

A STUDY OF CAUSTIC CORROSION OF CARBON STEEL WASTE TANKS

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ABSTRACT

Solution chemistry of wastes from US atomic weapons production is controlled to inhibit corrosion of carbon steel tanks used in containment and storage. The pH, nitrate ion and nitrite ion concentrations of fresh solutions are maintained within specified limits for this purpose. In the start up process for a new waste evaporator (RHLWE), non-radioactive solutions of similar chemistry will be circulated through carbon steel piping between a steel tank and the evaporator. The evaporator is fabricated from a corrosion resistant nickel base alloy. The equipment will be exposed continuously to the hot corrosive caustic solutions. Published corrosion rates for steel in pure caustic at the elevated temperatures indicate losses >1.3 mm/y. Because the total test period for start up is relatively short, penetration will not occur. However, concern exists because the rust particles will probably circulate and precipitate throughout the system.

A laboratory study was performed in order to determine corrosion to be expected for the specific waste solutions being used in start up testing of the new equipment. The test solutions used in the study were (A) 40% NaOH + 16% NaNO₃ by weight, representative of concentrate produced in the evaporator; (B) 40% NaOH, a control solution; and (C) 5% NaOH + 27% NaNO₃, representative of fresh waste. Corrosion rates for both simulant solutions at boiling are an order of magnitude less than for the control solution, indicating that nitrate ion significantly inhibits the effect of the hydroxide. Moreover, the corrosion rate for solution (A) is 1.5-2X that for solution (C), further emphasizing the importance of nitrate to hydroxyl ion ratio. Following determination of the corrosion rates, calculations of hydrogen gas generated as a result of the corrosion process together with analysis of the system showed that the explosive possibilities are remote.

In summary, the test results indicate that the corrosion rates for steel are acceptable for the short term simulant tests for the new evaporator. The amount of particulate is probably not a concern, though filtration is recommended as an option. The hydrogen formation is also not a concern because it is in a steam environment, and is continuously swept from the storage vessel.

1. BACKGROUND

Solution chemistry of wastes from US atomic weapons production must be controlled to inhibit corrosion of carbon steel tanks used in their containment. The pH, nitrate ion and nitrite ion concentrations of fresh solutions are maintained within specified limits for this purpose. After a year of storage in the waste tanks, during which natural radiation decay eliminates the relevance of short lived isotopes, the liquids are processed through an evaporator and concentrated to a specific gravity ranging between 1.4 and 1.7, or a minimum of about 40% by weight NaOH (1), before returning them to other waste storage tanks. A heel of solution is always present in a waste tank, so that the concentrate temperature falls immediately upon addition to the tank and the corresponding corrosivity of the mixture is reduced.

In the start up process for a new waste evaporator (RHLWE) (2), simulant non-radioactive waste solutions will be circulated between a steel receipt tank and the evaporator. This tank and connecting steel pipe will be exposed directly and continuously to the hot corrosive caustic solutions. Published corrosion rates at elevated temperatures for steel in pure caustic indicate losses >1.3 mm/y (3)(4). Although the rate is high, the total test period for start up is relatively short and penetration will not occur. However, concern exists because the corrosion produces iron oxide (rust) particles which may circulate with the solutions. Though rust may be 10 times as voluminous as the iron or steel that it replaces, the material that exfoliates will become broken up into small particles which are more dense and occupy only 1.5 to 2.3 times the space of the iron (5). Because a large amount of steel will be exposed in this start up process, the volume of oxide particles created and the possibility of agglomeration or settling needs to be addressed. The evaporator is constructed from alloys G3 and Hastelloy G30, which are resistant to corrosion in this environment.

Hydrogen gas will be generated at cathode sites. The amount will vary with the amount of corrosion, so there exists a possibility for formation of a significant quantity in the present case. The relationship between the corrosion rate of steel and the amount of hydrogen generated as a result of that corrosion is contained in Appendix I.

A laboratory study was conducted in order to determine corrosion to be expected for steel exposed to the specific waste solutions being used in start up testing and calibration of the new equipment. A steel vessel and piping are being used as a container in the full scale runs because of immediate availability. Lining the interior walls of the vessel in lieu of letting them corrode was considered but rejected. Knowledge of the corrosion rates will allow a determination of whether continuous filtration of the iron oxides will be needed and whether hydrogen will really be a problem.

2. EXPERIMENTAL SET-UP

A laboratory investigation was initiated to define corrosion rates for equipment being used in establishing RHLWE operating parameters. The test solutions used in the study were (A) 40% NaOH + 16% NaNO_3 by weight, representative of evaporator concentrate;

(B) 40% NaOH, a control solution; and (C) 5% NaOH + 27% NaNO₃, representative of new or fresh feed stock. These are bounding solutions based on those being used in the equipment test. Following determination of corrosion rates, calculations of the amounts of hydrogen gas formed will provide indications as to whether explosive possibilities exist.

The three solutions were made up in either flasks or beakers, and the tests were run on hotplates. Coupons were fully immersed in solution for each test. One steel coupon sample was used per beaker. All coupons were of ASTM A-516 Grade 70 steel.

Because hot concentrated hydroxides will attack glass very rapidly, modified stainless steel beakers were used for the tests. Inverted stainless steel funnels were welded to the beakers to support condensers used to minimize vapor loss. Stainless steel wire baskets were used to support the test coupons within the beakers. Water-cooled glass condensers (cold fingers) were placed at the top in the inverted funnel. RTV sealant was used at the condenser/funnel joint location and at a thermocouple penetration in the assembly, to mitigate steam escape. Tests were run at boiling and at 95°C. In spite of the precautions, steam was lost and concentrations drifted slightly during each test. The steam exit points were uncertain. During the tests, water was added to adjust concentrations.

Tests were conducted as follows:

<u>Exposure Time</u>	<u>Solution</u>	<u>Temperature</u>
06 hrs	A, B, C	boiling*
23 hrs	“	“
48 hrs + 96 hrs [∇]	“	95°C
96 hrs + 48 hrs ^θ	“	95°C

*boiling temperature varies with the solution:

135°C, 130°C, 110°C (A,B,C respectively)

[∇]Test consists in initial exposure of 48 hrs, followed by 96 hrs.

^θTest: 96 hrs, followed by 48 hrs.

3. RESULTS AND DISCUSSION

3.1 Steel Corrosion

Corrosion rates were determined using the weight loss method described in ASTM A262-93a (6). The short term corrosion rates obtained from exposure of the steel to boiling sodium hydroxide solutions were very telling. The results are contained in Table 1. From the results, the presence of nitrate inhibits the corrosion effect of the hydroxide alone. Note that sodium hydroxide is commonly used at the Savannah River Site to adjust pH of the radioactive waste in order to inhibit the stress corrosion cracking effects of nitrate ion on steel in the large steel waste storage tanks.

Table 1. Corrosion Rates for Steel in Caustic Solutions

<u>Solution</u>	<u>Time (hrs):</u>	<u>6</u>	<u>23</u>	<u>48</u>	<u>+ 96</u>	<u>96</u>	<u>+ 48</u>
	<u>Temp.</u> (boiling)	(boiling)		(95°C)		(95°C)	
A	135°C	2.39	0.76	0.178	0.076	0.127	0.051 mm/y
A	135°C	0.094	0.030	0.007	0.003	0.005	0.002 ipy
B	130°C	8.99	9.27	0.457	0.152	0.203	0.254 mm/y
B	130°C	0.354	0.365	0.018	0.006	0.008	0.010 ipy
C	110°C	0.051	0.457	0.0102	0.0102	0.0076	0.030 mm/y
C	110°C	0.002	0.018	0.0004	0.0004	0.0003	0.0012 ipy

Solution A: 40% NaOH + 16% NaNO₃

Solution B: 40% NaOH

Solution C: 5% NaOH + 27% NaNO₃

During testing, in spite of attempts to prevent it, water loss did occur, especially during vigorous boiling. Thus, solution volume and concentration varied with time. Some of the variation in corrosion rate could be related to this. The temperature was held at 95°C for longer exposures to reduce variations associated with the water losses and concentration fluctuations. Occasional additions of make-up water were made to maintain solution volume. No attack of the condenser glass was evident in any of the tests, probably as a result of the controlled water cooling.

The corrosion rates at 95°C for 48 hours, 96 hours, and 144 hours are also contained in Table 1, and all the data is included in Figure 1. The 95°C values are roughly an order of magnitude less than those found for boiling. There is a general tendency for corrosion rate to decrease substantially with time after very short exposure, and to level out at longer times, perhaps as corrosion products (ions) concentrate in the solution.

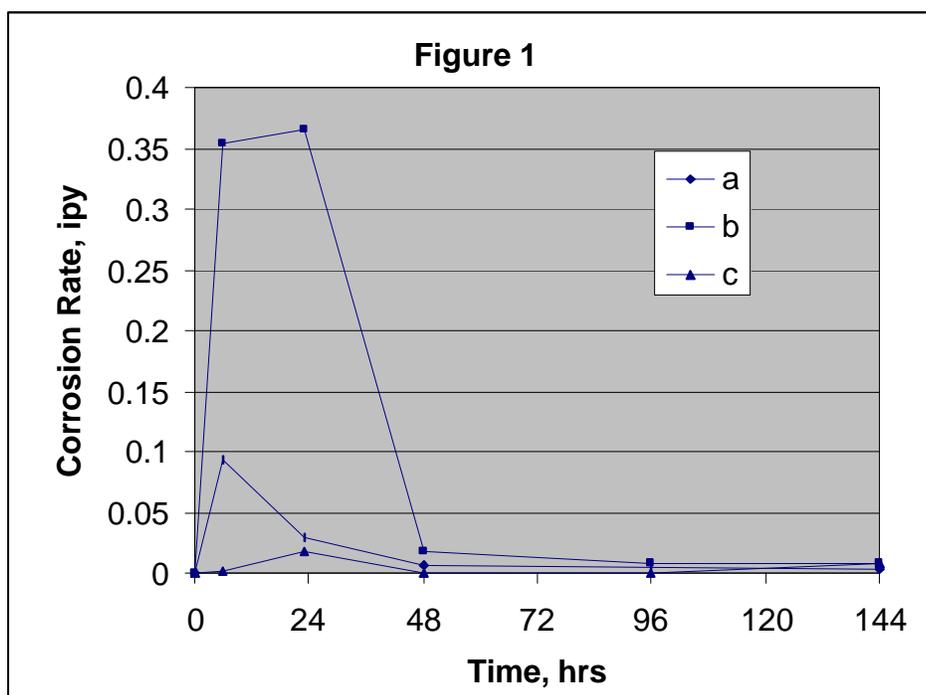
It is evident that nitrate inhibits hydroxide corrosion, though there is inconsistency with regard to the extent of inhibition. Decreasing the concentration of hydroxide is actually more effective in changing the rate of corrosion of the steel, Table 1 and Figure 1. However, inhibition reduces the quantity of rust or oxide sediments which develop.

As seen in the Table 1, corrosion rates for uninhibited hydroxide, solution B, are excessive at about 0.25 mm/yr. (0.01 in/yr.), even after six days exposure. Nitrate modified solution A, even with the same large OH⁻ content as solution B, has a significantly reduced corrosion rate. Solution C, with much lower OH⁻ and much higher NO₃⁻ contents, possesses the lowest corrosion rate of the three solutions. The measured corrosion rate for steel in solution B contraindicates its use for any long term exposures within the facility. From a corrosion standpoint, solution C is the preferred choice for extensive tests. The corrosion rate for solution A is also reasonable. The steel tank being considered for use in the RHLWE system has a diameter of 4m (13 ft). It will be filled to

a height of 1.83m (6 ft) with test solution. In addition, the interior surfaces of approximately 91.4m (300 ft) of 51 mm (2 in, sch 40) steel pipe will also be exposed to the solution from the tank. The respective areas subject to corrosion by the solutions are 35.1 m² (378 ft²) and 23.8 m² (256 ft²), for a total of 58.9 m² (634 ft²). The corrosion will result in rust and possible accumulation of rust particles. Some of the material will flow with the liquid, e.g. through the piping, but a deposit can be anticipated on the vessel bottom. Based on the measured corrosion rates and 3 months exposure, the volumes of iron and rust generated will be as shown in Table 2. Note that rust is substantially more voluminous than the iron it replaces. In a typical non-immersion atmospheric exposure, rust occupies about 10 times the space of the iron. The amount of rust is substantial, and filtration may be needed in order to collect it for disposal.

Table 2. Rate of corrosion and amount of rust created.

Solution	Corrosion Rate	thickness loss	Volume iron	Volume rust (10x)	Volume rust (2.3x)
B (2)(3)	1.27 mm/y	0.32 mm	187 cc	1870 cc	430 cc
B (2)(3)	50 mpy	0.0125 in	0.66 ft ³	6.6 ft ³	1.5 ft ³
A	0.76 mm/y	0.19 mm	113 cc	1130 cc	260 cc
A	30 mpy	0.0075 in	0.40 ft ³	4.0 ft ³	0.9 ft ³
C	0.46 mm/y	0.11 mm	68 cc	680 cc	156 cc
C	18 mpy	0.0045 in	0.24 ft ³	2.4 ft ³	0.55 ft ³



The rust will actually be suspended in the water solution. It will continuously circulate through the pump, piping and the two vessels. If feed to the evaporator is interrupted, the oxides will precipitate. It is anticipated that the precipitate will not accumulate to excess at any particular site but will rather be a general deposit throughout the system. Note that any accumulation to either the evaporator or tank bottoms will be directly lifted and will continue circulation.

Filtration of the oxides to remove them from the solutions may be considered. Inclusion of a filter in the recirculation system would mitigate some of the problems. However, to assure that plugging will not occur, filter cleaning or replacement is needed on a schedule to be determined during the tests. If filters are not used, the evaporator should be inspected to assure cleanliness before hot operations are initiated.

Because the steel receipt tank and piping will suffer wall loss, it is recommended that they not be used beyond these tests without first examining the vessel and derating it. However, the solutions being used, representative of actual process solutions, will not corrode or degrade other parts or equipment in the RHLWE system. Stainless steel process lines and evaporator alloys G3 and Hastelloy G30 will not be affected by the testing.

3.2 Hydrogen Gas

Concern about the generation of hydrogen relates to the possible extensive corrosion of the steel. The derivation of the relationship between corrosion rate of the steel and the quantity of hydrogen is shown in Appendix I. For a rate of 1.27 mm/y, the corresponding hydrogen per unit of corroding surface is 0.036 gm/cm²-yr.

The steel tank and piping together have an exposed area of approximately 589,000 cm². The amount of hydrogen "Q" (Appendix I) varies directly with the corrosion rate "CR" for the steel, so that

$$Q1 : CR1 :: Q2 : CR2 \quad (1)$$

Thus
$$Q2 = CR2 \times Q1/CR1 \quad (2)$$

Now, substituting the values from the Appendix, i.e. 1.27 mm/y (50 mpy) and 0.036 gm/cm²-yr, then

$$Q2 = CR2 \times 0.9327 \text{ lb.H}_2/\text{yr.} \quad (\text{CR2 in mpy}) \quad (3)$$

$$Q2 = CR2 \times 16.66 \text{ kg H}_2/\text{yr.} \quad (\text{CR2 in mm/y}) \quad (4)$$

For a corrosion rate of 1.27 mm/y (50 mpy), as much as 21.3 kg (47 lb.) of gas could be created, or 1.77 kg/mo. (3.9 lbs./mo.) The density of H₂ is 0.0899 gr./l (0.0056 lbs./ft³). Thus, 19.7 m³ (696 ft³) of gas per month might be generated. The partially filled 3.96 m (13 ft) diameter tank has 33.84 m³ (1195 ft³) of space above the liquid, so that full density

H₂ would fill 58% of the volume. That is, in one month, approximately half the volume would be hydrogen, which is an explosion concern when mixed with air. The possibility of simple recombination of hydrogen with oxygen is ignored as a conservative step, though some recombination will certainly occur.

Of more importance is the fact that the tank is vented to atmosphere through a 25-cm (10-inch) diameter penetration in the upper head. As a result, the pressurized recirculating feed will generate steam as it enters the tank. The vapor space above the liquid will be steam, not air. Moreover, the steam will exhaust through the 25-cm outlet and carry hydrogen with it. No accumulation of H₂ can occur as it continuously dissipates in the outside air.

To estimate the amount of hydrogen generated during an exposure, the mean values of corrosion rates were determined for each solution and temperature, using the relationship

$$CR_2 = \sum[CR(t)_i \times (t)_i] / \sum(t)_i \quad (5)$$

with “t” being time in hours for test “i”.

The calculated rates are contained in Table 3. In addition, the quantities of hydrogen that can be produced, based on the above relationships, are also included in the Table.

Table 3. Mean Corrosion Rates and Quantities of Hydrogen Gas As a Function of Temperature and Environment

<u>Solution</u>	<u>Temp.</u>	<u>Corr. Rate</u>	<u>H₂ Gas</u>	<u>Temp.</u>	<u>Corr. Rate</u>	<u>H₂ Gas</u>
A	95 C	0.107 mm/y	1.78 kg/y	135°C	1.097 mm/y	18.3 kg/y
A	"	0.0042 ipy	3.92 lb/y		0.0432 ipy	40.3 lb/y
B	"	0.236 mm/y	3.93 kg/y	130	9.21mm/y	153.4 kg/y
B	"	0.0093 ipy	8.67 lb/y		0.3627 ipy	338.3 lb/y
C	"	0.013 mm/y	0.21 kg/y	110	0.373 mm/y	6.21 kg/y
C	"	0.0005 ipy	0.47 lb/y		0.0147 ipy	13.7 lb/y

As evident in Table 3, the measured corrosion rate for 40% NaOH solution at 95°C is only about 1/5 that of the corrosion rate reported in the literature. The 40% NaOH, 16% NaNO₃ solution, has less than half the mean corrosion rate and amount of hydrogen of uninhibited NaOH. For both these cases, however, the H₂ exceeds 4% of the tank volume, which would be a problem were it not for the steam discharge. The corrosion rate for solution C, i.e. 5% NaOH + 27% NaNO₃, is 1/100 the literature value for NaOH. In one month, the hydrogen generated would be only 0.05% of the air-filled tank volume, and thus is below the 4% explosion limit. The steam discharge will remove the hydrogen.

Under boiling temperature conditions, even solution C at 110°C would cause enough corrosion in one month to provide a hydrogen concern, about 8% to 9% of the tank volume. The positive venting of the steam removes the gases and avoids the consequences.

In summary, the test results indicate that the corrosion rates for steel in the caustic solutions generally decrease with time and temperature of exposure. Nitrate ion is an inhibitor for hydroxide attack. The ideal OH^- to NO_3^- ratio will vary with temperature, just as does the amount of hydroxide required for preventing nitrate stress cracking of steel (6). The rates of corrosion are acceptable for the short term simulant tests for the new RHLWE system, for which it is proposed to use a carbon steel vessel and piping for containing and recirculating the cold run test solutions. The amount of rust sediment occurring as a result of the corrosion is probably large enough that filtration should be considered to remove concerns about plugging. The total amount of hydrogen gas theoretically formed in three months in the mild solution C is below the explosive limit in air, even if it was allowed to accumulate. However, solutions A and B will generate more H_2 in much shorter times. The positive removal of the gas which occurs with steam venting relieves the problem. Based on the corrosion rates and the hydrogen calculations, the steel vessel should be suitable for the run-in period for the outlined conditions.

4. CONCLUSIONS

The conclusions drawn from the experimental results and discussion are as follows:

- Steel corrosion in caustic solutions increases with time and temperature of exposure.
- Nitrate in solution is an inhibitor for caustic attack.
- The amount of rust resulting from corrosion is significant. However, the particles will remain suspended and will be recirculated with the solutions. Their presence will not affect cold test results.
- Before beginning actual hot operation, evaporator clean up might be necessary. This will be determined by an internal inspection after completion of the test runs. It is anticipated that cleaning will not be required.
- Hydrogen gas results from corrosion of the steel. In some cases, the quantities of gas would exceed the explosive limit in air. However, because the tank vapor space is filled with steam, and the gases vent and dissipate to atmosphere, explosive accumulations cannot occur.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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APPENDIX I

Hydrogen Generation During Corrosion of Steel

Hot caustic solutions will corrode steel. The corrosion in deaerated or acidic environments proceeds by the reduction of hydrogen. This cathodic reaction balances the anodic reaction of iron oxidation. Hydrogen gas forms and could be a concern in an enclosed container if the rate is significant. In a neutral solution, water and oxygen reduction could also occur as cathodic reactions. For a conservative approach, these reactions are not considered, and it is assumed that only hydrogen is involved in the process. The electrochemical reactions are:



The corrosion rate (CR) is dependent on the reaction rates of (1) and (2) occurring on the surface of the metal, i.e. the corrosion current (i_{corr}). The relationship is:

$$\text{CR} = (\text{K} \times i_{\text{corr}} \times \text{W})/\rho \quad (3)$$

where K is a constant, W is the equivalent weight of the metal and ρ is the density of the metal. For corrosion rates in the units of mils/year (mpy), the constant K has a value of 0.1288.

Both reactions (1) and (2) occur at the same rate or current: $i_{\text{corr}} = i_{(1)} = i_{(2)}$, which results from the electron flow. From reaction (1) a mole of H_2 is generated for every two moles of electrons. The relationship between the quantity Q gm/cm²yr of H_2 and i_{corr} is:

$$\text{Q} = (\text{C} \times i_{\text{corr}} \times \text{M})/(\text{n} \times \text{F}) \quad (4)$$

where C is a constant, equal to 31.54 when i_{corr} is in units of μA , M is the molecular weight (g/mole), n is the number of moles of electrons, and F is Faraday's constant, 95600 coulomb/gram-equivalent.

The quantity of H_2 as a function of corrosion rate of iron can be obtained by combining equations (3) and (4), or:

$$\text{Q} = (\text{D} \times \text{CR}_{\text{Fe}} \times \rho_{\text{Fe}} \times \text{M}_{\text{H}_2})/(\text{n} \times \text{W}_{\text{Fe}}) \quad (5)$$

where D is a constant equal to 2.53×10^{-3} , ρ_{Fe} is 7.86 gm/cm³, M is 2.016 g/mole, n is 2.0 moles, and W_{Fe} is 27.9. For a corrosion rate CR_{Fe} , of 50 mpy, the quantity of H_2 per unit of surface area of corroding steel per unit time is 0.036 gm/cm²-year. For the equivalent CR_{Fe} of 1.27 mm/yr, D is 0.1 and Q is the same.