Selenium Removal from Waste Waters by Chemical Reduction with Chromous Ions

by

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Abstract

Selenium can be released to the environment from both natural and industrial activities, resulting in increased selenium concentrations in surface and ground water. Even small concentrations of selenium can be toxic for many forms of aquatic life. Therefore, selenium contamination in the receiving environment is a key issue for many industries.

Selenium speciation in solution plays an important role in its removal. Selenite (SeO$_3^{2-}$, Se(IV)) and selenate (SeO$_4^{2-}$, Se(VI)) are the most important inorganic selenium species which are generally found in water and known to be toxic. Relative to the selenate, selenite can be quite easily removed from solutions using various treatment methods such as chemical reduction, precipitation and adsorption by ferrihydrite salts. However, these methods are not efficient for selenate removal. Typically, chemically based treatment processes for selenate removal require an initial reduction of selenate to the lower oxidation states (e.g., selenite, H$_2$Se).

Chromous ions have been known as a powerful reducing agent in the reduction of many organic compounds, oxides, and sulphide minerals and in many proposed novel hydrometallurgical processes. Therefore, there is a high potential for chromous ions to reduce selenate effectively.

In this study, the fundamental and practical aspects of the selenate reduction by chromous ions as a novel method to remove selenate from waste waters was investigated mainly in sulfate media. At first, the stoichiometry of selenate reduction by chromous ions was studied. Secondly, the kinetics of selenate reduction by chromous ions was studied over the wide range of acidity, chromous concentration, temperature and ionic strength. The reaction order with respect to the concentrations of selenate, chromous ions and hydrogen ions and the general rate law equation were determined. Furthermore, the effect of sulfate ions on the selenate reduction rate at different ionic strengths was studied. Thirdly, the reaction mechanism responsible for the reduction of
selenate by chromous ions was suggested. Finally, the removal of hydrogen selenide generated from the reduction of selenate with chromous ions was studied using three reagents. Additionally, a hydrometallurgy flowsheet incorporating chromous generation, selenate reduction, hydrogen selenide removal, and chromic precipitation units was proposed.


**Lay Summary**

The release of selenium from natural and industrial activities results in the environmental contamination. Selenite and selenate (SeO$_3^{2-}$, SeO$_4^{2-}$) are the most common inorganic selenium species which are generally found in water and known to be toxic. Selenite can be easily removed from water using various methods (e.g. chemical reduction, precipitation and adsorption). However, these methods are not effective for the selenate removal. There is a need to develop more effective processes to treat selenium-bearing solutions.

In this work, chromous as a strong reducing agent was used to reduce selenate. The reduction chemistry was carefully studied in both fundamental and practical aspects. Selenate can be effectively reduced to hydrogen selenide. Selenate reduction rate is proportional to the concentrations of selenate, hydrogen ions and chromous. The produced hydrogen selenide can effectively be removed using cuprous oxide. A novel selenate removal process has been successfully developed to solve selenium environmental contamination issue.
Preface

The original idea of this project was proposed to Seabridge Gold by Professor David Dreisinger. All the experimental works were developed and conducted in house with financial support received from Seabridge Gold and Mitacs-Accelerate Graduate Research Internship Program. The overall supervision of this research was provided by Dr. Dreisinger.

Dr. Lu and Dr. Wassink extensively helped with all aspects of the research work. The experimental apparatus and some of the experimental procedures have been developed with input from Dr. Lu.

Much of the work presented in this thesis as listed below has been filed as a U.S. patent or is presented as a conference paper.


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List of Symbols and Abbreviations

Symbols
A Prefactor in Arrhenius equation
α Activity
Y Activity Coefficient
E₀ Standard reduction potential
E Reduction potential
E_a Activation energy
ΔE Potential difference
F Faraday’s constant (96485 C/mol)
g Gram
ΔG₀ Standard Gibbs free energy
ΔG_f Standard Gibbs free energy of formation
ΔG₀ Gibbs free energy
ΔH°f Standard heat of formation
I Ionic strength
k Rate constant
K Equilibrium constant
Ksp Solubility product constant
L Litre
M Molarity
µg Micro gram
mg Milligram
[M]₀ Initial concentration of M
N Normality
P Pressure
pKa Acid dissociation constant
R Ideal gas constant
s Second
t Time
T Temperature (K or °C)
V Volt
zA charge of ion A [electron charge units]

Abbreviations
CCME Canadian Council of Ministers of the Environment
ICP-OES Inductively Coupled Plasma-Optical Emission Spectrometry
SHE Standard Hydrogen Electrode
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Dedication

To my loving parents, Ayat and Riyaz

for their kindness and devotion,

And

To my brothers, Ali and Saeed and My sister, Fatima

for their endless love and support
Chapter 1: Introduction

Selenium is an essential element that plays an important role for the health of organisms like fish, birds, mammals, and human however it can also be toxic in higher dosage. One of the important characteristics of Se is the very narrow range between sufficient and toxic concentrations. For humans and livestock, the factor between optimal and toxic doses of Se is in the range of 10 to 100 times. For fish the range is as low as 7 to 10 times optimal dietary requirements for fish. (Beatty and Russo, 2014). When selenium is released to the environment from both natural and industrial activities it can lead to increased concentrations in surface water, groundwater, soils, and vegetation and it can be toxic for many forms of aquatic life. Additionally, selenium accumulation to higher concentrations in wildlife species tissues leads to toxic levels for aquatic life, birds, and mammals including humans. In the interest of protecting aquatic environments, selenium discharge into the environment is closely controlled and monitored. (Beatty and Russo, 2014; IAEA, 2007; Tinggi, 2003)

Selenium in nature is mostly associated with metal sulfide minerals such as copper, iron, zinc, and lead sulfides (Zingaro and Cooper, 1974). The treatment of these ores to extract the metals of interest has the potential for selenium release and transport into surface and groundwater systems. Other sources of selenium contamination include coal mining, fossil fuel combustion, oil refining, and discharge of seleniferous drainage water from agriculture (Zingaro and Cooper, 1974). Selenium contamination in the receiving environment is a key issue for many industries and the treatment of wastewater contaminated with selenium is a growing challenge.

Selenium speciation in solution plays an important role in its removal as well as toxicology especially at low levels. Selenite (SeO$_3^{2-}$, Se(IV)) and selenate (SeO$_4^{2-}$, Se(VI)) are the most important inorganic selenium species which are generally found in water and known to be toxic
Relative to selenate, selenite can be quite easily removed from solutions using various treatment methods such as chemical reduction (e.g., zero valent iron and sulfur dioxide), and precipitation and adsorption by ferrihydrite salt. These methods are not efficient for selenate removal due to the high solubility of selenate in the solutions, its weak adsorption on the surfaces of precipitates, and slow kinetics of selenate reduction (Murphy, 1988; Sandy and DiSante, 2010). For example, ERM Rescan (BioTEQ, 2013; SeaBridge Gold, 2013) has studied the removal of selenium from iron-bearing wastewater and found that neutralization and precipitation of iron co-precipitates and removes selenium as selenite. However, the above treatment is not successful at removing selenate from the wastewater to meet the guidelines for selenium concentration. In Canada, the Canadian Council of Ministers of the Environment (CCME) has set Water Quality Guidelines, which for selenium are 1 µg/L in fresh water. In 2014, British Colombia updated its own guideline at 2 µg/L for fresh water and marine aquatic life (Beatty and Russo, 2014; CCME, 2009).

Typically, chemically based treatment processes for selenate removal require an initial reduction of selenate to the lower oxidation states (e.g., selenite, hydrogen selenide). The redox potential for the selenate/selenite couple is quite high; therefore, thermodynamically, selenate can be easily reduced to selenite (HSeO$_4^-$ to H$_2$SeO$_3$ or SeO$_4^{2-}$ to HSeO$_3^-$) by many reducing agents or electrochemically. However, kinetically, the reaction is known to be slow (Mokmeli et al., 2013; Sandy and DiSante, 2010). Consequently, reagents that are suitable to reduce selenite to elemental selenium or selenide are thermodynamically effective for selenate reduction as well, but reaction times are unacceptably long. For instance, Weir et al. (1982) reported that selenite can be quite easily reduced to elemental selenium using copper powder (99% after 1 min in 10-50 g/L sulfuric
acid at room temperature). In contrast, selenate reduction with metallic copper was much slower and required a higher temperature around the boiling point (Weir et al., 1983; Weir et al., 1982).

Various reagents have been studied for the reduction of selenate to its lower oxidation state. For example, Koyama and Kobayashi (2000) used copper, iron, zinc and aluminum powder to reduce selenate in HCl solution at pH 2 and found that elemental iron was the most efficient reductant. Elemental iron (known as Zero Valent Iron) has a high potential for the removal of selenate (up to 100% in laboratory testing). However, the presence of certain salts like phosphate ($\text{PO}_4^{3-}$) and nitrate ($\text{NO}_3^-$) reduces the efficiency of selenate removal significantly. Mondal et al. (2004) reported that the presence of 2.5 g/L sulphate in solution reduced the selenate removal by NiFe powder from 100% to 71.5% in a standard experiment. The other disadvantages of the use of metals in the reduction of selenate is that usually a large excess of metal is required per unit of selenate in the solution which increases the costs of reagents and introduces a significant challenge in waste management of the treatment sludge. For instance, Mondal et al. (2004) studied the reduction of selenate by NiFe powder and found the maximum selenate removal of 98% (10 min at an initial selenate concentration of 100 ppm) at a NiFe powder dosage of 5 g/L. However, at a lower NiFe powder concentration (0.6 g/L), the selenate removal decreased dramatically (80% after 2 h) and there was no further significant selenate removal at a longer residence time. The reduction of selenate by sulfur dioxide has also been studied and it was found that the reaction requires an autoclave at higher temperature (above 140 °C) and a long reaction time (several hours) is needed for a complete reduction (Weir et al., 1983b; Zingaro and Cooper, 1974).

Considering the problems associated with the current technologies available for selenate removal, it is necessary to develop more effective processes to treat selenium-bearing aqueous solutions.
Chromous ion is known to be a powerful reducing agent available for use in aqueous solutions (the standard potential for Cr^{3+}/Cr^{2+}: -0.42 V vs SHE). Chromous solutions have been used in the reduction of many organic compounds, oxides, and sulphide minerals and in many novel hydrometallurgical processes (Kelsall and Yin 1999b; Pedzana, 1988; Wells and Salam, 1968; Zabin and Taube, 1964). Therefore, there is a high potential for chromous ions to effectively reduce selenate. While chromous ion as a common reducing agent has been used for several important applications, there is nearly no information on the reduction of selenate by chromous ions available in the literature. The only information reported was that the reduction of selenate by chromous ions is not fast enough for the titration of selenate in HCl solution (Lingare and Niedrache, 1948).

According to the redox potentials of Cr(III)/Cr(II) and the selenium species, chromous ions should be able to reduce selenate to hydrogen selenide. The overall reaction can be written as:

$$8\text{Cr}^{2+} + \text{SeO}_4^{2-} + 10\text{H}^+ = \text{H}_2\text{Se} + \text{H}_2\text{O} + 8\text{Cr}^{3+}$$

However, as a novel method for selenate removal, the kinetics of the reduction of selenate by chromous ions is in need of careful study. The reduction of selenate by chromous ions results in the oxidation of chromous ions to chromic ions. Chromic ions can be easily removed from the solution by precipitation with base (Rai et al., 1987). The other benefit of the chromium system is that chromous ions can be electrochemically regenerated from a solution formed by leaching of chromic precipitates and thus is recyclable.

Considering the advantages of the use of chromous ions, it can be a promising alternative reducing agent for existing processes for selenate removal from waste water. As one example of the application of the studied selenate removal process, BioteQ (2013) disclosed an application for concentration of selenium in waste water by ion exchange (IX) treatment. In this process, the loaded ion exchange resin is eluted with a concentrated sulphate solution (1 M) to produce an
eluant containing about 10 ppm Se as selenate. The effluent of this process meets all the regulatory limits for selenium. However, the eluant needs to be treated to remove selenium in order to recycle the eluant. Therefore, the focus of this work was to develop an effective method for selenium removal from solutions containing sulfate and selenate, which might be suitable for process or economic reasons. Another example of the application of the studied method has been published by ERM Rescan (SeaBridge Gold, 2013). ERM have advocated the use of an ion exchange pre-treatment step to concentrate selenate. The wastewater from the ion exchange process meets all required selenium discharge standards. However, the eluant from the ion exchange process must be treated to remove the eluted selenate (5 ppm Se).

The current investigation focuses on the chemistry of selenate removal from sulfate bearing solution via chromous ions as a reducing agent. The solutions to be treated contain ppm levels of selenium as selenate and are largely free from the other anions except sulfate. A typical example is an eluant from an ion exchange process.

1.1 Objective of Research

To our knowledge there is no application of chromous ions for selenate removal. Therefore, the overall objective of this research was to study the selenate reduction by chromous ions and evaluate the feasibility and effectiveness of the use of chromous ions for selenate removal from solutions. The present research was undertaken with the following objectives:

1. To study the stoichiometry of selenate reduction by chromous ions under different conditions. The concentrations of chromous and selenate were varied, along with pH, to understand the overall reaction and potential products.

2. To study the kinetics of selenate reduction by chromous ions over the wide range of acidity of the solution, chromous concentration, temperature, ionic strength, and sulfate
concentration. The kinetic studies are important to evaluate the feasibility of chromous solutions in the industrial application for selenate reduction and removal from solution.

3. To determine the reaction mechanism responsible for the reaction of selenate reduction by chromous ions.

4. To study the removal of hydrogen selenide from solutions generated from the reduction of selenate with chromous ions. This was performed under simulated industrial conditions using CuO, Cu₂O, and CuSO₄ to verify the technical feasibility of copper selenide precipitation.
Chapter 2: Chemistry of Selenium and Chromous Ions

2.1 Selenium Chemistry

Selenium with the symbol of Se was discovered as an element in 1817 by Swedish chemists J.J Berzelius and J. G. Gahn. Selenium with atomic weight of 78.96 g/mol, atomic number of 34, melting point of 221°C, boiling point of 685°C, and density of 4.26-4.79 g/cm$^3$ belongs to the group VIA of the periodic table with the outer electron configuration of 4s$^2$4p$^4$. (Bueker and Kofron, 1958; Habashi, 1997; Zingaro and Cooper, 1974).

2.1.1 Properties

As a metalloid, selenium has intermediate chemical and physical properties between metals (e.g. semi-conductor) and non-metals (e.g. elemental selenium is dull, without metallic shine) (Zingaro and Cooper, 1974). Having the same electrovalence configuration as sulfur, selenium shows many similarities in atomic and physicochemical properties such as atomic sizes (both covalent and ionic bounds), bond energies, ionization potentials and electronegativities to sulfur (Bueker and Kofron, 1958; Tinggi, 2003). Like sulfur, selenium has four common oxidation states -2, 0, +4 and +6, and is present in the environment in both inorganic and organic forms. The inorganic forms are elemental selenium (Se$^0$), selenite (Se(IV), SeO$_3^{2-}$), selenate (Se(VI), SeO$_4^{2-}$), and hydrogen selenide (Se(-II), H$_2$Se).

Elemental selenium can exist in several allotropic forms, which are different molecular forms of selenium with different physical and chemical properties. As an example, red selenium is the amorphous allotrope of selenium while gray selenium has a crystalline hexagonal structure. Crystalline gray selenium shows the highest thermodynamic stability. The metastable allotropes of Se can be converted into the stable hexagonal form by heating or chemical reaction (Saji and Lee, 2013; Zingaro and Cooper, 1974).
Selenium can be present in a large number of compounds. The most stable and common compounds of selenium are the selenides with the elements of group IA and IIA and transition metals. Selenides of heavy metals such as mercury, silver, copper and cadmium are highly insoluble. Also selenium forms many stable compounds with electronegative elements (e.g., O, F and Cl) (Habashi, 1997; Sobolewski, 2000; Zingaro and Cooper, 1974)

Selenium shows a high resistance to oxidation up to its highest valence Se(VI) for all its oxidation states. This is a remarkable difference between selenium and sulfur. For example, S can be easily oxidized to H$_2$SO$_4$ by HNO$_3$; however, HNO$_3$ oxidizes Se only to H$_2$SeO$_3$. (Lange, 1966; Sobolewski, 2000).

2.1.2 Occurrence

Selenium is considered a rare element. In the earth’s crust, it is widely distributed but present in small concentrations with an abundance around $5 \times 10^{-5}$ weight percent. Selenium occurs in a wide range of minerals, as well as meteorites and volcanic matter, soils, plants, and fossil fuels (e.g., coal and crude oil) (Goodman 1996; International Atomic Energy Agency 2007; Lemly 2004; Terry 1997; Zingaro and Cooper 1974a).

Because of the similarities of selenium and sulfur in crystallochemistry and ionic radius (198 pm for Se vs. 184 pm for S) (Zingaro and Cooper, 1974), selenium can substitute for sulfur in sulfur-containing minerals, and thus the association of selenium with sulfur in the sulfide crystal lattice occurs. Mineral selenides are usually found in association with sulfide minerals such as chalcopyrite (CuFeS$_2$), pyrite (FeS$_2$), sphalerite (ZnS) and galena (PbS) (Lemly, 2004; Sobolewski, 2000; Zingaro and Cooper, 1974).

Copper sulfide is considered the main commercial source for selenium since it is from this mineral that selenium is mainly recovered through the treatment of anode slimes (containing Cu$_2$-
x, Ag₂Se, and CuAgSe phases). Anode slimes are produced through electrolytic refining of copper (Goodman, 1996; Habashi, 1997; Zingaro and Cooper, 1974).

The selenium level in soils is related to the geochemical cycle of selenium and its aqueous chemistry. Important factors such as selenium content of the host rock, pH and the nature of drainage water, and also the redox potentials influence the level of selenium in soils (Habashi 1997; Lemly 2004). Selenium exists in soils mainly as selenites, selenates, elemental selenium, selenides and organic selenium species such as selenomethionine, selenocysteine and, dimethyl selenide (CCME, 2009).

Selenium also is present in fossil fuels (coal and oil) in the concentration range between approximately 1 and 5 ppm; burning of these fuels is a source of selenium present in airborne dust. Consequently, the removal of selenium in fossil fuel combustion is important because of environmental impact of selenium that is released to the atmosphere from these sources (Zingaro and Cooper, 1974).

### 2.1.3 Toxicity

Selenium is an essential element that plays an important role for the health of organisms like fish, birds, mammals, and human in prevention of diseases. (Hatfield et al., 2012; Terry, 1997; Thompson-Eagle and Jr, 1992). For instance, the intake levels of Se recommended are 40-75 μg per day for men and 40-60 μg per day for women and the dietary selenium thresholds for fish and birds is 3-9 μg/g dw (dry weight of fish/bird) (Beatty & Russo, 2014; Tinggi, 2003). However, selenium can also be very toxic in higher dosage. In fact, one of the important characteristics of Se is the very narrow range between sufficient and toxic concentrations. For humans and livestock, the factor between optimal and toxic doses of Se is in the range of 10 to 100 times. For fish the range is as low as 7 to 10 times optimal dietary requirements for fish (Beatty and Russo, 2014;
IAEA, 2007). When selenium is released to the environment it can lead to increased concentrations and can be toxic for many forms of aquatic life. For instance, to protect the aquatic environments, the water guideline of 2µg/L and the dietary guideline of 4µg/g in food items are acceptable to wildlife species. (Beatty and Russo, 2014; IAEA, 2007).

Selenium toxicity depends directly on its composition, speciation and dosage. Selenium is most commonly found in the environment as selenate, selenite, selenide, and organo-selenides (Beatty and Russo, 2014). Selenate and selenite are the most commonly found species in polluted water and soils. Both are very soluble and toxic and display bioaccumulation and bioavailability. Selenate and selenite can easily be taken up by plants. Therefore, the presence of selenates and selenites in waste water is a serious problem. If left untreated, selenium will bioaccumulate and pose a threat to all aquatic life. Additionally, microorganisms reduce selenate and selenite to more toxic species such as selenides (Beatty and Russo, 2014). Volatile compounds such as hydrogen selenide and its organo-derivatives are the most poisonous compounds (Chapman, 2000). Organic selenides are highly bioavailable and may be rapidly incorporated into sediments or taken up by organisms (Beatty and Russo, 2014). Organoselenium species form toxic compounds, which are slowly released after they enters the human body and results in bad-smelling breath and sweating.

Selenium in the body is taken up by the kidneys, spleen and liver and can cause headache, nerve damage, vomiting, irritation of mucous membranes, and inflammation of the respiratory and digestive tract in humans (Geoffroy, 2011; Tinggi, 2003). Selenium interferes with the normal cellular metabolism of fish and waterfowl causing birth defects or mutation. Selenium is also very toxic for grazing cattle and causes serious disease and disorders in animals (Beatty and Russo 2014; Lemly 2004; Nathinal Academy Press 1983).
2.1.4 Applications

There are many applications of selenium in industry because of the variety of its physical, chemical and electrical properties. The principal applications of selenium are in glass manufacturing (accounting for about 50% of consumption), pigments, rubber, metal alloys, textiles, petroleum, photocells, xerography, rectifiers and solid state devices (Moore and Mahmoudkhani, 2011; Thompson-Eagle and Frankenbrger, 1992; Zingaro and Cooper, 1974). Nowadays, the use of Se-based pesticides has been largely restricted due to their instability in soils and thus contamination of food crops, and their toxicity to mammals and bird (Sobolewski, 2000).

2.1.5 Aqueous Chemistry of Selenium

The control of selenium in wastewater requires a deep understanding of the aqueous chemistry of selenium. The aqueous chemistry of selenium is complicated since it can exist in different oxidation states as well as many inorganic and organic compounds.

Selenium demonstrates four common oxidation states of -2 (H$_2$Se, HSe$^-$), 0 (Se), +4 (H$_2$SeO$_3$, HSeO$_3^-$, SeO$_3^{2-}$), and +6 (HSeO$_4^-$, SeO$_4^{2-}$) in aqueous systems. Selenium in its +5 (Se(V)) oxidation state is an unstable short-lived state (Klaning and Sehested, 1986). Organic forms of selenium are analogous to those of sulfate and include seleno amino acids and their derivatives, methyl selenides, methyl seleninic esters, methyl selenones, and methylselenonium ions (Cooke and Bruland, 1987; IAEA, 2007).

The aqueous chemistry of selenium is highly dependent on the reduction potential (Eh) and pH of the solution involved. The dissolved oxygen content of solution in addition to the presence of other ions directly influence the Eh of the solution. Combined with the presence of total dissolved solids (TDS) and microorganisms in the solution, they affect the selenium aqueous chemistry and its speciation (Cooke and Bruland, 1987; Sobolewski, 2000).
The Pourbaix diagram of the Se-H$_2$O system at 25 °C and a selenium species activity of $10^{-4}$ M is shown in Figure 2-1.

![Pourbaix diagram](image)

Figure 2-1: Eₜ-hₚ diagram of selenium at 25°C and selenium activity of $10^{-4}$ M. (derived from HSC Chemistry 6)

In acidic solutions with pH < 4, inorganic selenium mainly exists as biselenate (HSeO$_4^-$, pKa= 1.9), selenious acid (H$_2$SeO$_3$, pKa =2.5), elemental selenium and hydrogen selenide (pKa =3.89) depending on the potential of the solution. Selenic acid is a very strong acid (H$_2$SeO$_4$ (pK$_{a1}$=-3), analogous to sulfuric acid, and is easily deprotonated to biselenate. Biselenate is the most dominant species at high electrochemical potentials and pH range of -3 to 1.9. Selenate is the deprotonated form of biselenate and dominantly exists at pH>1.9 and high electrochemical potentials regions. At moderate potentials and pH<2.5, selenium (IV) mainly is present as selenious acid which deprotonates at pH> 2.5 to a single charged oxyanion, biselenite (HSeO$_3^-$, pKa=7.3). Biselenite is deprotonated above pH 7.3 and is mainly present as the double charged...
Elemental selenium is quite stable and can exist over a wide range of pH in a reducing environment. For example, elemental selenium cannot be attacked by hydrochloric and sulfuric acid, and usually very strong oxidizing conditions (such as fluorine (F₂), ozone (O₃), peroxide (H₂O₂), chromate (CrO₄²⁻), dichromate (Cr₂O₇²⁻), permanganate (MnO₄⁻), chlorate (ClO₃⁻), and perchlorate (ClO₄²⁻)) are needed in order to oxidize it to its higher oxidation states (Geoffroy, 2011).

Finally, under very strong reducing conditions, selenium can be present as selenide. Under acidic conditions (pH 0-3.89) H₂Se, and at pH 3.89-14 HSe⁻ are the dominant aqueous species. Se²⁻ is the predominant species after pH 15.16 (pKₐ₂=15.16 (Levy and Mysers, 1990)) and therefore it is not presented in the Figure 2-1. Hydrogen selenide gas has a very high solubility (7 g/L at 25 °C) in water and by far is the most toxic selenium compound and represents a serious safety hazard.

Oxyacids of selenium and sulfur show similar acid strengths (pKa 2.5 and pKa 2.9 for species with Se(IV) and S(IV), respectively; pKa -3 for both species with Se(VI) and S(VI)). Hydrogen selenide is a stronger acid (pKa 3.89) than hydrogen sulfide (H₂S, pKa 6.9)(Maghdy, 2011; Sobolewski, 2000; Tinggi, 2003). Hydrogen selenide is highly reactive and forms metal selenides with most transition metals. Most selenium-transition metal compounds are thermodynamically more stable than elemental selenium itself and are almost insoluble (Mokmeli et al., 2013; Zingaro and Cooper, 1974). In fact, almost all selenium minerals, including the two most common (clausthalite, PbSe and crookesite, Cu₇(Tl,Ag)Se₄), are selenide based and result from the substitution of Se(-II) into metallic sulfide minerals (Škácha, Sejkora and Plasil, 2017;
Moreover, Se(-II) species (H₂Se, HSe⁻ and Se²⁻) are rapidly oxidized to elemental selenium in air.

Because the kinetics of selenium redox transformations are relatively slow, both selenite and selenate are often found in polluted water and soils, regardless of redox conditions (IAEA, 2007). They exist in a wide pH range but selenate predominates in most natural and mine waters. The reduction of selenate to selenite is often thermodynamically favored because of its high standard reduction potential, but the kinetics of the reaction is very slow because of a high activation energy (Moore and Mahmoudkhani, 2011; Sandy and DiSante, 2010; Sobolewski, 2000). In fact, due to chemical polarity, selenite with an asymmetric hydration sphere has a more reactive structure than more oxidized selenate with a symmetric structure (Eklund and Persson, 2014). As a result, selenite can be easily reduced to gray selenium and, at more negative potentials, to red selenium. In fact, the reduction of both selenious acid and selenite by many reducing agents not only is thermodynamically favorable, but also the kinetics of reaction is fast (Cooke and Bruland, 1987; Klaning and Sehested, 1986; Sobolewski, 2000). Moreover, selenite salts are less soluble than the corresponding selenate ones. For example, the solubilities of ferric selenites (e.g., Fe₂(SeO₃)₃ (Kₚ = 2.0 ± 1.7× 10⁻³¹) and Fe₂(OH)₄SeO₃ (Kₚ = 10⁻⁶¹.7)) are extremely low, which is an important factor for the removal of selenite by precipitation (Škácha et al., 2017; Sobolewski, 2000).

2.2 Selenate Removal from Waste Waters

The main source of selenium in industrial wastewaters is from hydrometallurgical processing of sulfide minerals (e.g., copper and iron sulfide) (Zingaro and Cooper, 1974). As previously indicated, the removal of selenite ions has been found to be significantly easier than selenate. For example, various treatment methods such as chemical reduction (e.g. zero valent iron...
and sulphur dioxide), precipitation and adsorption by ferrihydrite salts have been successfully applied in the industrial scale for selenite removal. However, most of these methods are not efficient for the removal of selenate to the mandatory level for selenium in discharge solutions (e.g., 5 ppb and less). This is because of high solubility of selenate in the solutions, its weak adsorption on surfaces, and slow kinetics of selenate reduction to lower oxidation states (Murphy, 1988; Sandy and DiSante, 2010).

Various treatment methods including physical (e.g., membrane filtration, IX, adsorption on the surface), chemical (e.g., chemical reduction and co-precipitation with ferric salts), and biological treatments have been industrially applied for removal of selenate.

Physical treatment technologies can be classified into four groups: reverse osmosis, nanofiltration, ion exchange and evaporation. All of these technologies have been applied in industrial water treatment for removing inorganic contaminations; however, for selenium removal, most of these methods have only been developed to laboratory scale or pilot scale. Reverse osmosis is the only method among all these methods that has been extensively used for removing selenium from drinking and ground water in industrial scale (Geoffroy, 2011; Sandy and DiSante, 2010; Smith et al., 2009).

The effectiveness of ion exchange processes in the removal of selenium is strongly affected by the presence of other oxyanions in the solution. In many mining processes, the sulfate concentration of the solution is several orders of magnitude greater than that of selenium. This results in reducing the selenium removal efficiency due to competitive adsorption by sulfate. Ion exchange and other physical treatment methods are expensive when large volumes of solutions need to be treated. Usually in these methods, a contaminated eluent is produced which requires
further selenium removal before disposal, thus the selenium removal problem still exists but in a smaller volume of more highly concentrated solution (Golder Associates, 2009).

The most common types of chemical treatment technologies for selenium removal are reduction of selenate and selenite to a lower oxidation state by the use of reducing agents, and adsorption of the reduced species on the surface and precipitation. Cementation, electrocoagulation, and photoreduction are other types of treatments for selenium removal which have not been developed beyond the laboratory scale. Among these methods, ferrihydrite precipitation with concurrent adsorption of selenite and selenate on the ferrihydrite surface was selected by the U.S. Environmental Protection Agency (USEPA) as the “Best Demonstrated Available Technology” for selenium removal in the form of selenite from industrial wastewater (Sandy and DiSante, 2010; Sobolewski, 2000). However, there are some issues in the application of precipitation and adsorption processes. By way of contrast, laboratory and pilot plant tests have shown that chemical precipitation with the use of ferrihydrite salts, lime, ferrous sulfate or ferric sulfate is substantially ineffective for removing selenate from solution. In the presence of other anions such as sulfates, phosphates and nitrates, competitive adsorption on the surface occurs and consequently interferes with the adsorption of selenate on the surface. The concentration of anions in the solution as well as their intrinsic adsorption characteristics strongly influence their adsorption on the surface. Some studies on the interference due to adsorbing oxyanions on aluminum based oxides showed the following decreasing order of the preference to adsorption: phosphate > Se (IV) >> sulfate > Se (VI) > chloride > nitrate. The adsorption of selenate is strongly dependent on the ionic strength of the solution since selenate as a weakly sorbing anion forms weak outer-sphere ionic surface complexes which can be easily replaced by competing ions in the solution (Mondal et al., 2004; D. Peak & Sparks, 2002; Derek Peak, 2006; Tan, 2018). In addition
to this, the generation of a large volume of iron sludge, the long term stability of the selenium in this sludge and relatively high cost of reagents makes this approach questionable.

Biological treatment is considered as a cost-effective treatment option to remove selenium from the solution. In the biological treatment, both selenate and selenite can be removed to below regulatory standards by reducing the oxyanions and possibly volatilizing the reaction products. The presence of elevated nitrate concentrations found in agricultural and mining waters is known to be an important issue in the biological removal of selenium. Nevertheless, the recent research suggests the need for pre-treatment of nitrate can be overcome by proper selection of microbial communities (Golder Associate Inc., 2009).

Selenium speciation is an important factor in selenium removal from solutions and the feasibility and efficiency of different removal processes is often governed by this fact. Typically, chemically-based treatment processes require an initial reduction of selenate (stable) to selenite/hydrogen selenide (reactive) using strong reductants (e.g., zinc powder). The reduction of selenate and selenite species with the subsequent precipitation of metal selenides or elemental selenium appears to hold promise as a mine water treatment option.

2.2.1 Chemical Reduction of Selenate

Selenium removal from solution by chemical reduction has been studied using many known reducing agents. According to the Eh-pH diagram of selenium, selenate has a very high reduction potential and thermodynamically it can be reduced to a lower oxidation state by many reagents. However, the kinetics of the reduction of selenate is typically very slow. Therefore, most reagents found suitable to reduce selenite ions are theoretically effective on selenate but the reaction time is usually unacceptably long.

A possible reduction sequence of selenium species is given as follows (Bard et al., 1985):
\[
\begin{align*}
HSeO_4^- + 3H^+ + 2e &= H_2SeO_3 + H_2O & E^0 &= 1.094 \text{ V} \\
SeO_4^{2-} + 4H^+ + 2e &= H_2SeO_3 + H_2O & E^0 &= 1.151 \text{ V} \\
SeO_4^{2-} + 3H^+ + 2e &= HSeO_3^- + H_2O & E^0 &= 1.074 \text{ V} \\
H_2SeO_3 + 4H^+ + 4e &= Se + 3H_2O & E^0 &= 0.739 \text{ V} \\
HSeO_3^- + 5H^+ + 4e &= Se + 3H_2O & E^0 &= 0.777 \text{ V} \\
Se + 2H^+ + 2e &= H_2Se(aq) & E^0 &= -0.115 \text{ V}
\end{align*}
\]

Thermodynamically, any compound that has a reduction potential lower than that of any of the Se(VI)/Se(IV) or Se(IV)/Se couples can reduce selenate/selenite to elemental selenium. Application of a reduction potential below that of the Se/Se(-II) couple will allow reduction to selenide. In the application of metals as reducing agents for selenate reduction, the adsorption of selenate on the surface of the metals occurs and then selenite is reduced by the electrons which are donated from the metal (Mondal et al., 2004). Many metals, including Al, Cu, Ni, Fe, and Zn, and SO₂ gas have been tested for selenite and selenate reduction (Koyama et al., 2000; Sandy and DiSante, 2010; Twidwell and Mccloskey, 1999; Zhang et al., 2005). For instance, Koyama et al. (2000) studied the reduction of selenate by copper, iron, zinc and aluminum powder in HCl medium at pH 2. It was found that iron is the most effective reducing agent among these metals with selenate removal efficiency of 98.5%. Copper was the least effective one and the removal efficiency was only 2.5%.

In a related investigation, Mondal et al. (2004) studied the effectiveness of transition metals (Ni, Fe, Co and Cu) and nanoparticles of bimetallic NiFe on the reduction of selenate. With the use of NiFe nanoparticles, the selenate removal was 56% greater than that of Fe powder alone. The maximum selenate removal of 98% (10 min at an initial selenate concentration of 100 ppm, pH 7.7 and 25°C) was obtained at a NiFe solid dosage of 5 g/L. However, at a lower dosage of
NiFe nanoparticles (0.67 g/L; this represents a 4.5:1 molar ratio of NiFe to Se(VI) present for reaction, which is still 150% greater than the required stoichiometric ratio of 3:1), the selenate removal decreased dramatically (80% after 2 h) and no further significant reduction of selenate was observed at a longer residence time. In a low selenate concentration range, the reaction order with respect to selenate concentration is one for both Fe and Fe-Ni powders in neutral solution. However, the reaction order with respect to selenate concentration became zero at an initial concentration of selenate greater than 50 mg/L. Mondal et al. (2004) also found that the presence of 2.5 g/L sulphate reduced the selenate removal efficiency with the use of both powders by 30-50%. The competition for active metal sites by sulfate was indicated as the primary factor in the decrease in the selenium removal. To reduce the effect of competitive adsorption, significantly higher solids loading (active surface sites) must be used. However, this involves a larger amount of solids and is cost prohibitive.

Among all metals studied for selenate removal, elemental iron (or know as Zero Valen Iron) was used in the industrial scale to remove dissolved selenium from waste waters. It is economical and the reaction products are not environmentally harmful (Associate, 2009; Sandy and DiSante, 2010). Metallic iron added in the waste waters can act as both a catalyst and electron donor for the reduction of selenate (Frankenberger et al., 2004). Iron is oxidized to soluble Fe\(^{2+}\) and Fe\(^{3+}\) which subsequently reacts with OH\(^-\) forming a complex ferrous ferrihydroxide precipitate which is known as green rust. Green rust is generally formed as a function of pH, equilibrium concentrations of ferrous and ferric iron and the concentration of anions present in the solution. The green rust serves as a reducing agent to directly reduce selenate to selenite and selenite to elemental selenium. Additionally, green rust can adsorb selenite and selenate from solution. In a study by Refait et al. it was shown that selenate and selenite ions become a part of the rust’s
complex crystallographic structure (Refait et al., 2000). The efficiency of green rust in the removal of selenium can vary significantly depending on the oxidation state of the selenium as well as the presence of certain additional salts. Metallic iron will react with oxygenated compounds such as nitrate, perchlorate, carbonate, sulfate, phosphates and also oxygen if it is present in the solution. Consequently, these reactions consume metallic iron and more iron is required (Hansen et al., 1996; Koyama et al., 2000; Sobolewski, 2000; Zhang et al., 2005). The passivation of metallic iron may also occur, increasing the metallic iron usage. The passivation can be prohibited by applying a nitrogen atmosphere and pH control (NAMC White Paper Report Addendum, 2013; Sandy and DiSante, 2010).

In a laboratory scale study, the use of iron nanoparticles has shown promising results in the removal of selenate. The utilization of these nanoparticles can remarkably increase the surface area and consequently the rate of the reduction. With the use of iron nanoparticles, selenate ions are reduced to selenide and in the presence of iron, the product of iron selenide was obtained at pH 7. The reduction of selenate was fast and over 85% of selenate was removed in two hours (Olegario et al., 2010).

The use of copper has been patented in 1976 in Canada and it has been used at many sites globally to remove selenium from selenite/selenate containing solution in copper electrowinning processes (Rotrou et al., 1976). However, highly acidic solutions, elevated temperature (50 to 100 °C), and long reaction time are disadvantages of this process. Ladriere (1973) found that in a cupric sulfate solution, selenate is reduced by Cu⁺ (Cu + Cu²⁺ = 2Cu⁺) rather than directly by Cu. The rate equation is a second order rate law, first order in the concentrations of both Cu⁺ and Se(VI) with an activation energy of about 100 kJ/mol.
Mokmeli et al. (2013) studied the chemistry and kinetics of the reduction of selenate from copper sulfate-sulfuric acid solutions by cuprous ions and found that selenate is first reduced to selenite by cuprous ions and then further reduced to selenide. The rate-limiting step is the reduction of selenate to selenite and the mechanism is based on an initial one-electron transfer to form intermediate Se(V). The approximate reaction order with respect to the concentrations of Cu(I), Se(VI) and hydrogen ions were 2, 1 and 0.9 respectively. The activation energy was 86.0 kJ/mol. The relatively slow reaction kinetics for reduction of selenate and high air sensitivity of cuprous ions are the disadvantages of using cuprous.

Other reducing agents such as SO\textsubscript{2} can also be used to remove selenium from solutions (Mokmeli et al., 2013; Weir et al., 1982). With the addition of SO\textsubscript{2} at pH 5-6 and atmospheric pressure, selenite can be easily reduced to elemental selenium. However, selenate is not reduced under this condition and to achieve adequate selenate removal, the reaction requires a higher temperature (above 140 °C), an autoclave and a long reaction time (several hours) (Weir et al., 1983b; Zingaro and Cooper, 1974).

Another possible way to accelerate the rate of selenate reduction by common reagents is to use catalysts. As an example, a relatively effective selenate removal using SO\textsubscript{2} gas can be achieved in the presence of sufficient amounts of catalysts such as halide, thiourea or a mixture of chloride and ferrous ion (Weir et al., 1983b; Zingaro and Cooper, 1974). However, industrial applicability of these catalysts is nevertheless limited by high costs and handling problems. Thiourea (TU) can reduce selenate without the use of sulfur dioxide; however, a large amount of thiourea is required (Hollander and Lebedeff, 1958; Zingaro and Cooper, 1974). McGrew has studied selenate removal using iron powder as a reductant and found that the rate of selenate reduction by iron to selenium is
catalyzed by the presence of copper. However, as previously mentioned, the reduction by the use of solid metals involves a large amount of metals and is cost prohibitive.

2.3 Aqueous Chemistry of Chromium

In aqueous solutions, chromium mainly exists in three different oxidation states of +2, +3, and +6. In addition, compounds containing chromium in the -2, -1, 0, +4 and +5 oxidation states have been also reported (Dellien et al., 1976). Cr(III) and Cr(VI) are the most common oxidation states of chromium. Cr(III), is relatively nontoxic and less soluble whereas Cr(VI) is more toxic and soluble. Cr(VI) is also known to be carcinogenic by inhalation. (Avudainayagam et al., 2003; Shupack, 1991).

Thermodynamically, the (III) oxidation state is the most stable oxidation state of chromium in water and considerable energy is required to convert it to lower or higher states (Kotaś and Stasicka, 2000). Chromium (III) ion is relatively unreactive compared to most other metal ions. This can be attributed to its slow ligand displacement rate (hours to days at room temperature) (Avudainayagam et al., 2003). Chromium(III) appears in many compounds such as oxides, halides, sulfates, and nitrates. It is considered a hard Lewis acid which exhibits a strong tendency to form complexes with a variety of ligands (e.g., hydroxyl, sulfate, oxalate, ammonia, urea, tartrate and EDTA) (Balcerzak, 2000). The substitution reactions of many Cr(III) complexes are very slow, which results in the persistence of Cr(III) species for an extended time even where the conditions are not thermodynamically favorable (Kelsall et al., 1988b; Shupack, 1991).

The negative standard potential (E° = -0.42 V vs. SHE) of the Cr³⁺/Cr²⁺ couple indicates that Cr(II) is readily oxidized to Cr(III) and Cr(II) species are stable only in the absence of any oxidant (anaerobic conditions) (Kotaś and Stasicka, 2000; Weckhuysen et al., 1996).
Thermodynamically, aqueous Cr(II) is also not stable in the presence of H\(^+\) (low pH) as it could be oxidized by H\(^+\) to Cr(III) through the following reaction:

\[
2\text{Cr}^{2+} + 2\text{H}^+ = 2\text{Cr}^{3+} + \text{H}_2 (g) \quad \Delta G^\circ = -81.0 \text{ kJ/mol}
\]

However, it has been proved that the oxidation of Cr(II) by H\(^+\) is extremely slow and kinetically inhibited (Stone and Forstner, 1957). For instance, the long term (~600 hours) stability of Cr(II) ions in chloride solution has been investigated and it is reported that the reaction is kinetically very slow (Jalan et al., 1981).

The Eh-pH diagram for Cr-H\(_2\)O system is given in Figure 2-2. Although Cr\(_2\)O\(_3\) is more stable than Cr(OH)\(_3\), Cr(III) is precipitated as Cr(OH)\(_3\) in aqueous solution at room temperature and the equilibrium is established between Cr(OH)\(_3\) and the other chromium species. Therefore, Cr(OH)\(_3\) instead of Cr\(_2\)O\(_3\) has been considered in drawing the Eh-pH diagram. With increasing pH, the Cr(III) species shifts from Cr\(^{3+}\) to Cr(OH)\(^{2+}\), starts to precipitate as Cr(OH)\(_3\) around pH 5.4 and finally re-dissolves as Cr(OH)\(_4\)\(^-\) around pH 13. This is also shown in the experimental results given by Rai et al. (1987). Cr(OH)\(_2^+\) and Cu(OH)\(_3\)(aq) also exist as minor species. Cr(III) is present as an octahedral hexaquo ion Cr(H\(_2\)O)\(_6\)\(^{3+}\), in acidic solution.
The aqueous chemistry of Cr(II) has not been extensively studied because of its thermodynamic instability in the presence of oxygen. In the literature, it is indicated that chromous ions are present in water as octahedral hexaquo ions, $\text{Cr(H}_2\text{O)}^6{}^{2+}$ (Weckhuysen et al., 1996).

### 2.4 Application of Chromous as a Reductant

Chromous ion or divalent chromium is known to be a powerful reducing agents which is of interest in the area of fundamental chemistry and industry (Pedzana, 1988; Stone and Forstner, 1956). Because of its strong reducing power, aqueous chromous ions have been used as a reducing agent in the reduction of many organic compounds (Wells and Salam, 1968; Westheadt and Gray, 1972), oxides (Zabin, 1964), and sulphide minerals (Stone and Forstner, 1957), and in many proposed novel hydrometallurgical processes (Kelsall and Yin, 1999a).

Figure 2-2: Eh-pH diagrams for Cr-H$_2$O system at 298 K, with a dissolved Cr activity of 0.01 M. The data for Cr(OH)$_2^{2+}$, Cr(OH)$_2^{+}$ and Cr(OH)$_3^{(aq)}$ are from Berverskog and Puigdomenech (1997) while the other data are from Bard et al. (1984).
Zabin and Taube (1964) studied the reaction of chromous ions with many different metal oxides such as Pb$_3$O$_4$, V$_2$O$_5$, SnO$_2$, TiO$_2$, CrO$_2$ and Co$_3$O$_4$ in acidic solution (0.1 to 1M H$^+$, 0.02 to 0.08 M Cr(II) and 25 °C). They found that the reaction rates of all the oxides (especially less reactive oxide such as Fe$_2$O$_3$) can be accelerated in the presence of chloride and sulfate ions. The proposed mechanism is that the association of chloride ion with Cr(II) lowers the overall positive charge of Cr(II) and therefore reduces the activation energy necessary for the transfer of Cr(II) to the surface layer (Zabin and Taube, 1964).

Chromous ions have also been used to reduce PbS particles to elemental lead. It is reported that the complete reduction of 100 μm PbS particles with 0.8 M Cr$^{2+}$ takes less than 15 minutes under a nitrogen atmosphere (Kelsall and Yin, 1999a).

Cr(III) species are substitution inert (i.e. ligand exchange is very slow) and can provide evidence of bridging group involvement in homogeneous electron transfer reactions. Because of this, the Cr(III)/Cr(II) couple has been used widely in mechanistic studies of inorganic reactions. In addition, chromous ions have been also used in secondary batteries for energy generation (Kelsall and Yin, 1999a).

Stone and Forstner (1957) employed a chromous solution to study the reduction of sulfate to sulfide in acidic solution under the condition of 1.25 M Cr(II), 3.5 M SO$_4^{2-}$, 8 M H$^+$ and 50 °C. However, they found that the reaction suffers from slow reaction kinetics. To accelerate the reduction process, catalyzing the reaction with certain halides and phosphates, as well as increasing the sulfate, chromous and hydrogen ions concentrations and temperature was suggested. They suggested that the sulfate reduction by chromous ions occurs according to the overall reaction of:

$$8\text{Cr}^{2+} + \text{SO}_4^{2-} + 10\text{H}^+ = 8\text{Cr}^{3+} + \text{H}_2\text{S} + 4\text{H}_2\text{O}$$
They also found that the sulfate reduction rate by chromous ions is directly proportional to the concentration of sulfate, while the reduction rate is one half order with respect to the chromous and proton concentrations.

Wells and Salam (1968) studied the kinetics of reaction of chromous ions with some neutral molecules in sulfate media and found that chromous ions form a complex of CrSO$_4$ first and then takes part as a chromous sulfate in the reduction mechanism. They also pointed out that the reaction of the CrSO$_4$ complex with substrates is much faster than chromous ions. The rate equation suggested was a second order rate law, first order with respect to the concentrations of both Cr(II) and substrate. They also showed that the reaction rate is independent of ionic strength (ionic strength between 2.5×10$^{-6}$ to 1 M) of the solution in which this phenomenon was attributed to the existence of a neutral compound in the reaction.

Okamoto et al. studied the reduction kinetics of tropylium ions by chromous ions in 10% HCl. At the first step the chloride ion, which is loosely bound to Cr(II), would act as a weakly interacting electron transfer bridge (Okamoto et al., 1972).

Chromous ions have been studied and used as a reducing titrant for the determination of many metal ions such as Cu(II), mercury (II), iron(III), silver(I) and gold(III) (Malik and Abubacker, 1960; Pecsok, 1945). Lingate and Niedrach (1948) studied the titrimetric reduction of selenate and selenite by 0.1 M chromous sulfate solution and found that selenite was easily reduced by chromous ions to the elemental state in solutions acidified with both hydrochloric and sulfuric acid according to the reaction:

$$H_2SeO_3 + 4Cr^{2+} + 4H^+ = Se + 4Cr^{3+}$$

They observed that in the first two to three minutes, the steady potential in the titration curves was reached for selenite at room temperature and more rapidly at higher temperature. The titration in
sulfuric acid solution was not as satisfactory as in hydrochloric acid because of the slow reaction kinetics in sulfuric acid solution. The titration of selenate is reported to be more difficult than that of selenite because of the slow kinetics of reaction.

2.5 Chromous Generation

Chromous ions can be generated through chemical reduction of chromic or chromate ions using zinc powder and zinc amalgam under an inert atmosphere (Pecsok, 1945; Westheadt and Gray, 1972). However, the generation of chromous through these methods could introduce impurities into the generated chromous solution.

Electrochemical synthesis of chromous ions through the reduction of chromic ions in an electrochemical cell is a proven alternative method that does not require chromous solution to contact with any reagents, thus making it easier to control. Production of chromous ions through electro-reduction of chromic ions has been widely studied in different supporting electrolytes and utilizing different electrodes (Kelsall et al., 1988b; Kotaś and Stasicka, 2000). The standard potential for the Cr(III)/Cr(II) redox couple is approximately $-0.424 \text{ V vs. SHE}$ (Bard et al., 1985).

The kinetics and mechanism of the electron transfer for the Cr(III)/Cr(II) redox system depends strongly on the nature of the Cr(III) species and on the supporting electrolyte. Depending on the nature of the anions present in the electrolyte and the electrode materials, $\text{Cr}^{3+}/\text{Cr}^{2+}$ can undergo one-electron outer-sphere or inner-sphere transfer (Kelsall et al., 1988b; Yin et al., 2000).

In the outer-sphere reactions, the coordinated ligand of the reactant does not penetrate into the layer of solvent molecules, which are attached to the electrode surface, and therefore, electron transfer takes place with the reactant center located at the outer Helmholtz plan (OHP). In contrast with outer-sphere, in the inner-sphere mechanism, one or more of the ligands in the reactant's
primary coordination sphere penetrates the Helmholtz plane and is adsorbed on the electrode surface of the electrode (Tanimoto and Ichimura, 2013).

Many studies have been done to determine whether different chromium(III) complexes are reduced at the electrode by an inner-sphere or an outer-sphere mechanism. For example, Kelsall et al. (1998b) studied the reduction of Cr$^{3+}$ to Cr$^{2+}$ in chloride and sulfate media. They showed that the reduction of Cr$^{3+}$ starts at about -0.6 V vs. SCE and the current peak appears at -0.8 V vs. SCE, indicating that the reaction is irreversible. In comparison with Cr$^{3+}$/Cr$^{2+}$, the reduction of CrCl$^{2+}$/Cr$^{2+}$ or CrCl$_2^+$/Cr$^{2+}$ occurs at a less negative potential indicating that chloride complexation facilitates the electron transfer (Kelsall et al., 1988b; Kelsall and Yin, 1999a).

Although the complexation of chloride ions with Cr(III) ions occurs very slowly, the presence of chloride ions greatly enhances the kinetics of Cr$^{3+}$/Cr$^{2+}$ oxidation-reduction and also decreases the irreversibility of the Cr$^{3+}$/Cr$^{2+}$ reduction reaction. Depending of the type of electrode, the chloride ions are able to diffuse through the outer Helmholtz plane and attach to the electrode surface. As previously mentioned, these types of electrode reactions proceed via an inner-sphere chloride-bridged pathway which has the effect of providing a more efficient reaction pathway for reduction of Cr$^{3+}$ (Johnson and Reid, 1982; Kelsall et al., 1988b; Yin et al., 2000). In general, the rate of reactions which proceed as inner sphere reactions are significantly greater than those for outer sphere reactions (Weaver and Anson, 1976).

Weaver and Anson (1976) investigated the behavior of different chromium (III) complexes and found that, generally, the reduction of chromium complexed with H$_2$O, F$^-$ and SO$_4^{2-}$ follows the outer-sphere mechanism, while reduction with Cl$^-$, Br$^-$, NCS$^-$, N$_3^-$ and NO$_3^-$ complexation more likely exhibits the inner-sphere behavior.
Bae et al. (2002) investigated the effect of EDTA on the electrode kinetics of the Cr$^{3+}$/Cr$^{2+}$ couple using a graphite rod electrode. The kinetics of the reaction is noticeably enhanced by complexation with EDTA in the pH range of 4-7. The observed enhancement of reductions has been related to the inner sphere mechanism involved in the electron transfer.

Increasing the temperature is also another factor that could increase the reduction rate of the Cr$^{3+}$/Cr$^{2+}$ couple. Kelsall et al. (1988b) showed that increasing the electrolyte temperature from 298 K to 333 K increased the reversibility of the Cr$^{3+}$/Cr$^{2+}$ couple and also the peak current by about 45%. This phenomenon is caused by the acceleration of the transport process inside the Nernst diffusion layers as well as the charge transfer rate by increasing the temperature (Johnson and Reid, 1982; Kelsall et al., 1988a; Yin et al., 2000).

In addition to the electrolyte composition and temperature, the type of electrode is also an important factor as it has a substantial influence on the efficiency and kinetics of Cr$^{3+}$/Cr$^{2+}$ redox reaction. The chemical resistance, electrocatalytic activity and specific surface area of the electrode material are important factors which need to be considered in order to improve the efficiencies in a redox cell. Since the rate of reduction of Cr$^{3+}$ is slow on most surfaces, most of the electrodes need to be catalyzed (Johnson and Reid, 1982; Yin et al., 2000).

Since the standard reduction potential of Cr$^{3+}$/Cr$^{2+}$ couple (Eq. (2-1)) is 0.42 V lower than that of hydrogen evolution reaction in acidic solution (Eq. 2-2), thermodynamically hydrogen ions are much easier to be reduced than chromium(III) ions:

\[
\text{Cr}^{3+} + e = \text{Cr}^{2+} \quad E_0 = -0.42 \text{ V vs SHE} \quad (2-1)
\]
\[
2\text{H}^+ + 2e = \text{H}_2 \quad E_0 = 0 \text{ V vs SHE} \quad (2-2)
\]

Therefore, the evolution of H$_2$ gas on the cathode electrode decreases the coulombic efficiency and potentially introduces problems during the Cr(III) reduction. To prevent the evolution of
hydrogen on the cathode electrode, the employed cathode in the electrochemical cell must have a small exchange current and a high overvoltage for hydrogen generation.

Different electrodes such as hanging mercury drop, lead, gold, silver, titanium, and different types of carbon have been studied for electrochemical reduction of Cr(III) ions in the past few decades (Kelsall et al., 1988b; Yin et al., 2000; Zielinskaignaciuk and Galus, 1974). Among these electrodes, carbonaceous electrodes (graphite and carbon) are usually used in practical redox cells because they are economical and relatively durable in acidic electrolytes. Carbon electrodes have an adequate electrical conductivity and a large surface area because of high porosity. These materials have a fairly high hydrogen overpotential and therefore can act as a very promising cathode material for electrochemical reduction of chromium(III) ions in acidic aqueous solutions (Aldaz, 1991; Hong, 2015).

Yin et al. (2000) studied the electrochemical synthesis of Cr$^{2+}$ by reduction of Cr$^{3+}$ on vitreous carbon rotating disc and graphite felt electrodes and found that the electrochemical reduction of Cr$^{3+}$ on carbon electrodes is controlled mainly by charge transfer rather than mass transport.

### 2.6 Summary

Selenium is released to the environment from both natural and industrial activities, leading to the increased selenium concentrations in surface water, ground water, soils, and vegetation and hence causing environmental problems. Selenium speciation in solution plays an important role in its removal. Selenite (SeO$_3^{2-}$, Se$^{4+}$) and selenate (SeO$_4^{2-}$, Se$^{6+}$) are the most important inorganic selenium species which are generally found in water and known to be toxic. There are many methods such as chemical reduction, precipitation and adsorption to remove selenium from waste water. However, most of these methods are not efficient for selenate removal. Typically, in
chemically-based treatment processes, the pre-reduction of solution to convert selenate to lower oxidation states (e.g., selenite, H₂Se) is required in order to efficiently remove selenate from solution. The current successful methods for the selenate removal are the use of metallic iron or nickel-iron powder to reduce selenate. However, these methods are not very efficient in the presence of some certain salts like phosphate, sulphate, or nitrate. The other disadvantages of the use of metals in the reduction of selenate is that usually a large excess of metal is required per unit of selenate in the solution.

Chromous ions as a powerful reducing agent are used for the reduction of organic compounds, oxides and sulfide minerals. According to redox potentials of Cr³⁺/Cr²⁺ and the selenium species, selenate can be readily reduced to elemental selenium and hydrogen selenide by the use of chromous ions. The overall reaction can be written as:

$$8\text{Cr}^2+ + \text{SeO}_4^{2-} + 10\text{H}^+ = \text{H}_2\text{Se} + \text{H}_2\text{O} + 8\text{Cr}^3+$$

Chromous ions can be generated through the reduction of chromic ions in an electrochemical cell. The reduction of selenate by chromous ions resulted in the formation of chromic ions which can be removed from solution by precipitation as chromic hydroxide at pH 5-6. Chromic hydroxide is re-dissolved using sulfuric acid and chromous ions are regenerated electrochemically. There is very little information for the reduction of selenate by chromous ions available in the literature. The careful study of the chemistry and kinetics of reduction of selenate has to be conducted to verify the feasibility of the industrial application for the selenate removal from wastewater by the reduction of selenate by chromous ions.
Chapter 3: Experimental

In order to achieve the proposed objectives listed in Chapter 1, this work includes a comprehensive set of experiments to study (1) chromous generation using an electrochemical cell, (2) stoichiometry of the chromous reaction with selenate, (3) kinetics of selenate reduction with chromous, and (4) removal of hydrogen selenide from the solution using different reagents.

3.1 Materials

All chemicals used for the experiments were reagent grade or higher grade without any further purification.

In the chromous generation experiments, potassium chromium(III) sulfate dodecahydrate (KCr(SO$_4$)$_2$·12H$_2$O) from Alfa Aesar and 98% sulfuric acid from BDH were used to prepare catholyte and anolyte solutions. A Nafion N324 cation membrane from DuPont was used to separate catholyte and anolyte. A 6 mm thick graphite felt from CeraMaterials, USA was used as a cathode.

Sodium selenate (Na$_2$SeO$_4$, 99%) from Sigma-Aldrich, sodium sulfate (Na$_2$SO$_4$) from Fisher Scientific, perchloric acid (HClO$_4$, 61.2%) from Fisher Scientific, sodium perchlorate (NaClO$_4$·H$_2$O, HPLC grade) from Fisher Scientific and sodium hydroxide, all from Fisher Scientific, were used to prepare solutions for the kinetics studies.

Cupric oxide powder (CuO, 350 mesh) from Sigma Aldrich, cuprous oxide (Cu$_2$O, 75μm or less) from Alfa Aesar and copper sulfate from Fisher Scientific were used for the hydrogen selenide removal experiments.
NH₄Fe(SO₄)₂·12H₂O from Sigma-Aldrich was used to prepare ferric solution to oxidize chromous and hydrogen selenide to chromic and selenium, respectively. Standard cerium (IV) sulfate (0.1N) solution from Alfa Aesar was used to titrate ferrous ion from this reaction as an indirect indication of the content of chromous or hydrogen selenide reacted.

Ultra-high-purity argon 99.999% Ar (<3 ppm O₂) was used to purge the reactors and solutions to remove oxygen that would be expected to react with chromous and impact the reaction chemistry and kinetics.

3.2 Generation of Chromous Ions

The electrochemical generation of chromous ions was conducted to produce chromous solution for the selenate reduction experiments. The current efficiency and the power consumption of reduction of chromic to chromous as a function of time was calculated.

3.2.1 Electrochemical Cell

Chromous solution was generated by the electrochemical reduction of chromic solution in a divided electrochemical cell consisting of two anode compartments and one cathode compartment as shown in Figure 3-1. The schematic of the electrochemical cell is shown in Figure 3-2.
Figure 3-1: The electrochemical cell used for chromous generation

Figure 3-2: Schematic of the experimental setup for generation of chromous solution.  
1) Anode compartment, 2) Cathode compartment, 3) Cation exchange membrane, 4) Anode, 5) Cathode, 6) Argon sparging inlet, 7) Circulation tube, 8) Sampling port
The electrochemical cell consisted of four blocks and was constructed entirely of chlorinated polyvinyl chloride sheets. The anode and cathode chambers had a capacity of 500 ml (each anode) and 1L, respectively. The cathode compartment was equipped with three ports that were used for purging with argon gas, circulating the catholyte in the cathode compartment and collecting the generated chromous solution into a storage container. The circulation of chromous solution through the cathode was performed using a Masterflex pump at a rate of 100 mL/min to enhance the mass transfer. The superficial surface area of each of the anodes and the cathode were 114 cm².

Two titanium mesh frames (as shown in appendix A) were used to support and compress the graphite felt between the two cathode compartments and to conduct electricity to the graphite felt. The perforated area (184 mm x 60 mm) of the titanium frames have rectangular openings (26.6 x 4.8mm) which occupy 72% of the total cathode effective area. The titanium surface was painted using R-554T phenolic coating from Hersite Protective Coating except for the electrical contact area with the graphite felt. This was used to reduce the rate of formation of hydrogen on the titanium surface. No corrosion was observed on the titanium mesh after performing all chromous generation tests (approximately 80 hours of running the cell to generate enough chromous solution for this research).

A Nafion N324 cation membrane (DuPont Inc.) was used to separate the catholyte and anolyte. Two lead-silver alloy electrodes (1% Ag) from Teck were used as anodes while a 6-mm thick graphite felt electrode (CeraMaterials, USA) was used as a cathode. The graphite felt cathode was first washed using deionized water to remove any dust and then dried in the oven at 110°C for 24 hours to activate the graphite surface (Hong, 2015; Sun and Skyllas-Kazacos, 1992).
3.2.2 Experimental Procedure

The anolyte was prepared as a 0.1 M sulfuric acid solution using concentrated sulfuric acid solution and DI water. The catholyte contained 0.1M chromium (III) and 0.1 M sulfuric acid solution and was prepared using KCr(SO₄)₂·12H₂O and sulfuric acid. In this work, the focus was generation of chromous ions in a sulfate medium to maintain the compatibility with sulfate based selenium waste water. Therefore, the electrolyte for the reduction of chromium (III) was sulfate solution.

Each anode compartment was filled with the prepared anolyte solution using a volumetric cylinder. The catholyte was transferred into the cathode compartment using a peristaltic pump. The cell and catholyte were purged with ultra-pure argon gas for at least half an hour to remove oxygen from the solution and headspace of the cell before starting the experiment. A slow flow of argon gas was maintained across the headspace of the cell during the experiment to minimize oxygen ingress.

A DC power supply from GW Instek was used to apply a current density of nominally 200 A/m² (based on the overall superficial area) to the graphite felt. A logging multimeter and a standard resistor (5A, 100mV) were used to ensure that the currents flowing through the two anodes were the same. The electrolysis time was sufficiently long to ensure that almost all Cr(III) was converted to Cr(II). The generated chromous solution with the concentration of 0.1 M Cr(II) and 0.15 M of H₂SO₄ was then transferred into a glass container using a peristaltic pump under an argon gas atmosphere. The chromous solution was stored in a glass container under argon atmosphere to ensure no oxidation of chromous ions occurred by air ingress. The analysis of this solution after one month of storage showed that the chromous concentration did not change.
In the experiment for calculating the current efficiency and the power consumption of the cell, samples were taken periodically to monitor the concentration of generated chromous ions using the titration method as explained in the following section.

### 3.2.3 Chemical Analysis of Chromous Ions

The concentration of generated chromous solution was measured by a potentiometric titration method using Radiometer ABU 80 automatic burette. A known mass of chromous solution was mixed with a known mass of 0.15 M ferric solution under an argon atmosphere. The ferric solution was made by dissolving (NH₄)Fe(SO₄)₂·12H₂O salt into 2 M sulfuric acid solution and then purging with argon gas for 30 minutes to remove oxygen before introducing the chromous solution into it. Mixing with ferric solution, Cr(II) was converted to Cr(III) while Fe(II) was reduced to Fe(II), as shown in Eq. (3-1). The concentration of ferrous ions was determined by titration with Ce(IV) as shown in Eq. (3-2).

\[
\text{Fe}^{3+} + \text{Cr}^{2+} \rightleftharpoons \text{Cr}^{3+} + \text{Fe}^{2+} \quad (3-1)
\]

\[
\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Ce}^{3+} + \text{Fe}^{3+} \quad (3-2)
\]

The endpoint was indicated by a sharp jump in the potential of the solution around 500 mV. The end point was also double checked with the addition of one drop of ferroin (5×10⁻⁶ M) as indicator into the solution. Blank titration was used to correct for indicator error.

### 3.3 Stoichiometry Study of Selenate Reduction by Chromous Ions

The stoichiometry of the selenate reduction reaction by chromous ions was investigated at different initial concentrations of chromous ions and selenate and different pH of the solution. All the
experiments were performed at room temperature. The initial chromous concentration in all tests was 0.05M and the molar ratio of chromous ions to selenate was adjusted by varying the initial concentration of selenate ions.

3.3.1 Experimental Set-up and Procedure

To perform each stoichiometry experiment, a 60 mL syringe with its top sealed with a septum was used as a reactor. The schematic illustration of the set-up is shown in Figure 3-3. The sealed syringe was chosen as a reactor to ensure that there was no free headspace in the reactor to allow hydrogen selenide gas to escape from the solution into the headspace. A magnetic stirring bar was placed in the syringe to agitate the solution. Prior to starting the experiments, the syringe reactor was flushed with argon gas to remove the air and then placed in a glass cylinder. Both the top and bottom of the glass cylinder were sealed with threaded plastic caps and a slow flow of argon was maintained across the cylinder during the experiment. Argon gas was passed through the glass cylinder to prevent possible diffusion of oxygen into the syringe and subsequently to prevent the possible oxidation of chromous ions and hydrogen selenide by oxygen.
Figure 3-4 shows the actual experimental set-up.

Selenate solutions were prepared by dissolving a known amount of Na$_2$SeO$_4$ in deionized water at the desired concentrations and then purging with ultra-high purity argon gas for 30 minutes to remove oxygen from the solution.
To conduct a selenate reduction experiment, a syringe reactor was first flushed with ultra-high purity argon gas and then filled with a known mass of chromous solution through the septum. A known amount of selenate solution was then quickly injected into the syringe reactor through the septum and the solution was rapidly mixed with the chromous solution using a magnetic stirring bar. The solutions were added on a mass basis using a sealed syringe to minimize the oxidation of the chromous ions in contact with air. The densities of all the solutions were measured before and after purging argon gas to calculate the accurate volumes of the transferred solutions. The tests were conducted for variable times with intermediate sampling. Samples were taken through the septum using a syringe equipped with a needle. The syringe and needle were flushed with argon gas prior to the sampling to remove oxygen.

To investigate the potential reaction products at a Cr(II)/Se(VI) molar ratios of less than 8 (i.e., there is not enough Cr(II) present in the solution to completely reduce selenate to hydrogen selenide) and the effect of pH on the formation of different products, a substantial number of experiments were conducted at different pH and various initial molar ratios of Cr(II)/Se(VI).

3.3.2 Chemical Analysis of Samples

A series of samples were taken for analysis of Cr(II), H₂Se and Se(VI) during the tests. For the experiments with an initial molar ratio of Cr(II)/Se(VI) over 8 (i.e., an excess of Cr(II) present), after collection of the samples half of each sample was immediately mixed with a known mass of 0.15 M ferric sulfate and 2 M sulfuric acid solution to convert both Cr(II) and H₂Se to Cr(III) and Se, respectively, while Fe(III) was reduced to Fe(II). Standard cerium (IV) sulfate (0.1N) solution was used to titrate ferrous ion from these reactions as an indirect indication of the content of chromous or hydrogen selenide reacted. The other half of the sample was immediately mixed with a sufficient amount of 10 M NaOH. The Cr(II) was precipitated as Cr(OH)₂ while H₂Se was
converted to HSe\(^-\) and Se\(^2-\). In the acidic solution, the redox potential of H\(^+\)/H\(_2\) is 0.42 V higher than that of Cr\(^{2+}\)/Cr\(^{3+}\). However, hydrogen ions do not react with chromous ions because their reaction is kinetically inhibited. This is consistent with the work by Jalan et al. (Jalan et al., 1985). However, at a high pH, chromous ions were precipitated as Cr(OH)\(_2\) and then reacted with water to generate hydrogen gas. The hydrogen evolution was much faster in the presence of H\(_2\)Se, indicating that the reaction was catalyzed by H\(_2\)Se.

\[
2\text{Cr(OH)}_2 + 2\text{H}_2\text{O} = 2\text{Cr(OH)}_3 + \text{H}_2 \quad \Delta G^\circ = -100.8 \text{ kJ/mole} \quad (3-3)
\]

where the free energy change was calculated based on the data of Cr(OH)\(_2\) and Cr(OH)\(_3\) provided by Beverskog and Puigdomenech (1997) and those of H\(_2\)O and H\(_2\) given by Bard et al. (1985).

As hydrogen was dissolved in the solution and possibly adsorbed on the precipitate, the amount of hydrogen collected was about 5% less than that expected from reaction (3-3).

The hydrogen gas was collected using a set-up as shown in Figure 3-5. Two similar bottles were connected through a narrow tube from the caps. Both bottles were placed upside down. The first bottle for collecting hydrogen gas was totally sealed while the second bottle was open to the atmosphere. The positions of the two bottles were adjusted in such a way that the hydrogen pressure in the bottle for hydrogen collection was the same as the atmosphere. The bottle for hydrogen collection was first filled with water and weighed using a balance. After the hydrogen evolution was stopped from the sample, the hydrogen gas was injected into the first bottle. The injection of hydrogen gas into the first bottle caused the flow of the same volume of water to the
other one. The change in the mass of the water in the first bottle was measured using a balance. The volume of hydrogen gas is the mass change of water in the bottle divided by water density.

![Diagram of hydrogen collection setup](image)

**Figure 3-5:** Setup used for hydrogen collection.

After collecting all produced hydrogen gas, 5M H₂SO₄ solution was then added to the mixture to dissolve chromic hydroxides and convert HSe⁻/Se²⁻ back to H₂Se. The resulting solution, now free of chromous ions, was mixed with a known mass of ferric solution. Upon mixing with ferric solution, H₂Se was immediately converted to elemental Se, while Fe(III) was reduced to Fe(II). The solution was filtered through an Osmonics nylon 0.1 μm filter to remove elemental selenium and then the filtrate was analyzed for ferrous concentration by the titration with Ce(IV) using a Radiometer ABU 80 automatic burette (Eq. (3-2)). The concentration of chromous ions was calculated using the difference of the two titrations. The concentration of the remaining selenate in the solution was measured using ICP-OES.
3.4 Kinetics of Selenate Reduction with Chromous Ions

To study the kinetics of selenate reduction by chromous ions, a substantial number of experiments were conducted by varying the concentration of chromous ions, pH, sulfate concentration, ionic strength and temperature. All kinetics experiments were conducted using an in-house designed stopped-flow apparatus.

3.4.1 Stopped-Flow Technique and Procedure

To study the kinetics of a reaction, the time required to mix the reagents of the reaction should be negligible compared with the reaction time. Since the reaction of chromous ions with selenate is very fast under some conditions, the stopped-flow technique was used to study the reduction of selenate by chromous ions. A stopped-flow device is an apparatus for the rapid mixing of two solutions. Using the stopped-flow technique, the solutions are first forced from syringes into a mixing chamber. After several milliseconds, the observation cell is filled by a piston linked to a sensing switch that triggers the measuring device (e.g., a spectrometer) and the flow is stopped suddenly. Since commercial stopped-flow instruments are very expensive and usually used for mixing very small volumes of solutions (usually less than 1 mL), a stopped-flow device as shown in Figure 3-7 (the schematic illustration) and Figure 3-8 (the actual device) was designed and built in the Hydrometallurgy Laboratory at UBC.

In this study, a UV-spectrometer was initially used to monitor the concentrations of Cr(II) and Cr(III) ions in the solution. A large background interference with the detection of Cr(II) and Cr(III) by UV was observed, which was most likely due to the formation of H₂Se. Therefore, the ICP-OES analysis was used for analyzing the selenate concentration. A series of samples had to be taken and a large volume of solution (about 50 mL) was needed in each test, which was larger
than the capacity of commercially available stopped-flow devices. Using the designed stopped-flow device (Figure 3-7), 30 mL of chromous solution was mixed with 30 mL of selenate solution to produce 60 mL of mixed solution, providing enough solution samples.

Prior to running each experiment, two glass containers filled with water and placed in the water bath. The glass container was purged with argon gas and kept in the water bath at least for an hour. When the temperature of the water inside the glass container was the same as water bath, the syringes containing selenate and chromous solutions and sampling syringes were inserted in these two glass containers under an argon atmosphere for over 30 minutes to ensure that the temperature of two solutions stabilized at the target value before initiating the reaction. The setup is shown in Figure 3-6.

Figure 3-6: Glass containers to keep syringes under an argon atmosphere and at a constant temperature
As shown in Figure 3-7, with the use of a pneumatic cylinder, equal volumes of selenate and chromous solutions were driven from two syringes into a mixer in less than 5 seconds and then the mixture immediately flowed into a glass syringe reactor to initiate the reaction. The reactor was immediately inserted into the water bath to maintain the constant temperature (± 0.1°C) over the course of experiments. The top and bottom of the glass syringe reactor were sealed and also purged with argon to eliminate oxygen ingress and subsequent oxidation of chromous ions and
hydrogen selenide by oxygen. All the tubing connected to the reactor were flushed with argon gas prior to running the experiment in order to minimize oxygen in the system. The reactor was immersed in a water bath to maintain a constant temperature.

Sampling from the solution was accomplished by applying a positive pressure of argon gas to the reactor and forcing the solution to flow through a needle into a glass tube containing a known mass of approximately 0.30 M ferric solution to stop the reactions. The glass tube was flushed with argon gas to remove oxygen before introducing the sample. The ferric solution was also deaerated with argon gas for 30 minutes or longer before mixing with the sample. The density of the ferric solution was measured before and after purging argon gas to calculate the accurate volume of the transferred solution. The mixture of the sample and ferric solution was well shaken and then heated to about 60 °C to accelerate the oxidation of hydrogen selenide with ferric ions. The selenium concentration of each sample was determined by ICP-OES analysis.

3.4.2 Solution Preparation

Selenate solution was prepared according to the required solution composition using sulfuric acid, perchloric acid, sodium perchlorate and sodium sulfate. Considering the method detection limit of ICP-OES for selenium (> 100 ppb), the initial selenate concentration was selected as 0.0002 M (17 ppm) so that when 99% or less of selenate is removed from the solution, the selenate concentration can still be accurately determined. Despite the fact that a higher initial selenate concentration is better for the determination of selenate concentration by ICP-OES, at a higher concentration of selenate, the concentrations of chromous and hydrogen ions will change more as the reaction proceeds and they cannot be considered to be constant. The concentration of chromous was also chosen at a sufficiently high value compared to the selenate
so that the chromous concentration can be considered as constant when selenate is completely consumed.

As the chromous solution contained sulfuric acid and sulfate, the HSO₄⁻/SO₄²⁻ system was used as a pH-buffering pair to maintain a constant pH (i.e., a constant hydrogen ion concentration) over the course of reaction. The pH of the solution was measured at the end of each test and it was confirmed that the pH was maintained at a target value or with a little change (less than 0.05 unit). Sodium perchlorate was added to maintain a constant ionic strength. Perchloric acid is a strong acid which can completely dissociate without any further complexation with chromous ions. The speciation of each species in the solution has been considered in the calculation of the ionic strength. The determination of hydrogen ion concentration and ionic strength are discussed in detail in Appendix B. The solution compositions at different ionic strengths are also presented in Appendix B.

The selenate solution was purged with ultra-high purity argon for 30 minutes to remove oxygen from solution before mixing with the chromous solution. The chromous solution for each experiment was made as needed by diluting the original chromous solution, 0.1 M Cr(II) (in stock), with deoxygenated deionized water in a 50-mL flask while purging the headspace of the flask with ultra-high purity argon gas to maintain oxygen-free atmosphere during mixing. Based on the chromous solution composition (i.e., sulfate and proton concentrations), the selenate solution was prepared in such a way that the initial composition of the mixture reached the targeted value. The concentrations of all the solutions were validated by chemical analysis (ICP-OES and titration), and in all cases agreed well with the theoretical dilution values.
For the preparation of sulfate-free chromous solution, barium perchlorate was used to precipitate sulfate. The solubility product of barium sulfate is $1.08 \times 10^{-10}$ (Lide, 2005). In the presence of 0.001M of excess barium, the sulfate concentration can be reduced to about $1 \times 10^{-7}$ M. The excess of barium was analyzed by standard EDTA titration to make sure sulfate was completely removed. In the investigation of the effect of sulfate, barium perchlorate was used to precipitate such an amount of sulfate from chromous solution so that after mixing chromous and selenate solutions the sulfate concentration reached its target values. The solution compositions are presented in Appendix B.

3.4.3 Methodology of the Kinetics Study

At a molar ratio of Cr(II)/Se(VI) above 8 (i.e., in the presence of excess of Cr(II)), the reduction reaction of selenate can be expressed as:

$$\text{SeO}_4^{2-} + 8\text{Cr}^{2+} + 10\text{H}^+ = \text{H}_2\text{Se} + 8\text{Cr}^{3+} + 4\text{H}_2\text{O} \quad (3-4)$$

According to the above reaction, the rate of selenate reduction can be a function of several parameters including concentrations of Se(VI), H\(^+\), and Cr(II). Therefore, in the first step, the reaction orders with respect to Se(VI), H\(^+\) and Cr(II) need to be determined to obtain the reaction rate equation.

It is difficult to determine the rate equation when all three variables change. To simplify the rate equation, the dependence of rate on just one variable can be determined by having all other variables constant (Upadhyay, 2006). The reaction order with respect to selenate was first determined at constant concentrations of chromous ions and hydrogen ions. The constant concentrations of chromous and protons can be lumped into the effective rate constant, $K_{\text{eff}}$, and the rate equation may then be proposed as Eq. (3-5).
\[
\frac{d[\text{Se(VI)}]}{dt} = -k_{\text{eff}}[\text{Se(VI)}]^a \quad (3-5)
\]

where

\[
k_{\text{eff}} = k[\text{Cr(II)}]^b[H^+]^c \quad (3-6)
\]

and \(a, b, \) and \(c\) are the reaction order with respect to \([\text{Se(VI)}], [\text{Cr(II)}], \) and \([H^+]\) respectively.

Integrating the rate equation (Eq. 3-5) for assumed values of \(a\) and plotting the results versus time, the obtained linear plot for any assumed value of \(a\) indicates that value as reaction order respect to the selenate.

The reaction order with respect to chromous and hydrogen ions can be obtained by measuring the reduction rate across a series of experiments where one of them is varied while the other one is held constant. For example, to demonstrate the reaction order with respect to \([H^+]\), all the parameters except \(H^+\) can be lumped into \(k_2\).

\[
k_2 = k[\text{Cr(II)}]^b \quad (3-7)
\]

Substituting Eq. (3-7) into Eq. (3-6) and taking the natural logarithm of both sides of the equation yields the following equation (3-8).

\[
\ln k_{\text{eff}} = \ln k_2 + c \ln[H^+] \quad (3-8)
\]

The experiments were conducted at different \([H^+]\) to generate the corresponding \(k_{\text{eff}}\). The slope of the plot of \(\ln k_{\text{eff}}\) against \(\ln [H^+]\) represents the reaction order with respect to \([H^+]\). Similar procedures and calculations can be applied to determine the reaction order with respect to Cr(II).
3.5 Hydrogen Selenide Removal

Selenate is reduced to selenide using chromous ions, which forms hydrogen selenide in the acidic solution (pH<4). Therefore, the produced hydrogen selenide needs to be removed from the solution. All experiments for hydrogen selenide removal were carried out in a similar manner. The hydrogen selenide solution was first produced by the reduction of selenate by chromous ions and then the CuO or Cu$_2$O solids or CuSO$_4$ solution were introduced into the solution to remove hydrogen selenide from the solution as CuSe or Cu$_2$Se or perhaps Cu$_{2-x}$Se (0≤x ≤1).

3.5.1 Reduction of Selenate to Hydrogen Selenide

The same setup used for the stoichiometry study (Section 3.3.1, Figure 3-3) was also used to reduce selenate using chromous solution and produce hydrogen selenide solution. The time for the reduction of selenate by chromous ion was sufficiently long (4 hours) to ensure that almost all selenate was reduced to hydrogen selenide. A typical experiment first involved transferring of previously produced chromous solution into a reactor. A known amount of selenate solution was mixed with the chromous solution. The chromous ions were present in a quantity slightly higher than stoichiometrically required to completely reduce selenate ions to hydrogen selenide so that there was very little chromous ion left in the solution after the completion of the reactions.

To measure the concentration of produced hydrogen selenide, a sample was collected at the end of each reduction experiment and mixed with a sufficient amount of 10 M NaOH to precipitate any present Cr(II) as Cr(OH)$_2$. The Cr(OH)$_2$ then reacted with water to generate hydrogen gas and Cr(OH)$_3$ while H$_2$Se was converted to HSe$^-$ and Se$^{2-}$. A 5M H$_2$SO$_4$ solution was then added to the mixture to dissolve chromic hydroxides and convert HSe$^-$/Se$^{2-}$ back to H$_2$Se. The resulting solution, now free of chromous ions, was mixed with a known mass of ferric solution to
measure the concentration of H₂Se through titration with Ce(IV) as explained in section 3.2.3. The concentration of the remaining selenate in the solution was measured using ICP-OES.

### 3.5.2 Hydrogen Selenide Removal Experiments

A typical hydrogen selenide removal experiment was conducted by transferring 25 ml of previously produced hydrogen selenide solution into a sealed vessel, typically a 30-mL Pyrex bottle. The vessel contained three openings: one for addition of NaOH, CuO slurry, Cu₂O slurry and copper sulfate solution depending on the test, the second one for the pH probe, and the third one for purging of argon gas. The reactor was first purged with argon gas to remove air and then a low positive pressure of argon gas was maintained in the reactor.

The solution pH was adjusted to a desired value by adding deaerated 0.10 M NaOH solution at the beginning of the experiment as required. The pH was recorded at the beginning and end of each experiment. The experiments were conducted under constant agitation using a magnetic stirrer and tests were run at room temperature.

In order to create a slurry of copper oxide powder, 0.5 g of CuO or Cu₂O was mixed with 50 mL of deionized water in a separate sealed container and then the slurry was purged with argon gas for 30 minutes or longer. To ensure homogeneity of the added slurry to the reactor, a slurry was collected from the container using a 5-mL syringe while it was rapidly stirred. Starting immediately after addition of the known amount of copper oxide slurry, several samples were taken using a syringe to monitor the concentration of remaining hydrogen selenide in the solution. The samples were filtered through an Osmonics nylon 0.1 μm filter to remove solid particles and then the filtrate was analyzed for hydrogen selenide concentration by titration. Solids were
collected using a membrane filtration system and washed with deionized water and dried in air for x-ray diffraction (XRD) analysis.
Chapter 4: Generation of Chromous Ions

Chromium (II) salts are not available commercially for purchase because of their extreme sensitivity to the oxidation by air. Therefore, chromous ions were produced by the electrolytic reduction of chromium (III) in an electrochemical cell. The electrolytic reduction of chromium (III) to chromium (II) is a critical step to produce high purity chromous solution for selenate reduction in the industry. Therefore, it is important to understand the process in order to be aware of design constraints.

Electrochemical production of chromous ions in different media (e.g. chloride, sulfate, and perchloride) has been previously studied (Hong, 2015). In this work, the focus was generation of chromous ions in sulfate medium to maintain the compatibility with sulfate-based selenium waste water. Therefore, the electrolyte for the reduction of chromium (III) was sulfate solution. Sulfate medium was also selected for conducting the selenate reduction experiments.

4.1 Electrochemical Reduction in Sulfate Medium

The electrolytic reduction of chromium(III) can be described by the following half-cell reactions:

<table>
<thead>
<tr>
<th>Anode reaction:</th>
<th>H₂O = 0.5O₂ + 2H⁺ + 2e⁻</th>
<th>E₀ = 1.23 V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>membrane</td>
<td>2H⁺ (anolyte) = 2H⁺ (catholyte)</td>
<td></td>
</tr>
<tr>
<td>Cathode reaction:</td>
<td>Cr₂(SO₄)₃ + 2e⁻ + 2H⁺ = 2CrSO₄ + H₂SO₄</td>
<td>E₀ = -0.42 V vs. SHE</td>
</tr>
<tr>
<td>Side reaction:</td>
<td>2H⁺ + 2e⁻ = H₂</td>
<td>E₀ = 0 V vs. SHE</td>
</tr>
</tbody>
</table>

The standard reduction potential of Cr³⁺/Cr²⁺ is -0.42 V vs. SHE while that of H⁺/H₂ is 0 V vs. SHE. Thermodynamically, it is much easier to reduce H⁺ than Cr³⁺. To suppress the hydrogen evolution reaction, a cathode with a high hydrogen evolution overpotential should be used. In this
work, graphite felt was used as a cathode as it has a high hydrogen overpotential. The electrochemical reduction of 0.1M Cr(III) to Cr(II) resulted in the migration of 0.1M H\(^+\) from the anolyte through the cation membrane to the catholyte to maintain the charge balance. The reduction of 0.1M H\(^+\) to H\(_2\) also resulted in the migration of 0.1M H\(^+\) to the catholyte. The migrated H\(^+\) is equal to the amount of H\(^+\) reduced on the cathode to maintain the charge balance. Therefore, hydrogen evolution did not change the concentration of H\(^+\). If Cr(III) is fully reduced to Cr(II), the solution contains 0.1 M Cr(II) and 0.15 M H\(_2\)SO\(_4\).

The progress of the electrolysis reaction can be evaluated by two factors - current efficiency and conversion of chromium (III) to chromium(II). The current efficiency can be calculated by the use of the Eq. (4-1).

\[
\text{Current efficiency} = \frac{\Delta [\text{Cr(III)}] \cdot V \cdot F \cdot n}{I \cdot t} \quad (4-1)
\]

where V is the catholyte volume, \(\Delta [\text{Cr(III)}]\) the change in the concentration of chromium (III), n the change in the oxidation number of chromium (i.e. 1 for chromium (III) to chromium (II)), I the current (A), t the reduction time (s), and F Faraday’s constant (96485 Cmol\(^{-1}\) of e\(^-\)).

### 4.1.1 Current Efficiency of Chromic Reduction in Sulfate Medium

The current efficiency of chromic reduction in 0.1 M sulfuric acid medium was investigated under the conditions summarized in Table 4-1.

Table 4-1: Experimental conditions for the electrochemical reduction of Cr(III) to Cr(II)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density</td>
<td>200 A/cm(^2)</td>
</tr>
<tr>
<td>Cathode thickness</td>
<td>6 mm</td>
</tr>
<tr>
<td>Catholyte</td>
<td>0.1 M fresh KCr(SO(_4))(_2) +0.1 M H(_2)SO(_4)</td>
</tr>
<tr>
<td>anolyte</td>
<td>0.1M H(_2)SO(_4)</td>
</tr>
</tbody>
</table>
The conversion and current efficiencies of Cr(III) to Cr(II) as a function of time are shown in Figure 4-1. In the first 70 minutes, the conversion of Cr(III) to Cr(II) increased almost linearly with time to 80.3% while the current efficiency only decreased from 83.3 to 81.2%. After 70 minutes, the conversion of Cr(III) to Cr(II) increased slowly and reached almost 100% at 160 minutes. The current efficiency decreased from 81.2% to 43% with increasing time from 50 to 160 minutes. The energy consumption first increased slowly (from 3.41 to 3.83 kWh/kg over 80 minutes) and then it increased significantly as the current efficiency decreased. It finally reached 6.89 kWh/kg. In the conversion range of 80 to 90% which is probably sufficient for industrial applications, the current efficiency was 81 to 76% while the energy consumption was 3.5 to 3.83 kWh/kg Cr(III).
Figure 4-1: Current efficiency and conversion of chromium(III) to chromium(II) and energy consumption as a function of time. Initial catholyte: 0.1 M Cr(III) as sulfate and 0.05 M K$_2$SO$_4$ and 0.1 M H$_2$SO$_4$.

At a high hydrogen overpotential, the hydrogen evolution kinetics can be expressed by the high field approximation of the Butler-Volmer equation.

$$i_{H_2} = i_{o,H_2} \exp\left(-\frac{\alpha_{c,H_2} F (E - E_{H_2/H^+})}{RT}\right)$$  \hspace{1cm} (4-2)

where $i_{H_2}$ is the hydrogen evolution current, $i_{o,H_2}$ is the hydrogen evolution exchange current, $E$ the cathode potential, $E_{H_2/H^+}$ the hydrogen equilibrium potential, $\alpha_{c,H_2}$ the charge transfer
coefficient for hydrogen evolution, F the Faraday constant, R the gas constant and T the temperature (K).

The chromium(III) reduction kinetics can be expressed by the following Butler-Volmer equation (Eq. 4-3) incorporating a term involving the mass transport controlled current, $i_L$ to allow for local depletion of Cr(III) (A. J. Bard and Faulkner, 2001):

$$
\frac{i}{i_0} = \left(1 - \frac{i}{i_{L,c}}\right) \exp\left(-\frac{\alpha nF \eta}{RT}\right) - \left(1 - \frac{i}{i_{L,a}}\right) \exp\left((-\alpha)\frac{nF \eta}{RT}\right) \tag{4-3}
$$

where $i$ is electrode current density, $i_0$ exchange current density, $i_{L,c}$ the cathodic limiting current density, $i_{L,a}$ the anodic limiting current density, $\alpha$ cathodic charge transfer coefficient, $n$ number of electrons involved in the electrode reaction, $T$ absolute temperature, $K$, $F$ Faraday constant, $R$ universal gas constant and $\eta$ overpotential (electrode potential (E) – equilibrium potential (E$_{eq}$)).

At a high cathodic overpotential, the anodic current can be neglected and Equation 4-3 can be simplified as:

$$
\frac{i}{i_0} = \left(1 - \frac{i}{i_{L,c}}\right) \exp\left(-\frac{\alpha nF \eta}{RT}\right) \tag{4-4}
$$

By rearranging Equation 4-4, the current ($i$) can be expressed as an explicit function of overpotential($\eta$):

$$
i = \frac{i_0 \exp\left(-\frac{\alpha nF \eta}{RT}\right)}{1 + \frac{i_0}{i_{L,c}} \exp\left(-\frac{\alpha nF \eta}{RT}\right)} \tag{4-5}
$$

The current for the electrochemical reduction of Cr(III) to Cr(II) can be written as:
where \( i_{\text{Cr(III)}} \) is the Cr(III) reduction current, \( i_{0,\text{Cr(III)}} \) the exchange current, \( i_{L,\text{Cr(III)}} \) the Cr(III) reduction limiting current, \( \alpha_{c,\text{Cr(III)}} \) the Cr(III) reduction charge transfer coefficient, \( E \) the electrode potential and \( E(\text{Cr(II)/Cr(III)}) \) the equilibrium potential for Cr(II)/Cr(III) couple.

Chromic reduction was conducted in a constant volume batch reactor. The total chromium concentration (\( C_{\text{Cr, total}} \)) is constant. The exchange current for Cr(III) reduction, \( i_0 \), can be expressed as a function of conversion, \( X \) as shown in Eq. (4-7).

\[
i_{0,\text{Cr(III)}} = Fk_0[\text{Cr(III)}]^\alpha[\text{Cr(II)}]^{1-\alpha} = Fk_0C_{\text{Cr, total}}(1 - X)^\alpha X^{(1-\alpha)}
\]  

(4-7)

where \( F \) is the Faraday constant, \( X \) is the conversion factor, \( k_0 \) the rate constant, \( \alpha \) the charge transfer coefficient for Cr(III) reduction, and \( C_{\text{Cr}} \) the total chromium concentration.

Assuming that the charge transfer coefficient (\( \alpha \)) is 0.5, the exchange current as a function of conversion (\( X \)) are calculated and summarized in Table 4-2. It first increases with increasing \( X \), reaches a maximum at \( X = 0.5 \) and then decreases. The exchange current at a conversion of 0.99 is only 1/50 of that at a conversion of 0.5. As the conversion increases, the reduction of Cr(III) became more diffusion-limited and the equilibrium potential for Cr(III)/Cr(II) shifts to a more negative value. Therefore, the cathode potential needs to move to a lower value to maintain a constant current. Especially at a conversion of above 0.5, the exchange current density decreases with increasing conversion, the cathode potential needs to move to a much more negative potential.
so that hydrogen evolution increases much more and becomes the dominant electrode reaction, leading to a very low current efficiency of chromium (III) reduction.

Table 4-2: Exchange current of Cr(III)/Cr(II) as a function of conversion (X)

<table>
<thead>
<tr>
<th>Conversion (X)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>0.95</th>
<th>0.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i_0,\text{Cr(III)}/F\text{Cr(total)} k_0)</td>
<td>0.30</td>
<td>0.40</td>
<td>0.46</td>
<td>0.49</td>
<td>0.50</td>
<td>0.49</td>
<td>0.46</td>
<td>0.40</td>
<td>0.30</td>
<td>0.22</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The current efficiency calculated for chromium reduction in this work is slightly lower than that given by (Hong, 2015). Tin-coated stainless mesh frames were used to support the graphite felt and to conduct the electricity to the graphite felt while titanium frames were used in this study. The hydrogen evolution potential on tin is higher than titanium (Yin et al., 2000) and thus less hydrogen evolves on the tin frame than that on titanium. Hong (2015) treated the graphite felt in concentrated sulfuric acid at its boiling point (330 °C). Such treated graphite felt was probably more hydrophilic and had better catalytic effect on the reduction of chromium(III) to chromium(II). Therefore, the current efficiency of the reduction of chromium(III) to chromium(II) obtained was higher in his work. However, the coated tin was not stable and gradually dissolved in the solution. Also, the fiber of the graphite felt treated with concentrated sulfuric acid was very fragile. The tin-contaminated chromous solution is not suitable for the investigation of the selenate reduction by chromous ions. Therefore, in this work, the titanium frames were used instead.

4.2 Summary

Chromous solution was generated through the electrolytic reduction of chromium (III) to chromium (II) in an electrochemical cell. At an initial chromic concentration of 0.1M and a current density of 200 A/m², the current efficiency of chromic reduction to chromous ions was able to be maintained around 80% at a Cr(III) to Cr(II) conversion of 80%. The current efficiency slightly decreased with increasing conversion of Cr(III) to Cr(II). When the Cr(III) to Cr(II) conversion
exceeded 82%, the current efficiency decreased relatively faster with increasing conversion of Cr(III) to Cr(II). At a Cr(III) to Cr(II) conversion of 99.9%, the current efficiency decreased to 43%. In the real industrial application, chromic ions do not need to be completely reduced to chromous ions and a conversion of 80 to 90% is probably sufficient. In this conversion range, the current efficiency was 81 to 76% while the energy consumption was 3.5 to 3.83 kWh/kg. Therefore, chromous solution can be produced from sulfate solution without the introduction of additional impurities at a reasonably high current efficiency.
Chapter 5: Kinetics Study of Selenate Reduction by Chromous Ions

5.1 Objectives

As discussed in the literature review, chromous ions as a strong reducing agent have been used in the reduction of many organic compounds, oxides, and sulphide minerals and in many novel hydrometallurgical processes (Zabin and Taube, 1964; Pedzana, 1988; Wells and Salam, 1968; Westheadt and Gray, 1972). Therefore, there is a high potential for chromous ions to reduce selenate effectively. However, there is no data on the kinetics of the selenate reduction by chromous ions in the literature. To verify the feasibility of the use of chromous ions to remove selenate in industrial processes, it is necessary to investigate the kinetics of selenate reduction by chromous ions. It was therefore an objective of this research to investigate the kinetics of selenate reduction by chromous ions and identify the main factors that determine the reduction rate. In this chapter, the stoichiometry of selenate reduction by chromous ions, the kinetics of the reaction and the effects of acidity, chromous concentration, sulfate concentration, temperature and ionic strength on the removal rate will be discussed.

5.2 Stoichiometry of the Selenate Reduction with Excess Chromous Ions Present

The stoichiometry of selenate reduction by chromous ions was investigated at various initial molar ratios of chromous ions to selenate ions (from 9:1 to 36:1). The initial chromous concentration in all tests was 0.0500 M and the molar ratio of chromous ions to selenate was varied by changing the concentration of selenate ions. All the experiments were conducted at pH 1.0 (except where noted) and 20°C. The details of the experimental set-up, sampling and chemical analysis were explained in Chapter 3. The stoichiometry ratio was calculated by measuring the change in the
concentration of chromous ions in relation to the change in the concentration of selenate $\left(\frac{\Delta [\text{Cr(II)}]}{\Delta [\text{Se(VI)}]}\right)$ after the completion of the reaction. The results obtained from experiments conducted at pH 1.0 and at 20 °C are summarized in Figure 5-1. The data shown by red dashes are the stoichiometry ratios at different pH.

![Graph showing stoichiometric ratios](image)

Figure 5-1: Stoichiometry of the selenate reduction by chromous at different initial molar ratios of chromous to selenate at pH 1.0 and 20 °C (different pH data are referred to in the text).

As shown in Fig. 5-1, the average experimental stoichiometric ratio of chromous to selenate was 8.04. Within experimental uncertainty caused by factors such as the oxidation of chromous ions by oxygen during transferring the samples and chemical analysis the stoichiometric ratio of chromous to selenate is 8. Therefore, the overall reaction is written as Eq. (5-1)

$$\text{SeO}_4^{2-} + 8\text{Cr}^{2+} + 10\text{H}^+ = \text{H}_2\text{Se} + 4\text{H}_2\text{O} + 8\text{Cr}^{3+} \quad (5-1)$$
At an initial Cr(II)/Se(VI) ratio of 16 and room temperature, the reaction stoichiometry ratios of Cr(II) to Se(VI) were 8.02, 8.07, 8.04 and 8.01 for pH 0.7, 1.0, 1.3 and 1.6 respectively, which are shown as red dashes in the Figure 5-1. Within experimental uncertainty the reaction stoichiometry ratio of Cr(II) to Se(VI) is 8 and independent of the pH for initial chromous selenate molar ratio above 8 which confirms equation (5-1). This indicates that in the presence of even a small excess chromous all selenate is reduced to hydrogen selenide and there is no formation of elemental selenium.

The underlying chemistry of the reduction system can be explained using the Se-H₂O Eh-pH diagram (Fig. 2-1). At -0.42 V vs. SHE (i.e. the redox potential of Cr(II)/Cr(III)), the predominant reduction product is hydrogen selenide over the whole range of pH. It is noteworthy that no chromium-selenide solid is present in the diagram (Cr-Se-H₂O Eh-pH diagram) since such solid compounds have not been well characterized or studied from a thermodynamic point of view and thus are not present in established databases.

5.2.1 **Effect of the Acidity and Initial [Cr(II)]/[Se(VI)] on the Formation of Products**

The product of the reaction may change towards the formation of elemental selenium if there is not enough chromous available in the solution (lower than the required stoichiometry ratio, Cr(II):Se(VI) = 8:1) to completely reduce selenate to hydrogen selenide. The products of the reduction of selenate by chromous ions were investigated to find whether the reaction’s products are affected by the acidity and the ratio of chromous ions to selenate.

A substantial number of experiments were performed in order to establish the yields of hydrogen selenide and elemental selenium at different initial molar ratios of Cr(II) to Se(VI) and
pH values. The experiments were performed at an initial chromous concentration of 0.0500 M and 20 °C.

Table 5-1 shows the effect of pH on the yields of H₂Se and elemental Se at an initial molar ratio of Cr(II)/Se(VI) equal to 1. At a Cr(II)/Se(VI) molar ratio of 1 there is 8 times shortage of chromous ions present in the solution to reduce selenate compared to the stoichiometry ratio (Cr:Se = 8:1). The yield of H₂Se was analyzed by the titration method, which was previously explained in Chapter 3. The yield of elemental Se was calculated by subtracting the yield of H₂Se from the total selenate removal (measured based on the ICP-OES analysis of the remaining selenate in the solution) as only H₂Se and elemental Se can be produced. If selenite is produced in the solution, it reacts rapidly with H₂Se to produce elemental Se. The fraction of Cr(II) used for the formation of H₂Se was calculated assuming that 8 moles of Cr(II) are used to produce one mole of H₂Se according to the overall reaction (i.e., the reaction is equation (5-1) which goes to completion). The fraction of Cr(II) used for the formation of elemental Se was calculated by subtracting the chromous ions consumed for the formation of H₂Se from the total initial chromous concentration and assuming that there was no excess of chromous remaining in the solution after the completion of the reduction reaction.

<table>
<thead>
<tr>
<th>pH</th>
<th>H₂Se Yield (%)</th>
<th>Se Yield (%)</th>
<th>Fraction of [Cr(II)]i consumed for formation of H₂Se (%)</th>
<th>Fraction of [Cr(II)]i consumed for formation of Se (%)</th>
<th>Selenate removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>3.88</td>
<td>12.1</td>
<td>31.7</td>
<td>68.3</td>
<td>16.0</td>
</tr>
<tr>
<td>0.50</td>
<td>4.48</td>
<td>10.1</td>
<td>37.3</td>
<td>62.7</td>
<td>14.6</td>
</tr>
<tr>
<td>0.80</td>
<td>5.68</td>
<td>8.82</td>
<td>46.3</td>
<td>53.7</td>
<td>14.5</td>
</tr>
<tr>
<td>1.25</td>
<td>7.16</td>
<td>6.34</td>
<td>59.2</td>
<td>40.8</td>
<td>13.5</td>
</tr>
<tr>
<td>1.50</td>
<td>9.82</td>
<td>2.90</td>
<td>81.8</td>
<td>18.2</td>
<td>12.7</td>
</tr>
<tr>
<td>2.20</td>
<td>11.7</td>
<td>0.570</td>
<td>98.0</td>
<td>2.00</td>
<td>12.3</td>
</tr>
</tbody>
</table>
When the initial molar ratio of chromous to selenate is less than 8, the chromous was completely consumed, and both hydrogen selenide and red elemental selenium were produced.

As it is shown in Table 5-1, at pH 2.2, the fraction of chromous ions consumed for the formation of H₂Se (column 4) was close to 100%. This indicates that at pH 2.2 nearly all the chromous ions in the solution were consumed for the formation of H₂Se even when chromous ions were present in less than the required stoichiometry ratios (at an initial molar ratio of Cr(II)/Se(VI) equal to 1). A selenate removal of 12.3% was obtained at this pH (based on the ICP-OES results), which is in good agreement with the theoretical calculation (12.5% for an initial Cr(II)/Se(VI) molar ratio of 1). The yield of H₂Se obtained was 11.7% (based on titration method), proving that nearly all selenate was reduced to H₂Se.

The yield of H₂Se decreased dramatically with decreasing pH, while the yield of Se increased. For example, the yield of H₂Se at pH 0.1 was approximately 3.88 % while the yield of Se was 12.0%. Elemental selenium became a significant reaction product at pH 0.1 and an initial Cr(II)/Se(VI) molar ratio of 1.

The fraction of chromous ions consumed for the formation of H₂Se (%) at different [Cr(II)]/[Se(VI)] and pH is shown in Figure 5-2.
Figure 5-2: The fraction of chromous ions used for the formation of H$_2$Se as a function of the initial Cr(II)/Se(VI) molar ratio and pH

As shown in Figure 5-2, at pH 2.2, almost 100% of chromous ions were consumed for the formation of H$_2$Se in the Cr(II)/Se(VI) molar ratio range from 1 to 8. The fraction of chromous consumed for the formation of H$_2$Se and consequently the amount of produced H$_2$Se decreased with decreasing pH. In other words, more elemental selenium was produced at a higher hydrogen ion concentration. For example, at an initial Cr(II)/Se(VI) molar ratio of 4 almost 100% of chromous ions were consumed for the formation of H$_2$Se at pH 2.2, while at pH 0.10 only about 71% of chromous ions were used for the formation of H$_2$Se. The obtained trend indicates that there is a direct contribution of H$^+$ to the reaction pathway.
The above phenomenon is related to the multistep selenate reduction mechanism. The rate of each step changes differently with the pH and Cr(II) concentration, affecting the yields of the final products. Klaning and Sehested (1986) proved that Se(V) (SeO₅²⁻) is a short lived intermediate species in the reduction of Se(VI). Se(V) is very reactive and is rapidly reduced to Se(IV) in the presence of Cr(II). Se(IV) is further reduced to elemental selenium or hydrogen selenide. It is also quite possible that selenite reduces to Se(0) as an intermediate product first and then to H₂Se when there is enough chromous available in the solution. In our preliminary tests, it was observed that the reduction of selenite by chromous was almost instantaneous. Mokmeli et al., (2013) studied the reduction of Se(VI) by cuprous ions and found that the reduction of Se(VI) to Se(V) is the rate-determining step. Since Se(V) and Se(IV) are very reactive, the reduction of these two species by chromous is most likely not the rate-determining step. This will be discussed further in Chapter 6.

With decreasing pH, the reduction rate of Se(VI) to Se(V) which probably is the rate determining step increases faster than those of (some) intermediate products. Therefore, the concentrations of these intermediate products increase. When the total amount of reduced SeO₄²⁻ (intermediate) is more than that required for the reduction of SeO₄²⁻ to H₂Se by remaining Cr(II) according to Reaction 5-1, the intermediate products are not able to be reduced to H₂Se, but only to elemental selenium. More SeO₄²⁻ reacts with Cr(II) at a lower pH to produce more intermediate products and less Cr(II) is available to completely reduce SeO₄²⁻ to H₂Se. Consequently, the yield of H₂Se decreases with decreasing pH. It is noteworthy that, when the selenite solution was mixed with the H₂Se solution, elemental selenium was produced. This indicates that if Se(IV) is not reduced by Cr(II), it will react with H₂Se present in the solution to produce elemental selenium. This reaction chemistry mimics the Claus process where sulfur dioxide (S(IV)) is reacted with hydrogen sulfide (S(-II)) to produce elemental sulfur as a product (Gray and Handwerk, 1984).
As soon as elemental selenium was generated during the reduction of selenate by chromous, chromous solution was injected into the reactor to reduce elemental selenium. However, elemental selenium was not reduced to H$_2$Se. Selenate is probably reduced to selenium(0) as an intermediate product and then immediately further reduced to H$_2$Se in the presence of chromous ions. If selenium(0) as an immediate product is not immediately reduced to H$_2$Se, elemental selenium is produced.

5.3 Kinetics Study of Selenate Reduction by Chromous Ions

5.3.1 Determination of Reaction Order with Respect to Selenate Concentration

In order to determine the reaction order with respect to the selenate concentration, a selenate reduction test was conducted at a chromous concentration of 0.0475 M, pH 1.0, 20 °C and an ionic strength of 1.0 M. The selenate concentration of 0.220 mM was selected to be very low compared to chromous concentrations in order to maintain an approximately constant chromous concentration over the course of the experiment (only 3% of [Cr(II)] was reacted based on the 8:1 stoichiometry ratio). The HSO$_4^-$-SO$_4^{2-}$ system was used as a pH-buffering pair to maintain a constant pH (i.e., a constant hydrogen ion concentration). The details of experimental set-up and method were explained in the previous chapter. The solution compositions are given in Appendix B.

According to the selenate reduction reaction Eq. (5-1), the rate of selenate reduction by chromous ions can be affected by several parameters such as temperature and the concentrations of selenate, hydrogen ions and chromous ions. Therefore, the reaction rate can be a function of the concentrations of selenate, chromous ions and hydrogen ions and may be expressed as Eq. (5-2).
\[
\frac{\mathrm{d}[\text{Se(VI)}]}{\mathrm{dt}} = -k[\text{Se(VI)}]^a[\text{Cr(II)}]^b[H^+]^c
\]  
\tag{5-2}
\]

where \(a\), \(b\), and \(c\) are reaction orders with respect to \([\text{Se(VI)}]\), \([\text{Cr(II)}]\), and \([H^+]\) respectively.

At constant concentrations of chromous and hydrogen ions and a constant temperature, the reaction rate can be considered to be only dependent on the selenate concentration. Therefore, the general reaction rate can be simplified to the following equation.

\[
\frac{\mathrm{d}[\text{Se(VI)}]}{\mathrm{dt}} = -k_{\text{eff}}[\text{Se(VI)}]^a
\]  
\tag{5-3}
\]

where constant concentrations of chromous and hydrogen ions are combined with the rate constant to yield a single effective rate constant, \(k_{\text{eff}}\).

The classic technique for determination of reaction order is to integrate the rate equation (Eq. 5-3) for assumed values of \(a\) and plot the results versus time. A linear plot indicates a good fit to the assumed order.

When the assumed reaction order with respect to selenate concentration is 1 (\(a = 1\)), the integrated form of the general rate law can be expressed as Equation 5-5.

\[
\int_{[\text{Se(VI)}]_0}^{[\text{Se(VI)}]_t} \frac{\mathrm{d}[\text{Se(VI)}]}{[\text{Se(VI)}]} = \int_0^t -k_{\text{eff}} \mathrm{d}t
\]  
\tag{5-4}
\]

\[
\ln \left( \frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0} \right) = -k_{\text{eff}} t
\]  
\tag{5-5}
\]

By plotting \(\ln([\text{Se(VI)}]/[\text{Se(VI)}]_0)\) against time and applying the least square method, \(k_{\text{eff}}\) (i.e., the slope of the line) can be obtained.

Figure 5-3 shows a plot of \(\ln ([\text{Se(VI)}]/[\text{Se(VI)}]_0)\) against time. Indeed, the plot of \(\ln ([\text{Se(VI)}]/[\text{Se(VI)}]_0)\) had a linear relationship with time with a slope of -0.0695, indicating that the
reaction order with respect to selenate concentration is 1. The selenate concentration as a function of time is shown in Figure 5-4. The selenate concentration decreased from 0.220 mM (17.4 ppm) to 0.0130 mM (1.03 ppm) in 40 minutes.

Figure 5-3: ln([Se(VI)]/[Se(VI)]₀) as a function of time at [Cr(II)]₀=0.0475 M, [Se(VI)]₀ = 0.220 mM, pH 1.0, 20 °C, and an ionic strength of 1.0 M. [SO₄²⁻] = 0.137M, [HSO₄⁻] = 0.101M and [NaClO₄] = 0.45 M
5.3.2 Determination of the Reaction Order with Respect to Hydrogen Ion Concentration

The reaction order with respect to hydrogen ion concentration was investigated by varying the solution pH between 1.0 and 2.2 in a series of experiments at a chromous concentration of 0.0475 M, an initial selenate concentration of 0.210 mM, 20°C and an ionic strength of 1.0 M.

The selenate concentration as a function of time at pH 1.0, 1.3, 1.6, 1.9 and 2.2 are shown in Figure 5-5. Hydrogen ions are involved in the reduction of selenate by chromous as indicated by the overall reaction (Reaction 5-1) and hence the hydrogen ion concentration should have a significant effect on the selenate reduction rate. As shown in Figure 5-5, at pH 2.2, it took almost 6 hours for the selenate concentration (as Se(VI)) to decrease from 0.220 mM (17.4 ppm) to 0.0266 mM (2.10 ppm), while it only took less than 30 minutes at pH 1.0.

Figure 5-4: Selenate concentration as a function of time at [Cr(II)]₀=0.0475 M, pH 1.0, 20 °C, an ionic strength of 1.0 M, [SO₄²⁻] = 0.137M, [HSO₄] = 0.101M and [NaClO₄] = 0.450 M
The plots of $\ln([\text{Se(VI)}]/ [\text{Se(VI)}]_0)$ against time (Figure 5-6) are all linear with the slopes proportional to the hydrogen ion concentration.

Figure 5-5 Selenate concentration as a function of time at different pHs, $[\text{Cr(II)}]_0=0.0475$ M, 20 °C and an ionic of strength of 1.0 M. The determination of solution composition is given in Appendix B.
Figure 5-6: $\ln(\frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0})$ as a function of time at different pHs, $[\text{Cr(II)}]_0=0.0475$ M, $[\text{Se(VI)}]_0 = 0.220$ mM, 20 °C and an ionic of strength of 1.0 M. The determination of solution composition is given in Appendix B.

The regression lines and correlation coefficients, $R^2$ (R-Squared) of each plot are summarized in Table 5-2.

Table 5-2: Regression lines and corresponding R-Squared values for the plots of $\ln(\frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0})$ as a function of time at different pHs (Figure 5-6)

<table>
<thead>
<tr>
<th>pH</th>
<th>Regression Line</th>
<th>$R^2$</th>
<th>pH</th>
<th>Regression Line</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>$y = -0.0057x - 0.0345$</td>
<td>0.999</td>
<td>1.3</td>
<td>$y = -0.0371x - 0.1569$</td>
<td>0.9917</td>
</tr>
<tr>
<td>1.9</td>
<td>$y = -0.0117x - 0.1477$</td>
<td>0.9933</td>
<td>1.0</td>
<td>$y = -0.0695x - 0.0258$</td>
<td>0.999</td>
</tr>
<tr>
<td>1.6</td>
<td>$y = -0.0211x - 0.0654$</td>
<td>0.9944</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The calculated rate constants from these experiments are summarized in Table 5-3. As expected, the rate constant increases with increasing hydrogen ion concentration.
Table 5-3: Rate constant at different pHs, [Cr(II)] = 0.0475 M, [Se(VI)] = 0.220 mM, 20 °C and an ionic strength of 1.0 M ([H+] is calculated based on its activity coefficient (1.32) (see Appendix B)

<table>
<thead>
<tr>
<th>pH</th>
<th>2.16</th>
<th>1.86</th>
<th>1.59</th>
<th>1.34</th>
<th>1.04</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H+] / M</td>
<td>0.00524</td>
<td>0.0105</td>
<td>0.0195</td>
<td>0.0346</td>
<td>0.0683</td>
<td></td>
</tr>
<tr>
<td>k_{eff} /s^{-1}</td>
<td>0.0000950</td>
<td>0.000195</td>
<td>0.000352</td>
<td>0.000618</td>
<td>0.00116</td>
<td></td>
</tr>
<tr>
<td>k / M^{-2} s^{-1}</td>
<td>0.381</td>
<td>0.393</td>
<td>0.380</td>
<td>0.384</td>
<td>0.360</td>
<td>0.380</td>
</tr>
</tbody>
</table>

The plot of the ln(k_{eff}) against ln ([H^+]) gives a straight line with a slope of 0.972 (Figure 5-7).

The linear correlation between ln k_{eff} and ln [H^+] is shown in Eq. (5-6). Integrating Eq. (5-6) yields Eq. (5-7). The exponent of [H^+] in this equation shows the reaction order with respect to [H^+].

\[
\ln k_{eff} = 0.972 \ln([H^+]) - 4.13 \tag{5-6}
\]

\[
k_{eff} = 0.0161 [H^+]^{0.972} \text{ (S}^{-1}\text{) at [Cr(II)] = 0.0475 M} \tag{5-7}
\]

With the consideration of the experimental errors, the reaction order with respect to hydrogen ion concentration should be 1.

Figure 5-7: ln k_{eff} as a function of ln [H^+], [Cr(II)] = 0.0475 M, [Se(VI)] = 0.220 mM, 20 °C and an ionic strength of 1.0 M. The determination of solution composition is given in Appendix B.
5.3.3 **Determination of the Reaction Order with Respect to Chromous ion Concentration**

To determine the reaction order with respect to chromous ions, a series of experiments were performed by varying chromous concentration from 0.0475 to 0.00602 M at pH 1.0, 20 °C, an initial selenate concentration of 0.220 mM and an ionic strength of 1.0 M. The selenate concentration as a function of time at different chromous concentrations are given in Figure 5-8. The plots of \( \ln \left( \frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0} \right) \) against time give straight lines (Figure 5-9).

![Figure 5-8: Selenate concentration as a function of time at different chromous concentrations, pH 1.0, 20 °C, and an ionic strength of 1.0 M. The determination of solution composition is given in Appendix B.](image-url)
Figure 5-9: \( \ln([\text{Se(VI)}/[\text{Se(VI)}]_0]) \) as a function of time at different \([\text{Cr(II)}]_0\). pH 1, \([\text{Se(VI)}]_0 = 0.220 \text{ mM}\), 20 °C and an ionic of strength of 1.0 M. The determination of solution composition is given in Appendix B.

The regression lines and correlation coefficients, \( R^2 \) (R-Squared), of each plot are summarized in table 5-4.

Table 5-4: Regression lines and corresponding R-Squared values for the plots of \( \ln ([\text{Se(VI)}/[\text{Se(VI)}]_0]) \) as a function of time at different chromous concentrations. (Figure 5-9)

<table>
<thead>
<tr>
<th>[Cr(II)]</th>
<th>Regression Line</th>
<th>( R^2 )</th>
<th>[Cr(II)]</th>
<th>Regression Line</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00602</td>
<td>( y = -0.0095x - 0.0386 )</td>
<td>0.9934</td>
<td>0.0253</td>
<td>( y = -0.0438x - 0.039 )</td>
<td>0.9983</td>
</tr>
<tr>
<td>0.0122</td>
<td>( y = -0.0184x - 0.0265 )</td>
<td>0.9979</td>
<td>0.0475</td>
<td>( y = -0.0695x - 0.0258 )</td>
<td>0.999</td>
</tr>
</tbody>
</table>
The effective rate constant values ($k_{\text{eff}}$) at different chromous concentrations and a constant hydrogen ion concentration are calculated and summarized in Table 5-5. The rate constants are proportional to the chromous concentration.

Table 5-5: Rate constants at different chromous concentrations, pH 1.0, 20 °C, an initial selenate concentration of 0.220 mM and an ionic strength of 1.0 M

<table>
<thead>
<tr>
<th>[Cr(II)] / M</th>
<th>0.00602</th>
<th>0.0122</th>
<th>0.0253</th>
<th>0.0475</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{eff}}$ / s$^{-1}$</td>
<td>0.000158</td>
<td>0.000307</td>
<td>0.000730</td>
<td>0.00116</td>
<td></td>
</tr>
<tr>
<td>k / M$^2$ s$^{-1}$</td>
<td>0.385</td>
<td>0.372</td>
<td>0.399</td>
<td>0.360</td>
<td>0.378</td>
</tr>
</tbody>
</table>

The plot of $\ln(k_{\text{eff}})$ against $\ln([\text{Cr(II)}])$ (Figure 5-10) gives a straight line with a slope of 0.989. The correlation between $\ln(k_{\text{eff}})$ and $\ln([\text{Cr(II)}])$ is shown in Eq. (5-8) and (5-9), suggesting an effective first order relationship with respect to the chromous ion concentration with the consideration of the experimental errors.

\[
\ln(k_{\text{eff}}) = 0.990 \ln([\text{Cr}^{2+}]) - 3.68 \quad (5-8)
\]

\[
k_{\text{eff}} = 0.0252[\text{Cr}^{2+}]^{0.989} \quad \text{at } [\text{H}^+] = 0.0691 \text{ M} \quad (5-9)
\]

The rate constant values (k) at different chromous concentrations and a constant hydrogen ion concentration are calculated and summarized in Table 5-5 while these at different hydrogen ion concentrations and a constant chromous concentration are given in Table 5-3. At a constant temperature, the rate constant does not change with the concentrations of hydrogen and chromous ions. The average rate constant (k) at 20 °C are 0.380 M$^2$s$^{-1}$. 
Figure 5-10: $\ln (k_{\text{eff}})$ as a function of $\ln([\text{Cr(II)}])$ at pH 1.0, 20 °C, $[\text{Se(VI)}]_0 = 0.220$ mM and an ionic strength of 1.0 M. The determination of solution composition is given in Appendix B.

### 5.3.4 Effect of Temperature on Selenate Reduction Rate with Chromous Ions

The effect of temperature on the rate of selenate reduction by chromous ions was investigated in the temperature range from 10 to 50 °C at pH 1.6, an initial chromous concentration of 0.0475 M, an initial selenate concentration of 0.220 mM and an ionic strength of 1.0 M. The selenate concentration as a function of time is shown in Figure 5-11.
The plots of $\ln \left( \frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0} \right)$ against time (Figure 5-12) give linear lines, indicating that the reaction order with respect to selenate is 1 in the temperature range from 10 to 50 °C.
Figure 5-12: \( \ln \left( \frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0} \right) \) as a function of time at different temperatures, pH 1.6, 0.0475 M Cr(II), an initial selenate concentration of 0.220 mM and an ionic strength of 1.0 M. The determination of solution composition is given in Appendix B.

The regression lines and correlation coefficients, \( R^2 \) (R-Squared) of each plot are summarized in table 5-6.

Table 5-6: Regression lines and corresponding R-Squared values for the plots of \( \ln \left( \frac{[\text{Se(VI)}]}{[\text{Se(VI)}]_0} \right) \) as a function of time at different temperatures (Figure 5-12)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Regression Line</th>
<th>( R^2 )</th>
<th>T (°C)</th>
<th>Regression Line</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>( y = -0.0104x - 0.0131 )</td>
<td>0.9982</td>
<td>40</td>
<td>( y = -0.116x - 0.083 )</td>
<td>0.9948</td>
</tr>
<tr>
<td>20</td>
<td>( y = -0.0211x - 0.065 )</td>
<td>0.9944</td>
<td>50</td>
<td>( y = -0.217x - 0.0897 )</td>
<td>0.9902</td>
</tr>
<tr>
<td>30</td>
<td>( y = -0.055x - 0.0515 )</td>
<td>0.9977</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The \( k \) values at different temperatures are given in Table 5-7. The rate constant increased with increasing temperature.
Table 5-7: Rate constants at different temperatures, pH 1.6, 0.0475 M Cr(II), an initial selenate concentration of 0.220 mM and an ionic strength of 1.0 M.

<table>
<thead>
<tr>
<th>Temp. / °C</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁ / M⁻²s⁻¹</td>
<td>0.188</td>
<td>0.380</td>
<td>0.990</td>
<td>2.07</td>
<td>3.82</td>
</tr>
</tbody>
</table>

The dependency of the rate constant on the temperature can be expressed by the Arrhenius law:

\[
\ln k = \ln A - \left(\frac{E_A}{RT}\right)
\]

(5-8)

where \(E_A\) is the activation energy and \(A\) is the frequency factor.

The plot of \(\ln k\) against \(1/T\) is a straight line with the slope of \((-E_a/R)\), as shown in Figure 5-13. The activation energy and natural logarithm of the frequency factor are calculated as 58.7 kJ/mol and \(\ln A = 23.23 \text{ M}^{-2}\text{s}^{-1}\).

![Figure 5-13: \(\ln k_1\) as a function of \(1/T\) at pH 1.6, 0.0475M Cr(II), an initial selenate concentration of 0.220 mM and an ionic strength of 1.0 M.](image)
Such a moderate activation energy is consistent with the fairly rapid kinetics. Relatively high activation energies of 86 kJ/mol and 100 kJ/mol for the reduction of selenate by Cu$^+$ were reported by Mokmeli et al., (2013) and Ladriere (1973), respectively. The lower activation energy calculated in this study confirms that the selenate reduction by chromous is much faster than the selenate reduction with cuprous ions.

5.3.5 Proposed General Rate Equation:

According to the results obtained in the kinetics experiments, the overall rate equation for the reduction of selenate with chromous ions can be expressed as follows:

\[
\frac{d[\text{Se(VI)}]}{dt} = -k[\text{Se(VI)}][\text{H}^+][\text{Cr}^{2+}] \tag{5.9}
\]

where \( k \) is the rate constant \((\text{M}^{-2}\text{s}^{-1})\) and has the following relationship with temperature:

\[
k = 1.23 \times 10^{10} \exp \left( \frac{-5.87 \times 10^4}{RT} \right)
\]

The reaction rate was found to be first order with respect to the concentrations of selenate, hydrogen ions and chromous ions within the experimental errors.

In the previous kinetics experiments, the chromous concentration was chosen to be sufficiently high compared to selenate \((\text{Cr(II)}/\text{Se(VI)} = 250:1 \text{ to } 125:1)\) to maintain a nearly constant chromous concentration over the course of the experiments. To verify the above equation for industrial conditions, an experiment was conducted at a lower initial molar ratio of \(\text{Cr(II)}/\text{Se(VI)}\) \((16:1)\), an initial chromous concentration of 0.0230 M, an initial selenate concentration of 1.40 mM, ionic strength of 1.0 M, pH 1.0, and 20 °C. As the reaction proceeds, the concentration of chromous ions decreased significantly while the concentration of chromic ions increased. The practical validity of a proposed rate law can be tested by drawing the
theoretical concentration-time curve and comparing it with the one obtained experimentally under the same conditions. The mathematical calculation of theoretical rate curve is shown in Appendix D.

Figure 5-14: Comparison of experimental data at an initial Cr(II)/Se(VI) molar ratio of 16:1, pH=1.0, 20 °C and simulation results using the proposed rate equation (Eq. (5-11)).

Figure 5-14 shows a comparison of experimental data at low excess of chromous (Cr(II)/Se(VI)=16) to the rate law proposed in this study. The agreement between theory and experiment is sufficient to say that the rate equation can accurately predict the course of the selenate reduction by chromous ions.

The selenium concentration in the last sample (at 166 min) was slightly higher than the expected selenium concentration based on modelled rate. This is most likely attributable to the analytical error/uncertainty of measurement of selenium in the samples with high ferric and chromic
concentrations. When the selenate concentration is below 1 mg/L, it was difficult to accurately detect selenate after dilution as it approached the selenate detection limit.

5.3.6 Effect of Ionic Strength

The effect of ionic strength on the selenate reduction rate was investigated by changing the sodium perchlorate concentration to adjust the ionic strength at a constant initial chromous concentration of 0.0252 M, selenate concentration of 0.219 mM, [H+] = 0.101 M and 20°C.

The plots of ln ([Se(VI)]/[Se(VI)]0) against time at different ionic strengths are shown in Figure 5-16. The plots are linear and almost overlapping. By the use of the modified form of Bronsted-Bjerrum equation (Eq. 5-12), the plot of log(rate constant) against \( I^{1/2}/(1+I^{1/2}) \) gives a horizontal line, indicating that the ionic strength has no effect on the selenate reduction.

\[
\log(k) = \log(k_0) + 1.02Z_AZ_B I^{1/2}/(1+I^{1/2})
\]  

(5-10)

where \( k_0 \) is the rate constant of the reaction when the ionic strength is zero, and \( Z_A \) and \( Z_B \) are the charges of the reactants A and B respectively.
The invariance of rate constant with ionic strength suggests that one reactant involved in the rate equation must be neutral ($Z_A$ or $Z_B$ is zero) so that the reaction rate is not sensitive to the ionic strength. Wells and Salam (1968) reported that in the reduction of hydrazine by chromous ions, Cr(II) complexes with sulfate and the CrSO$_4$(aq) complex is involved in the reduction reaction. According to the similarity of selenate and sulfate, Cr(II) could also possibly complex with selenate.

To investigate which complex (CrSO$_4$ or CrSeO$_4$) is involved in the reaction, a series of selenate reduction tests were performed at different ionic strengths of solution in the absence of sulfate. Sulfate was removed to less than $2.5 \times 10^{-8}$ M by addition of barium perchlorate to the
chromous solution and the ionic strength was adjusted by the addition of sodium perchlorate. The initial solution compositions are given in Table B-7 in appendix B. The experiments were conducted at a constant initial chromous concentration of 0.0258 M, selenate concentration of 0.219 mM, constant hydrogen ion concentration of 0.0801 M and 20 °C.

The plots of ln([Se(VI)]/\([Se(VI)]_0\)) against time at different ionic strength are shown in Figure 5-16.

![Graph](image)

**Figure 5-16:** ln([Se(VI)]/\([Se(VI)]_0\)) as a function of time at different ionic strengths, 0.0801M H⁺, 0.0258 M Cr(II), \([Se(VI)]_0 = 0.219 \text{ mM, at 20 °C and in the absence of sulfate. The initial reaction compositions are given in Appendix B (Table B-7)}.

As shown in Fig. 5-16, the plots of ln([Se(VI)]/[Se(VI)]₀) against time gave straight lines with slightly different slope of the test at ionic strength of 0.5M. The ionic strength has a very
small effect on the reaction rate which suggests that one of the reactant involved in the rate-determining step should be a neutral species. Since there was no sulfate in the solutions, \( \text{CrSeO}_4^{(aq)} \) was more likely the neutral species which was involved in the reduction reaction. This suggests that the concentration of this neutral species decreased slightly with increasing ionic strength, resulting in a little decrease in the reaction rate. With increasing ionic strength, the activity coefficient of each species was changed, resulting in a change in the distribution of the reactive species. In this case, the concentration of the reactive species decreased. The effect of ionic strength in the absence of sulfate is slightly larger than that in the presence of sulfate, indicating that sulfate has a little influence on the concentration of reactive species. The rate-determining step and reactive species will be discussed further in Chapter 6.

5.3.7 Effect of Sulfate

Sulfuric acid and sulfates are commonly found in waste solutions and commonly used as reagents to minimize cost in commercial facilities. It would therefore be useful to understand the effect of sulfate on the selenate reduction by chromous ions. The focus of this work was to study the removal of selenate from the eluant of IX process which contains up to 1 M of sulfate. The effect of sulfate on the rate of selenate reduction by chromous ions was investigated by varying the concentration of sulfate from 0 to 0.150 M at a chromous concentration of 0.0257 M, selenate concentration of 0.220 mM, an ionic strength of 1, pH =1 and at 20°C. The plots of \( \ln([\text{Se(VI)}]/[\text{Se(VI)}]) \) against time at different sulfate concentrations (Figure 5-17) give straight lines which virtually overlapped.
Figure 5-17: ln([Se(VI)]/[Se(VI)]_o) as a function of time and different sulfate concentrations at [Cr(II)]_o=0.0257 M, [Se(VI)]_o = 0.220 mM, 20 °C pH 1.0 and an ionic of strength of 1.0 M.

The calculated rate constants k at different concentrations of sulfate are summarized in Table 5-8. The rate constant is almost independent of sulfate concentration thus sulfate practically has no effect on the selenate reduction rate. This means that there is no change in the underlying reaction mechanism in the presence of sulfate. Sulfate probably is not directly involved in a rate-limiting step. However, Wells and Salam (1968) found that Cr(II) complexes with sulfate and the CrSO_4(aq) complex enhance the reduction of hydrazine by Cr(II).

Table 5-8: Rate constants at different sulfate concentrations, pH 1, 0.025M Cr(II), an initial selenate concentration of 0.220 mM, 20°C, and an ionic strength of 1.0 M

<table>
<thead>
<tr>
<th>[SO_4^{2-}] M</th>
<th>0</th>
<th>0.0110</th>
<th>0.0247</th>
<th>0.0506</th>
<th>0.150</th>
</tr>
</thead>
<tbody>
<tr>
<td>k / M^2s^-1</td>
<td>0.382</td>
<td>0.391</td>
<td>0.388</td>
<td>0.380</td>
<td>0.398</td>
</tr>
</tbody>
</table>
Since the kinetics data also show that chromous ions does not reduce sulfate, the use of chromous ions may be useful for the selective removal of selenate in high sulfate concentration solutions.

In the use of ion exchange for selenate adsorption, the selenate-containing eluant can have a significant sulfate concentration (e.g. 1M sodium sulfate or 1M ammonia sulfate). Therefore, it is necessary to conduct the selenate reduction by chromous ions in the solutions containing higher sulfate concentrations. At pH above 2.2, the selenate reduction is quite slow. However, at a pH below 2.2, more sulfuric acid has to be used to attain the lower pH. Therefore, the selenate reduction was carried out at pH 2.2, an initial chromous concentration of 0.0475 M, an initial selenate concentration of 0.220 mM, and 20°C.

The plots of ln([Se(VI)]/[Se(VI)]0) against time at different sulfate concentrations (Figure 5-18) give linear lines which virtually overlapped.
Figure 5-18: $\ln([\text{Se(VI)}]/[\text{Se(VI)}]_0)$ as a function of time and different sulfate concentrations at $[\text{Cr(II)}]_0 = 0.0475\text{M}$, $[\text{Se(VI)}]_0 = 0.220\text{mM}$, 20 °C and pH 2.2.

The rate constants for the solutions containing different sulfates are summarized in Table 5-9. Sulfate has very little effect on selenate reduction with the consideration of experimental error limits.

Table 5-9: Rate constants at different sulfate-ammonia concentrations, pH 2.2, $[\text{Cr(II)}]_0=0.0475\text{M}$, $[\text{Se(VI)}]_0 = 0.220\text{mM}$, and 20 °C

<table>
<thead>
<tr>
<th>[SO$_4^{2-}$]M</th>
<th>0.150</th>
<th>0.998</th>
<th>1.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NH$_4^+$] M</td>
<td>0</td>
<td>0</td>
<td>2.00</td>
</tr>
<tr>
<td>Na$^+$ /M</td>
<td>0.85</td>
<td>2.00</td>
<td>0</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>0.450</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$k_1$ / M$^{-2}$s$^{-1}$</td>
<td>0.381</td>
<td>0.399</td>
<td>0.376</td>
</tr>
</tbody>
</table>
5.4 Summary

The stoichiometry of selenate reduction by chromous ions was investigated at various initial molar ratios of chromous to selenate. At an initial $\text{Cr}^{2+}/\text{SeO}_4^{2-}$ molar ratio of 8 or above, the product of the reduction of selenate by chromous ions was hydrogen selenide and the stoichiometry ratio was always 8 and independent of the hydrogen ion concentration. The stoichiometry of the reduction of selenate by chromous ions can be expressed as:

$$\text{SeO}_4^{2-} + 8\text{Cr}^{2+} + 10\text{H}^+ = \text{H}_2\text{Se} + 4\text{H}_2\text{O} + 8\text{Cr}^{3+}$$

At an initial $\text{Cr(II)}/\text{Se(VI)}$ molar ratio of less than 8, the products of the reduction of selenate by chromous ions were hydrogen selenide and elemental selenium. The yields of hydrogen selenide increased with increasing $\text{Cr(II)}/\text{Se(VI)}$ ratio and pH. At a higher $\text{Cr(II)}/\text{Se(VI)}$ ratio, more chromous ion are available to reduce intermediate products to hydrogen selenide. The effect of pH is related to the mechanism and kinetics of the reduction of selenate by chromous ions. At a lower pH, more chromous ions were consumed for the reduction of selenate and more intermediate products were produced. Therefore, a least amount of chromous ions was available for the reduction of intermediate products to hydrogen selenide.

The kinetics of selenate reduction by chromous ions was investigated at various concentration of chromous ions, pH, sulfate concentration, ionic strength and temperature to verify the feasibility of the use of chromous ions to remove selenate in industrial processes with different condition. The reaction order with respect to the concentrations of selenate, chromous ions and hydrogen ions was investigated and found to be 1 with respect to each of them.

The effect of temperature was also studied and the activation energy was calculated as 58.7 kJ/mole. The rate equation can be expressed as:
\[
\frac{d[\text{Se(VI)}]}{dt} = -k[\text{Se(VI)}][\text{H}^+][\text{Cr(II)}]
\]

where \( k_1 \) is the rate constant (M\(^{-2}\)s\(^{-1}\)) and has the following relationship with temperature:

\[
k = 1.23 \times 10^{10} \exp\left(\frac{-5.87 \times 10^4}{RT}\right)
\]

The effect of ionic strength on the selenate reduction rate was investigated in sodium perchlorate medium. Ionic strength has practically no effect on the reaction rate, indicating a neutral species involved in the rate-determining step.

A series of selenate reduction tests were performed at different concentrations of sulfate in the solution to study the effect of sulfate on the selenate reduction rate by chromous ions. The rate constant was almost independent of sulfate concentration. Thus sulfate practically has no effect on the selenate reduction rate. This means that sulfate probably is not directly involved in a rate-limiting step.
Chapter 6: Reaction Mechanisms

As discussed previously in the stoichiometry study (Chapter 5), the selenate reduction by chromous ions at an initial Cr(II)/Se(VI) molar ratio of 8 or above can be expressed as Eq. (6-1).

\[
\text{SeO}_4^{2-} + 8\text{Cr}^{2+} + 10\text{H}^+ = \text{H}_2\text{Se} + 8\text{Cr}^{3+} + 4\text{H}_2\text{O}
\]

The kinetics study showed that the rate of selenate reduction by chromous ions is directly dependent on the concentration of selenate, chromous, and hydrogen ions. This suggests that these species are involved in the underlying reaction mechanism. Therefore, in the reduction of selenate by chromous ions it might be expected that the rate determining step directly involves chromous, selenate and hydrogen ions. Since these ions are all involved in the reaction, the mechanism is complex. The probability of three or more molecules coming closer and colliding with one another at the same time is much less than in case of bi molecular reactions (Upadhyay, 2006).

To simplify the understanding of the mechanism, the electron transfer mechanism can be considered first and the effect of H\(^+\) can be considered later. At a constant proton concentration, the reaction rate depends on the concentration of selenate and chromous ions. Klaning and Sehested (1986) reported that the Se(V) species (SeO\(_3^{−}\)) as a short-lived intermediate of selenate can be produced at pH below 11 by pulse radiolysis. Mokmeli et al. (2013) suggested that the reaction between selenate and cuprous ions proceed through the formation of a short-lived intermediate species Se(V) which is reduced further by cuprous ions to yield the product, Cu\(_2\)Se. Therefore, it is reasonable to assume that the reduction of selenate with chromous also takes place as two subsequent one-electron transfers as shown in Eq. (6-2) and (6-3).
Step 1: \[ \frac{k_1}{k_{-1}} \text{Se}(\text{VI}) + \text{Cr}^{2+} \rightleftharpoons \text{Se}(\text{V}) + \text{Cr}^{3+} \quad (6-2) \]

Step 2: \[ \frac{k_2}{k_{-2}} \text{Se}(\text{V}) + \text{Cr}^{2+} \rightleftharpoons \text{Se}(\text{IV}) + \text{Cr}^{3+} \quad (6-3) \]

Mokmeli et al. (2013) reported that the reduction of Se(IV) with cuprous ions is extremely rapid. Ladriere (1973) showed that selenate reduction to selenite is the rate determining step and that all subsequent steps have faster rates. Also, in preliminary experiments in this work it was observed that, when selenite and chromous solution were mixed together, red selenium immediately formed. Therefore, the reduction of intermediate product Se(IV) by chromous ions is also expected to be rapid, but the products are different.

**First scenario:**

Assuming that the equilibrium in the first step (Eq. (6-2)) is rapidly established, while the second step (Eq. (6-3)) is slow and determines the rate of the overall reaction, the following relationship exists:

\[ k_1[\text{Se(IV)}][\text{Cr}^{2+}] = k_{-1}[\text{Se}(\text{V})][\text{Cr}^{3+}] \quad (6-4) \]

\[ [\text{Se}(\text{V})] = \frac{k_1[\text{Se(IV)}][\text{Cr}^{2+}]}{k_{-1}[\text{Cr}^{3+}]} \quad (6-5) \]

Therefore, the rate equation can be written as

\[ \text{Reaction rate} = k_2[\text{Se}(\text{V})][\text{Cr}^{2+}] = k_2 \frac{k_1[\text{Se}(\text{V})][\text{Cr}^{2+}]^2}{k_{-1}[\text{Cr}^{3+}]} - k_{-2}[\text{Se}(\text{IV})][\text{Cr}^{3+}] \quad (6-6) \]
Considering the reduction potential for Se(V)/Se(IV) (2.33 V vs. SHE) (Klaning and Sehested, 1986) is much higher than the standard potential of Cr(III)/Cr(II) (-0.42 V vs. SHE), \( k_2 \) is considered very small (zero) in the presence of a sufficient amount of chromous ions, and Eq. (6-6) can be simplified to:

\[
\text{Reaction rate} = k_2[\text{Se(V)}][\text{Cr}^{2+}] = k_2 \frac{k_1[\text{Se(V)}][\text{Cr}^{2+}]^2}{k_{-1}[\text{Cr}^{3+}]} \quad (6-7)
\]

In Eq. (6-6) and (6-7), the reaction order with respect to chromous concentration is in conflict with the first order reaction obtained in the kinetics experiments.

**Second scenario:**

If the Reaction (6-2) is not at equilibrium while the second step (Eq. (6-3)) is the rate-determining step, the rate equation can be expressed as:

\[
\text{Reaction rate} = k_1[\text{Se(VI)}][\text{Cr}^{2+}] - k_{-1}[\text{Se(V)}][\text{Cr}^{3+}] = k_2[\text{Se(V)}][\text{Cr}^{2+}]
\]

\[
[\text{Se(V)}] = \frac{k_1[\text{Se(VI)}][\text{Cr}^{2+}]}{k_{-1}[\text{Cr}^{3+}] + k_2[\text{Cr}^{2+}]}
\]

\[
\text{Reaction rate} = k_2[\text{Se(V)}][\text{Cr}^{2+}] - k_{-2} \text{[Se(IV)][Cr}^{3+}]
\]

\[
= \frac{k_1k_2[\text{Se(VI)}][\text{Cr}^{2+}]^2}{k_{-1}[\text{Cr}^{3+}] + k_2[\text{Cr}^{2+}]} - k_{-2}[\text{Se(IV)}][\text{Cr}^{3+}]
\]

The rate equation is more complicated. This is again in conflict with the first order reaction. With the consideration of \( K_2 \) as zero, the reaction rate equation can be simplified as:

\[
\text{Reaction rate} = \frac{k_1k_2[\text{Se(VI)}][\text{Cr}^{2+}]^2}{k_{-1}[\text{Cr}^{3+}] + k_2[\text{Cr}^{2+}]} \]
At $k_1/k_2[Cr^{3+}] \ll [Cr^{2+}]$, the reaction rate can further be simplified as:

\[
\text{Reaction rate} = k_1[\text{Se(VI)}][Cr^{3+}] = k_2[\text{Se(V)}][Cr^{2+}]
\]

The reaction rate of Step 1 is equal to that of Step 2. This is just a special case with negligible reverse reaction rates for both steps.

**Third Scenario**:

Assuming that step 1 is slow and determines the rate of the overall reaction, the rate equation can be expressed as:

\[
\text{Reaction rate} = k_1[\text{Se(VI)}][Cr^{2+}] - k_1[\text{Se(V)}][Cr^{3+}]
\]

(6-8)

The redox potential for Se(VI)/Se(V) (-0.03 V vs. SHE (Klaning and Sehested, 1986) is much higher than that of Cr(III)/Cr(II) (-0.42 V vs. SHE). Se(V) is very reactive and the redox potential for Se(V)/Se(IV) is 2.33 V vs. SHE. Se(V) should be immediately reduced by chromous ions and the Se(V) concentration is expected to be extremely low. Therefore, the reverse reaction is negligible and Cr(III) should not have any effect on the rate. The rate equation can be simplified as Reaction (6-9).

\[
\text{Reaction rate} = k_1[\text{Se(VI)}][Cr^{3+}]
\]

(6-9)

Based on this mechanism, the rate equation is first order with respect chromous ion concentration which is in consistence with the kinetics results. The kinetic expression, based on this mechanism, was derived and shown to fit the experimental kinetic data.

**6.1 Effect of Hydrogen ions**

$H_2SeO_4$ is strong acid (pKₐ = -3) and completely dissociates to $HSeO_4^-$ while the dissociation of $HSeO_4^-$ to $SeO_4^{2-}$ depends on the pH. According to the distribution of the selenate
species shown in Figure 6-1, the biselenate (HSeO$_4^-$) concentration increases with increasing proton concentration while the selenate (SeO$_4^{2-}$) concentration decreases with increasing proton concentration. In the reduction of Se(VI) with chromous ions either HSeO$_4^-$ or SeO$_4^{2-}$ could take part in the reaction. If the reaction of SeO$_4^{2-}$ with Cr(II) is the rate-determining step, the reaction rate should decrease with increasing proton concentration as the SeO$_4^{2-}$ concentration decreases. However according to the kinetics results discussed in Chapter 5, the reaction rate increases with increasing proton concentration. If the reaction of HSeO$_4^-$ with Cr(II) is the rate-determining step, the reaction rate should increase with increasing proton concentration at a decreasing rate. Based on the change in the HSeO$_4^-$ concentration with the proton concentration, the apparent reaction order with respect to the proton concentration are calculated from the slope of the curve and summarized in Table 6-1. The reaction order with respect to the proton concentration increases from 0.22 to 0.82 with decreasing proton concentration from 0.1 to 0.00625M. According to the kinetics results, the reaction order with respect to the proton concentration is calculated as 0.98. Therefore, the rate-determining step is not just the reaction of HSeO$_4^-$ or SeO$_4^{2-}$ with Cr(II).

Table 6-1: Reaction order with respect to the proton concentration at different proton concentrations based on the change in HSeO$_4^-$ concentration

<table>
<thead>
<tr>
<th>[H+] / M</th>
<th>0.1</th>
<th>0.05</th>
<th>0.025</th>
<th>0.0125</th>
<th>0.00625</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent reaction order</td>
<td>0.22</td>
<td>0.36</td>
<td>0.53</td>
<td>0.69</td>
<td>0.82</td>
</tr>
</tbody>
</table>
If the rate-determining step was the reaction of HSeO$_4^-$ or SeO$_4^{2-}$ with Cr(II), the reaction rate would significantly decrease with increasing ionic strength. In fact, based on the kinetics results (effect of ionic strength) the ionic strength has a very little effect on the reaction rate. Therefore, there is probably a neutral species that is involved in the rate-determining step so that the reaction rate is not sensitive to the ionic strength.

Wells and Salam (1968) reported that Cr(II) complexes with sulfate to form CrSO$_4$(aq) and the CrSO$_4$(aq) enhance the reduction of hydrazine by Cr(II). According to the similarity of selenate and sulfate, Cr(II) could possibly complex with Se(VI) first. Philippini et al. (2013) showed that the selenate ions can make uncharged complexes (MSeO$_4$) with divalent cations. Unfortunately, there is no thermodynamic data available on CrSeO$_4$ complexation. The CrSeO$_4$ complex may first form via a pre-equilibrium according to the following reaction:

![Figure 6-1: Fraction of HSeO$_4^-$ as a function of hydrogen ion concentration based on pKa$_2$ = 1.7 (Lide, 2005)](image-url)
\[
\text{Cr}^{2+} + \text{SeO}_4^{2-} \rightarrow \text{CrSeO}_4^{(aq)} \quad \text{(6-10)}
\]

Then CrSeO\(_4\) reacts with protons, resulting in the transfer of electrons from Cr(II) to Se(VI) to produce Se(V). Klaning and Sehested (1986) detected two Se(V) species as HSeO\(_4^{2-}\) at pH above 12 and SeO\(_3^{-}\) at pH below 11. SeO\(_4^{2-}\) can be reduced to HSeO\(_4^{2-}\) first and then converted to SeO\(_3^{-}\).

The following reactions can be proposed:

\[
\begin{align*}
\text{CrSeO}_4^{(aq)} + \text{H}^+ &\rightarrow \text{HSeO}_4^{2-} + \text{Cr}^{3+} \quad \text{(6-11)} \\
\text{HSeO}_4^{2-} + \text{H}^+ &\rightarrow \text{SeO}_3^{-} + \text{H}_2\text{O} \quad \text{(6-12)}
\end{align*}
\]

As a pre-equilibrium is established, there is the following relationship:

\[
K = \frac{a_{\text{CrSeO}_4}}{a_{\text{Cr}^{2+}}a_{\text{SeO}_4^{2-}}}
\]

where \(K\) is an equilibrium constant.

\[
[\text{CrSeO}_4] = \frac{\gamma_{\text{Cr}^{2+}} \gamma_{\text{SeO}_4^{2-}}}{\gamma_{\text{CrSeO}_4}} K[\text{Cr}^{2+}][\text{SeO}_4^{2-}]
\]

where \(\gamma_{\text{Cr}^{2+}}\) is the activity coefficient of \(\text{Cr}^{2+}\), \(\gamma_{\text{SeO}_4^{2-}}\) the activity coefficient of \(\text{SeO}_4^{2-}\), \(\gamma_{\text{CrSeO}_4}\) the activity coefficient of \(\text{CrSeO}_4\).

\[
\frac{d[\text{Se}(\text{VI})]}{dt} = -\frac{k \gamma_{\text{Cr}^{2+}} \gamma_{\text{SeO}_4^{2-}}}{\gamma_{\text{CrSeO}_4}} K[\text{H}^+][\text{Cr}^{2+}][\text{SeO}_4^{2-}]
\]

Therefore, if Reaction 6-11 is the rate-determine step, the reaction orders with respect to the concentrations of chromous ions, selenate and hydrogen ions are all one (as shown above) and the reaction rate is independent of ionic strength, which is consistent with the experimental results.

If Reaction 6-12 is the rate-determining step, the reaction order with respect to the concentration
of hydrogen ions is 2 and the reaction rate should change with ionic strength. Therefore, Reaction 6-11 is more likely to be the rate-determining step in selenate reduction with chromous ions.

CrSeO$_4$(aq) is a neutral species and therefore the ionic strength has very little effect on the reaction rate. This was observed in the kinetics experiments as in the absence of sulfate ions the reaction rate was found to be independent of the ionic strength. There is no data on the stability constant of Cr$_2^+$ - SeO$_4^{2-}$. The stability constant of CrSeO$_4$ complex should be very large so that the change in the pH and ionic strength have little effect on its concentration. The CrSeO$_4$ concentration decreases very slightly with increasing proton concentration and thus the apparent reaction order with respect to the proton concentration is slightly less than 1.0. It was also observed in the kinetics experiments that the reaction kinetics is independent of sulfate concentration, suggesting that the rate-limiting step does not directly involve sulfate. This result is consistent with the proposed mechanism.

Cr(II) is generally oxidized only to Cr(III), but in some cases, it is oxidized to Cr(IV) as a short-live intermediate (Cannon, 1980). Therefore, there is a possibility that Se(VI) is reduced to Se(IV) through two-electron transfer while Cr(II) is oxidized to Cr(IV). If two-electron transfer occurs for the reduction of selenate by chromous ions, there are the following possible reactions:

$$\text{CrSeO}_4 + H^+ \rightarrow \text{HSeO}_4^{3-} + \text{Cr(IV)} \quad (6-13)$$

$$\text{Cr(IV)} + \text{Cr(II)} \rightarrow 2\text{Cr(III)} \quad (6-14)$$

If reaction 6-13 is the rate-determining step, the rate equation is also consistent with the experimental results. If reaction 6-13 is not the rate-determining step, selenite species can be built up by the reaction of HSeO$_4^{3-}$ with hydrogen ions and there will be more complicated rate equation. Besides, selenite species rapidly react with Cr(II) to produce elemental selenium. This is not
consistent with the experimental results. Therefore, reaction 6-13 is more likely the rate-determining step. The reaction of Cr(IV) with Cr(II) produces Cr(III) dimer (Ardon and Plane, 1959). Therefore, there is a need to detect chromic dimer to confirm the possibility of the two electron transfer mechanism. In addition, the reduction potential of Cr(IV)/Cr(III) couple is 2.20 V vs. SHE (Bard et al., 1986). The oxidation of Cr(III) to Cr(IV) is less likely.

6.2 Reaction products

As discussed in the stoichiometry studies, at a Cr(II)/Se(VI) molar ratio of 8 or higher, H₂Se is only produced while at a Cr(II)/Se(VI) molar ratio of below 8 elemental selenium is also produced. The fraction of Cr(II) used for the formation of H₂Se decreases with decreasing Cr(II)/Se(VI) molar ratio and increasing hydrogen ion concentration. Although the reduction of Se(VI) to Se(V) as the rate-determining step is slower than those of the successive reduction steps, there might still be some intermediate products accumulated in the solution. If there is not a sufficient amount of Cr(II) in the solution to reduce all intermediate products to H₂Se, these intermediate products are only reduced to elemental selenium. At a lower Cr(II)/Se(VI) ratio, a lesser amount of chromous ions is available to reduce intermediate products to H₂Se.

The rate of the first step as the rate-determining step increases with increasing hydrogen ion concentration. If the rates of the reduction of intermediate products do not increase or increase less than the rate determining step, more intermediate products are produced at higher hydrogen ion concentration and a lesser amount of Cr(II) is available to reduce these intermediate products. This results in the formation of less H₂Se and more elemental selenium. When there is no Cr(II) available, intermediate products can react with H₂Se or even possibly reach with each other to produce elemental selenium.
6.3 Summary

The kinetics study showed that the rate of selenate reduction by chromous ions is directly dependent on the concentration of selenate, chromous, and hydrogen ions. Therefore, in the reduction of selenate by chromous ions the rate determining step involves chromous, selenate and hydrogen ions. The reduction of selenate with chromous also takes place as two subsequent one-electron transfers as shown below:

\[
\begin{align*}
\text{Step 1: } & \quad \text{Se(VI)} + \text{Cr}^{2+} \rightleftharpoons \text{Se(V)} + \text{Cr}^{3+} \\
& \quad k_1 \quad k_{-1}
\end{align*}
\]

\[
\begin{align*}
\text{Step 2: } & \quad \text{Se(V)} + \text{Cr}^{2+} \rightleftharpoons \text{Se(IV)} + \text{Cr}^{3+} \\
& \quad k_2 \quad k_{-2}
\end{align*}
\]

Based on the reaction kinetics data, the reduction of Se(VI) to Se(V) is the rate determining step. Therefore, the rate equation can be expressed as:

\[
\text{Reaction rate} = k_1 [\text{Se(VI)}][\text{Cr}^{2+}]
\]

Based on this mechanism, the rate equation is first order with respect to chromous ion concentration which is consistent with the kinetics results.

Ionic strength has a very little effect on the reaction rate, indicating that at least one neutral species is involved in the rate-determining step. The CrSeO₄ complex may first form via a pre-equilibrium established according to the following reaction.

\[
\text{Cr}^{2+} + \text{SeO}_4^{2-} = \text{CrSeO}_4^{\text{aq}}
\]

The CrSeO₄ reacts with protons, resulting in the transfer of electron from Cr(II) to Se(VI) to produce Se(V). Se(V) is further reduced to Se(IV).
CrSeO$_4$(aq) + H$^+$ → HSeO$_4^{2-}$ + Cr$^{3+}$

HSeO$_4^{2-}$ + H$^+$ → SeO$_3^{-}$ + H$_2$O

As the reaction of CrSeO$_4$ with protons is the rate-determining step, more chromous ions are consumed to reduce selenate at a lower pH and produced more intermediate products. Therefore, a lesser amount of chromous ions is available to reduce the intermediate products to hydrogen selenide.
Chapter 7: Industrial Applications for Selenate Removal Processes

7.1 Introduction

The process of removal of selenate by chromous ions has the potential to be considered as a new hydrometallurgical selenium removal technology. As discussed in chapter 5, selenate is completely reduced to hydrogen selenide by chromous ions. The reduction rate can be expressed as a function of temperature, and concentrations of selenate, chromous and hydrogen ions. Although selenate can be completely reduced to hydrogen selenide, the removal of hydrogen selenide from solution needs to be studied to show the viability of process as a method to remove selenium. Therefore, one of the objectives of this study was to find the feasibility of hydrogen selenide removal using different methods. The results are presented in the following section. Additionally, a simple overview flow sheet is also proposed, incorporating chromous generation, selenate reduction, hydrogen selenide removal, and chromic precipitation units. A schematic of the flow sheet and a brief description of each unit is given in the following section.

7.2 Hydrogen Selenide Removal from Solution

Hydrogen selenide is by far the most toxic inorganic compound of selenium and has to be removed from the solution. Different methods were investigated in this work to identify a feasible method for removing hydrogen selenide from solution.

In a set of preliminary tests, nitrogen gas was used at different flow rates and sparger pore sizes to remove hydrogen selenide from the solution. As hydrogen selenide solubility is quite high (7g/L at room temperature (Dubeau et al., 1971)), the removal of hydrogen selenide by purging N2 gas was not efficient to completely remove hydrogen selenide and a very long time (several hours) was needed.
Hydrogen selenide is highly reactive and forms metal selenides with most transition metals. Copper can also form very stable compound of copper selenide with selenium (Mokmeli et al., 2013). Cupric oxide, cuprous oxide and cupric sulfate can possibly react with hydrogen selenide to produce highly insoluble copper selenide. However, there is no information about the reaction of copper oxide and copper sulfate with hydrogen selenide in the literature.

The reaction of CuO, Cu$_2$O and CuSO$_4$ and H$_2$Se may be written as follows:

CuO + H$_2$Se = CuSe + H$_2$O \[ \Delta G^\circ = -161.5 \text{ kJ/mol} \quad K = 2.0 \times 10^{28} \] (7-1)

Cu$_2$O + H$_2$Se = Cu$_2$Se + H$_2$O \[ \Delta G^\circ = -161.3 \text{ kJ/mol} \quad K = 1.8 \times 10^{28} \] (7-2)

Cu$^{2+}$ + H$_2$Se = CuSe + 2H$^+$ \[ \Delta G^\circ = -128.6 \text{ kJ/mol} \quad K = 5.3 \times 10^{20} \] (7-3)

The free energy changes for the above reactions are calculated based on the data given in Table 7-1. The reaction free energies for all three reactions are very negative and therefore hydrogen selenide should be removed from the solution completely. However, according to the review by (Olin et al., 2005) the data for CuSe and Cu$_2$Se are quite uncertain.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H$^+$</th>
<th>H$_2$O</th>
<th>Cu$^+$</th>
<th>Cu$^{2+}$</th>
<th>Cu$_2$O</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Energy</td>
<td>0</td>
<td>-237.18</td>
<td>50.3</td>
<td>65.7</td>
<td>-148.1</td>
<td>-134</td>
</tr>
<tr>
<td>Compound</td>
<td>Se$^{2-}$</td>
<td>H$_2$Se</td>
<td>HSe$^-$</td>
<td>CuSe</td>
<td>Cu$_2$Se</td>
<td></td>
</tr>
<tr>
<td>Free Energy</td>
<td>128.6</td>
<td>21.5</td>
<td>43.5</td>
<td>-36.8</td>
<td>-50.9</td>
<td></td>
</tr>
</tbody>
</table>

*The data for selenium compounds are from Olin et al. (2005) while the other data are from Bard et al. (1985).

In aqueous solution, the following equations also need to be considered:

Cu$^{2+}$ + Se$^{2-}$ = CuSe \[ \Delta G^\circ = -231.8 \text{ kJ/mol} \quad K = 3.1 \times 10^{40} \] (7-4)

2Cu$^+$ + Se$^{2-}$ = Cu$_2$Se \[ \Delta G^\circ = -280.6 \text{ kJ/mol} \quad K = 1.1 \times 10^{49} \] (7-5)
The equilibrium constants of these reactions are so large which means the solubility of CuSe and Cu$_2$Se are very low. Furthermore, the concentration of Se$^{2-}$ in the solution is dependent on the pH of the solution. The hydrogen selenide dissociation in water is governed by the following reactions (Levy and Mysers, 1990; Lide, 2005):

$$\begin{align*}
H_2Se &= \text{HSe}^- + H^+ & K_1 = 1.3 \times 10^{-4} \\
\text{HSe}^- &= \text{Se}^{2-} + H^+ & K_2 = 6.9 \times 10^{-16}
\end{align*} \tag{7-6, 7-7}$$

In dilute solution, the concentrations of H$_2$Se and Se$^-$ can be expressed as follows:

$$\begin{align*}
[H_2Se] &= \text{[HSe}^-][H^+)/K_1 \\
[Se^{2-}] &= K_2\text{[HSe}^-]/[H^+] \\
[H_2Se] + [\text{HSe}^-] + [\text{Se}^{2-}] &= [\text{HSe}^-][H^+)/K_1 + [\text{HSe}^-] + K_2[\text{HSe}^-]/[H^+] = C_{\text{total H}_2\text{Se}} \\
[\text{HSe}^-] &= C_{\text{total H}_2\text{Se}} /((H^+)/K_1 + 1 + K_2/[H^+])
\end{align*}$$

The distribution of hydrogen selenide species as a function of pH is calculated based on the above equations and shown in Figure 7-1. At pH 2 or lower, over 99% of hydrogen selenide exists as H$_2$Se while at pH 4 to 6, HSe$^-$ is the main species. At pH 6 to 13, over 99% of hydrogen selenide exists as HSe$^-$ and finally at pH above 13, HSe$^-$ and Se$^{2-}$ are the main species. Figure 7-2 shows the fraction of Se$^{2-}$ as a function of pH. As shown in Figure 3, the fraction of Se$^{2-}$ is inversely proportional to the square of [H$^+$] at pH below 4 while it is inversely proportional to [H$^+$] at pH above 5. The fraction of Se$^{2-}$ at pH 0, 2, 4, 5, 6 and 8 is $8.6 \times 10^{-20}$, $8.5 \times 10^{-16}$, $5.6 \times 10^{-12}$, $3.7 \times 10^{-12}$, $6.5 \times 10^{-11}$ and $6.6 \times 10^{-8}$ respectively. Therefore, pH is one of the parameters that should affect the removal of hydrogen selenide significantly.
Figure 7-1: Distribution of hydrogen selenide as a function of pH

Figure 7-2: Fraction of $\text{Se}^{2-}$ as a function of pH
7.2.1 **Hydrogen Selenide Removal with the Use of Copper oxide**

Hydrogen selenide removal was studied by the addition of different amounts of cupric oxide at different pHs. All the experiments were performed at room temperature, constant stirring speed and under an argon atmosphere. The general procedures for the experiments are given in Chapter 3.

The hydrogen selenide removal as a function of time at different molar ratios of CuO to H$_2$Se is shown in Figure 7-3. It was observed that the hydrogen selenide removal increased rapidly within the first few minutes and then increased slightly over time. At pH 3.5 and an initial H$_2$Se concentration of 0.00220 M, the hydrogen selenide removal increased from 28% to only 53% with increasing CuO/H$_2$Se molar ratio from 10 to 25. However, according to the free energy of the reaction available in the literature, hydrogen selenide should be completely removed at this pH. The slow increase in the hydrogen selenide removal after several minutes probably resulted from the precipitation of CuSe on the surface of CuO that covers the active CuO surface and prevents the further reaction of CuO with H$_2$Se.
Figure 7-3: Hydrogen selenide removal as a function of time at CuO/H\textsubscript{2}Se molar ratios of 10, 15 and 25, an initial H\textsubscript{2}Se concentration of 0.0022 M, 20 °C and pH 3.5.

Figure 7-4 shows the effect of solution pH on the removal of H\textsubscript{2}Se by CuO from 0.00220 M H\textsubscript{2}Se solution at a CuO/H\textsubscript{2}Se molar ratio of 10. The hydrogen selenide removal increased from 28 to 99.9% with increasing pH from 3.5 to 8. This behavior can be attributed to the shift of hydrogen selenide species from H\textsubscript{2}Se to Se\textsuperscript{2-} with increasing pH as shown in Figure 7-1. Whether CuSe dissolves or precipitates in the solution directly depends on the concentrations of Cu\textsuperscript{2+} and Se\textsuperscript{2-} in the solution. If the product of Cu\textsuperscript{2+} and Se\textsuperscript{2-} concentrations is smaller than their Ksp, CuSe dissolves in the solution while if their concentration product is larger than their Ksp, CuSe precipitates. The fraction of Se\textsuperscript{2-} increases exponentially with increasing pH. For example, the fraction of Se\textsuperscript{2-} increases about 100 times with increasing pH from 2 to 3. Therefore, even if the total hydrogen selenide concentration at pH 3.0 is smaller than that of pH 2.0, the Se\textsuperscript{2-}...
concentration at pH 3.0 can still be maintained at a sufficiently high value so that the concentration product of Se\(^{2-}\) and Cu\(^{2+}\) is higher than their Ksp. Therefore, more hydrogen selenide can be removed at a higher pH.

![Figure 7-4: Hydrogen selenide removal as a function of time at a CuO/H\(_2\)Se molar ratio of 10, an initial H\(_2\)Se concentration of 0.0022 M, 20 °C and different pHs.](image)

The copper selenide formed at a higher pH blocked the CuO surface to a less degree and more CuO was available to react with H\(_2\)Se and hence more hydrogen selenide was removed at a higher pH. The copper concentration was below 0.10 mg/L at pH 4 or higher, indicating that very little CuO was dissolved in the solution. At pH 3.5, the copper concentration was 0.15 mg/L and again very small amount of CuO was dissolved into the solution.
From the XRD diffraction pattern of the reaction residue (Figure 7-5), the reaction residue consisted of about 97% CuO and 3% CuSe because the CuO/H₂Se molar ratio was 25 and most of the copper oxide did not react with H₂Se.

![XRD pattern](image)

Figure 7-5: XRD pattern of the residue after the reaction of CuO with H₂Se at a CuO/H₂Se molar ratio of 25, an initial H₂Se concentration of 0.0022 M, 20 °C and pH 3.5.

### 7.2.2 Hydrogen Selenide Removal with the Use of Copper Sulfate

To get insight into whether the hydrogen selenide removal was limited by the copper concentration in the solution, copper sulfate was added instead of CuO. The hydrogen selenide removal as a function of time at different pHs, CuSO₄ to H₂Se molar ratio of 6, and an initial hydrogen selenide concentration of 0.00220 M are shown in Figure 7-6. The reaction of hydrogen selenide with cupric ions was rapid as seen in the Figure 7-6. The hydrogen selenide removal increased from 24 to 96%
with increasing pH from 2 to 4.0. As the molar ratio of copper sulfate to hydrogen selenide was 6, the copper concentration in the solution was maintained around 0.012 M at pH of 2.0 to 4.0.

![Graph showing hydrogen selenide removal as a function of time at different pHs](image)

**Figure 7-6**: Hydrogen selenide removal as a function of time at a CuSO$_4$/H$_2$Se molar ratio of 6, 22 °C, an initial H$_2$Se concentration of 0.00220 M, 20 °C and different pHs

As indicated by Reaction 7-4, if the product of concentrations of Se$^{2-}$ and Cu$^{2+}$ is larger than their Ksp, copper selenide precipitates, otherwise Reaction 7-4 is under the equilibrium or copper selenide dissolves. The fraction of Se$^{2-}$ increases over 4000 times with increasing pH from 2 to 4 (Figure 7-2). Even if the total concentration of hydrogen selenide is very low at a higher pH, the concentration of Se$^{2-}$ can still be maintained at a sufficiently high value so that the concentration product of Se$^{2-}$ and Cu$^{2+}$ is higher than their Ksp, and CuSe still can precipitate or at least does not dissolve.
The product of concentrations of Cu\(^{2+}\) and Se\(^{2-}\) is \(1.1 \times 10^{-22}\), which is much higher than the CuSe Ksp value (3.1 \times 10^{-41}) calculated based on the free energy data. There are some uncertainties in the current free energy data available for CuSe (Olin et al., 2005). The free energy data used may be significantly higher than the real values. CuSe can be dissolved in hydrochloric acid with the evolution of H\(_2\)Se gas (Perry, 2011). The CuSe solubility may be much higher than that calculated by the available free energy data. There may be other reasons that cause hydrogen selenide not to be removed as expected from the thermodynamics data available. Further investigation should be conducted in the future to explore the inside chemistry. The quantitative XRD phase analysis (Figure 7-7) indicates that the precipitate consisted of CuSe (60.6%) and CuO (39.4%). The formation of CuO was probably due to the oxidation of CuSe by oxygen as the CuSe powder is very fine or somewhat amorphous.

Figure 7-7: XRD pattern of the precipitate after the reaction of CuO with H\(_2\)Se at a CuSO\(_4\)/H\(_2\)Se molar ratio of 6, an initial H\(_2\)Se concentration of 0.00220 M, 20 °C and pH 2.0.
7.2.3 **Hydrogen Selenide Removal with the Use of Cuprous Oxide**

Hydrogen selenide removal was also studied by addition of cuprous oxide to find whether cuprous selenide can be formed in order to improve the hydrogen selenide removal.

Figure 7-8 shows the hydrogen selenide removal efficiency as a function of time at different molar ratios of Cu$_2$O to H$_2$Se from a 0.00220 M H$_2$Se solution at pH 2. It was observed that hydrogen selenide was quickly removed within the first 10 minutes and then hydrogen selenide removal increased slightly over the time (Figure 7-8). Hydrogen selenide removal increased from 92 to 97% with increasing Cu$_2$O/H$_2$Se molar ratio from 6 to 15.

![Graph showing hydrogen selenide removal efficiency](image)

**Figure 7-8**: Hydrogen selenide removal as a function of time at a Cu$_2$Se/H$_2$Se molar ratio of 6 and 15, 22 °C, an initial H$_2$Se concentration of 0.00220 M, 20 °C and pH 2.
Hydrogen selenide removal as a function of time at pH 2.0 and 3.5 and Cu₂O to H₂Se molar ratio of 6 are shown in Figure 7-9. At pH 2.0, only about 90% of the hydrogen selenide was removed while at pH 3.5 hydrogen selenide was almost completely removed from the solution. As compared to the hydrogen selenide removal with CuO, using Cu₂O very better removal efficiencies were observed.

![Figure 7-9](image)

**Figure 7-9**: Hydrogen selenide removal as a function time at pH 2 and 3.5, an initial H₂Se concentration of 0.00220 M, 20 °C and Cu₂O/H₂Se molar ratio of 6.

The copper concentration in the solution at pH 2 reached 0.1 mg/l after 30 minutes and almost stabilized. During the reaction, some cuprous oxide dissolved and underwent the disproportionation reaction (2Cu⁺ = Cu + Cu²⁺). To avoid the dissolution of cuprous oxide in the solution, the hydrogen selenide removal with cuprous oxide can be done at a higher pH which also benefits from the higher reaction rate at an elevated pH.
The reaction residue consisted of Cu₂Se (52%), CuO(39%), Cu(5%) and Cu₃Se₂(4%) from the XRD quantitative phase analysis (Figure 7-10). The formation of metallic copper was due to the disproportional reaction of cuprous ions.

![XRD pattern of the precipitate after the reaction of Cu₂O with H₂Se at a Cu₂O/H₂Se ratio of 6, an initial H₂Se concentration of 0.0022M, 20 °C and pH 2.0](image)

Figure 7-10: XRD pattern of the precipitate after the reaction of Cu₂O with H₂Se at a Cu₂O/H₂Se ratio of 6, an initial H₂Se concentration of 0.0022M, 20 °C and pH 2.0

7.3 Industrial Application of the Method and Flow Sheet

The process of removal of selenate by chromous ions can be potentially considered as a new hydrometallurgical technology for selenium removal. Chromous ions can be generated by electrochemical reduction of chromic ions in an electrochemical cell. In Chapter 5, the kinetics of selenate reduction by chromous ions was investigated and it has been shown that selenate can be completely reduced to hydrogen selenide quite fast. The generated hydrogen selenide can be completely removed from solution by different methods such as Cu₂O addition.
In this section a simple overview of potential plant flow sheet is proposed, incorporating chromous generation, selenate reduction, hydrogen selenide removal, and chromic precipitation units. A schematic of the flow sheet is given in Figure 7-11 and a brief description of each unit is given below.

As one example\(^1\) of the application of the studied method, ERM Rescan (SeaBridge Gold 2013) has advocated the use of an ion exchange pre-treatment step to remove selenate. The wastewater from the ion exchange process meets all required selenium discharge standards. However, the eluant from the ion exchange process containing about 5-10 ppm of selenate needs to be treated to remove the eluted selenate.

A high-grade acidic chromous solution is mixed with the eluent of ion exchange process which contain 5-10 ppm of selenate to reduce selenate to hydrogen selenide. Selenate reduction reaction time can be estimated at different acidities, chromous concentration and temperatures using the suggested rate law and activation energy. By adjusting temperature and pH, the full reduction of selenate to hydrogen selenide can be completed in a reasonable time. As an example, using the suggested rate equation (Eq. 7-8 and 7-9) 10 ppm of selenate can be reduced to less than 10 ppb in one hour and half at pH 2.2, chromous concentration of 0.05 M and 50 °C. The high sensitivity of chromous to oxygen requires a proper sealed setup.

\[
\frac{d[Se(VI)]}{dt} = -k[Se(VI)][H^+][Cr^{2+}] \tag{7-8}
\]

\(^1\) As another example of the application of the studied selenium removal method, BioteQ (BioTEQ, 2013) reported an application with 363 ppb selenium in waste water before ionic exchange (IX) treatment to recover selenate. In this process, the loaded ion exchange resin is eluted with a concentrated sulphate solution (1 M) to produce an eluant containing about 10 ppm Se as selenate.
where $k_1$ is the rate constant ($\text{M}^{-2}\text{s}^{-1}$) and has the following relationship with temperature:

$$k_1 = 1.23 \times 10^{10} \exp \left( \frac{-5.87 \times 10^4}{RT} \right)$$

The reduced selenate solution ($\text{H}_2\text{Se}$ solution) is fed into another tank where it is covered, and properly sealed, to minimize oxidation of chromous/\text{H}_2\text{Se} by air. Cupric oxide or cuprous oxide can be used to remove hydrogen selenide as the precipitates of copper selenide. Probably there is a need for pH adjustment in this step since hydrogen selenide ($\text{H}_2\text{Se}$, $\text{HSe}^-$, $\text{Se}^{2-}$) is removed more efficiently at higher pH. Following hydrogen selenide removal, the copper selenide precipitates depending upon process pH, can be removed from the solution by any of known solid separations technique. After solid/liquid separation, the resulting filtrate is almost free of selenate and hydrogen selenide. The product has the composition of $\text{CuSe/Cu}_2\text{Se}$ and can be sold or stored indefinitely in this form. The copper oxide (either cuprous or cupric oxides) should be present in a quantity in excess of the stoichiometric requirements to remove all hydrogen selenide from the solution. Therefore, the product might contain $\text{CuO}$ or $\text{Cu}_2\text{O}$ as well. After the solid (copper selenide)-liquid separation, the solution is sent to a precipitation tank where the pH of the solution is adjusted to pH 5-6 for the removal of chromium from the solution. Since ammonium sulfate solutions are used to elute selenate from ion-exchange column, therefore the pH adjustment and precipitation can be accomplished through the addition of ammonium hydroxide. The resulting solution is almost free of chromic, and can be recycled to the IX circuit. The filter cake, consisting of solid $\text{Cr(OH)}_3$ can be dissolved in acidic solution to generate chromic solution and then recycled back to the chromous generation unit.
Summary

As discussed in chapter 5, selenate can be completely reduced to hydrogen selenide by chromous ions. The removal of hydrogen selenide from solution was studied to show the viability of the studied process as a method to remove selenium. From the available free energy data, hydrogen selenide should be readily removed from solution using copper (II) oxide. However, hydrogen selenide was only efficiently removed at pH higher than 6 and a higher CuO/H$_2$Se molar ratio (10 or higher) was required. The reaction of copper oxide with hydrogen selenide resulted in the
formation of cupric selenide (CuSe). The formation of CuSe on CuO particles possibly prevented the further reaction of CuO with H₂Se.

With the use of copper sulfate, the complete removal of hydrogen selenide had to be conducted at pH above 4 and a CuSO₄/H₂Se ratio above 6. The current available free energy data for CuSe may be much larger than the real one. The product of the reaction of cupric ions with hydrogen selenide was cupric selenide (CuSe).

Hydrogen selenide can be almost completely removed using cuprous oxide at pH 3.5 and Cu₂O/H₂Se molar ratio of 6 in less than 40 mins. The reaction products are cuprous selenide. Metallic copper and cupric ions are produced, due to the disproportional reaction of cuprous ions. As compared to the hydrogen selenide removal with CuO, using Cu₂O very better removal efficiencies were observed.
Chapter 8: Conclusions and Recommendations

The following are the principal conclusions resulting from the study of the electrochemical reduction of Cr(III) to Cr(II), kinetic study and mechanism of the reduction of selenate by chromous ions, and the removal of the generated hydrogen selenide from solution using copper oxide, cuprous oxide, and copper sulfate.

(1) At an initial chromic concentration of 0.1M and a current density of 200 A/m², the current efficiency of chromic reduction to chromous ions was around 80% at a Cr(III)/Cr(II) conversion of 80%. The current efficiency slightly decreased with increasing conversion of Cr(III)/Cr(II). When the Cr(III) to Cr(II) conversion exceeded 82%, the current efficiency of the reduction of chromic to chromous ions decreased relatively faster with increasing Cr(III) to Cr(II) conversion. At a Cr(III) to Cr(II) conversion of 99.9%, the current efficiency decreased to 43%. In the real industrial application, chromic ions do not need to be completely reduced to chromous ions and a lower conversion (80 to 90%) may be sufficient. In the conversion range of 80 to 90%, the current efficiency was 81 to 76% while the energy consumption was 3.5 to 5.6 kWh/kg. Therefore, chromous solution can be produced from sulfate solution through the electrolytic reduction of chromium (III) to chromium (II) and without the introduction of additional impurities at a reasonably high current efficiency.

(2) At an initial Cr(II)/Se(VI) molar ratio of 8 or above, the product of the reduction of selenate by chromous ions was always hydrogen selenide and it was independent of the solution pH. The stoichiometry of the reduction of selenate by chromous ions was found to be:

$$\text{SeO}_4^{2-} + 8\text{Cr}^{2+} + 10\text{H}^+ = \text{H}_2\text{Se} + 8\text{Cr}^{3+} + 4\text{H}_2\text{O}$$
(3) At an initial Cr(II)/Se(VI) molar ratio of less than 8, the products of the reduction of selenate by chromous ions were hydrogen selenide and elemental selenium. The yields of hydrogen selenide increases with increasing Cr(II)/Se(VI) ratio and pH. At a higher Cr(II)/Se(VI) ratio, more chromous ion are available to reduce intermediate products to hydrogen selenide. The effect of pH is related to the mechanism and kinetics of the reduction of selenate by chromous ions. At a lower pH, more chromous is consumed for the reduction of selenate and more intermediate products are produced. Therefore, a lesser amount of chromous ions is available for the reduction of intermediate products to hydrogen selenide.

(4) The reaction order with respect to the concentrations of selenate, chromous ions and hydrogen ions was investigated and found to be 1 with respect to each of them. The activation energy was investigated in the temperature range of 10 to 50 °C and calculated as 58.5 kJ/mole. The rate equation can be expressed as:

\[
\frac{d[Se^{6+}]}{dt} = -k[Se^{6+}][H^+][Cr^{2+}]
\]

where \(k_1\) is the rate constant (M\(^{-2}\)s\(^{-1}\)) and can be expressed as a function of temperature:

\[
k = 1.23 \times 10^{10} \exp\left(\frac{-5.87 \times 10^4}{RT}\right)
\]

(5) Ionic strength had almost no effect on the reaction rate, indicating that a neutral species perhaps CrSeO\(_4\) is involved in the rate-determination step. One possibility is that the CrSeO\(_4\) complex first forms and then a pre-equilibrium is established. CrSeO\(_4\) would then react with protons, resulting in the transference of an electron from Cr\(^{2+}\) to Se(VI) to produce Se(V).

\[
Cr^{2+} + SeO_4^{2-} = CrSeO_4(aq)
\]
\[
\text{CrSeO}_4^{(aq)} + \text{H}^+ \rightarrow \text{HSeO}_4^{2-} + \text{Cr}^{3+}
\]

\[
\text{HSeO}_4^{2-} + \text{H}^+ \rightarrow \text{SeO}_3^- + \text{H}_2\text{O}
\]

(6) The suggested reduction mechanism is based on the one electron transfer, to form short lived Se(V) species followed by reduction of Se(V) to Se(IV) and ultimately to H\(_2\)Se. As the transfer of the first electron is the rate-determining step, at lower pH the reaction is fast and thus more chromous ions are consumed to reduce Se(VI) and produce more intermediate products. Therefore, a lesser amount of chromous ions is available to reduce the intermediate products to hydrogen selenide.

(7) The generated hydrogen selenide was only efficiently removed with the use of CuO at pH above 6 and at a CuO/H\(_2\)Se molar ratio of 10 or higher. The reaction of copper oxide with hydrogen selenide resulted in the formation of cupric selenide (CuSe).

(8) With the use of copper sulfate, the complete removal of hydrogen selenide was achieved at pH above 4 and a CuSO\(_4\)/H\(_2\)Se molar ratio above 6. The product of the reaction of cupric ions with hydrogen selenide was cupric selenide (CuSe).

(9) Hydrogen selenide can be completely removed from solution using cuprous oxide at pH 3.5. The reaction product is cuprous selenide. Metallic copper and cupric ions are also produced, perhaps due to the disproportional reaction of cuprous ions. To avoid the dissolution of cuprous oxide in the solution the hydrogen selenide removal can be done at a higher pH of the solution.
8.1 Recommendations for Future Work

There are many factors that influence the electrochemical reduction of chromic to chromous. A high electrical conductivity of electrolyte can reduce the cell voltage and improve the current distribution on the three-dimension graphite felt and consequently can improve the cathodic current efficiency of the reduction of chromic to chromous. Therefore, supporting electrolyte should be used to increase the electrolyte conductivity for generation of chromous economically. Suitable supporting electrolyte can be selected according to the industrial application. Sodium and ammonium sulfate solutions are used to elute selenate from ion-exchange column. Therefore, it would be worthwhile to explore the generation of chromous ions using sodium or ammonium sulfate as supporting electrolytes.

Hydrogen evolution on the surface of cathode decreases the efficiency of chromous generation, therefore, an important focus of the future cell design should be the minimization of hydrogen evolution. Hydrogen evolution is dependent on the pH or acidity of the electrolyte. A higher pH or lower acid concentration results in a slower hydrogen evolution and consequently a higher current efficiency of chromic reduction to chromous. With increasing pH, the chromic species shifts from Cr$^{3+}$, Cr(OH)$^{2+}$ and Cr(OH)$_2^+$, which may affect the reduction of chromic. The effect of pH should be investigated in the pH range of 1 to 4 without the precipitation of chromic hydroxide.

The hydrogen evolution overpotential on graphite is higher than that on titanium and stainless steel. Therefore, titanium or stainless steel supporting frames for graphite felt can be coated with carbon paste to increase the hydrogen overpotential to suppress hydrogen evolution and consequently to improve the current efficiency of the reduction of chromic to chromous.
In the reduction of selenate by chromous ions, a neutral species (probably CrSeO$_4$ complex) is involved in the rate determining step. However, it has not been identified in current study. A future fundamental study could focus on the identification of the natural species involved in the reaction mechanism and evaluation of its stability using various methods and determination of formation constant to confirm the proposed mechanism.

Hydrogen selenide can be completely removed using cuprous oxide. However, only a few tests were conducted to investigate the feasibility of the proposed method. The usage of cuprous oxide for these tests was 6 times that stoichiometry required ratio and a portion of cuprous oxide was dissolved in the solution. A systematic investigation should be carried out to minimize the usage of cuprous oxide and understand the reactions occurring. Temperature and pH affect the removal of hydrogen selenide and the dissolution of cuprous oxide. Therefore, the effect of temperature and pH should be investigated to find an optimized condition. Furthermore, the effect of seeding on the removal efficiency of hydrogen selenide needs to be studied.

The product of concentrations of Cu$^{2+}$ and Se$^{2-}$ in the solution was 1.1×10$^{-22}$, which is much higher than the CuSe Ksp value (3.1×10$^{-41}$) calculated based on the free energy data. There are some uncertainties in the current free energy data available. The free energy data used may be significantly higher than the real values. The CuSe solubility may be much higher than that calculated by the available free energy data. There may be other reasons that cause hydrogen selenide precipitation as expected. Further investigation should be conducted in the future to explore the inside chemistry.

The work described in Chapter 7 could be extended to other industrial methods for hydrogen selenide removal such as purging of N$_2$ gas into the reduced selenate solution and
capturing of generated hydrogen selenide through Cu$_2$O or NaOH scrubbers to prevent the introduction of impurities into the selenate solution.

Although each of the steps from generating chromous ions to selenate reduction and hydrogen selenide removal have been proven individually, a test of the complete process is needed to show its viability as a whole. To achieve this and commercialize the selenate removal process with the use of chromous, the whole process needs to be performed in sequence starting with a chromous generation system continuously linked to the treatment of a real IX eluent containing selenate and sulfate, hydrogen selenide removal with cuprous oxide, precipitation of chromic ions as chromic hydroxide, the dissolution of chromic hydroxide and finally recycle of chromic back to the chromous generation cell.

8.2 Concluding Remarks
The reduction and removal of selenate using chromous ions shows great promise as a novel technique for the removal of selenium from selenium containing solutions. Chromous ions can be efficiently produced through electrochemical reduction of chromic ions. Selenate ions are effectively reduced to hydrogen selenide in a reasonable time comparing to the existing selenium removal processes. Using the proposed equation for the rate of selenate reduction by chromous, the selenate concentration can be well predicted over the course of reaction and finally the generated hydrogen selenide can be completely removed from solution using cuprous oxide and converted to a valuable product.

In combination with the current IX processes, selenate is first enriched using the ion-exchange method and then efficiently removed from waste water using the chromous solution. This provides a novel solution for effective selenate removal for wastewater treatment. Regarding the problem associated with the current technologies for the selenate removal, the invention of this
process is significant in the treatment of selenate-containing wastewater and further development of selenate removal using chromous ions would definitely worth further study with the view of implementing it.
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Appendix

Appendix A Different Components of Chromous Generation Electrolytic Cell

Block 1 and 2 view from left

Block 3 view from right

Painted metal frame

Carbon Graphite Cathode
Appendix B  Determination of hydrogen ion activity coefficients and sulfate species distribution

In order to maintain constant concentration of H⁺ in the kinetics experiments, different pH buffering solutions were made by the addition of H₂SO₄ to 0.150 M Na₂SO₄ solution. Under the condition studied in this work (pH<2.2), H₂SO₄ completely dissociates to HSO₄⁻ and H⁺. Therefore, the addition of HSO₄⁻ and H⁺ can be considered instead of addition of H₂SO₄ in the solution. The following equilibrium reaction needs to be considered for calculations:

\[
\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+ \quad \text{(B1-1)}
\]

I: C₁  C₂  C₁
E: C₁-x  C₂ + x  C₁ + x

\[
K_{a2} = \frac{(C₁ + x)(C₂ + x)}{(C₁ - x)} \quad \text{(B1-2)}
\]

\[
x^2 + (C₁+C₂+K_{a2})x +C₁(C₂-K_{a2}) = 0
\]

where C₁ is the initial concentration of H₂SO₄ or HSO₄⁻ and H⁺, C₂ is the initial concentration of Na₂SO₄ (0.150 M), and x is the change in the concentration. The sulfuric acid second dissociation constant (K_{a2}) is 0.0102 (Lide, 2005). Na⁺ can be associated with SO₄^{2-} to form NaSO₄⁻ ion pair. However, the association constant is only 0.22 (Leaist and Goldik, 2001). For instance, Garrels and Thompson (1962) found that only 1% of sodium is associated with sulfate at a sodium sulfate concentration of about 0.5M. Therefore, the association of Na⁺ with SO₄^{2-} is negligible in our studied concentrations and is not considered in ionic strength calculation.

In order to accurately calculate the distribution of sulfate species, the activity coefficients of all species needs to be determined. The accurate measurement of activity coefficients can be difficult and beyond the scope of this study. However, the hydrogen ion activity can easily be
measured using a pH meter. The activity coefficient of hydrogen can be well estimated using a similar solution with a known ionic strength and activity coefficient of hydrogen ions. In this study, the activity coefficient of hydrogen ions in $\text{H}_2\text{SO}_4$-$0.150 \text{ M Na}_2\text{SO}_4$ or $\text{H}_2\text{SO}_4$-$0.150 \text{ M Na}_2\text{SO}_4$-$\text{NaClO}_4$ solution is considered to be approximately the same as in the $\text{HClO}_4$-$\text{NaClO}_4$ solution with the equal ionic strength. If the pH and hydrogen ion activity coefficient are known, the hydrogen concentration can be calculated. According to the Reaction A1-1, the concentrations of $\text{HSO}_4^-$ and $\text{SO}_4^{2-}$ can be calculated by $2C_1 - [\text{H}^+]$ and $C_2 + [\text{H}^+] - C_1$ respectively.

At first, the concentrations of all sulfate species were calculated assuming that the activity coefficients of all species are 1. Based on the calculated concentrations of these sulfate species, the ionic strength contributed from the sulfate species and sodium ions is around 0.50 at pH 1 to 2.2. The pH values of perchloric acid and sodium perchlorate solutions with ionic strengths of 0.5, 1.0, 1.5 and 2.0 are summarized in Table B1. The corresponding activity coefficients calculated from the pH are 1.02, 1.32, 1.70 and 2.34 respectively. These four activity coefficients were used to calculate the proton concentration of the four solutions ($0.150 \text{M Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$, $0.150 \text{M Na}_2\text{SO}_4/0.50 \text{M NaClO}_4/\text{H}_2\text{SO}_4$ and $0.150 \text{M Na}_2\text{SO}_4/1.0 \text{M NaClO}_4/\text{H}_2\text{SO}_4$ and $0.150 \text{M Na}_2\text{SO}_4/1.50 \text{M NaClO}_4/\text{H}_2\text{SO}_4$) respectively. Knowing the $\text{H}^+$ concentration, the concentrations of $\text{HSO}_4^-$ and $\text{SO}_4^{2-}$ can be calculated based on Reaction B1-1.

$$[\text{H}_2\text{SO}_4] = C_1 - ([\text{H}^+] - C_1) = 2C_1 - [\text{H}^+]$$

$$[\text{SO}_4^{2-}] = C_2 + ([\text{H}^+] - C_1) = C_2 + [\text{H}^+] - C_1$$

The pH, $\text{H}^+$, $\text{HSO}_4^-$, $\text{SO}_4^{2-}$ and ionic strength as a function of sulfuric acid sulfuric acid are summarized in Tables B1-2 to B1-5. The ionic strengths of four solutions are nearly constant in the pH range from 1.0 to 2.2. They are very close to 0.5, 1.0, 1.5 and 2.0 respectively, which are the same as those of the corresponding $\text{HClO}_4$-$\text{NaClO}_4$ solutions given in Table 3.1. Therefore, it
is reasonable to use the activity coefficient of hydrogen ions in HClO₄-NaClO₄ solution to
determine the concentrations of hydrogen ions in Na₂SO₄-H₂SO₄-NaClO₄ solution with the same
ionic strength.

The liquid junction potential for the pH measurement is negligible (see Appendix D) and
therefore, the activity of hydrogen ions can be determined with a reasonable accuracy.

According to the chromous solution composition, the selenate solution was prepared in
such a way that the final composition, pH and ionic strength of the resulted mixture of the two
solutions reached the target values.

Table B-1: pH and proton activity coefficients (γ) of HClO₄ and NaClO₄ solutions at different
ionic strengths.

<table>
<thead>
<tr>
<th>Ionic strength = 0.50 M</th>
<th>HClO₄ /M</th>
<th>NaClO₄ /M</th>
<th>pH</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>0.4</td>
<td>0.45</td>
<td>0.475</td>
<td>0.4875</td>
<td>0.49375</td>
</tr>
<tr>
<td>0.99</td>
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<td>1.59</td>
<td>1.89</td>
<td>2.19</td>
</tr>
<tr>
<td>1.02</td>
<td>1.03</td>
<td>1.05</td>
<td>1.03</td>
<td>1.03</td>
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</table>

<table>
<thead>
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<th>HClO₄ /M</th>
<th>NaClO₄ /M</th>
<th>pH</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
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<td>0.975</td>
<td>0.9875</td>
<td>0.99375</td>
</tr>
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<td>0.88</td>
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<td>1.78</td>
<td>2.08</td>
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<td>1.33</td>
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</table>

<table>
<thead>
<tr>
<th>Ionic strength = 1.5 M</th>
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<th>NaClO₄ /M</th>
<th>pH</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>1.4</td>
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<td>1.475</td>
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<td>1.49385</td>
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<td>1.70</td>
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<td>1.68</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>HClO₄ /M</th>
<th>NaClO₄ /M</th>
<th>pH</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
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<tr>
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<td>1.95</td>
<td>1.975</td>
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<td>1.54</td>
<td>1.84</td>
</tr>
<tr>
<td>2.34</td>
<td>2.40</td>
<td>2.36</td>
<td>2.31</td>
<td>2.31</td>
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</table>
Table B-2: The concentrations of the species as a function of sulfuric acid concentrations at 0.15M Na\textsubscript{2}SO\textsubscript{4}

\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{Species} & \text{0.170} & \text{0.096} & \text{0.050} & \text{0.025} & \text{0.015} \\
\hline \text{[H\textsubscript{2}SO\textsubscript{4}] / M} & \text{1.0} & \text{1.3} & \text{1.6} & \text{1.91} & \text{2.19} \\
\hline \text{pH} & \text{0.097} & \text{0.049} & \text{0.024} & \text{0.012} & \text{0.006} \\
\hline \text{[H\textsuperscript{+}] / M} & \text{0.244} & \text{0.142} & \text{0.076} & \text{0.037} & \text{0.023} \\
\hline \text{[HSO\textsubscript{4}\textsuperscript{-}] / M} & \text{0.077} & \text{0.103} & \text{0.124} & \text{0.137} & \text{0.141} \\
\hline \text{[SO\textsubscript{4}\textsuperscript{2-}] / M} & \text{0.47} & \text{0.45} & \text{0.45} & \text{0.45} & \text{0.45} \\
\hline \text{Ionic strength / M} & \text{0.170} & \text{0.096} & \text{0.050} & \text{0.025} & \text{0.015} \\
\hline
\end{tabular}

Table B-3: The concentrations of the species as a function of sulfuric acid concentrations at 0.15M Na\textsubscript{2}SO\textsubscript{4} and 0.50M NaClO\textsubscript{4}

\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{Species} & \text{0.113} & \text{0.089} & \text{0.047} & \text{0.024} & \text{0.013} \\
\hline \text{[H\textsubscript{2}SO\textsubscript{4}] / M} & \text{0.88} & \text{1.00} & \text{1.30} & \text{1.63} & \text{1.88} \\
\hline \text{pH} & \text{0.100} & \text{0.076} & \text{0.038} & \text{0.018} & \text{0.0010} \\
\hline \text{[H\textsuperscript{+}] / M} & \text{0.126} & \text{0.101} & \text{0.057} & \text{0.030} & \text{0.016} \\
\hline \text{[HSO\textsubscript{4}\textsuperscript{-}] / M} & \text{0.137} & \text{0.137} & \text{0.141} & \text{0.144} & \text{0.147} \\
\hline \text{[SO\textsubscript{4}\textsuperscript{2-}] / M} & \text{0.104} & \text{1.01} & \text{0.98} & \text{0.96} & \text{0.96} \\
\hline \text{Ionic strength / M} & \text{0.113} & \text{0.089} & \text{0.047} & \text{0.024} & \text{0.013} \\
\hline
\end{tabular}

Table B-4: The concentrations of the species as a function of sulfuric acid concentrations at 0.15M Na\textsubscript{2}SO\textsubscript{4} and 1.0M NaClO\textsubscript{4}

\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{Species} & \text{0.148} & \text{0.082} & \text{0.041} & \text{0.021} & \text{0.010} \\
\hline \text{[H\textsubscript{2}SO\textsubscript{4}] / M} & \text{0.77} & \text{1.02} & \text{1.33} & \text{1.59} & \text{1.88} \\
\hline \text{pH} & \text{0.100} & \text{0.0562} & \text{0.0275} & \text{0.0151} & \text{0.0078} \\
\hline \text{[H\textsuperscript{+}] / M} & \text{0.196} & \text{0.107} & \text{0.055} & \text{0.026} & \text{0.013} \\
\hline \text{[HSO\textsubscript{4}\textsuperscript{-}] / M} & \text{0.102} & \text{0.124} & \text{0.136} & \text{0.144} & \text{0.147} \\
\hline \text{[SO\textsubscript{4}\textsuperscript{2-}] / M} & \text{1.50} & \text{1.48} & \text{1.46} & \text{1.46} & \text{1.46} \\
\hline \text{Ionic strength / M} & \text{1.48} & \text{0.041} & \text{0.021} & \text{0.010} & \text{0.005} \\
\hline
\end{tabular}

Table B-5: The concentrations of the species as a function of sulfuric acid concentrations at 0.15M Na\textsubscript{2}SO\textsubscript{4} and 1.50M NaClO\textsubscript{4}

\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{Species} & \text{0.158} & \text{0.064} & \text{0.033} & \text{0.017} & \text{0.008} \\
\hline \text{[H\textsubscript{2}SO\textsubscript{4}] / M} & \text{0.63} & \text{1.01} & \text{1.31} & \text{1.58} & \text{1.91} \\
\hline \text{pH} & \text{0.100} & \text{0.0418} & \text{0.0209} & \text{0.0112} & \text{0.00526} \\
\hline \text{[H\textsuperscript{+}] / M} & \text{0.216} & \text{0.086} & \text{0.046} & \text{0.022} & \text{0.010} \\
\hline \text{[HSO\textsubscript{4}\textsuperscript{-}] / M} & \text{0.092} & \text{0.128} & \text{0.137} & \text{0.145} & \text{0.147} \\
\hline \text{[SO\textsubscript{4}\textsuperscript{2-}] / M} & \text{1.99} & \text{1.97} & \text{1.96} & \text{1.96} & \text{1.95} \\
\hline \text{Ionic strength / M} & \text{1.99} & \text{1.97} & \text{1.96} & \text{1.96} & \text{1.95} \\
\hline
\end{tabular}

The generated chromous solution composition through electrochemical cell was: 0.1M CrSO\textsubscript{4}, 0.15M H\textsubscript{2}SO\textsubscript{4} and 0.05KSO\textsubscript{4}. To prepare an initial reaction solution with 0.025M CrSO\textsubscript{4}, 0.10M H\textsuperscript{+} and different ionic strengths, the chromous solution was first diluted two times and mixed with
a selenate solution containing H$_2$SO$_4$, Na$_2$SO$_4$ and NaClO$_4$. The initial solution compositions with different ionic strengths are given in Table A-6. The concentration of sodium perchlorate was adjusted so that the ionic strength reached the target values. The total sulfate concentration was maintained at 0.150M. Table A-6 Compositions of initial reaction solutions with a hydrogen ion concentration of 0.10 M

Table B-6: Compositions of initial reaction solutions with a hydrogen ion concentration of 0.10 M

<table>
<thead>
<tr>
<th>Ionic strength / M</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$ / M</td>
<td>0.175</td>
<td>0.113</td>
<td>0.148</td>
<td>0.158</td>
</tr>
<tr>
<td>CrSO$_4$ / M</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>K$_2$SO$_4$ / M</td>
<td>0.0125</td>
<td>0.0125</td>
<td>0.0125</td>
<td>0.0125</td>
</tr>
<tr>
<td>Na$_2$SO$_4$ / M</td>
<td>0.1125</td>
<td>0.1125</td>
<td>0.1125</td>
<td>0.1125</td>
</tr>
<tr>
<td>NaClO$_4$ / M</td>
<td>0</td>
<td>0.475</td>
<td>0.975</td>
<td>1.475</td>
</tr>
</tbody>
</table>

To prepare sulfate-free reaction solution, barium perchlorate was added to chromous solution to precipitate the sulfate anions, and most of potassium. After precipitation of sulfate, the chromous concentration decreased from 0.10 to 0.084M due to dilution while the sulfate concentration was below 1.0×10$^{-7}$ M. To prepare an initial reaction solution with 0.0258M Cr$^{2+}$, 0.0801 M H$^+$ and different ionic strengths, the chromous solution was first diluted and then mixed with the same volume of selenate solution containing HClO$_4$ and NaClO$_4$. The resulted initial solution compositions with different ionic strengths are summarized in Table B-7. The concentration of sodium perchlorate was adjusted so that the ionic strength reached the target values. The concentrations of potassium and barium were less than 0.0060 and 0.00025 M respectively and they are not considered in the calculation of ionic strength.

Table B-7: Compositions of initial reaction solutions without sulfate

<table>
<thead>
<tr>
<th>Ionic strength / M</th>
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<th>2.0</th>
</tr>
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<tbody>
<tr>
<td>HClO$_4$ / M</td>
<td>0.080</td>
<td>0.080</td>
<td>0.080</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
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<td>----------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>Cr(ClO$_4$)$_2$ / M</td>
<td>0.0258</td>
<td>0.0258</td>
<td>0.0258</td>
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</tr>
<tr>
<td>NaClO$_4$ / M</td>
<td>0.337</td>
<td>0.837</td>
<td>1.337</td>
<td>1.837</td>
</tr>
</tbody>
</table>
Appendix C  Calculation of liquid junction potential for pH measurement

The liquid junction potential arises from two different ionic solutions in contact due to different concentrations and mobilities of ions across the junction. The reference electrode is isolated from the working solution through a Luggin capillary or a porous plug. Hence, a liquid junction potential exists and affects the potential measurement of the working electrode. The direct potentiometric measurement of a junction potential is not possible as it is impossible to directly measure a single electrode potential. However, it is possible to estimate junction potentials based on assumptions about the geometry and distribution of the ions in the region of the junction. The basic equation relating the junction potential ($E_j$) between Phases $\beta$ and $\alpha$ to the transport number, charge and activity of the ions forming the junction is:

$$E_j = E_\beta - E_\alpha = \frac{-RT}{F} \int_\alpha^\beta \sum_{i=1}^{n} \frac{t_i}{z_i} d(\ln(a_i))$$  \hspace{1cm} (C-1)

Where $t_i$ is the transport number of Ion $i$, $z_i$ the algebraic value of the charge on the ion, $a_i$ the activity of the ion, and $n$ the number of the ions. It is almost too difficult to solve the above equation as it has to be known how the concentration, the activity coefficient and the transport number of each species vary in the junction region. If the activity coefficients are taken to be unity and the concentration of each ion is assumed to change linearly from $C_\alpha$ to $C_\beta$, the liquid junction potential can be expressed as:

$$E_j = \frac{-RT}{F} \sum_{i=1}^{n} \frac{|z_i|}{z_i} \frac{u_i}{u_i} (c_i^\beta - c_i^\alpha) \ln \frac{|z_i| c_i^\beta}{\sum_{i} |z_i| u_i c_i^\alpha}$$  \hspace{1cm} (C-2)

$$= \frac{-RT}{F} \sum_{i=1}^{n} \frac{|z_i|}{z_i} \frac{\lambda_i}{\lambda_i} (C_i^\beta - C_i^\alpha) \ln \frac{|z_i| \lambda_i c_i^\beta}{\sum_{i} |z_i| \lambda_i c_i^\alpha}$$
where $u_i$ is the mobility of Species $i$, $\lambda_i$ the equivalent conductivity of Species $i$ ($|z_i|u_i F$), $C^\alpha_i$ and $C^\beta_i$ the concentrations of Species $i$ in Phases $\alpha$ and $\beta$. For accuracy, the mobility or equivalent conductivity in the two phases. However, these data are lacking. As an approximation, the equivalent conductivities can be used to estimate the liquid junction potential.

The combination glass pH electrode can be dismantled into several components as shown in Figure 1. The potential difference across two electrodes consists of the following terms:

$$E = (E_{Ag} - E_1) + (E_1 - E_2) + (E_2 - E_3) + (E_3 - E_{Ag})$$

$$= K' + \frac{2.303RT}{F}(pH_1 - pH_2) + (E_2 - E_3)$$

$$= K - \frac{2.303RT}{F}pH_2 + (E_2 - E_3)$$

$$= K - \frac{2.303RT}{F}pH_2 - E_{j(2\rightarrow3)}$$

$$\frac{2.303RT}{F}pH_{meter} = - \frac{2.303RT}{F}pH_2 - E_{j(2\rightarrow3)}$$

$$pH_2 = pH_{meter} - \frac{F}{2.303RT}E_{j(2\rightarrow3)}$$

where $pH_{meter}$ is the reading from the pH meter, $E_{j(2\rightarrow3)}$ the liquid junction potential from Solution 2 to Solution 3, and $pH_2$ the true pH in the solution studied. The pH error is: $-F/(2.303RT)E_{j(2\rightarrow3)}$ ($- E_{j(2\rightarrow3)}/0.0591$ at 25 °C).
Solution 3 was 3M KCl while Solution 2 contained H⁺, Cr²⁺, K⁺, Na⁺, HSO₄⁻, SO₄²⁻ and ClO₄⁻. For the accurate estimation, the equivalent conductivities should be used at the concentration concerned. However, there are very limited equivalent conductivities of electrolytes available in the literature. Therefore, the equivalent conductivities at infinite dilution are used instead. The equivalent conductivities of these ions are given in Table C-1 (Lide, 2005). There is no equivalent conductivity data available for Cr²⁺. The radius of Cr²⁺ is similar to that of Fe²⁺. Therefore, the equivalent conductivity of Fe²⁺ is used for Cr²⁺.

The liquid junction potentials and corresponding errors at 25 °C for the HClO₄ and NaClO₄ solutions are summarized in Tables 2-5 for ionic strengths of 0.5, 1.0, 1.5 and 2.0 respectively. The pH errors were -0.012 to -0.0012, -0.025 to -0.016, -0.034 to -0.026 and -0.041 to -0.035 for ionic strengths of 0.5, 1.0, 1.5 and 2.0 respectively. The liquid junction potentials and corresponding errors for H₂SO₄, Na₂SO₄ and Na₂ClO₄ solutions are given in Tables 6-9 for ionic strengths of 0.5, 1.0, 1.5 and 2.0 respectively. The pH errors were 0.012 to 0.028, -0.0066 to
0.0047, -0.02 to -0.01 and -0.03 to -0.02 for ionic strengths of 0.5, 1.0, 1.5 and 2.0 respectively. These pH errors are nearly negligible. 0.025 or less M K₂SO₄ and 0.05 or less M CrSO₄ were introduced into the solutions to study the reduction of selenate by Cr²⁺. The solution ionic strength was maintained at constant (0.5, 1.0, 1.5 and 2.0) by changing the concentrations of Na₂SO₄ and NaClO₄ so that the activity coefficient of each species practically did not change. The liquid junction errors and corresponding pH errors for these solutions are summarized in Tables 10 to 17. With the introduction of such amounts of K₂SO₄ and CrSO₄, the liquid junction potential and corresponding pH errors nearly do not change.

Table C-1 Equivalent conductivities of ions in the solution studied (10⁻⁴ m² S mol⁻¹).

<table>
<thead>
<tr>
<th>Ion</th>
<th>H⁺</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Cr²⁺</th>
<th>Cl⁻</th>
<th>ClO₄⁻</th>
<th>HSO₄⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>350</td>
<td>73.5</td>
<td>50.1</td>
<td>54</td>
<td>76.3</td>
<td>67.3</td>
<td>52</td>
<td>80</td>
</tr>
</tbody>
</table>

Table C-2 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO₄ and NaClO₄ at an ionic strength of 0.5.

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>0.4</td>
<td>0.45</td>
<td>0.475</td>
<td>0.4875</td>
<td>0.49375</td>
</tr>
<tr>
<td>pH</td>
<td>0.99</td>
<td>1.29</td>
<td>1.58</td>
<td>1.89</td>
<td>2.19</td>
</tr>
<tr>
<td>H⁺ / M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na⁺ / M</td>
<td>0.4</td>
<td>0.45</td>
<td>0.475</td>
<td>0.4875</td>
<td>0.49375</td>
</tr>
<tr>
<td>ClO₄⁻ / M</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ej(3→2) at 25 °C</td>
<td>0.00072</td>
<td>0.00037</td>
<td>0.00020</td>
<td>0.00016</td>
<td>0.00007</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.012</td>
<td>-0.0062</td>
<td>-0.0033</td>
<td>-0.0027</td>
<td>-0.0012</td>
</tr>
</tbody>
</table>

Table C-3 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO₄ and NaClO₄ at an ionic strength of 1.0.

<table>
<thead>
<tr>
<th>Composition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>0.9</td>
<td>0.95</td>
<td>0.975</td>
<td>0.9875</td>
<td>0.99375</td>
</tr>
<tr>
<td>pH</td>
<td>0.88</td>
<td>1.18</td>
<td>1.48</td>
<td>1.78</td>
<td>2.08</td>
</tr>
<tr>
<td>H⁺ / M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na⁺ / M</td>
<td>0.9</td>
<td>0.95</td>
<td>0.975</td>
<td>0.9875</td>
<td>0.99375</td>
</tr>
<tr>
<td>ClO₄⁻ / M</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ej(3→2) at 25 °C</td>
<td>0.0015</td>
<td>0.0012</td>
<td>0.0011</td>
<td>0.0010</td>
<td>0.00095</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.025</td>
<td>-0.020</td>
<td>-0.018</td>
<td>-0.017</td>
<td>-0.016</td>
</tr>
</tbody>
</table>
Table C-4 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO$_4$ and NaClO$_4$ at an ionic strength of 1.5

<table>
<thead>
<tr>
<th>Composition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO$_4$/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO$_4$/M</td>
<td>1.4</td>
<td>1.45</td>
<td>1.475</td>
<td>1.4875</td>
<td>1.49375</td>
</tr>
<tr>
<td>pH</td>
<td>0.77</td>
<td>1.07</td>
<td>1.37</td>
<td>1.68</td>
<td>1.98</td>
</tr>
<tr>
<td>H$^+$ /M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na$^+$ /M</td>
<td>1.4</td>
<td>1.45</td>
<td>1.475</td>
<td>1.4875</td>
<td>1.49375</td>
</tr>
<tr>
<td>ClO$_4^-$ /M</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>$E_{j(3\rightarrow2)}$ at 25 °C</td>
<td>0.002</td>
<td>0.0018</td>
<td>0.0015</td>
<td>0.0016</td>
<td>0.0016</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.034</td>
<td>-0.030</td>
<td>-0.026</td>
<td>-0.027</td>
<td>-0.026</td>
</tr>
</tbody>
</table>

Table C-5 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO$_4$ and NaClO$_4$ at an ionic strength of 2.0

<table>
<thead>
<tr>
<th>Composition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO$_4$/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO$_4$/M</td>
<td>1.9</td>
<td>1.95</td>
<td>1.975</td>
<td>1.9875</td>
<td>1.99375</td>
</tr>
<tr>
<td>pH</td>
<td>0.63</td>
<td>0.92</td>
<td>1.23</td>
<td>1.54</td>
<td>1.84</td>
</tr>
<tr>
<td>H$^+$ /M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na$^+$ /M</td>
<td>1.9</td>
<td>1.95</td>
<td>1.975</td>
<td>1.9875</td>
<td>1.99375</td>
</tr>
<tr>
<td>ClO$_4^-$ /M</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$E_{j(3\rightarrow2)}$ at 25 °C</td>
<td>0.0024</td>
<td>0.0022</td>
<td>0.0021</td>
<td>0.0021</td>
<td>0.0021</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.041</td>
<td>-0.037</td>
<td>-0.036</td>
<td>-0.035</td>
<td>-0.035</td>
</tr>
</tbody>
</table>

Table C-6 Liquid junction potential and corresponding pH correction for the solutions containing 0.15M Na$_2$SO$_4$ and different amounts of H$_2$SO$_4$ at an ionic strength of 0.5 and different pHs

<table>
<thead>
<tr>
<th>pH</th>
<th>1.0</th>
<th>1.3</th>
<th>1.63</th>
<th>1.88</th>
<th>2.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$/M</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>H$_2$SO$_4$ / M</td>
<td>0.170</td>
<td>0.0955</td>
<td>0.0502</td>
<td>0.0246</td>
<td>0.0148</td>
</tr>
<tr>
<td>pH</td>
<td>1.0</td>
<td>1.3</td>
<td>1.6</td>
<td>1.91</td>
<td>2.19</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.0971</td>
<td>0.0487</td>
<td>0.0244</td>
<td>0.0119</td>
<td>0.00627</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[HSO$_4^-$] / M</td>
<td>0.244</td>
<td>0.142</td>
<td>0.0761</td>
<td>0.0373</td>
<td>0.0233</td>
</tr>
<tr>
<td>[SO$_4^{2-}$] / M</td>
<td>0.0767</td>
<td>0.103</td>
<td>0.124</td>
<td>0.137</td>
<td>0.141</td>
</tr>
<tr>
<td>$E_{j(3\rightarrow2)}$ at 25 °C</td>
<td>-0.00071</td>
<td>-0.0012</td>
<td>-0.0015</td>
<td>-0.0016</td>
<td>-0.0017</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>0.012</td>
<td>0.020</td>
<td>0.025</td>
<td>0.027</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Table C-7 Liquid junction potential and corresponding pH errors for the solutions containing 0.15M Na$_2$SO$_4$, 0.5M NaClO$_4$ and different amounts of H$_2$SO$_4$ at an ionic strength of 1.0 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.88</th>
<th>1.00</th>
<th>1.30</th>
<th>1.63</th>
<th>1.88</th>
<th>2.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$/M</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>H$_2$SO$_4$ / M</td>
<td>0.113</td>
<td>0.0886</td>
<td>0.0473</td>
<td>0.0236</td>
<td>0.0128</td>
<td>0.0059</td>
</tr>
<tr>
<td>NaClO$_4$/M</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.100</td>
<td>0.076</td>
<td>0.038</td>
<td>0.0178</td>
<td>0.01</td>
<td>0.0047</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>[H$_2$SO$_4^-$] / M</td>
<td>0.126</td>
<td>0.101</td>
<td>0.057</td>
<td>0.03</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>[SO$_4^{2-}$] / M</td>
<td>0.137</td>
<td>0.137</td>
<td>0.141</td>
<td>0.144</td>
<td>0.147</td>
<td>0.149</td>
</tr>
<tr>
<td>$E_{(3-2)}$ at 25 °C</td>
<td>0.00039</td>
<td>0.00015</td>
<td>-0.00007</td>
<td>-0.00019</td>
<td>-0.00025</td>
<td>-0.00028</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.0066</td>
<td>-0.0025</td>
<td>0.0012</td>
<td>0.0032</td>
<td>0.0042</td>
<td>0.0047</td>
</tr>
</tbody>
</table>

Table C-8 Liquid junction potential and corresponding pH correction for the solutions containing 0.15M Na$_2$SO$_4$, 1.0M NaClO$_4$ and different amounts of H$_2$SO$_4$ at an ionic strength of 1.5 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.77</th>
<th>1.02</th>
<th>1.33</th>
<th>1.59</th>
<th>1.88</th>
<th>2.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$/M</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>H$_2$SO$_4$ / M</td>
<td>0.148</td>
<td>0.0817</td>
<td>0.0414</td>
<td>0.0207</td>
<td>0.0103</td>
<td>0.00522</td>
</tr>
<tr>
<td>NaClO$_4$/M</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.100</td>
<td>0.076</td>
<td>0.038</td>
<td>0.0178</td>
<td>0.01</td>
<td>0.0047</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>[H$_2$SO$_4^-$] / M</td>
<td>0.196</td>
<td>0.101</td>
<td>0.057</td>
<td>0.03</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>[SO$_4^{2-}$] / M</td>
<td>0.102</td>
<td>0.137</td>
<td>0.141</td>
<td>0.144</td>
<td>0.147</td>
<td>0.149</td>
</tr>
<tr>
<td>$E_{(3-2)}$ at 25 °C</td>
<td>0.0011</td>
<td>0.00085</td>
<td>0.00069</td>
<td>0.00062</td>
<td>0.00057</td>
<td>0.00055</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.019</td>
<td>-0.014</td>
<td>-0.012</td>
<td>-0.010</td>
<td>-0.0096</td>
<td>-0.0093</td>
</tr>
</tbody>
</table>

Table C-9 Liquid junction potential and corresponding pH correction for the solutions containing 0.15M Na$_2$SO$_4$, 1.5M NaClO$_4$ and different amounts of H$_2$SO$_4$ at an ionic strength of 2.0 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.63</th>
<th>1.01</th>
<th>1.31</th>
<th>1.58</th>
<th>1.91</th>
<th>2.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$/M</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>H$_2$SO$_4$ / M</td>
<td>0.158</td>
<td>0.0640</td>
<td>0.0335</td>
<td>0.0167</td>
<td>0.00788</td>
<td>0.00394</td>
</tr>
<tr>
<td>NaClO$_4$/M</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.100</td>
<td>0.0418</td>
<td>0.0209</td>
<td>0.0112</td>
<td>0.00526</td>
<td>0.00324</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>[H$_2$SO$_4^-$] / M</td>
<td>0.216</td>
<td>0.0862</td>
<td>0.0460</td>
<td>0.0222</td>
<td>0.0105</td>
<td>0.00464</td>
</tr>
<tr>
<td>[SO$_4^{2-}$] / M</td>
<td>0.092</td>
<td>0.128</td>
<td>0.137</td>
<td>0.145</td>
<td>0.147</td>
<td>0.149</td>
</tr>
<tr>
<td>$E_{(3-2)}$ at 25 °C</td>
<td>0.0017</td>
<td>0.0014</td>
<td>0.0013</td>
<td>0.0012</td>
<td>0.0012</td>
<td>0.0012</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.028</td>
<td>-0.023</td>
<td>-0.021</td>
<td>-0.021</td>
<td>-0.020</td>
<td>-0.020</td>
</tr>
</tbody>
</table>
Table C-10 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO₄ and NaClO₄ at an ionic strength of 0.5

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>0.375</td>
<td>0.425</td>
<td>0.45</td>
<td>0.463</td>
<td>0.469</td>
</tr>
<tr>
<td>pH</td>
<td>0.99</td>
<td>1.29</td>
<td>1.58</td>
<td>1.89</td>
<td>2.19</td>
</tr>
<tr>
<td>H⁺ / M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na⁺ / M</td>
<td>0.375</td>
<td>0.425</td>
<td>0.45</td>
<td>0.463</td>
<td>0.469</td>
</tr>
<tr>
<td>Cr²⁺ / M</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>ClO₄⁻ / M</td>
<td>0.475</td>
<td>0.475</td>
<td>0.475</td>
<td>0.475</td>
<td>0.475</td>
</tr>
<tr>
<td>$E_{(3-\rightarrow 2)}$ at 25 °C</td>
<td>0.00047</td>
<td>0.00013</td>
<td>-0.00044</td>
<td>-0.00013</td>
<td>-0.00017</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.0080</td>
<td>-0.0021</td>
<td>0.00074</td>
<td>0.0022</td>
<td>0.0029</td>
</tr>
</tbody>
</table>

Table C-11 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO₄ and NaClO₄ at an ionic strength of 1.0

<table>
<thead>
<tr>
<th>Composition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>0.875</td>
<td>0.925</td>
<td>0.95</td>
<td>0.963</td>
<td>0.969</td>
</tr>
<tr>
<td>pH</td>
<td>0.88</td>
<td>1.18</td>
<td>1.48</td>
<td>1.78</td>
<td>2.08</td>
</tr>
<tr>
<td>H⁺ / M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na⁺ / M</td>
<td>0.875</td>
<td>0.925</td>
<td>0.95</td>
<td>0.963</td>
<td>0.969</td>
</tr>
<tr>
<td>Cr²⁺ / M</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>ClO₄⁻ / M</td>
<td>0.975</td>
<td>0.975</td>
<td>0.975</td>
<td>0.975</td>
<td>0.975</td>
</tr>
<tr>
<td>$E_{(3-\rightarrow 2)}$ at 25 °C</td>
<td>0.0013</td>
<td>0.00098</td>
<td>0.00086</td>
<td>0.0008</td>
<td>0.00076</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.021</td>
<td>-0.017</td>
<td>-0.015</td>
<td>-0.013</td>
<td>-0.013</td>
</tr>
</tbody>
</table>

Table C-12 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO₄ and NaClO₄ at an ionic strength of 1.5

<table>
<thead>
<tr>
<th>Composition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄/M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>1.375</td>
<td>1.425</td>
<td>1.45</td>
<td>1.463</td>
<td>1.469</td>
</tr>
<tr>
<td>pH</td>
<td>0.77</td>
<td>1.07</td>
<td>1.37</td>
<td>1.68</td>
<td>1.98</td>
</tr>
<tr>
<td>H⁺ / M</td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td>Na⁺ / M</td>
<td>1.375</td>
<td>1.425</td>
<td>1.45</td>
<td>1.463</td>
<td>1.469</td>
</tr>
<tr>
<td>ClO₄⁻ / M</td>
<td>1.475</td>
<td>1.475</td>
<td>1.475</td>
<td>1.475</td>
<td>1.475</td>
</tr>
<tr>
<td>Cr²⁺ / M</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>$E_{(3-\rightarrow 2)}$ at 25 °C</td>
<td>0.0018</td>
<td>0.0016</td>
<td>0.00149</td>
<td>0.00143</td>
<td>0.0014</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.031</td>
<td>-0.027</td>
<td>-0.025</td>
<td>-0.024</td>
<td>-0.024</td>
</tr>
</tbody>
</table>
Table C-13 Liquid junction potential and corresponding pH correct for the solutions with different concentrations of HClO₄ and NaClO₄ at an ionic strength of 2.0

<table>
<thead>
<tr>
<th>Composition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HClO₄/M</strong></td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td><strong>NaClO₄/M</strong></td>
<td>1.875</td>
<td>1.925</td>
<td>1.950</td>
<td>1.963</td>
<td>1.969</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>0.63</td>
<td>0.92</td>
<td>1.23</td>
<td>1.54</td>
<td>1.84</td>
</tr>
<tr>
<td><strong>H⁺ / M</strong></td>
<td>0.1</td>
<td>0.05</td>
<td>0.025</td>
<td>0.0125</td>
<td>0.00625</td>
</tr>
<tr>
<td><strong>Na⁺ / M</strong></td>
<td>1.875</td>
<td>1.925</td>
<td>1.950</td>
<td>1.963</td>
<td>1.969</td>
</tr>
<tr>
<td><strong>Cr²⁺ / M</strong></td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td><strong>ClO₄⁻ / M</strong></td>
<td>1.975</td>
<td>1.975</td>
<td>1.975</td>
<td>1.975</td>
<td>1.975</td>
</tr>
<tr>
<td><strong>Eₗ(3→2) at 25 °C</strong></td>
<td>0.0023</td>
<td>0.0021</td>
<td>0.002</td>
<td>0.0019</td>
<td>0.0019</td>
</tr>
<tr>
<td><strong>pH error at 25 °C</strong></td>
<td>-0.039</td>
<td>-0.036</td>
<td>-0.034</td>
<td>-0.032</td>
<td>-0.032</td>
</tr>
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</table>

Table C-14 Liquid junction potential and corresponding pH correction for the solutions containing 0.075M Na₂SO₄, 0.025M K₂SO₄, 0.05M CrSO₄ and different amounts of H₂SO₄ at an ionic strength of 0.5 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>1.0</th>
<th>1.3</th>
<th>1.63</th>
<th>1.88</th>
<th>2.21</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Na₂SO₄/M</strong></td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td><strong>H₂SO₄ / M</strong></td>
<td>0.170</td>
<td>0.0955</td>
<td>0.0502</td>
<td>0.0246</td>
<td>0.0148</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>1.0</td>
<td>1.3</td>
<td>1.6</td>
<td>1.91</td>
<td>2.19</td>
</tr>
<tr>
<td><strong>H⁺</strong></td>
<td>0.0971</td>
<td>0.0487</td>
<td>0.0244</td>
<td>0.0119</td>
<td>0.00627</td>
</tr>
<tr>
<td><strong>Na⁺</strong></td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>K⁺ / M</strong></td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Cr²⁺ / M</strong></td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>[HSO₄⁻]</strong> / M</td>
<td>0.244</td>
<td>0.142</td>
<td>0.0761</td>
<td>0.0373</td>
<td>0.0233</td>
</tr>
<tr>
<td><strong>[SO₄²⁻]</strong> / M</td>
<td>0.0767</td>
<td>0.103</td>
<td>0.124</td>
<td>0.137</td>
<td>0.141</td>
</tr>
<tr>
<td><strong>Eₗ(3→2) at 25 °C</strong></td>
<td>-0.00053</td>
<td>-0.0010</td>
<td>-0.0013</td>
<td>-0.0014</td>
<td>-0.0015</td>
</tr>
<tr>
<td><strong>pH error at 25 °C</strong></td>
<td>0.0090</td>
<td>0.017</td>
<td>0.021</td>
<td>0.024</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Table C-15 Liquid junction potential and corresponding pH correction for the solutions containing 0.075M Na₂SO₄, 0.025M K₂SO₄, 0.05M CrSO₄, 0.5M NaClO₄ and different amounts of H₂SO₄ at an ionic strength of 1.0 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.88</th>
<th>1.00</th>
<th>1.30</th>
<th>1.63</th>
<th>1.88</th>
<th>2.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄/M</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>H₂SO₄/M</td>
<td>0.113</td>
<td>0.0886</td>
<td>0.0473</td>
<td>0.0236</td>
<td>0.0128</td>
<td>0.0059</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>4.5</td>
<td>0.438</td>
<td>0.471</td>
<td>0.488</td>
<td>0.493</td>
<td>0.496</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.100</td>
<td>0.076</td>
<td>0.038</td>
<td>0.0178</td>
<td>0.01</td>
<td>0.0047</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.6</td>
<td>0.588</td>
<td>0.621</td>
<td>0.638</td>
<td>0.643</td>
<td>0.646</td>
</tr>
<tr>
<td>K⁺/M</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr²⁺/M</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>0.45</td>
<td>0.438</td>
<td>0.471</td>
<td>0.488</td>
<td>0.493</td>
<td>0.496</td>
</tr>
<tr>
<td>[HSO₄⁻] / M</td>
<td>0.126</td>
<td>0.101</td>
<td>0.057</td>
<td>0.03</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>[SO₄²⁻] / M</td>
<td>0.137</td>
<td>0.137</td>
<td>0.141</td>
<td>0.144</td>
<td>0.147</td>
<td>0.149</td>
</tr>
<tr>
<td>$E_{j(3-2)}$ at 25 °C</td>
<td>0.00043</td>
<td>0.00016</td>
<td>0.000052</td>
<td>0.000039</td>
<td>-0.00014</td>
<td>-0.00016</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.0073</td>
<td>-0.0027</td>
<td>-0.00088</td>
<td>-0.00066</td>
<td>0.0024</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

Table C-16 Liquid junction potential and corresponding pH correction for the solutions containing 0.075M Na₂SO₄ , 0.025M K₂SO₄, 0.05M CrSO₄ and different amounts of H₂SO₄ and NaClO₄ at an ionic strength of 1.5 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.77</th>
<th>1.02</th>
<th>1.33</th>
<th>1.59</th>
<th>1.88</th>
<th>2.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄/M</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>H₂SO₄/M</td>
<td>0.148</td>
<td>0.0817</td>
<td>0.0414</td>
<td>0.0207</td>
<td>0.0103</td>
<td>0.00522</td>
</tr>
<tr>
<td>NaClO₄/M</td>
<td>0.950</td>
<td>0.947</td>
<td>0.976</td>
<td>0.989</td>
<td>0.994</td>
<td>0.997</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.100</td>
<td>0.076</td>
<td>0.038</td>
<td>0.0178</td>
<td>0.01</td>
<td>0.0047</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>K⁺/M</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr²⁺/M</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>0.950</td>
<td>0.947</td>
<td>0.976</td>
<td>0.989</td>
<td>0.994</td>
<td>0.997</td>
</tr>
<tr>
<td>[HSO₄⁻] / M</td>
<td>0.196</td>
<td>0.110</td>
<td>0.057</td>
<td>0.03</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>[SO₄²⁻] / M</td>
<td>0.102</td>
<td>0.137</td>
<td>0.141</td>
<td>0.144</td>
<td>0.147</td>
<td>0.149</td>
</tr>
<tr>
<td>$E_{j(3-2)}$ at 25 °C</td>
<td>0.0012</td>
<td>0.0010</td>
<td>0.00081</td>
<td>0.00072</td>
<td>0.00068</td>
<td>0.00066</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.020</td>
<td>-0.017</td>
<td>-0.014</td>
<td>-0.012</td>
<td>-0.012</td>
<td>-0.011</td>
</tr>
</tbody>
</table>
Table C-17 Liquid junction potential and corresponding pH correction for the solutions containing 0.075M Na$_2$SO$_4$, 0.025M K$_2$SO$_4$, 0.05M CrSO$_4$ and different amounts of H$_2$SO$_4$ and NaClO$_4$ at an ionic strength of 2.0 and different pHs)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.63</th>
<th>1.01</th>
<th>1.31</th>
<th>1.58</th>
<th>1.91</th>
<th>2.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$ /M</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>H$_2$SO$_4$ / M</td>
<td>0.158</td>
<td>0.0640</td>
<td>0.0335</td>
<td>0.0167</td>
<td>0.00788</td>
<td>0.00394</td>
</tr>
<tr>
<td>NaClO$_4$ /M</td>
<td>1.450</td>
<td>1.480</td>
<td>1.492</td>
<td>1.494</td>
<td>1.497</td>
<td>1.497</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0.100</td>
<td>0.0418</td>
<td>0.0209</td>
<td>0.0112</td>
<td>0.00526</td>
<td>0.00324</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.600</td>
<td>1.630</td>
<td>1.642</td>
<td>1.644</td>
<td>1.647</td>
<td>1.647</td>
</tr>
<tr>
<td>K$^+$ / M</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr$^{2+}$ / M</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>1.450</td>
<td>1.480</td>
<td>1.492</td>
<td>1.494</td>
<td>1.497</td>
<td>1.497</td>
</tr>
<tr>
<td>[HSO$_4^-$] / M</td>
<td>0.216</td>
<td>0.0862</td>
<td>0.0460</td>
<td>0.0222</td>
<td>0.0105</td>
<td>0.0046</td>
</tr>
<tr>
<td>[SO$_4^{2-}$] / M</td>
<td>0.092</td>
<td>0.128</td>
<td>0.137</td>
<td>0.145</td>
<td>0.147</td>
<td>0.149</td>
</tr>
<tr>
<td>$E_{(3-2)}$ at 25 °C</td>
<td>0.0017</td>
<td>0.0014</td>
<td>0.0014</td>
<td>0.0013</td>
<td>0.0013</td>
<td>0.0013</td>
</tr>
<tr>
<td>pH error at 25 °C</td>
<td>-0.029</td>
<td>-0.024</td>
<td>-0.024</td>
<td>-0.022</td>
<td>-0.022</td>
<td>-0.022</td>
</tr>
</tbody>
</table>
Appendix D  Calculations of the graph of modelled Rate Equation

Proposed general rate equation: $\frac{d[Se^{6+}]}{dt} = -k_1 [Se^{6+}] [H^+] [Cr^{2+}]$

Assuming the $[H^+]$ is constant during the reaction, let $k = k_1 [H^+]$, then the rate equation can be expressed as

$$\frac{d[Se^{6+}]}{dt} = -k [Se^{6+}] [Cr^{2+}]$$

According to the stoichiometry of selenate reduction with chromous (Cr(II):Se(VI) = 8:1), the following reaction can be obtained.

$\Delta[Cr^{2+}] = 8\Delta[Se^{6+}] = 8([Se^{6+}] - [Se^{6+}]_0) = -8([Se^{6+}]_0 - [Se^{6+}])$  

$[Cr^{2+}] = [Cr^{2+}]_0 + \Delta[Cr^{2+}]$ 

$[Cr^{2+}] = [Cr^{2+}]_0 - 8([Se^{6+}]_0 - [Se^{6+}])$ 

Let $x = [Se^{6+}]_0$. 

$[Cr^{2+}] = [Cr^{2+}]_0 - 8([Se^{6+}]_0 - x) = 8(1/8 [Cr^{2+}]_0 - [Se^{6+}]_0 + x) = 8(b + x)$ 

where $b = 1/8 [Cr^{2+}]_0 - [Se^{6+}]_0$ 

$$\frac{d[Se^{6+}]}{dt} = \frac{dx}{dt} = -8kx(b + x)$$ 

$$\frac{dx}{x(b + x)} = -8kdt$$ 

$$\frac{1}{x(b + x)} = \frac{b}{bx(b + x)} = \frac{b + x - x}{bx(b + x)} = \frac{1}{bx} - \frac{1}{b(b + x)} = \frac{1}{b} \left( \frac{1}{x} - \frac{1}{b + x} \right)$$ 

$$\int_{x_0}^{x} \frac{1}{b} \left( \frac{1}{x} - \frac{1}{b + x} \right) dx = \int_{t_0}^{t} -8kdt$$ 

$$\frac{1}{b} \left( \ln \left( \frac{x}{x_0} \right) - \ln \left( \frac{b + x}{b + x_0} \right) \right) = -8kt$$
\[
\ln \left( \frac{x(b + x_0)}{x_0(b + x)} \right) = -b8k
\]

The above equation can be used in the industrial application to predict the selenate concentration during the reduction of selenate by chromous.