

Electrolytic recovery of iron from pickling solutions by tungsten carbide gas-diffusion anodes

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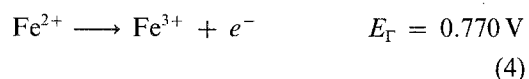
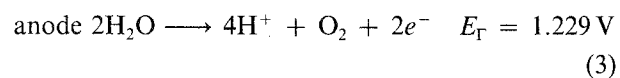
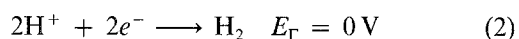
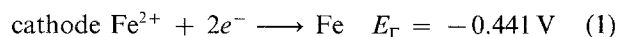
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The performance of gas-diffusion electrodes catalysed with tungsten carbide as anodes for the electrolytic recovery of iron from pickling solutions was investigated. The conditions under which the cathodic current efficiency of electrolytic cells utilizing such anodes increases significantly were determined. It was found that the energy consumption is two times lower than for a conventional electrolysis using lead anodes.

1. Introduction

The pickling of rolled steel sheet at metallurgical plants yields large amounts of ferric sulphate solution as a by-product. It can be separated as ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) upon cooling or by subjecting the waste liquor to vacuum treatment. Because the demand for ferrous sulphate heptahydrate is rather limited, the major part of the solid obtained is discarded, so that the problems of environmental pollution cannot be overcome by this method. Therefore its large-scale use is very much restricted. To utilize the waste ferric sulphate solutions, a method of electrolytic recovery of iron was developed, whereby the pickling acid is returned to the production cycle [1, 2]. The electrolysis is performed with steel sheet cathodes and rolled lead sheet anodes containing 1% Ag (Tainton anodes), separated by a diaphragm. Figure 1 presents a flow chart of the process and a plot of the concentration distribution of the electrolyte components at various sections of the chart [1, 2].

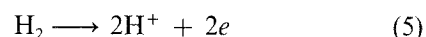
The following processes occur simultaneously



resulting in the establishment of mixed potentials at both electrodes.

The electrical energy consumption for Reactions 2 and 4 leads to a remarkable decrease of the overall process efficiency. For this reason a number of precautions were taken to suppress the hydrogen evolution rate at the cathode, such as the addition of $(\text{NH}_4)_2\text{SO}_4$ to the electrolyte, selection of a suitable

H_2SO_4 concentration, and close control of the flow rate from the cathodic to the anodic region [2]. As a result, the current efficiency is about 40%, the basic part of the energy losses being due to Reaction 4. Taking this into account, it can be assumed that the replacement of the lead anodes with electrodes upon which the anodic reactions occur at potentials substantially more negative than the thermodynamic potential of Reaction 4 may increase the process efficiency significantly. Hydrogen gas-diffusion electrodes may be considered a suitable replacement, since in this case instead of Reaction 3 the following reaction takes place:



with an equilibrium potential $E = 0 \text{ V}$.

The aim of the present investigation is to establish the feasibility of hydrogen gas-diffusion electrodes catalysed with tungsten carbide, proposed earlier as anodes for zinc electrowinning [3, 4], for the electrolytic recovery of iron from pickling solution.

2. Experimental details

The performances of two types of tungsten carbide gas-diffusion electrodes (GDE) have been investigated with single-layered electrodes developed at the Technical University (TU), Dresden, DDR, containing $800 \text{ mg WC cm}^{-2}$ [5] and double-layered electrodes developed at the Central Laboratory of Electrochemical Power Sources (CLEPS), Sofia, Bulgaria, containing $200 \text{ mg WC cm}^{-2}$ [6]. The carbides used as catalysts in the electrodes were synthesized from H_2WO_4 with the following surface areas: WC I ($S = 8 \text{ m}^2 \text{ g}^{-1}$) and WC II ($S = 4 \text{ m}^2 \text{ g}^{-1}$) (CLEPS, Bulgaria), and WC 164 ($S = 18.5 \text{ m}^2 \text{ g}^{-1}$) (TU, Dresden). The current-voltage characteristics of single-layered electrodes were obtained by using a plastic holder and a platinum contact ring. The electrodes

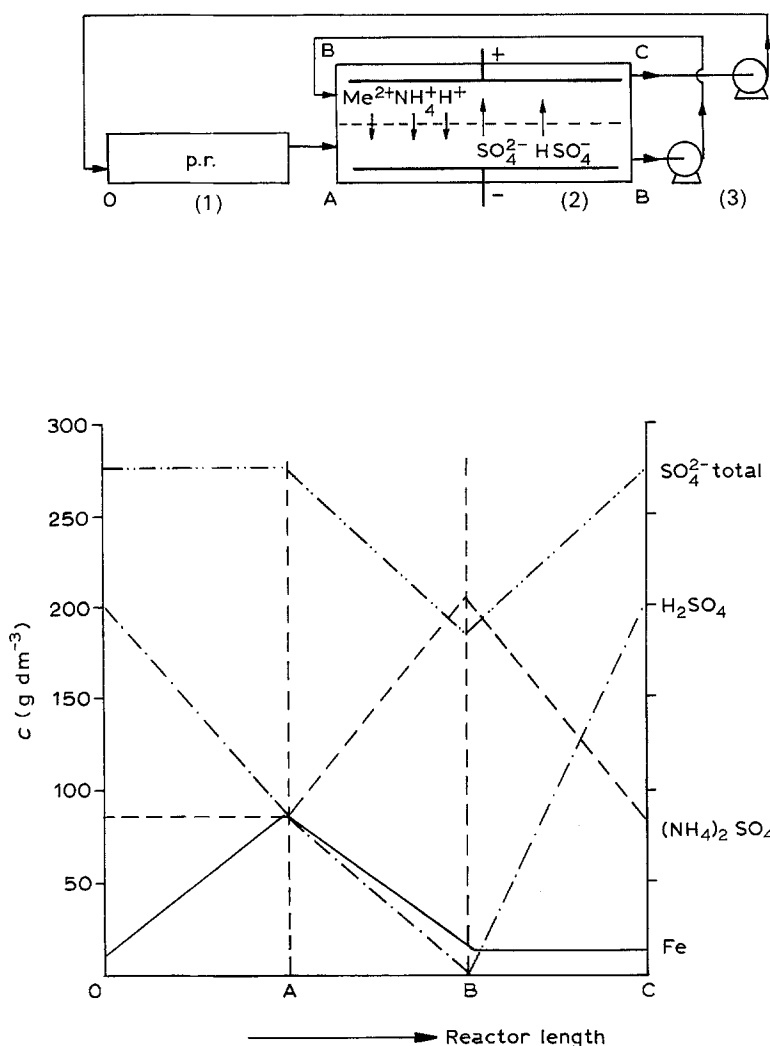


Fig. 1. Flow chart of the process and plot of the concentration distribution of the electrolyte components during electrolytic recovery of iron from pickling solutions. (1) pickling reactor; (2) electrolytic bath; (3) pumps.

operated at a hydrogen overpressure of 50–60 mm mercury. The double-layered electrodes were tested in half-cells with lead counter electrodes without applying hydrogen overpressure. The potential was measured against a $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode. All potentials were evaluated against the potential of a reversible hydrogen electrode (RHE). The long term tests were performed in cells with platinum cathodes.

The electrolytes used contained FeSO_4 (25–225 g dm^{-3}), $(\text{NH}_4)_2\text{SO}_4$ (80–230 g dm^{-3}) and H_2SO_4 (3–230 g dm^{-3}). These concentrations are similar to those of the catholyte and anolyte of the conventional electrolytic process.

The cathodic current efficiency was determined by weight gain of the deposited iron. The part of the anodic current utilized for the secondary Reaction 4 was estimated by the difference between the anolyte acidity during the electrolysis with tungsten carbide GDEs whereon Reaction 4 cannot occur, and that with Tainton anodes.

During the measurements of the cathodic current efficiency the gas-diffusion anodes (GDA) were wrapped in separators made of textile material commonly used in the electrolysis of pickling solutions [2]. This prevents the particles of the GDA from reaching the cathode, which would cause a large increase of the hydrogen evolution rate.

3. Results

Figure 2 presents the current-voltage curves of a single-layered tungsten carbide GDE and a Tainton anode, in electrolytes with compositions identical to those indicated in sections A, B and C of the plot shown in Fig. 1. Data for an electrolyte containing only sulphuric acid are given for comparison. The shape of the current-voltage curves obtained for the Tainton anode may be discussed in terms of a mixed potential as a result of Reactions 3 and 4. In the absence of Fe, Reaction 3 only occurs and the potentials are considerably more anodic. At high Fe concentrations, another extreme case can be observed — Reaction 4 dominates. In the other two cases, where the concentrations of the electrolyte components are similar to those at the inlet and outlet of the anodic chamber, both Reactions 3 and 4 take place. As can be seen from Fig. 2, the replacement of the Tainton anodes with hydrogen tungsten carbide GDAs leads to a decrease of the cell voltage by 1.5–1.7 V. Moreover, Reaction 4 cannot occur at the potentials at which the GDAs normally operate, while on the Tainton anodes together with Reaction 3 the oxidation of Fe^{2+} to Fe^{3+} (Reaction 4) may also occur. This is also confirmed by the data shown in Table 1. It can be seen that in the conventional process the

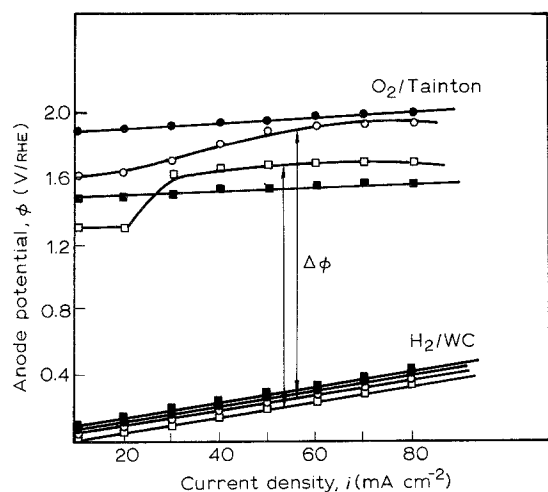


Fig. 2. Current-voltage curves of a single-layered tungsten carbide GDA and a Tainton anode in different electrolytes at $t = 70^\circ\text{C}$. Electrolyte compositions: (■) 82 g Fe + 80 g H_2SO_4 + 80 g $(\text{NH}_4)_2\text{SO}_4 \text{ dm}^{-3}$; (□) 9 g Fe + 5 g H_2SO_4 + 230 g $(\text{NH}_4)_2\text{SO}_4 \text{ dm}^{-3}$; (○) 10 g Fe + 230 g H_2SO_4 + 80 g $(\text{NH}_4)_2\text{SO}_4 \text{ dm}^{-3}$; (●) 80 g $\text{H}_2\text{SO}_4 \text{ dm}^{-3}$.

anodic current efficiency for Reaction 3 is lower. The result suggests that part of the current was utilized for Reaction 4, which is proved qualitatively by the $\text{Fe}_2(\text{SO}_4)_3$ precipitation. Figure 3 indicates the effect on the cathodic current efficiency. The latter parameter is presented as a function of the sulphuric acid concentrations used for both types of anodes. As can be seen, at sulphuric acid concentrations lower than 6 g dm^{-3} the cathodic current efficiency rises to 70% for the electrolysis carried out with a hydrogen GDA. At sulphuric acid concentrations below 6 g dm^{-3} the cathodic current efficiency declines remarkably, independently of the anode type. This can be attributed to the considerable increase of the hydrogen evolution rate at the cathode (Reaction 2).

It can be concluded that the replacement of Tainton anodes with hydrogen tungsten carbide GDAs will cause a significant decrease of the cell voltage and presumably an increase of the cathodic current efficiency at sulphuric acid concentrations lower than 6 g dm^{-3} .

Table 1. Influence of the acid concentration and type of anode on the anodic current efficiency at $t = 80^\circ\text{C}$, $i = 60 \text{ mA cm}^{-2}$. Electrolyte compositions: 14–16 g Fe dm^{-3} ; 160–200 g $(\text{NH}_4)_2\text{SO}_4 \text{ dm}^{-3}$; 3.3–10 g $\text{H}_2\text{SO}_4 \text{ dm}^{-2}$

C H_2SO_4 (g dm^{-3})	Anodic current efficiency (%)	
	WC	Tainton
3.30	100	55
4.73	100	70
6.01	100	70
9.90	100	70

Notes Solution remains clear green Solution becomes turbid up to 9.9 g $\text{H}_2\text{SO}_4 \text{ dm}^{-3}$. In all cases, the colour changes from green to brown very quickly.

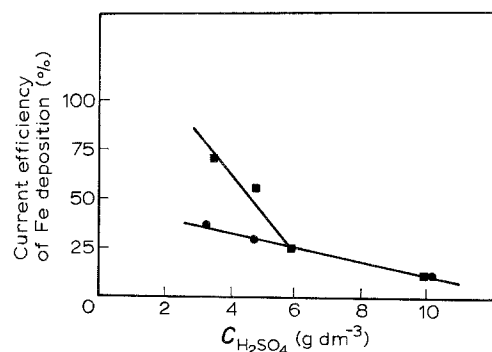


Fig. 3. Dependence of the cathodic current efficiency on the acid concentration at $t = 80^\circ\text{C}$, $i = 60 \text{ mA cm}^{-2}$, time of electrolysis 4–5 h. Electrolyte composition: 14–16 g Fe + 170–200 g $(\text{NH}_4)_2\text{SO}_4$ + 3–10 g $\text{H}_2\text{SO}_4 \text{ dm}^{-3}$. (■) tungsten carbide GDA; (●) Tainton anode.

An important point to be discussed further is the service life of the hydrogen tungsten carbide GDAs, which is dependent on two main factors: the structure of the electrode and the type of carbide used, the latter determining its corrosion resistance. Therefore investigations on electrodes with two different structures were carried out. The carbides used as catalysts were produced from the same raw material (H_2WO_4 – yellow modification), thus ensuring that their activity and corrosion resistance would be determined only by their specific surface area [7]. According to the results cited in [7] the carbide with the smallest surface area exhibits the lowest activity and the highest corrosion resistance.

Figure 4 shows the current-voltage curves of these electrodes in electrolyte with a composition identical to that of the anolyte at the inlet of the anode chamber in the Kerti process [1]. The electrolyte pH is approximately 2, which affects the GDE characteristics much more unfavourably than the pH values of 0–1. The single-layered electrodes catalysed with tungsten carbide with a surface area of $18.5 \text{ m}^2 \text{ g}^{-1}$ display almost the same activity as the double-layered ones with a surface area of $8 \text{ m}^2 \text{ g}^{-1}$. This may be attributed to the better gas supply provided by the double-layered electrodes. Moreover, the results given in Fig. 4 indicate

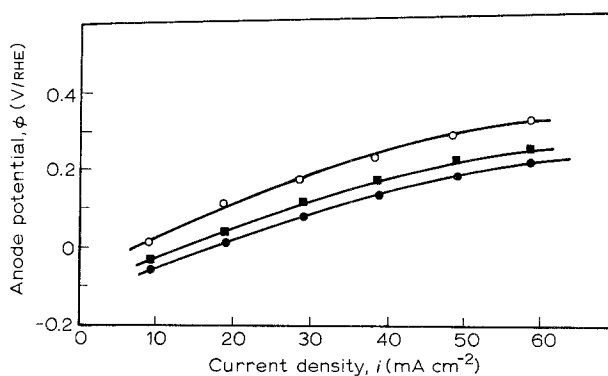


Fig. 4. Current-voltage curves of different types of tungsten carbide GDAs at $t = 60^\circ\text{C}$, $i = 60 \text{ mA cm}^{-2}$. Electrolyte composition: 15 g Fe + 6 g H_2SO_4 + 160–200 g $(\text{NH}_4)_2\text{SO}_4 \text{ dm}^{-3}$; pH = 2. (■) single-layered tungsten carbide GDA (WC 164); (●) double-layered tungsten carbide GDA (WC I); (○) double-layered tungsten carbide GDA (WC II).

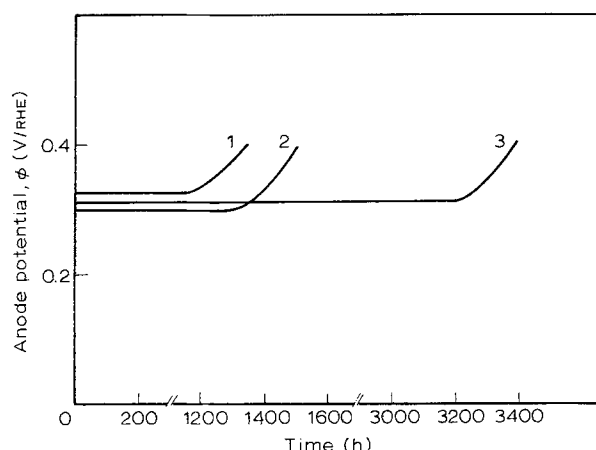


Fig. 5. Long term tests of different types of tungsten carbide GDAs at $t = 70^{\circ}\text{C}$. Electrolyte composition: 9–15 g Fe + 100–160 g $(\text{NH}_4)_2\text{SO}_4$ + 60–100 g H_2SO_4 dm^{-3} . (1) single-layered tungsten carbide GDA (WC 164), $i = 55 \text{ mA cm}^{-2}$; (2) double-layered tungsten carbide GDA (WC I), $i = 55 \text{ mA cm}^{-2}$; (3) double-layered tungsten carbide GDA (WC II), $i = 40 \text{ mA cm}^{-2}$.

that the electrode catalysed with the carbide with the smallest surface area, expected to have the longest service life, displays some 100 mV higher polarization at current densities of 40–60 mA cm^{-2} , which will not significantly affect the cell voltage.

Figure 5 presents the data obtained from the long term tests of the electrodes described. These were carried out in an electrolyte with a composition identical to that of the anolyte used for the electrolysis of pickling solutions. Because of the different activity of the three samples of tungsten carbide, the current density of the respective electrodes was selected within

the admissible limits, so that they would operate at close anodic potentials. This eliminated the influence of the potential on the corrosion resistance of the electrodes.

It can be seen from the figure that the single-layered electrode catalysed with WC 164 operated for over 1000 h without any deterioration in performance. The double-layered electrode catalysed with WC I operated for a slightly longer period. The service life of the third electrode catalysed with the carbide with the smallest surface area is three times longer. The X-ray diffractograms of the electrodes catalysed with WC I and WC II show that the deterioration of their characteristics after 1400 and 3200 h, respectively, is due to the deposition of tungsten oxides.

It can be concluded that the use of double-layered hydrogen gas-diffusion electrodes catalysed with tungsten carbide will ensure some 3000 h operation of the electrolytic cell at about 50% lower energy consumption.

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