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Electrolytic Cleaning and Conditioning of Gold Redox Probes in Flotation Circuits

By William K. Tolley and David A. Rice

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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**UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/m²	ampere per square meter	mm	millimeter
cm	centimeter	μm	micrometer
cm²	square centimeter	mV	millivolt
h	hour	mV/s	millivolt per second
L	liter	s	second
mA	milliampere	V	volt
min	minute		

ELECTROLYTIC CLEANING AND CONDITIONING OF GOLD REDOX PROBES IN FLOTATION CIRCUITS

By William K. Tolley¹ and David A. Rice²

ABSTRACT

The U.S. Bureau of Mines (USBM) is currently investigating the electrochemistry of mineral flotation. A significant need in this area is greater reliability of sensors. The USBM is testing electrolytic methods to clean and condition redox-sensing electrodes to improve the reliability and extend the service life of these instruments in the harsh physical and chemical environment of mineral processing slurries. A novel method for removing scale from fouled electrodes has been developed that includes anodic polarization to 1.2 V versus the Ag/AgCl reference potential, followed by brief potentiodynamic conditioning. Laboratory results show that this technique removes calcarious deposits from gold sensing electrodes and returns the electrodes to useful service within approximately 10 min. Mechanical abrasion to remove the scale is thereby avoided.

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INTRODUCTION

The effects of electrochemistry and redox potentials in the flotation of sulfide minerals have been described in many publications. A number of the notable publications are cited (1-12).³ The reasons for these electrochemical effects include the formation of hydrophilic or hydrophobic products on the mineral surface, and the electrochemical adsorption of reagents.

Plant operators must be able to measure the electrochemical state of the flotation slurry reliably before electrochemical control of the process is practical. Measurement of the electrochemical redox potential in mineral slurries commonly is done with noble metal electrodes in combination with standard reference electrodes. The noble metal sensing electrodes, however, often become coated or fouled (13), leading to faulty measurements and erroneous information.

Electrode technology has been significantly improved during recent years. Robust gel-filled electrodes are now in common use. "Self-cleaning" pH and oxidation-reduction potential (ORP) electrodes using fluid motion to reduce fouling of the electrode surface are available. However, fluid motion is inadequate in flotation circuits to

prevent accumulation of scale; the effects of fouling have been described elsewhere. The U.S. Bureau of Mines (USBM) is currently investigating electrolytic methods to further improve electrode reliability and extend service life in the harsh physical and chemical environment of mineral processing slurries. The purpose in the current research was to better understand fouling of redox-sensing electrodes in mineral slurries, and to develop methods to avoid fouling and improve reliability of redox potential control in flotation circuits. The procedure described here allows for in situ cleaning and conditioning of the electrode without introducing chemical cleaning reagents that could upset the chemistry of the flotation circuit.

Platinum, gold, and mineral electrodes all have been used as indicators of redox potential in mineral slurries (7, 14). The experience at the USBM's Salt Lake City Research Center has shown that gold works well; hence, gold was chosen for the sensing electrode material in this research.

This work was done as part of a USBM program to devise efficient and practical technology to economically recover minerals in an environmentally acceptable fashion.

EXPERIMENTAL

ELECTRODE MATERIALS

Three gold sensing electrodes were made from 3-mm gold rod. The rod was cut with a diamond wafering saw into 3-mm lengths, soldered to insulated copper wire, placed inside 9-cm lengths of 1-cm (outside diameter) Plexiglas⁴ thermoplastic polymer tubing, and cast inside the tubing with epoxy. After the epoxy set, the gold was polished with 600-grit emery paper. The exposed surface area of gold in the finished electrodes was 0.0707 cm².

A gel-filled, epoxy-body Ag/AgCl electrode was used as a reference electrode. The accuracy of this electrode was checked in Zobell standard redox solution using a freshly polished gold electrode. Unless otherwise indicated, all potentials are reported with respect to the Ag/AgCl reference potential.

PROCEDURES

Stability of the readings provided by the gold electrodes was measured in a molybdenite flotation slurry.

Molybdenite flotation concentrate was slurried in deionized water at 10% by weight MoS₂ pulp density in a Wemco 2-L glass flotation cell. The slurry was agitated by the flotation machine for approximately 8 h each day for the duration of the test. The slurry was open to the air during testing, but air was not introduced through the flotation machine. Ca(OH)₂ was added to the slurry to maintain pH 9.2; NaHS • xH₂O was added to maintain approximately -0.1 V measured against the AgCl reference electrode.

Three gold electrodes were prepared and tested simultaneously. The slurry potential was measured with each gold electrode against the AgCl reference electrode using a digital multimeter. The first gold electrode was connected to a strip chart recorder and immersed continuously in the slurry for continuous reading of the potential. The second gold electrode was immersed continuously in the slurry; however, potential measurements were made only occasionally using this electrode. This electrode was tested for electrolytic cleaning during the test. The third electrode was used as a standard for comparing the response of the other two electrodes and was stored in deionized water except when used for reading redox potentials of the slurry.

Anodic cleaning of the second electrode was accomplished with a potentiostat. The gold electrode functioned

³Italic numbers in parentheses refer to items in the list of references at the end of this report.

⁴Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

as the working electrode of the potentiostat. A graphite rod immersed in the slurry functioned as the counter electrode. The Ag/AgCl electrode functioned as the reference electrode for the potentiostat. Currents and voltages from

the potentiostat were recorded during and after the cleaning cycles. Following the test, the tip of each of the three gold electrodes was cut off with a wafering saw and examined under a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Laboratory research was undertaken to better understand fouling of redox-sensing electrodes in mineral slurries, and to develop methods to avoid fouling to allow for reliable redox potential control in flotation circuits.

In the laboratory tests, two gold electrodes were immersed in a molybdenite slurry. The potential as sensed by the first gold electrode (constantly immersed in slurry and connected to a strip chart recorder) is plotted in figure 1. For comparison, the potential as measured by the clean gold electrode is also plotted. An observable coating accumulated on the first electrode within 14 days. The potentials sensed by the two gold electrodes, however, did not differ greatly during the test period. This agrees with previous experience in flotation plants by USBM researchers and others (15), where gold electrodes performed more reliably than expected.

After 20 days of immersion in the slurry, the tip of the first electrode was cut off and examined under the SEM. A photomicrograph of the electrode tip is shown in figure 2. The gold cannot easily be distinguished in the

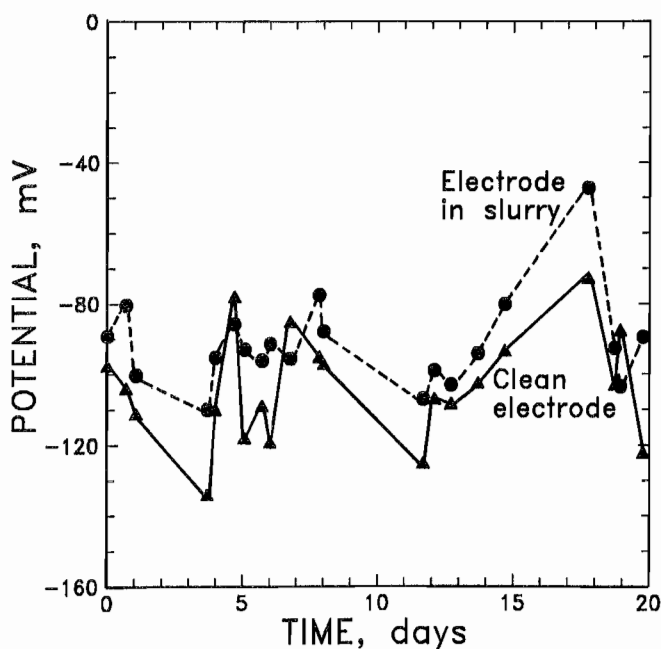


Figure 1.—Redox potentials sensed by gold electrode continuously immersed in molybdenite slurry and connected to chart recorder and by clean gold electrode stored in deionized water.

micrographs because of the coating. The gold occupies the lower portion of figure 2A; the box in the photograph straddles the edge of the gold. In the enlargement in figure 2B, a crack running nearly horizontally through the middle of the photo marks the interface between the gold (lower portion of the photograph) and the epoxy (upper portion) in the electrode. The electrode tip was uniformly coated with foreign material after 20 days in the flotation slurry. The coating was analyzed in the electron microscope by energy dispersive X-ray (EDX) analysis and found to contain a large amount of calcium, a small amount of sulfur, and trace amounts of copper and iron. The coating also fizzed in hydrochloric acid. Based on this information, the coating appears to be primarily CaCO_3 with a minor amount of CaSO_4 .

The potential sensed by the second gold electrode (constantly immersed in slurry but not connected to a strip chart recorder) is plotted in figure 3. A visible coating accumulated on this electrode within 14 days, as happened with the first electrode. At 14 days, electrolytic cleaning of the second electrode was attempted. Zhou and Chander (14) recommend anodic polarization to condition fresh electrodes. Following this recommendation, the gold electrode was anodically polarized to a potential of 1.0 V with respect to the standard hydrogen electrode (+800 mV versus Ag/AgCl) for 10 min. No visible change in the coating at the tip of the electrode was observable. The potential sensed by the electrode following this cleaning treatment was -22.8 mV compared with -93.4 mV for the clean gold electrode. The fouled electrode was also immersed in Zobell solution, where it produced a reading of +91 mV compared with +214 mV for the clean gold electrode. Thus, 800 mV versus Ag/AgCl was deemed insufficient for cleaning fouled gold electrodes.

In a modification of this treatment, the fouled electrode was anodically cleaned for 10 min at 1.2 V versus Ag/AgCl. The overall cell voltage for the cleaning was approximately 8 V. The current density averaged 9.1 mA for the electrode, or approximately $1,300 \text{ A/m}^2$. The potential of the electrode was monitored following the cleaning treatment until the potential stabilized. The potential readings are plotted in figure 4.

Approximately 30 min was required to reach a stable potential after cleaning at 1.2 V. The stabilized potential reading (-93 mV) agreed well with the potential of the standard gold electrode of -88 mV. Visual inspection of

the electrode tip indicated that the coating fouling the electrode tip had been removed. Several mechanisms are possible that would result in removal of the scale. The strong oxidation would cause anodic dissolution of metal sulfides in the scale. Anodic dissociation of water would

produce gaseous oxygen, which would force scale from the electrode surface.

This polarization treatment removed the coating on the electrode tip and restored proper functioning of the electrode; however, the time required to attain stable

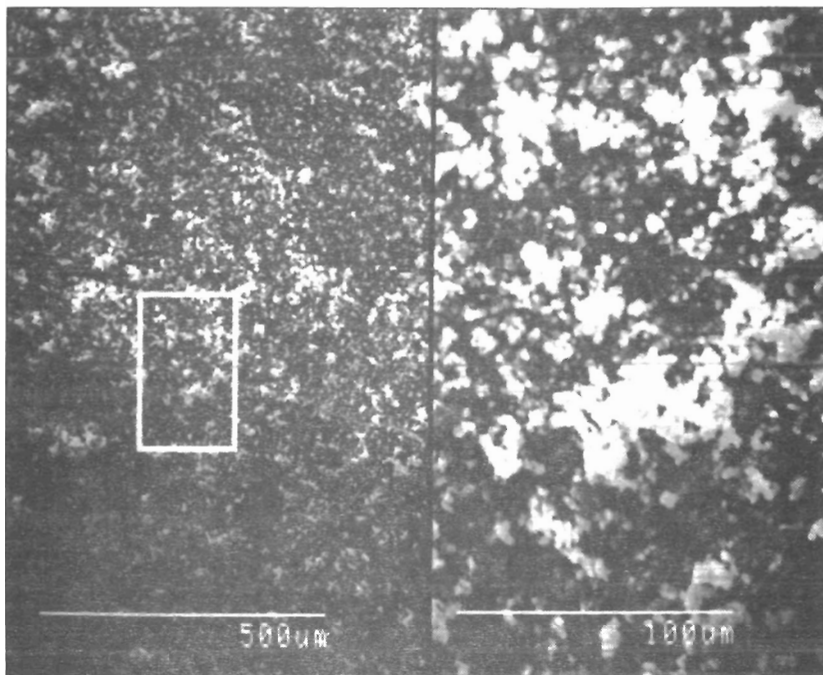


Figure 2.—Photomicrograph of gold electrode tip after 20 days in molybdenite slurry at pH 9.2.

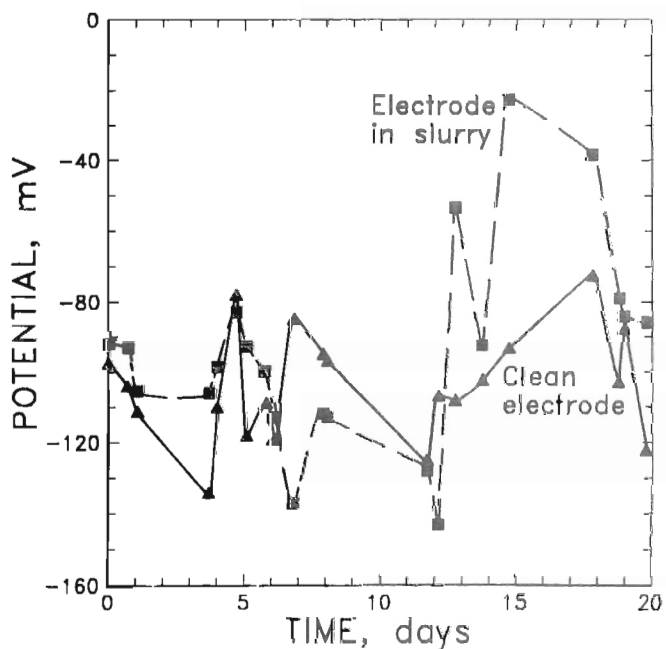


Figure 3.—Redox potentials sensed by gold electrode continuously immersed in molybdenite slurry and by clean gold electrode stored in deionized water.

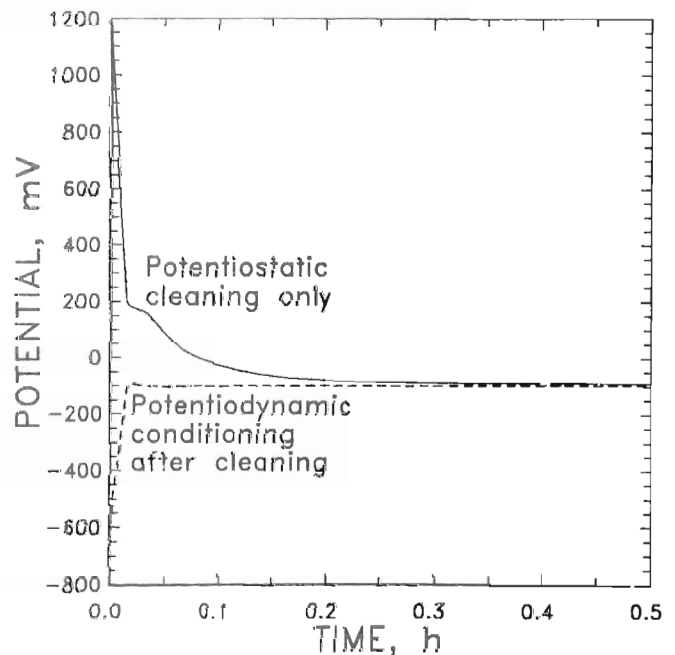


Figure 4.—Potential reading of gold electrodes following potentiostatic cleaning at 1.2 V versus Ag/AgCl, with and without potentiodynamic conditioning.

readings (≈ 30 min) is more than would be desirable in plant operation, where the electrode may be needed for continuous, on-line process control. In an attempt to reduce the stabilization time following potentiostatic cleaning, a potentiodynamic conditioning procedure described by Zhou and Chander (14) was tested. The previously cleaned second gold electrode was polarized in the molybdenite slurry for 10 min at 1.2 V as before. The anodic treatment was followed by 45 s of potentiodynamic cycling, during which the potential was oscillated between -600 mV and +800 mV at a 400-mV/s scan rate; six potentiodynamic cycles were completed. Following this combined potentiostatic-potentiodynamic treatment, the potential of the gold electrode was monitored. The plots in figure 4 show that the potential of the treated electrode stabilized within 1 min following the cycling treatment compared with 30 min stabilization time required without the potentiodynamic treatment. The potential sensed by the gold electrode in both the molybdenite slurry and the Zobell solution after cycling was found to be acceptable.

Following cleaning, the tip of the cleaned electrode was cut from the electrode and examined under the SEM. The photomicrographs in figure 5 show the gold to be free of

calcium deposits. The area free of coating extended approximately $10\ \mu\text{m}$ beyond the edge of the gold. The bulk of the electrically insulating epoxy material, however, remained coated with calcarious material. From EDX measurements, the composition of the coating was similar to that of the material observed in figure 2. For comparison, the tip of a freshly polished electrode was cut from the electrode and examined under the SEM; a photomicrograph of this electrode is shown in figure 6. The only observable difference is more debris from the polishing on the freshly polished electrode. Thus, electrolytic cleaning of the gold electrode followed by a brief period of rapidly cycled potential appears beneficial in maintaining gold redox-sensing electrodes in flotation slurries.

Ensuring a stable potential from the AgCl reference electrode in operation was critical to this test. The potential of the reference electrode was checked using a clean gold electrode in Zobell solution. Readings were stable over the course of several hours, but during 12 days of testing, the AgCl reference electrode drifted from +202 mV in Zobell solution to +220 mV. In general, however, the gel-filled, epoxy-body reference electrode appears to be robust in the flotation system.

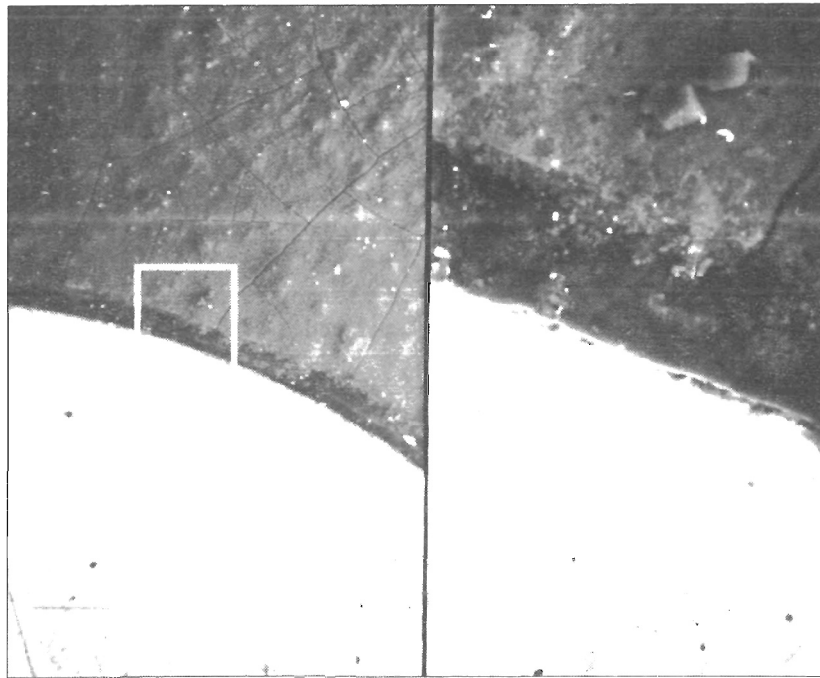


Figure 5.—Photomicrograph of electrode tip following potentiostatic cleaning at 1.2 V.

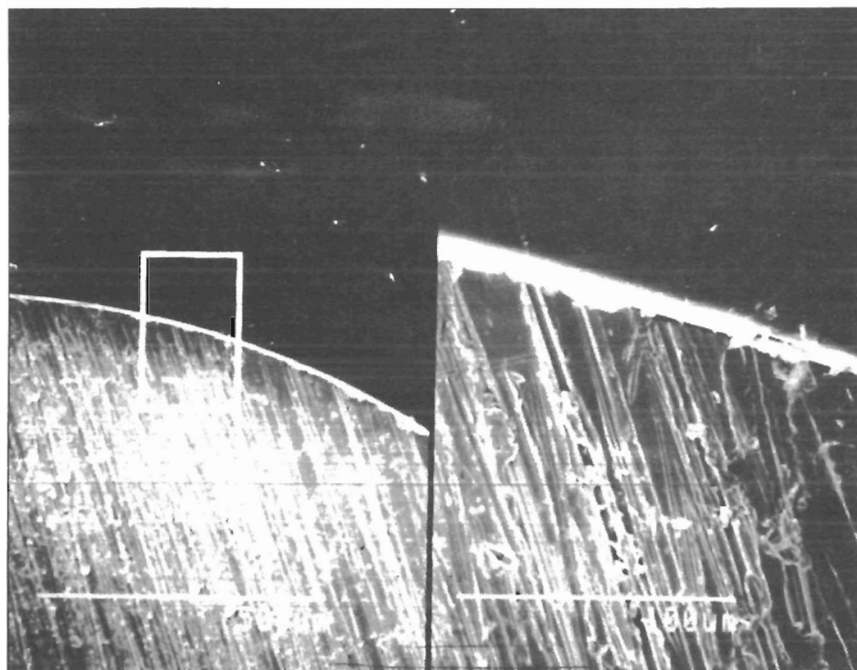


Figure 6.—Photomicrograph of freshly polished electrode tip.

CONCLUSIONS

Fouling of redox-sensing electrodes is a problem in monitoring and controlling the electrochemistry of sulfide flotation slurries. Recent laboratory work at the USBM has shown that gold electrodes may be cleaned by anodically polarizing the electrode to 1.2 V versus Ag/AgCl to remove the accumulated scale. To reduce the time required to attain stable readings following cleaning, a 45-s period of potentiodynamic cycling was included in the cleaning procedure. Examination under the electron microscope showed that this method is effective in removing accumulated scale from gold redox-sensing electrodes.

Electrochemical measurements following cleaning and cycling showed rapid return of the sensing electrode to stable, reliable potential readings. Work is continuing to assess the effectiveness of this procedure over an extended period of time and to test the procedure for cleaning of gold redox-sensing probes in control circuits at commercial flotation plants.

The optimum cleaning method will likely depend on pH, redox potential of the slurry, and chemical composition of the specific mineral systems.

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