WASTE MINIMIZATION
IN CHROMIUM PLATING INDUSTRY

WASTE MINIMIZATION IN CHROMIUM PLATING INDUSTRY

DISSERTATION

to obtain
the doctor’s degree at the University of Twente,
on the authority of the rector magnificus,
Prof. dr. W. H. M. Zijm,
on account of the decision of the graduation committee,
to be publicly defended
on Friday 3 June 2005 at 16.45

by

Ines Frenzel

born on 10 February 1977
in Freiberg, Germany

This dissertation has been approved by the promotor Prof. Dr.–Ing. M. Wessling and the assistant promotor Dr. D. Stamatialis

"Nothing in life is to be feared. It is only to be understood."

Marie Curie

This thesis was carried out at the company FuMA-Tech GmbH, Germany. The financial support by FuMA-Tech GmbH and by the European Commission in the GROWTH frame (G1RD-CT-2000-00196 and G1RD-CT-2000-00295) is gratefully acknowledged.

ISBN 90-365-2209-9

Printed by Print Partners Ipskamp, Enschede, The Netherlands

Contents

Chapter 1

Introduction

1.1 Chromium plating

Chrome plated parts are widespread in our everyday life and serve a lot in functional and decorative purposes. Almost all chromium layers are obtained by electrodeposition from a solution of chromic acid, sulphuric acid and possibly additives on metallic or non-metallic surfaces. Chromium layers produced by functional (hard) chromium electroplating are characterised by toughness and ultimate hardness. They have wear and heat resistance, low friction and anti-corrosion properties. Examples are printing cylinders, machine tool cutting surfaces, crankshafts, parts for hydraulic systems, shock absorbers and piston rings etc.. Decorative deposits have a bright, highly reflective surface and in addition to their decorative appearance, these layers are specifically used as conversion coatings or in corrosion protection systems on different materials. For example, such layers can be found on automotive parts or sanitary equipment. Besides, chromic acid is used in many other processes, e.g. anodising, acid cleaning, electropolishing and for steel and stainless steel blackening.

During the plating procedure hexavalent chromium is reduced in a multi-stage deposition reaction to elementary chromium. The concentration of chromic acid process solutions ranges from 250 to 400 g/l in functional (hard) chromium plating solutions and from 200 to 400 g/l in decorative (bright) chromium plating solutions [1]. During the electrodeposition process, trivalent chromium is formed and iron, copper, aluminium, zinc, nickel etc. could accumulate in the plating solution. Above certain concentrations, these impurities are undesirable since they could cause unacceptable layer quality and reduce the bath conductivity and the cathode current efficiency [2-14]. Therefore, replacement, replenishment or regeneration of the plating solution is required to improve and guarantee deposit quality [15]. Figure 1.1 schematically shows the plating process.

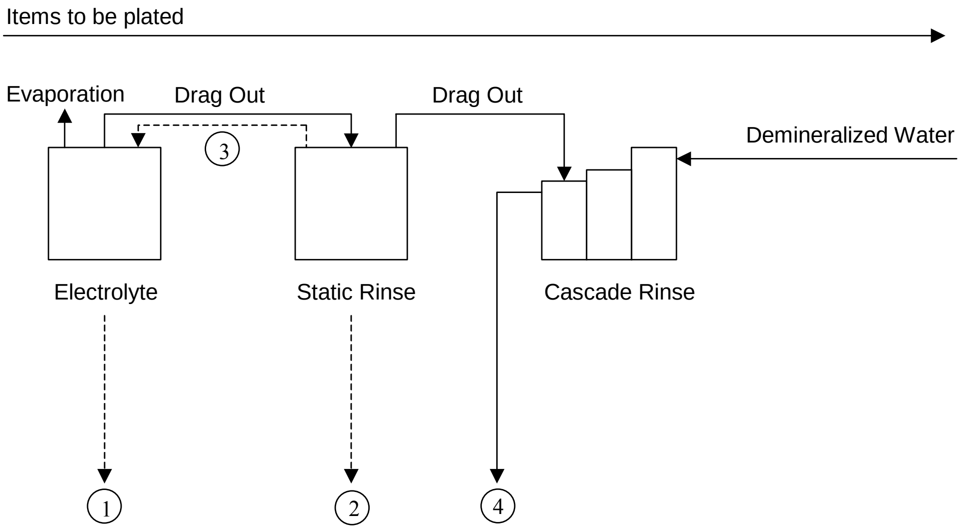


Figure 1.1. *Schematic diagram of the chromium plating process. (1) Exhausted plating solution (intermittent); (2) exhausted rinse water (intermittent); (3) recycling of concentrated rinse water into the plating bath (alternative); (4) exhausted rinse water from cascade rinsing (continuously).*

After chromium deposition, the surface of the parts is cleaned with demineralized water. This is realized by a number of rinsing steps, often by a combination of static and cascade rinsing or by cascade rinsing only [12, 16, 17] (see Figure 1.1). The contamination of the rinse water decreases along the path of the items to be plated and with increasing number of rinsing steps. Static rinses are concentrated and could contain up to 100 g/l chromic acid. Therefore, they have to be replaced regularly. Sometimes exhausted static rinse effluent is used for bath maintenance and is returned directly into the plating bath (compensation of evaporation and hexavalent chromium consumption). This procedure is only possible, if there are no process limiting impurities in the rinse (accumulation). Rinse water from final or cascade rinsing is continuously obtained and is much less concentrated. Therefore, it is more often recycled and reused (closed-loop rinsing).

Chromic acid is a strongly oxidizing, toxic and carcinogenic substance [18-20] and every plating company has to deal with these harmful effluents. More stringent environmental legislation, increasing government scrutiny, pressure of costs and moral obligations are the reasons for continuous research and development on waste minimization and prevention technologies towards zero discharge of waste. Additionally, in recent years, research activities increasingly focus on replacement of hexavalent chromium plating technology by different methods, e.g. deposition from trivalent chromium solutions, physical and chemical vapour deposition and thermal spray processes [1, 21]. However, in many applications, for instance in functional electroplating, electrodeposition from hexavalent chromium can not be replaced by other technologies due to excellent layer quality, easy handling of the process bath and perhaps most importantly cost reasons [2, 4].

1.2 State-of-the-art treatment and recycling technologies

Chromic acid containing waste effluents are generally treated by a combination of physicochemical methods:

- Acidification with sulphuric acid;
- Chemical reduction with sulfite sulfur compounds[1] or Fe(II) salts at $pH \leq 2.5$;
- Neutralization with sodium hydroxide solution or milk of lime (precipitation of metal hydroxides);
- Sludge separation and disposal

This waste water treatment procedure is chemical intensive and a considerable amount of sludge is produced, which has to be disposed. In addition to the government regulations due to the toxicity of the chromate, this is the reason for the effort to reduce the volume of chromate containing waste effluents. On the other hand, complete waste water reduction, aiming at zero liquid waste on-site, and consequently, relinquishment of waste water treatment, seems not feasible for plating companies, neither from practical or economical nor from an energetic standpoint [22, 23]. However, by favourable

---

[1] sodium sulfite (Na_2SO_3), sodium hydrogen sulfite as solution (sodium bisulfite, $NaHSO_3$), sodium disulfite (sodium metabisulfite, $Na_2S_2O_5$), sodium dithionite ($Na_2S_2O_4$), sulfur dioxide (SO_2)

combination of different recycling and treatment technologies, both reduction of waste water volume and plating process maintenance could be achieved.

In addition to measures directly on the plating line (for example, reduction of drag-out or rinse water volume flow) waste effluent reduction and impurity removal can be realized by different state-of-the art technologies [11, 15, 17, 22, 24]:

- Bath maintenance: ion-exchange, ion-transfer and membrane electrolysis;
- Recovery of chemicals: evaporation and ion-exchange;
- Closed-loop rinsing (final or flow-rinse): ion-exchange.

A study performed in 1994 concerning 318 plating companies in the USA [23] showed that the above technologies are not very widespread and physico-chemical treatment was preferred. However, Baral and Engelken [21] reported in 2002, that in the USA ‘a number of metal finishing industries, mainly large businesses, have adopted ‘greening’ as the principal philosophy of business management’. The authors stated that ‘greening is occurring slowly because of lack of personnel and capital resources, awareness, and technical competence, as well as organizational resistance, high costs of production, uncertainty about future regulatory activity, and substantial marketplace constraints’. From technical point of view, some of the following characteristics might have prevented the common use of these technologies in chromium plating industry:

- *Ion-Exchange* provides demineralized rinse water and is used as recycling method for closed-loop final rinses and for bath maintenance. Cations and anions are removed by cation- and anion-exchange resins respectively. Limitations arise from restricted resin stability. Thus, high concentrated chromium plating solutions can not be treated continuously [25] or should be diluted before treatment [17, 26]. Depending on the size of the plating business, ion-exchange columns are either regenerated automatically on-site or by an external company. In any case, regeneration chemicals (acid or caustic) are required and concentrated regenerates are produced, which have to be further treated by neutralization and precipitation [11, 15, 22, 27]. Often, hazardous sludge is produced, which should be disposed.

- *Evaporation* is either used for waste minimization towards zero liquid waste or as concentration technology for exhausted static rinse effluents in order to recover plating solution for reuse. The concentration does not provide selective removal of contaminants and in some cases impurities could accumulate in the plating bath resulting in a decrease of the plating performance. Therefore, evaporation is sometimes combined with ion-exchange to remove the impurities [28]. Evaporation is considered as energy and cost-intensive technology [22].

- *Ion-transfer systems* are separated electrochemical cells and used for bath maintenance [3, 10, 27, 29, 30]. The technology includes anodic oxidation of trivalent chromium to hexavalent chromium and removal of cationic impurities from the plating solution at the same time. The anode compartment is filled with exhausted plating solution and the cationic contaminants migrate towards the cathode through a separator. The cathodic solution is mostly alkaline and metal hydroxides precipitate. Commercial ion-transfer systems are either separated by ceramic diaphragms (porous pot method) or polyfluorocarbon membranes (e.g. Teflon®). The equipment is not very expensive and requires less chemicals and energy and it is therefore, suitable for small plating companies. However, the technology suffers from difficult maintenance, loss of plating solution [11] and has marginal separation efficiency [29].

In comparison to the previous technologies, *membrane electrolysis* systems are equipped with ion-exchange membranes allowing the permeation of cations (impurities) and/or anions (chromate). Therefore, this technology is more flexible and is either used for bath maintenance (similar to ion-transfer systems) or as recovery method for chromic acid from exhausted rinse water. The application of this technology for the recovery of chromic acid from rinse water was restricted up to now due to poor stability of anion-exchange membranes against chromic acid [3, 31].

1.3 Scope of this thesis

The chromic acid waste management is a significant challenge because of the solution characteristics (chromic acid is a powerful oxidizing agent) and the number of related challenges:

- Removal of impurities from chromium plating solutions;
- Re-oxidation or removal of trivalent chromium from plating solutions;
- Recovery and reuse of chromic acid dragged out from the plating bath;
- Rinse water purification and/or treatment

Different new technologies may be anticipated to solve the separate tasks. However, efficiency, engineering effort and suitability must be checked for each specific case. Often the general acceptance is rather low due to high operation costs and difficult handling [23] and discharging seems to be the easiest way. Concerning economy, simplicity and compactness membrane electrolysis (ME) is a promising technology because it requires less chemicals and energy. **Chapter 2** presents a literature review about chromic acid purification and recovery using ion-exchange membranes. Lab and pilot scale studies as well as commercial systems are reviewed.

Three-compartment electro-electrodialysis (EED) is a similar electromembrane process combining the characteristic and advantages of ME with purification of static rinse effluents. Chromic acid is recovered, impurities are removed and rinse water is purified at the same time (Figure 1.2). Therefore, EED is considered as high potential technology. Currently, the technology suffers mainly from poor resistance of the anion-exchange membrane (AEM) against chromic acid solutions. Therefore, **Chapter 3** presents the evaluation of various AEM membranes and discusses the optimum conditions to overcome the process limitations and achieve low-maintenance and long-term operation. The chapter also compares a new oxidation resistant AEM with currently used commercial ones. **Chapter 4** presents the evaluation of the EED process on pilot-scale with regard to long-term stability, process efficiency and economic feasibility.

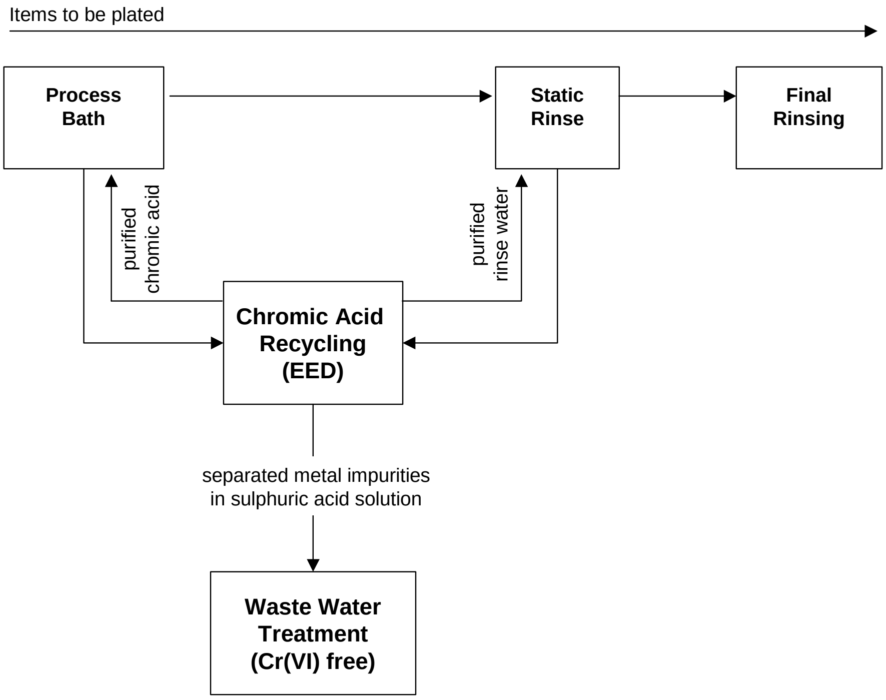


Figure 1.2. *Chromic acid recycling from static rinse water by three-compartment electro-electrodialysis (EED).*

As mentioned earlier, the diluted chromate containing rinse water is obtained from final or cascade rinsing (see Figure 1.1). It is either recycled by ion-exchange (closed-loop rinsing) or treated together with other chromate containing waste effluents by conventional waste water treatment including chemical detoxification, precipitation and sludge separation. This treatment method requires the use of reduction chemicals in excess and a considerable amount of sludge is produced, which has to be disposed. Therefore, **Chapter 5** discusses a new detoxification method - the electrochemical reduction of hexavalent chromate. The amount of chemicals and sludge and therefore, the treatment costs could be significantly decreased. As cathode material highly porous carbon felt is used. This method would be suitable for very diluted solutions since the carbon felt has a large specific surface area and high porosity. Chromate could be reduced below 0.1 ppm Cr(VI), which is for instance the German discharging level, in a very economical way. Figure 1.3 presents the integration of this technology in the existing treatment process.

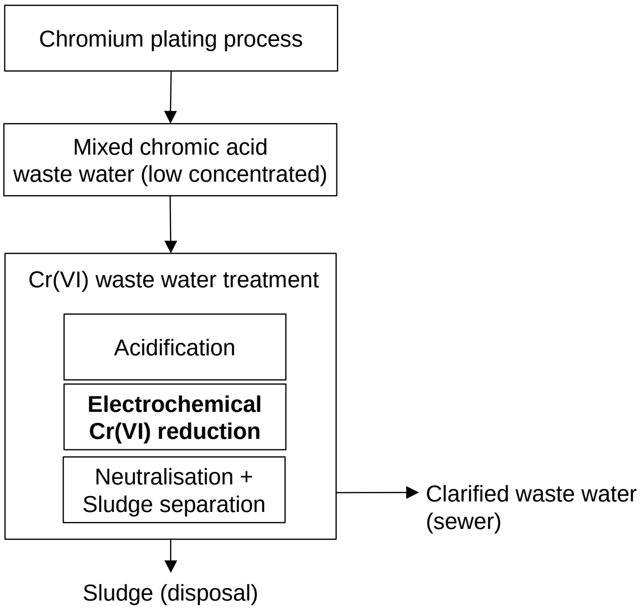


Figure 1.3. *Electrochemical Cr(VI) reduction instead of Cr(VI) reduction by chemicals.*

There are a lot of plating companies striving towards zero liquid waste for various reasons (to fulfil government regulations or for economical reasons). If separation of individual chromate containing effluents for recycling purposes is not possible, evaporation is currently used to minimize the amount of liquid waste. Since evaporation is an energy and cost intensive technology, membranes could be used for volume reduction prior to evaporation (Figure 1.4). **Chapter 6** discusses the combination of various pressure driven membrane processes (microfiltration, nanofiltration and reverse osmosis) in order to downsize the evaporation equipment and to reuse purified water as rinsing water. The recovered water has high quality and could be reused in the plating process.

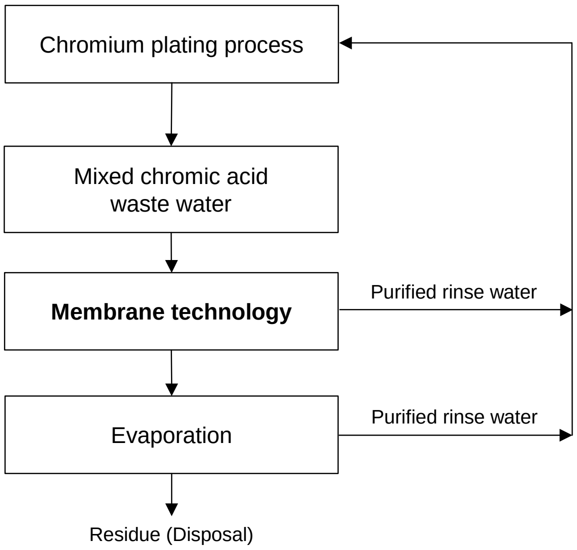


Figure 1.4. *Waste water treatment towards zero liquid waste by membrane technology, which is placed ahead the downsized evaporation.*

Finally, **Chapter 7** presents the conclusions of the thesis and recommendations for future work.

1.4 References

1. J.H. Lindsay, Decorative & Hard Chromium Plating, Plat. Surf. Finish. **86** (11) (1999) 40-42.
2. K. Stevens, Hard chrome plating - a clean bill of health, Trans. IMF (GB) **75** (2) (1997) B33.
3. V.S. Donepudi, N.R. Khalili, R. Kizilel and J.R. Selman, Purification of hard chromium plating baths - options & challenges, Plat. Surf. Finish. (4) (2002) 62.
4. N.V. Mandich, Practical problems in bright and hard chromium electroplating - Part I, Met. Finish. **97** (6) (1999) 100.
5. N.V. Mandich, Practical considerations in bright and hard chromium electroplating - Part II, Met. Finish. **97** (7) (1999) 42.

6. N.V. Mandich, Practical considerations in bright and hard chromium plating - Part III, Met. Finish. **97** (8) (1999) 42.
7. N.V. Mandich, Practical considerations in bright and hard chromium plating - Part IV, Met. Finish. **97** (9) (1999) 79.
8. N.V. Mandich, Practical considerations in bright and hard chromium electroplating - Part V, Met. Finish. **97** (10) (1999) 30.
9. N.V. Mandich, Practical considerations in bright and hard chromium electroplating - Part VII, Met. Finish. **98** (11) (2000) 46.
10. N.V. Mandich, C.-C. Li and J.R. Selman, Practical & theoretical aspects of regeneration of chromic acid plating solutions via electrolytic purification (porous pot method), Plat. Surf. Finish. **84** (12) (1997) 82-90.
11. A. Mühle, Passt Ihr Problem zu den angebotenen Lösungen? Regeneration und Standzeitverlängerung von Hartchromelektrolyten, Metalloberfläche **56** (10-12) (2002) 12-15 (in German).
12. G.A. Lausmann and J.N.M. Unruh, Die galvanische Verchromung. Schriftenreihe Galvanotechnik. 1998, Eugen G. Leuze Verlag, Saulgau, Germany (in German).
13. H. Horsthemke, Prozesssicherung sechswertiger Chromverfahren, Metalloberfläche **53** (4) (1999) 34 (in German).
14. P. Benaben and J. Popakul, Purification and recycling process for hexavalent chromium solutions using a low-cost chemical method, Plat. Surf. Finish. (12) (2000) 88.
15. E.C. Knill and H. Chessin, Purification of hexavalent chromium plating baths, Plat. Surf. Finish. **73** (8) (1986) 26-32.
16. A.W. Logozzo, Ideal layout for a hard chromium plating shop, Plat. Surf. Finish. (6) (2002) 10.
17. L. Hartinger, Handbuch der Abwasser- und Reyclingtechnik für die metallverarbeitende Industrie. 2 ed. 1991, München Wien, Carl Hanser Verlag (in German).
18. S.A. Katz and H. Salem, The toxicology of chromium with respect to its chemical speciation: a review, J. Appl. Toxicol. **13** (3) (1993) 217-224.

19. E. Nieboer and A.A. Jusys, Biologic chemistry of chromium, in "Chromium in the Natural and Human Environments", J.O. Nriagu and E. Nieboer, Editors. 1988, John Wiley & Sons, Inc.
20. E. Groshart, Finishing in the Green - Chromium, Met. Finish. **95** (3) (1997) 59-61.
21. A. Baral and R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environ. Sci. Pol. **5** (2) (2002) 121-133.
22. E.A. Cohen Hubal and M.R. Overcash, Net-waste-reduction analysis applied to zero-water discharge systems for chromic acid electroplating, J. Cleaner Prod. **3** (3) (1995) 161-167.
23. Pollution Prevention and Control Technologies for Plating Operations [Online]. Available: www.nmfrc.org/bluebook/tocmain.htm [2004, September, 2]
24. S. Beszedits, Chromium removal from industrial wastewater, in "Chromium in the Natural and Human Environments", J.O. Nriagu and E. Nieboer, Editors. 1988, John Wiley & Sons, Inc.
25. J. Jangbarwala, Ion exchange resins for metal finishing wastes, Met. Finish. **33** (11) (1997).
26. Entfernung von Eisen aus einem Hartchromelektrolyten, Galvanotechnik **87** (6) (1996) 1887 (in German).
27. A.R. Boyce and D.J. Kavanaugh (1988) Electrolytic regeneration of chromic/sulfuric acid etchant. AESF/EPA Conference on Environmental Control for the Metal Finishing Industry.
28. B. Jeanmenne and S. Perrone (1993) Caterpillar, Pennsylvania recovers hard chrome. 80th AESF Annual Technical Conference (Anaheim, CA, USA). (American Electroplaters & Surface Finishers Soc Inc).
29. S.L. Guddati, T.M. Holsen, C.-C. Li, J.R. Selman, and N.V. Mandich, The use of a porous ceramic diaphragm for the removal of metallic impurities from chromium plating baths, J. Appl. Electrochem. **29** (1999) 1129.
30. J. Pattanayak, K. Mondal, T. Wiltowski, S.B. Lalvani, and N.V. Mandich, Recovery of metallic impurities from chromium plating solutions by electromigration, Met. Finish. **98** (3) (2000) 39-45.

31. R. Audinos, Liquid waste concentration by electrodialysis, in "Separation and Purification Technology" N.N. Li and J.M. Calo, Editors. 1992, Marcel Dekker. p. 229-301.

Chapter 2

Chromic acid treatment and recovery by ion-exchange membranes – a literature review

Abstract

Membrane electrolysis (ME) is the only commercial technology using ion-exchange membranes for chromic acid recycling and recovery. On one hand, the technology has a number of promising advantages, but on the other hand, it has not yet gained common acceptance probably due to a lack of operation stability and efficiency. Published results of the research can be divided into three categories: lab scale studies, patents and systems, which have already been used at industrial scale. Furthermore, this literature review includes electro-electrodialysis (EED) and an overview about anion exchange membranes (AEM) used for applications with chromate containing solutions.

2.1 Membrane electrolysis

Membrane electrolysis (ME) combines electrolysis and dialysis. The technology is simple and includes impurity removal from the process and additionally, either anodic oxidation of trivalent chromium or chromic acid recovery from exhausted rinse water. Furthermore, the consumption of chemicals and energy is low. Two procedures are distinguished:

- Bath maintenance: exhausted plating solution is placed in the anode compartment, where trivalent chromium is oxidised. The other cations (impurities) migrate from the exhausted plating solution towards the cathode compartment through a cation-exchange membrane and accumulate there (Figure 2.1a). Some of the Cr(III) and Cr(VI) may be lost due to migration into the cathode compartment.
- Chromic acid recovery: exhausted chromic acid containing solution is placed in the cathode compartment. Chromate anions migrate from the waste water towards the anode through an anion-exchange membrane. In the anode compartment chromic acid is formed by protons generated at the anode (Figure 2.1b).

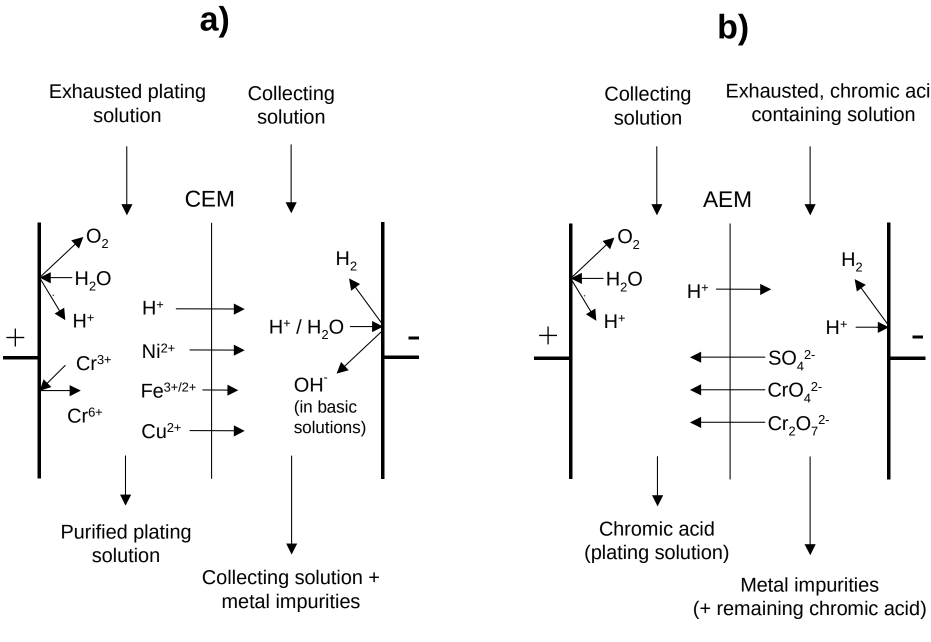


Figure 2.1. *Principles of membrane electrolysis with ion-exchange membranes. (a) Bath maintenance by anodic Cr(III) oxidation and removal of metal impurities using a cation-exchange membrane(CEM) and (b) chromic acid recovery using an anion exchange membrane.*

Lab-scale studies mostly aim on the improvement of process performance. In an early study, Ng and Snyder [1] investigated electrolysis (anodic Cr(III) oxidation) and dialysis (impurity removal) as two stage process. Later, research focused on electrode material for improved anodic re-oxidation of Cr(III) [2-5] and on the transport of cationic impurities through cation-exchange membranes (CEM). The transport of trivalent chromium through Nafion® 117, 417 and 450 was investigated by Dalla Costa et al. [6, 7] and Rodrigues et al. [8]. In addition, Huang et al. [9-11] studied the removal of Cu(II), Ni(II) and Fe(III) by Nafion® 117 in comparison to ceramic separators. The authors found better removal rates for the membrane than for the ceramic separator. Ahmed et al. [12] also used Nafion® 117 and developed a mathematical model to simulate impurity removal from chromium plating solutions. Additionally, the authors achieved higher process efficiency by a gas diffusion electrode [13, 14].

An alternative system was proposed by Renz et al. [15]. The authors used a combination of ME (equipped with a CEM) and ion exchange technology. As for standard ME, exhausted plating bath flows through the anode compartment and impurities migrate towards an ion-exchange cathode which contains a mixture of high surface area graphite particles and a cation-exchange resin. The advantage is, that high concentrated chromic acid does not touch the resin and sludge production at the cathode is avoided since the metal ions enter the resin.

Different systems were early patented and further developed, particularly by a number of German researchers and U.S. manufactures [16]. The plating bath was maintained by anodic oxidation of Cr(III) and by impurity removal using a CEM (membrane electrolysis) or a diaphragm (ion-transfer) [17-23]. Otherwise, chromic acid was recovered from exhausted effluents by migration of chromate anions towards the anode through an anion-exchange membrane (AEM) [24, 25] or a diaphragm [26, 27]. Another patent [28] describes a hybrid recovery process where hexavalent chromium is recovered from sludge, which contains only trivalent chromium and other metals. The trivalent chromium is oxidised in the anodic compartment of an electrolytic oxidation cell to hexavalent chromium and then further treated in a coupled transport module. This electrolysis cell is divided by the AEM IONAC MA-3475 and RAIPORE 4035.

Despite of the significant number of patents only few systems went beyond pilot scale and were used in electroplating companies. Cushnie [16] gives a detailed overview about industrial application of ME. In addition, up-scaled plants were reported from the Keihin Island in Japan [29], from Linnhoff [30] and Nonaka et al. [31]. The companies INNOVA Inc. [32, 33], Schering AG [34] and Kurion Technologies Ltd. [35] also reported up-scaled systems, partly sold as commercial systems. The commercial ME systems are ChromeNapper^{TM} from INNOVA Inc., CROMOX^{TM} from Kurion Technologies Ltd and the system 'Cat-Napper' [36], which is strictly speaking an ion-transfer technology [16]. Most systems provide modular cartridges hanging either in a separate, a catholyte solution containing tank or in exhausted rinse water. The operating principle of the systems differs in the type of separator. The ChromeNapper^{TM} works as recovery technology with an anion-exchange membrane. The maximum concentration of the recovered chromic acid is 75–100 g l^{-1}, in order to maximize the membrane life time [33]. The other two systems (CROMOX^{TM} and 'Cat-Napper') are equipped with a polyfluorocarbon membrane and operate with exhausted plating solution in the anode compartment. In the cathode compartment separated impurities (metal ions) accumulate, precipitate by increasing pH and form sludge, which has to be removed. Therefore, these systems require frequent cleaning of the cathode compartment and continuous operation (to prevent membrane scaling by fluorides). The CROMOX^{TM} system especially strives for long-term use of cathode solution by continuously removal of precipitated metals by a simply settler.

Two-compartment membrane electrolysis has not gained common acceptance in plating businesses, probably due to a lack of operation stability and efficiency. Therefore, research was continued, mainly by a number of German researchers [4, 37-40]. In addition, the promising three-compartment electro-electrodialysis (EED) became the focus of research and development.

2.2 Electro-electrodialysis

Actually, membrane electrolysis (ME) and electro-electrodialysis (EED) are based on the same principle. Both combine electrolysis reactions at the electrodes and electrodialysis. However, in the literature both terms are used independently and EED is distinguished into two- and three-compartment systems. In this part the literature concerning EED is briefly reviewed.

Two-compartment EED systems are equipped with an anion-exchange membrane (AEM), which allows the migration of chromate anions from exhausted solutions through the membrane towards the anode compartment (see Figure 2.1b). There, chromic acid is formed with protons generated at the anode. For instance, this technology was described by Audinos [41] proposing a two-compartment EED for chromic acid recovery up to 280 g l^{-1} and energy consumptions in the range of 10–20 kWh per kg_{CrO3}. Frequent AEM replacement was required since the membrane worked under very severe conditions. Audran et al. [25, 42] pointed out that poor AEM stability might prevent application of this technology and studied a two compartment EED system using an AEM by the company MORGANE (France). They could reach an average current efficiency of 48 % and power consumptions of 18 kWh per kg_{CrO3} at 40°C and 50 mA cm^{-2}. The maximum anolyte (product) concentration was 310 g l^{-1} CrO_3. The authors stated, that the membranes have been working for 4000 hours, however the performance during this long period was not reported and further commercialisation is not known. Cohen and Duclert [43] also described a two-compartment EED configuration equipped with anion exchange membranes from MORGANE (type ARA 17-10) and Sybron Co. (IONAC 3475 XL). Two applications for chromic acid recovery were briefly considered: re-concentration of chromic acid in the anode compartment from chromic acid plating solution (250 g l^{-1} at 58°C) and from a solution containing 8 g l^{-1} CrO_3 and 1.6 g l^{-1} Fe, which was re-concentrated to 323 g l^{-1} in the anode compartment. Using the high concentrated plating solution, the AEM MORGANE ARA 17-10 showed better transfer rates and lower power consumption than the IONAC MA 3475 XL. However, the authors did not mention the test duration and long-term stability of the membranes.

Other studies described the transport properties of anion-exchange membranes at low chromate concentration solutions. The AEM used were SB 6407 (Gelman Science), Neosepta AFN and ACM (Tokuyama Soda Co.) at 0.01 M $K_2Cr_2O_7$ [44], Raipore 1030 (RAI Research Co.) at 0.02 M Cr(VI) solutions [45, 46] and Selemion AMT (Asahi Glass Co.) in solution containing 1.7 g l^{-1} Cr(VI) [7]. Vallejo et al. [47] found that the membrane AW 11 (Solvay Co.) was not suitable for chromic acid recovery because of rapid increase of membrane resistance. However, Vallejo et al. [48] reported more promising results with the AEM IONAC MA-3475 (Sybron Co.). They showed that the Cr(VI) concentration in the anode compartment, the pH and temperature are critical parameter influencing the process. The maximum current efficiency achieved in acid environment was ~11 %. Roualdes et al. [49] tested a new AEM from plasma-grafted PVDF polymers with hexavalent chromium containing solutions obtaining Cr(VI) transport number of 0.16.

From a process design point of view, the *three-compartment* EED technology might be better for the plating industry, because it can manage three different tasks simultaneously: (i) removal of contaminants, (ii) chromic acid recovery and (iii) purification of static rinse water (Figure 2.2).

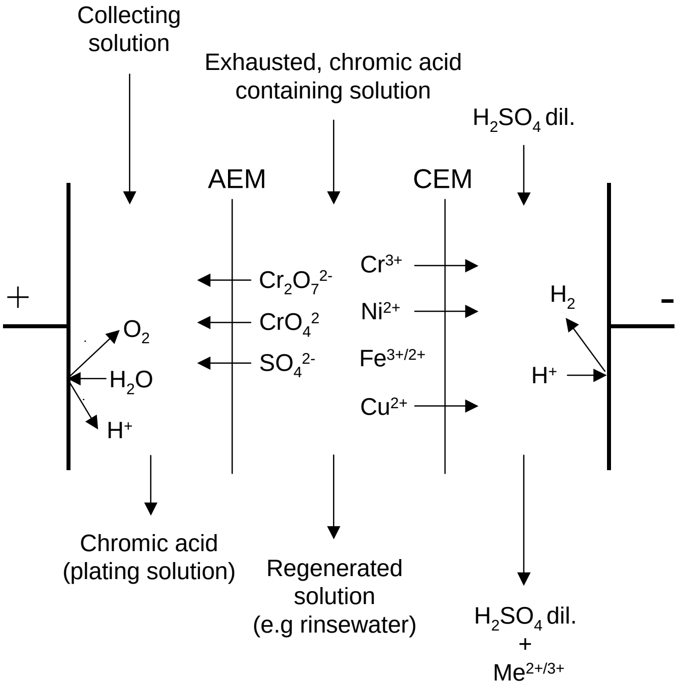


Figure 2.2. *Principles of three-compartment electro-electrodialysis (EED) for chromic acid recovery.*

Dalla Costa et al. [7] compared a two- and three-compartment configuration at lab-scale and found maximum process efficiency in the three-compartment system in the absence of sulfate ions. A publication and patent of Bergman and Iourtchouk [4, 50] describe a three-compartment cell for chromic acid recovery at bench-scale. The authors studied various electrode materials and compared a two- and three-compartment system using exhausted plating solution in the central compartment. They reported process limitations due to high voltage increase and current efficiencies between 12 % (chromating solution) and 20 % (hard chromium plating solution). However, the type of AEM, membrane stability and test duration was not stated. Shuster et al. [22] and Kidon et al. [23] also patented a three-compartment system, however, they used a porous diaphragm to separate the anode compartment.

Three-compartment EED seems better to meet the demands of the plating industry for successful and simple chromic acid recovery. However, up to now this technology was not yet industrially applied and the literature in this field shows, that the main reasons are poor anion-exchange membrane stability and process limitations by high voltage drop. Existing publications does not prove either long-term stability of commercially AEM and membrane modules nor propose solutions to overcome the process limitations. This thesis aims to evaluate suitable anion-exchange membranes regarding their stability, long-term performance and optimum process conditions and possible implementation of this technology in the industry.

Besides, alternative solutions for waste minimization in chromium plating industry are evaluated. The electrochemical reduction of chromate on carbon felt is an alternative method to the chemical chromate reduction and could help to reduce the amount of treatment chemicals used and the sludge produced. The combination of membranes and evaporation could be an efficient way to downsize the cost and energy intensive evaporation equipment. A combination of different membrane processes is studied for efficient reduction of the waste water volume before evaporation.

2.3 References

1. P. Ng and D. Snyder, Combining electrolysis and dialysis for regeneration of chromic acid etching solution, J. Memb. Sci. **13** (1983) 327-336.
2. K. Mondal, N.V. Mandich and S.B. Lalvani, Regeneration of hexavalent chromium using a Bi-doped PbO_2 anode, J. Appl. Electrochem. **31** (2001) 165-173.
3. Y. Van Andel and L.J.J. Janssen, Electrochemical regeneration of chrome etching solution, J. Appl. Electrochem. **32** (2002) 481-486.
4. T. Iourtchouk and H. Bergmann, Elektrochemische Regenerierung vorzugsweise chromhaltiger Systeme, in "Jahrbuch der Oberflächentechnik", A. Zielonka, Editor. 2003, Eugen G. Leuze Verlag, Bad Saulgau. p. 206-221 (in German).
5. D. Meyer, N. Nowack, S. Dressen and A. Rheindorf, Regenerierung chromsäurehaltiger Elektrolyte, Metalloberfläche **55** (10) (2001) 17 (in German).
6. R.F. Dalla Costa, J. Zoppas Ferreira and C. Deslouis, Electrochemical study of the interactions between trivalent chromium ions and Nafion perfluorosulfonated membranes, J. Memb. Sci. **215** (2003) 115-128.
7. R.F. Dalla Costa, M.A.S. Rodrigues and J.Z. Ferreira, Transport of trivalent and hexavalent chromium through different ion-selective membranes in acidic aqueous media, Sep. Sci. Technol. **33** (8) (1998) 1135-1143.
8. M.A.S. Rodrigues, R.F. Dalla Costa, A.M. Bernardes and J. Zoppas Ferreira, Influence of ligand exchange on the treatment of trivalent chromium solutions by electrodialysis, Electrochim. Acta **47** (5) (2001) 753-758.
9. K.-L. Huang, T.M. Holsen and J.R. Selman, Impurity partitioning in nafion and ceramic separators used for purification of spent chromium plating solutions, J. Memb. Sci. **210** (2002) 137-145.
10. K.-L. Huang, T.M. Holsen, T.-C. Chou and J.R. Selman, Comparing Nafion and ceramic separators used in electrochemical purification of spent chromium plating solutions: cationic impurity removal and transport, Environ. Sci. Technol. **37** (9) (2003) 1992-1998.

11. K.-L. Huang, T.M. Holsen and J.R. Selman, Impurity Diffusion through Nafion and ceramic separators used for electrolytic purification of spent chromium plating solutions, J. Memb. Sci. **221** (2003) 135-146.
12. M.I. Ahmed, H.T. Chang, J.R. Selman and T.M. Holsen, Electrochemical chromic acid regeneration process: fitting of membrane transport properties, J. Memb. Sci. **197** (2002) 63-74.
13. M.I. Ahmed, T.M. Holsen and J.R. Selman, Electrochemical chromic acid regeneration process with fuel-cell electrode assistance. Part I: Removal of contaminants, J. Appl. Electrochem. **31** (2001) 1381-1387.
14. M.I. Ahmed, T.M. Holsen and J.R. Selman, Chromic acid regeneration process with fuell cell electrode assistance. Part II: Electrochemical characterization, material compatibility and energy consumption, J. Appl. Electrochem. **31** (2001) 1389-1394.
15. R.P. Renz, T.M. Schumaker, J.J. Sun, J.D. Chromick, B.J. Grant, E.J. Taylor, P.O. Miller, and C.D. Zhou (1999) In-process recycling of a hexavalent chromium plating bath. (AESF SUR FIN - Proceedings).
16. Pollution Prevention and Control Technologies for Plating Operations [Online]. Available: www.nmfrc.org/bluebook/tocmain.htm [2004, September, 2]
17. F. Akira (1976) Process for the regeneration of exhausted chromium plating solutions by two-stage diaphragm electrolysis. Patent US 3948738
18. L.E. Lancy and E. City (1969) Apparatus and procedure for reconditioning metal treating solutions. Patent US 3481851
19. B.J. Swink and P.M. Phillips (1989) Chromium solution regenerator. Patent US 4857162
20. J.D. Troyer, A.A. Cochran and D.M. Soboroff (1982) Regeneration of waste metallurgical process liquor. Patent US 4337129
21. T. Zenon (1979) Apparatus for the electrolytic regeneration of hexavalent chromium compounds and recovery metals from waste bichromate solutions. Patent CA 1057234
22. N. Shuster, A.D. Babinsky and W.E. Kidon (1981) Chromic acid production process using a three-compartment cell. Patent US 4290864

23. W.E. Kidon, N. Shuster and A.D. Babinsky (1981) Production of chromic acid using two-compartment and three-compartment cells. Patent US 4 273 628
24. H. Iida (1998) Chromium plating solution, solution waste from chromium plating and closed recycling system for chromic acid cleaning water in chromium plating. Patent US 5 766 428
25. J. Audran, M.-M. Letord and A. Ducourroy (1992) Electrochemical cell, especially for recycling of chromic acid. Patent EP 0483015
26. J.I. Bishara, J.R. Brannan, R.J. Horvath, A.R. Sacco, and J.M. Hinden (1995) Electrolytic treatment of an electrolytic solution. Patent US 5 593 627
27. J.I. Bishara, R.J. Horvath, A.R. Sacco and J.M. Hinden (1998) Apparatus for electrolytic treatment of an electrolytic solution. Patent US 5 827 411
28. D.R. Kamperman and D.T. Friesen (1990) Hybrid chromium recovery process. Patent US 4948476
29. Die Keihin-Insel - Industriegebiet für Galvanisierbetriebe, Galvanotechnik **69** (5) (1978) 391 (in German).
30. F. Linnhoff, Anwendung der Electrodialysetechnik zur Rückgewinnung von Galvano-Elektrolyten., Metalloberfläche **34** (6) (1982) 284-286 (in German).
31. Y. Nonaka and T. Miyasaka, Regulating of bath concentration by electrodialysis of chromium plating solution, Kinki Aruminyumu Hyomen Shory, J. Alum. Finish. Soc. Kinki **138** (1989) 1-9 (in Japanese).
32. L. Hartinger, Handbuch der Abwasser- und Recyclingtechnik für die metallverarbeitende Industrie. 1991, Carl Hanser Verlag: München Wien. p. 530 (in German).
33. Bumper plater recovers chromic acid with new process, Plat. Surf. Finish. (April) (1980) 34-37.
34. G.A. Lausmann and J.N.M. Unruh, Die galvanische Verchromung, in "Schriftenreihe Galvanotechnik". 1998. p. 393 (in German).
35. CROMOX^{TM} regeneration system [Online]. Available: www.kurion.co.uk [2003, May 14]
36. T. Schwuch, Membranelektrolyse zur Reinigung und Standzeitverlängerung von Chromelektrolyten - Erfahrungsbericht aus der galvanotechnischen Praxis, Galvanotechnik **92** (5) (2001) 1260-1262 (in German).

37. G. Bormann and A. Möbius, Membranelektrolyse zur Instandhaltung von Hartchrombädern - Ein Beitrag zur drastischen Verringerung von Abwasser und Schlamm, Galvanotechnik **83** (1) (1992) 93-96 (in German).

38. H. Bergmann and T. Iourtchouk, Untersuchungen zur Regenerierung von Chromelektrolyten, Galvanotechnik **88** (3) (1997) 775-784 (in German).

39. H. Bergmann and T. Iourtchouk, Elektrochemische Regenerierverfahren in der Umweltschutztechnik, Galvanotechnik **89** (5) (1998) 1623-1633 (in German).

40. W. Blatt and L. Schneider, Geteilte Elektrolysetechnik, Metalloberfläche **50** (9) (1996) 694-696 (in German).

41. R. Audinos, Liquid waste concentration by electrodialysis, in "Separation and Purification Technology" N.N. Li and J.M. Calo, Editors. 1992, Marcel Dekker. p. 229-301.

42. J. Audran, P. Baticle and M.-M. Letord (1990) Recycling of chromic acid by electro-electrodialysis. Vth World Filtration Congress (Nice, France).

43. T. Cohen and F. Duclert, Récupération des acides et des métaux par de nouvelles membranes échangeuses d'ions, Rev. gén. électr. (3) (1992) 17-19 (in French).

44. Y. Çengeloglu, A. Tor, E. Kir and M. Ersöz, Transport of hexavalent chromium through anion-exchange membranes, Desalination **154** (3) (2003) 239-246.

45. E. Castillo, M. Granados and J.L. Cortina, Chromium(VI) transport through the Raipore 1030 anion exchange membrane, Anal Chim Acta **464** (1) (2002) 15-23.

46. E. Castillo, M. Granados and J.L. Cortina, Chemically facilitated chromium(VI) transport throughout an anion-exchange membrane: Application to an optical sensor for chromium(VI) monitoring, J. Chromatogr. **963** (1-2) (2002) 205-211.

47. M.E. Vallejo, P. Huguet, C. Innocent, F. Persin, J.L. Bribes, and G. Pourcelly, Contribution of raman spectroscopy to the comprehension of limiting phenomena occurring with a vinylpyridinium anion exchange membrane during the electrolysis of Cr(VI) solutions, J. Phys. Chem. B **103** (51) (1999) 11366-11371.

48. M.E. Vallejo, F. Persin, C. Innocent, P. Sistat, and G. Pourcelly, Electrotransport of Cr(VI) through an anion exchange membrane, Sep. Purif. Technol. **21** (2000) 61-69.

49. S. Roualdes, N. Kourda, J. Durand and G. Pourcelly, Plasma-grafted PVDF polymers as anion exchange membranes for the electrotransport of Cr(VI), Desalination **146** (2002) 273-278.

50. H. Bergman and T. Iourtchouk (1999) Verfahren und Zelle zur Regenerierung chromhaltiger Systeme. Patent DE 19733064 A1

Chapter 3

Chromic acid recovery by electro-electrodialysis I. Evaluation of anion exchange membrane*

Abstract

Electro-Electrodialysis (EED) is a promising technology for economic recovery of chromic acid in plating companies. It could potentially achieve chromic acid recovery, removal of metallic impurities and purification of static rinses in one step. There are however, process limitations. These are mainly, the poor stability of the applied anion exchange membrane (AEM) against the oxidative chromic acid solution and the increase of the AEM resistance, especially at the starting phase of the process, due to the formation of polychromates in the membrane.

In this work, various AEM are investigated for chromic acid recovery. The membrane fumasep® FAP (FuMA-Tech GmbH) seems to be the most efficient. Its current efficiency is much higher than those previously reported in the literature. Furthermore, the fumasep® FAP is used for process optimisation experiments. The process performance depends on the concentration gradient between product (anolyte) and central compartment (exhausted rinse water) and the temperature. Our results show that batch processing is recommended and the chromate transfer rates through the AEM could be significantly increased when increasing the temperature up to 50°C. Finally, low initial current density (10-20 mA cm^{-2}), feed flow rate higher than 7 cm s^{-1} could help overcoming the process limitations attributed to high AEM resistance.

---

* Parts of this chapter has been published in Journal of Membrane Science (in press).

3.1 Introduction

Safe handling of hexavalent-type chromium solutions is a big challenge for the chromium electroplating industry due to its toxicity and carcinogenicity [1-4]. 20–60 % of the chromic acid used in Europe is being wasted instead of re-used [5]. Since many years [6, 7] there are more and more legislative restrictions forcing for changes. At chromium plating process, hexavalent chromium is reduced in a multi-stage deposition reaction to elementary chromium. In this process besides trivalent chromium other undesirable impurities are present (iron, copper, aluminium, zinc, organics, chlorides etc.). Such impurities could accumulate during the deposition process and create deposits of unacceptable quality. Moreover, these impurities reduce the cathode current efficiency and the bath conductivity and increase resistance. Therefore, exhausted plating solutions should be replaced.

Electro-electrodialysis (EED) could be a promising technology for efficient chromic acid recycling. EED combines electrolysis and electrodialysis. It allows removal of chromic acid from the plating bath (together with impurities) and recovering it from static rinse solution. Figure 3.1 shows the process principles. One module consists of three compartments and the outer compartments include the electrodes. The rinse water from the plating process containing chromic acid and metallic impurities such as copper, iron, zinc, aluminium, nickel and trivalent chromium, flows through the central compartment. Cationic impurities migrate towards the cathode through the cation-exchange membrane (CEM). The cathode compartment is fed with diluted sulphuric acid to form dissolved metal sulphates. The acidic conditions prevent precipitation of metal hydroxides. Hexavalent chromium anions (chromates) migrate towards the anode through the AEM. There, chromic acid is formed by the chromate and dichromate anions and the protons generated at the anode. The treated rinse water is reused in the rinsing process and the pure chromic acid is returned to the plating bath. This process provides purification of chromium plating solutions and the treatment of the rinse water in a single step without need of either water or chemicals. Exhausted catholyte solutions can be treated by common physical-chemical treatment together with other effluents generated in plating companies. With respect to industrial requirements some process parameters are fixed. The concentration of the chromic acid recovered should be higher than 1 mol l^{-1} CrO_3 in order to avoid strong dilution of the process bath. The average concentration of the static rinse water is 0.1 mol l^{-1} CrO_3, but can strongly differ depending on the plating company.

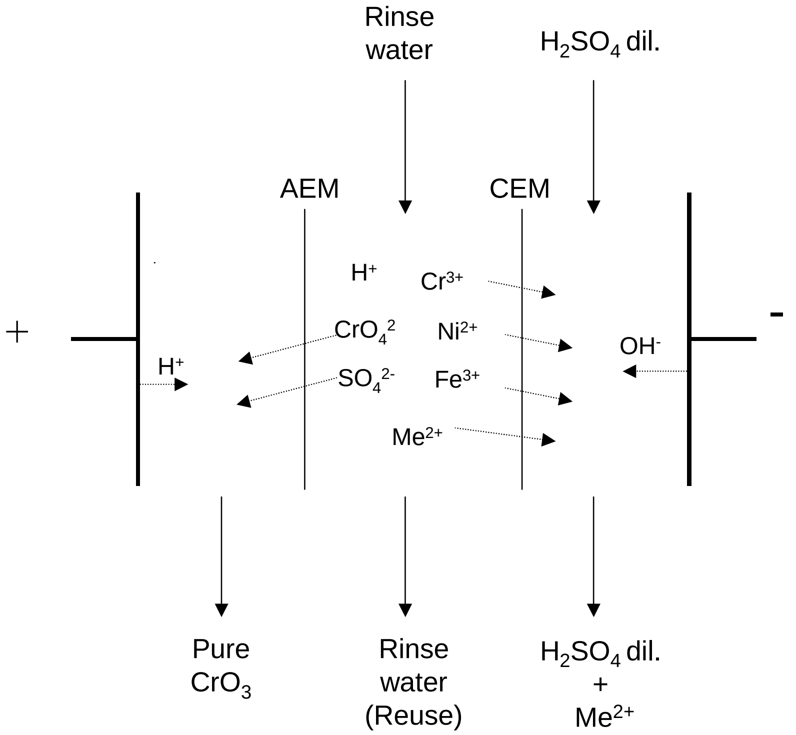


Figure 3.1. *Principles of electro-electrodialysis (EED) for chromic acid recovery.*

The EED process was described by Audinos [8] proposing a two-compartment EED with an anion exchange membrane for chromic acid recycling up to 228 g l^{-1} and energy consumptions in the range of 10–20 kWh per kg_{CrO3}. AEM replacement was frequently required due to deterioration. Audran et al. [9, 10] also studied a two compartment EED system using an AEM by the company MORGANE (France) and pointed out that poor AEM stability might prevent application of this technology. They could reach an average current efficiency of 48 % and power consumptions of 18 kWh per kg_{CrO3} at 40°C and 50 mA cm^{-2}. The maximum anolyte (product) concentration was 310 g l^{-1} CrO_3. Other studies described the transport properties of anion-exchange membranes at low chromium concentration solutions. The AEM used were SB 6407 (Gelman Science), Neosepta AFN and ACM (Tokuyama Soda Co.) at 0.01 M $K_2Cr_2O_7$ [11] and Raipore 1030 (RAI Research Co.) at 0.02 M Cr(VI) solutions [12, 13]. Dalla Costa et al. [14] studied the

Selemion AMT (Asahi Glass Co.) membrane in solution containing 1.7 g l^{-1} Cr(VI). They compared a two and three compartment configuration and found maximum process efficiency in the three-compartment system in the absence of sulfate ions. Vallejo et al. [15] found that the membrane AW 11 (Solvay Co.) was not suitable for chromic acid applications because of rapid increase of membrane resistance. However, Vallejo et al. [16] reported more promising results with the AEM IONAC MA-3475 (Sybron Co.). They showed that the Cr(VI) concentration in the anode compartment, the pH and temperature are critical parameters influencing the process. The maximum current efficiency achieved in acid environment was ~11 %. Roualdes et al. [17] tested a new AEM from plasma-grafted PVDF polymers with hexavalent chromium containing solutions obtaining Cr(VI) transport number of 0.16. Finally, it is worth noting that less membrane stability problems occur when using perfluorosulfonated CEM, which are stable in chromic acid. Nevertheless, the efficiency for the removal of cationic contaminants is low compared to the anodic electrolyse efficiency (anodic oxidation of Cr(III) to Cr(VI)) [14, 18-26].

In this work, the newly developed AEM (fumasep® FAP FuMA-Tech GmbH, Germany) is compared with other commercial membranes for the recovery of chromic acid by EED showing promising results and overcoming above described obstacles. In addition, the application of this membrane under various process conditions is studied aiming to the optimisation of the process and to the successful up-scaling.

3.2 Experimental

3.2.1 Membranes, chemicals and analysis

The IONAC MA 3475 (Sybron Co.), PC 100 D (PCA GmbH) and the newly developed fumasep® FAP FuMA-Tech membranes were selected for a membrane screening (see Table 3.1). The fumasep® FAP membrane could only be used at acidic environment, therefore the permselectivity, area resistance and IEC could not be determined by standard methods. As cation exchange membrane (CEM) reinforced Nafion®324 (Du Pont Polymers) was used (see Figure 3.1).

Table 3.1. *Characteristics of AEM used in membrane screening experiments.*

	PC 100 D	**IONAC MA-3475**	**fumasep® FAP**
Manufacturer	PCA GmbH	Sybron Chemicals Inc.	FuMA-Tech GmbH
Reinforcement	Reinforced	Reinforced	Plain film
Thickness (μm) [a]	110	570	46
Swelling (%)	39.8	27.2	30.4
Area resistance (Ω cm^2) [b]	1.87	30	n.a.*
Permselectivity (%) [c]	91.0	92.3	n.a.*
IEC (meq g^{-1})	1.45	1.26	n.a.*

*n.a: not available (see text)

Test conditions:

[a] membranes left for 24 h in measuring solution

[b] 0.5 N NaCl, 25 °C

[c] 0.1 N KCl / 0.5 N KCl, 25 °C

All solutions were prepared using deionized water. Synthetic rinsing solution was prepared from chromium (VI) oxide (Fluka Chemie GmbH, 27083, p.a.) and nickel(II) sulfate hexahydrate (VWR International, 106727, p.a.). Sulfuric acid was also from VWR International (100731, p.a.). The chromic acid was determined by iodometric potentiometric titration with thiosulphate using a combined Pt electrode (Mettler-Toledo GmbH, DL67 automatic titrator and ST20A sample changer). The chemicals used for this determination were potassium iodide (Riedel-de Haën, 30315, p.a.), sulfuric acid (VWR International, 100731, p.a.) and 0.1 N sodium thiosulfate solution (VWR International, 109950, Titrisol®). The proton concentration (acidity) was determined by acid-basic titration and the metals were analysed by ICP.

3.2.2 Equipment and process conditions

For the comparison of the AEM and the influence of temperature, current density and concentration, the tests cell consisted of three compartments divided by the AEM and the CEM. The cell frames were made of polypropylene pressed together with gaskets (Viton®) between two endplates (Figure 3.2).

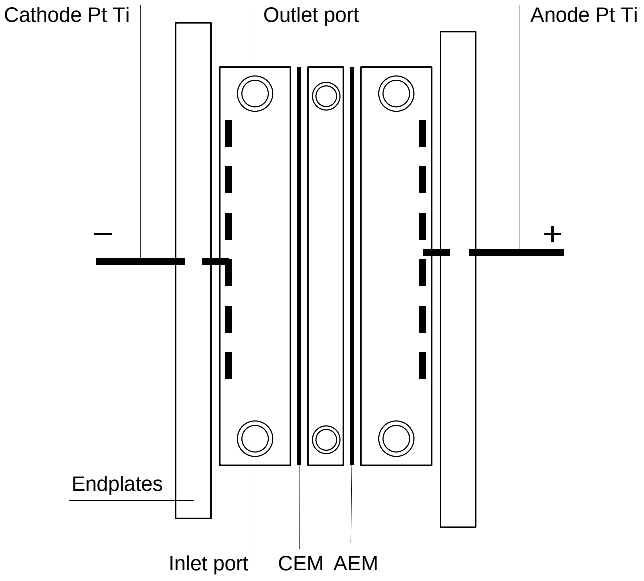


Figure 3.2. *Three-compartment test cell.*

The compartment thickness was 0.7 cm for the central and 1.2 cm for the outer compartments. Polypropylene spacers (Naltex® 3604) were used for turbulence improvement and membrane support. The effective membrane area was 100 cm^2. Haber-Luggin capillaries were installed to measure single membrane potentials. For this, and due to the strong chromic acid solution, a resistant solid electrolyte capillary filling was developed containing sodium trisilicate, potassium chloride and hydrochloric acid. The voltage drop over the AEM was measured with Ag/AgCl/KCl (saturated) reference electrodes. As electrode material platinised titanium was used (mesh type). The test equipment was designed for minimum dead volume (app. 0.4 l per compartment) in order to follow concentration changes within short experimental time (2 hours). All solution reservoirs were kept at constant temperature using double wall glass bottles and three magnetic drive pumps supplied the cell (flow velocity in all compartments was adjusted to 10 cm s^{-1}). Power was supplied by a Voltcraft laboratory rectifier (0–2.5 A, 0–30 V).

The experiments for optimisation of flow velocity were performed with the commercial Micro Flow Cell® from ElectroCell A/S, Denmark and an ED pilot plant which allow the adjustment of different flow velocities. The cell was equipped with a MOX coated Ti anode (DSA® for O_2) and a stainless steel cathode. The synthetic rinsing solution for the central compartment contained 0.1 M CrO_3, 0.01 M $NiSO_4$ and 10^{-4} M H_2SO_4 except one experiment where a mixture of 0.3 M CrO_3 and 0.003 M H_2SO_4 was used. The anolyte solution ranged from 0.1–1 M CrO_3 (pure). The catholyte solution was basically 0.05 M H_2SO_4, except for the experiments where cell voltage was followed. There, 0.2 M H_2SO_4 solution was used (see results). The experiments were performed for up to 3.5 h at 20–50°C. The current density was varied from 10 to 30 mA cm^{-2}. During all experiments, samples from each compartment were regularly taken and analysed for chromate and total acidity. Parallely, the current, voltage, temperature, conductivity and pH in each compartment were carefully monitored.

3.3 Theoretical background

The process performance could be evaluated on the basis of current efficiency (concerning formation of chromic acid in the anode compartment) and specific energy consumption (kWh kg^{-1}). The overall current efficiency for the product (chromic acid), Φ_P^e, is defined as the current carried by chromate ions relative to the total current used:

$$\Phi^e = \frac{m \nu_e F}{M I t} \tag{3.1}$$

where m is mass of product, M its molar mass, ν_e the stoichiometric number of electrons for the reaction, F the Faraday constant, I is the electric current and t the time [27]. In chromic acid solutions the chromium is present as different anionic species (monochromate, dichromate, trichromate, polychromate ions). The formation of large polychromate ions increases at higher chromic acid concentration and low pH, as described by Šarmaitis et al. [28, 29]. In fact, the following reactions take place:

$$\begin{aligned} H^+ + HCrO_4{}^- + Cr_2O_7{}^{2-} &\leftrightarrow Cr_3O_{10}{}^{2-} + H_2O \\ H^+ + HCrO_4{}^- + Cr_3O_{10}{}^{2-} &\leftrightarrow Cr_4O_{13}{}^{2-} + H_2O \end{aligned} \qquad (3.2)$$

This means that different chromate species may migrate through the anion exchange membrane depending on solution composition. Rinsing effluents used in this study contained 0.1 M CrO_3 of pH around 1.2. The chromate ions are either monovalent or bivalent charged. At these conditions, the chromate is present as monochromate (mainly $HCrO_4^-$, 20 %), as dichromate ($Cr_2O_7^{2-}$ and $HCr_2O_7^-$, 62 %) and to a lower extent (18 %) as trichromate ($Cr_3O_{10}^{2-}$). The valence regarding one mol of chromium is predominantly 1. Therefore the stoichiometric number $v_e = 1$ was used in all calculations. Nevertheless, it should be considered that the interstitial pH in the membrane phase could be much lower resulting in increased polychromate formation in the membrane [15].

The specific energy consumption, $E_{S,m}$ (in kWh mol_{CrO3}^{-1}) is essential for comparison of the efficiency of the EED with other recycling methods. Here, the total cell voltage, U_c, is an important factor of influence:

$$E_{S,m} = \frac{U_c \, \nu_e \, F}{M \, \Phi^e} \qquad (3.3)$$

3.4 Results and discussion

3.4.1 Membrane screening

Experiments with diluted and highly acidic solution in the anode compartment were performed. The experiments with diluted chromate solution (anode compartment: 0.1 M CrO_3, i = 30 mA cm^{-2}, T = 30°C) were used for screening of the AEM and for comparison with recent literature results. Figure 3.3 shows the increase of Cr(VI) concentration in the anode chamber for the studied membranes and Table 3.2 presents the overall results. The experiment with fumasep® FAP was performed for only 1 hour due to the fast depletion of the rinse water in the central compartment resulting at low electrolyte conductivity. For this membrane, the current efficiency was more than 2 times higher than for the other membranes. Both fumasep® FAP and PC 100 D membrane show promising results having low power consumption per mol CrO_3. The IONAC MA 3475 membrane shows the lowest current efficiency and the highest power consumption due to high voltage drop. It is important to note that for this membrane our results are in excellent agreement with those reported earlier in the literature [16].

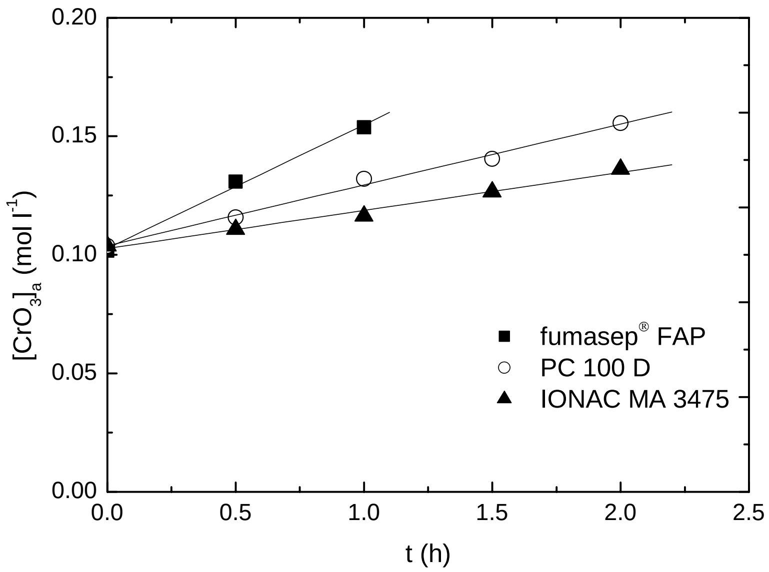


Figure 3.3. *Variation of CrO_3 concentration in the anode compartment. System parameters: 30 mA cm^{-2}, 30°C, anode compartment: 0.1 M CrO_3.*

Table 3.2. *Performance of the various AEM using 0.1 M CrO_3 in the anode compartment.*

	IONAC MA 3475	**PC 100 D**	**fumasep® FAP**
$\Phi^{e}_{CrO_3}$ (-) *	0.13	0.18	0.42
$E_{S,m}$ (kWh mol_{CrO3}^{-1})	3.7	1.0	1.1
Process parameters: i = 30 mA cm^{-2}, T = 30°C, (*) Overall current efficiency			

The performance of the PC 100 D, fumasep® FAP and IONAC MA 3475 membranes were then studied using 1 M CrO_3 concentration in the anode compartment. The experiments were conducted at lower current density (20 $mAcm^{-2}$) because high initial voltage increase was observed when using 30 mA cm^{-2}. In all cases, the current efficiency is lower compared to the previous experiments with 0.1 M CrO_3 solution (see Table 3.3). The fumasep® FAP shows the highest chromium transport and current efficiency and low power consumption. This membrane had the best overall performance; therefore it was further used in process optimisation experiments.

Table 3.3. *Performance of the various AEM using 1 M CrO_3 in the anode compartment.*

	IONAC MA 3475	**PC 100 D**	**fumasep® FAP**
$\Phi^{e}_{CrO_3}$ (-) *	0.10	0.08	0.14
$E_{S,m}$ (kWh mol_{CrO3}^{-1})	1.9	1.4	1.6
Process parameters: i = 20 mA cm^{-2}, T = 30°C (*) Overall current efficiency			

3.4.2 **Process optimisation**

3.4.2.1 Use of synthetic and industrial rinse water

Industrial rinsing solution was used in the central compartment to see whether the use of synthetic solution could effect the membrane performance. Depending on the bath type, the chromic acid solution could contain organic additives acting as reaction catalysts or wetting agents [30]. Fluoride surfactants could be present, which could cause fouling of the ion-exchange membranes [31-33]. The industrial solution for the central compartment was obtained from exhausted chromic acid bath from a plating company which produces chromium automotive accessories. The rinsing effluent was prepared by dilution. The composition of both synthetic and industrial solutions used in the central compartment is given in Table 3.4. The test parameters were the same as in membrane screening experiment. Table 3.5 presents the comparison showing that the current efficiency and the power consumption are comparable indicating the suitability of the membrane using industrial rinse solution.

Table 3.4. *Composition of effluents used in the central compartment (rinse solution).*

	Al	**B**	**Cr**	**Cu**	**Fe**	**Mg**	**Na**	**Ni**	**Pb**	**Zn**	**SO_4^{2-}**
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Synthetic	0	0	5730	0	0	0	0	651	0	0	1090
Industrial	< 3	15	5490	< 1.2	2.7	< 1	23	36	< 2	167	99

Table 3.5. *Effect of the type of rinsing solution on the performance of the fumasep® FAP membrane (1.0 M CrO_3 in the anode compartment).*

	Industrial rinse water	**Synthetic solution**
$\Phi^{e}_{CrO_3}$ (-) *	0.18	0.14
$E_{S,m}$ (kWh mol_{CrO3}^{-1})	1.1	1.6
Process parameters: i = 20 mA cm^{-2}, T = 30°C (*) Overall current efficiency		

3.4.2.2 Influence of chromic acid concentration in the anode compartment

The industrial process could be performed either in batch mode with fluctuating chromic acid concentration in the anode compartment (due to fluctuating acid recycling to the bath) or in continuous mode with permanent high acid concentration in the anode compartment (continuously acid recycling). Vallejo et al. [16] reported for the IONAC MA 3475 membrane that the current efficiency strongly depends on the anolyte concentration. In our experiments, the current efficiency for Cr(VI) transport decreases from 0.42 to 0.14 when the initial CrO_3 concentration in the anode compartment increases from 0.1 to 1 M (Figure 3.4).

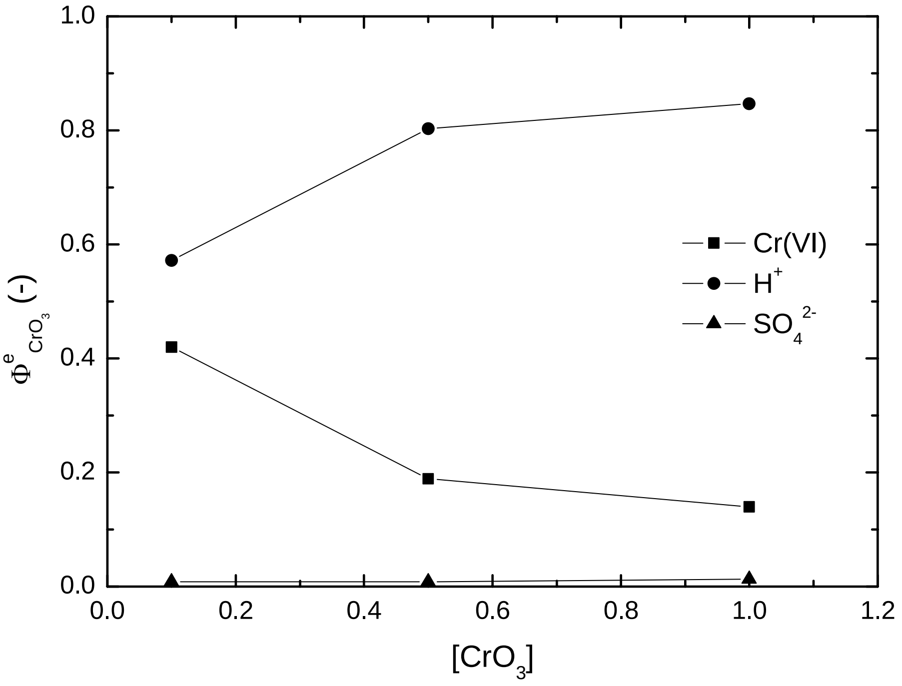


Figure 3.4. *Current efficiency for CrO_3, SO_4^{2-} and H^+ versus the initial CrO_3 concentration in the anode compartment. System parameters: AEM fumasep® FAP, 30 mA cm^{-2}, 30°C.*

The decrease of the current efficiency for Cr(VI) results in an increase of the current efficiency for protons from 0.57 to 0.85 whereas the sulphate transport remains generally low (Figure 3.4). Besides the proton leakage, a loss of water occurs in the anode compartment. Others [34] also studied the relationship between proton leakage and water flux at high acidic conditions and found that the proton flux increases while the water transport to the anodic side decreases, in agreement with our findings. Besides, the nature of chromic acid in the AEM is also important. Chromates could be present in many different species depending on pH and chromic acid concentration. At strong acid environment, the proton leakage could be enhanced by the formation of polychromates under dehydration acting as proton conductors [28, 29]. These large polychromates immobilised in the membrane could even reverse the AEM character due to their second negative charge. As a result, the membrane becomes highly permeable for protons and cations. Nevertheless, in our experiments no other cations besides protons where found in the anode compartment.

3.4.2.3 Influence of process temperature

Experiments with high chromic acid concentration in the anode compartment (~ 1 M) were performed, besides at 30°C (see earlier results), at 20 and 50°C, too. The CrO_3 concentration in the anodic compartment during the experiments is shown in Figure 3.5. Apparently, the product concentration increases much stronger at 50°C than at 20°C. Table 3.6 presents the current efficiencies and power consumptions.

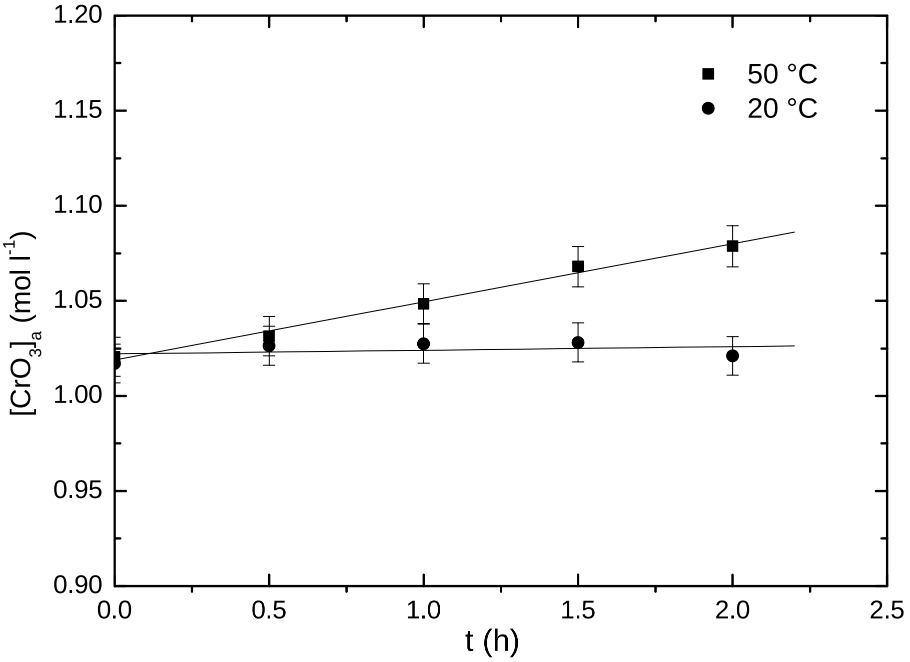


Figure 3.5. *Variation of CrO_3 concentration in the anode compartment at 20 and 50°C. System parameters: AEM fumasep® FAP, 20 mA cm^{-2}, anode compartment: 1.0 M CrO_3.*

Table 3.6. *Effect of temperature on the performance of fumasep® FAP membrane (1.0 M CrO_3 in the anode compartment).*

	20°C	**30°C**	**50°C**
$\Phi^{e}_{CrO_3}$ (-) *	0.04	0.14	0.33
$E_{S,m}$ (kWh mol_{CrO3}^{-1})	3.7	1.6	0.5
Process parameters: i = 20 mA cm^{-2} (*) Overall current efficiency			

The current efficiency was 0.33 at 50°C compared to 0.04 at 20°C. The increased chromium transport at higher temperatures could be attributed to lower proton leakage at higher temperatures [35]. The decrease of proton transport is mainly associated with reduced water organization at the membrane-solution interface at the anodic side [36]. Similar behaviour was also observed with the IONAC MA-3475 membrane [16] but not to this extent. For the latter, the current efficiency for hexavalent chromium was 0.16 at 50°C and 0.11 at 30°C using 0.1 M CrO_3 solution in the anode and central compartment. The difference in our case might be attributed to the high proton concentration in the anode compartment especially at the solution-membrane interface. The protons there have lower kinetic energy at higher temperatures and the entry into the membrane might be hampered.

In conclusion, the improved Cr transport at higher temperature could be exploited in the EED process. Nevertheless, the benefit from the improved transport should be weighed against long-term material stability (membranes and / or equipment) and extra heating costs of the process solutions.

3.4.2.4 Influence of current density – voltage drop

In all experiments, the voltage increases sharply during the first minutes. Both total voltage drop over the EED system and single voltage drop over the AEM were measured using Haber-Luggin capillaries. Figure 3.6 presents the first two hours of this experiment at 30 mA cm^{-2} showing that the increase of the cell voltage is parallel to the voltage increase over the AEM.

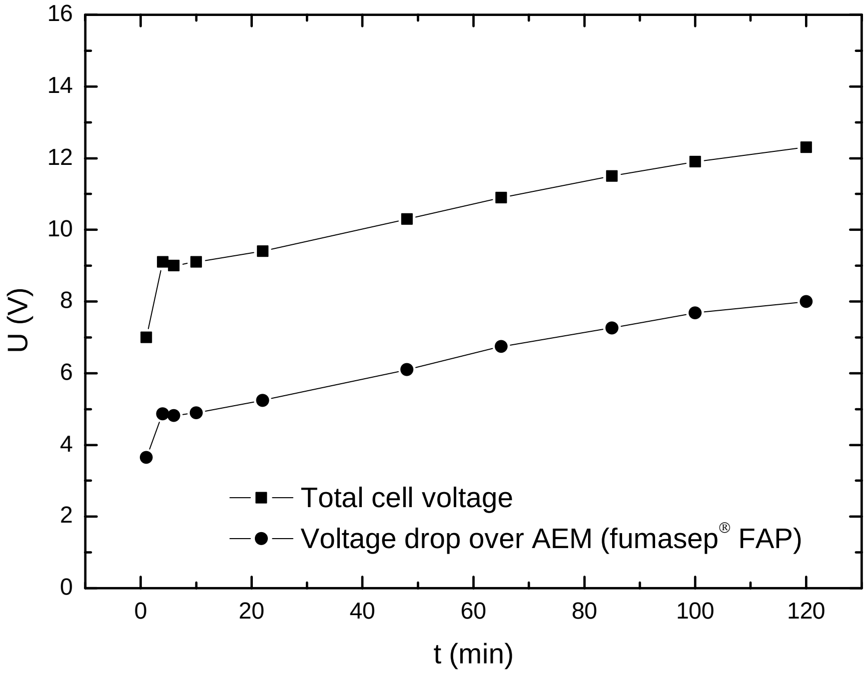


Figure 3.6. *The cell voltage at 30 mA cm^{-2}. Anode compartment: 1.2 M CrO_3 + 0.012 M H_2SO_4, central compartment: 0.3 M CrO_3 + 0.003 M H_2SO_4, cathode compartment: 0.2 M H_2SO_4 at 25°C*

Similar increase of resistance has been observed by Vallejo et al. [15], too. They attributed this phenomenon to the formation and accumulation of low mobility polychromate inside the membrane at high acidic conditions resulting to the deprotonation of the membrane active sides and increase of resistance. This was confirmed from the following experiments where a different AEM pre-treatment procedure is applied. A commercial test cell (Micro Flow Cell®) is used and 30 mA cm^{-2}

are applied. The first experiment is performed with 0.2 M H_2SO_4 in each compartment and the voltage stays constant at 2.7 V (Figure 3.7). A second piece of AEM is pretreated in 0.2 M H_2SO_4 and then directly overflowed with 0.1 M CrO_3 while the current starts passing. There is a strong increase in voltage observed in the beginning. The voltage reaches to 6 V in the first minute and remains at this level. Finally a piece of AEM is pretreated in 0.2 M H_2SO_4 and rinsed in 0.1 M CrO_3 for 2 h. Then, the experiment with 0.1 M CrO_3 is repeated and the voltage reaches very high level (18 V). From these results, we can conclude that the initial voltage is strongly associated with the chromic acid concentration inside the membrane and the formation of polychromates discussed earlier. It is worth to note, that De Körösy and coworkers [36, 37] also described the increase of the membrane resistance due to presence of multivalent ions in the membrane. However, they reported simultaneous breakthroughs of ions and change in membrane permselectivity, which we have not observed. Korngold et al. [31] have also reported similar behaviour for anionic membranes in the presence of insoluble acidic colloids.

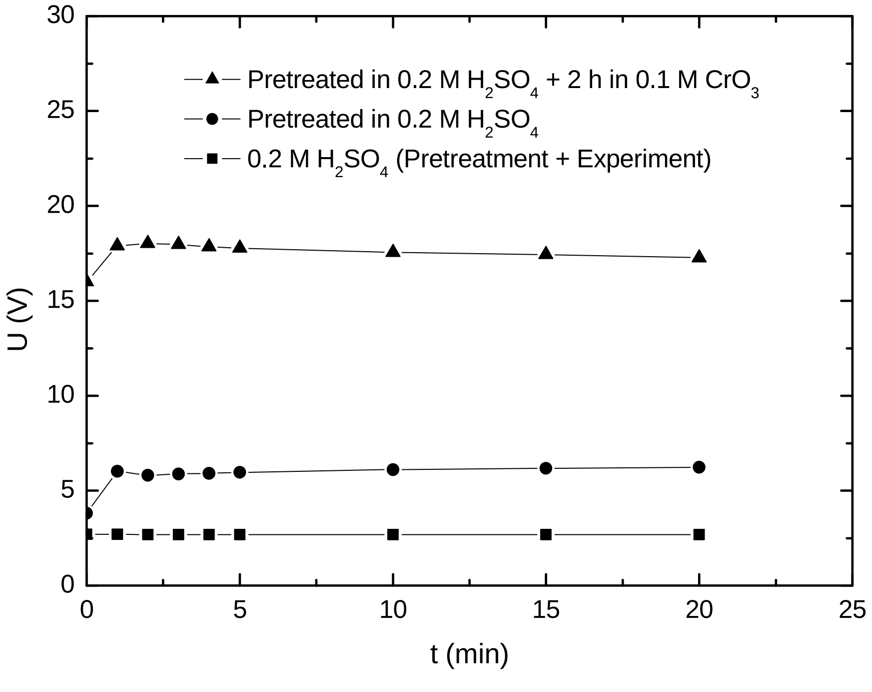


Figure 3.7. *The cell voltage at 30 mA cm^{-2}. System parameters: Micro Flow Cell®, AEM fumasep® FAP, 20°C, anode and central compartment: 0.1 M CrO_3 + 10^{-4} M H_2SO_4 or 0.2 M H_2SO_4; cathode compartment 0.2 M H_2SO_4, v = 7 cm s^{-1}.*

According to them the high initial membrane resistance could be reduced when using lower initial current densities and high flow rates. The following experiments aim to investigate this.

Figure 3.8 shows the variation of voltage in time at 20 and 30 mA cm^{-2} using 1 M CrO_3 anodic solution. The initial voltage increase is very rapid, especially for the higher current density. The average voltage drop is 7.7 V for 20 mA cm^{-2} and 13–15 V for 30 mA cm^{-2}. The increased current density (greater than 20 mA cm^{-2}) considerably improves the chromate transport (the chromate flux was around 30 % higher at 30 mA cm^{-2} in accordance to Faraday's law) but also results in a steadily growing high voltage drop over the EED system. This might cause damage on membranes and / or other equipment. Additionally, processing with increased voltage leads to high power consumptions. Table 3.7 presents the current efficiency and power consumption for these two current densities. Practically there are no differences in current efficiency between the two experiments. The power consumption was 1.6 kWh mol_{CrO3}^{-1} at 20 mA cm^{-2} and 2.5 kWh mol_{CrO3}^{-1} at 30 mA cm^{-2} due to higher cell voltage. All the above results show that the process should be operated at maximum 20 mA cm^{-2}.

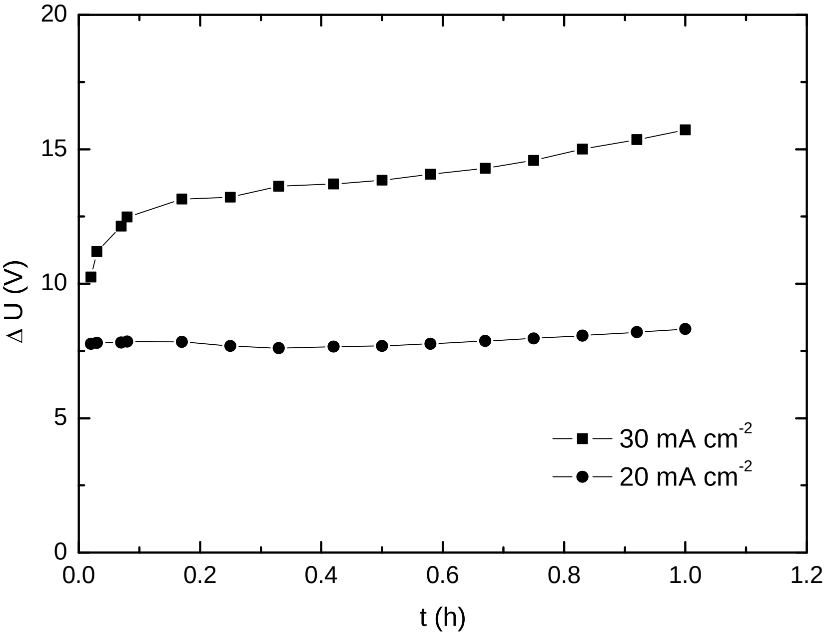


Figure 3.8. *The cell voltage at 20 and 30 mAcm^{-2}. System parameters: AEM fumasep® FAP, 30°C, anode compartment 1.0 M CrO_3, central compartment 0.1 M CrO_3 + 10^{-4} M H_2SO_4, cathode compartment 0.2 M H_2SO_4, v = 7 cm s^{-1}.*

Table 3.7. *Effect of the current density on the performance of fumasep® FAP membrane (1.0 M CrO_3 in the anode compartment).*

	20 mA cm^{-2}	**30 mA cm^{-2}**
$\Phi^{e}_{CrO_3}$ (-) *	0.14	0.14
$E_{S,m}$ (kWh mol_{CrO3}^{-1})	1.6	2.5
Process parameters: T = 30°C (*) Overall current efficiency		

The cell voltage was also measured in the Micro Flow Cell® at three different flow velocities. The superficial flow velocity was calculated for the empty space of the cell chamber. Before each experiment the voltage drop over the cell was determined using 0.2 M H_2SO_4 in all cycles at 30 mA cm^{-2} and found constant at 2.7 V. Then, 0.1 M chromic acid solution was placed into the anode and central compartment and the experiment started. After 20 minutes of operation, the cell voltage for velocities 5 and 7 cm s^{-1} was nearly the same and ~ 1 V higher than the voltage for 16 cm s^{-1} (Figure 3.9). At higher velocities, the concentration polarisation effects i.e. concentration decrease at the membrane surface facing the diluate compartment could be reduced and overall cell resistance could be kept lower [38]. In our application, the voltage could be only reduced by 1 V through application of higher flow rates.

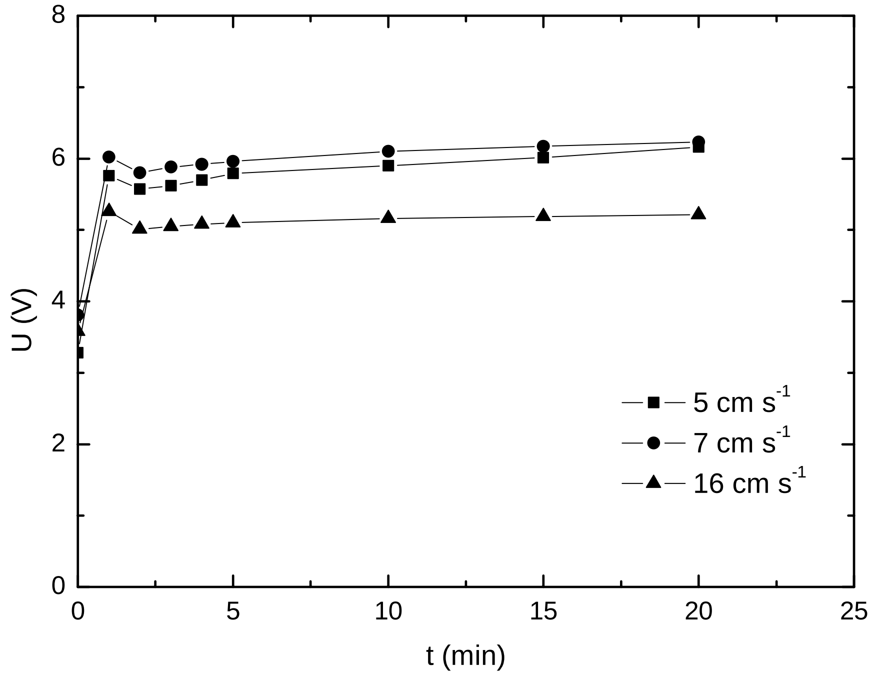


Figure 3.9. *The cell voltage at 30 mA cm^{-2}. System parameters: AEM fumasep® FAP, 20°C, anode and central compartment: 0.1 M CrO_3 + 10^{-4} M H_2SO_4, cathode compartment 0.2 M H_2SO_4.*

3.5 Conclusion and future work

Our work showed that the fumasep® FAP membrane seems to be a promising membrane for the chromic acid recovery EED process having better performance than the other two commercial membranes studied (IONAC MA 3475 and PC 100 D). The main factors influencing the current efficiency of the Cr transport seem to be the chromic acid concentration in the anode compartment and the process temperature. Low chromic acid concentration in the anode compartment and high temperature result in significantly higher chromate transport. A significant process limitation is the high membrane resistance due to the formation of polychromates inside the membrane. It was shown that low initial current densities and high flow rates could improve the process performance. Our results suggest that successful up-scaling of the EED process requires:

- Low initial current density (10–20 mA cm^{-2});
- High process temperature (between 40–50°C);
- High flow rates (above 7 cm s^{-1})

3.6 Acknowledgements

This work was financially supported by the company FuMA-Tech, Germany. The author wish to thank Steffi Ridder, Daniela Marks and Beate Scheiffelen for technical support and Dr. Dietmar Käshammer[†] for the helpful discussions on the membrane performance.

[†] diseased

3.7 References

1. V.S. Donepudi, N.R. Khalili, R. Kizilel and J.R. Selman, Purification of hard chromium plating baths - options & challenges, Plat. Surf. Finish. (4) (2002) 62.
2. S.A. Katz and H. Salem, The toxicology of chromium with respect to its chemical speciation: a review, J. Appl. Toxicol. **13** (3) (1993) 217-224.
3. E. Groshart, Finishing in the Green - Chromium, Met. Finish. **95** (3) (1997) 59-61.
4. E. Nieboer and A.A. Jusys, Biologic chemistry of chromium, in "Chromium in the Natural and Human Environments", J.O. Nriagu and E. Nieboer, Editors. 1988, John Wiley & Sons, Inc.
5. G. Pourcelly, R. Marquínez, B. Bauer, R. López, S. Viala, A. Mahiout, and G. Istvan (2003) Acid chromic recycling from rinse water in galvanic plants by electro-electrodialysis. Workshop on Environmentally Clean Technologies for Sustainable Production and Consumption (Vancouver, Canada). (CANMET-CARI-EUROPEAN COMMISSION).
6. A. Baral and R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environ. Sci. Pol. **5** (2) (2002) 121-133.

7. E.A. Cohen Hubal and M.R. Overcash, Net-waste-reduction analysis applied to zero-water discharge systems for chromic acid electroplating, J. Cleaner Prod. **3** (3) (1995) 161-167.
8. R. Audinos, Liquid waste concentration by electrodialysis, in "Separation and Purification Technology" N.N. Li and J.M. Calo, Editors. 1992, Marcel Dekker. p. 229-301.
9. J. Audran, P. Baticle and M.-M. Letord (1990) Recycling of chromic acid by electro-electrodialysis. Vth World Filtration Congress (Nice, France).
10. J. Audran, M.-M. Letord and A. Ducourroy (1992) Electrochemical cell, especially for recycling of chromic acid. Patent EP 0483015
11. Y. Çengeloglu, A. Tor, E. Kir and M. Ersöz, Transport of hexavalent chromium through anion-exchange membranes, Desalination **154** (3) (2003) 239-246.
12. E. Castillo, M. Granados and J.L. Cortina, Chromium(VI) transport through the Raipore 1030 anion exchange membrane, Anal Chim Acta **464** (1) (2002) 15-23.
13. E. Castillo, M. Granados and J.L. Cortina, Chemically facilitated chromium(VI) transport throughout an anion-exchange membrane: Application to an optical sensor for chromium(VI) monitoring, J. Chromatogr. **963** (1-2) (2002) 205-211.
14. R.F. Dalla Costa, M.A.S. Rodrigues and J.Z. Ferreira, Transport of trivalent and hexavalent chromium through different ion-selective membranes in acidic aqueous media, Sep. Sci. Technol. **33** (8) (1998) 1135-1143.
15. M.E. Vallejo, P. Huguet, C. Innocent, F. Persin, J.L. Bribes, and G. Pourcelly, Contribution of raman spectroscopy to the comprehension of limiting phenomena occurring with a vinylpyridinium anion exchange membrane during the electrolysis of Cr(VI) solutions, J. Phys. Chem. B **103** (51) (1999) 11366-11371.
16. M.E. Vallejo, F. Persin, C. Innocent, P. Sistat, and G. Pourcelly, Electrotransport of Cr(VI) through an anion exchange membrane, Sep. Purif. Technol. **21** (2000) 61-69.
17. S. Roualdes, N. Kourda, J. Durand and G. Pourcelly, Plasma-grafted PVDF polymers as anion exchange membranes for the electrotransport of Cr(VI), Desalination **146** (2002) 273-278.

18. R.F. Dalla Costa, J. Zoppas Ferreira and C. Deslouis, Electrochemical study of the interactions between trivalent chromium ions and Nafion perfluorosulfonated membranes, J. Memb. Sci. **215** (2003) 115-128.

19. P. Ng and D. Snyder, Combining electrolysis and dialysis for regeneration of chromic acid etching solution, J. Memb. Sci. **13** (1983) 327-336.

20. M.A.S. Rodrigues, R.F. Dalla Costa, A.M. Bernardes and J. Zoppas Ferreira, Influence of ligand exchange on the treatment of trivalent chromium solutions by electrodialysis, Electrochim. Acta **47** (5) (2001) 753-758.

21. K.-L. Huang, T.M. Holsen and J.R. Selman, Impurity partitioning in Nafion and ceramic separators used for purification of spent chromium plating solutions, J. Memb. Sci. **210** (2002) 137-145.

22. K.-L. Huang, T.M. Holsen, T.-C. Chou and J.R. Selman, Comparing Nafion and ceramic separators used in electrochemical purification of spent chromium plating solutions: cationic impurity removal and transport, Environ. Sci. Technol. **37** (9) (2003) 1992-1998.

23. K.-L. Huang, T.M. Holsen and J.R. Selman, Impurity diffusion through Nafion and ceramic separators used for electrolytic purification of spent chromium plating solutions, J. Memb. Sci. **221** (2003) 135-146.

24. M.I. Ahmed, H.T. Chang, J.R. Selman and T.M. Holsen, Electrochemical chromic acid regeneration process: fitting of membrane transport properties, J. Memb. Sci. **197** (2002) 63-74.

25. M.I. Ahmed, T.M. Holsen and J.R. Selman, Electrochemical chromic acid regeneration process with fuel-cell electrode assistance. Part I: Removal of contaminants, J. Appl. Electrochem. **31** (2001) 1381-1387.

26. M.I. Ahmed, T.M. Holsen and J.R. Selman, Chromic acid regeneration process with fuell cell electrode assistance. Part II: Electrochemical characterization, material compatibility and energy consumption, J. Appl. Electrochem. **31** (2001) 1389-1394.

27. H. Wendt and G. Kreysa, Electrochemical Engineering: science and technology in chemical and other industries. 1999, Heidelberg, Springer-Verlag.

28. R. Sarmaitis, V. Dikinis and V. Rezaite, Equilibrium in solutions of chromic acid, Plat. Surf. Finish. **83** (6) (1996) 53-57.

29. R. Sarmaitis, V. Dikinis, V. Rezaite and V. Stasiukaitis, Distribution of Cr(VI) particles in solutions of acids, Proceedings of the AESF Annual Technical Conference (1996). p. 89.

30. G.A. Lausmann and J.N.M. Unruh, Die galvanische Verchromung. Schriftenreihe Galvanotechnik. 1998. (in German)

31. E. Korngold, F. De Körösy, R. Rahav and M.F. Taboch, Fouling of anionselective membranes in electrodialysis, Desalination **8** (1970) 195-220.

32. H. Holdik (1999) Impedanzspektroskopische Charakterisierung von tensidverursachten Foulingvorgängen an Ionenaustauscher-Membranen. PhD Thesis, Saarland University (in German).

33. H. Strathmann, Ion-Exchange Membranes, in "Membrane Handbook", W.S. Winston Ho and K.K. Sirkar, Editors. 1992, Van Nostrand Reinhold: New York. p. 235.

34. B.J. Robbins, R.W. Field, S.T. Kolaczkowski and A.D. Lockett, Rationalisation of the relationship between proton leakage and water flux through anion exchange membranes, J. Memb. Sci. **118** (1996) 101-110.

35. Y. Lorrain, G. Pourcelly and C. Gavach, Influence of cations on the proton leakage through anion-exchange membranes, J. Memb. Sci. **110** (1996) 181.

36. F. De Körösy and E. Zeigerson, Breakthrough of poisoning multivalent ions across a permselective membrane during electrodialysis, J. Phys. Chem. **71** (11) (1967) 3706-3709.

37. D. Kertész, F. De Körösy and E. Zeigerson, Advances in the electrochemistry of permselective membranes, Desalination **2** (1967) 161-169.

38. W.S. Winston Ho and K.K. Sirkar, Membrane Handbook. 1992, New York, Van Nostrand Reinhold.

Chapter 4

Chromic acid recovery by electro-electrodialysis. II. Pilot scale process, development and optimisation*

Abstract

Electro-electrodialysis is a promising technology for chromic acid recovery and static rinse water purification. It combines the recovery of the plating chemicals from rinse water, the elimination of metallic impurities from the process and rinse water treatment in one step. Previous industrial use was restricted due to non-resistant anion-exchange membranes and process ineffectiveness. In this work, a stable and economical process is developed and high-quality chromic acid is recovered using a new oxidative stable anion exchange membrane (AEM Fumasep® FAP, FuMA-Tech GmbH). The membrane stability and performance is evaluated by a long-term experiment for 400 hours. Recovery rates were determined for batch and continuous operation and at different operation temperatures. The highest chromic acid production was reached by batch processing at 40°C. Both measures increase significantly the chromate transfer and result in lower equipment size and operational costs.

---

* Parts of this chapter has been submitted for publication to Separation and Purification Technology.

4.1 Introduction

The chromic acid recovery is an industrial challenge because of increasingly strict environmental legislation. Because of its toxic, carcinogen and strong oxidizing character, the chromium plating technology is under permanent government scrutiny. Therefore, the plating companies search for economical, easy to handle and reliable recycling and recovery technologies. Especially, the process cost effectiveness is very important, because 90 % of the European chromium-plating companies are small and medium-sized entities (SMEs) and need economical processes in order to remain competitive [1]. The requirements of the optimum technology for chromic acid recovery are:

- Removal of impurities from process solution;
- Recovery of chemicals and water;
- Low cost technology;
- No additional waste production;
- No use of extra chemicals;
- Easy handling;
- Long life - time

The contaminated effluents are generally treated by physical-chemical treatment involving chemical reduction of Cr(VI) to Cr(III), neutralization and precipitation at pH 7–9, followed by sedimentation and separation of metal hydroxides. This treatment method creates a considerable amount of sludge due to addition of treatment chemicals and neither the chromic acid nor the water is recycled. Simple measures, such as direct return of static rinse effluents to the plating bath, are applied, but are unable to remove impurities from the system.

The recycling technologies currently available are ion-exchange, evaporation, anodic oxidation of trivalent chromium in undivided and divided electrolytic cells and membrane electrolysis cells. They are operated either directly on the plating bath or with contaminated rinsing effluents from static or counter-flow rinses. These systems are compared in Table 4.1 in terms of their suitability for impurity removal, costs, waste production and maintenance [2-4].

Table 4.1. *Different commercial recycling technologies for chromic acid effluents (H: High, M: Medium, L: Low).*

	Technology	Impurity removal	Cost	Waste	Maintenance
Plating Bath	Impurity removal by ceramic diaphragms	Yes	M	H	H
	Anodic oxidation of Cr(III)	No	M	L	M
	Ion-exchange resins + evaporation	Yes	H	H	M
	Membrane electrolysis	Yes	H	H	H
Static Rinse	Evaporation (CrO_3 reuse)	No	H	L	M
	Ion-exchange resins (CrO_3 reuse)	Yes	M	H	M
	Direct return into the plating bath	No	L	L	M
Flow Rinse	Ion-exchange resins (water reuse)	Yes	M	H	M

Ion-exchange technology provides separation of metallic impurities and recovery of Cr(VI) oxo-anions by cation-exchange and anion-exchange resins, respectively. Chromium is recovered as sodium di-chromate and is post-treated by a second cation exchanger to form chromic acid. This technology has, however, limitations such as restricted resin stability at high concentrated chromic acid solution (dilution and frequent resin regeneration is necessary). Furthermore, extra chemicals are required and waste effluents are produced. Evaporation is a non-selective method to re-concentrate plating solution from exhausted rinses. The recovered solutions contain metallic contaminants, which could accumulate in the plating line. Therefore, this technology is sometimes combined with ion-exchange using strong acid cation-exchange resins. Usually, the evaporation technology is associated with increased energy consumption and in combination with ion-exchange it does not seem to be attractive for platers. Ion-transfer systems appear as a more economical alternative. Two-compartment electrolysis systems either separated by ceramic or plastic diaphragms or ion-exchange membranes are commercially available. However, depending on their construction, these systems have difficult maintenance (for instance removal of precipitated metal hydroxides, use of cleaning chemicals) and lack of operation reliability (unsatisfactory membrane stability, plugging).

A study of 1994 concerning 318 plating companies in USA [3] showed that eight companies used ion-exchangers for bath maintenance, six used membrane electrolysis and fifteen used other ion-transfer technologies. The same situation was found for chemical recovery. Twenty two companies used evaporation and only nine used ion-exchangers. It seems that the existing technologies are not attractive for the plating companies.

Electro-electrodialysis (EED) is a promising technology to meet the demands described earlier. It is an electromembrane process which combines electrolysis and electrodialysis [5]. Figure 4.1 illustrates its principle.

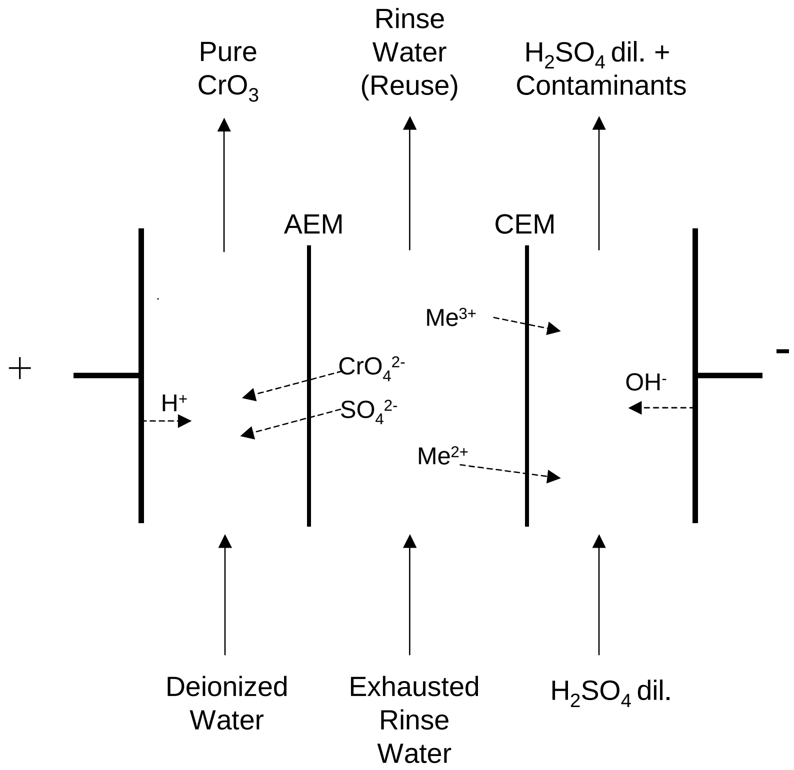


Figure 4.1. *The principle of electro-electrodialysis (EED) technology for chromic acid recovery.*

One repeating unit consists of three compartments, where the outer compartments include the electrodes. The rinse water flowing through the central compartment contains chromic acid and metallic impurities such as copper, iron, zinc, aluminium, nickel and trivalent chromium coming from the plating bath. Cationic impurities migrate towards the cathode through the cation-exchange membrane (CEM). The cathode compartment is fed with diluted sulphuric acid to form dissolved metal sulphates. Hexavalent chromium anions (chromates) migrate towards the anode through the AEM. There, chromic acid is formed by chromate and dichromate anions and protons generated at the anode. The treated rinse water is reused in the rinsing process and pure chromic acid returns back to the plating bath. Figure 4.2 shows a typical scheme of the process. Exhausted catholyte solutions can be treated by common physical-chemical treatment. The system manages three different tasks simultaneously: (i) removal of contaminants, (ii) chromic acid recovery and (iii) purification of static rinse water. In addition, membrane electrolysis technology has lower maintenance costs and does not require extra chemicals for regeneration [2, 6]. So far, the technology was not applied industrially due to poor AEM stability and low efficiency. In earlier work [7], the new antioxidant AEM Fumasep® FAP (FuMA-Tech GmbH) was compared in lab-scale EED experiments with other commercially available AEM: it showed very promising results. In this paper, the implementation of the process on a larger scale is discussed. Experiments are performed for a long time period using a commercial membrane electrolysis module aiming at the evaluation of the process performance, the equipment stability as well as the required costs.

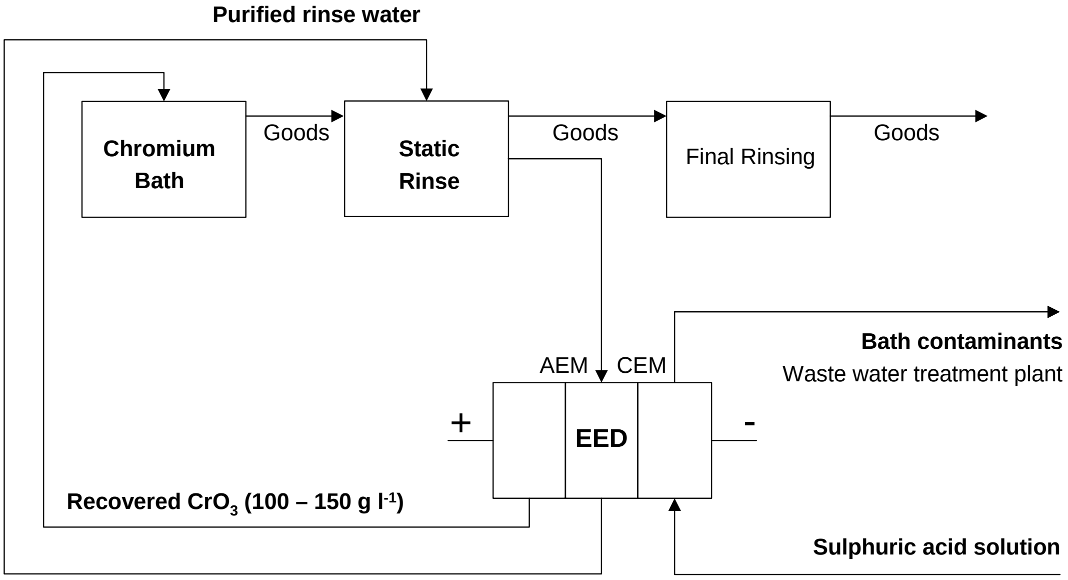


Figure 4.2. *Implementation of EED into chromium plating lines.*

4.2 Experimental

4.2.1 Materials, chemicals and analysis

A commercial multi-purpose plate and frame cell (MP-Cell® from ElectroCell A/S, Denmark) was used. The cell consisted of spacers made of polypropylene (PP) or polyvinylidene fluoride (PVDF) and gaskets compressed between two endplates. The gaskets were made of Viton®, fittings and tubes were made of Teflon® PFA. As electrodes, an oxygen stable DSA® anode and a stainless steel cathode were used. The cell had one repeating unit, divided into three compartments by the anion- and cation-exchange membrane. The effective membrane area was 100 cm². Figure 4.3 presents a schematic illustration of the pilot plant containing temperature-controlled glass vessels, flow meters and pumps. The anodic cycle was designed for minimum dead volume. For short batch experiments, the glass vessel had a capacity of 0.2 l. In the long-term experiments, the anodic solution capacity was similar to those of the other cycles.

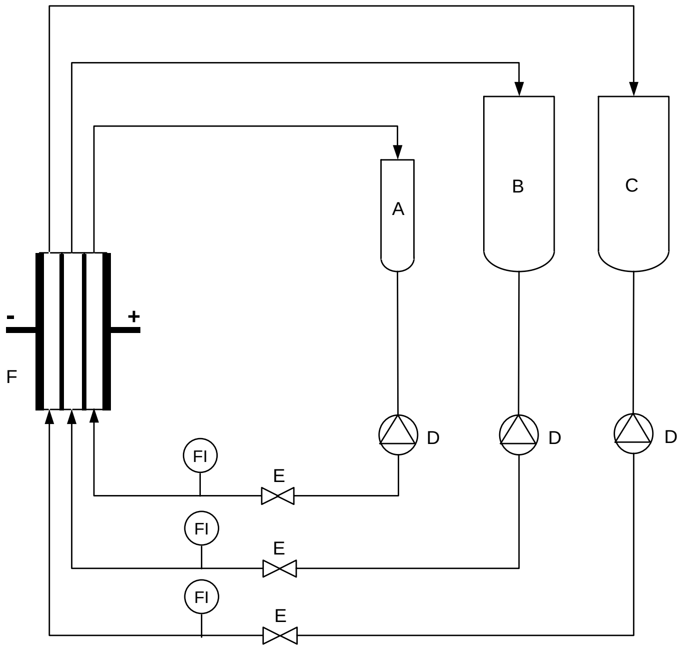


Figure 4.3. *Pilot-scale test equipment. (A) anolyte tank; (B) feed (rinse) tank; (C) catholyte tank; (D) pump; (E) valve; (F) membrane electrolysis cell (MP-Cell®, ElectroCell A/S); (FI - flow indicator).*

Fumasep® FAP membrane (FuMA-Tech GmbH, Germany) of 50 μm thickness was used as AEM and Nafion®324 (Du Pont Polymers) as CEM. Prior to use, both membranes were equilibrated in 0.2 M H_2SO_4. The AEM was additionally pre-treated in 0.1 M CrO_3 solution for 2 hours.

All aqueous solutions were prepared with deionized water. Chromic acid rinse water was prepared from exhausted chromium bath coming from a plating company producing chromium automotive accessories and sanitary equipment. Table 4.2 presents the composition of the plating solution. The anodic chromic acid starting solution was prepared from chromium(VI) oxide (Fluka Chemie GmbH, p.a.) and sulphuric acid for the cathodic solution was obtained from VWR International (p.a.). The chromic acid was determined by iodometric potentiometric titration with thiosulphate using a combined Pt electrode (Mettler-Toledo GmbH, DL67 automatic titrator and ST20A sample changer). The chemicals used for this determination were potassium iodide (Riedel-de Haën, p.a.), sulfuric acid (VWR International, p.a.) and 0.1 N sodium thiosulfate solution (VWR International, Titrisol®). Metals were analysed by ICP-OES (inductively coupled plasma optical emission spectrometry).

Table 4.2. *Analysis of the chromium plating solution used in the experiments (in g* l^{-1}*).*

Al	B	Cr	Cu	Fe	Mg	Mo	Na	Ni	Pb	Zn	SO_4^{2-}
0.228	0.344	144	0.183	0.085	0.252	0.013	0.540	1.02	0.026	5.27	7.20

4.2.2 Process Conditions

In the first part of this work, the long-term stability of the process was investigated. The experiment was performed for more than 400 h at 25 °C and was divided into two parts: (i) batch mode, concentrating the chromic acid in the anode compartment from 0.1 to 1.2 M CrO_3 for 200 hours and (ii) continuous mode, operating at constant high CrO_3 concentration (~ 1.2 M CrO_3) in the anode compartment for a further 210 hours. The equipment was filled with chromic acid solutions for a total of 1200 hours. Chromic acid rinse water was prepared by dilution of exhausted plating solution. The concentration was maintained between 0.1 and 0.15 M CrO_3. The cathode solution was 0.2 M H_2SO_4. The start volume of the anodic solution was 1.4 l, the rinse water effluent was 2.5 l and the cathode compartment cycle had a volume of 1.6 l. Previous lab scale work [7] showed that the initial current intensity should be low (10–20 mA cm^{-2}) and the feed flow velocity higher than 7 cm s^{-1} in order to overcome process limitations attributed to high AEM resistance. Therefore, the current density was initially 10 mA cm^{-2} at batch mode and later 20 mA cm^{-2} at continuous operation. The feed flow was 150 l h^{-1} corresponding to feed velocity of 7 cm s^{-1}. Furthermore, previous work [7] showed that treatment of chromium plating solution at high temperature can improve significantly the process performance. Therefore, in the second part of this work two long-term experiments at 25 and 40 °C were performed in batch mode (0.1–1.2 M CrO_3) using the same equipment and process conditions as in the first part (7 mA cm^{-2}, 150 l h^{-1}). The volume of the anodic solution was minimized to 0.4 l to achieve a complete batch within short time. The rinse water solution was replenished automatically every 3 hours.

During all experiments, samples of each compartment were regularly taken and analysed for chromate and total acidity. At the same time, the amperage, voltage, temperature, conductivity and pH in each compartment was monitored.

The overall current efficiency for the product (chromic acid), Φ^e, was defined as the current carried by chromate ions relative to the total current used:

$$\Phi^e = \frac{m \nu_e F}{M I t} \tag{4.1}$$

where m is mass of product, M its molar mass, ν_e the stoichiometric number of electrons for the reaction (assumed to be 1, [7]), F the Faraday constant, and I t the current quantity [8]. The specific energy consumption was calculated using:

$$E_{S,m} = \frac{U_c \nu_e F}{M \Phi^e} \tag{4.2}$$

where U_C is the total cell voltage.

4.3 Results and discussion

4.3.1 Long-term stability

Figure 4.4a shows the change of chromic acid concentration in the anode and central compartment during the long-term experiment. The first part of the run was performed in batch mode. After 200 hours of operation the CrO_3 target concentration of 1.2 M is reached. Figure 4.4b shows that the chromic acid production rate decreases with increasing chromic acid concentration in the anodic solution in agreement with the lab scale study [7]. The flux of Cr(VI) through the AEM decreases from 1.12 mol_{CrO3} m^{-2} h^{-1} (for 0.15 mol_{CrO3} l^{-1} in the anode cycle, measured after 13 hours) down to 0.22 mol_{CrO3} m^{-2} h^{-1} (for 1.2 mol_{CrO3} l^{-1} in the anode cycle after ~ 200 h, see Figure 4.4b). This corresponds to a decrease of efficiency from 0.30 to 0.06 due to increased acid concentration in the anode compartment. These results are in close agreement with results from lab-scale testing [7]. In the latter, the efficiency was ~ 0.04 at 20°C.

The long-term experiment was continued maintaining constantly high CrO_3 concentration in the anodic compartment (~ 1.2 M CrO_3) and applying a current density of 20 mA cm^{-2}. The increase of current density results in a double chromic acid transport through the AEM compared to that at 10 mA cm^{-2}, without loss in current efficiency [7]. Figure 4.4b shows the course of the CrO_3 production in the anode compartment for the continuous recovery. The chromate transport through the AEM remains nearly constant at ~ 0.4 mol_{CrO3} m^{-2} h^{-1} corresponding to a current efficiency of 0.05.

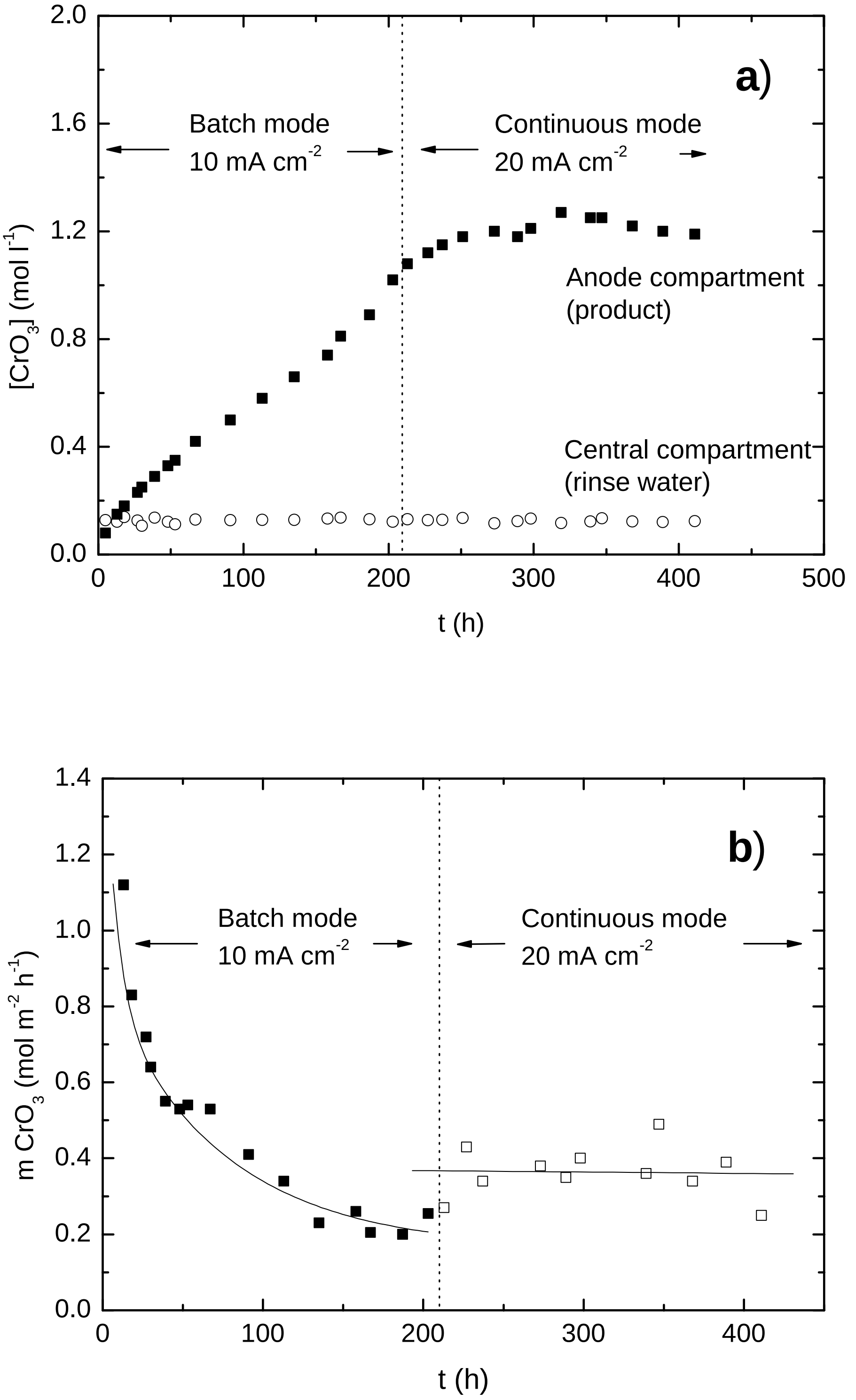


Figure 4.4. *The process performance during the long-term experiment. Process conditions: 10 mA cm^{-2} (0–200 h, batch mode), 20 mA cm^{-2} (200–420 h, continuous mode), 25°C, 7 cm s^{-1}. (a) Change of CrO_3 concentration and (b) Chromic acid recovery rate.*

The long-term experiment clearly shows that the chemical resistance of the AEM is no more the limiting factor of the technology. During the 1200 hours exposition to chromic acid solutions the membrane showed good performance. Further attention should be rather focused on cell materials and construction in order to guarantee long-term use. Chromic acid is highly corrosive and an oxidizing agent. During the long-term experiment, the equipment was exposed to chromic acid solutions for 1200 h, too. For concentrations above 1 M CrO_3 and temperatures higher than 20°C only fluorinated material seems to be sufficiently resistant. For 1 M CrO_3 solutions also PP and PE is recommended [9] (Table 4.3). During our tests, we observed that PP cell frames were generally stable, but reinforcement of the in- and outflow channels by more stable inserts were necessary to guarantee long-term stability. The frames made of PVDF were not resistant showing leakage after short-term running. The cell frames, however, provided good hydraulic condition and good support to the membrane. Besides, during the test runs, we observed formation of metal hydroxides on stainless steel and platinum coated titanium cathodes. Nonetheless, this layer could be removed by current-free circulation of 0.2 M H_2SO_4 cathode solution. The stronger the sulfuric acid concentration in the catholyte the lower the risk of sludge formation [10]. In our experiments, the control of acid concentration (pH < 1) was very important and when required, acid was added or the solution was replaced.

Table 4.3. *Material resistance in chromic acid solution at different temperatures (1 = resistant, 2 = practically resistant, 3 = partially resistant, 4 = not resistant) [9].*

	PVC	**PE-LD / PE-HD**	**PP**	**PVDF**	**PTFE**	**ECTFE**
10% chromic acid						
20°C	1	1 / 1	1	1	1	1
50°C	2	1 / 1	1	1	1	1
50% chromic acid						
20°C	1	3 / 3	3	1	1	1
50°C	3	4 / 4	3	1	1	1

4.3.2 Evaluation of batch and continuous mode

For a practical example, we compared both modes in terms of their chromic acid recovery rate and required membrane area. Table 4.4 presents some typical process parameters obtained by plating companies. The average weekly amount of chromium plating bath dragged out to the rinses is determined by the number of production batches per week, the number of workpieces per batch, the average surface area of each workpiece and the average volume of chromium solution remaining on the metal surface. This value is experimentally determined taking pieces with different size and shape into account. In this example, the total amount of chromic acid to be recovered is 2.35 kg_{CrO3} d^{-1}. The average static rinse water concentration should be app. 0.1 M CrO_3 as maintained in the long-term stability runs. If the plating company operates 14 h d^{-1}, but the recycling plant operates all day, the rinse water concentration increases during the day and decreases during the night. Table 4.5 gives the process conditions for the recycling plant and calculation results for both batch and continuous processing. In batch mode, the chromic acid production rate fluctuates according to the CrO_3 concentration in the anodic cycle and at continuous processing the rate remains constant (Figure 4.4b).

Table 4.4. *Typical process parameters obtained by plating companies.*

Drag out from the plating bath to the static rinse (l $week^{-1}$)	80
Drag out from the plating bath to the static rinse (l h^{-1}) [a]	0.67
Drag out from the plating bath (kg_{CrO3} h^{-1}) [b]	0.17
Daily amount of chromic acid to be recovered (kg_{CrO3} d^{-1}) [a]	2.35
[a] Working hours: 14 h d^{-1}, 5 days per week [b] Concentration of the plating solution: 250 g l^{-1} CrO_3	

Table 4.5. *EED process parameters for operation at batch and continuous mode at 25°C and 10 mA cm^{-2}.*

	Batch	**Continuous**
CrO_3 concentration range of the anode compartment (mol l^{-1})	0.1–1.2	1.2
Recycling of recovered solution to the plating bath	1 per day	Continuous
CrO_3 recovery rate (mol h^{-1} m^{-2})	0.2–1.1	0.2
Quantity of CrO_3 recovered per day (mol m^{-2})	10.1	4.8
Required membrane area (m²)	2.3	4.9

Based on our data obtained in the long-term experiment, in batch mode the daily amount of chromic acid recovered would be 10.1 mol$_{CrO3}$ m^{-2} d^{-1} (calculated by integration). The CrO_3 production rate for continuous recovery is expected to be 2 times lower (4.8 mol$_{CrO3}$ m^{-2} d^{-1}) due to the constant low chromate transport towards the high concentrated anolyte. Accordingly, for the continuous mode the effective membrane area should be much higher (4.9 m²) than for the batch mode (2.3 m^2). Thus, the continuous mode seems unfavorable especially in terms of investment costs. Additionally, the energy consumption increases with increasing membrane area and the number of repeating units. Besides, sustained loading of the membranes and fluid touched parts by high concentrated chromic acid should also not be underestimated at the continuous mode.

In conclusion, the batch mode seems to be more efficient both in terms of equipment size and expected energy consumption. The following paragraphs describe further optimisation aiming to increase chromium recovery rate.

4.3.3 Process optimisation

Increased transport of chromates can be further expected by increasing the current density and temperature [7, 11]. Therefore, two batch mode experiments at different temperatures were performed aiming at the improvement of the chromate transport. Figure 4.5 presents the results. The CrO_3 concentration in the anolyte increases and reaches 1.2 M CrO_3 much faster (43 h) at 40°C than at 25°C (69 h, see Figure 4.5a). The lower chromate transport at 25°C is also reflected in the process efficiency (see Figure 4.5b). From the beginning of the experiment the current efficiency is lower at 25°C than at 40°C. At the end, the efficiency is still 0.2 at 40°C compared to 0.08 at 25°C. When comparing the rate of chromic acid formation, this is 0.7 mol_{CrO3} m^{-2} h^{-1} at 40°C in comparison to 0.3 mol_{CrO3} m^{-2} h^{-1} at 25°C. These results are in good agreement with our earlier results, obtained during lab scale experiments [7] and other reported by Vallejo et al. [11] for the AEM IONAC MA-3475. The enhanced chromate transport could be attributed to lower proton leakage through the AEM at higher temperature, as discussed in Chapter 3.

Limitations in operational reliability and economical disadvantages could arise from the high electric resistance during the process [7, 12, 13]. Actually, when using a fresh piece of AEM, we observed an initial voltage increase followed by a slow decrease. As previously reported [7], suitable counter measures could be low initial current densities and increased superficial velocities. Therefore, the batch mode experiments were performed at 10 mA cm^{-2} and 7 cm s^{-1}. Figure 4.5c compares both experiments performed at 25 and 40°C. Interestingly, at 25°C the initial voltage increase is more pronounced than at 40°C. Generally, the high resistance is attributed to the formation of large polychromate molecules inside the membrane [11, 12]. The higher the acidity and the CrO_3 concentration of the solution the more polychromate formation is favoured [14]. The influence of the temperature on polychromate formation is not consistently discussed in the literature. It seems that the polychromates depolymerize upon heating [15]. This would result in formation of mono- and dichromates having higher mobility than polychromates. Therefore, the electric resistance of the AEM is lower at 40°C than at 25°C.

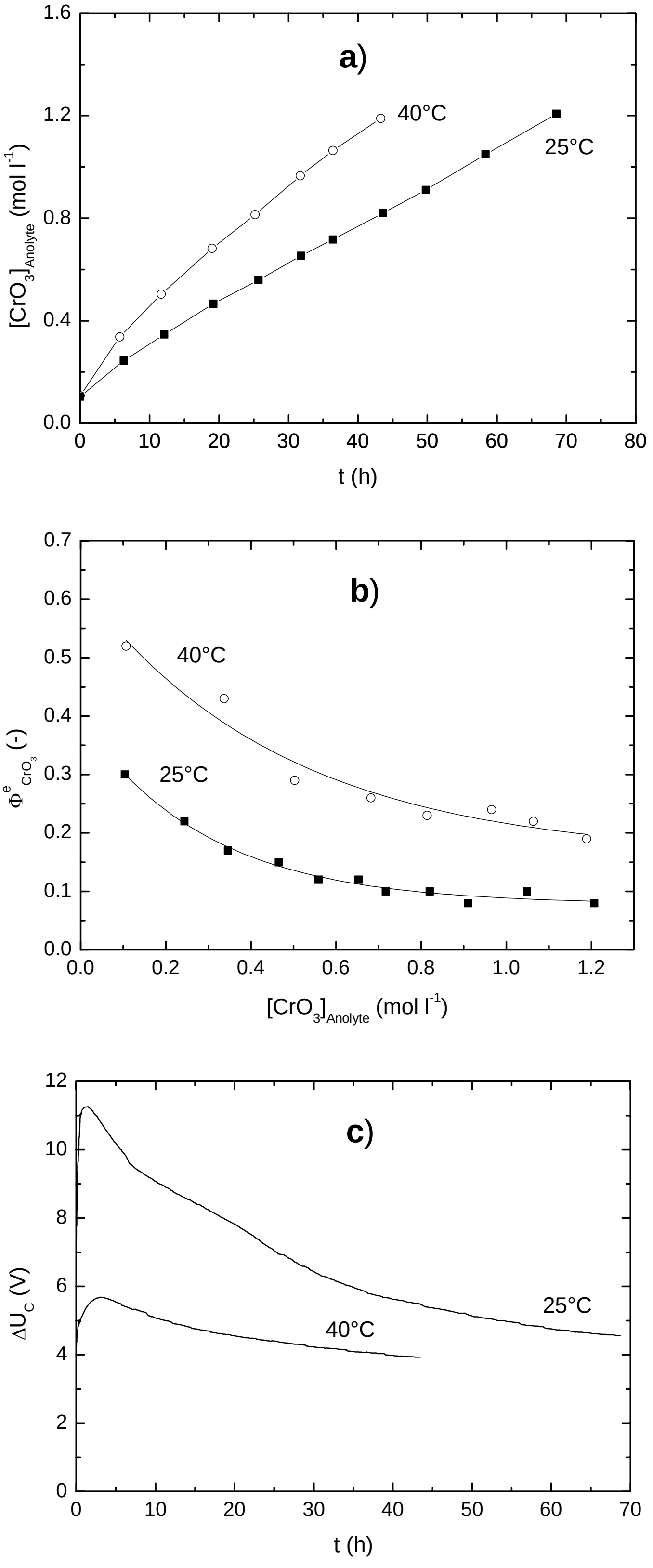


Figure 4.5. *Influence of temperature on process performance. (a)* CrO_3 *concentration in the anodic cycle. (b) Chromic acid recovery rate. (c) Cell voltage. Process conditions: batch mode, 10 mA* cm^{-2}*, 7 cm* s^{-1}*.*

The formation of polychromates in the AEM and possible change of its character towards amphoteric [11, 16] may lead to a loss in selectivity (co-ion leakage). Since the recovered chromic acid should be directly recycled into the plating bath, this is highly undesired. Table 4.6 presents the composition of the chromic acid solution obtained after the experiment at 40°C. The solution contains very low concentrations of metal ions in comparison to chromic acid rinse concentration. This indicates that no co-transport of positive charged ions occurs through the AEM. For sulphates, the concentration is only 0.2 % wt of the chromic acid content and is therefore lower than required. In a simple chromium plating bath, the concentration of H_2SO_4 should be 1 % of the chromic acid concentration. However, it is worth to note that the starting anode solution contained no sulphuric acid. By adding a certain amount of sulphuric acid to the anodic start solution the sulphuric acid concentration in the recovered solution could be maintained automatically.

Table 4.6. *Quality of industrial rinse water have to be treated and the final quality of chromic acid recovered in the anode compartment (in ppm).*

	Al	**B**	**Cr**	**Cu**	**Fe**	**Mg**	**Na**	**Ni**	**Pb**	**Zn**	**SO_4^{2-}**
Rinse	11	7	6580	8	4	88	28	43	< 1	208	880
Acid recovered	< 1.5	3	62000	< 0.6	0.6	10	4	< 0.5	< 1	0.25	250

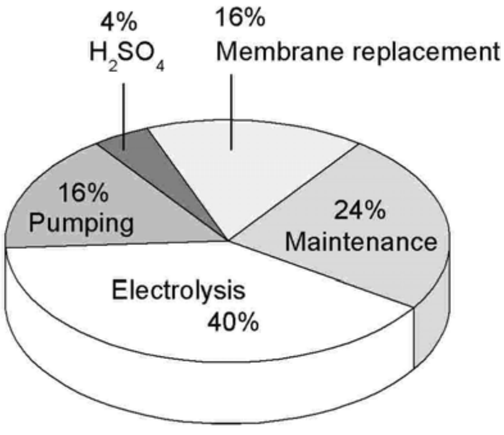
4.3.4 Economical evaluation

Various benefits could be achieved by implementing an EED recycling system:

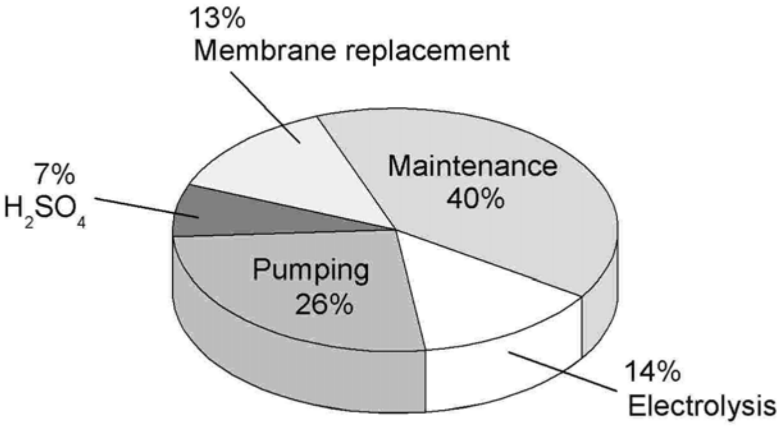
- Bath maintenance (removal of metallic impurities and therefore no disposal of the exhausted solution, bath replenishment by recovered chromic acid)
- Rinse water reuse (no discharge and treatment, no addition of fresh water)

The saving of costs would be obtained by lower costs for the bath chemical and water and by lower costs for waste water treatment and sludge disposal. Due to rather high variation in chromium plating operation (e.g. quantity of drag out, number of baths and rinses, management of waste effluents) savings of costs should be separately determined for each plating company. However, here we estimated the operation costs of this new technology involving the cost for electrolysis, pumping, consumption of H_2SO_4, membrane replacement and personnel (maintenance).

For the example in Table 4.4 (2.35 kg_{CrO3} d^{-1}) operational costs were estimated for batch processing at 25 and 40°C assuming a feed velocity of 7 cm s^{-1}, operation at 20 mA cm^{-2} and membrane area of 0.4 m² per repeating unit. The operational costs are expected to be 5.0 € kg_{CrO3}^{-1} at 40°C in comparison to 7.9 € kg_{CrO3}^{-1} at 25°C, due to increased chromate transfer and lower voltage drop at 40°C. For the recovery of 2.35 kg_{CrO3} per day at 40°C one repeating unit per EED module would be required. However, for the recovery of the same amount at 25°C, two repeating units in one module would be required. Thus, working at 25°C would result in significantly higher electrolysis costs. Figure 4.6 presents the composition of the operational costs at 25 and 40°C. The percentage of electrolysis costs in the total operation costs is 40 % at 25°C (Figure 4.6a) and only 14 % at 40°C (Figure 4.6b). Generally, no extra heat input is considered for operating at 40°C because the heat input coming from electrolysis and pumping would be higher than the loss of heat.



a) 25°C



b) 40°C

Figure 4.6. *Estimation of operating costs for process described in Table 4.6 (batch mode, recovery rate 2.35* kg_{CrO3} d^{-1}*, feed velocity 7* $cm\ s^{-1}$*, 20* $mA\ cm^{-2}$*). (a) Operation temperature 25°C (*U_C *= 10 V for two repeating units) and (b) operation temperature 40°C (*U_C *= 4 V for one repeating unit).*

Finally, it is important to note, that even an increase in current density to 30 mA cm^{-2} would result in significantly lower operational costs. For the example above (2.35 kg_{CrO3} d^{-1}), the operational costs would be 26 % lower in both cases (3.7 € kg_{CrO3}^{-1}

at 40°C and 6.2 € kg_{CrO3}^{-1} at 25°C). Earlier experiments showed that after a longer time period (~ 200 h) the overall resistance decreases and the current intensity can be increased without observing strong voltage fluctuation. Besides, the increase does not result in efficiency loss [7]. Figure 4.7 shows an estimation of operation costs for various daily CrO_3 recovery rates at 30 mA cm^{-2}, for the favourable batch mode at 40°C. The operation costs decrease with increasing daily recovery rates. This decrease is mainly influenced by the maintenance costs since they have a large share in the total operating cost (see Figure 4.6b) and the expenditure for maintenance is considered the same for all daily recovery rates (0.5 hours per week). The more chromic acid is recovered per day the lower the maintenance costs per kg CrO_3. Furthermore, the operation costs are influenced by the degree of utilization. The EED module could either consist of two or three repeating units with a standard size of 0.04 m² per unit (for recovery rates of 0.5 and 0.7 kg_{CrO3} d^{-1}, respectively), or consist of one repeating unit with a standard size of 0.4 m² for daily recovery rates above 1 kg_{CrO3} d^{-1}. In the estimation of Figure 4.7, the later case is considered and the specific operation costs (€ kg_{CrO3}^{-1}) for electrolysis, pumping and membrane replacement are lower due to better equipment utilization.

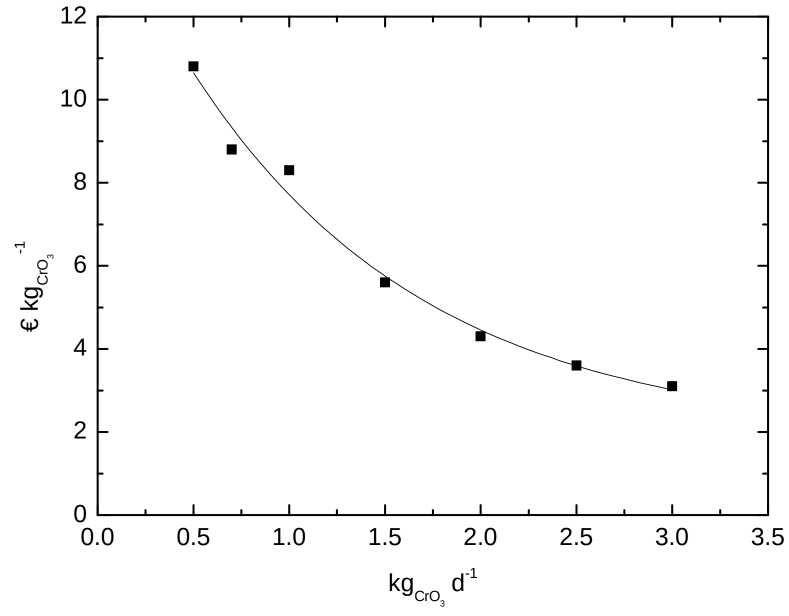


Figure 4.7. *Estimation of operation costs at various CrO_3 recovery rates for a batch mode process at 40°C using 30 mA cm^{-2} (feed velocity 7 cm s^{-1}, one repeating unit per EED module).*

4.4 Conclusions

In this work a stable pilot-scale study for chromic acid recovery for more than 400 hours was presented. Earlier results from lab-scale experiments were confirmed in batch mode. The recovery rates were strongly depending on the CrO_3 concentration in the anode compartment. The recovery rates were the highest in the beginning of a batch and decreased later when reaching the final concentration in the anode compartment. In continuous mode, however, the recovery rates remained constantly low requiring double membrane area.

It was shown that increased temperature (40°C) could significantly improve the process performance. The chromic acid recovery was more than double at 40°C in comparison to 25°C. For the target concentration of the recovered acid (1.2 M CrO_3), the chromate flux towards the anode was 0.7 mol_{CrO3} m^{-2} h^{-1} at 40°C in comparison to 0.3 mol_{CrO3} m^{-2} h^{-1} at 25°C. The start of operation with fresh membranes was accompanied by an initial increase of resistance, which was lower at 40°C than at 25°C.

The better process performance at 40°C was also reflected in the estimated operational costs. Due to the smaller size of the EED module, the percentage of electrolysis costs in the total operation costs were estimated to be lower at 40°C (14 %) than at 25°C (40 %). The operation costs for a daily recovery rate of 2.35 kg_{CrO3} d^{-1} at 40°C was estimated to be 3.7 € kg_{CrO3}^{-1} at 30 mA cm^{-2}.

4.5 Acknowledgements

The financial support by the European Commission DG XII in the GROWTH frame (G1RD-CT-2000-00196) and by the company FuMA-Tech GmbH, Germany, is gratefully acknowledged. The author wish also to thank Rosa Marquinez from LEIA (Spain) and the company CROPUSA (Spain) for their support.

4.6 References

1. G. Pourcelly, R. Marquínez, B. Bauer, R. López, S. Viala, A. Mahiout, and G. Istvan (2003) Acid chromic recycling from rinse water in galvanic plants by electro-electrodialysis. Workshop on Environmentally Clean Technologies for Sustainable Production and Consumption (Vancouver, Canada). (CANMET-CARI-EUROPEAN COMMISSION).
2. A. Mühle, Passt Ihr Problem zu den angebotenen Lösungen? Regeneration und Standzeitverlängerung von Hartchromelektrolyten, Metalloberfläche **56** (10-12) (2002) 12-15 (in German).
3. Pollution Prevention and Control Technologies for Plating Operations [Online]. Available: www.nmfrc.org/bluebook/tocmain.htm [2004, September, 2]
4. L. Hartinger, Handbuch der Abwasser- und Recyclingtechnik für die metallverarbeitende Industrie. 2 ed. 1991, München Wien, Carl Hanser Verlag (in German).
5. R. Audinos, Liquid waste concentration by electrodialysis, in "Separation and Purification Technology" N.N. Li and J.M. Calo, Editors. 1992, Marcel Dekker. p. 229-301.
6. W. Blatt and L. Schneider, Geteilte Elektrolysetechnik, Metalloberfläche **50** (9) (1996) 694-696 (in German).
7. I. Frenzel, D.F. Stamatialis, G. Pourcelly and M. Wessling, Chromic acid recovery by electro-electrodialysis I. Evaluation of anion exchange membrane, J. Memb. Sci., accepted (2005).
8. H. Wendt and G. Kreysa, Electrochemical Engineering: Science and Technology in Chemical and Other Industries. 1999, Heidelberg, Springer-Verlag.
9. Detailed list of resistances to 1600 media (September 28, 2004). [Online]. Available: www.buerkle.de [2004, October 8]
10. H. Bergmann and T. Iourtchouk, Untersuchungen zur Regenerierung von Chromelektrolyten, Galvanotechnik **88** (3) (1997) 775-784 (in German).
11. M.E. Vallejo, F. Persin, C. Innocent, P. Sistat, and G. Pourcelly, Electrotransport of Cr(VI) through an anion exchange membrane, Sep. Purif. Technol. **21** (2000) 61-69.

12. M.E. Vallejo, P. Huguet, C. Innocent, F. Persin, J.L. Bribes, and G. Pourcelly, Contribution of raman spectroscopy to the comprehension of limiting phenomena occurring with a vinylpyridinium anion exchange membrane during the electrolysis of Cr(VI) solutions, J. Phys. Chem. B **103** (51) (1999) 11366-11371.
13. T. Iourtchouk and H. Bergmann, Elektrochemische Regenerierung vorzugsweise chromhaltiger Systeme, in "Jahrbuch der Oberflächentechnik", A. Zielonka, Editor. 2003, Eugen G. Leuze Verlag: Bad Saulgau. p. 206-221 (in German).
14. R. Sarmaitis, V. Dikinis and V. Rezaite, Equilibrium in solutions of chromic acid, Plat. Surf. Finish. **83** (6) (1996) 53-57.
15. N.V. Mandich, Chemistry & theory of chromium deposition: Part I - Chemistry, Plat. Surf. Finish. **84** (5) (1997) 108-115.
16. F. Aouad, A. Lindheimer, M. Chaouki and C. Gavach, Loss of permselectivity of anion exchange membranes in contact with zinc chloride complexes, Desalination **121** (1999) 13-22.

Chapter 5

Electrochemical reduction of diluted chromate solutions on carbon felt electrodes[*]

Abstract

Carbon felt is a potential material for electrochemical reduction of chromates. Very diluted solutions could be efficiently treated due to its large specific surface area and high porosity. In this work, the up-scaling of this technology is investigated using a new type of separated cell and once-through flow of industrial rinse water.

A significant enhancement of the process is obtained due to copper deposition during long-term operation. The co-deposition and re-solution of copper occurs depending on the inlet chromate concentration. When previously deposited copper is present a current-free reduction of chromate takes place resulting in current efficiencies apparently above 100 %. Very high space time yields are obtained even for low concentrated effluents at optimised conditions (high flow rates and pH 2).

The economic feasibility of the technology is also considered. Flow-through operation results in lower energy requirements than batch processing. Besides, the economic potential of the process is evaluated in comparison with chemical detoxification of chromate. The operation costs for the electrochemical treatment of very diluted effluents on a carbon felt electrode are 30 % lower than for the chemical method.

---

[*] Parts of this chapter has been submitted for publication to Journal of Applied Electrochemistry.

5.1 Introduction

Chromic acid containing rinse water is almost exclusively treated by chemical reduction, followed by neutralization and sedimentation. Alternatively, electrochemical chromate reduction could help meeting the needs of the industry, as well as, environmental aspects. The advantages are detoxification without chemical reducing agents, minimization of salt freight and lower sludge production. This technology is being under investigation since many years using either planar electrodes [1-4], mesh type electrodes [3, 5] or packed beds with granular carbon [6-9]. Ibl and Frei [4] reported promising results with two-dimensional electrodes. They could reach chromate concentrations below 0.5 ppm and current efficiencies around 95 %, when using 100–1000 ppm CrO_3 solutions and pH below 1.5. For the treatment of 1 m^3 waste water per day, 1.25 m^2 electrode area was necessary. Robertson et al. [2] developed an up-scaled system, so called “Swiss Roll Cell” obtaining a current efficiency of 59 % with 100 ppm Cr(VI) and space time yield of 0.31 $g\ h^{-1}\ l^{-1}$. Besides, systems with soluble anodes were studied aiming at the chromate reduction by divalent iron [10-13]. However, the anode was steadily consumed and additional iron ions load the effluent.

Recent research work, however, was focused on highly porous materials, because space time yields obtained with very diluted waste effluents are often lower than industrial needs and the treatment of these streams is still ineffective. Especially chromate reduction on carbon felt [14-18] was promoted. Carbon felt provides a high specific surface area to electron transfer (app. 22000 $m^2\ m^{-3}$ [19]). High porosity enhances the convection of electroactive species to the electrode surface resulting in high conversion rates and extremely low outlet concentrations even for very diluted solutions. There are publications dealing with reduction and precipitation of chromium on carbon felt in a single or two stage process [14, 15]. The single stage process seems very promising because detoxification, precipitation and separation could be performed in a single step without adding of chemicals. Nevertheless a recent study [16] reported that the most critical factors in terms of efficiency are the pH and the electric current density. For effluents containing 50 ppm Cr(VI) the current efficiency was low (12 %) at the optimum pH (pH 3.5) and the final Cr(VI) concentration achieved was relatively high (5 ppm). Moreover, the risk of plugging the carbon felt was rather high. Therefore, a two stage process, consisting of (i) reduction in sulfuric acidic environment and (ii) separate neutralization and separation, should be considered. To the best of our knowledge, there is only one publication where the up-scaling of this technology was discussed [20]. A 50 ppm Cr(VI) solution was maintained over 17 days by continuous reduction of chromate on a carbon felt cathode cartridge (geometric surface area of 150 cm^2). At pH 2.6, reduction rates of Cr(VI) between 12 and 22 mg h^{-1} were obtained, corresponding to a space time yield of about 0.2 g h^{-1} l^{-1}. The present work focuses on the improvement of this technology to achieve higher space time yields and downsize equipment. The process parameters mainly influencing the mass transport to the surface (e.g. flow rate and initial Cr(VI) concentration) as well as the efficiency of reduction are evaluated. Besides, other distinctive features for up-scaling are taken into account. Performance limitations due to non-uniform current distribution, gas evolution, higher pressure drop or channeling in the material [21] are considered and finally a cost estimation for the treatment of very diluted chromate containing solutions is discussed.

5.2 Experimental

5.2.1 Material and equipment

A new type of separated plug-flow electrolytic cell was used (Figure 5.1). The quadratic cell was divided into anode and cathode compartment by a cation exchange membrane (CEM, type fumasep® FTN by FuMA-Tech GmbH, Germany) preventing Cr(III) reoxidation at the anode. The current passed perpendicular to the electrodes (flow-by reactor). The distinctive feature of this cell was the use of only one electrolyte cycle – the cathodic cycle.

The cathode electrode material was commercial carbon felt (GFA-10 from SGL Technologies GmbH, Germany). To prevent channelling, it was cut in 1 cm thick stripes and crossways placed in the cell. Various studies [22-24] showed that the current distribution within porous electrodes is determined by the ratio of conductivity between electrolyte and electrode material. The more these conductivities converge the more uniform the current distribution. The specific type of graphitised felt was preferred because its electric conductivity in the transverse direction (25 to 33 mS cm^{-1}) is in the same order to that of the acidified rinse water (4 to 5 mS cm^{-1}). The projected felt area was 180 cm^2. The other components were: cathode current connection made of a stainless steel plate and an impregnated graphite plate, which protects the stainless steel from chromic acid attack. The set-up of the anode consisted of a titanium mesh type electrode with mixed oxide coating (Ir) together with a titanium perforated plate for the anode current connection. All components were pressed together using PVC frames and stainless steel endplates.

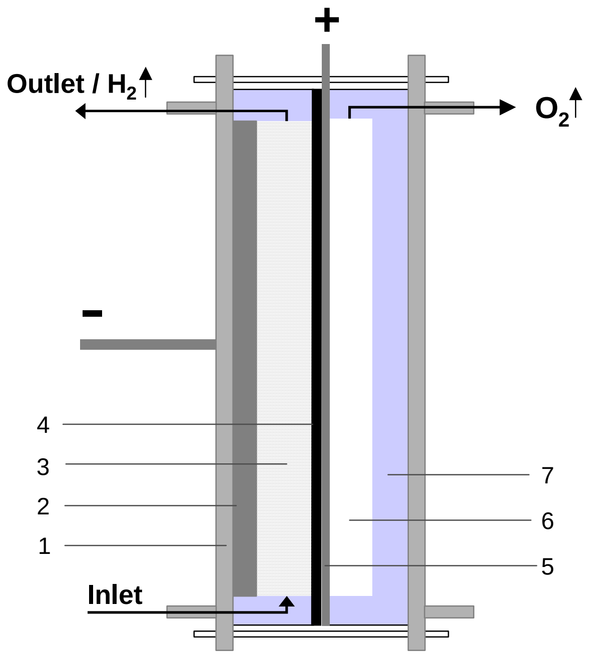


Figure 5.1. *Pilot plug-flow electrolytic cell (1: endplates, 2: cathode power supply, 3: carbon felt, 4: CEM, 5: anode power supply, 6: anode compartment, 7: frame).*

During our study, the anode compartment was wetted only once at the very beginning of the run by rinsing it with water, but later on, it was kept empty. The membrane remained humidified by water diffusion from the cathode compartment. The open cell design and perforated lid ensured, that anodic gas (oxygen) could easily escape from the reaction zone at the electrode. The pilot plant (Figure 5.2) was placed in a plating company producing decorative and hart chromium plated parts (Hartchrom GmbH, Karlsruhe, Germany). It consisted of a tank with mixer, an impeller pump for feed supply to the cell, a flow controller, flow meter, rectifier and PC for data acquisition (current, voltage, temperature, pH and conductivity). Samples were taken directly from the tank and the outlet stream. The Cr(VI) concentration was determined by UV-/VIS spectrophotometry (spectro-photometer CADAS 200, Dr. Bruno Lange GmbH, Germany, Test No. LCK 313 for 0.03–1 ppm Cr with formation of complexes with 1,5-diphenylcarbazide). Selected samples were analysed for Cu, Fe, Ni, Zn and Al by ICP-OES.

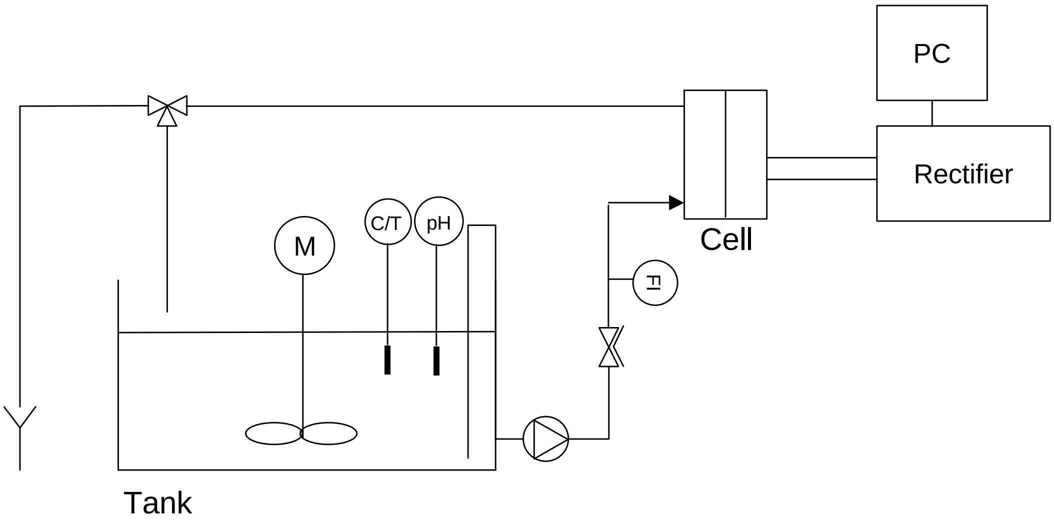


Figure 5.2. *Pilot plant for electrochemical chromate reduction (tank capacity: 400 l, FI - flow indicator, C/T - conductivity and temperature measurement, M - motor).*

5.2.2 Process conditions

The experiments followed the task plan earlier proposed by Simmrock [25] and previously used for electrochemical investigations of packed bed electrodes by Kreysa [26]. The rinse water (inlet stream) was manually mixed in a tank close to the production line. Thus, the initial conditions for this study were always the same. The concentration was adjusted to 3, 16 or 50 ppm Cr(VI) by dilution of exhausted chromium etching solution (see composition in Table 5.1). The pH was adjusted using technical grade sulphuric acid (pH 1.8 to 2.5). The experiments were either performed as flow-through experiments or batch experiments where the outlet stream was totally recycled to the tank until the discharge level was reached. Current densities were calculated based on the projected area of the carbon felt electrode. First, the optimum current density at each Cr(VI) concentration was experimentally determined and then used in all experiments at the specific concentration. The feed flow rates ranged from 10 to 50 $l\ h^{-1}$ corresponding to linear flow velocities from 0.3 to 1.5 $cm\ s^{-1}$ in accordance with other studies [16, 18]. The felt electrode was in contact with the process solution for 530 hours (total), from which, 120 hours under operation.

Table 5.1. *Composition of exhausted chromium etching solution used for preparing synthetic rinse water.*

Cr(VI) ($g\ l^{-1}$)	**Cr total** ($g\ l^{-1}$)	**Fe** ($g\ l^{-1}$)	**Cu** (ppm)	**Zn** (ppm)	**Ni** (ppm)	**Al** (ppm)
113	136	15.1	571	43	160	49

5.2.3 Theoretical background

The following reactions could occur at the electrodes:

Cathode

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O \qquad E° = 1.33\ V \qquad (5.1)$$

$$HCrO_4^- + 4\,H^+ + 3\,e^- \rightarrow Cr^{3+} + 4\,H_2O \qquad E° = 1.35\ V \qquad (5.2)$$

$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2 \qquad E° = 0.00\ V \qquad (5.3)$$

$$Cr^{3+} + e^- \rightarrow Cr^{2+} \qquad E° = -0.41\ V \qquad (5.4)$$

Anode

$$2H_2O - 4\,e^- \rightarrow O_2 \uparrow + 4\,H^+ \qquad E° = 1.23\ \text{V} \qquad (5.5)$$

The presence of Cr(II) according to equation (5.4) is generally not expected due to its fast oxidation by H^+ and chromate. The formation of $Cr(OH)_3$ is excluded due to the acidity of the solution. Various parameters could be used to describe the process performance [21, 27]:

1. Fractional conversion, X_A, defined as

$$X_A = 1 - \frac{n_A}{n_{A,0}} \qquad (5.6)$$

   where $n_{A,0}$, n_A is the starting and final molar amount of chromate, respectively.

2. Overall current efficiency, Φ^e, defined as the current required for chromate reduction relative to the total current applied:

$$\Phi^e = \frac{m\,\nu_e\,F}{M\,I\,t} \times 100 \qquad (5.7)$$

   where m is mass of the reduced chromate, M its molar mass, F the Faraday constant, I the applied current during time, t and ν_e the stoichiometric number of electrons necessary for the reaction. For the reduction of one mole of chromium, three electrons are required (see equations (5.1) and (5.2)). Therefore, the stoichiometric number, ν_e, is 3.

3. The space time yield (STY), ρ_{ST}, is the reduction rate per cell volume and may be expressed as:

$$\rho_{ST} = \frac{\Delta\,c\,M}{\tau_{ST}} \qquad (5.8)$$

where Δc is the Cr(VI) concentration change and τ_{ST} is the space or residence time, defined as the ratio of cell volume to volumetric flow rate. Generally, the STY is used for comparison of different systems and is expressed in kg m^{-3} s^{-1} or in g l^{-1} h^{-1}. However, it is important to note, that equation (5.8) contains no information about the initial effluent concentration, which could be one of the most important factors influencing the process.

4. The specific energy consumption, $E_{S,m}$:

$$E_{S,m} = \frac{U_c \nu_e F}{M \Phi^e} \tag{5.9}$$

where U_c is the total cell voltage.

5.3 Results and discussion

5.3.1 Determination of optimum current density

The limiting current densities could not be determined by direct measurement of current at different single electrode potentials using reference electrodes, because a pilot electrolytic cell was used. Instead, we determined the outlet concentrations (conversion rate) and current efficiencies at various current densities and at three inlet concentrations (3, 16 and 50 ppm Cr(VI)). Theoretically, the curves show maximum efficiency and maximum conversion rate at a certain current density, which is considered as the optimum current density. Figure 5.3 presents the typical conversion rate and current efficiency at 16 ppm Cr(VI).

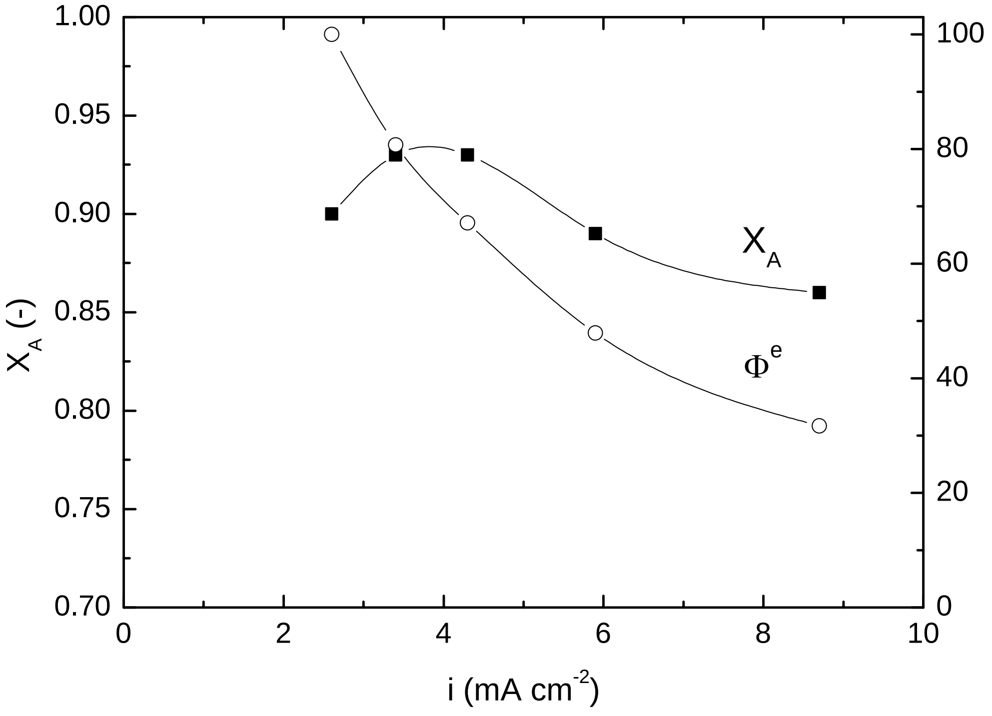


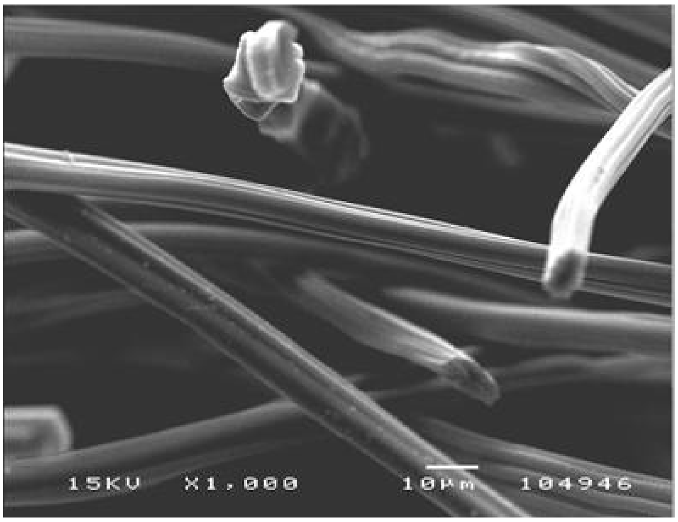
Figure 5.3. *Conversion rate,* X_A*, and current efficiency,* Φ^e*, at various current densities. Process parameters: Cr(VI) inlet concentration* c_i *= 16 ppm, pH 2.1, feed velocity u = 0.6 cm* s^{-1}*, fresh carbon felt as electrode, T = 26°C.*

The current efficiency was close to 100 % at 3 mA cm^{-2} and the conversion rate shows a maximum between 3.5 and 4.5 mA cm^{-2}. Therefore, the optimum current density for operation was assumed at 3.5 mA cm^{-2}. Similarly, at 50 ppm the optimum current density was found to be 8.6 mA cm^{-2}. At very low Cr(VI) concentration (3 ppm) no maximum conversion rate was found (the conversion rate was 0.99 at each current density). Therefore, 1.4 mA cm^{-2} was chosen as optimum current density, where the current efficiency was the highest.

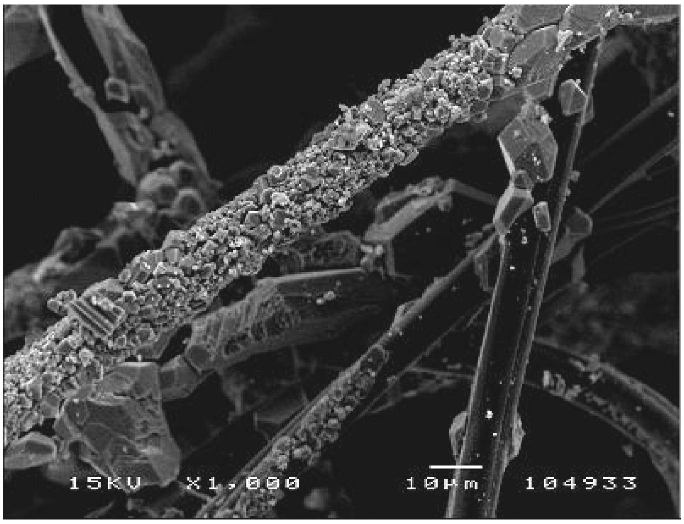
5.3.2 Influence of contaminants

Rinse water contaminants, especially copper could have a strong effect on process performance due to their deposition on the cathode even in acidic environment [20]. Copper coated fibers lower the specific surface area of the porous felt acting as solid electrode surface. This could result in decreasing limiting current density and lower reactant conversion [28]. In our experiments, we noticed a green coloured metal deposit on the carbon felt, which was removed by concentrated acid and analysed. The analysis showed that it was copper.

Furthermore, SEM pictures of the carbon felt were made (see Figure 5.4). Figure 5.4a shows an unused felt and Figure 5.4b shows a sample of the electrode used for 120 hours of operation, where the copper deposit on the fibres is obvious. The copper mainly deposits in the region near the entrance and the outlet of the electrode, in agreement with previous studies [28]. During the study, we observed apparent current efficiencies higher than 100 %. For instance 150 % for a inlet concentration of 16 ppm Cr(VI) working at pH 2.1 and 50 l h^{-1}. This indicates that current-free reduction of Cr(VI) must occur by alternative reductants. In order to investigate this, we placed two felt samples (one fresh and one used in process for 120 hours) in synthetic hexavalent chromium solution (50 ml, 16 ppm Cr(VI) prepared from chromic acid anhydrid) for 50 hours, under stirring. Table 5.2 presents the results. No hexavalent chromium is reduced with the unused felt, but the chromate is reduced almost completely with the felt having the copper deposit. This clearly shows that copper can additionally reduce the chromate.



(a)



(b)

Figure 5.4. *SEM photographs of carbon felt GFA 10. (a) Unused carbon felt and (b) used for 120 hours of operation.*

Table 5.2. *Current-free reduction of Cr(VI) at carbon felt GFA 10 (process conditions: 50 ml of 16 ppm Cr(VI) solution).*

Description	**[Cr(VI)] reduction**
carbon felt unused	0
carbon felt used in process solution for 120 hours	99 %

Moreover, it seems that both Cr(VI) reduction and copper deposition/dissolution happen simultaneously influenced by the chromate concentration in the feed. This behaviour is not surprising and can be explained based on the different standard electrode potentials of the reaction from equation (5.1) (1.33 V) and the copper deposition reaction:

$$Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0} \qquad E_e^{0} = 0.35\ \mathrm{V} \qquad (5.10)$$

According to the Nernst equation at constant temperature, the equilibrium potential shifts depending on the species concentration. At low chromate concentration, when the chromate is nearly completely reduced, the equilibrium electrode potential decreases and reaches that of copper resulting at copper deposition on the felt. If the inlet concentration is above 10 ppm Cr(VI), re-solution of previously deposited copper takes place. Figure 5.5 shows the course of a batch experiment lasting for 21 hours. The initial 300 l rinsing solution contained 50 ppm Cr(VI) and 0.3 ppm Cu. The felt was previously used in other experiments for 80 hours but the amount of the deposited copper was unknown. In the beginning of the experiment, the copper concentration in the tank increases whereas the hexavalent chromium concentration decreases as desired. After ~ 6 hours, the copper concentration in the tank reaches a maximum and later, after 15 hours, it starts to decrease due to its deposition on the felt (Figure 5.5a). Interestingly, despite the low initial copper concentration in the tank (0.3 ppm) the outlet stream contains 26 ppm Cu^{2+} (Figure 5.5b) mostly coming from copper resolved from the felt. As a result, the chromate concentration decreases relatively fast, the process has apparent current efficiency higher than 100 % and the Cr(VI) outlet concentration practically becomes zero after 13 h. At this point, the copper concentration in the outlet starts to decrease (Figure 5.5a) showing that the deposition becomes the main reaction again. These phenomena have significant importance for the practical long-term operation. Either undesired deposited copper should be reduced at the start of batch mode operation (self-cleaning) or the felt cathode could be easily cleaned when process solution flows current-free through the cell (potential cleaning procedure).

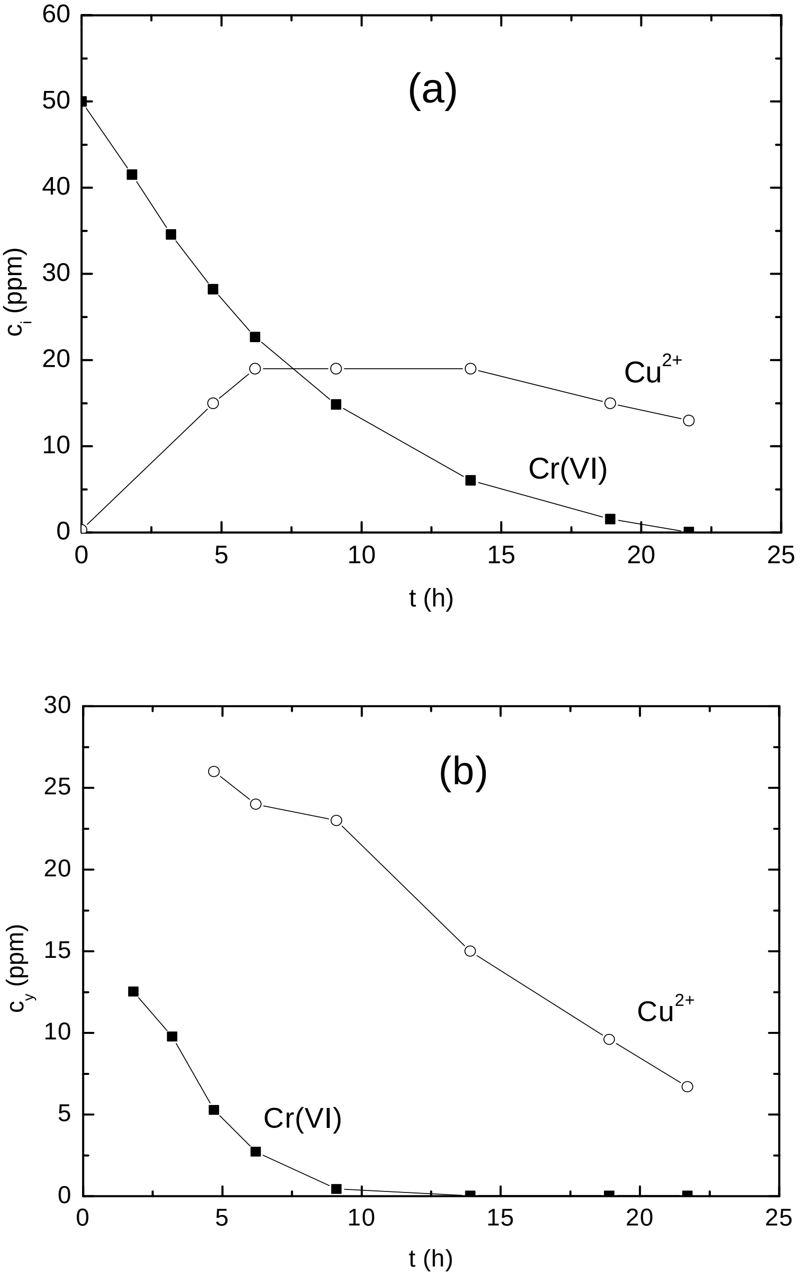


Figure 5.5. *The changes of Cr(VI) and* Cu^{2+} *concentration during a batch experiment. (a) In the tank (*c_i *= cell inlet concentration) and (b) in the outlet stream (*c_y *= cell outlet concentration). Process parameters:* $U_C = 2$ *V, u = 1.5 cm* s^{-1}*, i = 7.8 mA* cm^{-2} *(t = 0h) and 5.2 mA* cm^{-2} *(t = 21 h), pH 2.1, T = 26°C.*

Finally, it is worth noting that during all experiments we used the same cathode felt and the copper deposition and dissolution could not be controlled. Therefore, the measurement series taken at different operation times can not be directly compared.

However, the reactor performance in each measurement series shows always the same behaviour for the different influencing factors (inlet concentration, c_i, feed flow velocity, u, and pH) even if the parameters X_A, Φ^e and ρ_{ST} are fluctuating over the whole pilot study. Figure 5.6 presents a typical example, where the influence of the feed velocity on the process performance is studied at different operation times (all other process conditions are the same). Obviously, lower outlet concentrations (higher current efficiencies and conversion rates) are obtained when the felt is already used for a longer time (105 hours instead of 6 hours) indicating once more the additional chromate reduction by deposited copper. In addition, the influence of the flow rate seems to be different in these two cases. When the felt is only used for 6 hours, the outlet concentration increases strongly with the flow rate. However, after several hours of running (105 h), this effect is not as strong. It seems, that increasing feed flow rates results in increasing copper re-solution and therefore, lower Cr(VI) outlet concentrations compared to the fresh felt are obtained.

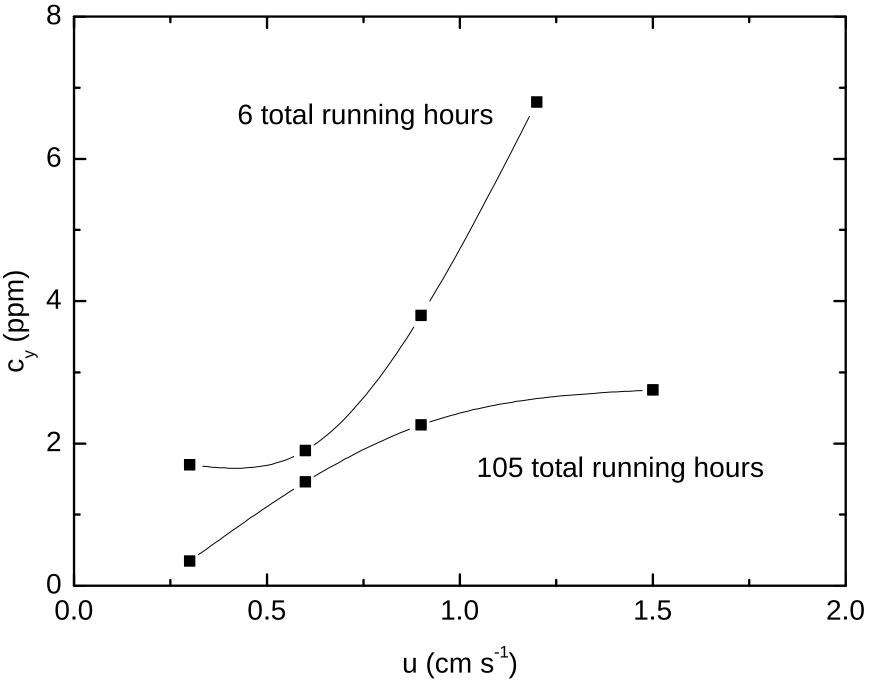


Figure 5.6. *Effect of feed velocity, u, on Cr(VI) outlet concentration, c_y, at different total running times. Process parameters: Cr(VI) inlet concentration c_i = 16 ppm, i = 3.5 mA cm^{-2}, pH 2.1, T = 26°C.*

5.3.3 Influence of process parameters

5.3.3.1 Effluent concentration and feed velocity

In plating companies, the concentration of waste effluent fluctuates strongly. In some cases, this could result in lower cell performance and outlet concentration above the maximum permissible levels. Figure 5.7 shows the variation of the space time yield at three different initial Cr(VI) concentrations for two feed flow rates. As expected, the STY increases with the increase of Cr(VI) concentration (see equation (5.8)) and this increase is stronger at higher flow rates. The highest Cr(VI) reduction rate (10.4 g l^{-1} h^{-1}) is found for 50 ppm and 50 l h^{-1} and is attributed to two effects. When the reactant concentration is low, the supply of reactant to the electrode surface becomes important (diffusion limitation). Therefore, the conversion improves at higher feed velocities (see Figure 5.6).

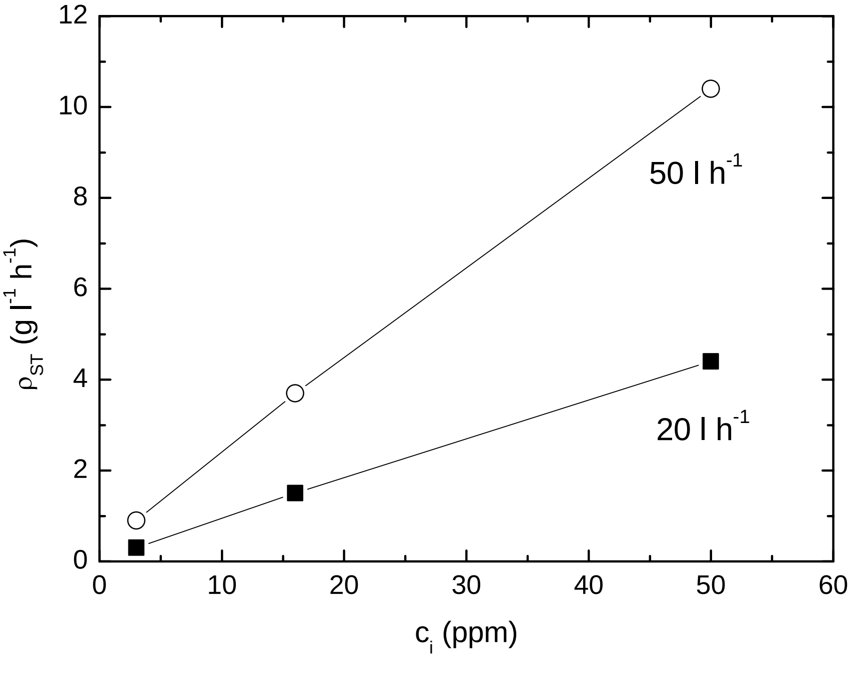


Figure 5.7. *Space time yield, ρ_{ST}, at different Cr(VI) inlet concentrations, c_i, and feed flow rates. Process parameters: Current density 1.4 mA cm^{-2} for 3 ppm, 3.5 mA cm^{-2} for 16 ppm and 8.6 mA cm^{-2} for 50 ppm Cr(VI), pH 2.1 and T = 26°C.*

The conversion improves at high flow rates due to increased copper re-solution resulting in a current efficiency of ~130 %. On the other hand, if the feed velocity is too high, especially at high inlet concentrations, the residence time might be too short to have effective conversion. Then, reduction of the flow rate (increasing residence time) might be required to reach lower outlet concentrations. Nevertheless, our results show that the outlet concentration at low concentrated solutions (3 ppm) is below the German discharge level (0.1 ppm) independent from the feed flow rate. Even when providing 50 l h^{-1} (1.5 cm s^{-1}), hexavalent chromium could not detected in the outlet stream.

5.3.3.2 Influence of pH

Protons are absolutely required for chromate reduction (see equations (5.1) and (5.2)). Therefore, both chemical and electrochemical reduction of diluted Cr(VI) effluents requires addition of sulphuric acid to pH < 2.5. One should always strive for optimised acid consumption. On one hand consumption of extra chemicals should be minimized, but on the other hand, the electrolyte pH must be low enough to ensure sufficient and complete chromate reduction.

This study describes experiments at pH 2.1. However, we also investigated the effect of excess of H_2SO_4. Samples were taken every 30 min after acid addition. Lowering the pH from 2.5 to 1.8 results in lower outlet concentrations (7.8 ppm to 2.0 ppm) and to increase of the conversion rate from 0.52 to 0.87 (Figure 5.8). The same behaviour was obtained for more diluted solutions, e.g. 3 ppm Cr(VI). The conversion rate was 0.96 at pH 2.1, but only 0.8 at pH 3 (both for 1.2 cm s^{-1}).

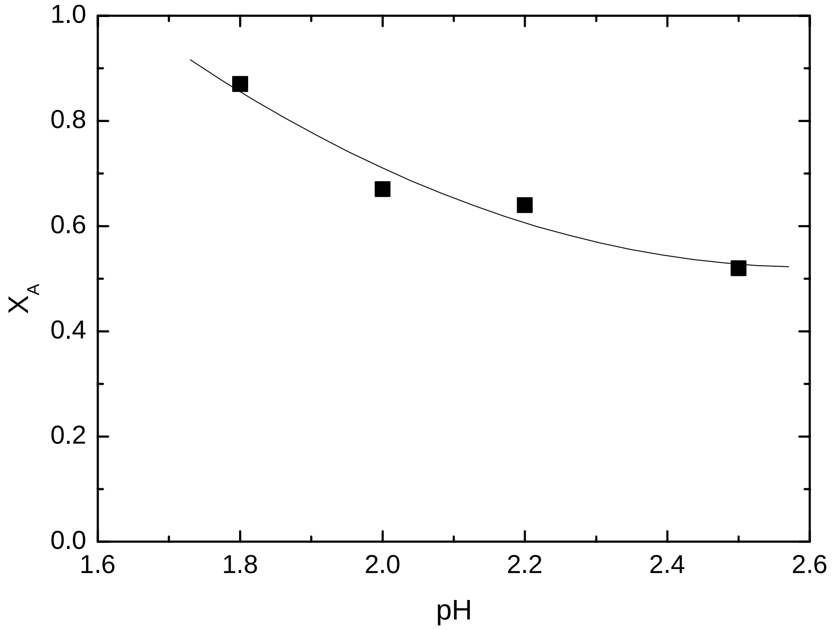


Figure 5.8. *The effect of rinse water pH on the conversion rate of Cr(VI). Process parameters: Cr(VI) inlet concentration* c_i *= 16 ppm, i = 3.5 mA* cm^{-2}*, u = 1.5 cm* s^{-1}*, T = 26°C.*

5.3.3.3 Potentiostatic vs. galvanostatic mode

For the estimation of energy requirements, we compared two batch mode experiments, where the Cr(VI) concentration in the tank was reduced from 16 ppm to below 0.1 ppm. The first experiment was performed at constant voltage of U_C = 1.6 V (potentiostatic mode) and the second experiment at constant current (galvanostatic mode). In the latter, the current was gradually lowered according to the concentration decrease in the tank simulating constant current operation as in industrial scale experiments. This process might have advantages, because the current density could be lowered stepwise according to the particular inlet concentration resulting at energy savings. Figure 5.9 shows that the decrease of Cr(VI) concentration in the tank is the same for both experiments despite the different electric operation. The overall STY for both experiments is 1.9 g l^{-1} h^{-1} and about 50 % lower than the STY of the flow-through experiments at constant Cr(VI) concentration (see Figure 5.7, STY ~ 3.5 g l^{-1} h^{-1} for 16 ppm Cr(VI) and 1.5 cm s^{-1}). This difference can be explained by the steady decrease of

Cr(VI) concentration in the tank resulting in decreasing STY according to Figure 5.7 and eventually in lower average STY. The total current efficiency is 93 % at batch mode and nearly 100 % at flow-through mode showing the good performance of this technology with very diluted waste effluents and indicating the balance of copper dissolution and deposition. In conclusion, it seems that the galvanostatic mode brings no additional benefits in terms of required carbon felt area (equipment size), however, gradual lowering of the current results in lower power consumption due to lower voltage drop.

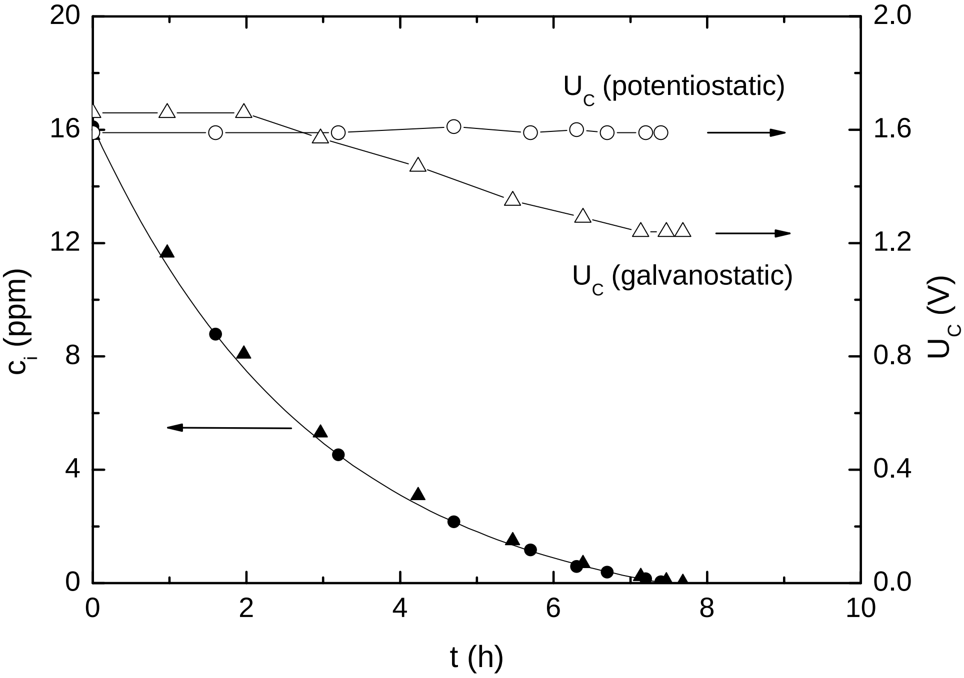


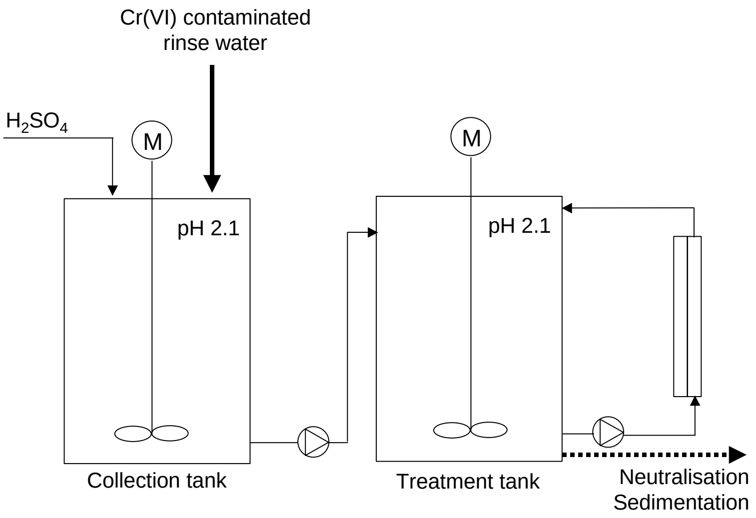
Figure 5.9. *Batch processing at different electric operation (circles: potentiostatic, triangles: galvanostatic mode). Other process parameters: Cr(VI) inlet concentration* c_i *=* *16 ppm (t = 0), pH 2.1, u = 1.5 cm* s^{-1}*, T = 26°C.*

5.3.4 Electrochemical Cr(VI) reduction at industrial scale - an example

5.3.4.1 Energy requirements for batch and flow-through operation

Generally the batch processing is promoted by legislative authorities. The reason is that the risk of the toxic chromate reaching the public sewers or receiving water seems less than continuous processing. By batch mode processing discharging levels could be safely maintained, even if the waste concentrations fluctuate. Figure 5.10 schematically presents future industrial-scale operation using either batch (Figure 5.10a) or flow-through mode (Figure 5.10b). The calculation is based on the STY of batch experiments of Figure 5.9 (1.9 g l^{-1} h^{-1}) assuming a waste water flow of 1 m^3 per hour. Flow-through processing requires only one small tank for pH adjustment, whereas batch processing requires two tanks able to collect the total waste stream for a certain time (1 h). For this example the carbon felt area is the same for both modes (~ 1.2 m^2) due to the same average STY (1.9 g l^{-1} h^{-1}). Batch operation is realized with one module (Figure 5.10a), whereas the flow-through configuration consists of three modules in series each running at different current density (Figure 5.10b). Accordingly, the three modules are smaller than the one module in batch mode.

(a) Batch operation



(b) Flow-through operation

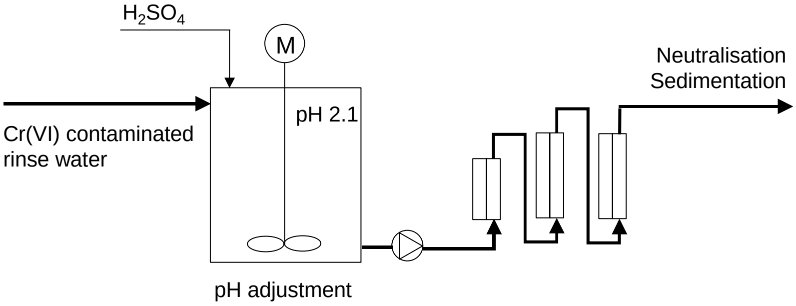


Figure 5.10. *Schematic presentation of electrochemical modes of operation. (a) Batch and (b) flow-through operation.*

Table 5.3 presents the calculations of energy requirements for both modes of operation. The consumed current was calculated from variation of current intensities by integration. The flow-through mode has economical advantages due to lower specific current at the inlet of each step. Besides higher current efficiency (~ 100 %), this results in slightly lower voltage drop and power consumption in comparison to batch mode (2.3 instead of 2.8 kWh $(kg_{Cr(VI)})^{-1}$, respectively). On the other hand, batch processing might have advantages in terms of operation reliability. In this mode, the deposited copper can be removed in the starting phase of the process (self-cleaning operation). In the flow-through mode most of the copper might be deposited in the last module and could be only removed by additional cleaning procedures. The successful industrial implementation requires further work focused on up-scaling of the electrolytic cell, especially on carbon felt multi-layer cathodes to provide sufficient large cross-sectional area.

Table 5.3. *Energy requirements for electrolytic chromate reduction at batch and flow-through mode for 1 $m^3\ h^{-1}$.*

	Batch	**Flow-Through**
Stages	1	3
I t (Ah)	27.4	24.7 (6.1 + 13.3 + 5.3)
U_c (V)	1.6	1.6 / 1.5 / 1.3
E (Wh)	44	37
$E_{S,m}$ (kWh $kg_{Cr(VI)}^{-1}$)	2.8	2.3
Calculation parameters: treatment of 1 $m^3\ h^{-1}$, c_i = 16 ppm, u = 1.5 cm s^{-1}, potentiostatic mode for batch operation and galvanostatic mode for flow-through operation		

5.3.4.2 Electrochemical vs. chemical detoxification of chromate

There are few literature data on the economics of other electrochemical methods, such as, chromate reduction on planar or mesh type electrodes, fixed beds (granular carbon) or soluble steel anodes. Table 5.4 presents some of them in comparison to our results. The power consumption for pure electrolysis per kg Cr(VI) are compared. Our method using carbon felt shows the lowest power consumption, 2.3 kWh per $kg_{Cr(VI)}$, followed by the reduction using graphite particles in a fixed bed.

Table 5.4. *Energy requirements for electrolytic Cr(VI) reduction using different electrochemical treatment methods.*

Cr(VI) reduction method	**Reference**	**Power consumption ($\mathbf{kWh\ kg_{Cr(VI)}^{-1}}$)**
Membrane electrolysis with mesh type cathodes	[5]	8–11 [a]
Soluble anodes (indirect reduction by Fe^{2+})	[13]	12 [b]
Fixed bed (granular carbon)	[9]	6 [a]
Carbon felt	[this work]	2.3 [c]

[a] Cr(VI) concentration not specified

[b] $c_{i,\ Cr(VI)}$ = 500 ppm Cr(VI)

[c] $c_{i,\ Cr(VI)}$ = 16 ppm (this work, Table 5.3)

Finally, the operation costs for chromate detoxification of very diluted effluents are considered (Table 5.5). Chemical and electrochemical treatment are compared using the results obtained during this work. The operation costs for electrochemical treatment are 30 % lower than for the chemical treatment. This is mainly due to the lower amount of produced sludge when reducing chromate without the use of reduction chemicals. The cost for electrolysis are very low compared to those of sludge disposal and practically do not influence the total costs. However, additional costs arise for the hydraulic supply of the electrolytic cell.

Table 5.5. *Operating costs for Cr(VI) detoxification by chemical and electrochemical reduction (in Euros per m^3).*

	Chemical treatment	**Electrochemical reduction on carbon felt (flow-through mode)**
Initial pH adjustment (pH 2.1)	0.08 (a)	0.08 (a)
Chemical for reduction ($NaHSO_3$)	0.08 (b)	–
Energy consumption for electrolysis	–	< 0.01 (c)
Energy for pumping through the cell	–	0.05 (d)
Chemical for precipitation (lime milk)	0.02 (e)	0.01 (f)
Sludge disposal	0.24 (g)	0.15 (h)
Total	**0.42**	**0.30**

Process parameter: c_i = 16 ppm Cr(VI), treatment of 1 m^3 h^{-1}, u = 1.5 cm s^{-1}, flow-through operation

(a) H_2SO_4 at 100 € t^{-1}

(b) $NaHSO_3$ (solid) at 1.3 € kg^{-1} (3.3 kg $NaHSO_3$ (kg Cr(VI))$^{-1}$ needed), including a factor for making-up and dosage of the liquid reduction chemical (factor 1.2)

(c) Example from Table 5.3 (2.3 kWh per kg Cr(VI)), 0.11 € kWh^{-1}

(d) Considering a pump consuming 0.5 kWh, 0.11 € kWh^{-1}

(e) 4.3 kg$_{Ca(OH)2}$ per kg$_{Cr(VI)}$, 35 % $Ca(OH)_2$, 65 € t^{-1}

(f) 2.1 kg$_{Ca(OH)2}$ per kg$_{Cr(VI)}$, 35 % $Ca(OH)_2$, 65 € t^{-1}

(g) 50 kg per kg$_{Cr(VI)}$, 20 % solids content, 300 € t^{-1}

(h) 32 kg per kg$_{Cr(VI)}$, 20 % solids content, 300 € t^{-1}

5.4 Conclusions

The electrochemical chromate reduction on highly porous carbon felt electrode is an efficient treatment method especially for very diluted solutions. In this work, we obtained high reduction rates of chromate, especially when the electrode felt was running over long-time and due to the copper deposition and re-solution in the felt (the copper in the rinse water comes from the chromium etching process). Copper deposited onto the cathode felt when chromate was completely reduced and dissolved when the chromate concentration increased, for instance when a new batch process started. The copper deposits significantly enhanced the process performance by this current-free reduction of chromate.

The economics of batch and flow-through operation were compared for effluents containing 16 ppm Cr(VI). For the flow-through operation, the energy requirements were estimated to be low (2.3 kWh per kg Cr(VI)). Finally, the electrochemical Cr(VI) reduction at carbon felt was compared to the chemical detoxification of chromate. The operation costs were estimated to be 30 % lower showing the promising economic potential of this technology.

5.5 Acknowledgements

The author wish to thank the company FuMA-Tech GmbH for financial support, Jörg Balster from the University Twente, Enschede, the Netherlands for making the SEM photographs, the company Hartchrom GmbH, Karlsruhe, Germany for active support during pilot experiments and Dr. Hans Holdik, FuMA-Tech GmbH, for the helpful discussions on the electrode processes.

5.6 References

1. I.M. Kolthoff and A.M. Shams El Din, Reduction of hexavalent chromium at the rotated platinum electrode. Permeability of the film formed, J. Phys. Chem. **60** (11) (1956) 1564-1568.
2. P.M. Robertson, F. Schwager and N. Ibl, A new cell for electrochemical processes, Journal of Electroanalytical Chemistry **65** (2) (1975) 883-900.
3. A.J. Chaudhary, N.C. Goswami and S.M. Grimes, Electrolytic removal of hexavalent chromium from aqueous solutions, Journal of Chemical Technology & Biotechnology **78** (8) (2003) 877 - 883.

4. N. Ibl and A.M. Frei, Untersuchung der elektrolytischen Reduktion chromhaltiger Abwässer, Galvanotechnik + Oberflächenschutz **5** (6) (1964) 117-122 (in German).

5. P. Kimmerl, H. Schade, W. Blatt and L. Schneider, Wirtschaftliche Lösungen auf dem Weg zur schadstoffarmen und abwasserfreien Galvanik, Galvanotechnik **85** (12) (1994) 4131-4140 (in German).

6. E.C.W. Wijnbelt and L.J.J. Janssen, Reduction of chromate in dilute solution using hydrogen in a GBC-cell, J. Appl. Electrochem. **24** (1994) 1028-1036.

7. K.N. Njau and L.J.J. Janssen, Electrochemical reduction of chromate ions from dilute artificial solutions in a GBC-reactor, J. Appl. Electrochem. **29** (1999) 411-419.

8. S. Reussard, J.F. Benezech and G. Lacoste, Removal of hexavalent chromium converting to chromium hydroxide by treatment in an electrochemical reactor, in "Electrochemical engineering and the environment 1992". 1992. p. 97-100.

9. E. Langefeld, Abwasserbehandlung mittels Elektrolyse bis auf die geforderten Einleitewerte, Galvanotechnik **83** (11) (1992) 3859-3865 (in German).

10. J. Dziewinski, S. Marczak, E. Nuttall, G. Purdy, W. Smith, J. Taylor, and C. Zhou, Developing and testing electrochemical methods for treating metal salts, cyanides and organic compounds in waste streams, Waste Management **18** (1998) 257-263.

11. N. Kongsricharoern and C. Polprasert, Electrochemical precipitation of chromium (Cr^{6+}) from an electroplating wastewater, Water Science & Technology **31** (9) (1995) 109-117.

12. N. Kongsricharoern and C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, Water Science & Technology **34** (9) (1996) 109-116.

13. C. Barrera-Díaz, M. Palomar-Pardave, M. Romero-Romo and S. Martínez, Chemical and electrochemical considerations on the removal process of hexavalent chromium from aqueous media, J. Appl. Electrochem. **33** (2003) 61-71.

14. D. Golub and Y. Oren, Removal of chromium from aqueous solutions by treatment with porous carbon electrodes: electrochemical principles, J. Appl. Electrochem. **19** (1989) 311-316.

15. M. Abda, Z. Gavra and Y. Oren, Removal of chromium from aqueous solutions by treatment with fibrous carbon electrodes: column effects, J. Appl. Electrochem. **21** (1991) 734-739.
16. E.P.L. Roberts and H. Yu, Chromium removal using a porous carbon felt cathode, J. Appl. Electrochem. **32** (2002) 1091-1099.
17. V.K. Varenzov, Detoxication of chromium-containing rinse water by means of electrolysis with carbon-fiber electrodes, Galvanotechnika i obrabotka poverchnosti (Russia) **10** (1) (2002) 29-33 (in Russian).
18. E.O. Vilar, E.B. Cavalcanti, H.R. Carvalho and F.B. Sousa, Cr(VI) electrochemical reduction using RVG 4000 graphite felt as the electrode, Brazilian Journal of Chemical Engineering **20** (3) (2003) 291-303.
19. J. González-García, P. Bonete, E. Expósito, V. Montiel, A. Aldaz, and R. Torregrosa-Maciá, Characterization of a carbon felt electrode: structural and physical properties, Journal of Materials Chemistry **9** (2) (1999) 419-426.
20. I.M. Dalrymple, J.G. Sunderland and M. Hendou (2003) The recovery and recycling of Cr(VI) from Dilute Waste Solutions. Canmet/Cari/European Commission Joint Workshop on "Environmental Technologies for a Sustainable Production and Consumption" (Vancouver (Canada)).
21. F. Walsh, A First Course in Electrochemical Engineering. 1993, The Electrochemical Consultancy.
22. V.S. Daniel-Bek, Polarisation of porous electrodes. Part I: Current and potential distribution within the electrode, Journal for Physical Chemistry (UdSSR) **22** (6) (1948) 697-710 (in Russian).
23. V.K. Varenzov, Use of voluminous porous flow-through electrodes for increased performance of electrochemical processes in hydrometallurgy, in "Increasing performance of electrochemical processes. Collection of scientific studies." A.P. Tomilov, Editor. 1988, Academy of Science of UdSSR. Institute for Electrochemistry "A.N. Frunkin". Moscow, Nauka. p. 94-118 (in Russian).
24. F. Walsh, Electrode Potential and Current Density Distribution, in "A First Course in Electrochemical Engineering". 1993, The Electrochemical Consultancy. p. 235.
25. K.H. Simmrock, Beispiele für das Auswerten und Planen von Versuchen, Chem.-Ing.-Tech. **40** (1968) 875-883 (in German).

26. G. Kreysa, Festbettelektrolyse - ein Verfahren zur Reinigung metallhaltiger Abwässer, Chem.-Ing.-Tech. **50** (5) (1978) 332-337 (in German).
27. H. Wendt and G. Kreysa, Electrochemical Engineering: Science and Technology in Chemical and Other Industries. 1999, Heidelberg, Springer-Verlag.
28. E.J. Podlaha and J.M. Fenton, Characterization of a flow-by RVC electrode reactor for the removal of heavy metals from dilute solutions, J. Appl. Electrochem. **25** (1995) 299-306.

Chapter 6

Water recycling from mixed chromic acid waste effluents by membrane technology[*]

Abstract

Approaching zero discharge waste on site requires economical treatment technologies for the plating industry, recovering high quality rinse water for reuse. The combination of membranes and evaporation could be an efficient way to downsize the cost and the energy intensive evaporation equipment. In this work a combination of different membrane processes is evaluated for efficient reduction of the waste water volume before evaporation. A stable process is developed showing that pre-concentration by 51 % is possible. Chemically stable membranes are evaluated and optimum process parameters are determined.

---

[*] Parts of this chapter has been submitted for publication to Separation and Purification Technology.

6.1 Introduction

During the chromium plating process toxic chromic acid is dragged out from the process bath into different rinsing baths. According to the required rinse water specification the exhausted rinse water should be replaced, detoxified and purified before discharging. This is commonly achieved by acidification, chemical detoxification, precipitation and sludge separation (Figure 6.1).

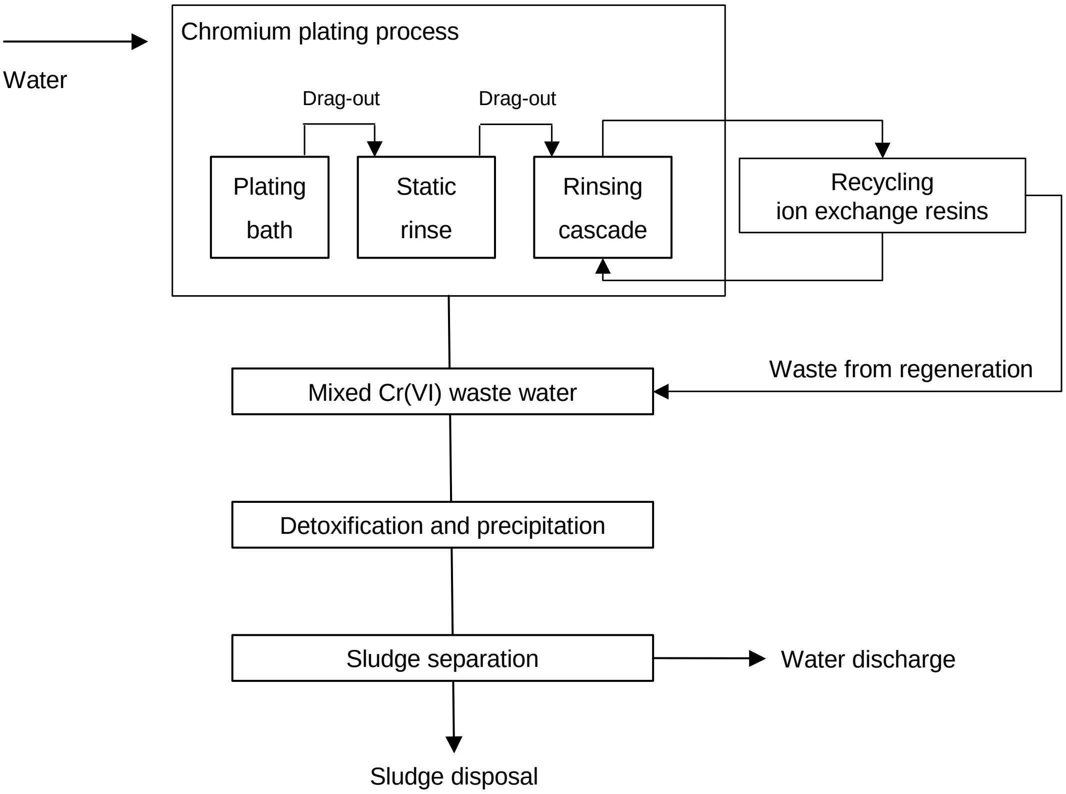


Figure 6.1. *Schematic diagram for the treatment of mixed chromic acid rinse water. Conventional waste water treatment.*

The clarified water is still saline and could not be reused in the rinsing process. Therefore, plating companies which are striving for "zero waste" management have to look for more advanced and efficient treatment technologies. Evaporation separates the waste water in a condensate, which is reused as rinsing water, and a concentrate, which is either reused in the plating process or disposed of depending on the waste management of the plating company. The acidic rinse water is directly evaporated when the concentrate does not contain undesired impurities and can directly be reused as plating chemical. In comparison, evaporation is operated as treatment technology, where the main objective is waste minimization and water reuse. Especially, the latter is applied for mixed chromic acid rinse waters containing a broad range of contaminants preventing recycling of the concentrate to the plating process. Here, the downsizing of the evaporation equipment seems to be an approach for net-waste and cost reduction. Cohen Hubal et al. [1] evaluated different scenarios with alternative treatment methods (evaporation and ion-exchange) concerning the production of additional waste and the extra energy consumption. They concluded that both technologies suffer from generation of hidden waste. Ion-exchange requires the use of additional chemicals and water. Evaporation requires high energy consumption resulting both in higher total waste production than conventional treatment. Therefore, technologies with lower energy consumption and minimized use of extra chemicals or water are necessary.

In this work, different membrane processes are investigated aiming to the efficient reduction of the waste water volume before evaporation (see Figure 6.2). The membrane technology should be able to recover high quality water suitable for reuse in rinsing processes. Usually, the recovered rinse water should have a specific conductance below 20 $\mu S\ cm^{-1}$ and pH 5–6. To keep these requirements pH adjustment before membrane filtration is necessary. Besides controlling the pH between 5 and 6, a precipitation and removal of metal hydroxides should be performed before NF or RO. For this microfiltration (MF) could be a sufficient method. Therefore in this work, the treatment of water by membrane technology is subdivided into three different stages:

- Stage 1: pH adjustment and removal of precipitates by MF
- Stage 2: removal of dissolved contaminants by NF or RO
- Stage 3: guaranteeing high water quality by final RO.

Our work focuses on membrane stability testing and process optimisation.

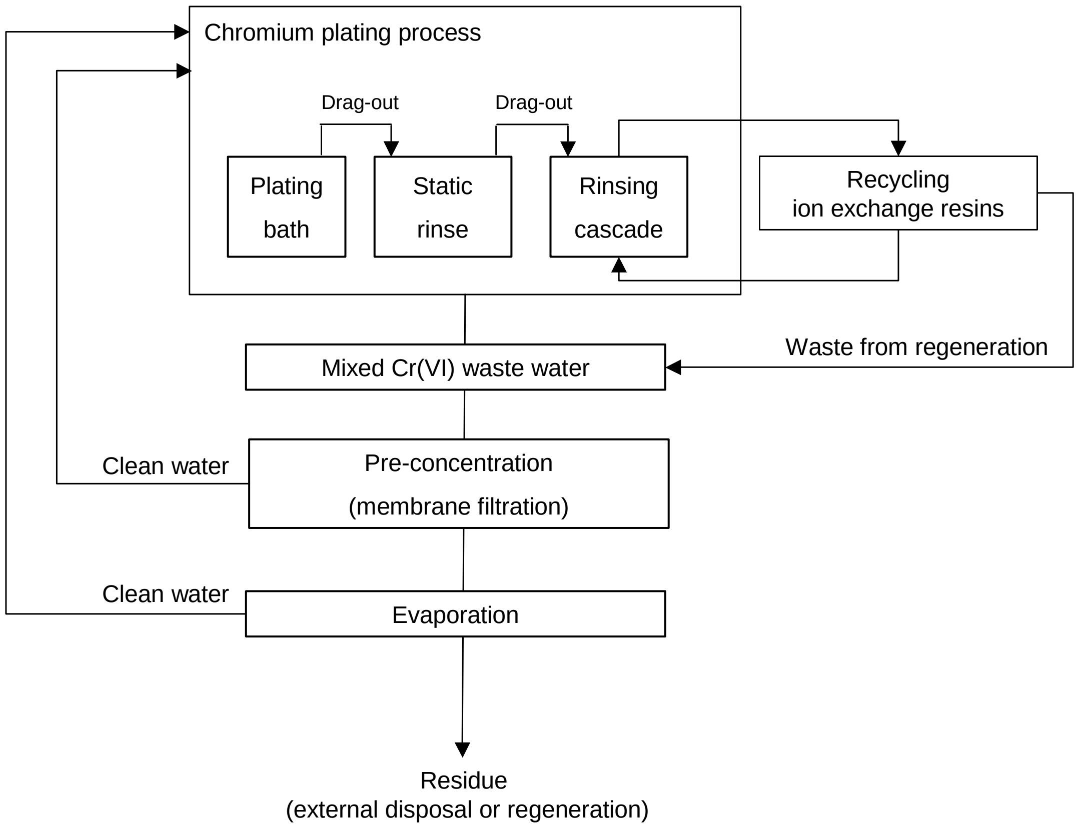


Figure 6.2. *Schematic diagram for the treatment of mixed chromic acid rinse water. Integration of membrane technology as pre-concentrating step and evaporation towards zero liquid waste.*

Micro- and ultrafiltration is widely used for separation of suspended solids and has been studied for chromium separation, either for the removal of precipitated $Cr(OH)_3$ [2, 3], which tends to cause membrane fouling or for direct separation of Cr(VI) using surfactant-enhanced ultrafiltration [4, 5], where the chromate anion is adsorbed to the surface of micelles. The application of RO for treatment and recycling of waste water from metal plating industry has been studied for several years [6-8]. In comparison, the treatment of chromate containing waste effluents by RO or NF is less studied, probably due to the expected, low chemical resistance of the membranes. In lab-scale, polyamide thin-film membranes have been tested by Hafiane et al. [9], cellulose acetate membranes were investigated by Ramani [10] and Gouxin et al. [11] developed a chromic acid resistant polysulfonamide membrane. However, there are few studies reporting pilot-scale studies [12] and industrial-scale application of RO or NF for chromic acid rinse waters [13, 14]. It seems that the membrane stability is still a crucial limitation. In this work a commercial spiral-wound module was tested for feasibility.

6.2 Experimental

6.2.1 Membranes, chemicals and analysis

Table 6.1 shows the various membrane types used in this work. A tubular microfiltration membrane made of PP with a standard pore size of 0.2 μm (type MD020TP2N from Microdyn-Nadir GmbH, Germany) was used for stage 1. The test module was equipped with three tubes each 5.1 mm in diameter (effective membrane area 360 cm^2). The NF spiral-wound membrane LES 90 HG from Nitto Denko Co. was used for the long-term nanofiltration experiments of stage 2. This membrane was selected due to its expected robustness in low oxidative media and their high salt retention compared to other NF membranes. The module size was 2540 (2.5 inch in diameter and 40 inch in length) and the effective membrane area was 1.6 m^2. Finally, the polishing of the NF permeate (stage 3) was performed using a low pressure RO membrane (ESPA 4 Nitto Denko Co.) used as flat sheet in a laboratory crossflow cell.

Table 6.1. *Membranes used in this study.*

Process step	**Type**	**Manufacturer**	**Used configuration**	**Membrane area (m^2)**
Stage 1 (MF)	MD020TP2N	Microdyn-Nadir	tubular	0.036
Stage 2 (NF)	LES 90 HG	Nitto Denko	spiral wound (2540)	1.6
Stage 3 (RO)	ESPA 4	Nitto Denko	flat sheet	0.004

Contaminated chromium plating rinse water was obtained from a hard chromium plating company (Ionhawk Oy, Finland). The effluent had no settleable solids, the pH was 2.5, the specific conductance ~ 22000 $\mu S\ cm^{-1}$ and the Cr(VI) concentration was 1700 ppm. The pH was adjusted (~ pH 5) using liquid, technical grade sodium hydroxide.

The chromic acid was determined by iodometric potentiometric titration with thiosulphate using a combined Pt electrode (Mettler-Toledo GmbH, DL67 automatic titrator). The chemicals used for this determination were potassium iodide p.a. (Riedel-de Haën), sulfuric acid p.a. (VWR International) and 0.1 N sodium thiosulfate solution (VWR International, Titrisol®). Sodium chloride (p.a.) for characterisation experiments was obtained from VWR International too. The metals were analysed by ICP.

6.2.2 Equipment and process conditions

During long-term investigation the permeate was recycled to the feed tank at a certain volume reduction factor (VRF) and for a certain time. Different VRF were adjusted by separate collection of permeate resulting in an increase of the concentration of the remaining effluent (retentate). During all experiments the temperature was kept constant by water cooling devices placed in the feed tank. The process conditions for all experiments are summarized in Table 6.2. The performance of the membranes was checked by determination of clean water flux and/or retention measurements with NaCl solution before and after treatment with the industrial effluent. Prior to the membrane characterisation the plant including the membrane was rinsed with deionized water for approximately 2 hours and the rinsing water was replaced several times.

Table 6.2. *Process conditions for all experiments in this work.*

Process Step	**Scale**	**Process conditions**	**Characterisation procedure**
Stage 1 (MF)	Lab scale	maximum VRF 9.4, $Q = 250\ l\ h^{-1}$, $T = 25 \pm 2°C$, pH 5	Clean water flux: 0.12 MPa, $T = 25 \pm 2°C$.
Stage 2 (NF)	Pilot scale	maximum VRF 4.4, $Q = 920\ l\ h^{-1}$, $p = 2.5$ MPa, $T = 25 \pm 2°C$, pH 5	Clean water flux: 2.5 MPa, $T = 25 \pm 2$ °C; Salt retention: $c_{NaCl} = 1000$ ppm (retentate conductivity 2 mS cm^{-1}), 2.5 MPa, $T = 25 \pm 2°C$
Stage 3 (RO)	Lab scale	maximum VRF 6.8, $Q = 350\ l\ h^{-1}$, $p = 1.4$ MPa, $T = 25 \pm 2°C$, pH 5.5	Flux and salt retention: $c_{NaCl} = 500$ ppm (retentate conductivity 1 mS cm^{-1}), 1.0 MPa, $T = 25 \pm 2°C$

Microfiltration experiments were performed with a SPS controlled test unit able to run both in dead-end or crossflow mode. The latter was used in this application. The plant provides different cleaning concepts, from which trans-membrane backflushing with permeate (inverse filtration) was used. The backflushing was performed with permeate flowing through a small, closed reactor, followed by a three-way valve, which let through either the permeate or compressed air (with adjustable pressure). Backflushing was automatically triggered (programmable) and clear permeate was pressed through the MF membrane in inverse direction for a certain time. The permeate samples were directly taken from the module.

The nanofiltration experiments of stage 2 were performed with a pilot-scale plant having a feed tank with a capacity of 150 l. The permeate was first collected in a small separate tank and then recycled to the feed tank by a transfer pump when an adjustable level (~ 3 l) was reached. The time between the start of the pump was automatically recorded by a PC and the average permeate flux was automatically calculated. The specific conductivity of the permeate and the temperature were also continuously recorded by the PC, whereas the retentate conductivity was measured manually each hour. The RO optimisation experiment (stage 3) aimed on the improvement of NF permeate quality and was performed on a multipurpose laboratory test rig equipped with a crossflow flat cell.

All experiments were carried out in batch mode and the volume reduction factor (VRF) was estimated:

$$\mathrm{VRF} = \frac{V_F}{V_R} \tag{6.1}$$

where V_F and V_R is the feed volume and retentate volume, respectively. The retention of contaminants was calculated using the concentration of the contaminant in the retentate, c_R, and comparing that value with the permeate concentration, c_P:

$$R = \frac{c_R - c_P}{c_R} \tag{6.2}$$

The permeate flux is the permeate flow related to one m² effective membrane area.

6.3 Results and discussion

6.3.1 Stage 1 (pH control and microfiltration)

6.3.1.1 pH control

The pH is adjusted to pH 5.2 using sodium hydroxide resulting partly in precipitation of metal contaminants forming a brown precipitate. The contaminants are not completely removed and mainly nickel and copper remain because their precipitation occurs at higher pH.

6.3.1.2 Operation mode

The solids retained by the membrane accumulate at the surface of the membrane resulting in concentration polarization and possibly cake formation. Concentration polarisation can be decreased by decreasing the pressure (lower flux), increasing the cross flow velocity on the membrane surface, by hydraulic (e.g. backflushing) or chemical cleaning [15]. When higher solid concentration is expected, as in our application, crossflow-microfiltration is recommended. The solid containing feed is pumped continuously and parallel to the membrane through the module with a certain speed keeping the formation of a filter cake slow and helping to prevent irreversible membrane plugging. According to the recommendations of the membrane manufacturer we operated the module in crossflow mode with a feed flow velocity of 1 $m\ s^{-1}$ (app. 250 $l\ h^{-1}$, Re = 6000).

6.3.1.3 Evaluation of working pressure and concentration factor

Both the current permeate flux and the long-term behaviour of the flux are influenced by the transmembrane pressure (TMP) and the volume reduction factor (VRF). A typical characteristic is observed when treating solid containing effluents by MF or UF. When the pressure increases the flux increases, up to a certain limit [15] called the limiting flux and beyond this flux sustained operation is not possible [16]. For long-term stable operation the determination of critical flux [17] is important and operation above this value should be avoided because irreversible flux reduction (membrane fouling) occurs. Therefore, first the optimum pressure was evaluated for the precipitates containing waste water. Figure 6.3a presents the variation of the flux with increasing transmembrane pressure at various VRF. The flux increases with increasing pressure and is lower at higher VRF due to the increased amount of solids concentrated in the retentate. At the maximum VRF (VRF 9.4) the permeate flux increases linearly up to ~ 0.14 MPa. At higher pressures the increase in permeate flux is lower indicating that the limiting flux is reached. Therefore, we further selected as working pressure 0.12 MPa. Figure 6.3b shows the variation of the permeate flux with increasing VRF at 0.12 MPa. The flux at VRF 9.4 is 58 l m^{-2} h^{-1} and app. 20 % lower than for the non-concentrated effluent (VRF 1). The permeate flux is relatively low, however, it remains stable for short-term operation (60 min). During the microfiltration experiments the solids are completely removed and a clear filtrate is obtained. The quantity of settleable solids in the concentrate is 940 ml l^{-1} at VRF 9.4. The concentrate should be further treated by the downsized evaporator.

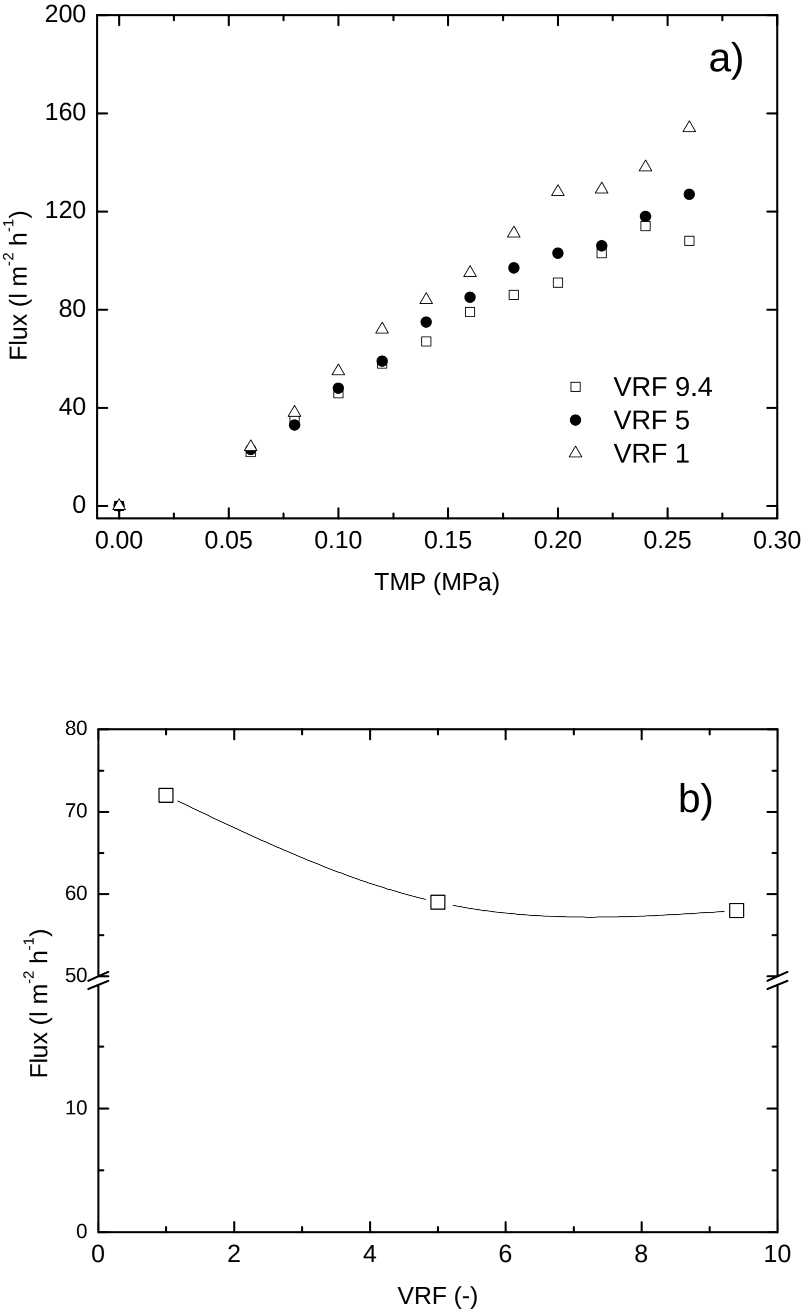


Figure 6.3. *Microfiltration after pH adjustment and precipitation (stage 1, process conditions: $Q = 250$ l h^{-1}, $T = 25 \pm 2$°C). (a) Flux versus transmembrane pressure (TMP) at different volume reduction factors (VRF) and (b) flux versus VRF at optimum pressure (0.12 MPa).*

6.3.1.4 Cleaning strategy

Trans-membrane backflushing is selected as cleaning strategy to guarantee stable long-term operation. At VRF 5, constant flux is achieved for 6 hours by backflushing every 30 min. At VRF 9.4, the time between backflushing is shortened to 10 min. Figure 6.4 shows the course of permeate flux for 6 hours continuous operation at VRF 9.4. Backflushing is triggered every 10 minutes, applying a pressure of 0.2 MPa for 15 s and results in a stable permeate flux with time. Finally, it is important to note that the MF membrane module operation was stable with the chromic acid effluent for almost 100 h. In the end of the experiments, the clean water flux through the MF module was evaluated and found to be the same as before the experiments with chromic acid effluents.

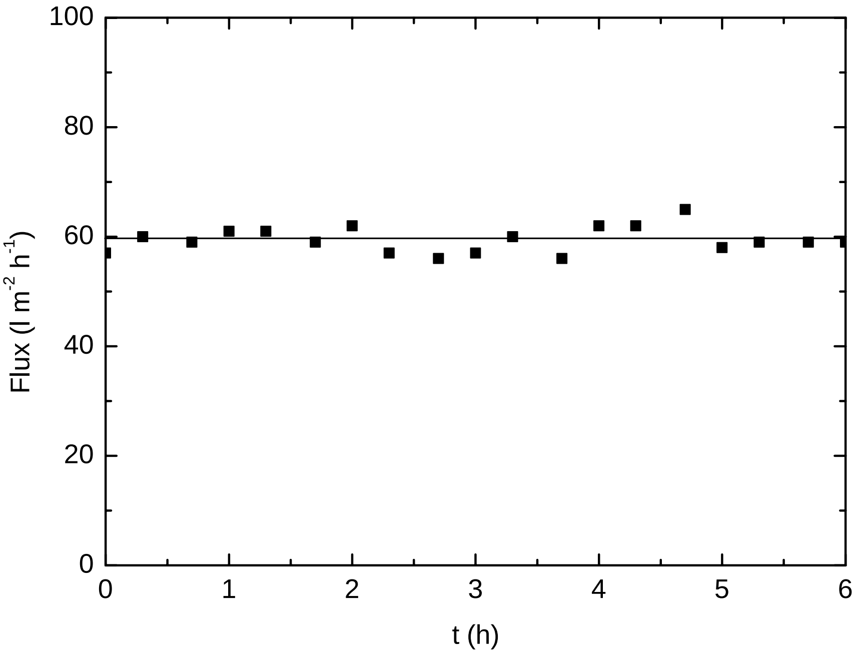


Figure 6.4. *Flux versus time for a MF experiment at VRF 9.4 (stage 1, process conditions: Q = 250 l h^{-1}, T = 25 ± 2°C, backflushing every 10 min for 15 s at 0.2 MPa).*

6.3.2 Stage 2 (nanofiltration)

During the long-term experiment, the NF membrane was exposed to the chromate containing rinse water for 310 hours at different VRF (stepwise increased from VRF 1.1 to 4.4). At each concentration step the VRF was kept constant and the permeate was recycled to the feed tank for a certain operation time.

The increasing VRF results in increased loading of the retentate indicated by higher electric conductivity. The higher the retentate concentration, the more impurities will pass the membrane resulting in decrease of permeate quality. Figure 6.5a shows this behaviour in our experiment. The permeate conductivity increases with increasing retentate concentration, which is nearly doubled from 16500 μS cm^{-1} (VRF 1.1) to 30700 μS cm^{-1} (VRF 4.4). However, the retention is steadily high during the whole experiment ($\geq$ 95 %). At VRF 4.4, the permeate has conductivity of 1670 μS cm^{-1} corresponding to a retention of 95.6 %. In comparison, at VRF 3.1 the permeate conductivity is lower by 58 % (660 μS cm^{-1}), however, still the required specification (20 μS cm^{-1}) is not achieved indicating that an additional purification stage is required. The membrane retention is generally high and only sodium, sulphate and chromate pass the NF membrane to a rather small extent. Figure 6.5b shows the variation in permeate flux depending on the VRF. The flux decreases with increasing retentate concentration due to the increase of retentate viscosity and osmotic pressure phenomena. At VRF 4.4 the flux is 50 % lower than at VRF 3.1. Therefore, a VRF of 3.1 should be selected due to a much better permeate quality and a higher permeate flux. Benefits could be the lower required membrane area and the reduced loading of the membrane in a further treatment step. Table 6.3 presents the compositions of the mixed chromic acid rinse water (feed) and the permeate obtained after purification by MF at VRF 9.4 and NF at VRF 3.1.

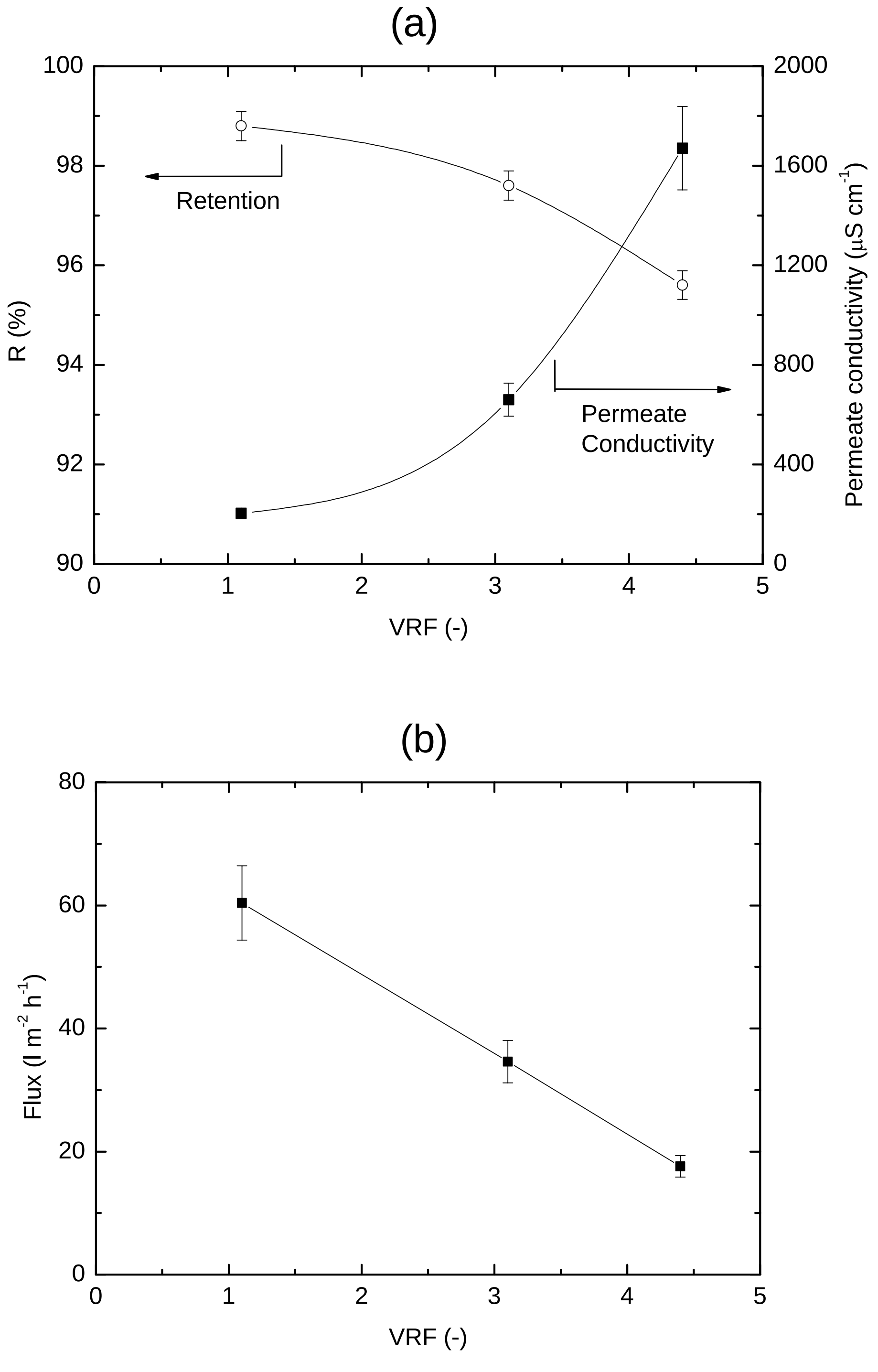


Figure 6.5. *Nanofiltration of mixed chromic acid rinse water after pre-treatment by MF (stage 2, process conditions: transmembrane pressure TMP = 2.5 MPa, T = 25°C ± 2°C, Q = 900 l* h^{-1}*, VRF: 1.1, for 45 h, VRF: 3.1, for 260 h and VRF: 4.4, for 175 h). (a) Average permeate conductivity and membrane retention and (b) average permeate flux.*

Table 6.3. *Compositions of exhausted rinsing effluent (feed) and permeate after treatment by MF (stage 1) and NF (stage 2).*

	Feed	**Permeate**$^{(a)}$	**Retention (%)**$^{(a)}$
pH	2.5	5.7	
Specific conductance (mS cm^{-1})	22	0.66	97
Al (ppm)	12	< 0.2	> 98
Cr total (ppm)	1900	44	98
Cr(VI) (ppm)	1700	44	97
Cu (ppm)	70	< 0.06	99.9
Fe (ppm)	210	< 0.05	99.9
Na (ppm)	1160	152	87
Ni (ppm)	62	0.1	99.8
SO_4^{2-} (ppm)	6600	49	99.3
Zn (ppm)	80	< 0.02	99.9
$^{(a)}$ measured after MF (stage 1, VRF 9.4) and NF (stage 2, VRF 3.1)			

Finally, it is important to note that the NF membrane stability was confirmed in two ways. During the experiment the permeate quality and the permeate flux remain constant at each VRF. Figure 6.6 presents a typical result of the variation of flux and permeate conductivity in time for a VRF of 3.1. Furthermore, the membrane stability was confirmed by retention measurement with NaCl solution before and after the chromium experiment (see Table 6.4). The salt retention remains constant at 98 % both initially and after 310 hours exposition to the chromic acid effluent. However, the clean water flux decreases from initially 122 l m^{-2} h^{-1} to 79 l m^{-2} h^{-1}.

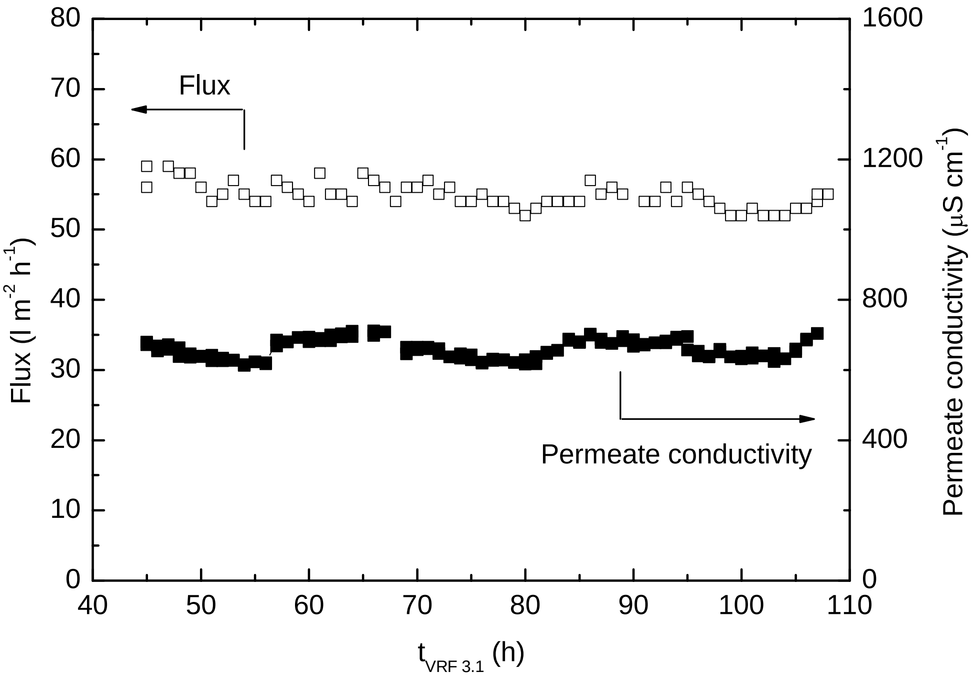


Figure 6.6. *Nanofiltration of mixed chromic acid rinse water at VRF 3.1 (stage 2, process conditions: TMP = 2.5 MPa, T = 25°C ± 2°C, Q = 900 l h^{-1}).*

Table 6.4. *Characterisation of the NF membrane LES 90 HG before and after use during stage 2 for 310 hours (~ 13 days).*

	Pre-Characterisation	**Post-Characterisation**
Clean water flux (l m^{-2} h^{-1})$^{(a)}$	122	79
Salt rejection (%)$^{(b)}$	98	98
$^{(a)}$ Conditions : 2.5 MPa, T = 20°C $^{(b)}$ Conditions : c_{NaCl} = 1000 ppm (retentate conductivity 2000 µS cm^{-1}), 2.5 MPa, T = 20°C		

6.3.3 Stage 3 (reverse osmosis)

The permeate of the NF (stage 2) does not fulfil the specifications for high-quality rinse water. Therefore, an additional polishing step was performed at lab-scale to improve the water quality. Since the chromate concentration was strongly reduced in stage 2, a low pressure and high flux reverse osmosis membrane can be used. During the experiment, the slightly contaminated effluent was concentrated up to VRF 6.8. Figure 6.7 shows the course of the permeate conductivity, which is 9 μS cm^{-1} in average. Even at high VRF the rinse water specification (20 μS cm^{-1}) is maintained. The conductivity at VRF of 6.8 is 13 μS cm^{-1}, the pH is 5.8 and no chromium could be detected in the permeate. The permeate flux is 90 l m^{-2} h^{-1} at VRF 6.8 (laboratory flat cell, high feed velocity, 1.4 MPa and 25°C) and decreases only slightly with increasing concentration due to general lower loading of the effluent. The membrane was in contact with the effluent for totally 70 hours, from which the concentration test lasted for 20 hours. The membrane stability within this period was confirmed by comparing the NaCl retention prior and after the chromium experiment. The salt retention was stable at 98 % before and after use (see Table 6.5).

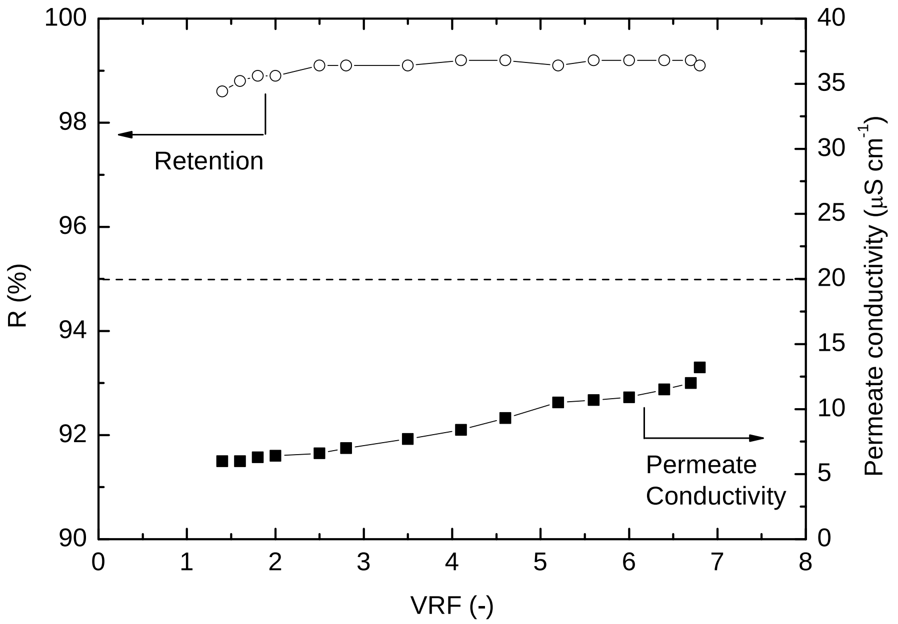


Figure 6.7. *Permeate conductivity and retention of contaminants during polishing of NF permeate by RO (stage 3, process conditions: TMP = 1.4 MPa, T = 25 ± 2°C for 20 h).*

Table 6.5. *Characterisation of the RO membrane ESPA 4 before and after use during stage 3 for 70 hours (~ 3 days).*

	Pre-Characterisation	**Post-Characterisation**
Flux (l m^{-2} h^{-1})	84	62
Salt rejection (%)	98	98
Conditions : c_{NaCl} = 500 ppm (retentate conductivity 1000 µS cm^{-1}), 1.0 MPa, T = 25°C		

6.3.4 Process performance and reflection

Figure 6.8 shows schematically, how the investigated membrane processes would fit into the water recycling system.

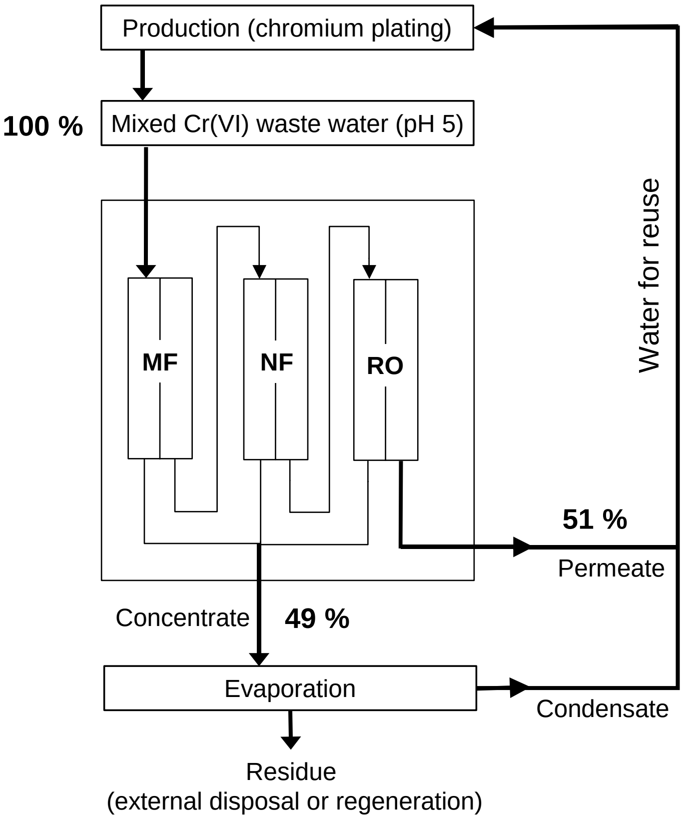


Figure 6.8. *Integration of the evaluated membrane processes into the water recycling process (stage 1: pH control and MF, stage 2: NF, stage 3: RO).*

The pH of the mixed chromic acid rinse water is controlled at pH 5 and suspended solids are removed in stage 1 (MF). Afterwards, most of the dissolved contaminants are retained during NF (stage 2). Finally, the NF permeate is polished during RO (stage 3) and the high quality permeate could be recycled to the production process. Table 6.6 summarizes the performance of the investigated membrane processes. For each stage the quality of the permeate and the VRF achieved at lab or pilot scale are listed. It seems that 51 % of the incoming waste effluent could be directly recycled and the remaining concentrates (49 %) could be treated by evaporation. This would result in significant lower investment and operational costs for the evaporation equipment because it is henceforth only half of the size.

Table 6.6. *Pre-concentration of mixed chromic-acid rinse water before evaporation by a combination of different membrane processes. Quality of the treated water after each step.*

	Mixed chromic acid rinse water	**Stage 1 (MF)**	**Stage 2 (NF)**	**Stage 3 (RO)**
Appearance	Clear, dark yellow	Clear, yellow	Clear, pale yellow	Clear, colourless
pH	2.5	5.3	5.7	5.8
Conductivity (µS cm^{-1})	22000	17000	660	13
VRF (-)		9.4	3.1	6.8

Figure 6.9 shows a cost estimation for the evaluated three-stage membrane process. Both capital and operation costs are calculated for various yearly flow volumes. The operation costs include energy consumption, maintenance and membrane replacement. For example, a three stage membrane plant able to treat 5000 m^3 a^{-1} mixed chromic acid rinse water would cost 44.000 € and could downsize the evaporation equipment by 51 %. In addition, Figure 6.10 presents a cost comparison between the single evaporation equipment and the combination of membrane technology and evaporation (downsized by 51 %) for the treatment of 5000 m^3 a^{-1} waste effluent. The data for the evaporation

equipment has been evaluated within an European project (G1RD-CT-2000-00295) aiming to clean up waste streams and to limit pollution in the first place [18-19]. Cost savings of app. 200 000 € for the capital costs and app. 50 000 € a^{-1} for the operating cost is expected to be achieved by implementation of membrane technology prior to evaporation. Besides having water of high quality for re-use, the plating companies would also have significant economical benefits.

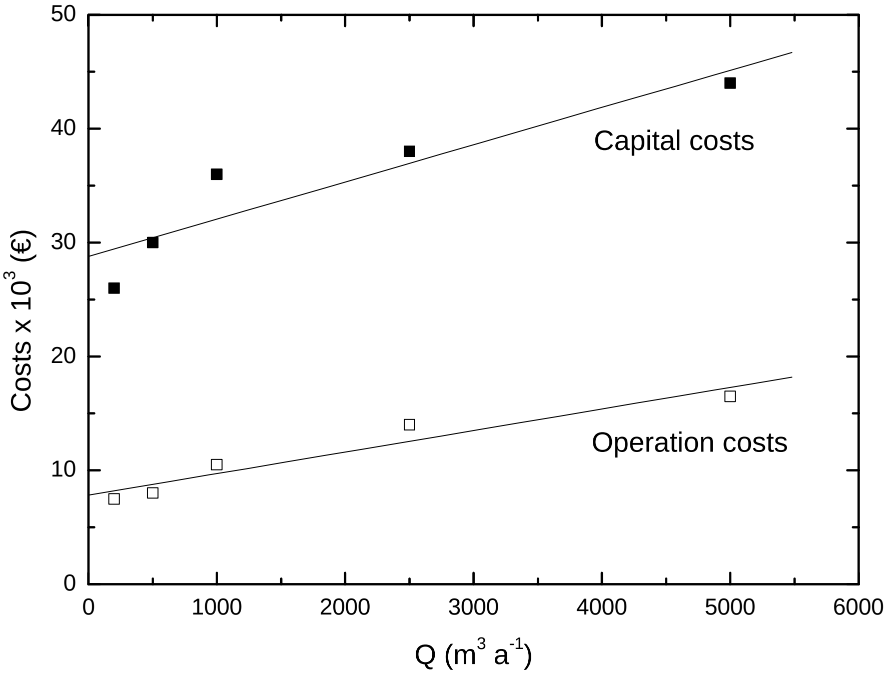


Figure 6.9. *Estimation of capital and operation costs of the evaluated three-stage membrane process (energy price 0.08 € kWh^{-1}, maintenance 100 h a^{-1} for 200–500 m^3 a^{-1}, 125 h a^{-1} for 1000–2500 m^3 a^{-1} and 150 h a^{-1} for 5000 m^3 a^{-1}, membrane replacement every 2.5 years).*

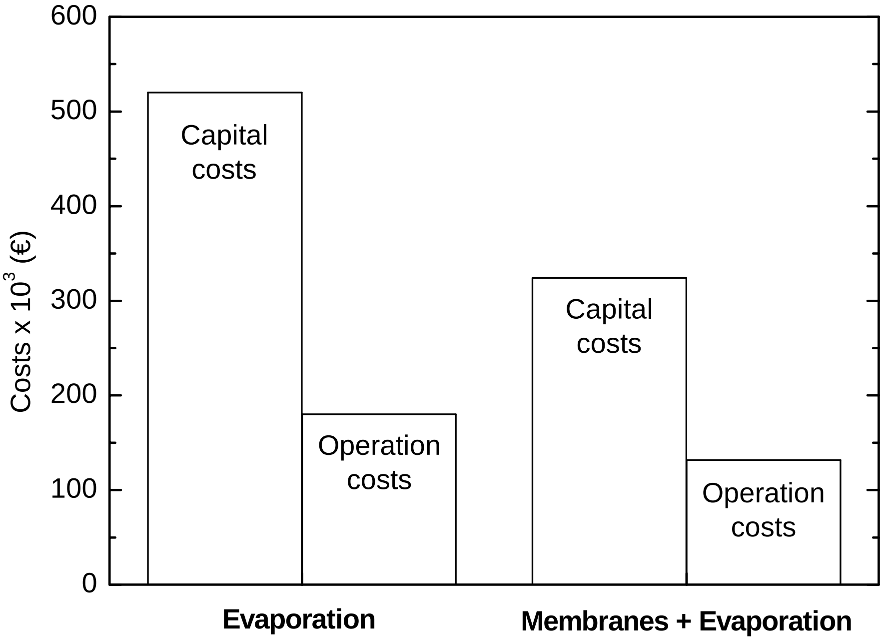


Figure 6.10. *Comparison of capital and operation costs for single evaporation equipment and the combination of membrane technology and downsized evaporation for 5000* m^3 a^{-1} *(assumption for evaporation [19]: energy price 0.08 €* kWh^{-1}*, maintenance 480 h* a^{-1} *(25 €* h^{-1}*) and costs for liquid waste disposal (concentrates) 200 €* t^{-1}*).*

6.4 Conclusions

Approaching zero discharge in plating industry can be achieved by water recycling. Since evaporation is cost intensive, in this work the suitability of membrane technology was investigated aiming to downsize of evaporation equipment. Mixed chromic acid rinse water could be successfully treated by a combination of various membrane technologies. The waste water concentration prior to evaporation includes the following stages: (i) controlling pH 5 and removal of suspended solids by MF (stage 1) (ii) removal of dissolved contaminants by NF (stage 2) and (iii) polishing of the NF permeate by RO to obtain high quality water for reuse in the production process (stage 3).

During stage 1 metal hydroxide precipitates could be totally removed by MF and a stable process was achieved by crossflow operation with backflushing every 10 minutes, applying a pressure of 0.2 MPa for 15 s. Afterwards in stage 2, most of the dissolved contaminants were retained by a chemically robust NF membrane, which has shown good performance during a 310 hours test run. At a VRF of 3.1 the permeate quality was 660 $\mu S\ cm^{-1}$ indicating that a final polishing stage is necessary to meet the required rinse water quality. This third stage (stage 3) was performed as low-pressure RO and it ensured a high quality permeate, even at high recovery (13 $\mu S\ cm^{-1}$ at VRF 6.8). The high quality permeate would be suitable for reuse as rinsing water in the chromium plating production. The waste water volume could be reduced by 51 % prior to evaporation using the membrane technology as a pre-concentration step.

6.5 Acknowledgements

The financial support by the European Commission in the GROWTH frame (G1RD-CT-2000-00295) and by the company FuMA-Tech GmbH, Germany is gratefully acknowledged. Besides, the author wish to thank Heidrun Klass and Jens Gebauer from FuMA-Tech GmbH, Germany and Heikki Leinonen from Ionhawk Oy, Finland for technical support.

6.6 References

1. E.A. Cohen Hubal and M.R. Overcash, Net-waste-reduction analysis applied to zero-water discharge systems for chromic acid electroplating, J. Cleaner Prod. **3** (3) (1995) 161-167.
2. R. Sondhi, Y.S. Lin and F. Alvarez, Crossflow filtration of chromium hydroxide suspension by ceramic membranes: fouling and its minimization by backpulsing, J. Memb. Sci. **174** (2000) 111-122.
3. C. Visvanathan, R. Ben Aim and S. Vigneswaran, Application of cross-flow electro-microfiltration in chromium wastewater treatment, Desalination **71** (1989) 265-276.

4. L. Gzara and M. Dhahbi, Removal of chromate anions by micellar-enhanced ultrafiltration using cationic surfactants, Desalination **137** (2001) 241-250.
5. B. Keskinler, U. Danis, A. Çakici and G. Akay, Chromate removal from water using surfactant-enhanced crossflow filtration, Sep. Sci. Technol. **32** (11) (1997) 1899-1920.
6. S. Beszedits, Chromium removal from industrial wastewater, in "Chromium in the Natural and Human Environments", J.O. Nriagu and E. Nieboer, Editors. 1988, John Wiley & Sons, Inc.
7. J.-J. Qin, M.-N. Wai, M.-H. Oo and F.-S. Wong, A feasibility study on the treatment and recycling of a wastewater from metal plating, J. Memb. Sci. **208** (2002) 213-221.
8. W.S. Winston Ho and K.K. Sirkar, Membrane Handbook. 1992, New York, Van Nostrand Reinhold.
9. A. Hafiane, D. Lemordant and M. Dhahbi, Removal of hexavalent chromium by nanofiltration, Desalination **130** (2000) 305-312.
10. K.V. Ramani, Recovery and reuse of chromium from electroplating waste using reverse osmosis, Indian Journal of Environmental Protection **12** (8) (1992) 604-608.
11. L. Gouxin and W. Jiangjing, The development of polysulfonamide membrane and its application in treating chromium plating wastewater, Desalination **62** (1987) 239-249.
12. R.G.J. Radier, C.W. van Oers, A. Steenbergen and M. Wessling, Desalting a process cooling water using nanofiltration, Sep. Purif. Technol. **22-23** (2001) 159-168.
13. Reverse osmosis in finishing (6/9/2003). [Online]. Available: www.pfonline.com/articles/089907.html [2004, November 25]
14. Approaching zero discharge in surface finishing (EPA 625/R-99/008) (November 2000). [Online]. Available: www.epa.gov [2004, November, 22]
15. M. Mulder, Basic Principles of Membrane Technology. 1996, Dordrecht, The Netherlands, Kluwer Academic Publishers.
16. J.A. Howell, Sub-critical flux operation of microfiltration, J. Memb. Sci. **107** (1995) 165-171.

17. R.W. Field, D. Wu, J.A. Howell and B.B. Gupta, Critical flux concept for microfiltration fouling, J. Memb. Sci. **100** (3) (1995) 259-272.
18. Effluent-free production to polish environmental performance of plating industry. [Online]. Available: http://europa.eu.int/comm/research/growth/pdf/cleantechnologies-conference/tozeliwa_en.pdf [2005, March 12]
19. Recommendations for implementing techniques to achieve zero liquid discharge on-site for surface treatment operations - “White Book” (G1RD-CT-2000-00295). Commission of the European Committees, submitted (2004).

Chapter 7

Conclusions and outlook

In this thesis the recovery and treatment of chromic acid containing solutions by various technologies was studied. Specific results of this research can be outlined as follows:

- Membrane electrolysis (ME) with ion-exchange membranes is used for chromic acid recycling for quite some time. The technology provides a number of advantages, however, it has not gained common acceptance in plating industry. The reason seems to be a lack of operation stability and efficiency. The literature review in *Chapter 2* shows, that research mainly focuses on process improvement, especially on transport of impurities through cation-exchange membranes. The similar electro-electrodialysis (EED) uses anion-exchange membranes and is not yet commercially applied. Here, the research mainly aims on the evaluation of suitable anion exchange membranes.

- The chromic acid recovery by three-compartment electro-electrodialysis (EED) provides chromic acid recovery, bath maintenance and rinse water treatment in one step (*Chapter 3*). However, the crucial issue is the stability of anion exchange membranes and their performance in chromic acid solutions. The membrane fumasep® FAP from FuMA-Tech GmbH, Germany, seems to be a promising membrane for this application having better performance than the other commercial membranes studied (IONAC MA 3475 and PC 100 D). The main factors influencing the current efficiency of the chromate transport seem to be the chromic acid concentration in the anode compartment and the process temperature. Low chromic acid concentration in the anode compartment and high temperature result in significantly higher chromate transport.

- High AEM membrane resistance due to the formation of polychromates inside the membrane is an important EED process limitation. However, low initial current densities and high flow rates could improve the process performance (*Chapter 3*). Our results suggest that successful up-scaling of the EED process requires:
    - Low initial current density (10–20 mA cm^{-2});
    - High process temperature (between 40–50°C);
    - High flow rates (above 7 cm s^{-1}).

- A stable pilot-scale study for chromic acid recovery by three-compartment EED for more than 400 hours is presented in *Chapter 4*. The recovery rates in batch mode strongly depend on the CrO_3 concentration in the anode compartment. The recovery rates are the highest in the beginning of a batch and decreases later when reaching the final concentration in the anode compartment. In continuous mode, however, the recovery rates remain constantly low requiring a double membrane area. It is shown that an increased temperature (40°C) could significantly improve the process performance. The chromic acid recovery is more than double at 40°C in comparison to 25°C. For the target concentration of the recovered acid (1.2 M CrO_3), the chromate flux towards the anode is 0.7 mol_{CrO3} m^{-2} h^{-1} at 40°C in comparison to 0.3 mol_{CrO3} m^{-2} h^{-1} at 25°C. The start of operation with fresh membranes is accompanied by an initial increase of resistance, which is lower at 40°C than at 25°C. The better process performance at 40°C is also reflected in the estimated operational costs. Due to the smaller size of the EED module, the percentage of electrolysis costs in the total operation costs are estimated to be lower at 40°C (14 %) than at 25°C (40 %). The operation costs for a daily recovery rate of 2.35 kg_{CrO3} d^{-1} at 40°C is estimated to be 3.7 € kg_{CrO3}^{-1} at 30 mA cm^{-2}.

- The electrochemical chromate reduction on a highly porous carbon felt electrode seems to be an efficient treatment method especially for very diluted solutions (*Chapter 5*). High reduction rates of chromate are obtained, especially when the electrode felt was running over long-time and due to copper deposition and re-solution in the felt (the copper in the rinse water comes from the chromium etching process). Copper deposited onto the cathode felt when chromate is completely reduced and dissolved when the chromate concentration increases, for instance when a new batch process starts. The copper deposits significantly enhance the process performance by this current-free reduction of chromate.

- The electrochemical chromate reduction on a carbon felt cathode provides economical advantages (*Chapter 5*). The economics of batch and flow-through operation are compared for effluents containing 16 ppm Cr(VI). For the flow-through operation, the energy requirements are estimated to be low (2.3 kWh per kg Cr(VI)). Besides, the electrochemical Cr(VI) reduction at carbon felt is compared to the chemical detoxification of chromate. The operation costs are estimated to be 30 % lower showing the promising economic potential of this technology.

- Approaching zero discharge in plating industry can be achieved by water recycling. Since evaporation is cost intensive, membrane technology is suitable to downsize the evaporation equipment (*Chapter 6*). Mixed chromic acid rinse water could be successfully treated by a combination of various membrane technologies. The waste water concentration prior to evaporation includes the following stages: (i) controlling pH 5 and removal of suspended solids by MF (stage 1) (ii) removal of dissolved contaminants by NF (stage 2) and (iii) polishing of the NF permeate by RO to obtain high quality water for reuse in the production process (stage 3). During stage 1 metal hydroxide precipitates could be totally removed by MF and a stable process is achieved by crossflow operation with backflushing every 10 minutes, applying a pressure of 0.2 MPa for 15 s. Afterwards in stage 2, most of the dissolved contaminants are retained by a chemically robust NF membrane, which has shown good performance during a 310 hours test run. At a VRF of 3.1 the permeate quality is 660 µS cm^{-1} indicating that a final polishing stage is necessary to meet the required rinse water quality. This third stage (stage 3) is performed as low-pressure RO and ensure high quality permeate, even at high recovery (13 µS cm^{-1} at VRF 6.8). The high quality permeate would be suitable for reuse as rinsing water in the chromium plating production. The waste water volume could be reduced by 51 % prior to evaporation using the membrane technology as a pre-concentration step.

This thesis presents three advantageous technologies, which could improve the waste management of chromium plating industry, however, there are still some issues to be addressed by others in the future:

- With regard to industrial EED implementation, the equipment, especially the membrane module, needs further optimisation concerning the materials used. During this work, the commercial available electrolysis equipment showed deterioration probably caused by the oxidative chromic acid and current flow.
- The new anion exchange membrane fumasep® FAP showed high resistance against chromic acid and could be used in many other applications where oxidative acting substances occur.
- In this thesis the chromate reduction on carbon felt is studied using a specific industrial rinse water. Strong enhancement of the process performance is observed due to copper co-deposition and re-solution reactions. However, the behaviour with mixed chromic acid waste effluents, possibly without copper, is not clear and should be further studied to obtain information about general use and the application boundaries.
- Industrial implementation of the three stage membrane process from Chapter 6 requires more work at pilot-scale to guarantee a high water quality and process stability for a longer time period.

Summary

Chromic acid is a strong oxidizing agent and plays an important role in metal finishing and plating industry. Chromate containing waste effluents are toxic and carcinogen and their treatment is chemical, energy and cost intensive. Therefore, waste prevention and waste treatment are in the focus of attention since many years. However, recycling systems and alternative treatment methods have not gained general acceptance.

This thesis investigates three technologies for the treatment of chromic acid solutions, which could combine economical and practical aspects with conservation of nature and natural resources.

Ion-exchange, evaporation, ion-transfer systems and membrane electrolysis are state-of-the-art recycling and recovery technologies for chromic acid solutions (*Chapter 1*). Due to low chemical and energy consumption and the ability to manage different recycling tasks at the same time, systems operating with ion-exchange membranes are further investigated. A review about the research and applications in this field is presented in *Chapter 2*. Three-compartment electro-electrodialysis (EED) most likely promises to meet the demands of the plating business and was therefore, further developed in *Chapters 3 and 4*. This technology combines recovery of dragged-out plating solution, elimination of metallic impurities from the process and rinse water treatment in one step. The evaluation of a suitable anion-exchange membrane and optimum process parameters are described in *Chapter 3*. The membrane fumasep® FAP (FuMA-Tech GmbH) seems to be the most efficient. Its current efficiency is much higher than those previously reported in the literature. The process performance depends on the concentration gradient between product (anolyte) and central compartment (exhausted rinse water) and the temperature. The results show that batch processing is recommended and the chromate transfer rates through the AEM could be significantly increased when increasing the temperature up to 50°C. Low initial current density and high feed flow rate

could help overcoming the process limitations attributed to high AEM resistance. *Chapter 4* presents the process optimisation. A stable and economical process is developed and high-quality chromic acid is recovered. The membrane stability and performance is evaluated by a long-term experiment for 400 hours. The highest chromic acid production was reached by batch processing at 40°C. Both measures increase significantly the chromate transfer and seem to result in lower equipment size and operational costs.

Conventional treatment of chromic acid containing waste effluents is chemical intensive and a considerable amount of sludge is created. Electrochemical reduction of chromate is an alternative method to reduce chemical consumption and the amount of sludge to be disposed. *Chapter 5* deals with the electrochemical reduction of Cr(VI) on highly porous carbon felt. Very diluted solutions could be efficiently treated due to the large specific surface area and high porosity of the felt. The up-scaling is simplified by the use of a new type of separated cell and once-through flow of industrial rinse water. A significant enhancement of the process is obtained due to copper deposition during long-term operation. The co-deposition and re-solution of copper occurs depending on the inlet chromate concentration. When previously deposited copper is present a current-free reduction of chromate takes place resulting in very high current efficiencies and space time yields. Finally, the economic potential of the process is evaluated in comparison with chemical detoxification of chromate. The operation costs for the electrochemical treatment of very diluted effluents on a carbon felt electrode seem to be 30 % lower than for the chemical method.

Waste minimization by evaporation is cost and energy intensive and downsizing of the equipment could be an efficient way to reduce costs. Thus, a combination of different membrane processes is evaluated in *Chapter 6* for efficient reduction of the waste water volume prior to evaporation. A stable process is developed showing that pre-concentration by 51 % is possible. High quality rinse water for reuse is obtained fulfilling the great demands on the rinsing process (electric conductivity of ~ 20 $\mu S\ cm^{-1}$). Chemical stable membranes are evaluated and optimum process parameters are determined.

Samenvatting

Chroomzuur is een zeer sterke oxidator en speelt een belangrijke rol in de industrie voor het afwerken en chromateren van metaal. Chromaat bevattende afvalstromen zijn toxisch en carcinogeen en de verwerking is chemisch, energetisch en economisch gezien zeer intensief. Vandaar dat het voorkomen en het verwerken van dit soort afval al jaren in de belangstelling staat. Desalniettemin zijn recirculatiemethoden en alternatieve verwerkingsmethoden nog niet algemeen geaccepteerd.

Dit proefschrift beschrijft het onderzoek naar drie technologieën om oplossingen van chroomzuur te verwerken, die economische en praktische aspecten mogelijk zouden kunnen combineren ten behoeve van het behoud van de natuur en natuurlijke bronnen.

Ion-uitwisselings-, verdampings- en ion-overdrachtsmethoden en membraanelektrolyse zijn ‘state-of-the-art’ technieken voor de recirculatie en de terugwinning van chroom uit oplossingen van chroomzuur (*Hoofdstuk 1*). Vanwege een laag chemicaliën- en energieverbruik en de eigenschap om verschillende recirculatietaken tegelijkertijd uit te kunnen voeren, zijn ion-uitwisselingsmembraansystemen verder onderzocht. Een overzicht van verricht onderzoek en toepassingen op dit gebied wordt gepresenteerd in *Hoofdstuk 2*. Elektro-elektrodialyse (EED) bestaande uit drie compartimenten lijkt het meest belovend om aan de eisen van de plating-industrie te voldoen en is om die reden verder ontwikkeld (*Hoofdstuk 3 en 4*). Deze technologie combineert het terugwinnen van meegesleurde plating-oplossing, het verwijderen van metaalverontreinigingen uit het proces en het in één stap spoelen van water. In *Hoofdstuk 3* wordt een evaluatie gemaakt van een geschikt anion-uitwisselingsmembraan en de meest optimale procescondities. Het membraan ‘fumasep® FAP (FuMA-Tech GmbH)’ lijkt het meest efficiënt te werken, aangezien de ‘current efficiency’ veel hoger is dan tot nu toe gepubliceerd in de literatuur. De prestatie van het proces hangt af van de concentratiegradiënt tussen product (‘anolyte’) en centraal compartiment (uitgeput spoelwater) en de temperatuur. De resultaten demonstreren dat batch-gewijze procesvoering aan te bevelen is en dat de overdrachtssnelheid door het anion-uitwisselingsmembraan van chromaat significant kan worden verhoogd door de temperatuur te verhogen tot 50°C. Een lage initiële stroomdichtheid en een hoge voedingsstroom zouden de proceslimiteringen, toe te kennen aan de hoge weerstand van het anion-uitwisselingsmembraan, kunnen verhelpen.

Hoofdstuk 4 geeft de optimalisering van het proces weer. Een stabiel en economisch proces is ontwikkeld waarbij chroomzuur van een hoge kwaliteit wordt teruggewonnen. De membraanstabiliteit en -prestatie zijn geëvalueerd aan de hand van een langetermijn experiment van 400 uur. De hoogste chroomzuurproductie werd behaald tijdens batch-gewijze procesvoering bij 40°C. Beide maatregelen laten de chromaatoverdracht significant toenemen en lijken te resulteren in kleinere apparaatafmetingen en lagere operationele kosten.

Conventionele behandeling van afvalstromen die chroomzuur bevatten is chemisch gezien zeer intensief waarbij een aanzienlijke hoeveelheid slijk wordt gecreëerd. Elektrochemische reductie van chromaat is een alternatieve methode om consumptie van chemicaliën en de hoeveelheid slijk dat moet worden afgevoerd te verminderen. *Hoofdstuk 5* behandelt de elektrochemische reductie van Cr(VI) op een zeer poreuze vilt van koolstof. Sterk verdunde oplossingen konden zeer efficiënt worden behandeld door middel van het grote specifieke oppervlak en de hoge porositeit van het vilt. Opschaling wordt vergemakkelijkt door het gebruik van een nieuw type gescheiden cel en het één keer doorstromen van industrieel spoelwater. Een significante verbetering van het proces werd behaald als gevolg van koperdepositie tijdens een langetermijn werking. Koperdepositie en het heroplossen van koper vindt plaats afhankelijk van de ingaande chromaatconcentratie. Een stroomvrije reductie van chromaat vindt plaats wanneer eerder afgezet koper aanwezig is, resulterend in zeer hoge ‘current efficiencies’ en ruimte-tijd opbrengsten. Tenslotte is de economische potentie van het proces geëvalueerd in vergelijking met het chemisch ontgiften van chromaat. De operationele kosten voor het elektrochemisch behandelen van zeer verdund effluent op een viltelektrode van koolstof blijken 30 % lager te zijn dan met de chemische methode.

Het minimaliseren van afval door verdamping is kosten en energetisch gezien intensief en het verkleinen van de apparatuur zou een efficiënte manier kunnen zijn om kosten te reduceren. Daarom wordt in *Hoofdstuk 6* een evaluatie gemaakt van een combinatie van verschillende membraanprocessen voor een effectieve reductie van het volume van afvalwater voor de verdamping. Een stabiel proces is ontwikkeld dat laat zien dat voorconcentreren tot 51 % mogelijk is. Een hoge kwaliteit spoelwater voor hergebruik wordt verkregen waarbij aan de hoge eisen van het spoelproces wordt voldaan (elektrische conductiviteit van ~ 20 μS cm^{-1}). Verder zijn chemisch stabiele membranen geëvalueerd en zijn de optimale procesparameters bepaald.

Acknowledgements

When I started working for FuMA-Tech four years ago I did not intend to write a thesis about the treatment and recovery of a strong oxidative and toxic chemical. However, the longer chromic acid was involved in my daily work the more I realized how important this ecological harmful chemical for the plating industry is, especially for small companies. Since the recovery of chromic acid is still a big challenge and the detoxification requires a large amount of chemicals I decided to make this topic to the subject of my thesis. On the way many people accompanied me giving me practical and theoretical support and bringing me forward in my professional and personal development.

I would like to thank my promotor, Prof. Matthias Wessling, for accepting me as an external PhD student, for his support and motivation. I am very grateful to Bernd Bauer for giving me the opportunity to carry out this thesis on the job, for fruitful discussions, for the trust in my work and the freedom to develop. I would not have completed my work without the help of Dimitris Stamatialis, who got involved in my chromium adventures again and again. I am greatly indebted to him for his patience and guidance, even if our long discussions on the telephone sometimes ended with great confusion. However, I appreciated his motivating emails shortly after. Furthermore, I would like to thank Prof. Marianne Nyström and Prof. Gerald Pourcelly for taking part in the promotion committee and for their support in different European projects. I wish to thank Prof. Andre de Haan, Prof. Geert Versteeg and Prof. van Swaaij for accepting my work as an external promotion.

It was great pleasure for me to give presentations for the Membrane Technology Group. I would like to thank the whole group for asking specific questions. I would like to express my special thanks to Jörg Balster for making the SEM pictures, to Tymen Visser for the “Samenvatting”, to Kitty Nymeijer for explaining me all formalities and to Greet Kamminga for being always ready to listen to my questions.

I wish to thank Rosa Marquinez from LEIA (Spain), Roberto López and Victor Manuel San Martin from CROPUSA (Spain), Heikki Leinonen from Ionhawk Oy (Finland), Peter Schmitt and Volker Frei from Hartchrom GmbH (Germany) for their active help during the pilot tests on site. Furthermore, I would like to thank Elena Vallejo for the helpful discussion on the valence of chromic acid species.

Den Mitarbeitern der FuMA-Tech GmbH danke ich für die Unterstützung in den letzten vier Jahren und die freundschaftliche Atmosphäre. Jens Gebauer danke ich besonders für die unkomplizierte Hilfe bei technischer Probleme mit den verschiedensten Pilotanlagen und für die Bereitstellung von Daten für Wirtschaftlichkeitsbetrachtungen. Karl Danz danke ich vor allem für die Beantwortung unzähliger Fragen zur Membrantechnik und Dimensionierung von Membrananlagen, schon während meiner Diplomarbeit. Frau Sonja Katzenwadel-Burkhardt danke ich für Ihre Hartnäckigkeit und gute Laune. Für die Unterstützung bei der Analytik danke ich Beate Scheiffelen, Daniela Bertram und Michael Renz.

Besonders möchte ich mich bei den Saarländern für die schöne Zeit bedanken. Ein herzlicher Dank gebührt Hans Holdik und Dietmar Käshammer, die mich fortwährend motivierten und mir jederzeit mit ihrem großen Wissen um Ionenaustauschermembranen und Elektrodenprozesse zur Seite standen. Martin Schmitz danke ich für die handwerkliche Umsetzung meiner Ideen in funktionstüchtige Membranstapel und Teststände. Mein Dank gilt auch Vladimir Barmashenko für die zahlreichen Diskussionen rund um das Kohlenstoff-Filz aus Kapitel 5. Die täglichen Höhen und Tiefen zu teilen war auch meinen Kolleginnen Steffi Ridder, Anette Collet, Daniela Marks und Michaela Bott vergönnt. Ihnen danke ich besonders für Ihre Unterstützung im Labor, die Gespräche über Gott und die Welt und für ihre Geduld mit mir, besonders im letzen Jahr. Gernot Ertl und Joanna Klein danke ich für den im Praktikum geleisteten Einsatz und Heidrun Klass für die wichtigen Daten, die sie in ihrer Diplomarbeit erarbeitet hat.

Martin Kaschek und Hans Holdik danke ich speziell für die Einweihung in die Geheimnisse der Messwerterfassung mittels WorkBench.

Ich möchte meiner ganzen Familie danken, insbesondere meinen Eltern für ihr Vertrauen und die Unterstützung während meiner Ausbildung. Meinem Bruder Andreas danke ich für den Beistand während der Verteidigung. Berit, Hege, Nico, Anna, Wolfram und Nadja möchte ich für die wunderbare Reise durch Island danken, auf der ich die nötige Energie für den Endspurt gesammelt habe.

Danny, ich danke Dir sehr für Deine Unterstützung, Deine unendliche Geduld und die geschickten Ablenkungsmanöver.

Ines Frentel