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Electrochemical ferrate generation for waste water treatment using cast irons with high silicon contents

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Abstract

This paper deals with the electrochemical preparation of ferrate in 15 M NaOH media, with a view to treatment of waste waters. Grey cast irons with high silicon contents were shown to allow current yields in the range 20–40% depending on the applied current density, up to 34 mA cm^{-2}. Ferrate solutions with contents up to 0.08 M could be produced in a divided cell of simple design, and provided with flat or packed-bed electrodes. Deactivation of the anode surface was shown to be of moderate significance for hour-long runs. The ferrate produced was tested for treatment of industrial liquid wastes: coagulation efficiency of the suspended matter was comparable with that of an electrocoagulation process with sacrificial Al anodes. The potential of waste water treatment by addition of ferrate is discussed.

1. Introduction

Numerous techniques can be used for treatment of waste waters. In particular, addition of suitable chemical agents allows treatment through various physicochemical processes (e.g., disinfection, oxidation of pollutants, or coagulation and flocculation of suspended particles). The agents to be added at low to moderate levels for this purpose, have to be harmless and to decompose to innocuous species. Ferrate species, Fe(VI), fulfils these requirements and possesses a high oxidation ability: this species has been shown to oxidize numerous organic compounds (e.g., alcohols [1], nitroanilic acid [2], cyanide [3]). In addition, ferric hydroxide, generated by ferrate decomposition, is an efficient flocculating agent at levels of the order of 10 ppm for various dilute wastes [4–6]. In most cases ferrate in the form of K_2FeO_4, was produced by chemical techniques, either by liquid phase oxidation of Fe(III) by chlorine or chlorinated agents, or high-temperature reaction with nitrate, oxides or hydroxides of alkali metals.

Reported first by Poggendorf in 1841, the synthesis of ferrate through electrodissolution of iron or iron alloys in concentrated alkaline media has been widely investigated [1, 7–15], and the best results have been obtained using 30–50 wt % NaOH electrolyte solutions. The yields reported vary over a broad range, depending on the reactor design and the operating conditions, namely the applied current density, the NaOH concentration and the temperature. Nevertheless reaction yields are known to be governed by the anode material. Comparison of various sources of data is often difficult because of the different materials used, and the presence of minor components may be missing. Surface deactivation by formation of an oxide layer was shown to be hindered by cathodic polarisation [11] or by using alternating current superimposed on direct current [14].

Compared with the various available processes for waste water treatment, the use of electrogenerated ferrate could be considered as competitive after improvement of current yields in long term operations. High production rates have to be obtained at the surface of low cost anodes for the production of concentrated ferrate solutions. In addition, the anode surface has to be stable enough to maintain high selectivity and to avoid passivation phenomena during continuous operation.

We suggest in this paper the use of grey cast irons with a high silicon content, which are currently produced at industrial scale. The presence of particular elements different from iron was shown to reduce the passivation of the anode [16], and it was hoped for the present investigation that silicon could have a similar role. Synthesis was conducted from NaOH solutions in a divided cell of a simple design, provided with flat or packed-bed anodes. Ferrate solutions with a concentration up to 10 g l^{-1} were produced without pretreatment of the electrode surface. The potential of electrogenerated ferrate, either in the form of the alkaline solution or as a potassium salt, for waste water treatment by coagulation, is then discussed.

2. Experimental section

2.1. *Chemicals*

Sodium and potassium hydroxide were of technical grade (Prolabo Normapur, Paris). Following most published works, NaOH concentration was fixed at 600 g l^{-1} i.e. 41.5 wt %. Concentration of ferrate was determined by the chromite method [17]: the reactants required for analysis, namely Cr(III) sulfate, iron(II)-ammonium sulfate, and ferroine were of analytical grade (Prolabo Rectapur). Fe(II) solution was regularly titrated using a calibrated Cr(VI) solution. Weighing the anode of the production cell before and after the electrochemical run yielded the amount of iron dissolved. Subtracting the amount of ferrate gave an indication of the amount of Fe(III) hydroxide.

2.2. *Anode materials*

Samples of grey cast iron were kindly provided by Pont-à-Mousson S.A. As shown in Table 1, the cast iron materials are produced either by moulding or by centrifugation. The Si content varied from 2 to 3%, whereas the carbon content was of the order of 3.5% (Table 1). Analysis of the samples revealed the presence of other elements (e.g., Mg or Mn), but at very low contents.

Table 1. Chemical composition of the alloys used

Cast iron	Production process	C/%	Si/%	Mg/%
1–1	Moulding	3.40	2.20	0.030
1–2		3.58	2.39	0.025
1–3		3.31	2.62	0.035
1–4		3.04	3.17	0.025
12–1	Centrifugation	3.60	2.07	0.015
2–2		3.60	2.30	0.021
2–3		3.56	2.53	0.026
2–4		3.85	2.60	0.032
2–5		3.65	2.80	0.022

Electrodes, either in the form of 5 mm thick slabs or as irregular metal chunks with dimension of about 15 mm, were prepared. The average area of a chunk was estimated at about 12 cm^2. The slabs were simply polished with coarse emery paper, whereas the chunks produced by sawing the alloy plates, were used without surface preparation.

2.3. *Electrochemical cells*

Preliminary tests were carried out with a laboratory U-cell, provided with a sintered glass separator. However, most runs were conducted using a Perspex cell consisting of two polymeric pieces which formed a rectangular pool 80 mm deep and (74 mm × 60 mm) in dimensions. A cationic membrane (Nafion® 450) was placed between the two cell parts. The temperature in the anodic compartment was continuously measured. An air stream was introduced through two small glass pipes for homogenisation of the anodic electrolyte solution.

A grid of Ti–Pt expanded metal being 70 mm × 80 mm acted as the cathode. Both flat electrodes and packed-bed anodes were used here. The area of one side of the flat anodes was varied from 15 to 56 cm^2 and the largest electrode being 70 mm × 80 mm was inserted tightly in the anodic compartment. The design of the packed-bed was derived from that of industrial electrolytic cells with sacrificial anodes, as used for the electrodeposition of metals (e.g., Zn), as follows. The packed-bed anode consisted of a basket prepared from a sheet of expanded Ti–Pt mesh, and alloy chunks (Figure 1). The basket sheet with an external area of 60 cm^2, acted as a current lead: a fraction of the applied current was consumed for oxygen evolution at the Ti–Pt grid, contributing to liquid circulation near the anode, in spite of the additional energy consumption. The area of the packed-bed structure could be varied from approx. 100 to 200 cm^2 by varying the number of alloy pieces. A polymeric mesh was inserted close to the membrane for mechanical protection from the anode chunks (Figure 1).

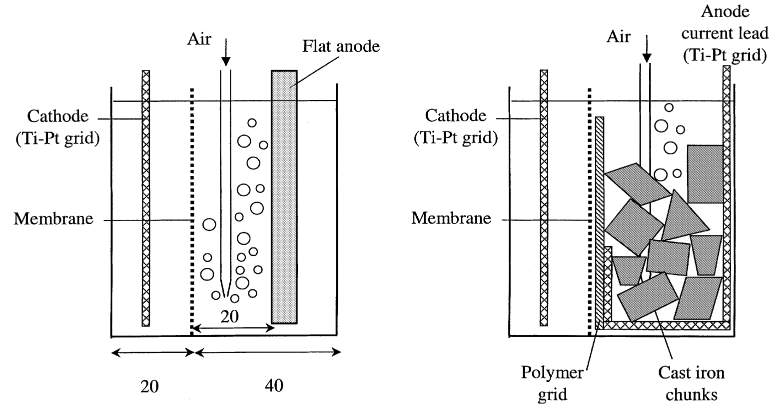

Fig. 1. Schematic view of the anode configuration in the Perspex cell for the electrochemical production of ferrate. Volume of the anode compartment: ~150 cm^3.

2.4. *Electrochemical run*

Most experiments were conducted batchwise. Fresh solution of sodium hydroxide was prepared before the run and allowed to cool. Traces of rust were removed from the cast iron pieces with a rotating steel brush. The electrodes were then installed in the cell. Flat anodes were located at 20 mm from the membrane, allowing a thermometer and the air injection pipes to be placed in the anode-to-membrane gap.

The volume of liquid in the anodic chamber of the Perspex cell varied from 120 to 150 cm^3, depending on the volume occupied by the electrode. The initial temperature of the solution had to be a compromised. The side formation of ferric hydroxide by iron dissolution was shown to be favoured over 60 °C; conversely an initial temperature at approx. 30 °C or less resulted in passivation of the electrodes, reducing their dissolution rates. The initial temperature of the alkaline solution was therefore around 45 °C. The solution temperature decreased regularly for the first hour before reaching a steady level which could vary from 27 °C at 0.8 A to 36 °C at 3 A, the higher current corresponding to the packed-bed anode.

The cell voltage in the Perspex cell was nearly constant for the batch run, in the range 2.5–3.6 V depending on the anode configuration and the current applied. Runs were carried out for 2 to 5 h, depending on the above conditions. As reported in previous papers (e.g., [10]), increasing reaction time over several hours did not result in higher ferrate concentrations: decomposition of the ferrate formed and partial inhibition of the electrode surface might explain the levelling-off of the ferrate amount in the anodic compartment. The viscosity of the solution was observed to increase, due to the presence of ferrate at concentrations up to 10 g per litre. This increase in viscosity might also be due to the side formation of poorly soluble Fe(III) hydroxo or oxo-compounds [18], or sodium carbonate formed by absorption of carbon dioxide from ambient air. Addition of sodium carbonate at 2 wt % had no effect on the yield, and the possible formation of this salt cannot be the cause of the low yields observed after a few hours.

The electrodes and the cell were thoroughly rinsed with deionised water after the run. Electrodes were wiped with paper cloth and the cell was rinsed with water, then filled with sulphuric acid at 3 wt % to remove traces of solid ferric species in the membrane, and to allow its hydration before the following run.

3. Electrochemical preparation of ferrate

3.1. *Effect of the electrode material*

Batch runs were carried out with the U-cell for two hours, with a flat anode 35 mm × 40 mm. The initial volume of the anode compartment was 50 cm^3. The current density calculated on the basis of the wetted area was fixed at 17 or 25 mA cm^{-2}. As shown in Figure 2, the silicon content, in the range investigated, appeared to be the key factor for ferrate production, regardless of the current density in the narrow range considered here. Additional runs carried on stainless steel or mild iron led to current yields below 4%. In addition, better results were obtained with alloys produced by centrifugation, and current yields up to 33% could be obtained with the 2.80% Si containing material. These yields are promising for ferrate generation in comparison with published results and taking into account the appreciable current densities.

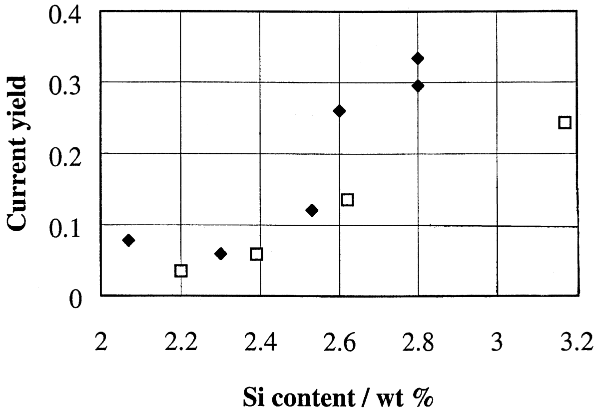

Fig. 2. Effect of the silicon content in the grey cast iron on the current yield for a two-hour run in the U-cell provided with a glass diaphragm. Volume of the anodic solution: 50 cm^3, electrode area: 30 cm^2; current density in the range 17–25 mA cm^{-2}. Key: (◆) centrifugation, (□) moulded.

SEM observations of material samples revealed the morphology of the alloy depending on its nature. Analysis of the surface by X-ray microprobe showed that the carbon was present in the material in the form of spheroidal graphite nodules, in agreement with [11]. The graphite nodules present in moulded cast irons are uniformly dispersed in the iron alloy, with a density of approx. 400 nodules per mm^2 and an average size around 25 μm (Figure 3(a)). The graphite particles in centrifugated alloys are quite smaller, with a surface density of approx. 1000 mm^{-2}. The nodules are of irregular shape in alloys with a moderate Si content (Figure 3(b)) and have a more circular aspect for the 2.80% Si material (Figure 3(c)). The higher yields observed with the centrifugated materials might be caused by the smaller size of the graphite inclusions, which are less accessible to ferrate species to decompose in ferric hydroxide, as suggested by Bouzek and Rousar [11].

The amount of Fe(III) produced over that of ferrate was in the range 0.20–0.50. The values for the molar ratio determined with a moderate accuracy, are of comparable order with published data. However, the values could not be correlated neither with the current density in the range considered, nor with the Si content, nor finally with the production process of the cast irons.

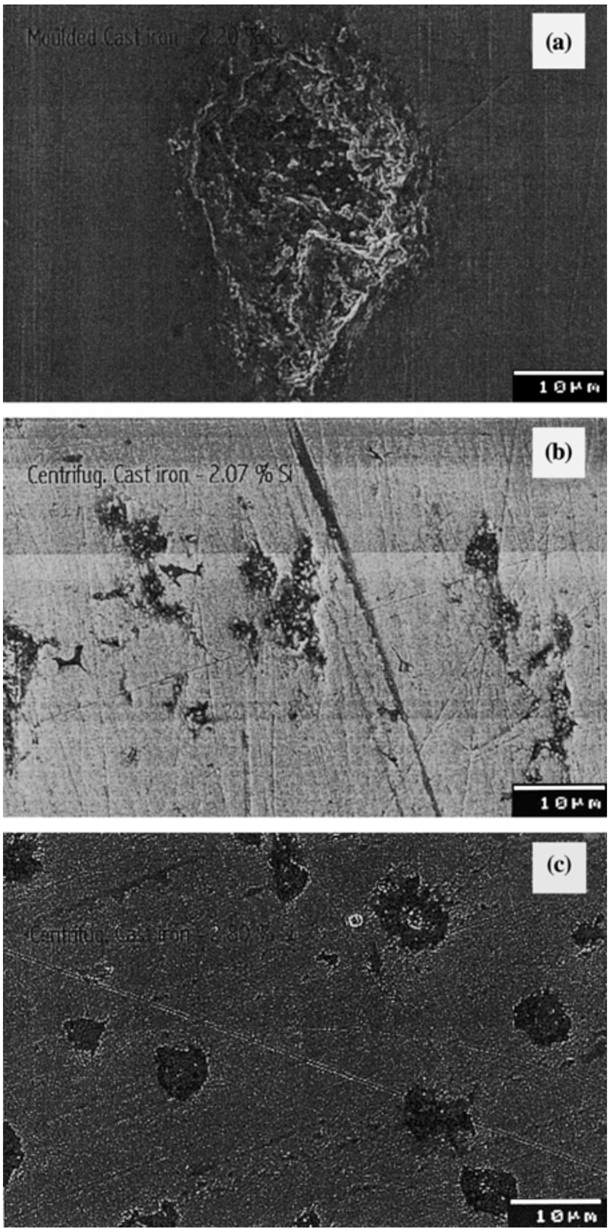

Fig. 3. SEM photographs of samples of grey cast iron. (a) Moulded cast iron with 2.20% Si, (b) centrifugated cast iron with 2.07% Si, (c) centrifugated cast iron with 2.80% Si.

3.2. *Effect of the current density*

Because of the design of the Perspex cell, with its narrow anodic compartment and the width of the electrode in comparison to that of the cell, the rear side of the anode was considered inactive for the estimation of the current density.

Two examples of data are given in Figures 4 and 5 with different cell configurations and electrode materials. Increasing the current applied to the anode led to higher production rates, corresponding to faster increase in the ferrate amount in the anodic compartment. Current yields calculated from the beginning of the batch run, exhibit slightly decreasing variations with time. The dependence on the applied current density was of moderate significance for the two examples considered, in particular above 15 mA cm^{-2}. Ferrate solutions at 0.04 M were produced in the glass U-cell with overall current yields varying from 25 to 20.5% whereas the cd was increased from 17 to 34 mA cm^{-2} (Figure 4). Synthesis in the Perspex cell with the largest flat electrode (wetted area at 49 cm^2) was conducted with current yields of 18.5% within 1% for current densities at 16, 20 and 30 mA cm^{-2} (Figure 5).

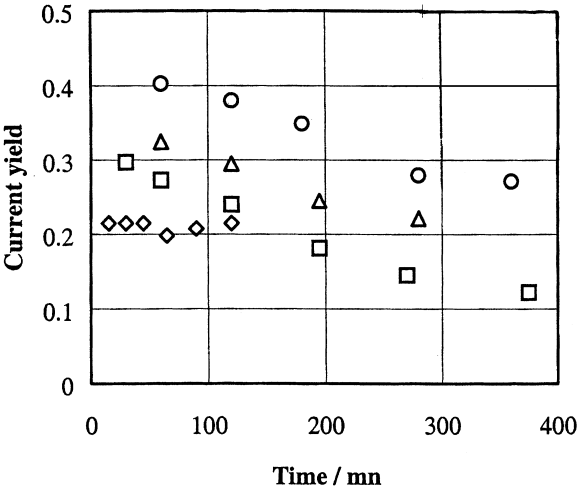

Fig. 4. Overall current yield against time, for batch synthesis of ferrate at fixed current density in the U-cell. Anode: centrifugated alloy with 2.80% Si. Volume of the anodic solution: 50 cm^3, electrode area: 30 cm^2. C.d.: (◇) 34, (□) 24, (△) 17 and (○) 10 mA cm^{-2}.

The differential yield of ferrate production was observed to remain roughly constant for ferrate concentrations below 0.05 M, before decreasing slightly over this concentration value. However, runs conducted at high current density allowed concentrated ferrate solutions to be produced with current yields as high as 15% at the end of the run. Examination of the experimental results showed that the decrease in pro-

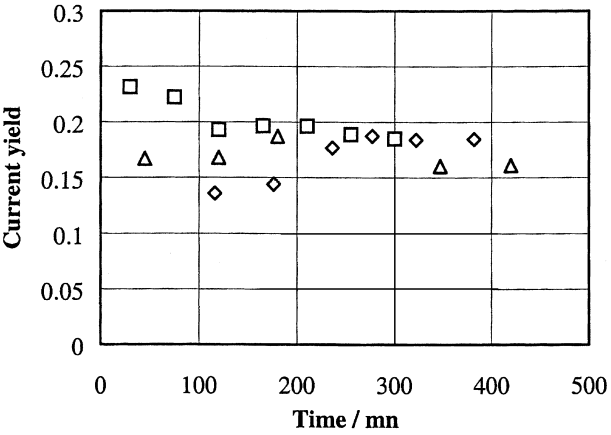

Fig. 5. Overall current yield against time, for batch synthesis of ferrate at fixed current density in the Perspex cell. Anode: centrifugated alloy with 2.60% Si. Volume of the anodic solution: 150 cm^3, electrode area: 45 cm^2. C.d.: (◇) 16, (□) 20 and (△) 30 mA cm^{-2}.

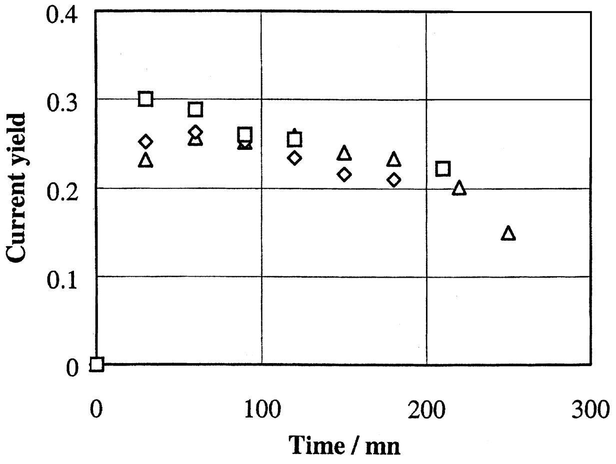

Fig. 6. Overall current yield against time, for batch synthesis of ferrate at fixed current density in the Perspex cell. Anode: packed bed of alloy chunks with a Si content at 2.60%. Volume of the anodic solution: 120–140 cm^3; applied current density around 13 mA cm^{-2}. Specific area: (△) 160, (◇) 103 and (□) 69 m^{-1}.

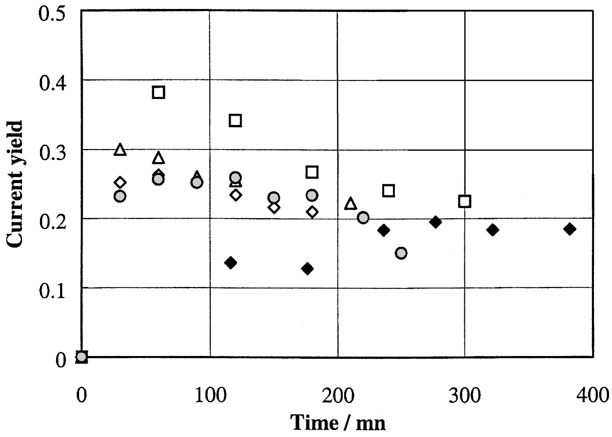

Fig. 7. Effect of the specific electrode area and the electrode configuration, on the current yield. Anode: centrifugated alloy with a Si content at 2.60%. The current density was in the range 12.5–15 mA cm^{-2}. Key: (◆) 33 m^{-1}, (□) 60 m^{-1}, (△) packed bed 69 m^{-1}, (◇) bed 103 m^{-1}, and (○) packed bed 160 m^{-1}.

duction rate observed in the batch runs was mainly caused by inhibition of the electrode surface after a long period, and also by the presence of ferrate at high concentration.

3.3. *Synthesis with packed-bed anodes*

The current density was calculated taking into account the area of the alloy chunks, and regardless of the Ti–Pt grid. Although an appreciable fraction of the current passed is consumed in oxygen evolution at the platinized grid, the yields obtained with the packed-bed structure were quite promising. Production rate was enhanced by enlarging the anode area from 96 to 192 cm^2, and a ferrate solution at 0.08 M (i.e., ~10 g l^{-1}), could be produced using the highest electrode area. The time variations of the current yield were not affected by the area, as shown in Figure 6. The performance of high area of the packed bed can be explained as follows: (i) ferrate production might be favoured by increasing the specific electrode area, as suggested by Gruber and Gmelin [8]; and (ii) the relative importance of the current lead (and of the side oxygen evolution on this surface) is reduced with a larger stack of alloy chunks.

Comparison of Figures 5 and 6 for current densities of the same order of magnitude (16 and 13 mA cm^{-2}, respectively) showed that the production rates offered by the packed-bed configuration are higher than those with flat anodes. The current yield for the production of 0.04 M ferrate solution was enhanced from 18% with the 49 cm^2 flat electrode, to 24% with the largest packed bed. The improved performance may be the fact of side oxygen evolution at the Ti–Pt grid which enhances mass transfer phenomena near the electrode, in contrast to the other configuration for which the sluggish circulation of the liquid prevails in the narrow anode-to-membrane gap.

3.4. *Effect of the specific area*

Although slow at moderate temperature, the chemical decomposition of ferrate is strongly accelerated by increasing temperature [1]. Because of the occurrence of this decomposition, anodes with a high specific area may be preferred for ferrate production. The results of various batch experiments carried out with a current density lying in the narrow range 13–16 mA cm^{-2}, and with a specific area varying from 33 to 160 m^{-1}, are given in Figure 7. Use of the 49 cm^2 anode, corresponding to a specific area of 33 m^{-1}, led to the lowest current yields. The other configurations with higher specific areas offered current yields of comparable order of magnitude. The weak effect of the specific area suggests that the performance is little hindered by the chemical decomposition of ferrate. The occurrence the ferrate reduction at the graphite nodules or the loss of activity of the electrode surface after a few hours may have a more significant influence on the ferrate yields.

3.5. *Continuous synthesis of ferrate production*

A continuous process for ferrate production was approached by drawing off a given volume of solution from the cell and introducing the same volume of fresh solution, at regular intervals. The experiment was conducted with a 192 cm^2 packed-bed electrode, with a total volume of solution of 120 cm^3 and the current was fixed at 2.5 A. First replacement of solution was carried out after three hours to allow high ferrate concentration in the anodic compartment. The volume of solution to be replaced every hour was fixed at 36 cm^3: this volume was estimated from the production rate observed previously for these operating conditions. The equivalent average residence time of the solution was of 200 min. The current yield of the process at time t

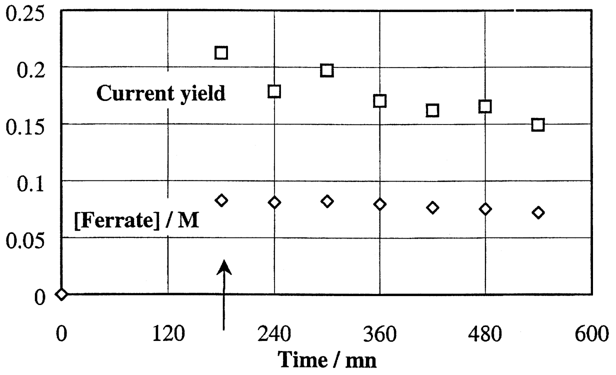

Fig. 8. Simulation of continuous synthesis with a packed-bed anode. Anode: centrifugated alloy with a Si content at 2.60%. Arrow corresponds to the first replacement of solution, with fresh NaOH solution (36 cm^3): the procedure was then repeated every 60 min. Parameters: (residence time) 200 min. (c.d.) 13 mA cm^{-2} and (S/V) 160 m^{-1}.

was calculated from the ferrate concentrations at times t and $t-\Delta t$, if Δt denotes the sampling interval, at one hour in the present case, and taking into account the volume of fresh solution introduced. The cell voltage was constant at 3.6 V within 0.1 V throughout the run.

The results of the nine hour-long experiment are given in Figure 8. The ferrate concentration slowly decayed from 0.082 to 0.072 M within six hours, but the current yield was observed to decrease more noticeably, from 21% at the first solution renewal, to 15% six hours later. This encouraging test shows that the continuous production of ferrate may be envisaged in spite of the likely inhibition of the cast iron surface. Considering an outlet concentration of ferrate at 10 g l^{-1} and taking into account the flow rate of electrolyte solution, allowed the electrical charge and the energy consumption to be estimated at 250 kA s and 25 kW h per kg ferrate, respectively.

4. Application of electrogenerated ferrate to waste water treatment

Preliminary tests of water treatment using electrochemical ferrate were carried out on industrial liquid wastes: these liquids were formerly investigated for the development of an electrocoagulation process with sacrificial aluminium anodes [19]. The effluents with respective COD at 6.7 and 22 g l^{-1} consisted mainly of soluble oils with a low content of suspended matter and a clear aspect.

Ferrate was first used in the form of the solution produced in the cell, with a content at 0.08 M. An alternative solution was offered by crystallization of ferrate through replacement by potassium as follows: 100 ml of the above solution was mixed to the same volume of saturated potassium hydroxide at 0 °C. Storage at this temperature for two days allowed formation of dark, small crystals which could be recovered by bench scale filtration in the form of a paste with an appreciable water content. Analysis of the paste by atomic absorption using a plasma torch, showed the presence of iron (7%), potassium (12%) and sodium (12%). Mossbauer spectroscopy revealed that 73% of the iron present in the solid was in the form of ferrate species.

The two liquid wastes were treated by addition of ferrate in one of the two forms at 10 and 40 ppm FeO_4^{2-} species in a jar test reactor, for coagulation and settling of the solid precipitates. The efficiency of the technique was compared with that offered by the electrocoagulation cell with dissolved aluminium. The efficiency of the various treatments was moderate only because of the nature of the wastes, in particular for liquid no. 1. Higher amounts of ferrate or dissolved aluminium did not result in higher abatement of the organic matter. Besides, addition of Fe(III) sulfate at 10 ppm Fe did not allow visible reduction in COD, which shows that the efficiency of the above tests was mainly due to the presence of ferrate.

The charge values given in Table 2 are only indicative since only a few tests were carried out. In spite of very different energy and charge consumptions, the two types of treatment allow comparable COD abatement. In addition, dissolution of Al at 1000 As l^{-1} did not result in significant treatment of the test liquids, contrary to the addition of ferrate (Table 2). However, the direct use of ferrate solution results in strong alkalination of the liquid waste, with a final pH at 12. Use of solid paste

Table 2. Treatment of two liquid wastes by electrocoagulation with dissolved aluminium [19] or by addition of electrogenerated ferrate, in the form of the solution recovered from the cell, or a solid paste produced by crystallization with potassium hydroxide. Initial COD at 22 g l^{-1} and 6.7 g l^{-1} for liquids 1 and 2, respectively. Initial pH 6.0

Properties of the treated wastes and charge consumed	Ferrate solution (10 ppm)	Solid paste (10 ppm)	Solid paste (40 ppm)	Electrocoagulation (92 ppm Al)	Electrocoagulation (500 ppm Al)
$[Na^+]$/ppm	290	8	32	–	–
$[K^+]$/ppm	–	8	32	–	–
pH	12	10.3	10.4	7.8	7.8
Charge consumed/As l^{-1}	250	250	1000	1000	5400
COD/g l^{-1}					
liquid 1	18.9	19.4	19.1	22.0	19.0
liquid 2	–	5.6	2.9	6.5	2.1

could be preferred over addition of ferrate solution, because of the more acceptable pH of the treated liquid (Table 2). Nevertheless, the precipitation of ferrate in the form of its potassium salt produces large volumes of concentrated mixed NaOH–KOH solutions.

5. Conclusion

Ferrate electrochemical synthesis was investigated for production purpose using grey cast iron with a high silicon content. The anode consisting of a packed bed of alloy chunks placed in a conducting basket, was shown to allow high production rates: the simple configuration of the anode was shown to be effective, and the side evolution of oxygen allowed efficient local stirring of the electrolyte solution. In spite of non-negligible deactivation of the anode, ferrate production can be carried out in a continuous reactor at appreciable current densities for several hours, with current yields over 15%.

The high coagulating properties of ferrate species allowed good COD abatement in waste liquid with low amounts of ferrate, corresponding to moderate energy consumption in the overall process. However, the two techniques relying upon addition of electrogenerated ferrate, were shown to be the source of further environmental issues. Conditions of the electrosynthesis have therefore to be improved for the production of more concentrated ferrate solutions and/or for its easy separation from the electrolytic phase, which could be recycled for further anodic dissolution of grey cast iron with high silicon contents.

Acknowledgements

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