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Electrodialysis of salts from heat-transfer medium solutions using ion-exchange membranes

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ABSTRACT

Recycling system that can recover the useful amount of glycol-based chemicals from the spent water-soluble heat-exchanging coolant liquids by electrodialysis (ED) is proposed in this paper. The majority of antifreeze liquids used is based on ethylene glycol (EG), but propylene glycol products are becoming more common. Glycol-based waste streams can originate from heat-exchanging liquids mediums, engine coolants or aircraft deicing fluids. Chemical additives as well as corrosion products and glycol degradation products were removed by ED with heterogeneous Ralex® AMH-PES and CMH-PES membranes, and pure glycol in water solution was produced. Laboratory experiments with model NaCl and EG solution were carried out. Real heat-transfer fluid from central heating equipment in the civil buildings was also demineralised by laboratory ED unit P EDR-Z (MemBrain s.r.o.). An efficient depletion of NaCl was achieved by reaching 99% desalination degree for the model EG solution. Ninety-eight per cent removal of salt additives was achieved by ED for EG sample from civil buildings cooling system.

Keywords: Electrodialysis; Heterogeneous ion-exchange membranes; Transport properties of IEMs; Glycol reuse

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1. Introduction

Electrodialysis (ED) is one of the important methods for desalination of water solutions, e.g. production of utility water from brackish water. The separation of electrolytes from organic solvents by ED became the focus of scientific and technical interest due to the development fuel cells containing alcohols, the removal of fermentation inhibitors like organic acids during or before bioethanol fermentation, as well as from other solvent systems. ED is increasingly being used for desalination of complex mixture of many components such as whey [1], wine, carbohydrates mixtures [2] and fruit juices [3] containing a number of organic and inorganic substances of complex chemical properties. Desalination of waste glycol is described in this paper as one of the promising applications of ED.

The treatment of waste-spent coolant liquids is an urgent problem due to the oil, organic additives substances and salts e.g. chlorine content in the solution

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[4]. The origin of spent glycol solutions are from heat-exchange fluids used in ventilation and air conditioning systems (HVAC), and from waste antifreeze mixtures for vehicle engine cooling. The main function of these fluids is to prevent fouling, clogging and the build-up of precipitated solids [5]. Chemical additives are used for corrosion protection of heat-exchange systems. Regardless of glycol type, heat-transfer liquid serves three main functions in pipes: heat transfer, freezing point decrease and corrosion protection. The majority of antifreeze solutions are based on ethylene glycol (EG) and propylene glycol (PG), but glycerol-based products are becoming more common too.

During incineration and other thermal treatment processing of waste antifreeze solutions, HCl and halogenated organic compounds are released, causing corrosion inside the treatment facility and harming human health and the environment [6]. In addition, the treated wastewater is often high in BOD (biological oxygen demand) and COD (chemical oxygen demand) values (e.g. BOD of pure PG is 1,000 g/l and COD is 1,850 g/l); therefore, it cannot be discharged into municipal water treatment systems.

2. Theory

ED is used to transport salt ions from one solution through ion-exchange membranes to another solution under the driving force of an applied electric potential difference. The ED plate-and-frame type cell (Fig. 1) consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by plastic spacers divided by an anion-exchange membrane (AM) and a cation-exchange membrane (CM).

In industrial-scale ED processes, multiple ED cells are arranged into a configuration called an ED module with large number of cells and electrode compartment and electrodes placed on both ends of the module.

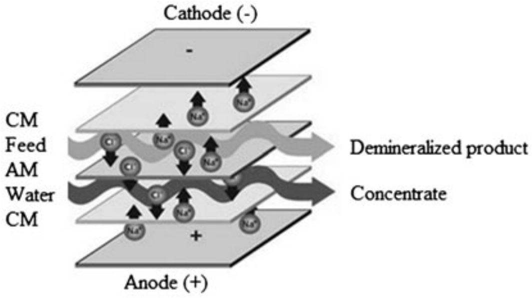

Fig. 1. Conventional salt ED principle.

3. Experimental

3.1. Materials

Heterogeneous RALEX® CM-PES cation-exchange membrane (CM, dry thickness: 0.42 mm, electric resistance: 7.6 Ω cm^2 in 0.5 M NaCl) and RALEX® AM-PES anion-exchange membrane (AM, dry thickness: 0.38 mm, electric resistance 7.4 Ω cm^2 in 0.5 M NaCl) was produced by MEGA as. Czech Republic were chosen for all experiments for their high mechanical strength, good chemical stability and good swelling properties in concentrated glycol solutions leading to low-electrical resistances.

Sodium chloride and EG p.a. grade were purchased from Lach-Ner, s.r.o. (Czech Republic). Model solution was prepared for the set of test with 50 wt% of monoethylene glycol (MEG) and 2.8 wt% of NaCl (see Table 1 for composition).

Chemical composition sample taken from HVAC fluid is reported in Table 2. Analytical matrix was chosen according to ASTM standard D6471-10 [7] and according to commonly used additives in antifreeze solutions [5].

3.2. Model solution desalination

ED was carried out on laboratory module EDR-Z/10-0.8 consisting of 11 CM and 10 AM membranes with an effective surface area of 64 cm^2. Membranes were placed between spacers with a thickness of 0.8 mm, which defined also the thickness of each single diluate and concentrate cell. Pt–Ti electrodes with the same active area were used in the module.

The diluate consisting of 1.828 kg of solution with 2 wt% NaCl and 50 wt% of MEG, and the concentrate made up with 350 ml of demineralised water with 3 g/l NaCl were circulated by a pump at flow rate of 58 l/h. Maximal voltage of the electric power supply was set on 10 V with maximal current density limit on 20 mA/cm^2. Samples were taken at the experiment end for analyses.

Table 1
Model NaCl and EG solution composition

	Unit	Value
pH		6
Conductivity	mS/cm	14.1
TDS	g/l	30
EG	g/l	531
Cl^-	g/l	18.2
Na^+	g/l	11.8

Table 2
Chemical composition of real feed HVAC solution

Parameter	Unit	Value
pH		8.30
Conductivity	mS/cm	5.4
NO_3^-	mg/kg	387.0
NO_2^-	mg/kg	60.6
NH_4^+	mg/kg	2.8
SO_4^{2-}	mg/kg	134.0
Cl^-	mg/kg	32.0
Zn^{2+}	mg/kg	1.38
Fe	mg/kg	5.00
MoO_4^{2-}	mg/kg	3.08
Ca^{2+}	mg/kg	86.0
Mg^{2+}	mg/kg	5.45
Na^+	mg/kg	1,470
K^+	mg/kg	2,120
SiO_3^{2-}	mg/kg	4,808
$B_4O_7^{2-}$	mg/kg	1,410
Tolyltriazole	mg/kg	532
Organic acids	mg/kg	322
MEG	g/kg	26.4
PG	g/kg	76.1

Solution conductivity and pH was determined by multimetre WTW pH/cond340 and the Mohr method titration was used for chloride concentration determination. Chosen ED products (concentrate, diluate and electrode solution) were analysed in the accredited laboratory ALS Global Česká Lípa.

3.3. HVAC sample desalination

The same ED module was used for real solution. The diluate consisting of 4.110 kg of HVAC sample and the concentrate was made up 500 ml of demineralised water. Both circuits were circulated at flow rate of 58 l/h. Maximal voltage of the electric power supply was set on 15 V with maximal current density limit on 20 mA/cm^2. Samples of diluate and concentrate were taken at the experiment end for analyses and analysed in accredited laboratory ALS Global Česká Lípa.

4. Results and discussion

4.1. Model solution

An efficient depletion of NaCl from the MEG solution was achieved, reaching about 99% desalting after 3 h at 10 V (Fig. 2). The sodium chloride removal was a linear function of time, during first 2 h of operation reaching 80% NaCl removal. The NaCl removal rate intensity was lower in third hour reaching 99% in the end of desalination.

The level of desalination continuously increased with time. However, it is visible that, for the high initial salt concentration, the maximum current density is reached, limiting the ion permeation through the membranes (Fig. 3).

The MEG loses from diluate were evaluated from 4 to 5% after 3 h of ED process. The MEG permeation will be increasing with the salt concentration.

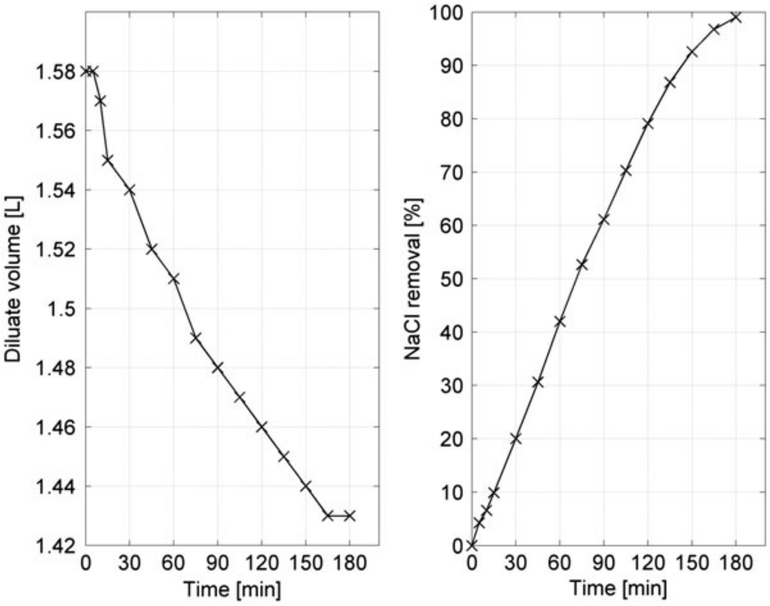

Fig. 2. Model solution volume decrease and NaCl removal as function of time.

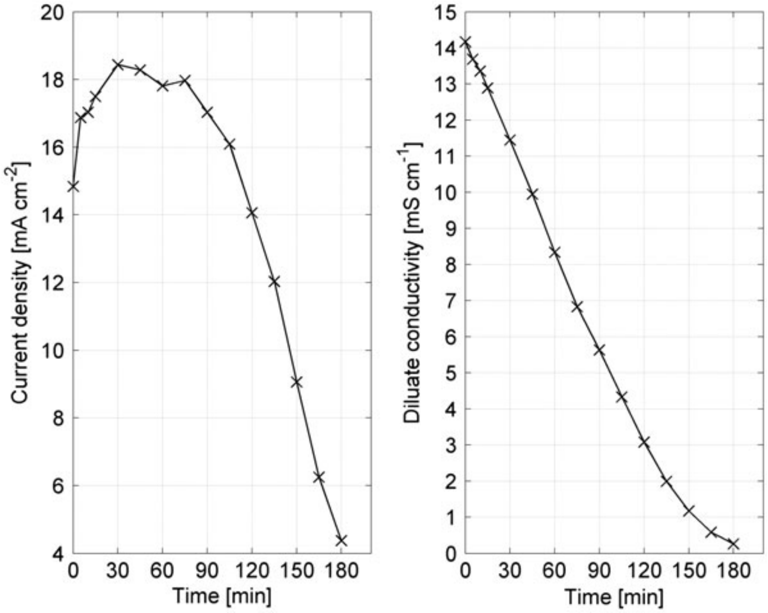

Fig. 3. Model solution current density and dilute conductivity.

In NaCl/water systems, usually three grams of water (solvent) are transported through membranes with one gram of salt. Since solvated ions carries MEG molecules when passing the membrane, the 3 g of water/MEG solution (solvent) is transported through membranes with 1 g of transported salt.

4.2. Real HVAC sample

An efficient decrease of PG-based HVAC liquid solution conductivity was achieved reaching about 98% desalination after 4.5 h at 15 V (Fig. 4) with final conductivity below 0.15 mS/cm. The compositions of key ions or molecules in desalted product are in Table 3.

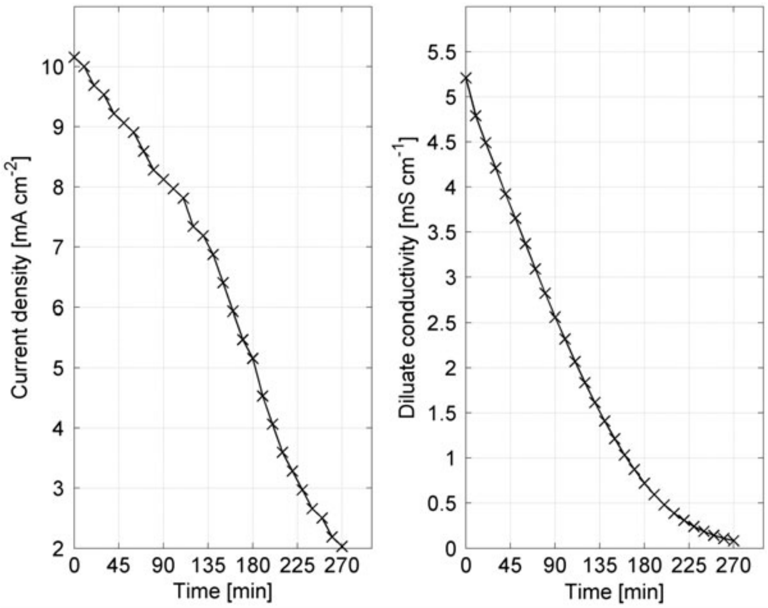

Fig. 4. Real solution current density and dilute conductivity.

Table 3
Real product species concentrations and removal efficiency

Species	Unit	Product	Species	Removal [%]
NO_3^-	mg/kg	1	NO_3^-	99
NO_2^-	mg/kg	1	NO_2^-	99
SO_4^{2-}	mg/kg	22	SO_4^{2-}	85
Cl^-	mg/kg	7	Cl^-	79
MoO_4^{2-}	mg/kg	1	MoO_4^{2-}	79
Ca^{2+}	mg/kg	44	Ca^{2+}	52
Mg^{2+}	mg/kg	4	Mg^{2+}	36
Na^+	mg/kg	38	Na^+	98
K^+	mg/kg	20	K^+	99
$B_4O_7^{2-}$	mg/kg	338	$B_4O_7^{2-}$	75
Tolyltriazole	mg/kg	66	Tolyltriazole	88
Organic acids	mg/kg	<10	Organic acids	98

Concentration of chlorides should be below 30 ppm and sulphates below 140 ppm according to ASTM standard D6472-10 [8]. Concentrations of chlorides and sulphates in desalted product were far below this limit.

ED was able to remove organic additives and also glycol degradation products, which behave like weak organic acids and are completely dissociated at pH > 7. Organic anions can be transported in electric field through heterogeneous ion-exchange membrane like any other inorganic anion.

5. Conclusions

The ED of NaCl and EG model solution was studied, when a high desalination ratio of 99% was achieved at capacity 9.5 kg/m^2 h at laboratory scale.

The ED of real spent glycol-based solution from civil building heating system was performed. The organic heat-transfer medium was consisting of PG and EG, non-depleted organic and inorganic additives, glycol degradation acids and metals. A conductivity decrease about 98% was reached and desalted product conductivity was lowered below 150 μS/cm. The final concentration of chlorides, sulphates and glycol degradation products are given below by using standard specification for recycled glycol-based products. Removal efficiency from 75 to 99% for key monovalent or multivalent anions was reached. This fact shows that ED with heterogeneous ion-exchange membranes RALEX® can be used as one step in the recycling of glycol-based fluids. ED capacity for this solution was 14.3 kg/m^2 h at laboratory scale.

Acknowledgements

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