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POLARIZATION MEASUREMENTS ON ASTM TYPE 6061-T6 ALUMINUM
ALLOY IN THREE ONTARIO MINE SHAFT WATERS

by

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ABSTRACT

Cathodic polarization measurements carried out on ASTM 6061-T6 aluminum alloy in three Ontario mine waters of different acidities and compositions provided a rapid estimate of relative corrosion rates even though these rates were too low to be readily measured by conventional weight-loss methods.

The results showed that corrosion rates in water from the Helen iron ore mine were much lower than those in waters from the two other mines. This correlated with the corrosion fatigue behaviour of ASTM 6061-T6 alloy in the same waters.

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Direction des mines

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MESURES DE POLARISATION D'UN ALLIAGE D'ALUMINIUM
DE TYPE ASTM 6061-T6 DANS LES EAUX DE TROIS
PUITS DE MINE EN ONTARIO

par

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RÉSUMÉ

Des mesures de polarisation cathodique effectuées sur un alliage d'aluminium de type ASTM 6061-T6 plongé dans les eaux d'acidité et de composition différentes de trois mines en Ontario ont permis de déterminer rapidement les vitesses de corrosion relatives même si ces vitesses étaient trop lentes pour être mesurées directement par les procédés ordinaires de perte de poids.

Les résultats ont montré que la vitesse de corrosion dans les eaux provenant de la mine de fer Helen est beaucoup plus lente que celle qui se produit dans les eaux des deux autres mines. Cet état de choses correspond au comportement à la fatigue-corrosion de l'alliage ASTM 6061-T6 dans les mêmes eaux.

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INTRODUCTION

Recent research at the Mines Branch into the corrosion fatigue properties of five metals commonly used in mine shaft conveyances has shown that the behaviour of ASTM 6061-T6 aluminum alloy is dependent on the type of mine shaft drain water used as corrodant during the tests (1).

In water from the Leitch* gold mine and Levack** nickel mine, corrosion fatigue endurances at 10^7 cycles were respectively 8,000 psi and 10,000 psi, and localized corrosion attack was observed.

However, in water from the Helen*** iron ore mine, resistance to corrosion fatigue was excellent, the corrosion fatigue endurance at 10^7 cycles exhibiting the high value of 15,500 psi, which was equal to the fatigue limit. Corrosion attack appeared to be slight, and an adherent black film soon developed on the specimens, which appeared to be highly protective.

Short-term (24-hr) corrosion tests showed the principal qualitative features of the corrosion attack in the three waters, but the weight losses in these tests were too low for measurement of comparative corrosion rates (1).

During the past decade, a number of workers have carried out polarization measurements in natural and process waters as a method of determining corrosion rates (2, 3, 4, 5, 6). Stern and co-workers (7, 8) have supplied a theoretical basis for this type of measurement and have also discussed its practical application, which involves the use of the equation:

$$R_p = \frac{\Delta E}{\Delta I} = \frac{B_a B_c}{2.3 (B_a + B_c) I_{corr}}$$

In this equation the quantity R_p , the "polarization resistance", is found by determining experimentally the linear slope $\frac{\Delta E}{\Delta I}$, which is observed when a corroding metal is polarized only slightly from E_{corr} , the rest corrosion potential. I_{corr} is the corrosion current, i.e. the rate of loss of metal

* Leitch Gold Mines, Co., Beardmore, Ontario.

** International Nickel Co., Levack, Ontario.

*** Algoma Ore Properties, Wawa, Ontario.

through corrosion expressed in terms of current density. B_a and B_c are respectively the anodic and cathodic "Tafel" constants, which can be either evaluated experimentally, or, in some cases, deduced from knowledge of the corroding system. It is claimed that this method can be used to estimate corrosion rates within a factor of 2 for most corroding systems, and that some knowledge of the electrochemistry of the system permits a much better estimate (8).

It was decided to use the techniques of Stern and co-workers to measure the corrosion rate of ASTM Type 6061-T6 aluminum alloy in the three Ontario mine waters that were utilized in the corrosion fatigue research. It could then be determined whether the superior resistance to corrosion fatigue observed in Helen water could be explained by a low rate of corrosion in that water.

EXPERIMENTAL

The ASTM Type 6061-T6 aluminum alloy was produced by the Aluminum Co. of Canada, Limited, as 1/4 in. sheet designated Alcan 65S-T6*. Semi-quantitative spectrographic analysis of the alloy gave results that showed good agreement with the chemical composition specified by the Aluminum Co. of Canada** for this alloy.

Detailed analyses of the three mine waters used in the measurements appear in Table 1.

Specimens used in the tests were rectangular. They incorporated a projecting arm containing a threaded socket extending along one side to facilitate electrical connection. Prior to tests, the specimens were ground to a uniform surface finish on water-cooled 120 grit silicon carbide paper lubricated with soap. They were then rinsed thoroughly in tap water, degreased in ultrasonically agitated carbon tetrachloride, and measured with a micrometer to determine the total immersed areas. These areas lay in the range 8-12 cm².

A schematic diagram of the apparatus appears in Figure 1. The potentiostat (Anotrol Model 311) is an instrument that can be used to hold a metal specimen, immersed in aqueous solution, at some selected potential with respect to a reference electrode. In this work, the reference was the

* Also Canadian Standards Association (CSA) HA.4 GS11N-T6.

** Cu, 0.15-0.40%; Fe, 0.70%; Mg, 0.8-1.2%; Mn, < 0.15%; Si, 0.40-0.80%; Ti, < 0.15%; Zn, < 0.20%; Cr, 0.15-0.35%; total other elements < 0.15% (9).

saturated calomel electrode. The electrical currents that were passed through the platinum auxiliary electrode to the specimen, or vice versa, to attain the selected potentials, were measured on a potentiometric chart recorder (Westronics, Model 511 A/U). The potentiostat was equipped for linear scan, so that a sweep could be carried out over a selected potential range at a constant rate, the current density being measured continuously.

The two-armed glass vessel in which the polarization measurements were carried out is shown in Figure 2. Specimens were contained in the left-hand arm, and an aluminum bar, threaded into the top of the projecting arm of the specimen, permitted electrical connection through the lucite cap. During measurements, all parts of the specimen and connecting bar above the water line were covered with paraffin wax to prevent vapour-phase corrosion. Measurement of the potentials of the specimens, relative to the saturated calomel electrode, were made possible by the installation of a Luggin probe, which was connected to the beaker containing the standard cell by means of a salt bridge.

The right-hand arm of the test vessel, which was separated from the left-hand arm by a sintered glass diaphragm, contained the auxiliary electrode of platinum foil. A platinum wire, welded to the upper part of the electrode, led through a rubber stopper to the external electrical circuit.

The measurements utilized the following rigidly controlled procedures:

1. The selected mine water (330 ml in all) was poured into the test vessel and allowed to stand for 1 hour. At the end of this time, the room temperature of $24^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ($75^{\circ}\text{F} \pm 2^{\circ}\text{F}$) had been attained.
2. The specimen of ASTM Type 6061-T6 alloy was immersed in the mine water for 1 hour. At the end of this time, the unpolarized corrosion potential E_{corr} was determined, using the vacuum tube voltmeter.
3. The potentiostat was adjusted to give a linear potential scan of 150 mV in 5 min (i.e. a rate of 1.8 V/hr), with the starting potential 100 mV more active (more cathodic) than E_{corr} .
4. The current was measured continuously during the scan, but the potentiostat was switched to the "standby" position as soon as the change of polarity from cathodic to anodic had taken place, thus preventing anodic polarization of the specimens.
5. After the conclusion of the scan period, a further five minutes was allowed to elapse. The value of E_{corr} was then measured and repeat scans were made until 8 consecutive scans had been carried

out for each specimen.

Two specimens of aluminum alloy from the same rolled sheet, termed specimens 1 and 2, were used in the work, and they were resurfaced for re-use as required. Both specimens were measured in each of the three mine waters, with eight replicate scans being carried out as described above in each water. A fresh supply of mine water was used for each group of eight scans.

RESULTS

Three model polarization curves, indicative of the different behaviour in the three mine waters, appear in Figure 3.

The values of R_p obtained from the polarization curves, along with the E_{corr} values determined just prior to the scans, using the vacuum tube voltmeter, are listed in Tables 2-4. For each group of 8 scans, the mean and standard deviation of R_p are calculated, and are presented rounded off to the nearest three significant figures.

In the aerated mine waters used in this work, the cathodic reaction is controlled by the diffusion rate of oxygen, and B_c is therefore equal to infinity. This information is sufficient, according to Stern and Weisert (8), to permit the calculation of corrosion rates accurate within 40%. Most values of B_a are stated to lie between 0.06 and 0.12, and the polarization resistance data of the present work should therefore yield I_{corr} values lying in the band shown in Figure 4.

Corrosion rates in the three mine waters, calculated from the mean polarization resistance values of Tables 2-4 using the method of Stern and co-workers, appear in Table 5.

DISCUSSION OF RESULTS

The results of Table 5 indicate that the corrosion rate of ASTM Type 6061-T6 aluminum alloy in Helen mine water is lower, by a factor of about 10, than the corrosion rates in the other two waters. This correlates with the previous observation of excellent corrosion fatigue resistance in

Helen mine water, as compared with the other two waters.

Corrosion rates in the Levack mine water, as compared with the Leitch mine water, did not appear to differ significantly. It bears mention, however, that the values of R_p , the polarization resistance, showed much greater consistency in the acid Levack water than in the high-chloride Leitch water (Tables 2 and 3).

It should be kept in mind that the corrosion rates that were measured were representative of behaviour during the second hour of immersion in a mine water, and that the rates would have probably become lower with more protracted immersion. In this regard it is worth mentioning that, in exploratory measurements, the aluminum alloy specimens were immersed overnight prior to measuring the polarization resistance, and corrosion rates were much lower in all three waters ⁽¹⁰⁾. In the exploratory measurements the successive scans incorporated anodic as well as cathodic branches, and employed a much slower scan speed of 0.6 V/hour, over the same range of 150 mV. Film formation and contamination of the mine water through dissolution during the anodic polarizations are believed to be responsible for the rather poor reproducibility that was then observed.

With respect to the present series, it is believed that reproducibility could have been improved still more if, rather than attempting to measure the slopes of the curves at the origin, which were questionable in a few cases, the potential at some definite current density had been measured, and the $\Delta E/\Delta I$ values resulting therefrom used in the Stern equation. Closer control of temperature and content of dissolved gases in the waters might also have improved reproducibility.

CONCLUSIONS AND FUTURE PROGRAM

Cathodic polarization measurements provided a rapid estimate of relative corrosion rates of ASTM Type 6061-T6 aluminum alloy in three mine waters, although the rates were too low to be measured conveniently by conventional weight-loss methods. The results correlated with the trends shown by corrosion fatigue measurements in the same waters. Because the primary objectives of the work have been attained, the work has been terminated.

Polarization measurements may be employed in future cases where a rapid estimate is required of the corrosion performance of some metal that corrodes at a relatively low rate in a natural water or chemical process solution.

ACKNOWLEDGEMENTS

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Discussions with Dr. M. Cohen of the Division of Applied Chemistry, National Research Council, Ottawa, and Mr. C.E. Makepeace, of Eldorado Mining and Refining Co., Ottawa, were very helpful.

REFERENCES

1. G.J. Bieffer, "Corrosion Fatigue of Structural Metals in Mine Shaft Waters", Mines Branch Research Report R 167, Department of Mines and Technical Surveys, Ottawa, Canada (July, 1965).
2. H.J. Engell, "Procedure for the Measurement of the Dissolution Velocity of Corroding Metals in Air-containing Solutions", *Archiv. fur das Eisenhüttenwesen* 9, 553 (Sept. 1958). In German.
3. R.V. Skold and T.E. Larsen, "Measurement of the Instantaneous Corrosion Rate by Means of Polarization Data", *Corrosion* 13, 139t (Feb. 1957).
4. T.P. Hoar and T.W. Farrar, "The Anodic Characteristics of Mild Steel in Dilute Aqueous Soil Electrolytes", *Corrosion Science* 1, 49 (1961).
5. P. Neufeld, "Application of the Polarization Resistance Technique to Corrosion Monitoring", *Corrosion Science* 4, 245 (1964).
6. S. Evans and E.L. Koehler, "Use of Polarization Methods in the Determination of the Rate of Corrosion of Aluminum Alloys in Anaerobic Media", *Journal of the Electrochemical Society* 108, 509 (June 1961).

REFERENCES (concluded)

7. M. Stern and A.L. Geary, "Electrochemical Polarization. I. A Theoretical Analysis of the Shape of Polarization Curves", Journal of the Electrochemical Society, 104, 56 (Jan. 1957).
8. M. Stern and E.D. Weisert, "Experimental Observations on the Relation between Polarization Resistance and Corrosion Rate", Proc. ASTM, 59, 1280 (1959).
9. Handbook of Aluminum, Second Edition, Aluminum Co. of Canada, Ltd., Montreal, Canada (1961).
10. G.J. Biefer and B.G. Olivier, "Polarization Measurements on 65S-T6 Aluminum in Mine Shaft Waters", Physical Metallurgy Division Internal Report PM-R-65-2, Department of Mines and Technical Surveys, Ottawa, Canada (Jan. 28, 1965).

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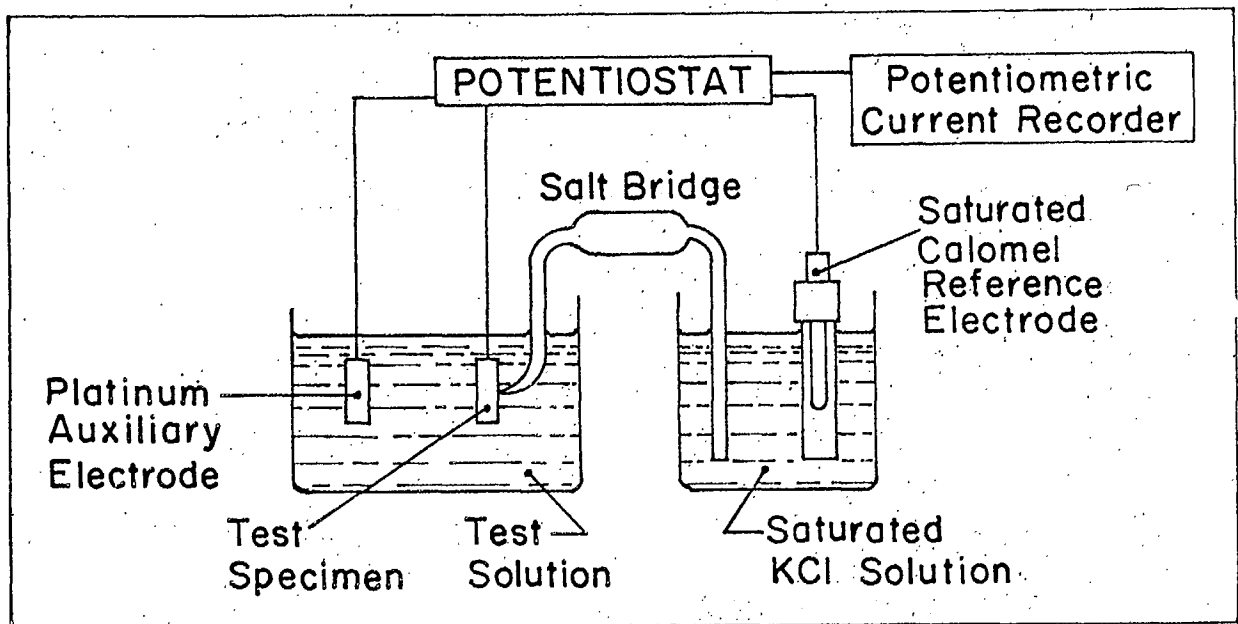


Figure 1. Schematic diagram of apparatus used to carry out the polarization measurements.

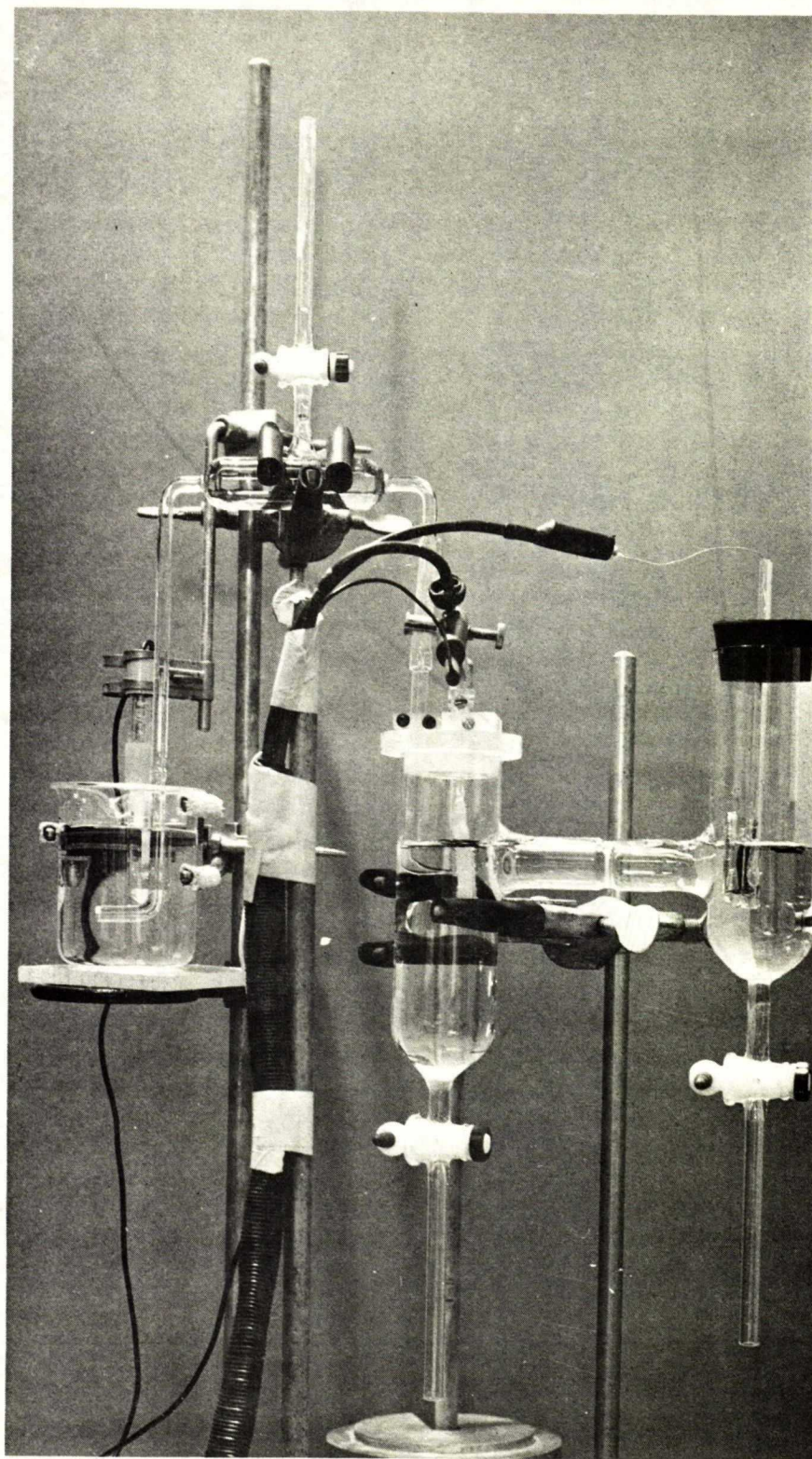


Figure 2. Equipment used in carrying out the polarization measurements.

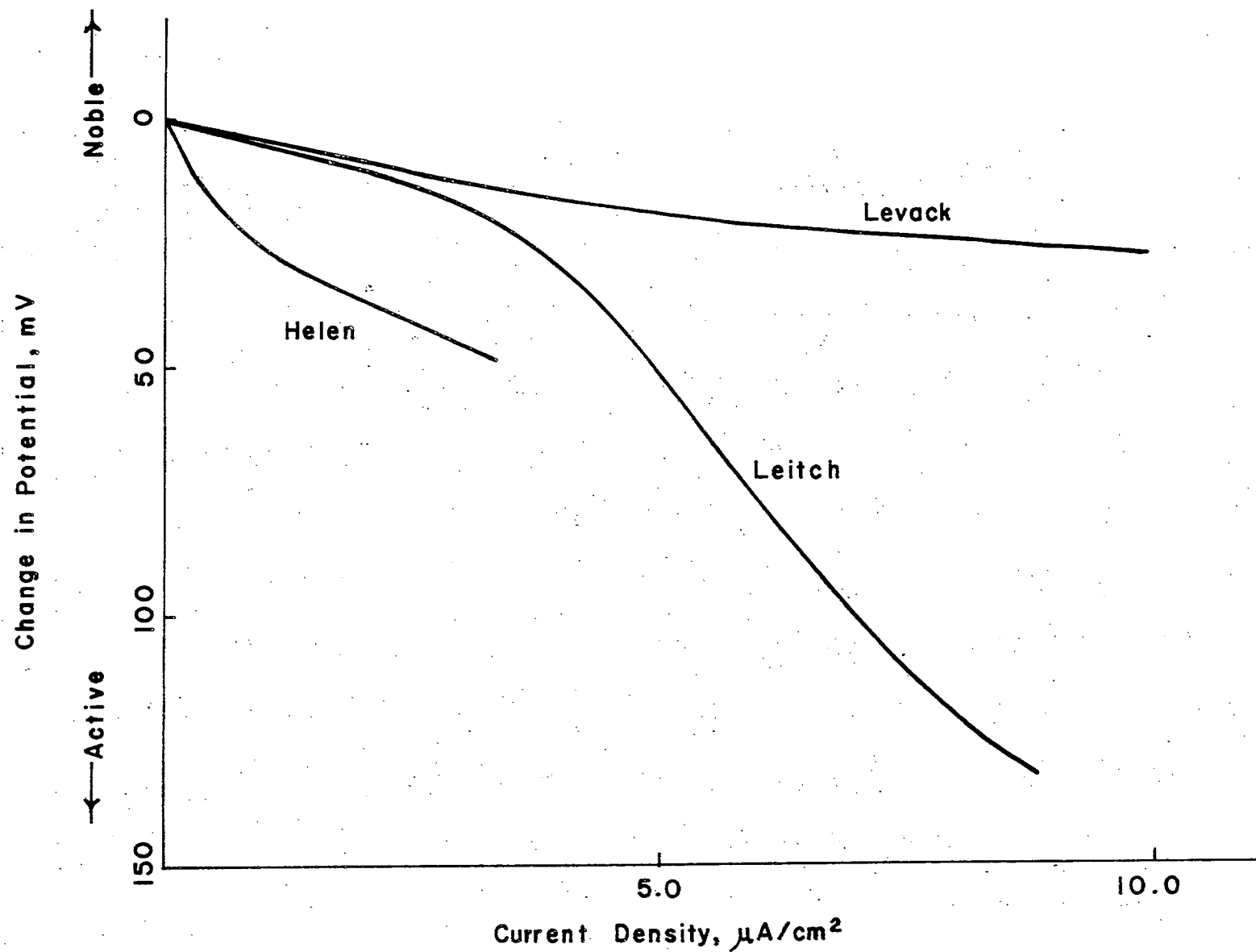
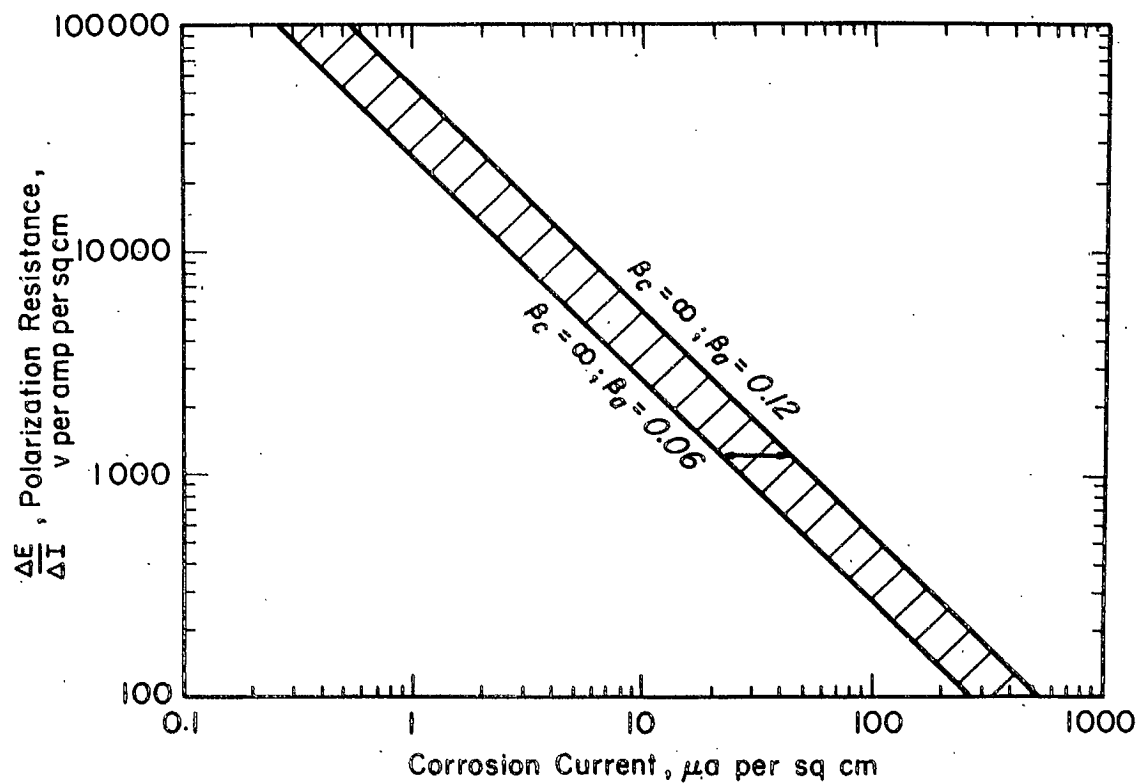


Figure 3. Model cathodic polarization curves in the three mine waters.



Limits Within Which the Relation Between Polarization Resistance and Corrosion Current Applies for a System with a Constant Cathodic β Value of Infinity (a limiting diffusion current) and an Anodic β Value Which Varies from 0.06 to 0.12 v.

Figure 4. Relationship of polarization resistance R_p and corrosion current I_{corr} , showing limiting values of I_{corr} for $B_c = \infty$, $B_a = 0.06$ to 0.12 .
(From reference 8)

TABLE 1
Analyses of Three Ontario Mine Waters (Levack, Helen, Leitch)

MINES BRANCH
MINERAL PROCESSING DIVISION

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

INDUSTRIAL WATERS SECTION
40 Lydia Street, Ottawa, Ont.

ANALYSIS OF WATER SAMPLE(S)
(in parts per million)

Location			
Source of water	Levack Mine	Helen Mine	Leitch Mine
Sampling point			
Reference			
Laboratory number			
Date of sampling			
Storage period (days)			
Temp. at sampling (°C)			
Temp. at testing (°C)	22.8	23.7	24.1
Appearance, odour, etc.			
Organic matter:			
Oxygen consumed (KMnO ₄)		4	
Chem. oxygen demand (C.O.D.) ..			
Ultra violet absorption (mu) ..			
Carbon dioxide (CO ₂), calculated		10	4
pH	3.4	7.2	7.6
Colour (Hazen units)	15	0	5
Turbidity (Units)	1.5	0	10
Alkalinity as (-Phenolphthalein	0	0.0	0.0
CaCO ₃ (-Total)	0	83.1	77.7
Susp. matter, dried at 105°C ..			
" " ignited at 550°C ..		1,644	
Res. on evap., dried at 105°C ..		353	
Loss on ignition at 550°C		1,897	31,000
Sp. conductance, micromhos at 25°C	3,040		
Hardness as (Total)	1,175	1,079	2,054
CaCO ₃ (Non-carbonate) ..	0.0	996	1,977
Calcium (Ca)	405	245	744
Magnesium (Mg)	42	113	48
Iron (Fe) Total	0.46	0.06	1.4
Dissoived	0.36	0.0	0.11
Aluminum (Al)	1.4	0.3	0.12
Manganese (Mn) Total	3.5	0.29	2.0
Dissoived	3.0	0.00	1.2
Copper (Cu)	1.58	0.005	0.05
Zinc (Zn)	0.54	1.7	0.05
Sodium (Na)	119	25.0	6,870
Potassium (K)	16.6	8.4	33
Ammonia (NH ₃)			
Nickel (Ni)	23.8		
Cobalt (Co)	0.56		
Carbonate (CO ₃)	0.0	0.0	0.0
Bicarbonate (HCO ₃)	0.0	101	94.7
Sulphate (SO ₄)	685	830	126
Chloride (Cl)	629	125	12,078
Fluoride (F)	0.4	0.18	0.37
Phosphate (PO ₄) Total	0.01	0.0	
Dissoived			
Nitrate (NO ₃)	0.3	37	19
Silica (SiO ₂)	20	3.1	5.6
Sum of constituents	1,950	1,440	19,921
% Sodium	16	4.8	88
Saturation index at test temperature		0.0	0.0
Stability index at test temperature		7.2	7.6
Sodium Absorption Ratio (SAR)		0.33	

*in parts per million unless otherwise stated:

NOTE: Details of the above terms and procedures are given in the booklet, procurable from the Industrial Waters Section, Mines Branch, 40 Lydia St., Ottawa 4, Ont., entitled "Industrial Water Resources of Canada, Water Survey Report No. 1, Scope, Procedure and Interpretation of Survey Studies", by J. F. J. Thomas, Report No. 833, Department of Mines and Technical Surveys, Ottawa, Canada (1953).

TABLE 2
Cathodic Polarization Measurements
in Leitch Mine Water

Scan No.	Specimen 1		Specimen 2	
	E_{corr} (mV)	R_p V/A/cm ²	E_{corr} (mV)	R_p V/A/cm ²
1	-710	4,650	-710	1,990
2	-710	2,740	-700	4,470
3	-700	4,960	-700	4,380
4	-700	3,340	-700	4,350
5	-700	4,250	-700	5,700
6	-700	4,750	-700	8,150
7	-700	4,000	-700	5,300
8	-700	5,450	-700	4,680
Mean		4,270		4,880
Standard Deviation		888		1,720

TABLE 3
Cathodic Polarization Measurements
in Levack Mine Water

Scan No.	Specimen 1		Specimen 2	
	E _{corr} (mV)	R _p V/A/cm ²	E _{corr} (mV)	R _p V/A/cm ²
1	-650	2,890	-730	2,520
2	-660	3,640	-700	2,520
3	-690	3,590	-720	2,710
4	-700	3,660	-680	2,120
5	-700	3,520	-680	3,370
6	-700	4,030	-640	2,640
7	-710	3,560	-630	2,420
8	-700	3,040	-700	2,980
Mean		3,490		2,660
Standard Deviation		363		378

TABLE 4
Cathodic Polarization Measurements
in Helen Mine Water

Scan No.	Specimen 1		Specimen 2	
	E _{corr} (mV)	R _p V/A/cm ²	E _{corr} (mV)	R _p V/A/cm ²
1	-500	25,800	-600	69,500
2	-530	51,500	-490	32,500
3	-520	45,000	-500	28,500
4	-530	41,500	-540	61,500
5	-530	44,800	-540	68,500
6	-530	46,900	-550	57,800
7	-530	40,400	-530	47,100
8	-530	46,200	-550	54,800
Mean		42,800		52,500
Standard Deviation		7,650		15,400

TABLE 5

Corrosion Rates of ASTM Type 6061-T6 Aluminum Calculated from Polarization Resistances

Mine Water	Specimen No.	Mean Polarization Resistance, $V/A/cm^2$	I_{corr} Range, $\mu A/cm^2$ *	Corrosion Rate Range, mdd **
Leitch	1	4,270	6.2 - 12	5.0 - 9.7
	2	4,880	5.4 - 10.5	4.4 - 8.5
Levack	1	3,490	7.6 - 15	6.1 - 12
	2	2,660	10 - 20	8.1 - 16
Helen	1	42,800	0.62-1.2	0.50-0.98
	2	52,500	0.51-0.99	0.41-0.80

* Utilizing Figure 4.

** mdd = milligrams/dm²/day. For aluminum, 100 mdd = 0.053/inches/yr.

A P P E N D I X

Statistical Analysis of the Polarization Resistance

Utilizing the methods and symbols described in the reference text*, an analysis of variance was carried out on the polarization resistance data which yielded the following results:

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square
Between Specimens	121, 380, 610	1	121, 380, 610
Between Waters	20, 499, 685, 219	2	10, 249, 842, 609
Errors	2, 366, 045, 260	44	53, 773, 756
Totals	22, 987, 111, 089	47	

Between Specimens, $F(1, 44) = 2.25$, which is less than the critical value of $F_{0.95}(1, 44) = 4.08$. Therefore the results obtained with specimen 1 do not differ significantly from the results obtained with specimen 2.

Between Waters, $F(2, 44) = 190.6$, which is greater than the critical value $F_{0.99}(2, 44) = 5.14$. The difference between the results obtained with the three waters is therefore highly significant.

It can be shown that the Helen water differs from the other two waters with a high degree of significance, but that they do not differ from each other, as follows:

* C.R. Hicks, "Fundamental Concepts in the Design of Experiments" Holt, Rinehart and Winston, New York, 1964.

(d) Leitch vs Levack (i. e. 2 vs 3) = 1,497 < 5,224.

Thus, there is no significant difference between the results obtained in the Leitch and Levack waters in this particular series of measurements.

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