Final Project
Redox Chemistry and the Treatment of Chrome Plating Wastes

The Chromalloy chrome plating plant in Boring, OR services a number of timber operations in Clackamas, Hood River, Deschutes, and east Multnomah counties as well as a local sawblade manufacturer. The sawblade manufacturer has lucrative contracts with many North American and Southeast Asian logging operations. Chromalloy itself has a payroll of 83 employees. Thus, Chromalloy has a significant, positive economic impact on Boring and its surrounding communities (see locator map at right.)

Chromalloy needs to develop an effective treatment for the water they use to rinse off sawblades and other machine parts after they are plated with hard chrome. The concentrated plating solution itself, when expended, has been (and continues to be) collected by a licensed hazardous materials treatment company and treated off-site under a contract with Chromalloy. However, the wash water is too dilute and of too great a volume to be effectively treated off-site. Prior to this time this relatively dilute solution has been mixed with the ordinary sanitary sewage from the Chromalloy plant and discharged to the Boring sewage treatment facility.

However, the sewage treatment plant operators have complained that occasional surges of Cr-containing wastes stun the population of bacteria needed to break down the sewage. Their complaints have cause DEQ to step in and demand that Chromalloy discharge water with no more than 50 ppb of total Cr to the sanitary sewage system. And the pH must be between 6 and 8. DEQ is prepared to shut down the operation by the end of June if a compliance plan is not prepared. Since this is the beginning of their busiest time of year, it is vital that Chromalloy get a compliance plan in place. Chromalloy is getting competitive bids from six environmental consulting firms, including the one you work for.

Chromalloy president C.R. "Red" Rivers has made it clear he is not paying for any studies until the bids are in and he has selected the winning contract. Your assignment is to perform a preliminary analysis of the problem so that your boss can present Chromalloy with a formal
proposal for the job. Another team of engineers is handling the structural and mechanical aspects. Your team’s task is to sort out the chemistry.

To that end, your group supervisor (Ms. Gail Creek) has requested the information and calculations listed below. Your report is to your boss and will not go directly to Chromalloy. However, Ms. Creek is very busy, not to say stressed out, and she wants a very clear, informative report from you that she can cut and paste into the final proposal with little or no editing. She also wants to see a formal presentation of your results so that she fully understands the proposal. This also means your firm will have the presentation “in the can” if the proposal wins and must be presented to DEQ on short notice. Your year-end bonuses are on the line.

**Characteristics of the Waste Stream:**

The working electroplate solution contains approximately 0.5 mol/L of potassium dichromate and 0.5 mol/L sulfuric acid. The parts are removed from the plating bath and washed down with high-quality water drawn from the nearby Clackamas River. The plating solution “carryover” (the volume of liquid that adheres to the blade) is fairly consistent on average and is approximately 1 fl.oz. per blade. The technical staff says an effective washing of each blade requires about 8 gal. of water which is then drained to the waste collection system. This is the wastestream to be treated. The plant plates an average of 200 blades per day, 6 days per week.

The staff has never had the input wash water analyzed (“We never had no problem with it; it’s always real clean” says operations manager Buck Sawyer) so you have no information about the background water chemistry other than that it is from a rural stretch of river that comes down off Mt. Hood. As yet the company has done nothing about the problem, so it also has no direct analyses of the waste wash water.
MEMORANDUM

From: Gail Creek, P.E.

To: Chromalloy Project Team

Subject: Information Needed for the Treatment Plan Proposal

I need this stuff ASAP! I want you to do a group presentation of your findings to the chief on next Thursday as a warm-up for the pitch to Chromalloy. I don’t think I need to remind you of the pending layoffs if we fail on yet another contract proposal.

1. I think we should know, to a first approximation, the composition of the wash water waste stream. We’ll need an estimate of the pH, pe, and chemical speciation of this water.

2. What happens if we tell them to just neutralize the pH by adding some base? That’s a very inexpensive approach. Will the discharge water then meet the DEQ guidelines? Why or why not? Does it depend on the choice of base we use?

3. The hard chrome plating process apparently includes small amounts of other metals beside Cr so I think it is best to go with the Fe(II) treatment process. (The Fe hydroxide sludge will take up any trace metals.) I don’t think the competition will propose this method and I feel we can sell the idea as a competitive edge our firm’s proposal. I would like you to do a thorough characterization of the process so the firm looks really smart in the pitch meeting next month.

   a. Prepare a data table and some sort of snappy looking graphics that show the results of titrating the Cr(VI) in the wash water waste solution with Fe^{2+} (i.e., perform a redox titration using Fe^{2+} as the titrant). The titration should sweep from conditions where the Cr(VI) dominates the chemistry to conditions where Fe(II) dominates. In the table and graph(s) I really want to see at least the pH, pe, and the major constituents of concern (e.g., [Cr(VI)]_t and [Fe(II)]_t), but you can include any other parameters you think are useful in the proposal. In your report discuss the meaning of the results, both in terms of the chemistry, and in terms of the practical issues of treating the waste stream to meet DEQ limits.

   Our goal here is to show the results of adding a range of Fe(II) reductant to the waste solution so that we know not only the optimal dosage but also the sensitivity of the system to variations in the ratio of reductant to oxidant. Remember, the concentration of waste is only approximately constant and will fluctuate from batch to batch and from day to day. This suggests to me a follow-up "titration"... (sorry guys)

   b. Perform a similar computed titration in which the [Fe^{2+}]_t is fixed at the dosage you decide is optimal but sweep the Cr(VI) concentration ± a factor of two (i.e., from one-half to twice the average concentration). Again plot up the pH, pe, and major components of interest, this time as a function of waste strength. The optimal amount is Fe(II) is your decision. Base it on the DEQ guidelines and the Fe(II) titration performed for Part (a).
4. After reducing the Cr(VI) we’ll obviously need to precipitate out the Cr(III) and end up with a supernatant that they can safely discharge to the sanitary sewer. Add some sort of base and figure out the optimal amount to achieve this. Report the resulting water conditions, pH, pe, etc. and comment on how this meets the desired standards. In choosing the base, consider the costs and other ramifications of various alternatives so that you can justify the cost analysis to Mr. Rivers at Chromalloy, who seems to be really anal retentive about such things.

5. Document the mass of sludge generated each month by the treatment regime you have designed. The so-called engineer in charge of the facility design says you can expect to have up to 50% water content in the sludge after the sedimentation basin and dewatering. Since you can’t be sure whether this is normal or just due to a pathetically poor design on his part, you’ll have to accept this number.

6. Calculate the total cost of chemicals and sludge disposal, per month, using the information I had our student intern provide us. I am asking that intern (what’s his name again?) To forward a memo to you with the cost info (attached).
Memo

From: Your long-suffering unpaid student intern
To: Da Boss
Re: Chemical and disposal costs

Hi, Gail told me you folks needed some help. Here’s what I managed to dig up by surfing the web. I also downloaded those "pics" you were too embarrassed to get for yourself. I’ll email them to your home computer so Gail doesn’t find ’em. ;-)

These numbers are pretty much up to date; we can fine tune later if we need to.

Lime: $55 per 50 lb. sack, about 90% Ca(OH)2
Soda ash: $11 per 50-lb sacks of dry powder, approx 95% Na2CO3.

Disposal of Cr(III) bearing sludge: I called the Arlington landfill and they said they would accept that sort of sludge at a cost of $225/ton. Jack Hawk Trucking said they would pick it up and deliver it for $75/ton. They recommended we accumulate loads of at least 2-3 tons because they might cut us a better deal. The guy I talked to sounded like a mafioso, so we might want to look around.

I did not look up the info on pickle licker (sp.?) for the Fe(II) because you said you already had data on the Fe(II)Cl2 form in your files. Thanks, because that sounds like a bizarre website.

OH! Almost forgot!!! I finally talked to that Ben Perkins guy in the Geology department at PSU. He said that those mineral phases K-jarosite and H-jarosite you asked about are not very likely to precipitate in a solution like ours when you raise the pH. He also said the only iron solid likely in the sludge would be amorphous iron hydroxide, whatever that is.