

Membrane Electrolysis – A promising Technology for Mine Water Treatment, Radionuclide Separation, and Extraction of valuable Metals

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Abstract

Membrane electrolysis processes can be appealing alternatives to other mine water treatment processes, especially for the selective separation and recovery of pollutants. The RODOSAN® process was developed for the simultaneous separation of sulfate and heavy metals and generation of buffering capacity. The process has been tested on a pilot scale and currently allows for sulfate separation at efficiencies of 40% to 60% with quantitative elimination of heavy metals. Sulfate is converted to ammonium sulfate, which can be used as a fertilizer. The regeneration processes have been optimized to allow more highly mineralized water to be treated in industrial membrane electrolysis cells without any process disruptions. Separation of radionuclides and valuable chemical elements from mine water, deep geothermal water and formation water is also possible using this process platform.

Key words: membrane electrolysis, sulfate removal, heavy metals, radionuclides, pilot tests

Introduction

Acidic, sulfur-rich, heavy metal-loaded mine water, or acid mine drainage (AMD), is a problem in lignite, bituminous coal, and sulfide ore mining operations around the world. If such water is allowed to flow into receiving streams without prior treatment, it can render them unsuitable as drinking or process water resources. Particularly in regions with low water availability, this can lead to massive water supply problems. Such large-scale problems are already known to exist e.g. in Chile, Peru, and South Africa. The semiarid and arid copper mining regions of Chile, for example, consume approx. 30 m³/s water for ore processing with the greater part being contaminated, which significantly impacts the water quality in the receiving streams (COCHILCO 2015).

The water quality of numerous streams in the watershed area of the Elbe river is also strongly affected by continuously high salt loading. Mineral weathering (pyrite oxidation) also occur over wide areas, resulting in highly loaded groundwater that is unfit for use as drinking or process water. The situation is particularly worse in some regions of Central and Eastern Germany, where centuries of extensive mining have left their mark and where mining operations are still expected to continue to a lesser extent over the next few decades. In part high inflows of primarily sulfate-rich water from the Lausitz and Central German lignite fields, the former ore mining regions e.g. of the Erzgebirge, and numerous others into the receiving streams are related to this, and even problems with sulfate concentration in drinking water in the German capital of Berlin can be traced back to it.

For some time now, this manifest water contamination has been resulting in demands for technical measures for limiting sulfate emissions. For water impacted by ore and bituminous coal mining operations, separation of heavy metal ions, naturally occurring radionuclides, and arsenic is being brought into focus. Conditioning of formation water and geothermal fluids in connection with the so called borehole mining is also gaining attention. These fluids often contain recoverable metals. Different approaches for developing membrane electrolysis methods for treatment of this water are reported below.

State of the Art and Current Research and Development

In Germany and in numerous other countries, the state of the art in treatment of mine water from coal and ore mining operations remains treatment by neutralization with lime and iron/aluminum precipitation. Sulfate normally cannot be separated to any significant extent because the solubility product for gypsum is usually not exceeded. Hardening inevitably occurs. Numerous other methods and approaches have been developed for treating mine water, but only a few are being used under specific application conditions. Hence, they will not be discussed further here. Besides lime precipitation, precipitation with barium salts, as schwertmannite, or with aluminates has been proposed (e.g., Wallhalla and SAVMIN process, Smit 1999). Apart from in part high process costs, the treatment and disposal of the sludge must be addressed. German BMBF has made considerable expenditures to drive the development of microbiological processes (passive and active processes). High-performance sulfate reduction according to the GEOS Freiberg process (www.geos.de) and autotrophic sulfate reduction according to the DGFZ process (F. Bilek et al. 2008) are in so far at the most advanced stage of development. These processes have not yet been implemented industrially in Germany. Passive processes in the form of constructed wetlands are being implemented in practice to some extent (Eden Project, GB). However, they have the disadvantages of low space-time yields, poor controllability, and hence they are not compliant with the need to treat larger water volumes that are typical for domestic mining and remediation operations.

Membrane processes such as reverse osmosis, nanofiltration, and electro dialysis have also been suggested. Water of drinking water quality can be generated at the diluate side, but, depending on plant capacity, larger volumes of concentrate may arise and must be disposed of unless discharge to rivers of sufficient capacity is possible. The costs (excluding costs of disposal) are as high as or higher than for electrolysis at the current stage of development. Over the last few years Vattenfall Europe Mining has been working with BTU Cottbus on the development of elaborate downstream precipitation processes for generating recoverable/disposable products from such a concentrate fraction, but this has proven to be difficult.

With considerable funding from BMBF, a process for electrochemical treatment of this water was developed and optimized. Tests were then performed on a pilot scale with multiple process variations and different mine water sources mainly on behalf of LMBV mbH. A number of process disturbances arose, especially in the treatment of water with lime and gypsum supersaturation, but have by now been solved.

Working Principle of the Electrochemical Sulfate Separation Process (RODOSAN® Process)

In the Rodosan® process, raw water is feed into the cathode chamber of a membrane electrolysis cell. When a sufficiently high cell potential is applied, (sulfate) anions migrate through specially selected anion exchange membranes into the anode chamber, where they are concentrated and then converted to ammonium sulfate either directly or in a subsequent stage with aqueous ammonia. While oxygen is formed at the anode (peroxydisulfate formation is also possible), pure hydrogen is formed at the cathode and can be utilized as a secondary energy source. As a result, the sulfate becomes depleted in the cathode chamber, the pH-value increases, and hydrolyzable cations are precipitated. Depletion of aluminum, iron, and manganese to trace amounts occurs. Feed-in of CO₂ into the cathode chamber is a proven method for further sulfate removal (gypsum splitting). So hydrogen carbonate partially substitutes sulfate in this process. Figure 1 illustrates the working principle.

With this process, also wastewater with elevated chloride concentrations can be treated to produce chlorine, chlorate, etc.

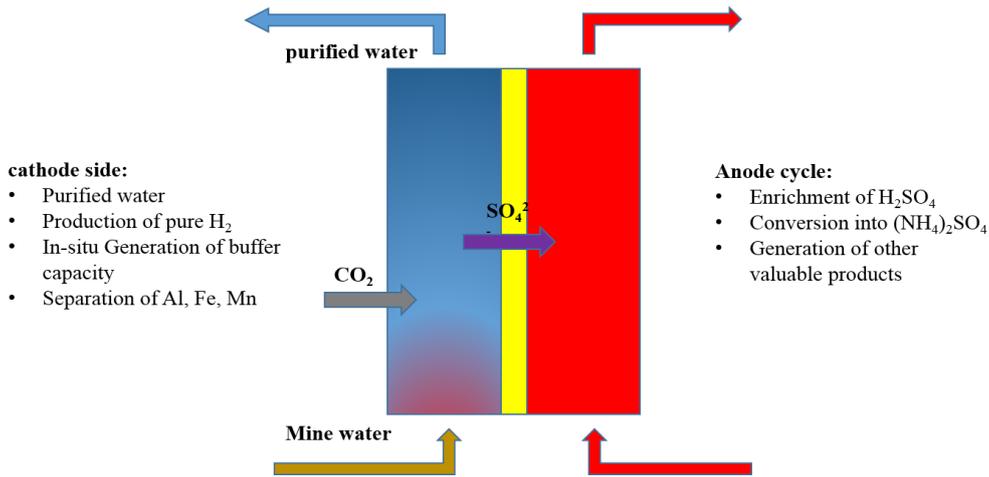


Figure 1 Schematic diagram illustrating the working principle of the Rodosan® process.

Figures 2 and 3 below show the membrane electrolyzers and the location of one of the pilot plant, respectively

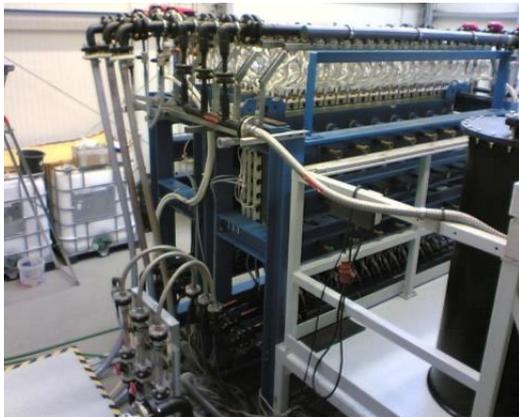


Figure 2 Uhde®-type electrolyzer



Figure 3 Plant location

The test facility capacity ranges from 2 m³/h to 6 m³/h, depending on the specific treatment objective and the starting hydrochemical parameters. Experience from around 20,000 hours of operation has been accumulated thus far.

Applications and Results

In the pilot tests performed up to now, several different water types with differing hydrochemistries from the Lausitz and Central German lignite fields were used. A considerably number of other water types was investigated on the laboratory scale.

The decommissioned open pit at Sedlitz (Lake Sedlitz) is in the Lausitz lignite field; the Lake Bockwitz is south of Leipzig. Its water has been neutralized with soda. In the Tzschelln mine water treatment plant (GWRA Tzschelln), the sump water from the Nochten strip mine is treated by lime neutralization. The parameters given in Table 1 apply to the plant process. Remarkable is the very high calcium content of the Tzschelln water after lime neutralization, which initially caused significant problems regarding process control.

Table 1 Hydrochemical data for treated water from strip mining operations.

Parameter	Lake Sedlitz	Lake Bockwitz	GWRA Tzschelln
pH	3.15	5.8	7.6
K _b 7.0 (mmol/L)	1.6	0.5	-1.4
Cl ⁻ (mg/L)	35.7	22	16
SO ₄ ²⁻ (mg/L)	890	1060	1880
Al ³⁺ (mg/L)	2.3	0.3	0.02
Fe _{total} (mg/L)	10.3	0.22	0.03
Mn ²⁺ (mg/L)	1.9	0.9	2
Ca ²⁺ (mg/L)	166	263	630

Figure 4 shows the mean sulfate removal ("dSO4") values and the volume-specific energy consumption ("Espez-V") values for electrochemical treatment of the water sources listed in Table 1.

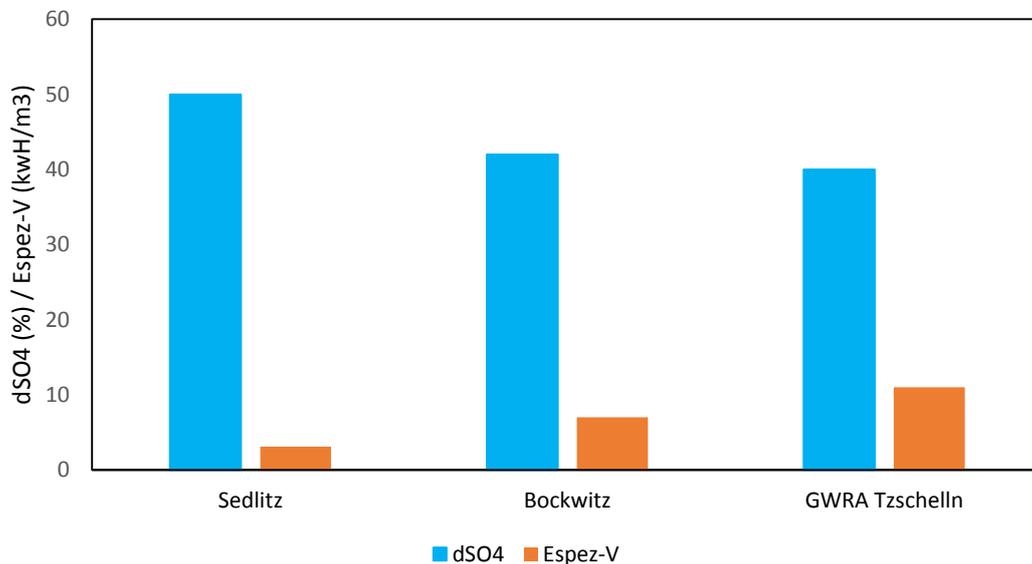


Figure 4 Sulfate separation and specific energy consumption

Sulfate separation efficiencies of between 40% (GWRA Tzschelln) and > 50% (RL Sedlitz) and specific energy consumption values of between 3.1 kWh/m³ and 11.3 kWh/m³ were obtained in continuous operation. Sulfate separation is hence a relatively energy-intensive process. Aluminum, iron, and manganese are removed down to trace amounts. At the same time buffering capacity (3–10 mol/m³) is generated during treatment.

In a further test series with water from GWRA Tzschelln, regeneration processes were optimized for the cells ("opt. regeneration") and a modified internal cell design ("opt. cell") was tested. This enabled stable process control with sufficient technical availability and led to a considerable decrease in the specific energy consumption (Figure 5) of nearly 40% (given as E relative), extending the applicability of the process to include treatment of more highly mineralized water.

With industrial use of the process, economically relevant amounts of coproducts are generated, as shown in Table 2. The values are based on a plant throughput of 0.5 m³/s for the given water sources.

Table 2 Coproducts generated in the treatment of 0.5 m³/s of each of the mine water sources and electrical power consumption values

Parameter	RL Sedlitz	RL Bockwitz	GWRA Tzschelln
dSO ₄ (%)	50	42	42
(NH ₄) ₂ SO ₄ (t/year)	7,800	9,600	15,300
H ₂ (millions of m ³ /year)	1.7	6.0	8.5
P _{el} (MW)	5.4	12.5	14.0

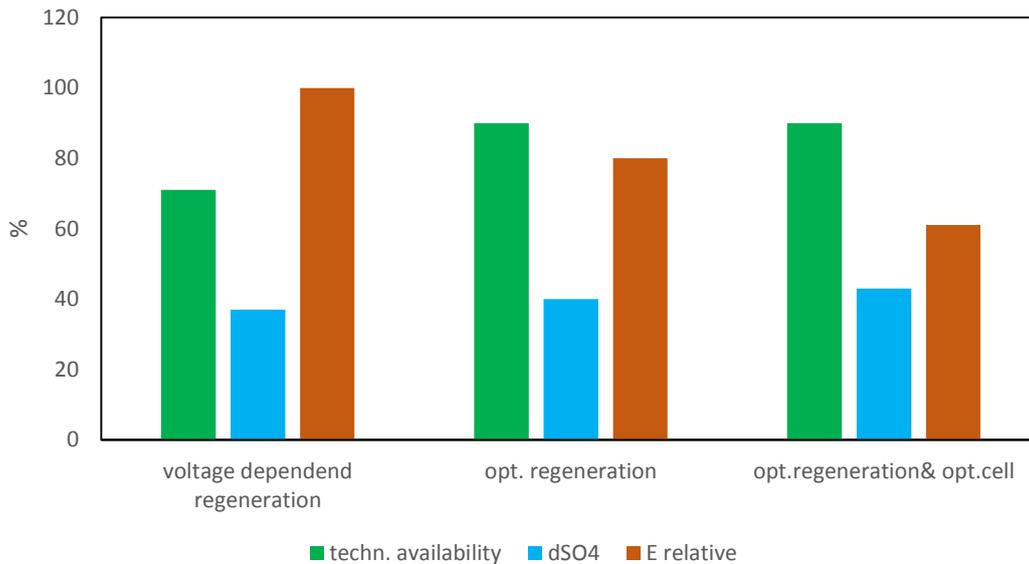


Figure 5 Performance improvements resulting from optimization of the regeneration process and the cell

The generated ammonium sulfate solution can be used as a fertilizer (if necessary, after further concentration). Tests are currently underway to determine its suitability as a fertilizer. Hydrogen is available as a secondary energy source. Because the plants can be operated flexibly, they could find use as buffer elements in energy supply networks.

With membrane electrolysis, heavy metals and radionuclides can also be removed efficiently from water. In the case of hydrolyzable cations ((Al), Fe, Mn), this occurs when the pH is raised in the cathode chamber. In laboratory tests with highly acidic mine water, it was shown that uranium and thorium could also be effectively removed (Table 3).

Table 3 Separation of uranium and thorium during membrane electrolysis of acid mine drainage

Parameter	Inlet	Outlet
UO ₂ ²⁺ (mg/L)	12.4	0.28
Th ⁴⁺ (mg/L)	0.21	< 0.005

Thorium is precipitated hydrolytically in the form of highly insoluble thorium hydroxide. In the case of uranium, overlapping of the coprecipitation of uranium and any iron present and precipitation as UO₂ following reduction of the uranyl cation in the cathode reaction occurs. Electrochemical kinetic investigations were performed to confirm this.

A modified version of the process was developed for separation of toxic heavy metals and radionuclides from highly saline waters such as are (co)extracted in geothermal plants at great depths or during natural gas extraction. Heavy metals contribute decisively to scaling; elimination of radioactive Pb-210-

containing scales is especially cumbersome. Treatment (conditioning) of the geothermal brines or formation water is a promising method for avoiding these problems, particularly in the case of Pb-210.

The process variant developed for this purpose differs from the previously described process primarily through the fact that precipitation occurs in a purely galvanic process. Further changes in the chemistry of the hydrochemical system are undesired and are avoided through appropriate membrane selection (e.g., cation exchange membranes instead of the normally used anion exchange membranes) and careful adjustment of mass transfer between anode- and cathode compartment.

The test equipment shown in Figure 6 was developed for practical testing on a small pilot plant scale under in situ conditions (approx. 100 °C and 10 bar).

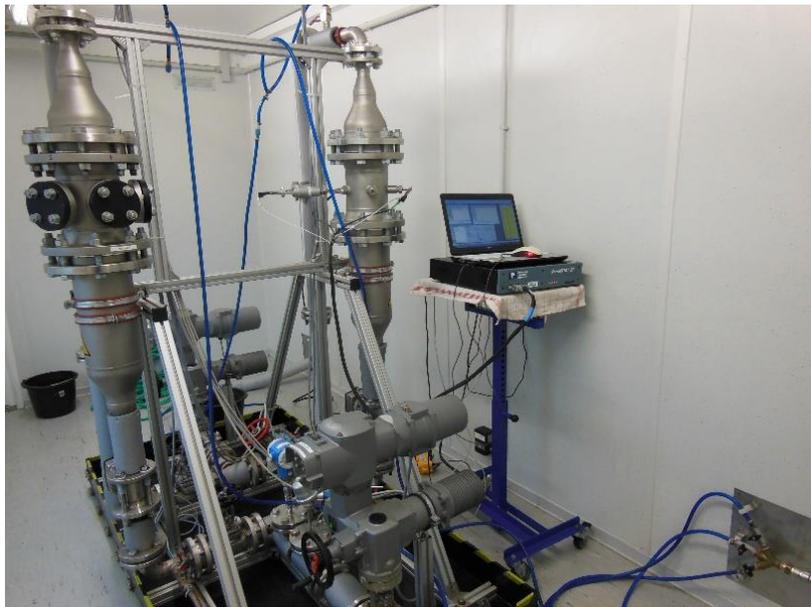


Figure 6 Test bench for in situ precipitation from geothermal brine

The test results obtained up to now show that both Pb-210 and other heavy metals can be separated with high efficiencies (Figure 7). Very short residence times are sufficient for precipitation of Pb-210.

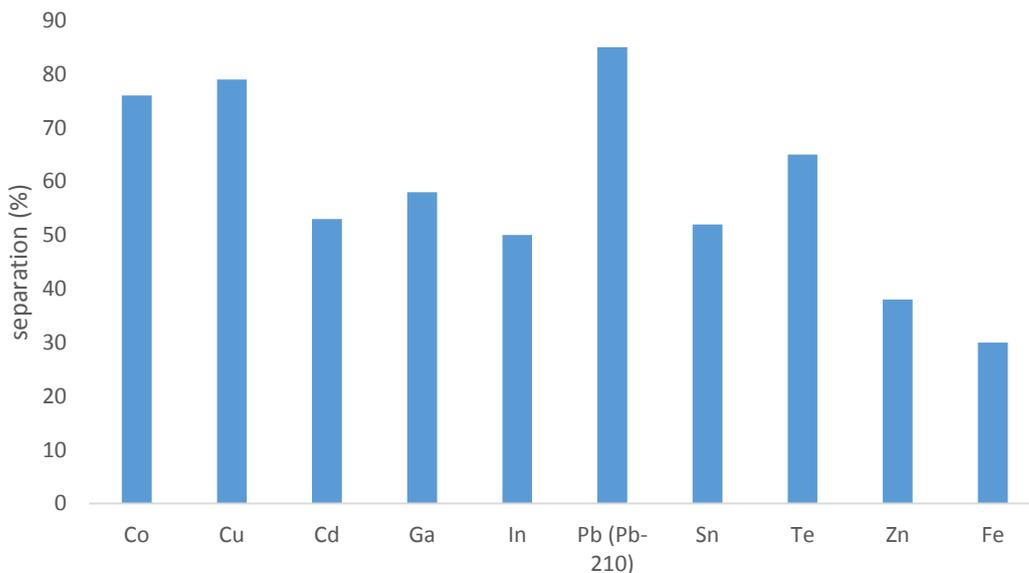


Figure 7 Separation of heavy metals from geothermal brine – borehole GSB1

The dominating factors for successful precipitation appear to be the residence time and the cathode material. Especially in the case of precipitation of Ga (and Tl), the cathode material may have to be chosen extremely carefully. Current efforts are being directed at optimizing the process on a pilot plant scale.

Conclusions

Electrochemical membrane processes are a promising technological route for environmentally sensitive treatment of mine waters or for conditioning of geothermal brines and formation water. They allow for at least nearly waste free operation and are capable to process greater water volumes due to the modular system design. Nevertheless energy consumption and costs of equipment should be reduced further to enable broader practical use. This are the main topics of current R&D.

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