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PROTECTION OF TYPICAL STAINLESS STEELS FROM CORROSION WHEN IN CONTACT WITH CERTAIN COMPLEX ORE LEACH SOLUTIONS

by

A. W. LUI

EXTRACTION METALLURGY DIVISION

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PROTECTION OF TYPICAL STAINLESS STEELS FROM CORROSION WHEN IN CONTACT WITH CERTAIN COMPLEX ORE LEACH SOLUTIONS

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SUMMARY

The research staff of Eldorado Mining and Refining Ltd. had hoped that large process tanks of stainless steels Types 304L, 316 and 347 containing six different acid solutions, used in ore leaching at a temperature of 80°C, could be largely prevented from corrosion by anodic protection. The problem of investigating this possibility was presented to this laboratory.

It was found

(1) that these tanks cannot be protected by the anodic protection method when they are in contact with solutions 5 and 6 because protective films are not formed on the surfaces of the tanks under such conditions.

(2) that these tanks can be protected by the anodic protection method when they are in contact with solutions 1, 2, 3 and 4.

(3) that there is no advantage in protecting these tanks by the anodic protection method because these steels become passive (and much more corrosive resistant) as soon as they come into contact with solutions 1, 2, 3 and 4 even without anodic protection.

(4) that the ease with which the anodic protection of these steels can take place is not greatly affected by partial immersion of the steel, welding of the steel with fairly similar weld metal or agitation of the solution. However anodic protection can take place more readily at lower temperatures (such as 25°C) than at higher temperatures (such as 80°C).

(5) the total sulphate contents of baths 5 and 6 were considerably less than those of baths 1, 2, 3 and 4. This seems to be the most probable explanation for the fact that protective films do not form on these steels in solutions 5 and 6 but do so in solutions 1, 2, 3 and 4.

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INTRODUCTION

A letter dated February 1, 1965, was received from Mr. C.E. Makepeace acting for Mr. J.M. Jardine, superintendent of the metallurgical laboratories of Eldorado Mining and Refining Ltd., Ottawa. In this it was stated that the company was interested in the anodic protection of certain stainless steel tanks from corrosion, and that any assistance in this regard from the Extraction Metallurgy Division of this Department would be appreciated.

Messrs R.R. Rogers and W. Dingley of the Corrosion Section of the Division attended a meeting at the Eldorado laboratories, at which this problem was discussed with personnel of the company, including Dr. A. Thunaes and Messrs. Jardine and Makepeace. It was stated by the company personnel that a process for the recovery of cobalt, nickel and silver from Cobalt area ores and concentrates had been developed, but that there were some doubts as to the corrosion resistance of the stainless steel tanks and pipelines which would be used, under the conditions which would exist during the continuous operation of the process. For this reason the company wished to learn whether it would be feasible to protect such equipment anodically from the corrosive action of the process materials, if the need should arise. The company was particularly interested in the protection of equipment of stainless steel Types 304L, 316 and 347.

It was agreed that this Corrosion Section would investigate the possibility and desirability of anodically protecting each of these three types of stainless steel when in contact with three different process solutions at 80°C. The latter, referred to as solutions 1, 2 and 3 in the present report, were known to the company personnel as "high emf" solutions and were taken from tanks 1-F-21, 1-F-23 and 6-F-14 respectively in their plant.

At a later date the company requested that similar experiments be performed using three additional solutions taken from their tanks 1-F-21, 1-F-23 and 1-F-24 at a different time. These, known to the company personnel as "low emf" solutions, are referred to as solutions 4, 5 and 6 respectively in the present report.

In due course 20 gal of each of the six solutions and samples of each of the three stainless steels (both welded and unwelded) were received from the company's Port Hope plant.

Since the anodic protection of metals has been discussed in publications by a number of authorities (1)(2)(3)(4)(5), it has not been considered necessary to include any general discussion of the subject in the present report.

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Since three steels and six solutions were submitted by the company it was necessary to investigate the possibility and desirability of anodic protection in eighteen different combinations of steel and solution. It was found to be impossible to protect steels anodically, i.e. to make them passive, in some of the solutions.

In the case of the other combinations of steel and solution

(1) the range of controlled potentials producing passivity in each steel in each solution was determined.

(2) the effects of certain variables on the width of each range, were determined.

(3) the corrosion rates of the steels when in the passive state in each solution, were determined.

(4) the corrosion rates of the steels at higher controlled potentials than those producing passivity (i.e. of the steels in the active state), were determined.

(5) the corrosion rates of the steels when the potentials were uncontrolled, were determined.

(6) the data obtained in (3) and (4) were compared to obtain some idea of the importance of having the steels in the passive state when in contact with the solutions.

(7) the data obtained in (3) and (5) were compared to determine the advantage of anodic protection of the steels in these particular solutions.

It should be pointed out that clear solutions were used in these experiments. It is possible that the results would have been somewhat different if the metal surfaces had been covered with solid particles during the experiments.

EXPERIMENTAL MATERIALS AND APPARATUS

The specimens of stainless steel of Types 304L, 316 and 347 supplied by the company, had the analyses given in Table 1. They included welded specimens of each type, the welding metal being of the same material as the welded metal in the case of the Type 316 and 347 steels. Type 308L steel was used as the welding metal when welding the Type 304L steel. All specimens used in the experiments were cut and machined so that the area of each side was 10 sq cm.

The analyses of solutions 1, 2 and 3 are given in Table 2A and those of solutions 4, 5 and 6 in Table 2B. This information was largely obtained by the company, the remainder being obtained by the Chemical Analysis Section of this Division.

TABLE 1

Analyses of Type 304L, 316 and 347 Stainless Steel

AISI Type	Analysis (%)						
	C	Mn	Si	Cr	Ni	Mo	Cb+Ta
304L	0.02	0.8	0.8	18.7	10.2		
316	0.05	1.8	0.5	16.7	13.1	2.5	
347	0.07	1.5	0.5	17.9	10.9		0.8

The inside diameter of the cylindrical glass electrolytic test cell was 6.2 cm, and the depth of the solution in it was 6.7 cm in the experiments in which the steel specimens were completely immersed. When the solution was agitated it was done by means of a magnetic stirrer on the bottom of the cell. The latter contained two platinum electrodes connected in parallel and, between these, an electrode of the stainless steel under investigation. The latter was suspended by a holder similar to that used by Riggs[6]. The reference electrode, consisting of a standard saturated calomel half-cell, was connected to the test cell by a salt bridge. The temperature of the solution in the test cell was maintained at the desired level by a regulated electric hot plate.

The potentials of some of the stainless steel specimens were controlled by a Model 4100 electronic potentiostat manufactured by the Anotrol Division of the Continental Oil Company. The accuracy of this instrument was within ± one millivolt. A Model G-22A dual channel recorder, manufactured by Varian Associates, gave a simultaneous record of the potential of the stainless steel specimen and the resulting current at the surface of the specimen.

EXPERIMENTAL PROCEDURE

The procedure for determining the uncontrolled potential of a metal in a solution is well known and need not be described here.

The same equipment was used when determining the range of the controlled potentials which would produce passivity in a stainless steel, except that a potentiostat was included to impress twelve different potentials from +0.45 to +1.00 volt on the steel. At each of these potentials a record was made of the resulting current density at the surface of the steel. It was assumed arbitrarily that the surface had become passive when the density of the current in either direction was less than 0.05 ma/cm^2, and a record was made of the range of the controlled potentials which produced this passivity.

TABLE 2A

Analyses of Leach Solutions 1, 2 and 3

(g/l)

Constituent	Solution 1	Solution 2	Solution 3
Cu	3.3	3.8	4.7
Ni	9.2	11.1	13.6
Co	13.3	16.8	20.1
Fe	31.1	33.5	37.9
As	33.0	35.5	42.5
Ag	2.8	1.9	0.1
Al	0.1	0.1	0.1
Ca	0.3	0.5	0.4
Mg	0.3	0.2	0.4
Mn	N.D.	N.D.	N.D.
Si	< 0.02	< 0.02	< 0.02
SO_4*	162.5	198.4	151.0
NO_3*	15.6	15.5	14.6
Cl*	< 0.01	< 0.01	0.19
Free acid (equiv. NaOH)*	72	76	58

* Analysis performed by the Chemical Analysis Section of the Extraction Metallurgy Division.

TABLE 2B

Analyses of Leach Solutions 4, 5 and 6

(g/l)

Constituent	Solution 4	Solution 5	Solution 6
Cu	1.8	1.0	0.4
Ni	16.7	14.1	8.8
Co	23.4	21.4	31.3
Fe	40.0	31.3	19.0
As	10.0	11.1	13.6
Ag	< 0.1	< 0.1	< 0.1
SO_4 *	107	70	41
NO_3 *	2.3	6.2	6.3
Cl *	0.005 approx	0.005 approx	0.005 approx
Free acid (equiv.NaOH)*	116	60	38

* Analysis performed by the Chemical Analysis Section of the Extraction Metallurgy Division.

Most of the above experiments were performed at 80°C since the solutions generally would be used at that temperature when the plant was in operation. However a few experiments were performed at 25°C to obtain information regarding the effect of temperature on the range of the controlled potentials which would produce passivity.

In most experiments the steel specimen was unwelded and completely immersed in the unagitated solution. However in some of them the specimen was only partially immersed or had been welded either vertically or horizontally. In still others the solution was agitated.

The effect of agitation on the breadth of the range of applied potentials producing passivity was investigated using a magnetic stirrer (2.6 cm long x 0.8 cm diam) on the bottom of the cell. Although the actual velocity of the solutions passing over the surface of the steel was not known, it was known that the minimum speed of the stirrer was zero r.p.m. and the maximum speed was very great (1280 r.p.m.).

The corrosion rate of each type of steel in each of the solutions 1, 2, 3 and 4 was determined at 80°C when

(1) the potential of the steel was uncontrolled

(2) the potential was maintained within a range of potentials approximating those which had been found to produce passivity (0.65 - 0.95 volt)

(3) the potential was maintained within a range of potentials which were higher than those producing passivity (1.00 - 1.10 volt), i.e. in a range of potentials which produced activity rather than passivity in the metal.

In each experiment in (2) and (3), the potential impressed on the steel was steadily increased from 0.65 to 0.95 volt (or from 1.00 to 1.10 volt) over a six-hour period.

All of the experiments in the investigation were performed in duplicate to ensure the accuracy of the results.

Immediately before each experiment the stainless steel specimen was treated in a trichlorethylene vapor degreasing unit manufactured by Canadian Hanson - VanWinkle Company. It then was blasted with a mixture of water and 220 mesh aluminum oxide at 80 lb/sq in pressure in a unit manufactured by the Lord Chemical Corp. Following this it was thoroughly washed with distilled water and then with ethyl alcohol, and finally dried in an air blast. It was immersed immediately in the process solution to be used in the experiment and then connected to the electrical equipment.

EXPERIMENTAL RESULTS

The Ranges of the Controlled Potentials Producing Passivity of the Steels in the Solutions Under the Simplest Conditions

The ranges of the controlled potentials which would produce passivity in the three unwelded and completely immersed stainless steels in each of the six unagitated solutions at 80°C were investigated.

It was found that passivity could not be produced in any of these steels when they were immersed in solutions 5 and 6.

The ranges of the potentials producing passivity in the three steels in solutions 1, 2, 3 and 4 are given in Table 3. (Experimental data typical of those required to determine these ranges are given in Appendix I)

It will be noted that the ranges of the controlled potentials producing passivity are fairly similar in the cases of the three steels in solutions 1, 2 and 3. However, in the cases of the steels in solution 4, the ranges are somewhat higher.

TABLE 3

Ranges of Applied Potentials Producing Passivity in the Completely Immersed, Unwelded Steels at 80°C

Solution	Ranges of Applied Potentials Producing Passivity (volts) *		
	Type 304L	Type 316	Type 347
1	0.65-0.90 (0.25)	0.60-0.85 (0.25)	0.65-0.85 (0.20)
2	0.60-0.80 (0.20)	0.60-0.85 (0.25)	0.65-0.80 (0.15)
3	0.60-0.85 (0.25)	0.60-0.80 (0.20)	0.65-0.85 (0.20)
4	0.70-0.90 (0.20)	0.75-0.95 (0.20)	0.75-0.95 (0.20)
5	no passivity		
6	no passivity		

* Width of ranges in brackets.

Effects of Variables on the Ranges of the Controlled Potentials Producing Passivity

Partial Immersion

As shown in Table 4, no great differences in these ranges were observed in most cases when the experiments were performed under conditions of partial immersion instead of total immersion. No passivity was produced in the cases of solutions 5 and 6.

Welding

As shown in Tables 5 and 6 the ranges obtained with the specimens which had been welded, both horizontally and vertically, were fairly similar to those in Table 3. It should be pointed out, however, that the ranges of potentials producing passivity were slightly narrower and that there was little difference between the effect of vertical welding and that of horizontal welding.

TABLE 4

Ranges of Applied Potentials Producing Passivity in the Partially Immersed, Unwelded Steels at 80°C

Solution	Ranges of Applied Potentials Producing Passivity (volts) *		
	Type 304L	Type 316	Type 347
1	0.65-0.90 (0.25)	0.60-0.85 (0.25)	0.60-0.80 (0.20)
2	0.60-0.95 (0.35)	0.60-0.80 (0.20)	0.60-0.80 (0.20)
3	0.60-0.85 (0.25)	0.60-0.75 (0.15)	0.55-0.80 (0.25)
4	0.70-0.90 (0.20)	0.70-0.90 (0.20)	0.75-0.95 (0.20)
5	no passivity		
6	no passivity		

* Width of ranges in brackets.

TABLE 5

Ranges of Applied Potentials Producing Passivity in the Welded Steels at 80°C

(Vertical Weld)

Solution	Ranges of Applied Potentials Producing Passivity (volts)*		
	Type 304L	Type 316	Type 347
1	0.65-0.80 (0.15)	0.65-0.80 (0.15)	0.60-0.80 (0.20)
2	0.65-0.80 (0.15)	0.60-0.80 (0.20)	0.65-0.80 (0.15)
3	0.65-0.80 (0.15)	0.60-0.75 (0.15)	0.60-0.75 (0.15)
4	0.75-1.00 (0.25)	0.75-1.00 (0.25)	0.70-0.85 (0.15)
5	no passivity		
6	no passivity		

* Width of ranges in brackets.

TABLE 6

Ranges of Applied Potentials Producing Passivity

in the Welded Steels at 80°C

(Horizontal Weld)

Solution	Ranges of Applied Potentials Producing Passivity (volts)*		
	Type 304L	Type 316	Type 347
1	0.65-0.85 (0.20)	0.70-0.90 (0.20)	0.60-0.80 (0.20)
2	0.65-0.80 (0.15)	0.65-0.80 (0.15)	0.65-0.80 (0.15)
3	0.65-0.85 (0.20)	0.60-0.75 (0.15)	0.60-0.75 (0.15)
4	0.80-1.00 (0.20)	0.80-1.00 (0.20)	0.65-0.85 (0.20)
5	no passivity		
6	no passivity		

*Width of ranges in brackets.

Agitation

It would have been very difficult to determine the actual velocities of the solutions passing over the surfaces of the steel specimens. However in some of these experiments these velocities were increased greatly by the use of a magnetic stirrer as referred to earlier. Such great increases in velocity had little effect on the ranges of potentials producing passivity in solutions 1, 2, 3 and 4, which were given in Table 3.

Temperature

Using specimens of Type 304L steel as an example, it was found that lowering the temperature of the solutions from 80 to 25°C produced a considerable widening of the ranges of potentials producing passivity in the typical solutions 1, 2 and 3, as shown in Table 7.

TABLE 7

Effect of Temperature on the Ranges of Applied Potentials Producing Passivity in Type 304L Steel

Solution	Ranges of Applied Potentials Producing Passivity (volts) *	
	25°C	80°C
1	< 0.45-0.90 (>0.45)	0.65-0.90 (0.25)
2	0.50-0.95 (0.45)	0.60-0.80 (0.20)
3	< 0.45-0.90 (>0.45)	0.60-0.85 (0.25)

*Width of ranges in brackets.

Uncontrolled Potentials of the Stainless Steels in the Leaching Solutions at 80°C

The uncontrolled potential of each of the stainless steels in each of the solutions 1 to 6 inclusive is given in Table 8. It will be noted that the potentials in solutions 1 to 3 inclusive vary between 0.65 and 0.75 volt, that those in solution 4 vary between 0.55 and 0.60 volt and those in solutions 5 and 6 vary between 0.30 and 0.40 volt.

CORROSION RATES OF STEELS

In the Passive State (Potential Controlled)

Unwelded steel Types 304L, 316 and 347 had been found to be passive at potentials which were maintained within the approximate range of 0.65-0.95 volt when totally immersed in solutions 1, 2, 3 and 4 and when the temperature was 80°C. The corrosion rates of the steels were found to be very low under these conditions (1.2 to 3.1 x 10^{-5} g/cm^2/hr) as shown in Table 9.

TABLE 8

Uncontrolled Potentials of the Stainless Steels in the Leaching Solutions at 80°C

Solution	Uncontrolled Potential (volts)		
	Type 304L	Type 316	Type 347
1	+0.70	+0.70	+0.75
2	+0.70	+0.65	+0.65
3	+0.70	+0.75	+0.70
4	+0.55	+0.60	+0.60
5	+0.35	+0.40	+0.35
6	+0.35	+0.30	+0.40

In the Active State (Potential Controlled)

These steels had been found to be active when immersed in the same solutions at a higher controlled potential (1.00-1.10 volt), the other conditions being the same as above. The corrosion rates of steel Types 304L and 316 were found to be comparatively high under these conditions (21 to 105 x 10^{-5} g/cm^2/hr) as shown in Table 9. In the case of steel Type 347 the rate was found to be much lower (2.0 to 6.0 x 10^{-5} g/cm^2/hr) although it was still somewhat higher than in the case of this same steel when in the passive state.

Potential Uncontrolled

The corrosion rates of the three steels in solutions 1, 2, 3 and 4, with their potentials uncontrolled, were very low (0.7 to 2.7 x 10^{-5} g/cm^2/hr) as shown in Table 9.

TABLE 9

Corrosion Rates of the Stainless Steels at Uncontrolled and Controlled Potentials

Solution No.	Controlled Potential (volts)	Average Corrosion Rate x 10^{-5} ($g/cm^2/hr$)		
		Type 304L	Type 316	Type 347
1	none	2.1	2.3	2.7
	0.65-0.95	1.6	2.2	2.6
	1.00-1.10	40	46	4.0
2	none	1.7	2.1	1.3
	0.65-0.95	1.5	2.2	2.0
	1.00-1.10	97	59	6.0
3	none	1.4	1.4	2.7
	0.65-0.95	1.4	3.1	2.0
	1.00-1.10	56	105	5.5
4	none	0.7	0.7	0.7
	0.65-0.95	1.3	1.3	1.2
	1.00-1.10	21	33	2.0

APPENDIX I

Effect of Applied Potential on the Current Density at Totally Immersed Steel Electrodes of Types 304L, 316 and 347 In Solutions 1, 2 and 3 at 80°C

Applied Potential (volt)	Current Density (ma/cm²)								
	Solution 1			Solution 2			Solution 3		
	Type 304L	Type 316	Type 347	Type 304L	Type 316	Type 347	Type 304L	Type 316	Type 347
0.45	-0.40	-0.40	-0.40	-0.35	-0.30	-0.50	-0.30	-0.40	-0.25
0.50	-0.20	-0.15	-0.20	-0.15	-0.20	-0.25	-0.10	-0.15	-0.10
0.55	-0.10	-0.05	-0.05	-0.05	-0.05	-0.10	-0.05	-0.05	-0.05
0.60	-0.05		-0.05			-0.05			-0.05
0.65									
0.70									
0.75	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
0.80									
0.85				0.05		0.05		0.05	
0.90		0.05	0.10	0.10	0.05	0.10	0.05	0.15	0.10
0.95	0.10	0.10	0.40	0.20	0.20	0.25	0.15	0.30	0.60
1.00	0.25	0.30	1.30	0.25	0.40	0.80	0.35	1.00	1.65

* [indicates a range of potentials producing passivity in a certain steel when immersed in a certain solution.

SUMMATION

The results of the experimental work described above are summarized as follows:

1. Stainless steel Types 304L, 316 and 347 were found to be active in solutions 5 and 6 regardless of the potential which was impressed on them. For this reason a tank of one of these steels, containing one of these solutions, could not be protected from corrosion anodically.

2. These three types of steel were found to be passive in solutions 1, 2, 3 or 4 when any potential between about 0.65 and 0.95 volt was impressed on them at 80°C.

3. The width of the range of potentials producing passivity, referred to in Item 2 above, was not greatly changed by partially immersing or welding the metal or by agitating the solution. The width of the range was considerably increased when the temperature was decreased from 80 to 25°C.

4. When steel Types 304L and 316 were immersed in solutions 1, 2, 3 or 4 and their potentials were controlled so that they would be in the active state (the range being between 1.00 and 1.10 volt) the corrosion rates greatly exceeded those obtained when the same steels were in the passive state.

5. When steel Type 347 was immersed in solutions 1, 2, 3 or 4 and its potential was controlled so as to be in the active state, (1.00 and 1.10 volt) its corrosion rate exceeded that of the same steel in the passive state by only a fairly small amount.

6. When steel Type 304L, 316 or 347 was immersed in solution 1, 2, 3 or 4, and when its potential was uncontrolled, its corrosion rate was approximately the same as that obtained when the potential of the steel was controlled within the range 0.65-0.95 volt.

CONCLUSIONS

On the basis of the above experimental evidence it is concluded that

1. No passive films are produced on tanks of stainless steel Type 304L, 316 or 347 containing solution 5 or 6 at 80°C. Consequently these tanks cannot be protected anodically under these conditions.

2. Passive films may be produced on tanks of these steels containing solution 1, 2, 3 or 4 at 80°C. Accordingly such tanks can be anodically protected. It was found that passive films can be produced on these steels when their potential is controlled to some value between about 0.65 and 0.95 volt.

3. Since the uncontrolled potentials of these steels in solution 1, 2, 3 or 4 are between 0.65 and 0.95 volt there would be no advantage in attempting to protect them anodically.

4. Pipe lines as well as tanks are protected from corrosion by passive films when, as in this case, protection is obtained without the use of controlled potentials.

5. The range of potentials producing passivity in a tank of stainless steel Type 304L, 316 or 347 when it contains solution 1, 2, 3 or 4 is not greatly affected by the extent of immersion of the steel in the solution or by the presence of vertical or horizontal welds (the weld metal being fairly similar to the welded metal). Neither is it affected greatly by the rate of agitation of the solution. On the other hand the width of this range of potentials is much greater at a lower temperature such as 25°C than at a higher temperature such as 80°C.

Actual tests showed that the corrosion rate of steel Type 304L, 316 or 347 in solution 1, 2, 3 or 4 has nearly the same low value whether anodic protection is used or not. Tests also showed that there is a very much higher corrosion rate when steel Type 304L or 316 is subjected to a potential between 1.00 and 1.10 volt, i.e. when the steel is active. It is of interest that the corrosion rate of steel Type 347 under these circumstances is very much lower than that of Type 304L or 316 under similar circumstances. However it still is somewhat higher than the corrosion rate obtained when Type 347 steel is rendered passive by controlling its potential between 0.65 and 0.95 volt, or when the potential of the steel remains uncontrolled.

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