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PROJECT COORDINATOR: AEA Technology -UK

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STMI - F
CNRS Laboratoire Pierre Sue - F
University of Reading -UK
Loughborough University of Technology -UK

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RECOVERY OF PRECIOUS AND BASE METALS FROM INDUSTRIAL LIQUORS USING ELECTROCHEMICAL ION EXCHANGE

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ABSTRACT

Electrochemical ion exchange (EIX) is an advanced ion exchange process for the treatment of liquid effluent. Until recently, applications of EIX were limited to the nuclear industry. The goal of this RTD project was to establish whether or not EIX is an appropriate technology for the treatment of a range of non-nuclear process liquors, containing base metals and/or precious metals.

Typical process liquors were analysed. Several novel sorbents were synthesised. Existing and novel sorbents were screened for their ability to remove the elements of interest (Cu, Ni, Zn, As, Se, Cr, Pt, Ir, Pal). Promising materials were incorporated into EIX electrodes and/or membranes. These were tested in prototype EIX (flow)cells. In parallel, mass transfer measurements and process modelling led to improvements in the flowcell design. Tests were conducted using simulant solutions and genuine process liquors. Good results were obtained for all three types: base metal cations, base metal anions, and precious metal anionic complexes. In the last year of the project, the Work Programme was modified to include continuous EIX (developed in a separate programmed). In the limited time available, most encouraging results were obtained for the base metal cations and the precious metal anionic complexes.

EIX is an energy efficient process which requires few added chemicals. It enables valuable metals to be recycled and toxic metals to be removed. The project has generated significant data on a wide variety of aqueous solutions. This will put us in a good position to design customised EIX plant for the treatment of specific process streams containing precious and/or base metals. Further development work is needed to enable this emerging technology to reach its intended markets in the non-nuclear sector.

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INTRODUCTION

Electrochemical ion exchange (EIX) is an advanced ion exchange process for the treatment of liquid effluent. Until recently, applications of EIX were limited to the nuclear industry. However, it was apparent that EIX technology would be of benefit in the non-nuclear sector, in the broader field of the metal/chemical industry,

On 2 April 1992, a proposal entitled "Recovery of Precious and Base Metals from Industrial Liquors using Electrochemical Ion Exchange" was submitted to the European Commission. In July 1992, we heard that the proposal had been rated A-1. After lengthy contract negotiations, the project commenced on 1 November 1992.

AEA Technology has coordinated this project. The other partners were W C Heraeus GmbH, STMI, CNRS (Laboratoire Pierre Sue), University of Reading, and Loughborough University of Technology. The first industrial partner runs a precious metal refinery and manufactures electrochemical process equipment, whilst the second industrial partner manufactures mineral ion exchangers for treatment of industrial effluent.

TECHNICAL DESCRIPTION

The goal of this RTD project was to establish whether or not EIX is an appropriate technology for the treatment of a range of non-nuclear process liquors. If successful, the technology would be developed to pilot plant scale, for the removal and recovery of base metals (Cu, Ni, Zn, As, Se, Cr) and precious metals (Pt, Ir, Pal). This 3-year project consisted of the following 12 tasks:

1. Analysis of industrial process liquors
2. Screening of existing sorbents for IX behaviour
3. Lab-scale preparation of novel sorbents
4. Screening of novel sorbents for IX behaviour
5. Investigation of ion fixation mechanisms
6. Large scale preparation of suitable sorbents
7. Manufacture of prototype EIX flowcells
8. Manufacture of EIX electrodes
9. Testing of EIX electrodes with simulant solutions
10. Testing of EIX electrodes with genuine process liquors
11. Mass transfer measurements and process modelling
12. Project management

RESULTS

The following is a concise summary of the most significant results:

Task 1: Analysis of industrial liquors

CNRS analysed 10 typical waste solutions, supplied by Heraeus, using a combination of neutron activation analysis (NAA) and inductively coupled plasma atomic emission spectrometry (ICP/AES).

The precious and base metal content is now known, together with the identity of interfering ions. In several cases, the results obtained deviated somewhat from the estimated compositions supplied by Heraeus. For example, NAA of solution 8 revealed the presence of antimony, in addition to the arsenic, selenium, and chromium known to be present. Solutions 9 and 10 actually contained negligible amounts of copper, nickel, and zinc (as would be expected in alkaline solutions). Higher concentrations could occur if completing agents were present - the identity of any such species should be determined.

Task 2: Screening of existing sorbents for IX behaviour

STMI's product range includes acids (e.g. polyantimonic acid), ferrocyanides (e.g. nickel ferrocyanide), oxides (e.g. titanium oxide) and phosphates (e.g. zirconium phosphate). Twenty two samples were sent to CNRS Laboratoire Pierre Süe, to be screened for their ability to remove the elements of interest (i.e. Pt, Ir, Pd, Cu, Ni, Zn, As, Se, Cr). Thirteen were available "off the shelf", whilst nine were prepared especially for the project.

At CNRS, initial experiments were conducted in columns. Several products had poor mechanical strength, and had to be tested batch-wise. From these studies, CNRS identified efficient sorbents for several of the selected elements:

- several oxides (polyantimonic acid, manganese dioxide, and titanium oxide) for the fixation of As and Se anions
- hydroxyapatite for the fixation of Cu
- zirconium, titanium, chromium, and tin phosphates for the fixation of Zn
- copper, cobalt, and nickel hexacyanoferrates for the fixation of Cu, Ni, and Pd
- chelating agents for the fixation of Cu, Ni, and Zn

Task 3: Lab-scale preparation of novel sorbents

Preparation of novel sorbents for anionic species was the responsibility of Reading University. Anions of interest included $PtCl_6^{2-}$, $IrCl_6^{2-}$, $PdCl_4^{2-}$, AsO_4^{3-}, SeO_4^{2-}, and CrO_4^{2-}.

As a general rule, weak ion exchangers are required for EIX, to facilitate electrochemical elution. For anion EIX, the exchangeable group is a weak base. At low pH, the protonated base forms an ion-pair with the anionic species. Increasing the pH results in elution. Several such exchangers were prepared, including:

Weak organic bases

• 2-Amino-5 -benzylmercapto- 1,3 ,4-thiadiazole	ABMT
• Cross-linked poly(4-vinylpyridine-N-oxide) (2%, 12%, and 25% cross-linked versions)	PVPO

Hydrous metal oxides

- Montmorillionite and titania-pillared montmorillionite
- Kanemite and derived materials
- Hydrous titania, hydrous zirconia, mesoporous titania, and mesoporous zirconia
- Manganese dioxide (cryptomelane type, prepared by CNRS)

Preparation of novel sorbents for cationic species was the responsibility of CNRS. Cations of interest include Cu^{2+}, Ni^{2+}, and Zn^{2+}.

CNRS synthesised pure phases of copper hexacyanoferrates by:

- direct precipitation
- local growth.

X-ray powder diffraction of the copper hexacyanoferrate sold by STMI indicated that this material was a mixture of $K_2CuFe(CN)_6$ and $Cu_2Fe(CN)_6$.

Task 4: Screening of novel sorbents for IX behaviour

ABMT performed well under IX conditions, so a further batch was prepared for examination under EIX conditions (by AEA Technology).

The various forms of PVPO were found to sorb $PtCl_6^{2-}$ from acid solution with rapid kinetics.

The exchange behaviour of Na^+ montmorillionite (the parent clay) and the titania-pillared derivative were investigated. Both were deemed poor sorbents for $PtCl_6^{2-}$.

Kanemite is a layered sodium silicate (ideally $NaHSi_2O_5.3H_2O$). It functions as a cation exchanger at high pH, and an anion exchanger at low pH.

Hydrous titania and hydrous zirconia both sorbed $PtCl_6^{2-}$ with reasonable kinetics. However, the mesoporous materials derived from HTO and HZO had little or no anion exchange capacity.

Selenite was selectively fixed on hydrous titania, even in 3M NaCl. However, this sorbent is moderately soluble in 1M HCI, which limits its usefulness.

Task 5: Investigation of ion fixation mechanisms

In Tasks 2 and 4, a wide variety of sorbents were screened for IX behaviour. In Task 5, the most promising candidates were subjected to more detailed mechanistic studies. CNRS demonstrated that the fixation mechanisms vary to a large extent, according to the type of sorbent:

With oxides, the formation of insoluble mixed oxides could be invoked in several cases:
. As on Mn oxides
. Se on Ti oxides

In the case of hexacyanoferrates, fixation can occur either by ion exchange or through an oxido-reduction process. The quantity of sorbed element is also an important factor. Consider the fixation of Pd: for small quantities, Pd exchanges with the K^+ in the hexacyanoferrate (where present). For larger quantities of Pd, a reorganisation of the structure occurs.

Task 6: Large scale preparation of suitable sorbents

STMI has specialised equipment for producing large quantities of mineral ion exchangers. Reproducibility is achieved by using very pure raw materials and strictly controlled production methods.

Previous studies by AEA Technology had demonstrated that amorphous zirconium phosphate was an excellent cation exchanger, likely to be suitable for treatment of waste waters containing base metal cations (Cu, Ni, Zn). STMI therefore synthesised 2.5kg of zirconium phosphate (0.5 :48), a form of the exchanger resistant to hydrolysis under EIX conditions.

In Task 2, CNRS identified polyantimonic acid and titanium oxide as suitable sorbents for base met al anions (As, Se). STMI therefore prepared 2. 5kg batches of each of these sorbents.

In Task 4, Reading University identified PVPO as a suitable sorbent for precious metal anions (e.g. $PtCl_6^{2-}$), and had already synthesised several small batches. In the third year of the project, STMI scaled up the process. PVPO (2% cross-linked) and PVPO (25% cross-linked) were synthesised, using an adaptation of the method developed by Reading University:

- reduction of acetic acid volume
- continuous hydrogen peroxide feed
- drying in a forced dry air oven

IR confirmed oxygenation of PVP to PVPO. This product recovered Pt as efficiently as PVPO made by the Reading procedure, The STMI modifications give rise to a considerable reduction in PVPO production costs.

Task 7: Manufacture of prototype flowcells

In the original Work Programme, AEA Technology was scheduled to make 3 types of prototype EIX flowcells:

- small flowcell (3)
- 5-module flowcell (1)
- improved flowcell (1)

In practice, AEA Technology produced 4 (different) types of prototype EIX flowcells:

- small flowcell (6)
- modified flowcell (3)
- improved flowcell (2)
- continuous EIX flowcell (1)

The simplest prototype is the small flowcell, which is made from Perspex. Three such cells were constructed. Ancillary equipment (power supply units, pumps, pH meters, valves, timer/switch units) was obtained and flowcell rigs assembled. One was delivered to Loughborough University and the other two were dispatched to W C Heraeus GmbH. The rigs were installed and commissioned by AEA Technology personnel.

For experiments with PGM solutions, the small EIX flowcell was modified to incorporate a cation transfer (CT) membrane. This prevented Pt deposition on the (cathodic) counter electrode during absorption and Cl_2 evolution on the (anodic) counter electrode during elution.

It was decided not to proceed with the manufacture of a 5-module EIX flowcell, since the 1-module EIX flowcell was sufficient for treatment of the individual PGM waste solutions (from electro-winning).

The improved flowcell actually consists of 3 small flowcells in series (C/A/C for cations and A/C/A for anions). This configuration was recommended by Loughborough University, following its mass transfer measurements and process modelling (Task 11).

In a separate programme, AEA Technology recently developed a technique known as continuous EIX. It was decided to modify the Work Programme of the BRITE-EURAM II project, to allow testing of this system. Two continuous EIX flowcells were required by AEA Technology, for concurrent tests on precious and base metals. A small continuous EIX flowcell (membrane area 50 cm^2) was manufactured specifically for the project, whilst a second cell was borrowed from another project,

Task 8: Manufacture of EIX electrodes

Some time ago, AEA Technology developed a simple, reproducible method for the fabrication of EIX electrodes, Powdered ion exchanger is mixed with a solution of a synthetic rubber in a solvent. The resulting slurry is poured into a mould containing a Pt/Ti mesh. The electrode is left overnight, in order to allow the solvent to evaporate.

Using this procedure, EIX electrodes were made from:

• Zirconium phosphate (0.5:48)	ZrP (0.5:48)
• 2-Amino-5-benzylmercapto-1,3,4-thiadiazole	ABMT
• Poly (4-vinylpyridine)	PVP
• Poly (4-vinylpyridine-N-oxide), 2% cross-linked	PVPO (2%)
• Poly (4-vinylpyridine-N-oxide), 12% cross-linked	PVPO (12%)
• Poly (4-vinylpyridine-N-oxide), 25% cross-linked	PVPO (25%)
• Reillex HPQ	
• Purolite PrAOH	
• Purolite PrCH	
• Purolite A-500	
• Purolite A-510	
• Purolite C-150	
• Eichrom Diphonix resin	
• Polyantimonic acid	
• Kanemite (layered sodium silicate)	
• Hydrous titanium oxide	
• Hydrous zirconium oxide	
• Zinc hexacyanoferrate (H)	ZnFe
• Nickel hexacyanoferrate (II)	NiFe
• Cobalt hexacyanoferrate (II)	CoFe
• Copper hexacyanoferrate (II)	CuFe
• Copper hexacyanoferrate (HI)	CuFe (III)

Some of these ion exchangers were commercially available, whilst others were prepared especially for the project.

In an independent programme, AEA Technology developed a new method for fabricating EIX electrodes, by means of hot-pressing, Powdered ion exchanger, synthetic rubber, and a small quantity of solvent are mixed together thoroughly. The resulting slurry is evaporated to dryness, and the product chopped up in a blender. EIX electrodes can be made from the powdered mix and a Pt/Ti mesh, by application of heat and pressure. Using this procedure, an EIX electrode was made from zirconium phosphate.

It is also possible to use hot-pressing as a post-treatment for EIX electrodes made by solvent evaporation. This procedure was used to make another zirconium phosphate electrode.

The new method confers several advantages. A membrane made by hot-pressing (d=1 ,7) is much denser than one made by solvent evaporation (d=1 .05). This implies greater particle-particle contact and lower resistance. Furthermore, uniform thickness is achievable.

In the last year of the project, the solvent evaporation method was used to prepare a number of continuous EIX membranes:

- PVPO
- Purolite PrAOH
- Purolite PrCH
- Purolite S-930
- Purolite S-950

Task 9: Testing of EIX electrodes with simulant solutions

Heraeus has 10 sample effluent streams, which require ion removal prior to discharge to the sewer. In Task 9, AEA Technology carried out a range of experiments, to ascertain whether EIX was effective for this purpose. Simulant solutions were used in these screening experiments. At the start (in the absence of accurate analytical data), the solution compositions were based on the ‘typical’ compositions supplied by Heraeus. In several cases, these data proved to be somewhat misleading and unrepresentative. Later experiments were based on the compositions determined by CNRS in Task 1.

During the project, 4 of these process streams were simulated: solution 9 (containing Cu, Fe, Ni, and Zn), solutions 7 and 8 (containing As, Se, and Cr), and solution 5 (containing Pt). Batch, flowcell, and continuous EIX experiments were performed.

Cationic Cu, Fe, Ni, and Zn

Batch experiments

In a typical batch cell experiment, 1l of solution was recirculated past the EIX module (EIX electrode + counter electrode) at a flowrate of 1.7l/min. Samples were taken periodically, for analysis.

A solution of metal (II) sulphate in water (10ppm M^{2+}) was used as simulant. Since the base metals were present as “cations, the EIX electrode was coated with a cation exchanger and was poised at cathodic potential during absorption. Almost complete success was achieved with the first exchanger tried - zirconium phosphate (ZrP).

The metals were treated singly, then in pairs, and finally altogether (10ppm Cu2+ + 10ppm Fe^{2+} + 10ppm Ni^{2+} + 10ppm Zn^{2+}). The cations were removed by the ZrP electrode and subsequently eluted (upon polarity reversal) into O. 1M HNO_3. Two slight problems were encountered:

- Fe^{2+} precipitated when the pH was allowed to rise >3 during elution.
- Cu metal deposited on the counter electrode during elution, but redissolved when the current was switched off.

These experiments were all conducted in the absence of high salt concentrations. Later experiments involved a considerable excess of alkali metal cations. At first, zirconium phosphate sorbed both base- and alkali-metal cations equally well. However, after several days operation, zirconium phosphate developed a significant preference for base metal cations. (N.B. It is unwise to draw sweeping conclusions on the basis of short experiments with new electrodes. Patience is required.)

Encouraging results were also obtained with the commercially-available chelating resins: Eichrom Diphonix, Purolite S-930 and Purolite S-950,

The hexacyanoferrates were uniformly awful under batch EIX conditions - the sorbent dissolved! This is believed to be a pH effect.

Flowcell experiments

AEA Technology assembled and tested the improved configuration (i.e. C/A/C) suggested by Loughborough University. Flowcells 1 and 3 contained Purolite S-930, whilst flowcell 2 contained Purolite PrAOH. The middle EIX flowcell was used to make the pH more alkaline, which improved the efficiency of ion exchange. With a feed solution containing 100ppm Na^+, it was possible to achieve a DF of 250 in a single pass. A DF of61 was attained for 141 ppm Zn^{2+}.

Continuous EIX

Preliminary continuous EIX experiments with solutions containing a mixture of alkali- and base-metal ions (Na^+/Zn^{2+} and Na^+/Ni^{2+}) gave most encouraging results. In the Na^+/Ni^{2+} system, it was possible to effect a separation of the two types of metal ions in a single pass through the cell. A control experiment demonstrated the importance of the electric field - the separation does not occur when the current is switched off.

Anionic As, Se, and Cr

Batch experiments

Experiments were conducted on 11 batches containing 100ppm of As(V), Se(IV), and/or Cr(VI). Since the base metals were present as anions, the EIX electrode was coated with an anion exchanger and was poised at anodic potential during absorption. Encouraging results were obtained with two anion exchangers: Purolite PrAOH and poly (4-vinylpyridine-N-oxide), 2% cross-linked. Both exchangers could be eluted by polarity reversal. PVPO is a very weak anion exchanger, and started to elute at open circuit. Addition of sulphate to the selenite feed resulted in slower kinetics.

Flowcell experiments

- Technical cooperation

Knowledge of the levels attainable by EIX is highly desirable. To this end, personnel from AEA Technology visited CNRS (Laboratoire Pierre Süe) for three weeks. During this period, experiments were performed and precise analysis carried out, using neutron activation analysis. Flowcells were operated in recycling mode (10 BV recirculating at 5 BV/h). The maximum current density was 3 mA/cm^2. With a PrAOH electrode, a 100ppm As feed was reduced to 20ppb in 23. 5h. Kinetics at PVPO were slightly poorer, reaching 99ppb after 23.3h. After 59.3h, the level had dropped to 2ppb. Similar results were obtained with a 100ppm Se feed. For both sorbents, rapid initial exchange was followed by a slower increase in fixation.

- Improved configuration

AEA Technology assembled and tested the improved configuration (i.e. A/C/A) suggested by Loughborough University. Flowcells 1 and 3 contained Purolite PrAOH, whilst flowcell 2 contained Purolite S-930. The middle EIX flowcell was used to make the pH more acidic, which improved the efficiency of ion exchange. A DF of 78 was achieved for 171 ppm Se (as SeO_3^{2-}) and a DF of **91** for 109ppm As (as AsO_4^{3-}).

Anionic Pt

Batch experiments

Experiments were conducted on 11 batches of K_2PtCl_6 solution (45ppm Pt, in 0.2M HCl). Since the precious metal was present as an anionic complex, the EIX electrode was poised at anodic potential during absorption. Two ion exchangers were tested in this way: zirconium phosphate and Purolite PrAOH.

- Zirconium phosphate (ZrP)

Zirconium phosphate is normally considered to be a cation exchanger. However, AEA Technology had demonstrated (in an independent programme) that ZrP EIX electrodes poised at anodic potential were able to remove anionic silver complexes. In this case, the soluble Pt concentration was reduced to <1 ppm in 2h. It was noted that some of the Pt had deposited on the counter electrode (the cathode) in the form of Pt black. Poorly adherent, some of the Pt black detached from the cathode and was seen circulating in the solution. Upon polarity reversal, very little elution was achieved.

- Purolite PrAOH

Purolite PrAOH is a Type 1 quaternary ammonium strong base ion exchanger. EIX electrodes fabricated from this material reduced the soluble Pt levels to 10ppm in 2h, and to 1ppm after 24h. No Pt black was observed in the solution . The counter electrode (the cathode) gained in weight, but the increase accounted for <50% of the reduction in soluble Pt concentration. Upon polarity, very little elution of Pt into 0.2M HCl was observed.

Flowcell experiments

Because of the toxicity of Pt solutions, subsequent experiments were conducted in flowcells (normal and/or modified with CT membranes).

Good results were obtained with EIX electrodes made from Purolite PrAOH and poly (4-vinypyridine-N-oxide), PVPO. Unfortunately, **2°/0** cross-linked PVPO swelled dramatically upon hydration/ion exchange, which caused the EIX membrane to peel away from the Pt/Ti mesh. A higher degree of cross-linking(12!A0 or 25%) was needed to overcome this problem.

Commercially-available Reillex HPQ was also tested, and the results compared with Purolite PrAOH. Upon polarity reversal, $PtCl_6^{2-}$ started to elute from the HPQ EIX electrode. However, the concentration of Pt in solution fell again, as Pt black formed.

Kanemite and hydrous titania were also screened for Pt removal. They were much poorer than Purolite PrAOH, in terms of both capacity and kinetics.

Continuous EIX

In a separate programme, AEA Technology recently developed a technique known as continuous EIX. Membranes fabricated from Purolite PrAOH gave most encouraging results. With a feed solution containing ~50ppm Pt (as $PtCl_6^{2-}$,in 0.2M HCl), it was possible to achieve a DF >10 in a single pass through the cell. Furthermore, this performance was sustainable - the cell operated continuously for 67 days! During this time, the effects of current density and permeation flowrate were systematically investigated. Impressive results were also obtained with PVPO membranes.

Task 10: Testing of EIX electrodes with industrial liquors

In the original Work Programme, Heraeus was scheduled to test EIX electrodes with 3 typical industrial liquors:

- dilute aqueous solutions containing low levels of Pt, Ir, Pd, As, Se, and Cr
- spent process liquors containing low levels of Pt, Ir, Pd, As, Se, Cr, and high levels of salt
- waste water containing base metals

Following the Mid-Term Assessment Meeting, Heraeus' rôle was enlarged, to include:

- treatment of dilute solutions containing base metals
- water softening

The following conclusions were drawn by Heraeus:

Dilute aqueous solutions containing low levels of Pt, Ir, Pd, As, Se, Cr

Pt extraction using PVPO EIX electrodes was considered unattractive, because of Cl_2 evolution during absorption and Pt deposition during elution. On the other hand, PVPO could be used as a conventional ion exchanger. It has been shown to offer high selectivity for $PtCl_6^{2-}$ compared with Cl^- and the base metal cations. Initial experiments have been performed in a production unit.

Spent process liquors containing low levels of Pt, Ir, Pd, As, Se, Cr and high levels of salt

Certain PGM effluents contain high levels of salt. Under these circumstances, the EIX cell performance was poor. It was concluded that EIX was not suitable for this purpose.

Waste waters containing base metals

Zirconium phosphate (ZrP) was shown to be a reversible ion exchanger for base metals, but in its H-form the sorbent showed no selectivity against alkali metals. This problem was overcome by using a chelating resin. Excellent results were obtained with 2 commercially-available exchangers of this type. They possessed the desired selectivity against alkali metals, even in the H-form. Better performance was achieved when the Na-form was used. It should be noted that there is no additional selectivity associated with electrochemical ion exchange: the selectivity observed is determined only by that of the ion exchanger incorporated in the EIX electrode.

Treatment of dilute solutions containing base metals

In the short term, where the EIX electrode was loaded to a very low extent only (<5%), the EIX process was extremely efficient. However, it was not possible to maintain this performance in the long term. For processes which allow reasonable flowrates (>5BV/h), hydroxide precipitation was observed. When the EIX electrodes were loaded to a considerable extent, metal hydroxide appeared on the electrode surface. Under adverse conditions, loosely adherent material might be washed off, thereby contaminating the outlet solution. In the standard flowcell, it was observed that metal ions migrated through the EIX membrane and into the gap between the back of the electrode and the cell wall. There they formed insoluble hydroxides, which were difficult to remove during the elution step.

Water softening

In order to examine a commercially-relevant system, Hanau drinking water was used as the feed solution. In the short term, EIX was effective for water softening, Eventually, calciferous precipitates formed, which reduced the cell performance. Heraeus therefore modified the cell design, in an attempt to produce deionised water without added chemicals. In this way, it was possible to elute 81% of the Mg^{2+} and 54% of the Ca^{2+}. Though much better, this approach is not a commercial viability.

Task 11: Mass transfer measurements, process modelling, and design of improved flowcell

Measurements

The following 6 parameters were studied in order to assess the performance of the existing flowcell:

- flowrate
- current density
- feed concentration

- feed pH
- electrode gap (between the 2 half-cells)
- membrane gap (between the EIX membrane and the counter electrode)

The range of values for these parameters can be seen in Table 1.

Initially, experiments were conducted to determine the time it took for the process to reach pseudo steady state. This was found to be around 10 to 20 minutes, depending on the process conditions. It was important to know this time, to ensure that samples were only taken after the process had reached equilibrium.

TABLE **1: Range of parameters used**

Parameter	**Minimum**	**Maximum**
Flowrate [l/h]	0.2	12
Current density [mA/cm’]	0.5	15
Electrode gap [mm]	3	8
Membrane gap [mm]	0	3
Feed concentration [g/l]	0	6
Feed pH	1	12

Flowrate

Increasing the flowrate resulted in poorer removal of cations (i.e. higher outlet concentrations). However, the electrical efficiency was better for the higher flowrates. This was thought to be because of the smaller pH swing which occurred between the inlet and outlet of the cell.

Current density

Increasing the current density resulted in improved removal of cations. However, the electrical efficiency decreased with increasing current density. Higher currents gave rise to lower pH’s, which meant that a greater proportion of the current was being carried by hydrogen ions.

Electrode gap

The performance of the cell was slightly better (by 4-5%) at smaller electrode gaps, particularly at low pH’s. This was thought to be due to improved mixing in the cell.

Membrane gap

For an alkaline feed (pH = 12) the removal of cations was improved by 5-17% as the membrane gap was increased. This was thought to be due to pH perturbations near the electrode. At lower pH’s, there was no significant improvement in the cell performance.

The cell voltage rose significantly as the membrane gap was increased. The higher power consumption led to an increase in temperature, particularly at high current densities and high feed pH.

Feed concentration

The percentage removal decreased with increase in feed concentration. The process performed very well under dilute feed concentrations: all the cations were removed to below the detection limit. Typical parameters: feed concentration = 20ppm sodium, flowrate = 0.2- 1.8 l/h, current density = 6 mA/cm^2, feed pH = 3, and electrode gap= 4.7 mm.

Feed pH

The removal of sodium ions was much better at higher pH. This was because there was less interference from hydrogen ions.

Concentration and pH profiles

In general, a steady decrease in both pH and concentration was observed along the length of the cell, in the same direction as the flow. In addition, there was some leakage of material from the back of the cell, back into the bulk of the solution in the centre of the cell. Indeed, when the sodium forms of Purolite S-930 and S-950 were used, the solution in the centre of the cell actually ended up more concentrated than the feed solution!

There was a gradual buildup of material at the back of the EIX electrode. For example, after a 6h experiment using zirconium phosphate electrodes, the concentration of sodium ions at the back of the electrode was of the order of 10 g/l (cf. 0.3 g/l in the feed).

Mixing

The flow patterns in the ceil were examined using a dye technique. Nigrosine dye was injected into different parts of the cell. Samples were then taken from the outlet at various time intervals. The quantity of tracer gave an indication of mixing within the cell under different process conditions. The results revealed a slow but definite leakage from the back of the cell, back into the bulk solution in the centre. The results also indicated that mixing within the cell was improved by generation of gas. At higher flowrates, the cell was like a plug flow reactor, with very little back mixing. Two factors affected the mixing within the cell:

- liquid flow
- gas generation (which is related to the current density)

Current distribution

Initially, a current follower technique was developed to measure the current in different parts of the cell. However, in situ calibration proved impossible. An alternative method was therefore developed. This involved dividing one half cell into five sections, and directly measuring the current flowing through each section. This gave a current profile, with minimum current readings in the centre section. The maximum readings were at the top and bottom of the cell.

Elution

Tests were carried out on EIX electrodes fabricated from zirconium phosphate, using various feed conditions and current densities. The rate of elution was found to be directly proportional to the current density. There was an ohmic relationship between the voltage and the current. This may have been due in part to the high acidic conditions in the bulk solution. With EIX electrodes made from the chelating resins, Purolite S-930 and Purolite S-950, it was found that zinc eluted only after most of the sodium had been desorbed from the membrane.

Additional tasks

The original Work Programme did not include work on different ion exchangers. However, after the Mid-Term Assessment Meeting it was decided to modify the Work Programme, to include work on two additional systems (Purolite S-930 and Purolite S-950) which appeared to work well under EIX process conditions. Both the hydrogen- and sodium-forms were assessed. On completion of these tests, Purolite S-930 was identified as being better suited for the removal of transition metals. Consequently, this ion exchanger was used in subsequent tests. In a series of selectivity tests, it was found that the selectivity improved with time (greater selectivity was observed in long experiments).

Processing modelling

A mathematical representation of the system was developed, based on the Nersnst-Planck transport equation. When the model was tested against a range of experimental data, it was found to predict the performance with considerable accuracy. The model was then used to test different configurations and process strategies.

The model was also applied to the experimental data generated by Heraeus. Once again, there was good agreement between predicted and experimental results[1].

Improvements in cell design

The data generated during the first 24 months was used to assess the cell design, conditions of operation, and operating strategies.

Cell design

A review of the experimental data gave some indication of how the cell should be arranged, and suggestions were made to modify the cell design. Experiments indicated that the gap between the half cells (the electrode gap) should be minimised, to ensure good mixing. The situation for the gap between the EIX electrode and the counter electrode (the membrane gap) was less straight-forward, since a small gap actually resulted in an improvement in performance. However, this was accompanied by an increase in power consumption. On balance, it was decided to minimise the membrane gap too.

The concentration and pH profiles indicated that leakage was occurring from the back of the EIX electrode to the bulk solution in the centre of the cell. In some cases, this resulted in a high pH and significant metal concentration at the bottom of the cell, When transition metals were used, metal precipitation occurred at this point. It was suggested that the bare part of the EIX electrode should be covered This strategy proved effective, and the precipitation was minimised.

In order to minimise leakage from the back of the EIX electrode, the membrane was sealed in the cell casing. A small opening was left at the top, to allow the gas to escape.

The counter electrode was bent over the top of the EIX electrode, to help reduce the local pH. As mentioned above, the bare part of the EIX electrode was covered by inert binder material. These measures drastically reduced solid formation.

Cell performance could be improved by having a more even current distribution along the length of the membrane. It was found that by changing the thickness of the membrane coating the metal mesh, more current passed through a thinner section than a thicker section (placed in the same location within the cell). Thus a possible approach would be to make the centre section thinner than the ends. This hypothesis has not been tested experimentally.

The original cell design already contained a number of features which enhanced the performance immensely:

- electrogenerated gas bubbles gave good mass transfer
- metal mesh electrodes facilitated mass transfer

Operating conditions

There are some general rules which can be applied when setting the process conditions:

- high flowrates improve the current efficiency, but at the cost of higher voltages, greater pumping cost and higher outlet concentrations
- higher current densities increase the removal of cations, but with lower electrical efficiency and higher power consumption
- during elution, high current densities increase the rate of elution, but with increased chance of metal precipitation

Two elution cycles were needed to elute completely Purolite S-930 EIX electrodes (total time 18h).

The mathematical model can be used to predict (reasonably accurately) the performance of the cell under different operating conditions. Hence it is possible to choose sensible operating conditions for the EIX process.

N.B. The absorption process should be operated so as to achieve reasonable loading of the ion exchanger.

Operating strategies

The mathematical model was used extensively to choose operating strategies which would improve the overall performance of an EIX plant. When intermediate anionic steps were used, the electrode area was reduced and less current was needed to remove the same amount of material. As a consequence, both the capital and operating costs of such a plant could be reduced. This was tested in the pilot plant. As predicted, using an anionic step improved the overall performance of the process.

The ultimate aim of an operating strategy must be to maximise removal and minimise operating costs. Hence the system should be in absorption mode, most of the time.

Assessment of process design

Pilot plant

A pilot plant was set up, as the culmination of Task 11. However, the system was not fully utilised, due to lack of time. The test loop was tested under a variety of process conditions. The results suggest scope for further improvements and optimisation. There were signs of precipitation within the system (which increased the overall removal of ions). Solid formation occurred absorption and electroplating during elution. Solid formation was drastically reduced by covering the bare part of the EIX electrode with inert binder material and by sealing the EIX membrane into the cell casing. The pilot plant was used on long runs without encountering any major operating difficulties.

Overall design

The pilot plant consisted of two cationic cells and one anionic cell in series (C/A/C). The loop was tested using a feed which contained just sodium or a combined feed containing sodium, copper, nickel, and zinc. The performance of the process was significantly enhanced by the inclusion of the anionic cell (which helped to increase the pH). There was clear evidence of selectivity, once the process had reached equilibrium. The removal of transition metal was **-70°/0** for a flowrate of 1.2-2 l/h, pH of 3, and feed concentration of 130-180ppm sodium, 10ppm copper, 10ppm nickel, and 10ppm zinc.

Safety

The handling of gases was not examined in any detail. This aspect is important in the detailed design, since the EIX process produces both oxygen and hydrogen. This potentially explosive combination must be treated with due care. One possibility would be to dilute the mixture with air, to below the lower flammable limit of hydrogen, oxygen, and air mixtures.

Task 12: Project management

Overall management of this BRITE-EURAM II project has been the responsibility of AEA Technology. In this capacity, the Coordinator has:

- compiled the original proposal
- undertaken contract negotiation
- produced a Collaboration Agreement acceptable to all parties
- called and chaired 7 Progress Meetings
- compiled 7 Progress Reports
- visited the other partners on a regular basis
- liaised with the EC Project Monitor on technical and financial matters
- received payment from the EC and disbursed the agreed amounts to the other partners

Coordination of a BRITE-EURAM II project has proved to be a very time-consuming activity!

CONCLUSIONS

EIX is an energy efficient process which requires few added chemicals. It enables valuable metals to be recycled and toxic metals to be removed. To date, applications of EIX have focused on the nuclear industry, where the technique has been used to remove radioactive cations and anions from nuclear waste. Pre-existing intellectual property is protected by an extensive patent portfolio - see Table 2.

The purpose of this project was to establish whether or not EIX is an appropriate technology for the treatment of non-nuclear process liquors, containing precious metals (Pt, Ir, Pd) and/or base metals (Cu, Ni, Zn, As, Se, Cr). Significant data has been generated on a wide variety of aqueous solutions. This will put us in a good position to design customised EIX plant for the treatment of specific process streams containing precious and/or base metals. However, further development work is needed to enable this emerging technology to reach its intended markets in the non-nuclear sector.

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REFERENCE

1. ‘A model to predict the performance of an electrochemical ion exchange cell’,
Iain W Cumming, Hadi Tai, and Michael Beier,
Transactions of the Institution of Chemical Engineers (1 995).

TABLE 2: EIX Patent Cover

Descriptor	Expiry date[a]	UK	Belgium	France	Germany	Netherlands	Italy	Spain
Separated cell	2004	✓		✓	✓			
Electrode Improvements	2004	✓		✓	✓			
Separate Resin	2006	✓						
Selective EIX	2007	✓						
Zr Phosphate Regeneration	2011	✓		✓	✓			
Li/Co Separation	2011	✓	✓	✓	✓	✓		
Asymmetrical Electrode	2011	✓	✓	✓	✓			
Composite Resin Structure	2011	✓	✓	✓	✓	✓		
Parallel Electrodes	2011	✓	✓	✓	✓	✓		
Continuous (Pending)	2015	✓	✓	✓	✓		✓	✓
Sodium Thiosulphate (Pending)	2015	✓	✓	✓	✓		✓	✓

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[a] Assuming necessary renewal fees are paid