1	<1	<1
Boron	112	103.5	52.1
Bromide	17.6	1.81	248
Cadmium	0.04502	0.0219	0.21
Calcium	3290	573	30180
Carbonate (as CaCO3)	<1	<1	<1
Chloride	11230	1033	122530
Chromium	0.02	0.014	0.231
Cobalt	<0.0010	<0.0010	<0.0025
Copper	0.149	0.128	0.54
Fluoride	9.5	5.3	12
Hydroxide (as CaCO3)	<1	<1	<1
Iron	<0.1	<0.1	<0.2
Lead	<0.0010	<0.0010	0.0067

Parameter	Raw FGD waste water	Processed water	Concnetraed brine
Units:	mg/L	mg/L	mg/L
Lithium	0.068	0.05	0.287
Magnesium	2,035	392	19,100
Manganese	0.02	<0.01	0.14
Mercury	0.0037	0.00013	0.06
Molybdenum	0.007	0.003	0.024
Nickel	0.089	0.039	0.864
Nitrate (as N)	11.6	1.11	202
Nitrite (as N)	<0.05	<0.005	<0.5
Phosphorus	1.3	1.2	4.1
Phosphate (Ortho)	0.06	0.025	0.08
Potassium	9	4	85
Selenium	0.086	0.079	0.06
Silica (Reactive)	17	17.3	5
Silicon	8	8	3
Silver	<0.004	<0.004	<0.010
Sodium	960	160	8320
Strontium	10.3	3.6	120
Sulfate	1845	1730	812
Thallium	0.002	0.001	0.0133
Tin	0.0035	0.0049	0.135
Titanium	<0.02	<0.02	<0.05
Uranium	0.0156	0.0049	<0.0005
Vanadium	<0.02	<0.02	<0.05
Zinc	0.89	0.41	8.53

Table 1. Water chemistry data for FGD Wastewater, processed water and reject brine

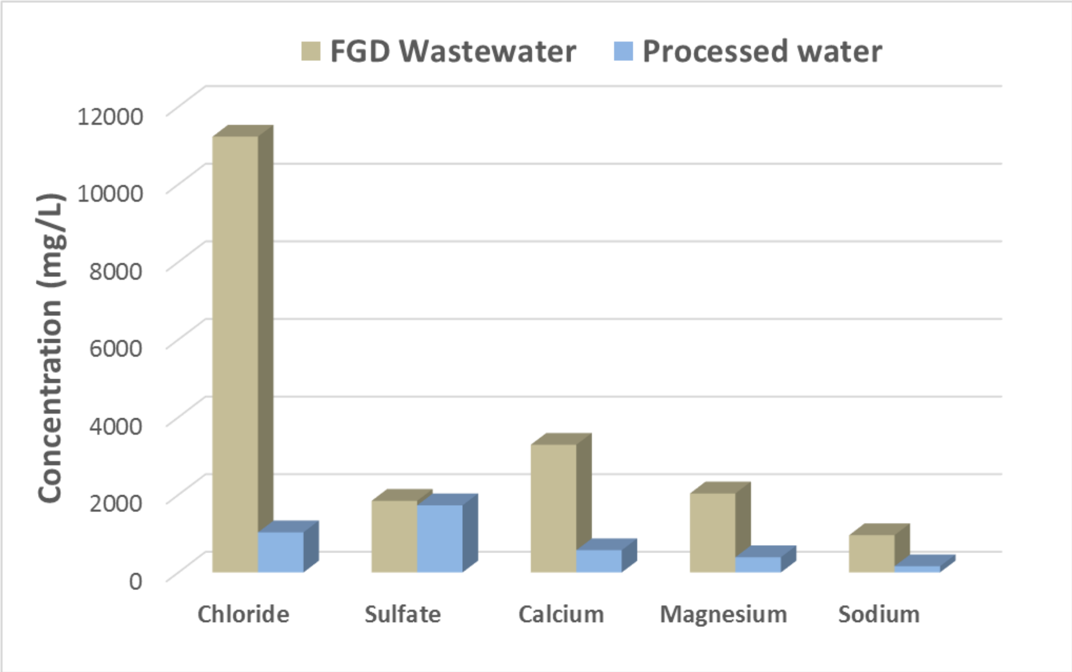


Figure 6. Comparison of major constituent concentrations in FGD wastewater and mEDR processed water

The test plant operated reliably without the need for chemical softening. The membranes demonstrated excellent monovalent anion selectivity – chlorides were reduced by more than 90%, while 94% of sulfates remained in the FGD water. On a molar basis, this means for every 200 chloride ions that were removed from the FGD wastewater, only 1 sulfate ion passed through the monovalent anion exchange membrane. This high monovalent selectivity is critical to realize chloride removal from FGD wastewater and concentrating calcium/magnesium/sodium chloride in the brine reject without scaling. No irreversible organic or inorganic fouling occurred, and preventive oxidant clean followed by a sodium chloride wash every 30 days will maintain performance.

FGD Wastewater Treatment Costs

Table 2 below compares capital and operating cost of all three options based on real FGD water, test data, and vendor prices assuming 300 m^3/day capacity (12.5 m^3/hr).

Costing is based on test data and water chemistry as shown in Table 1. The total cost of ownership is calculated assuming capital costs are depreciated over a 20-year life at 8% while adding in operating costs such as energy, chemicals, and membrane replacements. Installation, operating labour, and taxes are excluded. The mEDR installation desalting to 1500 mg/L chlorides requires six Saltworks' E200 stacks, while desalting to 500 mg/L requires twelve stacks. Flow rates larger than 300 m^3/day are readily achievable by adding more stacks.

Table 2. Comparison of FGD Wastewater Treatment Costs

Options:		1 **Chemical Soften - SWRO - UHPRO**	2 **Chemical Soften - SWRO - Evap**	3A **mEDR: Chlorides to 1,500 mg/L**	3B **mEDR: Chlorides to 500 mg/L**
Plant Availability	%	**95%**	**95%**	**95%**	**95%**
Total Inlet Flow	m3/day	300	300	300	300
FGD Wastewater Inlet TDS	mg/L	20,800	20,800	20,800	20,800
Brine Reject Flow	m3/day	61	35	30	38
Brine Reject TDS out	mg/L	130,000	180,000	150,000	150,000
Processed Water Flow	m3/day	239	265	300	300
Processed Water TDS	mg/L	581	~500	6,000	2,000
Processed Water Chlorides	**mg/L**	Permeate Quality	Permeate Quality	**1,500**	**500**
System Treated Water Recovery	%	80%	88%	91%	89%
mEDR Prefiltration Capital Cost (by Others)	$			$ 300,000	$ 300,000
mEDR Balance of Plant Capital Cost (by Others)	$			$ 887,407	$ 1,209,079
mEDR Stacks Capital Cost (By Saltworks)	$			$ 613,127	$ 1,229,702
mEDR Plant Capital Cost	$/m3 inlet			$ 1.76	$ 2.68
	RMB/tonne Inlet			¥ 11.75	¥ 17.88
Capital Cost (excludes install, taxes)	**$**	**$ 3,142,539**	**$ 5,788,329**	**$ 1,800,534**	**$ 2,738,781**
Total Chemical Cost	$/m3 inlet	$ 7.43	$ 7.43	$ 0.02	$ 0.02
Total Energy Requirement	kWh/m3 inlet	7.96	51.67	19.49	27.23
Total Energy Cost	$/m3 inlet	$ 0.40	$ 2.58	$ 0.97	$ 1.36
Total Membrane Replacement Cost	$/m3 inlet	$ 0.14	$ 0.03	$ 0.43	$ 0.86
Total Cost of Ownership (excludes install, labour, taxes)*	**$/m3 inlet**	**$ 11.04**	**$ 15.70**	**$ 3.18**	**$ 4.92**

*Costs assume pre-filtration and balance of plant built in China to Saltworks' specifications; Saltworks to supply membranes, stacks, process engineering (P&ID), and control PLC with program embedded

*Costs do not include: Install, labour, VAT – assumes equal impact to all options

*Costs assume economies of scale in orders and production

The results show potential that:

- mEDR can save up to 50% in capital (no need for chemical softening and thermal system) and operating cost for FGD wastewater treatment compared to options 1 and 2.

- mEDR can remove chlorides to very low levels, however that may not be the most economically practical. Once chlorides are reduced below 1,200 to 1,500 mg/L chlorides, the membrane flux is reduced and electrical resistance increases. This increases membrane area and power to reach lower chloride levels. Results show that although mEDR can readily desalt to 500 mg/L chlorides or lower, capital cost and energy increase by 50%. Since the treated fluid is being blended with higher chloride water inside the FGD system, and mEDR pre-treatment costs are low, it may not make economic sense to reduce chlorides much lower than 1,200mg/L to 1,500 mg/L.

mEDR Full Scale Implementation:

Full scale plants can be implemented as the foundation technology – electrodialysis - is not new and production systems are in placed as shown in Figure 7 below.

Figure 7. Full Scale Production of Electrodialysis Stacks

Standard mEDR skids are produced consisting of 6 Flex EDR E200 stacks, each with a hydraulic treatment capacity of 200 m^3/day per stack. Each stack will remove roughly 4,000 mg/L TDS per pass and multiple passes are required for higher removal. The monovalent ion exchange membranes are essential to the solution and Saltworks Ionflux membranes are recommended due to their high monovalent selectively, robustness, and oxidant tolerance balanced with their lower cost.

Saltworks owns a series of mobile pilot plants that are available to demonstrate any of the three options on site – RO, EVAP, or mEDR. The pilots are containerized (Figure 8) and recreate full scale processes including automation and controls.

Figure 8. Electrodialysis Pilot Plant

Conclusion:

mEDR technology, based on industrially available electrodialysis, shows much promise and compelling economics for FGD wastewater treatment at up to 50% cost savings. Field pilots in specific applications are recommended to determine the following:

- Optimum chloride reduction level for the process.
- Characterization of purge/blowdown to prevent accumulation of deleterious matter such as organics and other ions.

- Solidification requirements and recipe for the mEDR brine reject.

After a field pilot, full scale plants can be rapidly delivered as production is in place and electrodialysis has a long heritage of implementation. This article is intended as general guidance. Specific project needs, water chemistry, and site requirements will change economics. Contact projects@saltworkstech.com for further details.