

Chemical Engineering 378

Science of Materials Engineering

Lecture 32

Corrosion: Special Problems



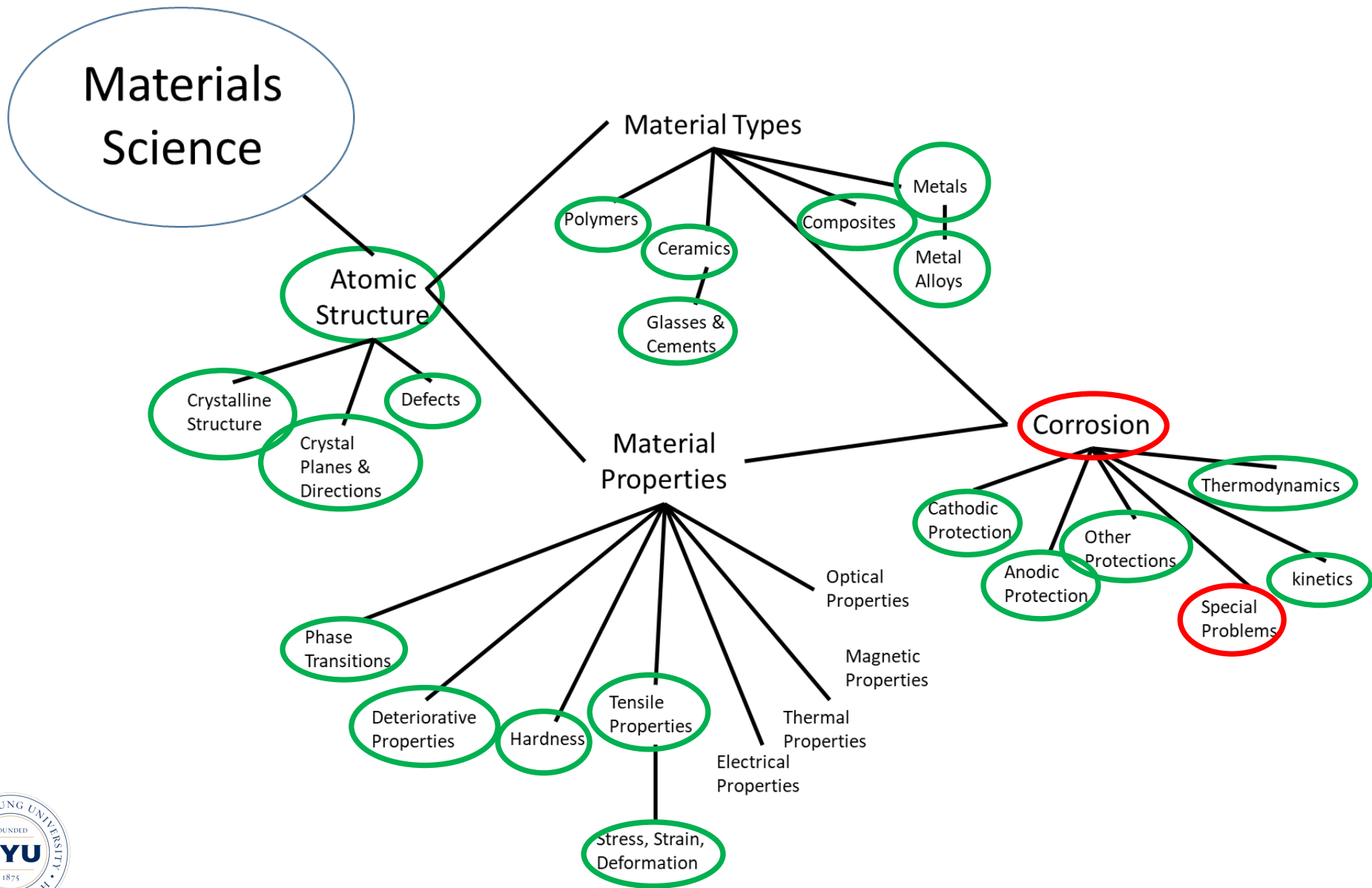
Spiritual Thought

D&C 68:29

And the inhabitants of Zion shall also observe the Sabbath day to keep it holy.



Materials Roadmap



Special Problem 7

1. You are assigned by your employer to design a better baffle for use in 1 N sulfuric acid contaminated with various oxidizing agents. It has been suggested by your boss that you use Type 316 stainless steel, for which you have several polarization curves (see below).

- (a) You notice that the potentials on the polarization curves are given versus an “SCE,” or Standard Calomel Electrode, and not relative to a Standard Hydrogen Electrode (SHE). Can you use this chart? Explain.



(b) The calomel electrode makes use of the half reaction: $\text{Hg} + \text{Cl}^- \rightarrow 1/2 \text{Hg}_2\text{Cl}_2 + \text{e}^-$

for which the standard half-cell potential (vs. the SHE) is +0.280V. If you needed to, could you convert the potentials in your polarization curves to the SHE scale? Prove it by giving the half-cell potential, relative to the SHE, at which the critical current occurs in 90° C sulfuric acid.

(c) After changing to the SHE scale in Part b, what is the critical current?



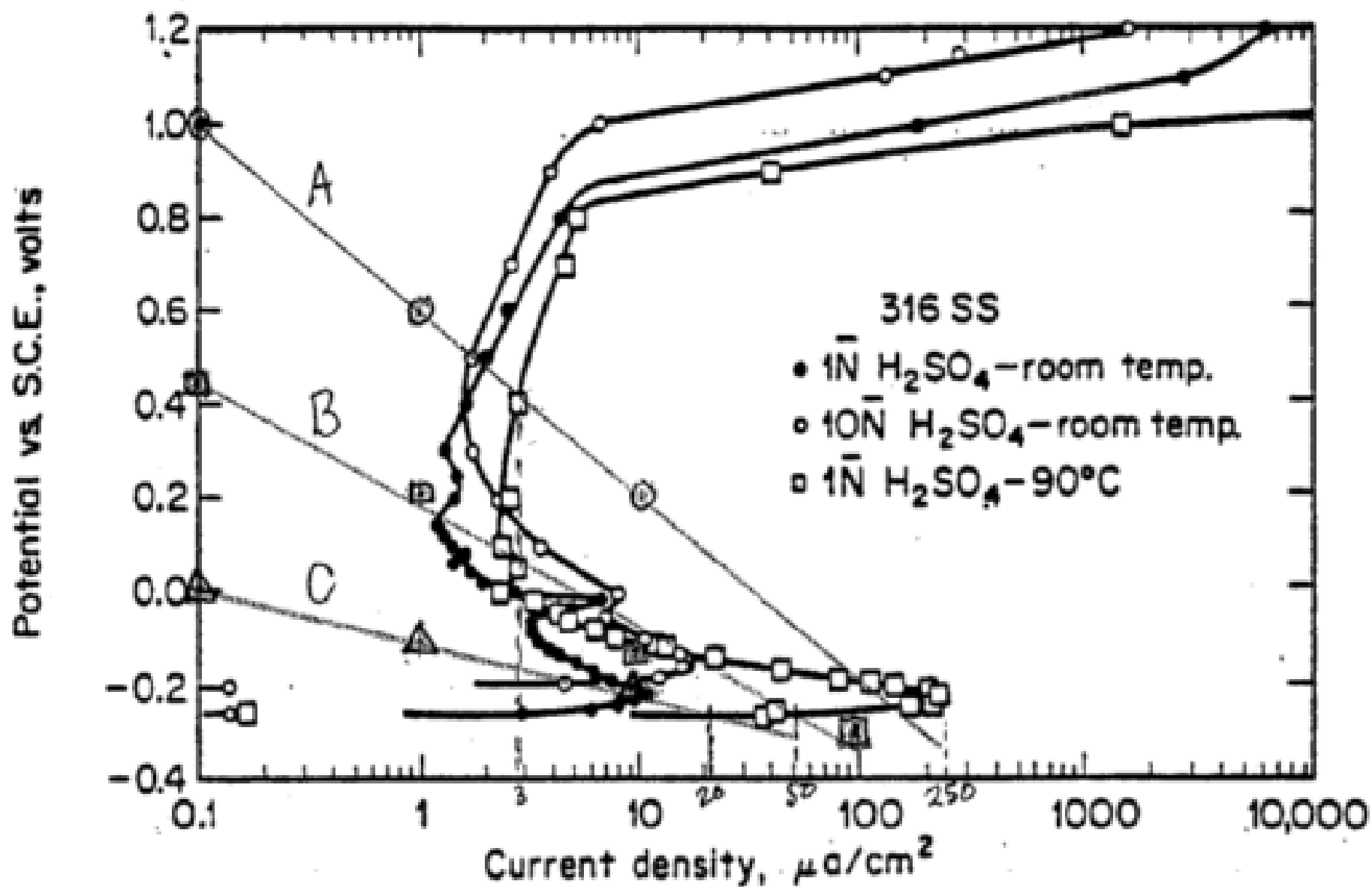
(d) You are especially concerned about the effect of three different oxidizing solutions (A, B and C) on your baffle. For each of these solutions, tell whether type 316 SS will be active or passive in 1 N sulfuric acid at 90° C, and give the corrosion current density.

(e) Suppose your solid baffle is made of 316 SS, with dimensions 5 x 5 x 0.2 cm. If it were placed in solution A at 90° C, how long would it take to completely corrode the baffle away? (Assume that the specific gravity of 316 SS is 8.02.)

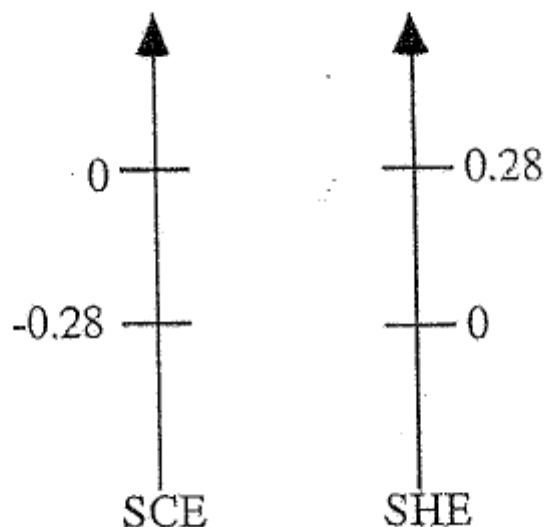


		Corrosive Solution A		
Current density ($\mu\text{A}/\text{cm}^2$)	0.1	1	10	100
Potential (vs. SCE)	1.0	0.6	0.2	-0.05
		Corrosive Solution B		
Current density ($\mu\text{A}/\text{cm}^2$)	0.1	1	10	100
Potential (vs. SCE)	0.45	0.2	-0.5	-0.3
		Corrosive Solution C		
Current density ($\mu\text{A}/\text{cm}^2$)	0.1	1	10	100
Potential (vs. SCE)	0.0	-0.1	-0.2	-0.3





(a) You notice that the potentials on the polarization curves are given versus an “SCE,” or Standard Calomel Electrode, and not relative to a Standard Hydrogen Electrode (SHE). Can you use this chart? Explain.



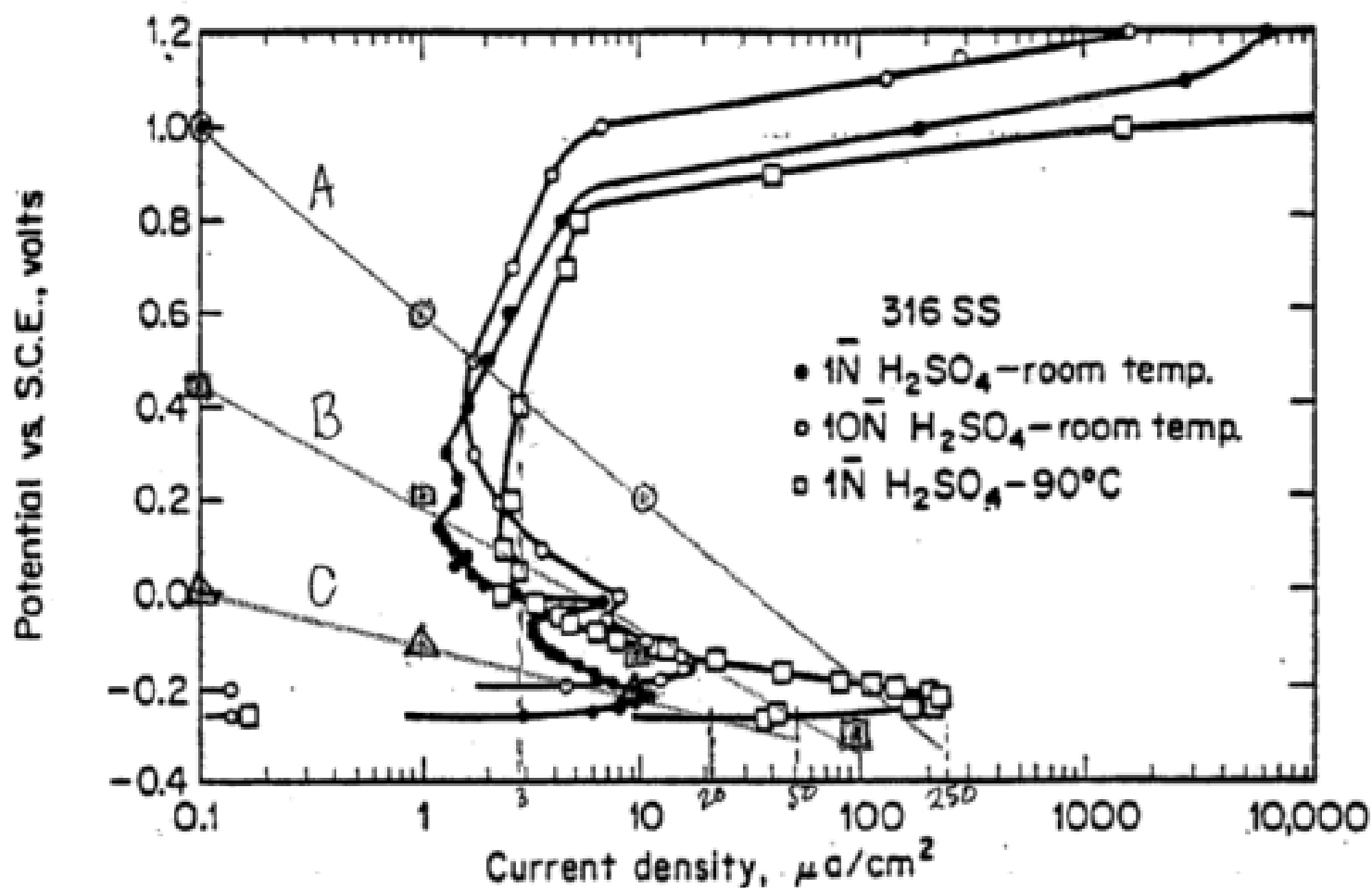
a) Yes, you just have to shift the Y-axis by adding +0.28 to all the values.

(b) The calomel electrode makes use of the half reaction: $\text{Hg} + \text{Cl}^- \rightarrow 1/2 \text{Hg}_2\text{Cl}_2 + \text{e}^-$

for which the standard half-cell potential (vs. the SHE) is +0.280V. If you needed to, could you convert the potentials in your polarization curves to the SHE scale? Prove it by giving the half-cell potential, relative to the SHE, at which the critical current occurs in 90° C sulfuric acid.

(c) After changing to the SHE scale in Part b, what is the critical current?





b) On the SCE scale, the i_{crit} is about -0.2 V, so $-0.2 \text{ V} + 0.28 \text{ V} = 0.08 \text{ V}$

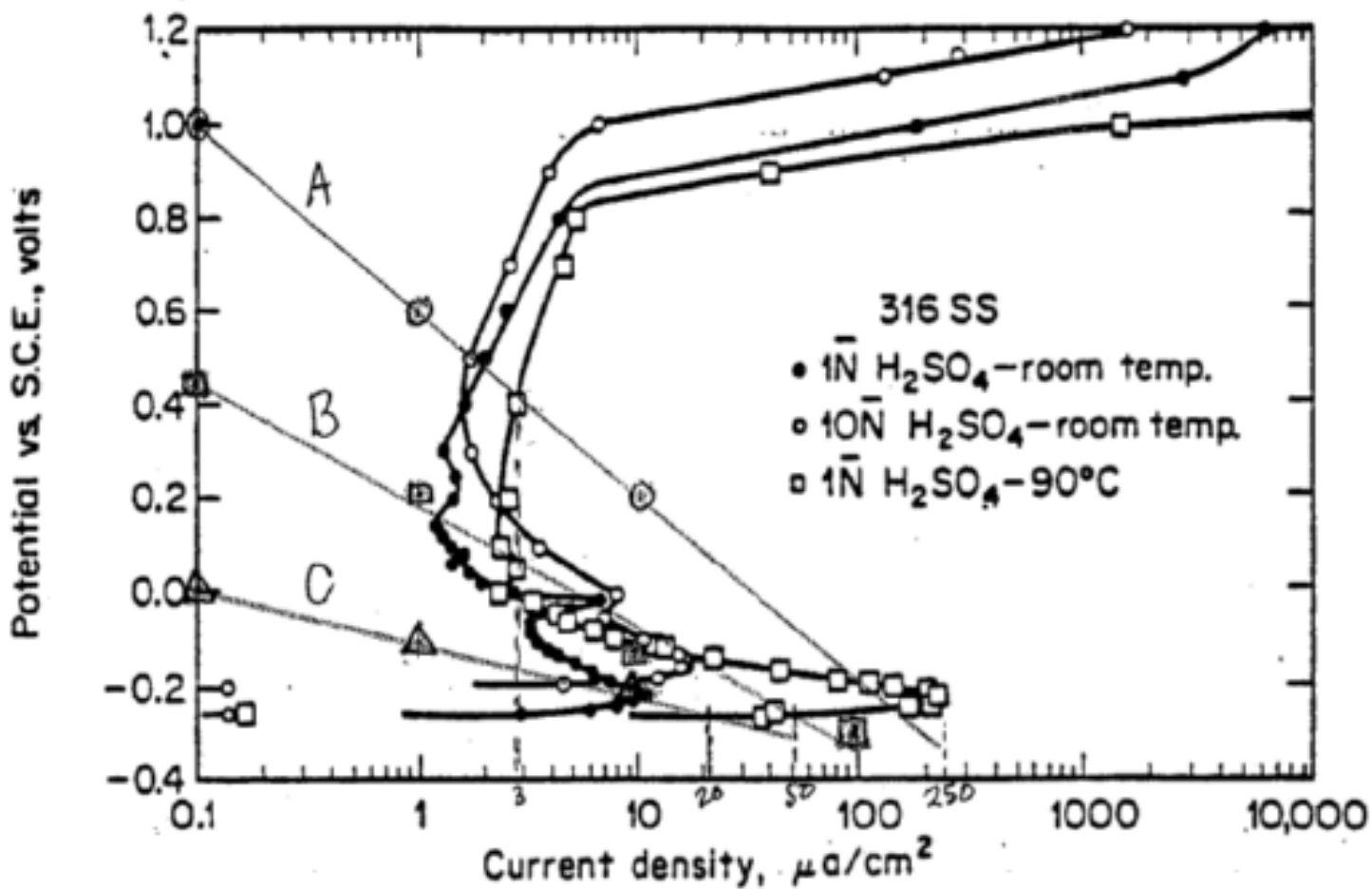
c) The current density doesn't change, it is $\sim 250 \mu\text{A}/\text{cm}^2$

(d) You are especially concerned about the effect of three different oxidizing solutions (A, B and C) on your baffle. For each of these solutions, tell whether type 316 SS will be active or passive in 1 N sulfuric acid at 90° C, and give the corrosion current density.

(e) Suppose your solid baffle is made of 316 SS, with dimensions 5 x 5 x 0.2 cm. If it were placed in solution A at 90° C, how long would it take to completely corrode the baffle away? (Assume that the specific gravity of 316 SS is 8.02.)



Solutions



d) A: Passive, $i_{\text{corr}} \sim 3 \mu\text{A}/\text{cm}^2$

B: Passive, $i_{\text{corr}} \sim 3 \mu\text{A}/\text{cm}^2$

C: Active, $i_{\text{corr}} \sim 20 \mu\text{A}/\text{cm}^2$

e) $SA = 54 \text{ cm}^2$, $r = i/nF$

$$r = 3 \mu\text{A}/\text{cm}^2 (54 \text{ cm}^2) / 2 (96,500 \text{ C/mol})$$

$$r = 8.39 \times 10^{-10} \text{ mol/s}$$

$$m = \rho V = (8.02 \text{ g/cm}^3)(5 \text{ cm}^3) = 40.1 \text{ g}$$

$$t = 40.1 \text{ g} (1 \text{ mol}/55.85 \text{ g}) (1 \text{ s}/8.39 \times 10^{-10} \text{ mol}) \\ \times (\text{hr}/3600 \text{ s}) (1 \text{ d}/24 \text{ hr}) (1 \text{ yr}/365 \text{ d}) = 27 \text{ yr}$$

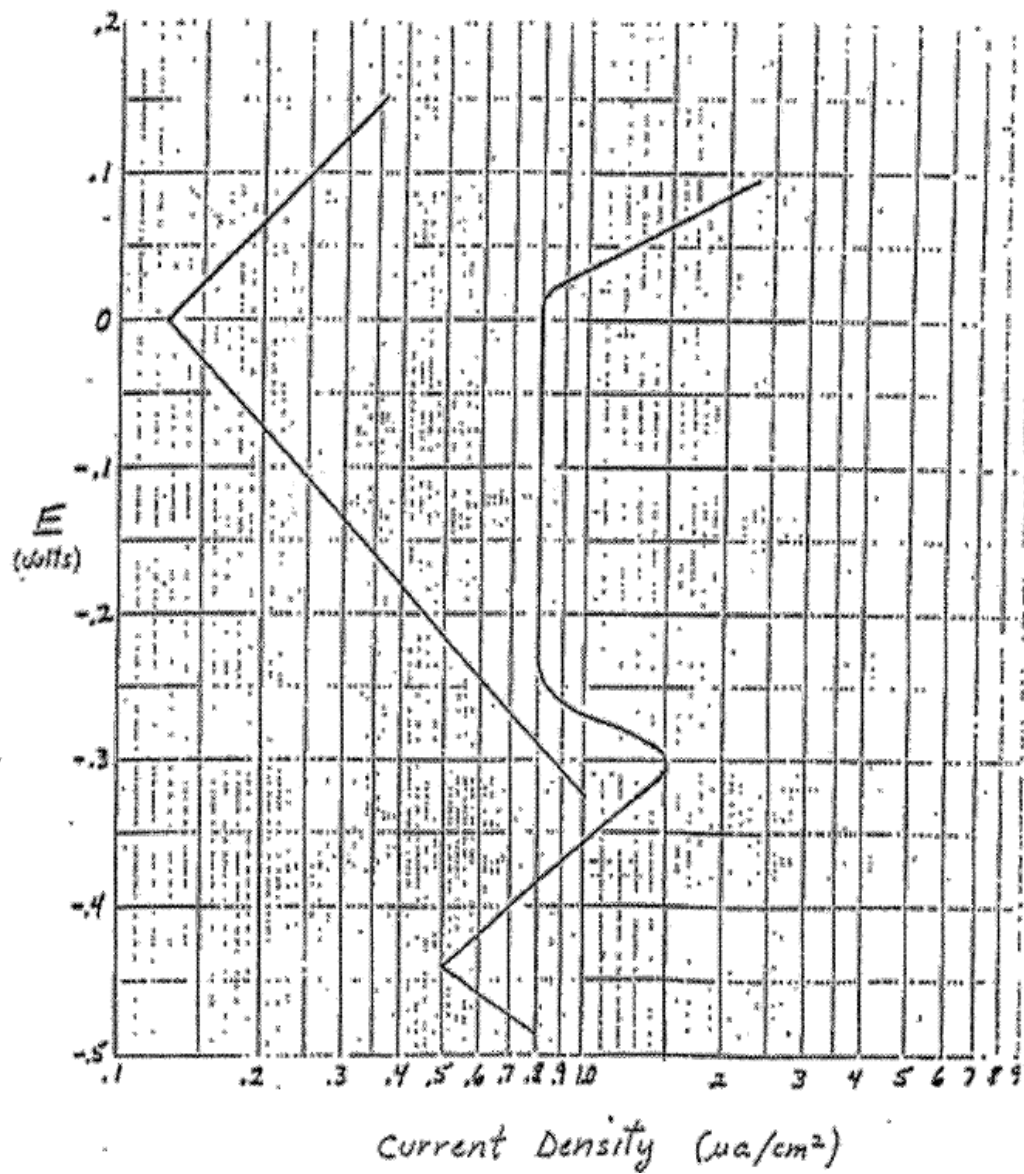


Special Problem #8

A rod of a particular stainless steel 18 cm long and 2 cm in diameter is submerged in an acid solution, and the polarization curves for the iron and acid half-reactions are found to behave as shown on the next graph. It is decided to protect the steel using anodic protection (i.e. forcing the steel into the passive range) as provided by external current from a current source device.

- What critical current must the current source device deliver to be able to begin to passivate the metal (critical current)?
- What is the minimum current the current source device must deliver to maintain protection of the steel (cheap anodic protection)?
- What is the change in voltage if you operate at $E = -0.1 \text{ V}$ (safe anodic protection)?
- What is the net power that you will consume to operate at safe anodic protection?
- What will be the initial corrosion rate (in g/yr) when the steel is successfully protected? (Assume that the steel has the same density and molecular weight as pure iron: 7.87 g/cm^3 and 55.85 g/mol .)





$$\text{Area} = \pi dL + 2\pi r^2 = \pi(2\text{cm})(18\text{cm}) + 2\pi(1\text{ cm})^2$$
$$A = 119\text{ cm}^2$$

$$\text{a) } I = A i_{\text{crit}} = (119\text{ cm}^2)(1.5\text{ }\mu\text{A/cm}^2) = 179\text{ }\mu\text{A}$$

$$\text{b) } I = A i_{\text{prot}} = (119\text{ cm}^2)(0.8\text{ }\mu\text{A/cm}^2) = 95.5\text{ }\mu\text{A}$$

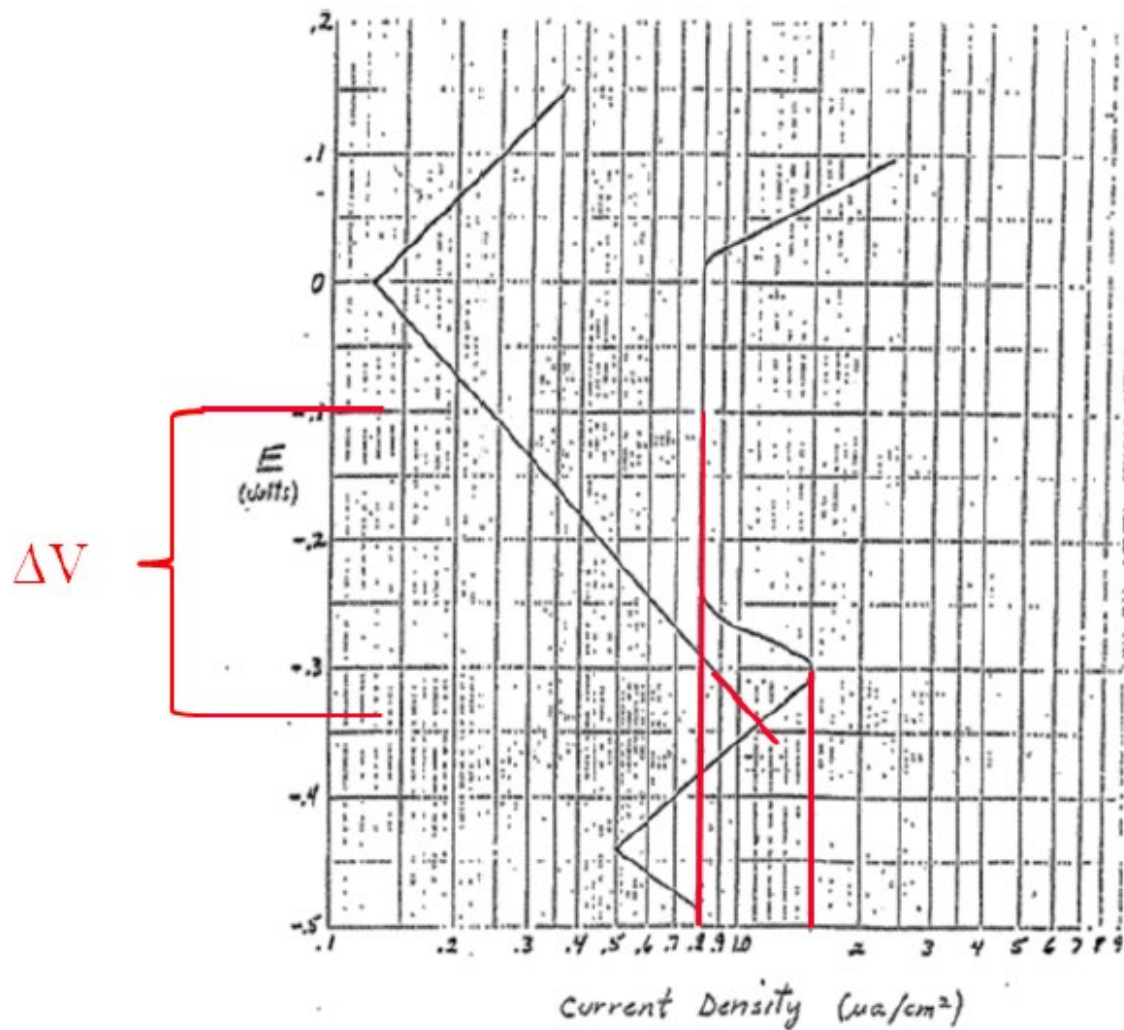


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$$c) \Delta V = V_{\text{safe}} - V_{\text{corr}} = (-0.1\text{V}) - (-0.34\text{V}) = 0.24\text{V}$$

d. What is the net power that you will consume to operate at safe anodic protection?

e. What will be the initial corrosion rate (in g/yr) when the steel is successfully protected? (Assume that the steel has the same density and molecular weight as pure iron: 7.87 g/cm³ and 55.85 g/mol.) 25

$$\text{d) Power} = i \Delta V = (0.8 \mu\text{A}/\text{cm}^2)(119 \text{ cm}^2)(0.24 \text{ V}) \\ = 23 \mu\text{W}$$

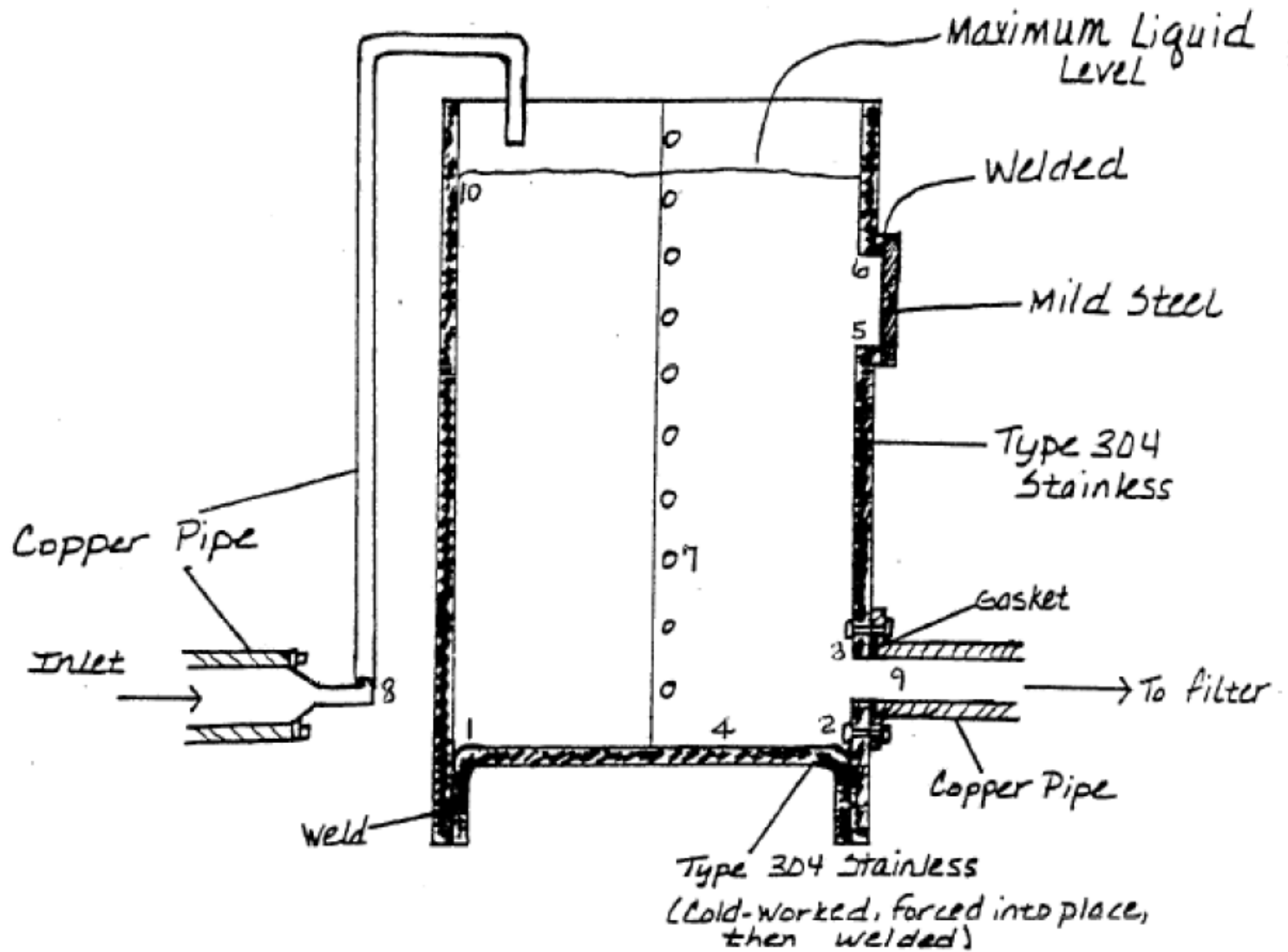
$$\text{e) } r = i/nF = \frac{(95.5 \times 10^{-6} \frac{\text{C}}{\text{s}})(55.85 \frac{\text{g}}{\text{mol}})(3600 \frac{\text{s}}{\text{hr}})(24 \frac{\text{hr}}{\text{d}})(365 \frac{\text{d}}{\text{yr}})}{2(96,500 \frac{\text{C}}{\text{mol}})} \\ r = 0.87 \text{ g/yr}$$



Special Problem #9

- a. If two dissimilar metals have to be joined together, what precautions must be observed to reduce the intensity of the attack on a less noble metal?
- b. What type of gasket materials would you recommend to prevent corrosion of steel-bolted joints in a petroleum processing plant? Temperature ranges up to 300° C, but little water is present. Give your reasons.
- c. The drawing below represents a proposed design for a tank to be used to hold a concentrated aqueous solution of suspended solids in brine which tend to settle out when the liquid slows down in the tank. The numbers on the drawing indicate where this system might develop corrosion problems. Describe the kind of corrosion that could occur at each spot (e.g., erosion corrosion, galvanic corrosion, etc.) Also suggest corrosion prevention or better design at each of these locations. Please give your answers in the space provided below the drawing.



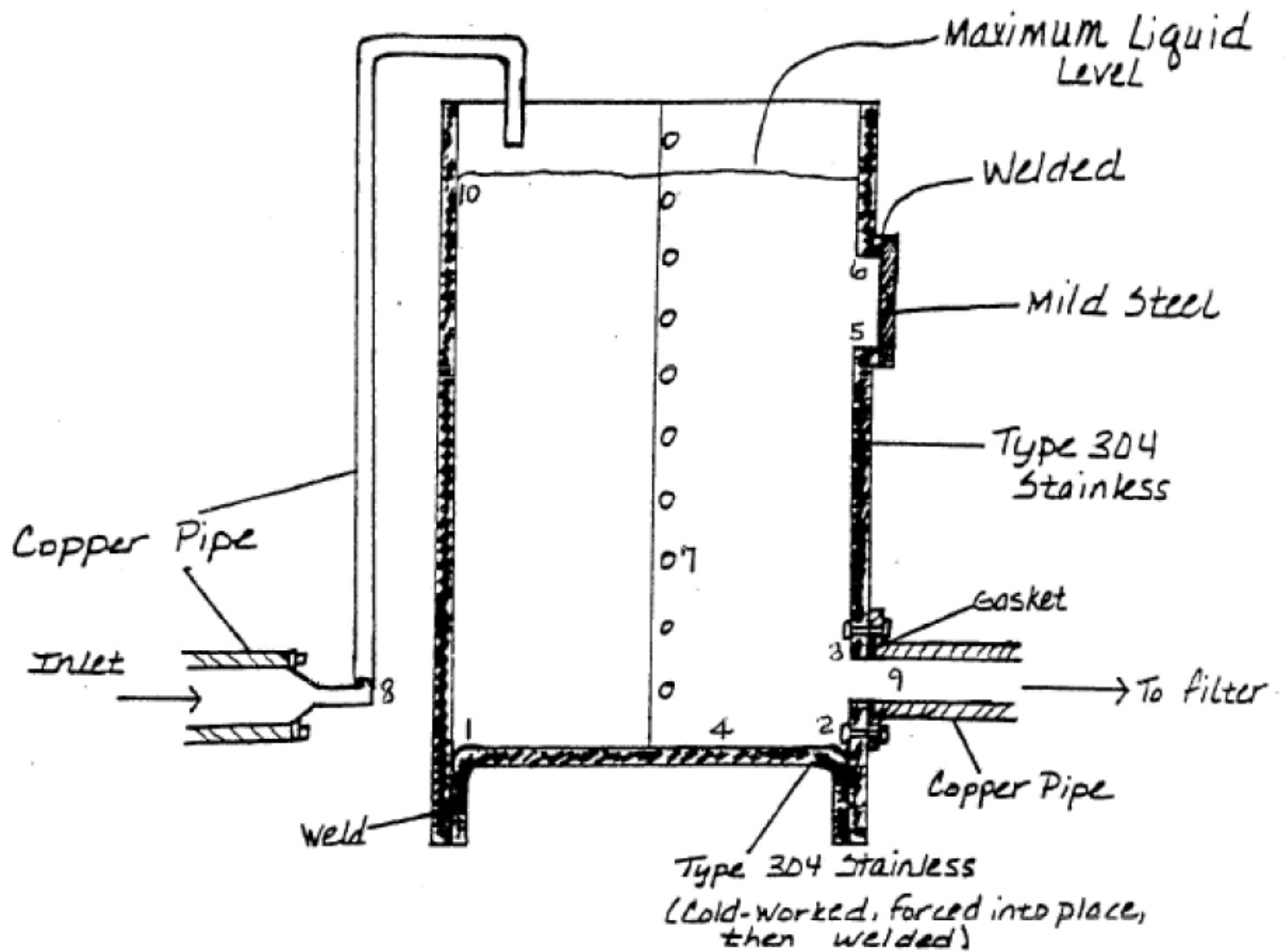


Solution

- a. If possible, the metals should be close together in the galvanic series. Also, when the materials are welded it would be important to completely seal the materials together, i.e., any cracks or areas where moisture could get between the metals should be avoided.

- b. A high-temperature polymer that is not reactive would be a must. It must be able to come in contact with chemicals and not break down. Also, to help prevent corrosion, it should be highly insulating. Also, a material with low cost would be desirable.





c.

Location #	Type of Corrosion	Remedy (Design or Material)
1	Crevice corrosion	Weld a T joint
2	Stress corrosion cracking	Don't force. Anneal to relieve stress.
3	Galvanic corrosion	Isolate, insulate the bolt which connects copper to stainless steel.
4	Pitting from particulate settling	Make a slanted bottom to the drain.
5	Pitting from particulate settling	Take out this protruding port or round ledges so that particles can't collect.
6	Galvanic weld rot	Don't connect stainless to mild steel. Anneal weld. Best to avoid weld; use insulated gasket.
7	Crevice corrosion around rivets	Weld properly instead of using rivets.
8	Erosion corrosion at sharp corner	Round out corner.
9	Erosion corrosion at sharp entrance	Smooth the corners.
10	Rust right below water level	Cover tank to keep air out; then fill tank completely.