PROGRESS REPORT

Related Studies to Cathodic Protection of Reinforced Concrete Structures No. 2

State Study 77-03-2

School of
CHEMICAL ENGINEERING
and
MATERIALS SCIENCE

The University of Oklahoma

202 West Boyd
Room 23
Norman, Oklahoma 73069

PROGRESS REPORT

Related Studies to Cathodic Protection of Reinforced Concrete Structures No. 2

State Study 77-03-2

To

Oklahoma Department of Transportation

by

Carl E. Locke
University of Oklahoma

January 5, 1977

Introduction

This progress report summarizes the work done on the project from its inception to the present time. The project has been divided into four sections: conductive layer, reference electrode, long-term current, and corrosion rate measurement. Each of these areas will be discussed below.

Conductive Layer Study

Two approaches to providing a conductive layer suitable for use as a current distribution system have been started. The first approach is to fill a polymeric membrane material with conductive particles such as coke breeze or carbon black. The second is to use carbon black or coke breeze with an asphaltic concrete to make it conductive. Each of these will be discussed below.

Conductive Polymeric Membrane

This work is a continuation of the study began in the summer of 1975. The results from this earlier study indicated that the polymeric membranes could be made to be electrically conductive by blending 40-50% by weight coke breeze or conductive carbon black. These materials were found to be as conductive as the conductive particles alone. However, the filled materials seemed to be too stiff to act as a reasonable material for bridge decks.

This study has been pointed towards developing a material that would be conductive and retain the desired flexibility requirements for bridge decks. The plan has been to work with the suppliers of membrane materials in developing a membrane mix to which we add carbon black or coke breeze. We have had talks with Carlisle Rubber, W. R. Grace, and Polyguard concerning the project. W. R. Grace has obtained samples of the materials we prepared in 1975 and has said they would send us conductive materials that hopefully would have the desired flexibility.

A few resistivity tests have been done using an apparatus constructed to hold a 3 x 2 x 1/2 inch specimen. Insufficient data has been taken to reach any quantative conclusions, but it does seem possible to make all the polymeric materials conductive. W. R. Grace has promised to send us some samples of conductive membrane material that will meet the present bending specifications of the Oklahoma Department of Transportation.

Conductive Asphalt

After conversations with the Oklahoma Department of Transportation personnel, we have changed the primary emphasis of this portion of the study slightly. It will be pointed toward development of a conductive asphaltic concrete that is sealed to prevent water intrusion. The conductive asphaltic concrete will be similar to that described in several publications and used by the Oklahoma Department of Transportation in the test installation of cathodic protection. The sealing will be similar to that previously used with rubber compounds or other suitable polymeric compounds.

We are presently in the midst of a literature survey concerning this area.

Reference Electrodes

This portion of the study is directed towards development of a solid reference electrode suitable to be permanently buried in the concrete. The electrode must be physically rugged, chemically stable in the high pH environment and electrically stable with respect to time and slight changes in chemical composition. We have manufactured and evaluated electrodes from silver-silver chloride (Ag/AgCl), molybdneum-molybdneum oxide (Mo/MoO) and carbon. Carbon proved to be completely unsatisfactory and will not be discussed further. In addition to those, we purchased Ag/AgCl electrodes manufactured for use with EEG instrumentation. These too proved unsatisfactory apparently due to defects in the manufacturing process. The Mo/MoO and Ag/AgCl manufactured in our laboratory will be discussed below.

Molybdneum-Molybdneum Oxide

These electrodes are manufactured by immersing electrical grade molybdneum in molten potassium nitrate. Some electrodes were also made the anode of an electrochemical cell to further oxidize the surface. There has been no detectable difference in the electrochemical performance of the electrodes prepared in these two ways. All results to be discussed below are from electrodes made in both procedures.

Figure 1 is a plot of the potential of eleven Mo/MoO electrodes compared to saturated calonel electrodes in saturated calcium hydroxide as a function of time. The electrodes are electrochemically stable and the potential very reproducible from electrode to electrode.

Figure 2 is a plot of the potential of several Mo/MoO electrodes in saturated calcium hydroxide as a function of chloride content. There is little effect on the potential by the chloride ions.

The potential of the electrodes are greatly affected by the pH of the environment. Figure 3 illustrates this when it is properly interpreted. Figure 3 is a plot of the Mo/MoO potentials as a function of time in saturated $Ca(OH)_2$ solutions for a period of 10 days. The same solution was used throughout the period of the test and due to reaction with CO_2 in the atmosphere, the pH of the $Ca(OH)_2$ changed.

Mo/MoO electrodes were buried in concrete cylinders with one rebar in each cylinder. The chloride ion level was varied from 0 to 0.5% weight percent. Figure 4 is a plot of potential versus chloride content about 15 days after the cylinders were poured. The potential of the rebar with respect to the saturated copper-copper sulfate ($Cu/CuSO_4$) electrode is shown. This potential varies with chloride content as previously found in the earlier study. The potential of the Mo/MoO electrode compared to the $Cu/CuSO_4$ was stable and not affected by the chloride ion.

Figure 5 is a plot of the potential of rebars and Mo/Mo electrodes compared to the $Cu/CuSO_4$ electrode as a function of time for cylinders containing 0 and 0.1% chloride ion. Time on the plot began when the cylinders were removed from the molds. They had been in the molds 15 days. Figure 6 is the same plot for cylinders containing 0.2 and 0.5% chloride ions. The Mo/Mo electrodes were found to be stable and reproducible.

Figure 7 is a plot of the potential of a rebar compared to Mo/MoO as a function of time beginning with the pouring date. These shifting potentials have been observed in the earlier studies and is due to the passivation of the rebar in the portland cement environment.

Silver-Silver Chloride Electrodes

Several manufacturing techniques have been tried for the silver-

silver chloride electrodes. Dipping fine silver wire in molten silver chloride has been the only technique that produces possibly satisfactory electrodes. Figures 8 and 9 are plots of potential data from silver-silver chloride electrodes manufactured in this method in saturated $Ca(OH)_2$ solutions with different levels of salt content. The electrodes are not as reproducible as the Mo/MoO and the potential is not as stable with respect to time. Also notice the potential is affected by chloride ion content.

Long-Term Current Tests

The effect of long-term DC currents of the magnitude expected in cathodic protection will be determined using pull out strength of rebars as a criteria. Apparatus has been partially constructed for the application of currents. The cylinders will be sent in a bed of coke breeze. This bed will be in an enclosed box to maintain an approximately constant humidity atmosphere. The cylinders will be poured shortly since we have now reached a decision on the chloride level of the cement to be used. The chloride ion content will be about 0.06% by weight.

Plans for Future Work

Conductive Layer

The literature survey will be completed. From this survey, material selections will be made and the mix design for the sealed, conductive asphaltic concrete will be developed. In addition, a mix design for conductive concrete will be developed.

Electrodes

Ag/AgCl electrodes will be buried in concrete cylinders containing a range of salt concentrations. Additional Mo/MoO electrodes will be placed in concrete cylinders to further check reproducibility of the manufacturing technique.

Long-Term Current

The cylinders for this test will be poured and the current test started. Plans are to pour enough cylinders so that five under current and five control cylinders will be subjected to pull out tests each three months for the five-year term of the test.

Corrosion Rate Measurement

Work has been delayed due to an instrument malfunction. This has been repaired and work will begin during the next period. Corrosion rate determinations will be started in saturated calcium hydroxide solutions containing various levels of chloride ion will be made using standard weight loss tests and the linear polarization measurements. This will lead to installing the linear polarization probes in concrete cylinders if the data from this method proves to be reliable.

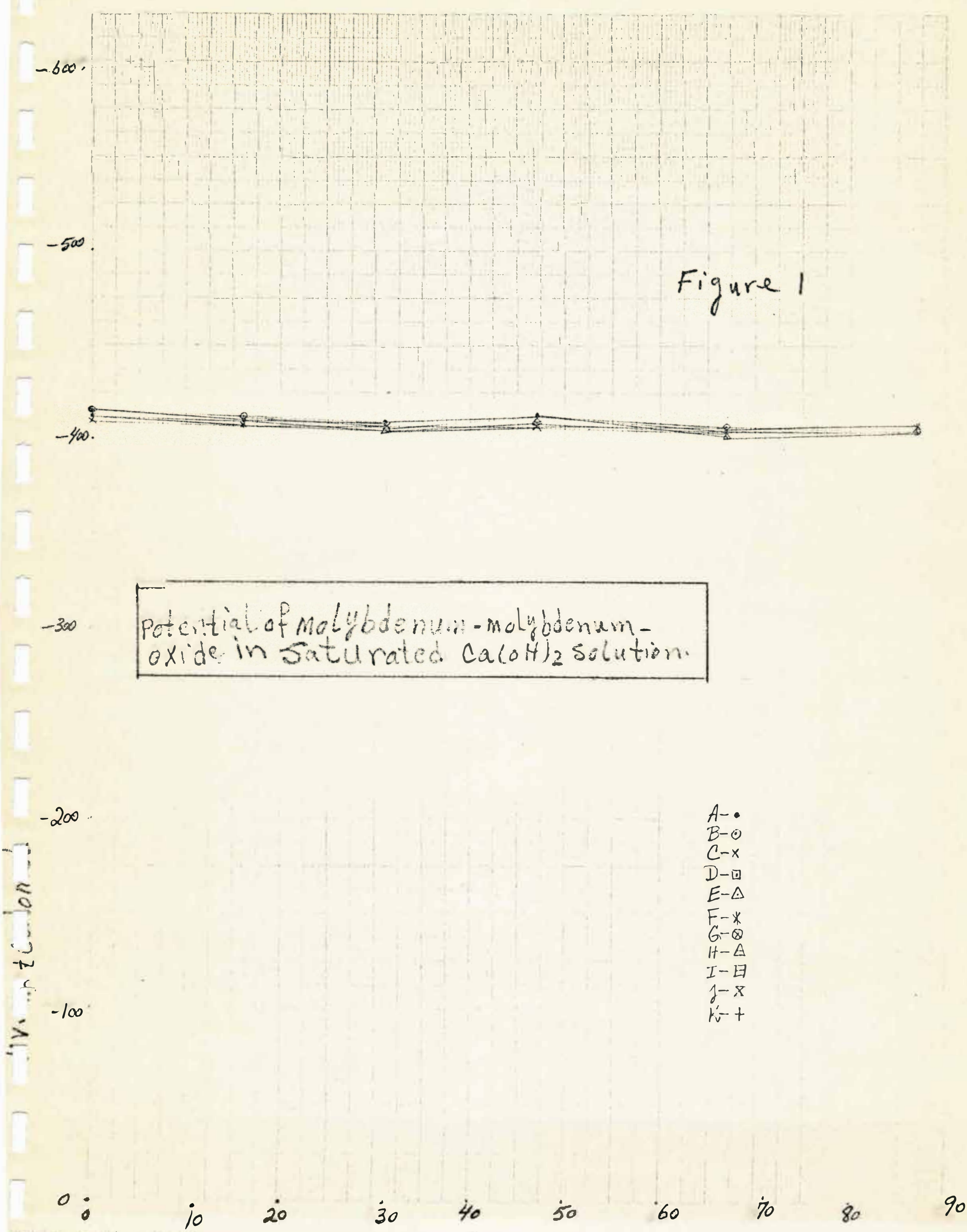
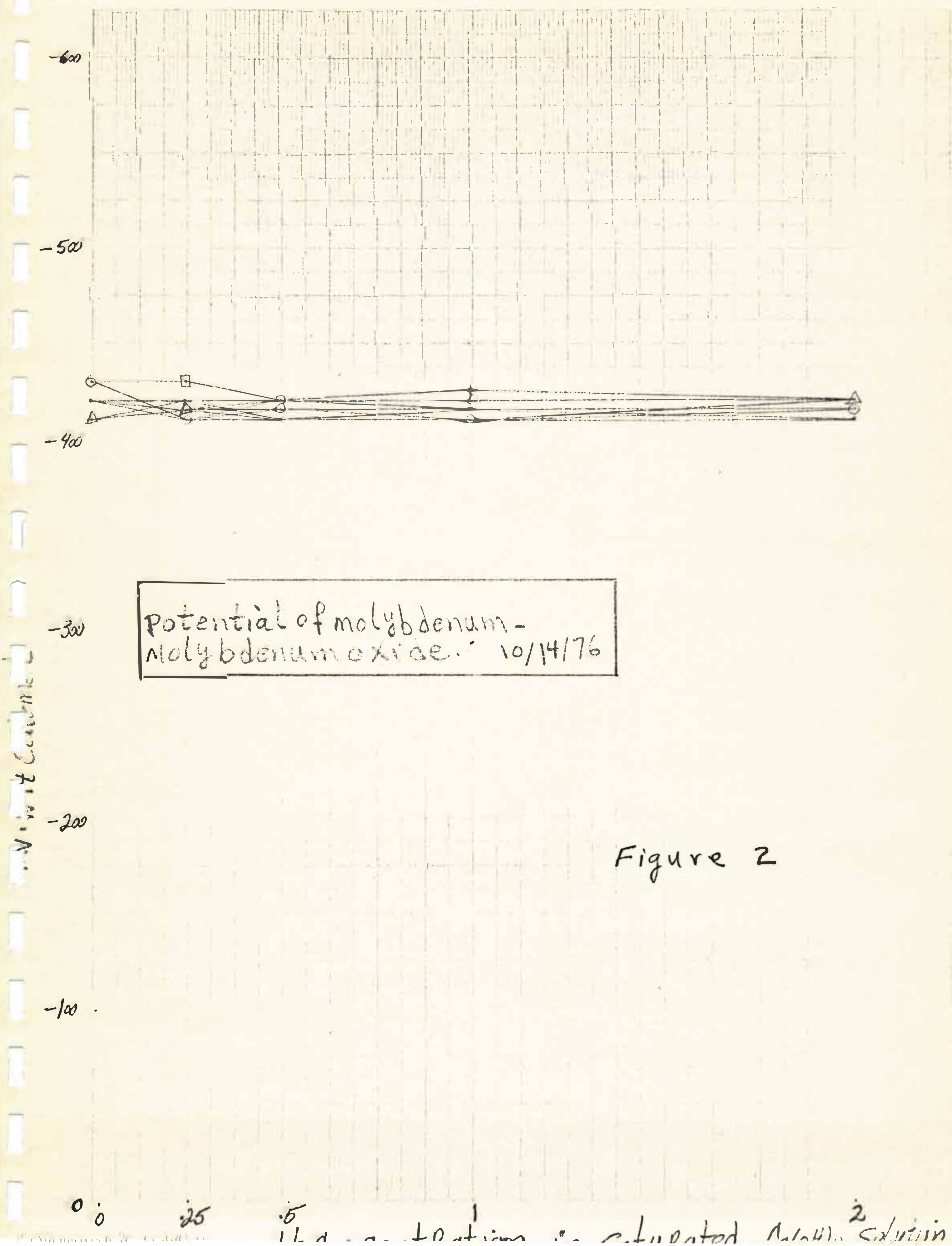


Figure 1

Potential of Molybdenum-molybdenum-oxide in Saturated $Ca(OH)_2$ solution.



-600
-500
-400
-300
-200
-100
0
0
.25
.5
1
2
potential of molybdenum-
molybdenum oxide. 10/14/76

Figure 2

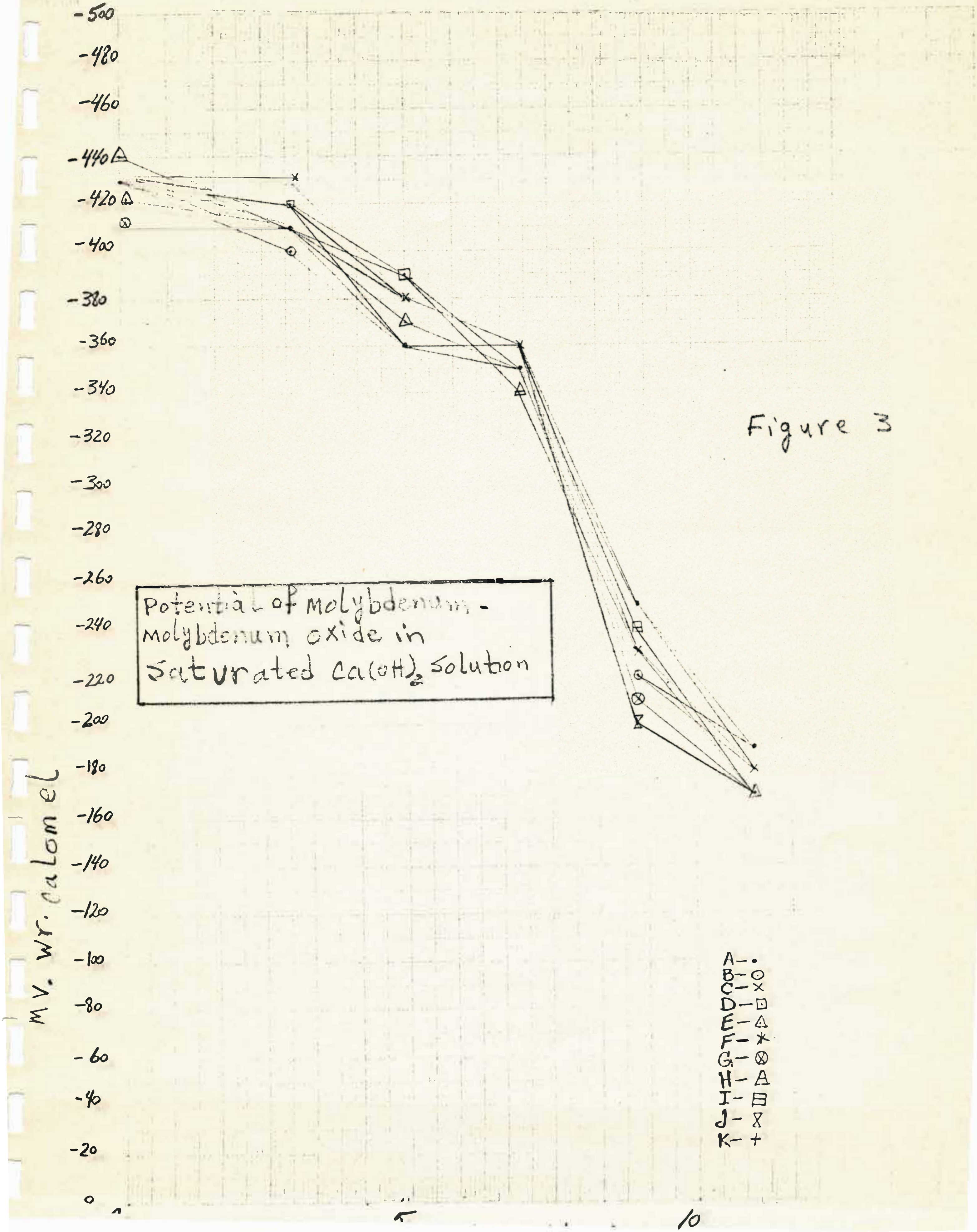
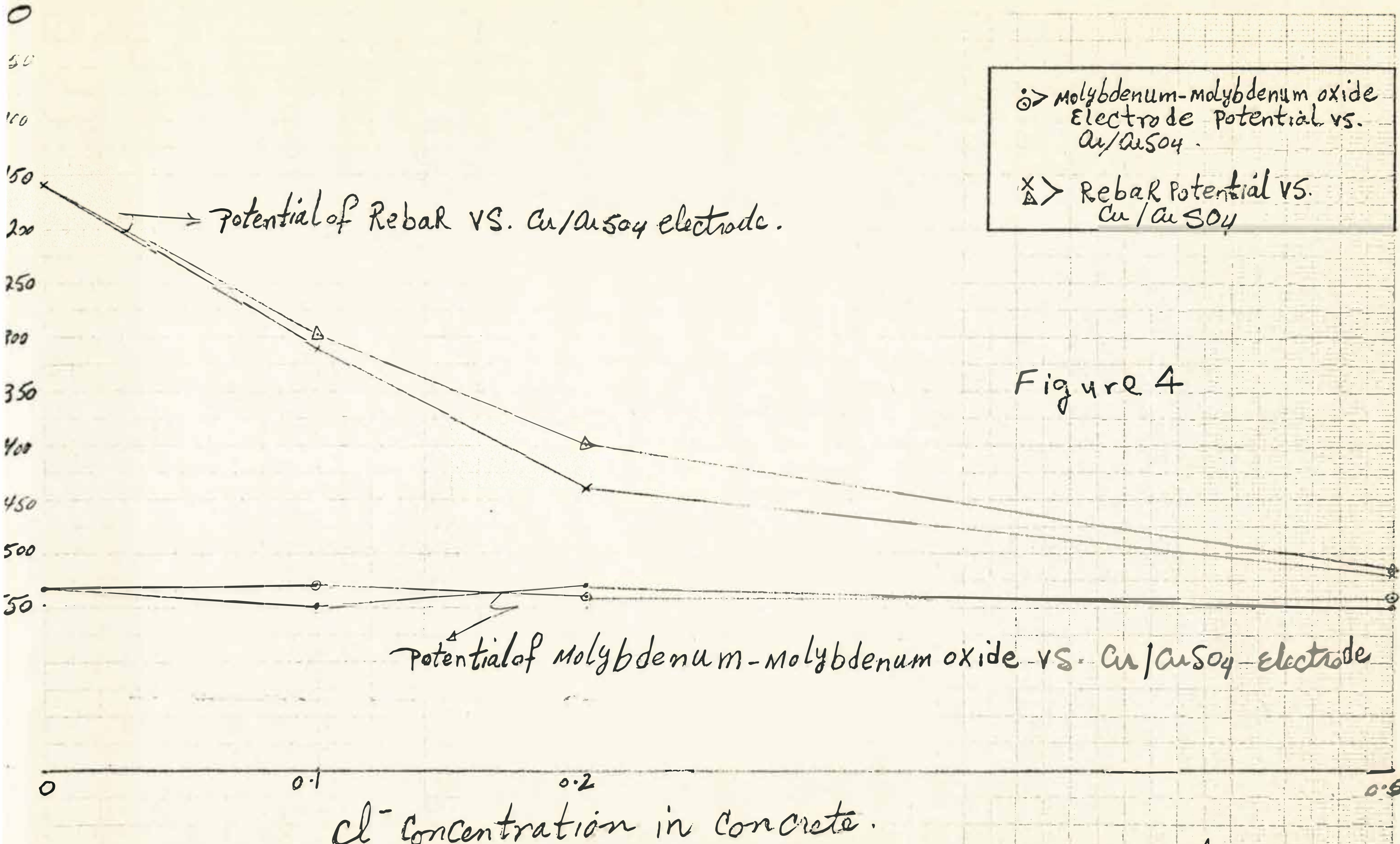

-500
-480
-460
-440
-420
-400
-380
-360
-340
-320
-300
-280
-260
-240
-220
-200
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
MV. wr. calomel
5
10
Potential of molybdenum-molybdenum oxide in saturated Ca(OH)2 solution
A- •
B- ⊙
C- ×
D- ⊡
E- ⊿
F- ✳
G- ⊗
H- A
I- ⊟
J- ⧗
K- +

Figure 3



Potential of Rebar and Molybdenum oxide Electrode vs. Cu/CuSO4 reference Electrode in different Salt Contaminated Concrete cylinder after Concrete cylinder got out of mold but still in water cabinet.

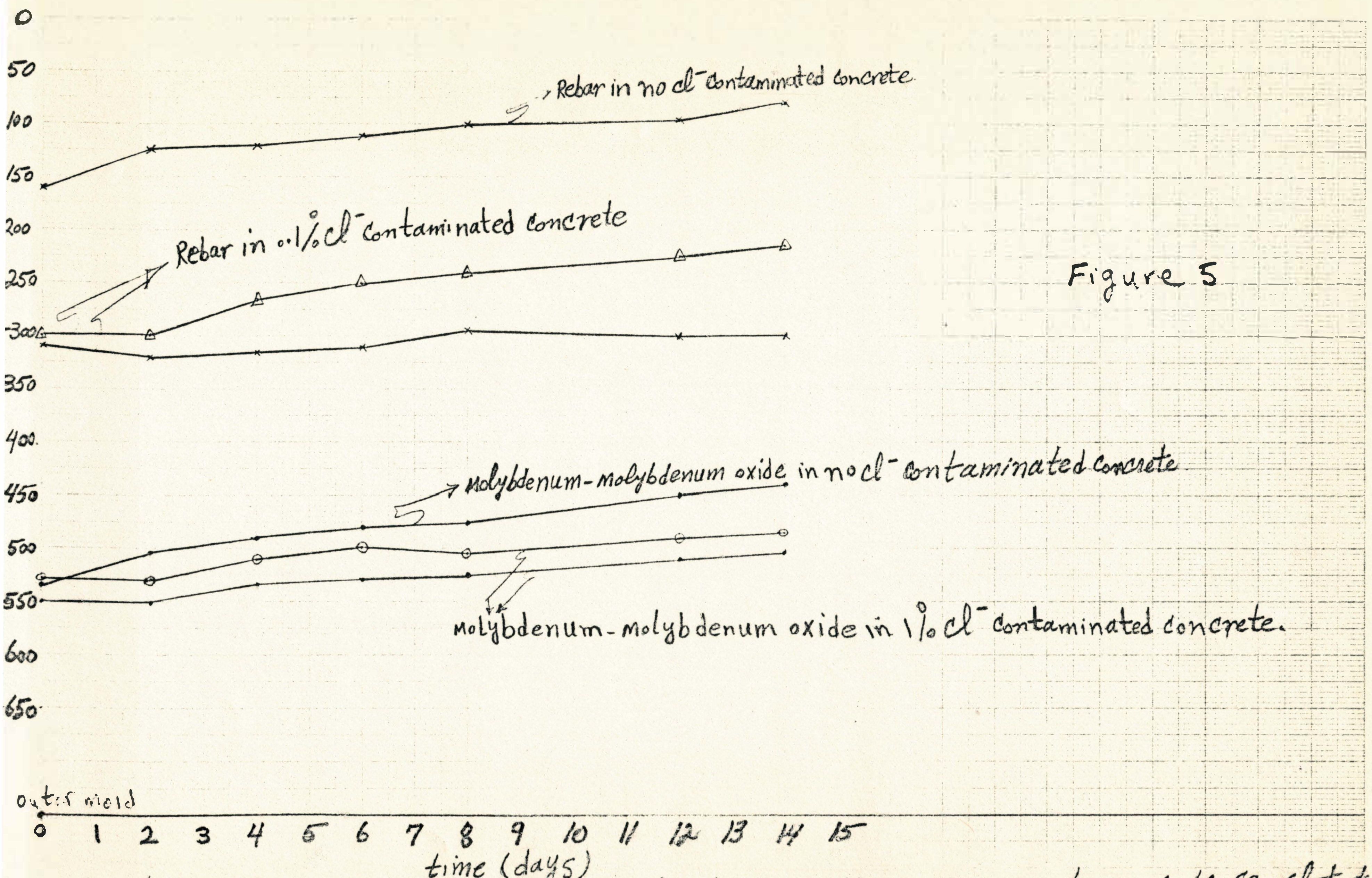
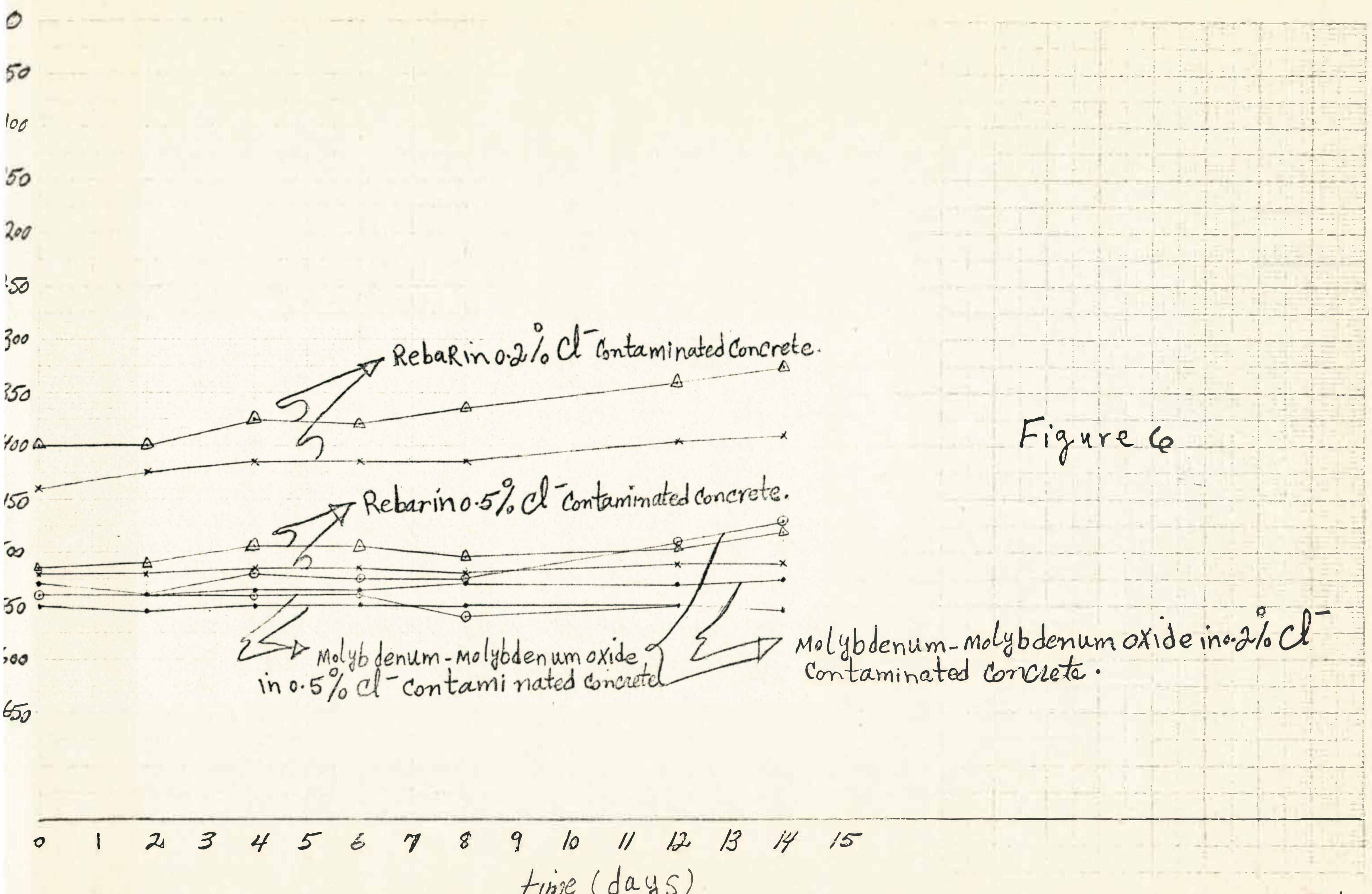


Figure 5

Potential(mv) of Rebar and Molybdenum-Molybdenum oxide in the Concrete vs. $Cu/CuSO_4$ Electrode
Concrete cylinders were taken out of mold but still kept in water Cabinet to Cure.
(15 days in Mold)



Potential (mv) of Rebar and Molybdenum-Molybdenum oxide in the Concrete vs. Cu/CuSO4 Electrode. Concrete cylinders were taken out of mold but still kept in water Cabinet to Cure.

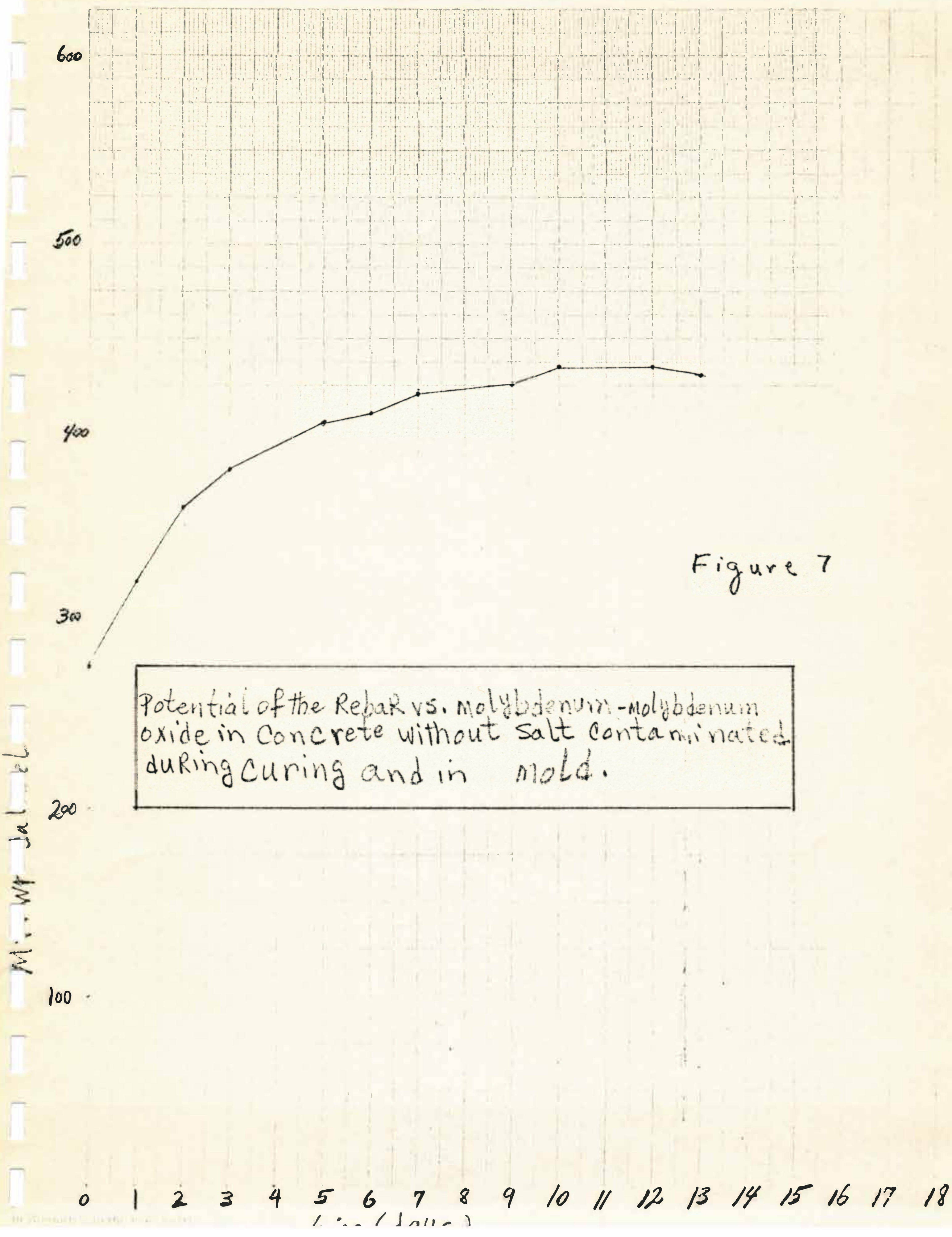
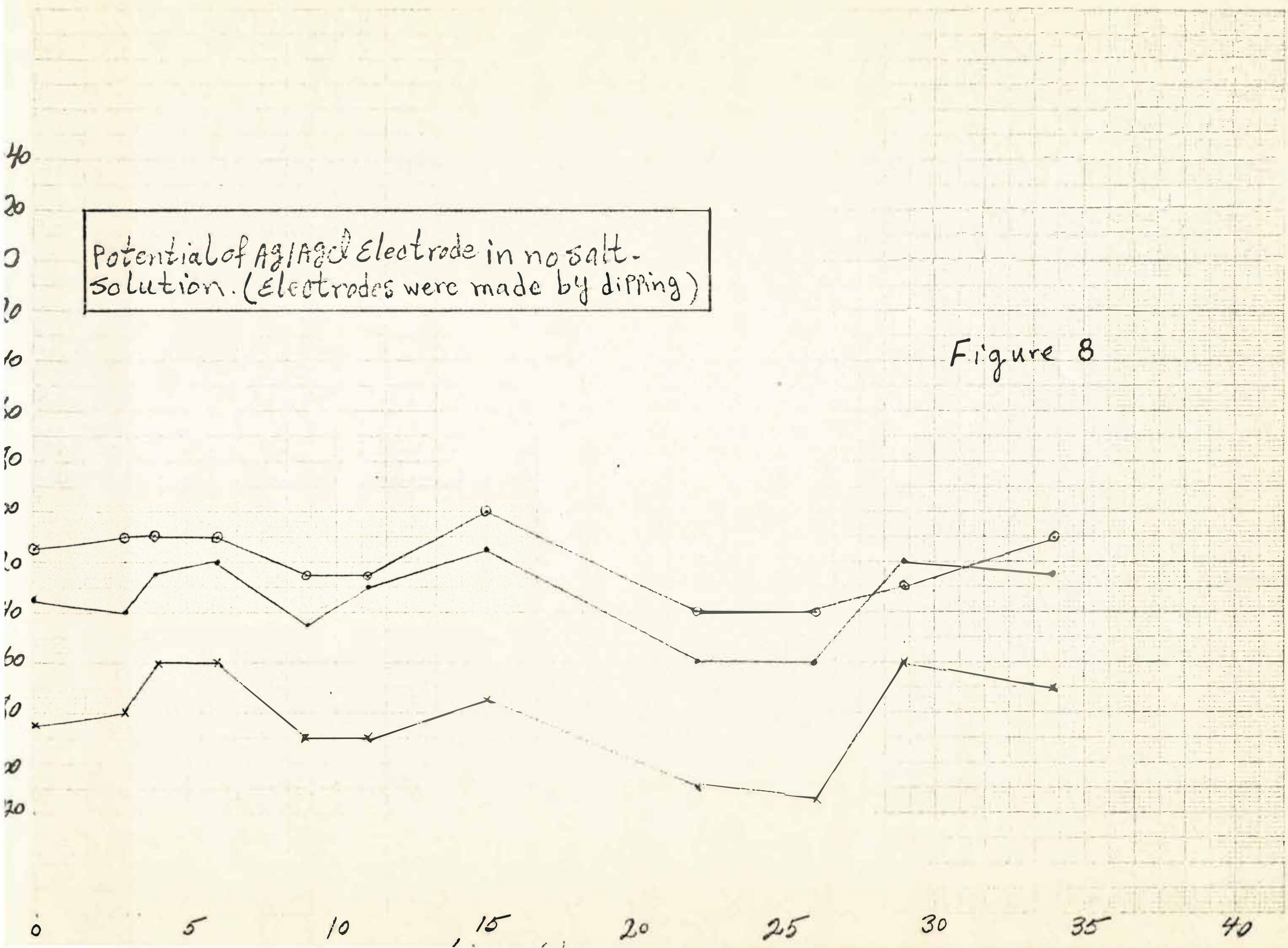


Figure 7

Potential of the Rebar vs. molybdenum-molybdenum oxide in Concrete without Salt contaminated during Curing and in mold.



Potential of Ag|AgCl Electrode in no salt solution. (Electrodes were made by dipping)
Figure 8
0
5
10
15
20
25
30
35
40

Potential of Ag/AgCl electrode in 0.25% salt solution (Electrodes were made by dipping).

Figure 9