



COMPARISON OF GOLD AND PLATINUM ELECTRODE RESPONSES IN ACTIVATED SLUDGE

A. Heduit*, B. Martin*, I. Duchamp* and
D. R. Thevenot**

* *Centre National du Machinisme Agricole, du Génie Rural, des Eaux et des Forêts (CEMAGREF), Division Qualité des Eaux, 14 avenue de Saint-Mandé, 75012 PARIS, France*

** *Université Paris XII, Val de Marne (U.P.V.M.), U.F.R. de Sciences et de Technologie, Laboratoire de Bioélectrochimie et Analyse du Milieu (LABAM), Avenue du Général de Gaulle, 94010 Créteil Cedex, France*

ABSTRACT

Gold and platinum were compared to ascertain how they expressed a stabilized potential in activated sludge. The comparison was based on electrochemical determination of the electron transfer rate (i.e. equilibrium exchange current density) and recording of potentials against time.

When both metals are treated in the same way, platinum gives equilibrium exchange current densities approx. 10 times higher than gold, both in aerated activated sludge and in treated water. For platinum, the equilibrium exchange current densities range from 0.1 to 0.25 $\mu\text{A}/\text{cm}^2$ immediately after polishing and decrease during prolonged contact with activated sludge subjected to alternating aeration/anoxia sequences.

The lower kinetics of electron transfer on gold go together with significant differences in response :

- In an aerobic medium a gold electrode potential is lower than that of a platinum electrode. In a strongly anaerobic medium, the reverse is true. Consequently, the amplitude of the potential variation between aerobic and anaerobic media is smaller for gold than for platinum. Under our experimental conditions this amplitude was approx 350 mV for gold and 850 mV for platinum.

- The slopes of the linear relationships between potential and pH or potential and the logarithm of the dissolved oxygen concentration are two or three times greater for platinum than for gold.

Although the values obtained with platinum electrodes cannot represent a veritable equilibrium state, the platinum electrode zero-current potential would seem to be far more sensitive to variations in the medium than that of the gold electrode; it is, therefore, more suitable for use in activated sludge.

KEYWORDS

Redox potential; platinum electrode; gold electrode; activated sludge; equilibrium exchange current density; zero-current potential.

INTRODUCTION

The zero-current platinum electrode potential is an attractive parameter for controlling the nitrification and denitrification processes in activated sludge (Charpentier *et al.*, 1989; Audic, 1992; Deguin, 1992).

Thermodynamically, gold is "nobler" than platinum. Nonetheless, bibliographic studies show that platinum is almost always used to measure potential in both water and activated sludge (Heduit, 1989). Authors rarely explain this choice.

Whitfield (1972) obtained estimations of the equilibrium exchange current densities on platinum (0.02 to 0.38 $\mu\text{A}/\text{cm}^2$) and on gold (0.003 to 0.008 $\mu\text{A}/\text{cm}^2$) by discharging natural redox cells through an external resistance. Buhler and Galster (1980) confirmed that platinum gave considerably higher equilibrium exchange current densities than gold in water. Coquery (1986) stopped using gold electrodes in activated sludge due to "their poor sensitivity to variations in the medium".

The aim of this project was to compare gold and platinum to ascertain how they expressed a stabilized potential in activated sludge: the comparison was based on electrochemical determination of the electron transfer rate (i.e. equilibrium exchange current density) and recording of potentials against time.

We therefore performed measurements of:

equilibrium exchange current densities (after polishing and after one week immersion in activated sludge)

zero current potentials in aerobic media (change after polishing, relationships potential vs pH and potential vs $\log [\text{O}_2]$)

zero current potentials in an anaerobic medium (change after polishing).

MATERIAL AND METHODS

Determinations of the Equilibrium Exchange Current Densities

Procedure. The equilibrium exchange current densities (J_0) were determined by recording low speed current potential curves (anode and cathode scans on either side of the equilibrium potential). The logarithm of the current densities was then plotted against the corresponding overpotential. The equilibrium exchange current densities were then determined by extrapolating these curves to zero overpotential. This technique has already been described in a previous paper (Heduit and Thevenot, 1989).

Electrochemical curve plotting equipment. The current-potential curves were plotted at low speed (1.25 mV/s) on a Tacussel PRG3 assembly comprising:

- a potential control unit (PRT 20-2X)
- an adaptor unit
- a voltage recorder (EPL 2) connected to the potential control unit.

Electrodes. The characteristics of the metal electrodes used are presented in Table 1.

TABLE 1 Metal Electrode Characteristics

TRADEMARK	TYPE	SHAPE	SIZE (mm)		AREA (cm ²)
			height	diameter	
INGOLD	Pt 805	ring	3	6	0.56
TACUSSEL	Pt 102	rod	12	1	0.38
INGOLD	Au 800/5	rod	5	2	0.34
INGOLD	Au 800/7	rod	7	2	0.47

The reference electrodes were Xerolyt Ingold electrodes (potential = + 210 mV/NHE at 20°C).

A Ponselle O2P oxygen-meter and a Schott CG 817 pH meter coupled to combined Ingold/Xerolyt pH electrodes, were used.

Preparatory treatment of electrodes. For the first series of tests, the metal electrodes were polished using bands of powdered abrasive (granularity 5 and 0.3 μm) fixed onto a plastic support (Tacussel BSC 3 and BAO 3 abrasive bands). The electrodes were then rinsed with distilled water. For the second series of tests, the electrodes were first polished and then left in alternately aerated sludge for 7 d.

Test cell. A 250 ml glass test cell was used. The cover contained 5 orifices for the measurement electrode, the reference electrode, the working electrode, the oxygen electrode and an air feed pipe. The air was provided by an aquarium compressor (adjustable flow) connected to a diffuser.

Activated sludge and treated water. The activated sludge and treated water were taken from an extended-aeration treatment plant (Maincy - Seine et Marne). The sludge was intermittently aerated (15 min aeration followed by 15 min with no aeration) for 2 to 4 d in a laboratory. Throughout this period, approx 100 ml of waste water per litre of sludge was added each day.

Measurement of Zero-Current Potentials in Aerobic Media

Procedure. The metal electrodes and the common reference electrode were connected:

either to high input impedance millivoltmeters (Knick 646), themselves connected to a multi-channel graphic recorder (Goerz Servogor 460 06), including variable-sensitivity racks (experiments on Maincy sludge),

or a Hewlett Packard HP 3421 A automatic data acquisition system (Central processor unit equipped with a 10-channel multiplexer card, internal resistance $10^{10} \Omega$, accuracy at the 3 V range: 0.3 mV) + HP 41 CV calculator + 82162 A thermal printer + 82161 A microcassette recorder (experiments on the Valenton sludge).

The electrodes were polished prior to each series of tests and then placed in the medium until the response stabilized.

A Schott CG 817 pH meter, coupled to a combined pH/Xerolyt Ingold electrode and Ponselle O2P and YSI 57 oxygen-meters were used. The dissolved oxygen concentration in the sludge was varied by decrementing *the air pump flow and then increasing it in the same sequence. The pH was varied by adding sulphuric acid* (Merck pro analysi) then soda (Prolabo Normapur). The potential was measured 20 to 30 min after changing the conditions in the medium.

Laboratory test cell. This is a 2-litre transparent PVC rectangular cell, capable of accommodating 10 electrodes. It was placed on a magnetic agitator and the liquid was stirred by a Teflon rod. It was thermostat-controlled for certain experiments (see results).

Activated sludge and treated water. The activated sludge and treated water were taken from biological treatment plants at Maincy (Seine et Marne) and Valenton (a low-loaded plant, Val de Marne). The sludge was stored in the laboratory as described previously.

Measurement of Zero-Current Potentials in an Anaerobic Medium

The sludge taken from the Valenton treatment plant was stored in the laboratory, under anaerobic conditions, for several days and periodically activated with wastewater taken at the station inlet. The electrodes were mounted on the above cell, containing this sludge plus 50 mg/l of potassium acetate (Prolabo Normapur) until the potential stabilized. The electrodes were then again polished and the potential from each was monitored using the data acquisition system.

RESULTS AND DISCUSSION

Equilibrium exchange current densities

Results. Figure 1 shows the equilibrium exchange current densities obtained, at various stabilized dissolved oxygen concentrations, from 2 platinum and 2 gold electrodes in the Maincy activated sludge, only a few minutes after polishing.

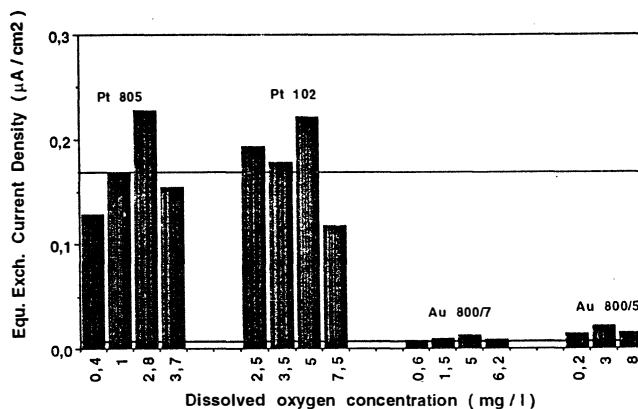


Fig.1. Equilibrium exchange current densities against dissolved oxygen concentration, for platinum and gold electrodes a few minutes after polishing (Maincy activated sludge).

The values obtained for platinum are between 0.12 and 0.24 $\mu\text{A}/\text{cm}^2$ (mean: 0.17 $\mu\text{A}/\text{cm}^2$). The results for gold are between 0.008 and 0.021 $\mu\text{A}/\text{cm}^2$ (mean : 0.013 $\mu\text{A}/\text{cm}^2$). The dissolved oxygen content does not seem to affect the measured values for either metal.

Table 2 shows the equilibrium current densities obtained from platinum and gold electrodes in treated water saturated with dissolved oxygen. The electrodes were first polished and then left a week in sludge alternately aerated and supplied with wastewater, before being placed in aerated treated water.

TABLE 2 Equilibrium Exchange Current Densities (in mA/cm²) from Platinum and Gold Electrodes in Aerated Treated Water, Immersed Directly after Polishing or after Polishing + 7 days in Maincy sludge.

Type of electrode	Pt 805	Pt 102	Au 800/7	Au 800/5
Treatment before voltametry in treated water				
Polishing	0.22	0.24	0.018	0.013
Polishing and 7 days in activated sludge	0.042	0.052	0.006	0.005

With both metals, the current densities are considerably lower after 7 d submersion.

Discussion. The current densities we measured during these two series of experiments were 0.04 to 0.24 $\mu\text{A}/\text{cm}^2$ for platinum and 0.005 to 0.018 $\mu\text{A}/\text{cm}^2$ for gold. These values must be compared with those Whitfield obtained: 0.02 to 0.38 $\mu\text{A}/\text{cm}^2$ for platinum and 0.003 to 0.008 $\mu\text{A}/\text{cm}^2$ for gold.

Heduit and Thevenot (1989) using unpolished platinum electrodes which were very probably contaminated by sulphur obtained $J_0 = 0.04 \mu\text{A}/\text{cm}^2$ in aerated sludge and $J_0 = 0.02 \mu\text{A}/\text{cm}^2$ in sludge held under anoxic conditions.

Consequently, provided both metals are treated identically, platinum gives equilibrium current densities approx 10 times higher than gold. In both cases, the density decreases after prolonged contact with activated sludge alternately subjected to aeration and anoxia.

Measurement of Zero-Current Voltages in an Aerobic Medium

Evolution in potential after polishing. Figure 2 represents changes in the electrode potentials, a few minutes after polishing, in sludge which was previously aerated and then no longer supplied with wastewater for several hours. For electrodes in the same metal and treated in exactly the same way, the potentials vary very little from one electrode to another.

The platinum potentials are far higher than those for gold. Under the experimental conditions ($\text{pH} = 7.8$, $(\text{O}_2) = 8 \text{ mg/l}$), the difference is approx 200 mV. After polishing, the potential varies in a similar way for both metals. This development is probably not representative of the large differences in current densities mentioned previously.

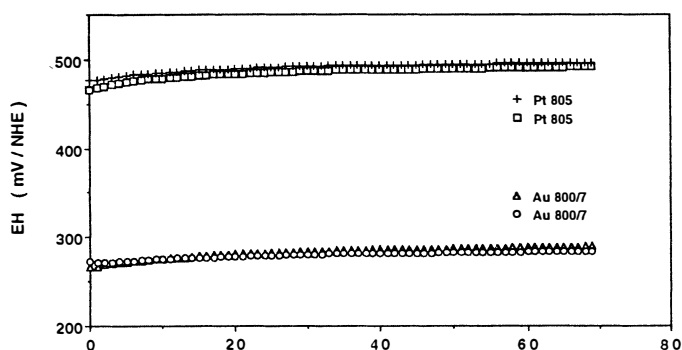


Fig. 2. Changes in the potential of polished platinum and gold electrodes (EH) a few minutes after polishing in aerated activated sludge (VALENTON activated sludge).

Effect of pH on potential. Figure 3 shows the effect of pH on the potential of platinum and gold electrodes in treated water from the Valenton treatment plant, at $27 \pm 0.1^\circ\text{C}$. The pH was varied by adding sulfuric acid or soda.

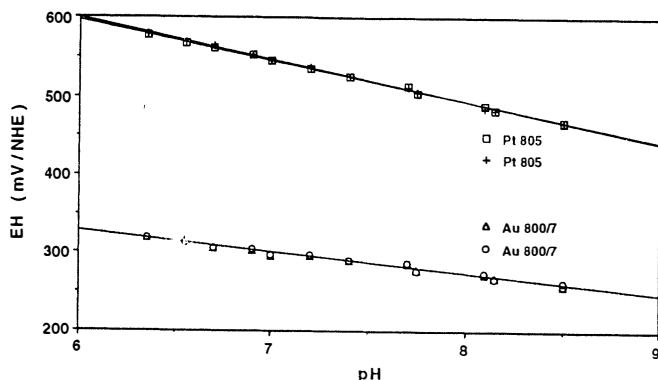


Fig. 3. Potential against pH at $27 \pm 0.1^\circ\text{C}$ in aerated treated water from the Valenton plant.

Table 3 summarizes the results obtained during this experiment and those obtained from a sample of treated water from the Maincy plant whose pH was varied in the same way.

TABLE 3 Results Pertaining to the Relationships Between Potential and pH in Treated Water from the VALENTON and MAINCY Plants when the pH is Varied Between 6 and 9.

Origin of water	Type of electrode	Equations of linear regression lines EH = A - B pH (mV/NHE)	EH at pH 7 (mV/NHE)	r ²	n	effluent content (mg/l)		
						NH ₄ N	NO ₂ N	NO ₃ N
VALENTON	Pt 805	EH = 903 - 51.1 pH	545	0.998	12	0.4	0.1	27
	Pt 805	EH = 915 - 52.7 pH	546	0.999	12			
	Au 800/7	EH = 489 - 26.8 pH	301	0.984	12			
	Au 800/7	EH = 487 - 26.5 pH	301	0.980	12			
MAINCY	Pt 102	EH = 884 - 58.5 pH	474	0.994	11	0.5	< 0.1	< 0.1
	Pt 805	EH = 885 - 58.6 pH	475	0.996	11			
	Au 800/7	EH = 524 - 32.8 pH	294	0.980	11			
	Au 800/7	EH = 482 - 28.6 pH	282	0.950	11			

These results confirm that in treated water the zero current potential is highly dependent on the metal of the electrode.

For platinum, although the experimental values of coefficients A and B in the $EH = A - B \text{ pH}$ equations are lower than the thermodynamic values corresponding to the Nernst equation for the Pt/PtO system ($EH \text{ (mV)} = 980 - 59 \text{ pH}$), this is still the most plausible electroactive system to explain the variation in potential with pH (Heduit and Thevenot, 1992). The correlation factors exceed 0.994 for both samples of treated water.

The slopes of the EH against pH lines obtained for gold are roughly half those obtained with platinum. This could reflect the low current densities with gold or the mixed nature of the potentials measured. The correlation factors for gold are not so good, possibly due to poorer stabilization of the potentials.

If the "sensitivity" of a sensor is considered as the strength of its response to changes in the medium, the polished platinum electrode is more sensitive to variations in pH than the gold electrode.

Effects of oxygen concentration on potential. As demonstrated previously (Heduit and Thevenot, 1989) the stabilized potentials generated by platinum electrodes when the pH is held constant is related to the dissolved oxygen concentration by a semi-logarithmic equation of the form $EH = C + D \log(O_2)$. The same result was demonstrated for the gold electrode.

Figure 4 gives the curves of EH against $\log(O_2)$ obtained from Valenton sludge. The oxygen content was stabilized at various levels by progressively reducing the flow from the air pump and then increasing it in the same sequence.

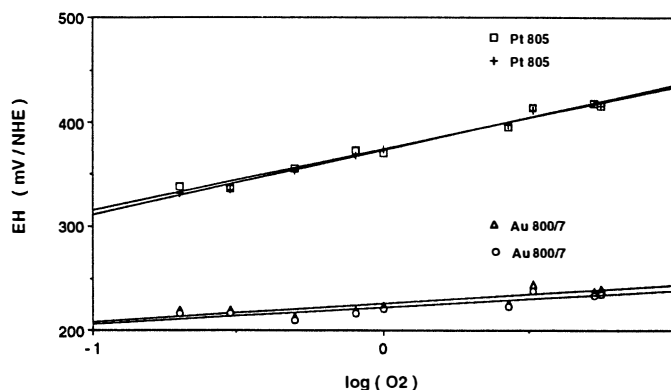


Fig. 4. Potential (EH) against $\log(O_2)$ (Valenton activated sludge).

Table 4 shows the results obtained from this experiment and those from the mean of 7 tests carried out on Maincy activated sludge. The pH varied between 7.6 and 8.15 during these experiments and, consequently, the measured potentials were corrected back to pH = 7.9 using the equations determined previously.

TABLE 4 Potential (EH) Against Log (O_2), Results Obtained from Valenton and Maincy Activated Sludge.

Origin of water	Type of electrode	Equations of linear regression lines $EH = C - D \log(O_2)$ (mV/NHE)	EH at 1 mg O_2 /l (mV/NHE)	r^2	n
VALENTON	Pt 805	$EH = 375 + 59.2 \log(O_2)$	375	0.975	9
	Pt 805	$EH = 373 + 62.3 \log(O_2)$	373	0.990	9
	Au 800/7	$EH = 225 + 17.6 \log(O_2)$	225	0.736	9
	Au 800/7	$EH = 221 + 15.7 \log(O_2)$	221	0.746	9
MAINCY	Pt 805	$EH = 482 + 68 \log(O_2)$	482	0.95	7
	Au 800	$EH = 316 + 29 \log(O_2)$	316	0.85	7

Except for factor D obtained for gold electrodes in Valenton activated sludge, the experimental coefficients are very different from the thermodynamic coefficients which represent the electrochemical reduction of dissolved oxygen:

$$EH = 730 + 15 \log(O_2) \quad \text{pH} = 7.9 \text{ at } 27^\circ\text{C}$$

(mV / NHE) (mg/l)

The values of factor D obtained for gold during the various experiments confirmed the very low current densities and, therefore, the mixed nature of the potentials measured.

Platinum is more sensitive to variations in dissolved oxygen concentration than gold. The correlation factors are generally better for platinum.

Measurement of Zero-Current Voltages in an Anaerobic Medium

Figure 5 shows the variation in the potential taken by mechanically polished electrodes in anaerobic sludge. Unlike the results from an aerobic medium, the platinum potentials are lower than gold (approx. 350 mV). For a given metal, the values obtained vary little from one electrode to another (differences are less than 10 mV). Under the experimental conditions, the platinum electrode potentials stabilized roughly 30 min after polishing while the gold electrode potentials initially stabilized and then continued to decrease slowly.

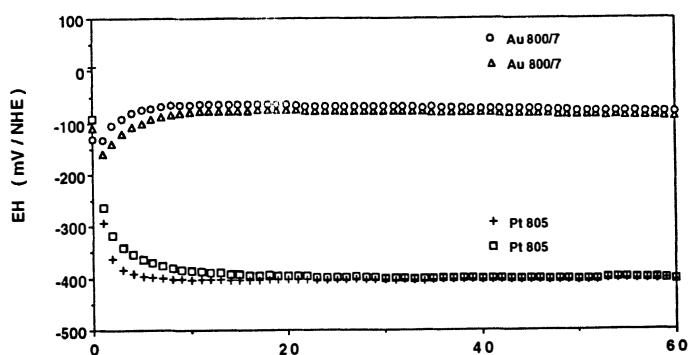


Fig. 5. Changes in the potential of polished platinum and gold electrodes (EH) a few minutes after polishing in anaerobic sludge (Valenton activated sludge).

CONCLUSIONS

The equilibrium exchange current densities and potential values obtained from a given type of electrode are highly repeatable after identical mechanical treatment or submersion in activated sludge. Platinum electrodes give current densities approx 10 times higher than gold.

As shown by the experiments conducted in various conditions of pH and dissolved oxygen concentrations, the lower kinetics of electron transfer on gold go together with significant differences in behaviour.

The potential of a gold electrode in an aerobic medium can be 200 mV less than that from a platinum electrode. In a strongly anaerobic medium, this situation reverses and the gold potential can be up to 350 mV higher than platinum. The difference between the potential in an aerobic medium and that in an anaerobic medium was, under our experimental conditions, 300 to 400 mV for gold and 800 to 900 mV for platinum.

The slopes of the linear relationships between potential and pH or potential and the logarithm of the dissolved oxygen concentration are lower for gold (29 ± 3 mV/pH and 22 ± 7 mV/decade (O_2)) than for platinum (55 ± 4 mV/pH and 60 ± 4 mV/decade (O_2)).

Although the values obtained with platinum electrodes do not represent a veritable equilibrium state, since they differ from those suggested by, for example, a Pt/PtO or O_2/H_2O system the platinum electrode nonetheless seems more sensitive to changes in the medium than the gold electrode and, therefore, more suitable for use in activated sludge.

REFERENCES

- Audic J.M. (1992). L'exemple d'une station entièrement automatisée. *TSM* 4, 195-199.
- Bühler et GASTER (1980). Mesures redox : bases et problèmes. *INGOLD Technique Ed.* 23 p.
- Charpentier J., Godart H., Martin G. and Mogno Y. (1989). Oxidation reduction potential (ORP) regulation as a way to optimize aeration and C, N and P removal : experimental basin and various full-scale examples. *Wat. Sci. Tech.* 21 (10/11). 1209-1223.
- Coquery, M. (1986). Limites et applications des mesures de potentiels d'équilibre dans les boues activées. *Mémoire de D.E.A. Sciences et Techniques de l'Environnement.* Université Paris Val de Marne - Agence Financière de Bassin Seine-Normandie - CEMAGREF - 63 p.
- Deguin A. (1992). Intérêt pratique de la mesure du REDOX pour la conduite de l'élimination de l'azote en boues activées. *TSM* 4, 187-194.
- Heduit A. (1990). Potentiel d'électrode de platine en épuration biologique. Thèse de Doctorat de l'Université Paris Val de Marne. CEMAGREF Collection Etudes n° 1 - 163 p.
- Heduit A. and THEVENOT D.R. (1989). Relation between redox potential and oxygen levels in activated sludge reactors. *Wat. Sci. Tech.* 21 (8/9), 947-956.
- Heduit A. and Thevenot D.R., (1992). Elements in the interpretation of platinum electrode potentials in biological treatment. *Wat. Sci. Tech.* 26 (5/6), 1335-1344.
- Whitfield M. (1972). The electrochemical characteristics of natural redox cells. *Limn. Oceanogr.*, 17, 383-393.