

FINAL
CONTRACT REPORT

**DEVELOPMENT OF AN
EMBEDDABLE REFERENCE ELECTRODE
FOR REINFORCED
CONCRETE STRUCTURES**

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(The opinions, findings, and conclusions expressed in this report are those of the authors and not necessarily those of the sponsoring agency)

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ABSTRACT

There is a concern that none of the existing concrete-embeddable reference electrodes that are being used as a convenient means for monitoring the condition of the reinforcing steel in concrete bridges or the operation of cathodic protection systems for permanently halting steel corrosion in these structures may have sufficient stability of at least 25 years. This study examines the possibility of using stable-potential galvanic couples (SPGC), which rely on different rate constants between the component metals of each couple to maintain stable potentials, as a new concept for developing better concrete-embeddable reference electrodes. Each SPGC relies on the different rate constants between the component metals to maintain a characteristic stable potential and can be classified as either noble-noble, noble/active-passive, noble-active or active-active.

The long-term and the short-term stability of the potentials of different galvanic couples (in saturated calcium hydroxide), relative to both a saturated calomel electrode and a commercial manganese dioxide electrode, were assessed. The cathode-to-anode area ratio aspects of some couples were also investigated and it was determined that the area ratio could be used to optimize couple stability. Mixed potential theory was used to characterize these electrodes and explain the stability behavior. Several potentially successful couples, that exhibited potential shifts of less than 10 mV, were identified and embedded in concrete (both with and without added chloride) for further investigation.

This resulted in the identification of three promising candidate couples (Cu-W, Ni-W, and Cu-Ni) that can be developed into very stable concrete-embeddable reference electrodes by optimizing the electrode design parameters such as anode-to-cathode area ratio and geometry.

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INTRODUCTION

The premature deterioration of many of the almost 600,000 bridges in existence in the United States as of 1995, as well as other reinforced concrete systems, gives rise to the growing concern about corrosion resistance in reinforced concrete. The reinforcing steel in concrete is protected by the alkalinity of the environment, but the ingress of chloride ions into the concrete has been found to prompt the breakdown of the passivity of the steel. The resulting corrosion products are larger in volume than the original steel by up to eight times. The increased volume places stress on the surrounding concrete and in severe cases may result in the spalling of the concrete cover. The deterioration of reinforced concrete structures increases each year as more deicing salts are deposited on roadways and environmental factors such as sea spray continue to add corrosive species to the structures.

A widely used method for assessing the possibility of corrosion on the reinforcing steel in a concrete structure is the measurement of the potential of the steel using a half cell or reference electrode. The underlying principle of this method is that corrosion involves an exchange of energy within different sections of the reinforcing steel; and, the relative energy levels can be determined in relation to a reference electrode with a stable electrochemical potential. Even though the potential of the steel in a structure is not a measure of the rate of corrosion of the steel, potential measurement made on the top surface of a concrete structure with a portable reference electrode (typically copper-copper sulfate electrode) is very useful and reliable for

delineating anodic and cathodic areas on the reinforcing steel, especially when used with other nondestructive or semidestructive inspection techniques.

In contrast to portable reference electrodes that are moved from point to point on the surface of the concrete structure, reference electrodes that can be embedded in concrete structures offer a unique advantage, in that they can be placed relatively close to the steel and, thereby, reduce errors in the measured potential caused by the resistance of the concrete. Even though the potentials measured by an embedded reference electrode are reflective only of the condition of the steel in its immediate vicinity, it is a very convenient way for monitoring the steel reinforcement because the need for traffic control to place a portable reference electrode on the surface of the concrete is eliminated.

In addition, embedded reference electrodes are extremely valuable for long-term evaluation of the performance of cathodic protection (CP) systems, since protection criteria are based upon shifts in the potential of the reinforcing steel. Furthermore, the greatest advantage of permanently embedded reference electrodes may be in their use to control the rectifiers and, therefore, the amount of applied current or potential at a "safe" level. This is particularly important in cathodic protection of prestressed concrete members, where overprotection of the high-strength prestressed steel tendons can cause generation of excessive hydrogen and, possibly, subsequent embrittlement of the tendons. Use of embedded reference electrodes also facilitates the use of remote monitoring devices that significantly reduce the need to visit bridge sites and, therefore, the cost of monitoring CP systems.

In general, a good reference electrode must have the following characteristics: (a) is governed by a reversible equilibrium that follows the Nernst equation, (b) have a stable potential that returns to a reversible value after any passage of small current through the electrolyte, (c) maintains a constant potential in spite of changes in temperature and moisture, (d) be rugged and permanent, (e) be reasonably small and unobtrusive to allow easy placement in a structure and (f) be inexpensive. Although many types of electrodes have been tested, none have been completely successful; in fact, there have been indications that some types of electrodes have become unstable after only several years of embedment in concrete.^{1,2} In view of the important role that embeddable reference electrodes have in the effective operation of CP systems, it is clear that development of a new effective and stable reference electrode is critical.

Galvanic couple reference electrodes represent a new concept in reference electrode technology. Unlike traditional reference electrodes, these electrodes are not based on thermodynamically reversible reactions but instead are bi-metallic couples that maintain a stable potential for a finite period of time. These can be made to be both rugged and cost effective. Furthermore, their stability is based on the specific environment of concrete, and can be explained and calibrated with electrochemical theory. In view of the potential application of this new type of electrodes in concrete, an investigation was recently conducted with the objective of identifying several viable galvanic couple electrodes that exhibit stable potentials for measurement in reinforced concrete and verifying the concept of potential stable galvanic couple electrodes in concrete. This report discusses the fundamentals of reference electrodes and the results of the investigation into the behaviors of a number of candidate galvanic-couple

electrodes in saturated calcium hydroxide solution and a selected subset of these electrodes in concrete. Electrode performance was analysed further by determining deaeration, chloride, and micro-polarization effects.

BACKGROUND

In any corroding system, the electrochemical reactions involved are defined by their characteristic potentials. As the passivity of the reinforcing steel breaks down, as a result of accumulation of chloride ions and shifts in pH and oxygen concentration in the concrete, a corresponding shift occurs in the electrochemical potential of the steel-and-concrete system. By monitoring the open-circuit potential of the steel, the corrosion state and behavior of the reinforcing steel can be determined without destroying the concrete structure. However, in all electrochemical systems, it is impossible to measure the absolute potential of a single electrode or reaction. For steel in concrete, this means that the absolute potential of the steel /concrete interface cannot be determined simply with the steel electrode alone; instead, it must be determined as the potential difference between the steel half-cell or electrode and an additional, separate electrode, which is called the reference electrode. Likewise, the “known” potential of this reference electrode is defined relative to a standard hydrogen electrode, which has a potential arbitrarily assigned as zero. To this end, the reference electrodes must be stable with time, reproducible, and unaffected by small currents that may be passed through the interfaces that constitute the reference electrodes in an electrochemical system.

Therefore, good reference electrodes, when embedded in concrete structures exposed to corrosive environments, provide a convenient, nondestructive means of monitoring the electrochemical parameters that govern the corrosion of steel in the concrete.

Existing Concrete-Embeddable Reference Electrodes

Several reference electrodes have been designed for, tested, and used in concrete structures. These reference electrodes can be classified as either (1) true reference electrodes, which include silver/silver chloride (SSC), manganese dioxide/manganese trioxide ($\text{MnO}_2/\text{Mn}_2\text{O}_3$) and copper/copper sulfate (CSE) electrodes, or (2) pseudo-reference electrodes, which include noble metal, mixed metal oxide, activated titanium, and graphite electrodes.

True Reference Electrodes

A true reference electrode obtains its stable potential from the thermodynamic equilibrium corresponding to a reversible electrochemical reaction of an ionic specie. Under a given concentration of the specie involved, the behavior of its electrode potential can be predicted by the Nernst equation:

$$E_r = E^*_{1/2} + (RT/nF) \ln (\alpha_{\text{ox}}/\alpha_{\text{red}}) \quad (1)$$

where E_r is the electrode's reference potential, $E_{1/2}^*$ is the standard equilibrium potential for the half-cell reaction at 25° C, α_{ox} and α_{red} are the activities of the oxidized and reduced species respectively, and R, T and F are the gas constant, temperature and Faraday's constant, respectively. As indicated by the Nernst equation, a true reference electrode requires a constant concentration of a given species to maintain a stable reference potential. The structure of a true reference electrode, therefore, generally consists of a metal wire in contact with an electrolyte medium that contains the active ionic species. In some cases, the metal ion is dissolved in the electrolyte solution, and in other cases the metal ion is contained in a salt film on the metal. For example, a silver/silver chloride (SSC) electrode consists of a silver wire covered with a deposited layer of silver chloride in solution with a chloride rich electrolyte. For this instance, the following reaction is maintained in equilibrium:



With a chloride concentration of 1.0 M, the reference potential is maintained at 0.235V, versus a normal hydrogen electrode.³

Both SSC and MnO₂ electrodes have been redesigned specifically for embedding in concrete, and extensive data exist about their performance.^{2,4,5} Copper sulfate electrodes have been used extensively as surface electrodes, but only limited data are available about the behavior of this electrode while embedded. As mentioned earlier, SSC require a chloride concentration cell to maintain a stable reference potential. However, because these electrodes are embedded in concrete, the standard glass encasing for liquid or gel electrolytes is not feasible. Embeddable silver chloride electrodes have been designed with a chloride rich electrolyte surrounded by a backfill that is contained in a concrete compatible form, usually a cotton bag.³ Figure 1 shows the structure of an embeddable SSC electrode.

Similarly, copper sulfate electrodes require a supply of copper ions. Because few of these electrodes have been embedded, the design for an embeddable copper sulfate electrode consists merely of a plastic (rather than glass) sheath for the copper ion containing electrolyte.²

Manganese dioxide reference electrode, which is based on the reaction between MnO₂ and Mn₂O₃ in an alkaline environment, has been used in alkaline battery technology for many years, and its stability has been well established. For compatibility with concrete, the electrode has a mortar tip, and the alkaline components of the electrode are housed in a polymer/metal casing to provide an electrical contact.⁵ Figure 2 shows a manganese dioxide reference electrode that is designed for use in concrete.

Even though these true reference electrodes provide all of the characteristics required for a good electrode, they do not behave as precisely in concrete as predicted by laboratory use. This is because none of these electrodes are based on the components found in concrete. Schell *et al.* determined that SSC electrodes suffer from two main problems in concrete: (a) the diffusion of chloride ions away from the electrode results in poor stability over extended time periods, and (b) the electrode tends to be unstable at cold temperatures.⁶

Arup et al., who developed the manganese dioxide electrode, found it to be an acceptable reference electrode because it could be embedded with minimal liquid junction potential errors.⁵ The manganese electrodes tested showed little deviation in reference potential between electrodes. Also, they found the manganese electrode to be stable even in mortar that had been deaerated by cathodic protection. Ansuini and Diamond found the manganese dioxide reference to be stable with time after two years in concrete both with and without chloride contamination.⁴ Myrdal and Videm found the manganese dioxide reference to be acceptable as well, but they noted that the reference potential was altered by pH shifts.⁷

It should be noted that most of these true reference electrodes perform well when designed, handled, and constructed properly; however, the proper design of the electrodes often means limiting their usage. Due to the complexity of the electrodes, they tend to be relatively expensive and are generally bulky. Both of these qualities make these electrodes difficult to apply extensively and cost effectively to cathodic protection systems.⁶

Pseudo Reference Electrodes

More pseudo reference electrodes than true reference electrodes have been used in reinforced concrete systems to determine potential distribution within the structure, because these electrodes tend to be durable for standard construction procedures and stable. Since they are simple to construct in various sizes, these electrodes are relatively less expensive. However, there are various drawbacks as well as the advantages to using these electrodes.

Pseudo reference electrodes are stable potential cells that do not have an identifiable reversible electrochemical reaction, such as the previous example for the SSC electrode. The behavior of these electrodes is not predictable by the Nernst equation, but can be shown, in some cases, to be stable through empirical observation. In some cases, the pseudo electrodes are corroding systems whose behavior may be explained by mixed potential theory. However, most of the data available for these electrodes are strictly empirical stability behavior and little data exist to explain the electrode potentials and potential shifts using theory. All pseudo reference electrodes are stable only in very specific environments. For instance, a pseudo reference electrode for concrete would not necessarily provide a stable reference potential in a less alkaline system, whereas a true reference electrode would generally be unaffected by a change in environment. While the true reference electrodes will have a liquid junction potential created by the interface of the electrode's electrolyte and the environment, pseudo reference electrodes do not have a liquid junction potential error because they rely on the pore solution for stability. Acceptable pseudo reference electrodes will vary only slightly with small changes in concrete porewater over time.

Several types of pseudo electrodes have been tested and some even implemented in concrete systems. These include several elemental electrodes (such as lead, gold, platinum, zinc or graphite) as well as mixed metal oxide (MMO) and titanium oxide electrodes. Some MMO electrodes are now commercially available.

For ease of implementation, pseudo reference electrodes can be designed quite simply with only a single element, i.e., consisting merely of the metal and an electrical connection to a potential monitoring system. Several single-metal pseudo reference electrodes that have been examined include gold, platinum, palladium, silver, nickel, stainless steel, and lead. White found that gold and platinum electrodes, although stable, were strongly influenced by oxygen and pH shifts.⁸ Similarly, Myrdal et al. found that the potential of platinum was strongly affected by oxygen partial pressure, but lead was not as sensitive.⁷ These investigators also determined that platinum, palladium, nickel, silver, gold and Type 316 stainless steel in concrete either lacked short term stability, were not consistent between electrodes, or/and did not return to their respective reference potentials after immersion in water.⁷

Graphite electrodes are similar in structure to noble metal electrodes. As illustrated in Figure 3, they consist mainly of a graphite block with a soldered connection to an electrical wire. The electrical connection is then protected with an epoxy plug. Schell *et al.* found that the potential of embedded graphite electrodes withstands large variations in temperature and in a wide range of chloride content.⁶ However, Ansuini et al. reported that graphite electrodes were only stable for about 3 months, and that over a period of 3 years the graphite electrodes deviated over a 100-mV span. They concluded that graphite cells should be used only for short-term relative measurements, such as the depolarization test.⁴ A separate study by Myrdal et al. concluded that while stable for up to a year, graphite electrodes tend to be sensitive to both oxygen and pH shifts⁷. Furthermore, since the specific reactions that determine the characteristic potential of this electrode are not well defined, there is another concern that concrete pore water composition (specifically, varying ion content) may alter the reaction behavior and thus the potential.⁶

Commercially available pseudo reference electrodes are of the mixed metal oxide (MMO) type. The exact structure of these commercial electrodes is proprietary, but some studies have been performed on activated titanium with mixed metal oxide surfaces. The activated titanium electrodes consist of a titanium rod that is covered with a mixed metal oxide of iridium. The reaction occurring on the surface should coincide with the following reaction:



Castro *et al.* found these electrodes to be acceptable embeddable reference electrodes – being less dependent on oxygen partial pressure than graphite is in neutral and high pH solutions, and appeared to have short- and long-term stability in concrete as well.⁹ Bennett et al. also found MMO electrodes to be suitable references, with reproducibility between electrodes of approximately 10 mV, and satisfactory behavior during micro-polarizability and hysteresis tests.² On the other hand, Arup and Sorensen found activated titanium electrodes to be strongly affected by deaeration and by cathodic polarization while embedded in concrete.⁵

Galvanic Couple Reference Electrodes

Galvanic couple reference electrodes (GCRE) are new pseudo reference electrodes that are based on a similar concept to graphite reference electrodes. These electrodes can be more stable and predictable than graphite and would be less expensive than true reference electrodes.

A galvanic couple is created when two dissimilar metals are electrically in contact with each other (providing an electronic path) and surrounded by an electrolyte that provides an ionic path. To maintain conservation of charge in all galvanic couples, the total reduction current must equal the total oxidation current – a condition which leads to the polarization of both metals to a combined potential E_{couple} .¹⁰ Figure 4 shows an Evans diagram to illustrate the polarization behavior of a set of couple halves (metals M and N) as well as for the entire couple. The more noble metal in this galvanic couple (M) will be polarized cathodically; therefore, it will be referred to as the cathode in this study. Similarly, the more active metal in the couple (N) will be polarized anodically resulting in a higher dissolution rate of this metal. This half of the electrode will be termed the anode.

Since the potential of the couple is determined by the point where the total anodic current is equal to the total cathodic current, and not by the current densities, the area of each couple half will have an effect on the couple potential. In other words, for the same current density an anode of 1 cm² will produce less total current than an anode of 10 cm². This area effect would shift the anodic currents to higher values at the same potentials and would decrease E_{couple} by lowering the point where the total cathodic and anodic currents intersect. The couple potential could also be affected by varying the cathodic area. For a galvanic couple reference electrode, this principle may be applied to create more stable or slower corroding electrodes.

The couple potential (E_{couple}) is the steady-state reference potential of a GCRE. To be a successful concrete-embeddable electrode, it must not only maintain a steady E_{couple} , but as a corroding electrode, other criteria must be met. First, the relevant cathodic and anodic processes must be understood so that any dependence on a species whose presence and availability in concrete may vary (e.g., oxygen) will be predictable. Secondly, the electrode must not lose metal or deplete ions from the surrounding environment at high rates.

Theoretically, GCRE should be able to maintain a steady state reference potential that could be used as a dependable reference in concrete. Even though the potential of a GCRE can not be predicted by Nernst equation, it may be predicted from their corresponding surface reactions, which are more straight forward to define than those on graphite electrodes. Unlike current true reference electrodes, theoretically, GCRE's do not require a supply of certain specific ion to maintain a stable potential. Furthermore, theoretically, these electrodes could be made to any size because the area ratio of the anode to the cathode is more important for maintaining a stable potential than the total area of the electrode. More important, since the life of a GCRE may be predicted by application of mixed potential theory, its service life in a concrete structure can be optimized by changing the ratio of the areas of the couple halves. Finally, these electrodes could be made to be mechanically durable and inexpensive.

EXPERIMENTAL DESIGNS

Electrode Designs

Galvanic couple reference electrodes were designed for testing in several different forms. The following section details those designs as well as the other electrodes required to characterize the behavior of a galvanic couple reference electrode.

Galvanic Couple Electrode Design and Materials

The initial design of a galvanic couple electrode consisted of two dissimilar metal wires wound together at one end and soldered to an insulated copper electrical wire. The electrical connection at the solder joint was then covered with a protective polymer coating to prevent interaction between the lead-tin solder and solution. Figure 5 shows a schematic representation of this electrode. PTFE/FEP Dual Shrink tubing was used as the polymer coating in initial tests. However, due to the high temperatures required to shrink this coating and the low melting temperature of certain metals used in the couples, later electrodes were protected with Pro-Coat™, a melted resin that solidifies around the couples upon cooling.

Electrodes were constructed from various combinations of the following metals: lead, gold, platinum, zinc, aluminum, nickel, tin, copper, silver, tungsten, molybdenum, and magnesium. Table 1 contains a complete listing of the electrodes considered. Electrodes that were considered in studies beyond the initial stability tests in tanks are noted.

Other Working Electrodes

Direct current electrochemical methods were used to characterize some of the galvanic half cells. The working electrodes used in these experiments were either galvanic couples that could be disconnected into separate halves (referred to as split couple electrodes) or electrodes consisting of only one element of the galvanic couple (referred to as single metal electrodes) that were never part of a couple. For a single metal electrode, insulated copper wire was soldered to one end of a metal wire sample. The electrical joint was then coated in Pro-Coat™. Split couple electrodes were made by connecting two single metal electrodes at the far end of the insulated electrical wire (not at a soldered junction). The split couple electrode and single metal electrode are depicted in Figure 6 (a) and (b), respectively.

Standards, Reference and Counter Electrodes

In all experiments, a reference electrode (for measuring potentials) and a standard electrode (against which the stability of the measured potential differences can be compared) were employed. Initially, a glass saturated calomel electrode (SCE) was used as a reference in all electrochemical tests done in calcium hydroxide. However, due to the aggressive nature of high

pH solutions on glass, these electrodes were later replaced with fresh electrolyte every two weeks. Commercial ERE 20 Manganese Dioxide reference electrodes, produced by Force Institutes, were used as standards in all stability tests. This electrode, which is shown to full scale in Figure 7, has a nominal standard reference potential of +160 mV vs. SCE at 23°C.

In the concrete stability tests, commercial Ag/AgCl electrodes (Electrochemical Devices, Inc.) were used as additional standards to the manganese dioxide reference electrodes. The nominal reference potential for embeddable SSC electrodes is -20 mV vs. SCE. Finally, for the three-electrode polarization experiment, where a counter electrode was required, a platinum coated niobium mesh electrically connected to a platinum coated titanium rod was used.

Experimental Design for Simulated Concrete Solution

To verify that galvanic couple electrodes could maintain consistent reference potentials in a high pH environment, many electrodes were tested at the same time in saturated calcium hydroxide solution. Subsequently, direct current electrochemical methods were performed on individual couples and single metals to further establish stability and to determine the relevant reaction kinetics. Micro-polarization experiments were performed on specific couples to verify that the stable reference potentials were unaffected by the application of small currents. These experiments were conducted in succession to show that after small variations in the reference potential, the original potential could be obtained again. Potentiodynamic tests on single metal samples were performed to determine the kinetics of the reactions occurring on each couple half. Similarly, potentiodynamic scans were performed with split couples that had been disconnected after reaching a steady state while coupled. These tests were designed to determine if the initial polarized state of the couple would affect the kinetic behavior of each couple half. From these experiments, mixed potential theory was used to account for the observed steady state behavior of the couple. The tank designs, cells and procedures used in these tests are all detailed in the following section.

Stability Tests: Procedure and Tank Design

The stability of each electrode was determined by monitoring the open circuit potential against a saturated calomel electrode in large reservoirs of solution. To avoid unwanted stirring and movement of the electrodes, glass boiling beads (3-6 mm diam., Fisher Scientific) were packed in the tanks. Figure 8 depicts one of the tanks of electrodes. Each 19-liter tank contained 12 to 16 galvanic couples and a MnO₂ electrode in approximately 2.5 liters of solution with a pH of 12.5.

The electrodes were allowed to reach a steady state while immersed in solution at ambient temperatures for at least two weeks. The open circuit potentials were then measured using a computer controlled data acquisition system. Potentials were taken at least every hour and at most every three minutes (more often if the reading had changed from the previous one) using the Monitor system (data acquisition software used with a multiplexing 16 channel DAQ board). The calomel references were changed and rejuvenated every two weeks. Stabilities for

each couple and the MnO₂ reference were then determined by calculating the standard deviations of the open circuit potentials over the last 60 days of 120 days of immersion. Stability tests were performed on all electrodes in saturated calcium hydroxide. A limited number of electrodes were then tested for increasing and decreasing stability with varying anode-to-cathode area ratios (0.1, 1.0, and 10).

The tank setup was also implemented to test a limited number of representative electrodes for stability with small temperature variations. In these cases, six couples at a time were immersed with a J type thermocouple in a 1.5-liter tank of glass beads and saturated calcium hydroxide. This tank in turn was placed in a water bath with a temperature-controlling pump. The circulating bath temperatures were held constant (± 0.2 °C) while the open circuit potentials and solution temperature were monitored for 24 hours.

Kinetics Experiments: Cell Designs and Procedures

Cell Designs, Hardware, and Software

The couples were individually tested for micro-polarizability and couple half kinetics. Single metal samples and split couple electrodes were allowed to reach a stable state (± 1 mV for two hours) in calcium hydroxide before being placed in either a three-port or five-port electrochemical cell for polarization tests. A three-port electrochemical cell was implemented for potentiodynamic scans and is shown schematically in Figure 9. Points A and B are porous and semi-porous frits, respectively. Compartments 1 and 3 contained the reference and counter electrodes, respectively. Compartment 2 provided ports for the working electrode as well as an inlet and outlet for deaeration.

The five-port electrochemical cell contains more solution and does not have separate compartments for electrodes. This cell has an individual port for deaeration, a reference electrode, a counter electrode, and the working electrode. Like the other cell, these ports are all air tight through glass joints and septum lids. All deaeration experiments were run in the larger, five-port cell. All potentiodynamic scans were run using E.G.&G. Princeton Applied Research (PAR) M352 Softcorr II™ corrosion software. A PAR Versastat™ and computer were used to obtain the data.

Potentiodynamic Scans on Single Metal Electrodes

Single metal electrodes were allowed to reach a steady state in solution for a twenty four hour period. The open circuit potential of the metal was then recorded for fifteen minutes. Following the open circuit test, a cathodic potentiodynamic scan was run on the sample. The electrode was polarized to -250 mV vs. open circuit. The sample was again allowed to reach a steady state for at least 24 hours, and the open circuit potential was monitored as before. If the open circuit was stable and within ± 5 mV of the previous scan, an anodic polarization was

applied. The anodic scan began at open circuit and stepped up to + 250 mV vs. open circuit. In both scans, the scan rate was 0.166 mV/s and the scan increment was 0.5 mV.

Potentiodynamic Scans on Coupled and Un-Coupled Split Electrodes

Connected split couple electrodes were allowed to reach steady state first in quiescent solution. A small voltage was then applied over the coupled electrode using the linear polarization and autoexecute options in the PAR software. A linear polarization loop was created to scan from -20 mV against the open circuit to +20 mV against the same open circuit. The reverse scan was then performed immediately to obtain a cyclic scan and the corresponding hysteresis loop.

After the micro-polarization test, the coupled electrode was again allowed to come to a steady state, as determined by two-hour open circuit monitoring. If the couple had not reached a steady state during this time, the open circuit monitoring was repeated as necessary. The split couple was then disconnected and the anode was used as the working electrode in a polarization scan. The anode was polarized from its open-circuit potential to just above the steady state reference potential of the coupled electrode. The scan rate in these experiments was 0.166 mV/s and the scan increment was 1.0 mV.

The electrode was recoupled at the end of the anodic polarization and allowed to reach steady state in the same manner as before. The couple was again disconnected, and the cathode was polarized. The cathode was polarized from its open circuit to below the measured open circuit of the couple or just above the open circuit of the anode whichever was lower. The same scan rates and increments were used in these polarizations as in the anodic polarizations.

Finally, couple kinetics in deaerated solution were determined. The couple was reconnected and allowed to reach a steady state again in the quiescent solution. Nitrogen was then bubbled through the saturated calcium hydroxide for 24 hours to deaerate the solution. After reaching steady state in this solution, the micro-polarizations, cathodic and anodic scans were repeated in the same manner as in the quiescent solution.

Experimental Design and Procedures in Concrete

After testing in solution, selected electrodes were cast in concrete to verify the behavior predicted by the simulated concrete solution. Three blocks constructed as shown in the schematic drawing in Figure 10 (a) were cast. All blocks were made of A-4 concrete mix used by the Virginia Department of Transportation. The first two blocks had no chloride added to them, but the third block contained 0.022 wt% Cl⁻ in the admixture. This chloride level corresponds to the threshold level observed to cause the transition from passive to active corrosion of steel reinforcement in concrete.

The electrodes were cast in the concrete as shown in Figure 10 (b). Each electrode was 50 mm (2 in.) away from the other electrodes. Due to size limitations, the commercial Ag/AgCl electrode was placed on its side along the bottom (just above concrete cover) of the center of the block. All other electrodes were 38 to 50 mm (1.5 to 2 in.) from the bottom.

After allowing the concrete to set in a temperature and moisture-controlled environment for one month, the various blocks were placed in water baths. The first two were placed in deionized water. The block containing admixed chloride was placed in 3.5 wt % NaCl solution. The electrodes and thermocouples were then connected to the data acquisition system. Two EXP 1800™ boards from Keithley Metrabyte multiplexed the inputs to a DAS1802 HR™ board within a computer. Labtech Notebook™ software was then used to control these boards and log the collected data. Open circuit potentials and temperature data were collected every hour for one- week periods at a time to reach a total of at least 2000 hours.

RESULTS AND DISCUSSION

Behavior of Galvanic-Couple Electrodes in Simulated Concrete Solution

Electrode Stability Results

The galvanic couple electrodes have been categorized by couple half behavior. The electrode stabilities are discussed with regard to these categories in the following sections. Open circuit potentials and standard deviations are discussed as well as couple potential control and the galvanic series for calcium hydroxide.

A Galvanic Series for Saturated Calcium Hydroxide

Each galvanic couple electrode was designated as either noble-noble, noble-active, active-active, or noble/active-passive metal pairs, according to the relative nobility of each component. To define the couple sets, an experimental galvanic series was obtained for saturated calcium hydroxide and is shown in Figure 11. Metals with higher open circuit potentials such as gold, silver, nickel, and copper were considered noble in this study. Molybdenum, tungsten, and lead were the only active metals considered. Normally, tin and zinc have extremely active open circuit potentials, but both exhibited passive behavior in the highly alkaline environment.

The galvanic series was then used to predict the anode and cathode in each couple. In this work, the couples have been designated as cathode-anode. For example, using this series, a Au-Cu couple would be classified as a noble-noble couple with a gold cathode and a copper anode.

Stability Behavior. The stability of the galvanic couples in saturated calcium hydroxide was analyzed in terms of the standard deviations of the open circuit potentials versus time. All of

the data shown in this section pertain to couples with an anode and cathode of the same area. To compare data between separate tanks, the standard deviation of each couple was normalized against the standard deviation of the commercial manganese dioxide reference electrode in each respective tank. Also, by normalizing the data, any temperature variations and SCE differences between tanks can be minimized for direct comparison between all electrodes. Large standard deviations can result from either gradual potential drift, potential steps, or noise of large amplitudes. As long as the amplitude of the noise is low, the frequency is less important, and the frequency of the noise can only be determined within the bounds of the frequency of data collection. In this study, the open circuit potential behavior with time and the normalized and true standard deviations were all considered to account for the different forms of potential variations. Figures 12 (a), (b), and (c) show the distributions of the normalized standard deviations for the three separate tanks of couples. The normalized standard deviations range from less than 1 to 60 mV/mV. Several couples performed equivalently to or better than the manganese dioxide reference electrodes with actual standard deviations under 5-12 mV.

The wide variations in couple performance, allowed the electrodes to be classified as successful, promising, and unsuccessful. Those couples with normalized deviations less than the manganese standard were all considered successful, and couples with standard deviations greater than twice that of manganese dioxide were classified as unsuccessful. Electrodes between these were classified as promising couples. Table 2 (a), (b), and (c) give the mean potentials of the successful, promising, and unsuccessful couples, respectively. These tables also list the true and relative standard deviations of the couples.

While the standard deviations provide a good estimate of couple stability, it is necessary to examine the actual potential behavior over time to ensure that the couple behavior is acceptable. To this end, the open circuit behavior was used to determine the cause of the standard deviations. Couples that maintain low standard deviations by slight noise are preferred to couples that deviate by a consistent drift, which is considered the equivalent of a non-steady state system and a reference potential cannot be obtained under such condition. However, low levels of noise can still be associated with a stable potential and can be accounted for by filtering the signal. Figure 13 shows the potential behavior for the last 60 days of immersion of two noble-noble couples and the standard MnO₂ reference. The difference in the plots of the Au-Cu and Cu-Ni couples shows the wide variation between successful and unsuccessful couples. The successful electrode has low noise and as little drift as the manganese dioxide reference electrode. The standard deviation produced by the successful Au-Cu couple is the result of low levels of noise and not a steady increase or decrease in potential. The Cu-Ni couple was unsteady by large amounts of noise after a steep potential jump.

Figure 14 presents the similarity in the potential behavior of the successful couples from the noble-active couple set. The potential behavior of the noble-active couples was controlled by the anodes. Plots for Ag-Pb and Cu-Pb are included as examples of lead (anode) controlled behavior seen in these couples. All of these couples have mean open-circuit couple potentials near the open-circuit potential of lead alone in saturated calcium hydroxide (near -740 mV vs. SCE). Cu-Mo also exhibits anode control and has a potential more near the open circuit of

molybdenum than that of copper. While the Au-W couple is also controlled by the open-circuit potential of the anode, it is inherently unstable by exhibiting potential drift.

Comparison of the plots of Cu-Mo and the lead couples provides a good example of the need for normalizing standard deviations for data comparison between tanks. The Cu-Mo couple was contained in Tank 2 while the lead couples were contained in Tank 1 and 3. The stability behaviors of the manganese dioxide reference electrodes are included as a reference to tank behavior and show an increase in the potential disturbances in Tank 2. Although the overall stability of the Cu-Mo couple appears to be less consistent than either of the lead couples, the tank behavior can be seen to be more erratic by the noise as seen in the manganese reference for Tank 2.

Figure 15 provides similar information for noble/active-passive couples. As seen by the data, the Pb-Sn couple was unsuccessful. This couple appears to be controlled more heavily by the tin and does not have an open circuit potential near that of lead. The Pb-Zn couple, on the other hand, is another couple that is lead controlled, but lead is the cathode in this instance. The Au-Sn couple is also cathode controlled by the gold. Finally, in Figure 16, stable and unstable active-active couples are plotted. Both of these couples are under mixed control.

Couple Stability Control

In many of the successful couples, the respective couple behavior was influenced more strongly by either the cathode or the anode. A summary of these couples is given in Table 3 along with the couple potential. The strongest occurrence of this is seen in couples containing lead. The lead (usually the anode) controls the potential behavior of these couples and maintains a reference potential that is very near its own open-circuit potential. The potential-controlling component of couples such as these can play a strong role in determining the stability of the couple as solution parameters are varied. A case in point, a couple that depends on the anodic kinetics of one of its components may be more stable in deaerated solutions than a couple whose steady state reference potential is strongly linked to cathodic control. Furthermore, by adjusting cathode to anode area ratios to maintain stable potential control, more stable or longer lived electrodes may be developed.

Kinetics Results

DC electrochemical techniques were used to further test the viability of galvanic couple electrodes and to explain the observed open-circuit behaviors. The electrode stability was tested using cyclic micro-polarizations and the results are detailed in the following sections. Mixed potential theory has been employed to explain the open circuit behaviors of the couples.

Micro-Polarization Effects. Ideally, reference electrodes should polarize very little with the application of small currents that might be passed in measuring electrical potentials. After small currents are applied, reliable reference electrodes should return to their reference potentials

almost immediately. In the case of corroding electrodes which are not in equilibrium, the most successful electrodes will be those that return to steady state quickly and do not shift far from that steady state during and after the application of small currents. From micro-polarization tests, these two parameters can be examined. Figure 17 shows a schematic micro-polarization for an ideal reference electrode. Small slopes on these curves represent low polarizability. Furthermore, ideal reference electrodes show no hysteresis; the reference potential returns immediately to its original value after the current is no longer applied. For steady state references, larger hysteresis loops correspond to either slow return to steady state or failure to return to the original reference potential. Both of these conditions are generally unacceptable. The micro-polarizability slopes are shown in Table 4.

The Cu-Au couple had excellent stability characteristics, and was examined in micro-polarizability experiments as a sample noble-noble couple. Figure 18 shows the micro-polarizability and hysteresis behavior of the Cu-Au couple in quiescent saturated calcium hydroxide. This couple exhibited some hysteresis between cathodic and anodic scans but repeats its respective cathodic and anodic behaviors in the second polarization loop. The polarizability was determined to be -6.0 for the anodic polarization and -6.9 mV/uA for the cathodic polarization. The couple was more difficult to polarize in deaerated solution as seen in Figure 19. The slopes on these curves were -0.95 mV/uA for the anodic polarizations and -0.67 mV/uA for the cathodic polarizations. This curve also had a significant hysteresis. Some of the hystereses may be accounted for by increased reduction or oxidation of the individual couple halves during the polarization. For example, if the film that has formed on the copper is easily reduced by the cathodic polarization, then the couple would require time to reform the film in order to return to the original steady state. The reverse could also be true of forming more oxide during the anodic polarization.

The Ag-Pb couple was investigated as a sample noble-active couple under micro-polarization effects. This couple is controlled by the anode, which is not readily polarizable. Figure 20 shows the micro-polarizability behavior of the Ag-Pb couple in quiescent solution. The anodic slope on this curve is -9.8×10^{-3} mV/uA and the cathodic slope is -6.6×10^{-3} mV/uA. Figure 21 shows the polarizability of this couple in deaerated solution. The slope of these curves is approximately -9.0×10^{-3} mV/uA.

Au-Sn was examined as a representative noble-passive couple. Figure 22 is the observed micro-polarizability behavior of the Au-Sn couple in quiescent calcium hydroxide. This couple has a slope of approximately 38.7 mV/uA. The hysteresis of the couple was limited, and the Au-Sn electrode appeared to return to the same steady state readily, even with polarizations as high as 20 mV. Figure 23 shows the same couple in deaerated solution. Under this condition the couple is less polarizable with a slope of -15.3 mV/uA. However, deaeration results in some hysteresis between the linear polarizations that start with cathodic currents and those that start with anodic currents. This may indicate some inability of the passive film on the tin to reform (after being reduced by the polarization) under deaerated conditions. Mixed potential experiments for this couple will reflect any effect of deaeration on the anodic kinetics of the tin.

Mixed Potential Results

Noble-Noble Couples. The mixed potential behavior of the Au-Cu couple was determined using split couple polarization (polarizing half of the couple after steady state was reached in coupled conditions). The couple initially reached a steady state of -195 mV vs. SCE. After the micro-polarizations, the mean measured steady state potential was -200 mV vs. SCE. The separate polarizations of the cathode and anode are shown in Figure 24. The couple potential is predicted by the intersection of the cathodic and anodic kinetics at -194.5 mV. The predicted, measured maximum and minimum (for all quiescent experiments), and measured mean potentials are all plotted as a reference. As seen in the plot, the couple potential as predicted by mixed potential theory corresponds well with the measured steady state values for this couple. The couple potentials predicted by mixed potentials after achieving steady state outside of the couple and the potentials expected for the couple in steady state were in slight disagreement. The steady state of the couple is affected by the immediate polarization of each half of the couple in solution. Figure 25 is the polarization behavior of the Cu-Au couple in deaerated calcium hydroxide. The deaeration caused the kinetics of the reduction of oxygen on the gold to switch from activation controlled to diffusion limited. Also, the open-circuit potential of the copper electrode half dropped from -218 mV to -358 mV. The corresponding effect is a drop in the couple potential. The predicted decrease in potential with decreasing oxygen content indicates that this couple has a strong dependence on oxygen concentration and may be adversely affected by the varying conditions in concrete.

Noble-Active Couples. Molybdenum, lead, and tungsten were examined as the active halves of noble-active couples. In most of these couples, the anode controls the steady state reference behavior. The Pb couples in particular show anode control and the lead appears to be highly non-polarizable. As an illustration of this behavior, the Pb-Ag couple was examined further. Figure 26 shows the couple half polarizations obtained for split couple electrodes of lead and silver in saturated calcium hydroxide after the joined couple had reached steady state. From this figure and the included open-circuit data it can be seen that lead does not readily polarize above its open circuit, and the couple potentials are therefore maintained very near the open circuit of lead. Figure 27 shows the polarization behavior of this couple in deaerated solution. The lead open circuit changed only negligibly with deaeration.

Figure 28 gives the single-metal polarization behaviors of Ag-Mo and the measured couple potentials. This couple also behaves as an anode controlled couple. With only a 18 mV difference between the couple potential and the Mo open-circuit potential. The predicted couple potential falls at the open circuit potential of molybdenum. The predicted behavior in Figure 28 shows that the anode controls these couples because of the intersection of the open-circuit potential of the anode with the (eventual) diffusion limited current density of the cathode.

Noble/Active-Passive Couples. For the successful noble-passive and active-passive couples investigated, the couple potential was controlled by the cathodic metal. The anode is highly polarizable in the passive region. When the cathodic current intersects the anodic current in this region, stable, cathode controlled couples are obtained. Figure 29 presents an example of this behavior as seen in single-metal polarizations for the Pb-Zn couple. Figure 30 shows the

polarization behavior of the Au-Sn couple, after a steady state couple potential has been reached. This couple behavior is dependent on a non-polarizable cathode to maintain stability as the solution parameters change. Figure 31 shows the deaerated split couple mixed-potential behavior of the Au-Sn couple. As can be seen by comparing Figures 30 and 31, the cathodic kinetics and open-circuit potential of gold are dependent on the oxygen content of the solution. The extreme change in the gold behavior can push the couple potential into a less stable region of the anodic curve, and results in a large drop in couple potential.

Effects of Area Ratio on Stability

Stability behavior was determined for three area ratios of a subset of the original couples. Table 5 gives the mean open-circuit potentials of the couples, the true standard deviations, and the normalized standard deviations at cathode-to-anode area ratios of 10:1, 1:1, and 1:10. Plots of the couple potentials versus time for all three area-ratios are also given for several couples. Figure 32 is the couple potential versus time data for the Au-Cu and couple. Figure 33 shows the data obtained for the Ag-Ni couple. Both of these are noble-noble couples, but the Ag-Ni couple was strongly affected by area ratio, whereas the Cu-Au couple remained at relatively the same stability. Figures 34 and 35 show the potential stability against time for noble-active couples, Ag-Mo and Cu-Mo, respectively. Noble-active couples tended to gain stability when the anode area, which controls the couple potential, was increased. Finally, Figure 36 gives the potential stability of active-active couple Mo-W at different area ratios.

The predicted effect of varying area ratios was plotted for five different couples (from three different sets of couples): Au-Cu (noble-noble), Ag-Mo, Cu-Mo, Ni-W (noble-active), and Mo-W (active-active). Figure 37 shows the predicted and observed noble-noble behavior. The predicted area ratio effects were found with split couple metal samples, and the area ratios were adjusted mathematically from the original data (multiplied by ten).

The area effect on the couple potentials follows the trend of mixed potential theory, in that a larger cathode would draw the couple potential toward more noble values. Similarly, a larger anode tended to pull the couple potential in the active direction. The open-circuit potential versus time plots show that the area ratios can be critical to the life of the couples. Couples like Cu-Mo and Ag-Mo become more noble, in a step function, when the cathode is much larger than the anode. One possible explanation for the step is an increase in the corrosion rate and subsequent decrease in area of the anode. Failure of the anode would result in a shift to more noble couple potentials with an upper limit at the single-metal open-circuit potential of the cathode.

A Final Note on Galvanic-Couple Electrode Behavior

As seen by comparing the stability, area, and mixed potential data, not all of the metallic couplings are consistent between different electrodes (of the same type). In other words, two separate Au-Cu couples may reach different steady state potentials. Table 6 illustrates this point

for several couples by comparing the open-circuit behaviors of two electrodes of the same type used in different tests. The inconsistency between electrodes may be a problem of construction practices, and preconditioning may reduce this inconsistency. Additional testing should be done to determine the best construction for each couple and any required conditioning treatments.

Finally, the mixed potential theory provides a means of selecting couples for further investigation. For example, it was determined that all of the active metals tend to control the couples and are highly non-polarizable. The passive metals were found to have excellent stability behavior when coupled to cathodes that controlled the couple and were within the range of passivity of the metal. These two types of behavior suggest that active, non-polarizable metals and passive metals would combine to make stable, low hysteresis couples. Mo-Sn and Pb-Zn couples are two examples of this combination, which performed relatively well in stability tests. Further testing on these couples is recommended.

Behavior of Galvanic-Couple Electrodes in Concrete

Electrode Stability in Plain Concrete

A test set of twelve successful and unsuccessful galvanic couple electrode types were embedded in concrete to obtain stability and couple potential data. The stability of these couples is discussed in the following sections, specifically with respect to the behavior of two commercial electrodes in the same concrete system.

Commercial Reference Electrodes

The reference potentials of two commercial embeddable reference electrodes were monitored along with the potential behaviors of the galvanic couples in concrete. The potentials of a SSC electrode and a manganese dioxide reference electrode were measured against a common manganese dioxide reference electrode. As in saturated calcium hydroxide, the standard deviations of the potentials were obtained and are presented for these electrodes in Table 7. First, the mean potentials and standard deviations for the MnO_2 and the SSC electrode, against the MnO_2 (common), are presented. Then the potential of the SSC against the first MnO_2 electrode is then presented. This potential is given to determine any errors specific to one electrode. The potentials of these electrodes are plotted with respect to time in Figure 38. The behavior of the SSC can be compared to that of MnO_2 through this graph by assuming constant MnO_2 (common) behavior. The relative behavior of the two manganese electrodes to one another can be compared through the SSC by assuming that the SSC is a consistent electrode. This figure shows the consistency between the two manganese reference electrodes, and similar stable behavior for all three electrodes. All of the electrodes had standard deviations that were very close. The behavior of these electrodes agreed with behaviors seen by other researchers.

Galvanic-Couple Electrodes

The stability behavior of the galvanic-couple electrodes in concrete was measured against the common manganese dioxide reference electrode. Then, this stability behavior is compared to that observed in saturated calcium hydroxide to determine the applicability of the behavior observed in simulated concrete solution. The potentials and standard deviations of the test set for both solution and concrete are presented in Table 8.

Although the values for the embedded situation in Table 8 were measured against a manganese reference, the potentials have been reported against SCE to simplify comparisons. Also, Figure 39 shows the ranking of the couples by their standard deviations. The bar plot shows that the stability of the couples in concrete varied from 5 mV to 300 mV. The last six galvanic couple electrodes in this plot had standard deviations greater than twice that of the manganese reference, but the other six had standard deviations under 12 mV. The Pb-Zn couple performed better than the manganese standard.

The open-circuit behavior of these electrodes was examined against time to determine the causes of the standard deviation (noise or drift). In the following sections, the electrode behaviors are discussed in reference to each class of couples.

Noble-Noble Electrodes. In Figure 41, the couple potential vs. time is plotted for the two noble-noble couples, Au-Cu and Cu-Ni. In simulated concrete solution, the Au-Cu couple was extremely stable and the Ni-Cu couple was unstable. In concrete, however, the particular Au-Cu couple that was monitored was unstable by noise. Large potential spikes characterize the behavior of this couple. The standard SSC behavior has been included in this plot and the magnitude of the noise spikes shown by the Au-Cu electrode were appreciable in comparison to the behavior of the standard. In contrast, the Ni-Cu couple was reasonably stable with a standard deviation under 10 mV, which is slightly less than twice that of the commercial standards.

Noble-Active and Active-Active Couples. Many noble-active couples were embedded to examine the behavior of different anodes within this couple type. As determined earlier in saturated calcium hydroxide, noble-active couples were anode-controlled. Therefore, different anode metals were examined in the embedded situation for similar cathodic elements. Figure 41 shows the couple potentials versus time for the noble-active couples containing lead and the active-active Mo-Pb couple in which lead and molybdenum had mixed control. Recall that of the Cu-Pb, Ag-Pb, and Mo-Pb couples, only the Mo-Pb couple was unsuccessful in calcium hydroxide. In the embedded environment, the opposite appears to be true. The Mo-Pb couple appears to have gained stability, but is no longer in a region of mixed lead and molybdenum control. The couple potential of this electrode is not near any predicted lead potential. On the other hand, the Ag-Pb and Cu-Pb couples that had been stable in solution were unstable in concrete. These two couples both exhibited reasonable stability that was interrupted by a potential step from approximately -880 mV to -360 mV (vs. MnO₂). The potential step is then followed by reasonable stability. The similar potential behavior of these couples indicates continued control by the lead half of the couple. Had the couples failed completely, it is not likely that their potential ranges would be so close together or so low. The predicted open circuit

behaviors of silver and copper in solution are -271 mV and -376 mV vs. MnO_2 , respectively. However, other copper controlled couples (such as Cu-Zn and Au-Cu) had much higher couple potentials. One possible explanation for the step change in couple potential is a change in the oxidation state of lead from PbO to Pb_3O_4 . Furthermore, the decay of the lead half by anodic dissolution would have resulted in gradual potential drift and not a sudden step.

Figure 42 shows the couple potential behavior of two noble-active couples containing molybdenum, Mo-Ag and Mo-Cu. The Mo-Pb couple is also included on this graph to show the control of molybdenum in this active-active couple. By comparing couple potentials, it can be seen that all of the molybdenum couples were behaving under molybdenum control. The mean stable couple potential is approximately -650 mV vs. MnO_2 for all three couples. The Mo-Pb and Mo-Ag couple remained stable throughout the 2000-hour experiment. The Cu-Mo couple, on the other hand, lost stability after 1000 hours, and the potential jumped from molybdenum control up to 8.8 mV vs. MnO_2 . The Ag-Mo and Mo-Pb couples were considered only promising and unsuccessful, respectively, in solution; but the Cu-Mo couple had been successful in solution.

The two couples under tungsten control that were investigated in concrete had high stabilities. Figure 43 shows the couple potential behavior for tungsten controlled Cu-W and Ni-W couples. In solution, the Cu-W couple was unsuccessful, and the Ni-W couple was successful. As with the noble-noble couples, the noble-active electrodes behaved somewhat differently in concrete than in the saturated calcium hydroxide solution. Initially, it was postulated that unstable electrodes in solution would generally be unstable in concrete as well. However, it has been shown that this is not necessarily the case and the electrode behavior must be examined in the concrete environment to determine the true embedded performance of the electrode.

Noble/Active-Passive Electrodes. Noble-passive and active-passive couples containing zinc and tin as the passive metals and various cathodic halves were embedded. The couple potential behavior with time is plotted for these couples in Figure 46. The Pb-Zn couple stabilized to the couple potential predicted by the calcium hydroxide experiments. The cathode controls the potential in this couple and it appears to be stable in both simulated concrete solution and in concrete. The Au-Sn and Cu-Zn couples also were cathode controlled; but neither of these couples remained stable. The Au-Sn shows slow breakdown of the high potential (within the passive region of the Sn), resulting in breakdown of the couple potential to the active region of Sn. While this couple had been stable in simulated concrete solution, the actual concrete behavior was unstable after 1000 hours. This couple may easily benefit by adjusting the cathode to anode area ratios to maintain a stable (passive) potential on the Sn. Cu-Zn exhibited unstable behavior in both environments, and as seen in Figure 45, the breakdown of the couple was caused by the polarization to a much more noble potential. The couple potential stepped up to 9.7 mV vs. MnO_2 (174.7 vs. SCE). This indicates that the couple is no longer held in steady state by the passive metal (the passivity may have broken down into dissolution), but rather is completely cathodically controlled and therefore unstable.

Electrode Stability in Chloride Contaminated Concrete

The same set of electrodes was embedded in chloride contaminated concrete blocks. The stability behaviors of these galvanic-couple electrodes and the commercial reference electrodes are discussed in the following sections in terms of electrode classes.

Commercial Reference Electrodes

The reference potentials of commercial Ag/AgCl and manganese dioxide electrodes were measured against a second commercial manganese dioxide reference to obtain potential behavior of standard electrodes in a chloride concrete environment. Table 9 shows the reference potentials for these electrodes in both concrete environments. Figure 45 shows the potential behavior over 1000 hours for both electrodes in the chloride system. Recall that the commercial SSC electrode is contained in a chloride-rich backfill, and therefore is relatively unaffected by the change in chloride content of the concrete.

Galvanic Couple Electrodes

The galvanic couple behaviors over the first 1000 hours in a chloride-containing concrete environment were as a whole similar to that seen in plain concrete with a few exceptions. Figure 46 shows the observed standard deviations for the potentials of all of the couples. The mean measured couple potentials and standard deviations are shown in Table 10. By comparing potential values in Table 10 and Table 8, it can be seen that many successful couples had high standard deviations, but not always too high enough to make them unsuccessful. On the other hand, several couples such as Au-Cu, Pb-Ag, Cu-Pb, Cu-Mo, Cu-Zn, and Au-Sn became more stable. Only five couples in this environment had standard deviations less than twice that of the manganese reference.

Noble-Noble Electrodes. The behavior of the noble-noble couples improved in the chloride and concrete environment. As seen by the standard deviations in Figure 46, the Cu-Ni couple is stable under these conditions as well, and the Au-Cu couple is more stable in this environment. The stability of these two couples can be seen in the open circuit behavior shown in Figure 47. The Au-Cu couple shows distinct improvement from the previous environment. However, the couple behaviors for this electrode were seen to vary from one Au-Cu couple to the next in calcium hydroxide solution, and the improvement in stability may be related more to the difference in the couples and not the difference in environment. The noise in both couples is slightly larger than before, but the overall standard deviation was within the bounds of stability. One theory that might explain this phenomenon is the increase in noise may be related to the increase in conductivity of the solution. The increased conductivity may lead to increased electrode sensitivity because of increased ionic transfer between the electrode halves.

Noble-Active Electrodes. As before, the noble-active couple behaviors have been examined for specific characteristics of electrodes with the same anode and various cathodic

elements. The couple potential behaviors of the lead controlled couples are shown in Figure 48. In chloride concrete, the lead couples display the same behavior seen in plain concrete. The Ag-Pb and Cu-Pb couples are unstable by a step in potential, but in the chloride environment the step occurs at an earlier time. The Mo-Pb couple does not exhibit this step behavior and is presumed to be controlled by the molybdenum as in plain concrete. The standard deviation of this couple is caused by the noise level, but in the chloride environment, the noise spikes are much greater than the previous potential disturbances. The behaviors of molybdenum controlled couples were examined in this environment and are shown in Figure 49. The Ag-Mo and Mo-Pb couples were not as noise resistant in the chloride environment. All of the molybdenum couples have large (~100 mV) noise spikes. The Cu-Mo couple again exhibits the most erratic behavior. Finally, the tungsten couples are shown in Figure 50. The tungsten-controlled couples had slightly higher noise levels in the chloride environment, but the potential behavior of these couples was generally stable. Both Ni-W and Cu-W ranked among the best couples in the chloride environment.

Noble/Active-Passive Electrodes. The noble-passive and active-passive couples that rely on large regions of passivity to maintain stable couple potentials are potentially the most vulnerable to the chloride environment. Pb-Zn, Au-Sn, and Cu-Zn couples were investigated for this effect. The potential behavior of these couples with time is shown in Figure 51. The Pb-Zn couple was strongly affected by the chloride addition. Compared this with the couple's behavior in plain concrete (Figure 44), it can be seen that the Pb-Zn couple breaks down both by potential drift (initial drop) and by the potential spikes that have been characteristic of lead. On the other hand, the Au-Sn and Cu-Zn couples are more stable in the chloride environment. The Cu-Zn couple while more stable in this environment, is still unacceptable, because of the small upward potential drift. The Au-Sn couple stability behavior was successful, but should be monitored for longer periods of time to determine the lifetime of the couple. The Au-Sn couple in Figure 44, for chloride free concrete, did not show signs of instability until after the period of time monitored for the chloride environment.

SUMMARY AND CONCLUSIONS

The main objective of this work was to determine the feasibility of using galvanic couples as stable permanent reference electrodes in concrete environment. To this end, the performance in saturated calcium hydroxide (for simulating concrete-pore solution) and later in concrete (with and without chloride admixed) of several candidate electrodes were investigated. The investigation has clearly demonstrated the viability of this new concept, within an acceptable potential deviation, for several different couples in both simulated concrete and real concrete environments for over 2000 hours. Galvanic couples that exhibited stable behavior in both environments include the Ni-W, Pb-Zn, and the Ag-Mo couples. However, in concrete without and with chloride present, only the tungsten couples were successful. Several other couples including Au-Sn and Au-Cu were successful in the chloride-contaminated concrete but not in the chloride-free concrete, or vice versa.

The controlling half of each couple was determined by the location of the couple potential relative to the open circuit potentials of its anode and cathode. In solution, noble-active couples were controlled by the anode. Generally, the anode in these couples is highly non-polarizable and the cathode is polarized down to the anodic potential. The couple potential in noble or active and passive couples was determined by the cathodic behavior. In these couples, the highly polarizable anode is held at a steady state within its passive region. No clear trend controls either the successful noble-noble or active-active couples. Mixed potential theory was used to show and explain the potential based control mechanisms. The couple behavior seen in concrete tended to follow these guidelines for anodic or cathodic control. However, in some cases, while the steady state potential was controlled by the same mechanism for the couple in concrete as in solution, the polarization behavior of the couple halves resulted in either gained or lost stability.

The noble-active couples containing lead were all lead controlled in saturated calcium hydroxide. Similarly, with the exception of Mo-Pb, all lead couples in concrete were also lead controlled. However, these electrodes behaved differently in solution and in concrete, even within the control of the lead. The couple potential is stable in concrete on either side of a potential step. All of the noble-active type of electrodes that contain lead have the same potential initially, and at different times their potentials step to a common value of -360 mV vs. MnO_2 . Because the couples all exhibit the same potentials on either side of the step, it is theorized that this step is a function of the oxidation state of lead, and that lead continues to control the couples after the step. Because the couples reach a new steady state, if the step could be forced to occur before the couple is embedded, these electrodes could still be used as pseudo reference electrodes. The potential step exhibited by these electrodes in the chloride environment occurs at earlier times.

Noble-Noble couples are very stable on an individual basis. However, these electrodes are not very reproducible between electrodes of the same material. In solution, the Au-Cu electrode was consistently stable, but the steady state reference potential varied for different electrodes by more than the standard deviation. The Cu-Au electrode in plain concrete was not stable, but the same electrode was stable in concrete with chloride. The chloride may have made the electrode more stable by increasing the conductivity of the environment, but without further testing there is no way of knowing if this effect is caused by the chloride or only the differences in the two Cu-Au electrodes.

Noble-passive and active-passive electrodes were stable in both solution and concrete environments when the cathodic element was extremely stable. The Pb-Zn and Au-Sn couples were stable in solution; the Au and Pb had stable kinetics. On the other hand, the Au does not maintain the potential within stable passivity in concrete. The Pb-Zn couple is more stable in concrete. It relies on the cathodic kinetics of the lead for stability, and does not have the potential step seen in lead anodic controlled couples. However, because these couples rely on passivity for stable steady state reference potentials, the introduction of chloride into the environment causes instabilities.

Finally, based on the potential control seen in both concrete and solution environments, it is probable that the stability and/or lifetime of these electrodes could be increased by adjusting

area ratios. As demonstrated in solution experiments, all of the noble-active couples became more stable with increased anodes relative to the cathode size.

RECOMMENDATIONS

To facilitate eventual development of a viable, concrete-embeddable galvanic-couple reference electrode, it is recommended that the following be investigated: (a) the effect of the concrete environment (pH, oxygen, and chloride content) on the behavior of this type of electrodes, and (b) optimization of electrode characteristics (stability and service life) by varying the anode-to-cathode area ratio and the geometry of the electrodes. This final developmental effort should be limited to a few particularly promising candidate electrodes that could be designed to provide optimum characteristics, specifically the Cu-W, Ni-W, and Cu-Ni couples. Since tungsten is often used as a component of thermocouples and the tungsten couples may exhibit shift in potential with temperature, these electrodes should also be monitored for temperature variations.

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FIGURES

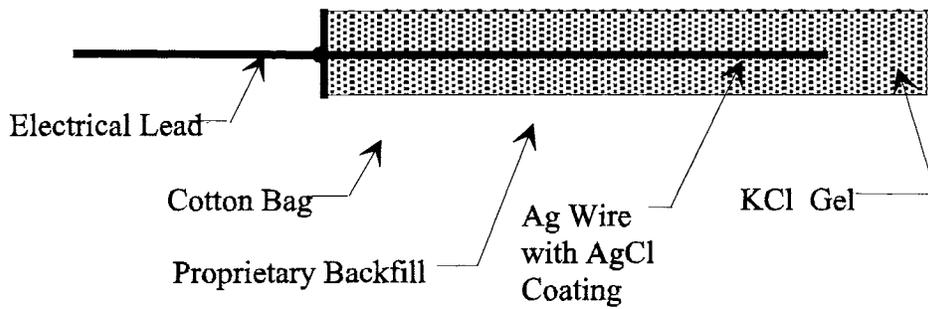


Figure 1. The structure of an embeddable silver-silver chloride electrode.

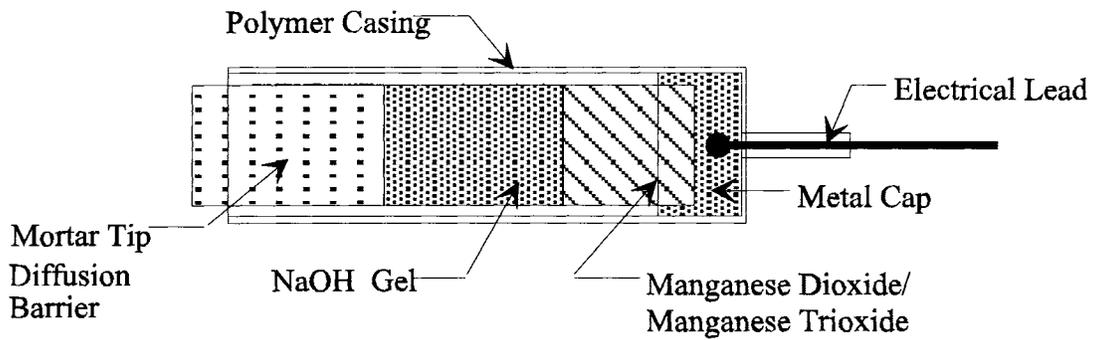


Figure 2. The structure of a $\text{MnO}_2/\text{Mn}_2\text{O}_3$ embeddable reference electrode.

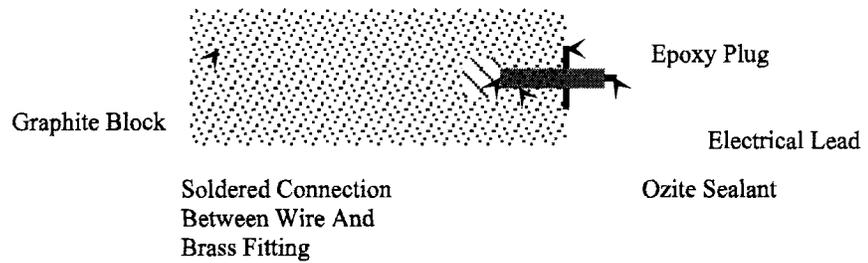


Figure 3. The structure of a graphite pseudo reference electrode.

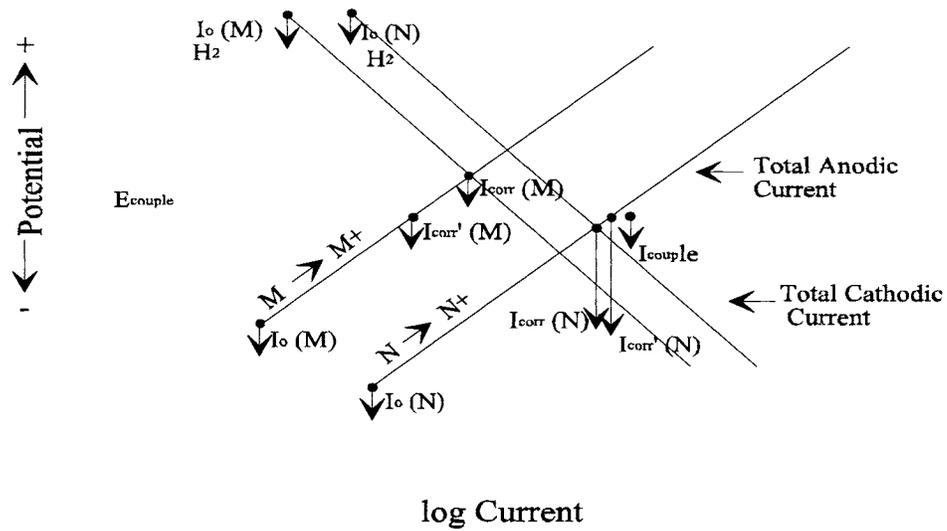


Figure 4. A schematic Evans diagram of a galvanic couple for metals M and N.

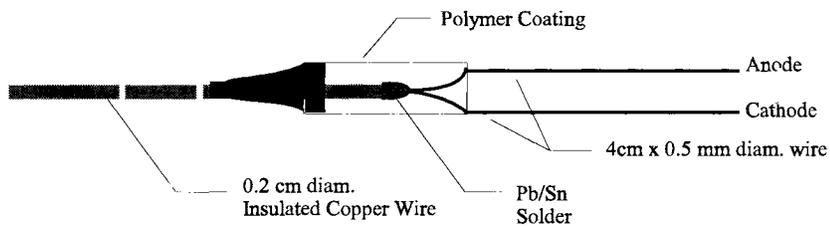


Figure 5. A schematic of the structure of an embeddable galvanic couple reference electrode.

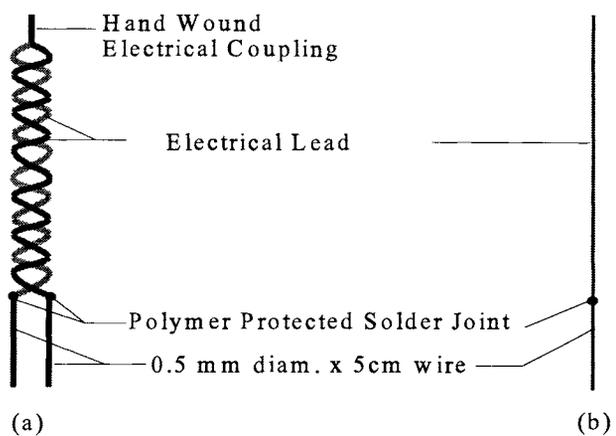


Figure 6. The form of split couple and single metal electrodes.



Figure 7. The ERE 20 Manganese Dioxide Reference Electrode. The porous cement frit is denoted by α .

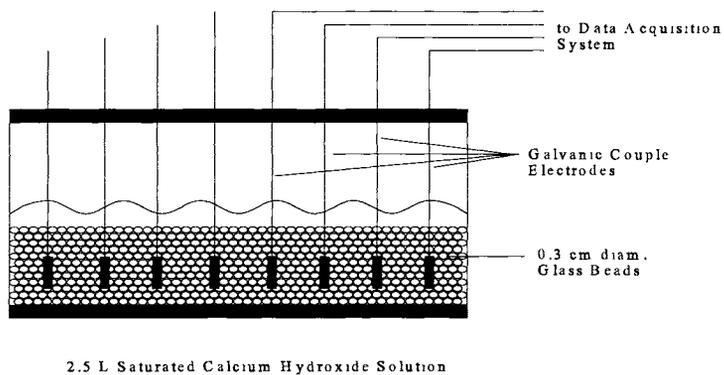


Figure 8. A schematic drawing of the tank setup for saturated calcium hydroxide stability tests.

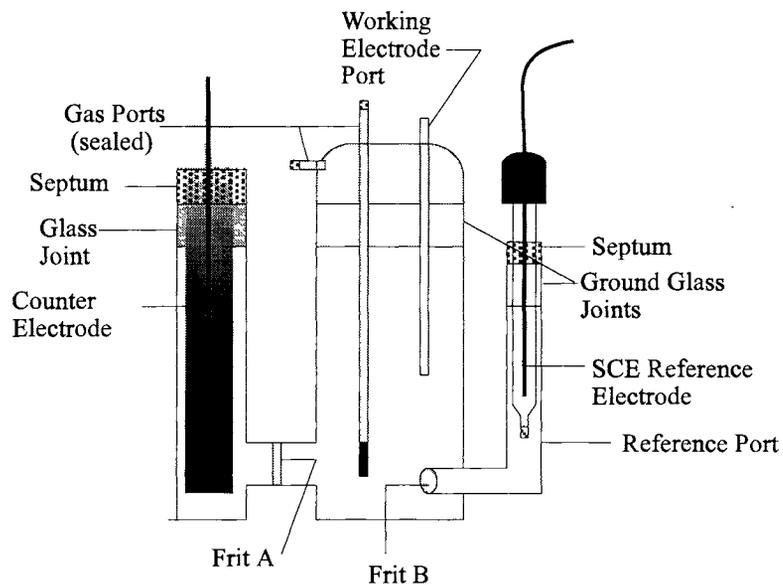
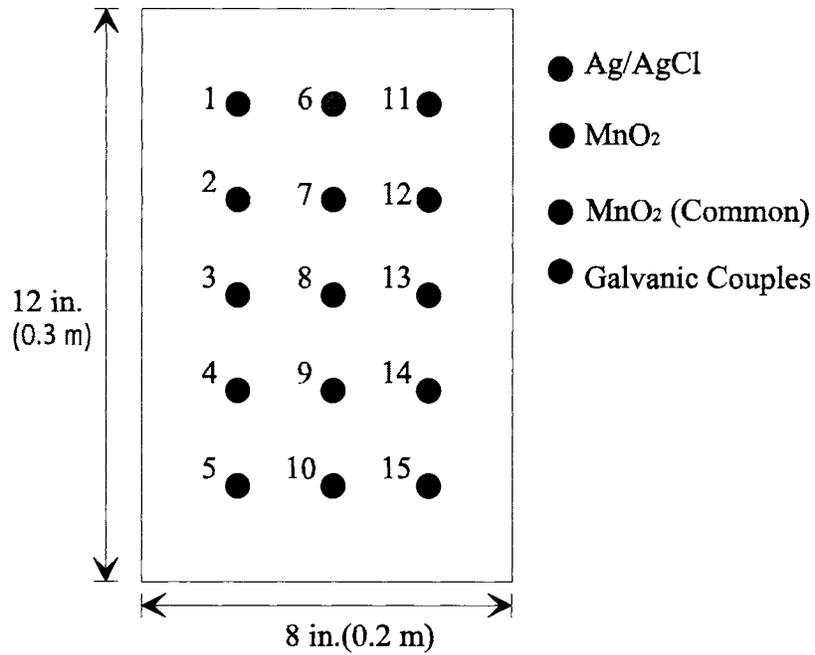
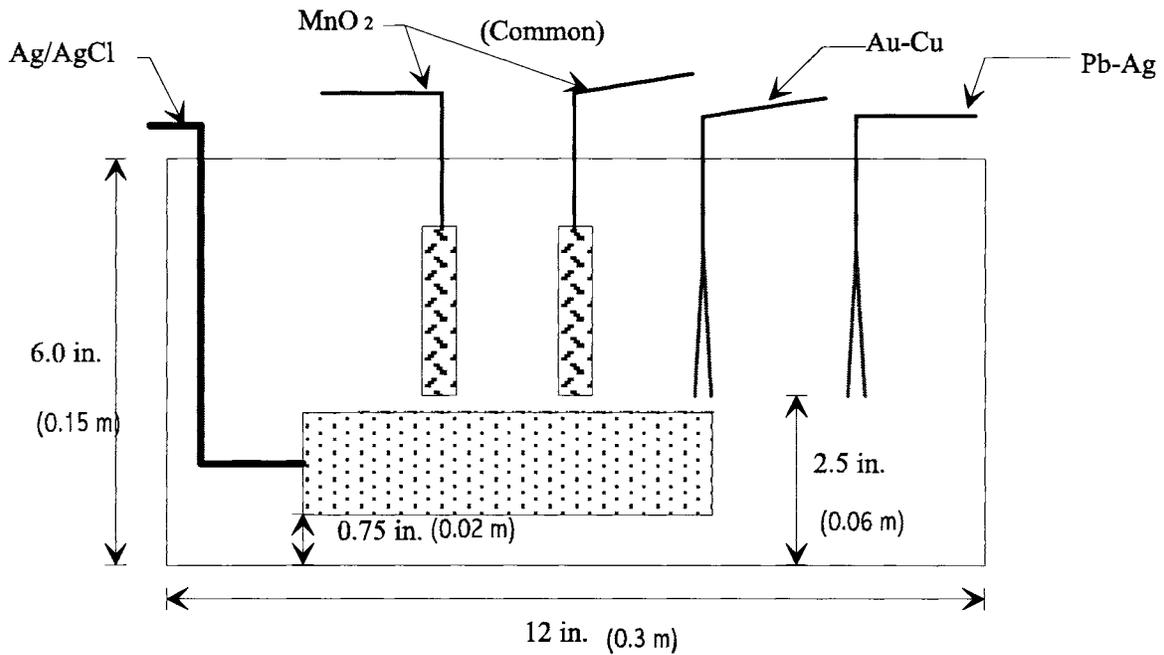


Figure 9. A schematic of the three-port electrochemical cell used in single metal electrode potentiodynamic scans.



(a)



(b)

Figure 10. the electrode setup within the concrete blocks: (a) the top view of the electrode, and (b) a cut-away view of the center row of electrodes.

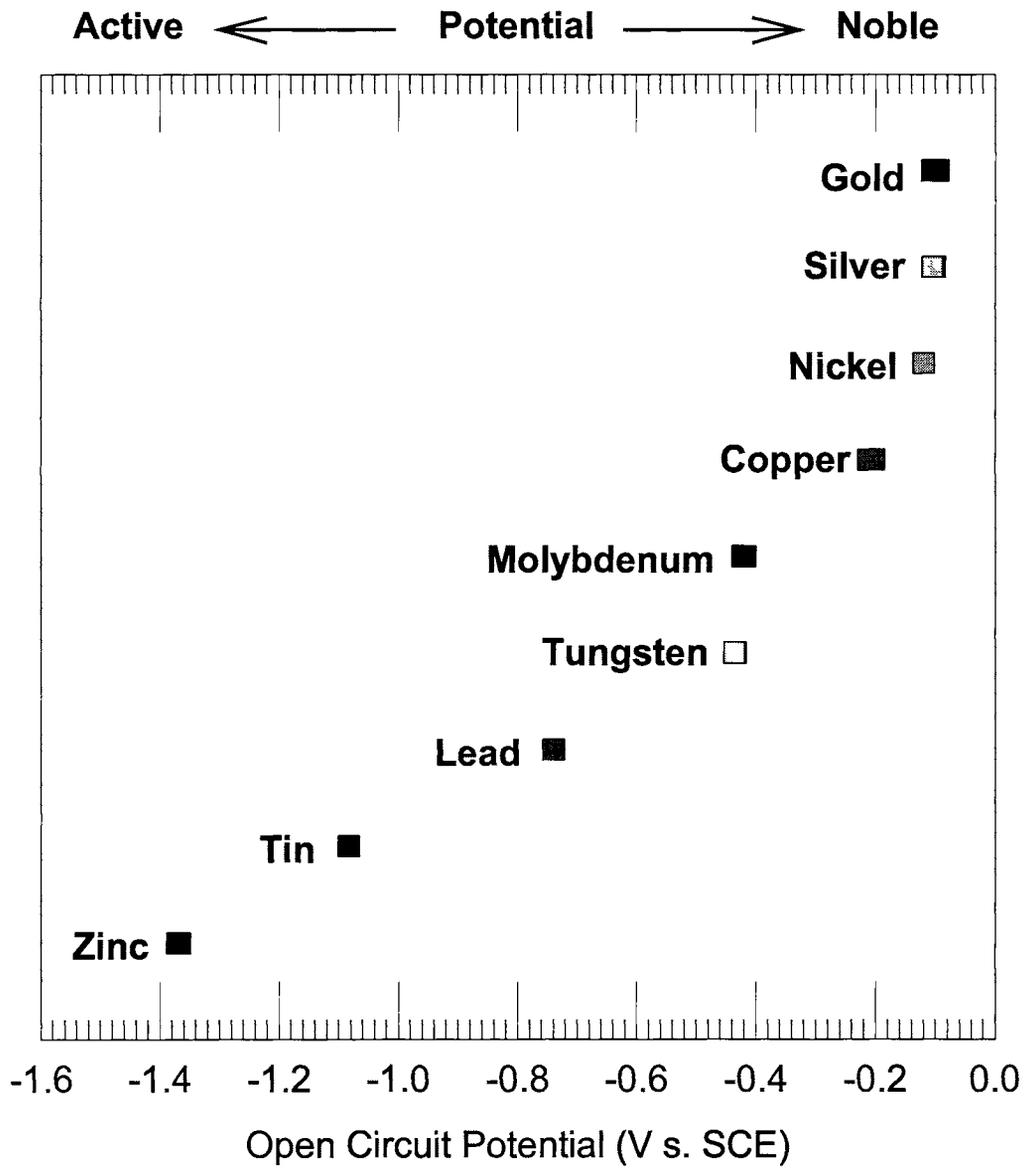


Figure 11. A galvanic series of couple components in saturated calcium hydroxide. More active metals are shown in the lower left and proceed upwards to the right in nobility.

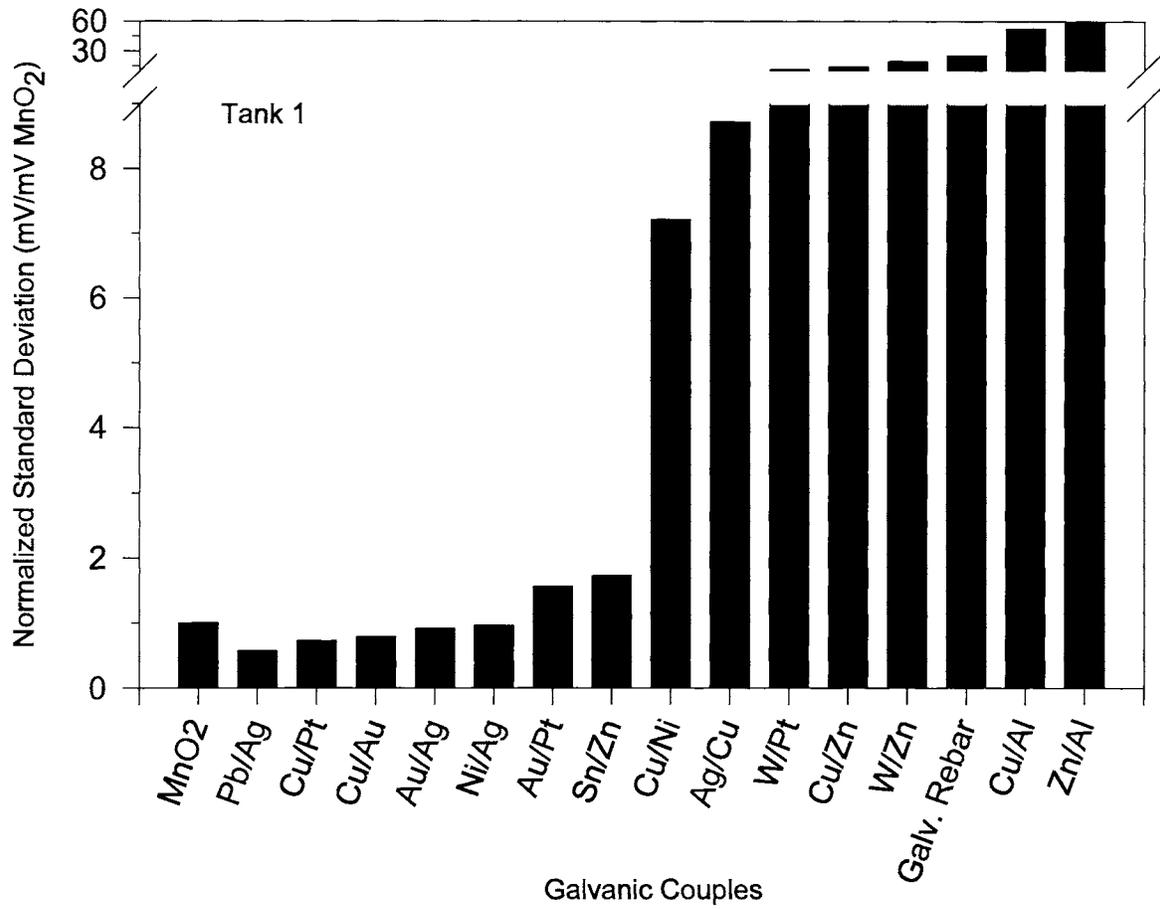


Figure 12. The normalized standard deviations for electrodes in (a) Tank 1, (b) Tank 2, and (c) Tank 3, range from less than 1 (better than the associated MnO₂ electrode) to greater than 60 mV/mV. The ranges of successful, unsuccessful, and promising electrodes can be obtained from these standard deviations.

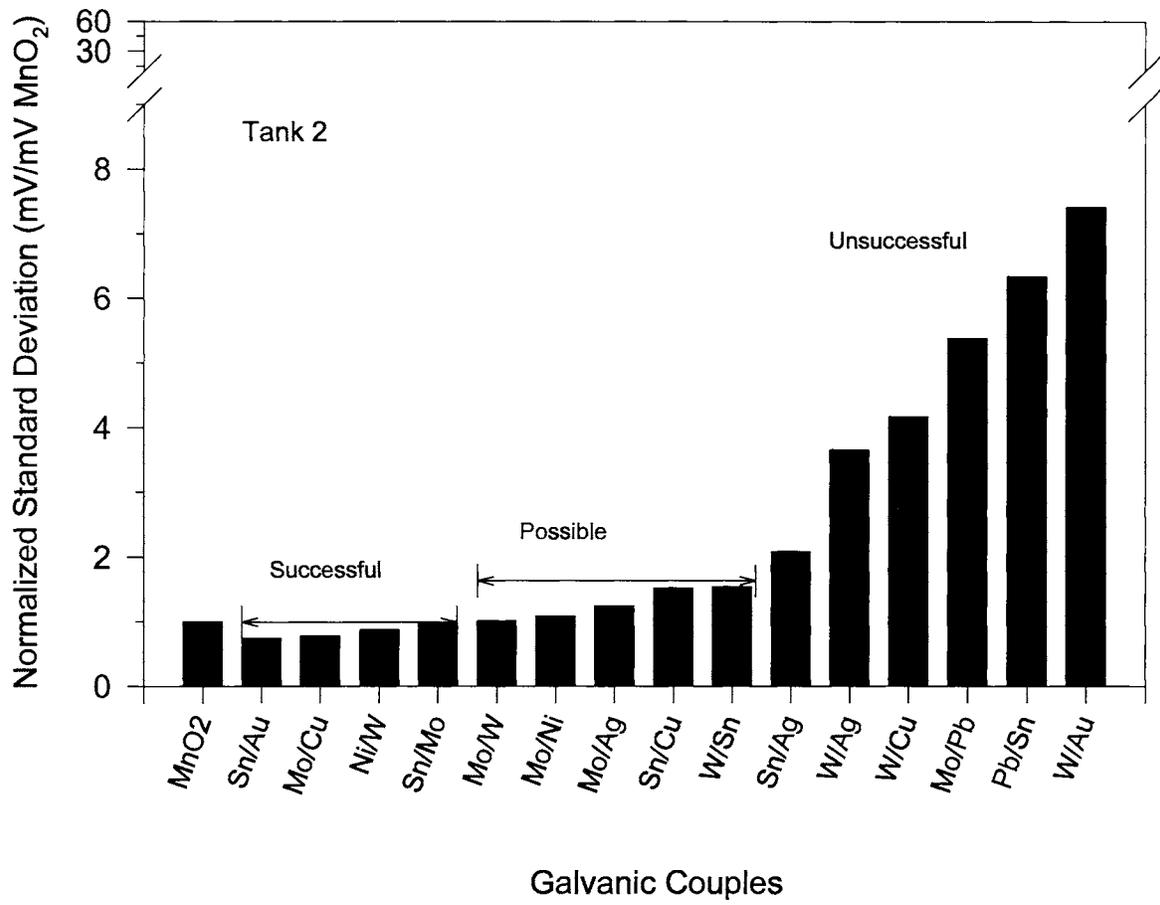


Figure 12 (b). Normalized standard deviations for Tank 2.

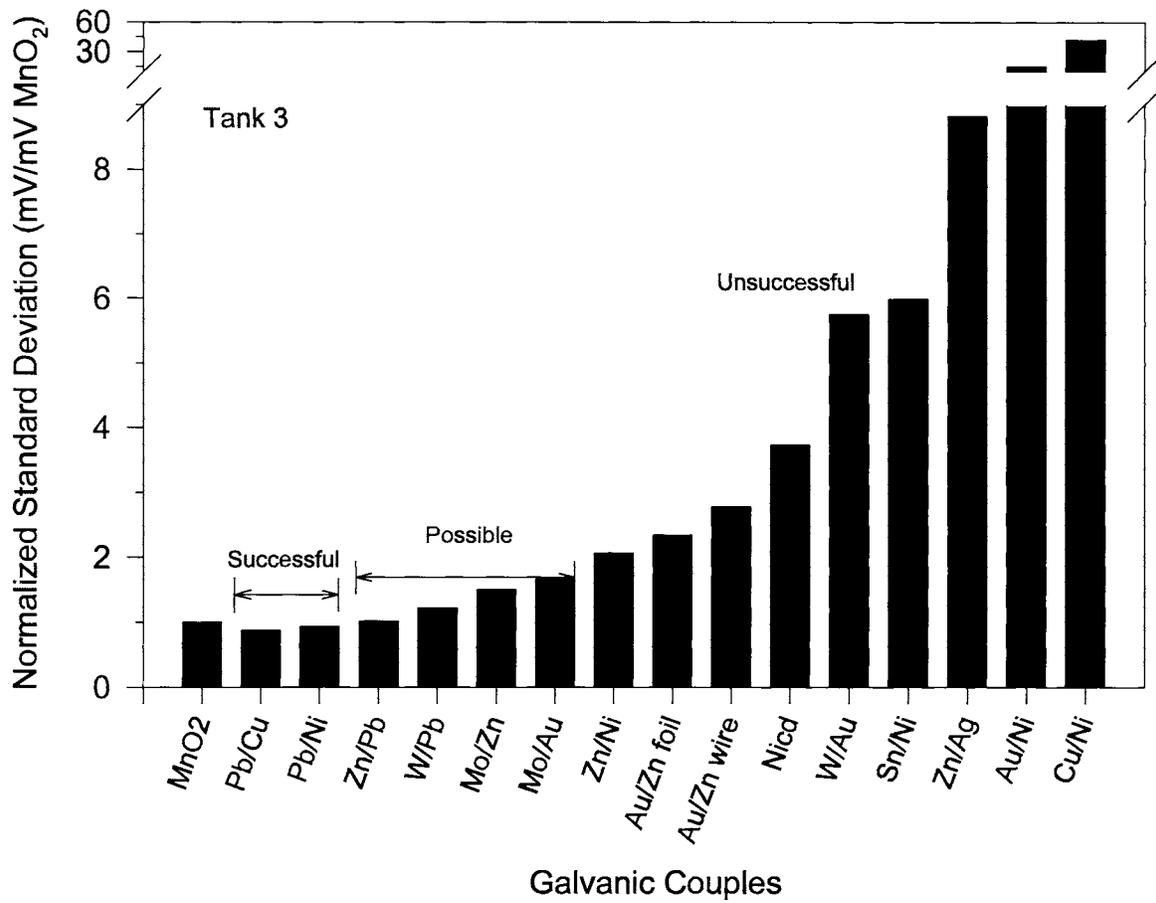


Figure 12 (c). Normalized standard deviations for Tank 3.

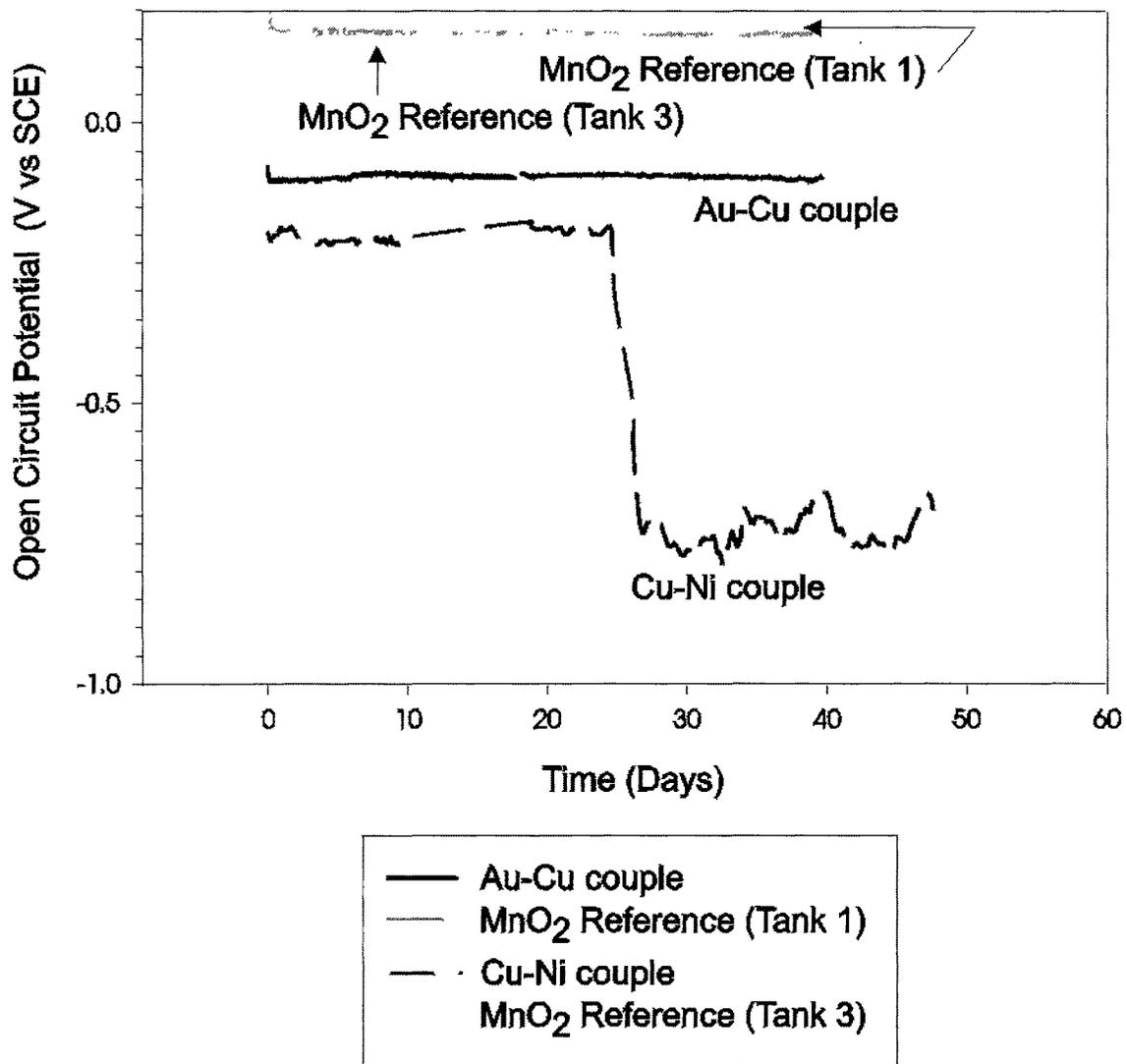


Figure 13. The open circuit behavior of successful and unsuccessful noble-noble galvanic couple electrodes. The unsuccessful electrode is marked by high noise and a large potential step. The successful electrode has low noise and as little drift as the manganese dioxide reference electrode.

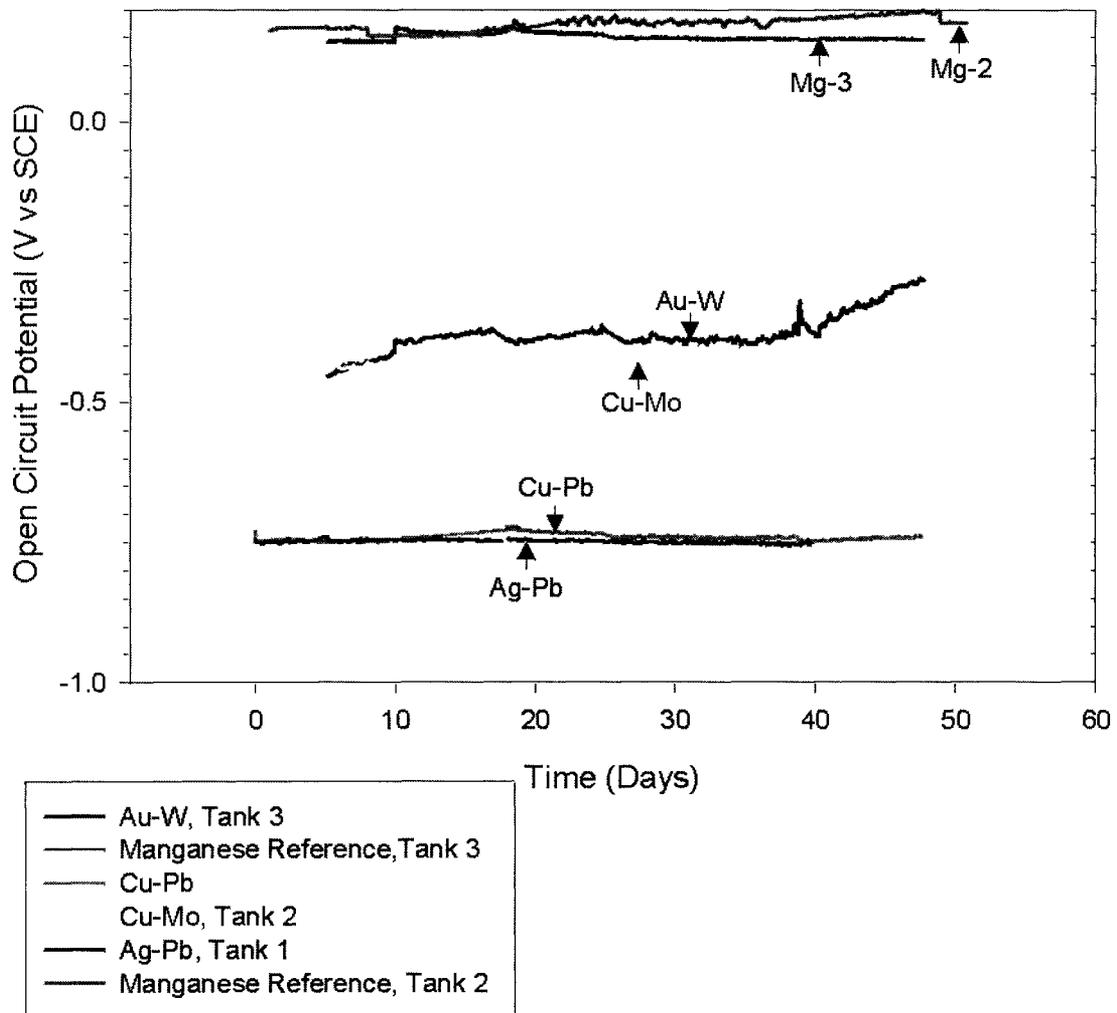


Figure 14. The open circuit behavior of noble-active couples. Successful couples have open circuit values that exhibit little drift and low standard deviations relative to the manganese dioxide reference. The unsuccessful couple has a steep drift in potential with time.

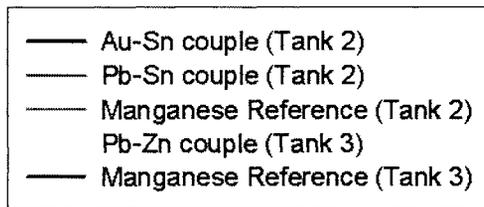
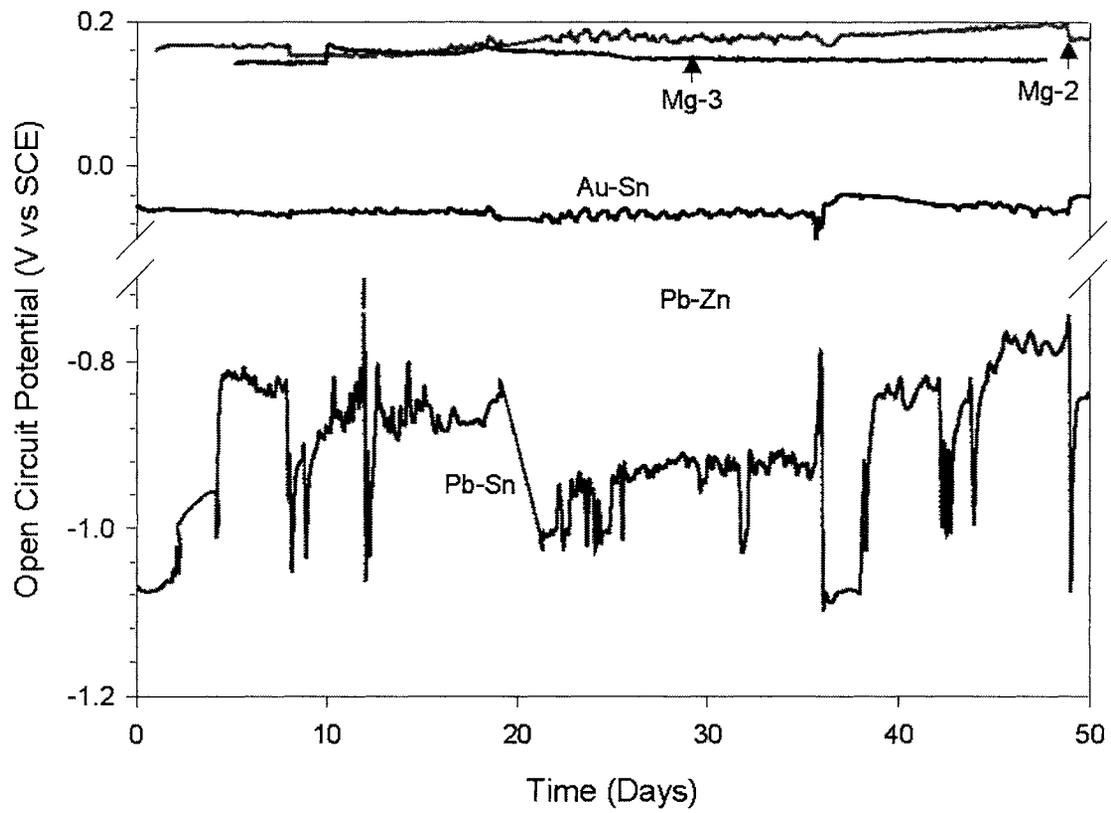


Figure 15. The stability behavior of noble/active galvanic couples in saturated calcium hydroxide. The open circuit behavior of the successful couples has extremely low noise (standard deviation) compared to the large variations seen in the unsuccessful Pb-Sn couple.

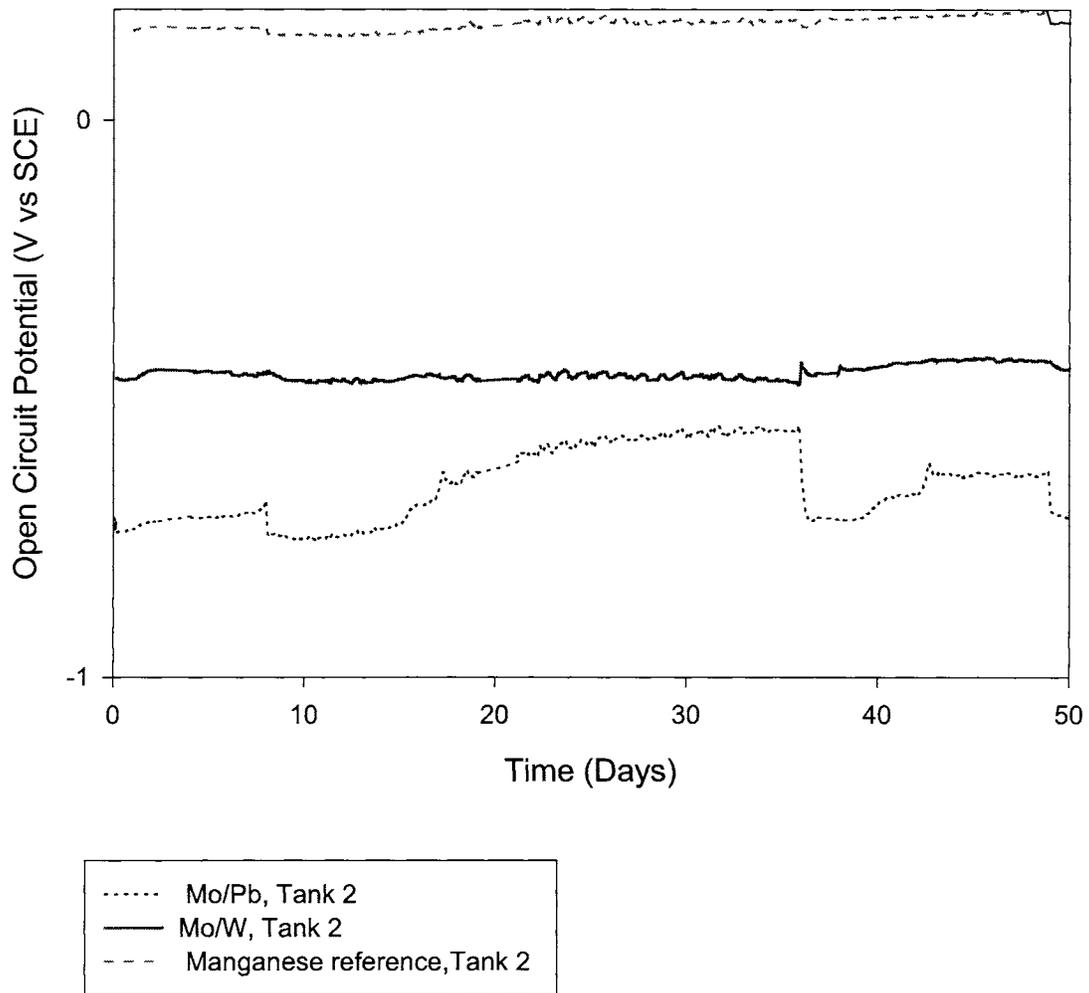


Figure 16. The stability behavior of active-active galvanic couples in saturated calcium hydroxide shows that stable couples (Mo-W) have steady open circuit potentials like the manganese dioxide reference electrode, but unstable electrodes (Mo-Pb) have large potential shifts.

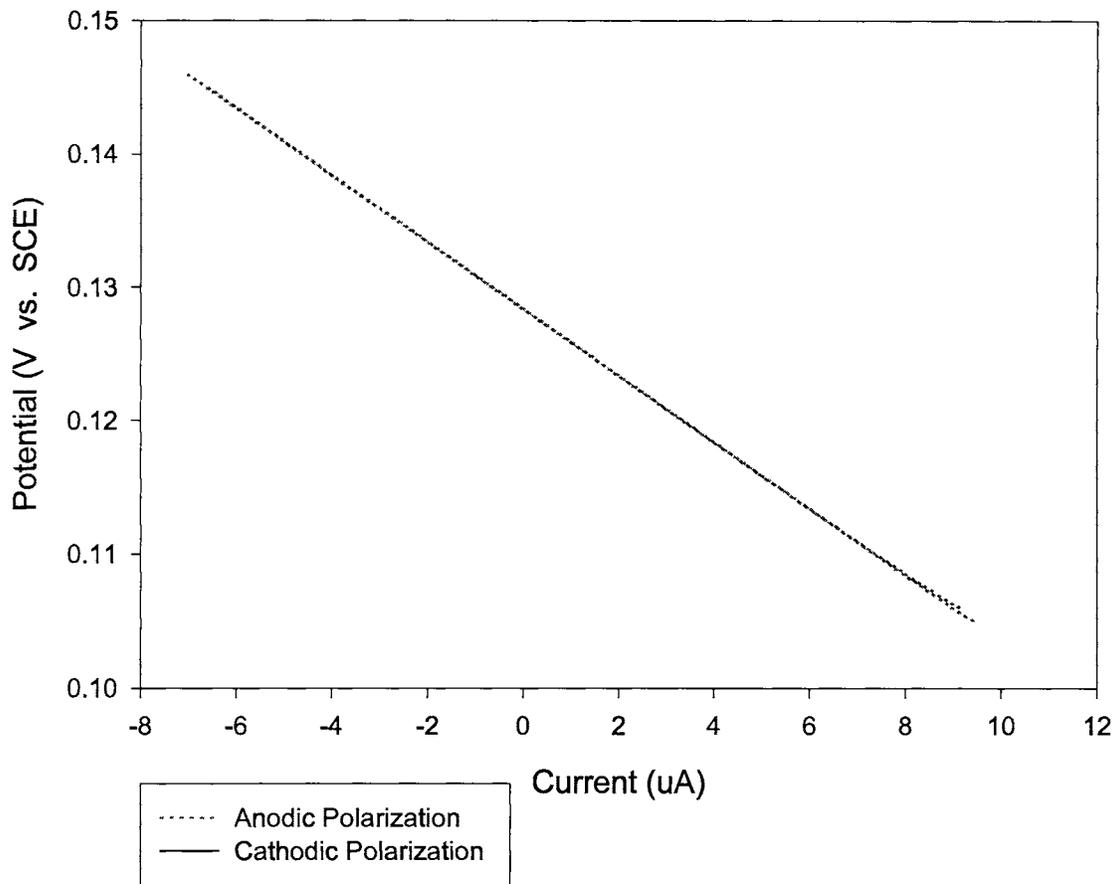


Figure 17. the micro-polarizability of true reference electrodes. The manganese dioxide reference electrode is shown.

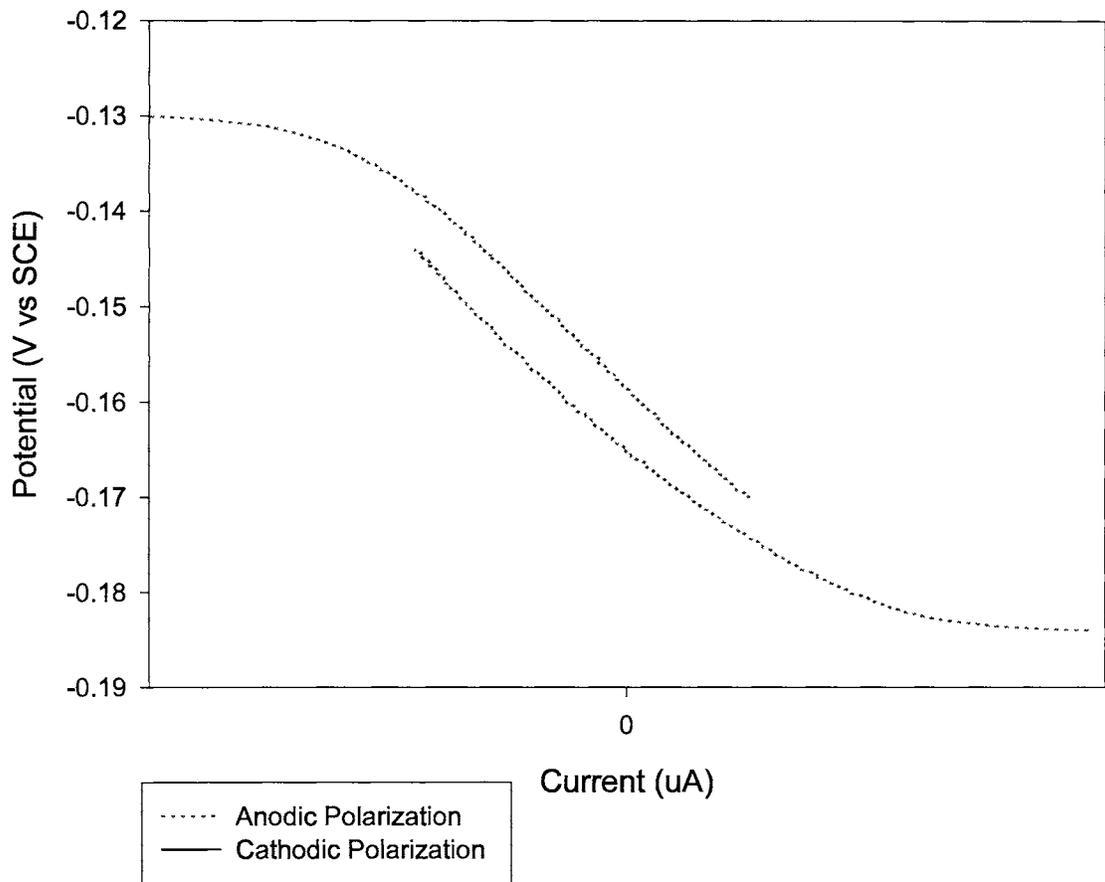


Figure 18. The micro-polarizations for a Cu-Au, noble-noble, couple in quiescent saturated calcium hydroxide. The hysteresis in the curve shows the recovery of the couple from the polarized state back to steady state.

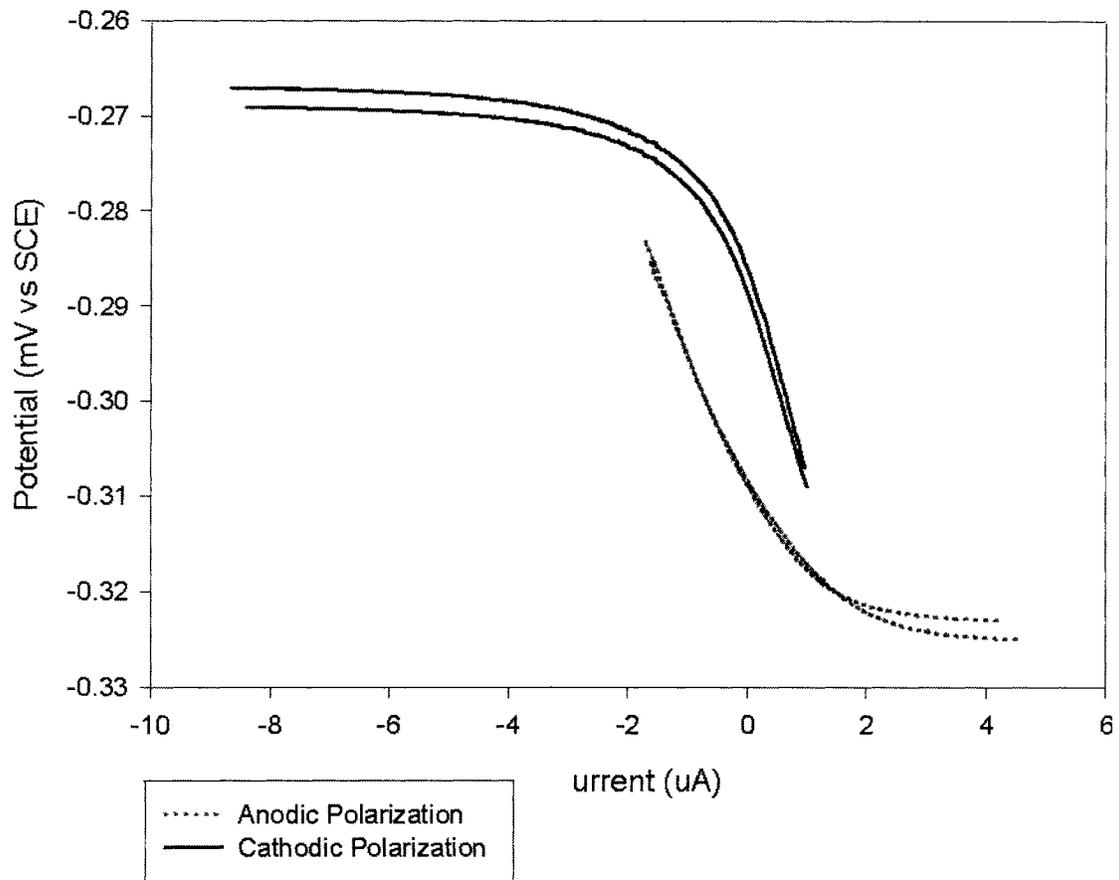


Figure 19. The micro-polarizability and hysteresis of the Au-Cu, noble-noble, couple in deaerated calcium hydroxide. The low slope seen in the polarization of this couple shows an increase in stability under deaerated conditions.

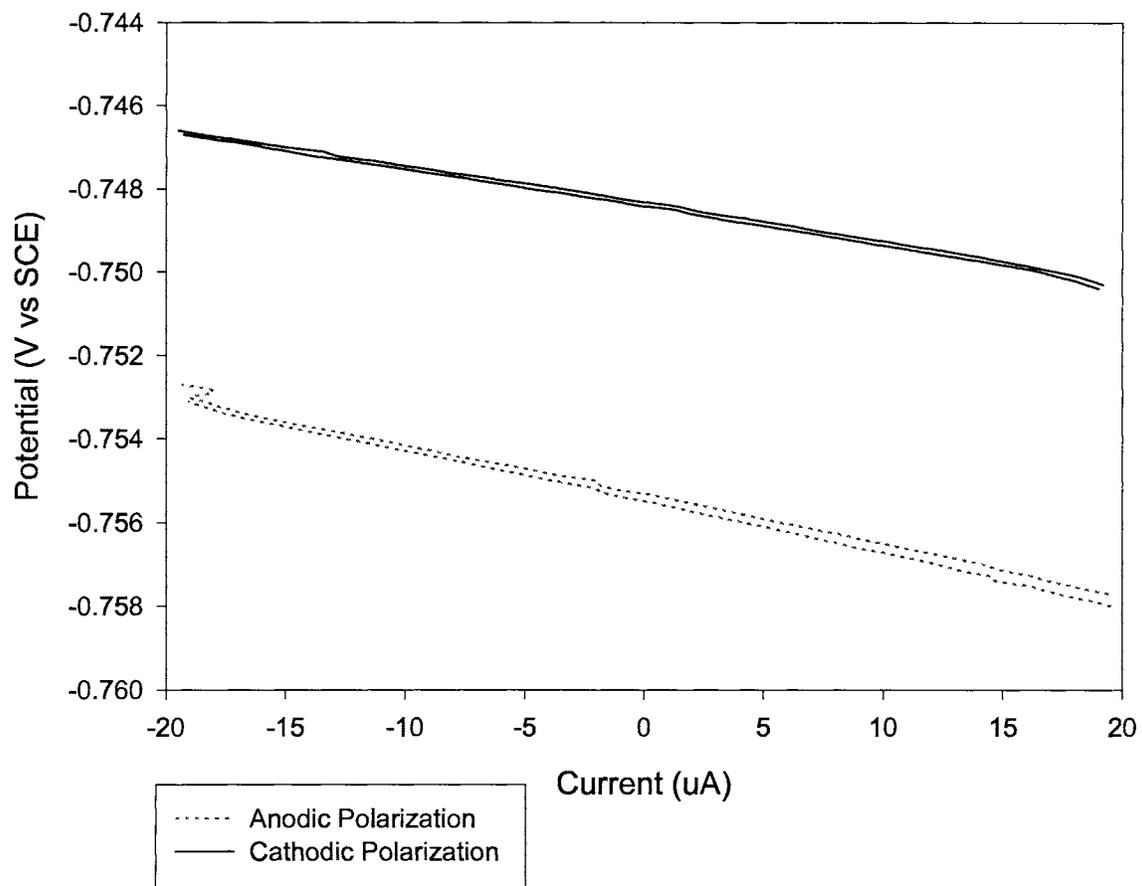


Figure 20. The micro-polarizability of the Ag-Pb, noble-active couple in quiescent saturated calcium hydroxide. The anode control of this couple provides high stability and low polarizability.

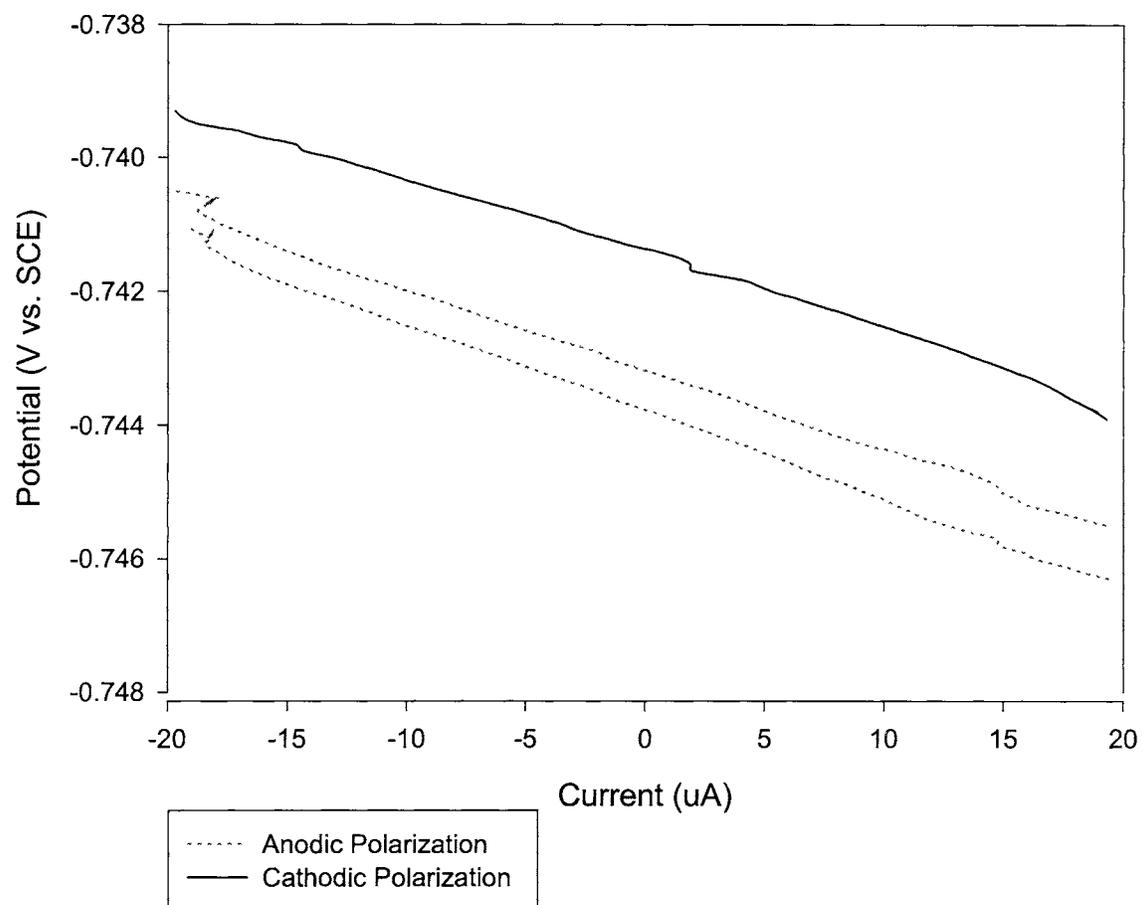


Figure 21. The micro-polarizability and hysteresis behavior of the Ag-Pb, noble-active couple in deaerated, saturated calcium hydroxide solution. This couple has a low polarizability in deaerated solution.

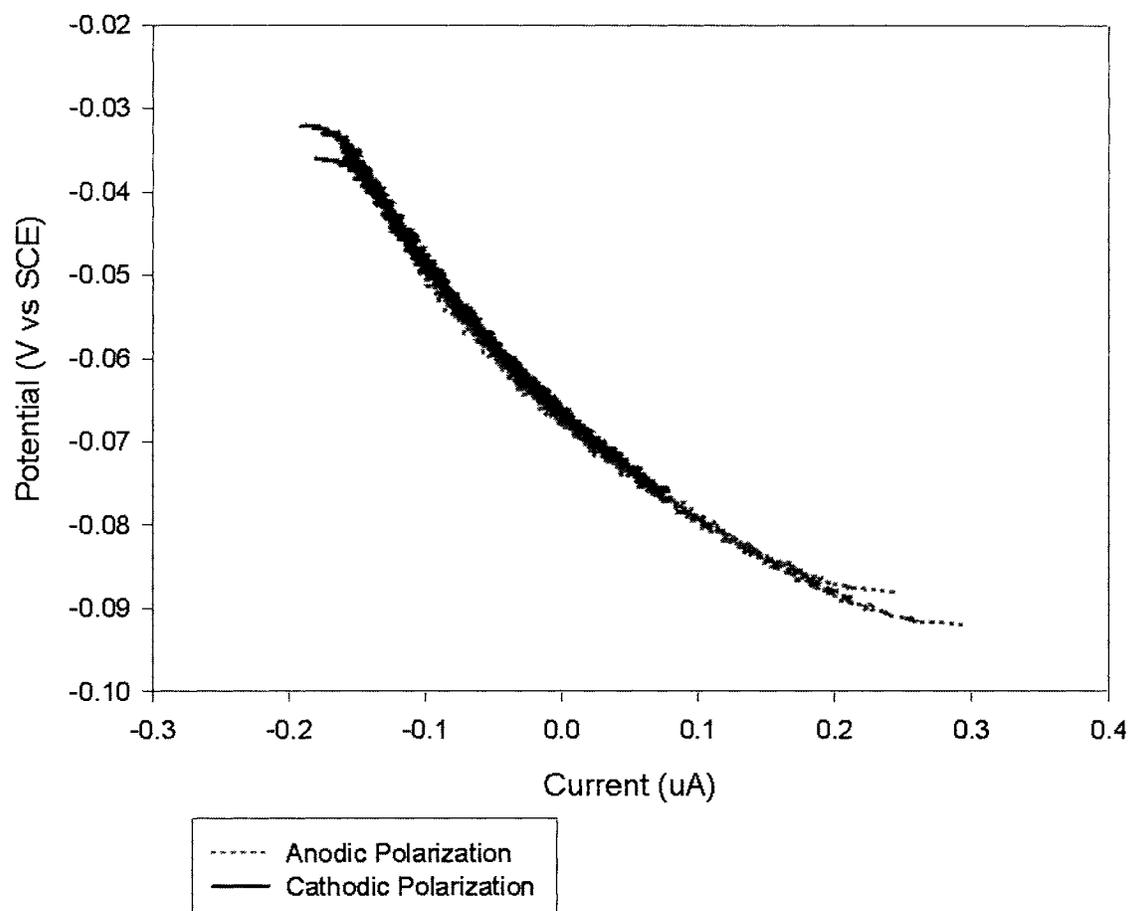


Figure 22. The micro-polarizability and hysteresis behavior of the Au-Sn, noble-passive couple in quiescent saturated calcium hydroxide. This couple exhibits limited hysteresis, returning to steady state readily.

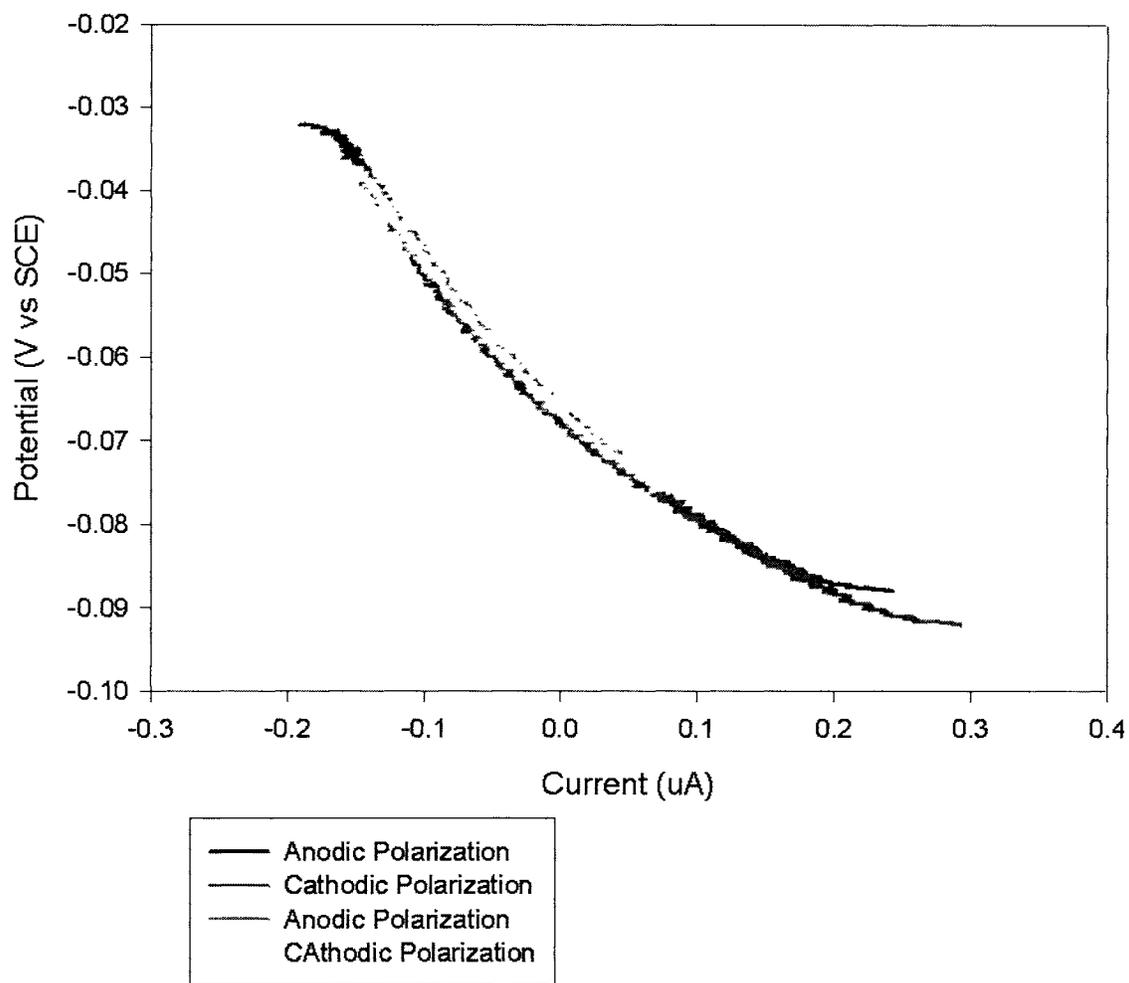


Figure 23. Micro-polarization and hysteresis behavior for the Au-Sn, noble-passive couple in decreased saturated calcium hydroxide. Greater hysteresis is observed in this situation than found in quiescent solution.

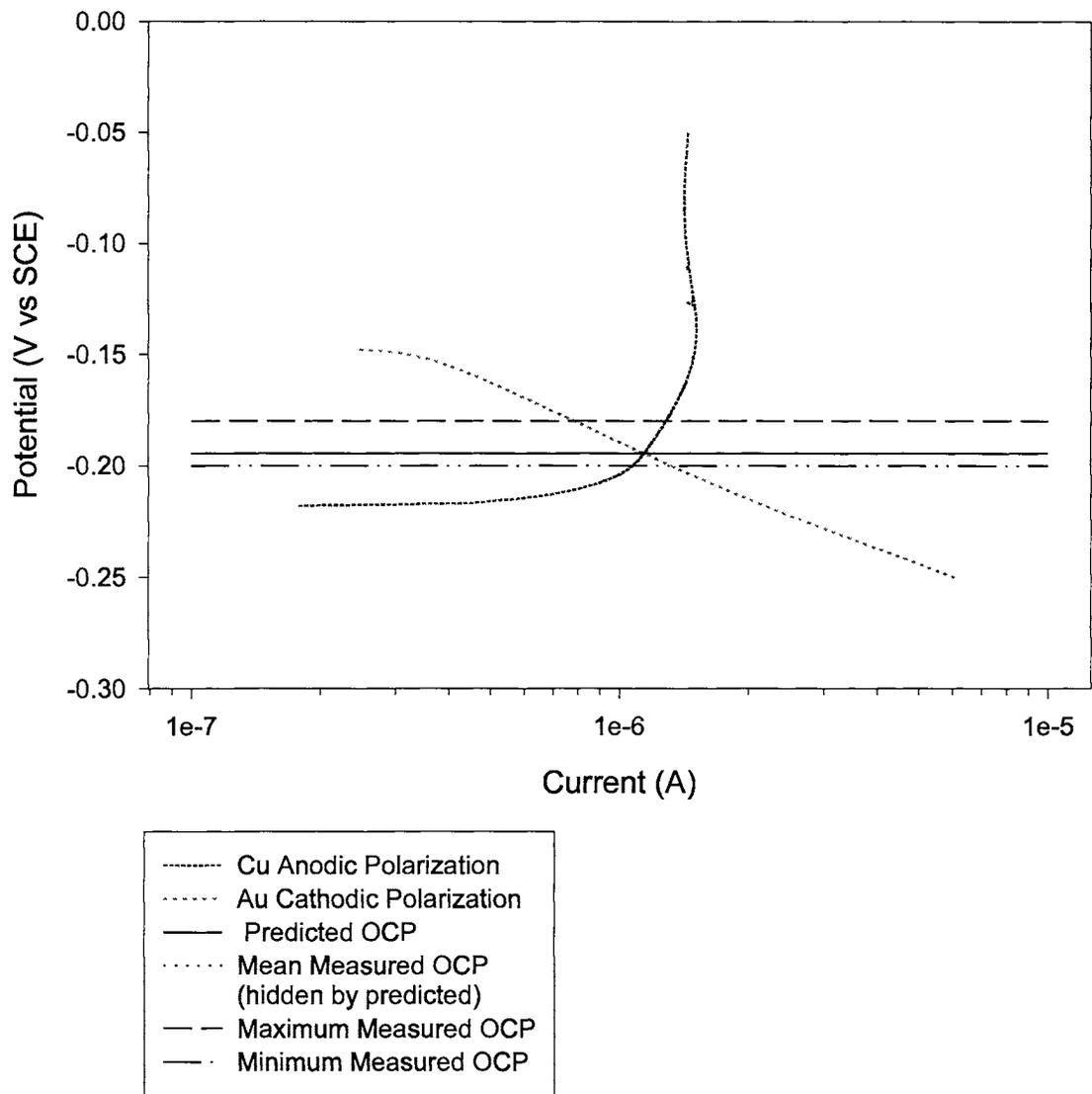


Figure 24. (a) The mixed potential behavior of the Au-Cu noble-noble couple in quiescent saturated calcium hydroxide, after reaching a steady state under coupled conditions. The predicted and measured couple potentials are shown.

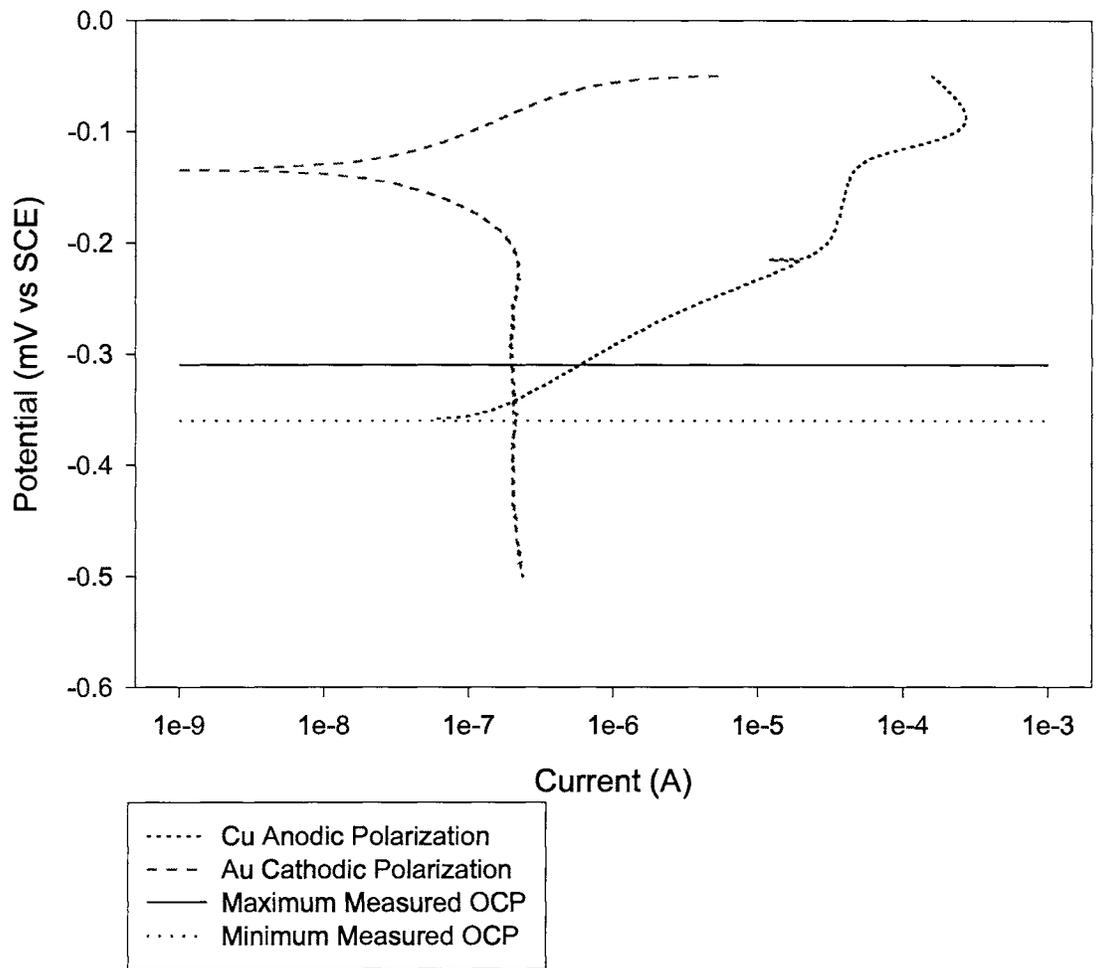


Figure 25. The mixed potential behavior of the Au-Cu couple after reaching steady state under coupled conditions in deaerated, saturated calcium hydroxide.

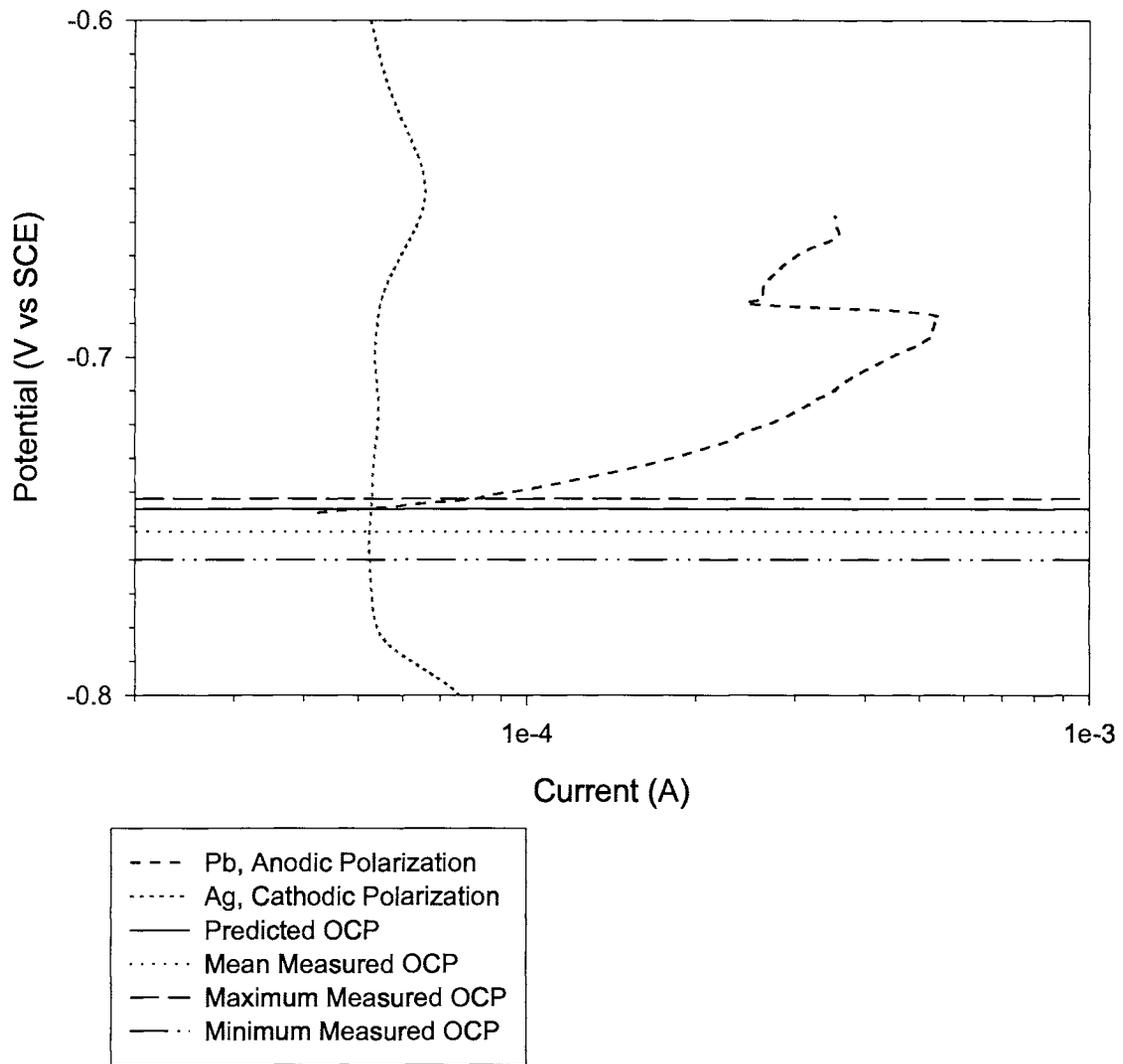


Figure 26. The polarization behavior of the anode and cathode of the Ag-Pb, noble-active couple after reaching steady state under coupled conditions. The intersection of the anodic and cathodic currents is plotted to show the predicted couple potential along with the mean, maximum and minimum measured couple potentials.

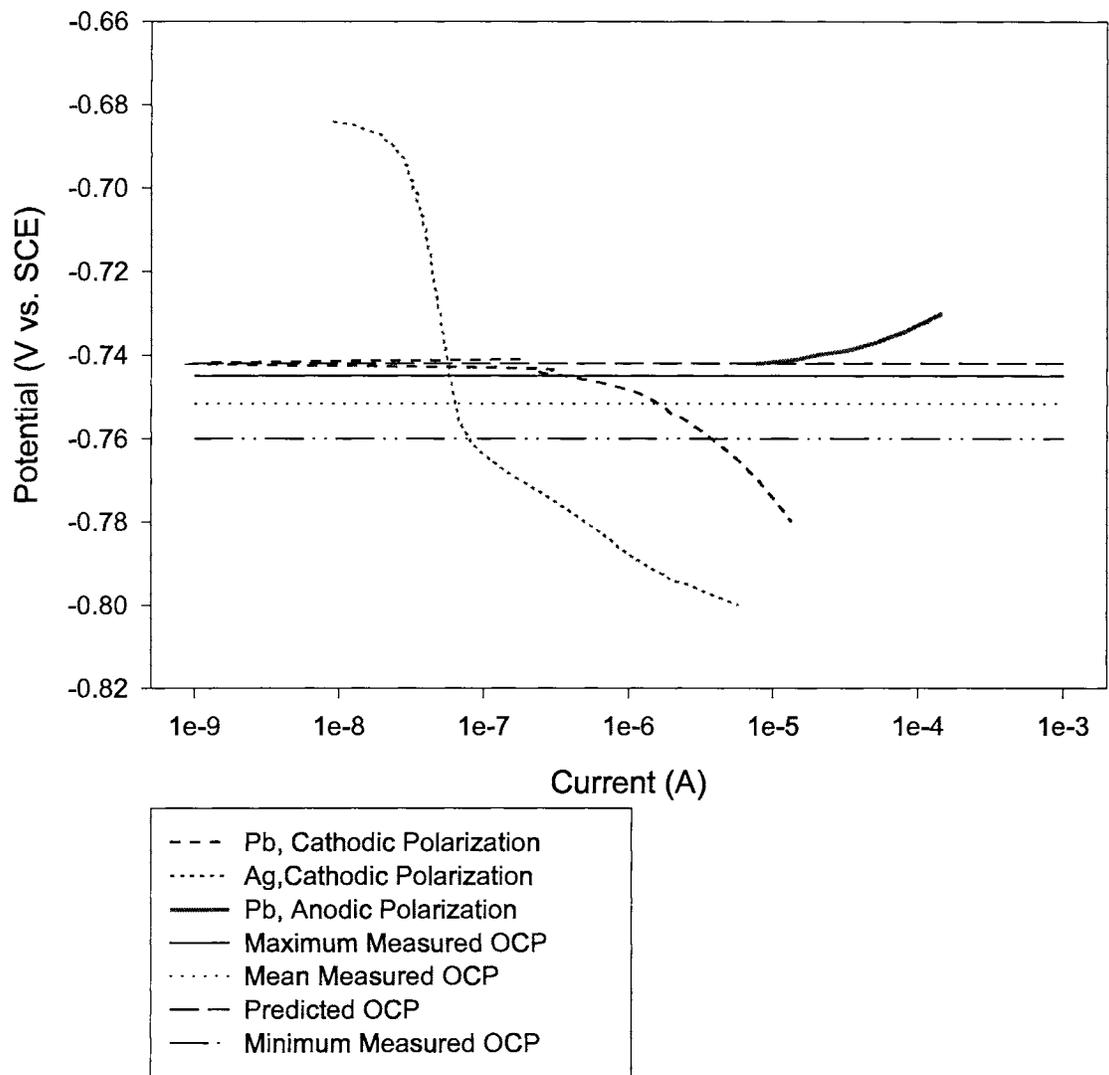


Figure 27. The polarization behavior for the split Ag-Pb, noble-noble couple, in deaerated saturated calcium hydroxide.

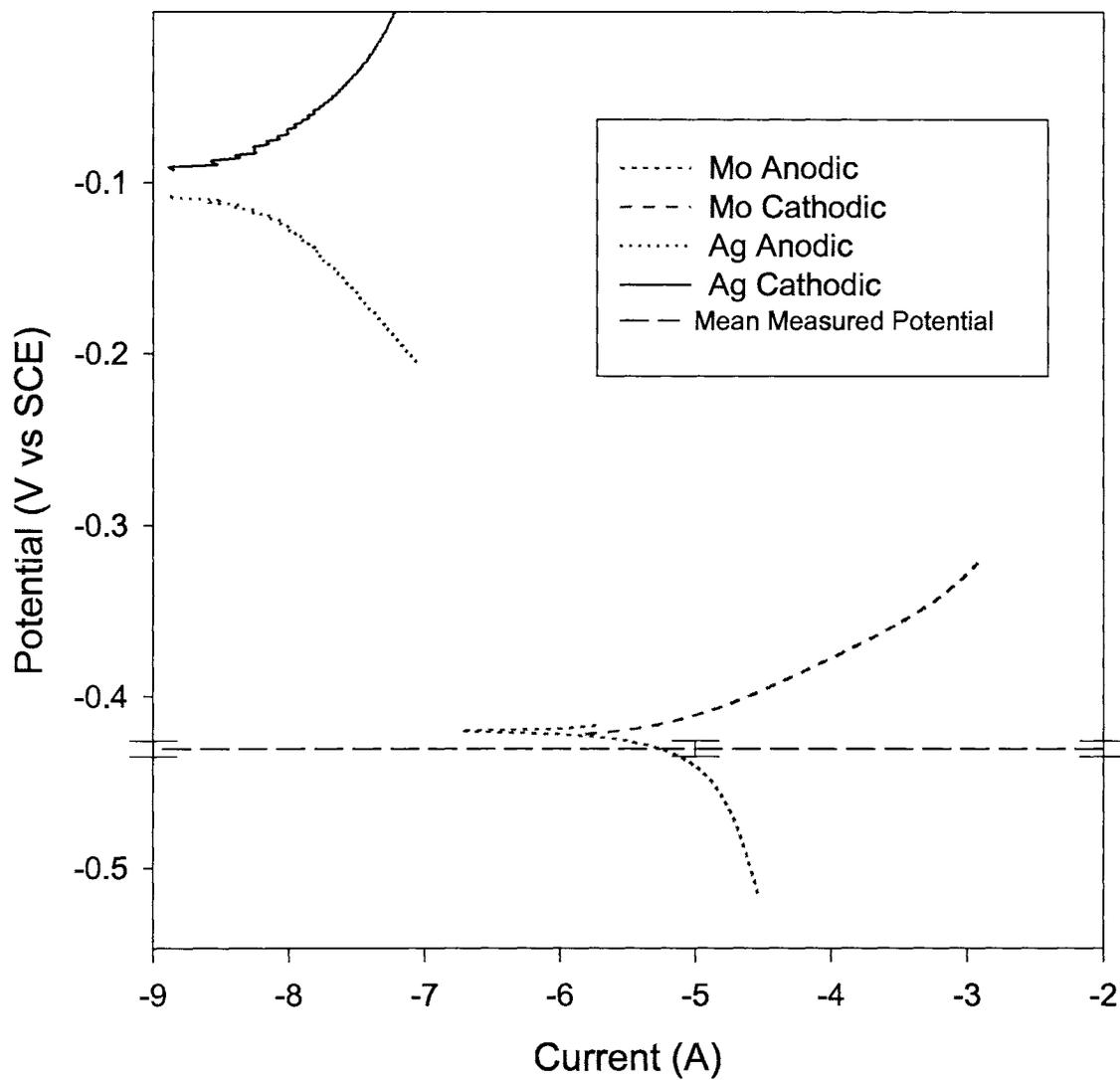


Figure 28. The separate polarization behaviors of Ag and Mo after reaching steady state under uncoupled conditions in saturated calcium hydroxide. The cathodic reaction is extrapolated to intersect the anodic reaction and determine the couple potential.

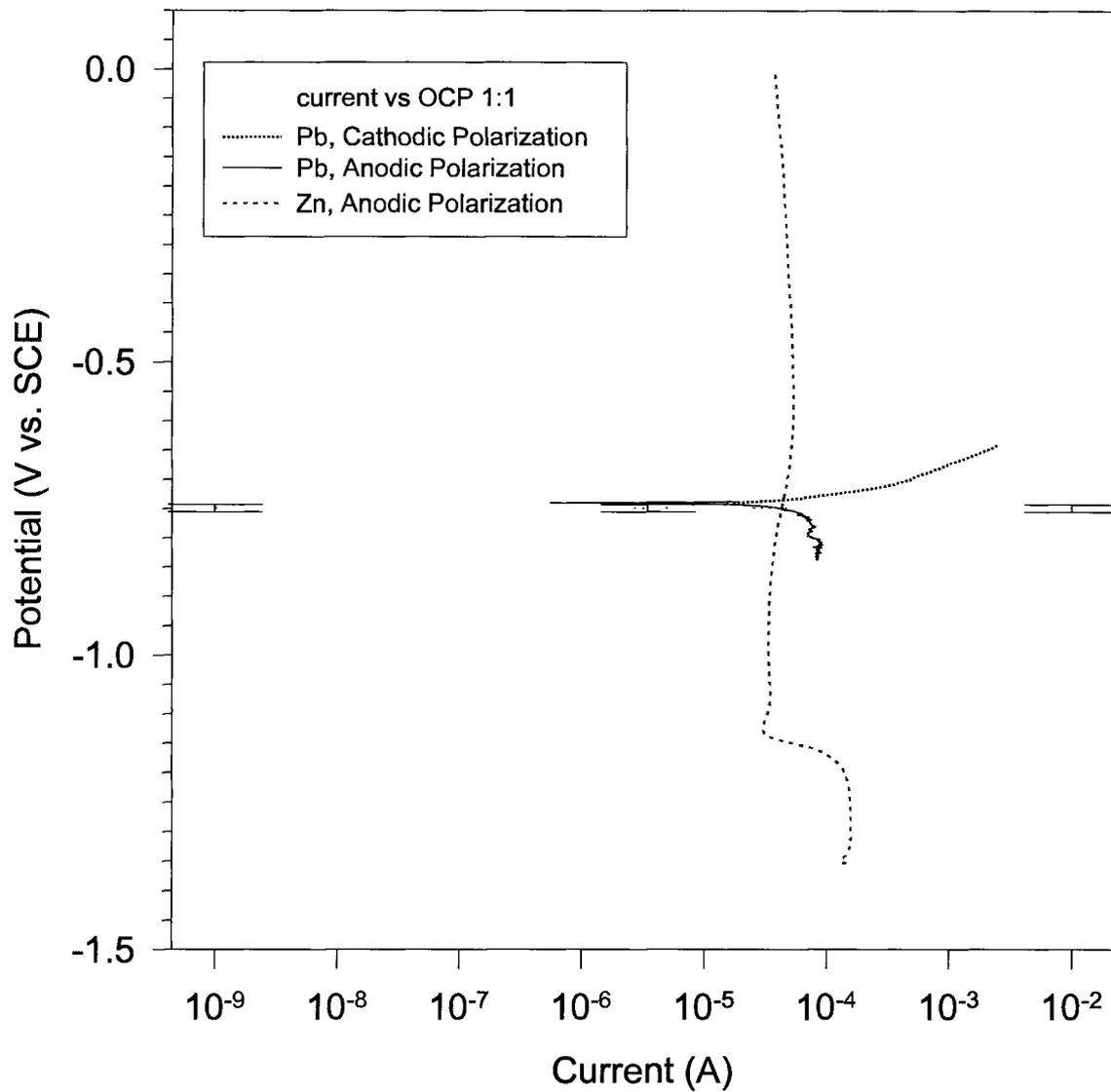


Figure 29. The single metal polarization behavior of Pb and Zn, showing the mixed potential behavior of the Pb-Zn (active-Passive) couple. The couple potential falls near the open circuit potential of Pb.

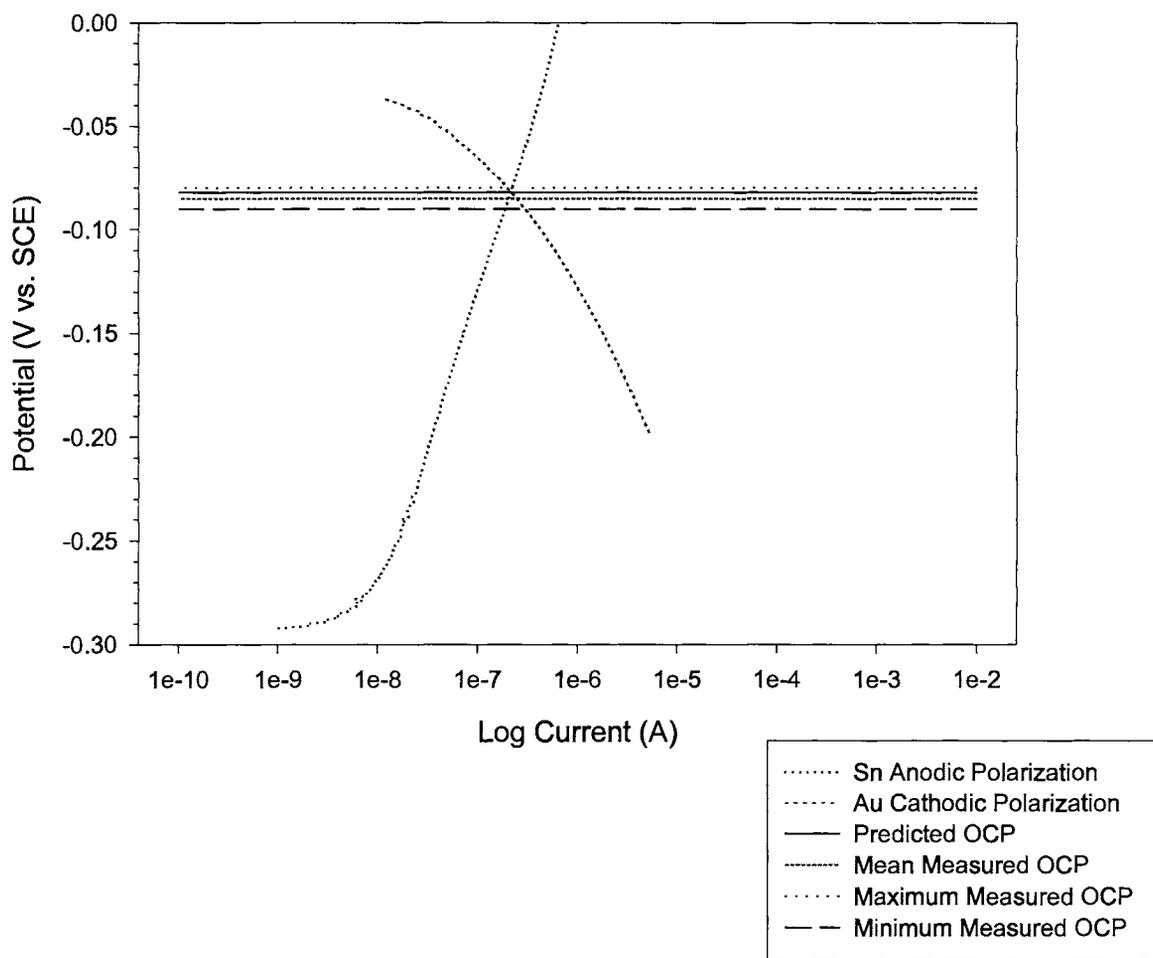


Figure 30. The mixed potential behavior of the Au-Sn, noble-passive, couple in quiescent saturated calcium hydroxide after reaching steady state under coupled conditions.

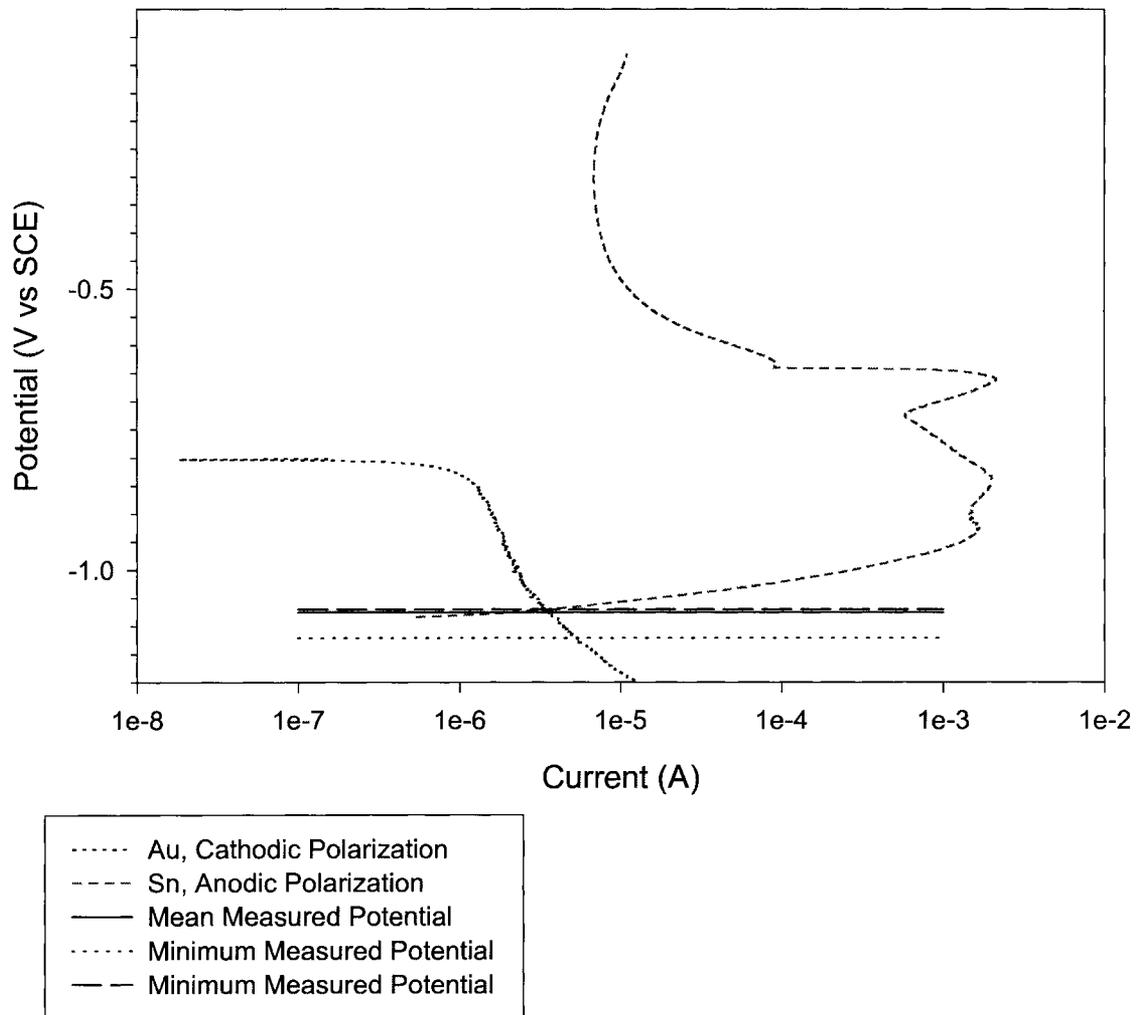


Figure 31. The mixed potential behavior of the Au-Sn, noble-passive, couple in deaerated saturated calcium hydroxide after reaching steady state under coupled conditions.

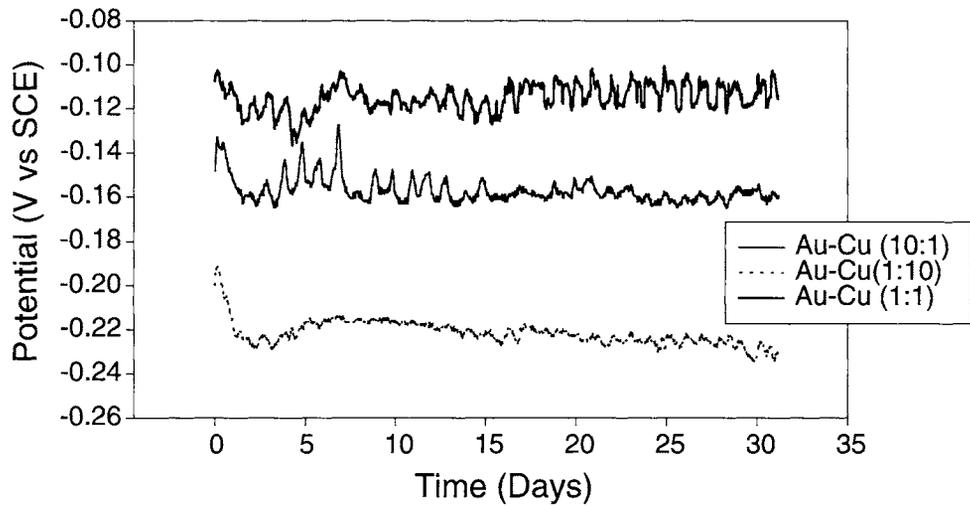


Figure 32. The open circuit potential of the Au-Cu (noble-noble) couple with cathode to anode ratios of 1:1, 1:10, and 10:1 in quiescent saturated calcium hydroxide.

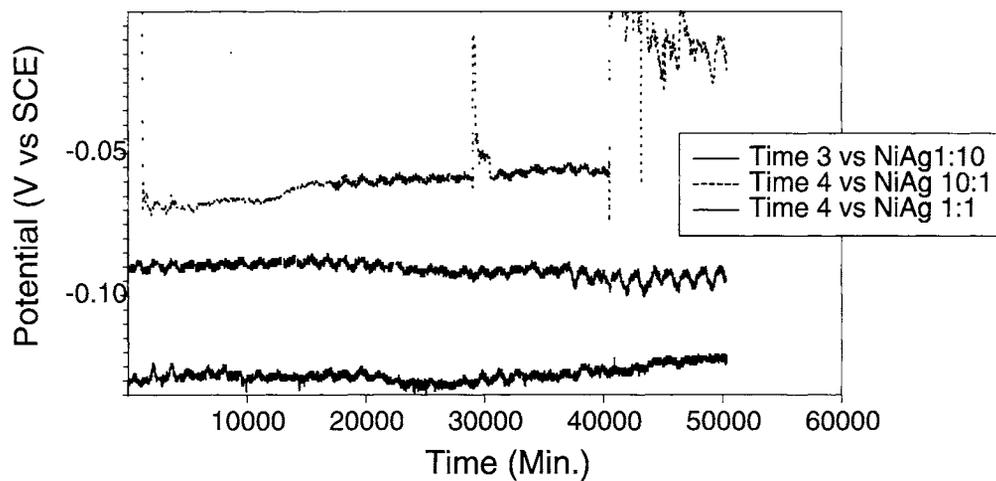


Figure 33. The open circuit potential behavior of the Ag-Ni (noble-noble) couple with cathode to anode ratios of 1:1, 1:10, and 10:1 in quiescent saturated calcium hydroxide.

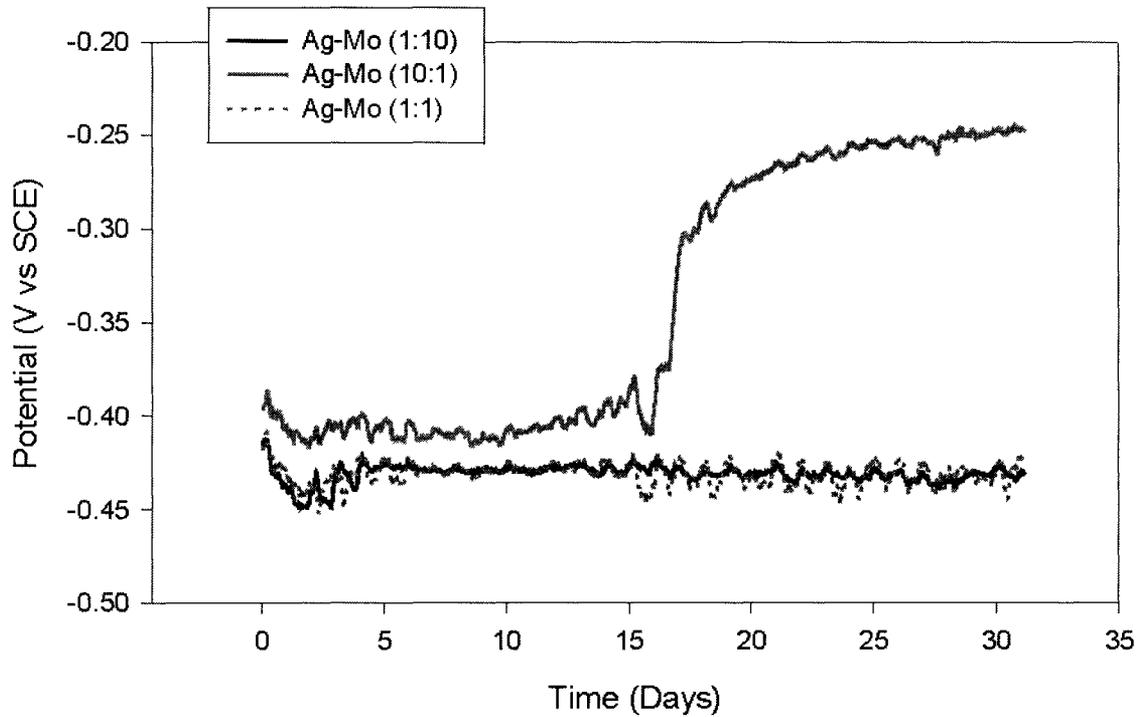


Figure 34. The effect of varying cathode to anode area ratios (1:1, 1:10, and 10:1) on the open circuit behavior of the Ag-Mo (noble-active) couple in quiescent saturated calcium hydroxide.

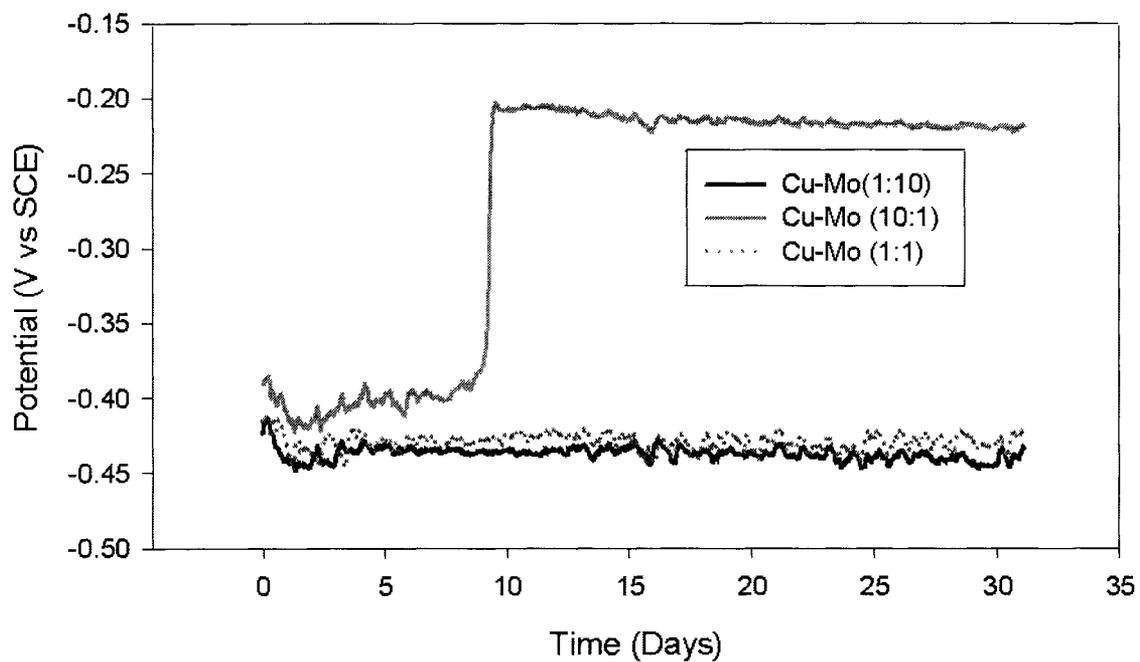


Figure 35. the effect of varying cathode to anode area ratios (1:1, 1:10, and 10:1) on the open circuit behavior of the Cu-Mo (noble-active) couple in quiescent saturated calcium hydroxide.

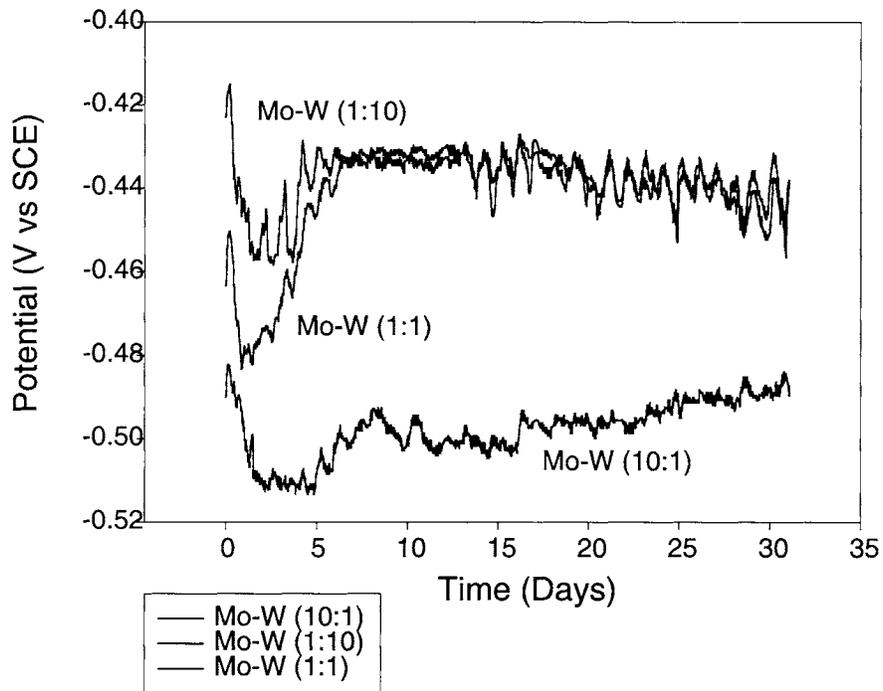


Figure 36. the effect of varying cathode to anode area ratios (1:1, 1:10, and 10:1) on the open circuit behavior of the Mo-W (active-active) couple in quiescent saturated calcium hydroxide.

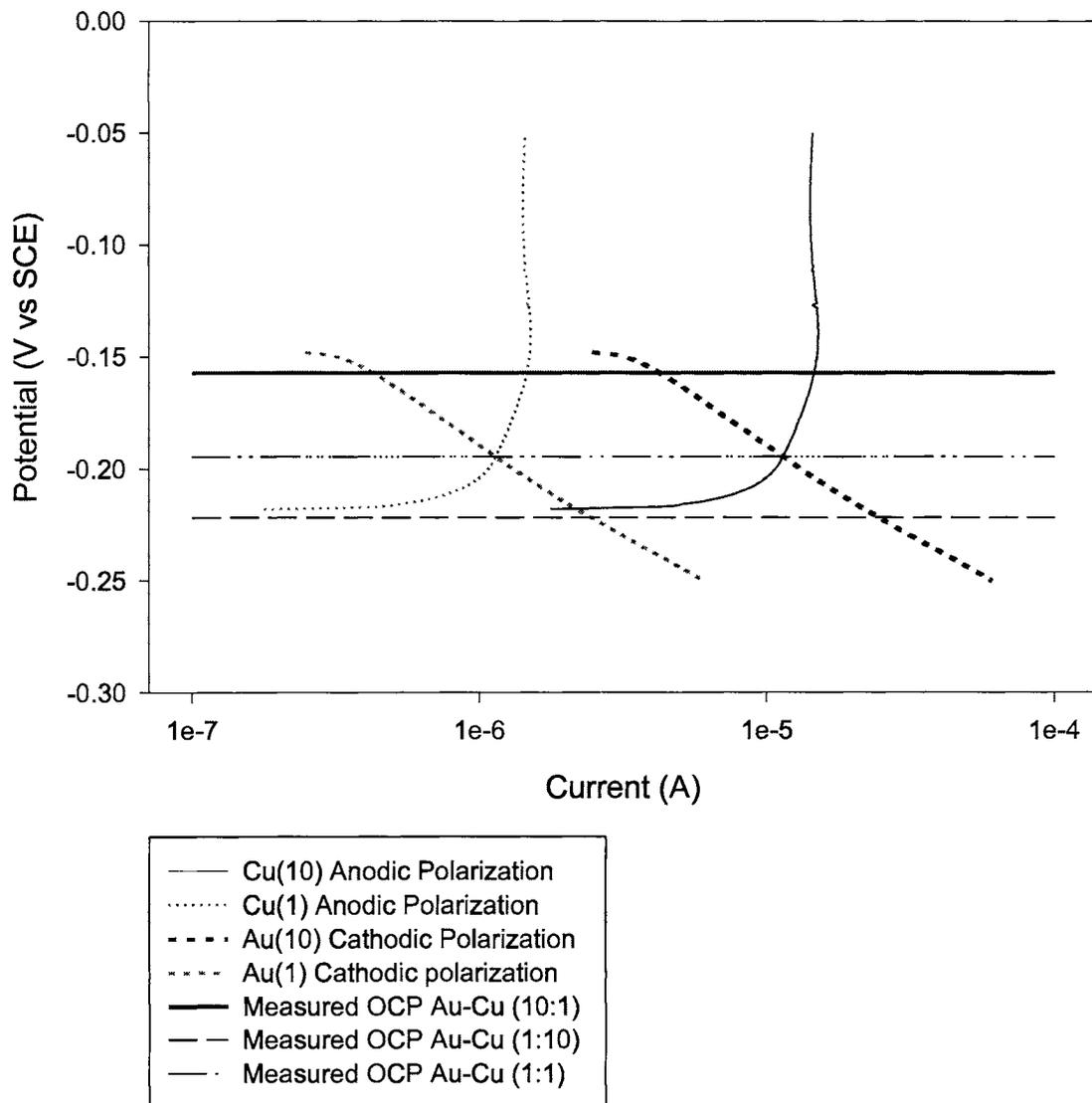


Figure 37. The effect of varying the cathode to anode area ratios of the Au-Cu couple in quiescent saturated calcium hydroxide as predicted by the mixed potential behavior of the individual couple halves after reaching steady state as a couple.

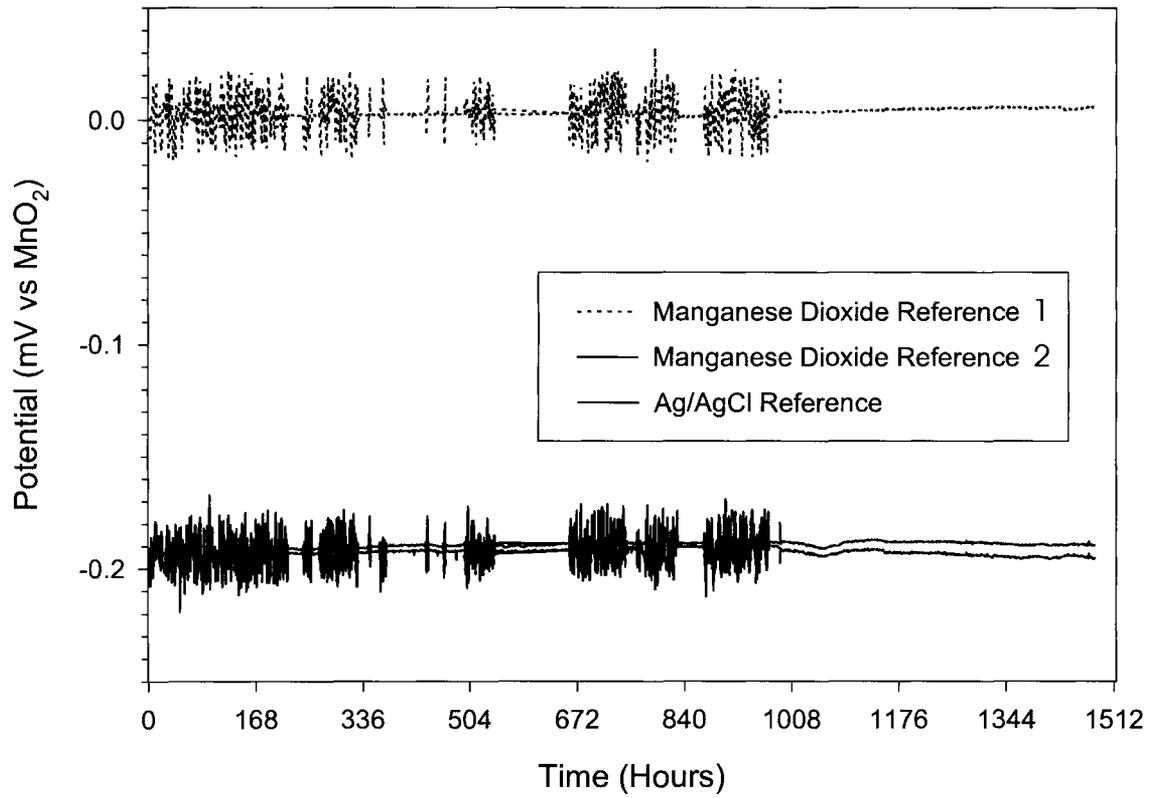


Figure 38. The reference potentials for the manganese dioxide and silver chloride commercial electrodes in concrete over 2000 hours. The stability of the Ag/AgCl electrode is plotted as determined against both manganese electrodes. All three electrodes show similar, stable behavior. The standard deviations of these electrodes are caused by noise and drift.

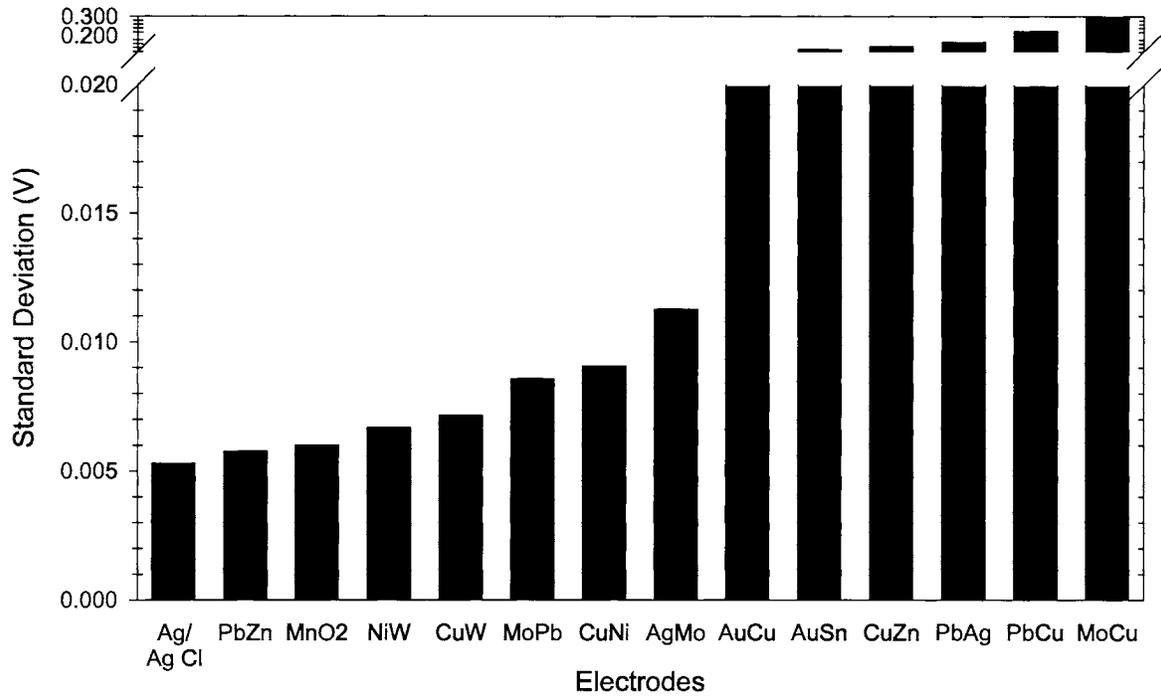


Figure 39. The standard deviations of the commercial and galvanic couple reference electrodes for 2000 hours in concrete.

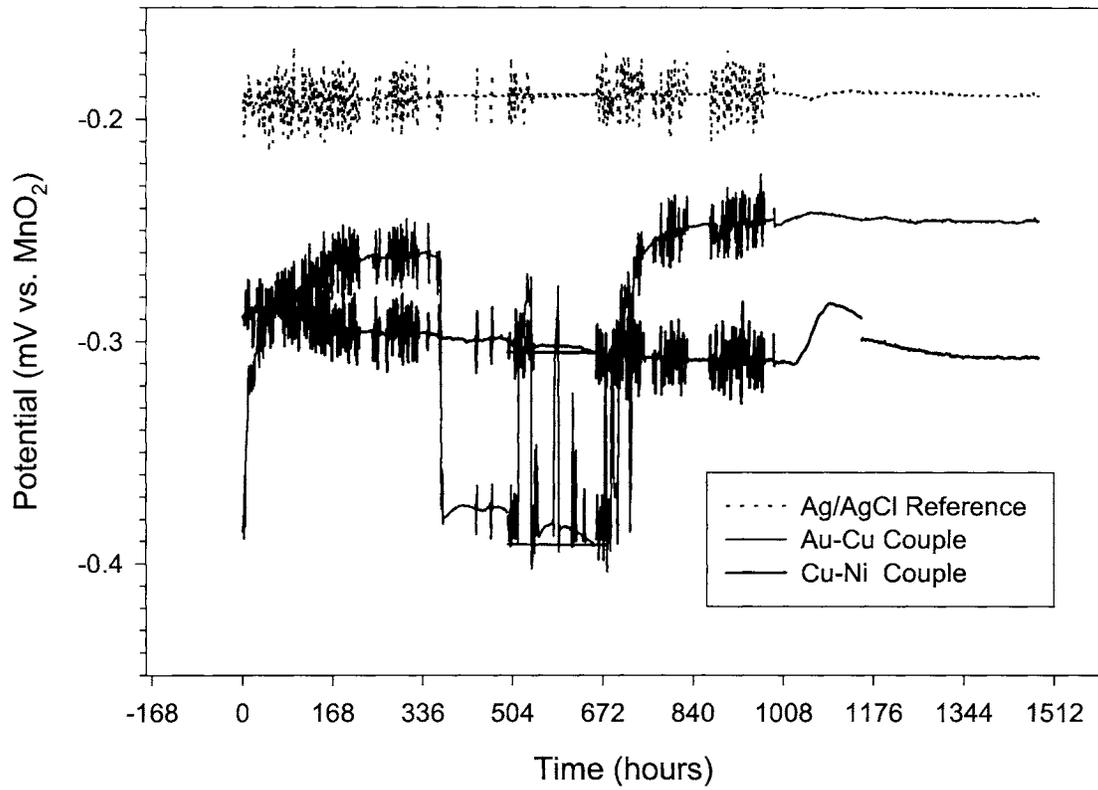


Figure 40. The potential behavior of Cu-Ni and Au-Cu, noble noble couples for 2000 hours in concrete. The Cu-Ni couple was stable, but the Au-Cu couple was unstable.

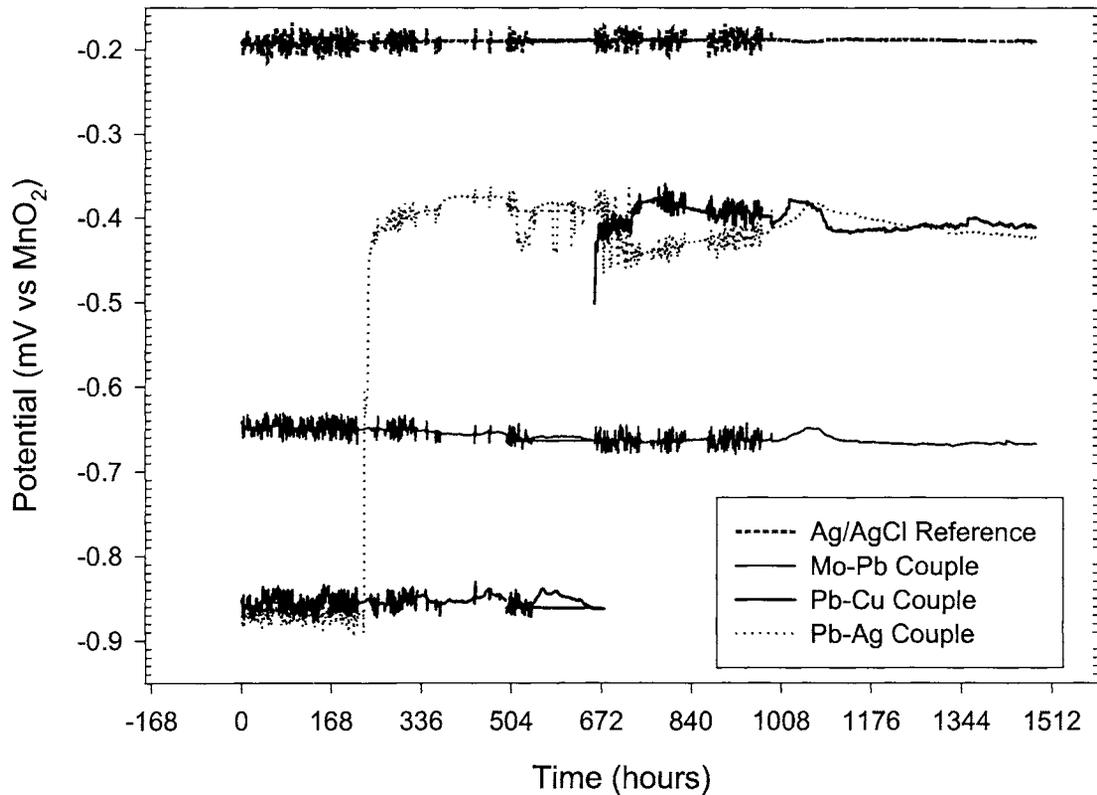


Figure 41. The potential behavior for 2000 hours in concrete of the noble-active and active-active couples that contain lead. The Ag-Pb and Cu-Pb couples were lead controlled in simulated concrete solution and remain lead controlled in concrete. The Ag-Pb and Cu-Pb couples are not stable in the concrete environment. The standard deviations of these couples were the result of a single potential step. The Mo-Pb couple gained stability in the concrete environment. The standard deviation of this couple was the result of noise.

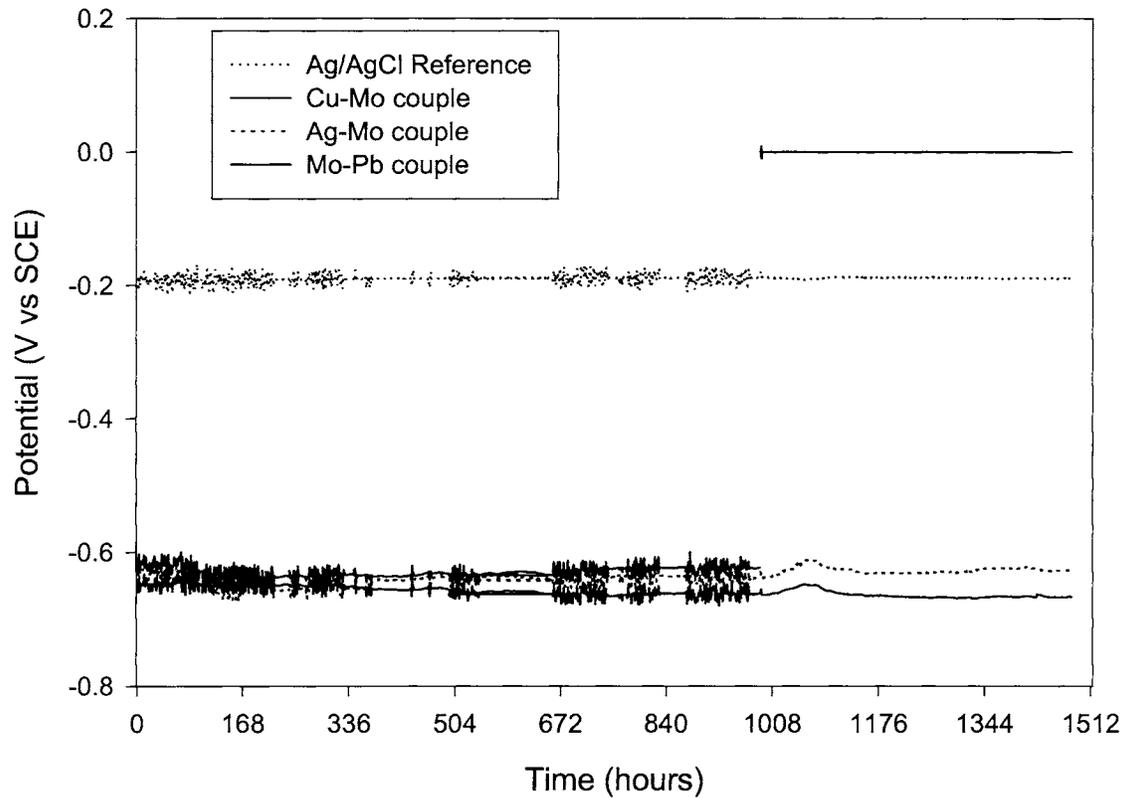


Figure 42. The potential behavior for 2000 hours in concrete of the noble-active and active-active couples that contained molybdenum. The Ag-Mo, Cu-Mo, and Mo-Pb couples were controlled by the molybdenum in this environment. The Cu-Mo couple was not stable in the concrete environment. The standard deviations of this couple was the result of a single potential step. The Mo-Pb, and Ag-Mo couple gained stability in the concrete environment. The standard deviations of these couples was the result of noise.

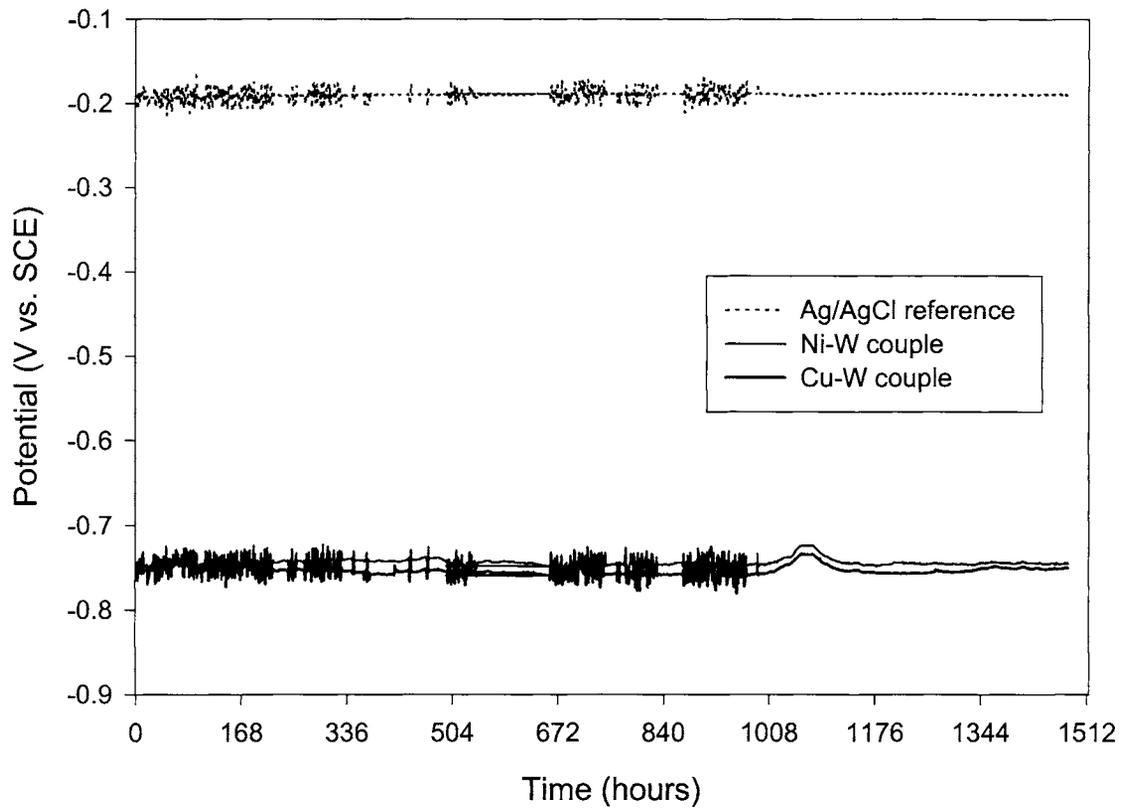


Figure 43. The potential behavior for 2000 hours in concrete of the noble-active couples that contained tungsten. The Ni-W and Cu-W couples both exhibit stable potentials in concrete. Their standard deviations occur as noise.

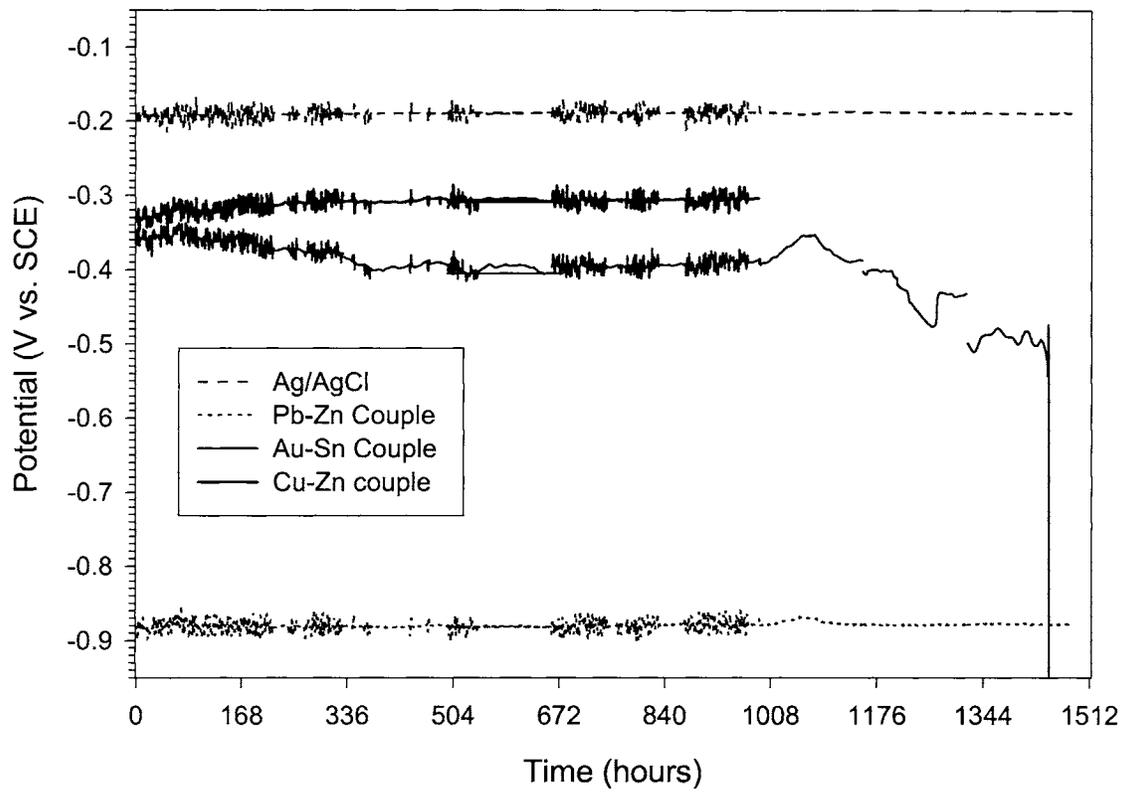


Figure 44. The potential behavior for the noble and active-passive couples in concrete for 2000 hours. The Pb-Zn couple exhibits stable behavior. The Au-Sn and Cu-Zn couples both lost stability in large potential shifts.

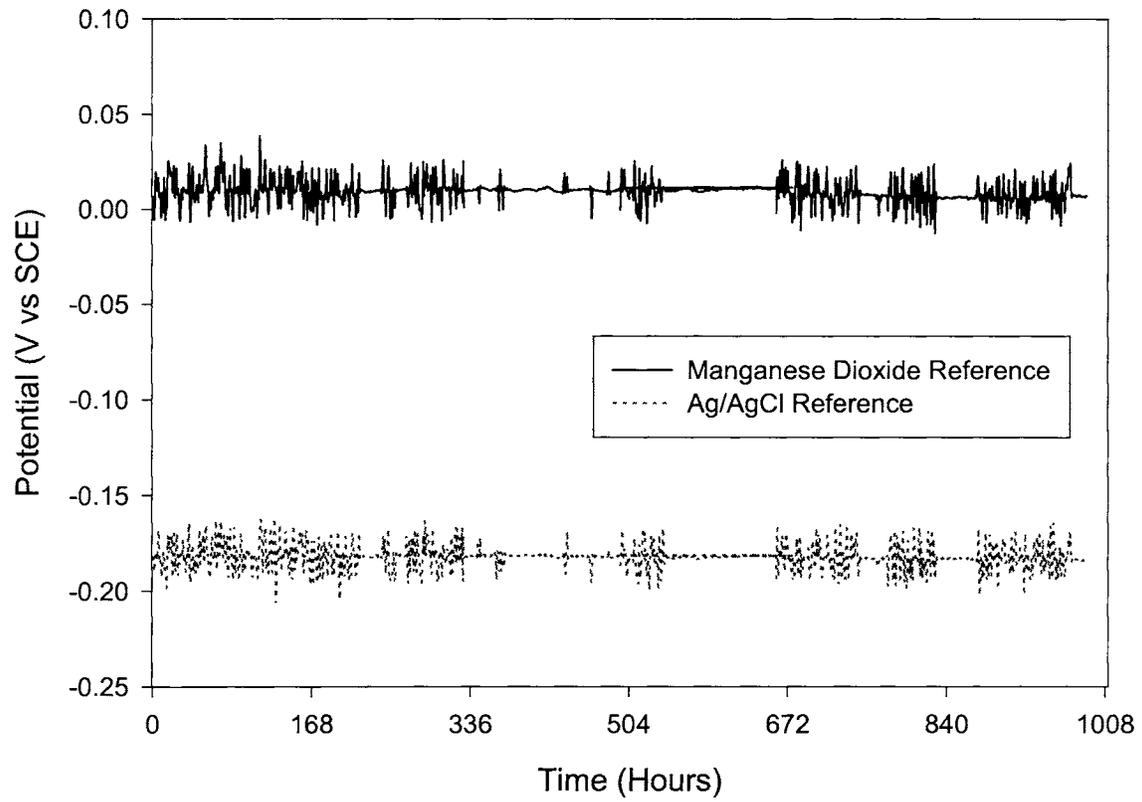


Figure 45. The reference potentials for the manganese dioxide and silver chloride commercial electrodes in concrete with chloride over 1000 hours. Both electrodes show similar, stable behavior. The standard deviations of these electrodes are caused by noise and not drift.

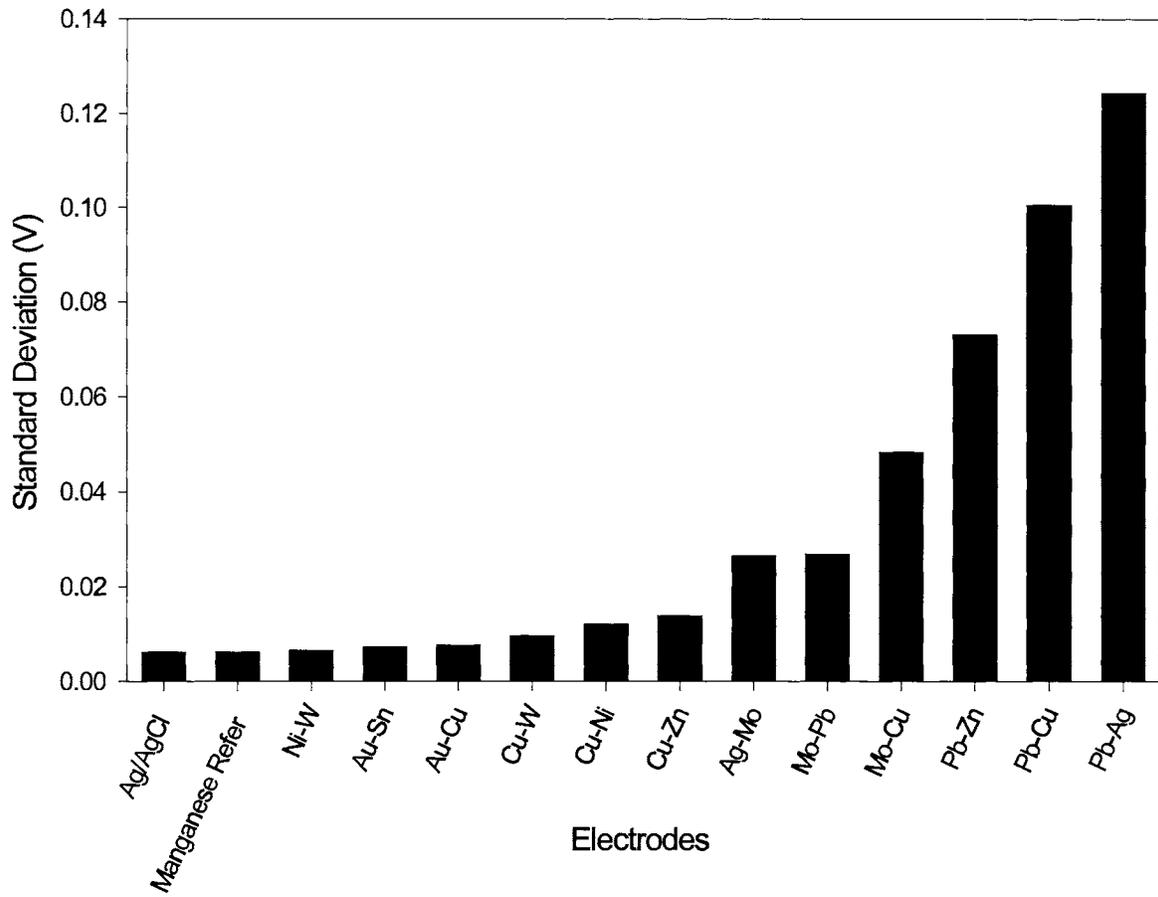


Figure 46. The standard deviations of the commercial and galvanic couple reference electrodes for 1000 hours in a chloride, concrete environment.

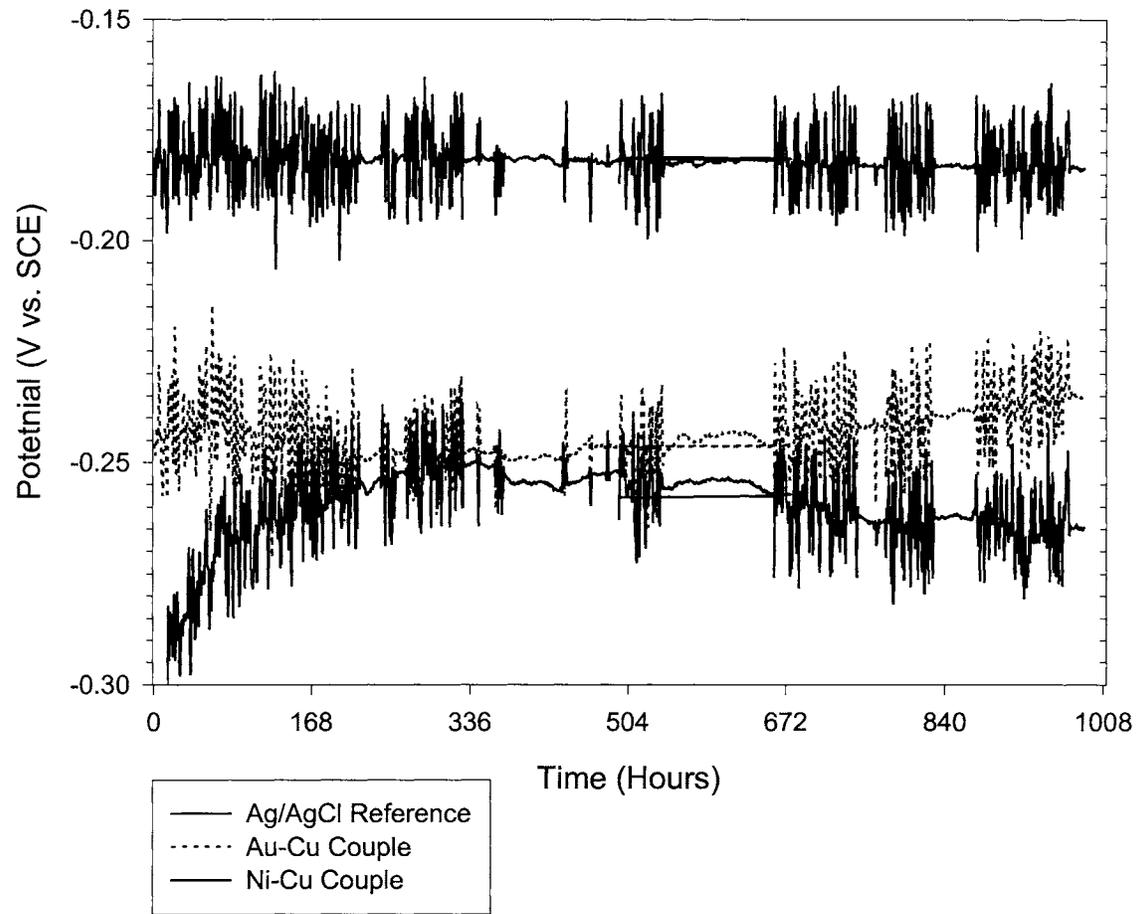


Figure 47. The potential behavior of Cu-Ni and Au-Cu, noble-noble couples for 1000 hours in concrete with chloride. The Au-Cu and Cu-Ni couples were reasonably stable in this environment. The standard deviations resulted from noise and a slight initial potential drift in the Cu-Ni couple.

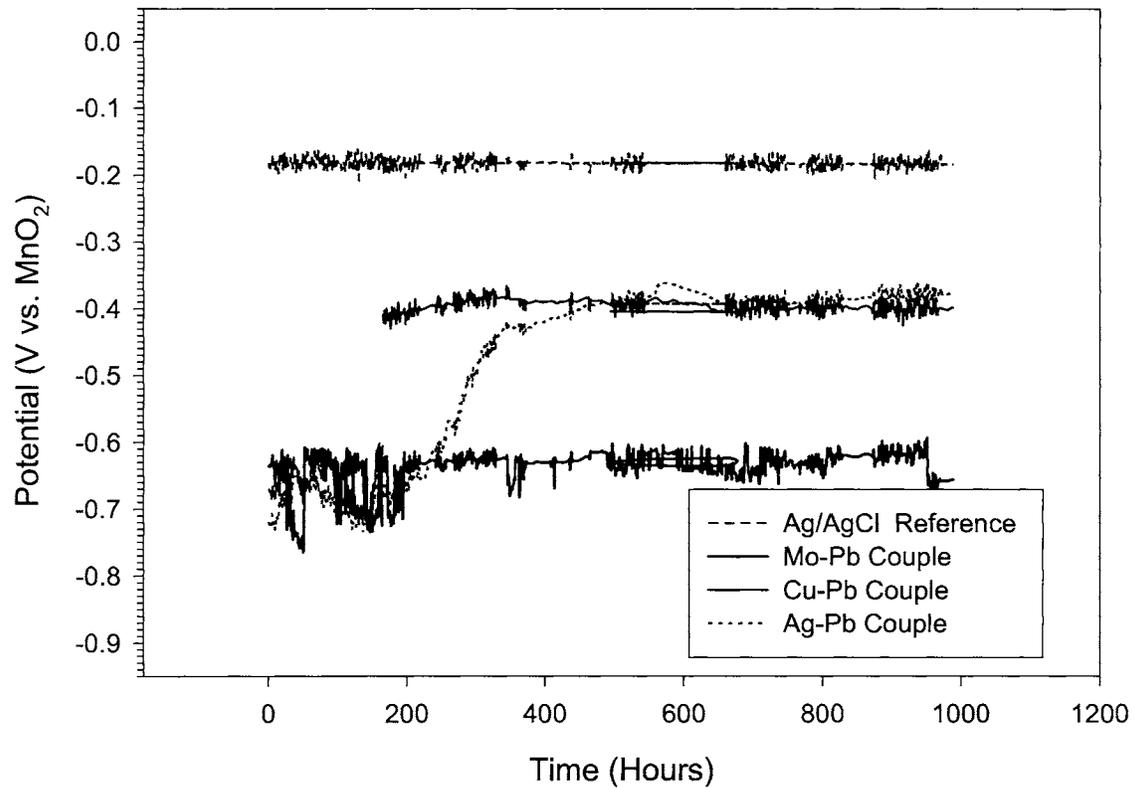


Figure 48. The potential behavior for 1000 hours in concrete with chloride of the noble-active and active-active couples that contained lead. The Ag-Pb and Cu-Pb couples were lead controlled in simulated concrete solution and remain lead controlled in concrete.

The Ag-Pb and Cu-Pb couples are not stable in this concrete environment either. The standard deviations of these couples were the result of a single potential step. The Mo-Pb couple is less stable than in the chloride free environment. The standard deviation of this couple was the result of high noise.

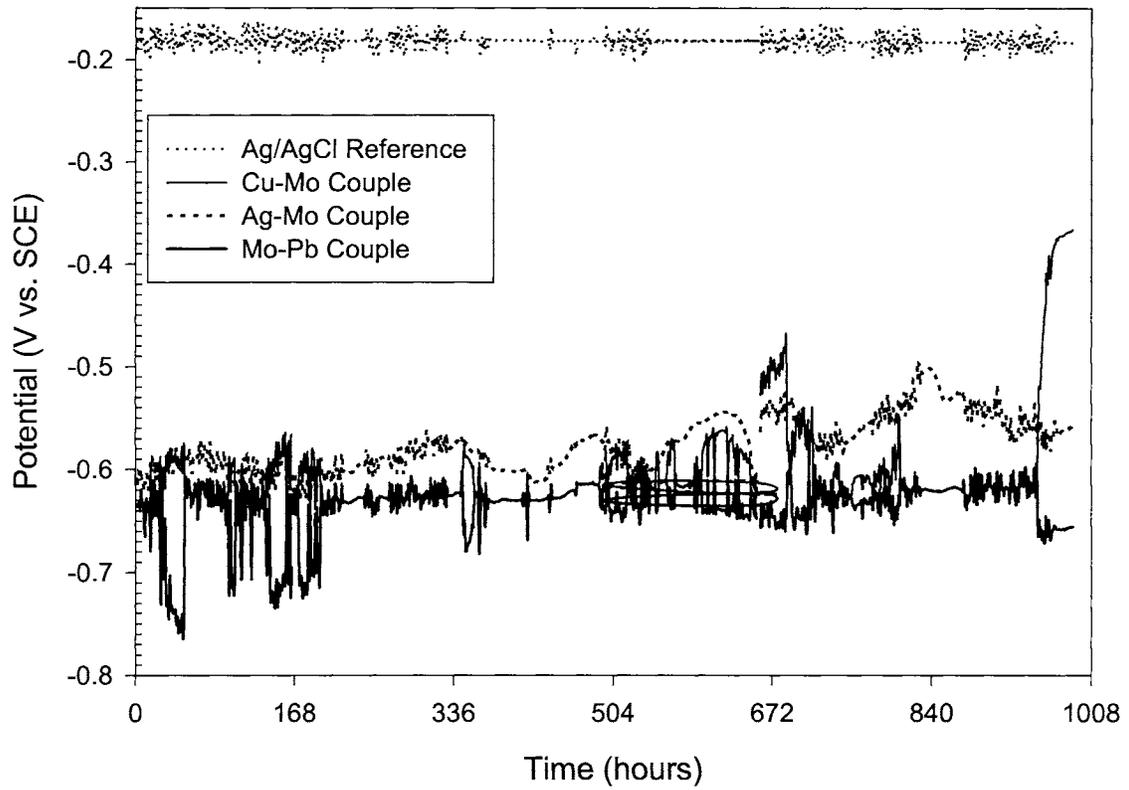


Figure 49. The potential behavior for 1000 hours in concrete with chloride of the noble-active and active-active couples that contained molybdenum. The Ag-Mo, Cu-Mo, and Mo-Pb couples were controlled by the molybdenum in this environment. All of these couples were unstable by large noise values.

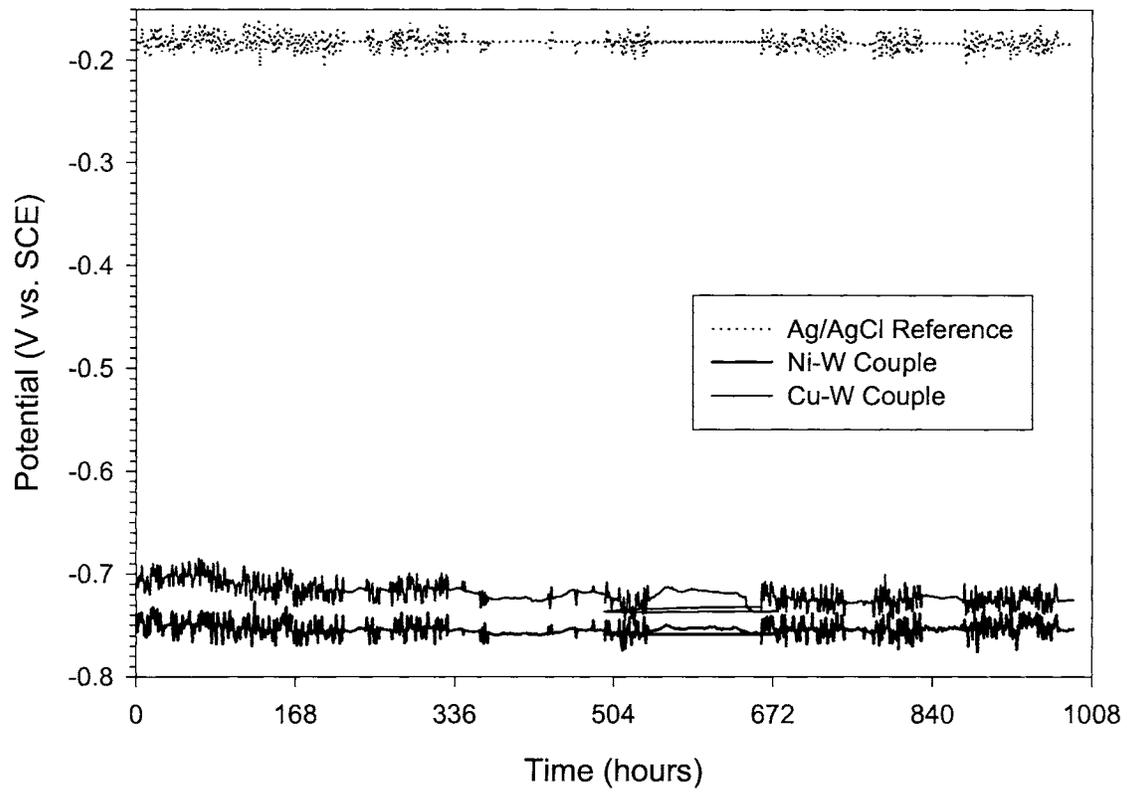


Figure 50. The potential behavior for 1000 hours in concrete with chloride of the noble-active couples that contained tungsten. The Ni-W and Cu-W couples both exhibit stable potentials in concrete. Their standard deviations occur as noise.

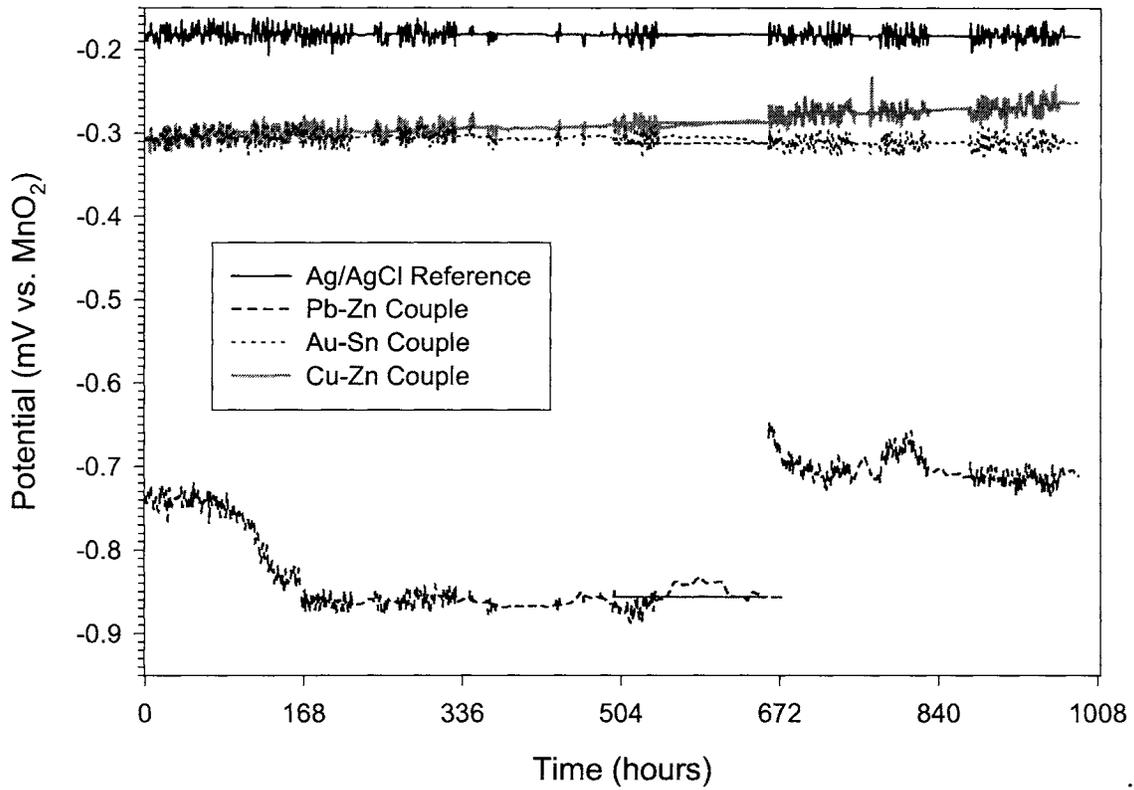


Figure 51. The potential behavior for the noble and active-passive couples in concrete with chloride for 1000 hours. The Pb-Zn couple exhibits unstable behavior by a large potential shift (similar to the lead anode couples). The Cu-Zn couple is more stable in this concrete block, but its standard deviation occurs both by slight drift and noise. The Au-Sn couple is stable, and its standard deviation occurs by noise alone.

TABLES

Table 1. Galvanic couple electrode test set.

Couple	Tank	Testing Continued ?	Couple	Tank	Testing Continued ?	Couple	Tank	Testing Continued ?
Ag-Pb	1	y	Au-Sn	2	y	Cu-Pb	3	y
Pt-Cu	1		Cu-Mo	2	y	Ni-Pb	3	
Au-Cu	1	y	Ni-W	2	y	Pb-Zn	3	y
Au-Ag	1		Mo-Sn	2		W-Pb	3	
Ag-Ni	1		Mo-W	2		Mo-Zn	3	
Pt-Au	1		Ni-Mo	2		Ni-Zn	3	
Zn-Sn	1		Ag-Mo	2	y	Au-Zn	3	
Cu-Ni	1	y	Cu-Sn	2		Au-Zn (foil)	3	
Ag-Cu	1		W-Sn	2		Au-W	3	
Pt-W	1		Ag-Sn	2		Ni-Sn	3	
Cu-Zn	1	y	Ag-W	2		Ag-Zn	3	
W-Zn	1		Cu-W	2	y	Au-Ni	3	
Cu-Al	1		Mo-Pb	2	y	Cu-Ni	3	
Al-Zn	1		Pb-Sn	2		Au-W	2	

Table 2 (a). The couple potentials and associated standard deviations for electrodes that were more stable than the commercial manganese dioxide reference electrode in saturated calcium hydroxide.

Couple	True Standard Deviation	Normalized Standard Deviations	Mean Measured Couple Potential
Noble-Noble			
Pt - Cu	3.4	0.72	-78.2
Au-Cu	3.7	0.79	-97.0
Au-Ag	4.3	0.91	-79.8
Ag-Ni	4.5	0.96	-115.4
Noble-Active			
Ag-Pb	2.7	0.57	-747.5
Cu-Mo	9.5	0.77	-431.7
Ni-W	10.7	0.87	-476.4
Cu-Pb	5.2	0.88	-741.6
Ni-Pb	5.6	0.93	-749.1
Active-Active			
Mo-W	12.4	1.0	-455.3
Noble/Active-Passive			
Au-Sn	9.1	0.74	-59.0
Mo-Sn	12.0	0.98	-433.9
Pb-Zn	12.4	1.0	-749.0

Table 2 (b). The couple potentials and associated standard deviations for electrodes that maintained potentials within twice the standard deviation of the commercial manganese dioxide reference electrode in saturated calcium hydroxide.

Couple	True Standard Deviation	Normalized Standard Deviation	Mean Measured Couple Potential
Noble-Noble			
Pt-Au	1.6	7.3	-50.9
Noble-Active			
Ni-Mo	13.3	1.1	-427.9
Ag-Mo	15.2	1.2	-440.7
Au-Mo	9.9	1.7	-424.7
Active-Active			
W-Pb	7.2	1.2	-750.9
Sn-Zn	8.1	1.7	-1062.8
Noble/Active-Passive			
Mo-Zn	8.9	1.5	-413.9
Cu-Sn	18.6	1.5	-145.0
W-Sn	19.0	1.5	-472.9
Ni-Zn	12.3	2.0	-306.7
Ag-Sn	25.6	2.0	-162.6

Table 2 (c). The potentials and standard deviations for couples that were unsuccessful relative to the commercial manganese dioxide reference electrode.

Couple	True Standard Deviation	Normalized Standard Deviation	Mean Measured Couple Potential
Noble-Noble			
Ni-Cu	33.9	7.2	-203.2
Ag-Cu	41.0	8.7	-164.4
Au-Ni	88.7	14.9	9.9
Ni-Cu	250.3	41.9	-543.0
Noble-Active			
Ag-W	44.9	3.6	
Cu-W	51.3	4.2	-445.0
Au-W	34.3	3.7	-316.2
Pt-W	54.1	11.5	-518.3
Cu-Al	246.7	52.5	-689.6
Active-Active			
Mo-Pb	66.1	5.4	-662.0
Noble/Active-Passive			
Au-Zn	16.6	2.8	-144.4
Ni-Sn	35.7	6.0	-221.1
Pb-Sn	77.9	6.3	-904.7
Ag-Zn	52.6	8.8	-217.3
Cu-Zn	68.0	14.5	-903.0
W-Zn	93.8	20.0	-626.2
Galvanized Rebar	118.8	25.3	-518.3

Table 3. Couple potential control.

Couples	Couple Potential	Couple Control
Pt-Cu	-78.2	Cathode
Au-Cu	-97.0	Mixed/Anode
Au-Ag	-79.8	Mixed
Ag-Ni	-115.4	Mixed/Anode
Ag-Pb	-747.5	Anode
Cu-Mo	-431.7	Anode
Ni-W	-476.4	Anode
Cu-Pb	-741.6	Anode
Ni-Pb	-749.1	Anode
Mo-W	-455.3	Mixed
Au-Sn	-59.0	Cathode
Mo-Sn	-433.9	Cathode
Pb-Zn	-749.0	Cathode

Table 4. Electrode micro-polarizability in quiescent and deaerated solution.

Electrode	Slope Quiescent Saturated Ca(OH) ₂ (mV/μA)	Slope Deaerated Saturated Ca(OH) ₂ (mV/μA)
MnO ₂	-2.49	-----
Au-Cu	-6.45	-0.81
Ag-Pb	-8.2 x 10 ⁻³	-9.7 x 10 ⁻³
Au-Sn	-38.7	-15.3

Table 5. The effect of cathode-to-anode area ratio on the couple potentials and true standard deviations of galvanic couple electrodes. (1:1, 1:10, and 10:1 area ratios as well as the original stability data from a separate test are given.)

Couple	1:1 Area Ratio (Original Stability)		1:1 Area Ratio		1:10 Area Ratio		10:1 Area Ratio	
	OCP	Std. Dev.	OCP	Std. Dev.	OCP	Std. Dev.	OCP	Std. Dev.
Ag-Mo	-440.7	15.2	-431.6	6.3	-430.6	4.7	-332.6	71.3
Mo-W	-455.3	12.4	-441.6	12.7	-438.2	6.5	-497.9	6.9
Cu-Mo	-431.7	9.5	-429.5	5.7	-436.9	4.8	-273.9	87.0
Au-Cu	-97.0	3.7	-115.1	6.2	-221.6	5.9	-157.0	5.9
Ni-W	-476.4	10.7	-486.3	8.5	-499.3	3.5	-377.3	53.6
Ag-Ni	-115.4	4.5	-80.9	17.0	-27.0	46.8	-117.5	14.2
Pt-Cu	-77.2	3.3	-88.3	19.9	-110.3	20.4	-69.8	15.1
Ni-Mo	-428.0	13.3	-432.5	9.2	-439.1	8.1	-401.3	25.6
Pt-Au	-50.9	7.3	-50.3	20.1	-58.1	16.2	-37.3	16.8
Au-Ag	-79.3	3.8	-44.0	19.2	-56.7	22.6		

Table 6. Electrode consistency. (The couple potentials are given for two different 1:1 versions of several couples to show variations in reference potential.)

Couple	Potential 1	Potential 2
Au-Cu	-97.0	-115.1
Ag-Pb	-747.5	-760.0
Au-Sn	-59.0	-85.5
Ag-Mo	-440.9	-431.6
Cu-Mo	-431.7	-429.5
Ag-Ni	-115.4	-80.9

Table 7. Reference electrode potentials in concrete

Reference vs. Reference	Mean Potential (mV)	Standard Deviation (mV)
MnO ₂ (1) vs. MnO ₂ (common)	3.4	6.0
Ag/AgCl vs. MnO ₂ (common)	-189.6	5.3
Ag/AgCl vs. MnO ₂ (1)	-193.0	4.9

Table 8. Comparison of galvanic-couple electrode behavior in concrete (for 2000 hours) and in solution.

Couple	In Concrete		In Solution	
	Electrode Potential (mV vs. SCE)	Standard Deviation (mV)	Electrode Potential (mV vs. SCE)	Standard Deviation (mV)
References				
MnO ₂ /Mn ₂ O ₃	168.4	6.0	163.1	4.7
Ag/AgCl	-24.6	5.3	-----	-----
Noble-Noble				
Au-Cu	-116.8	51.9	-97.0	3.7
Cu-Ni	-135.5	9.0	-543.0	250.3
Noble-Active				
Ag-Pb	-314.5	168.0	-747.5	2.7
Cu-Pb	-437.1	224.5	-741.6	5.2
Ag-Mo	-472.2	11.3	-440.7	15.2
Cu-Mo	-254.4	296.8	-431.7	9.5
Cu-W	-588.1	7.1	-445.0	51.3
Ni-W	-579.1	6.7	-476.4	10.7
Active-Active				
Mo-Pb	-493.8	8.6	-662.0	66.1
Noble/Active-Passive				
Pb-Zn	-714.5	5.7	-749.0	12.4
Cu-Zn	-41.3	146.3	-903.0	68.0
Au-Sn	-253.1	129.6	-59.0	9.1

Table 9. Commercial reference electrode behavior in concrete with chloride.

Reference vs. Reference	In Concrete w/ Chloride		In Plain Concrete	
	Potential (mV vs. MnO ₂)	Standard Deviation (mV)	Potential (mV vs. MnO ₂)	Standard Deviation (mV)
MnO ₂ (1) vs. MnO ₂ (common)	9.3	6.3	3.4	6.0
Ag/AgCl vs. MnO ₂ (common)	-182.0	6.2	-189.6	5.3
Ag/AgCl vs. MnO ₂ (1)	-191.2	5.0	-193.0	4.9

Table 10. Galvanic-couple electrodes' mean measured potentials and standard deviations in concrete with and without chloride.

Couple	In Concrete w/ Chloride		In Plain Concrete		Potential Change Between Cl ⁻ and non-Cl ⁻ Environments (mV)
	Mean Measured Potential (mV)	Standard Deviation (mV)	Mean Measured Potential (mV)	Standard Deviation (mV)	
Reference					
MnO ₂ (1)	174.3	6.3	168.4	6.0	5.9
Ag/AgCl	-17.0	6.2	-24.6	5.3	7.6
Noble-Noble					
Au-Cu	-78.9	7.6	-116.8	51.9	37.9
Cu-Ni	-95.3	12.1	-135.5	9.0	40.2
Noble-Active					
Ag-Pb	-307.2	124.4	-314.5	168.0	7.3
Cu-Pb	-274.2	100.7	-437.1	224.5	162.9
Ag-Mo	-410.6	26.6	-472.2	11.3	61.6
Cu-Mo	-436.8	48.5	-254.4	296.8	-182.4
Cu-W	-554.0	9.6	-588.1	7.1	34.1
Ni-W	-588.4	6.6	-579.1	6.7	-9.3
Active-Active					
Mo-Pb	-471.0	26.9	-493.8	8.6	22.8
Noble/Active-Passive					
Pb-Zn	-627.0	73.2	-714.5	5.7	87.5
Cu-Zn	-122.6	13.9	-41.3	146.3	-81.3
Au-Sn	-142.2	7.2	-253.1	129.6	110.9