FLUIDIZED BED ELECTROLYSIS FOR THE REMOVAL OR RECOVERY OF METALS FROM DILUTE SOLUTIONS

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ABSTRACT : Akzo Zout Chemie has developed a new electrolysis technology based on the fluidized bed principle. As scaling-up problems have been solved the process is suitable for industrial application. Features of fluidized bed electrolysis (FBE) are a high specific active cathode area and a high mass transfer rate due tu turbulence created by the moving metal particles, which function as the cathode. Therefore FBE is particularly suited for the selective recovery or removal or metals which are present in low concentrations in large volume proccess streams. FBE can be applied both in solving waste water problems (e. g. mine water) and in hydrometallurgical processes. An important advantage of FBE over conventional techniques is the economic and simple one-step conversion of a dilute metal solution into a rather pure metal product.

RESUME : Akzo Zout Chemie a développé une technologie nouvelle d'électrolyse basée sur le principe de couche fluidifiée. Etant donné que les problèmes de "scale-up" ont été résolus, le processus est propre à être appliqué. Les caractéristiques de ces cellules électrolytiques de couche fluidifiée (FBE) sont : une grande surface de cathode active spécifique, et un grand taux de transfert de masse dû à la turbulence créée par les particules de métal en mouvement, qui fonctionnent en tant que cathode. Par conséquent, la cellule de FBE est particulièrement adaptée à la récupération sélective ou l'extraction de métaux qui se trouvent présents, en faible concentration, dans des eaux de cours à grand débit. Le FBE peut s'appliquer tant pour résoudre des problèmes d'eaux résiduelles (par exemple eaux de mine) que dans des processus hydrométallurgiques. Un avantage important du FBE sur les techniques conventionnelles est la conversion économique, par un simple passage d'une solution métallique diluée à un produit métallique très pur.

RESUMEN : Akzo Zout Chemie ha desarrollado una nueva tecnología de electrólisis basada en el principio del lecho fluidizado. Como sea que los problemas del "scale up" han sido resueltos, el proceso resulta apropiado para aplicaciones. Las características de estas células electrolíticas de lecho fluidizado (FBE)

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son : un gran área de cátodo activo específico, y una gran tasa de transferencia de masa debido a la turbulencia creada por las partículas de metal en movimiento, que funcionan como cátodo. Por consiguiente, la célula de FBE está particularmente adaptada para la recuperación selectiva o extracción de metales que se hallen presentes, en baja contracción, en aguas de procesos con gran caudal. El FBE puede aplicarse tanto a resolver problemas de aguas residuales (por ejemplo aguas de mina) como en procesos hidrometalúrgicos. Una importante ventaja del FBE sobre las técnicas convencionales es la conversión económica, por un simple paso, de una solución metálica diluida en un producto metálico muy puro.

Introduction

Akzo Zout Chemie is a producer of salt, chlorine and chlorinated hydrocarbons. Therefore, many of its process streams and waste waters are highly concentrated chloride solutions. Some of them also contain metal ions in low concentrations, as is illustrated in figure 1 for a process stream of a mercury cell chlor-alkali electrolysis plant and for a waste water stream from a chlorinated hydrocarbons plant.

A)	$Cl^- = 160$ g/l pH = 2-3	Hg = 1-2 ppm
B)	$Cl^- = 5\text{-}30$ g/l pH = 0-1	Cu = 30-100 ppm

Figure 1. Composition of a Mercury Chlorine Electrolysis Process Stream (A) and a Waste Water Stream from a Chlorinated Hydrocarbons Plant (B)

Lowering of the metal concentration in these solutions can be necessary because of technical requirements or because of environmental regulations. Especially, environmental regulations are expected to become more strict in the future. Therefore, it appeared necessary to develop a process to lower these metal concentrations.

Suitable processes for the removal of metals in low concentrations from streams with a high flow rate are ion exchange, solvent extraction, precipitation and fluidized bed electrolysis. Fluidized bed electrolysis was chosen because of our electrolysis experience. It was soon realized that fluidized bed electrolysis (FBE) can also be applied to the separation and winning of metals from hydrometallurgical process streams. This extended the scope of our research and development work.

Principle of fluidized bed electrolysis

The FBE cell (figure 2) consists of an anode and cathode compartment, which are separated from each other by a diaphragm. In the cathode compartment metal particles are fluidized by the process stream or waste water to be treated. The bed expansion, which is defined as increase in bed height x 100/ static bed height is varied between 10 and 30%.

The diameter of freshly added particles is about 0.5 mm. By deposition of the metal the particles grow to a diameter of about 1 mm. In consequence the particles become heavier during electrolysis and sink gradually to the bottom of the cathode compartment. The process can be operated continuously by adding small particles at the top of the cathode compartment and discharging grown particles from the bottom.

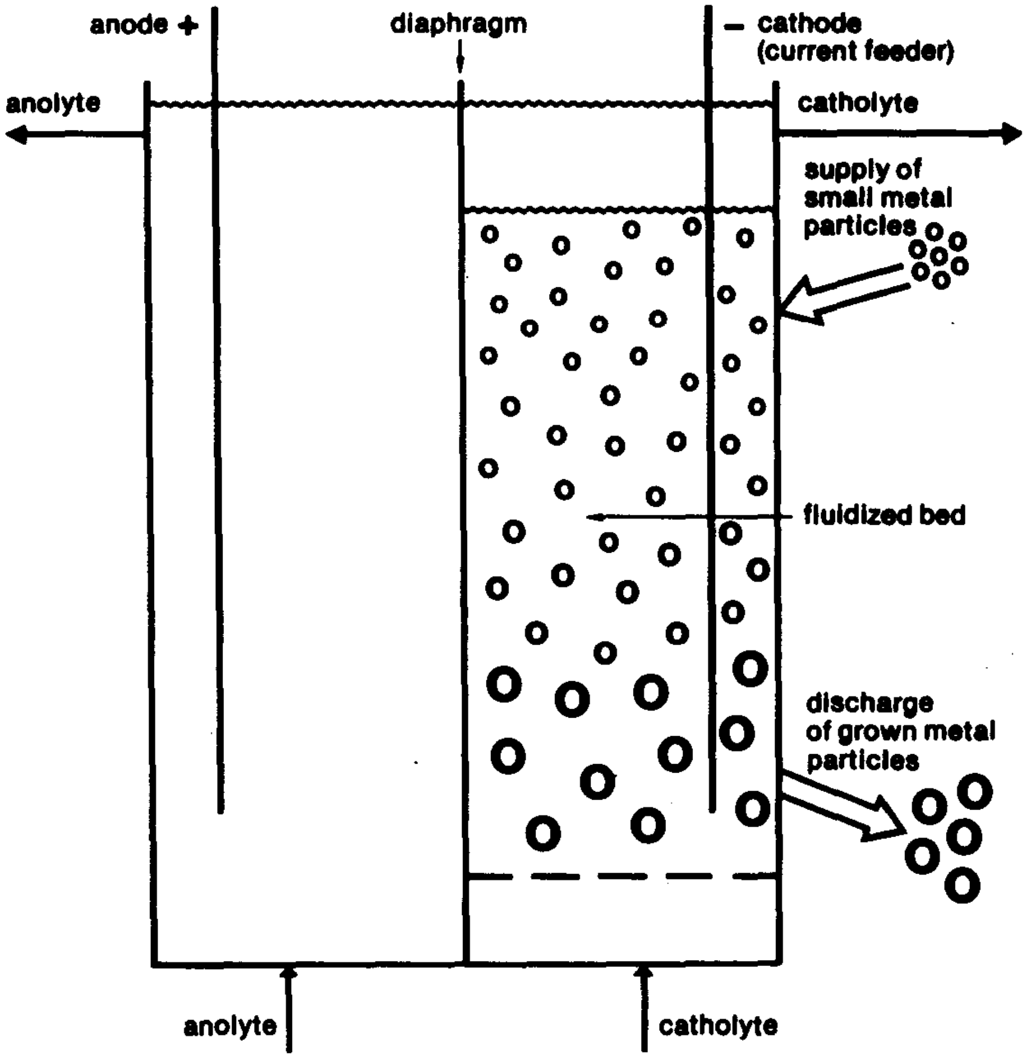

Figure 2. Schematic View of an FBE Cell

In general the material of the fluidized particles will be the same as the metal to be deposited. The electrical charge which makes the particles function as a cathode, result from their contact with the current feeders as well as from contact of particles with each other.

Features of fluidized bed electrolysis

The one-step conversion of a diluted metal solution into a rather pure metal product is an important general advantage of FBE. Other techniques, such as precipitation, cementation, ion exchange and solvent extraction, result in derived problems. The product of precipitation or cementation is a sludge or cake that requires quite some further processing before a salable metal product is obtained. The same is more or less true of the concentrated metal solutions produced by ion exchange or solvent extraction.

In comparison with other electrolytic processes, such as porous bed electrolysis or conventional planar electrolysis, the FBE cell has a high specific active cathode area.

Another characteristic feature of fluidized bed electrolysis is the high mass transfer rate due to the turbulence of the moving particles. Therefore, as compared with planar electrodes, higher local current densities can be applied without approaching the limiting current density range.

The high specific active cathode area results in low cathodic current densities at high current intensities, where current intensity is defined as the ratio of current load to cell volume. The combination of the high specific active cathode area and the high mass transfer rate, make FBE particularly suited for electrochemical reactions with a low reaction rate per unit of electrode area. The reasons for a low reaction rate can be either a high activation energy required or a low metal concentration. As a consequence, even at low metal concentrations, an FBE cell can operate at high current efficiencies.

Comparison of FBE with conventional electro-winning cells (figure 3) shows that the specific cathode area of a fluidized bed electrode is some 200 x as high as that of a conventional planar electrode. Therefore, local current densities in an FBE cell are about 40 x as low, even though the current intensity in an FBE cell is 5 x as high! With planar electrodes metals can be recovered at acceptable current efficiencies from solutions containing 30-150 g/l of metal. Because of the high specific cathode area and the high mass transfer rate in an FBE cell this concentration range is extended downwards to concentrations as low as 1 mg/l! However, planar electrolysis will in general be the most economical electrolysis process to recover metals from concentrated solutions. In case of solutions containing less than several g/l of metal FBE will be more attractive.

Characteristics	Type of Electrode	
	Planar Electrode	FBE
Cathode area/m^3 cell	16 m^2/m^3	3500 m^2/m^3
Current intensity	2.5-10 kA/m^3	15-50 kA/m^3
Metal concentration	30-150 g/l	0.001-150 g/l

Figure 3. Comparison of FBE with Conventional Electro-winning Cells

Further advantageous operating characteristics of FBE are:

— There is no clogging of the bed by solid impurities, which may be present in the process stream.

— Due to the short contact times, agglomeration of particles does not occur.

— As already mentioned before, the process can be operated continuously supplying fresh and discharging grown particles at respectively the top and the bottom of the cell.

The diaphragm

Up to now, scale-up of FBE to industrial size has been troubled by problems with diaphragms or membranes, which have to meet many requirements. The diaphragm developed by Akzo Zout Chemie solves many of the usual problems, as can be seen from the following list of properties.

a. The mechanical strength is high. The diaphragm withstands the pressure of the fluidized bed and is resistant to the erosion of the moving particles. In addition the high mechanical strength makes it possible to subject the anode compartment to overpressure in order to prevent contamination of the anolyte by the catholyte. An example is chloride transport from the cathode compartment through the diaphragm resulting in chlorine evolution at the anode. This is undesirable in many circumstances.

b. The diaphragm is made of materials with a high chemical resistance. Therefore, the diaphragm is not attacked by aggressive media, such as chlorine gas and concentrated acids, like sulphuric or hydrochloric acid.

c. The hydrodynamic permeability is very low: approximately 10^{-2} m^3 water per hour and per m^2 of diaphragm at a pressure difference of 1 atmosphere. The low hydrodynamic permeabillity is required in order to prevent a substantial loss of catholyte to the anode compartment due to pressure differences over the diaphragm of up to 0.5 atmosphere.

   The very low permeability of this diaphragm allows operation with a high bed-height so that a high depletion per pass can be achieved. Moreover, the anolyte can be chosen irrespective of the catholyte. In general, sulphuric acid is chosen as anolyte because of its high electrical conductivity and the absence of chlorine gas evolution.

d. The structure of the diaphragm is such that the electrical resistance factor is low, i.e. about 2.5, whereas the permeability is very low (c). In consequence the contribution of the diaphragm to the cell voltage is small.

e. The smooth diaphragm surface prevents adhesion of particles, wich causes scaling that may spread over the entire cell.

Cell construction

The following targets were aimed for during the development of the cell:

1. Scale-up should be economically advantageous. For many chemical processes the ratio of plant costs of different capacities is roughly proportional to the ratio of the capacities to a power between 0.6 and 0.7. A much lower scale-up advantage is available in electro-chemical processes because of the dependence of capacity on electrode area and the need to locate these electrodes accurately in the equipment. The FBE cell developed shows a scale-up advantage comparable to that of chemical plants: the ratio of plant costs is proportional to the ratio of the capacities to the power 0.73!

2. Cell construction and process control should be simple.
3. Particle agglomeration should be prevented. This objective requires round corners, smooth surfaces and uniform fluidisation.
4. The cell should be closed. One reason is the desired possibility to subject the anode compartment to overpressure. Another reason is chlorine evolution at the anode in case of metal removal from concentrated chloride solutions. Therefore, in the case of chloride hydrometallurgical applications, a closed cell construction is a necessity.

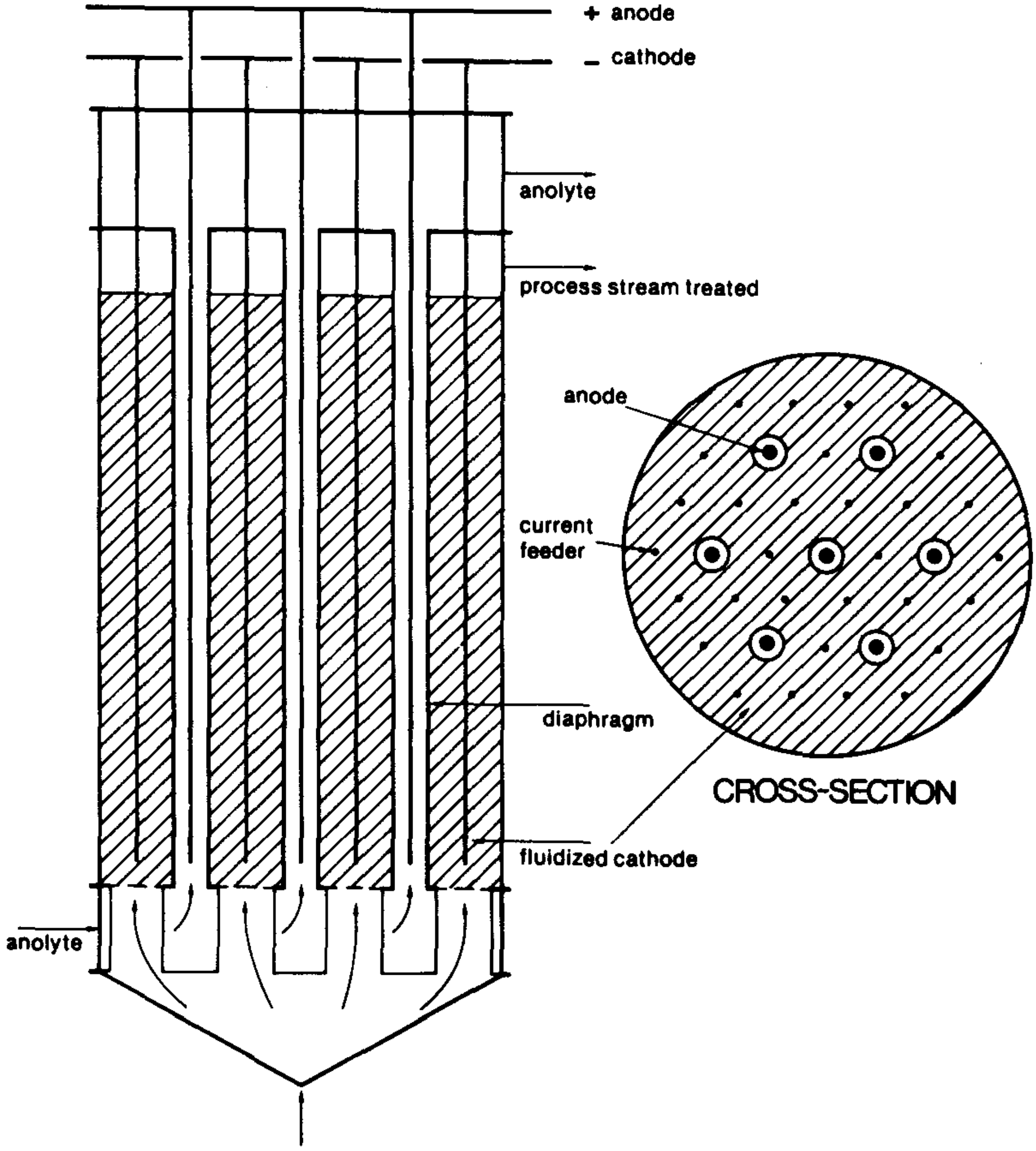

Figure 4. Cell Configuration of FBE Cell

The final result of our cell development, which meets the aforementioned requirements, is a cell configuration as shown in figure 4. The main characteristics of this configuration are the cylindric diaphragm construction and the possibility to install many diaphragms in one cathode compartment. This type of cell construction allows simple enlargement of units, while both large and small units require only one catholyte supply. This is an important advantage over filter press type FBE cells.

The anodes are placed in the centre of the diaphragms. In consequence, the anode area needed is small, which makes it possible to apply stable, but relatively expensive anode materials. Around each diaphragm six bar-shaped contact electrodes or current feeders are installed to supply the fluidized bed with current.

Figure 5 shows the largest FBE test cell of the Research Department of Akzo Zout Chemie. This cell contains 7 diaphragms, while the height of the fluidized bed is about 1.2 m. The diameter of the cell is 0.35 m. In general the operational conditions are a current load of 1000-2000 A and a flow rate of 10-20 m^3/h.

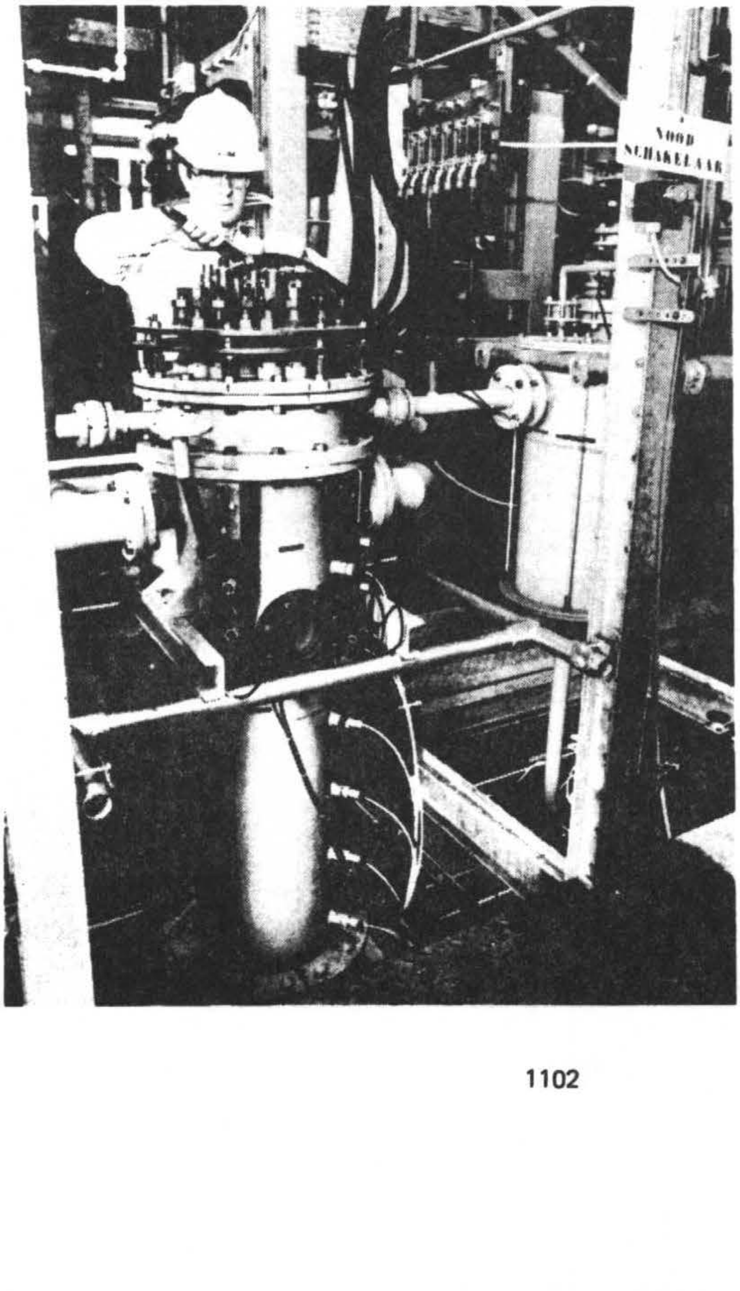

Figure 5. FBE test cell, containing 7 diaphragms, at the research laboratories of Akzo Zout Chemie

The process flow diagram of a complete fluidized bed electrolysis unit is given in figure 6. The installation is composed of an FBE cell, which makes the heart of the unit, an anolyte circuit and a catholyte circuit. The two circuits are separated from each other and due to the low diaphragm permeability the anolyte can be chosen irrespective of the catholyte. Moreover, the anode compartment can be subjected to overpressure in order to prevent a flow of catholyte through the diaphragm. Recirculation of catholyte is necessary to keep the fluidization velocity constant, even when the supply varies. Both the anolyte and the catholyte recirculation tank function also as a gas-liquid separator.

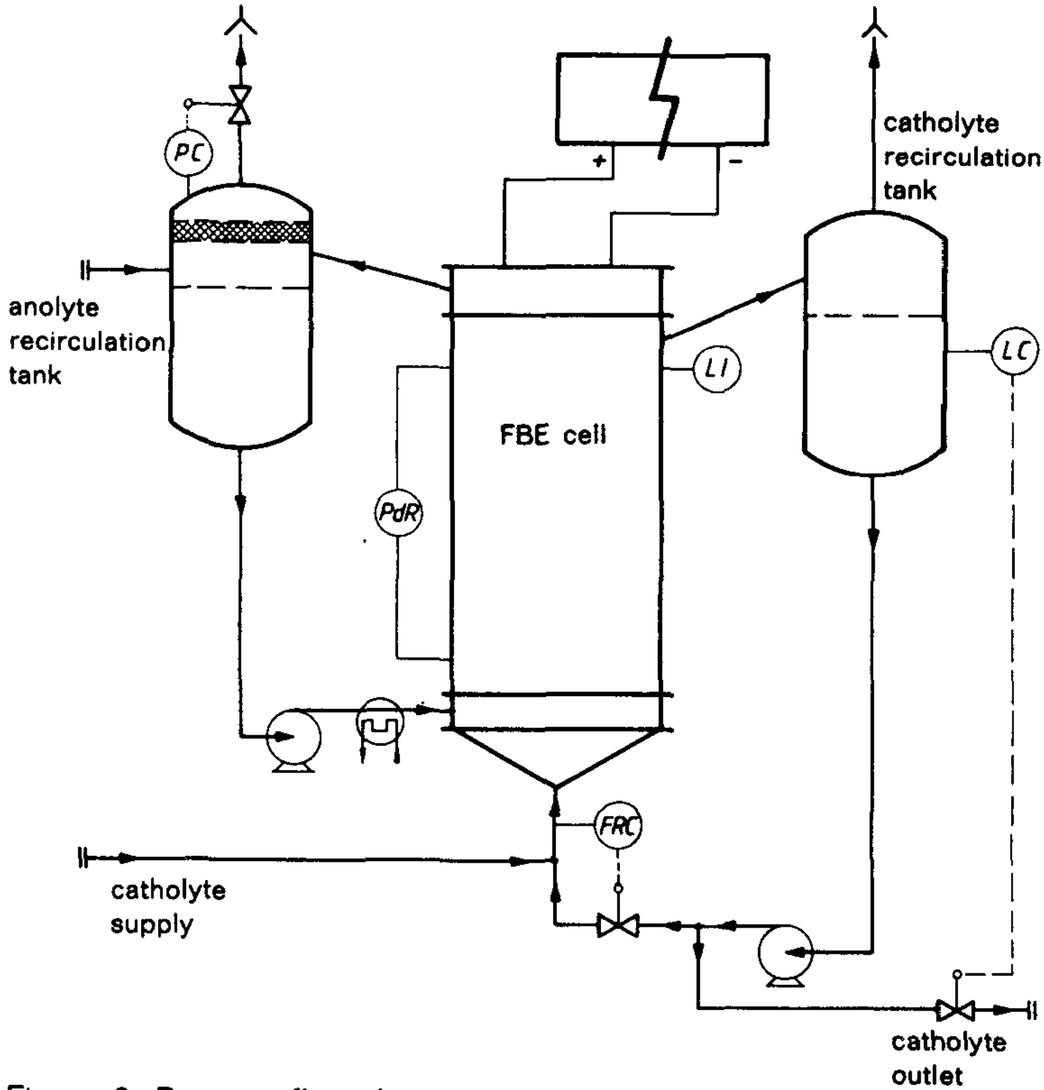

Figure 6: Process flow diagram of an FBE unit

Test results

The first process flow, which we examined and subsequently treated in a test unit in situ, was a copper containing waste water stream from a plant for chlorinated hydrocarbons (figure 7). In this test unit with a capacity of about 1 m^3/h, the copper content was lowered from 100 to less than 1 mg/l in one pass. The vast quantities

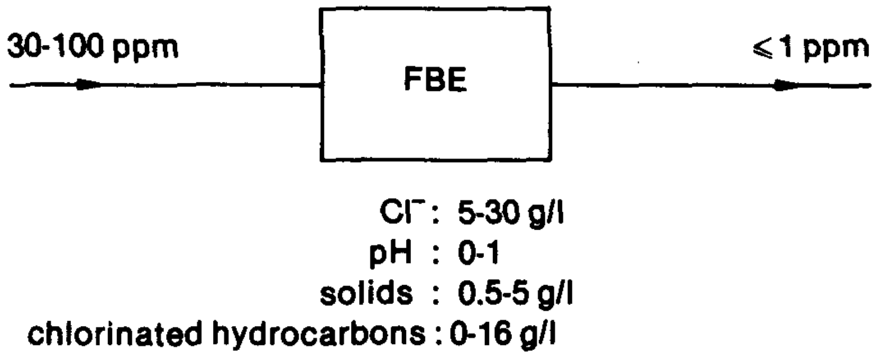

Figure 7. Copper Removal from a Process Stream in a Plant for Chlorinated Hydrocarbons

of solid particles and chlorinated hydrocarbons present in this stream did not interfere. A current efficiency of some 70% has been obtained. Chlorine evolution at the anode was greatly suppressed by the use of overpressure in the anode compartment. The copper particles were allowed to increase in weight by a factor 10, which corresponds to an increase in particle diameter of about 2.

Till now this copper removal has been performed by precipitation/filtration. However, the filtration of the precipitated $Cu(OH)_2$ sludge is rather troublesome. Moreover, cost comparisons we made for the treatment of 15 m^3/h demonstrate that:

- the investment costs of FBE are about $ 200,000 lower than in the case of precipitation, while
- the operational costs of FBE are $ 200,000 per year lower.

An FBE-unit has also been tested in a brine stream of the mercury cell chlor-alkali electrolysis plant at our Hengelo (Netherlands) site. This unit (figure 8) has already been in operation for almost two years and up to now we did not meet any major problem. The FBE cell, removing mercury from this process stream, contains 1 diaphragm and the height of the fluidized bed is 1.2 m. The mercury content of the brine is reduced from 5 mg/l to about 0.05 mg/l (figure 9). Both the ionic and the metallic mercury species are deposited onto the copper particles, with which they amalgamate. Recovery of mercury is obtained by distillation of the amalgamated particles.

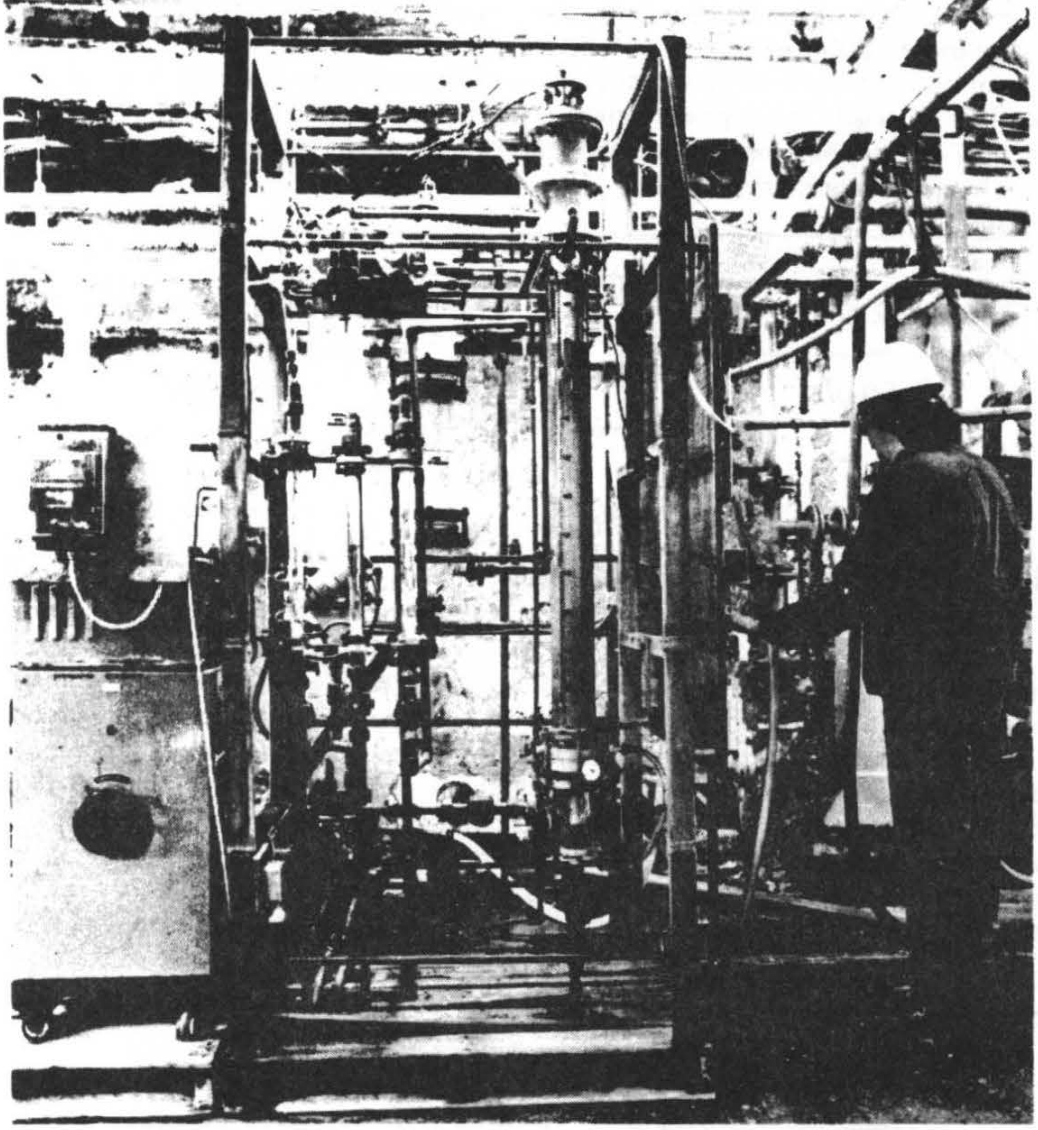

Figure 8. FBE-unit removing mercury from a brine stream

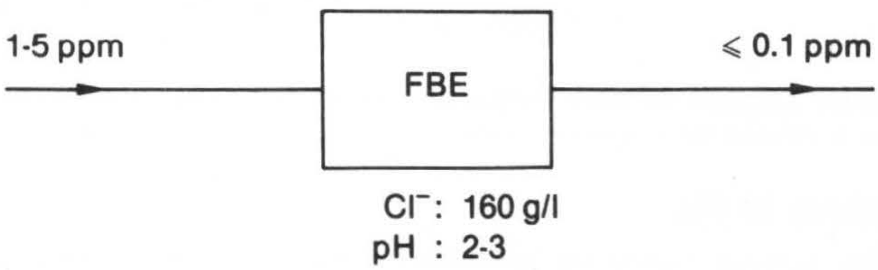

Figure 9. Mercury Removal from a Process Stream in a Mercury Cell Chlor-Alkali Electrolysis Plant

Another example of the technical possibilities of fluidized bed electrolysis is the separation of copper and nickel in a nickel electrolyte (figure 10). At a nickel concentration of some 50 g/l the copper concentration was lowered from 2 g/l to less than 0.1 mg/l. The copper content of the copper deposit was 99%. This example, just as the next one, proves that FBE can be an attractive technique to solve hydrometallurgical problems!

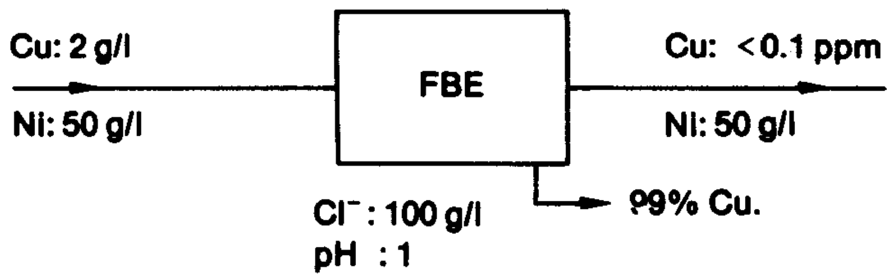

Figure 10. Copper-Nickel Separation

The presence of arsenic in copper electrolyte can be a great problem in copper hydrometallurgy because of arsenic hydride evolution during copper electrolysis of a tankhouse bleed. FBE, however, appeared to be capable of separating copper from arsenic without arsenic hydride evolution. In an electrolyte containing 5 g/l of both copper and arsenic FBE reduced the copper concentration to 10 mg/l (figure 11). Evolution of arsenic hydride did not occur until the copper concentration was further lowered to less than 0.1 mg/l. Up to copper concentrations of 10 mg/l the deposited copper appeared to be rather pure: the arsenic content was less than 0.3%

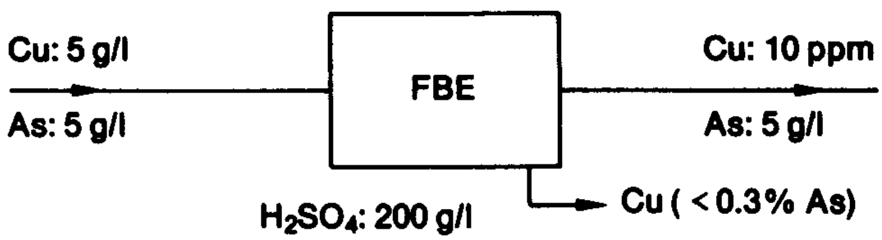

Figure11. Copper-Arsenic Separation without AsH_3 Evolution

Feasibility of FBE

Besides technical aspects the feasibility of a technique is also determined by economics. The potential attractiveness of FBE in waste water treatment will be demonstrated by a case of copper removal from a sulphuric acid solution. The feasibility of FBE in hydrometallurgical applications will be illustrated by the removal of copper and cadmium from a zinc electrolyte.

Two FBE cells, each containing 7 diaphragms, will be installed in a plant at the Wuppertal (West Germany) site of Enka Glanzstoff. Each unit will have to remove about 1 kg/h of copper from 3 m^3/h of a 100g/l sulphuric acid solution. By reducing the copper concentration from some 300 mg/l to less than 5 mg/l re-use of the sulphuric acid solution will be possible. Up to now this copper has been removed by ion exchange. However, ion exchange requires neutralisation of the solution, for instance by ammonia, and therefore re-use of the sulphuric acid is impossible. Due to a decrease in consumption of sulphuric acid and ammonia, replacement of ion exchange by FBE will result in annual savings in operational costs of some $ 200,000 per FBE unit. Investment costs of FBE and ion exchange are about the same.

The second example of the feasibility of FBE is the removal of copper and cadmium from a zinc electrolyte.
Previously cementation with zinc dust has been used to perform this removal (figure 12). The outlet of a copper-cadmium cementation in an electrolytic zinc plant contains 1 mg/l of copper and 10 mg/l of cadmium. The addition of 3 g/l zinc dust results in an increase of the zinc concentration with about 2 g/l leaving part of the zinc in the copper-cadmium cement. Treatment of this cement results in copper and cadmium products of low quality and therefore of low value. Higher proceeds can be obtained by further costly refining.

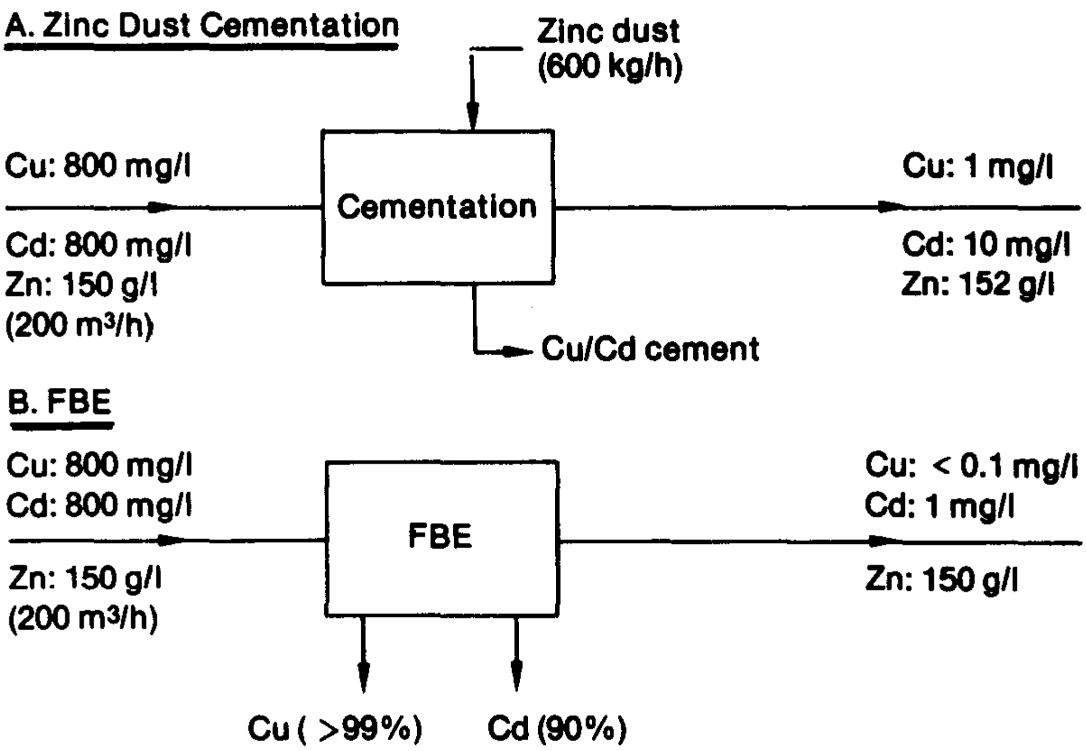

Figure 12. Copper-cadmium Removal from Zinc Electrolyte by Means of Zinc Dust Cementation (A) and Fluidized Bed Electrolysis (B)

Fluidized bed electrolysis results in lower copper and cadmium concentrations (figure 12), namely less than 0.1 mg/l of copper and 1 mg/l of cadmium. The copper deposit has a copper content of more than 99%, while the cadmium deposit contains some 90% of cadmium. Current efficiencies of copper and cadmium deposition are 70 and 40% respectively.

	Zinc Dust Cementation	FBE
Investment	— $8 million	— $6 million
Operational Costs (excluding Depreciation)	— $0.8 million/year	— $1.3 million/year
Increase in Zinc Output		+ $2 million/year
Increase in Copper and Cadmium Quality		+ $1.2 million/year

Figure 13. Cost Comparison between Zinc Dust Cementation and FBE for Copper-Cadmium Removal from Zinc Electrolyte in a Zinc Electro-Winning Factory of 150,000 MTPA of Zinc

From these technical results a cost comparison between FBE and zinc cementation has been made for a zinc electro-winning factory of 150,000 MTPA of zinc (figure 13). It appears that the estimated investment of FBE is substantially lower, whereas the operational costs of cementation are about $ 500,000 per year lower at an energy price of $ 0.02 per kWh. Besides the lower investment FBE offers some further advantages over the conventional zinc dust cementation.

Firstly, there is an increase in marketable zinc output, since FBE does not require zinc dust. In consequence the part of the zinc electrolysis, required for zinc dust production, can now also yield a salable product! At an addition of 3 g/l of zinc dust to an electrolyte flow of 200 m^3/h application of FBE results in an extra yield of 5000 MTPA compared to cementation. This extra zinc output requires only an equivalent amount of zinc concentrate and a part of the low variable costs. Therefore, the profit margin on these 5000 MTPA is about equal to the added value, which is estimated at some $ 400 per metric ton of zinc.

A second advantage of FBE over cementation is the better quality of the copper and cadmium products. It is estimated that the value of the 99% copper produced by FBE is about $ 400 per metric ton higher than the copper cake of the cementation. At a copper production of 1000 MTPA this results in extra proceeds of $ 400,000 per year. It is also estimated that refining of the 90% FBE cadmium will cost some $ 2000 per metric ton less than in the case of the cementation cadmium cake. At a cadmium output of some 400 MTPA the 90% FBE cadmium will result in profits $ 800,000 per year higher than the cementation cadmium cake.

Furthermore, the cadmium concentration in the FBE outlet is 9 mg/l lower than in the case of cementation. This means that FBE will give a 15 MTPA higher cadmium output and hence extra proceeds of about $ 90,000 per year at a cadmium price of $ 6000 per MT.

Cost comparison between FBE and zinc dust cementation for copper-cadmium removal in a zinc electro-winning factory results in the following conclusion: the investment of FBE is $ 2 million lower, while the net annual operating profits of FBE are some $ 2.8 million higher!

Conclusions

We have demonstrated that the FBE technique developed can be an attractive solution to many environmental and hydrometallurgical problems. Cost comparisons showed that for removal of metals from waste waters, in many cases FBE is cheaper than alternative processes such as precipitation or ion-exchange. The data presented on the copper-nickel separation and the copper-arsenic separation without arsenic hydride evolution, as well as the feasibility study of the copper-cadmium removal from zinc electrolyte illustrate that FBE can also be a very attractive process for separation and recovery of metals from hydrometallurgical process streams.