REMOVAL OF NICKEL CATIONS AND SILVER COMPLEX ANIONS FROM DILUTE PROCESS WATERS USING AN ION-EXCHANGE ELECTRODIALYSIS SYSTEM.

L.J.J. Janssen

Workgroup Electrochemical Technology, Process Development Group, Eindhoven University of Technology, P.O.Box 513, 5600 MB Eindhoven, The Netherlands

Electrochemical technology has succesfully contributed to the removed of heavy metals from industrial process waters. The usefullness of the various electrochemical techniques depends strongly on the nature of the metal to be removed and the composition of the liquid to be purified [1].

Due to the formation of solid deposits on the electrode, the two-dimensional electrode with mass transfer promoters is the most favourable configuration. For solutions with single metal salt concentrations higher than about 2 mol m^{-3} , an undivided cell is favourable when a metal deposit is preferred and an electrodialysis cell when a concentrated metal ion solution is preferred.

For concentrations lower than about 2 mol m⁻³ an ionexchange assisted electrodialyser (IXED-cell) has been found very successfully for the removal of nickel ions to concentrations lower than 0.02 mol m⁻³. Experimental results with an IXED-cell (a three compartment cell) are presented for nickel removal from dilute rinse water from a galvanic Watts bath. The IXED-cell was loaded with organic-exchangers (a rigid macroporous cationexchanger resin, Amberlist 15, and a flexible and low cross-linking cation-exchanger resin, Dowex 50X-2) and inorganic exchangers based on zirconium phosphate (ZrPh-205 solid).

It was found that the mass transport of nickel ions through a bed of cation-exchanger can be well described by a simplified Nernst-Planck relationship [2].

The mobility of nickel ions in the bed has found to be strongly dependent on the nature of the ion-exchanger. For a completely loaded bed at 298 K the nickel mobility is $3.0x10^{-12} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Amberlyst 15 with $c_{Ni} = 670 \text{ mol m}^{-3}$ [3], $4.4 \times 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Dowex 50X-2 with $c_{Ni} = 534 \text{ mol m}^{-3}$ [4] and $4.2x10^{-11} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ZrPh-205 with $c_{Ni} = 65 \text{ mol m}^{-3}$ [5].

From these results it follows that Dowex 50X-2 is the most useful ion-exchanger to remove nickel ions from dilute liquids. One of the greatests problems in this process is the formation of nickel hydroxide in the bed near the cation selective membrane. The use of Dowex 50X-2 allows the electrolysis to occur with the highest current density through the bed without the formation of nickel hydroxide.

The ion-exchange electrodialysis system with Dowex 50X-2 was tested on-site at a galvanic plant and was used to treat a rinse solution containing 0.1 mM Ni. It operated continuously without the need for maintenance for a period of 3 months and was able to remove nickel to concentrations less than 0.004 mM.

Moreover, it has been concluded that the use of tap water strongly decreases the effectiveness of the ion-exchange assisted electrodialysis. Therefore, it is necessary to close the nickel rinse water system resulting in a very strong decrease in fresh water use. Silver can also be recovered from thiosulfate fixing bath's used in photographic processes. Using the various ionisation constants [6] it can be calculated that in an excess of thiosulfate almost all silver ions are present as the $Ag(S_2O_3)_2^{-3}$ complex. Because of its negative charge, an anion-exchanger (Bayer Lewatit MP 500), loaded with 40 mol m⁻³ Ag, was used in the center compartment of the electrodialysis cell. It was found [7] that from the start of electrodialysis with a cell voltage of 30 V a black deposit, viz. Ag₂S, was formed in the anion-exchange bed and no silver ions were transported to both the anolyte (0.1 M H₂SO₄) and catholyte (0.1 M H₂SO₄) in both outer cell compartments. The same results were obtained for a constant current density experiment (0.32 mA cm⁻²). It is likely that the first step will be:

$$Ag(S_2O_3)_2^{-3} \rightarrow Ag(S_2O_3)^{-1} + S_2O_3^{-2}$$

and the second and third step under the potential gradient over the bed possibly [8]:

$$2 \operatorname{AgS}_2\operatorname{O}_3^{-} \to \operatorname{Ag}_2\operatorname{S}_2\operatorname{O}_3 + \operatorname{S}_2\operatorname{O}_3^{-2}$$
$$\operatorname{Ag}_2\operatorname{S}_2\operatorname{O}_3 + \operatorname{H}_2\operatorname{O} \to \operatorname{Ag}_2\operatorname{S} + \operatorname{SO}_3^{-2} + 2 \operatorname{H}$$

From the results for silver removal it follows that in general heavy metal complex anions cannot be removed with anion-exchange assisted electrodialysis without the formation of a precipitate, since the complex adsorbed on the ion-exchanger dissociates under a potential gradient over the bed where an insoluble heavy metal compound is formed.

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