

CANADA

A CORROSION STUDY IN PROCESSING URANIUM ORE

by

I. I. TINGLEY AND R. R. ROGERS EXTRACTION METALLURGY DIVISION



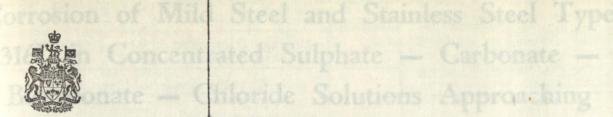
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- Chloride Solutions Approaching

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I. I. Tingley and R. R. Rogers

Extraction Metallurgy Division

Reprint of Paper "Corrosion of Mild Steel and Stainless Steel Type 316L in Concentrated Sulphate - Carbonate -Bicarbonate - Chloride Solutions Approaching Those Used in Grinding and Leaching Uranium Ore" in The Canadian Mining and Metallurgical Bulletin, January 1960 (C.I.M.M. Transactions, Volume LXIII, 1960, pp. 16-21)

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Corrosion of Mild Steel and Stainless Steel Type 316L in Concentrated Sulphate — Carbonate — Bicarbonate — Chloride Solutions Approaching Those Used in Grinding and Leaching Uranium Ore*

By I. I. TINGLEY and R. R. ROGERS§

(Transactions, Volume LXIII, 1960, pp. 16-21).

INTRODUCTION

TABLE I .- ANALYSIS OF PLANT GRINDING AND LEACHING SOLUTIONS

SERIOUS CORROSION prob-Alem recently arose in the plant of one of the leading uranium mining companies of Canada. Grinding and leaching equipment, constructed largely of iron and mild steel, had undergone corrosion, including severe pitting. Deterioration of large, mild steel pachucas was particularly serious. Assistance in solving this problem was requested from the Corrosion Laboratory of the Pyrometallurgy and Corrosion Subdivision, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys.

It was decided that the investigation should be divided into two parts:

1.—An inspection of the corrosion taking place at the plant.

2.—A laboratory investigation at the Mines Branch to obtain information which, it was hoped, would lead to an understanding of the mechanism of the corrosion reaction, as well as to the solution of the corresion problem at the plant.

Inspection at the plant revealed that:

(1) Pitting corrosion had occurred underneath deposits of wet, finely-divided uranium ore which had adhered tightly to the steel in certain areas.

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Solution	Sodium Sulphate	Sodium Carbonate	Sodium Bicarbonate
	(Na ₂ SO _{ll})	(Na ₂ CO ₃)	(NaHCO3)
	(g/liter)	(g/liter)	(g/liter)
Grinding	110	40	5
Leaching	125	25	15 to 20

TABLE II.—Compositions of Corroding Solutions Used

	•			
Na ₂ SO ₄ (g/liter)	Na ₂ CO ₃ (g/liter)	NaHCO3 (g/liter)	Na2CO3 NaHCO3 Ratio	рН
110 to 125	40	5 to 6.1	6.6 to 8	10.1
110 to 125	25	16.9 to 18	1.4 to 1.5	9.5
125	13•2	27.3	0.5	8.6
125	0	37.8	0	. 7.5
60	59.6	20.6	2.9	10.0
60	41.2	32.6	1.3	9.5
60	6.6	61.0	0.1	8.5
60	0	67.6	0	7.5

*In some of the tests about 3 g/1 of sodium chloride was added to the solutions at the request of the plant management.

(2) This pitting corrosion was particularly serious in the area near the weld between the cylindrical and conical portions of the pachuca examined. Here the combination of ore and leaching solution did not circulate as rapidly as it did elsewhere in the tank, and consequently there was a greater tendency for the ore to settle on the surface of the steel.

In the laboratory investigation, the corrosive effects on mild steel and on stainless steel Type 316L of concentrated synthetic solutions containing sulphate, carbonate, bicarbonate, and chloride were studied. Many of these solutions approached in composition those used in grinding and leaching uranium ore at the plant. The concentrations of the ions in the plant grinding and leach-

ing solutions are given in Table I. The solutions used in the investigation are listed in Table II. The solutions containing 60 g/liter of sodium sulphate were studied because the concentration of this material in the plant solutions was reduced to this figure during the time of the investigation.

The experiments were performed at room temperature (72° ± 5°F.) rather than at the somewhat higher temperature used at the plant (125°F.), since it would have been difficult to maintain such a large number of test panels at the higher temperature.

Panels of mild S.A.E. 1025 steel (containing 0.22 to 0.28 per cent carbon), and of stainless steel Type 316L, were used in the investigation. Some panels were partially immersed and others totally immersed, the latter being vertical in some cases and horizontal in others. Other panels were L-shaped, with the vertical part partially immersed.

PROCEDURE

Flat test panels 2 in. by 1 in. (for total immersion tests) and 31/2 in. by 1 in. (for partial immersion tests) were cut from a 0.035-inch sheet of S.A.E. 1025 hot-rolled steel and from a stainless steel Type 316L sheet. After having a 1/16inch hole drilled through it near one end for suspension, each panel was degreased in trichlorethylene liquid, blasted with fused alumina grit, degreased, and washed in trichlorethylene vapour, dried in a desiceator, and weighed. It then was quickly dipped in 10% hydroehlorie acid solution to activate the surface, rinsed thoroughly with distilled water, and suspended in the test solution by means of a saran cord. In the case of unaerated solutions, each panel was totally or partially immersed in 325 ml. of solution in a 400-ml. beaker. A half-inch portion of each partially immersed panel extended into the air. To datermine the effect of aeration, additional panels were each totally immersed in 285 ml. of solution in a 500-ml. Erlenmeyer flask. A stream of air was bubbled constantly through the solution. Visual observations were made and recorded frequently during the experiment, and evaporation losses were made up at short intervals with distilled water.

At the conclusion of the experiment each panel was removed from the solution, photographed if desired, rinsed with water, brushed

TABLE III.—AVERAGE CORROSION RATES OF VERTICAL PANELS IN UNARRATED SOLUTIONS CONTAINING 110 TO 125 g/l Na₂SO₄ (98-day test.

рН	Average Corrosion Rate (ipy)*	Type of Corrosion
	Totally Immer	sed Specimens
10.1	0.0003	General corrosion
9.5	0.005	General corrosion and
		slight pitting
8.6	0.0009	General corrosion and
ر		slight pitting
7.5	0,0011	General corrosion and
		slight pitting
	Partially Imme	rsed Specimens
10.1	0,0003	General corrosion
9.5	0.0019	General corrosion and
	_	pitting
8•6	0,0016	General corrosion and
	1	pitting
7.5	0.0024	General corrosion and
		pitting

^{*}Inches per year.

with a bristle brush, treated for ½ to 1½ hours in boiling 30% Alka-Deox solution (an alkaline rust remover), dried, cooled, and weighed. It was then photographed again if desired, to show the appearance of the surface after cleaning.

Other test panels, in the form of 'tables', were produced by cutting rectangular pieces of the mild-steel sheet 5 in. by $1\frac{1}{2}$ in. and bending down each end. Each of the resulting 'tables' had a horizontal part 3 in. by $1\frac{1}{2}$ in. and a 1 in. by $1\frac{1}{2}$ in. leg at each end. These test panels were each immersed in 600 ml. of solution in a 1 liter beaker. The horizontal surface of each table was about 2 inches from the surface of the liquid.

Each of the L-shaped test panels of both mild and stainless steel had a horizontal portion 1 in. by 2 in., which was covered by ½-inch of ground uranium ore, and a vertical portion 3½ inches long. The latter extended ½ inch out of the solution. The vertical portions of some of these L-shaped panels were 1 inch wide, of others were ½ inch wide, and of still others ¼ inch wide, so that the immersed areas of these vertical portions were 6, 3, and 1.5 square inches, respectively.

These 'tables' and L-shaped test

panels were treated in the same way as the flat panels before and after the tests.

RESULTS

Mild Steel Panels

The average corrosion rates of the flat vertical panels tested in unaerated solutions, calculated from the weight losses, are given in Table III for the solutions containing 110 and 125 g/liter of sodium sulphate; and in Table IV for the solutions containing 60 g/liter of sodium sulphate. The average corrosion rates for the flat vertical panels totally immersed in aerated solutions are given in Table V.

The corrosion of the flat, vertical panels in the unaerated highsulphate solutions followed a very interesting pattern. During the first few days of the experiments, the immersed parts of the panels became uniformly covered with a dark corrosion product which was almost blue in some cases. Later, this material changed to a rusty red colour, the time required for the change varying with the pH of the solution. Still later, pustules appeared on all except the panels in pH 10 solution. These started as black spots in the rust coating, then developed into mounds of hard rust. After a few days, filaments, varying in colour from black through hluc-

green to white, grew out of some of the pustules, an elongation of three inches occurring in a single night in some cases. Within a few hours after their formation, the filaments changed to a yellow colour. In most cases they grew downward, but a few turned and grew upward again. One filament crossed over itself, forming a complete loop, and then divided into three branches. The pustules from which filaments did not grow became larger and sometimes joined together to form clusters. Pustule formation took place more frequently at the edges and liquid-air interfaces than elsewhere, on the panels partially immersed in solutions with comparatively highpH (but not pH 10). However, they were located more at random on the surfaces of panels which had been totally immersed in solutions with comparatively low pH values. It is important to note that pitting took place underneath the pustules and filaments, and only at these locations.

In Figure 1 are shown two panels which had been partially immersed, with large pustule clusters at the interfaces and long filaments running almost to the bottom edges. Also are shown two panels which had been totally immersed, with pustules but without filaments. In Figure 2 are shown panels which had been in solutions of pH 10. The absence of pustules and filaments on the three specimens at the left will be noted. The pH of the solution in which the fourth panel had been tested had decreased and a pustule cluster and short filament had developed after a fairly long period. In Figure 3 are shown some panels after they had been cleaned. The pitting and local attack which had taken place under the pustules and filaments are quite apparent.

Examination by X-ray diffraction showed that the red corrosion product covering most of the surfaces, and also the major constituent of the pustules, was goethite $(\alpha-Fe_2O_3.H_2O)$. A whitish-coloured material also present in the pustules was found to be a hydrated ferrous sulphate $(FeSO_4.4H_2O)$. A minor constituent present in the pustules could not be identified.

In the aerated solutions, the development of red corrosion product was much faster than in unaerated solutions. In those with high sulphate contents and the lower pH values, pustules were formed in about half the time required in the

TABLE IV.—AVERAGE CORROSION RATES OF VERTICAL PANELS IN UNAFRATED SOLUTIONS CONTAINING 60 g/l Na₂SO₄ (98-day test).

рН	Average Corrosion Rate (ipy)	Type of Corrosion
	Totally Immersed Specimens	
10.0 9.5 8.5 7.5	0.0006 0.0004 0.0003 0.0003	General corrosion General corrosion General corrosion General corrosion
	Partially Imme	rsed Specimens
10.0 9.5 8.5 7.5	0°000f 0°000f 0°0002	General corrosion General corrosion General corrosion General corrosion

TABLE V.—AVERAGE CORROSION RATES OF PANELS TOTALLY IMMERSED IN AERATED SOLUTIONS (100-day test).

рН	Average Corrosion Rate (ipy)	Type of Corrosion
•	Solutions containing	125 g/liter Na ₂ SO ₁
10.1	0.0001	General corrosion
9.5	0.0005	General corrosion
8.6	0.00/12	General corrosion
		and severe pitting
7.5	0.0066	General corrosion
		and severe pitting
	Solutions containing	60 g/liter Na ₂ SO ₁
10.0	0,0003	General corrosion
9.5	0.0008	General corrosion
8.5	0.0004	General corrosion
7.5	0.0003	General corrosion

TABLE VI.—AVERAGE CORROSION RATES OF TABLE-SHAPED PANELS TOTALLY IMMERSED IN UNAERATED SOLUTIONS CONTAINING 100 to 125 g/l Na₂SO₄ (84-day test).

На	Average Corrosion	Type of Corrosion
	Rate (ipy)	
10.1 9.5	0.0005 0.000L	General corrosion General corrosion

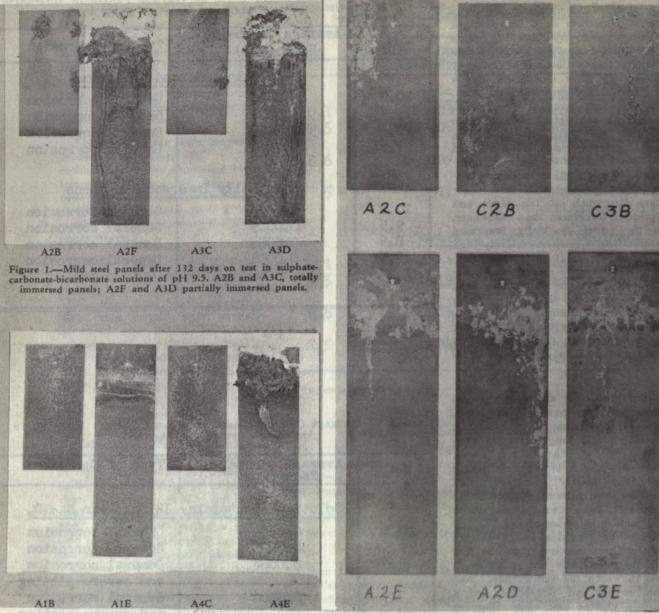


Figure 2.—Mild steel panels after 132 days on test in sulphatecarbonate-bicarbonate solutions of pH10, A1B and A4C, totally immersed panels; A1E and A4E, partially immersed panels.

Figure 3.—Mild steel panels, cleaned, after 50 days on test in suiphate-carbonate-bicarbonate solutions of pH 9.8. A2C, C2B, and C3B totally immersed; A2E, A2D, and C3E partially immersed. C2B, C3B, and C3E were tested in solutions containing 2.94 g/l NaCl. Ligt areas show the severe local corrosion which took place under pustules and filaments.

unaerated solutions. Short filaments grew from the pustules, none longer than ½ inch; but the pustules grew larger, and more appeared, until from half to three-quarters of the surface was covered with a rough crust formed by the pustules growing together. After cleaning, it was seen that the panels were heavily pitted under these pustules. In one case perforation of the panel had occurred.

In the low-sulphate solutions, only general corrosion occurred, with no pustules or filaments, as indicated by the Tables. Aeration

TABLE VII.—AVERAGE CORROSION RATES OF TABLE-SHAPED PANELS TOTALLY IMMERSED IN UNAERATED SOLUTIONS CONTAINING 125 g/l Na₂SO₄ When Partially Covered With Solid Material (75-day test).

pH	Average Corrosion Rate (ipy)	Type of Corrosion
la i	Specimens Partly Cov	ered with Uranium Ore
9.5	0.0006 Specimens Partly Cov	General corrosion wered with Quarts Sand
9.5	0,0006	General corrosion

and pH had no effect on the corrosion behaviour of the panels in these solutions.

In experiments with table-shaped panels in unaerated solutions, no local attack occurred, and the corrosion rates were low at pH values of both 9.5 and 10, as shown in Table VI. The effect of covering part of the surface of such panels with finely-divided uranium ore or with finely-divided quartz sand was quite small, as shown in Table VII. No local attack occurred. However, Tables VIII and IX show that local attack did occur when the solutions were aerated by bubbling a stream of air through them. Obviously, the oxygen concentration became much greater at the uncovered metal surface than underneath the uranium ore or quartz, resulting in oxygen concentration cells. The local attack took place at the anodic areas of these cells. A number of identical experiments are listed in each of these tables to show how closely the results could be duplicated.

The effect of differential aeration also was shown in the tests with the L-shaped panels in which the horizontal part of each panel was covered with finely-divided uranium ore, and the vertical part had free access to a plentiful supply of oxygen. The average corrosion rates of the panels are given in Tables X and XI. The effect of the area of the surface exposed to the aerated solution is shown also in these Tables, the greater the area the higher the rate of corrosion of the horizontal part of the panel.

In Figure 4 is shown the appearance of the under surfaces of the horizontal parts of the three Lshaped specimens at the end of the experiment (the area of the exposed surface increasing in going from left to right), and in Figure 5 are shown the same surfaces after they had been cleaned.

The effect on the corrosion rate of a small chloride ion concentration (about 3 g/liter NaCl) was found to be small. When experiments similar to those described above were performed in solutions containing this amount of sodium chloride, the general corrosion rate increased slightly but the frequency of pitting was decreased.

Other experiments showed that, even under the most corrosive conditions, no local attack, or pustule or filament formation, took place

TABLE VIII.—CORROSION RATES OF TABLE-SHAPED PANELS IN AERATED SOLUTIONS CONTAINING 125 g/l Na2SO4 (90-day test).

рН	Average Corrosion Rate (ipy)	Type of Corrosion
9.5	0.0013	Some local attack at edges
9.5	0.0006	General corrosion only
9.5	0.0007	Very slight local attack
9.5	0.0011	Some local attack
9.5	0.0009	Some local attack
9.5	0.0018	Considerable local attack

TABLE IX.—CORROSION RATES OF TABLE-SHAPED PANELS IN AERATED SOLU-TIONS CONTAINING 125 g/l Na₂SO₄ When Partially Covered With Solid Materials.

A Dayrest	Duration o	f	Average Corrosion	T	ype of Corresion
рН	Duration of Test (Days)	Av	erage Corrosion Rate (ipy)	Туре	of Corrosion
	Panels	Pa	rtially Covered	with	Uranium Ore
9.5 9.5 9.5 9.5 9.5 9.5	29 29 29 29 29 29 29	9.5	0.0026 0.0016 0.0019 0.0016 0.0017 0.0019	Some Some Some	local attack local attack local attack local attack local attack local attack
9.5 9.5 9.5 9.5 9.5 9.5	Panels 15 15 15 15 15 15	Pa	0.0038 0.0033 0.0051 0.0037 0.0029 0.0031	Most Some Loca Most Most	Quartz Sand ly general local attack l attack ly general ly general ly general

removed from the surface soon after they had been formed.

Stainless Steel Panels

Experiments with partially and totally immersed panels of stainless steel Type 316L (extra low carbon) in aerated and unaerated solutions, and also experiments with Lshaped panels of the same metal, were performed. In 183 days no corrosion of the stainless steel occurred under any of the experimental conditions.

DISCUSSION AND CONCLUSIONS

The experiments outlined above give a clear indication as to the mechanism by which the severe pit-

if the solid corrosion products were ting corrosion took place at the plant. It was shown that the composition of the solution must be within a certain range for the phenomenon to occur; also that the surface of the metal must be partly covered by a wet layer of solid material such as iron corrosion product, powdered quartz, or (as at the plant) powdered uranium ore; and finally that the metal covered by this solid material must be in electrical contact with an area of bare metal which is in contact with the solution. These conditions existed in the pachuca at the plant in which severe pitting corrosion was observed. Obviously, the oxygen concentration beneath the uranium ore or other solid material was very low; and that in the solution next to the bare metal was comparative-





Figure 4.—Under surfaces of horizontal parts of L-shaped panels after 61 days on test in unaerated sulphate-carbonate-bicarbonate solution.

Figure 5.—Under surfaces of horizontal parts of L-shaped panels after cleaning; same specimens as shown in Figure 4. Light areas were the most deeply corroded.

Table X.—Corrosion Rates of Horizontal Parts of L-Shaped Panels in Solutions Containing 125 g/l Na₂SO₄

ly high. In this way an oxygen concentration cell was produced, the	
corrosion pits being formed at the	he
anodic areas, where the oxygen co- centration was least.	n-
The last of the same of the sa	

The lack of pitting on the unaerated table-shaped panels was due to the oxygen concentration being about the same at the metal underneath the uranium ore as it was elsewhere in the solution, i.e., no oxygen concentration cells existed. It was possible for such cells to exist, however, on the L-shaped panels. Here the most severe pitting observed on a horizontal metal surface covered with ore corresponded with the largest surface of bare metal which was in contact with the solution containing dissolved oxygen.

These experiments show that pitting corrosion of this particular type may be prevented by:

- (1) Using a sufficiently low sulphate content in the solution
- (2) Using a sufficiently high pH in the solution
- (3) Preventing the formation of solid deposits on the metal surface
- (4) Preventing the formation of exygen concentration cells by eliminating aeration of the solution or by other means
- (5) Using Stainless Steel Type 316L instead of ordinary mild steel.

pН	Aerated or not		Av. Corrosion Rate (ipy)	
H	The same	Immersed Area	of Vertical Pa	rt 6 sq. in.
9.5	Unaerated	61	0.0041	Pitting on under surface
9.5	Aerated	53	0.0096	Pitting on both top and bottom surfac
	1 85	Immersed Area	of Vertical Par	t 1.5 sq. in.
9.5	Unaerated	61	0.0010	General corrosion
9.5	Aerated	41	0,0031	Pitting on both top and bottom surfac

Table XI.—Corrosion Rates of Horizontal Parts of L-Shaped Panels in Solutions Containing 60 g/l Na₂SO₄ (50-day test)

рН	Aerated or not	Average Corrosion Rate (ipy)	Type of Corrosion or Horisontal Part
	Imm	ersed Area of Vertica	al Part 6 sq. in.
8.0	Unaerated	0.0009	General corrosion
8.0	Aerated	0.0113	Pitting on both top and bottom surface
10.0	Unaerated	0.0000	in his faces and smile to the August
10.0	Aerated	0.0000	
	Immer	rsed Area of Vertical	Part 1.5 sq. in.
8.0	Unaerated	0,0006	General corrosion
8.0	Aerated	0.0035	Pitting on both top
10.0	Unaerated	0,0000	- In Souton Dataco
	Aerated	0,0000	NAME OF TAXABLE PARTY OF TAXABLE PARTY.

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