

RECOVERY OF RAW MATERIALS FROM COAL MINE WASTE WATERS

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Coal mine waste waters

- Dewatering generates saline waste waters
- Hard coal mining is the largest source of salinity in Vistula river
- Closing down the mines won't make the problem disappear





Pilot plant in "Bolesław Śmiały" coal mine









http://zerobrine.eu

What was tested?

- pilot scale: pretreatment, ultrafiltration, decarbonization, two-pass nanofiltration, reverse osmosis, two-stage electrodialysis
- bench scale: magnesium recovery (CrIEM and conventional precipitation), salt recovery by EFC



























Two-pass nanofiltration

- nanofiltration can be safely operated at high permeate recovery (80%), without the observable scaling,
- two-pass nanofiltration system has shown very high rejection coefficients with respect to divalent ions, even above 95%, and relatively low rejection coefficients of univalent ions



		Recovery in first-pass nanofiltration							
		NF2 retentate recycled			NF2 retentate not recycled				
		60%	70%	80%	60%	70%	80%		
Rejection [%]	Cl-	23.5%	6.6%	20.7%	20.5%	9.0%	3.9%		
	SO ₄ ²⁻	98.4%	98.5%	98.1%	98.4%	97.3%	97.3%		
	Na+	20.2%	1.8%	16.5%	16.5%	4.8%	1.4%		
	K+	18.0%	4.0%	12.7%	14.8%	4.1%	6.3%		
	Mg ²⁺	95.6%	98.6%	95.9%	95.6%	95.7%	96.0%		
	Ca ²⁺	95.7%	89.2%	96.5%	93.9%	92.5%	90.3%		



Electrodialysis

- Electrodialytic concentration of the reverse osmosis retentate can be achieved with low energy consumption
- Additional evaporator might be required





Magnesium recovery

flow rate range of 0.2 l/h to 1.5 l/h













magma density

3.94

4

1.29

3

test number [-]

3.20

5

2.60

6

Purity in Mg







Boron recovery

Boron content in magnesium oxide is limited thus it has to be removed from saline waste waters before MgO recovery



Removal of boron from highly saline solution on commercially available sorbent Purolite S108.

Desorption of boron using 0.5 M HCI. Our know- how let Mixture of boric and hydrochloric acid is separated us split the eluate into three fractions during continuous desorption process without online boron determination. The second fraction contains about 90% of the total desorbed boron and hydrochloric acid.



using electrodialysis – as the result diluate contained of pure boric acid (<0.07 mS/cm) and concentrate of high conductivity are obtained.

Boric acid solution is concentrated on an evaporator and next B is crystalized as very pure boric acid (proven pharmaceutical grade, chemical purity >99,95%)





Boron recovery

from Flue Gas Desulfurization (FGD) wastewater - pilot scale



Boron sorption/desorption column located in power plant (capacity about 1000 l/h of purified wastewater). Eluate from desorption was divided into three fractions)

The second fraction form desorption was transported to our lab equipped with pilot plant for boron recovery.

Mixture of boric and hydrochloric acid was separated using electrodialysis (our pilot plant consisted of electrodialyzer EDR-X/50-0.8 (MemBrain), containers for diluate, concentrate and electrode solutions, pumps, pressure, flow and conductivity metres, power supply as well as venting and cooling systems).

Boric acid solution is concentrated on an evaporator and next B is crystalized as boric acid. Several kilograms of very pure (proven pharmaceutical grade, chemical purity >99,95%) boric acid was obtained.

- Carlos - Carlos

Chosen treatment train

Comparison with reference technology

Technology	Energy consumption [kWh/m ³ of treated brine]	Bivalent impurities in the concentrate stream [g/dm ³ as Ca+Mg]	Salt recovery [%]	Magnesium hydroxide recovery [%]	Water recovery (not including crystallizer) [%]	Recovered gypsum [kg/m ³ of treated brine]
"Dębieńsko"	16.7	8.25	81.0	0	92.4	1.36
"ZERO BRINE" coupled with "Dębieńsko" evaporator "ZERO BRINE" coupled	12.9 12.0	0.036	56.9 56.9	96.7 96.6	75.7 75.7	0.002
evaporator and crystallizer						
"ZERO BRINE" with intermediate gypsum precipitation and modern evaporator	11.2	0.104	92.8	94.9	90.6	0.84

Environmental impact

- CO_2 emission decreased by about 340 kg CO_2 per ton of NaCl
- Energy consumption decreased by 33%
- Demineralized water recovery: 0.91 m³/m³ of treated brine
- Avoiding the discharge of 20.64 kg of NaCl/m³ of treated brine into the environment

Business case & policy impact

- Decreased energy consumption,
- Decreased environmental fees,
- New revenue streams: magnesium, boron
- Results may be used to develop new policies for coal mining industry,

Scaling up: KWK Piast-Ziemowit

Thanks for the attention

