DIVISION S-2—NOTES

CONTROLLED ENVIRONMENT POTENTIOSTAT TO STUDY SOLID–AQUEOUS SYSTEMS

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Abstract

We designed a redox apparatus that controls electropotenial (Eh), pH, and temperature. The apparatus is fully automated and can be assembled from equipment found in most soil analytical laboratories. The reactor can maintain environmental conditions used to evaluate the chemical fate of contaminants under natural conditions (natural attenuation) or adjust them to a new steady state to evaluate the effect of engineered remediation on a subsurface system. It can operate within a wide range of redox potential values (-400 to 400 mV) and at any pH value. The stability and accuracy of the instrument was tested by performing Eh–pH titrations on MnO_2 suspensions. Results indicated that Eh could be controlled within 1 to 2 mV, pH within 0.05 to 0.1 unit, and temperature within 0.1°C for weeks or months.

Many chemical constituents, both inorganic and organic, are subject to electron transfer reactions that occur within the Eh range of natural systems (about -400 to 600 mV). These oxidation–reduction (redox) reactions are of environmental importance, since they are often responsible for the mobilization–immobilization of chemical contaminants, and in some cases the degradation of organic material. Study of redox reactions requires control of temperature, pH, and Eh to adequately access reaction mechanisms and characterize resulting reaction products. This is especially significant if in situ remediation of aquifers is to be considered, because associated chemical reactions are dependent on the conditions present within the aquifer. We designed a redox apparatus that controls temperature, pH, and Eh. Although similar units have been developed (Patrick et al., 1973; Dragun, 1993), the apparatus illustrated below is fully automated and can largely be assembled from equipment found in most soil analytical laboratories. It can be constructed using inexpensive parts available at any electronics store. This results in a relatively low-cost apparatus, and our design allows for flexibility in selection of the components used to build the complete unit.

Methods and Materials

The system designed for controlling Eh, pH, and temperature is illustrated in Fig. 1. The redox cell allows the control of the redox potential by controlling the flow of oxidizing and reducing gases into the cell. Compressed air or O_2 was used

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as the oxidizing gas; a reducing environment was created with a mixture (3:97) of H_2 and Ar.

The glass cell had a working volume of 500 to 600 cm^3 (Fig. 2). The main body consisted of two pieces connected by a ground glass joint to ensure a gas-tight seal. The lower section contained the working volume, and was surrounded by a glass water jacket. The water jacket was connected to a temperature-controlled water bath by a lower inlet and upper outlet port (Model 9110, Fisher Scientific, Pittsburgh, PA), that circulated water around the cell to maintain a constant set temperature. The upper section contained seven Ace glass thread connectors. Four Size 7 (7-mm i.d.) connectors housed the platinum electrode, acid–base dispenser, gas diffuser inlet, and gas diffuser outlet lines. Three Size 18 (18-mm i.d.) connectors housed the reference electrode, pH electrode, and sampling port. A nylon bushing and a rubber O-ring created a gas-tight seal around each instrument. The working electrode in the main body was separated from the side chamber (≈ 70 cm^3) containing the reference electrode with a sintered-glass frit. The reference electrode was secured in a Size 18 thread connector.

A schematic of the circuitry is illustrated in Fig. 3. An Analog Devices (Norwood, MA) dual precision high-speed BiFET AD712 operational amplifier ("op-amp") was used to compare an input (V_{in}) voltage (platinum electrode voltage relative to a saturated calomel electrode) to two reference or threshold voltages (V_{ref1} and V_{ref2}). Setting the threshold voltages on either side of the desired Eh created a voltage window. When V_{in} rose or fell below V_{ref1} and V_{ref2}, there were a number of output states from the AD712. The truth table shown in Table 1 illustrates this for a cell Eh of 200 mV. Thus, for example, when the measured cell Eh was 220 mV, which exceeded V_{ref2} by 10 mV, the output at Pin 1 (Fig. 3) was positively saturated and conversely the output at Pin 7 was negatively saturated.

Since the analog signal from the platinum electrode was relatively low (± 500 mV), resolution (for switching purposes) within the AD712 was improved using a second AD712 as a noninverting amplifier. An output voltage gain of 4 to 5 V was used for the input signal. An equal component Sallen–Key low-pass filter with a frequency cutoff (fc) of ≈ 1000 Hz was used to filter noise from the power supply (switching power supply from a computer) before reaching the relays. Following the low-pass filter, a unity gain amplifier (LM741) buffered the window comparator from the impulsive interference generated from the inductive "kick" when solenoids closed.

The LM741 supplied the small base current to the TN 3904 transistor necessary to pull 5 V across the relay. A Potter and Brumfield T75 series 14-amp miniature dip relay (SPDT, Potter and Brumfield, Siemens Co., Switzerland) powered the normally closed two-way direct ASCO Red-Hat II (Automatic Switch Co., Florham Park, NJ) solenoid valves (Figure 1). Relay coil voltage was 5 V. Because of the high current load (0.8–1.0 A) required to open the solenoids, a transistor was used to power the relay, which electrically isolated the solenoids from the rest of the circuit. A diode (PR6007) was placed across the solenoid to protect and lengthen the life of the relay from the inductive "kick" when the solenoid closed. The impulsive interference generated from the inductive "kick" was filtered with the low-pass filter. Green and red LEDs were used to indicate whether the solenoids were opened or closed.

Voltage regulators with outputs of 5 V (LM805) and -5 V (LM7905) ensured that the AD712 detected a stable input
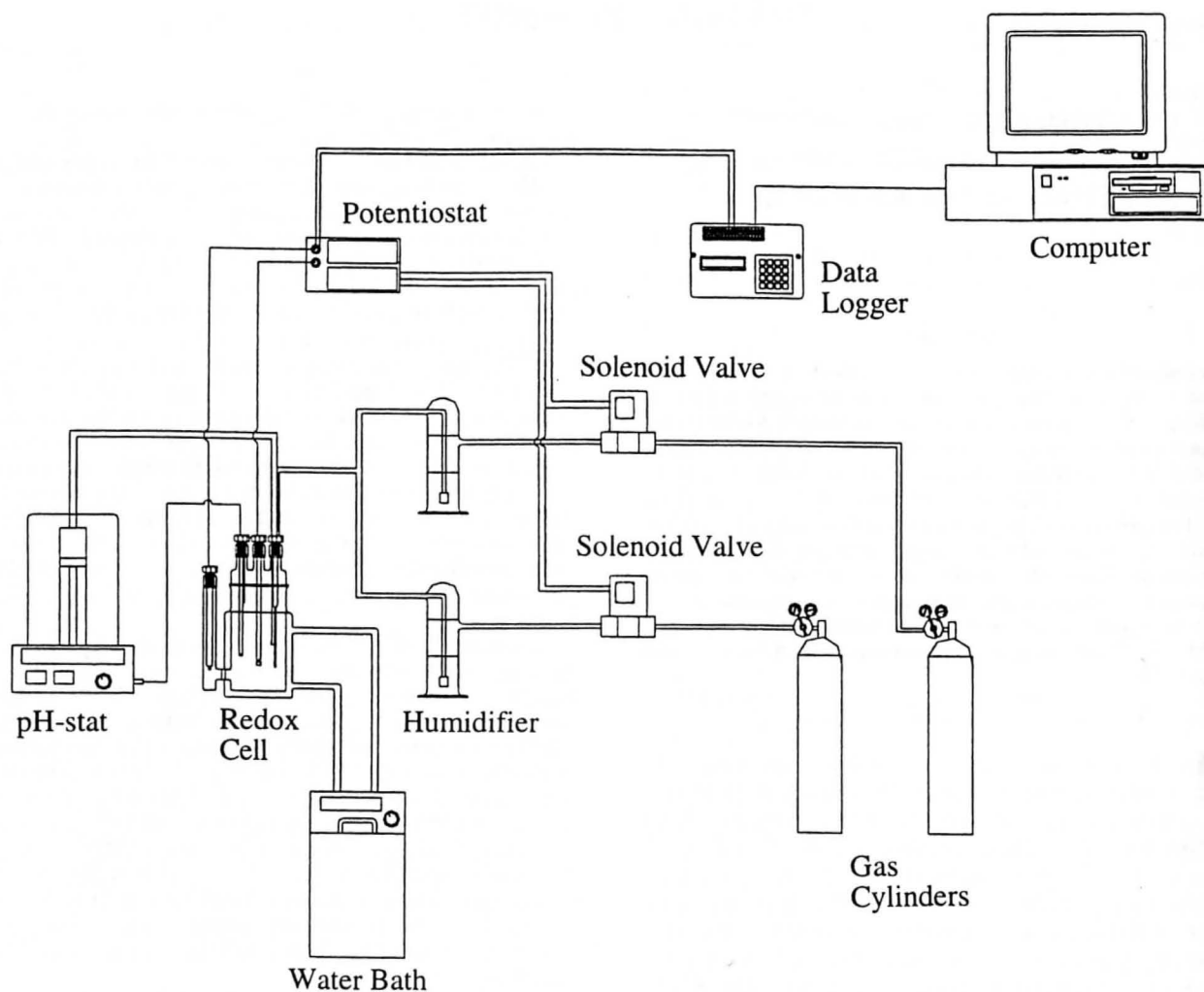
Fig. 1. Combination potentio- and pH-stat with temperature control.

reference voltage. Without the voltage regulators, small variations in power supply input voltage would result in incorrect output swings in the AD712 window comparator when cell voltage was close to either reference voltage. Erratic solenoid switching would reduce the stability of the cell Eh. The 0.1-μF capacitor across the output improved the transient response and kept impedance low at high frequencies. Bourns Model 3590s 10-turn wirewound precision potentiometers (10 KΩ, Bourns Inc., Logan, UT) were used as panel controls for the two reference potentials.

The redox potential was measured with an electrode pair consisting of an inert electrode and a reference electrode (saturated calomel) (Fig. 1). The inert electrode was made from bright platinum foil (0.0254-mm thickness, catalog no. 13-761-10A, Fisher Scientific, Pittsburgh, PA) to create an electrode with a surface area of 1 cm^2. Approximately 7 mm of platinum wire (36 gauge, Fisher catalog no. 13-766-11A) was spot welded (microspot welder, Model 8200, Weller, The Cooper Group, Apex, NC) with ≈3-mm overlap onto foil. The free end of the platinum wire was then soldered to bare copper wire. A hollow glass rod supported the electrode. The copper wire was threaded through the rod and the glass was melted to enclose the platinum wire at one end, creating a seal impervious to gas and liquid. The heated wire was positioned to expose only platinum foil and 3 to 4 mm of platinum wire, preventing leakage inside the electrode during immersion and ensuring that platinum acted as the sole indicator electrode. The bare copper wire was soldered onto shielded copper wire

(for external connection to the potentiometer). Finally, the shielded wire was sealed into the top of the glass rod with silica sealant.

A titrino (Model 716 DMS, Metrohm Ltd., Zurich, Switzerland) used to measure and regulate the pH within the reaction cell consisted of an exchange unit and pH electrode electronically connected to a microcomputer. This instrument was programmed to perform as a pH-stat autotitrator. The exchange unit automatically responded to changes in pH by dispensing small amounts of acid or base until the preset pH was reached. A computer RS232 interface allowed pH monitoring and recording. An extra-long combination pencil gel electrode (Accumet, Fisher catalog no. 13-620-293) was used to measure the pH within the cell.

Five hundred and thirty milliliters of a 0.025 g/L of MnO_2 suspension were used for the Eh–pH titration. The MnO_2 was prepared according to the method of Whelan (1992). The MnO_2 was characterized by x-ray diffraction and found to be a weakly crystalline birnessite with a surface area of 121 m^2/g (Cramer, 1995) as determined by a Brunauer–Emmett–Teller (BET) adsorption isotherm. The background electrolyte concentration was fixed using 0.02 M NaCl. The titration was performed at 11°C, simulating groundwater temperatures used in additional experiments. At the beginning of the experiment, the pH was adjusted to 5.0 with 0.1 M HCl, and during the titration the pH-stat adjusted the pH back to 5.0 as necessary with 0.01 M HCl. Redox potentials ranged from −200 to 400 mV during the titration. The potential was fixed by the
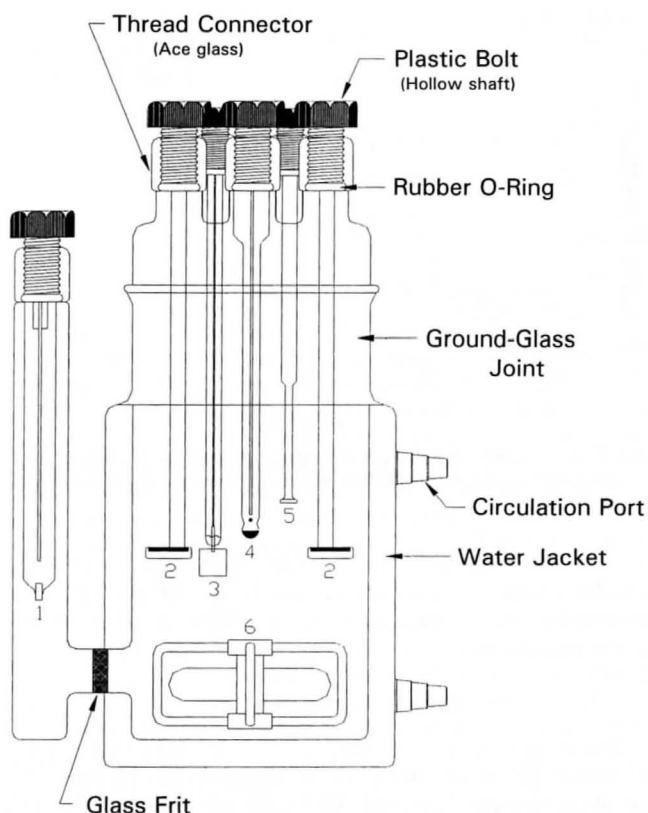
Fig. 2. Schematic cell design for redox potential control unit: (1) calomel reference electrode; (2) gas diffuser; (3) platinum electrode; (4) pH electrode; (5) acid–base dispenser; (6) floating magnetic stir bar.

Table 1. Truth table for example cell voltage of 200 mV, reference voltage 1 (V_{ref1}) = 190 mV and reference voltage 2 (V_{ref2}) = 210 mV; V_{in} is the input voltage.

Voltage, mV	AD712 output saturation	
	Pin 1	Pin 7
$V_{in} > 210$	positive	negative
$190 < V_{in} < 210$	negative	negative
$V_{in} < 190$	negative	positive

potentiostat at -200 mV for 48 h, after which the potential was increased in 100-mV steps to 400 mV.

Additional redox experiments were performed by adding 0.025 g/L pentachlorophenol (PCP) to 530 mL of a 0.025 g/L MnO_2 suspension. The Eh–pH titrations were performed at pH values of 4.5, 5.0, 6.0, and 7.0, and Eh values of -300, -100, 100, and 300 mV. For every permutation of Eh–pH, a 48-h titration was performed. Experiments were conducted as described above except that once the desired pH was reached, PCP was added by syringe through a rubber septum to the reaction cell. After 48 h, 20 mL of the suspension mixture were extracted from the reaction cell and filtered through a Gelman Supor-200 0.2-μm 25-mm filter disk (Gelman Sciences, Ann Arbor, MI). The filtered extract was acidified to pH 3 by dropwise addition of 1 M $NH_2OH \cdot HCl$ in 0.1 M HNO_3 and stored at 4°C. The filtered extract was analyzed for soluble Mn(II) by emission spectroscopy with inductively coupled plasma (ICP/6000, Perkin Elmer, Norwalk, CT). Emission spectra were analyzed at 257.610 nm for Mn.

Results and Discussion

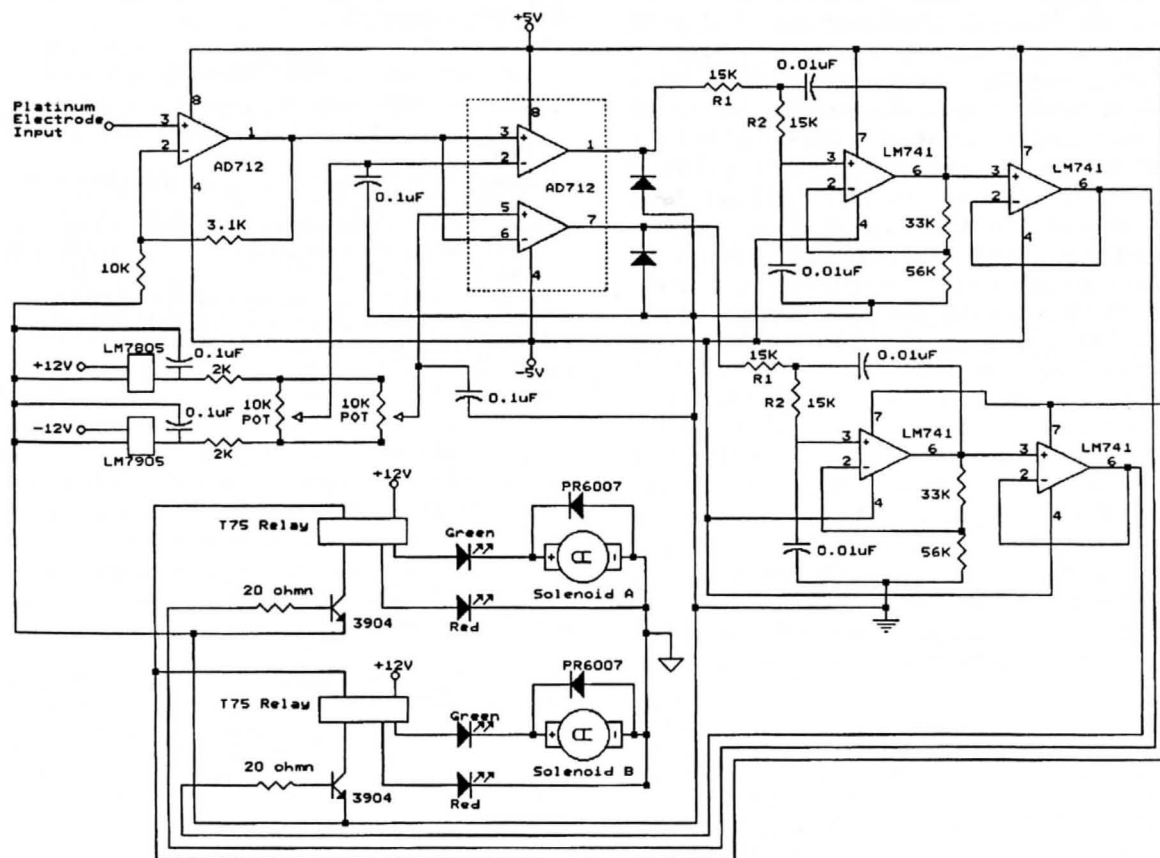The potentiostat described here used passive control of redox potential, rather than passing a current or volt-

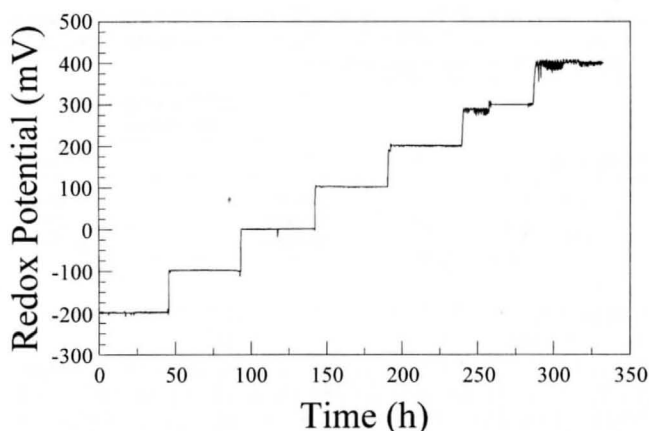Fig. 3. Voltage comparator and solenoid driver circuit.

Fig. 4. Example of redox potential control at pH 5 during MnO_2 dissolution. There is a 48-h interval between each redox potential value.

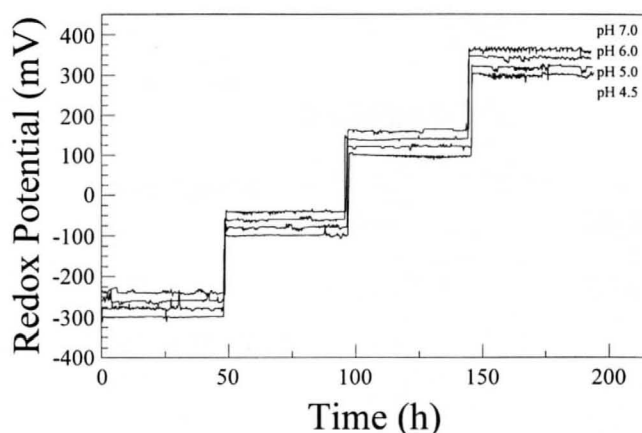

Fig. 5. Redox potential control over environmentally relevant Eh and pH values during the oxidation of pentachlorophenol and reduction of MnO_2.

age between two electrodes, to obtain a desired potential. The redox potential is simply a function of the ratio of hydrogen and oxygen in the reaction cell and the potential they exert between a platinum and calomel reference electrode. Hydrogen gas (3%) induced low redox potentials; conversely O_2 (as compressed air) added to the reaction cell increased the redox potential. By varying the ratio of these gases in the cell, redox potentials ranged from -400 to >400 mV. The use of an accurate potentiostat ensured that the desired potential could be maintained within 1 to 2 mV for an indefinite period of time.

An Eh titration conducted on a MnO_2 suspension demonstrated the ability of this system to control redox potential during MnO_2 dissolution at pH 5.0 (Fig. 4). The desired redox potential was maintained for consecutive 48-h periods from -200 to 400 mV. Little noise in the redox signal was observed during the experiment. Electrode poisoning contributed to the signal noise at the 400-mV step since the platinum electrode performed normally after an acid rinse (0.1 M HNO_3) and flame annealing. Experiments conducted at pH 4.5, 6.0, and 7.0 (data not shown) performed similarly. The Eh–pH titrations carried out with an oxidant (MnO_2) and a reductant (PCP) also exhibited good redox potential control (Fig. 5). Again, most of the signal noise was

associated with higher potentials (300 mV). As long as the platinum foil was cleaned regularly, electrode poisoning and consequent signal noise were kept to a minimum.

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