

The effect of vanadium oxidation states on the conversion of hydrogen sulphide to elemental sulphur

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DECLARATION

I Petrus Makondelele Ndou, hereby declare that the dissertation entitled:

“The effect of vanadium oxidation states on the conversion of hydrogen sulphide to elemental sulphur”

Submitted in fulfilment of the requirements for the degree of Master in Chemical Engineering, is my own work, except where acknowledged in the text and has not been submitted to any other tertiary institution either in part or as a whole.

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ABSTRACT

The formation of toxic hydrogen sulphide (H_2S) gas as a by-product is unavoidable during production of fuels and other chemicals from coal, crude oil, and natural gas. There are different processes available to recover H_2S of which the StretfordTM process is one of them. The concentration of vanadium (V^{5+}) plays a crucial role in the StretfordTM process during H_2S absorption and conversion to elemental sulphur. However, the effect of vanadium oxidation states (V^{4+} and V^{5+}) on hydrogen sulphide ions (HS^-) conversion to sulphur product and its quality has not been systematically studied hence the purpose of this study was to understand these effects. A series of experiments was conducted using sodium ammonium vanadate (SAV) and vanadyl sulphate (VOSO_4) as sources of V^{5+} and V^{4+} respectively. The analytical techniques used to determine the quality of elemental sulphur were X-ray powder Diffraction Spectroscopy (XRD), Differential Scanning Calorimetry (DSC), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), gravimetric and Particle Size Distribution (PSD) analyses.

The first set of experiments was conducted at variable V^{5+} concentrations with impurities (Na_2SO_4 and NaSCN) added to the synthetic StretfordTM solutions to determine the best V^{5+} concentration to achieve maximum conversion of HS^- to sulphur of good quality. The H_2S absorption and sulphur production were found to increase as the concentration of V^{5+} increased. However, the elemental sulphur particle sizes were finer and the purity decreased as the V^{5+} concentration increased. The elemental sulphur particle sizes and purity were affected by the impurities in the technical SAV that was used as a source of V^{5+} . Some of these impurities in SAV include Na, NH_3 , K, Al, Si, Mg, and Fe. The impurities in SAV interfered with the sulphur sol nucleation and Ostwald ripening process. The nucleation and Ostwald ripening process facilitates the formation of coarse elemental sulphur. However, the elemental sulphur formed during the experimental work was crystalline and melted at approximately 122°C , which was comparable to 120.6°C reported in the literature.

A second set of experiments was conducted at best V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$ to investigate the effect of impurities (Na_2SO_4 and NaSCN) on H_2S conversion to elemental sulphur. The sulphur production was slightly higher without impurities added in synthetic StretfordTM solution. The elemental sulphur particle sizes slightly shifted to the coarser side but the thermal behavior, crystallinity, and colour were comparable. The elemental sulphur produced without impurities was also of high purity compared to sulphur produced with impurities. The best concentration of V^{5+} , which is based on the experimental results obtained, is $0.029 \text{ mol.dm}^{-3}$. This concentration of V^{5+} was also selected for the experiments at variable V^{5+} to V^{4+} molar ratios

without the addition of sodium salt of 2,7 Anthraquinone Di-Sulfonic Acid ($\text{Na}_2[\text{ADA}]$) to the StretfordTM aqueous solution; vanadium re-oxidation catalyst to the simulated StretfordTM liquor. The H_2S conversion to elemental sulphur reduced as the V^{5+} to V^{4+} molar ratios decreased. There was high loss of total vanadium concentration (5 - 27%) due to the precipitation of V^{4+} and the free OH^- from the simulated StretfordTM liquor-containing NaOH in the form of $(\text{VO}(\text{OH})_2)$. The loss of total vanadium due to precipitation decreased as the V^{5+} to V^{4+} molar ratios decreased. The HS^- conversion to elemental sulphur decreased as the V^{5+} to V^{4+} molar ratios decreased. The elemental sulphur particle sizes were coarse and comparable to elemental sulphur particle sizes produced at the V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$.

Elemental sulphur was crystalline and melted at temperature similar to sulphur produced at V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$ with $\text{Na}_2[\text{ADA}]$ added in solution. In addition, the elemental sulphur product was filtered with difficulty from the sulphur slurry due to precipitation of V^{4+} ions which react with free hydroxides to form a dark colloidal precipitate $(\text{VO}(\text{OH})_2)$. The formation of this precipitate resulted in sticking and blinding the filter paper during filtration of the sulphur slurry. The dominant V^{5+} species in all solutions in this study were the dimer, tetramer, and pentamer. V^{5+} ions in the solutions were qualified by ^{51}V NMR using the NMR literature data to predict dimer, tetramer, and pentamer in these solutions.

A thermodynamic model was developed using the OLI studio analyzer. This model showed that V^{5+} is stable in both acidic and alkaline conditions. However, vanadium in its reduced oxidation state (V^{4+}) is only stable in acidic conditions. Traditionally, the StretfordTM process is operated in alkaline conditions and this explains why V^{4+} precipitated at higher pH (8.2 - 9.5). Hydrogen peroxide which was released from $\text{Na}_2[\text{ADA}]$ oxidizes V^{4+} to V^{5+} in solutions. The statistical models confirmed the experimental findings that H_2S absorption and elemental sulphur production were proportional to the concentrations of V^{5+} in all experiments in this study.

Therefore, the experiments that use StretfordTM aqueous solution should be operated at the best V^{5+} to HS^- molar ratios (between 4.8 and 7.3 in stoichiometry) with $\text{Na}_2[\text{ADA}]$ to oxidizes V^{4+} to V^{5+} in the aqueous solutions. This will subsequently result in the significant production efficiency of the elemental sulphur. The oxidation of almost all of V^{4+} to V^{5+} can minimise the sodium based salts and V^{4+} precipitations. The low stoichiometry V^{5+} to HS^- molar ratios (below 1) results in high hydrogen sulphide emission. The StretfordTM aqueous solution which does not contain $\text{Na}_2[\text{ADA}]$ which can release hydrogen peroxide cannot oxidize V^{4+} to V^{5+} and eventually V^{4+} precipitates in the form of $\text{VO}(\text{OH})_2$. The sodium based salts can co-precipitate together with $\text{VO}(\text{OH})_2$, while the elemental sulphur particles formed can settle at the bottom of the simulated StretfordTM aqueous

solution. Generally, the precipitation of V^{4+} requires an increase in make-up vanadium to achieve best H_2S absorption.

Key words: StretfordTM process, vanadium, oxidation states, precipitation, impurities, elemental sulphur and $Na_2[ADA]$

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LIST OF ABBREVIATIONS

<u>Acronym</u>	<u>Description</u>
^{51}V NMR	Vanadium Nuclear Magnetic Resonance
ATM	Atmosphere
CdS	Cadmium Sulphide
COA	Certificate of Analysis
DCTA	Trans-1,2-Diamino-Cyclohexane Aetra-acetic Acid
DSC	Differential Scanning Calorimetry
ENDOR	Electron Nuclear Double Resonance
EPR	Electro Paramagnetic Resonance
ESEEM	Electron Spin Echo Envelope Modulation
GRI	Gas Research Institute

ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
Na ₂ [ADA]	Anthraquinone Disulfonic Acid, Disodium Salt
NWU	North West University
PAR	Pink Monosodium Salt Monohydrate
PFD	Process Flow Diagram
pH	Power of Hydrogen
PPM	Parts Per Million
PSD	Particle Size Distribution
SASOL	South African Synthetic Oil Limited
SAV	Sodium Ammonium Vanadate
SDS	Sodium Dodecyl Sulphate
SEM	Standard Error of the Mean
SHE	Standard Hydrogen Electrode
SOV	Sodium Ortho Vanadate
Std dev	Standard Deviation
TA	Total Alkalinity
TTDD	Trisodium Triammonium Decavanadate (V) Dodecahydrate
TVT	Trisodium Vanadate Trihydrate
UV	UltraViolent
VHS	Vanadium Hydrogen Sulphide
V ^{Total}	Total Vanadium
XRD	X-Ray Powder Diffraction
XRF	X-Ray Fluorescence

LIST OF SYMBOLS

<u>SYMBOLS</u>	<u>DESCRIPTION</u>
°C	Degree Celcius
µm	Micrometer
dm ³	Cubic decimeter
g	Gram
S-1	Solution 1
S-2	Solution 2
S-3	Solution 3
S-4	Solution 4
S-5	Solution 5

S-6	Solution 6
S-7	Solution 7
S-8	Solution 8
S_{∞}	Polymerized elemental sulphur
S-A	Sample A
S-B	Sample B
S-C	Sample C
S-D	Sample D
S-X	Solution X
V^{Total}	Total vanadium
$\alpha\text{-S}_8$	Orthorhombic elemental sulphur
$\beta\text{-S}_8$	Monoclinic elemental sulphur
μl	Microliter

CHAPTER 1: BACKGROUND AND MOTIVATION

1.1 Introduction

In this chapter the background and motivation, problem statement and hypothesis are discussed. The chapter further discusses the dissertation objectives and scope of work. The chapter will also provide a preview of subsequent chapters.

1.2 Background and motivation

During the production of fuels and other chemicals from coal, crude oil and natural gas, the production of hydrogen sulfide gas (H_2S) as a by-product is unavoidable (Gary, J., (2005), Trofe, T. W., et al., (1987), Taback, H.J., et al., (1985)). H_2S is a colourless and toxic gas that is very harmful to the environment as well as to human beings at certain concentrations. It is a weak acid and marginally soluble in water (Carter, C.N., (1966)). Over the years as countries developed and industrialized, production of H_2S as a by-product increased significantly and countries started to introduce stricter legislations on the H_2S emissions limits to protect the environment. The introduction of the stricter legislations forced industries to start investigating methods that can recover H_2S and convert to elemental sulphur as far back as the early 19th century (Gary, J., (2005), Trofe, T. W., et al., (1987)). There have been different processes (Claus, Unisulf, Lo-Cat, Hiperion Iron oxide box, Ferrox, Fischer, Thylox, Sulfolin, and many others) developed since 1927 to recover H_2S and convert the absorbed H_2S to elemental sulphur with some still in use today and others discontinued as a result of high operational costs (Gary, J., (2005)). The higher costs of operating processes that are associated with Claus, Unisulf and Iron oxide boxes led to the invention of a new method in the 1950's called StretfordTM process (Trofe, T. W., et al., (1987), Trofe, T. W., et al., (1986)).

The StretfordTM process uses an aqueous solution comprising of sodium bicarbonate (NaHCO_3) and carbonate (Na_2CO_3) in the molar ratio of 3:1, vanadium salts containing (V^{5+}) and sodium salts of the 2,6 and 2,7 isomers of anthraquinone disulfonic acid ($\text{Na}_2[\text{ADA}]$), (Nicklin, T., et al., (1961)). The process is based on the absorption of H_2S in the alkaline aqueous solution at pH values between 8.2 and 9.5, followed by oxidation of the hydrogen sulphide ions to sulphur product by V^{5+} and regeneration of V^{4+} . The V^{5+} and V^{4+} redox circuit by dissolved oxygen (O_2) molecules and hydrogen peroxide (H_2O_2) is driven by $\text{Na}_2[\text{ADA}]$ which is an oxidant (Gary, J., (2005)). V^{5+} plays a very crucial role in the overall StretfordTM chemistry during absorption and conversion of H_2S to elemental sulphur. This places V^{5+} at the heart of the StretfordTM process (Nicklin, T., et al., (1963A), (Nicklin, T., et al., (1963B)). By 1993 more than 100 StretfordTM plants

(63 plants in United States of America, 11 plants in Japan, 6 plants in Britain, 4 plants in Canada, 3 plants in Germany, 2 plants in South Africa and other countries) were still in operation (Trofe, T. W., et al., (1993)). A lot of research work has been done in the middle of 1980's by Gas Research Institute (GRI) to further improve and reduce the operational problems of the Stretford™ process as the industries that produce H₂S were either expanding or new plants were built (McKay, A.E., (1989)).

Previous research on the Stretford™ process did not fully address the vanadium speciation and how it affects production of elemental sulphur. This work will attempt to provide a detailed understanding of the effect of vanadium oxidation states on H₂S absorption and conversion to elemental sulphur. The physical, chemical and mineralogical properties of the elemental sulphur will be investigated to check the quality. The research will assist the Stretford™ operators to further understand how to optimize H₂S conversion to elemental sulphur whilst ensuring that the quality is not compromised.

1.3 Problem statement

In the Stretford™ aqueous solution containing low concentration of V⁵⁺ and high concentration of V⁴⁺ small elemental sulphur fines are formed. These fine particles causes handling challenges, equipment blockages, low sulphur production efficiency and filtration problems that can subsequently lead to high H₂S emissions. The chemistry of vanadium species in a Stretford™ aqueous solution is complex since mono-nuclear and various poly-nuclear anions occur in equilibrium (Vermaire, S., et al., (1988), Habayeb, M.A., et al., (1980)). This equilibrium depends not only on the vanadium concentration, but also on the pH values, the temperature, and the ionic strength of the Stretford™ aqueous solution. Reliable information exists for both the effects of pH values and vanadium concentrations (V⁵⁺), but the effects of vanadium oxidation states on elemental sulphur production and its quality have not been investigated in detail. At low concentrations of V⁵⁺ below 0.029 mol.dm⁻³, there are insufficient of V⁵⁺ ions derived from SAV stoichiometric to oxidize HS⁻ to elemental sulphur and this will result in incomplete oxidation of HS⁻ in the oxidizing tank at high HS⁻ loading (Scheffel, F.A., et al., (1986), Trofe, T.W., et al., (1993), Cruywagen, J.J., et al., (1998), Trofe, T.W., et al., (1987)).

1.4 Hypothesis

The low proportions of vanadium cations (<0.029 mol.dm⁻³ of V⁵⁺) and high content of V⁴⁺ (>0.0003 mol.dm⁻³) in the Stretford™ process could negatively affect the absorption efficiency of H₂S and its initial conversion to elemental sulphur. However, the ratios of vanadium cations (V⁴⁺

to V^{5+}) could have effects on the conversion of the absorbed HS^- to produce different forms of elemental sulphur particles. This hypothesis was not adequately investigated in the past.

1.5 Objectives

The main objective of the study was to determine the effect of vanadium cations (V^{4+} and V^{5+}) on the conversion of the absorbed HS^- to form the elemental sulphur particles containing different properties (physical, chemical and mineralogical) in the simulated Stretford™ aqueous solutions. In order to achieve the goals of this objective in this study, the following steps were conducted:

- Effect of V^{5+} concentrations on H_2S absorption and conversion of HS^- to elemental sulphur.
- Effect of impurities (Na_2SO_4 and $NaSCN$) on H_2S absorption and conversion of HS^- to elemental sulphur.
- Effect of vanadium oxidation states on H_2S absorption and conversion of HS^- to elemental sulphur.
- Comparative method of studying of the chemical, mineralogical, and physical properties of elemental sulphur particles produced from the experiments and the commercial elemental sulphur was followed.
- Develop H_2S speciation model as a function of pH using OLI studio analyzer to simulate the H_2S species that are oxidized to elemental sulphur using V^{5+} species.
- Develop vanadium speciation model as a function of pH using OLI studio analyzer to simulate vanadium species in the simulated Stretford™ aqueous solution.
- Develop statistical model to determine the effect of vanadium cations (V^{4+} and V^{5+}) on H_2S absorption and conversion of HS^- to elemental sulphur formation and to validate experimental results.

1.6 Scope of work

- At fixed concentrations of operating parameters (H_2S , pH, total alkalinity, $NaSCN$, Na_2SO_4 , and Na_2ADA concentrations) and temperature but variable V^{5+} concentrations - to determine the effect of V^{5+} concentrations on H_2S conversion to elemental sulphur and its quality.
- At fixed concentrations of operating parameters but variable V^{5+} concentration without $NaSCN$ and Na_2SO_4 added- to determine the effects of impurities on H_2S conversion to elemental sulphur and its quality.
- At fixed concentrations of operating parameters but variable V^{5+} to V^{4+} molar ratios without $Na_2[ADA]$ - to determine the effects of vanadium oxidation states on H_2S conversion to elemental sulphur and its quality.

- Simulation of H₂S speciation as a function of pH in water using the OLI stream analyzer software. This is to understand the type of H₂S species in the Stretford™ aqueous solution at different pH ranges that get oxidized to elemental sulphur.
- Simulation of vanadium oxidation states stability as a function of pH in water using the OLI stream analyzer software - to simulate stable vanadium species across the Stretford™ aqueous solution pH range, which oxidized absorbed H₂S to elemental sulphur.
- Develop H₂S absorption and sulphur production statistical models as a function of V⁵⁺ concentrations in Stretford™ solution.

1.7 Dissertation outline

Chapter 1 gives the introduction of the dissertation. The literature review is given in Chapter 2. Chapter 3 discusses the procedures used to perform the experiments, the analytical techniques, experimental repeatability, and the characterizations of the chemicals used for the experimental work. Results and discussions are given in chapter 4. Chapter 5 outlines the OLI studio analyzer and statistical models. Chapter 6 gives conclusions and recommendations of the dissertation. Figure 1.1 is an overview of the dissertation.

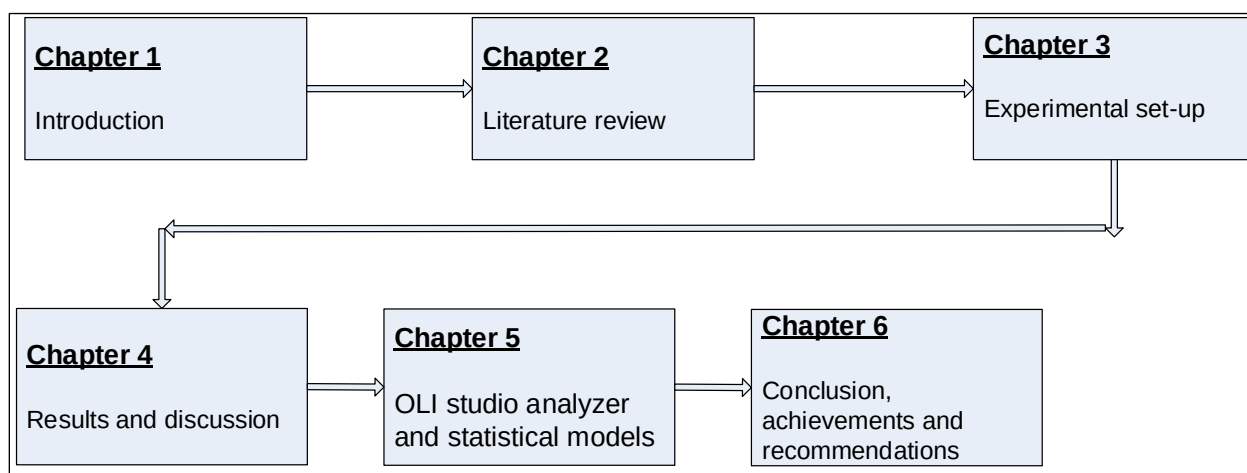


Figure 1.1: Outline of the dissertation in the research study

CHAPTER 2: LITERATURE STUDY

2.1 Stretford™ process description

Chapter 2 discusses the details and insights of the Stretford™ process. The Stretford™ process can be divided into H₂S absorption, elemental sulphur formation, slurry/separation, melting and granulation systems. The process flow diagram (PFD) of a typical Stretford™ process is given in Figure 2.1 (Trofe, T.W., et al., (1986)). This study will focus more on the process chemistry of the H₂S absorption in the absorbing contactor, HS⁻ conversion to elemental sulphur in the reaction tank and reduction-oxidation chemistry between vanadium species, oxygen molecules, and Na₂[ADA] in the oxidizing tank. The chapter will end with a summary outlining the shortcomings observed in the literature that require further investigation.

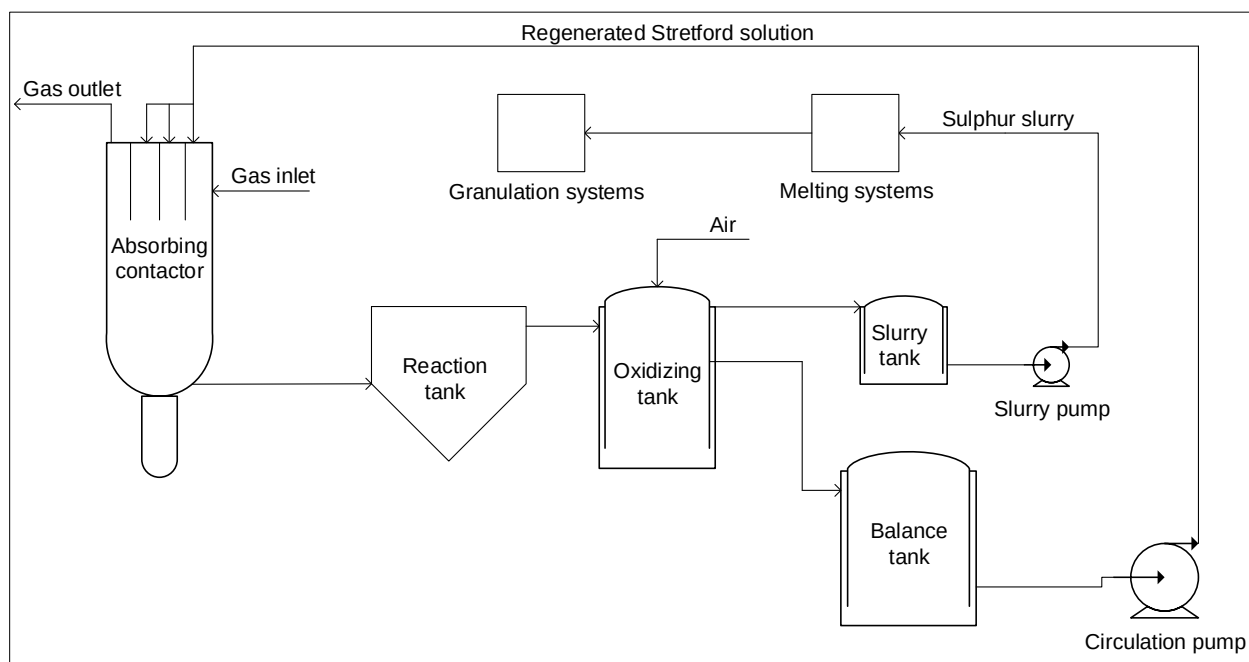


Figure 2.1: Overview of typical Stretford™ process (Trofe, T.W., et al. (1993))

The feed gas which contains H₂S, carbon dioxide (CO₂) and other gases enters the gas/liquid absorption contactor on the side while the Stretford™ aqueous solution containing total alkalinity, NaSCN, Na₂SO₄, V⁵⁺, O₂⁻ molecules and Na₂[ADA] enters on top of the absorbing contactor. The H₂S is absorbed by the Stretford™ aqueous solution counter or concurrently (Trofe, T.W., et al., (1993)). The absorption of H₂S in the Stretford™ aqueous solution is a function of pH value. Chemically the Stretford™ aqueous solution can absorb all H₂S, provided the stoichiometric amount of V⁵⁺ is available to react with HS⁻. The physical design of the absorbing contactor determines the absorption efficiency (Vermaire, S., et al., (1988), Trofe T.W., et al., (1987), Carter, C.N., (1966)). Treated gas exits the absorbing contactor at the top to a smoke stack or it is sent

for further processing, whilst the Stretford™ aqueous solution with the absorbed hydrogen sulphide starts to dissociate to HS^- and exits at the bottom of the absorbing contactor (McKay, A.E., (1989)).

As the HS^- in the Stretford™ aqueous solution exits the bottom of the absorbing contactor, V^{5+} starts to oxidize HS^- to elemental sulphur and the reaction reach completion at the reaction tank (Kohl, A.L., et al., (1997)). The Stretford™ aqueous solution exits the reaction tank to the oxidizing tank with V^{5+} reduced to V^{4+} . Atmospheric air is introduced at the bottom of the oxidizing tank to float the sulphur froth and dissolved the O_2 molecules to regenerate V^{4+} back to its active form of V^{5+} . The oxidizing tank has a dual function and also purges the CO_2 gas (Gary J., (2005)). The reaction between V^{4+} and O_2 radicals back to V^{5+} is not direct; it requires $\text{Na}_2[\text{ADA}]$ to act as a catalyst (Kohl, A.L., et al., (1997)). After oxidation of V^{4+} to V^{5+} , $\text{Na}_2[\text{H}_2\text{ADA}]$ is also regenerated back by dissolved O_2 molecules to its active form $\text{Na}_2[\text{ADA}]$ (Kohl, A.L., et al., (1997)).

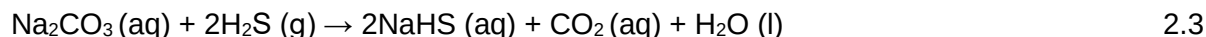
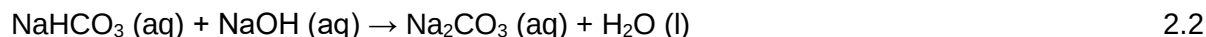
The sulphur froth floats on top of the Stretford™ aqueous solution and overflows together with Stretford™ aqueous solution to the slurry tank that acts as a buffer for the centrifuge or pan vacuum filter. The Stretford™ circulation solution underflows to the balance tank which serves as online Stretford™ aqueous solution buffer after regeneration of V^{4+} back to V^{5+} and $\text{Na}_2[\text{H}_2\text{ADA}]$ back to $\text{Na}_2[\text{ADA}]$. The spent air exits the oxidizing tank at the top to the atmosphere together with purged CO_2 (Trofe, T.W., et al., (1993)). The regenerated Stretford™ circulation solution exits the balance tank back to the absorbing contactor for absorption of H_2S containing gas. The pH of the Stretford™ solution is controlled by adding sodium hydroxide (NaOH) or Na_2CO_3 as it will slowly drop as Na_2CO_3 gets depleted (McKay, A.E., (1989)). The sulphur slurry from the slurry tank which still contains Stretford™ solution is first separated from the Stretford™ solution through the centrifuge or pan vacuum filter before being sent to the melting system to process it to liquid sulphur (McKay, A.E., (1989), Trofe, T.W., et al., (1987)). The elemental sulphur slurry is melted by direct contact with medium pressure steam and liquid sulphur is produced. Liquid sulphur is then pumped or transported for filtration and granulation or sent to the market as is (Scheffel, F.A., et al., (1986)).

The focus of this study will exclude the melting, filtration and granulation part of the Stretford™ process systems and will focus only on the absorption and circulation systems of the process.

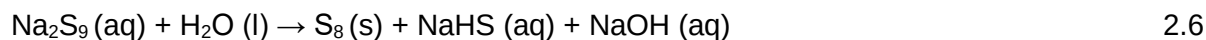
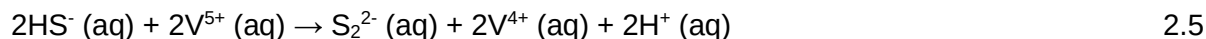
2.2 Stretford™ process chemistry

In the Stretford™ process, under ideal conditions sulphur is mainly formed in the absorbing contactor and the reaction tank. Prior to that, H_2S is absorbed by the Stretford™ aqueous solution

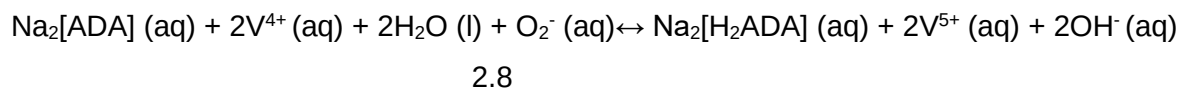
in the absorbing contactor. The oxidation of HS⁻ leads to polysulphide anions, which are eventually oxidized to sulphur in the reaction tank as indicated by Reactions 2.1 to 2.3 below (Nicklin, T., et al., (1963A), Nicklin, T., et al., (1963B), Trofe, T.W., et al., (1987)).



The absorbed H₂S dissociate to HS⁻ then followed by series of oxidation and disproportionation reactions. The disproportionation as indicated by Reaction 2.4 is catalytically accelerated by V⁵⁺ as indicated by Reaction 2.5. By a number of disproportionation and further oxidation reactions, long-chain of hydrophilic polysulphide are formed which eventually split off to hydrophobic α-S₈ ring molecules at a pH value below 8 in the reaction tanks as indicated by Reaction 2.6 (Hoffman, M.R., (1977)).



In Reaction 2.5, other V⁵⁺ ions are reduced to V⁴⁺ ions during polysulphide conversion to elemental sulphur. It is extremely important that V⁴⁺ be re-oxidized by dissolved O₂⁻ molecules and H₂O₂ back to V⁵⁺ in the oxidizing tank, otherwise other V⁴⁺ ions can precipitate in the form of sodium salts (Trofe, T.W., et al., (1993), Trofe, T.W., et al., (1987)). The H₂O₂ is formed during regeneration of inactive Na₂[H₂ADA] as shown in Reaction 2.7. V⁴⁺ alone is too slow to be oxidized back to V⁵⁺ in direct contact with dissolved O₂⁻ molecules. The O₂⁻ radical's anion is capable of oxidizing V⁴⁺ to V⁵⁺ as per Reaction 2.8 (Kohl, A.L., et al., (1997)).



2.2.1 H₂S absorption chemistry

The H₂S containing gas is absorbed into Stretford™ solution present in the absorbing contactor and dissociates to HS⁻ ions that are subsequently converted to elemental sulphur (McKay, A.E., (1989), Trofe, T.W., et al., (1993)). The summary of the absorption, dissociation and

disproportionation of H_2S in a StretfordTM aqueous solution is shown by Reactions 2.9, 2.10 and 2.4 (Nicklin, T., et al., (1961), Trofe, T.W., et al., (1987)).



HS^- is the main species that is present in the pH range of 8.2 to 9.5 following the absorption of H_2S in the StretfordTM aqueous solution. The absorption capacity is enriched by oxidation of HS^- by V^{5+} to elemental sulphur as indicated by Reaction 2.5. If oxidation of HS^- to elemental sulphur does not happen quickly enough, an equilibrium condition can be reached and limit the absorption of H_2S (Stumm, W., et al., (1970), Trofe, T.W., et al., (1993), Trofe, T.W., et al., (1987)). Laboratory studies reported in the literature have indicated that HS^- concentration in a solution containing NaHCO_3 and Na_2CO_3 was about $0.0018 \text{ mol.dm}^{-3}$ without V^{5+} and $\text{Na}_2[\text{ADA}]$, while in the same solution with V^{5+} and $\text{Na}_2[\text{ADA}]$ added, there was less than $0.000018 \text{ mol.dm}^{-3}$ of HS^- in the solution. The study confirms that the dissociation of H_2S to HS^- as indicated by Reaction 2.10 and the oxidation of HS^- by V^{5+} to elemental sulphur as indicated by Reaction 2.5 play a crucial role in the overall absorption of H_2S (Fenton, D.M., et al., (1979), Keene, D.E., (1992)). The pH, total alkalinity, and temperature are the other crucial parameters in the absorption, dissociation and conversion of HS^- to elemental sulphur (details of the roles of pH, total alkalinity, and temperature are discussed in Sections 2.3 - 2.5).

2.2.2 Conversion of HS^- to elemental sulphur in the reaction tank

The conversion of HS^- to elemental sulphur starts at the absorbing contactor and it is completed at the reaction tank. The oxidation reaction of HS^- to elemental sulphur takes place in an aqueous phase with V^{5+} reducing to V^{4+} . Reaction 2.5 shows the overall HS^- oxidation and V^{5+} reduction cycles, but does not show the detailed information about the reactants or products speciation or the kinetics behind the chemical process (Trofe, T.W., et al., (1993), Trofe, T.W., et al., (1987), Nicklin, T., et al., (1961)). Detailed laboratory studies were conducted to understand the reaction kinetics between V^{5+} and HS^- by Schwarzenbach. The complete overall results indicated that the reaction takes place in a series of steps with vanadium hydrogen sulphide species (VHS) and disulphide (S_2^{2-}) acting as intermediates as shown by Reactions 2.11 and 2.12 (Schwarzenbach, G., et al. (1960)).



The first step after H_2S is absorbed and dissociates to HS^- is indicated by reversible Reaction 2.11 to form a VHS species. After the formation of the VHS species it can combine by internal oxidation to a chain and react with itself and produce di-sulphide (S_2^{2-}) species as shown by Reaction 2.12. The series of oxidation and disproportionation chain reactions continues until S_9^{2-} is formed as indicated by Reaction 2.4. The S_9^{2-} is known to disproportionate to $\alpha\text{-S}_8$ (elemental sulphur in solution) and HS^- as indicated by Reaction 2.6 (Trofe, T.W., et al., (1993)). Further studies done by Kelsall and Thompson also confirmed the reaction between V^{5+} and HS^- to form VHS species which then continues to form polysulphide and elemental sulphur. The experiments were done using electrochemical methods to determine the presence of polysulphide (S_2^{2-}), (Kelsall, G.H., et al., (1989), Trofe, T.W., et al., (1993)).

The polysulphide concentration increases at the beginning and decreases thereafter with a simultaneous formation of elemental sulphur in the StretfordTM aqueous solution being observed (Schwarzenbach, G., et al., (1960), Trofe, T.W., et al., (1987)). The oxidation of HS^- (Reaction 2.11) was found to be faster than the oxidation of polysulphide (Reaction 2.12) to elemental sulphur (Trofe, T.W., et al., (1993)). Therefore, the StretfordTM solution always contains unreacted polysulphide at equilibrium with each other (Schwarzenbach, G., et al., (1960)). The rate of reaction between V^{5+} and polysulphide increases as the pH values of the StretfordTM aqueous solution decreases (Ryder, C., et al., (1962), Steudel, R., (1996), Trofe, T.W., et al., (1993)).

The observation done in most StretfordTM plants confirmed plugging of the absorber and reaction tank with a mixture of sodium salts precipitate and fine sulphur due to lower pH values. The pH values decrease due to hydrogen cyanide (HCN), CO_2 and H_2S absorbed in a StretfordTM aqueous solution, which are acidic (Trofe, T.W., et al., (1993), Trofe, T.W., et al., (1989)). The optimum pH values for the good conversion of HS^- to elemental sulphur is between 7.2 and 7.5 in the reaction tank (Trofe, T.W., et al., (1986)). The absence of excess V^{5+} can result in slip out of the HS^- to the oxidizing tank and promotes formation of by-products.

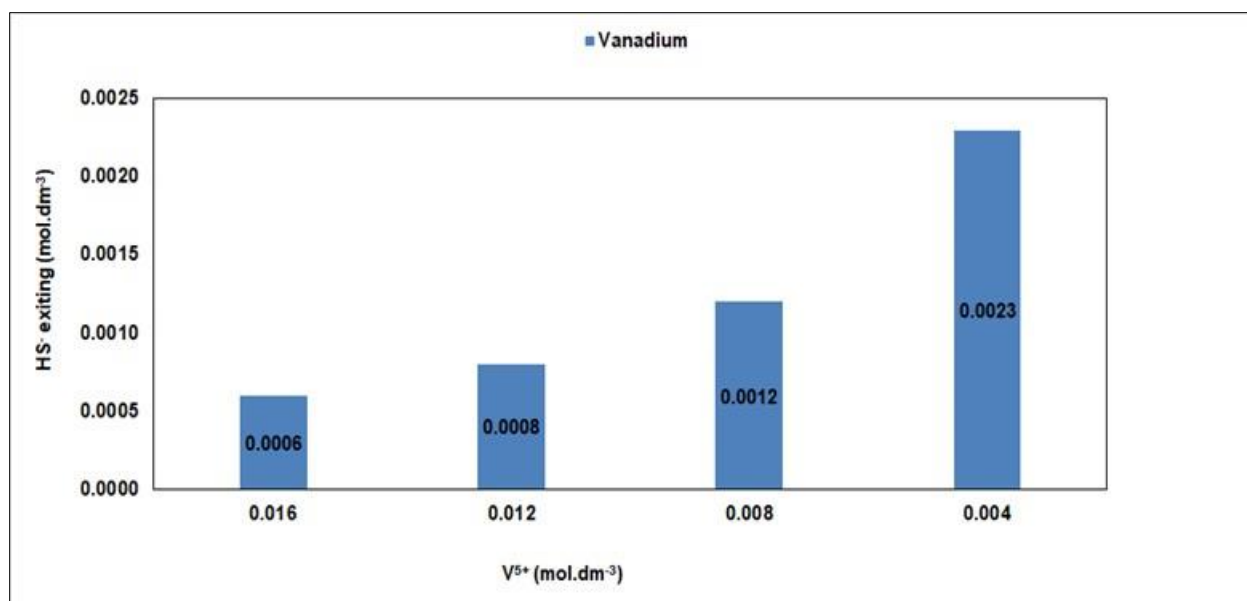
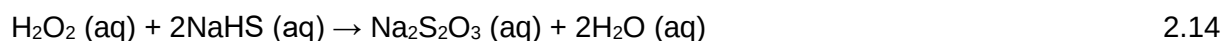
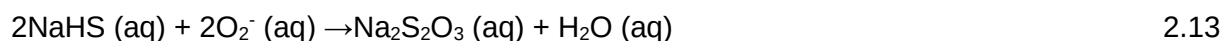
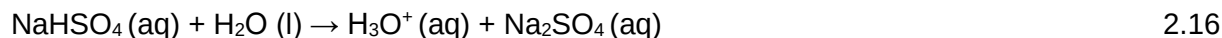
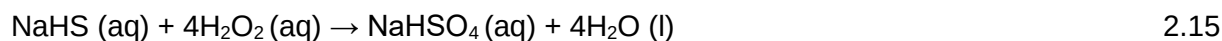


Figure 2.2: Role of excess V⁵⁺ during conversion of HS⁻ to elemental sulphur (Scheffel, F.A., et al., (1986))

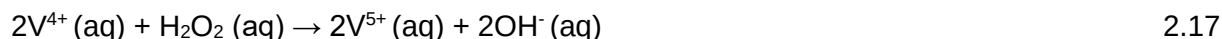
Figure 2.2 clearly shows that the slip out of HS⁻ from the reaction tank is a result of insufficient V⁵⁺ in the Stretford™ aqueous solution. For example, when V⁵⁺ concentration is 0.016 mol.dm⁻³ and HS⁻ loading of 0.015 mol.dm⁻³, the HS⁻ slipped out from the reaction tank to the oxidizing tank is about 0.0006 mol.dm⁻³. However, when V⁵⁺ concentration is reduced to 0.004 mol.dm⁻³ at the same amount of HS⁻ loading, the HS⁻ slipped out from the reaction tank exponentially increased to about 0.0023 mol.dm⁻³ (Trofe T.W., et al., (1986)). The residence time in the reaction tank is also very importance for the good operation of the process in preventing slip out of HS⁻ to oxidizing tanks (Steudel, R., (1996), Trofe, T.W., et al., (1993), Nicklin, T., et al., (1963A)). If the residence time is too long, it may lead to the precipitation of vanadium species and if the residence time is too short, it may lead to slip out of HS⁻ to the oxidizing tank which will react with dissolved O₂⁻ radicals or H₂O₂ and will convert to by-products such as sodium thiosulphate (Na₂S₂O₃) and Na₂SO₄ as per Reactions 2.13 to 2.16. Without sufficient V⁵⁺ to meet stoichiometry requirements of conversion of HS⁻ to elemental sulphur in the absorbing contactor as indicated by Reaction 2.5, some HS⁻ ions and polysulphide present in the oxidizing tank are oxidized to thiosulphate and sulphate. These sulphates react with sodium ions to form Na₂S₂O₃ and Na₂SO₄ salts (Reactions 2.13-2.16), (Trofe, T.W., et al., (1987), Trofe, T.W., et al., (1991), Trofe, T.W., et al., (1993)). The optimum residence time in most Stretford™ processes is 8-20 minutes (Trofe, T.W., et al., (1993), Nicklin, T., et al., (1963), Ryder, C., et al., (1962)).





2.2.3 Oxidation of V^{4+} and precipitation of $\alpha\text{-S}_8$ in the oxidizing tank

The H_2O_2 that is formed during regeneration of $\text{Na}_2[\text{ADA}]$ as per Reaction 2.7 re-oxidizes V^{4+} present in the oxidizing tank to V^{5+} as shown by Reaction 2.17. The $\text{Na}_2[\text{H}_2\text{ADA}]$ is easily re-oxidized back to $\text{Na}_2[\text{ADA}]$ with dissolved O_2 molecules as shown by Reaction 2.7 (Zwicky, J.F., et al., (1980), Moyes, A.J., et al., (1973), Trofe, T.W., et al., (1993)).



The overall Reactions 2.7, 2.8 and 2.17 take place in the oxidizing tank before the Stretford™ solution can be pumped back to the absorbing contactor for absorption of H_2S (Vancini, C.A., et al., (1985), Trofe, T.W., et al., (1993)). The elemental sulphur froth is separated from Stretford™ aqueous solution by density differences. Figure 2.3 shows HS^- converted to elemental sulphur with V^{5+} as an oxidizing agent, which then loses an electron and reduced to V^{4+} as indicated by the grey area. The elemental sulphur precipitation and nucleation ripening process start and finish at the oxidizing tank. The formation of bubbles by the air cause elemental sulphur to form froth floatation and elemental sulphur continue to agglomerate through an Ostwald ripening process (Zwicky, J.F., et al., (1980)).

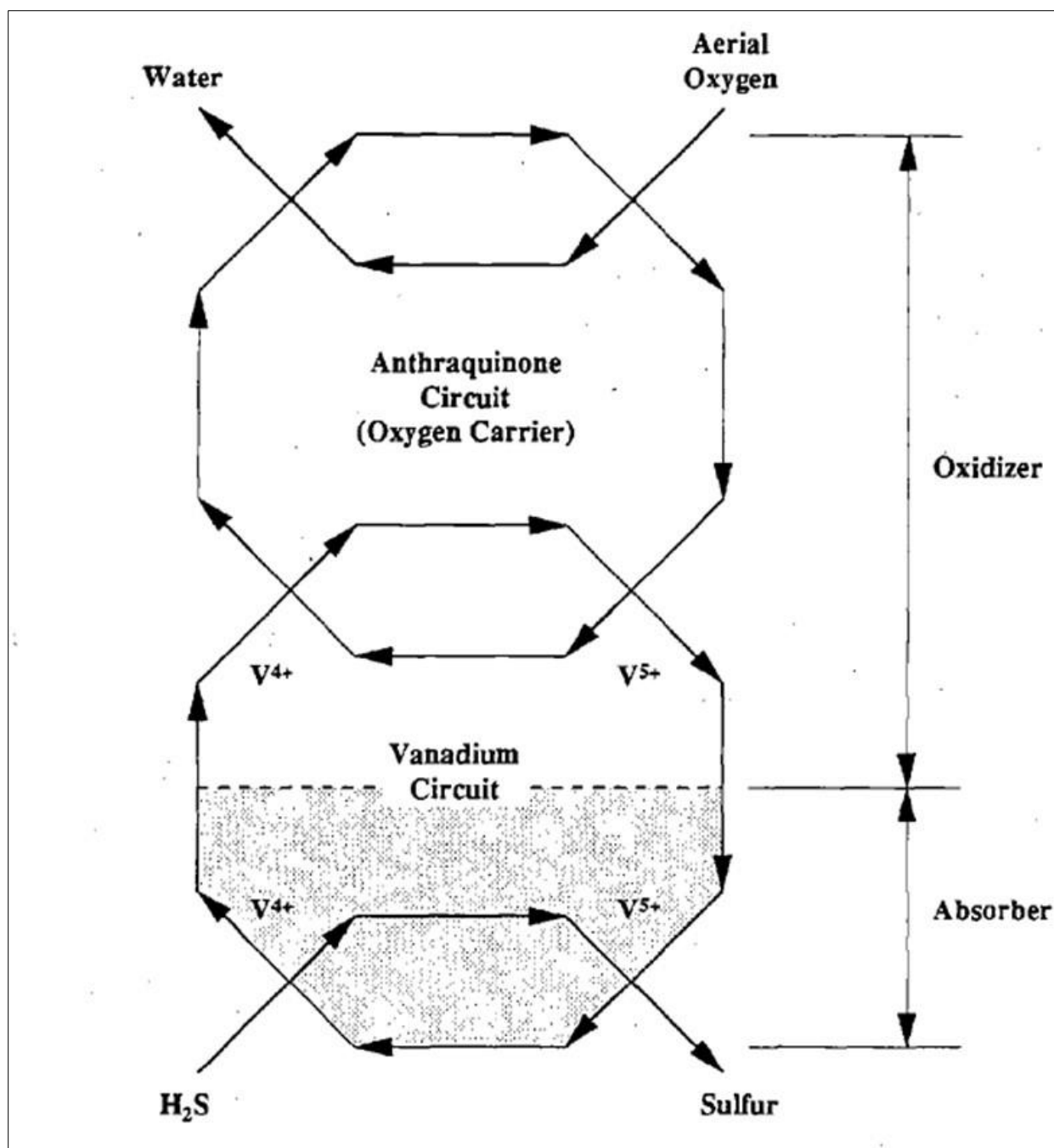


Figure 2.3: Overall redox cycle between V^{4+} , V^{5+} , O_2^- and $Na_2[ADA]$ in the Stretford™ aqueous solution (Trofe, T.W., et al., (1993))

2.3 Role of pH on absorption of H_2S and oxidation of HS^- to sulphur

The speciation of H_2S in water is represented by Reactions 2.9, 2.10 and 2.18 (Carter, C.N., (1966)).



As expected, the dominant H_2S species is dependent on the pH value of the solution. It was found that at pH values between 9 and 12 there was more than 99% HS^- in the aqueous solution (Carter, C.N., (1966), Stumm, W., (1970)). A study was carried out to establish the degree of ionization of hydrogen sulphide species at pH values between 0.3 to 14 as indicated by Figures 2.4 and 2.5.

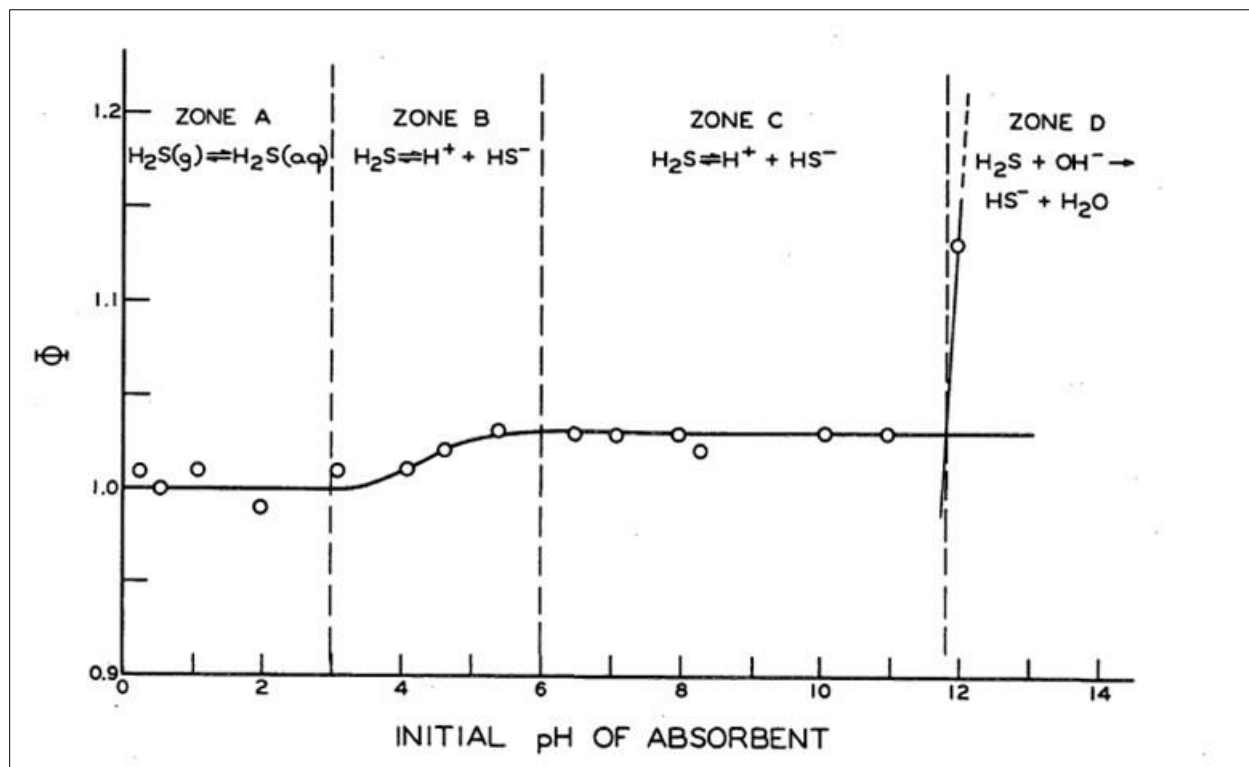


Figure 2.4: Effect of pH on absorption and ionization of H_2S (pH (0.3-11.8), (Carter, C.N., (1966))

Note: Zone A (pH, 0-3); Zone B (pH, 3-6); Zone C (pH, 6-11.8); Zone D (pH, 11.8-14); Θ ; (Rate constant)

The results of the study were divided into Zones A to D. In Zone A ($\text{pH} < 3$) as indicated by Figure 2.4, the H_2S is absorbed into acidic solution and does not dissociate to HS^- as indicated by reversible Reaction 2.9 (Carter, C.N., (1966), Spalding, C.W., (1961)). This means the absorption of H_2S in Zone A is not influenced by the rate of dissociation to HS^- in Reaction 2.10. The degree of ionization in pH less than 3 is negligible and as a result, there is equilibrium between H_2S in gaseous and aqueous form (Carter, C.N., (1966)). The function Θ on the y-axis was calculated by dividing the experimental rate of H_2S absorption by the rate of absorption without chemical reaction. As the pH increases to greater than 3 the dissociation of H_2S in the aqueous solution, starts to occur as indicated in Zone B. The dissociation of H_2S to HS^- occurs until the pH of 11.8 as indicated in Zone C. At pH value above 6, the curve is a straight line until pH of 11.8, which indicates that the reaction rate over the pH ranges is almost not changing. Over the pH range of 6 to 11.8, Reaction 2.10 is such that reverse reaction is negligible and can be considered irreversible (Carter, C.N., (1966)). Figure 2.5 shows that at the pH value above 11.8, the rate of

absorption increase exponentially. Reaction 2.18 is a neutralization reaction and possibly has a faster reaction rate than Reaction 2.10. The neutralization Reaction 2.18 will outshine the impact of ionization in Reaction 2.10 on the rate of absorption. When hydroxide ions react with acidic absorbed H_2S , the reaction has an infinitely fast rate (Nijsing, R. A. T. O., et al., (1959), Spalding, C.W., (1961)).

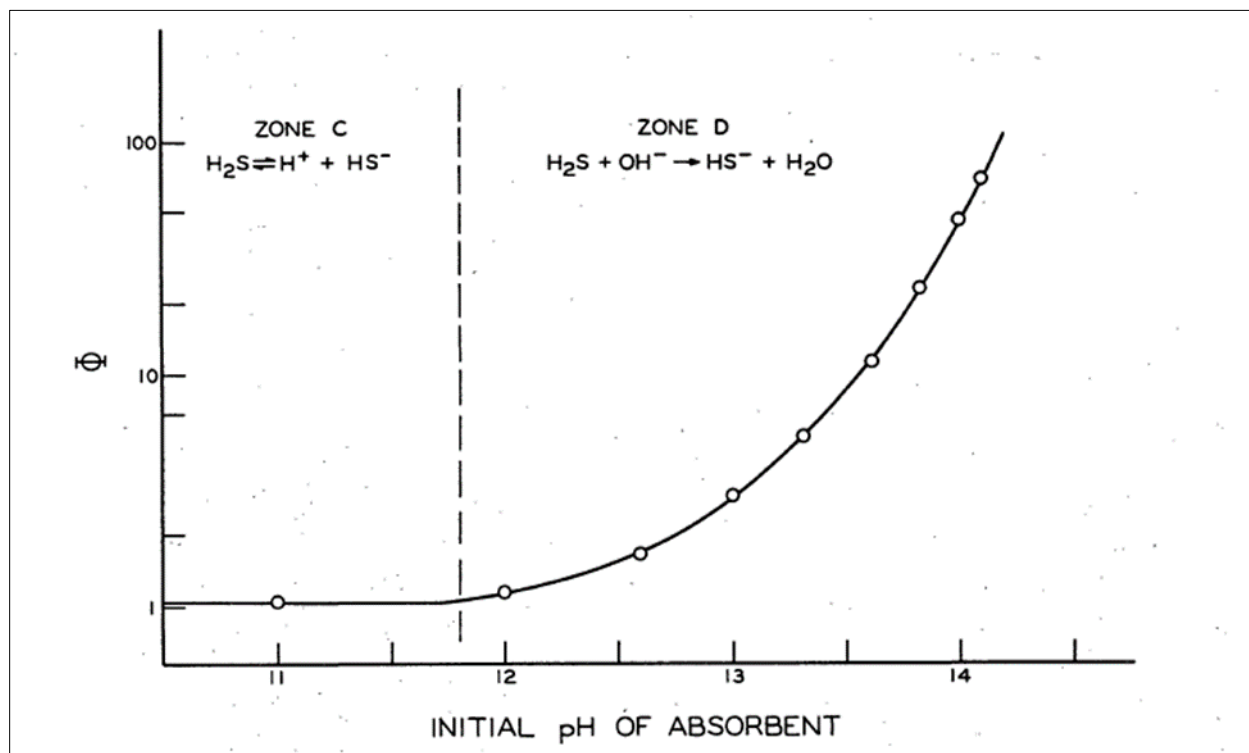


Figure 2.5: Effect of pH on absorption and ionization of H_2S gas ($\text{pH} > 11.8$), (Carter, C.N., (1966))

The StretfordTM aqueous solution is controlled between 8.2 and 9.5 in the absorbing contactor inlet and the dominant species is HS^- (Kohl, A.L., et al., (1997)). It is very important to operate the StretfordTM aqueous solution at an optimum pH between 8.2 and 9.5 at the inlet of the absorbing contactor to guarantee maximum absorption of H_2S (Trofe, T.W., et al., (1993), Carter, C.N., (1966)). The rate of conversion of HS^- to elemental sulphur is favored as pH value decreases as indicated by Figure 2.6 (Kohl, A.L., et al., (1979)). When the pH of the solution is 10, the rate constant of HS^- to elemental sulphur is $2500 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{hr}^{-1}$, while the reaction rate constant is $12000 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{hr}^{-1}$, at pH value of 7 (Nicklin, T., et al., (1961), Ryder, C., et al., (1962)). On the contrary, the absorption rate of H_2S is high at the high pH as indicated in Figures 2.4, 2.5 and 2.7. However, good conversion of the absorbed HS^- is achieved at low pH as indicated by Figure 2.6 (Chen, K.W., et al., (1972), Giggenbach, W., (1972), Ryder, C., et al., (1962)). If the pH is too high, HS^- slips out of the reaction tank and oxidizes to sodium based by-products as indicated by Reactions

2.13 - 2.16. However, if pH is too low the elemental sulphur might be formed in the absorbing contactor and cause fouling (Kohl, A.L., et al., (1997)).

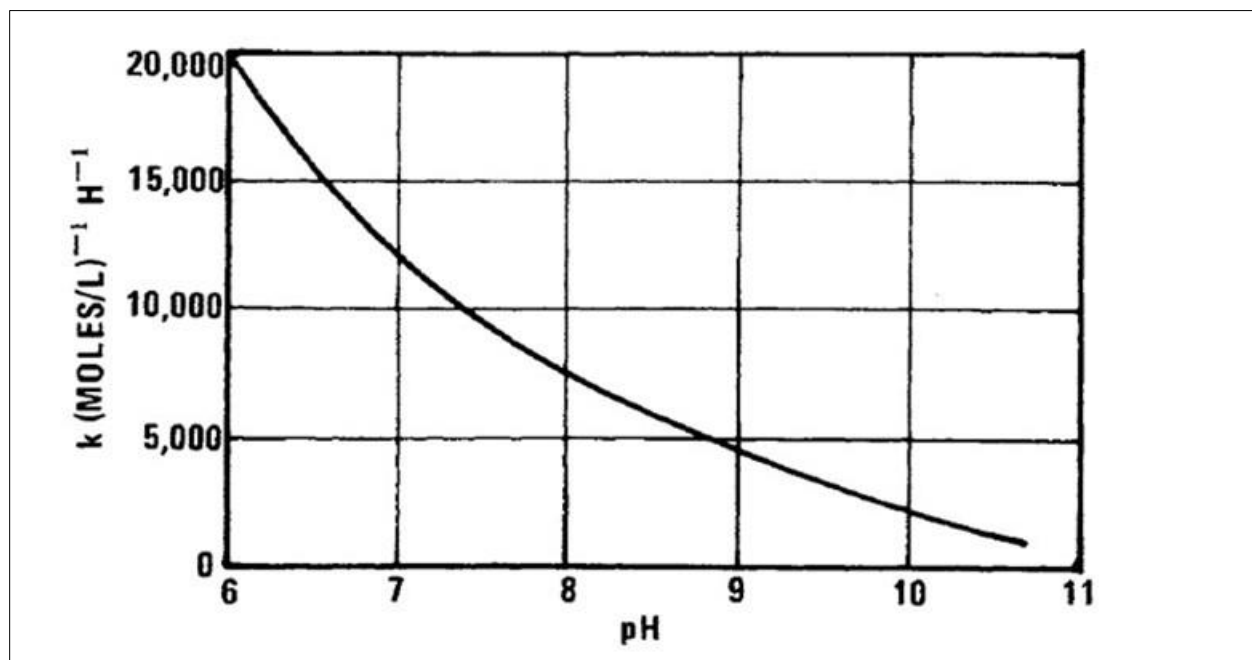


Figure 2.6: Rate of oxidation of HS^- to sulphur by V^{5+} increases as pH decreases (Kohl, A.L., et al., (1979))

Figure 2.7 indicates the overview of H_2S species in StretfordTM aqueous solution as a function of pH values. The H_2S acidity constants of 1×10^{-7} and 1×10^{-13} at 20°C were used to construct species distribution diagram (Stumm, W., et al., (1970)). It can be clearly seen that above pH of 9 that all of the H_2S is absorbed and dissociate to hydrogen sulphide ions which is in support of Figures 2.4 and 2.5 theories on Zones C and D as already explained (Trofe, T.W., et al., (1987)).

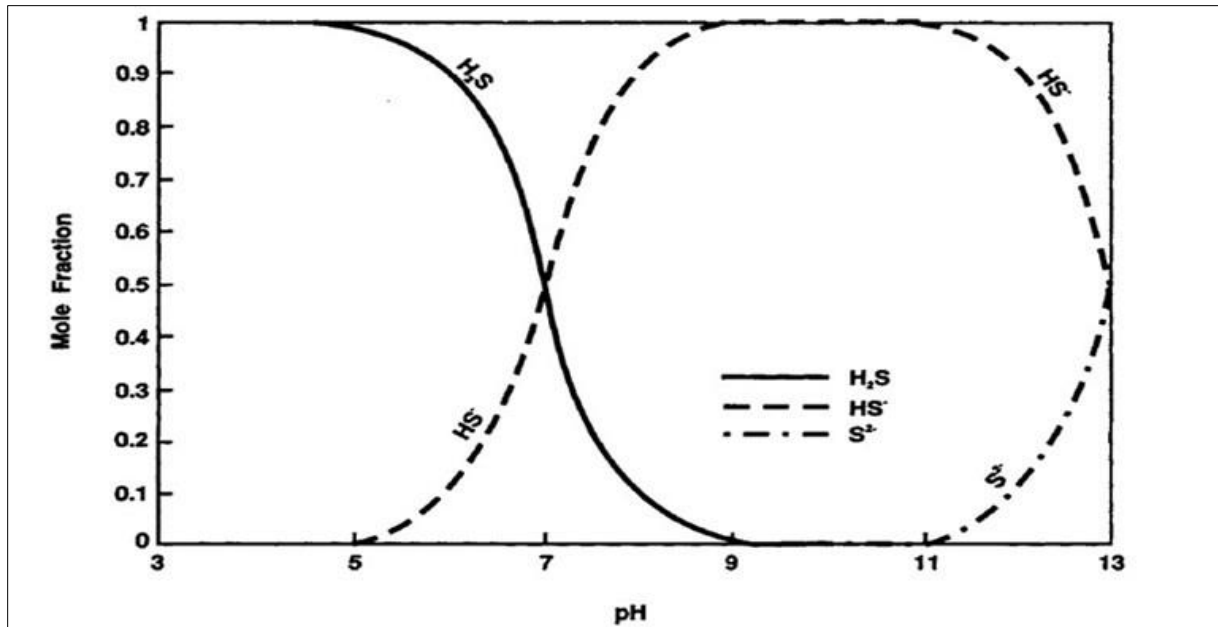
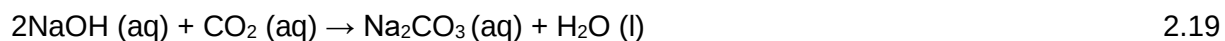


Figure 2.7: H₂S speciation distribution diagram at 25°C as a function of pH (Troffe, T.W., et al., (1987))

2.4 Role of total alkalinity in the Stretford™ process

The total alkalinity (NaHCO₃ + Na₂CO₃) content is maintained by the addition of NaOH, NaHCO₃ and Na₂CO₃ to the Stretford™ aqueous solution on a daily basis and it acts as a buffer to control the pH of the Stretford™ aqueous solution” (Rice, E.W., et al., (2012), Carter, C.N., (1966)). The NaOH solution, which is added to the Stretford™ solution, can also react with CO₂ or H₂O₂ and form Na₂CO₃, H₂O and sodium peroxide (Na₂O₂) as shown by Reactions 2.19 and 2.20.



Carbon dioxide is absorbed in the Stretford™ solution together with H₂S and HCN in the absorbing contactor. It is very important not to operate the Stretford™ process at low total alkalinity concentration (<0.11 mol.dm⁻³) which is a buffer for pH as it will increase absorption of CO₂ in the absorbing contactor (Trofe, T.W., et al., (1993)). If NaOH is not added to the Stretford™ solution on a daily basis, CO₂ is absorbed and further lower the pH value. Figure 2.8 shows that when there is no CO₂ in the feed gas, the pH of the Stretford™ aqueous solution is 9.6 in the reaction tank. However, when CO₂ concentration in the feed gas increased to 50%, the pH of the Stretford™ aqueous solution dropped to 7.6 (Trofe, T.W., et al., (1993)).

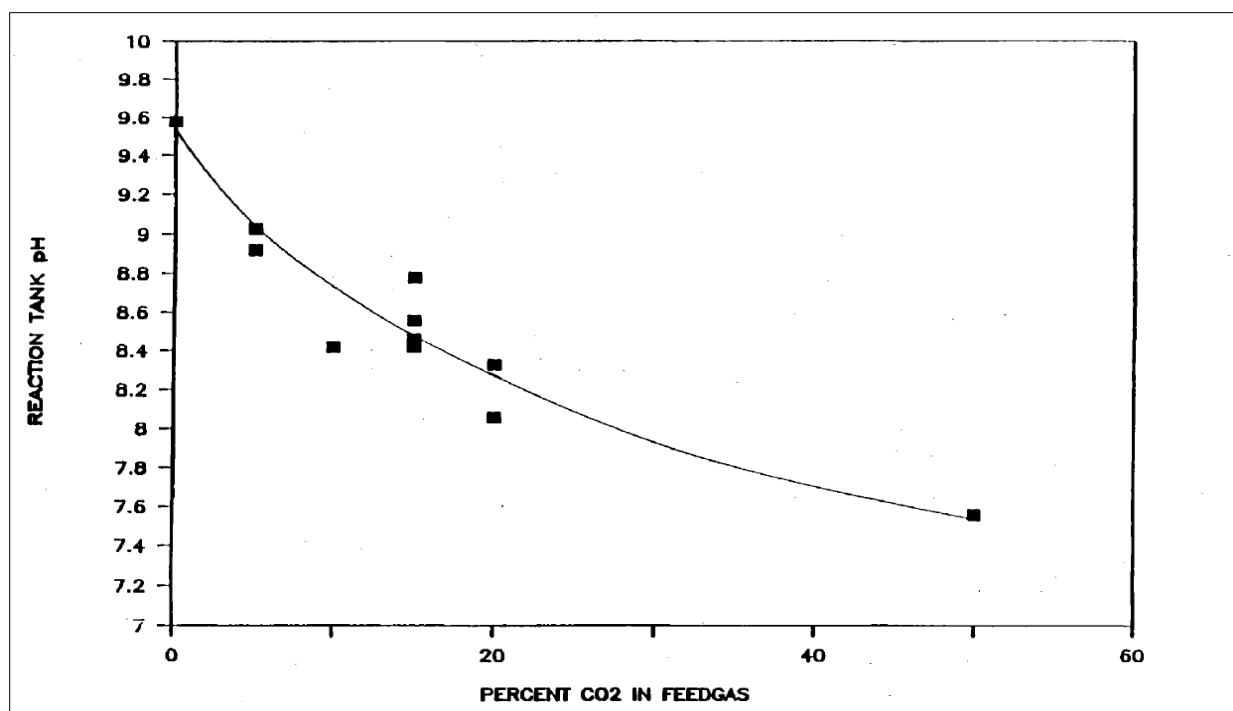


Figure 2.8: Impact of high concentration of CO₂ on Stretford™ aqueous solution pH (Trofe, T.W., et al., (1993))

The absorption efficiency of H₂S in the Stretford™ process is affected at low pH values due to a high absorption efficiency of CO₂. Absorption and dissociation of H₂S in the Stretford™ aqueous solution is a function of pH values. On the other hand, high total alkalinity in the Stretford™ aqueous solution is responsible for the formation of sodium based by-products at high pH values (pH>8.9), (Nicklin, T., (1963B)). Figure 2.9 show that when total alkalinity increased from 0.189 to 0.473 mol.dm⁻³ per day, the formation of sodium sulphate increased from 0.00092 to 0.0023 mol.dm⁻³ per day. The control of the upper and lower limits in the Stretford™ solution has differed depending on the plant vendor and individual plant experience. Different Stretford™ plants have operated between 0.11-0.28 mol.dm⁻³ total alkalinity, with preferred limits between 0.19-0.24 mol.dm⁻³ by most Stretford™ plants (Trofe, T.W., et al., (1993)).

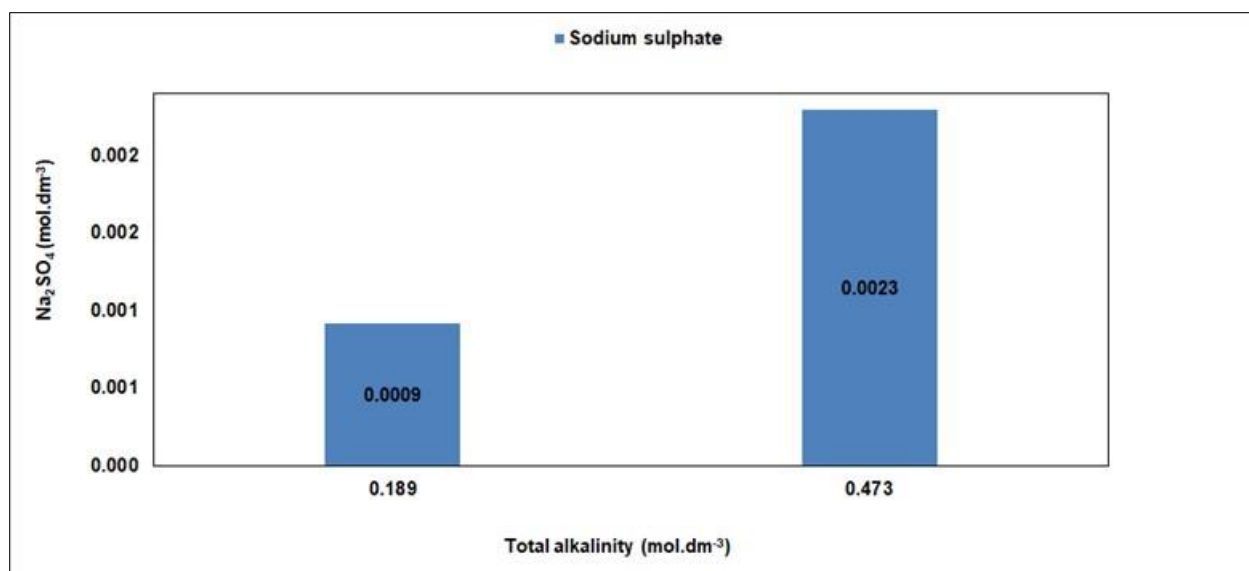


Figure 2.9: Effect of high total alkalinity on the formation of Na₂SO₄ (modified), (Trofe, T.W., et al., (1993))

The concentration of CO₂ in the H₂S containing gas must be <90% to absorb high amounts of H₂S and to maintain an acceptable pH value of the Stretford™ aqueous solution. An acceptable high concentration of total alkalinity significantly improves the removal efficiency of H₂S from the feed-gas by reducing pH depression caused by CO₂ and H₂S absorption as indicated by Figure 2.10 (Trofe, T.W., et al., (1989), Moyes, A.J., et al., (1974), Taback, H.J., et al., (1985)).

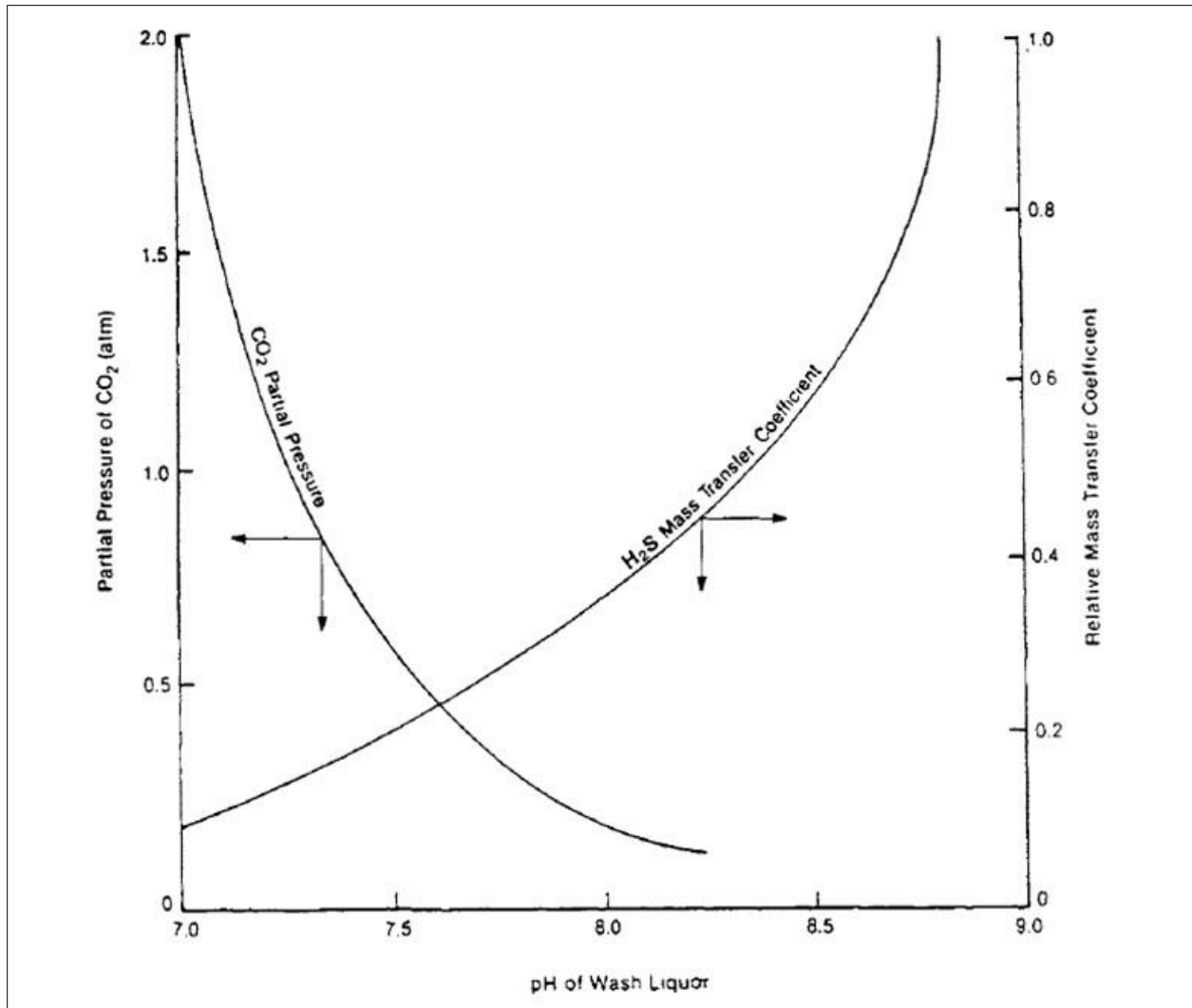


Figure 2.10: Impact of CO₂ partial pressure on the solution pH and H₂S absorption (Moyes, A.J., et al., (1974))

The most dominant species at a pH between 8.2 and 9.5 is NaHCO₃ as indicated by Figure 2.11 (Vermaire, S., et al., (1988)). In most Stretford™ processes, the ratio of bicarbonate (HCO₃⁻) to carbonate (CO₃²⁻) is maintained at 3:1 (Nicklin, T. et al., (1961)). Figure 2.11 shows that below the pH 4, the only species that exist is H₂CO₃. As the pH approaches 5, HCO₃⁻ species starts to appear and H₂CO₃ disappearing at the same ratio until a pH of about 8, where only HCO₃⁻ species exists. As the pH starts to increase above 8, CO₃²⁻ starts to appear with HCO₃⁻ diminishing at the same ratio until a pH of about 12, where only CO₃²⁻ is the species present (Rice, E.W., et al, (2012)). The absorption of H₂S into Stretford™ aqueous solution is followed by dissociation to HS⁻ as explained in Section 2.3. The dissociation of absorbed H₂S takes place as a reaction with Na₂CO₃ as indicated by Reaction 2.3. Na₂CO₃ plays a crucial role in reaction with absorbed H₂S than NaHCO₃ (Astarita, G., et al., (1964), Taback, H.J., et al., (1985)).

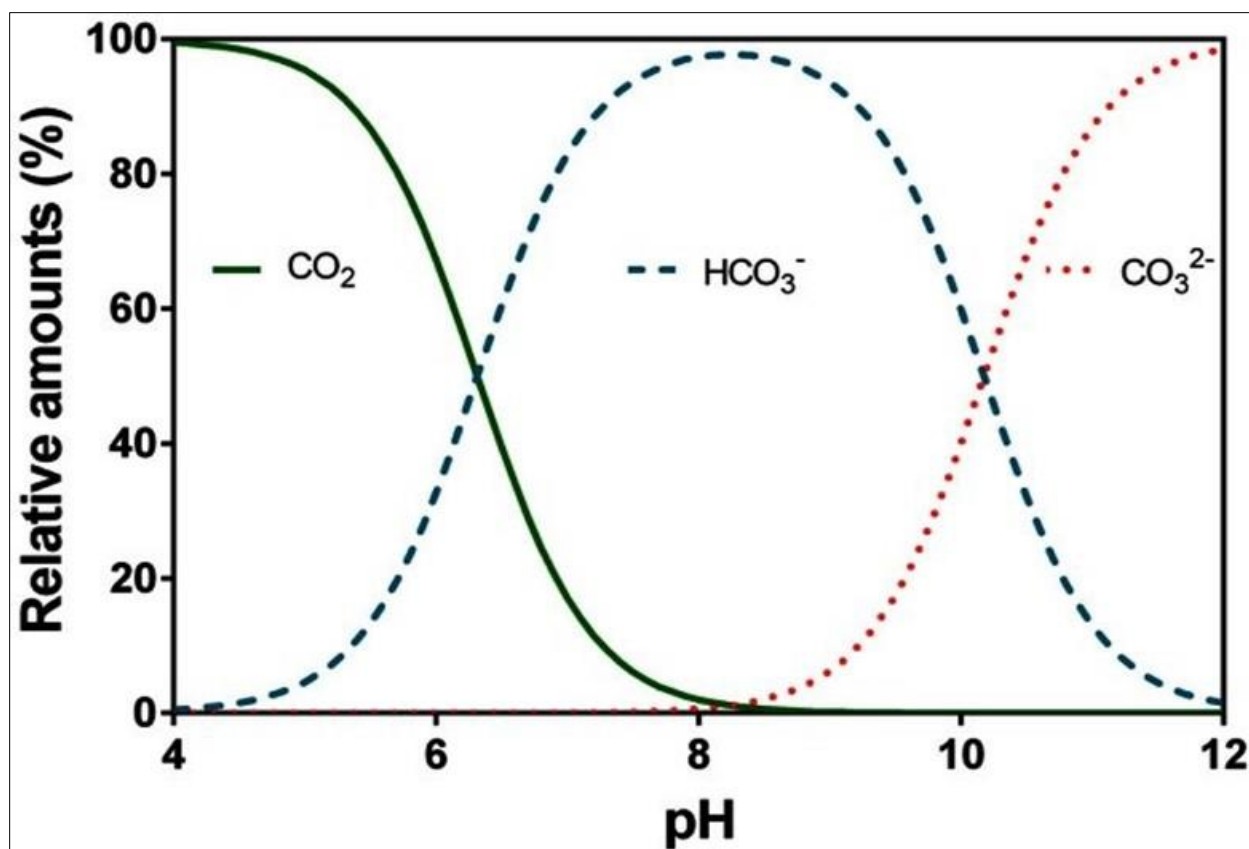


Figure 2.11: Molar ratio of HCO_3^- to CO_3^{2-} in a StretfordTM aqueous solution (Nicklin, T., et al., (1961))

2.5 Role of temperature on H_2S conversion to elemental sulphur

A higher temperature of the StretfordTM aqueous solution reduces the absorption and dissociation of H_2S to HS^- . However, the higher the temperature (above 46°C) of the StretfordTM aqueous solution, the higher the rate of conversion of HS^- to elemental sulphur (Gary, J., (2005), Trofe, T.W., et al., (1989)). The higher temperatures of the StretfordTM aqueous solution assists in re-oxidation of V^{4+} to V^{5+} depending on the concentration of $\text{Na}_2[\text{ADA}]$ in the StretfordTM aqueous solution. Figure 2.12 shows that as the temperature of the StretfordTM aqueous solution increases, that the rate of formation of by-products increases. Most StretfordTM processes that operate between 30 and 40°C to oxidize HS^- to elemental sulphur do not experience high rate of formation of by-products (sodium sulphate and sodium thiosulphate). As the temperature of the StretfordTM solution increases to above 46°C , the amount of by-products increases exponentially as shown by Figure 2.12 (Trofe, T.W., et al., (1993), Trofe, T.W., et al., (1989), Nicklin, T., et al., (1961)).

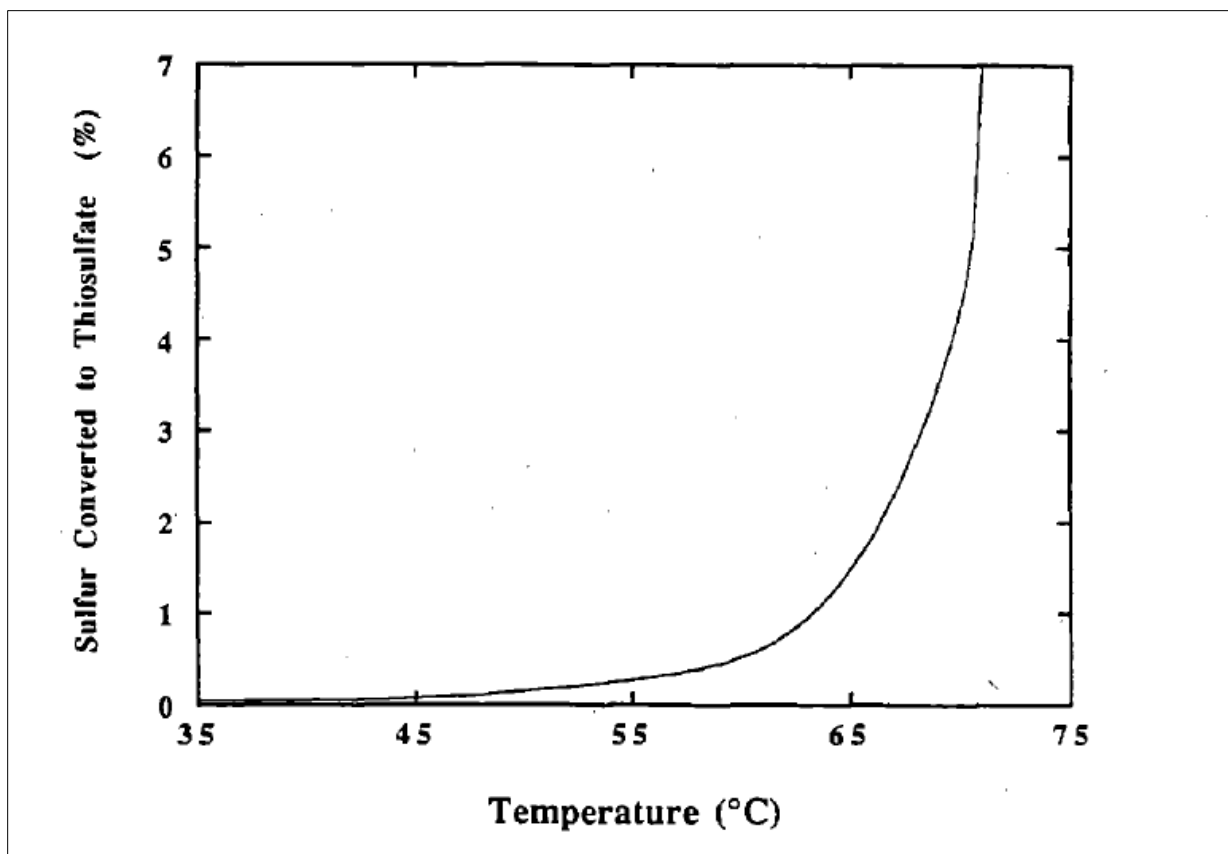


Figure 2.12: HS^- conversion to sodium thiosulphate as a function of temperature (Trofe, T.W., et al., (1993))

2.6 Chemistry of vanadium in the aqueous phase

Vanadium ions exist naturally in different oxidation states (V^{3+} , V^{4+} , and V^{5+}). Vanadium species in the minerals exist as oxides, but it assumes the role of metal cation sometimes. Vanadium exists in rivers, lakes, and oceans in the monomeric V^{5+} oxoanion, vanadate and given the pH of natural water ranges between 6.5 and 8.5, the common vanadium species is vanadate (H_2VO_4^-), (Tracey, A.S., et al. (1998)). When vanadium compounds are dissolved in water, vanadium ions in different oxidation states (V^{3+} , V^{4+} and V^{5+}) undertake hydrolytic, acid/base condensation and reduction reactions as indicated by the Pourbaix diagram in Figure 2.13 at different pH levels.

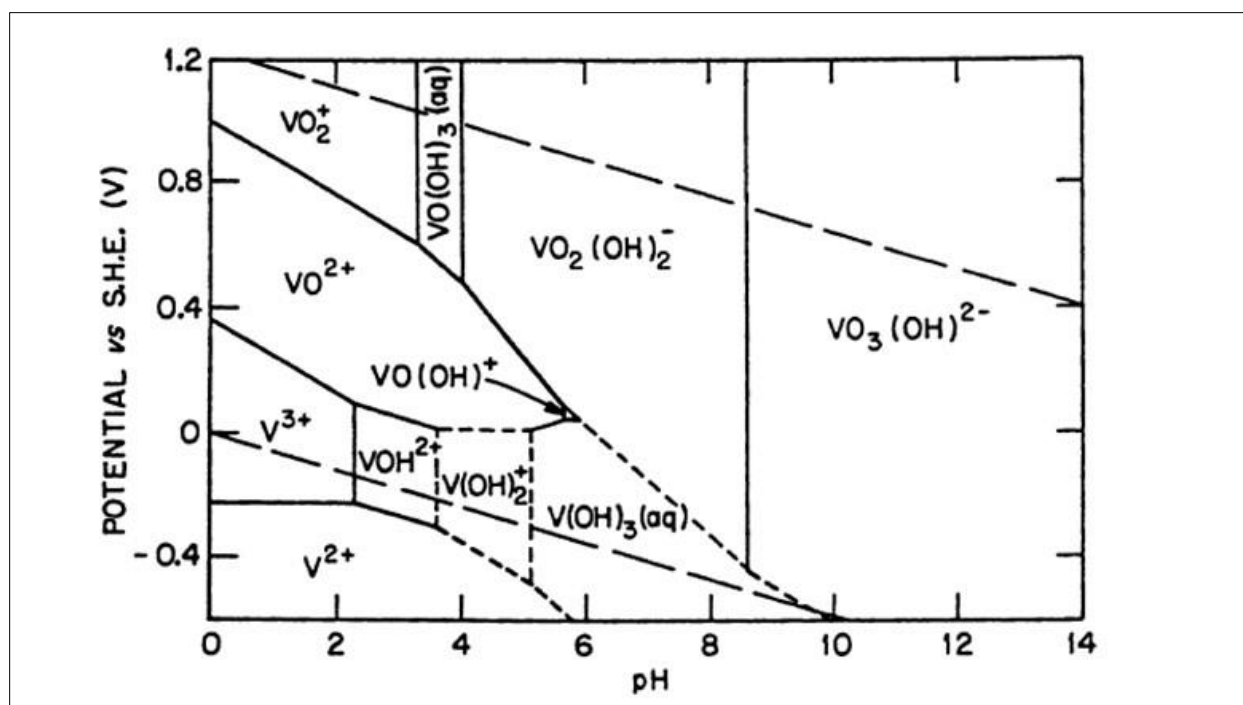


Figure 2.13: Vanadium speciation as a function of pH values at 25°C (Crans, D.C., et al., (1998))

Figure 2.13 shows that at the boundary lines, the ions in adjacent areas are present in equivalent concentrations. Boundaries represented by short dashed lines are less definite than those indicated by bold lines. The top and bottom longer dashed lines show the stability ranges of water (Crans, D.C., et al., (1998), Baes, C.F., et al., (1976)). The chemistry of vanadium species differs significantly upon dissolution in the aqueous solution. This is demonstrated in aqueous phase as V^{3+} and V^{4+} species are cationic while V^{5+} species is anionic. V^{5+} is a diamagnetic ion and is studied by vanadium nuclear magnetic resonance spectroscopy (^{51}V NMR). The V^{4+} species are a paramagnetic ion and is studied by electro paramagnetic resonance (EPR) spectroscopy, vibrational spectroscopies, electron spin echo envelope modulation (ESEEM) and electron nuclear double resonance (ENDOR), (Chasteen, N.D., (1990)). The techniques available to study paramagnetic V^{3+} species are more limited for use in structural characterization. In this study ^{51}V NMR was used to identify V^{5+} species.

2.7 V^{3+} species in aqueous solution

A major difficulty encountered during the study of V^{3+} species chemistry in the aqueous solution is the stable pH range. The number of species formed during the hydrolytic reactions in aqueous solution of this oxidation state seems to be both monomeric and higher oligomeric cationic species $(V(\text{OH})_2(\text{H}_2\text{O})_4)^+$. This is the main monomeric species that is stable in the neutral pH range. The deprotonation of the monomeric species $(V(\text{H}_2\text{O})_6)^{3+}$ and $(V(\text{OH})(\text{H}_2\text{O})_5)^{2+}$ happens willingly as

the pKa values are almost 2.6 and 4.6 respectively as shown in Figure 2.14. V^{3+} species is more stable at the pH less than 3 according to the speciation diagram in Figure 2.13 and turn green when dissolved in Sulphuric acid solution (Sigel, A., et al., (1995)).

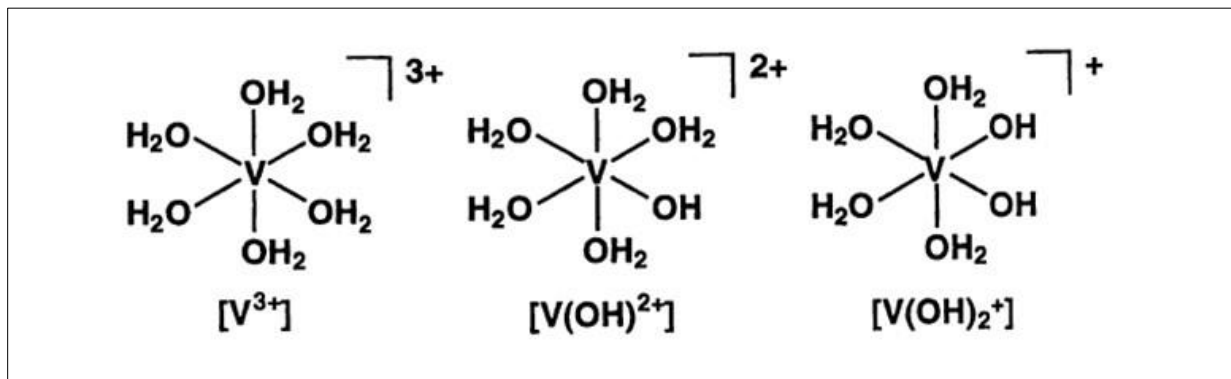


Figure 2.14: Hydrated structure of V^{3+} , $(V(H_2O)_6)^{3+}$, $(V(OH)(H_2O)_5)^{2+}$ and $(V(OH)_2(H_2O)_4)^+$, (Sigel, A., et al., (1995))

2.8 V^{4+} species in aqueous solution

By dissolving V^{4+} species in acidic solution it resulted in formation of hydrated vanadyl cation $(VO(H_2O)_5)^{2+}$ commonly abbreviated as VO^{2+} as is indicated by Figure 2.15. Figure 2.15 shows the hydrated structure of V^{4+} ions in aqueous solution (Chasteen, N.D., (1981)).

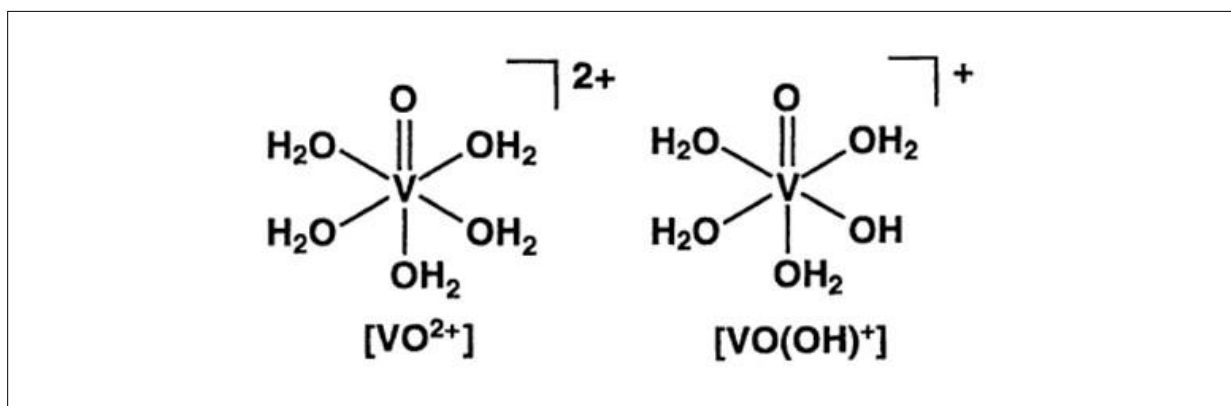


Figure 2.15: Hydrated structure of VO^{2+} , $(VO(H_2O)_5)^{2+}$ and $(VO(OH)(H_2O)_4)^+$, (Chasteen, N.D., (1981))

The strong vanadyl oxygen bond remain intact even with V^{5+} species (Cotton, F.A., et al (1966). When titration was done on VO^{2+} by adjusting pH with NaOH the soluble and insoluble ions as indicated by Reactions 2.20 and 2.21 were formed. The insoluble species is the one that normally precipitate as a black product in Stretford™ process due to its instability in basic solution. It was also found that on adding NaOH into the solution which contain VO^{2+} on a ratio of 1:1 more precipitation of insoluble $VO(OH)_2$ was observed (Ducret, L., (1951), ((Falkiner, R.J., (1978)).



The previous studies on V^{4+} speciation in StretfordTM aqueous solution has found the existence of vanadium isopolyanions ($\text{V}_4\text{O}_9^{2-}$) and ($\text{V}_2\text{O}_5^{2-}$). There is equilibrium of the two isopolyanions and it is highly reliant on the pH value of the solution. Reactions 2.22 shows equilibrium relationship as a function of a pH between insoluble $\text{VO}(\text{OH})_2$ and isopolyanions $\text{V}_2\text{O}_9^{2-}$ (Walker, T.A., (1983), (Ducret, L., (1951), (Iannuzzi, M.M., et al., (1975)).



V^{4+} species is stable in acidic solution and increasing the pH to just above neutral yields, few oligomeric and polymeric spin paired species that are EPR quiet (Crans, D.C., et al., (1998)). Other polymeric forms are highly insoluble and they precipitate (Boyd, D.W., et al., (1984)). In the neutral pH range, the aqueous equilibrium limit the concentration of hydrated monomeric VO^{2+} is between 1×10^6 and $1 \times 10^9 \text{ mol.dm}^{-3}$ depending on specific pH regardless of the amounts of V^{4+} species added to the aqueous solution (Boyd, D.W., et al., (1984)). However, because of V^{4+} ions high affinity for most oxygen-, nitrogen-, and sulphur containing ligands, complexation can prevent the formation of the polymeric precipitates (Crans, D.C., et al., (1998)).

2.9 V^{5+} species in aqueous solution

V^{5+} ions occurs in a monomeric form as H_2VO_4^- anion vanadate at a physiological pH range in aqueous solution. The above is correct even when sodium metavanadate (NaVO_3), ammonium vanadate (NH_4VO_3), sodium orthovanadate (Na_3VO_4) and vanadium pentoxide (V_2O_5) are used to prepare the aqueous solution (Crans, D.C., et al., (1998)). The stoichiometric charges, pK_a values, chemical shifts, and formation constant of V^{5+} species in aqueous solutions are shown in Table 2.1.

Table 2.1: V^{5+} species chemical shifts in aqueous solution (Crans, D.C., et al., (1998))

Species	p,q	$\log b_{pq}^b$	pK_a	$d(^{51}\text{V})(\text{ppm})^c$
VO_4^{3-}	(1, 1)	-21.31		-541.2
HVO_4^{2-}	(1, 0)	-7.91	13.4	-538.8
H_2VO_4^-	(1, .1)		7.91	-560.4
VO^{2+}	(1, 3)	6.97		-545
$\text{V}_2\text{O}_7^{4-}$	(2, 0)	-15.13		-561
$\text{HV}_2\text{O}_7^{3-}$	(2, 1)	-5.39	8.74	-563.5

$\text{H}_2\text{V}_2\text{O}_7^{2-}$	(2, 2)	2.9	8.29	-572.7
$\text{V}_4\text{O}_{13}^{6-}$	(4, 2)	-8.5		-566 to -585 ^d
$\text{HV}_4\text{O}_{13}^{5-}$	(4, 3)	0.4	8.9	-566 to -585 ^d
$\text{V}_4\text{O}_{12}^{4-}$	(4, 4)	10.04		-577.6
$\text{V}_5\text{O}_{15}^{5-}$	(5, 5)	12.43		-586
$\text{V}_3\text{O}_{10}^{5-}$	(3, 1)	51.98		-422, -496, -513
$\text{V}_6\text{O}_{18}^{6-}$	(6, 6)	58.12	6.14	-424, -500, -516

Note: ^b log b for the equilibrium $\text{pH}^+ + 1(\text{H}_2\text{VO}_4^-) = (\text{H}^+)\text{p}(\text{H}_2\text{H}_2\text{VO}_4^-)\text{q}$, ^c V relative to VOCL_3 , ^d A value in the indicated range has been reported, ^{pq} equilibrium constant

Figure 2.16 shows some of the proposed V^{5+} anions structures. In an acidic aqueous condition between pH of 3 and 6, the dominant species is decavanadate ($\text{V}_{10}\text{O}_{28}^{6-}$). This complex anion is the major V^{5+} oxoanion that has a yellow-orange colour. Between pH 6 and pH 10, the dominant species is dimer ($\text{V}_2\text{O}_7^{4-}$), cyclic tetramer ($\text{V}_4\text{O}_{12}^{4-}$) and cyclic pentamer ($\text{V}_5\text{O}_{15}^{5-}$) which are all colourless (Crass, D.C., et al., (1995), Vermaire, S., et al., (1988)). Above pH 10, the anionic monomer is the favored species, whereas below pH 3 the cationic monomer is the major species (Crans, D.C., et al., (1998), Vermaire, S., et al., (1988)). Colourless oxovanadium ions interconvert in aqueous solution and stock solutions may contain a variety of oxoanions that quickly generate H_2VO_4 upon dissolution into an in vitro or in vivo system at neutral pH value. However, when obtaining coloured (yellow-orange) stock solutions, heating is often necessary to convert the hydrolytically more resistant decavanadate ($\text{V}_{10}\text{O}_{28}^{6-}$) to the colourless oxoanions (Crans, D.C., et al., (1998)). These anions (tetra-, pentameric and mono-) are comprises the metal atoms in four co-ordination. However, the decavanadate ($\text{V}_{10}\text{O}_{28}^{6-}$) has the vanadium atoms of six-coordinate. The pentamer and tetramer are cyclical and their common formula is $(\text{VO}_3)_n^{n-}$ (Crans, D.C., et al., (1998), Vermaire, S., et al., (1988)).

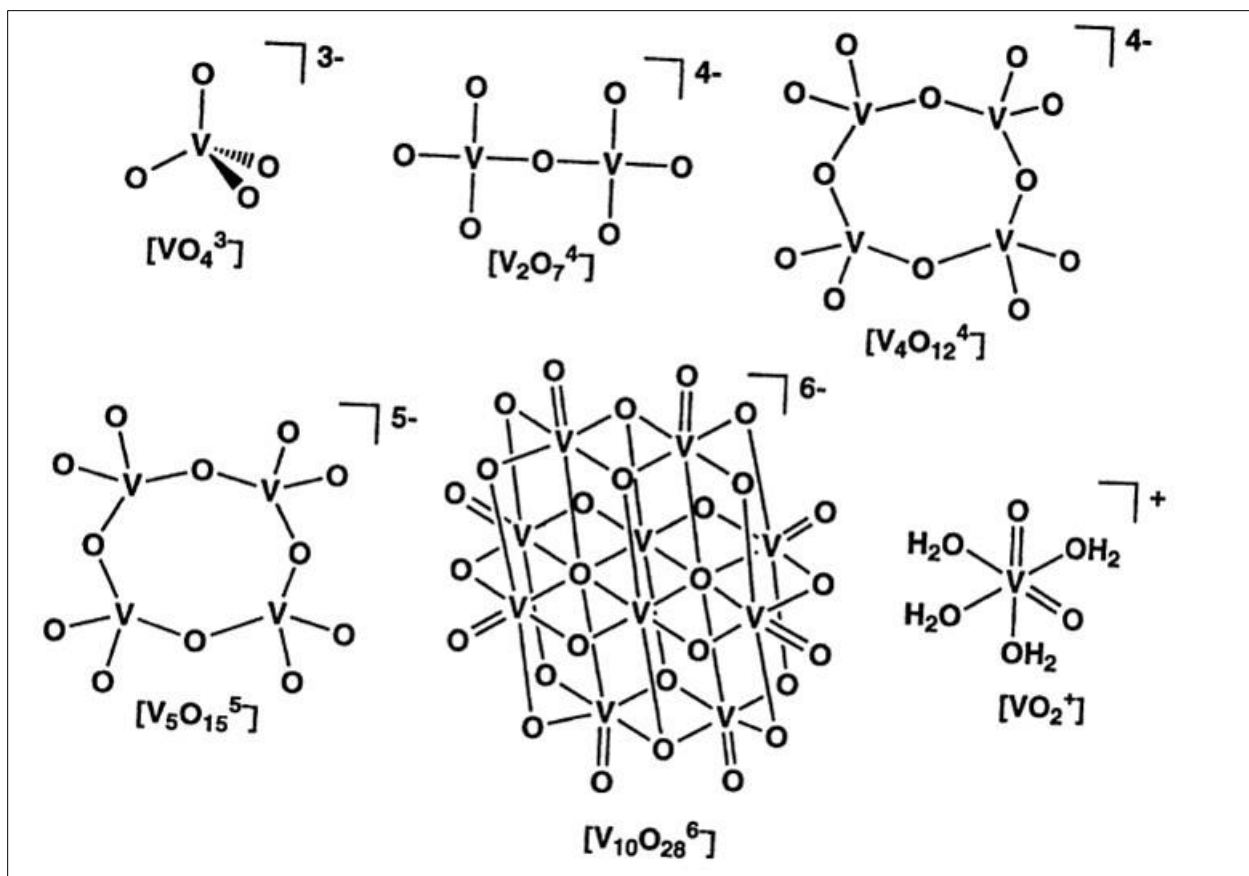
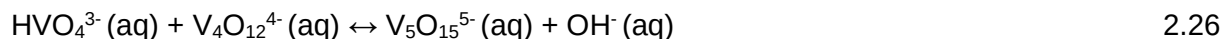
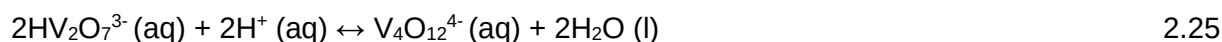
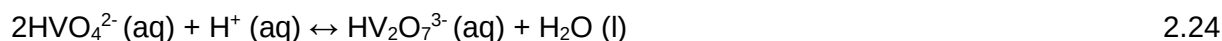


Figure 2.16: Structure of some polyoxidovanadate in aqueous solution in equilibrium (Vermaire, S., et al., (1988))

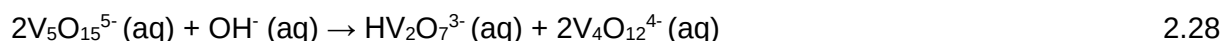
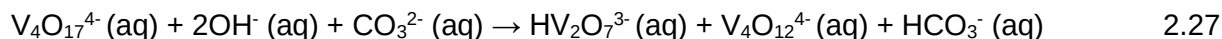
2.10 Chemistry of vanadium ions in the Stretford™ process

In the Stretford™ aqueous solution of pH between 8.2 and 9.5, the orthovanadate anion VO_4^{3-} exists in equilibrium with di- and polynuclear species which are formed as per Reactions 2.23 to 2.26 (Cruywagen, J., et al., (1998), (Lingane, J.J., (1945))).



^{51}V NMR studies have indicated that the inter conversion of the species indicated by Reactions 2.23 to 2.26 are too slow to be identified separately in a solution (Crans, D.C., et al., (1998)). The existence of other salts (e.g. Na_2CO_3 , NaSCN , Na_2SO_4 , $\text{Na}_2[\text{ADA}]$, e.t.c) in the Stretford™ aqueous solution possibly influences the equilibrium in Reactions 2.23 to 2.26 even though the details are not known. Literature indicates that the high total dissolved salts concentration (above

0.76 mol.dm⁻³) results in precipitation of vanadium species, most especially at a pH above 8.5 (McKay, A.E., (1989)). Previous aqueous V⁵⁺ ions studies in the StretfordTM aqueous solution using ⁵¹V NMR spectrographic techniques indicated that dimer (HV₂O₇³⁻) and tetramer (V₄O₁₂⁴⁻) are the main species present at a pH between 8.2 and 9.5 in the StretfordTM aqueous solution as per Figure 2.17 (Pope, M.J., et al., (1968)). The hexamer and pentamer can dissociate to the dimer and tetramer as indicated by Reactions 2.27 and 2.28 (Vermaire, S., et al., (1988), Petterson, L., et al., (1983)).



The hatched area in Figure 2.17 represents the vanadium species (dimer and tetramer) found in the pH ranges of the StretfordTM process (Pope, M.J., et al., (1968)). It was found that the dimer and tetramer are in equilibrium with each other and they are a function of total vanadium and V⁵⁺ as indicated by Reaction 2.29. The tetramer was the dominant species in a high concentrated aqueous solution with vanadium at a pH of 8.5. However, the dimer was more stable at high carbonate to vanadium ratio (Vermaire, S., et al., (1988), Petterson, L., et al., (1983)).



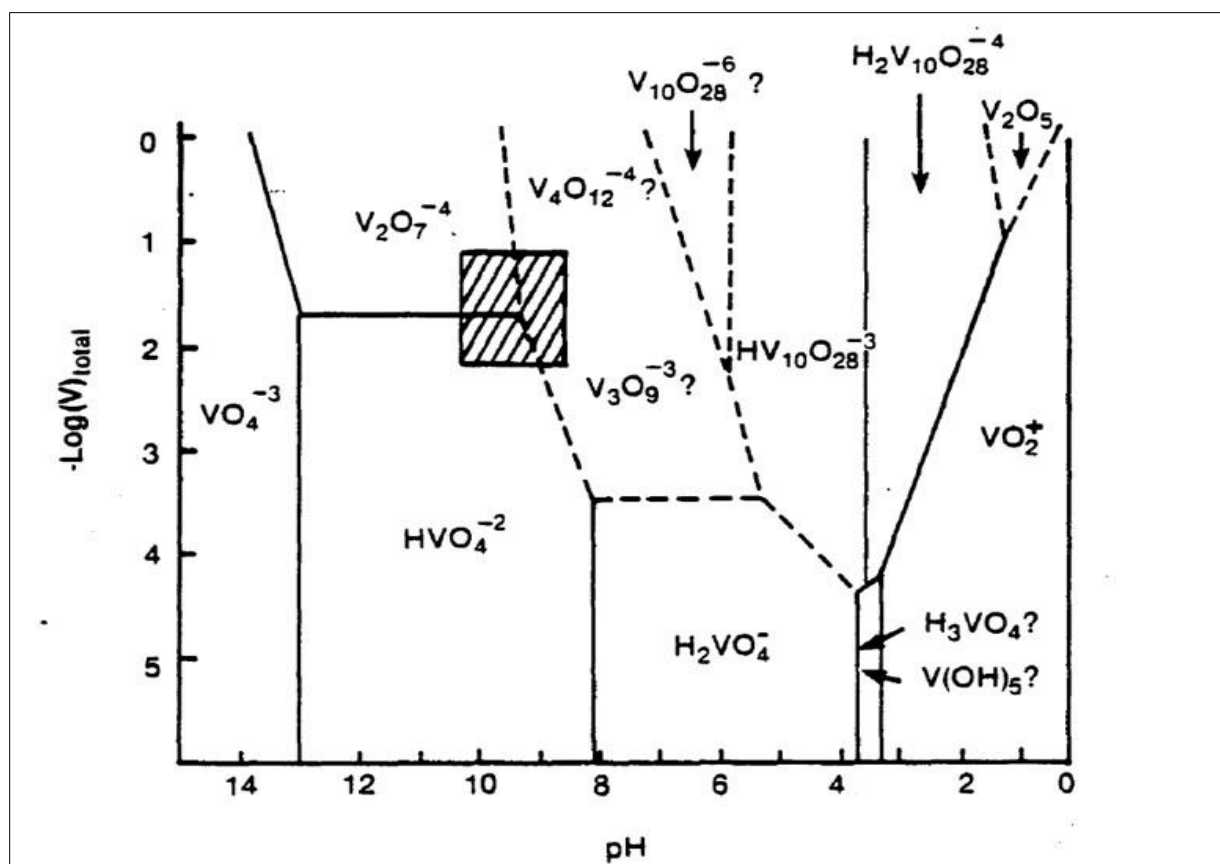


Figure 2.17: V^{5+} species as a function of pH values at 25°C (Pope, M.J., et al., (1968))

The concentration of V^{5+} ions in the Stretford™ process is dependent on H_2S concentration in the feed-gas to the absorbing contactor (Trofe, T.W., et al., (1986)). The various molecular spreading of various V^{5+} anions as a function of pH is also indicated in Figure 2.18 at the V^{5+} concentration of 0.03 mol.dm^{-3} at 25 °C. The numbers in brackets in below figure represent equilibrium constant of vanadium species. Between pH values of 7 and 7.5, the common vanadium species are $V_2O_{12}^{4-}$ (4 , 4) and $V_5O_{15}^{5-}$ (5 , 5). As the pH approaches 8, there is a disappearance of $V_2O_{12}^{4-}$ and $V_5O_{15}^{5-}$ while HVO_4^- , $V_2O_7^{4-}$, $HV_2O_7^{3-}$, $V_4O_{13}^{6-}$ and $V_3O_{10}^{5-}$ start to appear (Cruywagen, J.J., et al., (1998)). HS^- ions form various thio- and thio-oxivanadate at alkaline pH levels of cold aqueous solution of V^{5+} anions e.g. orange-yellow $VO_2S_2^{3-}$ and the purple VS_4^{3-} .

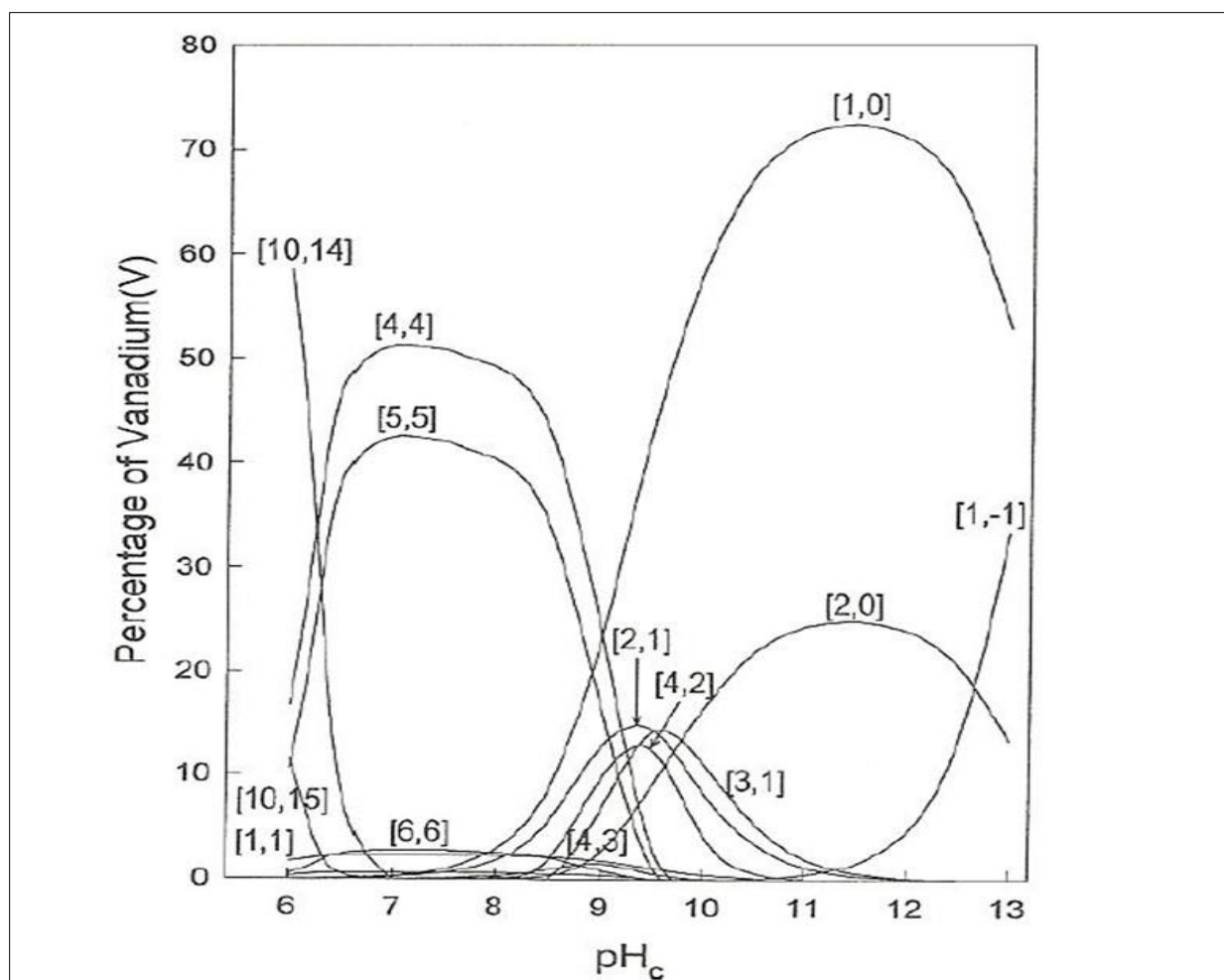
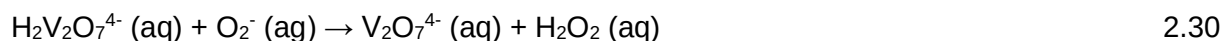


Figure 2.18: Distribution of V^{5+} species as a function of pH values at 25°C (Cruywagen, J.J., et al., (1998))

At higher total alkalinity, the V^{5+} ion that dominate is the dimer but as the total alkalinity diminishes, the tetramer dominates. When the dimer is reduced, it re-oxidizes faster than the tetramer and prevents the less active tetramer from forming. The probability is that during the conversion of HS^- to sulphur that the dimer reacts faster with HS^- than the tetramer (Trofe, T.W., et al., (1993)). After oxidizing hydrogen sulphide to elemental sulphur, V^{5+} ions are reduced to V^{4+} ions and need to be re-oxidized to V^{5+} ions. The probable reaction that takes place between O_2^- radicals and vanadium species with $Na_2[ADA]$ in the StretfordTM aqueous solution is shown by Reaction 2.30 (Kelsall, G.H., et al., (1993)). The H_2O_2 formed in Reaction 2.7 plays a role in the re-oxidation of V^{4+} to V^{5+} as discussed in Section 2.2.3.



The use of V^{5+} ions in a StretfordTM aqueous solution allows for maximum loading of HS^- to elemental sulphur (up to 0.03 mol.dm^{-3}). Literature has reported that V^{5+} concentration should be

at least 2 or 3 times the concentration of HS^- by weight (Trofe, T.W., et al., (1993)). The optimum value of V^{5+} ions reported in the literature is up to $0.059 \text{ mol.dm}^{-3}$ (Stavros, J., (2006)). Figure 2.19 below indicates the increase in the rate of conversion of HS^- to elemental sulphur as the concentration of V^{5+} increases at a constant pH, $\text{Na}_2[\text{ADA}]$ and temperature.

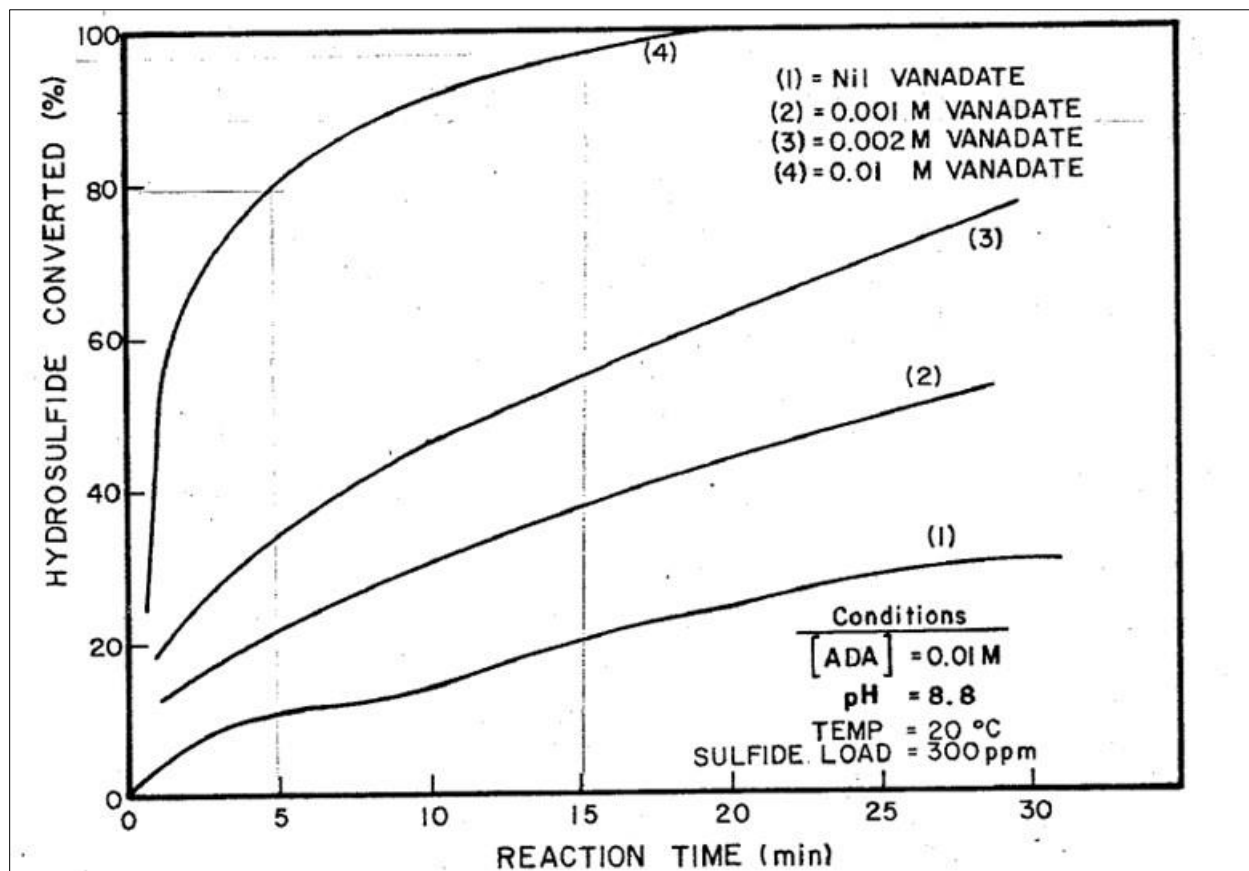


Figure 2.19: Hydrogen sulphide loading as a function of V^{5+} concentration (Trofe, T.W., et al., (1993))

Figure 2.20 demonstrates the importance of keeping high V^{5+} to HS^- loading ratio. When V^{5+} ions was $0.024 \text{ mol.dm}^{-3}$ with other parameters constant (HS^- loading, pH, $\text{Na}_2[\text{ADA}]$ and temperature), the formation of sodium sulphate was $0.0069 \text{ mol.dm}^{-3}$ per day, but when V^{5+} was increased to $0.055 \text{ mol.dm}^{-3}$ the formation of sodium sulphate reduced to less than $0.003 \text{ mol.dm}^{-3}$ per day with other conditions remaining constant (Trofe, T.W., et al., (1993)).

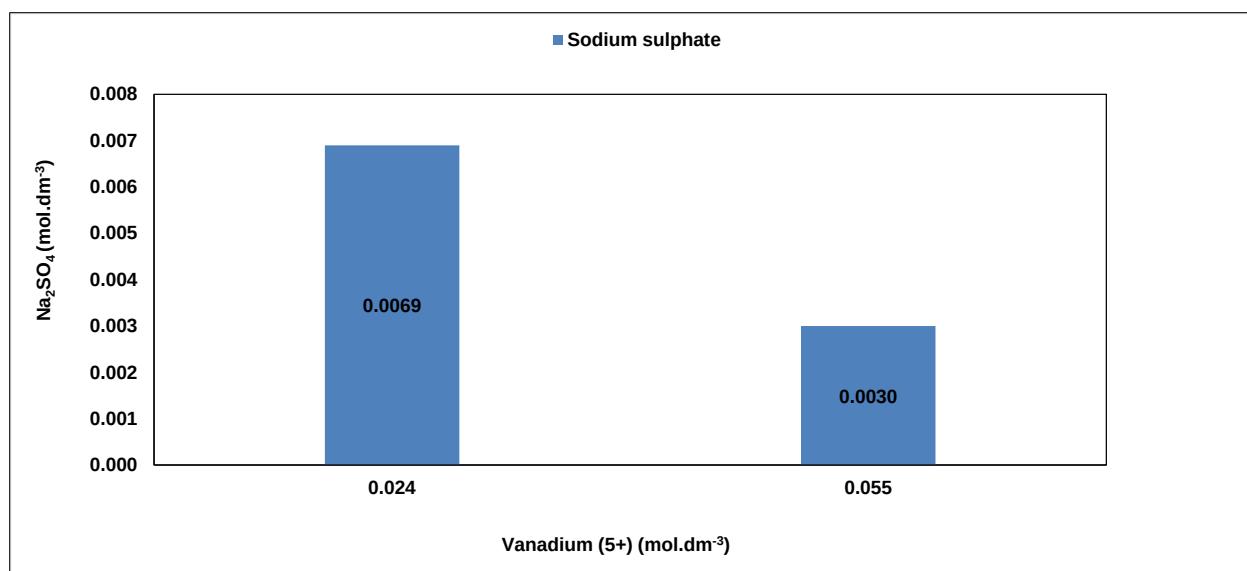


Figure 2.20: Effect of V⁵⁺ concentration on by-products formation (modified), (Trofe, T.W., et al., (1993))

The real existence of the various oxido-anions of vanadium in the Stretford™ aqueous solution depends on the V⁵⁺ concentration, the ionic-strength, the pH value, the presence of other salts, and the temperature. There is limited information on the V⁴⁺ ions in the Stretford™ aqueous solution in comparison to V⁵⁺ ions. Kinetic studies reported on the oxidation of hydrogen sulphide by V⁵⁺ indicated that the reaction fits a second order rate equation. The reaction rate decreases with an increase in pH values and increases with an increase in temperature as discussed in Sections 2.3 and 2.5. The experiment demonstrates the redox between V⁵⁺ and hydrogen sulphide anions. At higher V⁵⁺ concentrations (0.01-0.1 mol.dm⁻³) the reaction of V⁵⁺ ions with sodium sulphide (Na₂S) of the same molar concentration resulted in a green-brown mixture (from which on addition of more Na₂S) a brown-black solid precipitated which dissolved in hydrochloric acid (HCl) to form a blue solution (Kelsall, G.H., et al., (1993)). Evidently, in these experiments insoluble black V⁴⁺ compounds have been prepared which on dissolution in aqueous H₂SO₄ produced the well-known blue vanadyl cation (VO(H₂O)₅)²⁺ containing the metal atom in the V⁴⁺ oxidation state. Due to the high pH values (8.2 to 9.5) in the Stretford™ aqueous solution, V²⁺ and V³⁺ do not exist and the chemistry of these species were not discussed in more detail in the Stretford™ processes.

2.11 Interaction of V⁵⁺ and V⁴⁺ in the Stretford™ processes

The lack of knowledge from literature and previous studies on the optimal V⁵⁺ to V⁴⁺ molar ratio has resulted in precipitation of vanadium species in the Stretford™ process. Vanadium ions has been reported to precipitate and found in a stagnant area as a black product which has been

associated with insoluble $\text{VO}(\text{OH})_2$. Experiments were conducted to test rate of precipitation with fully oxidized and reduced vanadium solutions. The fully oxidized solution did not contain any black products while the solution with V^{4+} species contained precipitates of vanadium compounds. The test indicated that the deposit contain 30-41% of V^{4+} and V^{5+} compounds, 10-25% of sodium, 0.64% of carbon, 2.08% of hydrogen, 1.22% of elemental sulphur and 0.03% of nitrogen (Falkiner, R.J., (1978), (Hileman, O.E., (1967)). V^{4+} and V^{5+} on a ratio of 2 to 1 co-precipitated with $(\text{NH}_4)_2\text{V}_4\text{O}_9$ compounds (Ducret, L., (1951), (Ostrowetsky, J., et al, (1964)).

The prevention of vanadium precipitation has been attempted by adding organic complex agent in a Stretford™ aqueous solution like citrate or oxalate. The citrate has been found not to interfere with other Stretford™ parameters but more stable at pH less than 8, which is lower than operating pH of Stretford™ plants. Oxalate was found to form 2 to 1 metal complex that was stable at pH of around 6.5 (Nikolova, D.M., et al., (1966), Ducret, L., (1951), Ballhausen, C.J., et al., (1962)). Three experiments were done by Falkiner to check rate of precipitation of vanadium compounds. The first experiment was changing ratio of V^{4+} to V^{5+} from 9:1 to 1:9 at pH 9 in a 0.24 mol.dm^{-3} sodium carbonate solution. The precipitates yielded maximum black products at a ratio of 2:1. The analysis indicated the precipitates contain 26% of V^{4+} and 12% of V^{5+} species, which represented 2:1 molar ratio of V^{4+} to V^{5+} in solution (Falkiner, R.J., (1978)).

The second experiments was to check the impact of vanadium precipitation by changing the solution pH. The pH values were varied from 8.0 - 10 with incremental changes of 0.25. The solution was prepared on a ratio of 2:1 of V^{4+} and V^{5+} . The total vanadium was 0.05 mol.dm^{-3} in 0.24 mol.dm^{-3} sodium carbonate solution. The results indicated that when the pH of the solution was increased the rate of precipitation also increased. On analyzing the total vanadium after each experiments, it was found that at pH of less than 9.4 more that 80-95% of vanadium total was still in solution. However, above pH of 9.4 the solutions contained 15-55% of total vanadium that was present before experiments (Falkiner, R.J., (1978)).

The third experiment was done with citrate solution. The total vanadium was maintained at 0.05 mol.dm^{-3} in 0.24 mol.dm^{-3} of sodium carbonate solution. The ratio of V^{4+} to V^{5+} was maintained at 2:1. The ratio of organic citrate to total vanadium was varied from 0.1 to 1 on the equal increment of 0.1. The lower the citrate to total vanadium was found to increase the rate of precipitation. The problem with citrate was not stable at a pH range of the Stretford™ process and interfere with V^{5+} analysis (Falkiner, R.J., (1978)). The form of V^{5+} species that get reduced during oxidation of elemental sulphur plays a very crucial role in minimizing the rate of precipitation in a Stretford™ process. If the reduced V^{5+} was from the tetramer, these species is slow to re-oxidizes and will

precipitate. However, if the reduced V^{5+} was from the dimer species it re-oxidizes faster than tetramer. The tetramer and dimer are in equilibrium with each other and are a function of carbonate ratio as discussed in Section 2.7 (Vermaire, S., et al., (1988)).

2.12 Chemistry of $Na_2[ADA]$ in the Stretford™ process

The mixture of the organic isomers 2,6 and 2,7 $Na_2[ADA]$ increases the oxidation capacity of the Stretford™ aqueous solution due to the fact that it is an oxidant. This leads to faster oxidation of V^{4+} to V^{5+} , which increases the H_2S absorption capacity. Due to the high oxidation capacity of $Na_2[ADA]$, the addition is an ideal technique to prevent V^{4+} from precipitation which is not stable in an alkaline solution (Trofe, T.W., et al., (1993)). Sufficient total vanadium ($0.059 \text{ mol.dm}^{-3}$) must be present in the circulation Stretford™ aqueous solution for the $Na_2[ADA]$ to be effective. Figure 2.21 gives the chemical structures of oxidized 2,7 $Na_2[ADA]$ and reduced 2,7 $Na_2[H_2ADA]$, (Trofe, T.W., et al., (1986)). Most Stretford™ plants in South Africa, Great Plains plant in Beulah, Stretford™ plants in the United State of America, China, Europe and Asia use 2.6 and 2.7 $Na_2[ADA]$ due their higher solubility and stability in water.

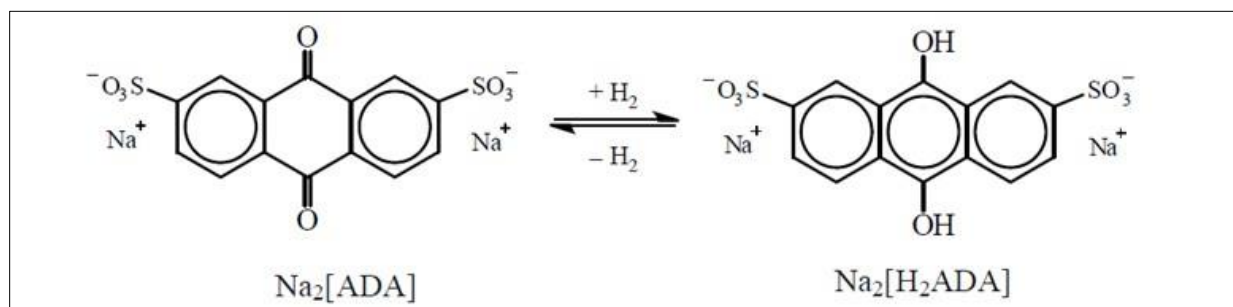
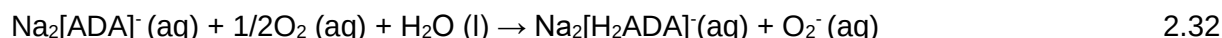


Figure 2.21: Oxidized (left) and reduced (right) structure of Na_2ADA (Trofe, T.W., et al., (1986))

The $Na_2[ADA]$ reacts with electron donors in the Stretford™ aqueous solutions including water and form free radicals anion ($Na_2[ADA]^{\cdot-}$) as shown by Reaction 2.31. The free radical $Na_2[ADA]^{\cdot-}$ anion undergoes electron exchange with dissolved O_2 to form free radicals $O_2^{\cdot-}$ as shown by reaction 2.32. The radicals $O_2^{\cdot-}$ and H_2O_2 that is formed during regeneration of $Na_2[H_2ADA]$ is the one that oxidized V^{4+} to V^{5+} species (Trofe, T.W., et al., (1986)).



2.13 Elemental sulphur allotropes

2.13.1 Chemistry of elemental sulphur

Elemental sulphur is a chemical with the largest number of allotropes, of up to 30 known homocyclic rings (Steudel, R., et al., (2003)). Elemental sulphur can exist as a solid, liquid and gas. The sulphur allotropes can be determined by their melting temperatures (Meyer, B., (1975)). The literature review on elemental sulphur focuses on the most stable form of crystalline elemental sulphur (α -S₈). Some elemental sulphur allotropes thermal behavior was summarized. The concentration of V⁵⁺ plays a very crucial role In the Stretford™ process during conversion of H₂S to elemental sulphur. The formation of elemental sulphur depends on the reaction between HS⁻, polysulphide and V⁵⁺ concentration. The rate and particle sizes of the elemental sulphur formed in the Stretford™ process is not determined by the concentration of HS⁻ but the concentration of polysulphide, which is an intermediate (Trofe, T. W., et al., (1986), Steudel, R., et al., (2003)). Reactions 2.4 to 2.6 in Section 2.2 represent formation of polysulphides up to S₉²⁻, which splits to α -S₈. The polysulphide species are not stable at pH below 7.5 and start to convert to α -S₈. This follows a nucleation theory until agglomerate to large crystals (Steudel, R., et al., (2003)).

It is very crucial that the solution does not contain impurities to prevent interference during nucleation and crystallization of elemental sulphur (Steudel, R., et al., (2003)). The nucleation of elemental sulphur is also delayed due to a complex structure of α -S₈, which is composed of 16 molecules that need to follow a specific order to form crystals. To form a big elemental sulphur crystal a rapid growth is required. However, impurities in the Stretford™ aqueous solution will delay the nucleation, crystallization, and Ostwald ripening process of elemental sulphur particles. The rate of hydrophobic colloidal sulphur precipitation and crystallization should be greater than the rate of conversion of HS⁻ to hydrophilic polysulphide by V⁵⁺ to prevent delay in nucleation process. (Steudel, R., et al., (2003), Steudel, R., et al., (1996), (Trofe, T. W., et al., (1986)). Garcia in 2014 supported the work done by Steudel. He also reported that the formation of elemental sulphur involved hydrophilic polysulphide which escape to hydrophobic colloidal sulphur. The elemental sulphur formation process is represented by Reaction 2.33. He reported that the nanoparticles start to agglomerate through nucleation and Ostwald ripening process. The study was in agreement with what was discussed in Section 2.2 during oxidation of HS⁻ to elemental sulphur by V⁵⁺.



Note: x = 2-9

Garcia found in the beginning elemental sulphur combines following a nucleation theory before the aggregation and Ostwald ripening process starts. He further studied the effect of surfactants on the elemental sulphur particle sizes using sodium dodecyl sulphate (SDS), triton-X-100 and pine needle extract as surfactant. The effect of surfactants was studied using dynamic light scattering technique. All experiments with surfactants show smaller particle sizes than experiments without surfactants as it is shown in Figure 2.22. He found that the elemental sulphur particle sizes grow overtime and if there are surfactants in solution the nucleation and Ostwald ripening process will be interfered with (Garcia, A.A. et al., (2014)).

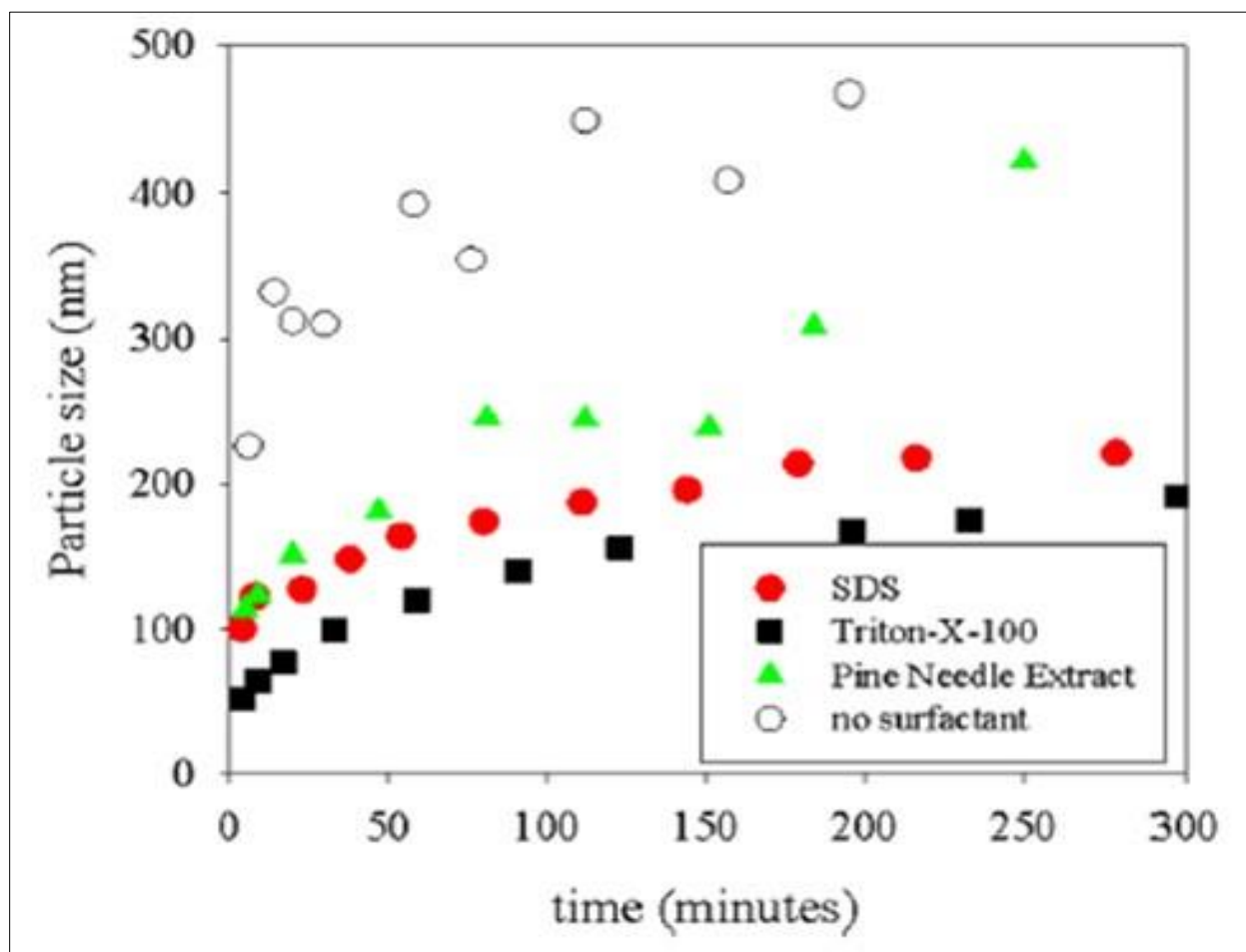


Figure 2.22: The effect of surfactant on the PSDs the elemental sulphur particles using dynamic light scattering analyses (Garcia, A.A. et al., (2014))

Note:

SDS

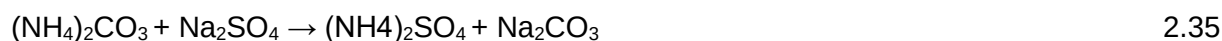
Triton-X-100

Pine needle extract

No surfactant



The source of contamination in the Stretford™ process can be due to impurities like hydrocarbon in feed gas, process chemicals added like vanadium catalyst, by-products formed in the process like Na₂SO₄ and NaSCN and sulphur bacterial growth. Sodium based salts will co-precipitate with elemental sulphur. If elemental sulphur is not washed thoroughly it can contain some residuals of vanadium as V⁵⁺. If the V⁴⁺ salt (VO₂SO₄) was added to the simulated Stretford™ aqueous solution, V⁴⁺ does not oxidize rapidly to V⁵⁺, the elemental sulphur particles from this solution will co-precipitate with VO(OH)₂. The source of V⁵⁺ like SAV contain impurities like ammonium, iron, silicon, magnesium, and chloride, which can also co-precipitate with elemental sulphur. Reactions 2.34 and 2.35 represents possible reactions that can take place and co-precipitate with elemental sulphur (Hyne, J. B., (1991), Trofe, T.W., et al., (1993)). In this study, the impurities by the feed gas was not be applicable because the gas contained N₂ and H₂S only.



The presence of these impurities delay the nucleation process, which end-up precipitating small elemental sulphur crystals (less than 10 µm). The smaller elemental sulphur crystals that are called “fine sulphur” are difficult to float but still melt at the same temperature as large crystals. Suspended elemental sulphur forms a primary crown in solution with a size of less than 10 µm. The crown elemental sulphur then agglomerates until a large froth size particles are formed up to greater than 100 µm. The impurities contaminate elemental sulphur which normally causes operational problems and responsible for elemental sulphur change from yellowish to greyish. The physical properties of elemental sulphur is highly affected by impurities ((B. Meyer, (1976)), Steudel, R., et al., (2003), (Hileman, O.E., (2003))).

The colour change also depend on the elemental sulphur particle sizes, the finer the elemental sulphur the lighter the colour impression. The temperature also plays a role on the colour of elemental sulphur. Elemental sulphur that contain 2% and 98% of S₇ and α-S₈ respectively at ambient temperature will contain no S₇ if the elemental sulphur is heated to above 39°C which is S₇ melting point and will decompose to α-S₈ above this temperature. There is normally some small proportion of S₆ and S₇, which precipitate with α-S₈ particles. (Steudel, R., et al., (1996), (Steudel, R., et al., (1988))). The different types of sulphur species varies from deep yellow of S₆ to pale yellow of S₁₂ as indicated in Table 2.2 (Steudel, R., et al., (2003), (Meyer, B., (1976))).

Table 2.2: Melting points of elemental sulphur species (Steudel, R., et al., (2003))

Elemental sulphur allotropes	Melting points (°C)	Colour
S ₆	50-60	Orange
S ₇	39	Yellow
α-S ₈	<96.3	Yellow
β-S ₈	120.6	Yellow
S ₉	Not reported	No information
S ₁₀	109	No information
S ₁₁	63	No information
S ₁₂	148	Pale yellow
S ₁₃	114	No information
S ₁₄	117	No information
S ₁₅	Not reported	No information
α-S ₁₈	126-128	Lemon yellow
S ₂₀	124-126	Pale yellow
S _∞	100-110	Yellow

2.13.2 Elemental sulphur (α-S₈) melting properties

The most stable sulphur element is orthorhombic (α-S₈) which converts to monoclinic (β-S₈) above 96.3°C. Monoclinic (β-S₈) which melts at temperatures of 120.6°C is the major elemental sulphur species found in the Stretford™ plants (Schmidt, M., et al., (1973), (Steudel., R, et al., (2003)). The transition temperature from α-S₈ to β-S₈ depend on the heating rates and it starts above 96.3°C as observed by differential scanning calorimetry (DSC), (Thackray, M., et al., (1970)). Heating α-S₈ below the melting point does not result in decomposition of eight-numbered ring (Ralf Steudel., et al., (2003), Prins J.A., et al., (1957)). Pure elemental sulphur can be kept in a liquid form below melting point at 50°C for twenty minutes without crystallization. When the temperature is close to the melting point, the super-cooling period is extended (Bacon, R.F., et al., (1942)). Above 159°C the monoclinic species starts to form amorphous sulphur (S_∞) of which it becomes the major species above 170°C (Prins J.A., et al., (1957)).

The insoluble sulphur is dark-brown in colour, viscous and insoluble in carbon disulphide. The thermal behavior depends on its formation since amorphous sulphur is a long chain molecule. When the dark-brown liquid is quenched by cold water, the molecules does not have time to organize in orthorhombic crystals. However, after few days at room temperature the amorphous sulphur can revert back to α-S₈. At higher temperatures above 300°C, S₁, S₂, S₃, and S₄ species can detected spectroscopically as they only exist in vapor form. Homocycles between S₆ to S₂₀

can be prepared as a solids at moderate temperature (Steudel, R., et al., (2003)), (Kozhevniko V.F., et al., (2004)). Elemental sulphur (α -S₈) can be melted at lower temperature than 120.6°C but the process takes longer. The melting points of elemental sulphur also depend on the heating rate, external pressure and during the process it may decompose. The lower the heating rate, the lower the melting point. Only in a case of pure α -S₈ constant triple point temperature of 115°C can be measured since the composition at the melting point reaches an equilibrium after plus or minus 10 hours (Steudel, R., et al., (2003)).

2.13.3 Other elemental sulphur allotropes melting properties

Other elemental sulphur species decompose to α -S₈ and S_∞ as a primary products from which other rings are then formed. The S₇ and α -S₈ has a reversible melting temperature if heating rate is too fast and cooling is so quickly before the last crystals disappear. All other sulphur allotropes decompose already at below melting temperature if kept at the temperature for some time except α -S₈ (Steudel, R., et al., (2003)). The experimental ionization patterns, theoretical calculations and thermodynamic considerations indicated that S₆-S₁₂ exist as a rings in all stages. S₇, S₉ and S₁₀ suffer from unfavorable distances and contain unequal molecules. Experimental results also show that α -S₈, S₁₂ and S₆ are the most stable bonds in that order. The thermal behavior or kinetic stability does not increase with molecular sizes (Berkowitz, J., et al., (1969), Berkowitz, J., (1975)). The structure of α -S₈ is the only one with equal angles across all eight atoms as indicated in Figure 2.23 (Schmidt, M., et al., (1973)).

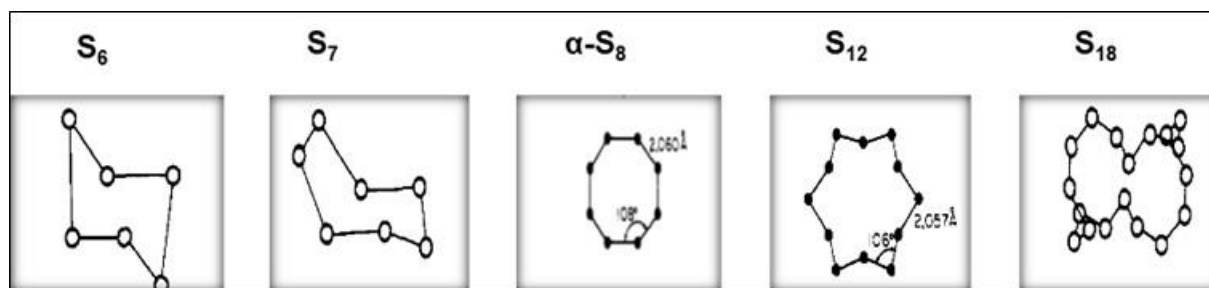


Figure 2.23: Ring structures of some elemental sulphur allotropes (Schmidt, M., et al., (1973))

2.14 Summary of literature review

For the Stretford™ plant to operate stably crucial parameters such as V⁵⁺, Na₂[ADA], total alkalinity, temperature and pH need to be optimized. The literature study for this dissertation has revealed that the Stretford™ chemistry is very complex. V⁵⁺ plays a very crucial role during absorption of H₂S in the absorbing contactor, ionization, and conversion of HS⁻ to elemental sulphur in the reaction tank. The redox cycle between V⁵⁺, V⁴⁺ and Na₂[ADA] as a catalyst is very important. The oxidation of V⁴⁺ to V⁵⁺ is catalyzed by Na₂[ADA]. The actual active oxidants are

the peroxide radicals that are released in the redox cycle. V^{5+} is reduced to V^{4+} during HS^- conversion to elemental sulphur in the absorbing contactor and reaction tank. It is very important that V^{4+} be re-oxidized back to V^{5+} in the oxidizing tank to prevent precipitation of V^{4+} with the elemental sulphur. The pH plays a very crucial role during absorption, dissociation, and conversion of H_2S to elemental sulphur. A higher pH was found to exponentially increase absorption of H_2S but reduced the conversion rate of HS^- to elemental sulphur. If the concentration of V^{5+} is stoichiometrically lower than the HS^- , the rate of converting HS^- to elemental sulphur will be slower than the rate of absorption of H_2S . This will cause an equilibrium condition to be reached in the absorbing contactor. When an equilibrium condition is reached between H_2S in the gaseous phase and that in the aqueous phase, the benefit of high H_2S absorption due to high pH will be reversed as H_2S will not be absorbed further. It is therefore, very important that the concentration of V^{5+} is always 2 to 3 higher than the absorbed H_2S in stoichiometry.

Total alkalinity is important as a buffer for pH in the Stretford™ aqueous solution. A higher total alkalinity was found to stabilize vanadium species but also increases the rate of formation of by-products. Temperature plays a crucial role during H_2S absorption and conversion to elemental sulphur. A higher temperature was found to increase the rate of re-oxidation of V^{4+} to V^{5+} and conversion of HS^- to elemental sulphur. However, it reduces H_2S absorption and exacerbates formation of by-products. It was found that elemental sulphur contained large number of allotropes, with more than 30 known homo-cyclic rings and can exist as a solid, liquid, and gas. Orthorhombic crystalline elemental sulphur α - S_8 was found to be the most stable allotrope.

Previous research on the Stretford™ process did not fully focus on the vanadium speciation and how it affects formation and production of elemental sulphur. This work will attempt to provide a detailed understanding of the effect of vanadium oxidation states on elemental sulphur production and its quality. The physical, chemical and mineralogical properties of produced elemental sulphur will be analyzed using ICP-OES, gravimetric, XRD, DSC and PSD. The thermodynamic models will be developed using the OLI studio analyzer to understand the stability of different H_2S and vanadium species at given conditions. The statistical model will also be developed to establish the relationship between total vanadium and V^{5+} concentrations on H_2S absorption and elemental sulphur production.

CHAPTER 3: ANALYTICAL TOOLS AND EXPERIMENTAL METHODS

3.1 Introduction

The chemicals and equipment that were used in this study are outline in this chapter. Sections 3.2 and 3.3 give the materials and the experimental method. Section 3.4 discusses the synthetic Stretford™ aqueous solution preparations. Section 3.5 discusses analytical techniques that were used to characterize the synthetic Stretford™ aqueous solutions and the elemental sulphur. Sections 3.6 and 3.7 gives overview of OLI studio analyzer and statistical models development. Section 3.8 is a summary of Chapter 3.

3.2 Materials

The semi-batch experiments were performed using a synthetic Stretford™ aqueous solutions containing concentrations of V^{5+} , V^{4+} , $Na_2[ADA]$, $NaSCN$, total alkalinity and Na_2SO_4 . Gas cylinders containing 1.5% H_2S and 98.5% N_2 balance were used to conduct all the experiments. The air which contains 21% O_2 and 79% N_2 was used. All chemicals that were used in this study are listed in Table 3.1 with their respective purities. SAV $(NH_4)(Na_3)(V_4O_{11})_2$ and $VOSO_4$ were used as a source of V^{5+} and V^{4+} respectively.

Table 3.1: List of chemicals compounds

Chemical compounds	Purity (wt%)	Grade
[SAV]*	99	Technical
H_2SO_4	98	Analytical
Na_2SO_4	98.8	Analytical
Na_2CO_3	99	Analytical
$NaSCN$	99.4	Analytical
$NaHCO_3$	99	Analytical
$[VOSO_4]**$	97	Analytical
$Na_2[ADA]***$	90	Technical
$[Cd(CH_3COO)_2]****$	99	Analytical

Note:

* - Sodium Ammonium Vanadate

** - Vanadyl (IV) sulphate

*** - Disodium salt of 2.6 and 2.7 isomers of Anthraquinone disulfonic acid

**** - Cadmium acetate

The concentrations of the trace elements are given in Table 3.2. The concentrations of K, Ca, Si, B, Cd, As and Zn in the SAV salt could contaminate the elemental sulphur particles produced during the oxidation of the absorbed H_2S in the Stretford™ aqueous solution. The trace elements

in NaSCN, Na₂SO₄, Na₂CO₃ and NaHCO₃ were low. There was trace elements like K, As, Mg, Ca, Cd, Li, Si in Na₂[ADA] also.

Table 3.2: Chemical trace elements by ICP-OES

Elements (ppm)	SAV	VOSO ₄	NaSCN	Na ₂ SO ₄	Na ₂ CO ₃	NaHCO ₃	Na ₂ [ADA]
AS	3763	0.00	1.30	1.10	0.00	0.00	2619
B	12022	3535	0.00	0.00	131.7	19.76	1008
Ba	428	1724	0.00	0.00	0.20	0.20	197
Ca	27097	4051	2.00	1.10	30.3	74.14	4988
Cd	6161	171	0.10	1.20	0.20	0.59	4301
Co	420	260	0.10	0.10	0.00	0.00	249
Cr	0.00	0.00	0.10	0.00	1.10	0.00	0.00
Cu	332	0.00	0.30	2.10	0.00	0.59	0.00
Fe	1032	223	1.40	69.00	6.60	4.89	581
Hg	0.00	0.00	0.10	0.00	0.00	0.00	0.00
Li	103	33	0.20	0.40	8.40	2.15	0.00
Mg	9744	275	0.30	3.30	5.30	5.87	2599
Mn	325	86	0.10	0.20	0.20	0.39	78.0
Mo	0.00	0.00	0.10	0.40	0.00	0.00	0.00
Ni	856	862	0.10	40.00	0.00	0.00	0.00
Pb	856	0.00	0.10	20.00	1.50	1.17	1271
K	45466	0.00	260	10.40	0.00	53.0	22766
Se	0.00	0.00	1.70	30.2	0.00	0.00	282
Si	17975	0.00	0.10	12.3	0.00	0.00	1655
Sr	1166	200	0.00	23.0	1.80	0.00	1661
Zn	2914	258	0.00	34.0	0.20	0.20	1212
Cl	100	350	20.0	49.0	0.30	0.40	123

Figure 3.1 shows the XRD results of SAV and Na₂[ADA]. The diffractograms of VOSO₄, NaSCN, Na₂SO₄, Na₂CO₃ and NaHCO₃ are given in Appendix G (Figures G-1 to G-5). The XRD results shows all chemicals compounds were crystalline except Na₂[ADA] which contained organic carbon. Based on Figure 3.1, Na₂[ADA] is amorphous material because it contain organic carbon. The peaks observed in this figure are for the silicon standard which was spiked into the sample to quantify proportions of amorphous during the quantitative XRD analysis. The SAV contained oxovanadium sulphate, ammonium vanadate and sodium amidosulphate species.

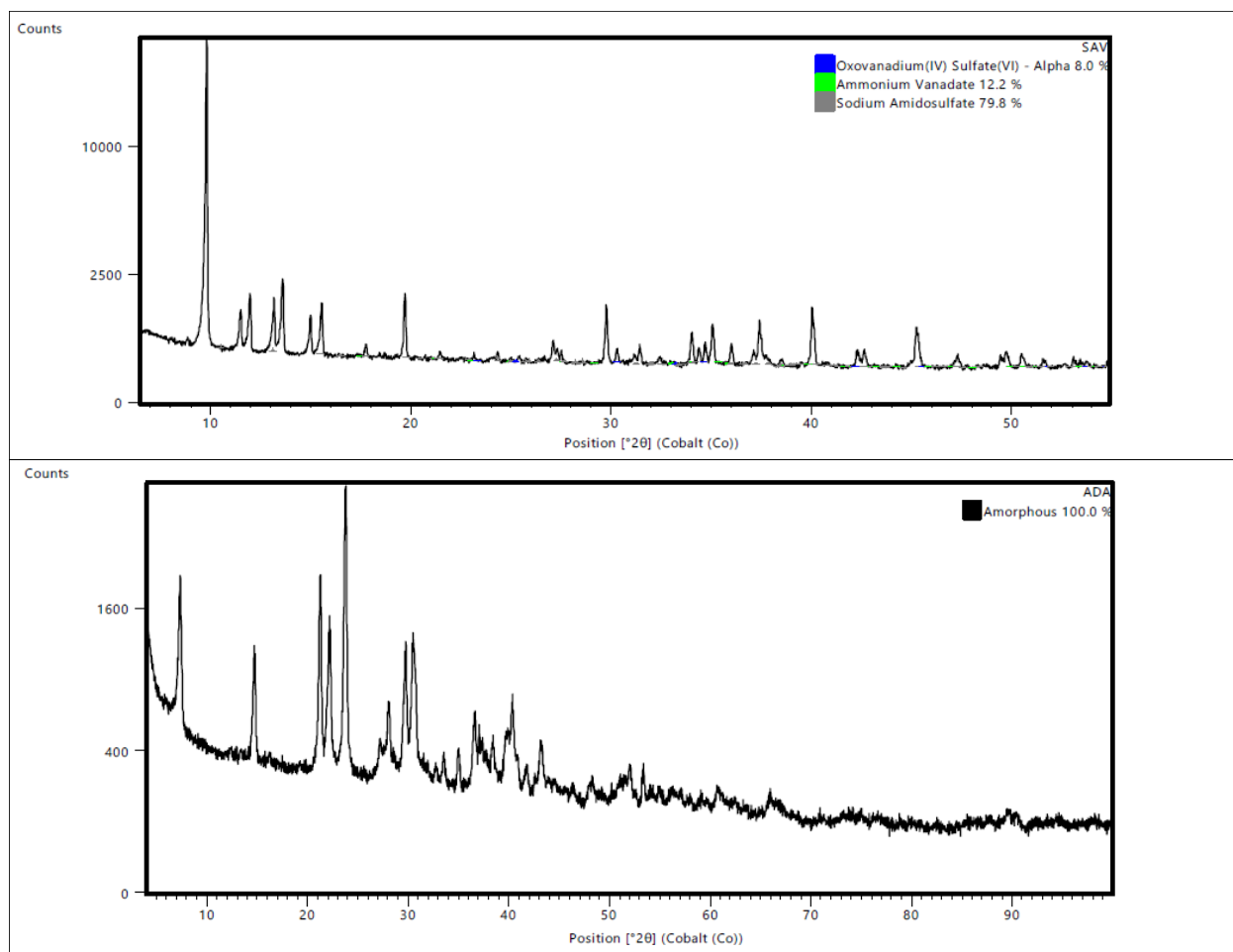


Figure 3.1: The diffractograms of SAV (top) and Na₂[ADA] (bottom) used to prepare synthetic Stretford™ solution

3.3 Experimental methods

3.3.1 Experimental set-up

Figure 3.2 shows an experimental flow diagram that was used to conduct all the experiments in this study. The actual picture of the experimental set-up is given in Appendix A. The experiments were repeated four times with similar conditions using a laboratory unit consisting of an absorbing contactor, peristaltic pump, reaction, oxidizing and balance tanks. The laboratory unit was filled with 6.5 dm³ of the Stretford™ aqueous solution. The absorbing contactor, reaction tank, oxidizing tank and balance tank were all made of transparent glass. The Stretford™ aqueous solution was circulated from the balance tank to the top of the absorbing contactor using a peristaltic pump. The H₂S containing gas was introduced on the side of the closed absorbing contactor co-currently with the synthetic Stretford™ aqueous solution.

The flow of the H₂S containing gas and Stretford™ solution were maintained constant at 7 and 1.3 dm³.min⁻¹ respectively. The gas exited at the bottom of the absorbing contactor and bubbled into 1 mol.dm⁻³ of cadmium acetate solution before release to the atmosphere. The cadmium acetate solution was used to absorb the unabsorbed H₂S in order to calculate the H₂S absorption efficiency. The Stretford™ aqueous solution with absorbed H₂S flow to the top of the reaction tank gravitationally for conversion of HS⁻ to elemental sulphur. The closed reaction tank was placed higher than the oxidizing tank and the oxidizing tank was higher than the balance tank for the liquid to flow gravitationally.

The oxidizing and balance tanks were open to atmosphere. The solution from the bottom of the reaction tank flowed to the bottom of the oxidizing tank via a transparent flexible pipe. The air was introduced at the bottom of the oxidizing tank using four air frits. The purpose of the air was to oxidizes V⁴⁺ to V⁵⁺, inactive Na₂[H₂ADA] to active Na₂[ADA] and float elemental sulphur slurry. Spent air exited the oxidizing tank to atmosphere while the solution with elemental sulphur slurry overflowed to the balance tank. The temperature of the solution was maintained by a thermostatic water bath at 40°C throughout. The air flow into the oxidizing tank was controlled constant at 6 dm³.min⁻¹. The temperature of the solution was measured by thermocouples (TI) that were installed at the absorbing contactor, reaction tank, oxidizing tank and balance tank. The air and gas flows were measured by flow meters (FI). The pH values of the solutions were measured continuously at the balance tank. The elemental sulphur slurry floating on top of the oxidizing and balance tanks solutions were filtered for different analyses.

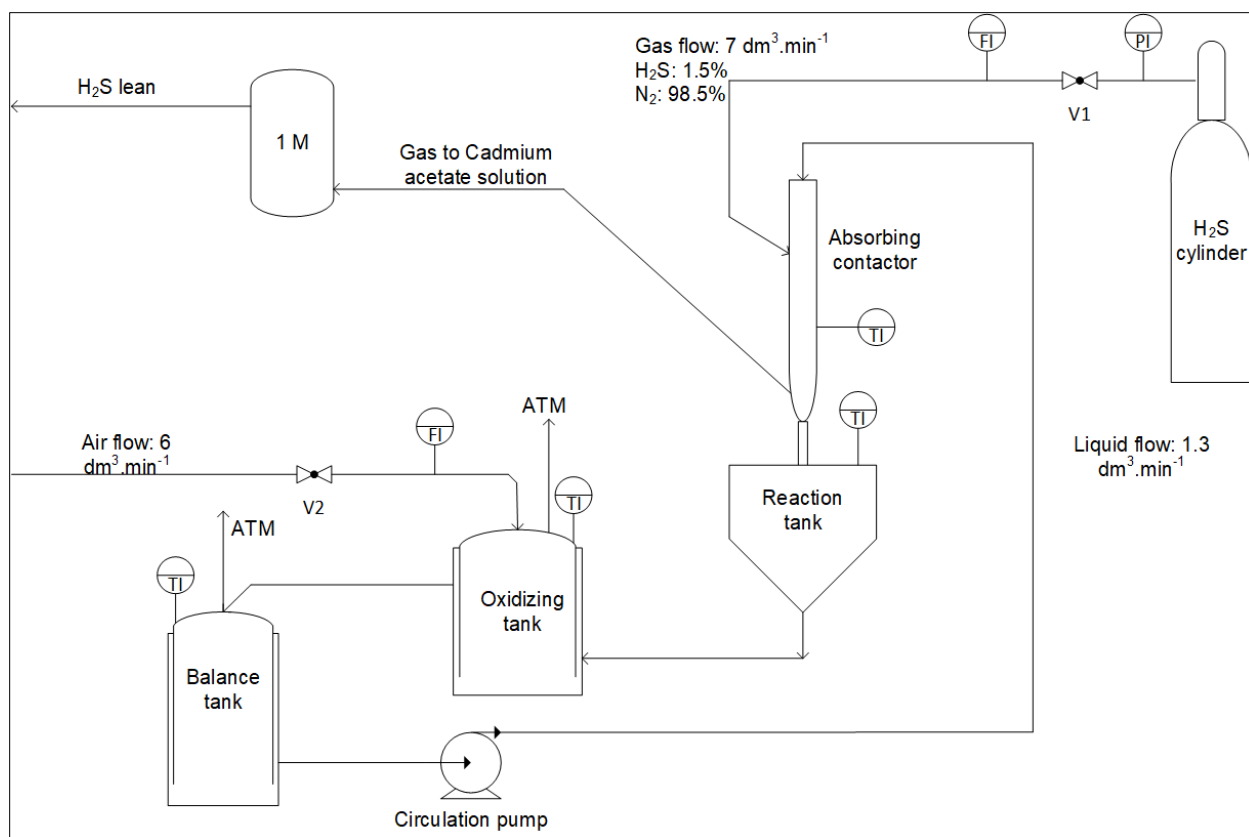


Figure 3.2: Apparatus used to simulate Stretford™ process during experimental work

3.3.2 Experimental procedure

1. 7 dm³ of the synthetic Stretford™ aqueous solution was filtered through a Whatman 42 filter paper to remove suspended solids.
2. The pH value of the Stretford™ aqueous solution was measured at 40°C using a pH meter.
3. A sample was taken to quantify the concentrations of total vanadium, V⁵⁺, NaSCN, Na₂SO₄, Na₂[ADA] and total alkalinity.
4. The water bath was filled to 96% with de-ionized water and set at 43°C.
5. 6.5 dm³ of the Stretford™ aqueous solution was transferred into the reaction, oxidizing and balance tanks.
6. Peristaltic pump was started and set at 1.3 dm³.min⁻¹ to circulate synthetic Stretford™ aqueous solution.
7. The air valve was slowly opened to the oxidizing tank and set at 6 dm³.min⁻¹.
8. The peristaltic pump was kept running for 20 minutes while stabilizing the pH of the solution.
9. The H₂S gas valve was opened at 7 dm³.min⁻¹ for 5 hours as soon as all four temperature indicators were at 40°C.
10. After 5 hours, the H₂S gas valve was closed.

11. The peristaltic pump was kept running and the air kept open for 20 minutes to ensure absorbed H_2S in solution oxidizes to elemental sulphur and V^{4+} oxidizes to V^{5+} .
12. Samples were taken to quantify the concentrations of total vanadium, V^{5+} , NaSCN , Na_2SO_4 , $\text{Na}_2[\text{ADA}]$ and total alkalinity.
13. Both floating and sinking elemental sulphur particles fractions were filtered and washed off with de-ionized water.
14. Elemental sulphur particle sizes were measured by the Malvern 2000 particle sizer.
15. Elemental sulphur was dried in the oven at 70°C for 12 hours and weighed.
16. Physical properties of elemental sulphur was determined by DSC.
17. Crystallinity of the elemental sulphur particles were determined by an XRD technique.
18. Elemental sulphur purity was determined by gravimetry technique.
19. Residual ash trace elements were determined by an ICP-OES technique.

3.4 Synthetic Stretford™ aqueous solutions preparations

3.4.1 Variable V^{5+} concentration with added impurities

Table 3.3 shows chemical concentrations of the synthetic Stretford™ aqueous solutions prepared. The impurities in this study was referring to Na_2SO_4 and NaSCN that are formed as a side product during conversion of HS^- to elemental sulphur. Four experiments were conducted to determine the effect of V^{5+} on H_2S conversion to elemental sulphur. The Stretford™ aqueous solutions were prepared with de-ionized water and contained total alkalinity, NaSCN , Na_2SO_4 , V^{5+} and $\text{Na}_2[\text{ADA}]$.

The difference between the concentrations total vanadium and V^{5+} was assumed to be V^{4+} in this study. The concentration of V^{5+} was varied as indicated in Table 3.3. The characterization of all solutions prepared in this section are given in Section 4.2.1. The total of 7 dm^3 of de-ionized water was measured in a 10 dm^3 glass beaker and heated to 40°C . The chemicals were added while stirring de-ionized water in a magnetic hotplate for each solution prepared. The following procedure was used to prepare synthetic Stretford™ aqueous solutions in this study:

- 490 g of NaSCN was slowly added into the de-ionized water and stirred until dissolved.
- 490 g of Na_2SO_4 was slowly added into the solution and stirred until dissolved.
- 318.5 g of NaHCO_3 was slowly added into the solution and stirred until dissolved.
- 20.3 g of Na_2CO_3 was slowly added into the solution and stirred until dissolved.
- 2.1 g of $\text{Na}_2[\text{ADA}]$ was slowly added into the solution and stirred until dissolved.
- 18.8, 28.1, 46.9, and 93.8 g of SAV were added in Solutions 1, 2, 3, and 4 respectively.

Table 3.3: Theoretical Stretford™ aqueous solutions results at variable V⁵⁺ concentrations

Solutions	mol.dm ⁻³							pH
	V ^{Total}	V ⁵⁺	V ⁴⁺	Na ₂ [ADA]	Na ₂ SO ₄	NaSCN	TA	
S-1	0.020	0.019	0.0003	0.001	0.47	0.89	0.17	8.32
S-2	0.029	0.029	0.0004	0.001	0.49	0.88	0.16	8.34
S-3	0.047	0.046	0.0004	0.001	0.50	0.84	0.17	8.33
S-4	0.096	0.096	0.0006	0.001	0.50	0.88	0.16	8.32

Note: V^{Total}-Total vanadium; TA-Total alkalinity; S-1 (Solution 1); S-2 (Solution 2); S-3 (Solution 3); S-4 (Solution 4)

3.4.2 Optimal V⁵⁺ concentrations without added impurities

One experiment was conducted using synthetic Stretford™ aqueous solution without impurities at V⁵⁺ concentration of 0.029 mol.dm⁻³. The aim was to determine the effect of impurities on H₂S conversion to elemental sulphur and use the experiment as a control. The operating parameters were similar to Solution 2 except NaSCN and Na₂SO₄ were not added. The characterization of the solution without impurities (S-X) is given in Section 4.2.2.

3.4.3 Vanadium oxidation states without Na₂[ADA]

Table 3.4 displays chemical concentrations of the synthetic Stretford™ aqueous solutions in the absence of Na₂[ADA]. The V⁵⁺ to V⁴⁺ molar ratios were varied from 0% (Solution 5), 20% (Solution 6), 40% (Solution 7) and 100% (Solution 8) of the V⁴⁺ concentrations in total vanadium. The 20% of V⁴⁺ in total vanadium means V⁵⁺ was 80% while 40% of V⁴⁺ in total vanadium means V⁵⁺ was calculated as 60%. The characterization of the solutions prepared in this study are given in Section 4.2.3. Four experiments were conducted to determine the effects of vanadium oxidation states on H₂S conversion to elemental sulphur. The concentration of total vanadium was maintained at 0.029 mol.dm⁻³ while changing the concentrations of V⁵⁺ and V⁴⁺ respectively. The amounts of SAV and VO₂SO₄ that were added in Solutions 5, 6, 7 and 8 are shown in Table 3.5.

Table 3.4: Concentrations of Stretford™ aqueous solutions results at V⁵⁺ to V⁴⁺ molar ratios

Solutions	mol.dm ⁻³							pH
	V ^{Total}	V ⁵⁺	V ⁴⁺	Na ₂ [ADA]	Na ₂ SO ₄	NaSCN	TA	
S-5	0.029	0.027	0.001	0.00	0.49	0.86	0.16	8.32
S-6	0.028	0.022	0.006	0.00	0.49	0.86	0.17	8.29
S-7	0.028	0.016	0.011	0.00	0.49	0.87	0.16	8.33
S-8	0.028	0.001	0.027	0.00	0.50	0.86	0.17	8.30

Note: S-5 (Solution 5); S-6 (Solution 6); S-7 (Solution 7); S-8 (Solution 8)

Table 3.5: Amount of SAV and VOSO₄ added

Solutions	SAV (g)	VOSO ₄ (g)
S-5	26.3	0.0
S-6	21.0	7.5
S-7	15.8	15.1
S-8	0.0	37.7

3.5 Analytical techniques

3.5.1 Determination of vanadium concentrations by UV-Visible Spectrophotometry

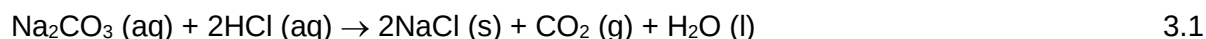
UV-Visible spectrophotometry was used to determine the concentrations of total vanadium and V⁵⁺. The technique uses the light close to ultraviolet (UV) and infrared ranges to measure concentrations of the compound (McKay, A.E., (1989), Skoog A.D., et al., (2007)). The method was established on the intensity of colour that materials displayed. The intensity of colour is then correlated to concentration and quantitatively determines the concentrations of the chemical species according to Beer Lambert law (Settle, F.A., (1997)). Total vanadium and V⁵⁺ control standards of 0.029 mol.dm⁻³ were prepared and used as the reference to ensure reliability of the chemical results.

The concentration of total vanadium was quantified by mixing 0.001 dm³ of a diluted Stretford™ sample solution with 0.015 dm³ of ammonium acetate solution. The total vanadium and ammonium acetate solution was mixed with 0.005 dm³ of sodium triphosphate (Na₃P₃O₉) to reduce all V⁵⁺ to V⁴⁺. The Gallic acid (0.01 dm³) was added to the Stretford™ aqueous solution and forms V⁴⁺ Gallic acid complex with blue colour. The intensity of the blue colour was relative to the concentration of V⁴⁺ and was determined by spectrophotometer in 10 mm glass cells at the wavelength 595 nm. The intensity of the blue colour of the Stretford™ aqueous solution was compared to that of standard total vanadium solution used to prepare a calibration curve to ensure accuracy (Perkin, E., (1982)).

The concentration of V⁵⁺ was determined by mixing 0.02 dm³ of 4-(2-pyridylazo) resorcinol monosodium salt monohydrate (PAR) and 0.01 dm³ of trans-1,2-diaminocyclohexane tetra-acetic acid (DCTA) with 0.01 dm³ of diluted Stretford™ aqueous solution and forms a pink colour compound. The pink colour compound was determined with a spectrophotometer using 10 mm glass cuvette at a wavelength of 540 nm. The intensity of the blue colour of the Stretford™ aqueous solution was also compared to that of standard V⁵⁺ solution used to prepare a calibration curve to ensure accuracy (Perkin, E., (1982)).

3.5.2 Determination of total alkalinity concentration by titration

The total alkalinity, which is, expressed as Na₂CO₃ concentration buffer the pH of the Stretford™ aqueous solution. The determination of the Na₂CO₃ concentration forms the foundation of total alkalinity measurements (Andrews, M., et al., (1988)). The concentration of total alkalinity was determined by acid-base titration. During titration, a titrant with a known concentration and volume is added to the solution that has a known volume but unknown concentration (analyte). The concentration and volume of the titrant added to the analyte is used to calculate the concentration of the analyte by stoichiometry (McGraw, H., (2011)). The filtered Stretford™ aqueous solution sample was titrated with hydrochloric acid (HCl) from initial pH (approximately 8.3) to end-point pH of 3.8 and the results were reported as mol.dm⁻³ of Na₂CO₃. The indicator which was added to the liquid sample during the titration analysis is methyl orange bromo-cresol-green. The titration was conducted at 40°C which is within Stretford™ process operating temperature. The final result calculations was based on the volume of Stretford™ aqueous solution sample used together with the concentration and volume of HCl consumed as per below reaction (Ritter, T.J., et al., (1988)).



By stoichiometry, the concentration of Na₂CO₃ was calculated as follow:

$$\text{Total alkalinity as Na}_2\text{CO}_3, \text{ mol.dm}^{-3} = (V_1 \times M_1) \div (2 \times V_2) \quad 3.2$$

Note: V₁ (Volume of HCl solution in dm³), M₁ (Molarity of 0.1 M HCl solution in mol.dm⁻³), V₂ (Volume of Stretford™ aqueous solution in dm³)

3.5.3 Automated discrete spectrophotometry for Na₂SO₄ concentration determination

The concentrations of Na₂SO₄ was determined in the Stretford™ aqueous solution using automated discrete spectrophotometry at 40°C. The automated discrete photometric analyzer is pre-programmed to follow automated photometric principle to measure Na₂SO₄ concentrations at 420 nm wavelength (Settle, F.A., (1997)). The technique is suitable to quantify Na₂SO₄ in Stretford™ aqueous solution in the concentration ranges from 0.04 to 1.41 mol.dm⁻³. The measurement of the control standard is done against the appropriate calibration curve and the result automatically calculated by the instrument. The control standard of 1.23 mol.dm⁻³ was used. 0.01 dm³ of Stretford™ aqueous solution was diluted with 0.15 dm³ of de-ionized water. 0.01 dm³ of diluted sample in a plastic test tube was put into calibrated automated photometric analyzer for analysis (Settle, F.A., (1997)).

3.5.4 Quantification of NaSCN by Argentometric titration

The concentration of NaSCN was determined in the Stretford™ aqueous solution sample using Argentometric titration. Acidified diluted Stretford™ aqueous solution sample was titrated with silver nitrate solution (AgNO_3) to a potentiometric end-point at 40°C . This method is suitable to determine the sodium thiocyanate of Stretford™ aqueous solution samples in the range of 0.06 to 2.47 mol.dm^{-3} as NaSCN. The volume and concentration of AgNO_3 was known while the volume of NaSCN was not known. The results calculation were based on the volume of Stretford™ aqueous solution used together with the concentration and volume of AgNO_3 consumed (Harris, D.C., (2003)). The concentration of NaSCN was calculated by stoichiometry as per below Reaction 3.3.



By stoichiometry, the concentration of NaSCN was calculated as follow:

$$\text{NaSCN (mol.dm}^{-3}\text{)} = (V_3 \times M_1) \div (2 \times V_4) \quad 3.4$$

Note: V_3 (Volume of AgNO_3 solution in dm^3), M_1 (Molarity of 0.1 M AgNO_3 solution in mol.dm^{-3}), V_4 (Volume of Stretford™ aqueous solution in dm^3)

3.5.5 Quantification of $\text{Na}_2[\text{ADA}]$ concentrations by colorimetry

$\text{Na}_2[\text{ADA}]$ is used in the Stretford™ aqueous solution as the oxidant during oxidation of V^{4+} to V^{5+} . The $\text{Na}_2[\text{ADA}]$ was reacted with the sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) which is a reducing agent and form a red complex in a highly alkaline solution (Andrews, M., (1989)). The alkalinity was increased by adding sodium hydroxide solution. The technique cannot identify different $\text{Na}_2[\text{ADA}]$ organic isomers but can quantify the concentration of reduced $\text{Na}_2[\text{ADA}]$, (Trofe, T.W., et al., (1986)).

The intensity of the red colour complex was determined spectrophotometrically at 448 nm. The absorbance calibrations curve of standard $\text{Na}_2[\text{ADA}]$ solution was determined at the concentrations of $0.0013 \text{ mol.dm}^{-3}$. Total of 0.01 dm^3 Stretford™ aqueous solution sample was filtered and mix with 0.01 dm^3 of 30% sodium hydroxide solution. 0.1 gram of $\text{Na}_2\text{S}_2\text{O}_4$ was added and mixed for one minute. 0.005 dm^3 solution was transferred into 0.01 dm^3 glass cell and determined spectrophotometrically at 448 nm. The method is suitable to determine the concentration of $\text{Na}_2[\text{ADA}]$ in a range between 0.0003 to 0.2 mol.dm^{-3} (Ritter, T.J., et al., (1988)).

3.5.6 Determination of elemental sulphur particle sizes

The elemental sulphur particles sizes were measured using a Malvern 2000 particle sizer. The elemental sulphur particles passed through a laser beam, which results in the laser light scattered at different angles. The detectors are placed at fixed angles and measure the intensity of light scattered at that position. The instrument captures the actual scattering pattern from the field of sulphur particles and calculates the sizes of each particle. The Malvern particle sizer measure particles from sizes 0.972 to 704 μm . The elemental sulphur particle sizes is reported as a percentage. The lower detection limit of the instrument is 0.972 μm . For example, the elemental sulphur particles sizes ranged between 0.972 and 704 μm are reported as a percentages. This data is then analyzed to calculate the size of the particles that created the scattering pattern in percentage. The elemental sulphur produced was filtered and washed with de-ionized water. The instrument was started to open water and clean the sampling slot. When the ready to add sample appear on the screen, 2 grams of elemental sulphur slurry was added into sample slot and run for 3 minutes. When completed the results automatically generated (Malvern Instrument Ltd., (2007)).

3.5.7 Measurement of pH values of the Stretford™ aqueous solutions

The pH value of the synthetic Stretford™ aqueous solutions was determined at 40°C. The pH value is used to measure the degree of acidity or alkalinity of a Stretford™ aqueous solution in this study. The pH of the Stretford™ aqueous solutions is monitored to ensure H_2S absorption and dissociation occur in the absorber. The acidic solution contains hydronium ions (H_3O^+) activity while alkaline solution contains hydroxide (OH^-) activities (Cammack R, et al., (2006)). Two buffer solutions at a pH of 4 and 10 were prepared and used to calibrate the pH meter at 40°C. The Stretford™ aqueous solution was heated to 40°C and the pH was measured (Andrews, M., (1989)).

3.5.8 Thermal analysis of elemental sulphur by DSC

The DSC is an analytical tool in which the difference in the amount of energy needed to increase the temperature of the sample and the indium reference standard sample are measured. Elemental sulphur sample and reference standard are maintained at the same temperature. The reference sample should have a well-defined heat capacity over the range of temperatures to be investigated (Dean J.A., (1995)). The DSC gives a peak at that particular temperature when the elemental sulphur particles changes phase from a solid to a liquid or polymer. This particular temperature will be a melting or polymerization point. In this study, the Mettler Toledo DSC 827^e

high-pressure with FRS5 sensor was used to determine the melting and polymerization points of elemental sulphur particles. Analysis was performed under an inert atmosphere of N₂ using standard 40 µl aluminum pans with pierced lids. The elemental sulphur and reference were heated to 30°C at 10°C per minute and held for a minute. The temperature of the sample and standard were 30°C and heated to 380°C with heating rate of 10°C per minute. There was a hold point of a minute at 380°C and the samples cooled down uncontrolled (Dean J.A., (1995)).

3.5.9 Investigation of vanadium species using ⁵¹V NMR

⁵¹V NMR was used to identify different types of V⁵⁺ species in the Stretford™ aqueous solutions. The method is based on measurement of absorption of electromagnetic radiation in the frequency of approximately 4 to 900 MHz. The technique depends on the magnetic resonance to provide detailed structures of the species (Harald G., (2013), Skoog A.D., et al., (2007)). An Agilent Unity-Inova 600 NMR spectrometer with a H¹ frequency of 600 MHz and a V⁵¹ frequency of 157.8 MHz was utilized. The instrument was equipped with a 5 mm dual channel broadband probe with each sample equilibrated and shimmed at 40°C before acquisition. A Solution of VOCl₃ was used as a standard and gave a chemical shift of 0 ppm. The Stretford™ aqueous solutions were heated to 40°C and 700µl then transferred to a new ⁵¹V NMR tube using pipettes. The structures of V⁵⁺ species were determined by studying the peaks of ⁵¹V NMR spectra (Harald G., (2013), Brand, D.J., (2018)). The procedure by Brand is given in Appendix H.

3.5.10 Analysis of elemental sulphur using XRD

XRD spectroscopy was used to determine the crystallinity and amorphous of elemental sulphur particles and other solid precipitates. The XRD has the power to identify and characterize the crystalline phases of different solid compounds using X-rays. The structure is crystalline when the atoms are ordered and amorphous structure is not arranged in regular arrays. A different chemical gives different peaks in XRD that is independent of other chemicals (Settle, F.A., (1997)). Single crystal diffractometer and powder are two different classes of XRD. The single crystal is used to determine the molecular structure of materials while the powder diffractometer is used for phase identification and quantification of the crystalline phase in solid samples (Settle, F.A., (1997)). In this study, the elemental sulphur was analyzed using a Panalytical X-pert pro X-ray diffraction instrument. The elemental sulphur was crushed to less than 75 µm and transferred to sample holder and spiked with 20% silicon standard. The micronisation was used to homogenise the samples. The spiked chemical was added to the sample to determine the proportion of amorphous material in the sample using a HighScore Plus and International Center for Diffraction Data at two

theta angle. The quantification of the phases were done following Rietveld method (Rietveld, H.M., (1969), Speakman, S.A., (2012)).

3.5.11 Analysis of elemental sulphur purity by gravimetric

The gravimetric analytical technique was used in this study to determine the purity of elemental sulphur product. The technique can quantify the amount of chemical elements through the measurement of mass. The principle behind gravimetric analysis is that the mass of an element in a compound can be determined and then used to find the mass percent of other elements by difference (Skoog, D., et al., (1996)). A 200 g silica crucible was put inside the oven at 100°C to remove all moisture and cooled down inside silica desiccant. An amount of 20 g milled elemental sulphur sample was weighed in an MS-semi micro advanced analytical balance and added into silica crucible. The elemental sulphur was burned in a furnace at 900°C for 1 hour. After an hour, all elemental sulphur particles were oxidized and only inorganic elements which are impurities reported to the residual ash (Skoog, D., et al., (1996)). The trace elements in the residual ash were identified by ICP-OES discussed in the next section. The mass of dried residue was weighed. The elemental sulphur purity was calculated as per Equation 3.5:

$$\text{Sulphur purity (\%)} = (20 \text{ g} - \text{mass of impurities}) * 100 \div (20 \text{ g}) \quad 3.5$$

3.5.12 Analysis of residual ash by ICP-OES

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is a technique that can determine the composition of inorganic elements in a variety of different samples in aqueous phase. The technique exploits the fact that excited atoms emit photons of a particular wavelength as they return to the ground state after excitation by a high temperature argon plasma that can reach electron temperatures of up to 9726°C. Each element emits photons of specific wavelengths different to its atomic character and the measured emission intensities are then compared to the intensities of element standards of known concentration to obtain the corresponding concentrations in the sample (John, W.O., (1991)). The ICP-OES was used to identify and quantify chemical elements in the residual ash. All residual ash particles dissolved completely in 0.01 dm³ HCl. 0.09 dm³ of de-ionized water was added. The 0.1 dm³ of HCl acid solution was pumped by a peristaltic pump for the analysis of the elements (John, W.O., (1991)).

3.5.13 Elemental sulphur mass balance

The H₂S gas reacted with cadmium acetate as indicated by Reaction 3.6 and form CdS yellow precipitate (Matjie R.H., et al., (2018)). 1 mol.dm⁻³ of cadmium acetate solution (Cd(CH₃COO)₂)

was prepared in de-ionized water to scrub the H₂S gas before exiting to atmosphere. 143 g of Cd(CH₃COO)₂·2H₂O (99% assay) was added in 1 dm³ beaker and mix with 0.5 dm³ of deionized water. The CdS precipitates was allowed to settled at the bottom of the glass bottle for 5 hours filtered out of the solution and dried at 50°C together with filter paper. The dried CdS with the filter paper was weighed at the scale. The known mass of the filter paper was subtracted. The amount of elemental sulphur in CdS precipitate was calculated. The volume and concentration of H₂S to the absorber was known and it was used to calculate total elemental sulphur to close the mass balance. The details H₂S absorption efficiency calculations are given in Appendix B.



3.6 OLI studio analyzer

OLI studio analyzer is a thermodynamic predictive framework that has capacity to determine the physical and chemical properties of organic and inorganic behavior of multi-phase chemicals in water. OLI is utilized in different applications for aqueous chemistry at high temperature, pressure, and concentration ranges. The OLI database contains proprietary coefficients for the prediction of physical properties of 80 inorganic elements and their associated aqueous species as well as over 8000 organic species (OLI Analyzer Studio., (2011)). In this study, the H₂S speciation graph was developed to simulate the type of H₂S species that are oxidized to elemental sulphur by V⁵⁺ at different pH ranges. A vanadium stability graph in water as a function of pH was also developed to simulate the type of vanadium species in a Stretford™ aqueous solutions. One of the limitations of the OLI model is the exclusion of Na₂[ADA] which is a very crucial parameter in the redox cycles between V⁴⁺ and V⁵⁺ in the oxidizing tank. However, in this study the OLI was not utilized to study the redox reaction between V⁴⁺ and V⁵⁺.

3.7 H₂S absorption and elemental sulphur production statistical models

In Chapter 2 it was discussed that the speciation of vanadium could negatively affect the H₂S absorption and elemental sulphur production. Therefore, this hypothesis was tested by developing a vanadium statistical model using data from the experiments. The two responses considered were elemental sulphur production and H₂S absorption for the statistical modelling. A linear plus interaction statistical model was fitted on the responses as a function of the total vanadium and V⁵⁺ concentrations variables. The analysis of the variance (ANOVA) was conducted to assess the statistical significance of the variables. An ANOVA quantifies the variance explained of a variable relative to the variance in the experimental error. Therefore, the F-test gives the ratio of the mean sum of the squares variance divided by the mean sum of the squares error. The F-value was

compared to the F-distribution to produce the P-value which is the probability that the effect of the variable on the response. Therefore, a p-value smaller than or equal to 0.05 indicates that there is 95% confident that the variables has an effect on the elemental sulphur production and H₂S absorption, (Lane, D.M., et al (2013)).

3.8 Summary

The materials, experimental set-up and procedure that were used and discussed in this study. The details of the calculated concentrations of the synthetic Stretford™ aqueous solutions used in this study were given. Three sets of synthetic Stretford™ aqueous solutions were prepared. The first set was the Stretford™ aqueous solutions prepared to determine the effect of V⁵⁺ on H₂S conversion to elemental sulphur with impurities. Impurities referring to NaSCN and Na₂SO₄. The second experiment was the Stretford™ aqueous solution prepared at the V⁵⁺ concentration without added impurities to determine their effect on H₂S conversion to elemental sulphur at best V⁵⁺ concentration (0.029 mol.dm⁻³) in this study. The last set was the synthetic Stretford™ aqueous solutions prepared at the variable V⁵⁺ to V⁴⁺ molar ratios without Na₂[ADA] to determine the effect of vanadium oxidation states on H₂S absorption and quality of elemental sulphur produced. The analytical tools used for the analyses of the Stretford™ aqueous solutions and elemental sulphur produced were described in detail. Chapter 4 will discuss the results obtained from this experimental work. Summary of how OLI studio analyzer and vanadium statistical models function were discussed.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

The literature study in Chapter 2 showed that concentration of V^{5+} plays a very crucial role during absorption of H_2S gas and conversion of HS^- to elemental sulphur in the StretfordTM process. It was discussed that the loss of vanadium in the form of V^{4+} due to precipitation has been observed previously in the StretfordTM process (Scheffel, F.A., et al., (1986)). It was further indicated that in the past there was never a focus to investigate the effect of vanadium oxidation states in the production of elemental sulphur and its effects on elemental sulphur quality. Therefore, the results obtained from this work are outlined to provide the details on the effects of vanadium oxidation states on H_2S absorption, elemental sulphur production and its quality. The details of materials, experimental methods, and analytical tools were given in Chapter 3. The chapter is made up of the following sections:

- Section 4.2 focuses on the characterization of the synthetic StretfordTM aqueous solutions before the experiments.
- Section 4.3 discusses the results obtained of the liquid samples during the repeatability experiments.
- Section 4.4 discusses the effect of V^{5+} concentrations on H_2S conversion to elemental sulphur.
- Section 4.5 discusses the effect of impurities on H_2S conversion to elemental sulphur.
- Section 4.6 discusses the effect of vanadium oxidation states on H_2S conversion to elemental sulphur.
- Section 4.7 discusses quality of elemental sulphur produced in this study compared to commercial sulphur.
- Section 4.8 gives a summary of the findings in this research.

4.2 Characterization of synthetic StretfordTM aqueous solutions

4.2.1 Variable V^{5+} concentration

Figure 4.1 shows the physical appearance of StretfordTM aqueous solutions at different V^{5+} concentrations with $Na_2[ADA]$, $NaSCN$, Na_2SO_4 , and total alkalinity fixed. The orange colour in Solutions 1, 2, 3, and 4 was an indication of vanadium at its highest oxidation state (5+). The colour of a highly oxidized StretfordTM aqueous solution with V^{5+} is wine-red to orange while the colour of a reduced vanadium (4+) StretfordTM aqueous solution is dark-blue to grey (Hileman, O.E., (2003)). Solution 1 was light orange while Solution 4 was deep orange. The deep orange

colour in Solution 4 could indicate high concentration of V^{5+} in the Stretford™ aqueous solution as compared to Solutions 1, 2, and 3.



Figure 4.1: Stretford™ aqueous solutions physical appearance at different V^{5+} concentrations

Note: S-1 (Solution 1); S-2 (Solution 2); S-3 (Solution 3); S-4 (Solution 4)

Table 4.1 shows actual concentrations and pH values of Stretford™ aqueous solutions that were used to determine the effect of V^{5+} concentration on H_2S absorption and elemental sulphur product quality. The concentrations of total vanadium were varied from 0.02 to 0.096 mol.dm⁻³. The concentrations of V^{5+} were varied from 0.02 to 0.096 mol.dm⁻³. The difference between total vanadium and V^{5+} concentrations in Solutions 1, 2, 3, and 4 was negligible which confirmed what was observed in Figure 4.1 that the orange colour indicates solutions with vanadium species at their highest oxidation state (5+).

Table 4.1: Stretford™ aqueous solutions chemical results at different V^{5+} concentration

Solutions	mol.dm ⁻³							pH
	V^{Total}	V^{5+}	V^{4+}	$Na_2[ADA]$	Na_2SO_4	$NaSCN$	TA	
S-1	0.020	0.020	0.0	0.001	0.47	0.89	0.17	8.32
S-2	0.029	0.029	0.0	0.001	0.49	0.88	0.16	8.30
S-3	0.047	0.046	0.0	0.001	0.50	0.84	0.17	8.28
S-4	0.096	0.096	0.0	0.001	0.50	0.88	0.16	8.31

Figure 4.2 shows the chemical shifts of the V^{5+} compounds that were present in Stretford™ aqueous Solution 2. Only ^{51}V NMR result for Solution 2 was selected as the best V^{5+} concentration (0.029 mol.dm⁻³) to conduct further experiments. There were four chemical shifts resonances at -565.6, -577.5, 570.4, and -588.4 ppm. The resonances at -565.6, -577.5, -570.4, and -588.4 ppm are associated with the dimer ($V_2O_7^{4-}$), cyclic tetramer ($V_4O_{12}^{4-}$), pentamer ($V_5O_{15}^{5-}$), and hexamer

($V_6O_{17}^{4-}$) species, (Vermaire, S., et al (1988), Petterson, L., et al., (1983)). The dimer, pentamer, cyclic tetramer and hexamer heights were 3407, 1943, 2608 and 2. The dimer had a biggest peak followed by the tetramer and pentamer respectively. The V^{5+} species identified by the ^{51}V NMR analysis are in agreement with what other authors found previously, (Vermaire, S., et al., (1988)). The details of the ^{51}V NMR spectra are given in Appendix C.

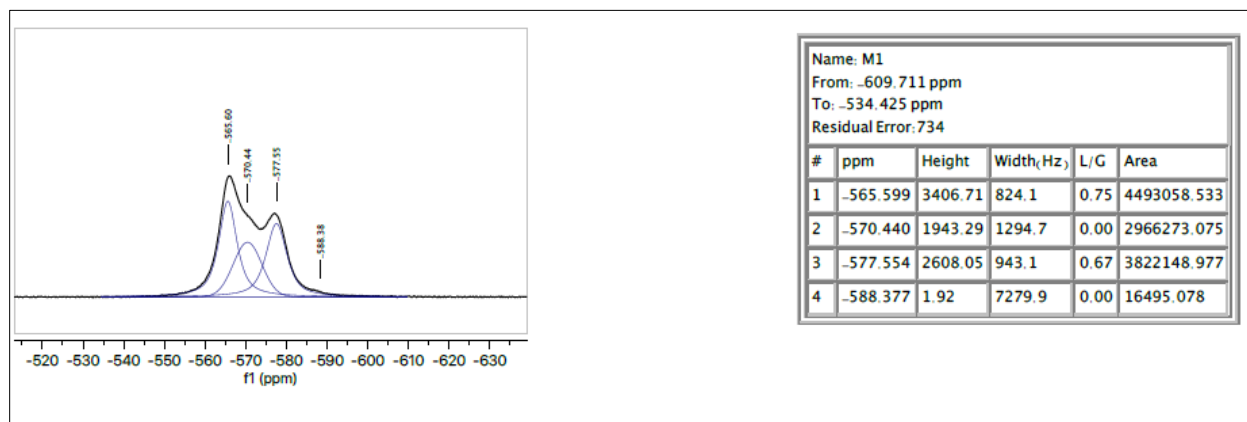


Figure 4.2: Solution 2 vanadium (5+) species chemical shifts

4.2.2 Best V^{5+} concentration without impurities

Figure 4.3 shows the StretfordTM aqueous solution at V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$ without impurities added (Na_2SO_4 and $NaSCN$). The sample was orange in colour similar to the colour of synthetic StretfordTM aqueous solution at V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$ with impurities added. The absence of the impurities did not affect the colour of the StretfordTM aqueous solution. The average concentrations of total alkalinity, V^{5+} and $Na_2[ADA]$ were 0.17, 0.029 and $0.001 \text{ mol.dm}^{-3}$ which were similar to the concentrations with impurities. The average pH value was 8.47, which was higher by 1.7 compared to the pH of StretfordTM aqueous solution with impurities at V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$. The pH values of Na_2SO_4 and $NaSCN$ in de-ionized water were measured and found to be at 7.4 and 8.1 respectively at 40°C . StretfordTM aqueous solution without impurities was high which can explain the cause of higher average pH value.



Figure 4.3: Synthetic Stretford™ aqueous solution without impurities (Na_2SO_4 and NaSCN)

4.2.3 V^{5+} to V^{4+} molar ratios without $\text{Na}_2[\text{ADA}]$

Figure 4.4 shows the physical appearance of the synthetic Stretford™ aqueous solutions at the different V^{5+} to V^{4+} molar ratios without $\text{Na}_2[\text{ADA}]$. These experiments were not part of the initial plan. However, due to the fact that V^{4+} oxidized to V^{5+} on experiments with $\text{Na}_2[\text{ADA}]$ and produced good quality elemental sulphur against expectation these experiments had to be done. The results of the effect of vanadium oxidation states on H_2S conversion to elemental sulphur with $\text{Na}_2[\text{ADA}]$ are given in Appendix D. Solution 5 shows a light yellow colour sample which is contrary to Solution 2 discussed in Section 4.2.1 which was orange in colour. The samples in Solutions 2 and 5 had similar chemical parameters except Solution 2 contained $\text{Na}_2[\text{ADA}]$ while Solution 5 did not. This means that $\text{Na}_2[\text{ADA}]$ is responsible for the deep orange colour. Solutions 6, 7 and 8 were light orange to blue, dark and mild blue. The change in colour as the V^{5+} to V^{4+} molar ratios reduced was an indication of different vanadium oxidation states.

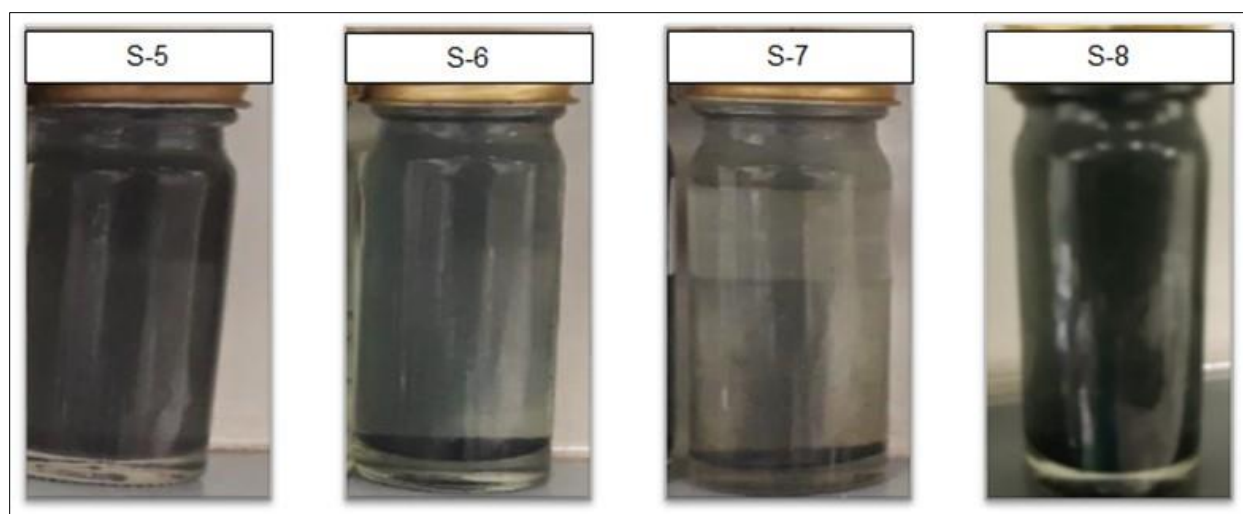


Figure 4.4: Solutions at different V^{5+} to V^{4+} molar ratios in the absence of $Na_2[ADA]$

Table 4.2 shows the chemical analyses of Stretford™ aqueous solutions without $Na_2[ADA]$ added. The total vanadium concentration used while changing the molar ratios of V^{5+} to V^{4+} was $0.029 \text{ mol.dm}^{-3}$. The concentrations of total vanadium shows stability similarly to the concentration of total vanadium in Solution 2 given in Section 4.2.1. The concentrations of V^{5+} was going down which confirms the addition of V^{4+} species in the Stretford™ aqueous solutions.

Table 4.2: Stretford™ aqueous solutions' parameters in the absence of $Na_2[ADA]$

Solutions	mol.dm ⁻³							pH
	V^{Total}	V^{5+}	V^{4+}	$Na_2[ADA]$	Na_2SO_4	$NaSCN$	TA	
S-5	0.029	0.027	0.001	0.00	0.49	0.86	0.16	8.32
S-6	0.029	0.022	0.006	0.00	0.49	0.86	0.17	8.28
S-7	0.028	0.016	0.011	0.00	0.49	0.87	0.16	8.32
S-8	0.028	0.001	0.027	0.00	0.50	0.86	0.17	8.34

Table 4.3 gives the V^{5+} species chemical shifts and the heights for Solutions 5, 6, 7 and 8. The same V^{5+} species (dimer, pentamer, tetramer, and hexamer) identified in Solutions 2 were also identified in Solutions 5, 6, 7, and 8. The dimer, pentamer, and tetramer had peaks at -566, -570, and -575 ppm in Solution 5. In Solutions 6, 7, and 8 the dimer, pentamer and tetramer had almost similar chemical shifts like in Solution 2 and 5. There was hexamer peak in Solutions 6 and 7 at -587 ppm respectively, which did not appear in Solutions 5. In Solution 8, there were resonances of the dimer and tetramer at -566 and -576 ppm. As the V^{5+} to V^{4+} molar ratios reduces the heights of the dimer and pentamer also reduces. The estimated drop of V^{5+} heights were in agreement with drop of V^{5+} concentrations shown in Table 4.2. The details of the ^{51}V NMR spectra are given in Appendix C.

Table 4.3: V^{5+} species at variable V^{5+} to V^{4+} molar ratios in the absence of $Na_2[ADA]$

Solutions	Resonance	V^{5+} species			
		$V_2O_7^{4-}$	$V_4O_{13}^{5-}$	$V_4O_{12}^{4-}$	$V_6O_{17}^{4-}$
S-5	Peak (ppm)	-566	-570	-575	-
	Height	864	183	479	-
S-6	Peak (ppm)	-564	-569	-579	-587
	Height	797	550	470	49.2
S-7	Peak (ppm)	-565	-570	-579	-587
	Height	559	382	197	8.1
S-8	Peak (ppm)	-566	-	-576	-
	Height	202	-	141	-

4.3 Experiments repeatability

Tables 4.4 to 4.14 shows the mean, standard deviations (Std dev) and standard error of the mean (SEM) for the H_2S absorption, elemental sulphur production, PSDs, DSCs and gravimetric results. The DSC curves are given in Appendix E. A minimum of four experiments were conducted with similar conditions to ensure repeatability and enough elemental sulphur analyses. Overall, the SEM was low for all the experiments, which indicated low variation of the results. The SEM was calculated using Equation 4.1.

$$SEM = Std\ dev \div \sqrt{n} \quad 4.1$$

Note: n is the number of runs.

The elemental sulphur results by XRD and gravimetric were done in duplicate. One experiment produced approximately 18 g of elemental sulphur on average. The elemental sulphur produced from two runs with similar operating conditions were mixed to make one sample for XRD and gravimetric analyses. The concentrations of total vanadium, total alkalinity, $NaSCN$, Na_2SO_4 and V^{5+} were determined for each run. The average of each of these concentrations were taken. The pH values of each solution was measured continuously during experiment but the initial and final pH values were reported. The elemental sulphur produced commercially at different conditions were used as a reference. The aim was to check if elemental sulphur produced in this study was different to purified and unpurified elemental sulphur.

Table 4.4: H₂S absorption at different V⁵⁺ concentrations

Solutions (%)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
S-1 (0.019)	99.1	99.4	99.1	99.3	99.2	0.15	0.08
S-2 (0.029)	99.8	99.7	99.6	99.8	99.7	0.10	0.05
S-3 (0.042)	99.8	99.8	99.7	99.7	99.8	0.06	0.03
S-4 (0.096)	99.8	99.8	99.7	99.8	99.8	0.05	0.02

Table 4.5: Elemental sulphur production at different V⁵⁺ concentrations

Solutions (mol)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
S-1 (0.019)	0.849	0.868	0.860	0.860	0.859	0.008	0.004
S-2 (0.029)	0.861	0.858	0.865	0.860	0.861	0.003	0.001
S-3 (0.042)	0.869	0.849	0.870	0.860	0.862	0.010	0.005
S-4 (0.096)	0.859	0.869	0.860	0.860	0.862	0.005	0.002

Table 4.6: H₂S absorption at different V⁵⁺ to V⁴⁺ molar ratios

Solutions (%)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
S-5	81.8	82.5	82.3	82.4	82.3	0.311	0.155
S-6	68.6	68.4	68.6	68.1	68.4	0.236	0.118
S-7	54.1	53.8	54.9	54.3	54.3	0.465	0.232
S-8	3.93	4.35	3.96	4.15	4.10	0.194	0.097

Table 4.7: Elemental sulphur production at different V⁵⁺ to V⁴⁺ molar ratios

Solutions (mol)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
S-5	0.650	0.692	0.690	0.648	0.670	0.024	0.012
S-6	0.550	0.570	0.560	0.562	0.561	0.008	0.004
S-7	0.392	0.399	0.380	0.398	0.392	0.009	0.004
S-8	0.031	0.034	0.023	0.040	0.032	0.007	0.004

Table 4.8: Solutions 1 and 2 elemental sulphur PSD values

Size (µm)	Solution 1 (%)							Solution 2 (%)						
	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
704	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
498	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
352	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
249	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
176	97	98	98	98	98	0.5	0.2	96	100	96	99	98	2.1	1.0
125	85	93	86	92	89	4	2	89	93	90	92	91	1.8	0.9
88	72	76	72	76	74	2.4	1.2	77	80	77	80	78	2.1	1.1
62	56	60	56	60	58	2.1	1.0	59	63	60	63	61	2.1	1.0
44	43	47	43	47	45	2.3	1.2	42	45	42	45	43	1.8	0.9
31	33	35	33	36	34	1.7	0.8	26	28	26	28	27	1.6	0.8
22	22	25	21	25	23	2.1	1.0	13	16	13	17	15	2.0	1.0
16	13	15	12	16	14	1.9	0.9	6	9	6	9	8	1.7	0.8
11	6	7	5	7	6	0.9	0.5	2	4	2	4	3	1.0	0.5
7.8	2	3	3	3	3	0.3	0.1	0.3	2.5	0.6	2.2	1.4	1.1	0.6
5.5	1	2	1	2	2	0.3	0.1	0.4	0.8	0.3	0.9	0.6	0.3	0.1
3.9	0.8	1.4	0.9	1.3	1.1	0.29	0.15	0.2	0.3	0.2	0.3	0.3	0.02	0.01
2.8	0.4	1.0	0.5	0.9	0.7	0.29	0.15	0.0	0.0	0.0	0.0	0.0	0.00	0.00
1.945	0.2	0.4	0.1	0.5	0.3	0.18	0.09	0.0	0.0	0.0	0.0	0.0	0.00	0.00
1.375	0.0	0.1	0.0	0.1	0.1	0.03	0.01	0.0	0.0	0.0	0.0	0.0	0.00	0.00
0.972	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.00	0.00

Table 4.9: Solutions 3 and 4 elemental sulphur PSD values

Size (µm)	Solution 3 (%)							Solution 4 (%)						
	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
704	100	100	100	100	100	0.0	0.0	93	94	92	94	98	6.4	3.2
498	100	100	100	100	100	0.0	0.0	92	98	91	99	95	4.1	2.0
352	100	100	100	100	100	0.0	0.0	88	95	87	95	91	4.4	2.2
249	100	100	100	100	100	0.0	0.0	82	90	83	89	86	4.1	2.0
176	96	100	97	99	98	1.8	0.9	78	84	79	84	81	3.1	1.6
125	88	91	88	92	90	2.0	1.0	73	80	74	79	76	3.6	1.8
88	75	79	76	79	77	1.9	1.0	69	74	68	75	71	3.5	1.8
62	62	66	62	66	64	2.5	1.2	63	69	64	69	66	3.3	1.6
44	52	54	51	55	53	1.9	0.9	58	64	59	63	61	2.9	1.5
31	41	45	39	47	43	3.7	1.8	52	55	51	56	53	2.4	1.2
22	31	36	30	36	33	3.1	1.6	42	46	42	47	44	2.5	1.2
16	22	26	21	27	24	2.7	1.4	33	37	32	38	35	3.0	1.5
11	13	16	12	17	15	2.4	1.2	23	27	23	27	25	2.6	1.3
7.8	7.3	10.3	6.8	10.8	8.8	2.0	1.0	15	19	15	19	17	2.4	1.2
5.5	4.4	7.0	4.0	7.4	5.7	1.7	0.9	8	14	9	13	11	2.9	1.5
3.9	3.1	5.3	3.3	5.1	4.2	1.2	0.6	5.5	9.3	5.2	9.6	7.4	2.4	1.2
2.8	2.1	4.3	2.3	4.1	3.2	1.2	0.6	3.1	6.9	2.7	7.3	5.0	2.4	1.2
1.945	1.6	3.2	1.5	3.3	2.4	1.0	0.5	1.6	5.2	1.9	4.9	3.4	1.9	1.0
1.375	1.3	2.3	1.1	2.5	1.8	0.7	0.4	1.4	3.8	1.1	4.1	2.6	1.6	0.8
0.972	1.0	1.8	0.8	2.0	1.4	0.6	0.3	1.1	3.1	1.2	3.0	2.1	1.1	0.5

Table 4.10: Solutions X and 5 elemental sulphur PSD values

Size (µm)	S-X (%)							Solution 5 (%)						
	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
704	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
498	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
352	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
249	99	100	99	100	99	0.2	0.1	99	100	99	100	99	0.2	0.1
176	94	96	94	96	95	0.9	0.4	92	98	93	98	95	3.1	1.6
125	85	85	84	85	85	0.37	0.18	82	88	82	87	85	3.4	1.7
88	68	69	68	69	68	0.18	0.09	66	71	65	72	68	3.6	1.8
62	48	52	48	52	50	2.60	1.30	47	53	47	52	50	3.3	1.6
44	30	36	31	35	33	2.78	1.39	30	36	31	35	33	2.8	1.4
31	18	21	17	22	20	2.19	1.09	18	22	17	22	20	2.4	1.2
22	9	12	8	13	11	2.32	1.16	9	13	9	13	11	2.5	1.2
16	3.5	8.3	2.8	9.0	5.9	3.20	1.60	3.8	8.0	2.9	8.9	5.9	3.0	1.5
11	0.8	5.0	0.9	4.9	2.9	2.37	1.18	0.5	5.3	1.1	4.7	2.9	2.4	1.2
7.8	0.4	3.6	0.2	3.2	1.9	1.80	0.90	0.4	3.0	0.5	2.9	1.7	1.4	0.7
5.5	0.5	1.7	0.4	1.8	1.1	0.75	0.38	0.4	1.8	0.4	1.8	1.1	0.8	0.4
3.9	0.6	1.0	0.4	1.2	0.8	0.37	0.18	0.6	1.0	0.4	1.2	0.8	0.4	0.2
2.8	0.4	0.6	0.2	32.5	8.4	16.05	8.03	0.2	0.8	0.3	0.7	0.5	0.3	0.1
1.945	0.2	0.3	0.1	0.3	0.2	0.10	0.05	0.2	0.3	0.1	0.4	0.2	0.1	0.1
1.375	0.1	0.1	0.0	0.1	0.1	0.02	0.01	0.1	0.1	0.0	0.1	0.1	0.0	0.0
0.972	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 4.11: Solutions 6 and 7 elemental sulphur PSD values

Size (µm)	Solution 6 (%)							Solution 7 (%)						
	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev (±)	SEM (±)
704	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
498	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
352	100	100	100	100	100	0.0	0.0	100	100	100	100	100	0.0	0.0
249	100	100	100	100	100	0.2	0.1	100	100	100	100	100	0.0	0.0
176	94	100	95	99	97	2.9	1.5	98	99	98	99	99	0.9	0.4
125	85	92	86	91	89	3.3	1.6	93	93	92	93	93	0.4	0.2
88	71	76	70	77	73	3.4	1.7	81	81	81	81	81	0.2	0.1
62	51	57	52	57	54	3.3	1.6	63	68	63	68	65	2.6	1.3
44	33	39	34	38	36	2.9	1.5	46	51	46	50	48	2.8	1.4
31	19	22	18	23	20	2.1	1.1	30	33	29	34	31	2.2	1.1
22	9	12	8	13	11	2.3	1.2	16	19	15	20	18	2.3	1.2
16	4	8	3	9	6	2.9	1.5	6	11	6	12	9	3.2	1.6
11	0.8	5.0	0.9	4.9	2.9	2.4	1.2	1.4	5.6	1.5	5.5	3.5	2.4	1.2
7.8	0.6	3.8	0.4	3.4	2.0	1.8	0.9	0.5	3.7	0.3	3.3	1.9	1.8	0.9
5.5	0.7	1.9	0.6	2.0	1.3	0.8	0.4	0.5	1.7	0.4	1.8	1.1	0.8	0.4
3.9	0.7	1.1	0.5	1.3	0.9	0.4	0.2	0.6	1.0	0.4	1.2	0.8	0.4	0.2
2.8	0.5	0.7	0.4	0.8	0.6	0.2	0.1	0.4	0.6	0.3	0.7	0.5	0.2	0.1
1.945	0.2	0.4	0.2	0.4	0.3	0.1	0.0	0.2	0.4	0.2	0.4	0.3	0.1	0.0
1.375	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.3	0.3	0.3	0.3	0.3	0.01	0.01
0.972	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.3	0.3	0.4	0.3	0.04	0.02

Table 4.12: DSC results at different V^{5+} concentrations

Solutions ($^{\circ}C$)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev ($\pm$)	SEM ($\pm$)
S-1	122.4	122.2	121.8	122.2	122.1	0.26	0.13
S-2	122.3	122.2	123.0	120.7	122.1	0.97	0.49
S-3	122.8	122.3	122.9	122.6	122.7	0.27	0.13
S-4	122.9	123.9	122.5	122.7	123.0	0.60	0.30

Table 4.13: DSC results at V^{5+} to V^{4+} molar ratios and V^{5+} concentrations without impurities added

Solutions ($^{\circ}C$)	Run 1	Run 2	Run 3	Run 4	Mean	Std dev ($\pm$)	SEM ($\pm$)
S-5	124.4	124.2	123.4	123.9	124.0	0.43	0.21
S-6	123.8	124.1	122.9	123.2	123.5	0.56	0.28
S-7	122.3	122.3	121.8	122.0	122.1	0.24	0.12
S-8	121.5	121.8	121.7	121.6	121.6	0.13	0.06
S-X	121.4	121.3	121.5	121.1	121.3	0.17	0.09

Table 4.14: Gravimetric results at different V^{5+} concentrations

Solutions	Composition (%)	Run 1	Run 2	Mean	Std dev ($\pm$)	SEM ($\pm$)
S-1	S	96.4	96.6	96.5	0.141	0.10
	Ash	3.3	3.7	3.5	0.283	0.20
S-2	S	93.1	93.9	93.5	0.566	0.40
	Ash	6.6	6.4	6.5	0.141	0.10
S-3	S	93.3	87.1	90.2	4.384	3.10
	Ash	10.5	10.1	10.3	0.283	0.20
S-4	S	87.4	80	83.7	5.233	3.70
	Ash	15.9	16.6	16.25	0.495	0.35

4.4 Effect of V^{5+} concentrations on H_2S absorption to elemental sulphur

4.4.1 StretfordTM circulation solution

Figure 4.5 shows the physical appearance of StretfordTM circulation solutions after the experiments at variable V^{5+} concentrations with other parameters fixed. The StretfordTM circulation solutions still showed an orange colour after the experiments. The colour of all the StretfordTM circulation solutions indicated vanadium at its highest oxidation state similar to synthetic StretfordTM aqueous solutions discussed in Section 4.2.1.



Figure 4.5: StretfordTM circulation solutions appearance at different V^{5+} concentrations

Note: S-1: $0.019 \text{ mol.dm}^{-3} V^{5+}$, S-2: $0.029 \text{ mol.dm}^{-3} V^{5+}$, S-3: $0.042 \text{ mol.dm}^{-3} V^{5+}$, S-4: $0.069 \text{ mol.dm}^{-3} V^{5+}$

4.4.2 Chemicals results of Stretford™ circulation solutions

Table 4.15 gives the fixed results of the Stretford™ circulation Solutions 1, 2, 3, and 4 at variable total vanadium and V^{5+} concentrations. The concentrations of $Na_2[ADA]$, $NaSCN$, Na_2SO_4 , and total alkalinity after experiments were almost similar to the concentrations before the experiments as discussed in Section 4.2.1. The changes in pH values for all four solutions were negligible. The concentrations of total vanadium and V^{5+} are graphically shown in Figure 4.6.

Table 4.15: Stretford™ circulation solutions results at different V^{5+} concentrations

Solutions	mol.dm ⁻³					pH
	$Na_2[ADA]$	$NaSCN$	Na_2SO_4	TA	V^{4+}	
S-1	0.001	0.89	0.49	0.17	0.001	8.33
S-2	0.001	0.86	0.49	0.16	0.001	8.34
S-3	0.001	0.88	0.50	0.17	0.001	8.32
S-4	0.001	0.86	0.48	0.17	0.001	8.31

The concentrations of total vanadium in Solutions 1, 2, 3 and 4 were 0.02, 0.029, 0.047, and 0.096 mol.dm⁻³ and the concentrations of V^{5+} were 0.019, 0.029, 0.047, and 0.096 mol.dm⁻³. The concentrations of total vanadium and V^{5+} in the Stretford™ circulation Solutions 1, 2, 3, and 4 were comparable to the concentrations of the synthetic Stretford™ circulation solutions discussed in Section 4.2.1. The ^{51}V NMR analysis for the Solution 2 shows the V^{5+} species was still the dimer, tetramer, pentamer, and hexamer. The concentrations of total vanadium and V^{5+} showed stability in all Stretford™ circulation solutions.

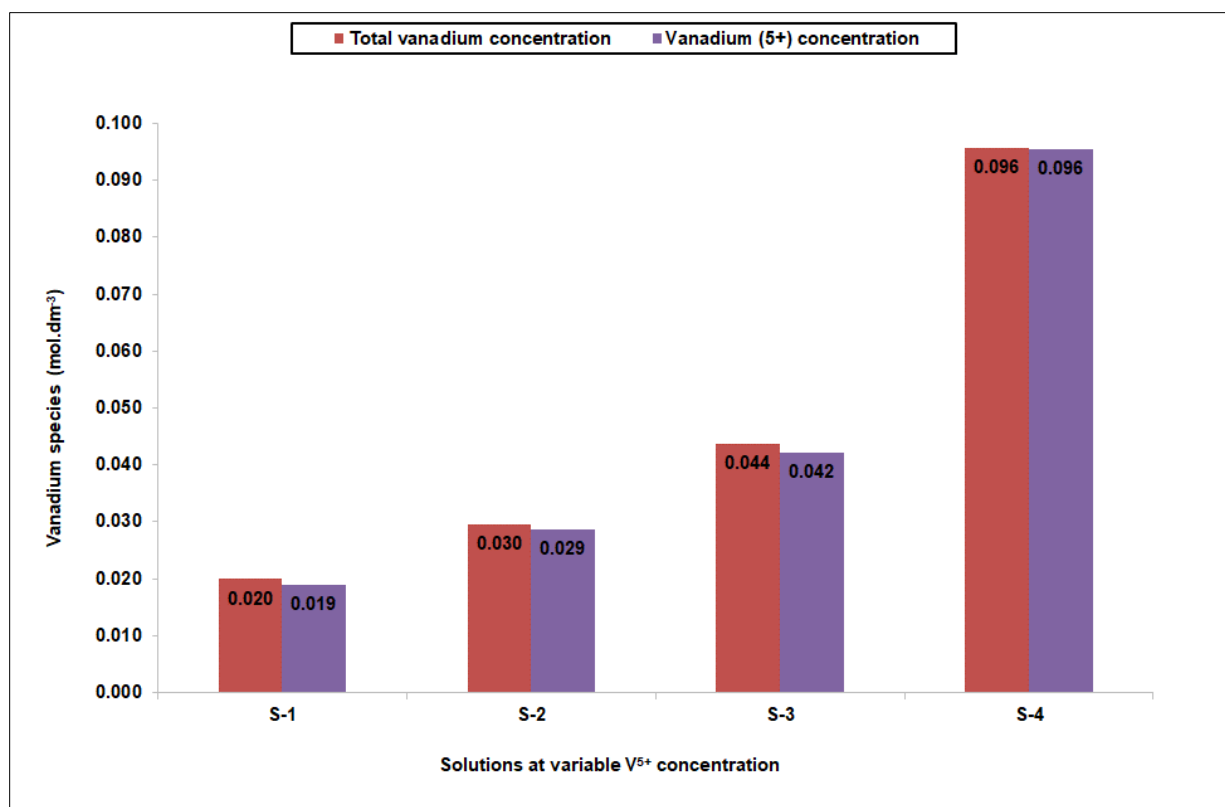


Figure 4.6: Stretford™ circulation solutions total vanadium and V⁵⁺ concentrations

4.4.3 H₂S absorption and elemental sulphur production

Figure 4.7 shows the effect of V⁵⁺ concentrations on H₂S gas absorption and elemental sulphur production. The H₂S absorption efficiency was 99.2, 99.7, 99.8, and 99.8% in Solutions 1, 2, 3 and 4 respectively. Example of how H₂S absorption was calculated is given in Appendix B. The elemental sulphur produced in Solutions 1, 2, 3, and 4 were 0.859, 0.861, 0.862, and 0.862 mol. The H₂S absorption was within similar range in all solutions. The elemental sulphur production was slightly low in Solution 1 compared to Solutions 2, 3 and 4. The H₂S absorption and dissociation is dependent on the pH value of the Stretford™ aqueous solution as discussed in Section 2.3 (Rice, E.W., et al., (2012), Carter, C.N., (1966)). The pH was constant in this study. However, the slight drop in elemental sulphur production was a confirmation of role of V⁵⁺ during H₂S absorption and HS⁻ conversion to elemental sulphur as discussed in Section 2.2.1 (Fenton, D.M., et al., (1979), Keene, D.E., (1992)). The V⁵⁺ to HS⁻ stoichiometric molar ratios were 4.8, 7.3, 10.7, and 24.1 for Solutions 1, 2, 4, and 5 respectively. There was sufficient concentration of V⁵⁺ to oxidize HS⁻ concentrations in all solutions. The detail stoichiometric calculations results are displayed in Appendix F.

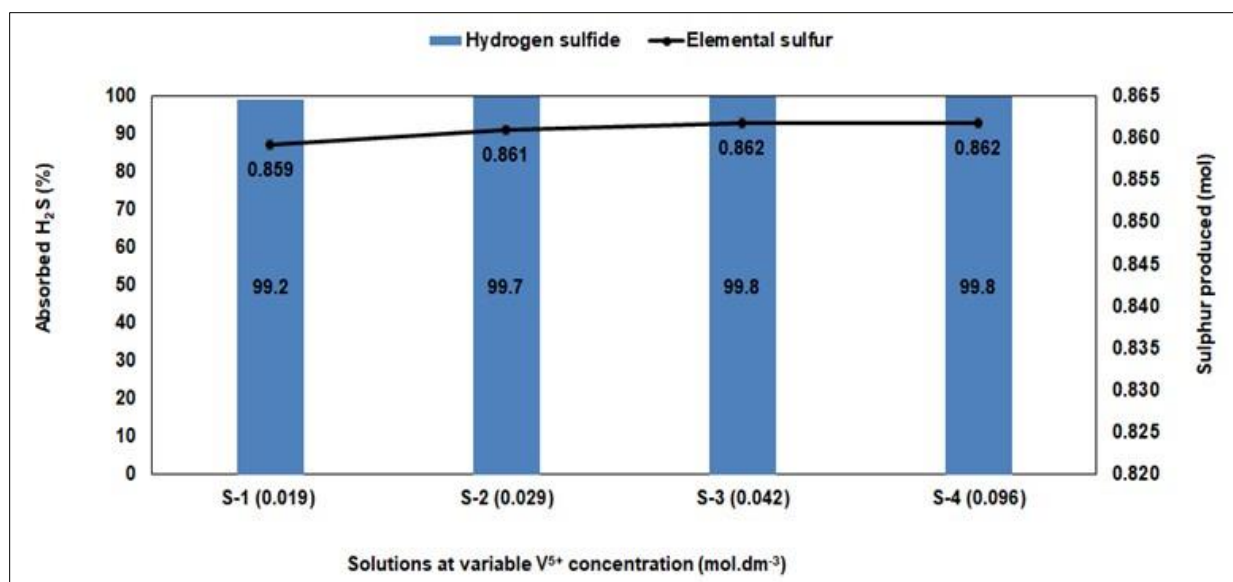


Figure 4.7: H₂S absorption and elemental sulphur produced at variable V⁵⁺ concentration

4.4.4 Elemental sulphur physical appearance

Figure 4.8 shows elemental sulphur physical appearance produced in Solutions 1, 2, 3, and 4. The numbers in brackets (e.g. 0.019) on the below figure will be used throughout in this chapter and will be representing concentrations of V⁵⁺ in mol.dm⁻³ unless stated otherwise. Elemental sulphur produced in Solutions 1 and 2 was yellowish while elemental sulphur produced in Solutions 3 and 4 was greyish. The colour difference is determined by level of impurities in the final product as reported in Section 2.13 not an indication of amorphous sulphur (Steudel, R., et al., (1988)). The causes of elemental sulphur colour differences were not discussed in details because it was out of scope of this study.

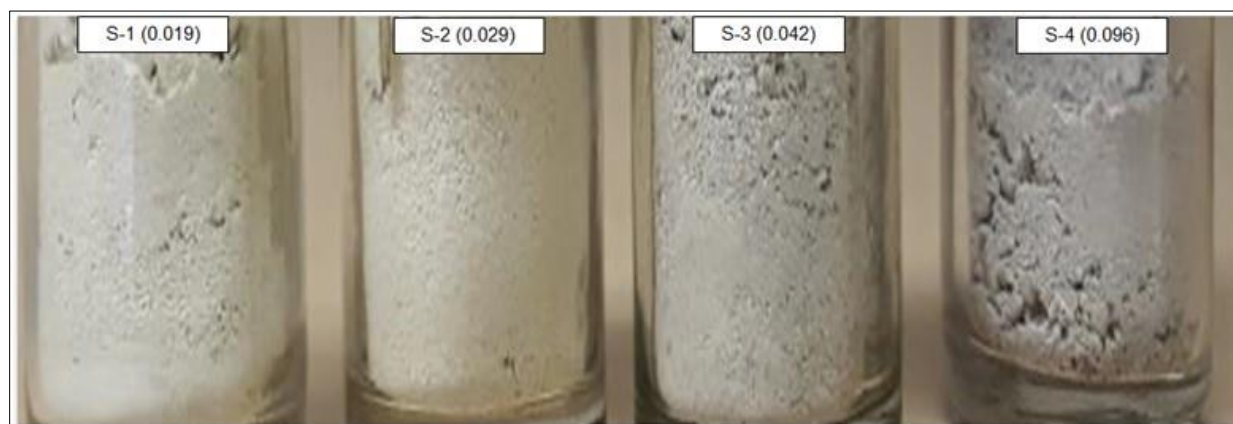


Figure 4.8: Elemental sulphur appearance at variable V⁵⁺ concentrations

Figure 4.9 shows elemental sulphur in the oxidizing tank in Solutions 1 and 4 during experiments. The oxidizing tank in Solution 1 shows a yellowish elemental sulphur while Solution 4 shows

greyish elemental sulphur, which was foaming. The excess V^{5+} concentration and impurities caused foaming in Solution 4. Foaming is the physical or chemical changes of substances when the reactions occurred after bubbling air through the Stretford™ aqueous solutions. The formed small bubbles with gases and air will subsequently be foamed and gases emitted. During the addition of SAV and air to the simulated Stretford™ aqueous solution containing hydrogen peroxide, hydroxides, sodium carbonate and SAV could release carbon dioxide and ammonia as indicated by S-4 in Figure 4.5 at V^{5+} concentration of $0.096 \text{ mol.dm}^{-3}$. Foaming in Stretford™ process can be caused by surfactants due to high bacteria or from organics in feed gas (Steudel, R., et al (1996), Garcia, A.A., et al., (2014)). However, in this study foaming was caused by excess amount of commercial/technical SAV with impurities, as it was the only changing variable. The foaming was observed visually during the experiment. The ICP-OES results of the sulphur foaming products contained similar impurities found in SAV.

The elemental sulphur also stuck on the wall of the reaction, oxidizing, and balance tanks in Solution 4. The cause was due to other impurities in SAV and excess vanadium. The V^{5+} to HS^- stoichiometry molar ratio was 24 for the Solution 4 and 4.8 for the solution 1. This means that Solution 4 contained high proportion of the impurities than that of Solution 1. This explains the foaming and elemental sulphur stuck on the side of the walls of the oxidizing and balance tanks caused by impurities in SAV. The elemental sulphur that stuck on the wall was finer and blocked the filter papers.

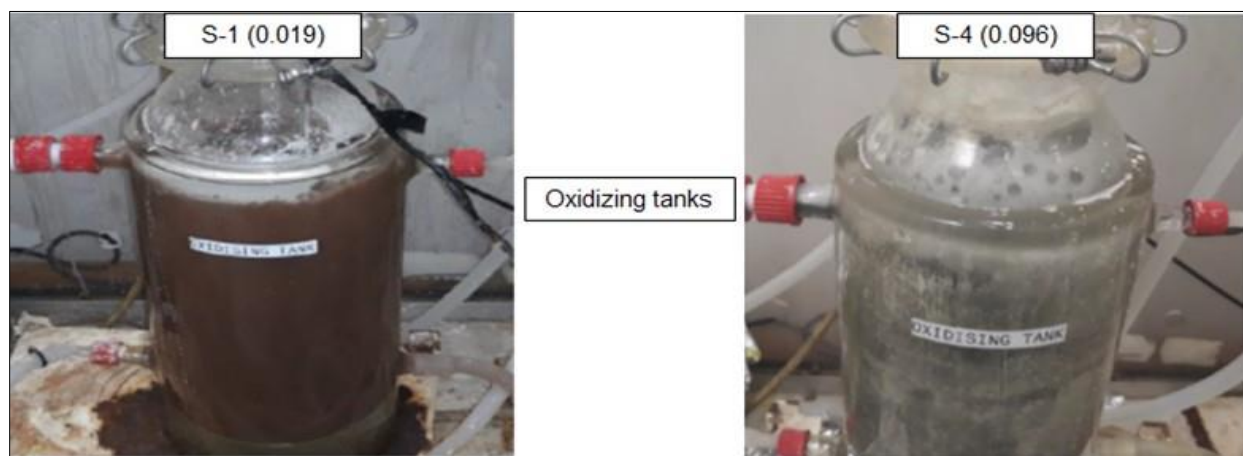


Figure 4.9: Elemental sulphur forming at higher V^{5+} concentrations

Note: S-1 on the left (Non-foaming) and S-4 on the right (Foaming)

4.4.5 PSD curves at variable V^{5+} concentration

Figure 4.10 display the particles sizes of the elemental sulphur produced in Solutions 1, 2, 3 and 4. The results shows as the concentrations of V^{5+} increased the elemental sulphur particles sizes shifted to the left. The elemental sulphur PSDs shift to the left was to the finer side. There was high elemental sulphur production in Solutions 3 and 4 but with fine elemental sulphur particles. The elemental sulphur PSDs shifted to the finer part was an indication that the excess impurities in SAV interfered with nucleation and Ostwald ripening processes. To form a big elemental sulphur crystal a rapid growth is required as discussed in Chapter 2 (Steudel, R., et al., (1996)). The rate of hydrophobic colloidal sulphur precipitation and crystallization should be greater than the rate of conversion of HS^- to hydrophilic polysulphide by V^{5+} to prevent delay in nucleation process (Trofe, T. W., et al., (1986), (Steudel, R., et al., (1996))). The source of impurities like Na, K, Si, Mg, Fe, and Al were from SAV. The elemental sulphur produced in Solutions 1 and 2 was yellowish while elemental sulphur produced in Solutions 3 and 4 was greyish.

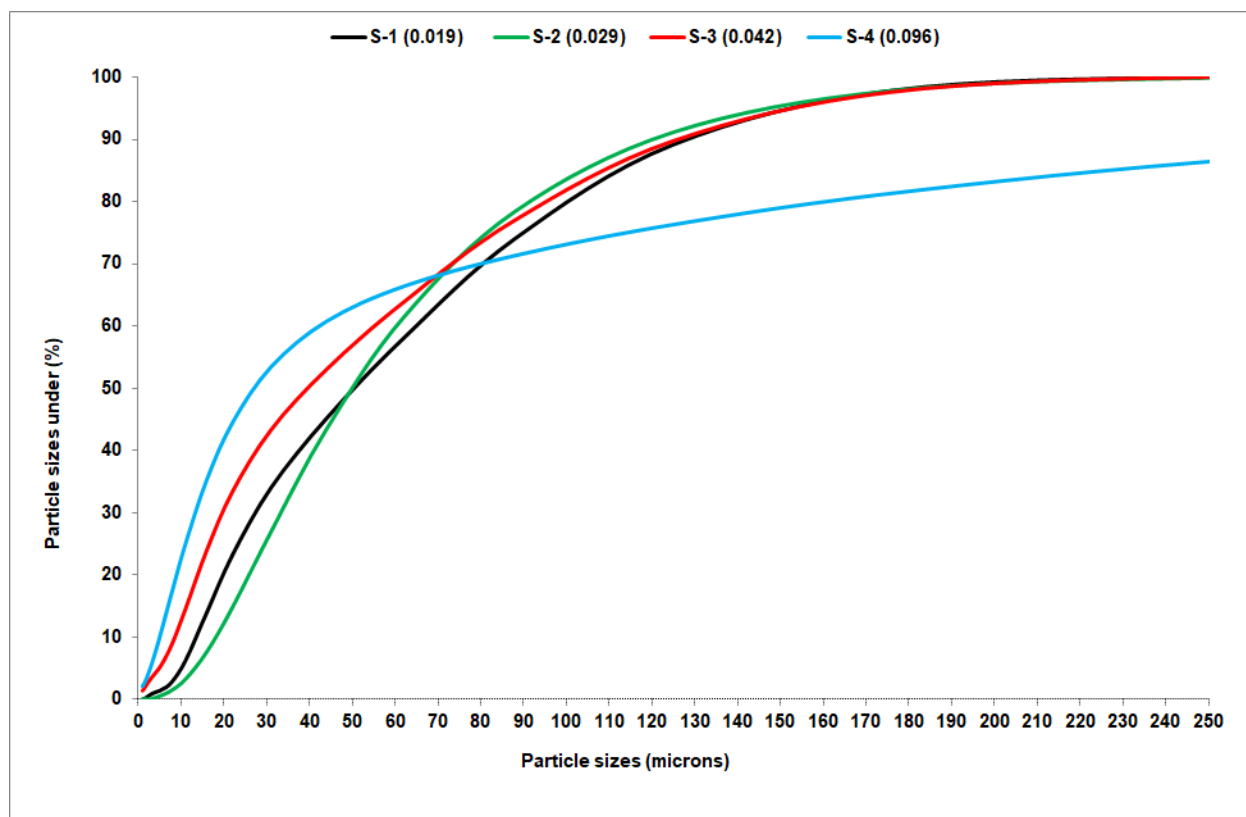


Figure 4.10: PSD curves of elemental sulphur produced product at different V^{5+} concentrations using SAV

4.4.6 DSC results at variable V⁵⁺ concentration

Table 4.16 show the DSC results for elemental sulphur produced in Solutions 1, 2, 3, and 4. Solutions 1, 2, 3, and 4 had peaks at 111.2, 111.6, 110.1, and 112°C. These peaks are associated with transitions from orthorhombic (α -S₈) to monoclinic (β -S₈) elemental sulphur, (Ralf Steudel, et al., (2003)). The second peaks for the same solutions in a similar sequence were at 122.4, 122, 122.4, and 122.8°C. The DSC curves are given in Appendix E.

Table 4.16: DSC results for elemental sulphur produced at variable V⁵⁺ concentrations

Transition temperature(°C)	S-1 (0.019)	S-2 (0.029)	S-3 (0.042)	S-4 (0.096)
α -S ₈ → β -S ₈	111.2	111.6	110.1	112.0
Melting point	122.4	122.0	122.4	122.8
Polymerization	164.7	175.0	174.0	171.9

The second peaks are the melting points of elemental sulphur. Literature has reported elemental sulphur (α -S₈) to melt at temperature between 116 and 120.6°C (Meyer, B., (1976)). The melting point temperatures in Table 4.16 are in agreement with literature melting points of between 116 and 120.6°C. The melting of the elemental sulphur products at 164.7, 175, 174 and 171.9°C could be associated with the transition from monoclinic to polymerization type of elemental sulphur (S_∞) or impurities contained in these products (Steudel, R., et al., (2003)). Polymerization of the elemental sulphur could start at temperature above 159°C as discussed in Section 2.13.2 and ends at temperatures around 170°C (Jansen, D., et al., (1973)). The results in Table 4.16 shows consistency with literature in terms of transition from orthorhombic to monoclinic, melting to polymerization points.

Literature reported elemental sulphur melting and polymerization points to be delayed by impurities, external pressure and heating rates (Carson, C.M., et al., (1907), (Steudel, R., et al., (2003)). The pressure and heating rate were constant throughout the experiments. The transition temperatures show orthorhombic elemental sulphur (α -S₈) was produced in all solutions. As the concentrations of impurities in the sulphur products increased after the addition and dissolution of SAV into the simulated Stretford™ aqueous solution, the melt points of elemental sulphur products with impurities were increased. Based on the results, the impurities from SAV contained in the elemental sulphur products contribute positively to physical (melting points) and chemical properties of these products. This meant when elemental sulphur is contaminated more energy is required to melt it.

4.4.7 Elemental sulphur diffractograms at variable V^{5+} concentration

Figure 4.11 shows the diffractograms of elemental sulphur produced in Solutions 1, 2, 3, and 4. Elemental sulphur produced in all solutions was crystalline orthorhombic (α -S₈). As expected, the smaller elemental sulphur particle sizes (<0.972 μ m) and its colour at different V^{5+} concentrations did slightly affect the crystals of the elemental sulphur.

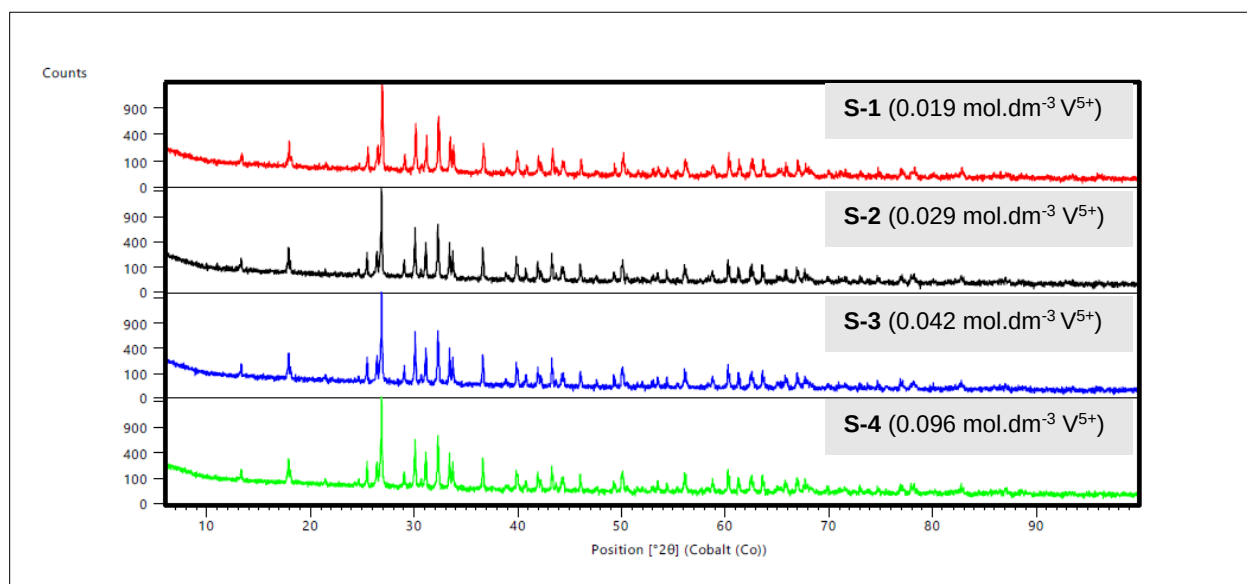


Figure 4.11: Diffractograms for elemental sulphur products at different V^{5+} concentrations

4.4.8 Elemental sulphur purity by gravimetric analysis

Table 4.17 shows the elemental sulphur purity results. The results indicate that elemental sulphur purity reduced as significant amount of the commercial SAV increased in the synthetic Stretford™ aqueous solutions. This confirms that the impurities in SAV and excess vanadium were the cause of a colour change and formation of finer elemental sulphur. The commercial SAV which was used as a source of V^{5+} contained high concentrations Na, K, V, Si, Mg, Fe, and Al as showed in Table 3.2 in Chapter 3. The composition of ash is given in Section 4.4.9 in Table 4.18.

Table 4.17: Purity results for elemental sulphur produced at variable V^{5+} concentrations

Composition (%)	S-1 (0.019)	S-2 (0.029)	S-3 (0.042)	S-4 (0.096)
α -S ₈	96.5	93.5	89.7	83.7
Ash	3.5	6.5	10.3	16.3

4.4.9 Ash results by ICP-OES

Table 4.18 outline the chemical composition of ash samples of the elemental sulphur products produced from the experiments. The ash contained a high proportion of sodium, potassium, vanadium, silicon, magnesium, iron, aluminum, chloride, and other elements in small proportions.

It is crucial to control the concentrations of vanadium at optimal to prevent contamination of the elemental sulphur by SAV impurities and vanadium compounds. The high proportion of sodium, potassium, vanadium, silicon, magnesium, iron, aluminum, and chloride was observed when the concentration of V^{5+} was increasing. This was a confirmation that the impurities in SAV and excess vanadium do affect the quality of elemental sulphur in terms of PSDs and physical appearance. There was a slight delay on the melting of elemental sulphur produced at higher concentration of V^{5+} . However, the impurities did not affect the elemental sulphur crystallinity.

Table 4.18: Ash results by ICP-OES for sulphur produced at variable V^{5+}

Elements (ppm)	S-1 (0.019)	S-2 (0.029)	S-3 (0.042)	S-4 (0.096)
Na	1100	21400	27727	29187
K	183	456	491	551
V	149	297	481	528
Si	52	261	272	292
Mg	12	131	236	270
Fe	40	73	93	105
Al	35	66	110	122
Cl	6	9	19	26
Ti	2.8	4.7	5.9	6.5
Cr	1.7	3.3	4.2	4.7
Ba	1.3	2.6	3.3	3.6
Cu	1.1	2.0	8.1	12.3
Sr	0.3	0.7	1.7	5.7
Ca	0.2	0.4	1.0	1.4

4.5 Effects of impurities (Na_2SO_4 and NaSCN) in a Stretford™ aqueous solution

4.5.1 Effect of impurities on appearance and vanadium redox reaction

Figure 4.12 shows the physical appearance of Stretford™ circulation solutions without impurities at V^{5+} concentration of $0.029 \text{ mol.dm}^{-3}$ in this study. The Stretford™ circulation Solution X without impurities shows vanadium was at its highest oxidation state similar to Solution 2. The result of Solution X was compared with the Solution 2 results discussed in Section 4.4. The concentrations of V^{5+} , total alkalinity and $Na_2[ADA]$ were 0.029 , 0.17 , and $0.001 \text{ mol.dm}^{-3}$ respectively. The concentrations were slightly similar to the concentrations in Solution 2. The chemical results were in support of the observation in Figure 4.12 on the vanadium concentration at its highest oxidation state. The pH values of the Stretford™ circulation solution was 8.46 , which was still higher by 1.6 after the experiments. The pH values of Na_2SO_4 and NaSCN were measured to be 7.4 and 8.1

respectively in de-ionized water. The absence of Na_2SO_4 and NaSCN caused pH of the Stretford™ aqueous solution to increase.



Figure 4.12: Stretford™ circulation solutions appearance with and without impurities at V^{5+} of $0.029 \text{ mol.dm}^{-3}$

4.5.2 Effect of impurities (Na_2SO_4 and NaSCN) on elemental sulphur appearance

Figure 4.13 shows elemental sulphur appearance produced without impurities added. Elemental sulphur was yellowish similar to the elemental sulphur produced with impurities added. The absence of these impurities did not affect colour change of elemental sulphur. The trace elements in SAV were the cause of elemental sulphur colour change not Na_2SO_4 and NaSCN .



Figure 4.13: Elemental sulphur produced concentrations with and without impurities

4.5.3 Effect of impurities (Na_2SO_4 and NaSCN) on H_2S conversion to elemental sulphur

The H_2S absorption and elemental sulphur production were 99.8% and 0.87 mol respectively without impurities. The H_2S conversion to elemental sulphur without impurities was slightly higher than conversion with impurities discussed in Figure 4.7 in Section 4.4. The higher H_2S absorption was due to a slightly higher pH that was observed without impurities. The higher pH improved the dissociation of H_2S to HS^- that leads to easier absorption of H_2S . This was a confirmation on the role of pH on H_2S absorption and conversion to elemental sulphur.

4.5.4 Effect of impurities (Na_2SO_4 and NaSCN) on elemental sulphur PSD curves

Figure 4.14 shows the PSD values of the elemental sulphur produced at V^{5+} concentrations of $0.029 \text{ mol.dm}^{-3}$ with and without impurities. The elemental sulphur PSDs in StretfordTM aqueous solutions with and without impurities were coarse. However, the particle sizes with impurities were slightly finer compared to the particle sizes without impurities. The cause of the PSDs shifting to the left was due to impurities that interfered with elemental sulphur nucleation, crystallization and agglomeration processes. The colour of elemental sulphur was not influenced by the presence of Na_2SO_4 and NaSCN . However, the particle sizes of the elemental sulphur were affected.

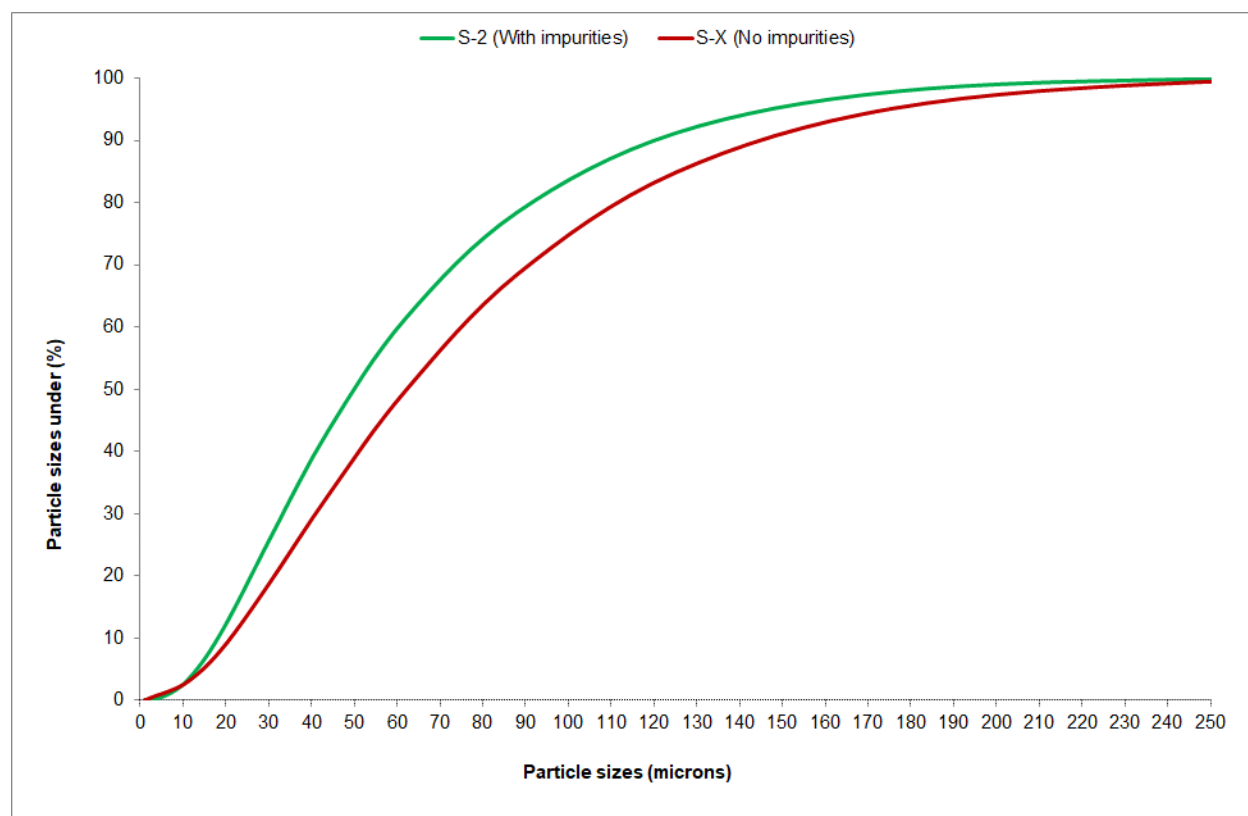


Figure 4.14: PSD curves of elemental sulphur produced with and without impurities added

4.5.5 DSC results

Table 4.19 shows the DSC results for elemental sulphur produced at V^{5+} concentration ($0.029 \text{ mol.dm}^{-3}$) without impurities. The elemental sulphur produced with and without impurities, melting and polymerization points were comparable at 122 and 175°C . The low impurity content did not significantly change the elemental sulphur melting points but energy requirements as they are shown in the curves in Appendix E. The energy requirements for the elemental sulphur produced with impurities added in solution was higher than elemental sulphur produced without impurities added in solution.

Table 4.19: DSC results for sulphur produced without impurities

Transition temperature (°C)	S-X (Without impurities)	S-2 (With impurities)
$\alpha\text{-S}_8 \rightarrow \beta\text{-S}_8$	113	112
Melting point	122	122
Polymerization	175	175

4.5.6 XRD results

Figure 4.15 shows the diffractograms of elemental sulphur produced at best V^{5+} concentration without impurities. The text indicated as 'Run 10 (E)' in below figure was used to differentiate samples by the analyst at the lab. Most of the XRD results in this study were described in a similar way. The diffractograms was comparable to diffractograms of sulphur produced in Solution 2. Elemental sulphur was crystalline orthorhombic which is in agreement with DSC results discussed in Section 4.5.5. The impurities does not affect the crystallinity of elemental sulphur.

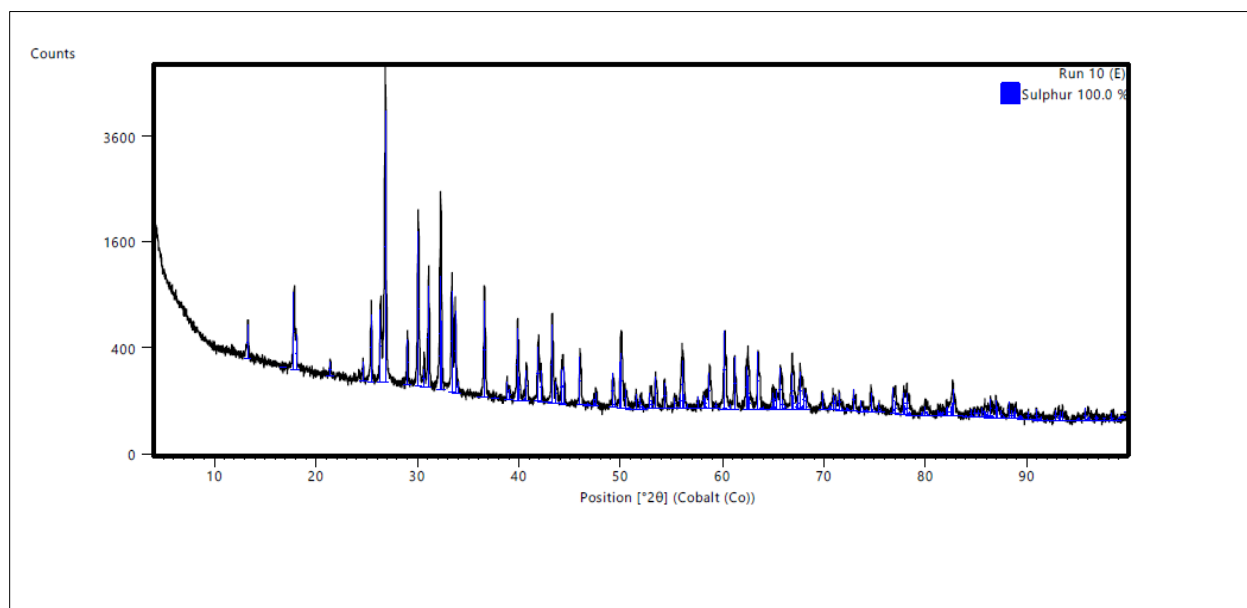


Figure 4.15: Diffractograms for elemental sulphur product produced at V^{5+} concentrations ($0.029 \text{ mol.dm}^{-3}$) without impurities

4.5.7 Elemental sulphur purity by gravimetric analysis

Table 4.20 shows the elemental sulphur purity results. Elemental sulphur produced without impurity was higher quality than elemental sulphur produced with impurities added. The details of the composition of elemental sulphur residual ashes produced with and without impurities are given in the next section.

Table 4.20: Results for sulphur produced without impurities added in Stretford™ solution

Composition (%)	S-X (Without impurities)	S-2 (With impurities)
α -S ₈	99.2	93.5
Ash	0.8	6.5

4.5.8 ICP-OES results

Table 4.21 shows the chemical composition of ash obtained from elemental sulphur produced with and without impurities. The big difference between elemental sulphur produced in a Stretford™ aqueous solution with and without impurities was sodium. The sources of sodium were Na₂SO₄, NaSCN, SAV, Na₂CO₃, NaHCO₃ and Na₂[ADA]. There was no additional sodium from Na₂SO₄ and NaSCN in this experiment. Without impurities, the sodium in ash was low at 1000 ppm while with impurities it was 21400 ppm. The high impurities confirm the cause of PSD in Solution 2 shifting to the finer part. The other impurities like potassium, vanadium, silicon, magnesium, iron, and aluminum were slightly similar to elemental sulphur produced with impurities. The reason was that the amount of SAV added with and without Na₂SO₄ and NaSCN was same and fixed.

Table 4.21: Ash results by ICP-OES for sulphur produced without impurities added

Elements (ppm)	S-X (Without impurities)	S-2 (With impurities)
Na	1000	21400
K	366	456
V	287	297
Si	258	261
Mg	133	131
Fe	74	73
Al	63	66
Cl	6.7	9
Ti	7.7	4.7
Cr	2.4	3.3
Ba	1.6	2.6
Cu	1.2	2.0
Sr	0.4	0.7
Ca	0.3	0.4

4.6 Effects of vanadium oxidation states on H₂S conversion to sulphur without Na₂[ADA]

4.6.1 Circulation solutions

Figure 4.16 shows physical appearance of the circulation solutions at the different V⁵⁺ to V⁴⁺ molar ratios. Solution 5 was dark-blue colour and contained dark-grey precipitates. Solutions 6 and 7

were more light blue with dark-grey precipitates at the bottom. Solution 8 was deep blue but without precipitates at the bottom. Solution 8 before showed dark-blue colour, which indicated that it was concentrated with V^{4+} species. Literature reported V^{4+} species to turn blue when dissolved in water (Kelsall, G.H., et al., (1993)).

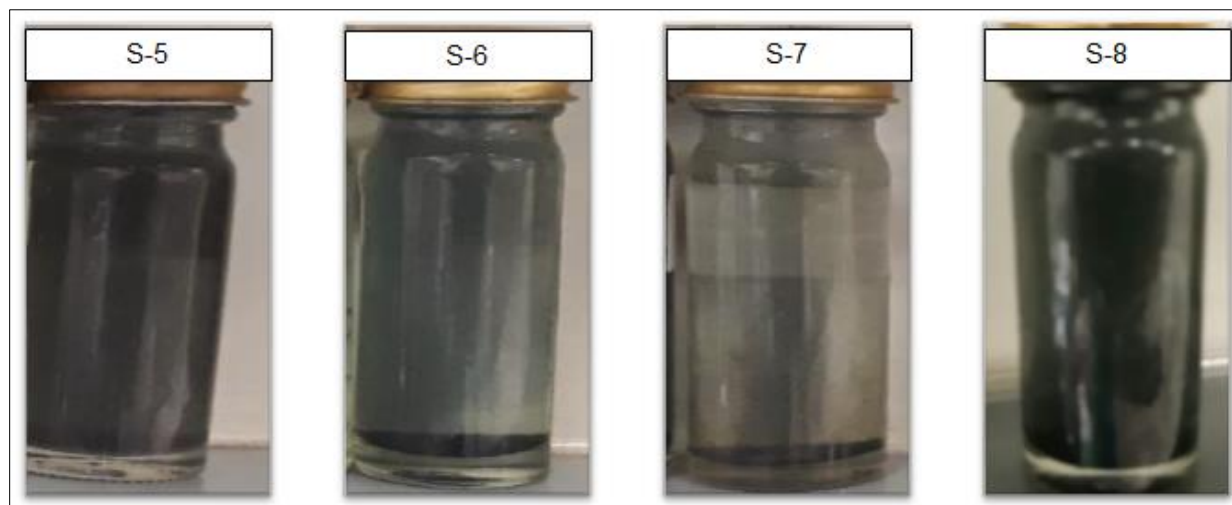


Figure 4.16: Circulation solutions at variable V^{5+} to V^{4+} molar ratios without $Na_2[ADA]$

Note: V^{5+} : V^{4+} molar ratios, **S-5** (100%:0%); **S-6** (80%:20%); **S-7** (60%:40%); **S-8** (0%:100%)

The blue colour in Solution 8 was an indication of the presence of V^{4+} species. This was an indication of slow redox cycle between V^{5+} , V^{4+} , H_2O_2 and O_2^- radicals without $Na_2[ADA]$ added in solution which is an oxidant. The redox cycle between V^{5+} , V^{4+} , H_2O_2 and O_2^- radicals was rapid with $Na_2[ADA]$ added in solutions. The circulation Solutions 5 conditions were similar to Stretford™ circulation Solutions 2 except absence of $Na_2[ADA]$. However, the Stretford™ circulation Solutions 2 was orange which was an indication of vanadium at its highest oxidation state (5+) after the experiment. The $Na_2[ADA]$ is responsible for producing O_2^- radicals and H_2O_2 .

4.6.2 Chemical results of circulation solutions

Table 4.22 shows fixed concentrations and pH values of the circulation solutions that were used to determine the effect of vanadium oxidation states on the H_2S absorption to elemental sulphur. The concentrations of total vanadium and V^{5+} are graphically shown in Figure 4.17. The total vanadium concentration in Solution 5 was $0.029 \text{ mol.dm}^{-3}$ before the experiment and dropped to $0.003 \text{ mol.dm}^{-3}$ after the experiment. The drop of total vanadium concentrations equates to 89.4% loss in total vanadium.

Table 4.22: Circulation results at variable V^{5+} to V^{4+} molar ratios without $Na_2[ADA]$

Solutions	mol.dm ⁻³					pH
	$Na_2[ADA]$	$NaSCN$	Na_2SO_4	TA	V^{4+}	
S-5	0.00	0.87	0.49	0.16	0.001	8.36
S-6	0.00	0.86	0.50	0.17	0.006	8.34
S-7	0.00	0.86	0.49	0.17	0.02	8.41
S-8	0.00	0.85	0.50	0.17	0.026	8.32

The loss of total vanadium was huge in comparison with less than 1% loss in Solution 2 under similar conditions but with $Na_2[ADA]$. In Solution 6, the total vanadium dropped from 0.029 to 0.008 mol.dm⁻³ after the experiment. The loss of total vanadium in Solution 6 was 72.8%. Solution 7 total vanadium dropped from 0.028 to 0.022 mol.dm⁻³, which equate to 20.8% loss of total vanadium. Solution 8 total vanadium dropped from 0.028 to 0.027 mol.dm⁻³, which equate to 2.8% loss of total vanadium.

The drop in total vanadium content in Solution 7 after the experiments, further confirms there is insufficient amount of $Na_2[ADA]$ to oxidize V^{4+} to V^{5+} at fast rate. The concentrations of V^{5+} dropped in Solutions 5, 6, and 7 together with the total vanadium content. The concentration of V^{5+} in Solution 8 increased marginally after the experiments, which indicated there was V^{4+} oxidation that took place. The rate of the V^{4+} precipitation was high in the Solution 5 compared to Solutions 6, 7, and 8. The drop in V^{4+} concentrations after the experiments was an indication of the crucial role of $Na_2[ADA]$ which was not added to these solutions. $Na_2[ADA]$ in the simulated StretfordTM aqueous solution releases hydrogen peroxide which oxidises V^{4+} to V^{5+} .

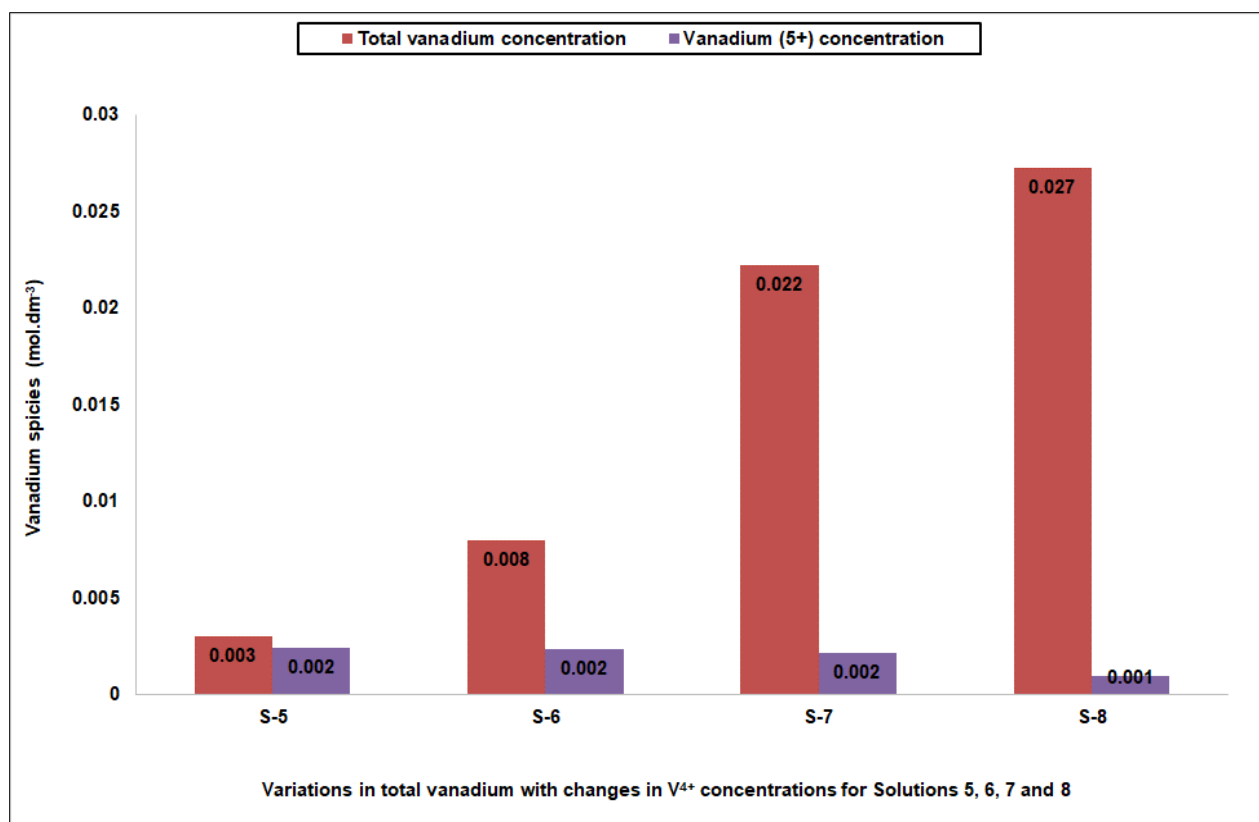


Figure 4.17: Concentrations of total vanadium and V⁵⁺ in circulation solutions without Na₂[ADA]

Note: V⁵⁺:V⁴⁺ molar ratios, S-5 (100%:0%); S-6 (80%:20%); S-7 (60%:40%); S-8 (0%:100%)

4.6.3 ⁵¹V NMR results

Table 4.23 shows the summary of chemical shifts and heights of the V⁵⁺ species in Solutions 5 to 8 respectively. It was observed that the similar V⁵⁺ species (dimer, tetramer, pentamer, and hexamer) identified before experiments were similar after the experiments with almost similar chemical shifts. The heights of the vanadium species were getting smaller when VOSO₄ was added as discussed in Section 4.2.3. The heights of the V⁵⁺ species in the Stretford™ circulation Solutions 5, 6, and 7 were even smaller after the experiments. The decrease in heights was an indication that V⁴⁺ species added did not oxidized to V⁵⁺. The decrease in heights was a further confirmation of the observed loss of total vanadium discussed in Section 4.6.2. However, the heights of circulation Solution 8 increased which was in agreement with low total vanadium precipitation observed in Sections 4.6.1 and 4.6.2. The details of the ⁵¹V NMR spectra are given in Appendix C.

Table 4.23: Stretford™ circulation solution ⁵¹VNMR results in the absence of Na₂[ADA]

Solutions	Resonances	V ⁵⁺ species			
		V ₂ O ₇ ⁴⁻	V ₄ O ₁₃ ⁵⁻	V ₄ O ₁₂ ⁴⁻	V ₆ O ₁₇ ⁴⁻
S-5	Peak (ppm)	-564	-	-575	-
	Height	117	-	84	-
S-6	Peak (ppm)	-563	-569	-576	-
	Height	448	104	143	-
S-7	Peak (ppm)	-559	-568	-577	-
	Height	551	237	287	-
S-8	Peak (ppm)	-562	-569	-576	-
	Height	795	267	400	-

4.6.4 H₂S absorption and elemental sulphur production

Figure 4.18 shows the H₂S gas absorbed and elemental sulphur produced as V⁵⁺ to V⁴⁺ molar ratios reduced. The H₂S absorption was low in all experiments compared to the experiments with Na₂[ADA]. The H₂S gas absorptions in Solutions 5, 6, 7, and 8 were 82, 68, 54, and 4.1% respectively. The elemental sulphur produced in Solutions 5, 6, 7 and 8 were 0.674, 0.561, 0.389, and 0.035 mol respectively. The low H₂S gas absorption and elemental sulphur production in all experiments reduced as the V⁵⁺ to V⁴⁺ molar ratios reduced. The H₂S gas absorption was higher in the beginning of the experiment in Solution 5. However, 60 minutes before the end of the experiment the H₂S gas monitor on top of the oxidizing and balance tanks started to detect H₂S gas. This was an indication that HS⁻ slipped-out of the reaction tank due to low V⁵⁺ concentration, which plays a very crucial role in shifting the equilibrium during absorption and conversion of H₂S to elemental sulphur. If the concentration of V⁵⁺ is not sufficient in stoichiometry to HS⁻, the absorbed HS⁻ saturate the Stretford™ solution and circulate back to the absorber (Trofe, T.W., et al., (1987)). The saturated Stretford™ solution with HS⁻ cannot absorb H₂S gas and as a result, it will exit at the absorber outlet and result in higher H₂S emission. The low H₂S absorption and elemental sulphur production can be explained by the sub stoichiometric condition between V⁵⁺ to HS⁻ molar ratios in all solutions. The molar ratios were 0.62, 0.6, 0.54, and 0.24 between V⁵⁺ to HS⁻ in Solutions 5, 6, 7 and 8.

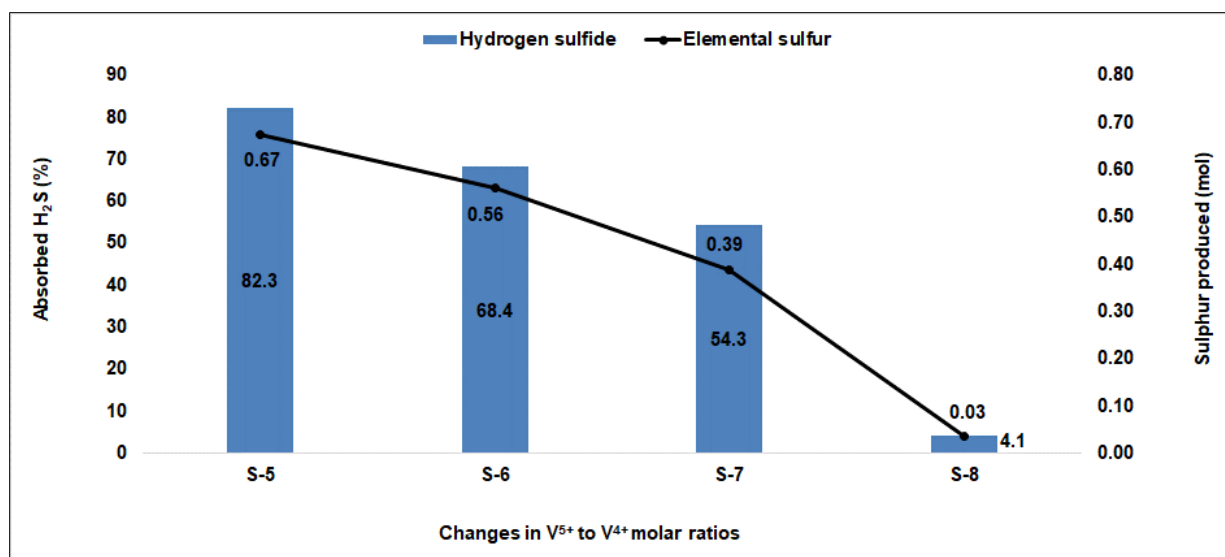


Figure 4.18: H₂S absorption and sulphur production at variable V⁵⁺ to V⁴⁺ without Na₂[ADA]

Figures 4.19 shows the dark-grey precipitates at the bottom of the balance tank for Solutions 5, 6, 7, and 8 at the end of experiments. The visual observation in Figures 4.19 confirms loss of total vanadium due to precipitation discussed in Section 4.6.2. Solutions 5, 6, and 7 clearly shows dark-grey precipitates settled at the bottom of the balance tank. There was high vanadium precipitation in Solutions 5 and 6, which correlate with total vanadium losses discussed in Section 4.6.2.

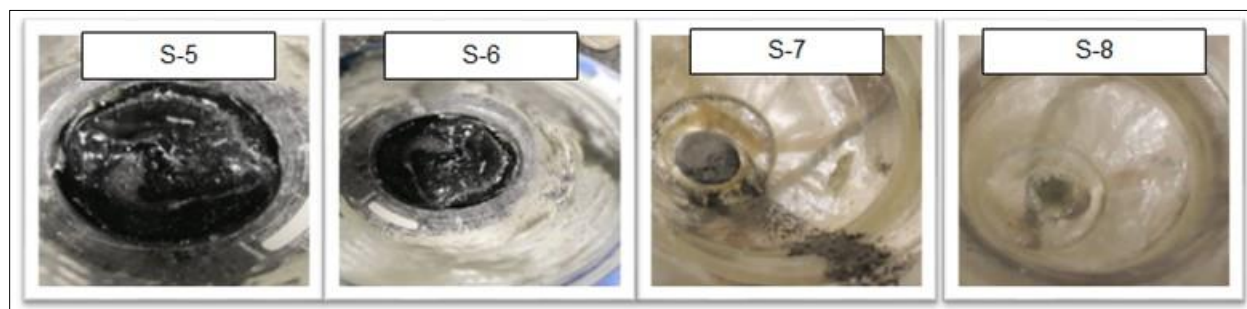


Figure 4.19: Dark-grey precipitates after the experiments at V⁵⁺ to V⁴⁺ molar ratios for Solutions 5, 6, 7, and 8

There was an indication of precipitation starting to occur on the side of the balance tank in Solution 8. Total vanadium precipitation reduces as the V⁵⁺ to V⁴⁺ molar ratios reduces. The absorption of H₂S and elemental sulphur production rate were high in Solutions 5 and 6 due to high concentration of V⁵⁺. However, there was high rate of precipitation in Solutions 5 and 6 as shown in Figure 4.20. Elemental sulphur is hydrophobic and acted as a precursor for vanadium and other sodium based salts precipitation. V⁴⁺ is not stable in an alkaline solution.

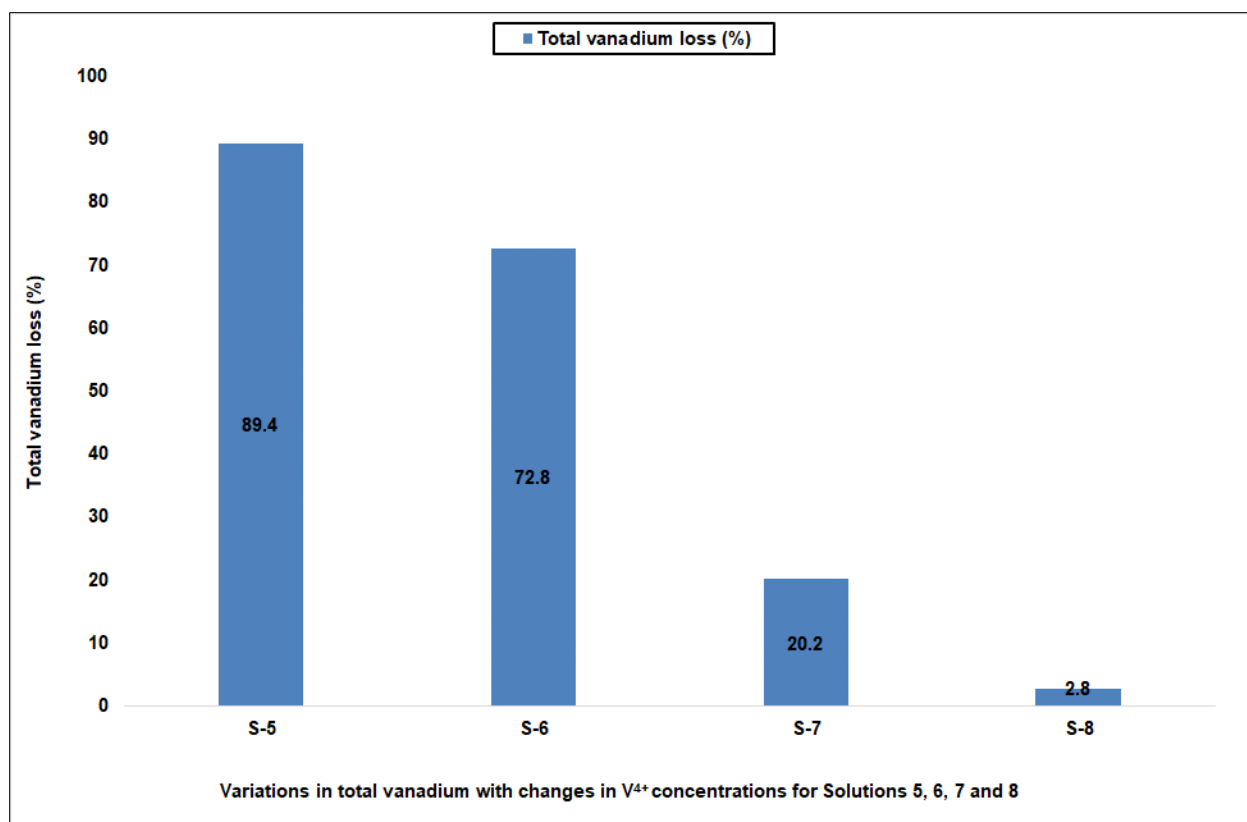


Figure 4.20: Total vanadium loss after the experiments at V^{5+} to V^{4+} molar ratios

The dark-grey precipitates were dried and dissolved into 0.51 mol.dm^{-3} of Sulphuric acid and the colour turned blue to green as shown in Figure 4.21. There was a visual observation of approximately 40% of the precipitate that did not dissolve in sulphuric acid and was floating. On analyzing the dark precipitates with XRD, it was found to contain V^{4+} compounds and elemental sulphur. The dark precipitates that did not dissolve in sulphuric acid contained elemental sulphur compounds. The undissolved compound was washed with de-ionized water and dissolved in carbon disulphide. The dissolution of the elemental sulphur in carbon disulphide was a confirmation that the dark precipitates that did not dissolve were crystalline elemental sulphur products.



Figure 4.21: Sample of a dry and a dissolved precipitates after experiments

It was difficult to filter elemental sulphur in Solutions 5, 6 and 7 due to dark precipitates. The filter papers were replaced three to six times per experiment. The four air frits that were used to supply air for regeneration of vanadium compounds and $\text{Na}_2[\text{ADA}]$ with dissolved oxygen was also blocked by the dark-grey precipitates. The blockage of the air frits was a simulation of what could be the cause of air boxes blockages that has been reported by the Stretford™ plants operators. Some of the dark-grey precipitates could be observed on the elemental sulphur slurry floating in the balance tank but most of it sank. The formation of a sulphur sol could not be observed in Solution 8 throughout the experiment. That was an indicator that H_2S gas was absorbed in solution but not converted to elemental sulphur due to low V^{5+} concentration in stoichiometry with HS^- .

The H_2S gas could be detected by portable H_2S gas monitor inside the fume hood. H_2S gas was also smelt when elemental sulphur was filtered out of the solution in all the experiments. The detection of H_2S on top of the oxidizing and balance tanks was another indication that H_2S gas was absorbed but not converted to elemental sulphur. This was a further confirmation on the role of the V^{5+} during absorption of H_2S and conversion of HS^- to elemental sulphur. The role of V^{5+} is to ensure that all three steps which are absorption, dissociation, and disproportionation of the H_2S happened fast enough to prevent equilibrium conditions (Stumm, W., et al., (1970), Trofe, T.W., et al., (1993)). When V^{5+} to V^{4+} molar ratios reduced, HS^- could not be converted to polysulphide which is a precursor for precipitation of the vanadium and other sodium based salts. This was the reason there was almost no precipitation of total vanadium in Solution 8. Figure 4.22 shows the diffractograms of the dark-grey precipitates collected at the bottom of the balance tank after the experiment. The black products that were precipitated and settled at the bottom of the balance tank at the end of the experiments, contained non-crystalline phase (amorphous material) as

shown in Figure 4.22. Without $\text{Na}_2[\text{ADA}]$, the reduced V^{5+} compounds precipitated from the circulation solutions as shown in Figure 4.19.

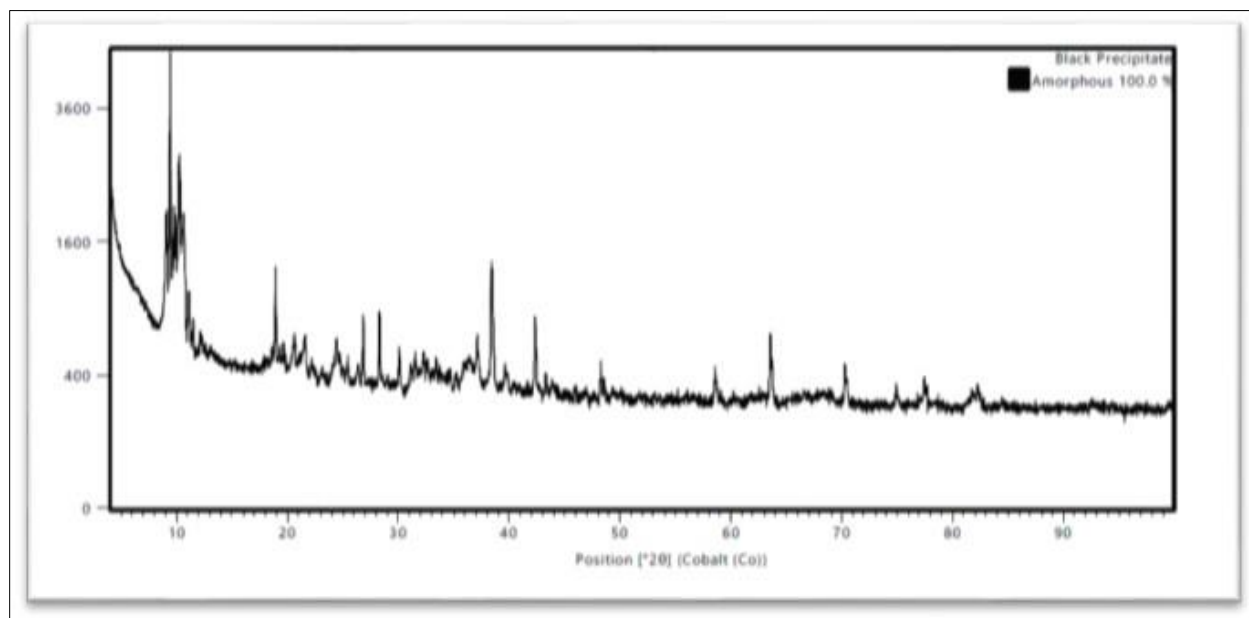


Figure 4.22: Diffractograms of the dark-grey precipitates produced during experiments

4.6.5 PSD curves at different V^{5+} to V^{4+} molar ratios

Figure 4.23 shows the particles sizes of the elemental sulphur produced in Solutions 5, 6 and 7. The elemental sulphur produced in Solution 8 was not enough for PSD analysis, only DSC and XRD analyses were done. Solution 5 produced coarse elemental sulphur particles almost similar to elemental sulphur produced in Solution 2. The decrease in V^{5+} to V^{4+} molar ratios did not affect the elemental sulphur PSDs similar to the impurities in SAV and excess vanadium concentration.

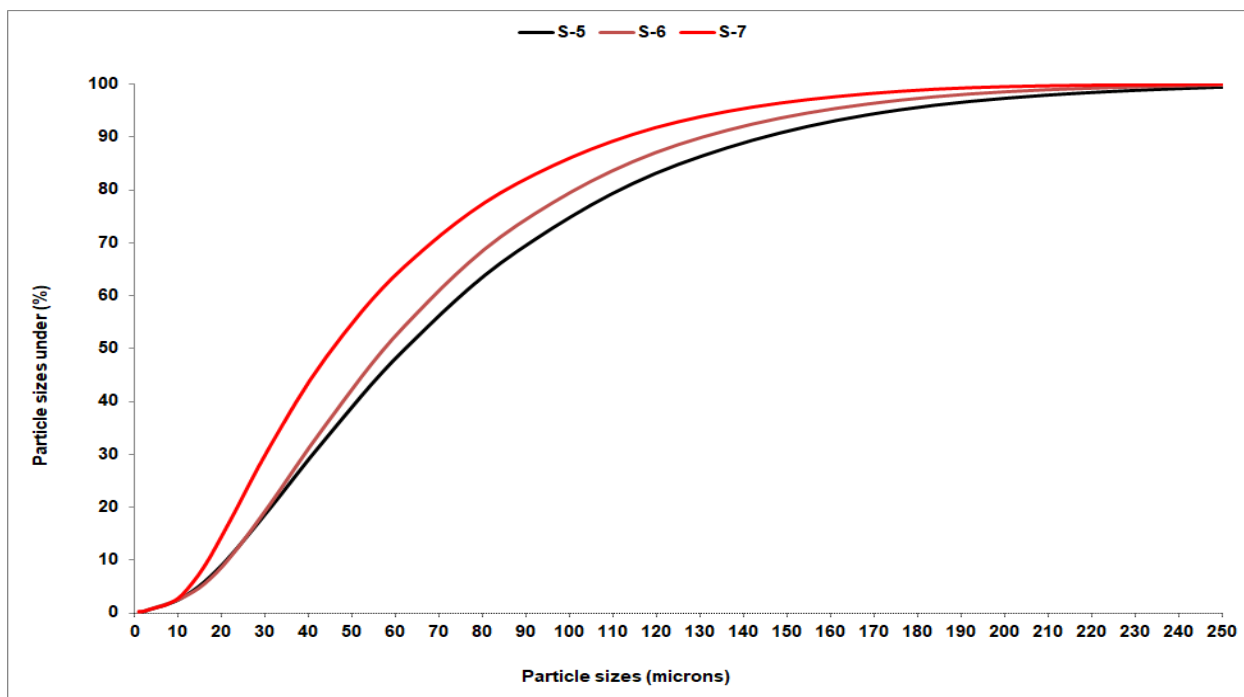


Figure 4.23: PSD curves of elemental sulphur produced at different V^{5+} to V^{4+} molar ratios

Figure 4.24 shows physical appearance of elemental sulphur slurry produced in Solutions 5 and 7 five minutes after samples were shaken. Solution 5 shows black precipitates on the wall of the bottle. There was no visibility of the black precipitates on the elemental sulphur slurry in Solution 7. This observation was in agreement with observation made in Section 4.6.4 that Solution 5 had high vanadium precipitation than Solutions 6, 7, and 8.

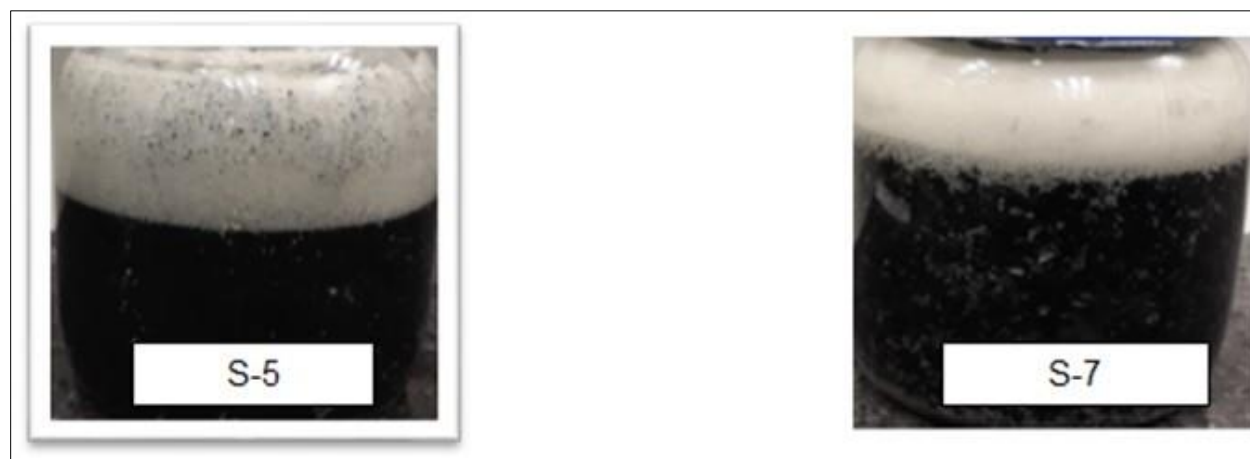


Figure 4.24: Elemental sulphur slurry at variable V^{5+} to V^{4+} molar ratios

4.6.6 Elemental sulphur physical appearance

Figure 4.25 shows the elemental sulphur produced as the V^{5+} to V^{4+} molar ratios reduced. The elemental sulphur samples were in support of the dark-grey precipitation discussed in Section

4.6.4. The elemental sulphur produced in Solutions 5 and 6 was dark-greyish whilst Solution 7 and 8 produced normal yellowish elemental sulphur. It took longer to filter the elemental sulphur produced in Solutions 5, 6, and 7 due dark-grey precipitates that blinded the filter papers. The filter papers that were used to recover elemental sulphur had to be replaced three to six times due to blockages by the dark-grey precipitates.

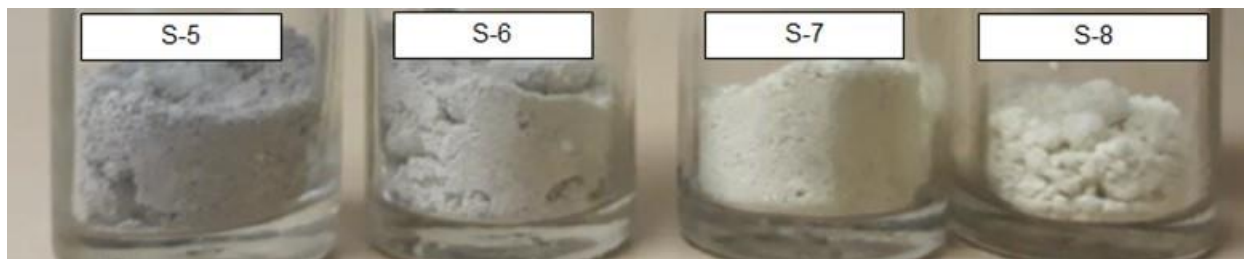


Figure 4.25: Elemental sulphur appearance at different V^{5+} to V^{4+} molar ratios

4.6.7 DSC results

The results in Table 4.24 show the average transition temperatures of elemental sulphur from orthorhombic to monoclinic and finally to polymerized product. The average transition temperature from orthorhombic to monoclinic was 113.9°C. This was an indication that even though elemental sulphur samples look different in colour it was still orthorhombic as discussed in Section 2.13. The colour difference was due to dark-grey precipitates, which co-precipitated with elemental sulphur produced. The average melting temperature of elemental sulphur in all solutions was 123.1°C. The average elemental sulphur melting point was closed to 120.6°C as it is reported in the literature (Steudel, R., et al., (2003)). There was a time delay in melting elemental sulphur and it reduced as the V^{5+} to V^{4+} molar ratios reduced. This was a further confirmation that the impurities or contaminants does not change the elemental sulphur melting points but delay it.

Table 4.24: DSC results for elemental sulphur produced at different V^{5+} to V^{4+} molar ratios

Transition temp (°C)	S-5	S-6	S-7	S-8
$\alpha\text{-S}_8 \rightarrow \beta\text{-S}_8$	113.8	113.8	114.2	113.6
Melting point	122.3	121.8	124.1	124.2
Polymerization	179.9	173.1	171.3	173.9

4.6.8 XRD results at V^{5+} to V^{4+} molar ratios

Table 4.25 shows the summary of XRD results for the elemental sulphur produced in Solutions 5, 6, 7, and 8. The results confirmed the observations made in Section 4.6.6 that elemental sulphur produced was contaminated. Figure 4.26 diffractogram shows crystalline elemental sulphur was

produced but with sodium based contaminants in Solution 5. The XRD curves for Solutions 6, 7, and 8 are given in Appendix G (Figures G-6 to G-8).

Table 4.25: Results for elemental sulphur produced at V^{5+} to V^{4+} molar ratios

Components (wt%)	S-5	S-6	S-7	S-8
α -S ₈	99	99.4	99.7	99.8
Metathenardite	0.4	0.1	0.3	-
Nahcolite	0.2	0.1	-	-
[TVT] ^{5*}	0.3	-	-	-
Burkeite	-	0.4	-	0.2
[TTDD] ^{6*}	0.1	-	-	-
Total	100	100	100	100

Note: 5*- Trisodium vanadate trihydrate ; 6*- Trisodium triammonium decavanadate (V) dodecahydrate

The purity of elemental sulphur produced in Solutions 5, 6, 7, and 8 were 99.0, 99.4, 99.7, and 99.8% respectively. The results in above table indicate that the sodium based salts contamination decreased as the V^{5+} to V^{4+} molar ratios decreases. The contamination of elemental sulphur was a confirmation that precipitation of polysulphide was the initiator of the precipitation of other sodium salts including V^{5+} compounds.

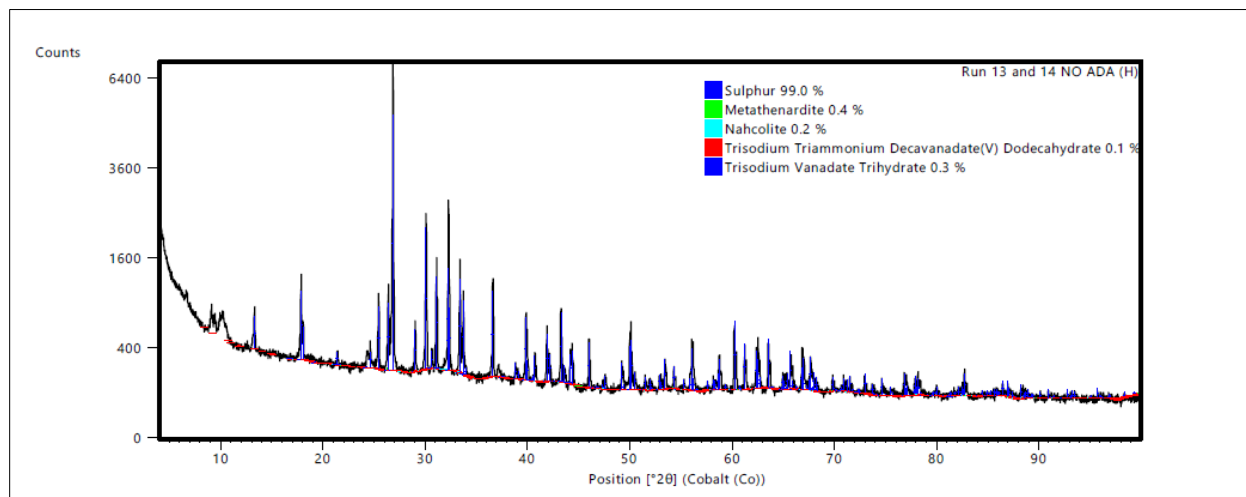


Figure 4.26: Diffractograms of the elemental sulphur (S-5) produced at different V^{5+} to V^{4+} molar ratio

4.7 Quality of elemental sulphur produced in this study compared to commercial sulphur

Elemental sulphur produced in this study was compared with commercial purified and unpurified elemental sulphur. DSC, XRD, gravimetric and ICP-OES techniques were used to analyze the commercial elemental sulphur and the elemental sulphur produced in this study. The objective was to confirm if the elemental sulphur produced in this study was similar or different to elemental

sulphur produced commercially in terms of purity and physical properties. The comparison was done with elemental sulphur produced at vanadium concentration with $\text{Na}_2[\text{ADA}]$ added in solution. The conditions that were used to produce commercial sulphur are not known.

4.7.1 Elemental sulphur physical appearance

Figure 4.27 shows the commercial purified and unpurified elemental sulphur in comparison with elemental sulphur produced in this study. The elemental sulphur produced in this study (S-D) was physically comparable to unpurified commercial elemental sulphur (S-C) produced commercially in a Stretford™ plant. The purified commercial elemental sulphur S-A and S-B were slightly comparable. S-A and S-C were the same sulphur and the difference was elemental sulphur S-C was not purified while S-A was purified through melting process. The purified elemental sulphur was bright yellow than unpurified elemental sulphur, which confirmed the cause of colour difference was due to impurities.

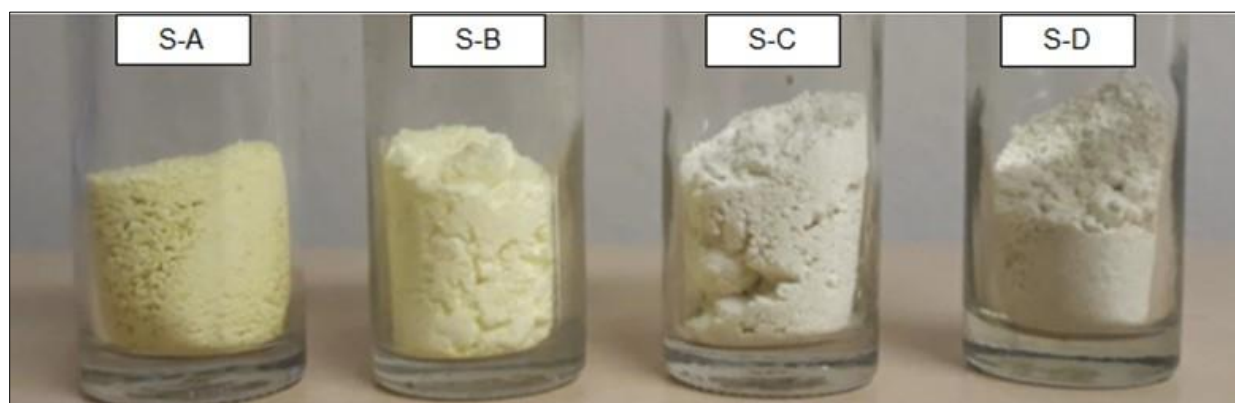


Figure 4.27: Comparison of commercial elemental sulphur and sulphur produced in this study

Note: S-A: Purified liquid sulphur, S-B: Purified Sigma Aldrich sulphur, S-C: Unpurified commercial sulphur, S-D: Unpurified sulphur produced in this study

4.7.2 DSC results

Table 4.26 shows S-A, S-B and S-C changing from orthorhombic to monoclinic elemental sulphur at 109, 111 and 112°C respectively. The elemental sulphur from Sigma Aldrich (S-B) was supplied with certificate of analysis (COA) for purity and melting temperature. The melting temperatures for S-A, S-B and S-C from orthorhombic to monoclinic were comparable to melting temperatures for elemental sulphur produced in this study (S-D). The melting and polymerization temperatures for S-A, S-B and S-C were also comparable to S-D as indicated above. However, S-C has a fourth melting temperature at 297°C that can be ascribed to the melting or decomposition of impurities contained in the elemental sulphur products. The melting temperature on the COA for S-B was 119°C. The melting temperature for S-B was measured by DSC and it was 121°C, which was 2°C

higher than the temperature on the COA. The heating rate and external pressure used to measure S-B melting temperature on the COA was not known. Perhaps if similar heating rate and external pressure was used to analyze elemental sulphur produced in this study, the melting and polymerization temperatures could have been lower by 2°C. The details DSC curves are attached in Appendix E.

Table 4.26: Comparison of commercial sulphur and sulphur produced in this study using DSC

Transition temperature(°C)	S-A	S-B	S-C	S-D
α -S ₈ → β -S ₈	109	111	112	114
Melting point 1	123	121	124	123
Polymerization	167	165	166	168
Melting point 2	-	-	297	-

4.7.3 Elemental sulphur curves using XRD technique

Figure 4.28 shows the diffractograms of commercial elemental sulphur and sulphur produced in this study. The commercial sulphur diffractograms were crystalline similar to the elemental sulphur produced in this study. This was a confirmation that elemental sulphur produced in this study was comparable to elemental sulphur produced commercially. The clear XRD diffractograms for S-A, S-B, S-C and S-D are given in Appendix G (Figures G-9 to G-12).

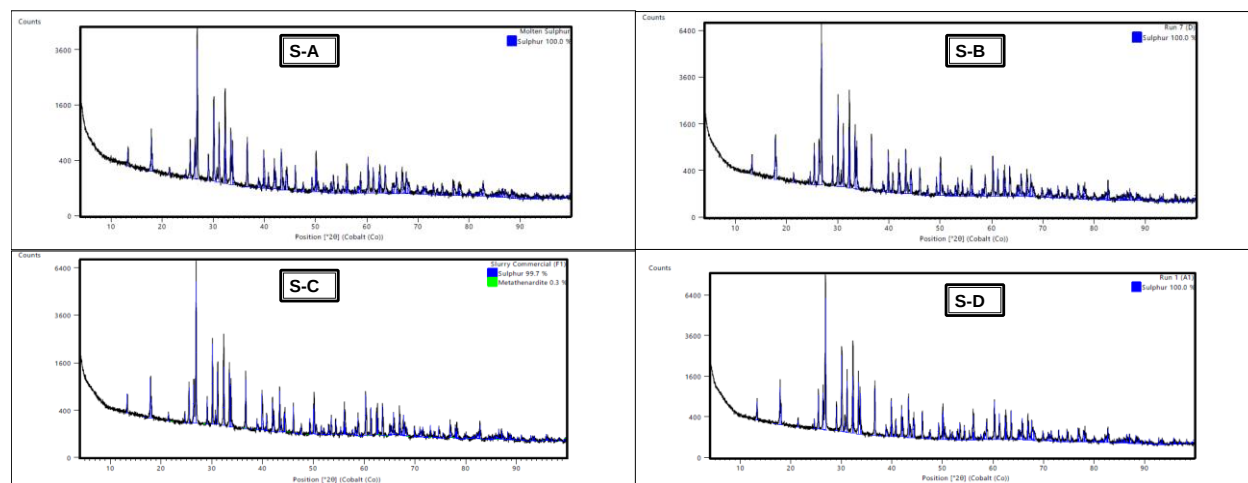


Figure 4.28: Diffractograms of the purified and unpurified elemental sulphur

4.7.4 Elemental sulphur purity results

Table 4.27 shows the purity results of commercial elemental sulphur and elemental sulphur produced in this study. The commercial unpurified elemental sulphur (S-C) was comparable to elemental sulphur produced at V⁵⁺ concentration of 0.029 mol.dm⁻³ in this study (S-D). After the unpurified elemental sulphur was purified through melting and filtration, the purity increased from

93.34 to 99.95%. The COA from the elemental sulphur supplier (S-B) showed purity to be above 99.8%. The gravimetric analysis for S-B was 99.98%, which is in agreement with the COA results. The composition of ash is given in Section 4.7.5.

Table 4.27: Elemental sulphur purity results by gravimetry

Composition (%)	S-A	S-B	S-C	S-D
α -S ₈	99.95	99.98	93.34	93.49
Ash	0.05	0.02	6.66	6.51

4.7.5 ICP-OES results

Table 4.28 shows the chemical composition of residual ash for commercial and elemental sulphur produced in this study. There were high concentrations of the sodium, potassium, vanadium and iron in unpurified (S-C) and elemental sulphur produced in this study (S-D).

Table 4.28: Composition of ash samples of the elemental sulphur products using ICP-OES

Chemical composition of ash (ppm)				
Elements	S-A	S-B	S-C	S-D
Si	111	19.3	110	261
Al	29.5	15.8	39.8	66.1
Fe	41.1	10.2	106	72.8
Ti	1.44	1.11	2.39	4.68
Ca	12.9	10.2	16.18	0.20
Mg	2.69	3.73	11.64	131
Na	22.9	18.2	25500	21400
K	18.3	12.6	158.4	457
Mn	0.41	0.22	6.19	8.87
P	0.23	0.16	0.00	0.00
Ba	0.44	0.00	1.33	2.6
Cr	0.63	0.02	3.99	3.25
Cu	5.50	0.12	0.67	1.95
Ni	0.02	0.00	0.00	0.00
Pb	0.06	0.00	0.00	0.00
Sr	0.07	0.03	0.00	0.65
V	0.35	0.00	318	298
Z	0.32	0.00	0.67	0.00

4.8 Summary

The details of the calculated concentrations of the chemicals in the synthetic Stretford™ aqueous solutions used in this study were given. The experimental results of the samples from the repeatability experiments are discussed below and the mean, standard deviation and the standard error of the mean are presented. The standard errors of the mean for elemental sulphur

production in mol (<0.06 mol), absorption in % (<0.3%), particle sizes in % (<3.3%), purity in % (<3.8%) and thermal behavior in °C (<0.5°C) were low, which shows low variation of the results. All synthetic Stretford™ aqueous solutions prepared in this study were characterized before and after the experiments using different analytical techniques. The research revealed as the concentration of V^{5+} increased the H_2S absorption and elemental sulphur production also increased. However, as the elemental sulphur production increases the particle sizes shift towards finer particles and the colour of elemental sulphur changes from yellowish to greyish. The changes of elemental sulphur particle sizes and colour was due to impurities in SAV and excess vanadium as shown by ICP-OES results. Elemental sulphur foaming occurred as the concentration of V^{5+} increased due to significant amount of impurities in the commercial SAV. The concentrations of total vanadium and V^{5+} before and after the experiments determined by UV-Visible spectrophotometry were almost the same. The gravimetric results showed elemental sulphur purity decreased as the amount of SAV added in synthetic Stretford™ solutions increased. The XRD results indicated that the elemental sulphur ($\alpha-S_8$) produced from all Stretford™ circulation solutions was crystalline and orthorhombic. The DSC results showed elemental sulphur melting point did not differ significantly as the concentration of impurities increased. However, the energy requirements to melt one gram of elemental sulphur increased as the concentration of impurities increased. The ICP-OES results shows that the elemental sulphur was contaminated by sodium, vanadium, potassium, silicon, magnesium and iron.

The pH value of the Stretford™ aqueous solutions increased when impurities (Na_2SO_4 and $NaSCN$) were not added. This indicated that without addition of these impurities the pH of the Stretford™ circulation solution was high which improved the H_2S absorption and dissociation. The elemental sulphur PSD values obtained from the Stretford™ circulation solution without added impurities were coarser. However, the colour of elemental sulphur was not affected by the absence of the impurities. The DSC results shows that the melting points of the elemental sulphur produced without impurities was slightly similar to the melting points of elemental sulphur produced with impurities. However, the energy requirements of the elemental sulphur produced without impurities was low. This result showed the effect of impurities from SAV and excess vanadium were higher than the effect of Na_2SO_4 and $NaSCN$ as impurities on H_2S conversion to elemental sulphur and its quality.

The H_2S absorption and elemental sulphur production decreased as the V^{5+} to V^{4+} molar ratios decreased when $Na_2[ADA]$ was not added. However, elemental sulphur particle sizes were coarse. The concentrations of total vanadium and V^{5+} decreased after the experiments as

determined by UV-Visible spectrophotometry. The decrease in total vanadium and V^{5+} concentrations was due to precipitation. The precipitates were confirmed to be a mixture of elemental sulphur and V^{4+} compounds by XRD and ICP-OES results. The precipitates also blocked the air frits in the oxidizing tank during experiments. The amount of precipitates decreased as the V^{5+} to V^{4+} molar ratios decreased. The elemental sulphur precipitation was found to initiate the precipitation of V^{4+} compounds in higher V^{5+} to V^{4+} molar ratios. The XRD results shows elemental sulphur produced in all solutions without $Na_2[ADA]$ was crystalline and orthorhombic ($\alpha-S_8$) but contaminated with sodium salts and V^{5+} compounds. The DSC results showed that the product sulphur with high amount of precipitates melted slower than that with low amount. The time delay in melting meant higher energy requirements to melt elemental sulphur. The XRD, DSC, gravimetry, and ICP-OES results showed elemental sulphur produced in this study was comparable to the unpurified elemental sulphur produced commercially in terms of physical, mineralogical, and chemical properties. The ^{51}V NMR results indicated that the dimer, tetramer, and pentamer were the main types of V^{5+} species in all solutions in this study. The results showed that different vanadium oxidation states did not influence the type of V^{5+} species present in solutions.

Therefore, to achieve optimal absorption and conversion of H_2S to elemental sulphur of good quality, V^{5+} to HS^- molar ratios must be maintained (between 4.8 and 7.3 in stoichiometry). The best V^{5+} to HS^- molar ratios was between 4.8 and 7.3 in this study. The redox cycle between V^{5+} , V^{4+} and O_2 is dependent on the presence of $Na_2[ADA]$. Without $Na_2[ADA]$ vanadium 5+ species reduced and precipitated together with elemental sulphur.

CHAPTER 5: THERMODYNAMIC (OLI) AND STATISTICAL MODELS

5.1 Introduction

The results and discussion in Chapter 4 concluded that as the concentration of V^{5+} increased the H_2S absorption and elemental sulphur production increases. The results further concluded that without $Na_2[ADA]$ in StretfordTM aqueous solution V^{4+} precipitates. In this study, the H_2S speciation model was developed to simulate the type of H_2S species that are oxidized to elemental sulphur by V^{5+} species in a StretfordTM circulation solution at different pH values using OLI studio analyzer. A vanadium stability graph in water as a function of pH was also developed to simulate the type of vanadium species in a StretfordTM circulation solution using the OLI studio analyzer. The vanadium model was used to validate experimental findings. The effect of vanadium oxidation states on H_2S conversion to elemental sulphur was also tested statistically to validate the experimental findings on the effect of vanadium oxidation states on H_2S absorption and elemental sulphur production. The data points inputs for the statistical models were the concentrations of vanadium (V^{Total} and V^{5+}) in $mol.dm^{-3}$ and the output were H_2S absorption and elemental sulphur production in moles.

The chapter consists of the following sections:

- Section 5.2 discusses OLI studio models.
- Section 5.3 discusses the H_2S and elemental sulphur production statistical models.

5.2 OLI studio models development

5.2.1 H_2S speciation as a function of pH

Figure 5.1 shows the simulation of H_2S stability as a function of pH in water at 25°C. The graph shows that between pHs of 2 and 6 the H_2S gas dissolves but does not dissociate. Between pHs of 6 and 11 the H_2S gas starts to dissociate to HS^- . Above pH of 11, the HS^- further dissociates to S^{2-} as indicated by Reactions 2.9 and 2.10 discussed in Chapter 2. The pH of the StretfordTM aqueous solutions in this study was 8.3 on average. The pH of 8.3 is where H_2S gas was absorbed in the StretfordTM aqueous solution and dissociated to HS^- . The role of V^{5+} was to oxidized HS^- to elemental sulphur and allow absorption of more H_2S gas. Without sufficient V^{5+} concentration in stoichiometry to HS^- , dissolved H_2S was emitted in the oxidizing and balance tanks. This was observed in this study as the V^{5+} to V^{4+} molar ratios decreased. The H_2S gas was detected by portable H_2S meters on top of the oxidizing and balance tanks as the V^{5+} to V^{4+} molar ratios declined. The H_2S absorption in the StretfordTM circulation solution is dependent on the pH. However, without sufficient V^{5+} in stoichiometry to HS^- , the H_2S absorption efficiency declined as

discussed in Section 4.6.4. Figure 5.1 is in line with what was reported in literature (Troffe, T.W., et al., (1987)).

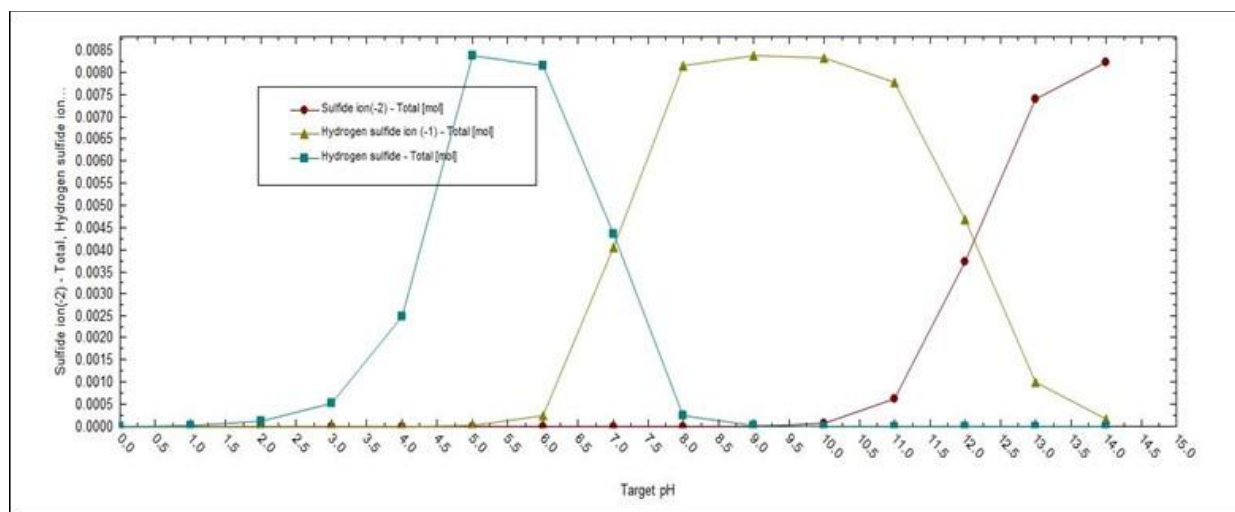


Figure 5.1: Effect of pH on H₂S speciation

Note:

Sulphide ion (-2)-total (mol)



Hydrogen sulphide – total (mol)



Hydrogen sulphide ion (-1)-total (mol)



5.2.2 Vanadium stability as a function of pH

Figure 5.2 shows the vanadium oxidation states as a function of pH values. The graph shows V²⁺ is stable below a pH of 7.2. Above a pH of 7.2 the model shows V²⁺ is not stable and it can precipitate as VO(s). Below a pH of 2 vanadium (3+) is stable in solution as V³⁺. Between a pH of 2 and 4.8 vanadium (3+) is stable as VO²⁺. Above a pH of 4.9, V³⁺ is not stable and can precipitate as V₂O₃ (s). Vanadium (4+) is stable as VO₂⁺ between pHs 1 and 5.2. Above a pH of 5.2, V⁴⁺ is not stable and can precipitate as V₂O₄ (s) and VO (OH)⁺. Vanadium (5+) is stable across all the pH ranges.

In acidic conditions, the dominant V⁵⁺ species exist as VO₂⁺, H₃VO₄ and H₂VO₄⁻ and in alkaline conditions it exists as HVO₄²⁻ and VO₄³⁻. The pH of the StretfordTM aqueous solution in this study was around 8.3 which means the HVO₄²⁻ was the dominant species that existed. The HVO₄²⁻ is the species where the dimer, tetramer and pentamer were formed as discussed in Section 2.10 in Chapter 2. The model confirmed the ⁵¹V NMR results on the V⁵⁺ species, which was identified around pH of 8.3. The OLI model also confirms the precipitation of V⁴⁺ compounds that were observed in experiments without Na₂[ADA] added. The reason for the V⁴⁺ not to precipitate in the StretfordTM circulation solution with Na₂[ADA] added was probable due to the rate of oxidation of

V^{4+} to V^{5+} faster than the rate of V^{4+} precipitating or V^{4+} form a complex with $Na_2[ADA]$. Figure 5.2 is in line with what was reported in literature (Crans, D.C., et al., (1998)).

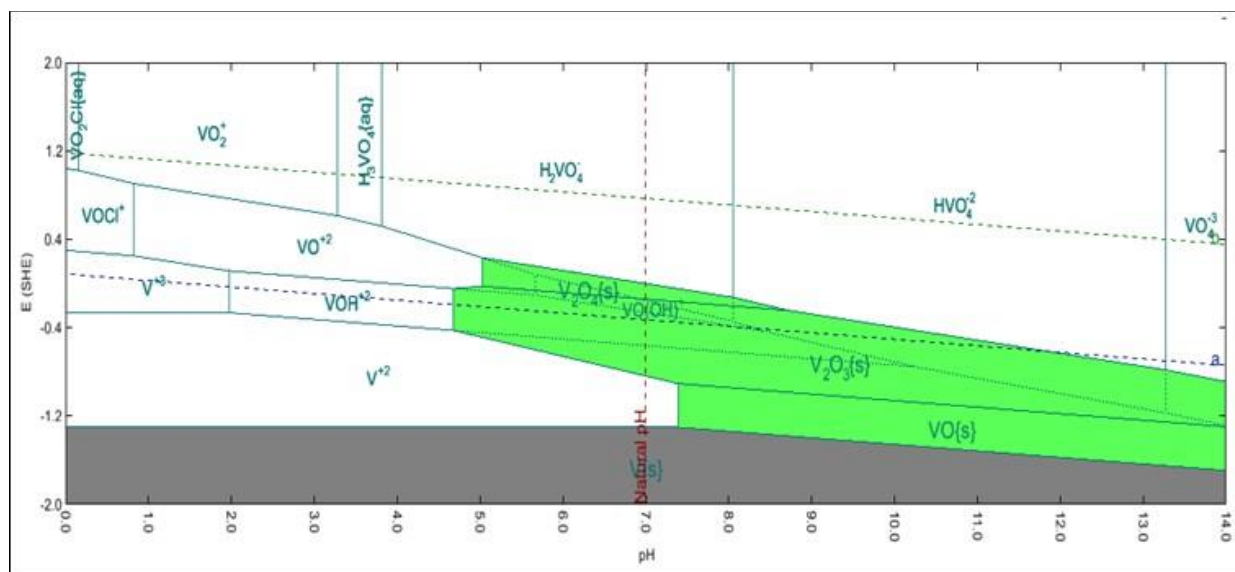


Figure 5.2: Effect of pH on stability of vanadium species

Note:

Natural pH

5.3 H₂S absorption and elemental sulphur production efficiency statistical models

5.3.1 Effect of vanadium oxidation states on H₂S absorption

Figure 5.3 shows the relationship between H₂S absorption and vanadium concentration (V^{Total} and V^{5+}). The statistical model shows that when V^{5+} concentration increased the H₂S absorption also increased. The P-value was 0.01 which indicate model was at 99% confidence that V^{5+} influenced the H₂S absorption. V^{5+} concentration plays a very crucial role in the absorption and conversion of H₂S to elemental sulphur. The model supports the findings discussed in Chapter 4 on the role of V^{5+} concentration on H₂S absorption and elemental sulphur production.

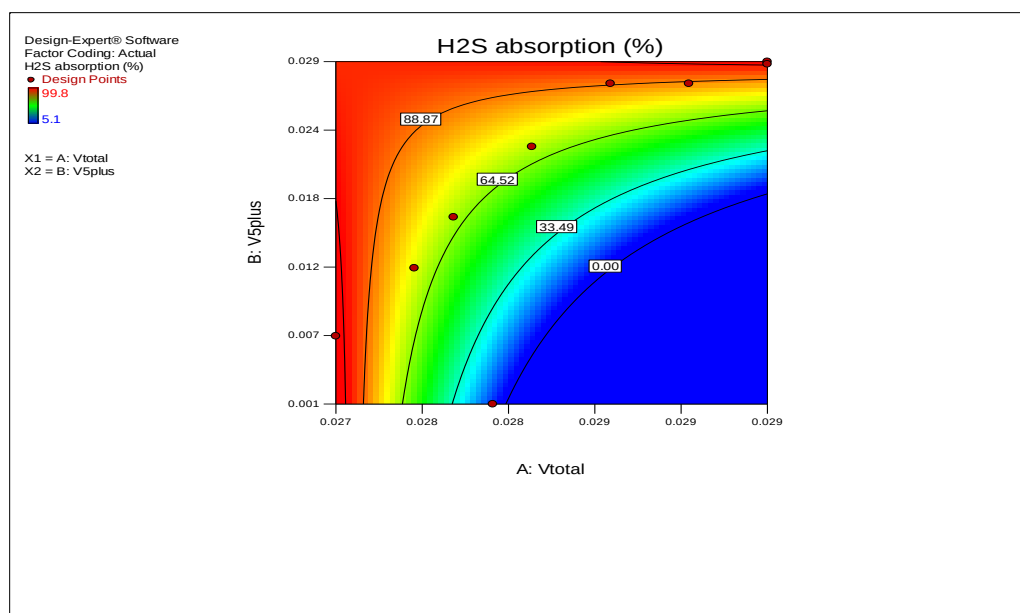


Figure 5.3: Effect of vanadium oxidation states on H₂S absorption

Figure 5.4 shows the actual H₂S absorbed against the predicted H₂S absorbed by the model. The calculated R² was 87% which indicate the model was 87% accurate in predicting the H₂S absorption as a function of total vanadium and V⁵⁺ concentration. Therefore, Equation 5.1 can be used to predict H₂S absorption as a function of total vanadium and V⁵⁺ by the Stretford™ operators.

$$Y_A = 3682 - (130973 \cdot X_1) - (126328 \cdot X_2) + (4614265 \cdot X_1 \cdot X_2) \quad 5.1$$

Note:

Y_A : H₂S absorbed (mol)

X_1 : Total vanadium (mol.dm⁻³)

X_2 : V⁵⁺ (mol.dm⁻³)

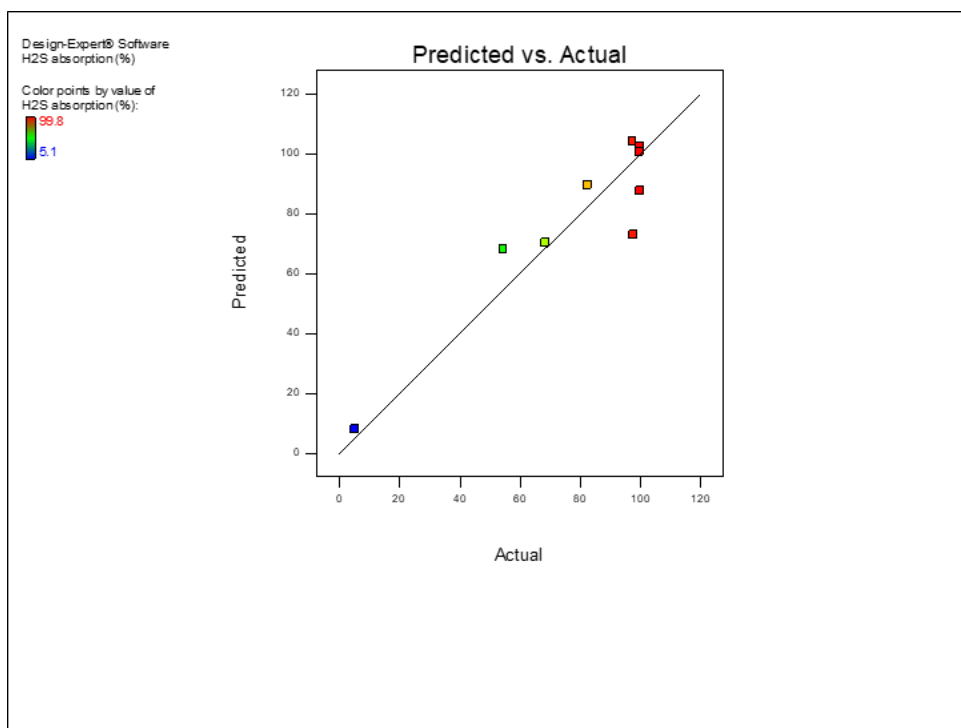


Figure 5.4: Actual H₂S absorption against model prediction

5.3.2 Effect of vanadium oxidation states on elemental sulphur production

Figure 5.5 shows the effect vanadium oxidation state on elemental sulphur production. The statistical model shows that when V⁵⁺ concentration increases the elemental sulphur production was increasing. The P-value was 0.019 which indicate model to be 98.1% confidence that V⁵⁺ concentration influenced the elemental sulphur production. The model support the findings discussed in Chapter 4 on the role of V⁵⁺ concentration on conversion of absorbed H₂S gas to elemental sulphur.

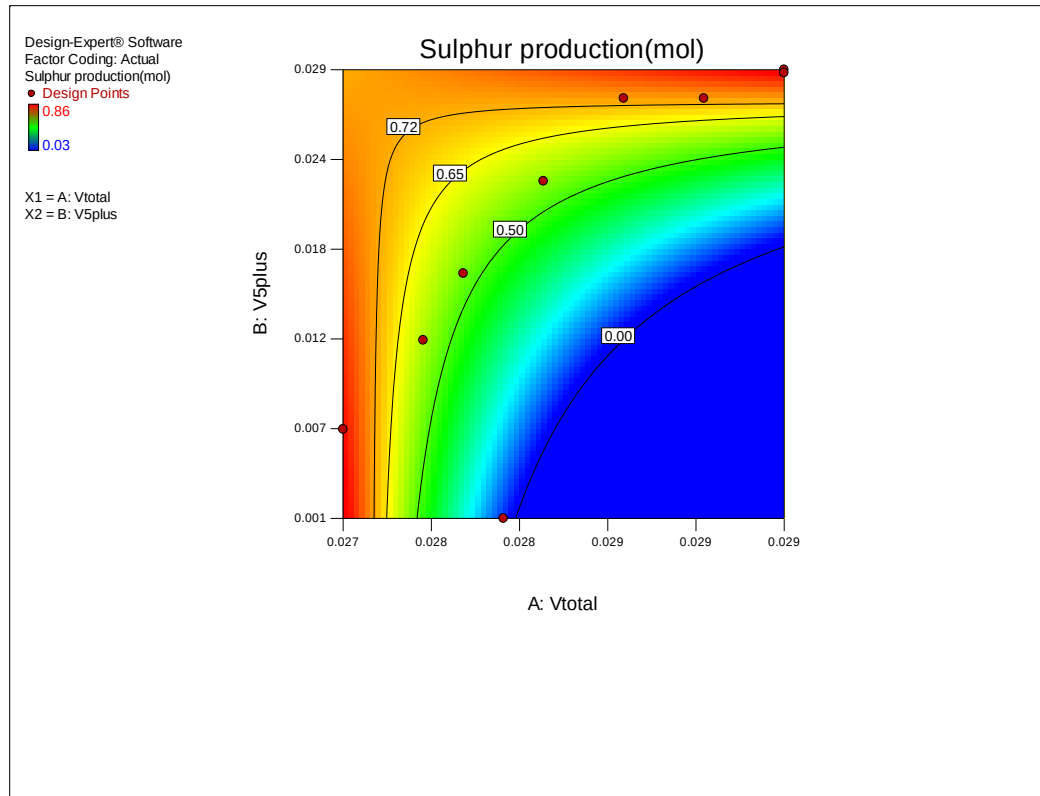


Figure 5.5: Effect of vanadium oxidation states on elemental sulphur production

Figure 5.6 shows the actual elemental sulphur produced against the predicted elemental sulphur by the model. The R^2 was 84% which indicate the model was 84% accurate in predicting elemental sulphur production as a function of total vanadium and V^{5+} concentration. Equation 5.2 can be used to predict elemental sulphur production as a function of total vanadium and V^{5+} by the Stretford™ operators.

$$Y_B = 30.7 - (1091 \cdot X_3) - (1103 \cdot X_2) + (40214.5 \cdot X_3 \cdot X_4) \quad 5.2$$

Note:

Y_B : Sulphur production (mol)

X_3 : Total vanadium (mol.dm⁻³)

X_4 : V^{5+} (mol.dm⁻³)

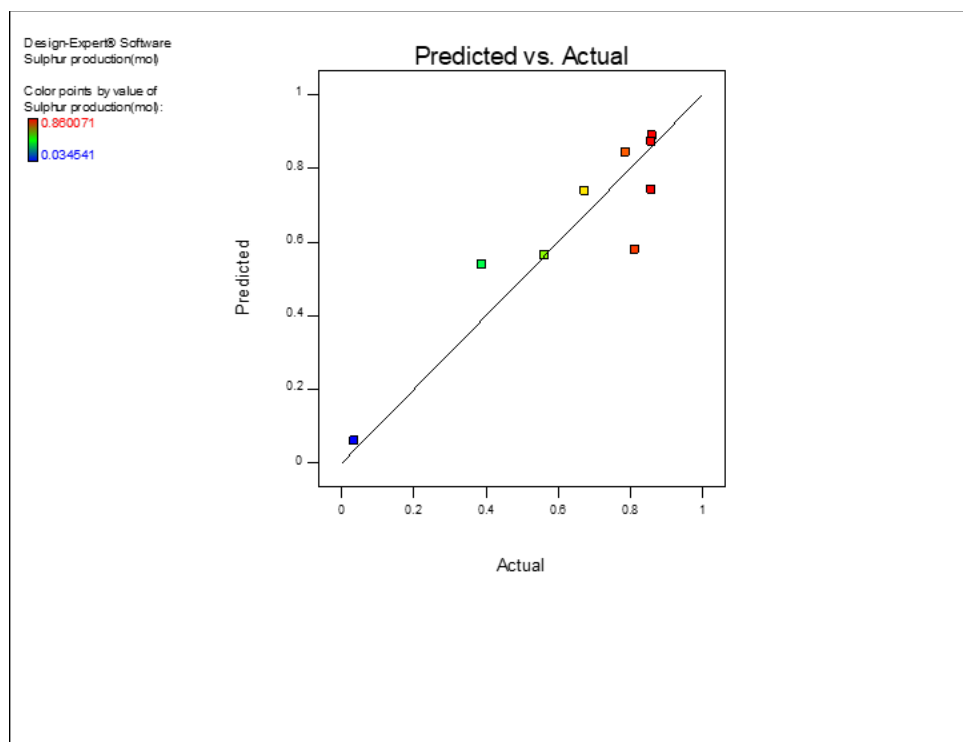


Figure 5.6: Actual elemental sulphur production against model prediction

5.4 Summary

The thermodynamic OLI studio analyzer model showed that V^{5+} was stable in both acidic and alkaline conditions but as different species. In this study, it was confirmed that the HVO_4^{2-} was the dominant species of V^{5+} at a pH of 8.3. From the model, it could be seen that V^{4+} was unstable at a pH of 8.3. The experimental findings showed that the oxidation of V^{4+} to V^{5+} was slow without $Na_2[ADA]$ added in solution hence more V^{4+} precipitation. When $Na_2[ADA]$ was added there was no precipitation of V^{4+} which means the rate of oxidation of V^{4+} to V^{5+} could be faster than the rate of V^{4+} precipitation or V^{4+} compound form complex with $Na_2[ADA]$. The species that easily gets oxidized to elemental sulphur is HS^- as was shown by the speciation graph at different pH values. The H_2S absorption and elemental sulphur production statistical models results were in line with experimental findings. As the concentrations of V^{5+} increased, the H_2S absorption and elemental sulphur production increased.

CHAPTER 6: CONCLUSIONS

The concentration of V^{5+} in the StretfordTM process is crucial for oxidation of HS^- to elemental sulphur. The study successfully proved that the H_2S absorption efficiency and conversion of the absorbed HS^- to the elemental sulphur with high quality increased as the concentration of V^{5+} increased. However, the physical properties (PSD values) of the elemental sulphur shifted to the finer particles as the concentration of V^{5+} using SAV in the simulated StretfordTM aqueous solution increased. As expected, the finer PSD values of the elemental sulphur products and different melting point values of these products were due to the impurities contained in the commercial SAV. Based on the mineralogical results, the elemental sulphur produced when using the simulated StretfordTM aqueous solutions containing low and high concentrations of V^{5+} was crystalline and orthorhombic (α - S_8). However, a low production efficiency of the elemental sulphur product was achieved when using the simulated StretfordTM aqueous solution containing low concentration of V^{5+} . The physical properties (colour) of produced elemental sulphur changed from yellowish to greyish based on the amount of SAV added to the aqueous solutions. The quality of elemental sulphur produced in this study was similar to that of the technical elemental sulphur produced from the plants in terms of physical, mineralogical, and chemical properties. As expected, the quality and colour of the elemental sulphur products were found to be further improved by the purification method.

The foaming of sulphur slurry resulted in the formation of the small bubbles and emission of gases, after addition of a significant amount of SAV with impurities and air during the absorption of H_2S and conversion of the absorbed HS^- to the elemental sulphur. As the concentration of V^{5+} increased, the melting points did not change drastically but the energy requirements increased due to impurities in the elemental sulphur products.

The pH of the StretfordTM aqueous solutions increased when impurities (Na_2SO_4 and $NaSCN$) were not added to these solutions. However, the H_2S absorption and conversion of HS^- to the elemental sulphur were observed to increase as the pH values increased in the absence of these impurities. The chemical property of the elemental sulphur produced without impurities favourably compared to that of the elemental sulphur produced with impurities, due to the small amount of SAV added to the StretfordTM aqueous solution.

As expected, without the addition of $Na_2[ADA]$ into the StretfordTM aqueous solutions, there was low H_2S conversion to the elemental sulphur due to the reduction of V^{5+} to V^{4+} . The V^{4+} ions react with hydroxide in the solution to form the colloidal precipitates of $VO(OH)_2$. These precipitates

subsequently resulted in the higher loss of total vanadium (5 - 27%). Without $\text{Na}_2[\text{ADA}]$ added to the aqueous solution, the hydrophobic elemental sulphur co-precipitated with vanadium (V^{4+}) hydroxide, and sodium salts (Na_2SO_4 , Na_2CO_3 and NaHCO_3) as dark precipitates. The dark precipitates caused the colour of the elemental sulphur to change from yellow to dark brown. The dark precipitates also contribute to the blockage of the air frits that were used to supply air for the oxidation of the absorbed H_2S in the StretfordTM aqueous solution to the elemental sulphur particles. In this research, the main types of V^{5+} species were found to be the dimer, tetramer, and pentamer at low and high concentrations of V^{5+} , which were in line with what other researchers found. The type of V^{5+} species was found to be dependent on the pH values of the solution hence the V^{5+} species did not change at different concentrations because pH values were almost similar.

A thermodynamic OLI studio analyzer model proved that V^{5+} was stable in both acidic and alkaline conditions as expected. In acidic conditions, OLI found the dominant V^{5+} species to exist as VO_2^+ , H_3VO_4 and H_2VO_4^- but in alkaline conditions, it existed as HVO_4^{2-} and VO_4^{3-} . However, V^{4+} species was found to be only stable in acidic conditions as VO^{2+} . The StretfordTM circulation solution was alkaline which can explain the cause of V^{4+} compounds precipitation in the absence of $\text{Na}_2[\text{ADA}]$. When $\text{Na}_2[\text{ADA}]$ was added there was no precipitation of V^{4+} compounds which means the rate of oxidation of V^{4+} to V^{5+} by peroxide radicals was faster than the rate of V^{4+} species precipitate. The experimental findings were confirmed by the OLI model, which showed the stability of vanadium species at different pH ranges. The model also showed the dominant H_2S species that is oxidized to elemental sulphur by V^{5+} to be HS^- . The statistical model validated the increase in H_2S absorption and the elemental sulphur production as concentration of V^{5+} increases. The statistical models can be used to predict H_2S absorption and elemental sulphur production as a function of total vanadium and V^{5+} .

Therefore, the StretfordTM process must always be operated at best V^{5+} to HS^- stoichiometric molar ratios (4.8 - 7.3), pH value of (8.2 - 9.5), $\text{Na}_2[\text{ADA}]$ content ($0.001 \text{ mol.dm}^{-3}$) and other parameters to prevent low H_2S absorption and conversion of HS^- to the elemental sulphur of low quality. In addition, this prevents V^{4+} and other sodium based salts precipitation, which will cause equipment blockages and increase cost of operating StretfordTM plants. The impact of low V^{5+} concentration will results in high hydrogen sulphide emission, which is detrimental to human, and environment.

6.1 Achievement of objectives

- The study successfully proved that the concentration of V^{5+} plays a crucial role from H_2S absorption, dissociation, and conversion to elemental sulphur of good quality.
- It is not the concentration of V^{5+} , which is important in converting HS^- to elemental sulphur, but the V^{5+} to HS^- molar ratio.
- To maximize elemental sulphur production and its quality, the V^{5+} to HS^- molar ratios should be maintain between 4.8 and 7.3 in stoichiometry.
- The elemental sulphur can be fine or contaminated but it is still a crystalline and orthorhombic.
- The impurities affect the quality of elemental sulphur for example particle sizes.
- The low concentration of V^{5+} does not affect the particle sizes of elemental sulphur but H_2S absorption and elemental sulphur production.
- The excess V^{5+} concentration in stoichiometry to HS^- and impurities in a source of V^{5+} like SAV does negatively affect the PSD values of elemental sulphur.
- The study further shows that $Na_2[ADA]$ is crucial in the redox cycle between V^{4+} , V^{5+} and dissolved oxygen in preventing loss of vanadium due to precipitation.
- Elemental sulphur melting point does not change due to impurities but energy requirements change.
- The colour of elemental sulphur is determined by impurities.
- There H_2S absorption and elemental sulphur production can be predicted with a models.

6.2 Recommendations

- The rate of formation of Na_2SO_4 and $NaSCN$ should be investigated further at longer run times to observe their effect on elemental sulphur quality.
- Kinetic studies using purer sources of V^{5+} (e.g. $NaVO_3$ or Na_3VO_4) should be conducted to determine the effect impurities on elemental sulphur quality.
- Effect of vanadium speciation on H_2S conversion to elemental sulphur should be conducted using pure H_2S gas that contain CO_2 gas to simulate commercial Stretford™ plant conditions.

CHAPTER 7: REFERENCES

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APPENDICES

APPENDIX A: Experimental set-up

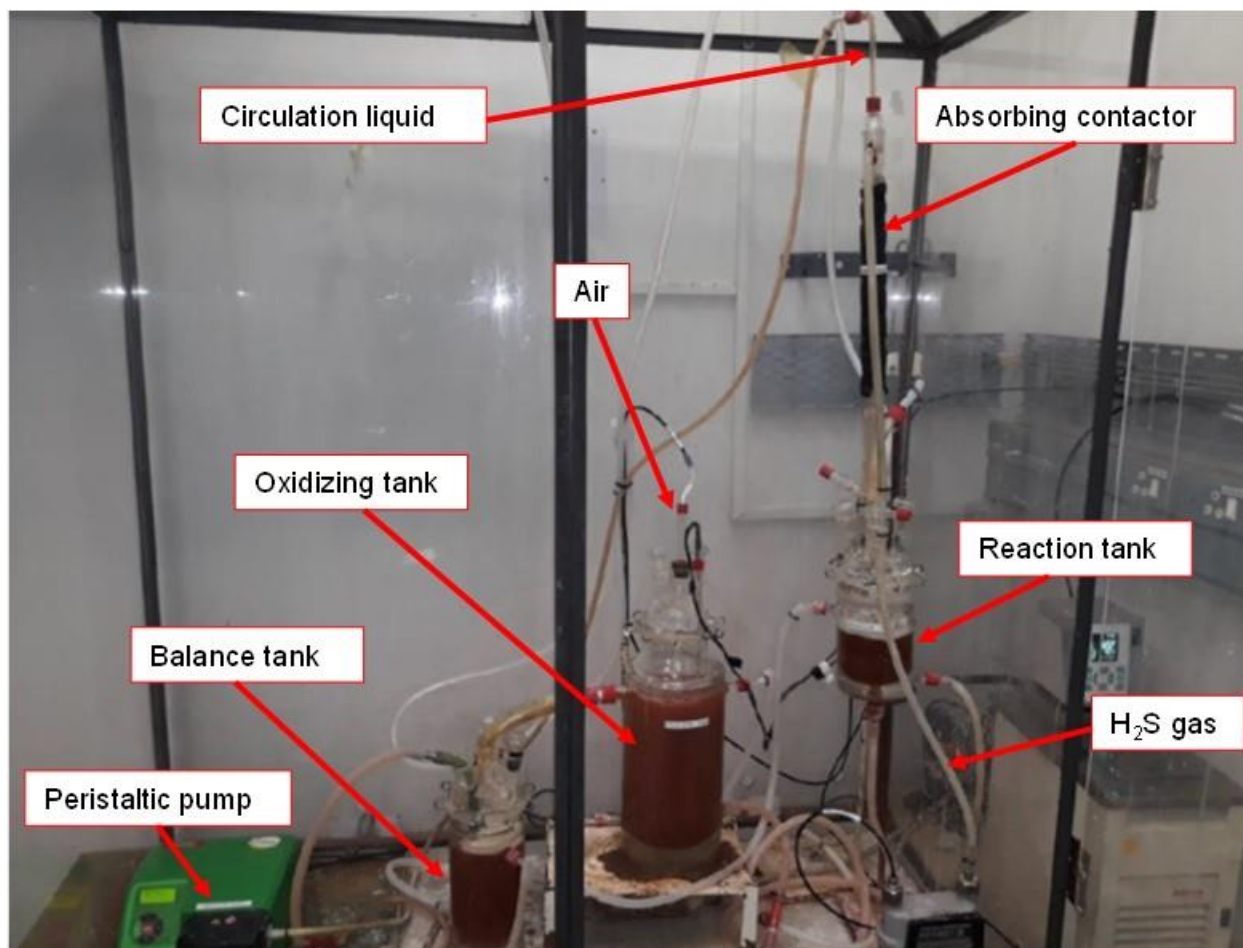


Figure A-1: Apparatus used to conduct experiments

APPENDIX B: H₂S absorption efficiency calculations

Below is the example step by step calculations that were followed to determine the absorption efficiency based on the mass balance.

Total volume of gas introduced = 1384 dm³

H₂S concentration = 1.5%

N₂ balance = 99.6%

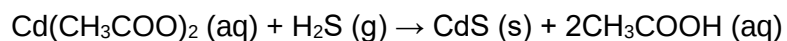
H₂S molecular weight = 34.1 g.mol⁻¹

Total H₂S in gas = 1384 × 0.014

Total H₂S in gas = 19.4 dm³

Total mole of H₂S in feed = 19.4 ÷ 34.1

Total mole of H₂S in feed = 0.568 mol



B.2

Mass of CdS after experiments = 4.51 g

$$M_{\text{wt}} (\text{CdS}) = 141.5 \text{ g.mol}^{-1}$$

$$n_{\text{CdS}} = 4.51 \div 141.5$$

$$n_{\text{CdS}} = 0.031 \text{ mol}$$

1 mol of H₂S is require to form 1 mol of CdS as per equation B.2.

Therefore.

$$0.031 \text{ mol of CdS} = 0.031 \text{ mol of H}_2\text{S}$$

$$\% \text{ of H}_2\text{S to atmosphere} = (0.031 \div 0.568) \times 100$$

$$\% \text{ of H}_2\text{S to atmosphere} = 5.5\%$$

$$\text{Total H}_2\text{S not absorbed} = 19.4 \times 0.055$$

$$\text{Total H}_2\text{S not absorbed} = 1.065 \text{ dm}^3$$

$$\text{Total unabsorbed H}_2\text{S in total gas} = (1.065 \div 1384) \times 100$$

$$\text{Total unabsorbed H}_2\text{S in total gas} = 0.07\%$$

$$\text{Total absorbed H}_2\text{S in Solution 2} = 100 - 0.07$$

$$\text{Total absorbed H}_2\text{S in Solution 2} = 99.7\%$$

APPENDIX C: ^{51}V NMR results

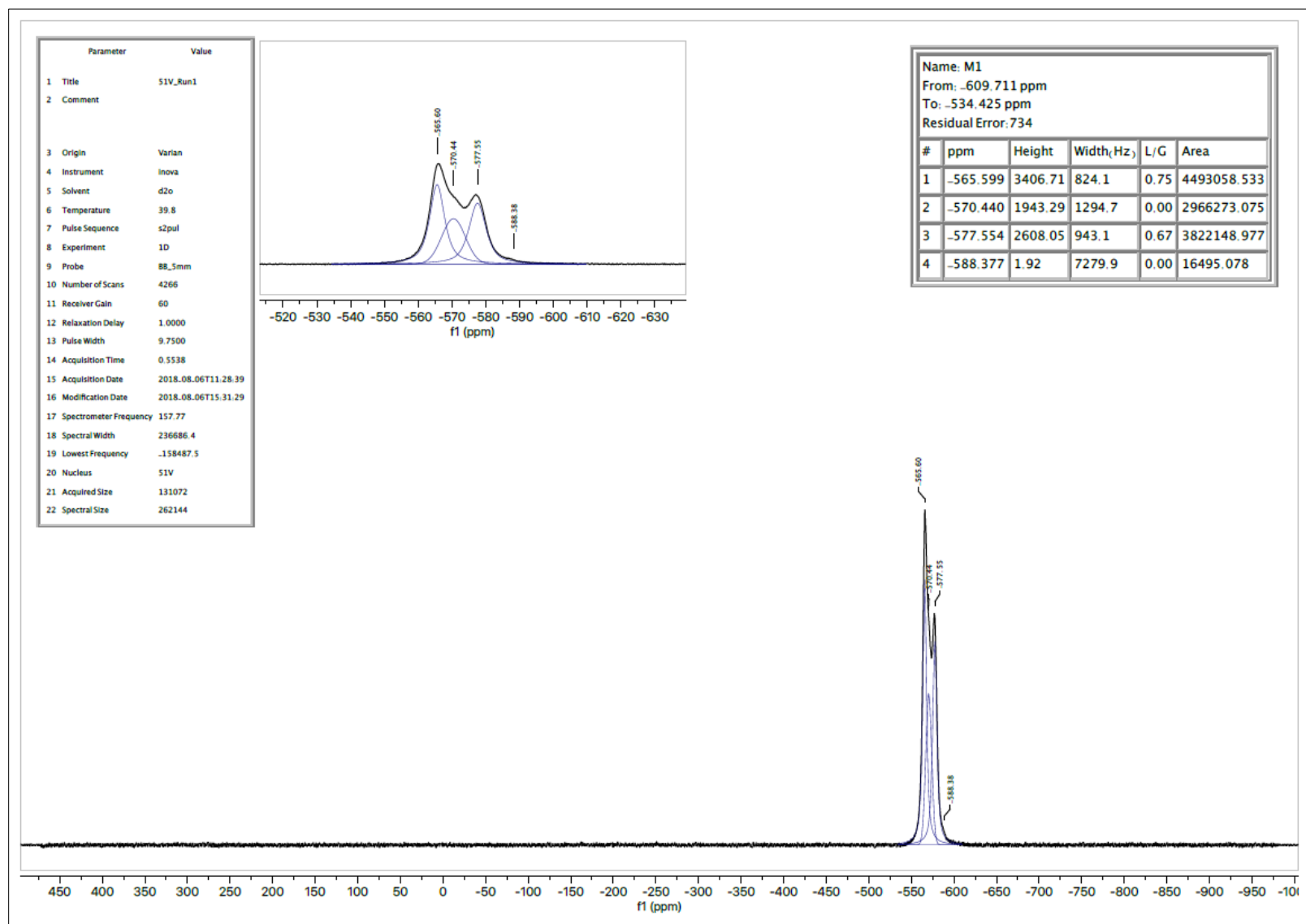


Figure C-1: Solution 2 vanadium 5+ spectra before the experiment

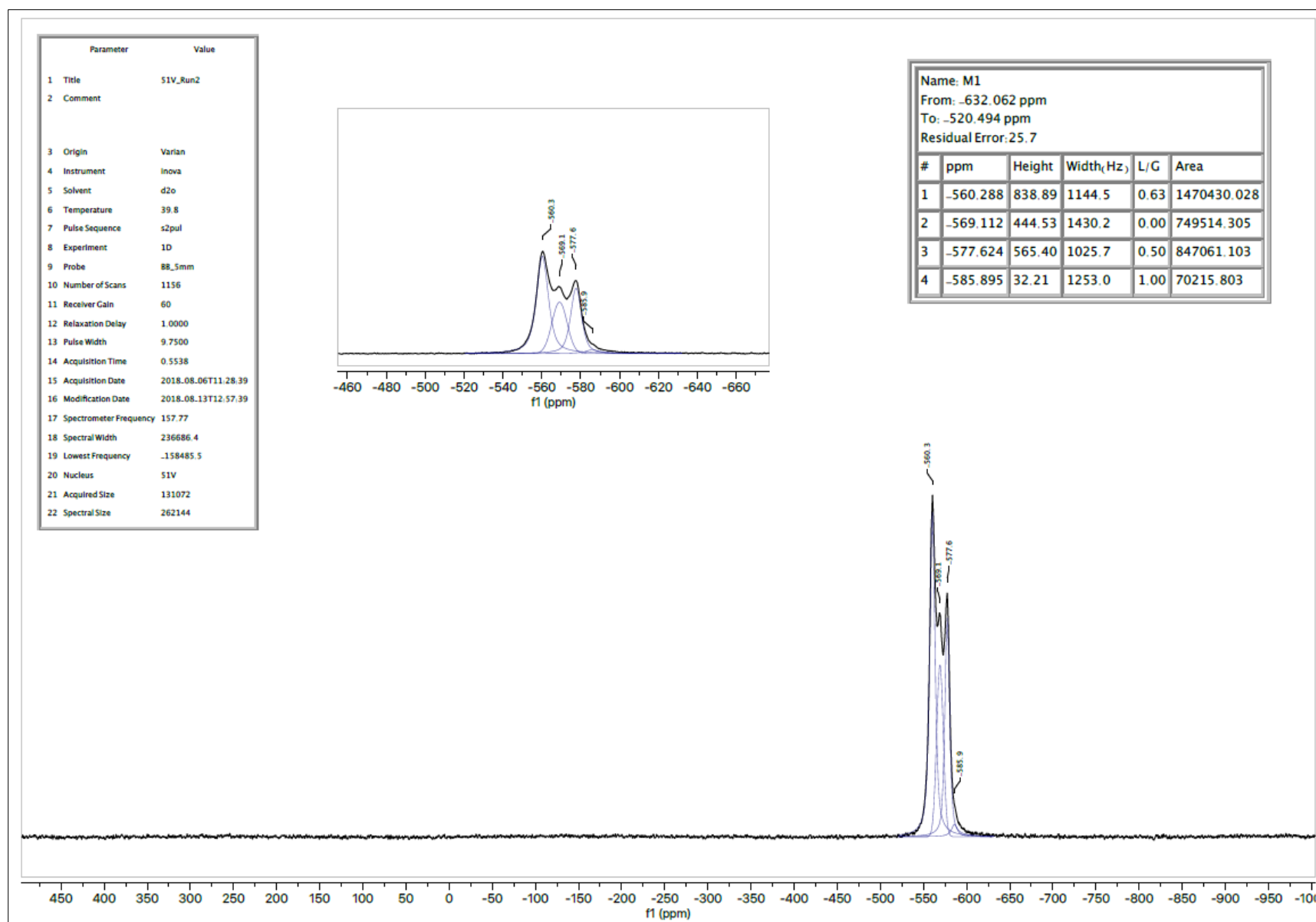


Figure C-2: Solution 2 vanadium 5+ spectra after the experiment

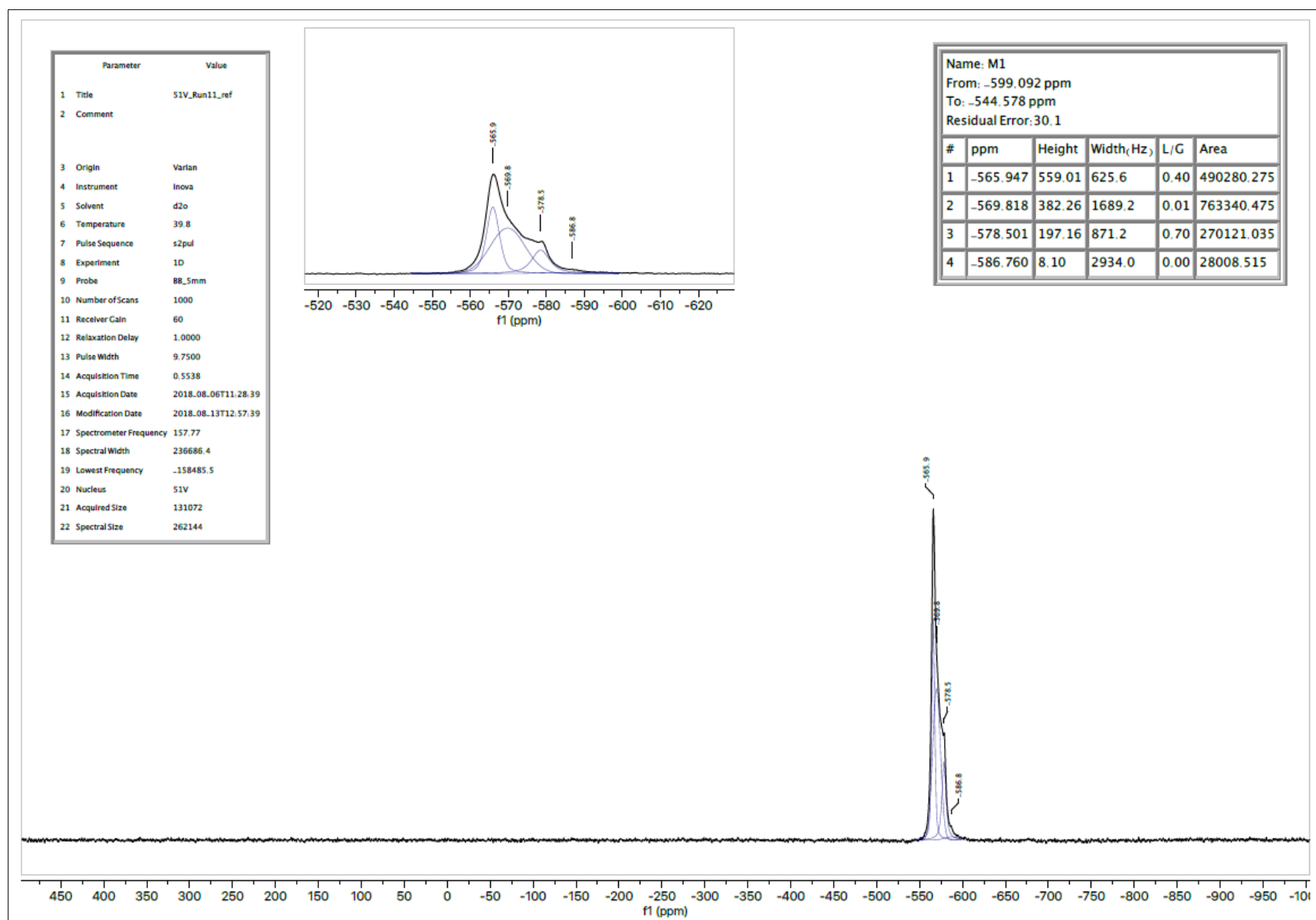


Figure C-3: Solution 5 vanadium 5+ spectra before the experiment

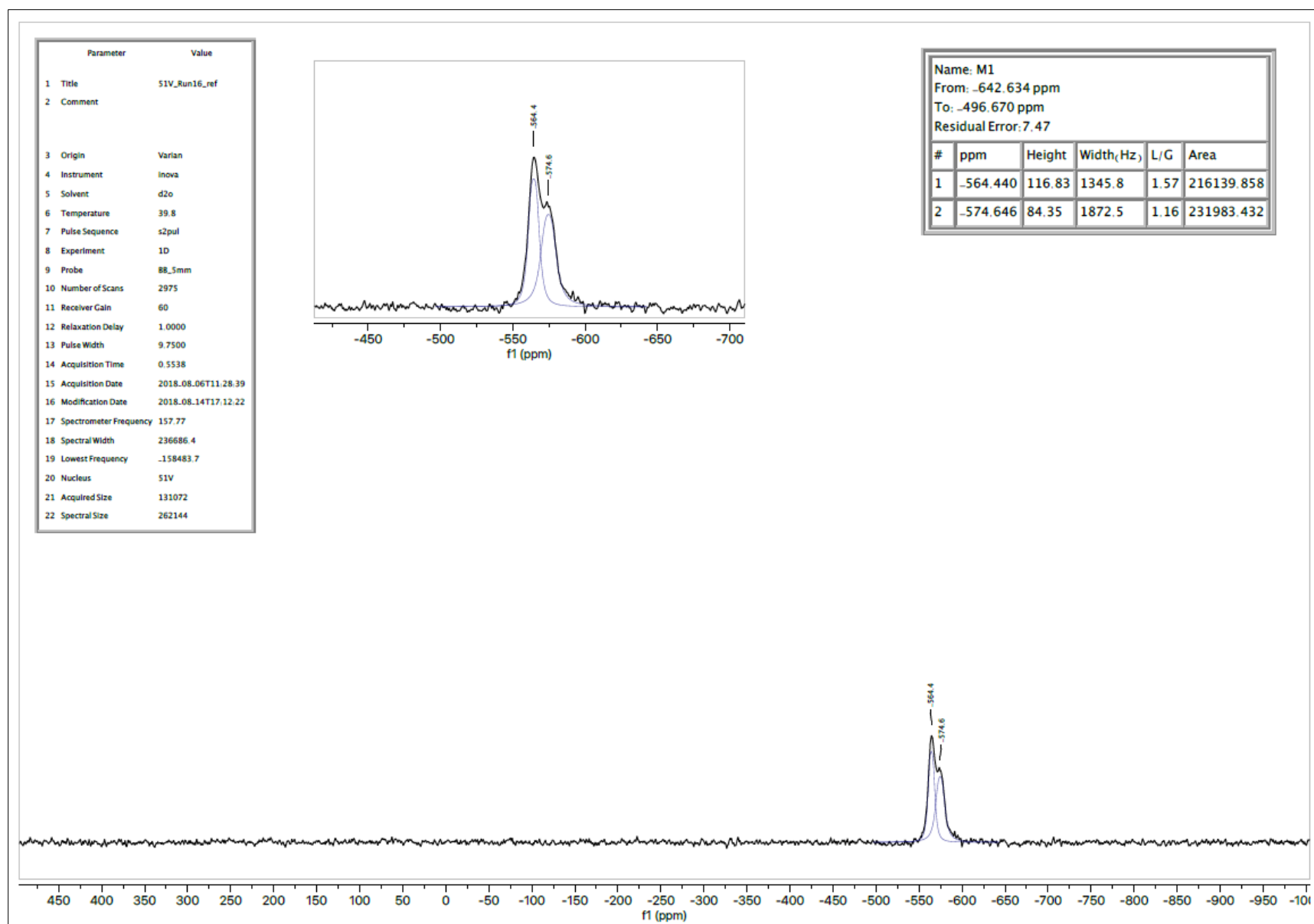
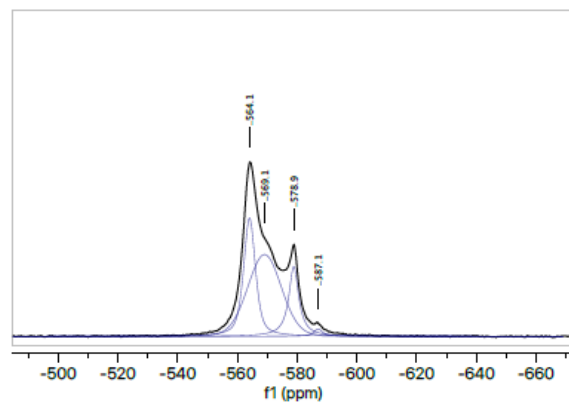


Figure C-4: Solution 5 vanadium 5+ spectra after the experiment

Parameter	Value
1 Title	S1V_Run13_ref
2 Comment	
3 Origin	Varian
4 Instrument	Inova
5 Solvent	d2o
6 Temperature	39.8
7 Pulse Sequence	s2pul
8 Experiment	1D
9 Probe	88_5mm
10 Number of Scans	1200
11 Receiver Gain	60
12 Relaxation Delay	1.0000
13 Pulse Width	9.7500
14 Acquisition Time	0.5538
15 Acquisition Date	2018.08.06T11:28:39
16 Modification Date	2018.08.14T15:10:03
17 Spectrometer Frequency	157.77
18 Spectral Width	236686.4
19 Lowest Frequency	-158483.7
20 Nucleus	51V
21 Acquired Size	131072
22 Spectral Size	262144



Name: M1
From: -669.093 ppm
To: -477.707 ppm
Residual Error: 19.5

#	ppm	Height	Width (Hz)	L/G	Area
1	-564.058	796.53	721.8	0.55	854991.975
2	-569.086	549.89	2084.4	0.11	1420649.667
3	-578.872	470.00	611.7	1.00	500195.388
4	-587.055	49.22	548.2	1.00	46947.346

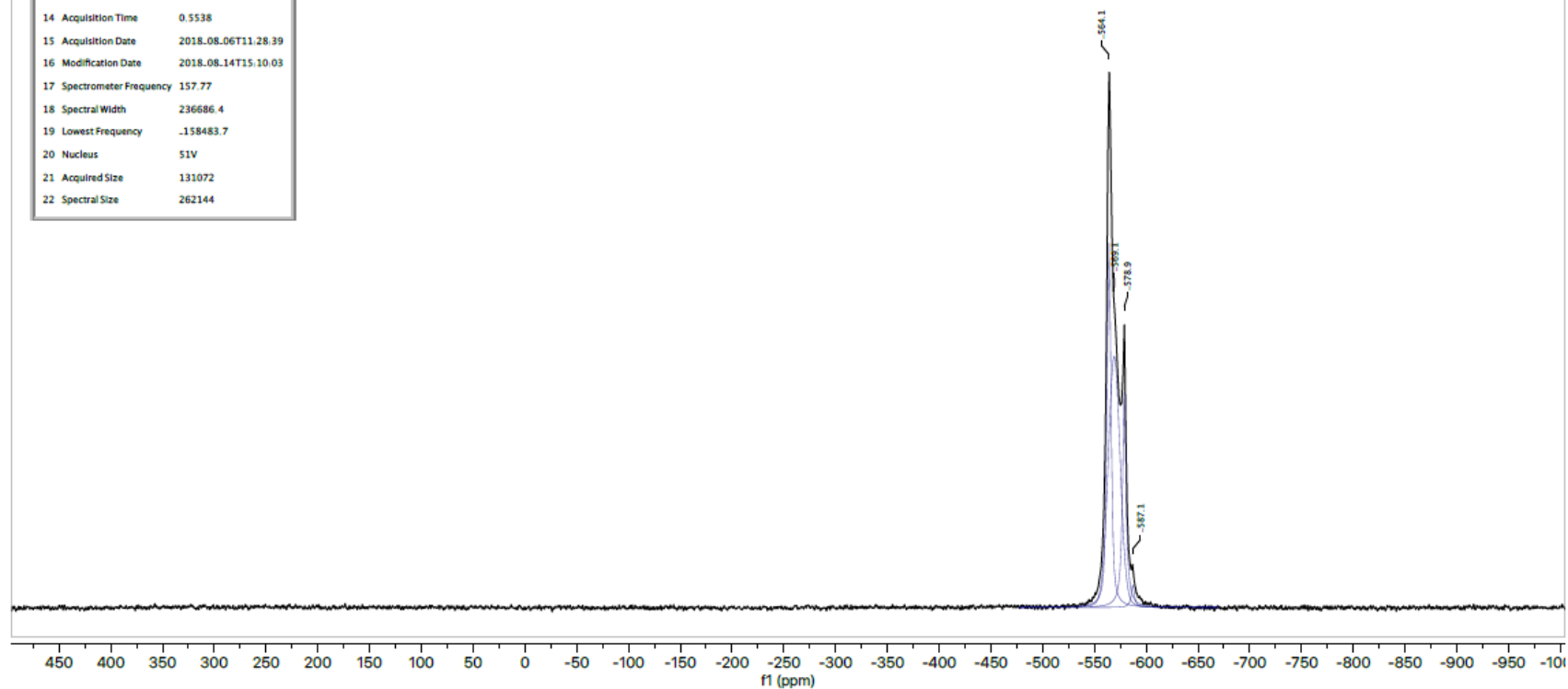


Figure C-5: Solution 6 vanadium 5+ spectra before the experiment

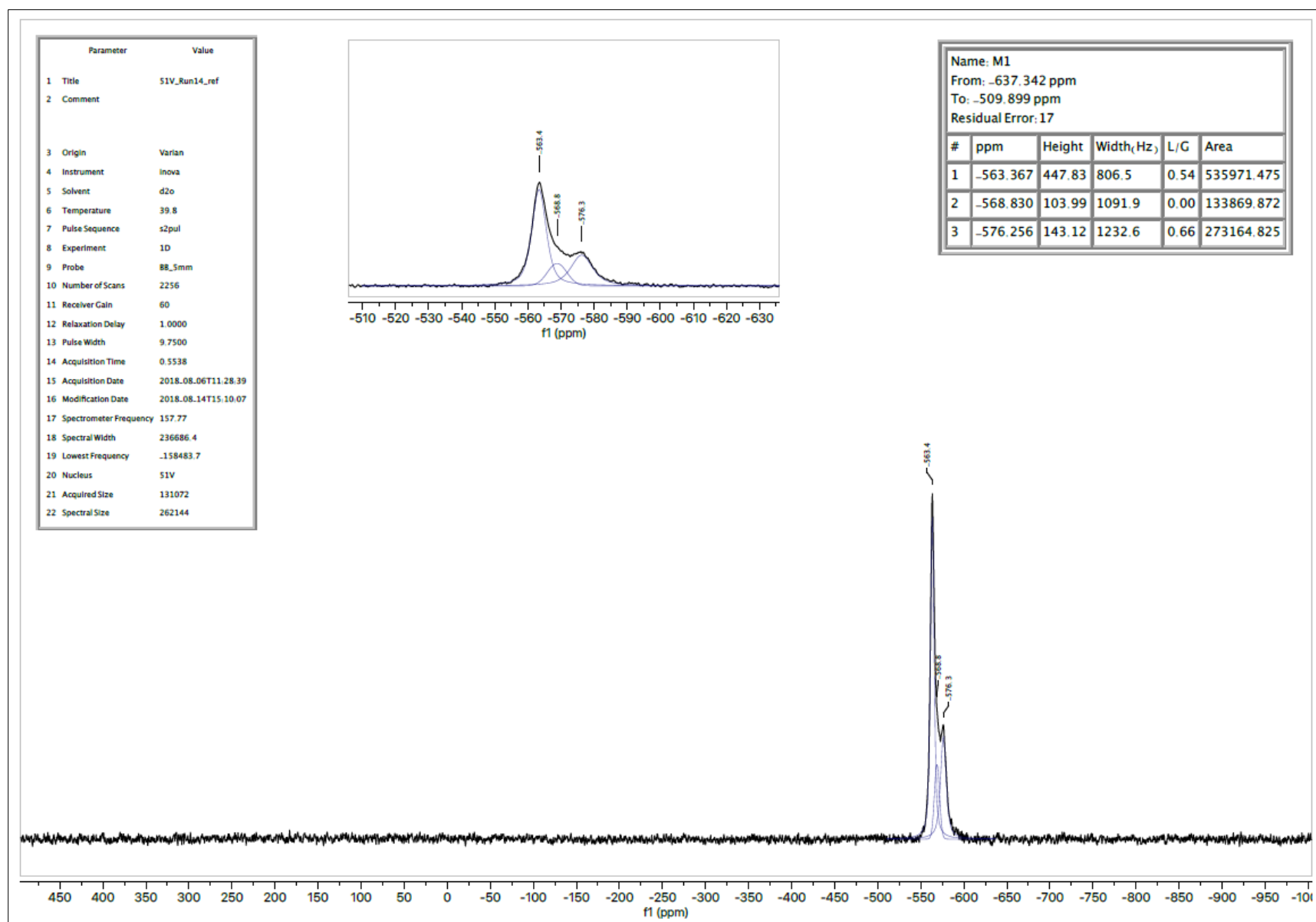


Figure C-6: Solution 6 vanadium 5+ spectra after the experiment

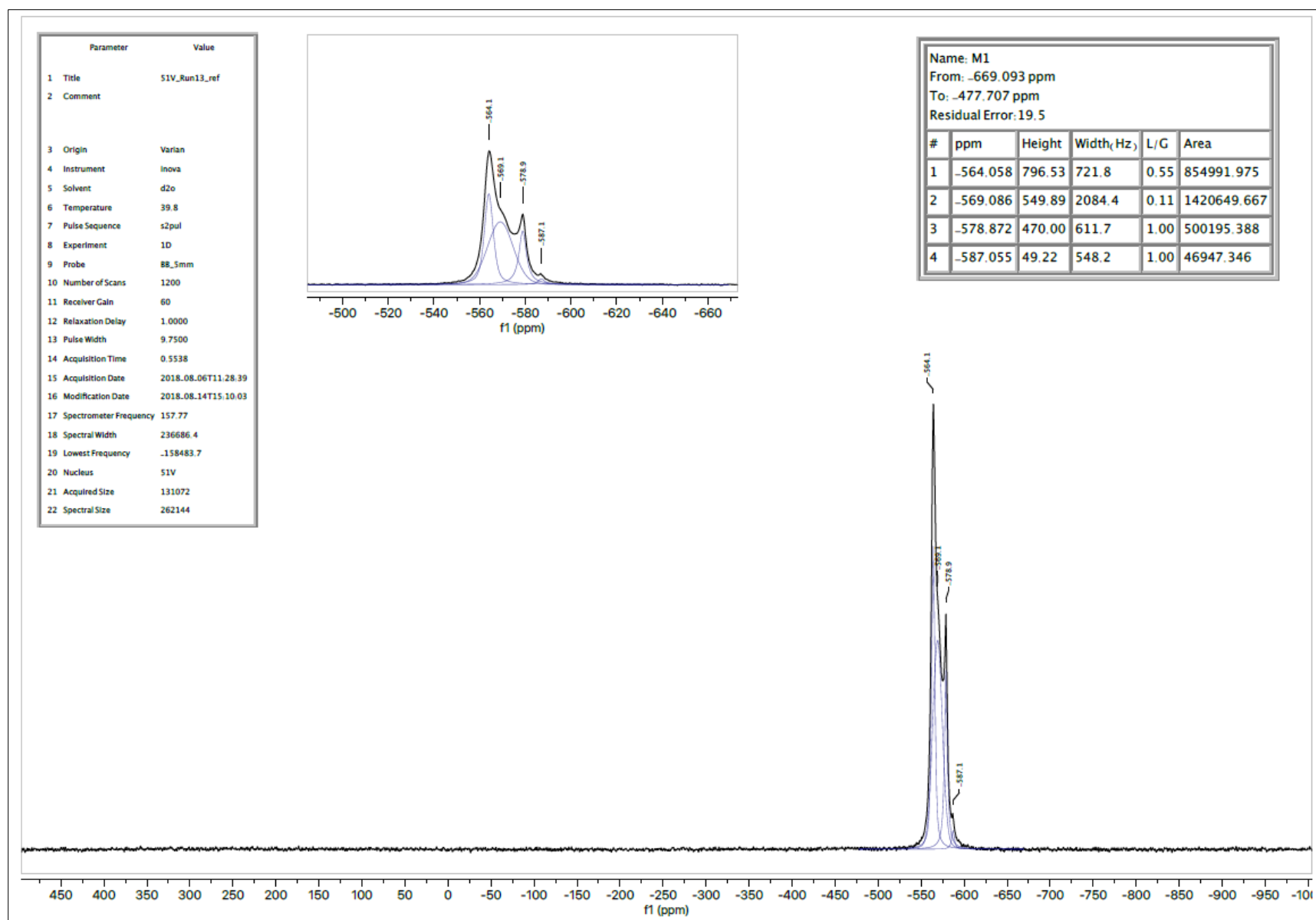


Figure C-7: Solution 7 vanadium 5+ spectra before the experiment

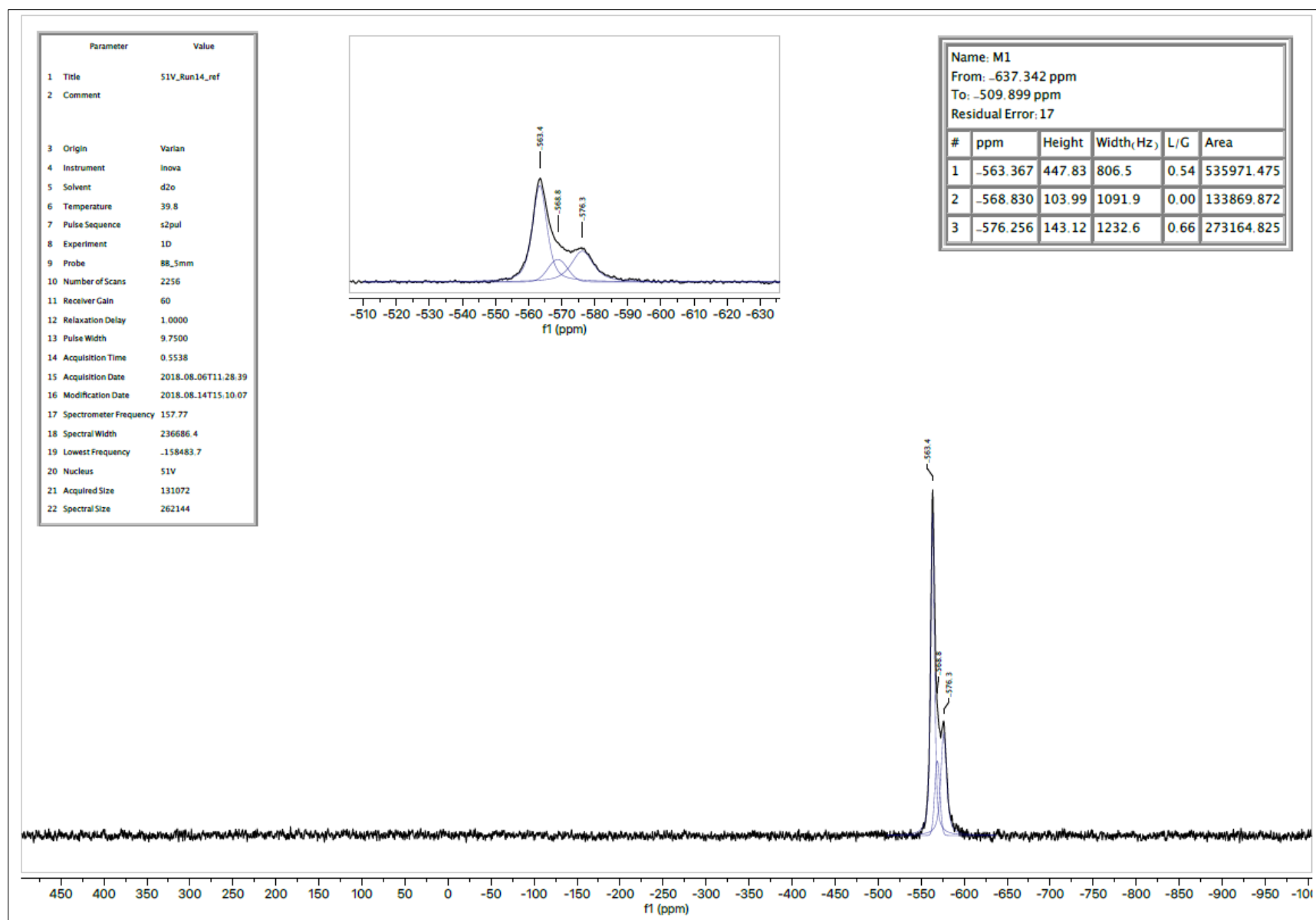


Figure C-8: Solution 7 vanadium 5+ spectra after the experiment

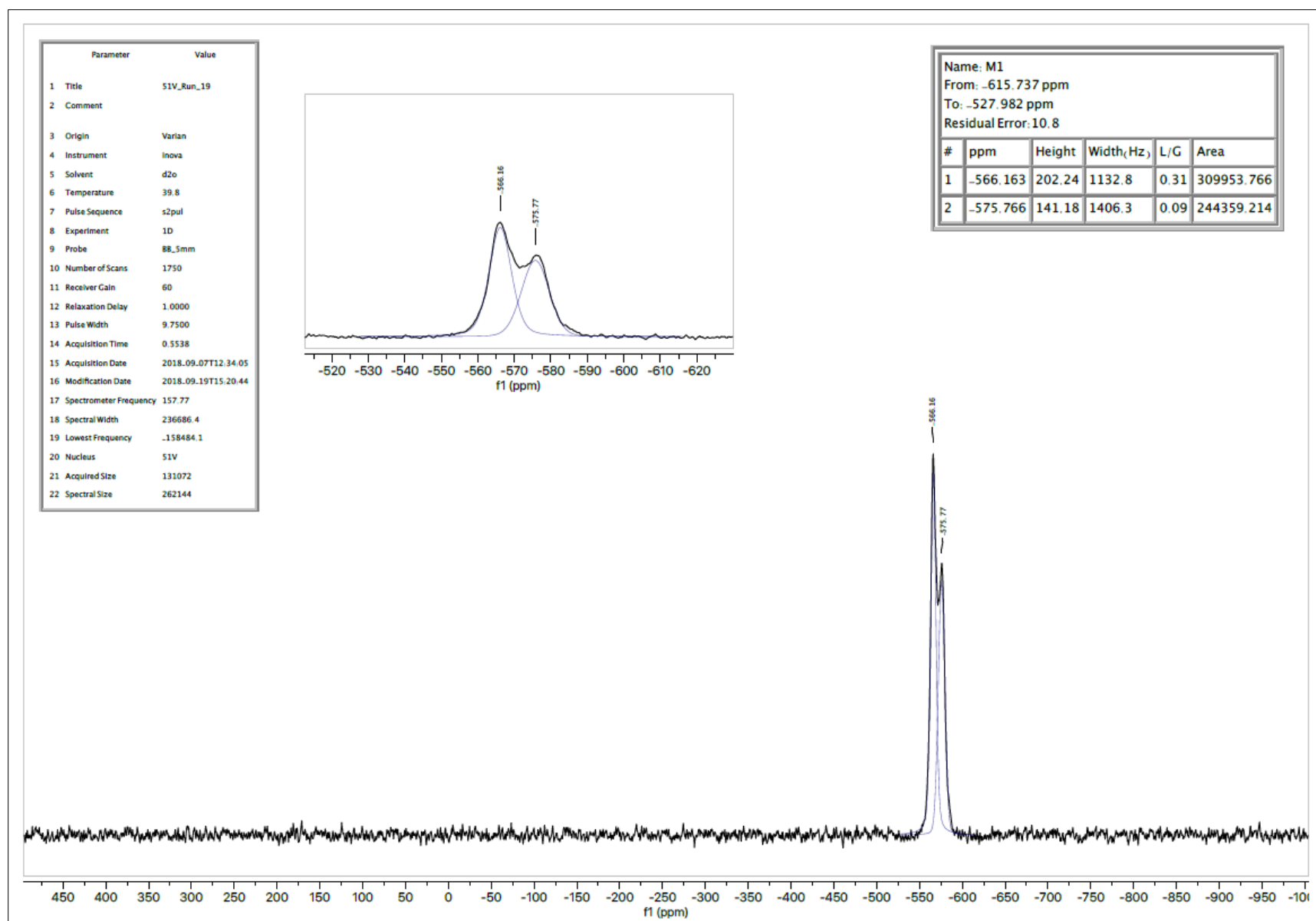


Figure C-9: Solution 8 vanadium 5+ spectra before the experiment

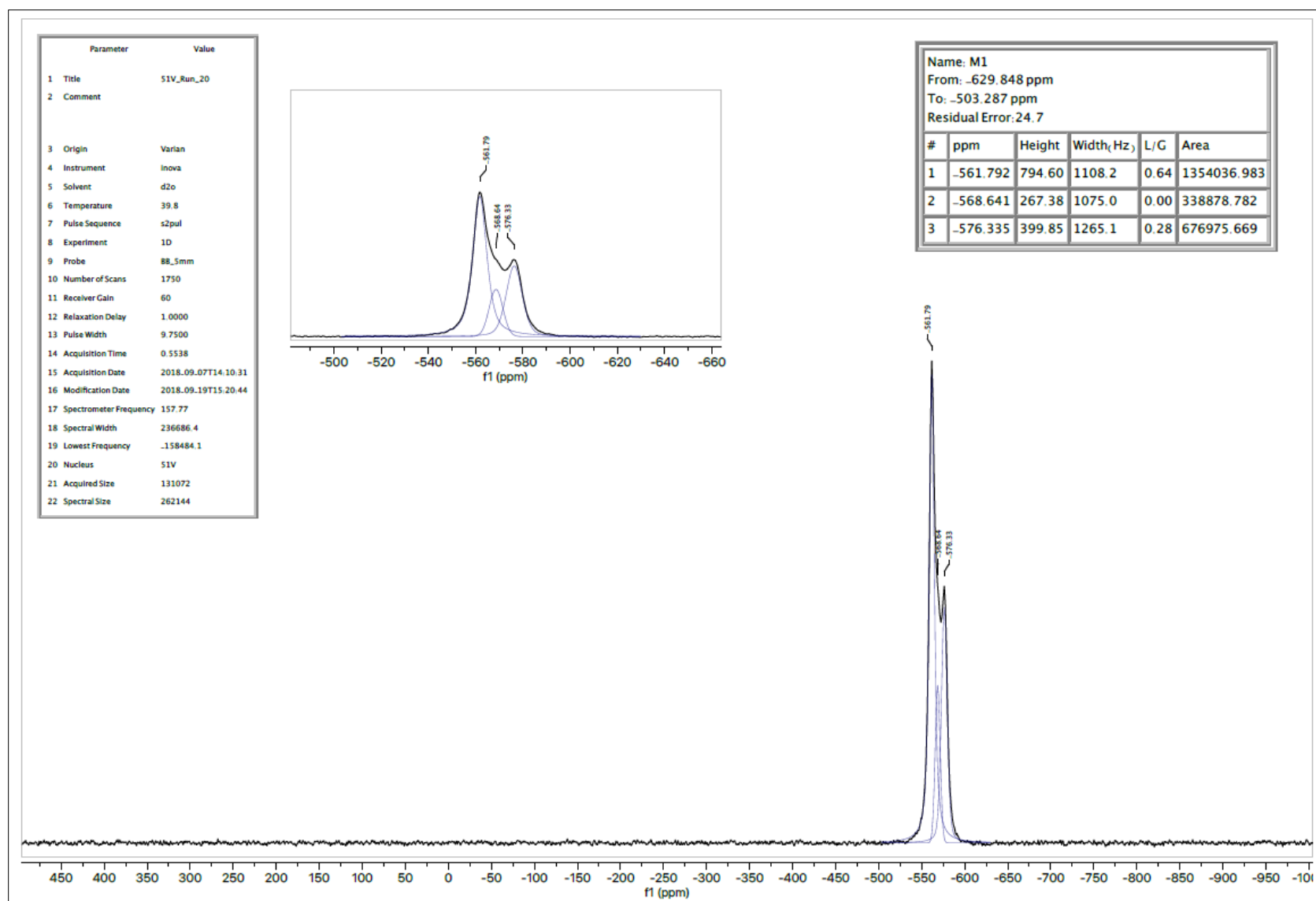


Figure C-10: Solution 8 vanadium 5+ spectra after the experiment

APPENDIX D: Effect of vanadium oxidation states on H₂S conversion to elemental sulphur with Na₂[ADA]

A. Stretford™ aqueous solutions characterization before experiments

Physical appearance

Figure D1 shows the appearance of the synthetic Stretford™ aqueous solutions at the different V⁵⁺ to V⁴⁺ molar ratios. The concentration of 0.029 mol.dm⁻³ of V⁵⁺ was selected to vary molar ratios of V⁵⁺ to V⁴⁺. As more V⁴⁺ was added with reduction in V⁵⁺ the solutions changes from light grey to dark-grey/blue colour as shown in Figure D-1. Solution D-4 that had 100% of V⁴⁺ added was not as dark-grey/blue as Solution D-3 that had 60% of V⁴⁺ added. This was a confirmation of interaction between V⁵⁺ and V⁴⁺ which form sparingly soluble isopolyanions (V₄O₉²⁻) that give a deep dark-grey/blue colour, (Walker, T.A., (1983), Ducret, L., (1951), Lannuzzi, M.M., et al (1975)). V⁴⁺ solution give blues colour when dissolved in water while V⁵⁺ gives light yellow colour when dissolved in water, (Kelsall, G.H., et al. (1993)).

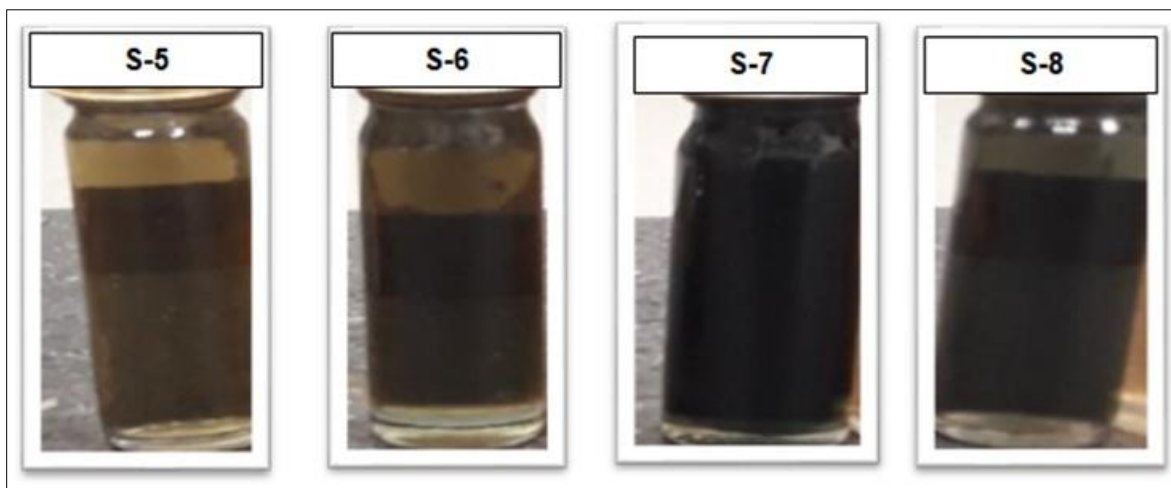


Figure D1: Stretford™ aqueous solutions' appearance at different V⁵⁺ to V⁴⁺ molar ratios.

Stretford™ aqueous solutions results

Table D1 details the chemical results of the synthetic Stretford™ aqueous solutions at a different V⁵⁺ to V⁴⁺ molar ratios. The concentrations of V⁵⁺ in Solutions D-5 and D-6 were close to the concentrations of total vanadium. However, there was a big gap between total vanadium and V⁵⁺ concentration in Solutions D-3 and D-4. The total vanadium concentration in all four Stretford™ aqueous solutions was within the same range. There was low concentrations of V⁴⁺ in Solutions D-1 and D-2 but high concentration of V⁴⁺ in Solutions D-3 and D-4. The results confirm the observation in Figure D1 that as the concentration of V⁴⁺ increased the solutions changes from orange to dark-blue/grey. Some of the V⁴⁺ added started to oxidized to V⁵⁺ in Solution D-4. There

was no V^{5+} added in Solution D-4 but the results shows $0.007 \text{ mol.dm}^{-3}$ of V^{5+} species. The oxidation of V^{4+} to V^{5+} was expected with the solutions prepared under atmospheric condition. The rate of oxidation of V^{4+} to V^{5+} by dissolved oxygen was increased by the presence of $\text{Na}_2[\text{ADA}]$ as discussed in Chapter 2, (Gary, J., (2005)).

Table D1: StretfordTM aqueous solutions parameters in the presence of $\text{Na}_2[\text{ADA}]$

Solution	Chemical analysis (mol.dm^{-3})							pH
	V^{Total}	V^{5+}	V^{4+}	$\text{Na}_2[\text{ADA}]$	Na_2SO_4	NaSCN	TA	
D-1	0.029	0.029	0.001	0.001	0.49	0.86	0.17	8.28
D-2	0.029	0.027	0.002	0.001	0.49	0.87	0.17	8.29
D-3	0.029	0.012	0.015	0.001	0.50	0.86	0.15	8.33
D-4	0.029	0.007	0.020	0.001	0.48	0.88	0.17	8.32

StretfordTM aqueous solution $^{51}\text{VNMR}$ results

Table D2 outline the chemical shifts and heights of the V^{5+} species for Solutions D-1 to D-2. There were four different V^{5+} species that were identified by $^{51}\text{VNMR}$ results which are dimer ($\text{V}_2\text{O}_7^{4-}$), pentamer ($\text{V}_4\text{O}_{15}^{5-}$), cyclic tetramer ($\text{V}_4\text{O}_{12}^{4-}$) and hexamer ($\text{V}_6\text{O}_{17}^{4-}$). The dimer, pentamer, cyclic tetramer and hexamer resonated at -563, -570, -578 and -586 ppm. The dimer heights in Solutions D-1, D-2, D-3 and D-4 were 805, 737, 230 and 128 respectively. The pentamer heights in Solutions D-1, D-2 and D-3 were 553, 379 and 246. The cyclic tetramer heights were 581, 399, 125 and 101. The heights of the three dominant V^{5+} species (dimer, pentamer and tetramer) in Solutions D-1, D-2, D-3 and D-4 were getting smaller as the concentration of V^{5+} added was getting less with simultaneous increase in V^{4+} concentration. The results in Table D2 are in agreement with the V^{5+} results discussed in Table D1. The decrease in heights was an indication of decrease in V^{5+} concentration.

Table D2: V^{5+} species at variable V^{5+} to V^{4+} molar ratios in the presence of $\text{Na}_2[\text{ADA}]$

Solution	Resonance	V^{5+} species			
		$\text{V}_2\text{O}_7^{4-}$	$\text{V}_4\text{O}_{13}^{5-}$	$\text{V}_4\text{O}_{12}^{4-}$	$\text{V}_6\text{O}_{17}^{4-}$
D-1	Peak (ppm)	-563	-570	-578	-586
	Height	805	443	581	44
D-2	Peak (ppm)	-564	-570	-578	-585
	Height	737	379	399	22
D-3	Peak (ppm)	-565	-568	-577	-
	Height	230	246	125	-
D-4	Peak (ppm)	-567	-	-575	-
	Height	128	-	101	-

B. Stretford™ aqueous solutions characterization after experiments

Physical appearance

Figure D2 shows the Stretford™ circulation solutions appearance after the experiments. The Stretford™ circulation Solutions D-1, D-2, D-3 and D-4 indicate the present of V^{4+} species before the experiments as indicated in Section A. After the experiments all Stretford™ circulation solutions changed colour to orange which indicate vanadium at its highest oxidation state (V^{5+}). Even Solution D-4 that did not contain SAV which is a source of V^{5+} in the beginning change colour from blue to orange. The colour change to orange was a confirmation that V^{4+} was oxidised to V^{5+} by dissolved oxygen.

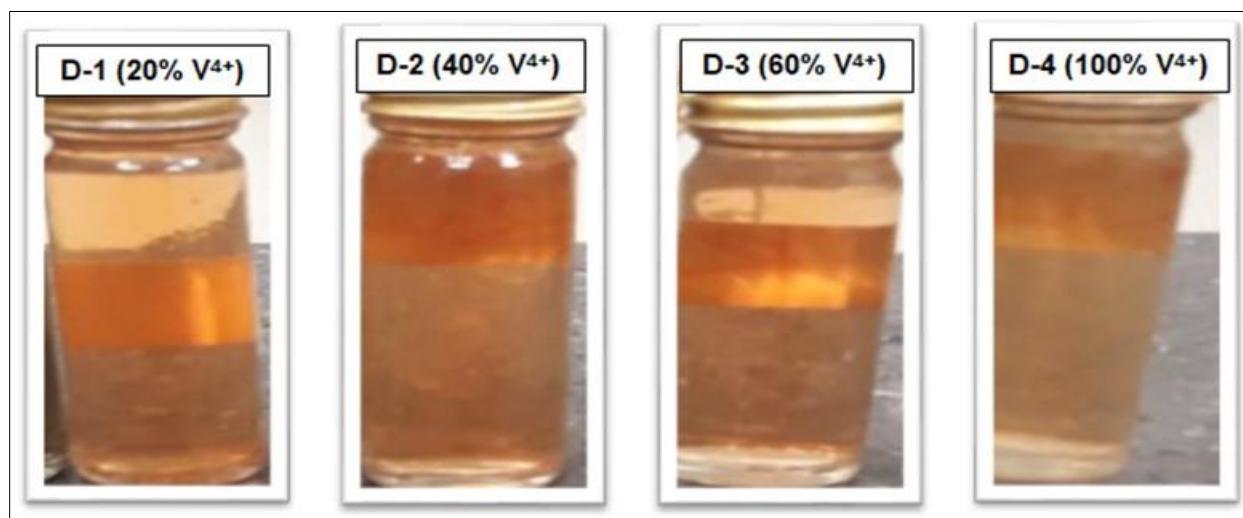


Figure D2: Stretford™ circulation solutions at variable V^{5+} to V^{4+} molar ratios with $Na_2[ADA]$ added

Note: V^{5+} : V^{4+} molar ratios, D-1 (80%:20%); D-2 (60%:40%); D-3 (20%:80%); D-4 (0%:100%)

Stretford™ circulation solutions results

Table D3 shows fixed concentrations and pHs of the Stretford™ circulation Solutions D-1, D-2, D-3 and D-4. The concentrations of $Na_2[ADA]$, $NaSCN$, Na_2SO_4 and total alkalinity after experiments were similar to the concentrations before experiments. The concentrations of total vanadium and V^{5+} are shown in Figure D3.

Table D3: Stretford™ circulation results at variable V^{5+} to V^{4+} molar ratios

Solution	mol.dm ⁻³					pH
	$Na_2[ADA]$	$NaSCN$	Na_2SO_4	TA	V^{4+}	
D-1	0.001	0.86	0.50	0.16	0.0001	8.32
D-2	0.001	0.86	0.49	0.17	0.0001	8.33
D-3	0.001	0.85	0.50	0.16	0.0001	8.30
D-4	0.001	0.89	0.49	0.17	0.0001	8.31

Figure D3 summarizes the average concentrations of total vanadium and V^{5+} for Solutions D-1 to D-4. The concentrations of V^{5+} after the experiments were almost equal to the concentrations of the total vanadium. Almost all V^{4+} species added in Solution D-1 oxidized to V^{5+} species before the experiment. The observation indicates that the oxidation of 20% of V^{4+} occurred during solution preparation. However, when the concentration of V^{4+} was increased to 40, 60 and 100% the concentrations of V^{4+} were 0.0018, 0.0153 and 0.0204 mol.dm⁻³ respectively. After the experiments the concentrations of V^{4+} in Solutions D-2, D-3 and D-4 were reduced to 0.0001 mol.dm⁻³ while V^{5+} concentrations increased to 0.029 mol.dm⁻³. The observation indicated V^{4+} oxidized to V^{5+} during experiments. The oxidation of V^{4+} to V^{5+} was catalyzed by the organic isomer Na₂[ADA] which acts as an oxidizing agent, (Zwicky, J.F., et al. (1980), Moyes, A.J., et al. (1973A), Trofe, T.W., et al (1993)). The Na₂[ADA] plays a very crucial role in maintaining the stability of total vanadium and prevent vanadium precipitation which confirm what has been reported by the literature as the role of Na₂[ADA], (Carpentier, W., et al. (2003), Trofe, T.W., et al. (1993)).

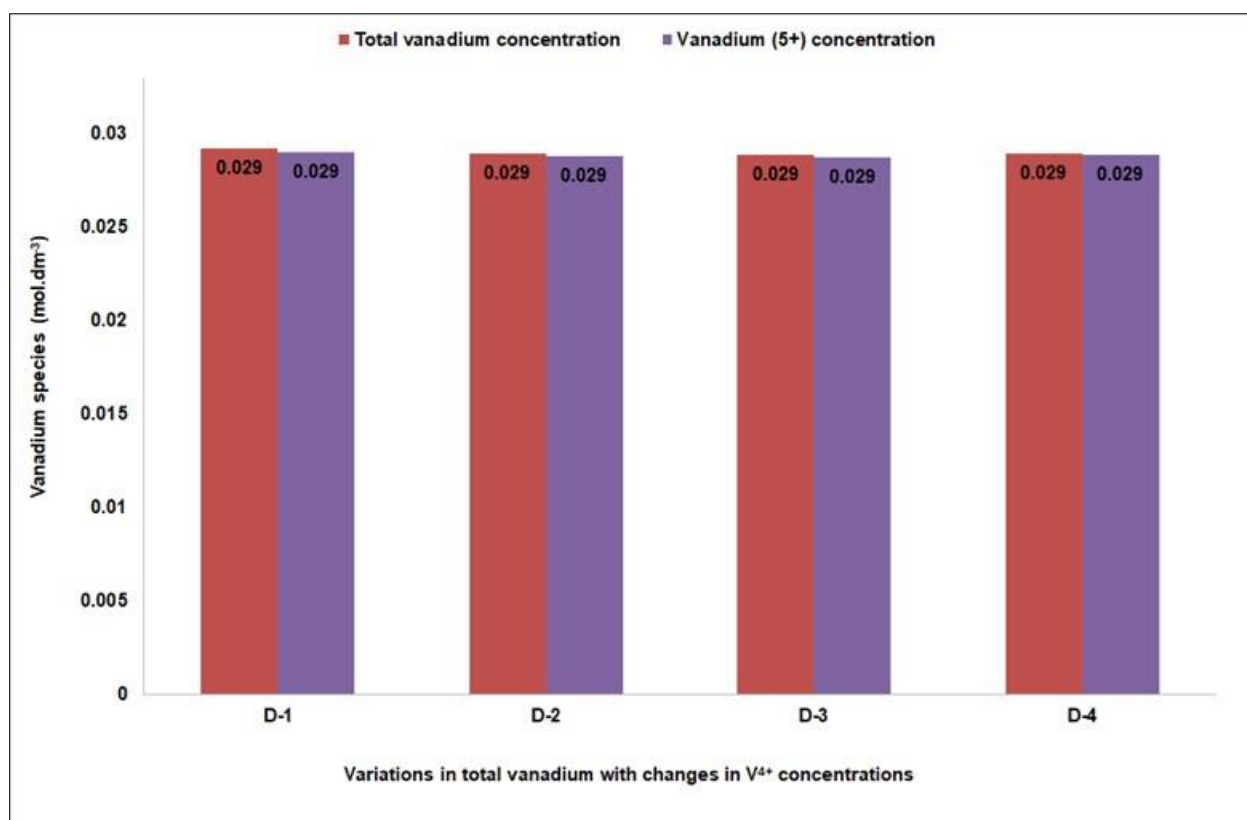


Figure D3: Variation in total vanadium and V^{5+} with changes in V^{4+} concentrations with Na₂[ADA] added

⁵¹V NMR results after experiments

Table D4 shows the summary of chemical shifts and heights of the V⁵⁺ species for Solutions D-1 to D-4. The similar V⁵⁺ species (dimer, tetramer, pentamer and hexamer) identified before experiments were also identified after the experiments with almost similar chemical shifts. The heights of the different V⁵⁺ species were getting smaller when VOSO₄ was increased before experiments. However, after the experiments the heights of the V⁵⁺ species for Solutions D-2, D-3 and D-4 were higher than before experiments. The increase in height was a confirmation that V⁴⁺ did oxidized to V⁵⁺.

Table D4: V⁵⁺ species chemical shifts

Solution	Resonances	V ⁵⁺ species			
		V ₂ O ₇ ³⁻	V ₄ O ₁₃ ⁵⁻	V ₄ O ₁₂ ⁴⁻	V ₆ O ₁₇ ⁴⁻
D-1	Peak (ppm)	-560	-569	-578	-
	Height	735	350	466	-
D-2	Peak (ppm)	-562	-569	-578	-586
	Height	803	397	405	42
D-3	Peak (ppm)	-558	-568	-577	-
	Height	577	232	281	-
D-4	Peak (ppm)	-559	-568	-577	-
	Height	551	237	287	-

C. Effect of vanadium oxidation states on H₂S conversion to elemental sulphur

H₂S absorption and elemental sulphur production

Figure D4 shows H₂S absorbed and elemental sulphur produced in Solutions D-1, D-2, D-3 and D-4 with Na₂[ADA] added. The absorbed H₂S gas in all solutions was between 97.3 and 99.5%. The low H₂S gas absorption in Solutions D-3 and D-4 compared to Solutions D-1 and D-2 was not as significant as the drop in elemental sulphur produced. The elemental sulphur produced in Solutions D-1 and D-2 was within similar range at 0.860 and 0.858 mol respectively. However, there was a downward step change in elemental sulphur produced in Solutions D-3 and D-4. The step change in elemental sulphur production in Solutions D-3 (0.812 mol) and D-4 (0.786 mol) correlate with the step changes of V⁵⁺ concentrations before the experiments. The elemental sulphur production reduced as the V⁵⁺ to V⁴⁺ molar ratios decreased. This was a confirmation of the literature on the role of V⁵⁺ during H₂S gas absorption and HS⁻ conversion to elemental sulphur, (Fenton, D.M., et al. (1979), Keene, D.E., (1992)). The minimal drop of H₂S absorption

in Solutions D-3 and D-4 was due to low initial V^{5+} concentrations. The H_2S gas absorption and dissociation is dependent on the pH of the StretfordTM aqueous solution, (Rice, E.W., et al. (2012), Carter, C.N., (1966)). The role of V^{5+} is to shift the equilibrium condition by oxidizing HS^- to elemental sulphur, (Scheffel, F.A., et al. (1986)). The H_2S gas was detected by the H_2S gas monitor on top of the oxidizing and balance tanks during the first 15 - 50 minutes in Solutions D-3 and D-4. That was an indication of H_2S gas absorbed in StretfordTM aqueous solution but not converted to elemental sulphur due to low V^{5+} to V^{4+} molar ratios in the beginning of the experiments.

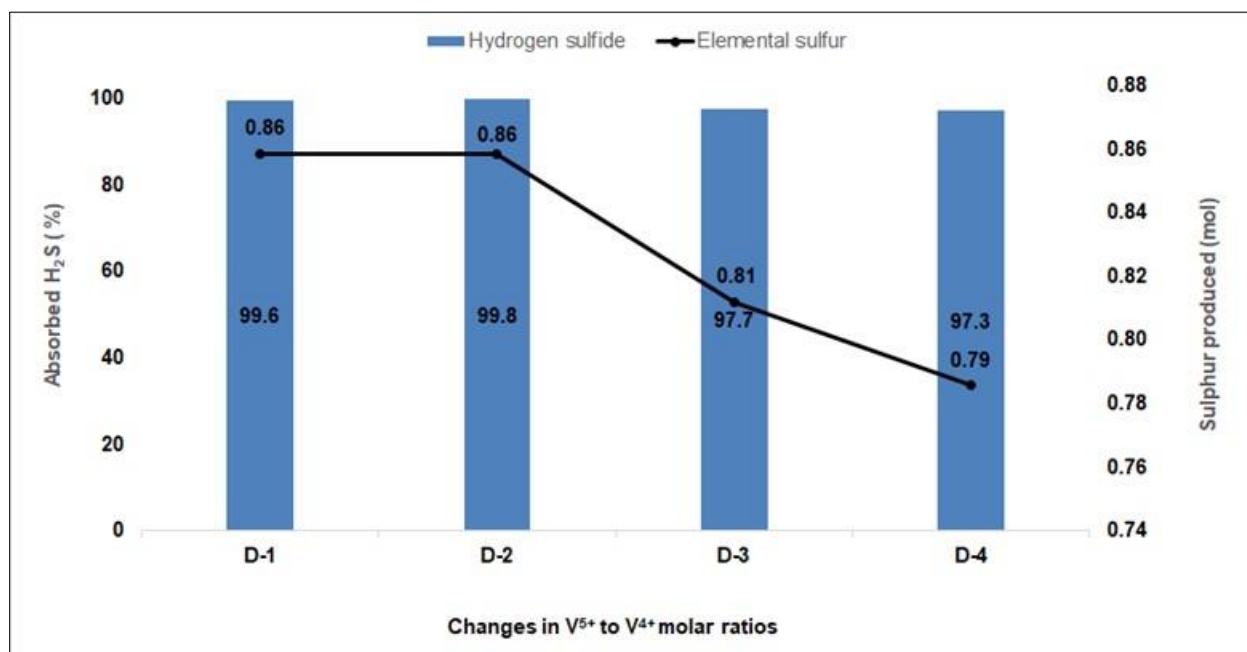


Figure D4: H_2S conversion to elemental sulphur at different V^{5+} to V^{4+} molar ratios

Figure D5 display the PSDs' of the elemental sulphur produced in Solutions D-1, D-2, D-3 and D-4. The PSD's of elemental sulphur produced at V^{5+} to V^{4+} molar ratios were comparable to commercial PSD. The initial low V^{5+} to V^{4+} molar ratios did not affect the elemental sulphur particle sizes at the end of experiment but floatation and production. These results indicate that if there is V^{5+} in solution, the oxidation of HS^- to elemental sulphur does take place. The elemental sulphur particle sizes get affected during precipitation and crystallization process if there is excess vanadium or impurities as discussed in Chapter 4.

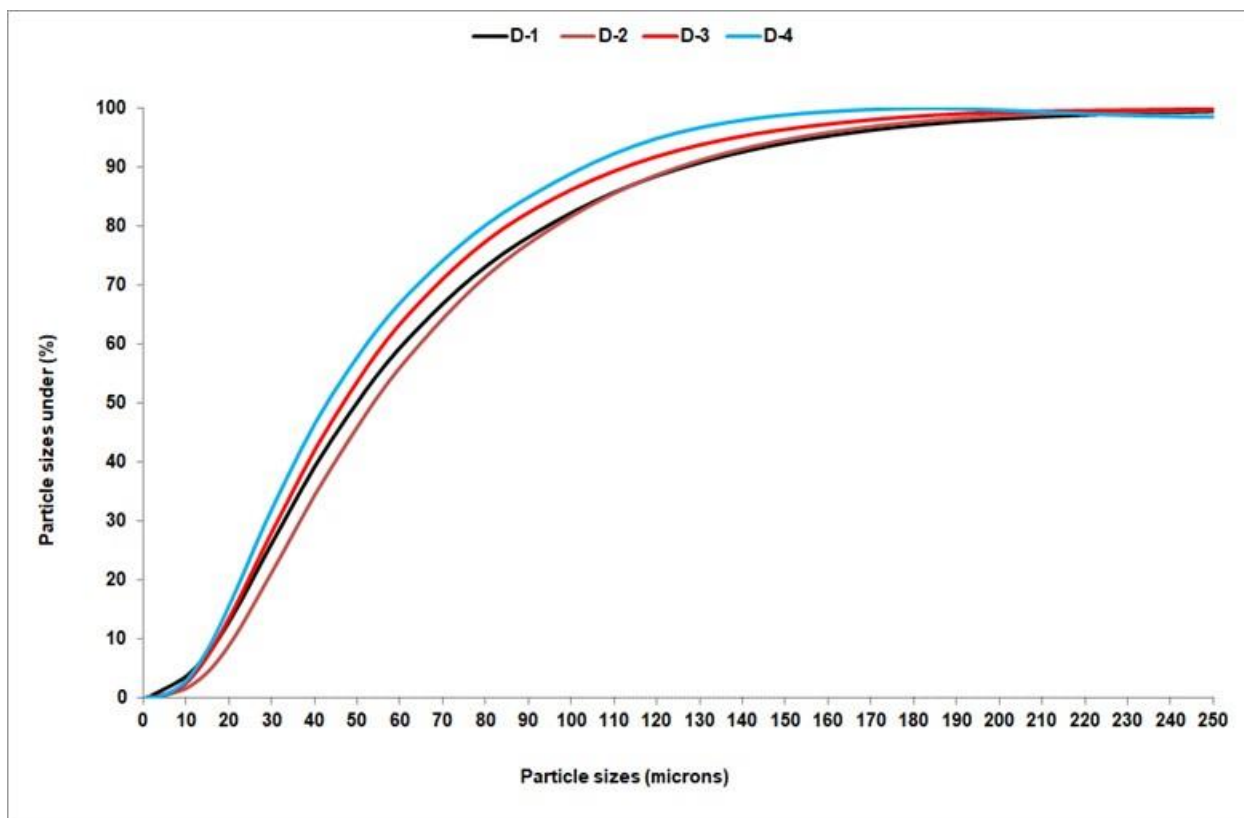


Figure D5: Elemental sulphur particles size at different V^{5+} to V^{4+} molar ratios with $Na_2[ADA]$

Figure D6 shows elemental sulphur samples shaken and picture was taken after five minutes. As the initial V^{5+} to V^{4+} molar ratios decreases the amount of sinking elemental sulphur increases as shown by Solutions D-3 and D-4. The sinking elemental sulphur was observed in the first 15-50 minutes of the experiments at the bottom of the balance drum while V^{5+} to V^{4+} molar ratios were low. However as the V^{5+} to V^{4+} molar ratios increases the conversion of HS^- to elemental sulphur increases. The low concentration of polysulphide delayed elemental sulphur crystallization and agglomeration process in the oxidizing tank to form a froth. The delayed crystallization and agglomeration led to small elemental sulphur particles overflowing to the balance tank which did not have air to assist with floating and formation of froath. However, the sinking elemental sulphur at the bottom of the balance tank did agglomerate to a coarse materials overtime.

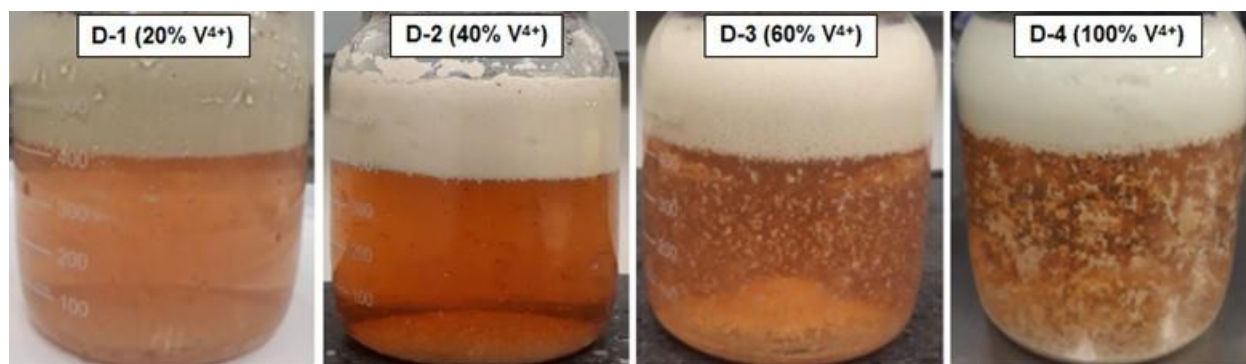


Figure D6: Sinking and floating sulphur slurry at variable V^{5+} to V^{4+} molar ratio with $Na_2[ADA]$ added

Elemental sulphur DSC results

Table D5 shows the melting and polymerization points of elemental sulphur. The results shows consistency with literature in terms of transition from orthorhombic to monoclinic, melting and polymerization points. The transition temperatures indicate only elemental sulphur ($\alpha-S_8$) was produced in all experiments. The small elemental sulphur particles that did float which are called “fine sulphur” were still crystalline orthorhombic ($\alpha-S_8$).

Table D5: Elemental sulphur transition temperatures with $Na_2[ADA]$ added

Transition temperature ($^{\circ}C$)	D-1	D-2	D-3	D-4
$\alpha-S_8 \rightarrow \beta-S_8$	113.2	114.2	112.5	113.8
Melting point	121.5	122.4	122.1	122.7
Polymerization	172.8	171.1	165.3	165.1

Elemental sulphur appearance

The colour of elemental sulphur produced in Solutions D-1 and D-2 was light yellow. However, the elemental sulphur produced in Solutions D-3 and D-4 gave a deep yellow colour as indicated in Figure D7. The colour difference is determined by level of impurities in the final product as reported not an indication of amorphous sulphur, (Holz B., et al (1988)).

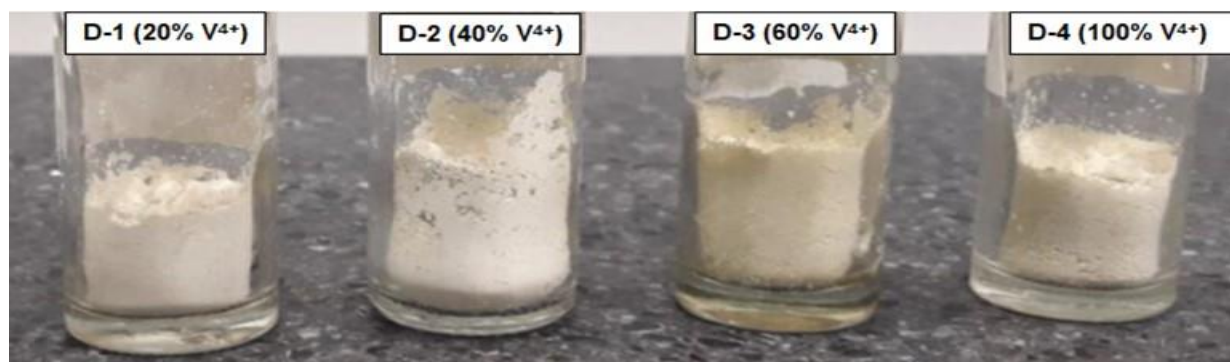


Figure D7: Elemental sulphur appearance at different V^{5+} to V^{4+} molar ratio with $Na_2[ADA]$

XRD results

Figure D8 shows diffractograms of elemental sulphur produced in Solutions D-1 to D-4. The XRD results shows 100% crystalline orthorhombic elemental sulphur. The result shows crystalline elemental sulphur was produced which is in agreement with DSC analysis discussed in Section C5. Even elemental sulphur produced in Solution D-4 which did not contain V^{5+} compound in the beginning produced crystalline elemental sulphur of good quality.

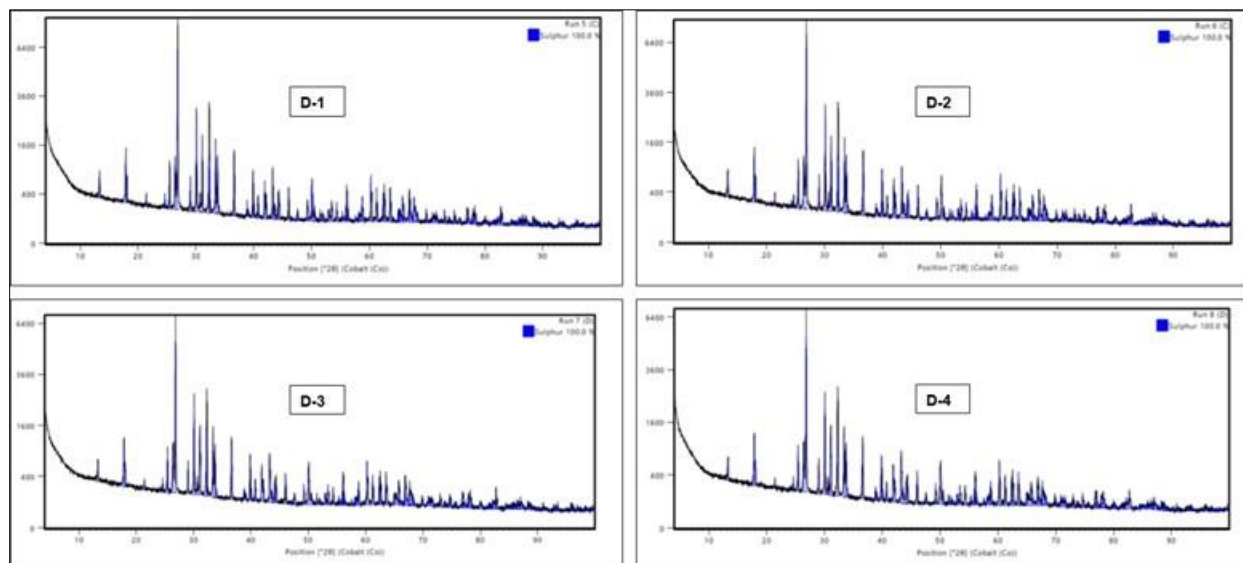


Figure D8: Elemental sulphur diffractograms at different V^{5+} to V^{4+} molar ratios with $Na_2[ADA]$

Elemental sulphur purity results

Table D6 shows purity of elemental sulphur results. The results shows as the V^{5+} to V^{4+} molar ratios reduces the purity of elemental sulphur increases. Elemental sulphur produced in Solution D-1 was following similar trend of elemental sulphur produced in Solutions 1, 2, 3 and 4 discussed in Chapter 4. However, from Solutions D-2 the purity of elemental sulphur increased to over 99.92%. These results confirms that impurities in SAV was the source of contamination of elemental sulphur. Elemental sulphur production was high when the SAV to $VOSO_4$ ratios (V^{5+} to V^{4+} molar ratios) was high. However the quality of elemental sulphur was high at the low SAV to $VOSO_4$ ratios. The high elemental sulphur quality was also observed on the colour of elemental sulphur that was changing to more yellowish as discussed in Figure D7.

Table D6: Elemental sulphur purity results

Composition	D-1	D-2	D-3	D-4
S (%)	95.8	99.92	99.97	99.98
Ash (%)	4.2	0.08	0.03	0.02

ICP-OES results

Table D7 shows chemical composition of ash. The ash content in elemental sulphur produced in Solution D-1 shows high concentrations of sodium, potassium, vanadium, silicon and iron. From Solutions D-2 the quality of elemental sulphur was almost similar. The results is a further confirmation that impurities in commercial SAV affected the quality of sulphur. All The concentrations of silicon, iron, sodium, potassium and vanadium were getting low as the SAV to VOSO₄ ratios were decreasing.

Table D7: Elemental sulphur purity results by ICP-OES

Chemical composition of ash (ppm)				
Elements	D-1	D-2	D-3	D-4
Si	67.7	48.7	44.9	37.25
Al	34.9	14.9	8.34	8.63
Fe	44.01	45.9	9.77	9.56
Ti	3.02	0.66	0.28	0.30
Ca	42.28	5.63	9.50	8.40
Mg	12.14	1.21	12.71	10.40
Na	13900	6.75	2.03	2.30
K	218.4	6.12	1.85	1.68
Mn	0.32	11.39	0.35	0.35
P	0.00	0.23	0.55	0.35
Ba	0.42	0.99	0.05	0.05
Cr	1.68	0.51	0.21	0.46
Cu	2.52	3.51	0.1	0.08
Ni	0.00	0.11	0.05	0.16
Pb	0.00	0.00	0.03	0.00
Sr	0.42	0.07	0.03	0.02
V	208.93	0.12	0.35	0.42
Z	0	0.49	0.21	0.16

APPENDIX E: DSC results

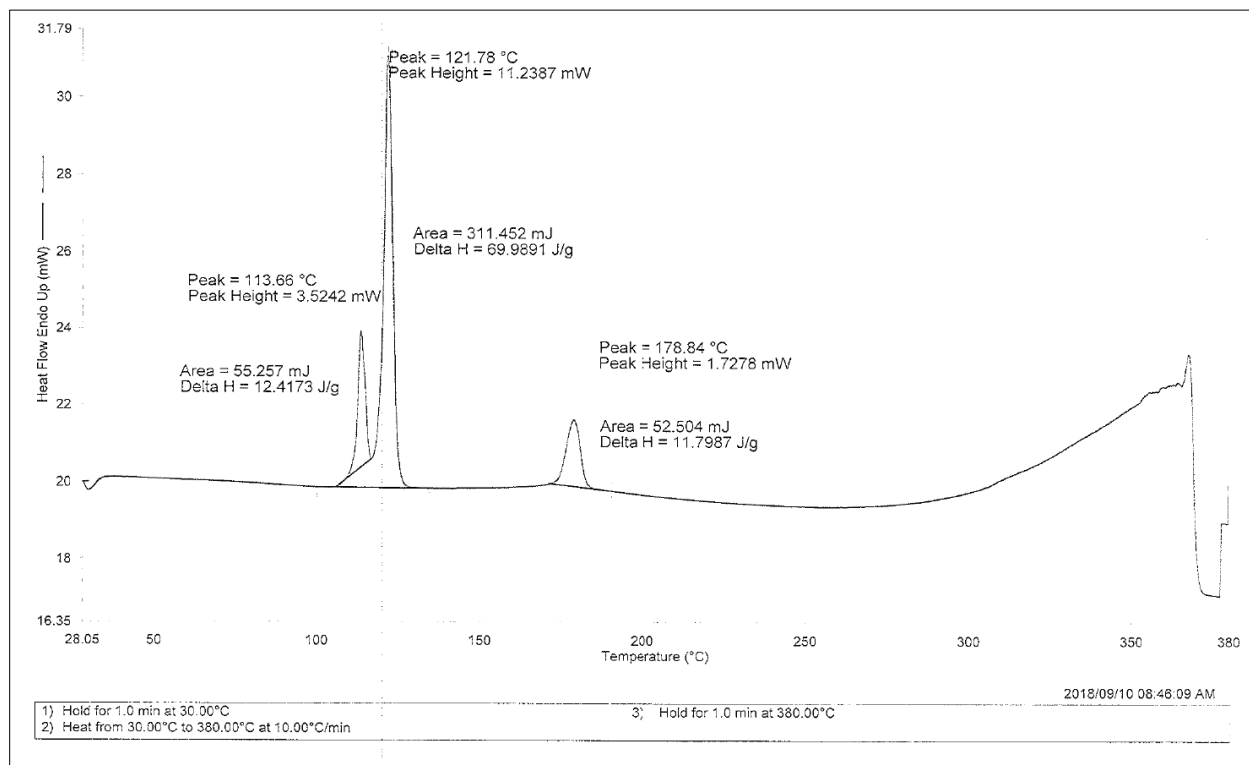


Figure E-1: Elemental sulphur melting and polymerization points for Solution 1

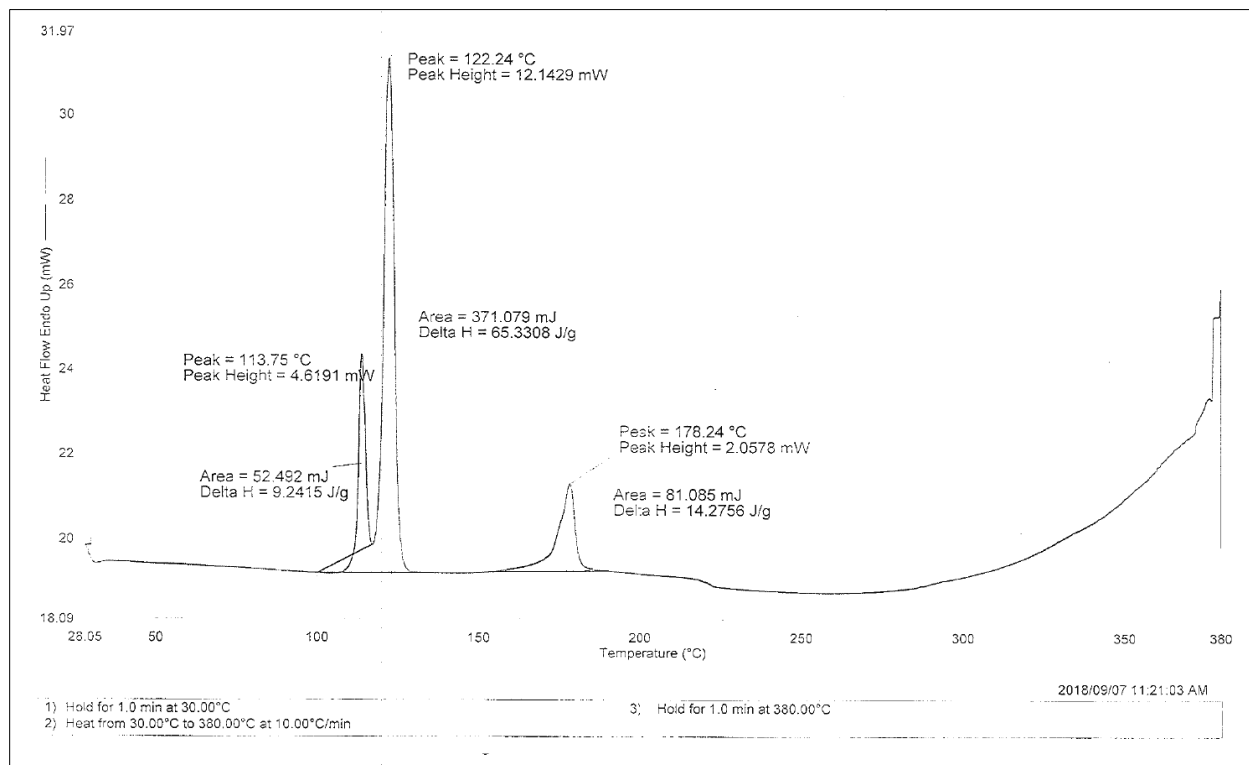


Figure E-2: Elemental sulphur melting and polymerization points for Solution 2

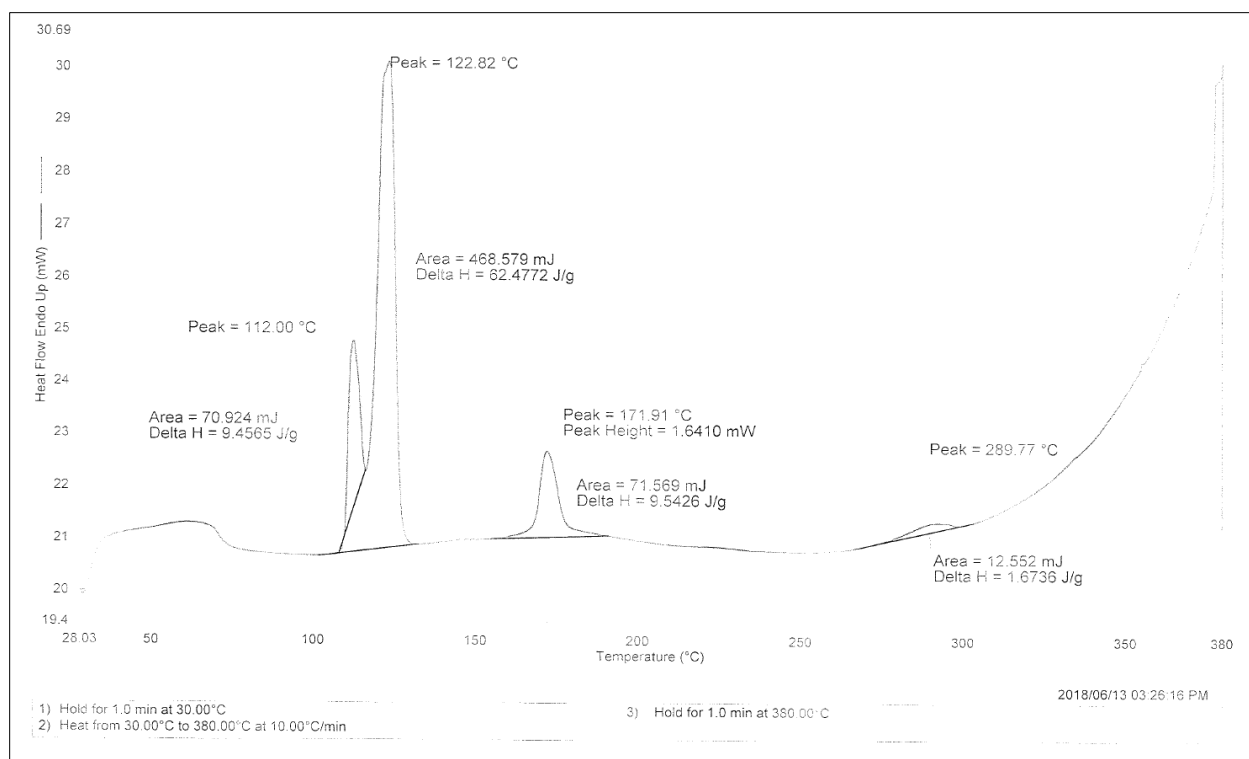


Figure E-3: Elemental sulphur melting and polymerization points for Solution 3

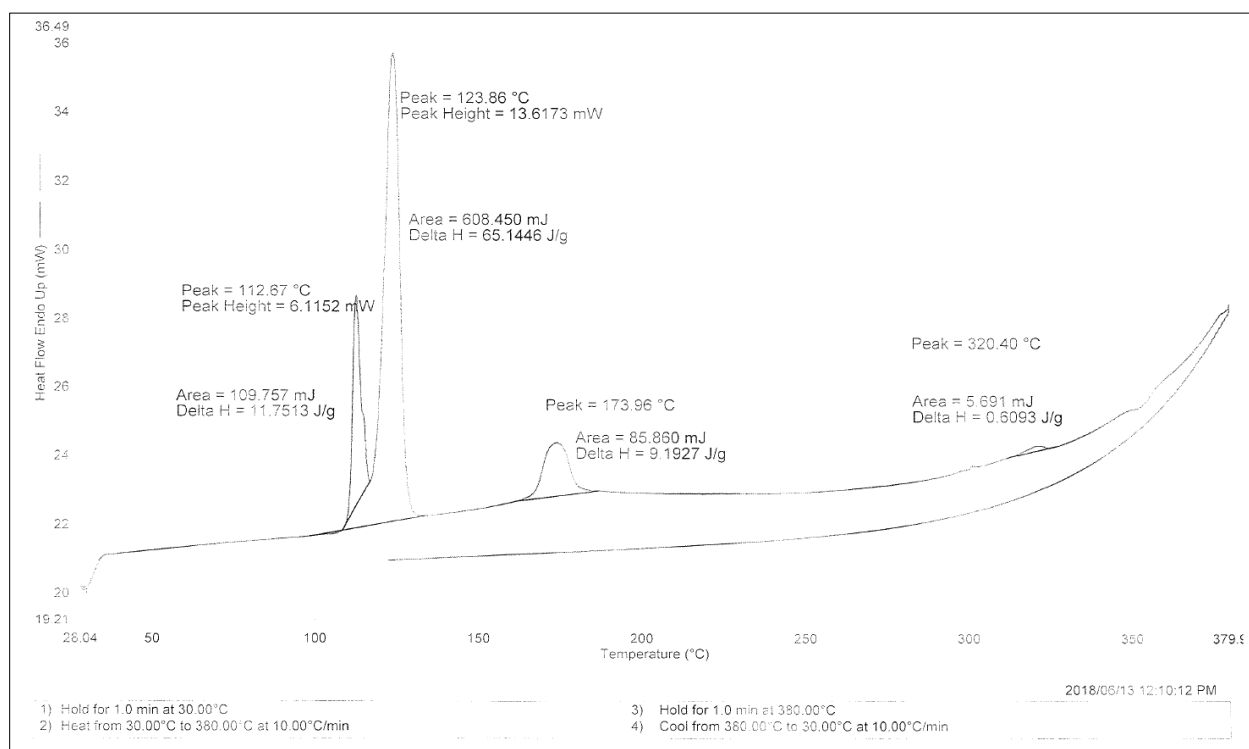
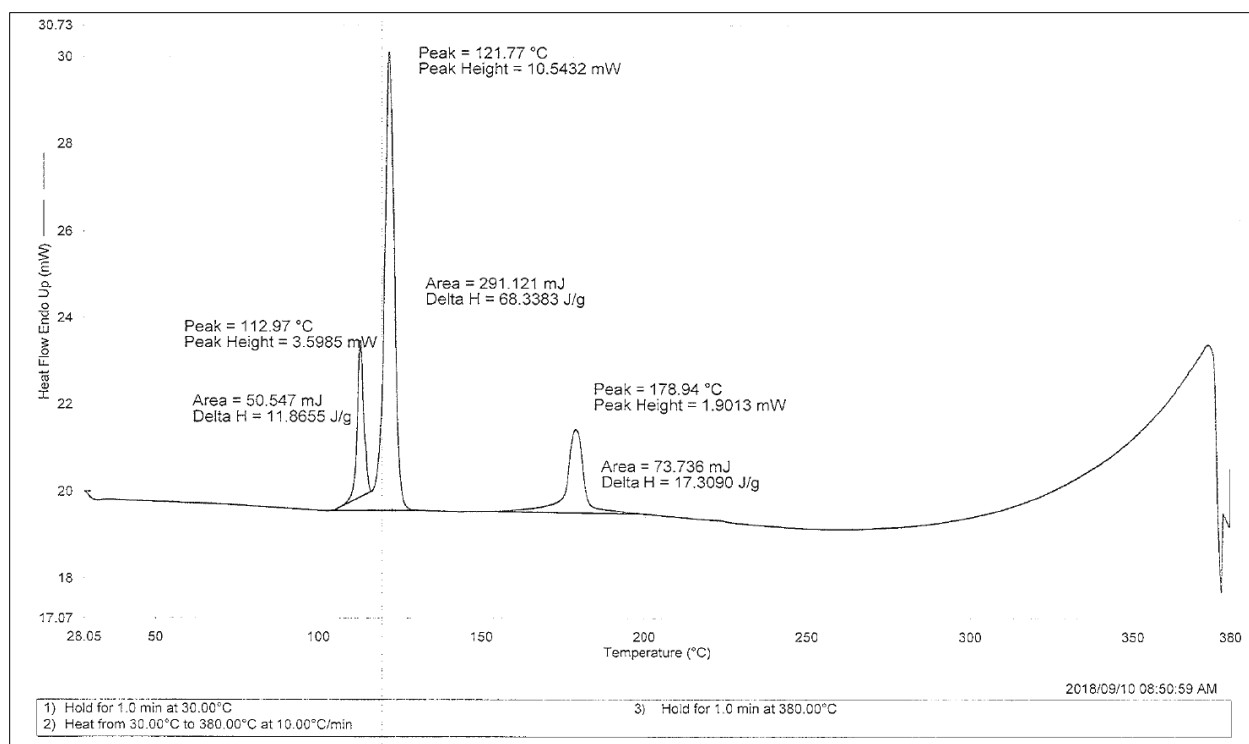
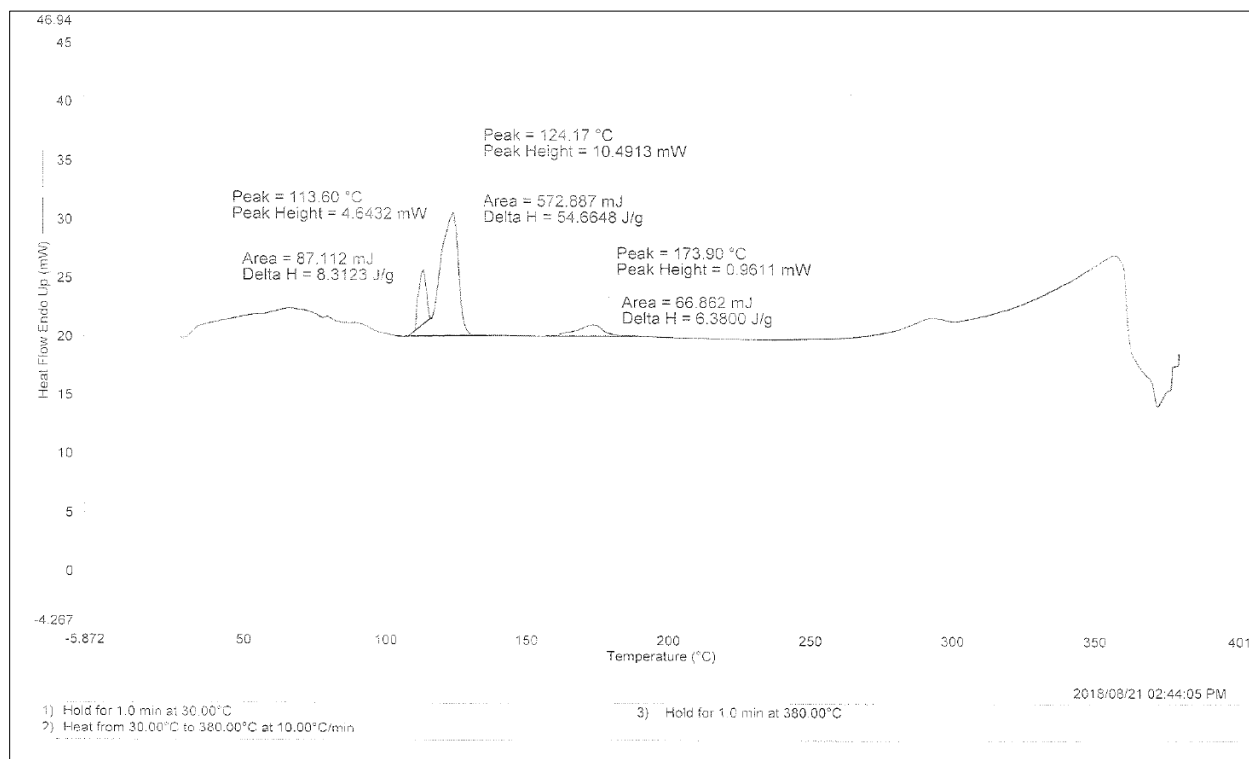


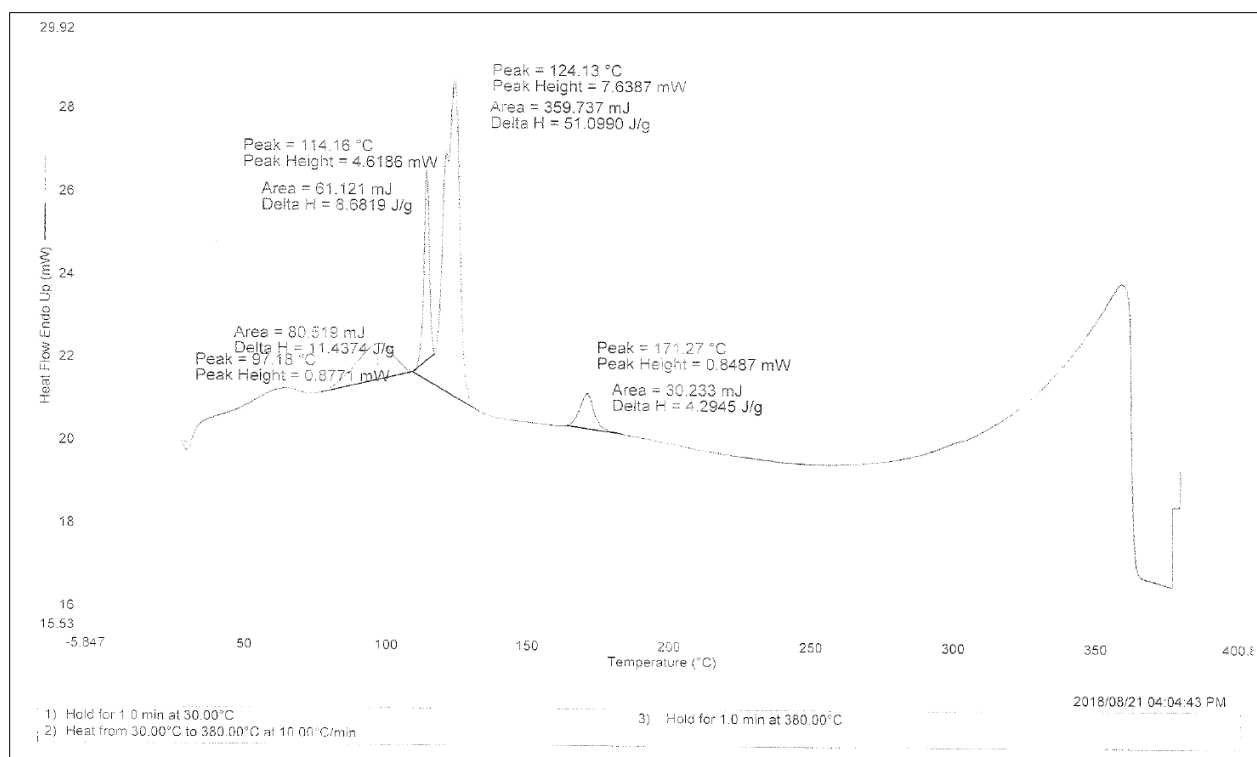
Figure E-4: Elemental sulphur melting and polymerization points for Solution 4



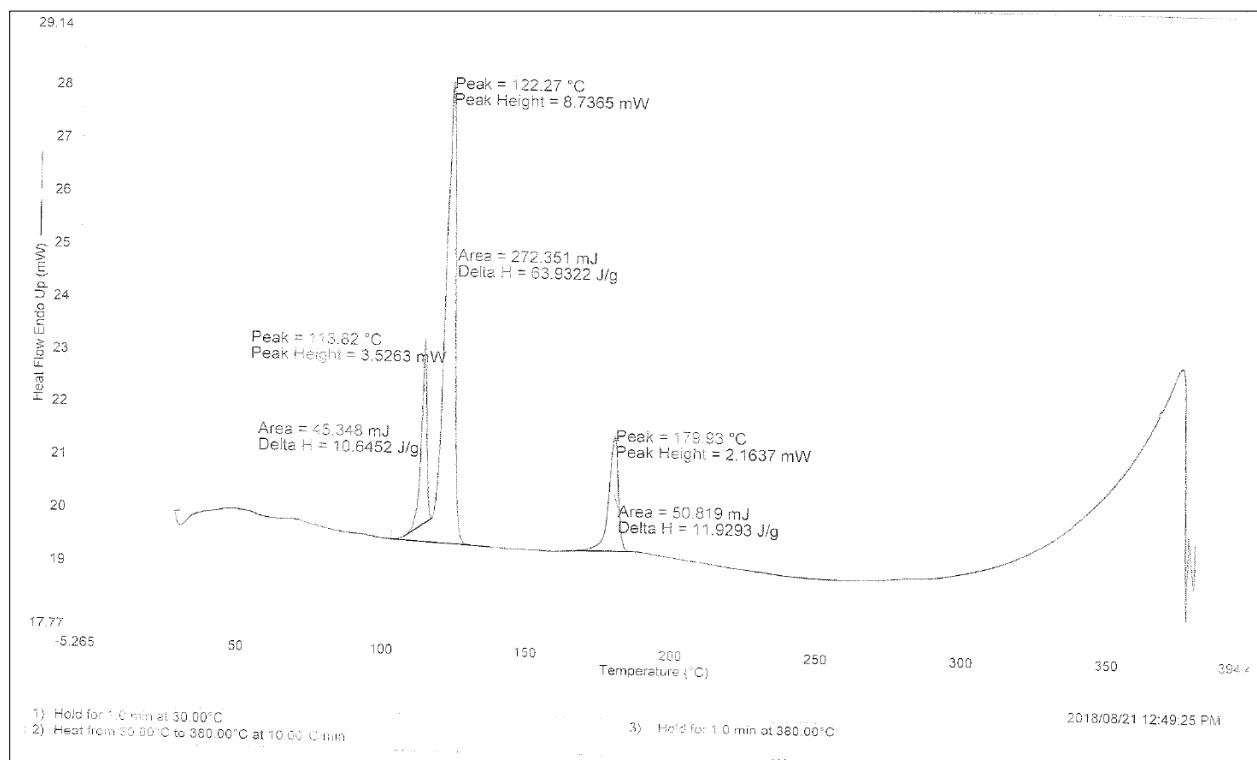
E-5: Elemental sulphur melting and polymerization points for Solution X without impurities



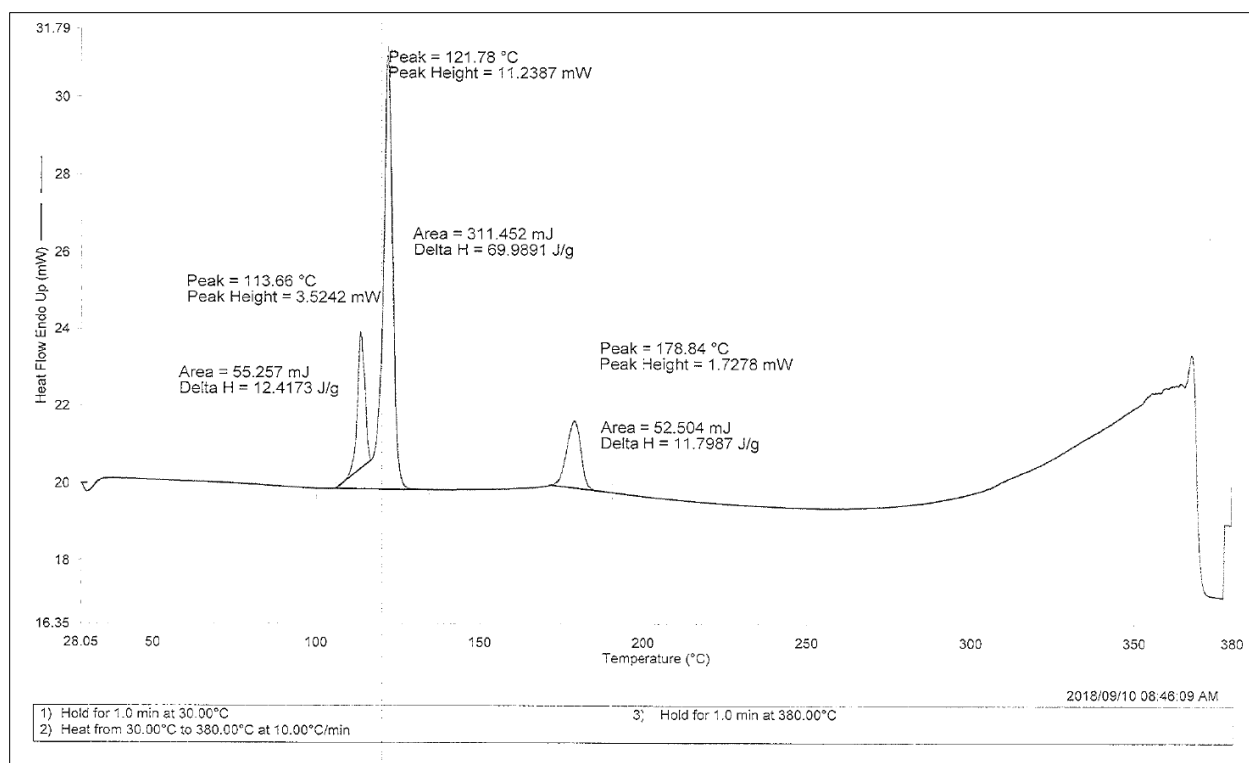
E-6: Elemental sulphur melting and polymerization points for Solution 5



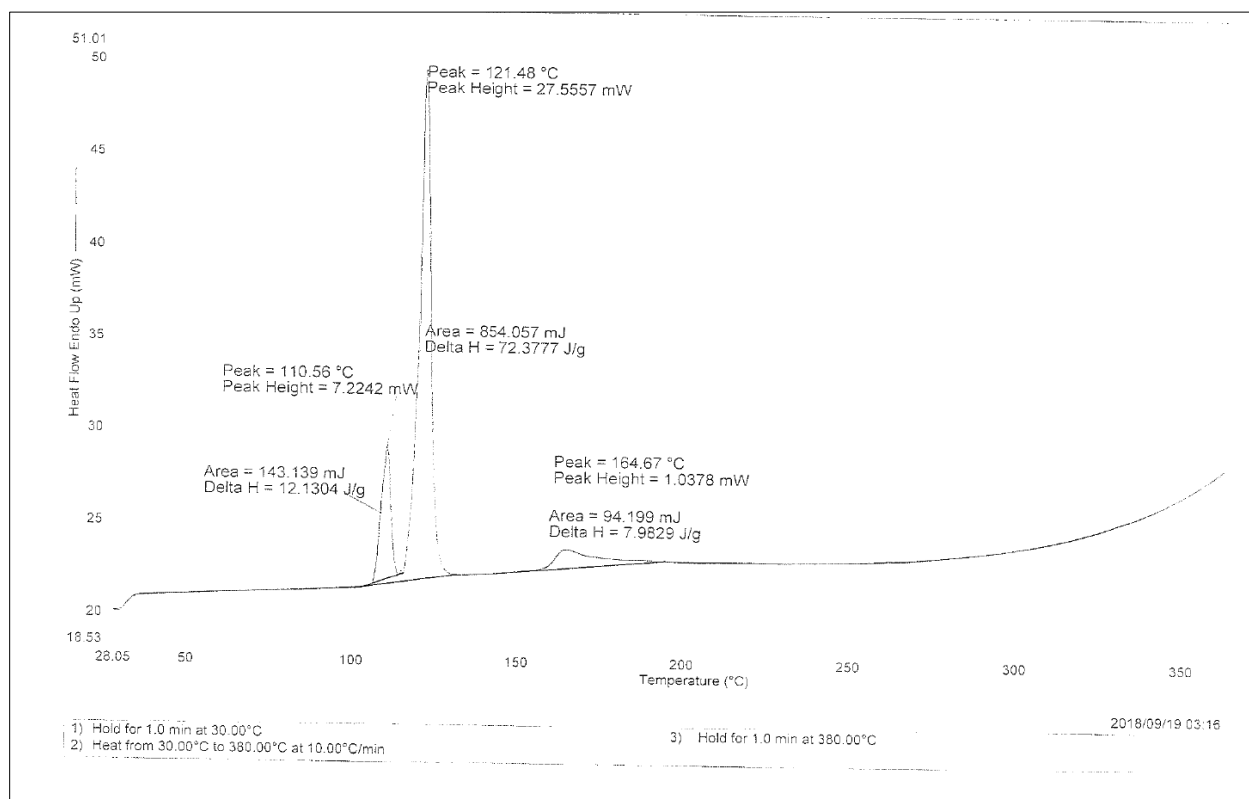
E-7: Elemental sulphur melting and polymerization points for Solution 6



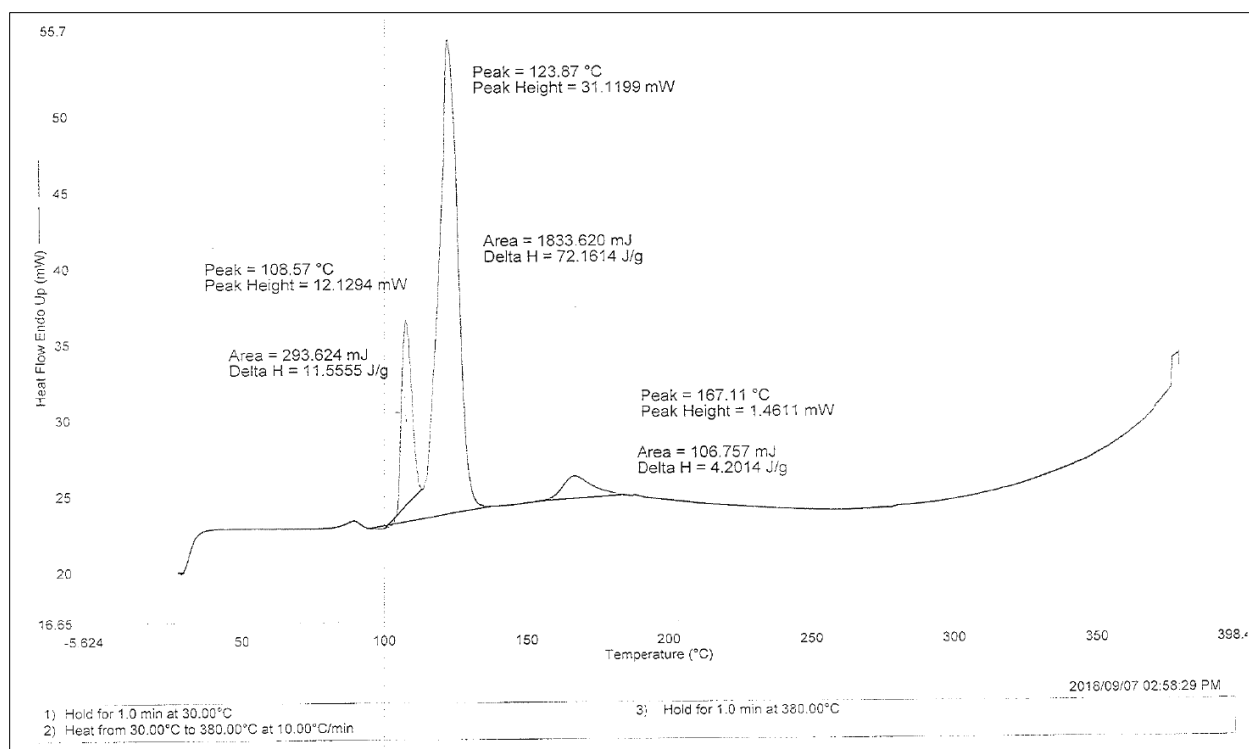
E-8: Elemental sulphur melting and polymerization points for Solution 7



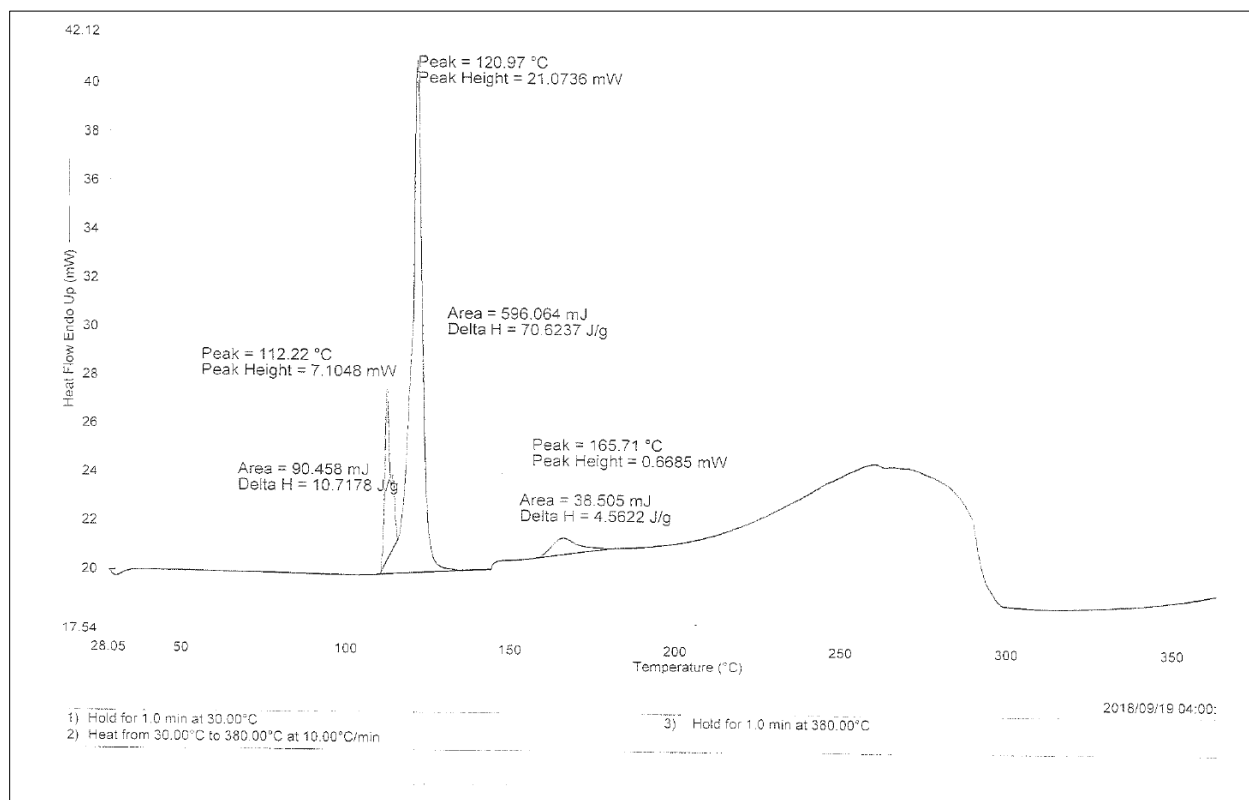
E-9: Elemental sulphur melting and polymerization points for Solution 8



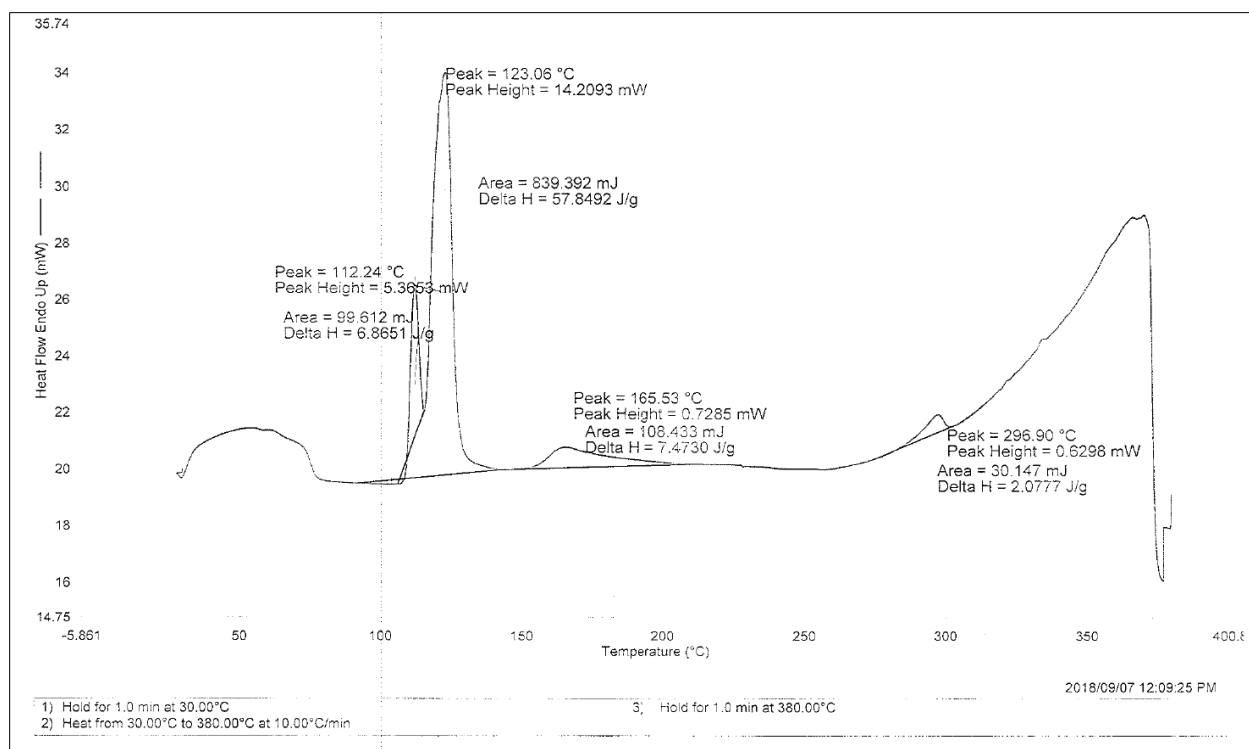
E-10: Elemental sulphur melting and polymerization points for Solution 8



E-11: Commercial elemental sulphur melting and polymerization points (S-A)



E-12: Commercial elemental sulphur melting and polymerization points (S-B)



E-13: Commercial elemental sulphur melting and polymerization points (S-C)

APPENDIX F: HS⁻ loading calculations

Below calculations are examples of how V⁵⁺ to HS⁻ molar ratio for Solution 1 was calculated. The molar ratios for Solutions 2, 3, 4, 5, 6, 7 and 8 were similar to Solution 1 and results are given in Table F-1.

Gas (G) = 7 dm³.min⁻¹; StretfordTM circulation (L) = 1.3 dm³.min⁻¹; H₂S (X) = 1.5%; HS⁻ (M_{wt}) = 33 g.mol⁻¹

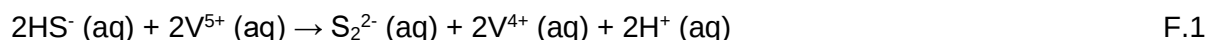
V⁵⁺ concentration (C) = 0.019 mol.dm⁻³

HS⁻ loading = (G ÷ M_{wt}) × (X ÷ 100) × (33 ÷ 22.414)

HS⁻ loading = (7 ÷ 33) × (1.6 ÷ 100) × (33 ÷ 22.414)

HS⁻ loading = 0.005 mol.min⁻¹

Two moles of V⁵⁺ is required to produce one mole of S₂²⁻ as per below equation F.1



Therefore

V⁵⁺ required = 2 × 0.005

V^{5+} required = 0.01 mol.min⁻¹

V^{5+} circulating = $C \times L$

V^{5+} circulating = 0.019×1.3

V^{5+} circulating = 0.02 mol.min⁻¹

V^{5+} to HS^- molar ratio = $0.02 \div 0.005$

V^{5+} to HS^- molar ratio = 4.8

Table F-1: V^{5+} to HS^- molar ratios

Solution	dm ³ .min ⁻¹	dm ³ .min ⁻¹	mol.dm ⁻³	mol.min ⁻¹	mol.min ⁻¹	mol.min ⁻¹	Molar ratio
	Feed flow	Circulation	V^{5+} concentration	HS^- loading	V^{5+} required	V^{5+} available	$V^{5+} : HS^-$
1	7	1.3	0.019	0.0052	0.0103	0.02	4.8
2	7	1.3	0.029	0.0052	0.0103	0.04	7.3
3	7	1.3	0.042	0.0052	0.0103	0.05	10.7
4	7	1.3	0.096	0.0052	0.0103	0.12	24.1

Table F-1: V^{5+} to HS^- molar ratios without $Na_2[ADA]$

Solution	dm ³ .min ⁻¹	dm ³ .min ⁻¹	mol.dm ⁻³	mol.min ⁻¹	mol.min ⁻¹	mol.min ⁻¹	Molar ratio
	Feed flow	Circulation	V^{5+} concentration	HS^- loading	V^{5+} required	V^{5+} available	$V^{5+} : HS^-$
5	7	1.3	0.0024	0.0052	0.0103	0.00	0.62
6	7	1.3	0.0024	0.0052	0.0103	0.00	0.60
7	7	1.3	0.0021	0.0052	0.0103	0.00	0.54
8	7	1.3	0.0010	0.0052	0.0103	0.00	0.24

APPENDIX G: XRD diffractograms

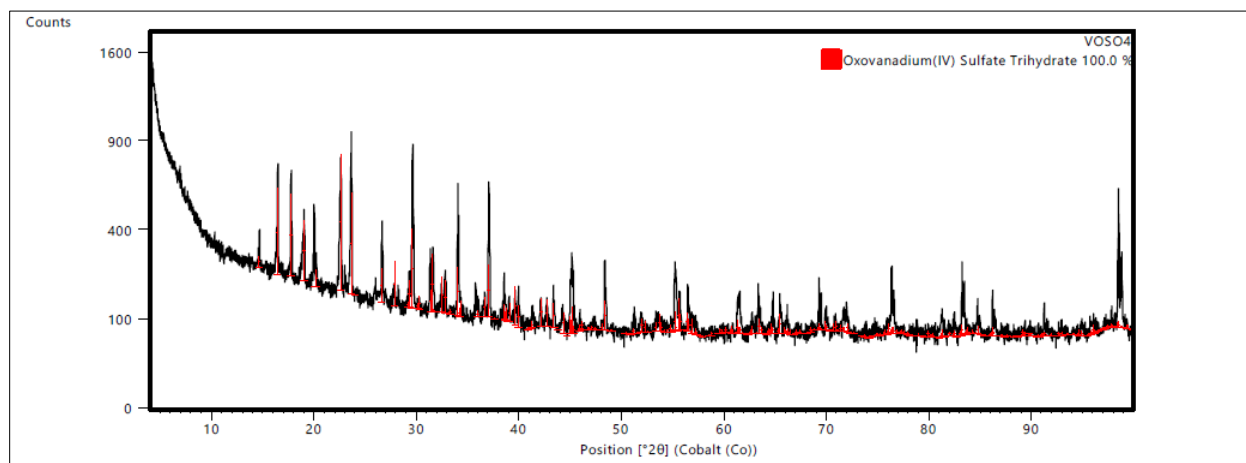


Figure G-1: Diffractogram of $VOSO_4$

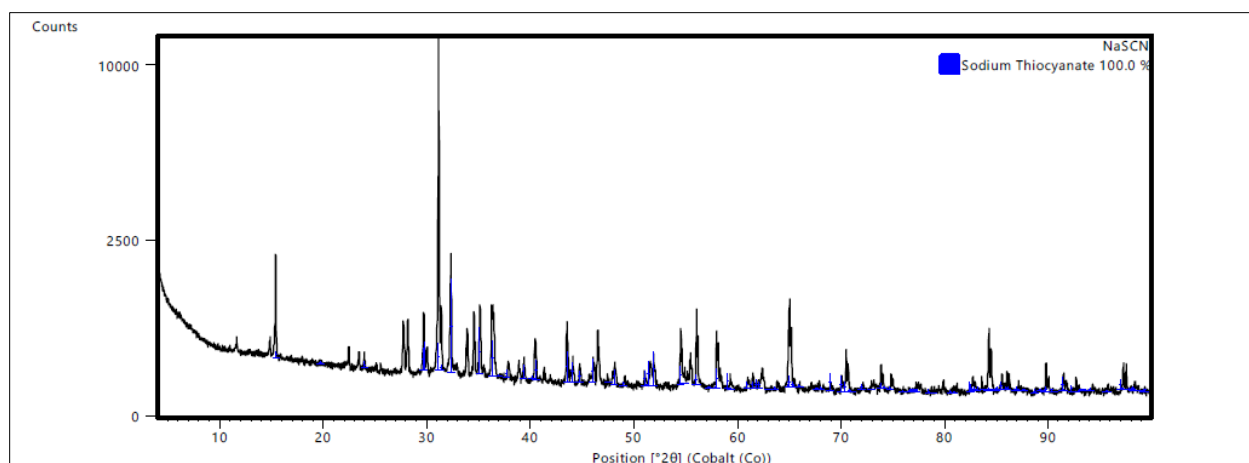


Figure G-2: Diffractogram of NaSCN

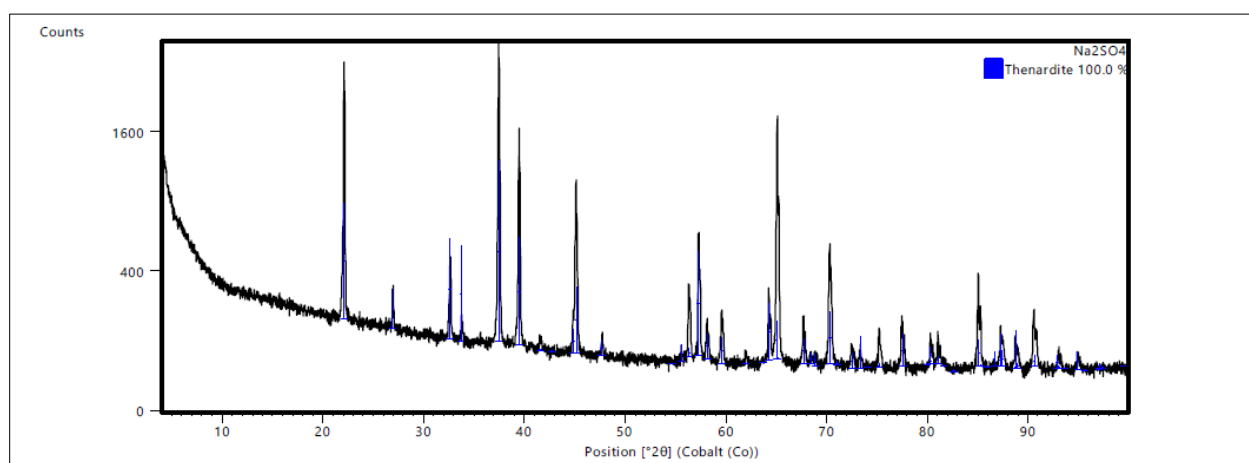


Figure G-3: Diffractogram of Na₂SO₄

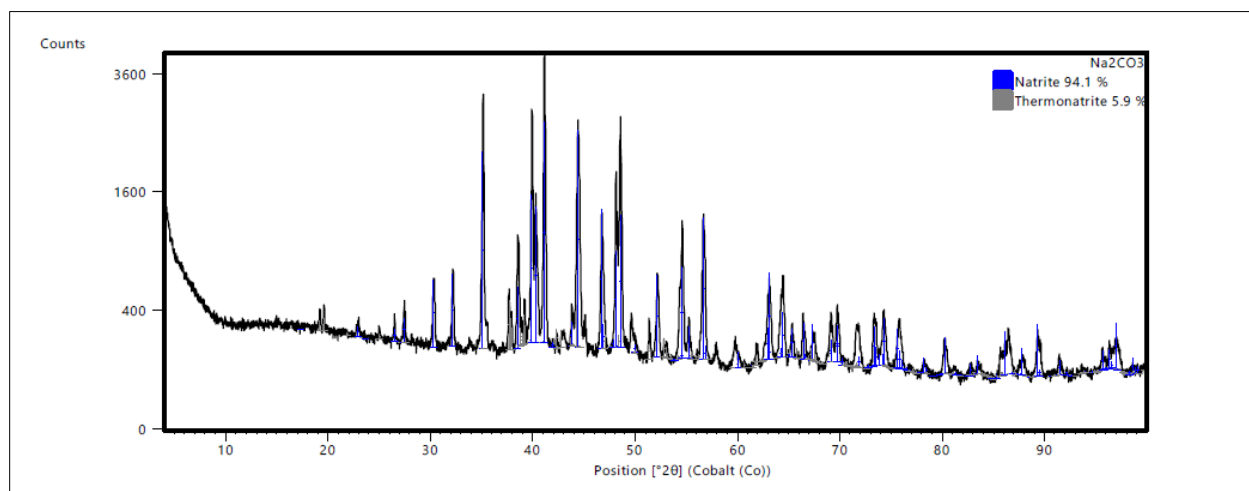


Figure G-4: Diffractogram of Na₂CO₃

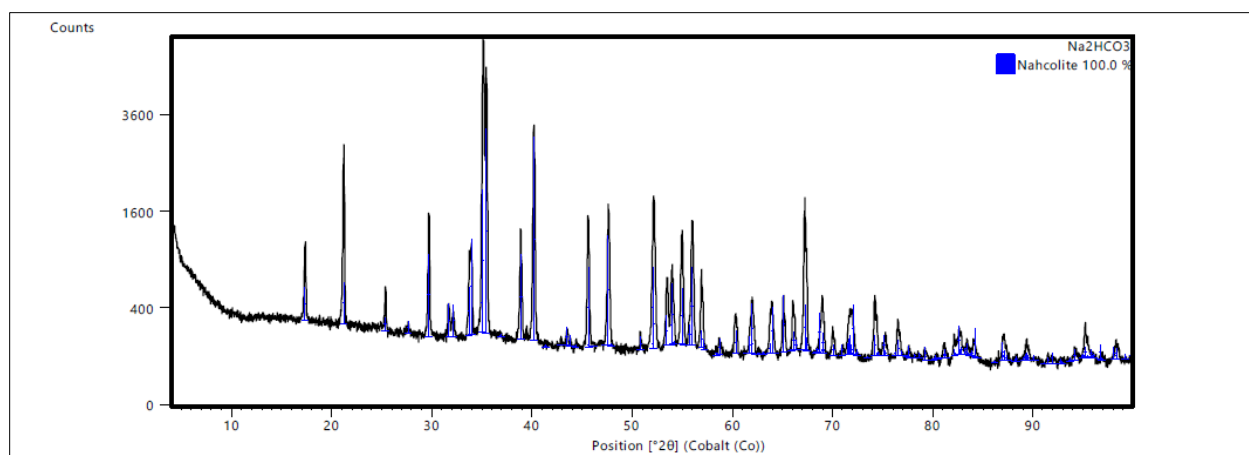


Figure G-5: Diffractogram of Na_2HCO_3

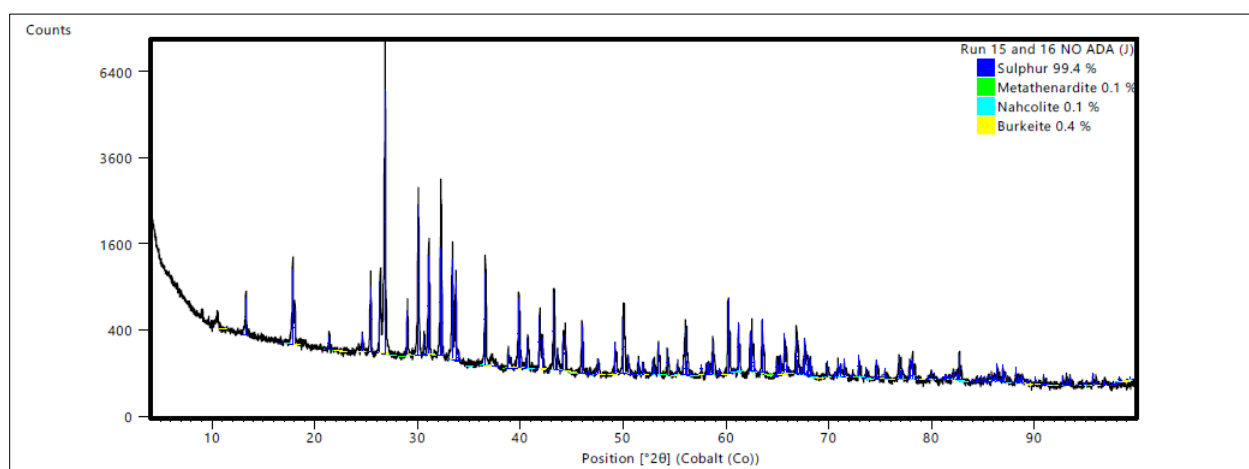


Figure G-6: Diffractogram of sulphur produced in Solution 6 at different V^{5+} to V^{4+} molar ratios

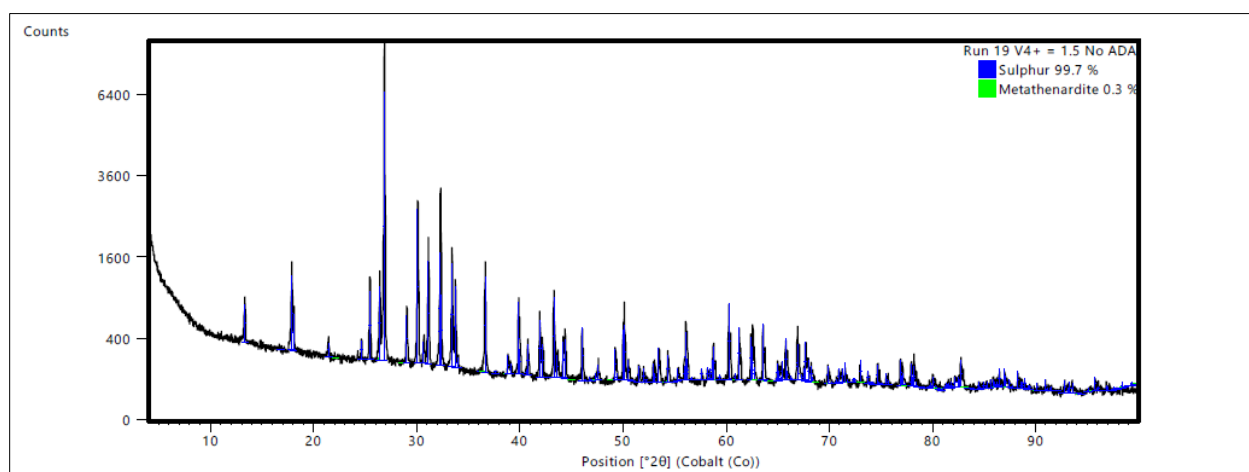


Figure G-7: Diffractogram of sulphur produced in Solution 7 at different V^{5+} to V^{4+} molar ratios

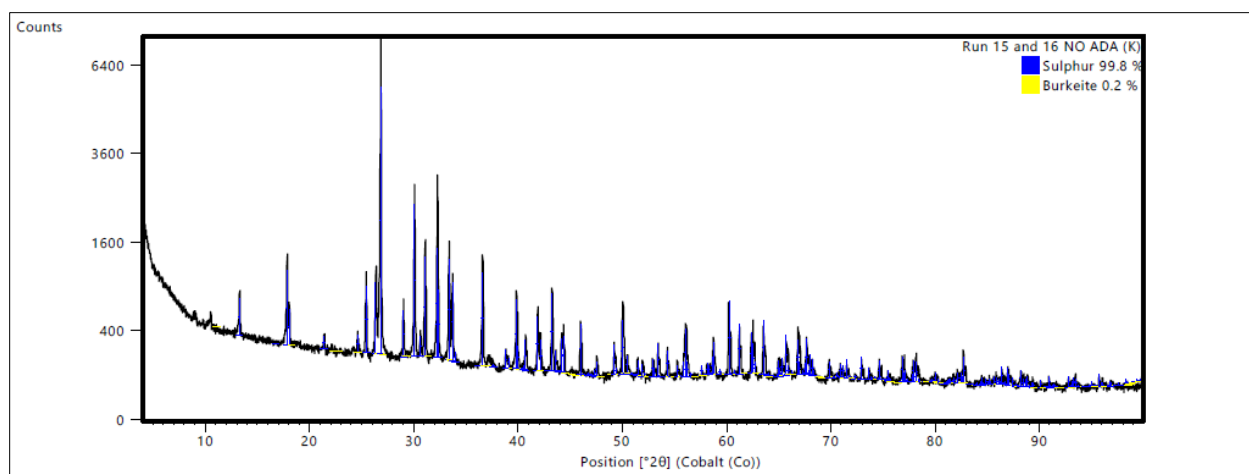


Figure G-8: Diffractogram of sulphur produced in Solution 8 at different V^{5+} to V^{4+} molar ratios

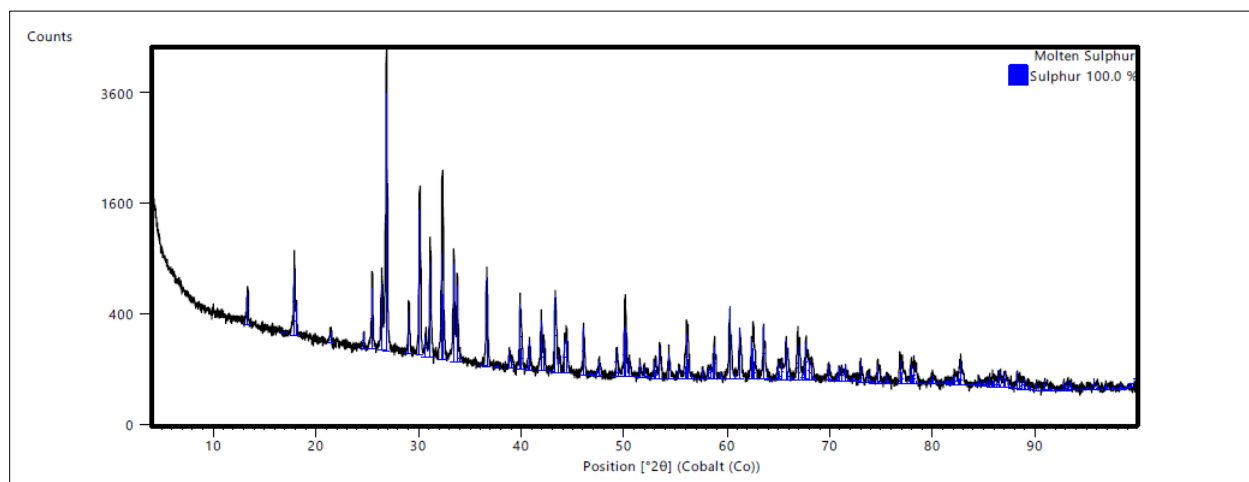


Figure G-9: Diffractogram of purified sulphur produced (S-A)

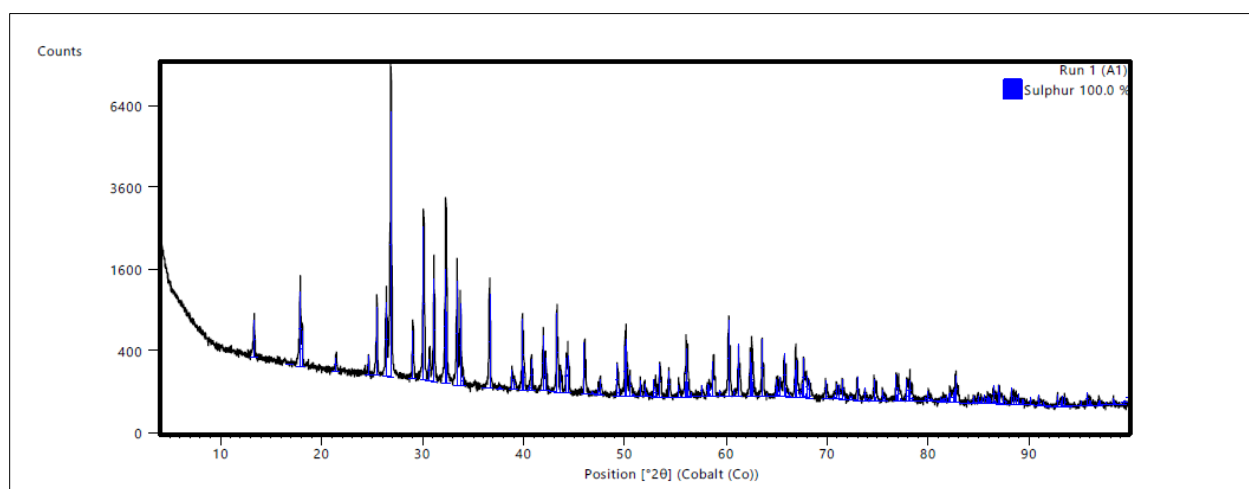


Figure G-10: Diffractogram of purified sulphur produced (S-B)

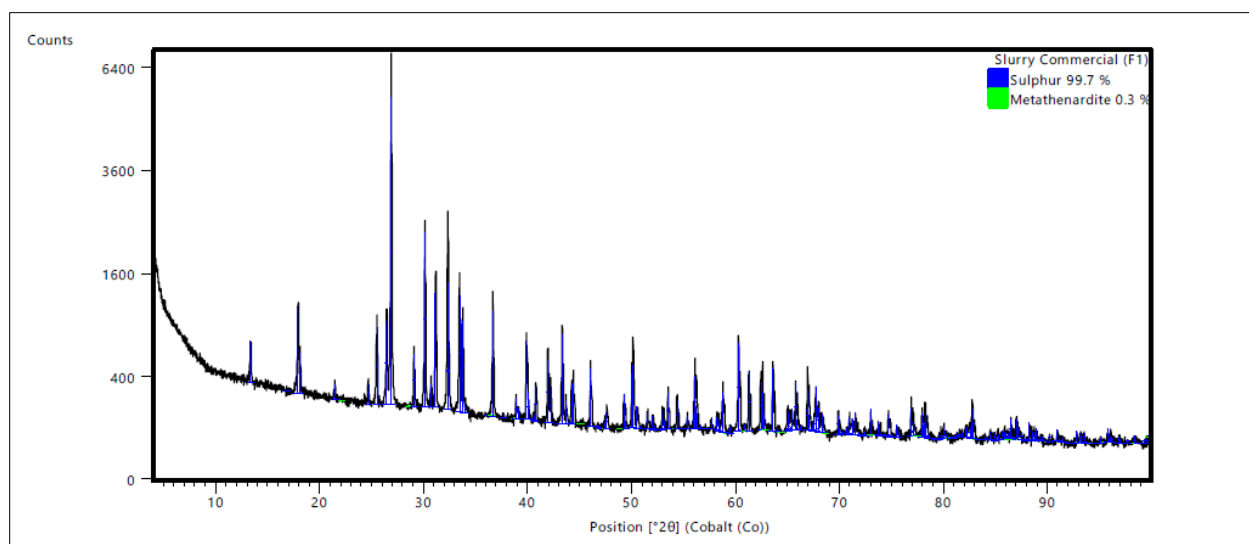


Figure G-11: Diffractogram of un-purified sulphur produced (S-C)

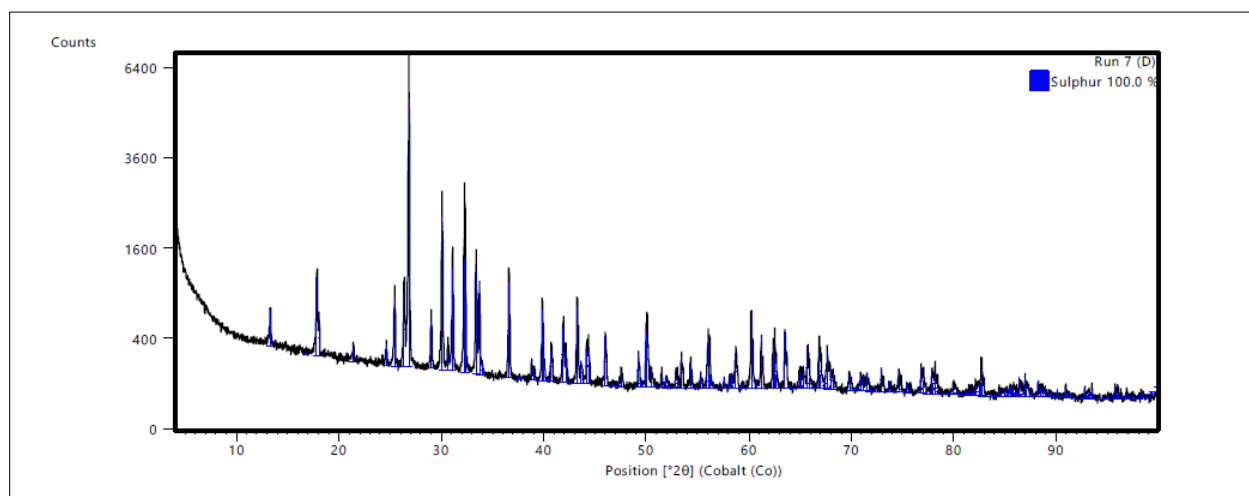


Figure G-12: Diffractogram of purified sulphur produced (S-D)

APPENDIX H: ^{51}V NMR procedure

  Central Analytical Facilities STELLENBOSCH UNIVERSITY																									
14 August 2018																									
Jonine Badenhorst Buyer Refurbishment Secunda Synfuels Supply Chain Services																									
Tel +27 17 610 6478 Fax +27 086 504 4985 E-mail: jonine.badenhorst@sasol.com																									
RFQ number 6002287868																									
Report:																									
Recording of ^{51}V (V) NMR spectra for 16 aqueous samples. Makonde Ndou (CAF ID: 18-94452)																									
Samples:																									
• Run 1-16																									
Sample preparation: The samples are heated to 40°C and 700µl are then transferred to new NMR tubes using new Pasteur pipettes. A C_6D_6 filled glass insert are added to the sample for locking and shimming purposes and the tube capped.																									
Instrumentation: An Agilent <i>UnityInova</i> 600 NMR spectrometer with a ^1H frequency of 600 MHz and a ^{51}V frequency of 157.8 MHz is utilised, equipped with a 5mm dual channel Broadband probe, with each sample equilibrated and shimmed at 40°C before acquisition.																									
Experiment(s): The 9.75µs 90° pulse of ^{51}V was determined using commercial VOCl_3 dissolved in C_6D_6 . The VOCl_3 signal was referenced to 0 ppm and used as external reference for the 16 Vanadium samples provided. All ^{51}V spectra was recorded using the acquisition parameters given below.																									
<table border="1"><thead><tr><th>Channels:</th><th>Observe ☒ 2</th><th>Decouple ☒ 2</th></tr></thead><tbody><tr><td>Nucleus / freq</td><td>^{51}V 157.774 MHz</td><td>^1H 599.966 MHz</td></tr><tr><td>Offset</td><td>85365.70 Hz</td><td>0.00 Hz</td></tr><tr><td>Det on/off</td><td></td><td>☒ rrv ☐ Hom</td></tr><tr><td>Det modulation</td><td></td><td>w</td></tr><tr><td>90 deg. at pwr</td><td>9.75 µs at 5.3</td><td>76.4 µs at 47</td></tr><tr><td>Waveform</td><td>Homodec</td><td>- 1.3100</td></tr><tr><td>at resolution</td><td>degrees</td><td>wahz16 90.00 degrees</td></tr></tbody></table>		Channels:	Observe ☒ 2	Decouple ☒ 2	Nucleus / freq	^{51}V 157.774 MHz	^1H 599.966 MHz	Offset	85365.70 Hz	0.00 Hz	Det on/off		☒ rrv ☐ Hom	Det modulation		w	90 deg. at pwr	9.75 µs at 5.3	76.4 µs at 47	Waveform	Homodec	- 1.3100	at resolution	degrees	wahz16 90.00 degrees
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NMR Laboratory Room 1001 (1014), Mike De Vries Bldg., Private Bag X1, Matieland, 7602, South Africa Tel: +27 21 808 3338/2661 Fax: +27 21 808 3360 dbrand@sun.ac.za www.sun.ac.za/caf																									

Figure H-1: ^{51}V NMR procedure used