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Abstract

Kverneland Group requires a reduction of Cr(VI) in their waste water and this work investigated the reduction of Cr(VI) in aqueous solution by Ferrous sulfate and elemental iron powder at range pH 12, 7 and 6. Reduction by Ferrous sulfate was possible at all pH levels with increasing efficiency at lower pH values ranging from 70% Cr(VI) remaining at 12 pH, and 17.3% remaining at pH 6. By contrast the reduction by Zero Valent Iron proved ineffective with no discernable reduction of Cr(VI) at pH values at and above 6. Lower pH levels were not able to be tested due to the production of nitrous gas at pH 5.

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1. Preface

I would like to thank my adviser Roald Kommedal for the excellent guidance and support during this process. I would like to thank my institution, The University of Stavanger, faculty of science and technology, for letting me use the laboratory during my thesis work. I would also like to thank Kristin Torgersen Ravndal and Erling Berge Monsen for helping and guiding me all the way until the end of my laboratory work. Without your help, this study would have been significantly harder. Special thanks to my husband for motivating me and taking on the family duties freeing me to concentrate on my lab work and writing.

2. Introduction

Chromium plays an important role in the steel making industry, as a way of creating various alloys like stainless steel and hardening steel. The popular Chrome finish on cars and motorcycles is achieved by plating with Chrome on steel. The properties of hardness and corrosion resistance are useful characteristics for metals used in in plowshares or other implement exposed to the elements constantly with physical impacts.

Unfortunately the Cr(VI) ion is considered poisonous and found to be involved in skin rashes (Achmad et al., 2017), kidney, liver and lung cancer (Kim et al., 2018) among others. And it is also poisonous to environment and species found in water ways. In contrast Cr(III) is used in various biological functions by animals and humans. It is found in large concentrations in the cooling/hardening baths at Kverneland group due to the metal leeching out during the hardening process.

The Kverneland hardening process consist of dipping the metallic alloy while between 830 and 890 °C into Caustic sodabath and a Salt bath, promoting hardening of the hardening of the alloy. During this process some heavy metals are leached/exchanged from the high temperature stainless steel alloy and retained in the bath. The wash water from these bath and the overall waste water contains large amounts of Cr(VI), Nitrates and salts. The waste water has to be sent to a specialist vendor to treat, as it is not permissible to release into the local water-net at those concentrations. Figure 1 shows a very simplified view of the process

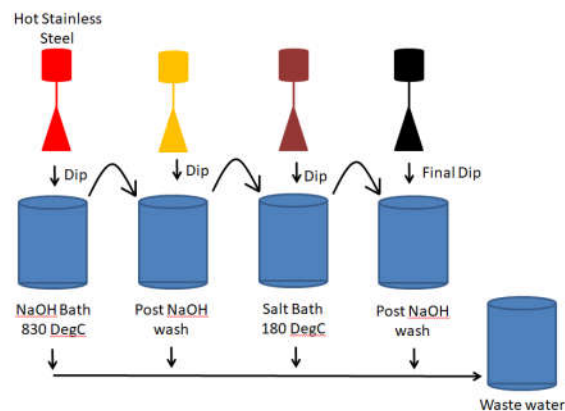


Figure 1: Simplified Kverneland Stainless steel hardening process

Due to the poisonous nature of the metal there are regulatory concentration limits (0.05 mg/l) on the effluent water from the facility. At the time of writing the concentration is higher than the allowed limit (>600 mg/L) and Kverneland wants to reduce the concentration within the allowable limits to avoid fines and environmental concerns to allow for discharge into local water, rather than sending the water internationally to have it treated.

The Kverneland Group is therefore interested in exploring methods of reducing the Cr(VI) to the more environmentally friendly Cr(III) thus removing the Cr(VI) from the effluent and showing the authorities improvement in the outlet concentration if not completely bringing it below the required concentration.

The wastewater at Kverneland has a high pH and many other ionic species and contaminants. The yards contain ample supply of pure iron. The solution should meet the following requirements:

1. Not create an additional environmental issue
2. Be efficient and low cost
3. Not create a new novel hazard in the process

A reduction of the Cr(VI) will be achieved chemically with readily available methods and chemicals.

The report is built up around using known methods to reduce the Cr(VI) and seeing which of these work with Kverneland samples, what additional steps to prepare the samples are required and what concentration it can be reduced to.

3. Theory

Kverneland supplied the following data for their various water streams. In table 1 the regulatory limits are also present showing the constraints the Kverneland Group is working against. Of particular note is the maximum Cr(VI) value of 0.05 mg/l and the pH range of 6.5 to 9.5 for discharge in the local water-net. Table 2 shows the composition of the Soda- and Salt-baths, which show that both of the water streams are above the regulatory limits.

Table 1: Waste- and wash-water composition and regulatory discharge limits

Item	Regulatory limit for discharge	Measured Wash Water	Measured Waste Water
pH	6.5 - 9.5	>11	>11
Residual metal embers (mg/L)	30	-	-
P (mg/L)	5	-	-
Fe (mg/L)	5	<1	<1
Ni (mg/L)	0.5	0.26	<0.06
Cr (Total) (mg/L)	0.5	82.9	961
Cr(III) (mg/L)	-	32.3	286
Cr(VI) (mg/L)	0.05	50.6	676
N (total) (mg/L)	40	6360	94100
Non Polar Oil ((mg/L)	20	-	-

Table 2: Soda and salt bath composition and analysis method received from Kverneland

Parameter	Prøve 1 Salt Bath Result	Prøve 2 NaOH bath Result	Detection Limit	Method uncertainty	Analysis method
pH	11.5	12.1	2 - 12	+/- 0.2	NS-EN ISO 10523
Temp @ pH measurement (degC)	18.7	18.5	-	-	NS-EN ISO 10523
Residual metal embers (mg/L)	69	120	10	+/- 20%	NS-4733 2 ed
P (mg/L)	0.47	0.49	0.02	+/- 20%	NS-EN ISO 17294-2
Fe (mg/L)	19	42	0.001	+/- 20%	NS-EN ISO 17294-2
Ni (mg/L)	15	12	0.0002	+/- 15%	NS-EN ISO 17294-2
Cr (Total) (mg/L)	72	26	0.00004	+/- 10%	NS-EN ISO 17294-2
Cr(VI) (mg/L)	60	20	0.01	+/- 20%	En 16192, EPA 7199
Nitrite-N (mg/L)	4000	1.4	0.01	+/- 15%	NS-EN 13395
Nitrate-N (mg/L)	700	14	0.01	+/- 15%	NS-EN 13395
Total-N (mg/L)	4700	16	0.015	+/- 15%	Internal (NS-EN ISO 11905-1)

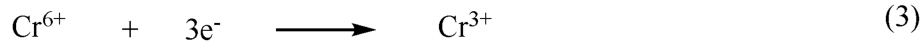
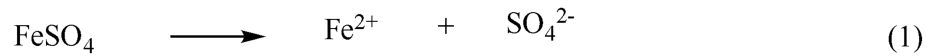
Testing for the concentration of Cr(III) and Cr(VI) traditionally relies on complexation and selective extraction prior to analyzing the samples (Soares et al., 2009), which is a laborious process. Instead the method suggested in the same paper by Soares et Al (2009), will be used to produce quick reliable results.

Complexing Cr(III) with EDTA and reacting Cr(VI) diphenylcarbazide solution yields species capable of being detected in a Spectrophotometer (Soares et al., 2009). It provides a reasonably fast and accurate method which can be used qualitatively and quantitatively to detect differences in Cr(III) and Cr(VI) when performing reduction experiments. The method does not make it possible to detect Cr(III) and Cr(VI) in the same sample and therefore 1 sample per species must be prepared.

To determine the actual concentration from the Absorbance measurements of the unknown samples, samples with known concentrations of Cr(III) and Cr(VI) are prepared from CrCl₃ and K₂CrO₄.

Once calibrated the line equation will be used to determine concentration of unknown samples. The unknown samples will be subjected to the same preparations as the known samples. Due to the high concentrations of Cr(VI) measured by Kverneland, the samples will be diluted to be within testable range of the method as per (Soares et al., 2009). Kverneland has provided concentration from other lab work, however that data is on the basis of an average day not specifically the provided sample. Once prepared samples tested for Cr(III) will show readings in the 540nm range. In contrast Cr(VI) samples should show readings in the 543nm range.

According to (Mitra et al., 2011) and (Qin et Al., 2005) it is possible to reduce Cr(VI) using iron in various states as a reducing agent. As these are reduction reactions a low pH will shift the equilibrium to the right in the case of equations 1-3 and 4-6. This requires shifting the pH of the wastewater solution, requiring a use of chemicals. One possibility is using ferrous sulfate as described in (Qin et Al., 2005) which will proceed according to the following reaction;



Equation 1: Ferrous Sulphate Equations 1, 2 & 3

It is noted in (Qin et Al., 2005) that while ferrous sulfate is effective at reducing Cr(VI) to Cr(III), but the removal of Cr(III) is difficult. The presence of Fe^{3+} and SO_4^- in solution can increase the readings of Cr(III) but does not appear to interfere with the readings of Cr(VI) (Soares et al., 2009) and thus will not create issues for measuring the Cr(VI) concentrations. Ferrous sulfate will be added in a 1 to 1 mol ratio to each sample and samples shaken in a benchtop incubation shaker. Testing for Cr(III) and Cr(VI) will be done at 2 hrs, and again at 24 hrs after adding ferrous sulfate.

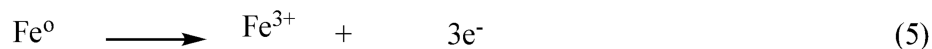
Elemental Iron is also possible to use, but the area available determines the potential for reaction, and has the potential to become saturated as per (Mitra et al., 2011). As there is elemental iron available at the Kverneland site this is a favorable option, though the size of the metal pieces presents a challenge as area to volume is not favorable as for powdered iron, and having to reduce the pH significantly may introduce issues.

This can be seen with equation 4, depending on the area. (Mitra et al., 2011)

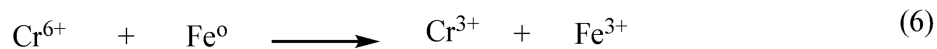
$$\frac{d[\text{Cr(VI)}]}{dt} = -k[\text{Cr(VI)}]^{0.5} [\text{H}^+]^{0.5} (\text{Area}). \quad (4)$$

Equation 2: Rate reaction 4 for Cr(VI) with Zero Valent Iron

Elemental iron reduces Cr(VI) as listed below in equations 5 & 6;



Redox reaction:



Equation 3: Zero Valent Iron Reaction 5 & 6

The zero valent iron will be added in a 1 to 1 mole ratio as per the ferrous sulfate and in the same number of pH levels and parallels. Testing for Cr(III) and Cr(VI) will be done at 2 hrs, and again at 24 hrs after adding the zero valent iron.

In (Jiang, B. et al., 2019) it is possible to reduce the Cr(VI) to Cr(III) using carboxylic acids. The acid would act as an electron donor to the Cr(VI), and the acids are environmentally neutral, thus not creating a new environmental concern. This method relies on low pH, high temperature, presence of

other ionic species, gas atmosphere and light to increase the reduction and as such present a large investment in new equipment for Kverneland that would defeat the purpose of removing Cr(VI) on site. As such this method was found unsuitable for the work.

The use of activated carbon is known in many industries for its potential to absorb heavy metals, and is readily available in large quantities from many suppliers. K, Selvi. (2001) explores the use of activated carbon in removing Cr(VI) from solution, and was found effective particularly at a pH value of 3. Due to the nature of activated carbon the Cr(VI) is not reduced but instead absorbed within the carbon. It would require filtering and potential transport to other facility for recovery of the absorbed Cr(VI) meaning the problem is moved but not solved and new equipment like filters pumps, activated carbon storage etc are required to make this a feasible solution. For this work it is considered initially unsuitable, but may have future applicability.

Biological methods using microorganisms to remove heavy metals are possible (Elahi, A et Al., 2020). These use various bacterial organisms to reduce Cr(VI) in to Cr(III), through various biological processes such as fermentation and respiration. The drawbacks include potential large equipment investments to encourage a bacterial environment to flourish and reduce the Cr(III). Due to the weekly waste water flow rate of approximately 1 m³ it may not be feasible to sustain the bacteria. It has been deemed unsuitable for this work, but could be of interest in future work as Biological Cleaning Facilities are known in Norway.

Electrocoagulation is a method of using an Iron Electrode with a current applied causing the Cr(VI) to coagulate (El-Taweel, Y et al., 2015). This method has the optimum working conditions at very low pH, El-Taweel, y et al (2015) stating the optimum being a pH of 1. This does not appear to be a feasible solution as this requires a very corrosive environment for the coagulation to take place, creating additional hazards at site.

The objective of this study is to use the methods described above to reduce the amount of Cr(VI) found in the Kverneland Group wastewater samples to a reasonable level. The study will attempt to quantify what amount of reduction is possible at various pH levels, including the natural pH of the wastewater. In addition this should provide an optimum level of pH for reduction given the wastewater characteristics, and be useful for Kverneland to establish a procedure to apply at site.

Finally the study will likely provide insight to unknown variables that have not been accounted for in the initial setup and give options for further study to eliminate uncertainties or strengthen the conclusion within.

4. Materials and Methods

This section describes in detail the equipment and procedures used to perform the experiment and collect data. The location for all experiments is the laboratories at the University of Stavanger, with wastewater samples delivered from Kverneland site.

4.1. Materials and Methods for creating calibration data

All the solutions were prepared with analytical reagents with ultra pure water (Purelab Flex by ELGA Labwater, VWS United Kingdom). Standard stock solutions containing 1000mg L^{-1} for Cr(III) using CrCl_3 were prepared from titrisol concentrate (Merck, Darmstadt, Germany) and for Cr(VI) containing 1000mg L^{-1} using K_2CrO_4 and fixanal concentrate from (Riedel-de-Haën Seelze Germany). Intermediate low concentration solutions of Cr(III) and Cr(VI) were prepared by dilution of the corresponding stock solution with ultra pure water. The chemicals used were Sulfuric acid, EDTA (Merck, Darmstadt, Germany) DPC (VWR, Leuven Belgium) and acetone (VWR International, Fontenay-sous-Bois, FRANCE). A 0,45M sulfuric acid was made by diluting with purified water in 100ml volumetric flask. DPC solution were prepared by dissolving 0,250g of the reagent into 50ml of acetone.

To make Cr(III) stock solution, a mass of 0,3045g of CrCl_3 was transferred into 100ml Volumetric flask and diluted with ultrapure water. Using automatic Pipette, stock solutions of (50,100,500,1000,2000,3000) μL into 100 ml Volumetric flask and diluted to 100ml with ultra pure water to achieved concentrations of (0.5,1.0,5.0,10,20,30)mg/L ideally. Due to a measuring error the actual concentrations have become (0.3, 0.6, 3.0, 6.0, 12.0, 18.0)mg/L. This has no effect as the measurements were within the range of the method. For Cr(VI), a mass of 0,3735g of K_2CrO_4 was transferred into 100ml volumetric flask and 100 ml ultra pure water added. 10 ml of this solution was pipetted into a 100 ml volumetric flask and diluted to 100ml. Stock solutions were then prepared according to the same method as Cr(III). Using automatic Pipette, standard solutions of (5, 10, 50, 100, 200, 300) μL with the concentration of (0.005, 0.01, 0.05, 0.10, 0.20, 0.30)mg/L, each transferred into 100ml Volumetric flask and diluted using purified water.

In this test, aliquots of 25ml were taken from the sample and was transferred into 50ml plastic beaker. For Cr(III) complexation 0,065g EDTA was added. The pH adjusted using 0,45M H_2SO_4 and 2,0M NaOH solutions until pH 4.5 (Soares et al., 2009) The solution was transferred into 50ml volumetric flask and was heated using water bath with the temperature between 87-90°C for 16 minutes. The solution cool down until it reached room temperature then top up with purified water. For the Cr(VI), the pH must be in range 2.18-2.23 (Lace et al., 2019). Then 1ml of DPC solution was added to react with Cr(VI). The solutions stands for 30 minutes then it was transferred into using 2.5 ml macro cuvette for spectrophotometric analysis. The deionized water was used as a blank then followed by the standard solutions. The mixed standard solutions used in analytical work were in the table below. Table 3 shows the overview of concentrations and figure 2 shows the absorbance spectra.

Table 3: Cr(III) and Cr(VI) concentration list for calibration

Number	Cr(III) with EDTA		Cr(VI) with DPC solution	
	Concentration (mg/L)	Volume (ml)	Concentration (mg/L)	Volume (ml)
1	0,3	0,005	0,005	0,0005
2	0.6	0,1	0,01	0,001
3	3	0,5	0,05	0,005
4	6	1	0,1	0,01
5	12	2	0,2	0,02
6	18	3	0,3	0,03

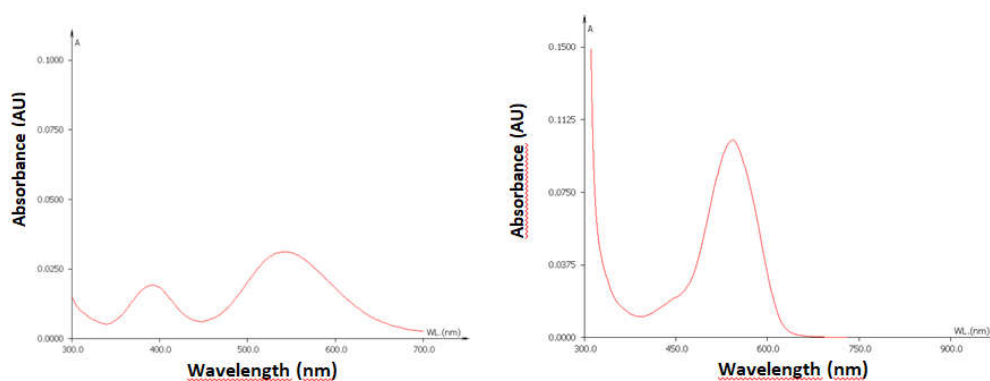


Figure 2: Wavelength of Cr(III) using EDTA at 392nm and 540nm, for Cr(VI) using DPC solution at 543nm

4.2. Material and Method for testing with Ferrous Sulfate

The waste water sample from Kverneland Group was prepared by transferring 100ml sample in each 12 vessels. The samples were measured in pH 12, 7, 4, 2. The samples were titrated using 2.0M HCl (Hydrochloric Acid, VWR International, Fontenay-sous-Bois, FRANCE). Unfortunately, lowering the pH to 5 produces nitrogen dioxide due to high concentration of nitrate in wastewater. The samples therefore titrated until roughly around pH 7 and 6. All of them were in 3 parallels. The wastewater samples must measure the before and after adding the reduction agent, then the analysis tests performed.

The first reducing agent to test was Ferrous sulfate. A mass of 0,0448g of FeSO₄ (Iron(II) sulfate heptahydrate, Merck, Darmstadt, Germany) was added into 30ml of wastewater sample and was transferred into 100ml borosilicate glass(from VWR) and put in in a benchtop incubation shaker(CERTOMAT, B. Braun Biotech International) under constant temperature at 26°C for 2 hours and then for 24 hours to monitor the reduction values. To calibrate the spectrophotometer at zero absorbance, a deionized water was used as a blank using 2.5 ml macro cuvette(BR759005

BRAND® macro-cuvette, Merck, Darmstadt, Germany) then followed by the mixed standard solutions. The wavelength was set at 540nm for Cr(III) and 543 nm for Cr(VI). All the tests were performed 3 parallels for accurate results. This was repeated for 0.030g of zero valent iron.

5. Results and Discussion

The data collected for the calibration using the method outlined in (Lace et al., 2019) and (Soares et al., 2009), is shown in figure 3,

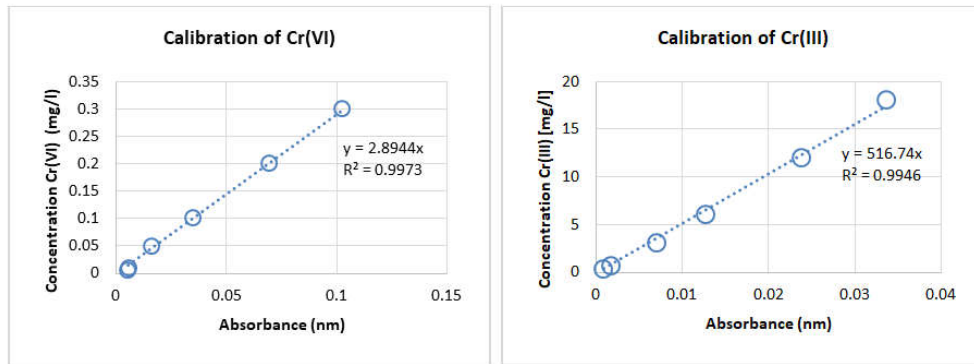


Figure 3: Calibration Curves for Cr(VI) and Cr(III) with linear calibration equation R2 values

The recorded data forms a straight line enabling the use of the linear calibration to be used for calculating the concentrations in the tested unknown samples.

The titration curve is in figure 4, shows 2 buffer regions, indicating some buffering capacity in the waste water.

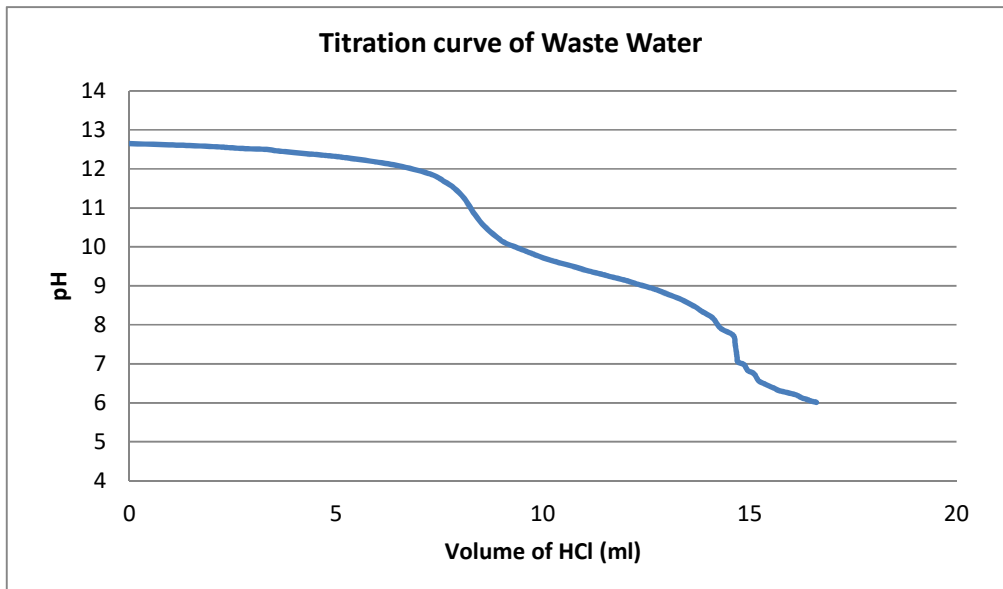


Figure 4: Titration Curve of Waste Water showing plateaus

5.1. Ferrous Sulphate Testing

The samples for the Ferrous Sulphate testing were analysed prior to adding Ferrous Sulphate, denoted as 0 hrs, and drawn at 2 hrs and 24 hrs of reaction time. Table 4 contains the data for Cr(III). The Cr(VI) data is placed in Table 5. Data was averaged over three individually independent samples per pH level and standard deviation estimated. Note it was initially attempted to have samples at pH values of 5 and 2 as well, however it was discovered that a reddish/brown gas was created and these low pH level samples were disposed of and not used in the experiment.

Table 4: Cr(III) testing with Ferrous Sulfate at pH 12,7 & 6 at 0, 2 and 24 hrs

pH	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)
	0 Hrs		2 Hrs		24 Hrs	
12.74	733	42	994	280	1205	113
7.04	817	62	989	35	1022	31
6.06	787	67	864	30	783	13

Table 5: Cr(VI) testing with Ferrous Sulfate at pH 12,7 & 6 at 0, 2 and 24 hrs

pH	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)
	0 Hrs		2 Hrs		24 Hrs	
12.74	567	10	321	45	397	90
7.04	581	71	139	18	124	2
6.06	635	12	145	19	110	19

The Cr(III) shows an upward trend for all parallels with the exception of pH 6. The data show that higher pH levels shows higher increases in Cr(III), but in all cases there is an increase in Cr(III) at all pH levels, with the exception noted earlier. The standard deviation is noticeably higher for Cr(III) than for Cr(VI) for pH level 12 at the 2 hr mark. This is likely due to a reading error for 1 sample.

As predicted the Cr(VI) shows a downward trend. Lower pH values showing a more significant decrease in Cr(VI) concentration. In this case the concentrations at pH 12, indicate that the reduction of Cr(VI) is lower after 2 hrs compared to 24 hrs. This is likely due to the high pH pushing the equilibrium towards less Cr(VI) as per equations 1-3. In all cases the data shows the concentration less than original concentration. The reduction efficiency, ie percent Cr(VI) remaining, at pH 12, 7 and 6 is 70%, 21.3% and 17.3% respectively.

There is not a 1 to 1 correspondence in the concentration reduction of Cr(VI) and increase of Cr(III). This can be due to an over-reading of the Cr(III) results which according to (Soares et al., 2009) can be caused by presence of other ion in the solution such Cu(II), Ni(II) and SO_4^{2-} or by the formation of other species of Chrome. Also, Cr(III) precipitation may have occurred during pH manipulation.

5.2. Zero Valent Iron Testing

Zero Valent Iron testing is collected in table 6 for Cr(III) measurements and table 7 for Cr(VI) measurements. Data was averaged over the samples per pH level.

Table 6: Cr(III) testing with Zero Valent Iron at pH 12,7 & 6 at 0, 2 and 24 hrs

pH	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)
	0 Hrs		2 Hrs		24 Hrs	
12.74	673	72	665	49	1319	46
7.04	817	62	1400	24	1345	81
6.06	792	68	1105	5	892	59

Table 7: Cr(VI) testing with Zero Valent Iron at pH 12,7 & 6 at 0, 2 and 24 hrs

pH	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)	Average concentration (mg/L)	Std Deviation (mg/L)
	0 Hrs		2 Hrs		24 Hrs	
12.74	558	18	548	8	623	24
7.04	581	71	700	10	715	14
6.06	635	12	666	37	680	28

The Cr(III) concentrations using zero valent Iron have increased at the end of the 24 hr period. It shows the same trend as for the Ferrous Sulfate results, with higher pH levels trending towards larger increases in Cr(III) concentration. At pH 7 and 6 it also shows a trend of having more Cr(III) when tested at 2 hrs versus 24 hrs. This indicates that equilibrium is not established until after several hours, which allows for a batch process for Kvernland, which can likely be achieved using barrels or current storage containers. As there is no reduction of Cr(VI) measured, the increase in Cr(III) could be caused as by other ions in solution as stated earlier, though according to Soares et Al (2009), this would be on the order of 5 to 20%. Alternatively other species of Chrome could be reducing/oxidising into Cr(III).

Cr(VI) testing with zero valent iron shows, in contrast to the testing with Ferrous Sulfate, a rising trend in concentration of Cr(VI). The rise is not large, between 3 and 15%, but significant for the 24 h sample. In (Mitra et al. 2010), it is noted that a Cr(VI) reduction of 47.8% is possible at pH 3, but only 1.7% at pH 5.5. This suggests that the reduction of Cr(VI) at pH 6 and above is not possible using elemental iron. The issues with rising Cr(III) measurements may also translate to Cr(VI) in the presence of higher concentrations of ions than tested for in (Soares et al., 2009).

5.3. Other result and future work

The reddish/brown gas generated at pH values below 6 was likely a nitrous gas formed in redox reactions at the lower pH levels in the presence of reducing agents such as iron and high levels of nitrates, NO_3^- and NO_2^- , as seen in the Kverneland sample compositions as shown in Figure 1 and Figure 2. This is likely to occur with any reducing agent once the pH level is below 6. Due to the health risks involved it is not recommended to test the Kverneland samples or for Kverneland to establish a process based around a pH value below 6 as there will be significant equipment changes to mitigate the risks.

A potential process for Kverneland is shown in figure 5. This includes placing an amount of waste water in barrels or other container, then adding HCl to reduce the pH to around 7. This pH is unlikely to cause corrosion or degradation of a container but material compatibility should be investigated. Also the pH level will be within the regulatory guidelines. Once the pH level has been established Ferrous Sulphate should be added to the container and the solution agitated with a simple mixer unit for 24 hrs. The time to establish equilibrium may depend on how well mixed the solution is. This will bring the Cr(VI) concentration down to approximately 125 mg/L, that may result in options to ship the water to national heavy metal removal sites for processing. Establishing at what time the equilibrium is reached will also ensure a more efficient batch process.

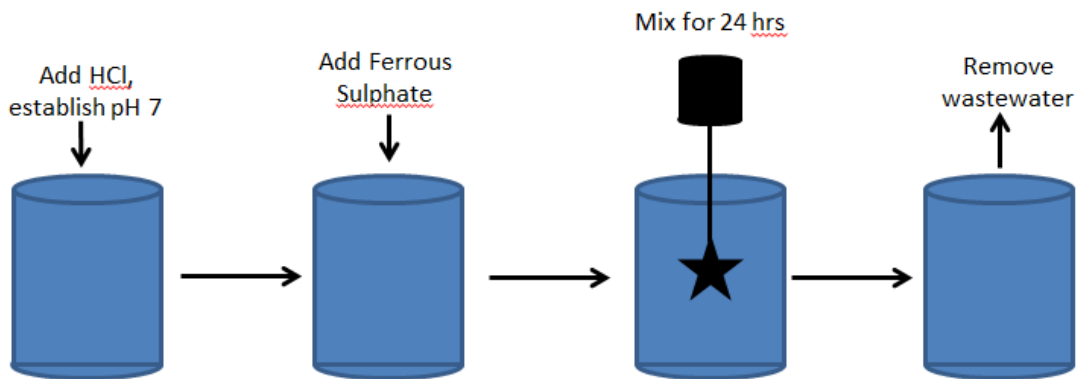


Figure 5: Batch process suggestion for Kverneland based on ferrous sulphate

Future work should include investigation of whether or not other species of Chrome are created during the reduction reactions, and if it is possible to do a Chrome balance with the different species. The chrome balance would confirm if there are other potential issues created during the reduction.

Further investigating options to avoid the production of the Nitrous gas at lower pH and thereby enable testing of the effectiveness of Zero Valent Iron, would bring options to use the available scrap iron at site and in addition the efficiency of ferrous sulphate at lower pH levels. Nitrates are possible to remove via microbiological processes, or other methods such as Ion exchange or reverse osmosis though these are all intensive processes that may not work due to the presence of other ionic species. It is worth noting that according to table 1 the regulatory limits for nitrates are also currently being exceeded and would require to be solved.

Using an organic reduction agent like methanol or formic acid other in the same manner as the ferrous sulphate to provide further options for use at Kverneland should be attempted. These may have the potential to reduce Cr(VI), though the interaction with the nitrates at low pH may create a potential explosive atmosphere.

The use of activated carbon should be investigated, both on its own and as a continuation of the potential batch process laid out in figure 5. As a small batch process the filtering and storing of active carbon used in absorbing Cr(VI) may be feasible, and could bring the Cr(VI) concentration below regulatory guidelines and allow for discharge into the local water drain, assuming the other criteria are met.

6. Conclusion

Based on the data above we conclude that Ferrous Sulphate is effective at reducing Cr(VI) at pH 7 and below, and can also reduce Cr(VI) to a lesser extent at pH 12. The percent Cr(VI) remaining at pH 12, 7 and 6 is 70%, 21.3% and 17.3%. Zero valent Iron is not effective at reducing Cr(VI) above pH 6. Kverneland samples produce a yellow/brownish gas below pH 6.

Further the equilibrium is not established quickly therefore a process with Ferrous Sulphate would require a batch process, preferably with agitation.

It is not possible to reduce the pH of the Kverneland waste water sample below 6 in the presence of reducing agents as nitrous gases will form due to the high levels of nitrates in the sample.

7. References

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