

Oxidation of sodium thiocyanate (NaSCN) in high ionic-strength process aqueous liquor

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Declaration

I, Raksha Sunderlall, hereby declare that the dissertation entitled:

Oxidation of sodium thiocyanate (NaSCN) in high ionic-strength process aqueous liquor

which I herewith submit to the North-West University in fulfilment of the requirements for the degree, M.Sc. in Chemistry, is my own original work, and has not been previously submitted to any other educational institution. Recognition is given to all sources.

Date:

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Abstract

The use of liquid redox processes (Stretford Process) for the absorption of H_2S from gaseous streams and converting the absorbed H_2S into elemental sulphur is widely used. The chemistry of Stretford process aqueous liquors is very complicated and maintaining the critical chemical parameters is imperative. Sodium thiocyanate (NaSCN) is used for bacterial control and for reducing the consumption of sodium anthraquinone 2,7-disulphonate ($\text{Na}_2[\text{ADA}]$) in Stretford process aqueous liquors.

A series of experiments were conducted to investigate the degree of oxidation of NaSCN in aqueous solutions and Stretford process aqueous liquors using oxidants such as hydrogen peroxide (H_2O_2), air, intermediate H_2O_2 from sodium ammonium vanadate (SAV) and sodium anthraquinone 2,7-disulphonate ($\text{Na}_2[\text{ADA}]$). A decrease in the total alkalinity and $\text{Na}_2[\text{ADA}]$ concentration was also observed under these oxidising conditions. Some of the techniques employed during the study were X-ray diffraction (XRD), X-ray fluorescence (XRF), Ion Chromatography (IC), Fourier Transform Infrared (FTIR), automated titration and Gas Chromatography-Mass Spectrometry (GC-MS).

The products formed from the oxidations were identified. The FTIR and XRD results confirmed that a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ was formed as an intermediate when NaSCN solutions were oxidised with H_2O_2 . XRD and XRF results confirmed the presence of Na_2SO_4 as a major product from the H_2O_2 oxidation of NaSCN solutions. NaSCN in the Stretford process aqueous liquor is oxidised to form sodium sulphate, burkeite and mascagnite when using air and H_2O_2 . When HCl and NaOH were used at pH values of 7.0 and 9.0 respectively, the concentration of NaSCN remained predominantly unaffected.

The oxidation of NaSCN using increased concentrations of $\text{Na}_2[\text{ADA}]$ and SAV did not impact the NaSCN concentration. Small amounts of H_2O_2 are liberated from $\text{Na}_2[\text{ADA}]$ and SAV during the re-oxidation of $\text{Na}_2[\text{ADA}]$ using SAV. These liberated H_2O_2 concentrations are not sufficient to facilitate NaSCN oxidation using increased concentrations of these catalysts (i.e. $\text{Na}_2[\text{ADA}]$ and SAV). During oxidation of Stretford process aqueous liquors using air and H_2O_2 , the concentration of NaSCN steadily decreased while the concentration of Na_2SO_4 increased. During the oxidation of Stretford process aqueous liquor using H_2O_2 , HCN was found to be the main gas liberated. The formation of $\text{Na}_2\text{S}_2\text{O}_3$ during the oxidation of Stretford process aqueous liquors using H_2O_2 was not found to be significant since the conditions of increased pH and temperature that facilitate its formation were not met.

Key Words: Stretford, Oxidation, Peroxide, Catalyst, Sulphate

Opsomming

Die gebruik van vloeistofreduksieprosesse (Stretford Proses) vir die absorpsie van H_2S vanaf gasagtige strome en om die geabsorbeerde H_2S na elementêre swael te omskep word algemeen gebruik. Die chemie van Stretford prosesvloeistowwe is ingewikkeld en dit is dus noodsaaklik om die chemiese veranderlikes konstant te hou. $NaSCN$ word gebruik vir bakeriële beheer en om die gebruik van natriumantraquinoon 2,7-disulfonaat ($Na_2[ADA]$) in Stretford prosesvloeistowwe te verminder.

‘n Reeks eksperimente is uitgevoer om die graad van oksidasie van $NaSCN$ in waterige oplossings en Stretford vloeistowwe te ondersoek deur gebruik te maak van die volgende oksidante: waterstofperoksied (H_2O_2), lug, intermediêre H_2O_2 gevorm uit natriumammoniumvanadaat (SAV) en natriumantraquinoon 2,7-disulfonaat ($Na_2[ADA]$). ‘n Afname in die algehele basisiteit en in die konsentrasie van $Na_2[ADA]$ is waargeneem onder hierdie oksiderende kondisies. Sommige van die tegnieke wat gebruik is tydens die studie sluit in XSD, XSF, IC, FTIR, automatiese titrasies en GC-MS.

The produkte wat gevorm is deur die oksidasie prosesse is geïdentifiseer. Die FTIR resultate het bevestig dat kolloïdale polimeriese $(NaSCN)_x$ en $(SCN)_x$, wat bekend staan as tiosianogeen, gevorm is as ‘n tussenproduk tydens die oksidasie van Na_2SO_4 oplossings met H_2O_2 . Die XSD en XSF resultate het bevestig dat Na_2SO_4 as ‘n hoofproduk teenwoordig is tydens die H_2O_2 oksidasie van $NaSCN$ oplossings. $NaSCN$ in die Stretford prosesvloeistowwe is geoksideer om natriumsulfaat, burkeit en maskaniet te vorm tydens die gebruik van lug en H_2O_2 . Met die gebruik van HCl en NaOH by pH waardes van 7.0 en 9.0 afsonderlik, het die konsentrasie van $NaSCN$ grootendeels onveranderd gebly.

Die oksidasie van $NaSCN$ met die gebruik van toenemende konsentrasies van $Na_2[ADA]$ en SAV het nie die $NaSCN$ konsentrasie geaffekteer nie. Klein hoeveelhede van H_2O_2 is vrygestel uit $Na_2[ADA]$ en SAV tydens die heroksidatie van $Na_2[ADA]$ met SAV. Die vrygestelde H_2O_2 konsentrasies was nie genoeg om die oksidasie van $NaSCN$ in sterker konsentrasies van die betrokke katalisator ($Na_2[ADA]$ en SAV) te veroorsaak nie. Tydens die oksidasie van Stretford prosesvloeistowwe met die gebruik van lug en H_2O_2 , het die konsentrasie van die $NaSCN$ geleidelik afgeneem terwyl die konsentrasie van Na_2SO_4 toeneem het. Tydens die oksidasie van Stretford prosesvloeistowwe met die gebruik van H_2O_2 , is daar vasgestel dat HCN die vernaamste gas is, wat vrygestel was. Daar is bevind dat die vorming van $Na_2S_2O_3$ tydens die oksidasie van Stretford prosesvloeistowwe met die gebruik van H_2O_2 nie beduidend genoeg is nie, omdat ‘n toename in pH en temperatuur wat die vorming fasiliteer, nie plaasgevind het nie.

Sleutel Woorde: Stretford, Oksidasie, Waterstofperoksied, Katalisator, Sulfaat

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“It always seems impossible until it is done”

Nelson Mandela

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Nomenclature

ADA	Anthraquinone Disulfonic Acid
ATR	Attenuated Total Reflectance
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
GRI	Gas Research Institute
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrophotometry
IPCS	International Programme on Chemical Safety
IR	Infrared
Na₂[ADA]	Anthraquinone disulfonic acid, disodium salt
PAR	Pink Monosodium Salt Monohydrate
ppb	parts per billion
ppm	parts per million
RF	Radiofrequency
SAV	Sodium Ammonium Vanadate
SOB	Sulphur Oxidising Bacteria
TDS	Total Dissolved Solids
UV	Ultraviolet
Vis	Visible
XRD	X-ray diffraction
XRF	X-ray fluorescence

Chapter 1

Problem Statement and Hypothesis

1.1. Problem Statement and Substantiation

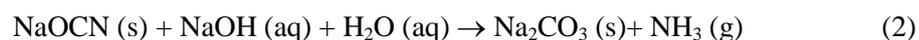
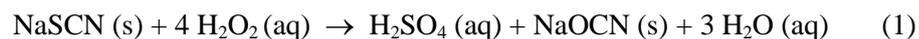
The Stretford process is a continuous process that removes large amounts of H₂S from gas streams. The Stretford process employs a solution containing dissolved vanadium salts and dissolved anthraquinone disulfonic acid (Na₂[ADA]) to facilitate the absorption of H₂S into an alkaline solution [Speight, 2007].

The concentration of sodium thiocyanate in the Stretford aqueous liquor was adjusted to the acceptable levels by the addition of sodium thiocyanate to this aqueous liquor. A high concentration of sodium thiocyanate (NaSCN > 0.61 mol.dm⁻³) is required for the prevention of bacterial growth and to act as a solvent of fines formed in the system during the recovery of elemental sulphur from bisulphide ions [Wilson and Newell, 1984; Weber, 1985].

In addition to its bacteriostatic activity, thiocyanate ions also protect Na₂[ADA] from degradation by reactive peroxide radicals and also to catalyse the oxidation of thiosulphate to sulphate under Stretford conditions. This is probably the reason why the concentration of thiosulphate in other sulphur plants is very low. Thus thiocyanate in the Stretford process has many functions. During the addition of the sodium thiocyanate to the Stretford aqueous liquor, the sodium thiocyanate concentration was decreased due to the oxidation of the dissolved sodium thiocyanate to sodium sulphate and other cyanate salts.

Sodium thiocyanate (NaSCN) in the Stretford process aqueous liquor can react with dissolved oxygen or H₂O₂ (hydrogen peroxide) to form sticky sodium salts [Cristy and Edgeberg, 2000]. Some of these salts include sodium sulphate (Na₂SO₄), sodium thiosulphate (Na₂S₂O₃) and sodium cyanate (NaOCN) [Cristy and Edgeberg, 2000].

The most likely mechanism for the oxidation of NaSCN in process aqueous liquor is presented in the following series of reactions [Cristy and Edgeberg, 2000]:



The hydrogen peroxide (H₂O₂) is expected to be formed in the oxidizers due to an oversupply of air and oxidation of anthraquinone disulfonic acid (Na₂[ADA]). Molecular oxygen can react with

$\text{Na}_2[\text{ADA}]$ species to form hydrogen peroxide. Reaction (1) can explain the drop in pH on dosing with NaSCN due to the formation of sulphuric acid (H_2SO_4). Dosing with NaSCN crystals in the process aqueous liquor is responsible for the high concentrations of sodium thiocyanate and sodium sulphate. In this case, sulphate, carbonate, ammonia gas /ions and even nitrate ions have been observed as oxidation products. The sodium cyanate (NaOCN) formed in reaction (1) may accumulate in the process aqueous liquor or may be hydrolysed (See Reaction 2) [Cristy and Edgeberg, 2000]. The hydrolysis of aqueous cyanate with urea ($\text{CO}(\text{NH}_2)_2$) as an intermediate is well-described in the chemical literature [Wen and Brooker, 1994].

The free ammonia (NH_3) formed in reaction (2) is expected to either evaporate from the alkaline solution at high pH (>9.5) or is oxidised by hydrogen peroxide as is evident in reaction 3 [Cristy and Edgeberg, 2000].

Combining chemical reactions (1) to (3) implies that NaSCN is turned into sulphate species (H_2SO_4), carbonate (Na_2CO_3) and nitrogen (N_2) which are components of the Stretford aqueous liquor. All three reactions may be catalysed by vanadium complexes present in the system.

In order to better understand the oxidation of NaSCN in the process aqueous liquor with high ionic-strength, laboratory experiments, using an artificial process aqueous liquor containing the salts $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ and Na_2SO_4 , will be investigated. Monitoring the oxidation of NaSCN under the impact of vanadate ions, salts of anthraquinone disulfonic acid ($\text{Na}_2[\text{ADA}]$), H_2O_2 , O_2 or mixtures of these should be conducted.

1.2. Basic Hypothesis

The addition of NaSCN to Stretford aqueous liquor that contains high dissolved oxygen concentrations in the form of hydrogen peroxide can result in the oxidation of NaSCN to form sodium sulphate. Sodium thiocyanate (NaSCN) in the process aqueous liquor can react with dissolved oxygen or H_2O_2 (hydrogen peroxide) to form sticky fine sodium salts and co-precipitated fine sulphur. Some of these salts from the oxidation of sodium thiocyanate may include sodium bisulphate (NaHSO_4), sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium sulphate (Na_2SO_4), and sodium cyanate (NaOCN). The oxidation of NaSCN using inorganic acids (H_2O_2 , HCl), $\text{Na}_2[\text{ADA}]$ and vanadium ions could result in the formation of significant quantities of $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_4 in the Stretford aqueous liquor. Na_2CO_3 (used to express total alkalinity) may decompose to form sodium ions and carbon dioxide during the oxidation of the dissolved sodium thiocyanate. The spent liquid containing sodium sulphate salts from the oxidation process could be recycled back into the sulphur recovery plants and sodium sulphate plants.

1.3. Research aims

In order to better understand the oxidation of NaSCN in process aqueous liquor, laboratory experiments using artificial Stretford process aqueous liquor containing the salts Na_2CO_3 and Na_2SO_4 will be used. The oxidation of NaSCN under the impact of Na_2CO_3 , Na_2SO_4 , vanadate, $\text{Na}_2[\text{ADA}]$, H_2O_2 , O_2 or mixtures of these will be conducted and monitored. The factors that promote and minimise the oxidation of NaSCN will be identified and investigated. From these, the ideal conditions for the promotion and minimisation of the oxidation of NaSCN will be determined.

1.4. Research objectives

The objectives of the investigations are:

- Monitoring the oxidation of NaSCN in water using H_2O_2 as an oxidising agent.
- Monitoring the oxidation of NaSCN in Stretford aqueous solutions at a pH of approximately 8.3 using hydrogen peroxide.
- Monitoring the oxidation of NaSCN in Stretford aqueous solutions at a pH of approximately 7.0 using hydrochloric acid.
- Monitoring the oxidation of NaSCN in Stretford aqueous solutions at a pH of approximately 9.0 using sodium hydroxide.
- Monitoring the oxidation of NaSCN in Stretford aqueous solutions at a pH of approximately 8.5 using increased concentrations of $\text{Na}_2[\text{ADA}]$.
- Monitoring the oxidation of NaSCN in Stretford aqueous solutions at a pH of approximately 8.5 using increased concentrations of vanadium.
- Monitoring the oxidation of NaSCN in Stretford aqueous solutions at a pH of approximately 8.5 using air.
- Monitoring the evolution of gases using the alkaline scrubber (potassium hydroxide solution) during the oxidation of NaSCN in the Stretford aqueous solutions using hydrogen peroxide.
- Evaporating the solution samples from the experiments in order to form crystals for analyses using X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier Transform Infrared (FTIR) spectroscopy.
- Determination of the concentration of the unwanted by-product $\text{Na}_2\text{S}_2\text{O}_3$ in Stretford aqueous solutions.

The concentrations of Na_2CO_3 , Na_2SO_4 , Vanadium, $\text{Na}_2[\text{ADA}]$, H_2O_2 and O_2 will be varied. This will be done to observe the effect of varying the above parameters on the oxidation of NaSCN . The techniques that will be used for analyses of the samples will include Ion Chromatography (IC), Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES), X-ray diffraction (XRD), X-ray fluorescence (XRF), Gas Chromatography-Mass Spectrometry (GC-MS), spectroscopic techniques, titrimetry and Fourier Transform Infrared (FTIR) and other general wet chemistry techniques such as pH determination and dissolved oxygen analysis.

Chapter 2

Literature Review

2.1. Introduction

H₂S is a colourless gas with a characteristic odour. It undergoes a number of oxidation reactions to yield primary products such as SO₂, H₂SO₄, and elemental sulphur. The rates of the reactions and formation of products depend on the nature of the oxidising agent and operating conditions [IPCS, International Programme on Chemical Safety- environmental health criteria 19, 1981].

H₂S is produced as an undesirable by-product although it is an important intermediate in some processes. It usually forms as a by-product from the production of coke from sulphur-containing coal, the refining of sulphur containing crude oils and in the Kraft process that produces wood pulp [ICPS, International Programme on Chemical Safety- environmental health criteria 19, 1981]. An area of particular concern is the release of sulphur and its associated compounds into the atmosphere during the refining of petroleum, the sweetening of sour natural gas, the processing of ore and the destructive distillation of coal [Fenton and Vaell, 1977].

Demands have been placed on industry to produce products in a safe pollution free manner, due to increasing concerns over the pollution of the atmosphere [Fenton and Vaell, 1977]. There is strict governance and environmental regulations imposed on companies with regards to emitting H₂S into the atmosphere and its emissions have to be controlled in order to meet regulatory requirements. Due to these regulations H₂S must be removed from gas streams before they are discharged [Harmon and Brinkman, 2003]. H₂S as a component of gas streams can also prevent the use of the gas streams in other processes, as H₂S is known for its capability to deactivate catalysts [Harmon and Brinkman, 2003].

H₂S therefore has to be removed or converted to a less harmful product. The Ferrox or Stretford processes are continuous processes that remove large amounts of H₂S from gas streams. The Stretford process employs a solution containing dissolved vanadium salts and dissolved anthraquinone disulfonic acid (Na₂[ADA]) to facilitate the absorption of H₂S into an alkaline solution [Speight, 2007].

This chapter reviews the Stretford process and the complex chemistry via reduction-oxidation (redox) reactions that occur in this process. The Stretford aqueous liquor contains dissolved salts of various compounds such as vanadium salts, Na₂[ADA], sodium sulphate (Na₂SO₄), sodium thiocyanate (NaSCN), sodium bicarbonate (NaHCO₃) and sodium carbonate (Na₂CO₃). The chemistry of the

process is complicated and there are many chemical reactions that occur and influence the process. One such reaction is the oxidation of sodium thiocyanate in Stretford aqueous liquor to form sodium sulphate, sodium bisulphate and sodium thiosulphate (“sticky” sodium salts). This is the primary reaction that is dealt with and discussed in this study.

2.2. Stretford Process Chemistry

2.2.1. Stretford Process Summary

As early as the beginning of the 1900’s, there has been continuous work and research to develop a liquid phase regenerative process for converting H_2S into pure elemental sulphur [Nagl, 2005]. There have been over 25 different processes, most of which have had little commercial success. During the late 1940’s, the North Western Gas Board and the Clayton Aniline Company developed the Stretford process [Wilson and Newell, 1984]. Many process operational and environmental problems accompanied the process but it became fairly popular in the 50’s, 60’s and 70’s [Nagl, 2005]. Some of the other processes include the Chelated Iron Process (CIP), which makes use of chelated irons, the LO-CAT[®] process and the Sulferox process [Nagl, 2005].

It has been established that the Stretford process is the most versatile for converting H_2S into elemental sulphur. This process has a removal efficiency rate of 99% for a wide variety of conditions [Nagl, 2005]. In the Stretford process, air is used to oxidise H_2S in process gases to elemental sulphur.

The H_2S gas is absorbed into an alkaline solution at a pH of approximately 8.5-9. During dissolution, H_2S is deprotonated to form HS^- ions. The alkaline solution, where dissolution of H_2S takes place, contains dissolved V^{5+} salts and $Na_2[ADA]$. These salts are water soluble. They act as catalysts and facilitate a reduction reaction with HS^- ions. The resulting reduced solution is passed into an oxidation reactor where air reacts with it to form elemental sulphur [Kelsall, *et al*, 1993]. The reduced solution contains V^{4+} and H_2ADA which are re-oxidised in the presence of air to V^{5+} and $Na_2[ADA]$. The regenerated solution is re-cycled back to the absorption stage, where it is ready for further contact with H_2S . The elemental sulphur formed is hydrophobic and concentrates in a froth flotation layer at the liquid surface, where it is recovered and filtered [Kelsall and Thompson, 1993a].

2.2.2. Detailed Process Description

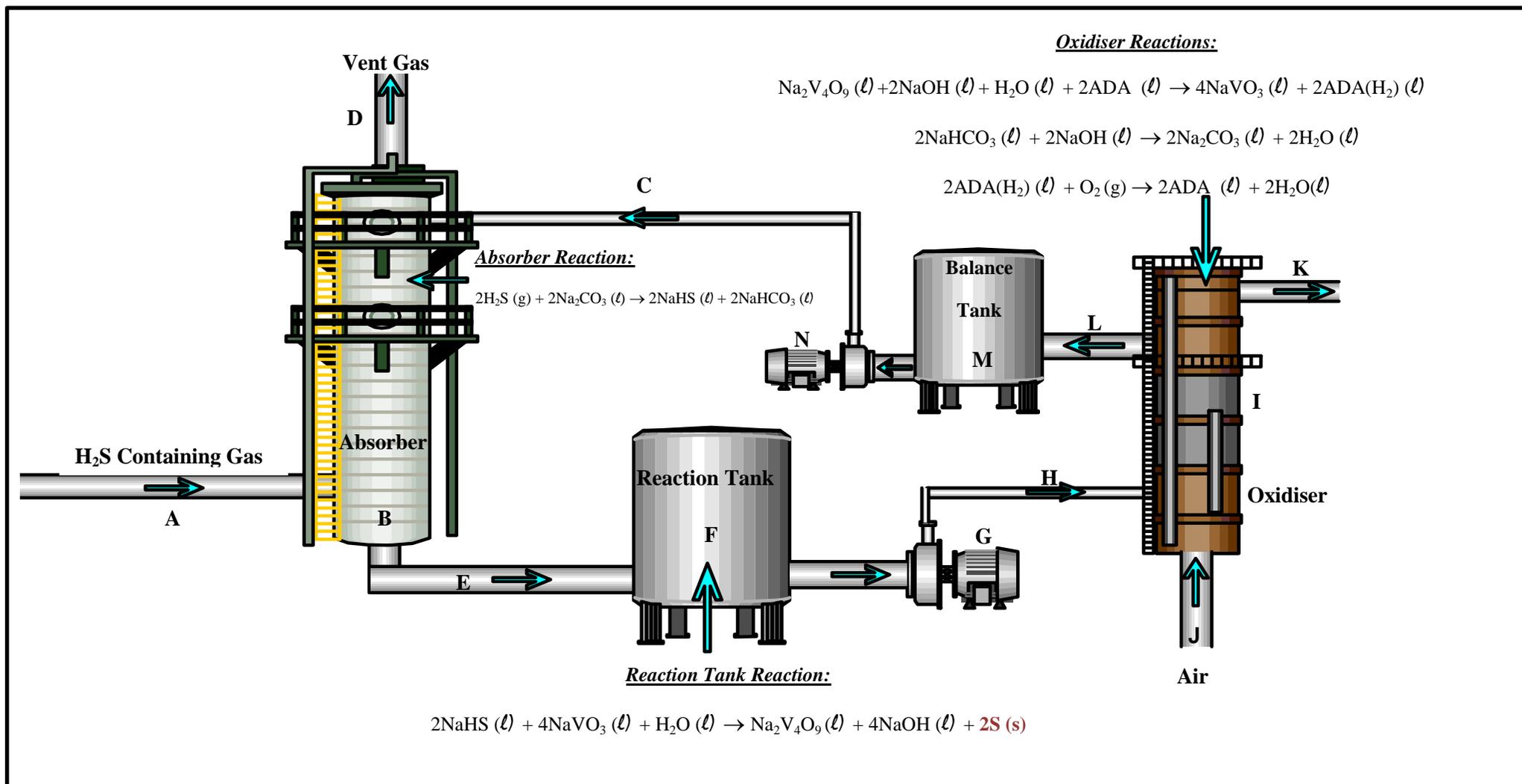


Figure 2.1: A simplified process flow diagram with basic reactions for the Stretford Process [Harmon and Brinkman, 2003].

Figure 2.1 is a simplified process flow diagram for equipment typically employed in the Stretford process [Harmon and Brinkman, 2003]. With reference to Figure 2.1, H₂S containing gas is introduced into the bottom of the absorber (B) via stream (A). A washing solution (i.e. Stretford process aqueous liquor) is introduced into the top of the absorber (B) via stream (C). The Stretford washing solution, essentially the liquid that scrubs and absorbs the H₂S gas flows counter current downwards in the absorber (B), while H₂S gas flows upwards. In an ideal situation all the H₂S gas is absorbed into the Stretford washing solution. The vent gas that is free of H₂S is released into the atmosphere via outlet (D) [Harmon and Brinkman, 2003].

After the absorption of H₂S has taken place, oxidative reactions convert H₂S into elemental sulphur. The oxidation reactions occur as a result of certain constituents such as ADA and V⁵⁺ in the Stretford aqueous liquor. Refer to Section 2.2.3 for details of chemical reactions that take place in the Stretford aqueous liquor [Harmon and Brinkman, 2003; Kelsall, *et al*, 1993].

After the oxidation reactions have taken place, the reduced Stretford aqueous liquor is removed from the absorber (B) via stream (E) into a reaction tank (F). The purpose of the reaction tank is to allow the completion of oxidation of H₂S into elemental sulphur and this normally takes 10-15 minutes to happen [Harmon and Brinkman, 2003].

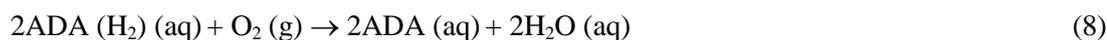
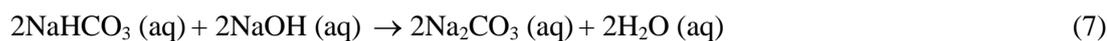
The reduced circulation aqueous solution and entrained sulphur come into contact with air introduced into the bottom of the oxidiser (I) via inlet stream (J). The air oxidises the spent Stretford aqueous liquor and regenerates the ADA and V⁵⁺. It also has the dual role of floating the elemental sulphur, which is formed, to the top of the oxidiser. A slurry of sulphur is thus formed and withdrawn from the oxidiser at stream (K) [Harmon and Brinkman, 2003; Kelsall, *et al*, 1993].

The regenerated solution is removed from the oxidiser (I) and recycled back to the absorber (B) via stream (L) using a recycle pump (N). An optional surge tank (M) may serve as a tank for Stretford aqueous liquor which is eventually recycled back to the absorber (B) [Harmon and Brinkman, 2003].

2.2.3. Reactions in Stretford Aqueous Liquor

As mentioned in the introductory section, Stretford aqueous liquor is a complex solution containing an aqueous solution of sodium vanadate (NaVO₃), ADA and sodium carbonate (Na₂CO₃). The key reactions that occur to remove H₂S from a gas stream are represented by the chemical reactions shown below: [Kohl and Riesenfeld, 1974, and Kelsall, *et al*, 1993].





Reaction (4) represents the absorption of H_2S in an alkaline solution (i.e. hydrogen sulphide is absorbed by sodium carbonate). The rate of absorption is favoured by a high pH of approximately 8.5, however the rate of conversion of absorbed H_2S to elemental sulphur is adversely affected by pH values above 9.5. The rate of conversion to form elemental sulphur is rapid and essentially a function of the vanadate concentration [Kohl and Riesenfeld, 1974]. Figure 2.6 represents the reaction rate as a function of vanadate concentration. Two moles of sodium vanadate are required to oxidise each mole of sodium hydrogen sulphide to sulphur [Kohl and Riesenfeld, 1974].

During conversion of the absorbed H_2S to elemental sulphur, there is reduction of vanadium from the pentavalent to the quadrivalent oxidation state (Reaction 5). The reduced vanadium is re-oxidised to the pentavalent oxidation state by ADA which acts as a catalyst (Reaction 6). The air introduced into the oxidiser re-oxidises the $\text{ADA}(\text{H}_2)$ back to ADA [Kohl and Riesenfeld, 1974]. Reactions (4)-(8) require the ionised forms of the reactants in aqueous solution. The liquid redox chemical mechanism for vanadium ions and ADA can be seen in Figure 2.2. The diagram depicts in a simplified manner the gas cleaning, conversion to sulphur and liquid regeneration phases during the Stretford process. All concentrations, especially ADA and the vanadium (5+) ions must satisfy the overall H_2S removal reaction (Reaction 9).

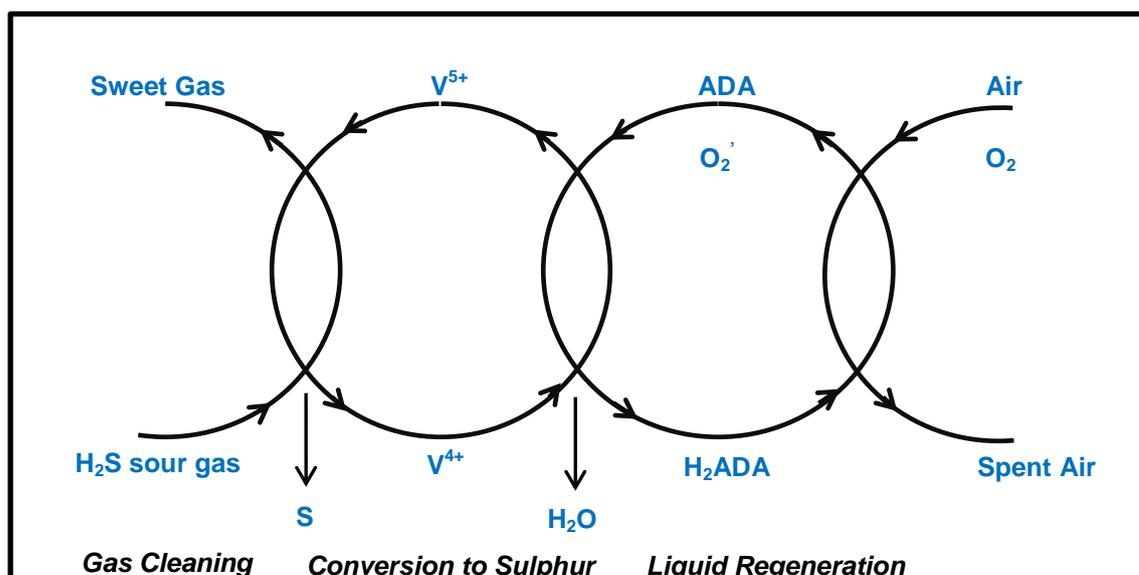
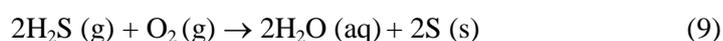


Figure 2.2: Liquid redox chemical mechanism diagram for vanadium ions and ADA transformations during the Stretford process [Kelsall, *et al*, 1993].

Although the Stretford process is effective in removing H₂S from gas streams in industry, it is costly to maintain the Stretford aqueous liquor and this contributes to increased operating costs. Unwanted side chemical reactions can result in a portion of the absorbed H₂S and the product sulphur/salts being converted to water soluble sulphur containing salts such as sulphates, thiosulphates and polythionates [Harmon and Brinkman, 2003].

The chemical reactions of the process have to be controlled optimally to maintain absorption efficiency and hydrogen sulphide and sulphur production efficiency. Several side reactions occur in the Stretford process which degrades the absorbing solution. The various side reactions that occur will be discussed in further detail in this chapter.

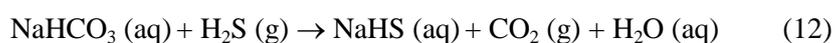
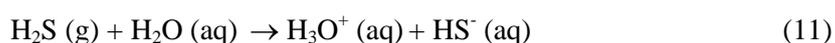
2.2.4 Properties and Functions of the Stretford Process Chemicals

a) Sodium Carbonate (Na₂CO₃), Sodium Hydrogen Carbonate (NaHCO₃), and Hydrogen Sulphide (H₂S)

The Stretford process solution has to be made alkaline to pH values above 8. The preferred pH for this aqueous solution is between 8.5- 9.0. This is achieved by the addition of alkalis such as sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonia (NH₃), or sodium, potassium or ammonium carbonates or bicarbonates. The most common alkalis used are sodium carbonate or bicarbonate. A mixture of the two in the ratio of 0.0094-0.075 mol.dm⁻³ sodium carbonate to 0.12-0.36 mol.dm⁻³ sodium bicarbonate is an example of an acceptable mixture [Fenton and Vaell, 1977]

Carbonates (i.e. Na₂CO₃ and NaHCO₃) contribute to the total alkalinity of the Stretford aqueous liquor. Typical values for total alkalinity in Stretford aqueous liquor lie between 0.24 mol.dm⁻³ and 0.33 mol.dm⁻³. The alkaline solution makes conditions appropriate for the absorption of H₂S in the Stretford aqueous liquor.

The following reactions (10), (11) and (12) explain the dissociation of Na₂CO₃, H₂S and the absorption of H₂S from the feed gas: [Trofe, *et al*, 1993]



The formation of CO_2 (See Reaction 42) is critically important. Carbon dioxide is absorbed into the sodium carbonate alkaline solution to form sodium bicarbonate. This results in the lowering of the solution pH and lowers the H_2S absorption efficiency from the feed gas [Kohl and Riesenfeld, 1997].

b) Sodium Hydroxide (NaOH)

Since the pH in the Stretford circulation solution is so critical for the formation of elemental sulphur and for the prevention of premature sulphur formation, NaOH is added to the Stretford circulation solution to maintain the pH at 8.0-8.5. The pH should therefore be increased and controlled at 8.3 optimally by the addition of NaOH. The carbonate ions exist mainly as HCO_3^- at a pH of approximately 8.3, by stabilizing and creating a buffer capacity for the Stretford aqueous liquor. As a result the critical pH parameter of the Stretford aqueous liquor is controlled (see Figure 2.3 below) [Rice, *et al*, 2012].

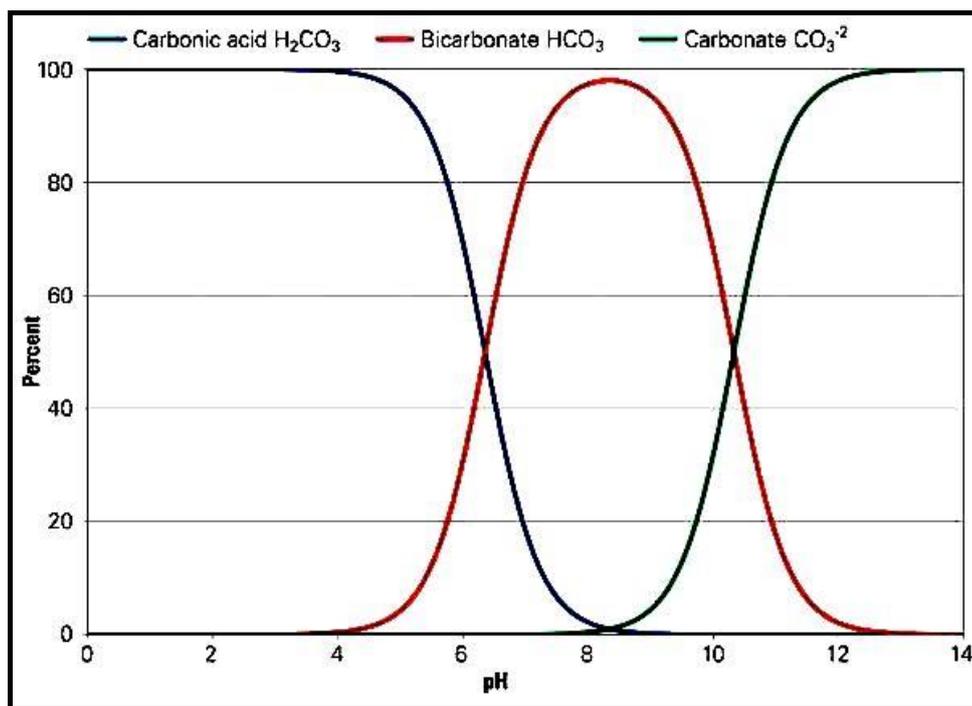


Figure 2.3: The Carbonate-Bicarbonate buffering system [Rice, *et al*, 2012].

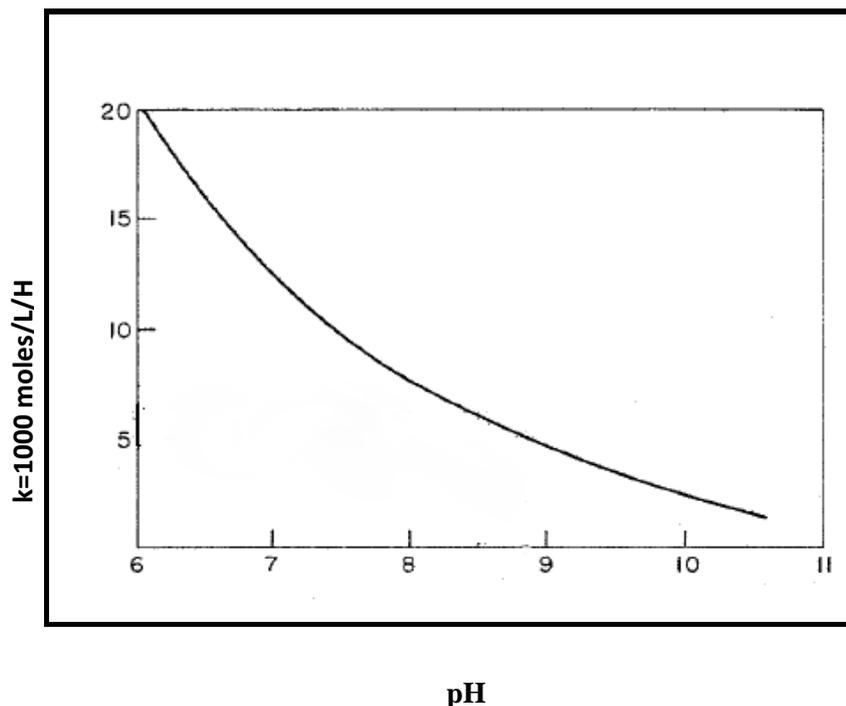


Figure 2.4: The effect of pH on the hydrogen sulphide reaction rate constant [Kohl and Riesenfeld, 1974].

From Figure 2.4 it can be seen that the H_2S absorption reaction rate decreases exponentially with an increase in pH [Kohl and Nielsen, 1997]. The speciation diagram which is shown in Figure 2.5 also illustrates that the bisulphide anions (HS^-) form optimally at a pH of approximately 8.

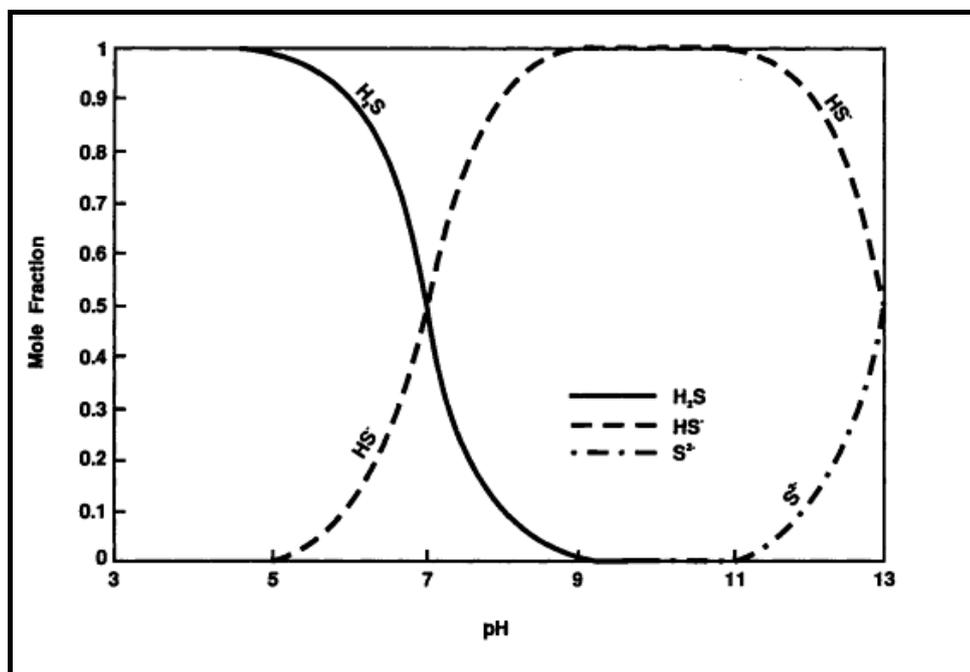


Figure 2.5: The hydrogen sulphide speciation diagram at 25 °C [Kohl and Riesenfeld, 1997].

c) Sodium Vanadate (NaVO_3)

V^{5+} is used as a catalyst for the oxidation of H_2S into elemental sulphur. During this oxidation to elemental sulphur, V^{5+} is reduced to V^{4+} . Due to the fact that the various mononuclear and polynuclear anions exist in equilibrium with each other, the chemistry of vanadium species in the aqueous liquor is very complex. These equilibria depend on many factors, such as vanadium species concentrations, the ionic strength, pH, other salts concentrations and temperature [Cruywagen, *et al*, 1998]

Scientific literature mentioned that vanadium concentrations of up to $0.059 \text{ mol.dm}^{-3}$ are optimum for the Stretford process [Stavros, 2006]. The V^{5+} concentration is maintained in the Stretford process by adding the vanadium salt in the form of an aqueous solution. The V^{5+} concentration should be at least twice as high as the concentration of the hydrogen sulphide anions (HS^-) in the gas feed [Kohl and Riesenfeld, 1974]. Therefore the dosing of vanadium salts in the circulation liquor depends on the H_2S content in the feed gas.

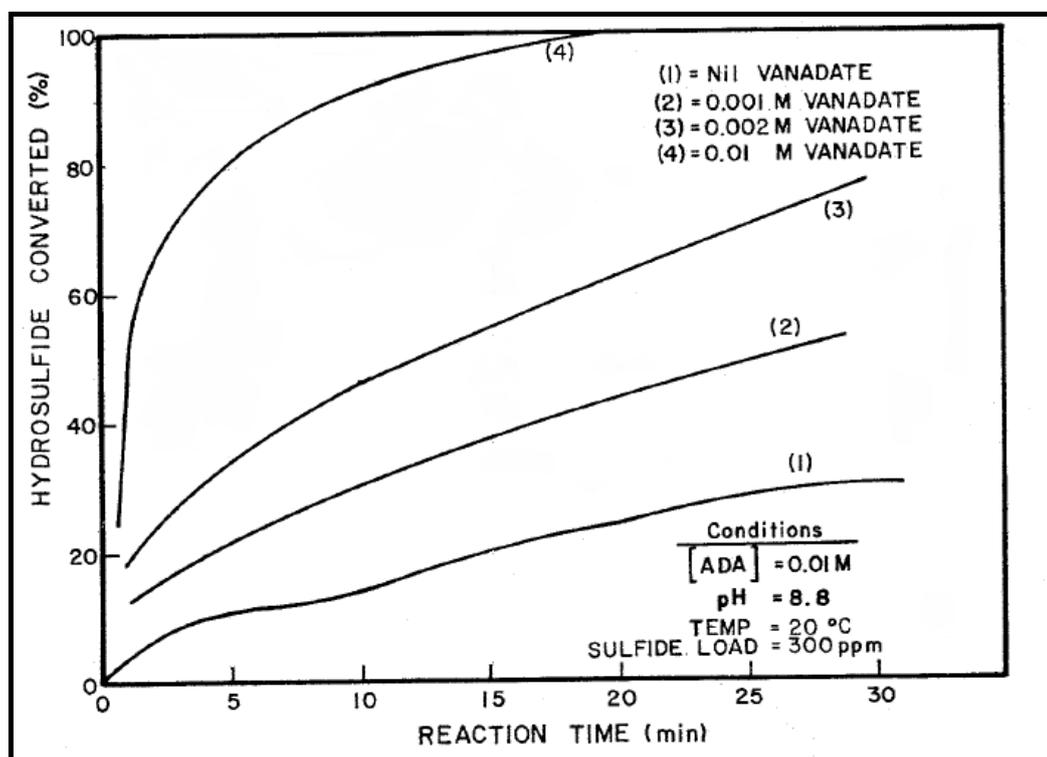
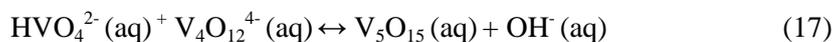
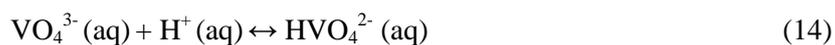


Figure 2.6: Rate of conversion of hydrogen sulphide as a function of vanadate concentration [Kohl and Riesenfeld, 1974].

The ortho-vanadate anion VO_4^{3-} exists in equilibrium with the di- and poly-nuclear species in aqueous solutions of pH 6-10. The di- and poly-nuclear species are formed by the protonation, condensation and insertions reactions shown below: [Cruywagen, *et al*, 1998]



The tetramer and pentamer are cyclic and of the general formula $(\text{VO}_3)_n^{n-}$. The two ions are commonly abbreviated as V^{4+} and V^{5+} respectively. [Cruywagen, *et al*, 1998].

The mono-, di-, tetra- and pentameric anions are colourless, while the decameric species $[\text{V}_{10}\text{O}_{28}]^{6-}$ is yellow [Cruywagen, *et al*, 1998]. At high pH, V^{5+} is the most stable form of vanadium in aqueous solution, whereas at low pH, V^{4+} is the more favoured species. From pH 2-6, the major V^{5+} species is the decamer $[\text{V}_{10}\text{O}_{28}]^{6-}$ and its protonated forms. This is a highly yellow-orange coloured species and is thermodynamically unstable at neutral and alkaline pH [Crans, *et al*, 2004].

At high V^{5+} concentrations (0.01-0.1 mol.dm⁻³), the reaction of V^{5+} with Na_2S of similar molar concentration results in a green brown mixture. Upon addition of more Na_2S , a brown-black solid precipitates. This solid dissolved in hydrochloric acid to form a blue solution [Kelsall, *et al*, 1993].

These insoluble black V^{4+} compounds produce the well-known blue vanadyl cation, $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ upon dissolution in hydrochloric acid [Kelsall, *et al*, 1993].

d) Anthraquinone disulfonic Acid, disodium salt ($\text{Na}_2[\text{ADA}]$)

Figure 2.7 gives the chemical structure of anthraquinone disulfonic acid, disodium salt. The chemical formula for anthraquinone disulfonic acid, disodium salt ($\text{Na}_2[\text{ADA}]$) is $\text{C}_{14}\text{H}_6\text{Na}_2\text{O}_8\text{S}_2$ and the molecular weight is 412 g.mol⁻¹

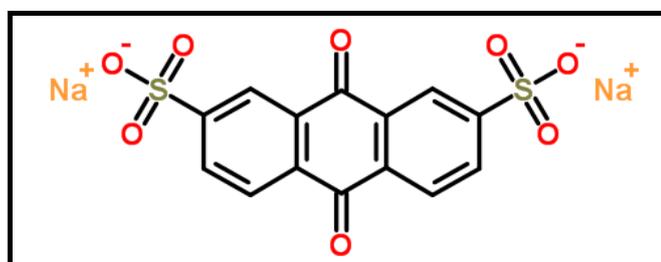


Figure 2.7: Chemical Structure of anthraquinone disulfonic acid, disodium salt [Chemspider, 2014].

As mentioned, gas streams containing H_2S are brought into contact with an aqueous circulation solution (i.e. Stretford liquid) which has an alkaline composition and contains one or more dissolved anthraquinone disulfonic acids. During the absorption process, hydrogen sulphide is oxidised and sulphur is liberated. The reduced anthraquinone disulfonic acid (H_2ADA) or acid is re-oxidised by oxygen to ADA (Refer to Figure 2.8).

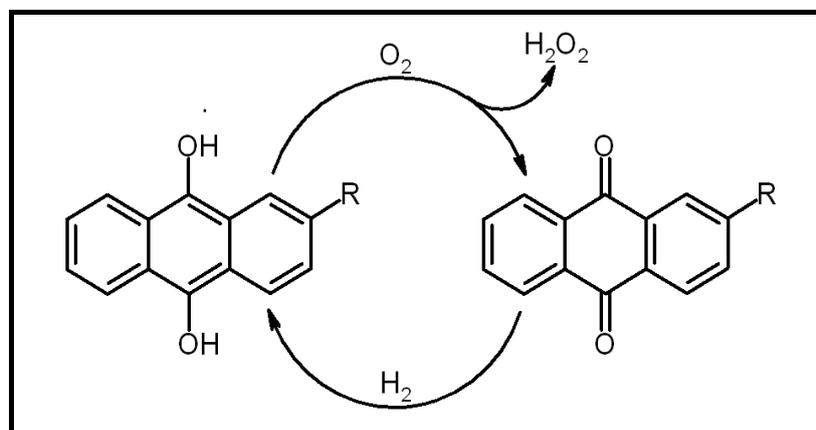


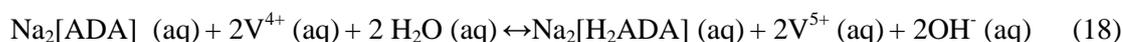
Figure 2.8: The oxidised and reduced forms of ADA [Wikipedia, 2014].

There are many different isomers of anthraquinone disulfonic acids. They include anthraquinone- 1,5 disulfonic acid, anthraquinone- 1,6 disulfonic acid, anthraquinone- 1,7 disulfonic acid, anthraquinone- 2,6 disulfonic acid and **anthraquinone- 2,7 disulfonic acid** [Nicklin, *et al*, 1961]. Some of the isomers or mixtures are suitable for the process, however the anthraquinone- 2,6 disulfonic acid and anthraquinone- 2,7 disulfonic acid have higher reactivity with sulphide and are preferred materials. The anthraquinone- 2,7 disulfonic acid is the most soluble in water and hence the most preferred out of all the anthraquinone disulfonic acid salts [Fenton and Vaell, 1977]. The concentration of $Na_2[ADA]$ in the Stretford aqueous liquor, calculated as the disodium salt (see Figure 2.7) can be as high as $0.012 \text{ mol.dm}^{-3}$, but the preferred range is between $0.00073\text{-}0.0073 \text{ mol.dm}^{-3}$ [Fenton and Vaell, 1977].

$Na_2[ADA]$ has the following properties and these make them particularly suitable for use in the Stretford aqueous liquor [Nicklin, *et al*, 1961].

- Due to the fact that they do not undergo substantial decomposition in the presence of iron and alkali and can be re-used indefinitely with no loss, they can be classified as stable compounds.
- They are non-toxic.
- Anthraquinone- 2,7 disulfonic acid is soluble in water in the reduced and oxidised states.
- The two sulfonate groups (SO_3^-) increase the solubility as well as the oxidation potential.
- The Stretford process can be carried out economically viable due to the fact that they have fast reactions for both the oxidation and reduction reactions.

The primary function of Na₂[ADA] in the Stretford aqueous liquor is its catalytic function for the re-oxidation of reduced V⁴⁺ ions. The equation shown below illustrates the reaction for the re-oxidation of V⁴⁺ to V⁵⁺:

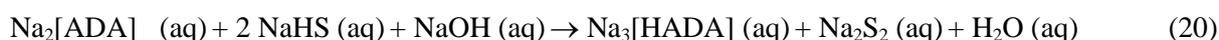


One of the two phenolic OH⁻ groups of the reduced Na₂[ADA], Na₃[HADA], is deprotonated. This deprotonation occurs at alkaline pH due to the fact that phenols are weak acids. The mechanism is shown below in reaction 19 [Kellsall and Thompson, 1993b].



The concentrations of the H₂ADA²⁻, HADA³⁻ and ADA⁴⁻ are pH dependent and the concentrations have been determined by UV-Vis spectroscopy [Gamage, *et al*, 1991]. The pK_a(1) and pK_a(2) values for H₂ADA at 25°C have been determined as 7.4 and 10.8 respectively. The pK_a value of 7.4 implies that at a pH of 7.4, the ratio of H₂ADA²⁻ and HADA³⁻ is 1:1 [Kellsall and Thompson, 1993b]. 80% of the doubly reduced Na₂[ADA] exists as HADA³⁻ and 20% remains as undissociated H₂ADA²⁻ at a pH of approximately 8 for Stretford aqueous liquors. At Stretford aqueous solution pH values, ADA⁴⁻ can be neglected as it will only exist at pH values exceeding 11 [Kellsall and Thompson, 1993b].

Due to Na₂[ADA] solutions being a strong oxidant, with increased oxidation potential as a result of the SO₃⁻, it is easily able to oxidise sodium hydrogen sulphide (NaHS) (reaction 20).



It is important to note that Na₂[H₂ADA] and Na₃[HADA] are known to react with molecular oxygen (air) back to Na₂[ADA]. H₂O₂ is liberated under certain conditions (refer to Figure 2.8) and this is an important reaction that has consequences in the Stretford aqueous liquor [Kellsall, *et al*, 1993]



The concentration of Na₂[ADA] can be determined using spectrophotometry after reduction to the highly coloured H₂ADA²⁻ form in a strong alkaline solution.

$\text{Na}_2[\text{ADA}]$ is one of the principal components of Stretford aqueous liquors. $\text{Na}_2[\text{ADA}]$ is chemically consumed in Stretford aqueous liquors after the treatment of tail gases, and with hydrogenated Claus process tail gas in particular. $\text{Na}_2[\text{ADA}]$ is expensive and has to be added to Stretford aqueous liquors to maintain proper concentration of this constituent [Fenton and Vaell, 1977]. Thiocyanate ion precursors have been added to Stretford aqueous liquors which contain an insufficient amount of thiocyanate ions to prevent the consumption of the $\text{Na}_2[\text{ADA}]$. By increasing the concentration of thiocyanate in Stretford aqueous liquors, the rate at which $\text{Na}_2[\text{ADA}]$ is chemically consumed is reduced [Fenton and Vaell, 1977].

e) Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide is a colourless liquid, slightly more viscous than water with the chemical formula H_2O_2 . It is the simplest known peroxide and has the structure given in Figure 2.9.

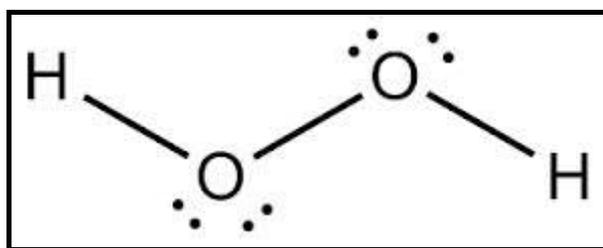
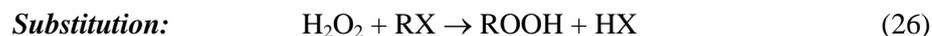


Figure 2.9: Electron distribution diagram of hydrogen peroxide [Chemistry stack exchange, 2014].

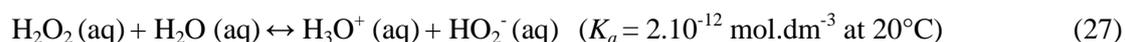
Due to their exceptional reactivity and oxidative capacity, inorganic and organic peroxides are widely used in laboratories and in industry [Clark, 2001]. It has a weak oxygen-oxygen linkage with a bond dissociation energy of 20-50 kcal/mole. This is characteristic of organic and inorganic peroxides. Inorganic peroxides react with organic compounds to generate organic peroxide and hydro-peroxide products. Peroxides are exceptionally prone to violent decomposition initiated by several mechanisms, including heat, mechanical shock or friction. Knowledge of their dangers is imperative and handling and storage precautions must be exercised when working with them [Clark, 2001].

The O-O bond of hydrogen peroxide is covalent. The persalts of alkali metals (M_2O_2) are ionized to the mono-positive alkali metal ion, M^+ , and the di-negative peroxide ion, O_2^{2-} . Due to its versatility, H_2O_2 has a high oxidative capacity over a wide pH range. Its oxidation potential at pH=0 is 1.763 V and pH =14 is 0.878 V. Hydrogen peroxide can undergo a number of reactions, depending on the type of substrate. These include decomposition, oxidation, molecular addition, reduction and substitution reactions. The basic mechanisms for these are shown below in equations 22-26: [Campos-Martin, *et al*, 2006]

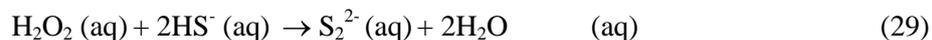


In the Stretford aqueous liquor, hydrogen peroxide is formed from $\text{Na}_2[\text{ADA}]$ and molecular oxygen in the oxidisers (refer equation 21). This results in the regeneration of $\text{Na}_2[\text{ADA}]$, which is a compulsory oxidant for the Stretford process.

H_2O_2 is a strong oxidant and a weak acid in water. Reaction 27 shows the dissociation of H_2O_2 in water with its associated ionization constant:



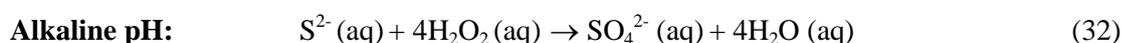
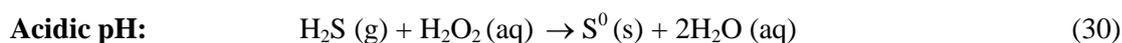
Due to its reactivity in water, H_2O_2 produces water or its components if it is reduced. An example of the reduction can be seen below with V^{4+} and bisulphide ions.



From Reaction 28, it can be seen that hydrogen peroxide is very effective in re-oxidising V^{4+} back to V^{5+} [Trofe, *et al*, 1987]. It is generally assumed that $\text{Na}_2[\text{ADA}]$ is predominantly a catalyst for the re-oxidation of the V^{4+} ion. However the role of $\text{Na}_2[\text{ADA}]$ can also be to produce H_2O_2 by reaction of reduced $\text{Na}_2[\text{ADA}]$ (i.e. $\text{Na}(\text{HADA})$) which is formed in the reaction tank with molecular oxygen from the oxidisers (refer to Reaction 21 for the mechanism) [Trofe, *et al*, 1993].

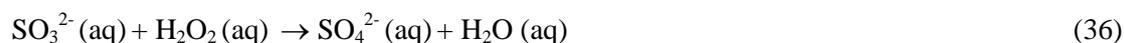
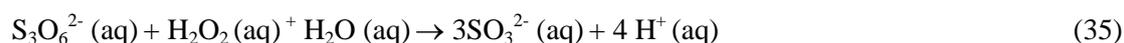
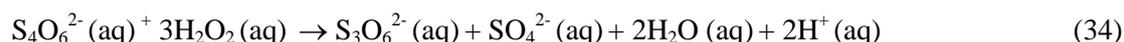
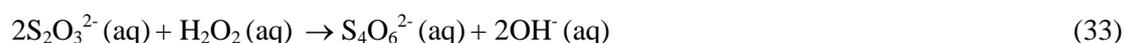
Sulphides and polysulphides exist in equilibrium with their basic and protonated forms in solution. This equilibrium is dependent on the pH of the solution (refer to Figure 2.5). Therefore the reaction of sulphide species with hydrogen peroxide is also influenced by the pH. Under acidic or neutral conditions, sulphide species are predominantly oxidised to sulphates. Polysulphides react with hydrogen peroxide in a similar way as sulphides and form sulphate or elemental sulphur, depending on the pH of the oxidation [Jones, 1999].

The key reactions that occur at the various pH values are outlined below: [Jones, 1999]



The pH where oxidation of sulphide species occurs therefore affects the quantity of hydrogen peroxide required. This means that under neutral conditions a mass ratio of between 1.1:1 and 1.3:1 ($\text{H}_2\text{O}_2/\text{S}$) is required. This ratio changes to 4.25:1 under alkaline conditions [Jones, 1999].

During the oxidation of thiosulphates by hydrogen peroxide, a series of reactions take place. Tetrathionates are formed first followed by trithionates, sulphites and finally sulphates [Jones, 1999]. The oxidation of thiosulphates is shown below: [Jones, 1999].

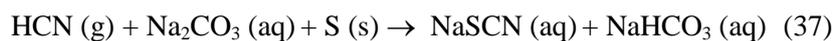


The tetrathionate stage is reached under acidic to alkaline conditions whereas the oxidation of thiosulphate proceeds to form sulphates under alkaline conditions. Polythionates are an intermediate species in the oxidation of thiosulphates. An example is trithionate. The oxidation of sulphites to sulphates using hydrogen peroxide takes place and is not dependent on the pH [Jones, 1999].

f) Sodium Thiocyanate (NaSCN)

Sodium thiocyanate is the chemical compound with the formula NaSCN. The crystals are colourless and odourless. NaSCN is one of the primary sources of the thiocyanate anion and as a result is used as a precursor for the synthesis of pharmaceuticals and other speciality chemicals (MSDS – www.sigmaaldrich.com).

The presence of HCN in the feed gas to the Stretford aqueous liquor results in the formation of NaSCN and total dissolved salts (TDS) and this leads to substantial increase in Stretford purge requirements to control increases in total dissolved solids [Kohl and Riesenfeld, 1974]. NaSCN is formed in Stretford aqueous liquors by the following equation:



The SCN^- anion is said to have bacteriostatic properties and is therefore added into the Stretford aqueous liquor to control the growth of sulphur oxidising bacteria (SOB's) in the Stretford aqueous liquors. NaSCN at a concentration of 0.62 mol.dm^{-3} has been reported as being sufficient for the control of sulphur oxidising bacteria [Wilson and Newell, 1984].

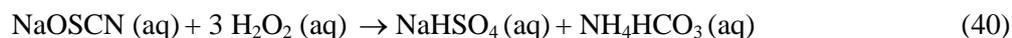
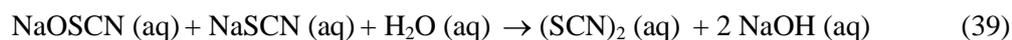
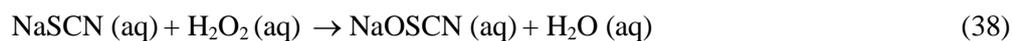
It has also been reported that the addition of NaSCN to the Stretford process facilitates the solubilisation of vanadium compounds and reduces sulphur by-product formation [Weber, 1985]. The formation of thiosulphate in the simultaneous scrubbing and oxidation of H_2S is suppressed by the addition of thiocyanate. These can be added in the form of sodium, potassium or ammonium thiocyanate. The addition of thiocyanate in the concentration of $0.06\text{-}0.5 \text{ mol.dm}^{-3}$ was shown to be advantageous, however $0.3\text{-}0.4 \text{ mol.dm}^{-3}$ is preferred [Weber, 1985].

The microbial thiocyanate utilization under highly alkaline conditions was examined [Sorokin, *et al*, 2001]. It was found that there were three types of alkaliphilic bacteria that were able to utilize thiocyanate (SCN^-) at pH 10. These bacteria were found in highly alkaline soda (sodium carbonate) lake sediments and soils. They were obligate heterotrophs, obligate autotrophic sulphur-oxidising alkaliphiles and obligate autotrophic sulfur-oxidising alkaliphilic bacteria. The three types utilized thiocyanate as a nitrogen source while growing at pH 10 with acetate as carbon and energy sources, utilized thiocyanate nitrogen during growth with thiosulfate as the energy source and utilized thiocyanate as a sole source of energy, respectively. The use of alkaliphilic bacteria to degrade thiocyanate under highly alkaline conditions proves useful in improving bio-removal of thiocyanate from alkaline wastewater.

The oxidation of NaSCN in alkaline solutions has been studied many times due to its physiological importance; however the oxidation of NaSCN in Stretford plants has not been investigated in more detail. The mechanism of its oxidation and the responsible oxidant is not clear. The most probable oxidants working on thiocyanate in the Stretford aqueous liquor will be the peroxy radicals resulting from the reduction of O_2 by $\text{Na}_3[\text{HADA}]$ to form hydrogen peroxide (see Reaction 21).

The peroxide radicals react with NaSCN to form NaOSCN, commonly known as hypo-thiocyanite or cyanosulfoxylate in literature. The OSCN^- is a powerful anti-microbial agent and may probably be the bacteriostatic reagent in the Stretford process [Kalmár, *et al*, 2013].

The following reaction sequence has been proposed for the oxidation of SCN^- ions by hydrogen peroxide to form NaHSO_4 and NH_4HCO_3 [Kalmár, *et al*, 2013; Wilson and Harris, 1960; Orban, 1986; Barnett and Stanbury, 2002 and Nagy, *et al*, 2006]



Reaction (38) was not confirmed as the rate determining step. NaOSCN is observed as an intermediate and can therefore not be isolated as a pure material. Several spectroscopic techniques such as NMR and UV-Vis have been used to detect NaOSCN and it has also been separated by electrophoresis. [Cristy and Egeberg, 2000].

(SCN)₂ is a thiocyanogen and is unstable at 25°C. It polymerizes easily and is hydrolysed to HSCN and HOSCN in water. From the reactions (38-40) it is evident that ammonium ions, sulphate and carbonate are the major soluble by-products [Wilson and Harris, 1960; Orban, 1986; Barnett and Stanbury, 2002 and Nagy, *et al*, 2006]. A decrease in pH is expected when NaSCN is dosed into Stretford aqueous liquor for bacterial control because hydrogen sulphate (NaHSO₄) and sulphuric acid (H₂SO₄) are strong acids while ammonium hydrogen carbonate (NH₄HCO₃) has a pH of approximately 7.0 - 7.8 in water.

The thiocyanate oxidation by hydrogen peroxide generated in gas diffusion electrode in alkaline media has been studied [Kenova and Kornienko, 2002]. Ecologically safe methods to purify industrial wastewater of hazardous substances have become critical. The most common method of disposing of toxic wastes such as cyanides and thiocyanates in the form of cyanide complexes is chlorination [Kenova and Kornienko, 2002]. Other methods such as treatment with mixtures of air and sulphur dioxide are not as efficient. The rate of indirect oxidation of thiocyanates in a cell with cation exchange membranes is considerably lower than in a cell without such membranes. It was also found that the rate and efficiency of thiocyanate destruction increased in the presence of hydrogen peroxide generated from oxygen in a gas diffusion electrode [Kenova and Kornienko, 2002].

The efficiency of cyanide oxidation by hydrogen peroxide depends on a number of factors including concentration of the oxidising agent and substrate, pH, temperature, and presence of acceptors of oxy radicals. The consumption of H₂O₂ for thiocyanate oxidation in an alkaline medium is more than 10 mol/mol SCN⁻ [Kenova and Kornienko, 2002]. Cyanates, ammonium ions, sulphites, sulphates, carbonates and water are the products formed from the oxidation of thiocyanate by hydrogen peroxide [Kenova and Kornienko, 2002].

As a result of being used in many industrial processes, thiocyanate (SCN⁻) is commonly found in industrial and mining wastewaters. It occurs as a result of the interaction between free cyanide (CN⁻) and dissolved sulphur or polysulphides. In gold ore concentrators, sulphur dioxide (SO₂) is used to

convert CN^- to SCN^- . Due to its toxic effects, SCN^- must be removed from wastewater [Kuyucak and Akcil, 2013].

The direct oxidation of thiocyanate by molecular oxygen can be eliminated unless traces of metal ions such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ are present and facilitate the reaction as catalysts. The oxidation of thiocyanate by Fe^{6+} and Fe^{5+} has been studied extensively. Environmentally friendly oxidants namely Fe^{6+} and Fe^{5+} were used to determine oxidation of thiocyanate. Such a study was performed under anaerobic conditions using stopped-flow and premix radiolysis techniques [Sharma, *et al*, 2002]. Conclusions from the study indicated that the rate of oxidation of SCN^- by Fe^{5+} was approximately 3 orders of magnitude faster than Fe^{6+} . If appropriate one electron reducing agents are used, then oxidation of SCN^- with Fe^{6+} can be enhanced. The results suggest effective removal of SCN^- by Fe^{5+} and Fe^{6+} [Sharma, *et al*, 2002].

Following the previous study, the destruction of cyanide and thiocyanate by ferrate (Fe^{6+}) was also investigated. Once the processing of gold in the mining industry has been completed, chemically contaminated effluents containing cyanide (free or metal complexed species) are generated. Due to its toxic effects, cyanide has to be removed from the effluent before discharge into the aquatic environment. The traditional methods of natural degradation, sulphur based, hydrogen peroxide, ozonation and alkaline chlorination were not sufficient and therefore a new chemical oxidant utilising iron in the +6 oxidation state was studied for the purposes of oxidising cyanides in gold mill water [Sharma, 2003].

It was found that complete removal of cyanide and thiocyanate were achieved in seconds to minutes with the formation of less harmful products, making ferrate (Fe^{6+}) suitable as a new environmentally friendly oxidant [Sharma, 2003].

An article on cyanide and removal options from effluents in gold mining and metallurgical processes was also compiled [Kuyucak and Akcil, 2013]. Cyanide is converted to thiocyanate after reaction with sulphur species. Thiocyanate is seven times less toxic than cyanide. Sulphide minerals include chalcopyrite (CuFeS_2), chalcocite (Cu_2S) and pyrrhotite (FeS). Their oxidation products include polysulphides and thiosulphate. These can be found in soil and provide a source of sulphur. All sulphides minerals, except lead sulphide, have the potential to generate thiocyanate, where production is accelerated if inadequate aeration is allowed in conjunction with low alkalinity conditions. It may break down chemically and biologically, producing ammonia, nitrate, carbonate and sulphate [Kuyucak and Akcil, 2013].

The photocatalytic oxidation of cyanate to nitrate over TiO_2 was also investigated [Bravo, *et al*, 1994]. The observations indicate that the photocatalytic oxidation of cyanate ions in an aqueous solution and in the presence of TiO_2 takes place by two different reaction pathways. This oxidation of cyanate is

however dependent on the pH of the solution. NH_4^+ is formed during the hydrolysis of OCN^- . It was found that nitrate instead of N_2 is the main oxidation product at pH values lower than 10. In a strongly basic medium, the photo-oxidation of OCN^- to N_2 appeared to be faster. NH_4^+ is rarely oxidised and remains very stable in solution at pH values lower than 5 [Bravo, *et al*, 1994].

Raman spectroscopy was used in a study that investigated the rate constants for cyanate hydrolysis to urea [Wen and Brooker, 1994]. It was found that peaks related to cyanate became less intense and those attributed to urea, carbamate and carbonate became more intense as time passed. It was also confirmed that cyanate hydrolysis occurred slowly and spontaneously at room temperature. There was formation of urea, carbamate and carbonate without the additional ammonium ions. The hydrolysis of cyanate with water and the reaction of cyanate with aqueous ammonia were found to be first and second order kinetic reactions, respectively.

It can be concluded from the information above that thiocyanate is useful for its bacteriostatic properties and also its ability to protect $\text{Na}_2[\text{ADA}]$ from degradation by reactive peroxide radicals. Sodium thiocyanate in the Stretford liquor acts as a solvent for the sodium based salts (fine sodium sulphate, fine sodium thiosulphate), undissolved V^{5+} particles, V^{4+} precipitate and $\text{Na}_2[\text{ADA}]$ sludge (water insoluble $\text{Na}_2[\text{ADA}]$ isomers). It therefore has two important functions, namely minimising fine salts formation and controlling bacterial growth.

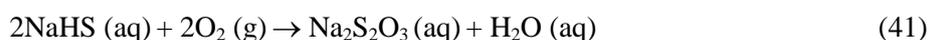
NaSCN serves a dual function in the Stretford aqueous liquor and hence its importance in facilitating the chemical balance in Stretford aqueous liquors is critical.

2.2.5. Unwanted Side Reactions in Stretford aqueous liquors

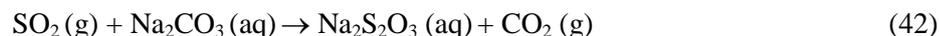
There are several side reactions that occur in the Stretford aqueous liquor that degrade the treating solution or reduce its efficiency in the absorption of hydrogen sulphide (H_2S). Compounds such as sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium thiocyanate (NaSCN) and sodium sulphate (Na_2SO_4) build up in the solution as a result of side reaction and reduce the ability of the Stretford aqueous liquor to remove H_2S . A purge stream is thus required either for further treatment or to recover the above mentioned chemicals for disposal or purification and re-sale [Kohl and Riesenfeld, 1974].

a) Sodium Thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$)

Thiosulphate is an unwanted by-product in the Stretford process resulting from a reaction between NaHS and molecular oxygen. When HCN is negligible in the feed gas, the major problem is the formation of thiosulphate represented by equation 41 [Kohl and Riesenfeld, 1974]:



The presence of SO₂ in the feed gas also degrades the solution by forming sodium thiosulphate as shown below [Kohl and Riesenfeld, 1974]:



The reaction product from (reactions 41 and 42), namely sodium thiosulphate, build up in the Stretford aqueous liquor and reduce its capacity to absorb H₂S from the feed gas efficiently. The formation of sodium thiosulphate is dependent on the solution pH, temperature and the amount of unreacted sodium hydrogen sulphide (NaHS) [Kohl and Riesenfeld, 1974].

The effects of Stretford aqueous liquor temperature and pH on the relative amount of sodium thiosulphate formed is shown in Figure 2.10 [Kohl and Riesenfeld, 1974].

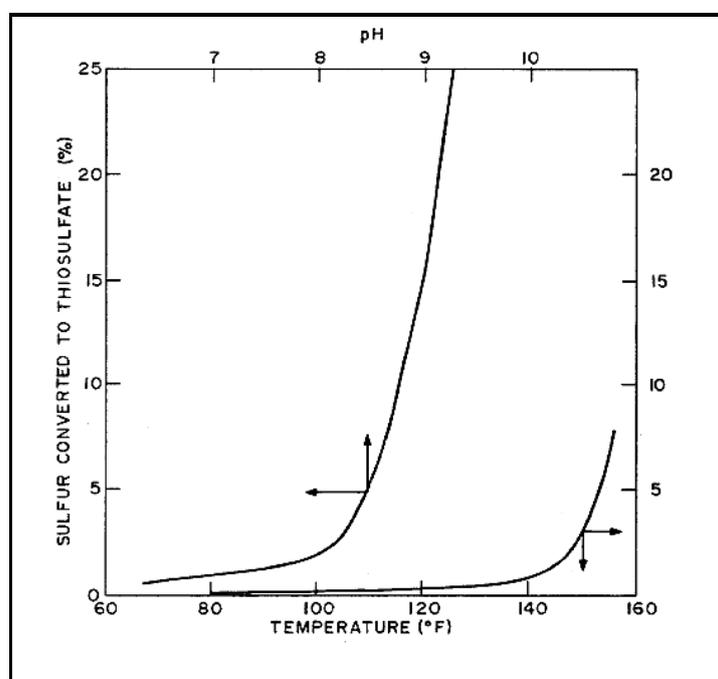


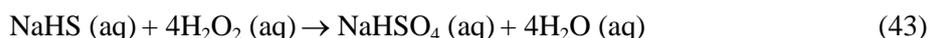
Figure 2.10: The relative production of thiosulphate as a function of temperature and pH [Kohl and Riesenfeld, 1974].

The rate of thiosulphate formation increases with increasing pH and increasing temperature.

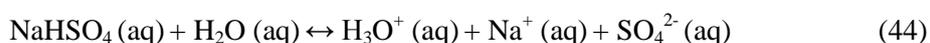
Sodium thiosulphate cannot be removed by simple crystallisation processes due to its high solubility. Simple purging processes cannot be adopted easily due to the high biological oxygen demand of sodium thiosulphate. This means that the solution cannot simply be discarded. It is therefore imperative that steps should be taken to minimise its formation altogether in Stretford aqueous liquors [Weber, 1985].

b) Sodium Hydrogen Sulphate (NaHSO₄) and Sodium Sulphate (Na₂SO₄)

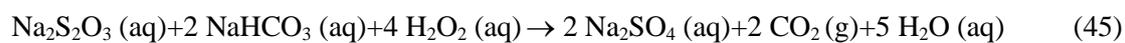
Part of the hydrogen sulphide is oxidised to sodium sulphate, which is a by-product of the overall Stretford process. It accumulates in the Stretford aqueous liquor over time and must be removed to maintain the absorption efficiency of the Stretford aqueous liquor. Sodium sulphate is a by-product from the oxidation of polysulphides and thiosulphate, but also forms from the reaction of hydrogen sulphide ions with hydrogen peroxide [Hoffman, 1977]. The reaction is shown below:



Sodium hydrogen sulphate is an acidic salt in water and will therefore contribute to a reduction in pH values.



Thiosulphate can undergo further oxidation to form sulphates. This oxidation occurs in the oxidisers by the following reaction:



The accumulation of inevitable by-products leads to an increase in the TDS content in the Stretford aqueous liquor. A purge stream is required to prevent the accumulation of these salts. It allows a bleed off, of undesirable high TDS Stretford aqueous liquor and the introduction of fresh Stretford aqueous liquor into the absorbers.

If the concentration of sulphates and thiosulphates is allowed to increase, it may result in the precipitation of insoluble V⁴⁺ compounds in the absorber or reaction tank. If the concentration of Na₂SO₄ increases considerably, then it may be removed from the Stretford aqueous liquor via crystallisation techniques [Weber, 1985]. The disadvantage of the crystallisation abilities of Na₂SO₄ is that once they increase considerably in the Stretford aqueous liquor, they can crystallise out, and cause equipment blockages and plant downtime [Kohl and Riesenfeld, 1974].

Conclusively, it is of critical importance to limit by-product formation in the Stretford aqueous liquors. The rate of by-product formation increases with increased temperature and by-product concentration. The efficiency of the Stretford plants is increased with lower by-product formation and the cost decreased [Kohl and Riesenfeld, 1974].

Chapter 3

Experimental Procedures and Analytical Techniques

This chapter gives a description of the experimental procedures that were followed in this study. Some sodium thiocyanate crystals that were added to the over-oxidised Stretford aqueous liquor, containing the dissolved $\text{Na}_2[\text{ADA}]$ and dissolved sodium ammonium vanadate, were oxidised to form sodium sulphate and other sodium cyanate species. The concentration of the dissolved sodium thiocyanate was slightly increased after the addition of sodium thiocyanate crystals to this aqueous liquor. The research focuses primarily on the effect of the addition of oxidants (hydrogen peroxide (H_2O_2), air) to the Stretford aqueous liquor samples to observe its effect on the oxidation of NaSCN in the Stretford aqueous liquor. The working temperature range is between 40°C and 50°C . All experiments were performed on a laboratory scale.

In this chapter a literature background is given of the chemical, physical and analytical techniques and experimental procedures performed on the samples in this study. Brief descriptions are given of the various experimental apparatus and the analytical methods that were followed to determine the concentrations of inorganic elements/substances in the samples from the experiments.

3.1 Materials

Stretford aqueous liquor containing sodium sulphate, sodium thiocyanate, sodium carbonate, sodium hydrogen carbonate, vanadium and $\text{Na}_2[\text{ADA}]$ species were used in this research study. The chemicals that were used in the experimental investigation and chemical analyses are listed in Table 3.1.

Table 3.1: Chemical names, chemical purity and supplier of chemical species used in this study.

Chemical species	Purity (%)	Supplier
Analytical reagent NaSCN	98.5	Merck
Technical grade, Na ₂ [ADA] Powder	90.0	London Chemicals and Resources LTD
Analytical reagent vanadium pentoxide and sodium ammonium vanadate	>99.0	Merck
	68-75	Vanchem Vanadium Products (PTY) LTD
Analytical reagent Na ₂ SO ₄	≥99.0	Sigma Aldrich
Na ₂ CO ₃ Anhydrous-*platinum line (AR)	≥99.5	Ace Chemicals
H ₂ O ₂ - **gold line (CP)	50% V/V	Ace Chemicals
HCl-platinum line (AR)	32% V/V	Ace Chemicals
Analytical reagent H ₂ SO ₄	≥95.0	Sigma Aldrich
Na ₂ S ₂ O ₃ -gold line (CP)	99.0	Ace Chemicals

* **Platinum Line:** Analytically pure quality - supplied with "warranty certificate"

** **Gold Line:** Chemically pure quality - supplied with "typical analysis"

3.1.1. Oxidation of NaSCN in de-ionised water using H₂O₂ as an oxidising agent

Two separate concentrations of NaSCN solutions were prepared in de-ionised water. The respective concentrations of the solutions were 0.99 mol.dm⁻³ and 1.97 mol.dm⁻³ NaSCN. The solutions were prepared by weighing 80 g and 160 g of NaSCN (98.5% purity) into two 1000 ml volumetric flasks respectively. The flasks were made up to the mark using de-ionised water.

Approximately 200 ml each, of the 0.99 mol.dm⁻³ NaSCN solution was measured and decanted into 5 separate bottles. The same procedure was followed for the 1.97 mol.dm⁻³ NaSCN solution.

Table 3.2 illustrates the volumes and concentrations of 50 % v/v hydrogen peroxide which was added to the respective NaSCN solutions. The resulting solutions as listed in Table 3.2 were placed in an oven at a temperature of 50°C for an hour in order to prevent salt crystallisation/precipitation before the chemical analyses. The samples were taken from the oven after an hour and were submitted for the NaSCN, Na₂SO₄, Na₂S₂O₃ and total alkalinity (which is expressed as Na₂CO₃) analyses; and pH measurements using the analytical methods that are detailed in Section 3.3 of this chapter.

Table 3.2: Volumes of hydrogen peroxide added to the respective NaSCN solutions.

Volume (ml) of NaSCN solution	[NaSCN] (mol.dm ⁻³)	Volume (ml) of H ₂ O ₂ which was added to the NaSCN solution	[H ₂ O ₂] (mol.dm ⁻³) in the NaSCN solution
200	0.99	0	0
200	0.99	10	0.83
200	0.99	20	1.66
200	0.99	30	2.49
200	0.99	40	3.32
200	1.97	0	0
200	1.97	10	0.83
200	1.97	20	1.66
200	1.97	30	2.49
200	1.97	40	3.32

3.1.2 Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.3 using hydrogen peroxide

The pH of the solution was approximately 8.3. The experiment was performed in two individual Stretford aqueous solutions with varying concentration of NaSCN. The oxidation of NaSCN in Stretford aqueous solutions which contained Na₂CO₃ + NaHCO₃ (total alkalinity), Na₂SO₄, Na₂S₂O₃, NaSCN, vanadium species, and Na₂[ADA] was monitored using H₂O₂ as an oxidising agent. Table 3.3 shows the concentrations of the sodium based salts and total vanadium present in the two Stretford aqueous liquors (i.e. A and B) used. The pH values of Stretford aqueous liquors A and B were 8.29 and 8.26 respectively.

Table 3.3: Concentrations of total alkalinity, sodium sulphate, sodium thiocyanate, total vanadium and Na₂[ADA] in the two working Stretford aqueous liquors (i.e. A and B).

Sodium based salts and total vanadium	Stretford aqueous liquor A concentration (mol.dm ⁻³)	Stretford aqueous liquor B concentration (mol.dm ⁻³)
Total alkalinity	0.28	0.33
Na₂SO₄	0.86	0.61
NaSCN	0.93	1.90
Total vanadium	0.024	0.028
Na₂[ADA]	0.00078	0.0012

Approximately 200 ml each of Stretford aqueous liquor A was measured and decanted into 5 separate bottles. The same procedure was followed for Stretford aqueous liquor B. Table 3.4 shows the volume and concentration of 50 % v/v hydrogen peroxide added to Stretford aqueous liquors A and B.

The resulting solutions, shown in Table 3.4 were placed in an oven at a temperature of 50°C for an hour to prevent salt crystallisation/precipitation prior to NaSCN, Na₂SO₄, Na₂S₂O₃, total alkalinity, total vanadium and Na₂[ADA] analyses; and pH measurements. The samples were taken from the oven after an hour and were subsequently submitted for the chemical analyses using all analytical methods that are detailed in Section 3.3 of this chapter.

Table 3.4: Volumes and concentrations of hydrogen peroxide that were added to the respective Stretford aqueous solutions containing different concentrations of NaSCN.

Solution Identity	Volume (ml) Stretford aqueous solution	[NaSCN] (mol.dm ⁻³) in the Stretford aqueous solution	Volume (ml) of H ₂ O ₂ added to the Stretford aqueous solution	[H ₂ O ₂] (mol.dm ⁻³) in the Stretford aqueous solution
Stretford aqueous liquor A	200	0.93	0	0
Stretford aqueous liquor A	200	0.93	10	0.83
Stretford aqueous liquor A	200	0.93	20	1.66
Stretford aqueous liquor A	200	0.93	40	3.32
Stretford aqueous liquor A	200	0.93	60	4.98
Stretford aqueous liquor B	200	1.90	0	0
Stretford aqueous liquor B	200	1.90	10	0.83
Stretford aqueous liquor B	200	1.90	20	1.66
Stretford aqueous liquor B	200	1.90	40	3.32
Stretford aqueous liquor B	200	1.90	60	4.98

Note: Important considerations when performing the experimental procedures are:

- H₂O₂ is a powerful oxidising agent resulting in highly exothermic reactions.
- When peroxide is added to aqueous solutions or Stretford aqueous solutions, vigorous, exothermic reactions occur.
- The reaction takes approximately 1-2 minutes to proceed after the initial addition of hydrogen peroxide to the respective solutions.
- Therefore the addition of hydrogen peroxide to the solutions was done carefully and slowly to avoid possible spillage of the sample during the reactions.

- The addition of hydrogen peroxide to the aqueous solutions or to the Stretford aqueous solutions was done in an ice bath as the temperature of the solution increased significantly during these reactions.

3.1.3 Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 7.0 using HCl

Hydrochloric acid (HCl) was added to the Stretford aqueous liquor until a pH of approximately 7.0 was reached. The pH was monitored using a Mettler Toledo pH meter with Expert Pro pH electrode. The addition of HCl was done slowly and carefully to prevent the pH decreasing below a pH value of 7.0. The addition was done drop wise to obtain the desired pH value of approximately 7.0.

The oxidation of NaSCN in Stretford aqueous solutions which contained total alkalinity, Na₂SO₄, NaSCN, vanadium species, and Na₂[ADA] was also monitored at a pH of approximately 7.

The experiment was performed using two individual Stretford aqueous liquors A and B with varying concentrations of NaSCN (See Table 3.3).

The resulting solutions (Table 3.5) were placed in an oven at a temperature of 50°C for an hour to prevent salt crystallisation/precipitation. The samples were taken from the oven after an hour and were subsequently submitted for the NaSCN, Na₂SO₄, Na₂S₂O₃, total alkalinity, total vanadium and Na₂[ADA] analyses; and pH measurement (See Section 3.3).

Table 3.5: Volumes of the Stretford aqueous solution containing the different concentrations of NaSCN at pH 7 using HCl.

Solution Identity	Volume (ml) Stretford aqueous solution	[NaSCN] (mol.dm ⁻³) in the Stretford aqueous solution	pH
Stretford aqueous liquor A	200	0.93	7.0
Stretford aqueous liquor B	200	1.90	7.0

3.1.4. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 9.0 using NaOH

Sodium hydroxide (NaOH) was added to the Stretford aqueous liquor until a pH of approximately 9.0 was reached. The pH was monitored using a Mettler Toledo pH meter with Expert Pro pH electrode. The addition of sodium hydroxide was done slowly and carefully to prevent the pH increasing to above a pH value of 9.0. The experiment was performed in two individual Stretford aqueous liquors A and B with varying concentrations of NaSCN (see Table 3.3).

The oxidation of NaSCN in Stretford aqueous solutions which contained total alkalinity, Na_2SO_4 , NaSCN, total vanadium, and $\text{Na}_2[\text{ADA}]$ was also monitored at a pH of approximately 9.0.

The resulting solutions (Table 3.6) were placed in an oven at a temperature of 50°C for an hour to prevent salt crystallisation/precipitation prior to analyses. The samples were taken from the oven after an hour and were subsequently submitted for the NaSCN, Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, total alkalinity, total vanadium and $\text{Na}_2[\text{ADA}]$ analyses; and pH measurement.

Table 3.6: Solutions prepared for NaOH addition to obtain pH values of approximately 9.0.

Solution Identity	Volume (ml) Stretford aqueous solution	[NaSCN] ($\text{mol}\cdot\text{dm}^{-3}$) in the Stretford aqueous solution	pH
Stretford aqueous liquor A	200	0.93	9.0
Stretford aqueous liquor B	200	1.90	9.0

3.1.5. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.40 using increased concentrations of $\text{Na}_2[\text{ADA}]$

The oxidation of NaSCN in Stretford aqueous solutions which contain total alkalinity, Na_2SO_4 , NaSCN, and total vanadium was monitored by addition of $\text{Na}_2[\text{ADA}]$. The $\text{Na}_2[\text{ADA}]$ concentration in the Stretford aqueous liquor was adjusted from $0.0010 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2[\text{ADA}]$ to 0.0024, 0.0049, 0.012, 0.024 and $0.049 \text{ mol}\cdot\text{dm}^{-3}$ by adding varying amounts of $\text{Na}_2[\text{ADA}]$ powder into five separate bottles to adjust the $\text{Na}_2[\text{ADA}]$ concentration to the desired level (See Table 3.8). The pH of the $0.0010 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2[\text{ADA}]$ solution was 8.40.

Table 3.7: Concentrations of the total alkalinity, Na₂SO₄, NaSCN and total vanadium in the Stretford aqueous solutions for Na₂[ADA] addition experiment.

Sodium based salts and total vanadium	Stretford aqueous solution concentration (mol.dm ⁻³)
Total alkalinity	0.32
Na ₂ SO ₄	0.86
NaSCN	0.94
Total Vanadium	0.024
Na ₂ [ADA]	0.0010

The resulting solutions (Table 3.8) were placed in an oven at a temperature of 50°C for an hour to prevent salt precipitation/crystallisation. The samples were taken from the oven after an hour and were submitted for the NaSCN, Na₂SO₄, total alkalinity, total vanadium and Na₂[ADA] analyses and pH measurement (See Section 3.3).

Table 3.8: Concentrations of Na₂[ADA] in the Stretford aqueous solution.

Volume (ml) Stretford aqueous solution	Na ₂ [ADA] (mol.dm ⁻³) in the Stretford aqueous solution
200	0.0010
200	0.0024
200	0.0049
200	0.012
200	0.024
200	0.049

3.1.6. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.40 using sodium ammonium vanadate (SAV)

The oxidation of NaSCN in Stretford aqueous solutions which contain total alkalinity, Na₂SO₄, NaSCN and total vanadium was monitored by increasing the concentrations of total vanadium in the Stretford liquor by the addition of varying amounts of sodium ammonium vanadate. The vanadium concentration in the Stretford aqueous liquor was adjusted by the addition of varying amounts of

sodium ammonium vanadate powder into four separate bottles to adjust the vanadium concentration to the desired level (See Table 3.9). The pH of the 0.028 mol.dm⁻³ vanadium solution was 8.40.

The resulting solutions (Table 3.9) were placed in an oven at a temperature of 50°C for an hour to prevent salt crystallisation/precipitation. The samples were taken from the oven after an hour and were submitted for the NaSCN, Na₂SO₄, total alkalinity, total vanadium and Na₂[ADA] analyses; and pH measurement (See Section 3.3).

Table 3.9: Concentrations of total vanadium in the Stretford aqueous solutions.

Volume (ml) Stretford aqueous solution	[Vanadium] (mol.dm ⁻³) in the Stretford aqueous solution
200	0.028
200	0.039
200	0.098
200	0.20
200	0.39

3.1.7. Air Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.3

The oxidation of NaSCN in Stretford aqueous solutions which contain total alkalinity, Na₂SO₄, NaSCN, Na₂S₂O₃, total vanadium, and Na₂[ADA] was monitored using air as an oxidising agent. The pH of the solution was approximately 8.3. The experiment was performed in two individual Stretford aqueous solutions with varying concentration of NaSCN. Table 3.10 shows the concentrations of the various compounds present in the two Stretford aqueous liquors C and D used. The pH values of Stretford aqueous liquors C and D were 8.29 and 8.26 respectively.

Table 3.10: Concentrations of total alkalinity, Na₂SO₄, NaSCN, total vanadium and Na₂[ADA] in the two Stretford aqueous liquors (i.e. C and D).

Sodium based salts and total vanadium	Stretford aqueous liquor C Concentration (mol.dm ⁻³)	Stretford aqueous liquor D Concentration (mol.dm ⁻³)
Total alkalinity	0.31	0.33
Na₂SO₄	0.88	0.57
NaSCN	0.99	1.74
Vanadium	0.029	0.029
Na₂[ADA]	0.0012	0.00097
pH	8.29	8.26

Approximately 2000 ml (2 L) of Stretford aqueous liquor C was measured and decanted into four separate 2000 ml beakers. The same procedure was followed for Stretford aqueous liquor D. Table 3.11 shows the duration of bubbling for the Stretford aqueous liquors C and D. The solutions were bubbled while keeping the temperature between 40°C- 50°C on a hotplate.

The samples were taken from the hotplate after the stipulated durations of oxidation with air and were subsequently submitted for the NaSCN, Na₂SO₄, Na₂S₂O₃, total alkalinity, total vanadium and Na₂[ADA] analyses and pH measurement (See Section 3.3).

Table 3.11: Duration of oxidation of NaSCN in Stretford aqueous liquors C and D with air.

Solution Identity	Volume (ml) Stretford aqueous solution	Duration of oxidation with air (hours)
Stretford aqueous liquor C	2000	0
Stretford aqueous liquor C	2000	2
Stretford aqueous liquor C	2000	6
Stretford aqueous liquor C	2000	12
Stretford aqueous liquor C	2000	24
Stretford aqueous liquor D	2000	0
Stretford aqueous liquor D	2000	2
Stretford aqueous liquor D	2000	6
Stretford aqueous liquor D	2000	12
Stretford aqueous liquor D	2000	24

3.1.8. Evolution of gases during the oxidation of NaSCN in the Stretford aqueous samples using hydrogen peroxide

During the oxidation of NaSCN in Stretford aqueous solutions using hydrogen peroxide, there was evolution of gases. In order to identify these gases qualitatively, the volatilised gases were injected onto a GC-MS. The gases evolved were collected using a syringe while adding 3.32 mol.dm⁻³ H₂O₂ (40 ml) to a 200 ml Stretford aqueous solution containing total alkalinity, Na₂SO₄, NaSCN, Na₂S₂O₃, total vanadium and Na₂[ADA]. The concentrations of total alkalinity, Na₂SO₄, NaSCN, total vanadium, and Na₂[ADA] were 0.31, 0.88, 0.99, 0.029 and 0.0012 mol.dm⁻³ respectively. The pH of the solution before the hydrogen peroxide addition was 8.29.

The volatilised gases were analysed for gases such as hydrogen cyanide and ammonia.

3.1.9. Crystallisation of sodium based salts from the aqueous samples

The sequence of aqueous solutions (Refer to Table 3.2) was prepared from 1.97 mol.dm^{-3} NaSCN. These solutions were subsequently evaporated in an oven at 105°C to obtain crystals. The same procedure was followed for the sequence of solutions (Refer to table 3.4) prepared from Stretford aqueous liquors A and B. All resulting crystals were prepared and submitted to Setpoint laboratories for XRD and XRF analyses. The XRD analysis was done to determine the crystalline phases of sodium based salts present in the crystals formed after evaporation of the solutions produced from the oxidation study. The XRF analysis was used to determine the concentrations of the inorganic elements in the crystals.

3.1.10. Determination of the concentration of the unwanted by-product sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) in the Stretford aqueous liquor samples

Sodium thiosulphate is an unwanted by-product that forms in the Stretford aqueous liquor. $\text{Na}_2\text{S}_2\text{O}_3$ was quantified during this study using an ion chromatographic technique (See section 3.3). The resulting solutions, namely Stretford aqueous liquor A, Stretford aqueous liquor B, Stretford aqueous liquor A + 4.98 mol.dm^{-3} H_2O_2 , Stretford aqueous liquor B + 4.98 mol.dm^{-3} H_2O_2 , Stretford aqueous liquor C, Stretford aqueous liquor D, Stretford aqueous liquor C-oxidised with air for 24 hours and Stretford aqueous liquor D-oxidised with air for 24 hours were analysed for $\text{Na}_2\text{S}_2\text{O}_3$. The ion chromatograph (IC) was used to identify the presence of $\text{Na}_2\text{S}_2\text{O}_3$ in the resulting oxidised solutions. Quantification of $\text{Na}_2\text{S}_2\text{O}_3$ was done when the thiosulphate species was positively identified in the oxidised solutions.

3.2. Analytical Techniques

Many different instruments were used to determine the concentrations inorganic elements, sodium compounds, ions and crystalline phases in the liquid and solid samples from this study. In this section a brief description is given of the various experimental apparatus and the analytical techniques are also discussed briefly.

The analytical techniques that were used in this study are:

- Inductively coupled plasma optical emission spectrophotometry (ICP-OES);
- X-ray diffraction (XRD);
- X-ray fluorescence (XRF);
- Fourier Transform Infrared (FTIR);
- Gas Chromatography-Mass Spectrometry (GC-MS);
- Ion chromatography (IC);
- UV-Visible Spectrophotometry;
- pH; and
- Auto-titration.

Table 3.12: Equipment used with their model names and suppliers.

Equipment Type	Equipment Model	Supplier
ICP-OES	Optima 5300 DV	Perkin Elmer
XRD	XRL-X'tra	Thermo-Scientific
XRF	ARL™ 9800XP	Thermo-Scientific
FTIR	Perkin Elmer Spectrum 400 FTIR	Perkin Elmer
GC-MS	7890A GC System and 5975C MSD with Triple-Axis Detector	Agilent Technologies
Ion Chromatograph- (anions + cations)	882 Compact IC Plus with 858 Professional sample processor	Metrohm
Spectrophotometer	Macherey-Nagel Nanocolor Spectrophotometer NVIS1021	Separations-Promolab
pH meter	Mettler Toledo seven multi with pH cartridge and expert pro electrode	Microsep
Alkalinity Autotitrator	809 Titrando with 800 Dosino and 772 pump connected to a 814 USB sample processor	Metrohm
NaSCN Argentometric/Potentiometric Autotitrator	702 SM Titrino with electrode	Metrohm
Discrete Photometric Analyser- Na ₂ SO ₄	Thermo Scientific Aquakem 250/600	Anatech
Dissolved oxygen meter	Cyberscan 110	Eutech Instruments

3.2.1. Inductively coupled plasma optical emission spectrophotometry (ICP-OES)

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is a powerful technique which is used for the determination of inorganic elements in a variety of different sample matrices [Hou and Bradley, 2000]. The basic steps during the ICP-OES analysis of liquid samples can be seen in Figure 3.1. A liquid sample is injected into a radiofrequency (RF) - induced argon plasma. The sample introduction is done via one of a variety of different nebulizers. Due to the high temperature of approximately 10000 K in the plasma, the mist was vaporized and energized through collisional excitation [Hou and Bradley, 2000]. The excited atoms are promoted to higher electronic energy levels [Settle, 1997]. When the excited electrons in these elements fall back into the lower energy levels, they emit light. The emission emanating from the plasma is viewed in either a radial or axial

configuration. These emissions are collected with a lens or mirror that image onto the entrance slit of a wavelength selection device [Hou and Bradley, 2000].

A simple monochromator - photomultiplier detector will allow for single measurement determination while a polychromator and array detector will result in the determination of 70 elements simultaneously [Settle, 1997].

Some of the general uses of the ICP-OES are the simultaneous qualification and quantification of over 70 elements in virtually any sample is less than 2 minutes. It can easily determine the concentrations of elements in the samples ranging from part per billion (ppb) levels to weight % without pre-concentration or dilution depending on the sample introduction kit used. Although it is a destructive technique, only a few milligrams of sample are required [Settle, 1997]. Figure 3.2 is a photo of the ICP-OES used in this study to determine the concentration of elements such as vanadium in the Stretford aqueous liquor.

When ICP-OES is employed as a technique, no information is obtained on the oxidation states and structures of the compounds. Gaseous compounds and carbon are generally not determined. Interferences from major components may result in overlapping of emission lines, causing upsets in the detection limits and matrix differences between samples and standards may alter plasma background emission or analyte responses [Settle, 1997]. The limitations must be carefully considered before using ICP-OES as a technique.

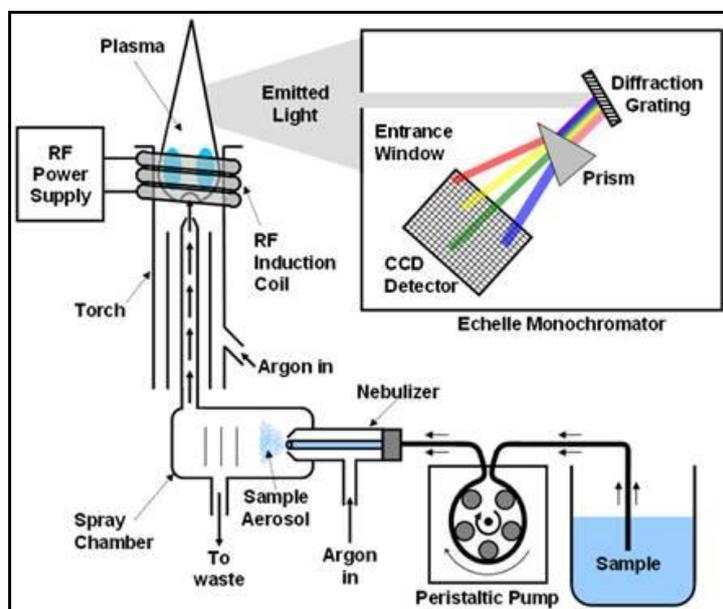


Figure 3.1: Basic process flow diagram for ICP-OES [Analytical Chemistry Laboratory Manual, Concordia College, Minnesota].

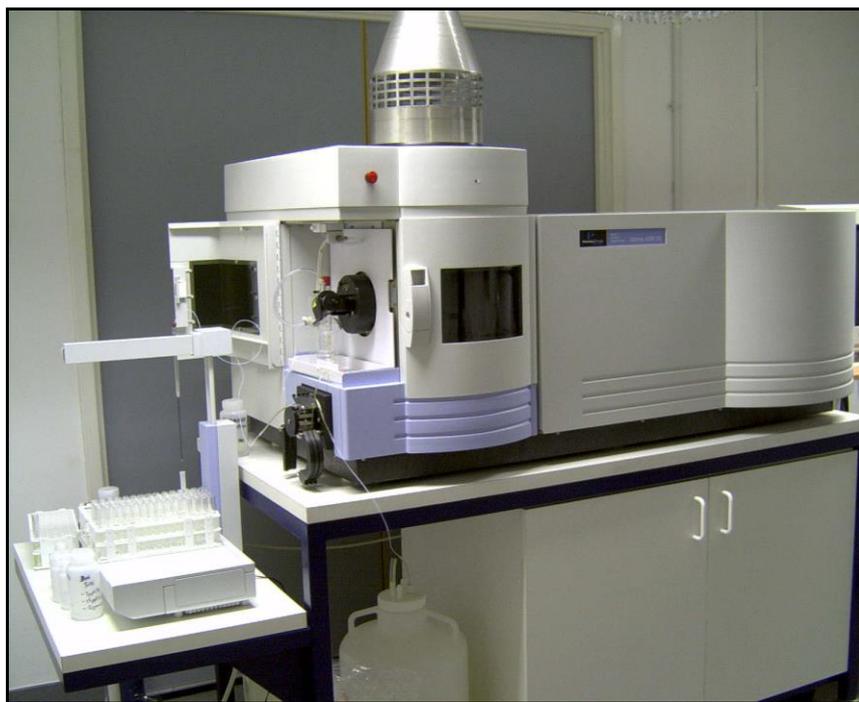


Figure 3.2: The ICP-OES instrument used to analyse the Stretford aqueous liquor.

3.2.2. X-ray diffraction (XRD)

X-ray diffraction is a versatile analytical technique used for the qualification and quantification of the crystalline phases in solid samples. These include ceramics, metals, mineral ores, geographical materials, organics and polymers [Settle, 1997]. Unknown samples crystal lattice spacing is determined by calibrating the XRD apparatus with crystal samples of known lattice spacing [Huggins, 2002]. There are two classes of X-ray diffractometers, namely, single crystal and powder. The molecular structure of materials is determined by single crystal and powder diffractometers they are also used for phase identification and quantification of the crystalline phase in solid samples. Powder diffractometers can be configured to also obtain texture [Settle, 1997]. Figure 3.3 is an image of the Thermo-Scientific XRL-X'tra XRD equipment used for the qualitative and quantitative XRD analyses in this study. Figure 3.4 shows a simplified diagram of the optical arrangement for an X-ray diffractometer.

The common applications of XRD include identification of unknown peaks, quality control (qualitative and quantitative analyses), characterization of polycrystalline thin films, quantification of texture and orientation in metals and polymers and temperature studies to determine thermal expansion, stability and phase diagrams [Settle, 1997].

Depending on the instrument configuration and analytical XRD methods, the analysis may vary from minutes to days. There are limitations for the use of XRD, such as amorphous materials not yielding useful diffraction data; peak overlapping hindering phase identification and quantitative analysis;

matrix effects (i.e. the obscuration of weak diffracting materials by strong ones); and saturation and increased background counts as a result of sample fluorescence in certain detector types [Settle, 1997].



Figure 3.3: The Thermo-Scientific XRL-X'tra used for XRD analysis [Thermo Scientific, 2014].

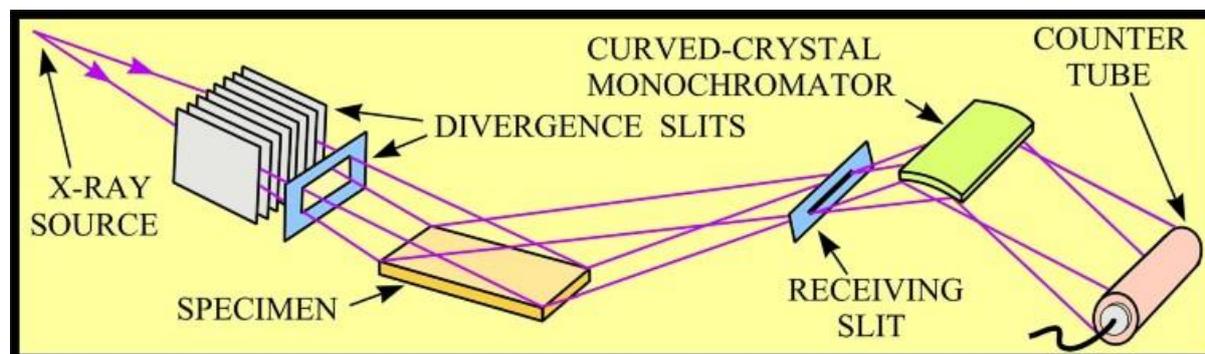


Figure 3.4: The optical arrangement for an X-ray diffractometer [Poppe, *et al*, 2002].

3.2.3. X-ray fluorescence (XRF)

When XRF is used, an element is identified by the measurement of its characteristic X-ray emission wavelength or energy [Gunzler and Williams, 2002]. The basic principle of XRF is emission and detection [Settle, 1997]. A sample is bombarded with X-ray beams and the re-emitted X-radiation is measured. An X-ray fluorescence spectrometer requires an X-ray source, a means of dispersing the X-rays and a detector [Gunzler and Williams, 2002].

Some of the general uses of XRF include qualification and quantification of the elements in the solid and liquid samples; determination of sulphur in diesel; quality control and customer support for catalyst manufacture; process control of steel and cement manufacture; sorting of metal alloys and support of mineralogical and geological exploration and waste site field evaluation [Settle, 1997].

Figure 3.5 is a photo of a standard XRF apparatus. The illustration in Figure 3.6 is a simplified diagram of how the technique works. The polychromatic spectrum is incident upon the detector. The detector has the capability of registering the energy of each photon that strikes it. These energies are expressed in a histogram using the X-ray spectrum. The number of counts versus energy is plotted [Guthrie, 2010].

The time taken for analyses will depend on the instrument and can last 30 minutes on a sequential wavelength dispersive instrument for 15 elements whereas it can take 5 minutes for the same number of samples on a simultaneously measuring instrument.

The elemental range is limited to boron and up and this can be a limitation. Some other limitations include matrix interferences and in certain instances for quantitative analysis, the standards may not match the unknown matrix.



Figure 3.5: Photo of the ARL™ 9900 Simultaneous-Sequential XRF Series [Thermo Scientific, 2014].

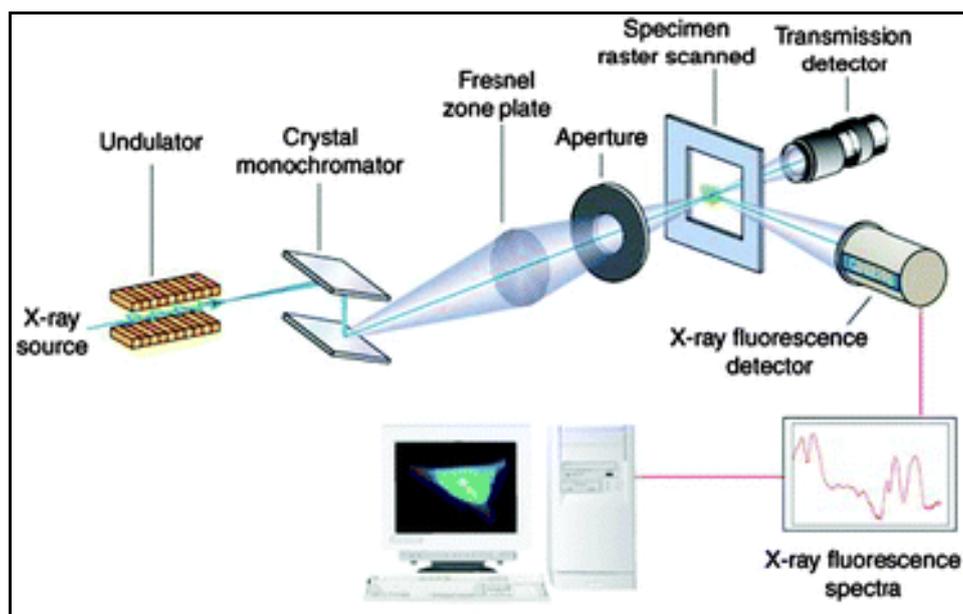


Figure 3.6: Diagram of typical X-ray fluorescence spectrometer [Chen, *et al*, 2012].

3.2.4. Ion chromatography-anion separation (IC)

One of the most ideal methods for analysing anions, cations and other polar compounds is ion chromatography. It is reliable through a wide concentration range and its robustness has made it a popular choice in many applications. A variety of anions and cations present in the samples can be qualified and quantified in a single determination [Theory of Ion Chromatography, 2014].

The basic principle involves the injection of a sample into a stream of eluent which is then passed through a series of ion exchangers. Based on their affinities for a low capacity, strongly basic anion exchanger (guard and analytical column), the anions of interest will separate. A separator device provides continuous suppression of the eluent conductivity and as a result the analyte responses are enhanced. The separated analytes are detected using a conductivity detector [Rice, *et al*, 2012].

Anion chromatography particularly for sulphates has been suggested as there are few other techniques that provide the sensitivity, simplicity and selectivity for its determination [Theory of Ion Chromatography, 2014]. Figure 3.7 is an image of the Metrohm ion chromatograph which is used in the analyses of anions in this study.

Some of the general uses of IC include separation and detection of ions and ionisable species, simultaneous determination of the concentrations of several ions in a mixture and the determination of ionic species in samples of low concentrations [Settle, 1997].

The most common applications for IC include, monitoring of water quality, determination of the composition of industrial wastes, quality of intermediates in industrial processes, and identification of ionic impurities [Settle, 1997].

There are a few limitations to the use of the technique. The determination is sequential and not simultaneous as each ion separates based on its affinity for the column, analytes can be misidentified and their quantities incorrectly determined if separation is not good [Settle, 1997].



Figure 3.7: Photo of a Metrohm ion chromatograph [Theory of Ion Chromatography, 2014].

3.2.5. Ultraviolet (UV) and visible (Vis) molecular absorption spectrophotometry

One of the earliest methods of identifying materials qualitatively was molecular absorption spectrophotometry. This was based on the intensity of colour that materials exhibited. The intensity of colour was then related to concentration and hence quantitative determination of compounds became possible [Settle, 1997].

Depending on the application, modern spectrophotometers are designed to cover many laboratory applications. A wide range of spectrophotometers are now available and they have the capability of performing ultraviolet and visible (UV/Vis) measurements. The Macherey-Nagel Nanocolor Spectrophotometer in Figure 3.8 was used for all spectrophotometric determinations.

The general applications for UV/Vis spectrophotometry include the quantitative determination of mixtures of analytes, identification of chromatographic eluents and identification of many types of organic and inorganic molecules and ions [Settle, 1997].

There are few limitations to this technique. The sample concentrations for measurements must be low (i.e. absorbance units less than 2) in order to obtain reliable results. Photosensitive compounds are also difficult to analyse [Settle, 1997].



Figure 3.8: Photo of Macherey-Nagel Nanocolor Spectrophotometer [Laboratory and Environment, 2014].

3.2.6. pH determination

The measurement of pH is one of the most frequent and important measurements in water chemistry. A pH meter is used to measure the degree of acidity or alkalinity of a sample.

At a given temperature, the intensity of acidic or basic nature of a solution is indicated by pH or hydrogen ion activity. Acidic solutions will have a higher number of hydrogen (H^+) while alkaline (basic) solutions will have higher hydroxyl (OH^-) ions [Rice, *et al*, 2012].



Figure 3.9: Photo of Mettler Toledo pH meter [Mettler Toledo, 2014].

3.2.7. IR determination

One of the most common spectroscopic techniques used by organic and inorganic chemists is infrared (IR) spectroscopy. This type of spectroscopic analysis is used to determine functional groups in a sample. Each functional group absorbs a characteristically different frequency. [Settle, 1997]. Solid, liquid and gaseous samples can be determined using IR, depending on the sample accessories used. Due to this flexibility, IR has become a popular tool for structural and compound identification [Settle, 1997].

IR is commonly used to identify compounds by matching the spectrum of an unknown compound with a reference spectrum. Some other common applications include identification of reaction components and kinetic studies of reactions, identification of polymers, plastics, and resins and analysis of formulations such as insecticides and copolymers [Settle, 1997].

Some of the general limitations are that the molecule must be active in the IR region, background or solid matrix must be transparent in the spectral region of interest, and minimal elemental information is given for most samples [Settle, 1997].

3.2.8. Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS is a hyphenated technique that can be used for the quantification and identification of volatile and semi-volatile organic components. The Gas Chromatograph (GC) separates components with good resolution but is unable to identify them. The Mass Spectrometer (MS) provides detailed structural information on most compounds. This assists in accurately identifying these compounds [Settle, 1997].

The structural determination using MS is done by matching the spectra obtained with reference spectra in the MS database [Settle, 1997].

Common applications include quantification of pollutants in drinking and wastewater, quantification of drugs in blood and urine, forensic applications, identification of reaction products from synthetic organic chemistry and for analysis of industrial products for quality control purposes [Settle, 1997].

Some of the limitations with the technique include determining positional substitution of aromatic rings and correctly identifying certain isomers. The technique can only be used when compounds have vapour pressures exceeding 10^{-10} torr [Settle, 1997].



Figure 3.10: Photo of an Agilent 7890A gas chromatograph with 5975C MSD [Mass Spectrometry, 2015]

3.3. Analytical Methods

The Gas Research Institute (GRI) has developed a handbook on the chemistry and analytical methods for monitoring the chemical composition of the Stretford aqueous liquor. Information on the process chemistry as well as sampling, preservation, and analytical methods are presented in this handbook. The compilation includes the analytical methods for the determination of the concentrations of sulphur species, of $\text{Na}_2[\text{ADA}]$, of vanadium ions, of carbonates in the Stretford aqueous liquor and of gases in the feed gas. A brief description of the analytical methods used for the determination of sodium based salts and vanadium species in Stretford aqueous liquor is given below.

The analytical methods used are as follows:

- NaSCN analysis;
- $\text{Na}_2\text{S}_2\text{O}_3$ analysis;
- Na_2SO_4 analysis;
- Na_2CO_3 analysis;
- $\text{Na}_2[\text{ADA}]$ analysis;

- Vanadium analysis;
- pH determination;
- FTIR;
- XRD and
- XRF.

3.3.1. NaSCN, Na₂S₂O₃ and Na₂SO₄ analyses using ion chromatography

One of the most sensitive and selective methods for the analyses of sulphates, thiosulphates and thiocyanates is ion chromatography. This technique was employed for the analyses of sulphates, thiosulphates and thiocyanates in Stretford aqueous liquor. The ions were separated on an anion exchange resin using conductivity detection on a Metrohm 882 Compact IC Plus connected to an 858 Professional sample processor. An A-Supp 5 column was used with a guard column. The eluent comprises of Na₂CO₃ and NaHCO₃.

The guard column traps particulate matter and organic contaminants to prevent damage to the column. Once the sample injection has taken place, the anion size and resin affinity can determine the degree of separation of the various anions. The separated analytes are detected based on conductivity and quantified using external calibrations [Andrews, 1988].

3.3.2. Na₂CO₃ Total alkalinity (NaHCO₃ and Na₂CO₃) analysis by acid titration

The total alkalinity concentration which is expressed as Na₂CO₃ concentration is directly related to the capacity of the Stretford aqueous liquor to absorb H₂S. The measurement of the Na₂CO₃ concentration forms the basis of alkalinity measurements [Andrews, 1988].

There are two titration endpoints namely for the determination of the concentration of NaHCO₃ and Na₂CO₃ which occur at pH values of 8.3 and 4.5 respectively. The titration is performed using a standardised solution of hydrochloric acid (HCl) [Andrews, 1988; Rice; *et al*, 2012].

An aliquot of alkaline Stretford aqueous liquor was titrated in a beaker using a standardised hydrochloric acid solution. A pH electrode connected to a pH meter was used to monitor the pH during the titration.

The total alkalinity was analysed by titrating the Stretford aqueous liquor with HCl using a Metrohm autotitrator 809 Titrando with 800 Dosino and 772 pump connected to a 814 USB sample processor.

The final result calculations were based on the volume of sample used together with the concentration and volume of HCl consumed during the titration. The total alkalinity is expressed as concentration of Na₂CO₃ in the Stretford aqueous liquor [Andrews, 1988].

3.3.3. Na₂[ADA] analysis by visible spectrophotometry

Re-oxidation of V⁴⁺ to V⁵⁺ occurs in the presence of Na₂[ADA] which acts as a catalyst. The Na₂[ADA] in Stretford aqueous liquor is analysed colorimetrically by reacting with a suitable reducing agent and measuring the absorbance photometrically. The technique cannot differentiate between the various isomers but can determine the concentration of reduced Na₂[ADA] that is present in Stretford aqueous liquor [Trofe, 1986]. The total Na₂[ADA] isomers are chemically reduced at high pH and form a highly coloured red solution [Andrews, 1988].

The absorbance of the red coloured sample was determined spectrophotometrically and the concentration was calculated by means of an external calibration prepared using standards of known Na₂[ADA] concentrations [Andrews, 1988]. The Stretford aqueous liquor was heated to 40°C and filtered through a Whatman 42 filter paper. The Na₂[ADA] was reduced using sodium dithionate in a strongly alkaline solution obtained by the addition of sodium hydroxide (NaOH) to the Stretford aqueous liquor. The resulting solution was a red coloured solution and its absorbance was determined at 448 nm using a 10 mm glass cuvette [Andrews, 1988].

The method is suitable for the determination of Na₂[ADA] concentrations that are greater than 0.00012 mol.dm⁻³. The calibration was obtained by preparing various standards that cover the possible concentration range of Na₂[ADA] to be determined. The absorbance of these samples is related to concentration and is used to obtain a linear plot used to determine the concentration of Na₂[ADA] in the sample [Andrews, 1988].

3.3.4. Vanadium analysis (total vanadium concentration determination)

The concentration of total vanadium must be monitored to ensure that it is present in sufficient concentrations for the oxidation of the absorbed hydrogen sulphide (HS⁻) [Andrews, 1988].

UV visible spectroscopy can be used to screen for total vanadium species in Stretford aqueous liquors [Trofe, 1986]. The Gallic Acid Method (approved standard method 3500-V B) was employed to determine total vanadium in the Stretford process aqueous liquor. The concentration of total vanadium was determined by measuring the catalytic effect it exerts on the rate of oxidation of gallic acid by persulphate in an acid solution. The extent of oxidation of gallic acid is proportional to the concentration of total vanadium. Total vanadium concentration was then determined by measuring the absorbance of the resulting blue coloured complex at 415 nm and compared with standard solutions treated in the same way [Rice, *et al*, 2012].

The method is suitable for the determination of a total vanadium concentration in the range of 0.00020-0.039 mol.dm⁻³ vanadium. The total vanadium content was also confirmed using ICP-OES.

3.3.5. Vanadium analysis (V^{5+} concentration determination)

The V^{5+} concentration is monitored in the Stretford process aqueous liquor using an analytical method whereby it forms a pink coloured complex upon the addition of 4-(2-pyridylazo) resorcinol monosodium salt monohydrate (PAR) to a filtered Stretford aqueous liquor. The resulting pink coloured complex was measured with a spectrophotometer using a 10 mm glass cuvette at a wavelength of 540 nm. The method is suitable for the determination of the concentration of V^{5+} in the range of 0.00078-0.029 mol.dm⁻³. A standard of known concentration was prepared and reacted with PAR reagent to obtain a pink coloured complex. The absorbance of the standard was measured and this was used as a reference for the determination of the concentration of the samples [Gavazov, *et al*, 2006].

3.3.6. pH value measurement

The pH was measured potentiometrically using a standard hydrogen electrode or glass electrode with a reference electrode. A combination electrode was also used. Certified buffer solutions were used for the calibration. The potential of the solution is measured in millivolts and converted to pH units. The pH meter was calibrated using buffer solutions of pH 4.01, 7.00 and 9.21. The samples were analysed at a temperature of 40°C to ensure that there was no crystallisation of sodium based salts when taking the pH measurement.

It is important to note that temperature has an effect on pH and therefore all measurements must be temperature compensated. Electrode responses are known to be affected by temperature and the pH of aqueous solutions also changes with temperature. pH values should therefore always be reported with temperature [Andrews, 1988]. An Inlab 413 with a built in temperature sensor was used for the determination of pH in this study.

3.3.7. Chemical composition using FTIR

The chemical composition of pure sodium thiocyanate and washed yellow precipitate (mixture of $(NaSCN)_x$ and amorphous polymeric $(SCN)_x$), obtained during the addition of hydrogen peroxide to sodium thiocyanate solution was completed using Fourier Transform Infrared (FTIR) analysis on a Perkin Elmer spectrum 400 FTIR, equipped with a universal Attenuated Total Reflectance (ATR) sampling accessory. About 1 mg of each sample was placed on a sample holding hole and pressed by means of gauge force arm mounted on the instrument in order to ensure maximum contact with the detector. The spectra for both samples were recorded in the range of 4000 cm⁻¹ to 400 cm⁻¹.

3.3.8. XRD Analysis

Solid samples obtained from the experiments and NaSCN crystals were subjected to mineralogical analysis using X-ray diffractometry (XRD), with the Rietveld-based X'Pert HighScore Plus Software [Speakman, 2012].

3.3.9. XRF Analysis

Solid samples obtained from the experiments were fused into a borosilicate disk [Norrish and Hutton, 1969] and analysed by X-ray fluorescence (XRF) spectrometry techniques.

Chapter 4

Results and Discussion

This study focused mainly on the oxidation of NaSCN in aqueous solution samples using oxidants such as hydrogen peroxide (H_2O_2), air, sodium ammonium vanadate (SAV) and $\text{Na}_2[\text{ADA}]$. Ion Chromatography (IC), Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES), X-ray diffraction (XRD), X-ray fluorescence (XRF), Gas Chromatography-Mass Spectrometry (GC-MS), spectroscopic techniques, titrimetry and Fourier Transform Infrared (FTIR) and other general wet chemistry techniques such as pH determination were also performed to characterise liquid and solid samples resulting from the experiments. In this chapter all results obtained are presented and discussed.

4.1. Oxidation of NaSCN in de-ionised water using H_2O_2 as an oxidising agent

After following the steps described in Section 3.1.1, the concentrations of sodium based salts in the aqueous solution samples containing 0.99 mol.dm^{-3} and 1.97 mol.dm^{-3} NaSCN were quantified. The pH of the individual solutions was also measured and recorded.

The results are graphically depicted in Figure 4.1 and Figure 4.3. From Figure 4.1 and Figure 4.3, it is clear that as the concentration of hydrogen peroxide in the individual solution samples were increased from 0.00 mol.dm^{-3} to 3.32 mol.dm^{-3} , the concentration of NaSCN decreased while the concentration of sodium sulphates ($\text{Na}_2\text{SO}_4 + \text{NaHSO}_4$) steadily increased. This provides evidence that hydrogen peroxide is responsible for oxidising NaSCN present in the aqueous solution samples into sodium and ammonium salts. Previous studies show that H_2O_2 was used to oxidise potassium thiocyanate to form SO_4^{2-} and OSCN^- species [Hu, *et al*, 2014]. The degree of oxidation of NaSCN also varied between the two solution samples. As expected, the pH dropped as the concentration of hydrogen peroxide (i.e. weak acid) increased.

The degree of oxidation of NaSCN in the 0.99 mol.dm^{-3} and 1.97 mol.dm^{-3} NaSCN solutions also varied. In the 0.99 mol.dm^{-3} NaSCN solution samples, the oxidation of NaSCN to Na_2SO_4 went to completion with oxidation of NaSCN to a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ species occurring intermittently as is illustrated in Figure 4.2.

After an addition of 3.32 mol.dm^{-3} of hydrogen peroxide to the 200 ml of the 0.99 mol.dm^{-3} NaSCN solution sample, almost of all NaSCN species present in this sample was oxidised to Na_2SO_4 . Figure 4.1 clearly shows that as the H_2O_2 addition to the 0.99 mol.dm^{-3} NaSCN solution increased to 3.32

$\text{mol}\cdot\text{dm}^{-3}$, the initial concentration of $0.99 \text{ mol}\cdot\text{dm}^{-3}$ NaSCN decreased to $0.00 \text{ mol}\cdot\text{dm}^{-3}$ and the initial concentration of $0.03 \text{ mol}\cdot\text{dm}^{-3}$ Na_2SO_4 increased to $0.74 \text{ mol}\cdot\text{dm}^{-3}$. Since no NaSCN was detected after this addition, it was concluded that full oxidation from NaSCN to Na_2SO_4 occurred. A proposed reaction sequence for the oxidation of SCN^- ions by hydrogen peroxide to form NaHSO_4 and NH_4HCO_3 is cited in literature. According to this series of reactions, NaHSO_4 and NH_4HCO_3 are formed when NaSCN is reacted with H_2O_2 [Kalmár, *et al*, 2013; Wilson and Harris, 1960; Orban, 1986; Barnett and Stanbury, 2002 and Nagy, *et al*, 2006].

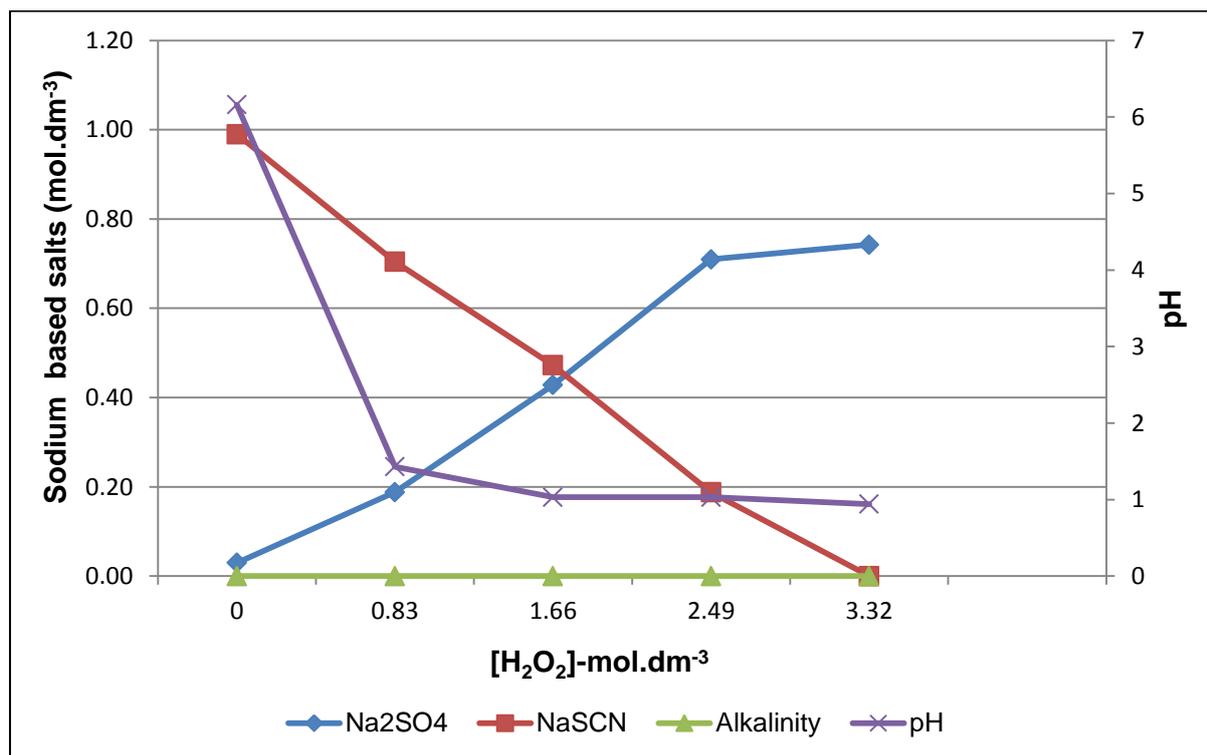


Figure 4.1: The concentrations of sodium based salts and pH values in the aqueous solution samples after the addition of H_2O_2 to $0.99 \text{ mol}\cdot\text{dm}^{-3}$ NaSCN solution.

The resulting solution samples after H_2O_2 additions to the $0.99 \text{ mol}\cdot\text{dm}^{-3}$ NaSCN solution samples are given in Figure 4.2. Solution 1 is an aqueous solution of $0.99 \text{ mol}\cdot\text{dm}^{-3}$ NaSCN and is clear in colour. No H_2O_2 has been added to solution 1. The yellow coloured slurry samples in Figures 4.2 and 4.4 clearly indicated formation of a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ as H_2O_2 oxidised the sulphur species in NaSCN to a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ (Refer to Figure 4.2(a), Figures 4.5 – 4.8 and Table 4.2).

The water washed yellow precipitate (a mixture of amorphous polymeric $(\text{SCN})_x$ and $(\text{NaSCN})_x$) formed in this study has the same colour as the crystalline elemental sulphur (S_8). Figure 4.2(a) illustrates the spectra for pure NaSCN crystals and the polymeric species formed. From the spectra a sharp defined peak (strong infrared absorption band) with a wavenumber of approximately 2000 cm^{-1}

is observed for the pure NaSCN crystals. The polymeric species has a medium intensity peak with a wavenumber in the region of 1000 cm^{-1} to 1500 cm^{-1} . These spectra were compared to literature and it was confirmed that the polymeric species of $(\text{SCN})_x$ absorbs IR radiation in the mid IR region of approximately 1000 cm^{-1} to 1500 cm^{-1} [Miller and Wilkins, 1952]. This confirms the formation of amorphous polymeric $(\text{SCN})_x$ during the oxidation of NaSCN with H_2O_2 .

Some researchers added thiocyanate salt solutions to either the organic liquids or aqueous solutions during the synthesis of various polythiocyanogen $(\text{SCN})_2$ species under different polymerization conditions in various laboratories [Pandey, *et al*, 2011; Früchtl, *et al*, 2009; Bowman, *et al*, 2006; Echeverri, 2012; Zhou and Tian, 2012; Tudela, *et al*, 1984; Cataldo and Heymann, 2001]. These authors found that thiocyanate radicals rapidly polymerized at low temperatures into amorphous products and the colours of the formed polymeric products ranged from yellow to orange to red to black. Excess concentrations of H_2O_2 in solutions 4 and 5 (see Figure 4.2) with limited concentrations of NaSCN resulted in all NaSCN being converted to Na_2SO_4 with mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ formation observed.

Literature indicates that in Stretford process liquors, intermediate H_2O_2 from vanadium species and $\text{Na}_2[\text{ADA}]$ catalyse the formation of H_2S to yellow elemental sulphur particles [Kelsall, *et al*, 1993]. Under acidic and neutral conditions H_2S is oxidised to yellow hydrophobic elemental sulphur (see reactions 30 and 31) [Jones, 1999]. In the experiments performed in Section 3.1.1 formation of a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ occurred as a result of H_2O_2 oxidising NaSCN to sodium sulphate.

The presence of high concentrations of elemental sulphur (reported as SO_3) and yellow $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ are confirmed by XRF and XRD results presented in Tables 4.1 and 4.2. The X-ray diffraction patterns for the solid products formed from the reactions between NaSCN and H_2O_2 are shown in Figures 4.5 to 4.8.

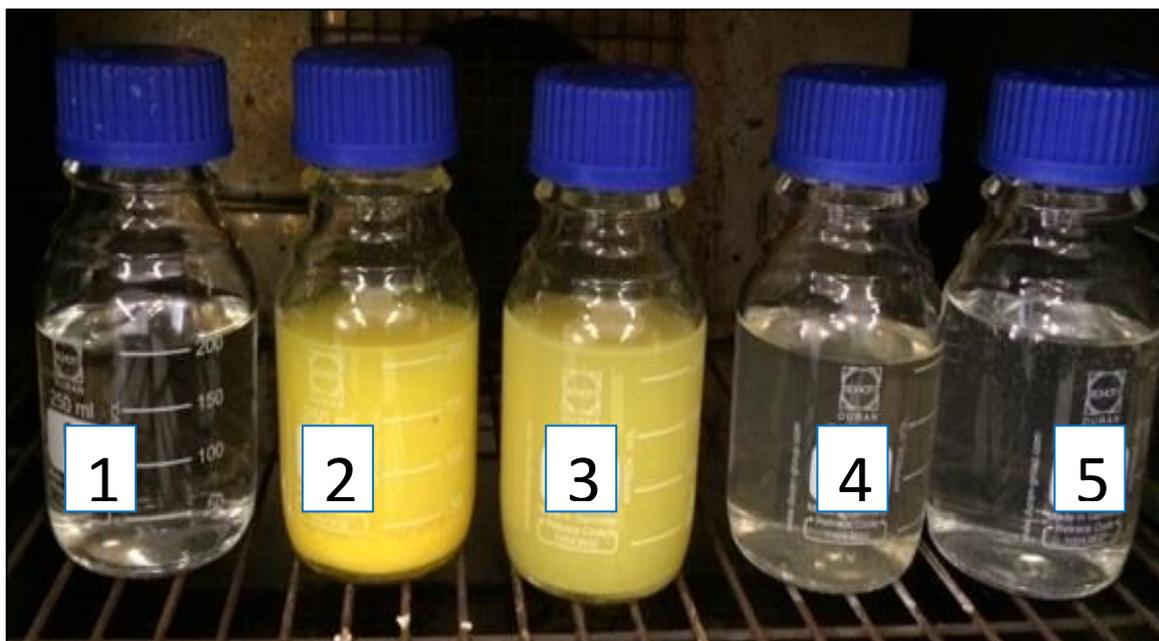


Figure 4.2: NaSCN solution and slurry samples were formed after the addition of H_2O_2 to 0.99 mol.dm^{-3} NaSCN solution.

Note:

- a) **Solution sample 1:** 0.99 mol.dm^{-3} NaSCN solution
- b) **Slurry sample 2:** 0.99 mol.dm^{-3} NaSCN solution + 0.83 mol.dm^{-3} H_2O_2
- c) **Slurry sample 3:** 0.99 mol.dm^{-3} NaSCN solution + 1.66 mol.dm^{-3} H_2O_2
- d) **Solution sample 4:** 0.99 mol.dm^{-3} NaSCN solution + 2.49 mol.dm^{-3} H_2O_2
- e) **Solution sample 5:** 0.99 mol.dm^{-3} NaSCN solution + 3.32 mol.dm^{-3} H_2O_2

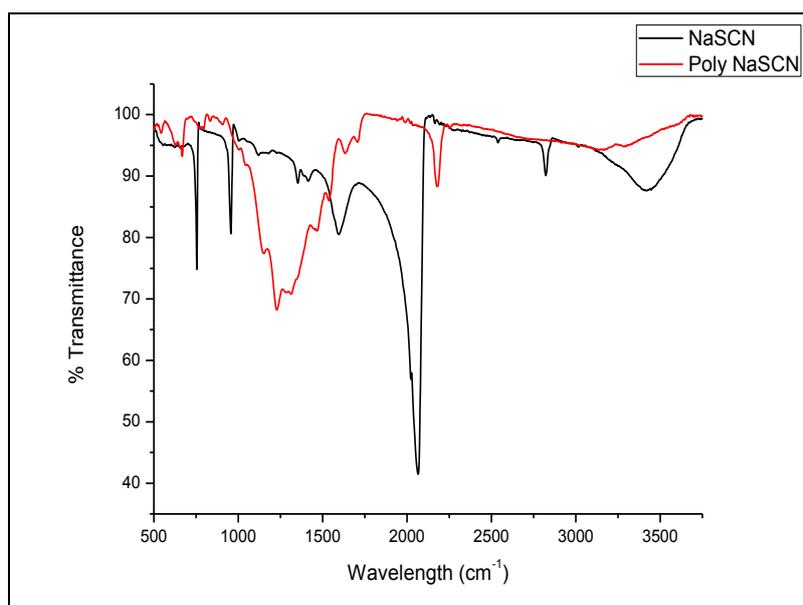


Figure 4.2(a): FTIR analysis results for the washed colloidal polymeric $(\text{SCN})_x$.

From Figure 4.3 it is clear that the dissolved NaSCN concentrations and pH values in the aqueous solution samples decreased with an increase in the concentrations of H_2O_2 due to partial oxidation of other NaSCN species to Na_2SO_4 . The concentrations of the sodium sulphate formed in the aqueous solution samples were gradually increased after the addition of H_2O_2 to these samples.

Upon the addition of 0.83 mol.dm^{-3} H_2O_2 to the 1.97 mol.dm^{-3} NaSCN solution, the initial concentration of 1.97 mol.dm^{-3} NaSCN decreased to 1.39 mol.dm^{-3} and the initial concentration of 0.03 mol.dm^{-3} Na_2SO_4 increased to 0.17 mol.dm^{-3} . As the H_2O_2 addition to the 1.97 mol.dm^{-3} NaSCN solution was increased to 3.32 mol.dm^{-3} , the initial concentration of 1.97 mol.dm^{-3} NaSCN decreased to 0.52 mol.dm^{-3} and the initial concentration of 0.03 mol.dm^{-3} Na_2SO_4 increased to 0.54 mol.dm^{-3} . As expected, the pH of the resulting aqueous solution decreased as the concentration of H_2O_2 increased. H_2O_2 is a weak acid and will affect the pH values by decreasing it as a result of this characteristic [Gamage, *et al*, 1991].

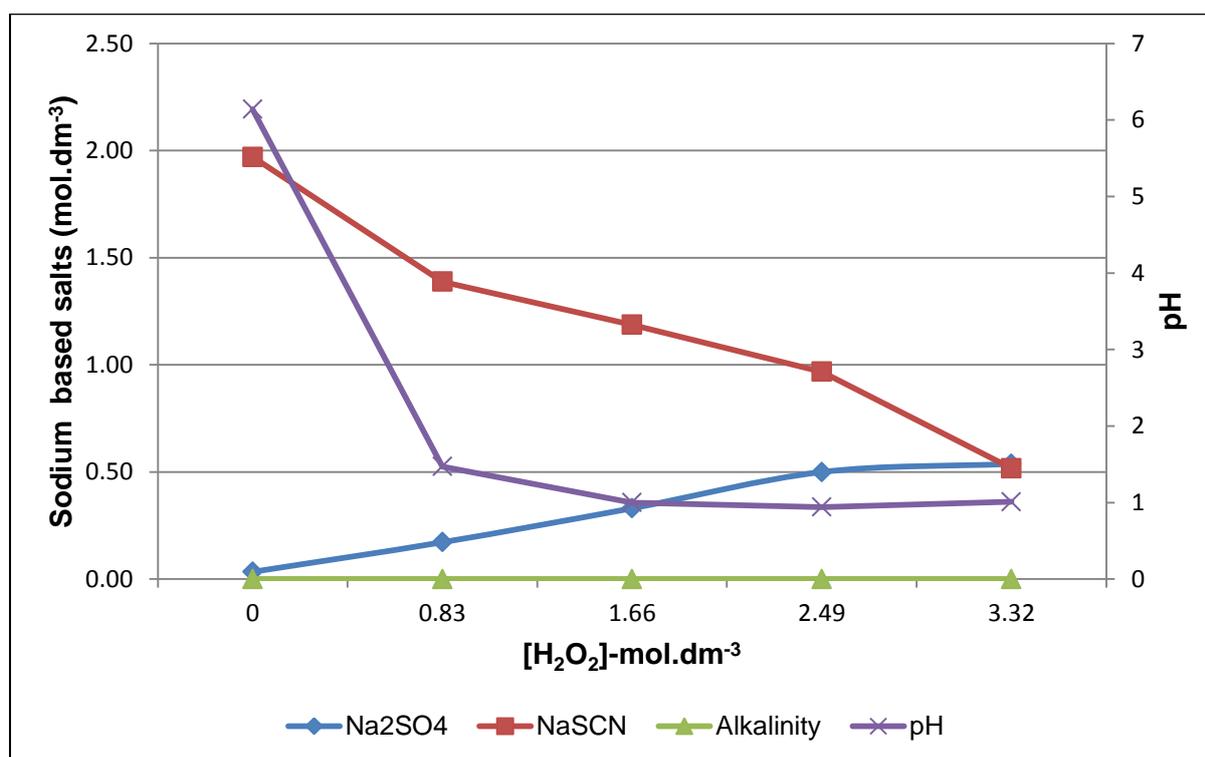


Figure 4.3: The concentrations of sodium based salts and pH values in the aqueous solution samples after the addition of H_2O_2 to 1.97 mol.dm^{-3} NaSCN solution.

The resulting aqueous solution and slurry samples that were formed after H_2O_2 addition to the 1.97 mol.dm^{-3} NaSCN solution samples can be seen in Figure 4.4. Solution 6 is an aqueous solution of 1.97 mol.dm^{-3} NaSCN and is clear in colour. No H_2O_2 has been added to solution 6. The yellow coloured solution samples marked 7, 8, 9 and 10 clearly indicated formation of a mixture of

(NaSCN)_x and amorphous polymeric (SCN)_x as H₂O₂ oxidised the sulphur species in NaSCN to sodium sulphates and a mixture of (NaSCN)_x and amorphous polymeric (SCN)_x species. Since only partial oxidation of NaSCN to Na₂SO₄ was observed with the 1.97 mol.dm⁻³ NaSCN solution due to H₂O₂ not being present in excess concentrations, the formation of a mixture of (NaSCN)_x and amorphous polymeric (SCN)_x (amorphous product) was visually observed for all samples produced after the H₂O₂ addition to these solution samples (Refer to Figure 4.4). The presence of the amorphous content is also confirmed in the diffraction patterns (Figures 4.5 to 4.8). 2-Theta (angle -degrees) is plotted on the x-axis while intensity (counts per second) is plotted on the y-axis for Figures 4.5 to 4.8. It was evident, that as the hydrogen peroxide addition increased, more amorphous material started to form. It was found that hydrogen sulphide reacted with oxygen to form white amorphous sulphur in the absence of V⁵⁺ catalyst [Mercieca, 2004; Hiner and Warren 1970].

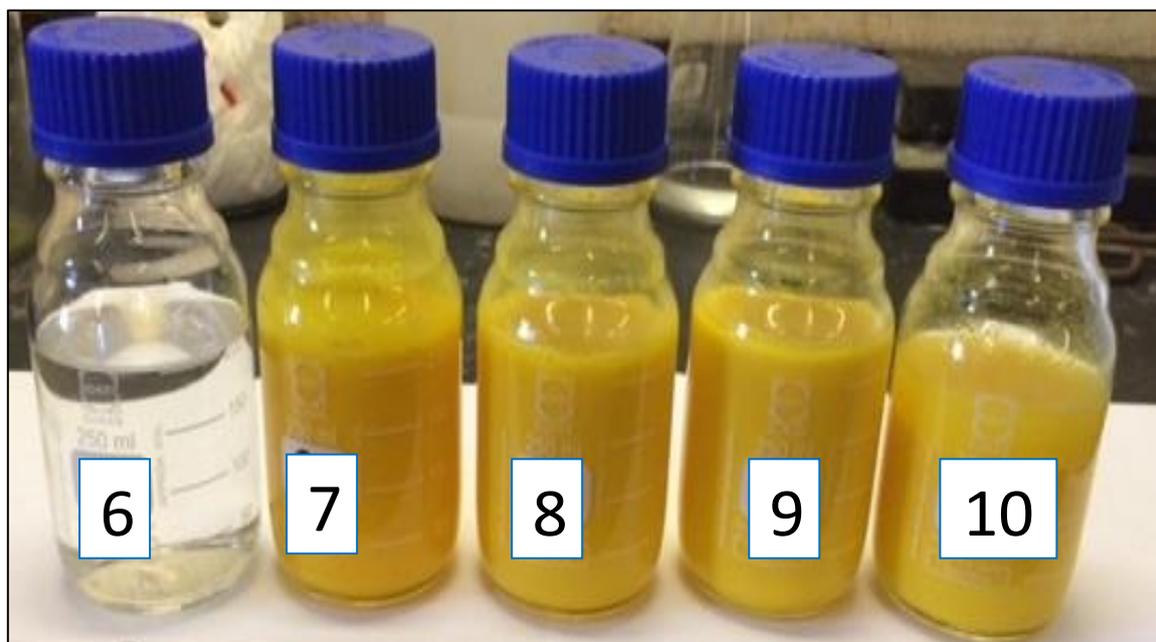


Figure 4.4: NaSCN solution and slurry samples were formed after the addition of H₂O₂ to 1.97 mol.dm⁻³ NaSCN solution.

Note:

- a) **Solution sample 6:** 1.97 mol.dm⁻³ NaSCN solution
- b) **Slurry sample 7:** 1.97 mol.dm⁻³ NaSCN solution + 0.83 mol.dm⁻³ H₂O₂
- c) **Slurry sample 8:** 1.97 mol.dm⁻³ NaSCN solution + 1.66 mol.dm⁻³ H₂O₂
- d) **Slurry sample 9:** 1.97 mol.dm⁻³ NaSCN solution + 2.49 mol.dm⁻³ H₂O₂
- e) **Slurry sample 10:** 1.97 mol.dm⁻³ NaSCN solution + 3.32 mol.dm⁻³ H₂O₂

The solid samples that were produced during the evaporation of the NaSCN solution (Section 3.1.9) and slurry samples formed after the addition of H₂O₂ to the NaSCN solution (Figure 4.4) were submitted for the XRF and XRD analyses. It should be noted that the XRD results for the solids

sample produced after evaporation of aqueous NaSCN and slurry samples that are reported in this study are semi-quantitative. The concentrations of elements in the solid samples were determined by X-ray fluorescence analysis and are also reported as elemental oxides by default.

The XRF and XRD results for the solid samples are presented in Table 4.1 and Table 4.2. The XRF results for the solid samples clearly indicate that these solid samples contained mainly sodium and sulphur elements (Table 4.1). When expressed as its common elemental oxide (Na_2O), sodium oxide makes up 10.36% and 4.05% of the solids that were produced from the 0.83 mol.dm^{-3} and $3.32 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ solution samples respectively. The concentrations of sulphur (SO_3) in the solid samples that were formed from the 0.83 mol.dm^{-3} and $3.32 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ solution samples are 88.3% and 94.14% respectively. The XRD results also indicate that the amorphous material in the formed solid samples increased as the concentrations of hydrogen peroxide in the 1.97 mol.dm^{-3} NaSCN solution increased.

The XRD results confirmed the presence of a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ product as a major component in the solid samples that were formed from the evaporation of the NaSCN solution and the slurry samples (Figures 4.5 to 4.8). As the concentration increased from $0.83 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ to $3.32 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$, the defined peaks (i.e. crystalline material) in the X-ray diffraction patterns in Figure 4.5 started to broaden and became undefined as shown in Figure 4.8. The broad peaks confirmed the formation of amorphous (i.e. non-crystalline material) content as the H_2O_2 concentration increased.

The crystalline phases (minerals) that were detected in the solid samples as major constituents are sodium sulphate and sodium thiocyanate. The minor constituents are trona ($\text{Na}_2\text{CO}_3\text{NaHCO}_3(\text{H}_2\text{O})_2$), sulphur oxide (SO_2), sodium cyanide hydrate ($\text{NaCN}(\text{H}_2\text{O})_2$), sulphur amide ($\text{S}_4(\text{NH})_4$), sulphur imide ($\text{S}_6(\text{NH})_2$). Ammonium based salts are known to form from the oxidation of NaSCN using H_2O_2 [Kalmár, *et al*, 2013; Wilson and Harris, 1960; Orban, 1986; Barnett and Stanbury, 2002 and Nagy, *et al*, 2006].

Table 4.1: X-ray fluorescence results of the solid samples that were formed from the evaporation experiments of NaSCN solution and slurry samples of NaSCN solution and H₂O₂.

Mass %	Sample Identification			
	7	8	9	10
Fe₂O₃	0.02	<0.01	0.01	<0.01
MnO	<0.01	<0.01	<0.01	<0.01
Cr₂O₃	0.05	0.04	0.05	0.03
V₂O₅	0.07	0.06	0.06	0.04
TiO₂	<0.01	<0.01	<0.01	<0.01
CaO	<0.01	<0.01	<0.01	<0.01
K₂O	<0.01	<0.01	<0.01	<0.01
P₂O₅	0.0021	0.0026	0.0041	0.0077
SiO₂	<0.1	<0.1	<0.1	<0.1
Al₂O₃	<0.1	<0.1	<0.1	<0.1
MgO	1.24	1.35	1.55	1.7
Na₂O	10.36	9.86	8.3	4.05
Cl	0.029	0.027	0.024	0.027
SO₃	88.3	88.66	90	94.14

Note:

7. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 0.83 mol.dm⁻³ H₂O₂
8. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 1.66 mol.dm⁻³ H₂O₂
9. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 2.49 mol.dm⁻³ H₂O₂
10. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 3.32 mol.dm⁻³ H₂O₂

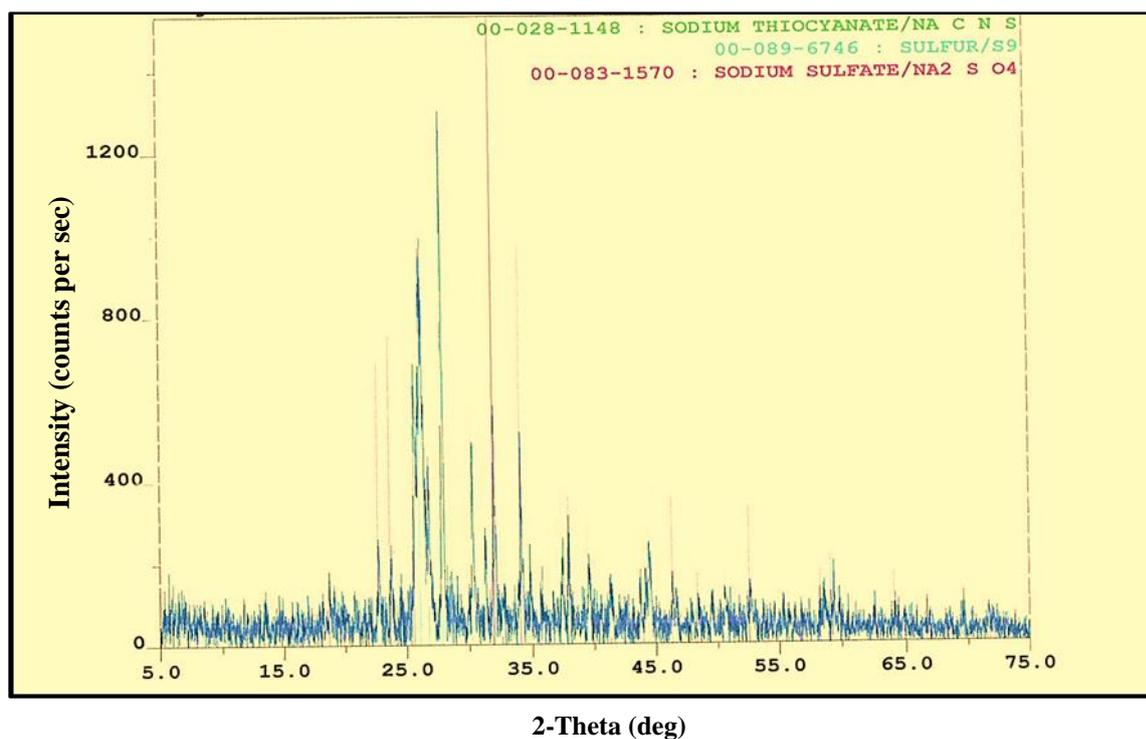


Figure 4.5: X-ray diffraction pattern for the solid product formed from the evaporation experiment of $1.97 \text{ mol.dm}^{-3} \text{ NaSCN} + 0.83 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$.

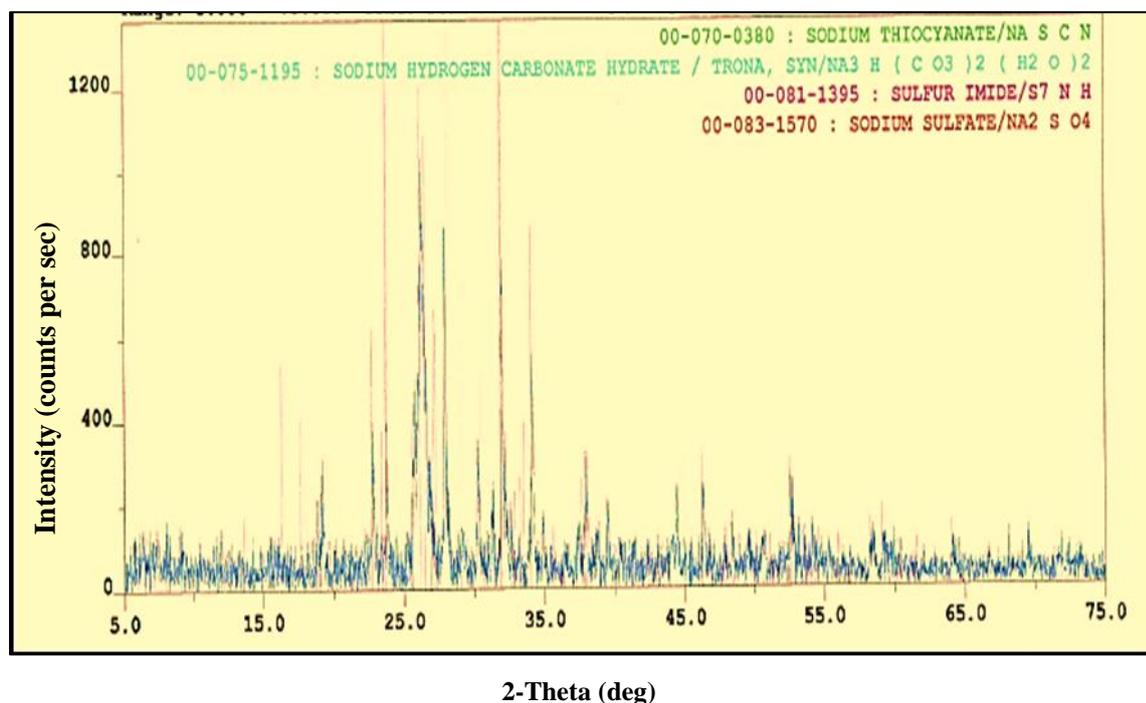


Figure 4.6: X-ray diffraction pattern for the solid product formed from the evaporation experiment of $1.97 \text{ mol.dm}^{-3} \text{ NaSCN} + 1.66 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$.

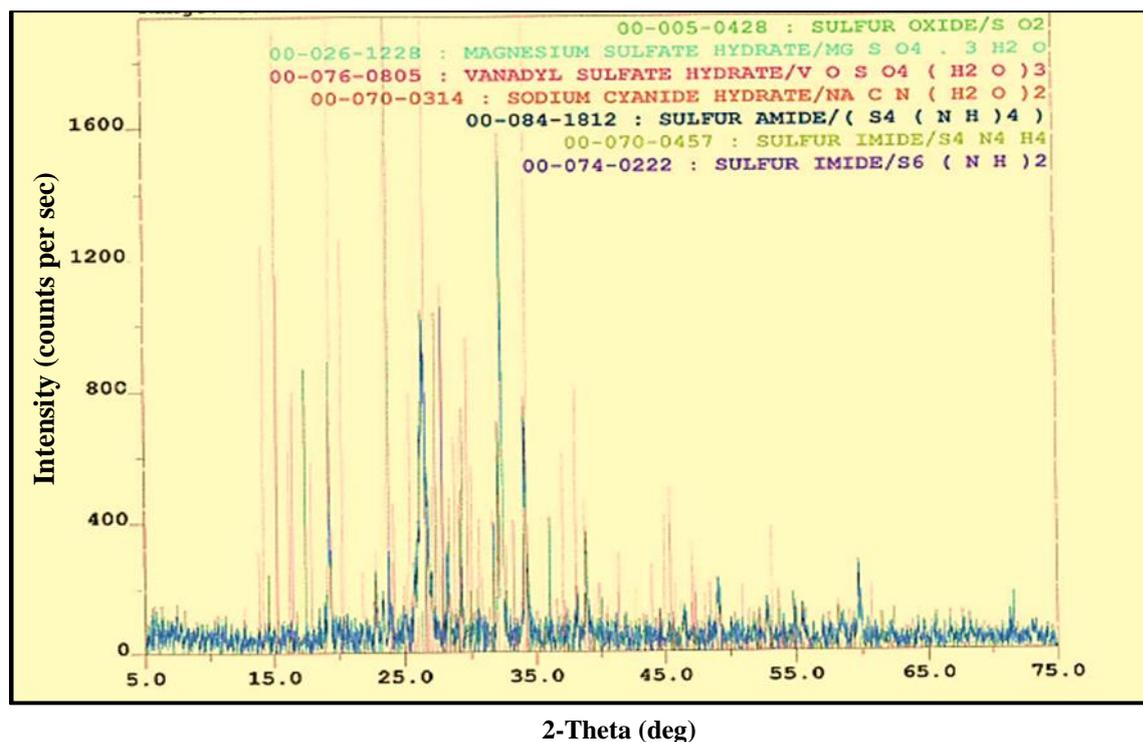


Figure 4.7: X-ray diffraction pattern for the solid product formed from the evaporation experiment of $1.97 \text{ mol.dm}^{-3} \text{ NaSCN} + 2.49 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$.

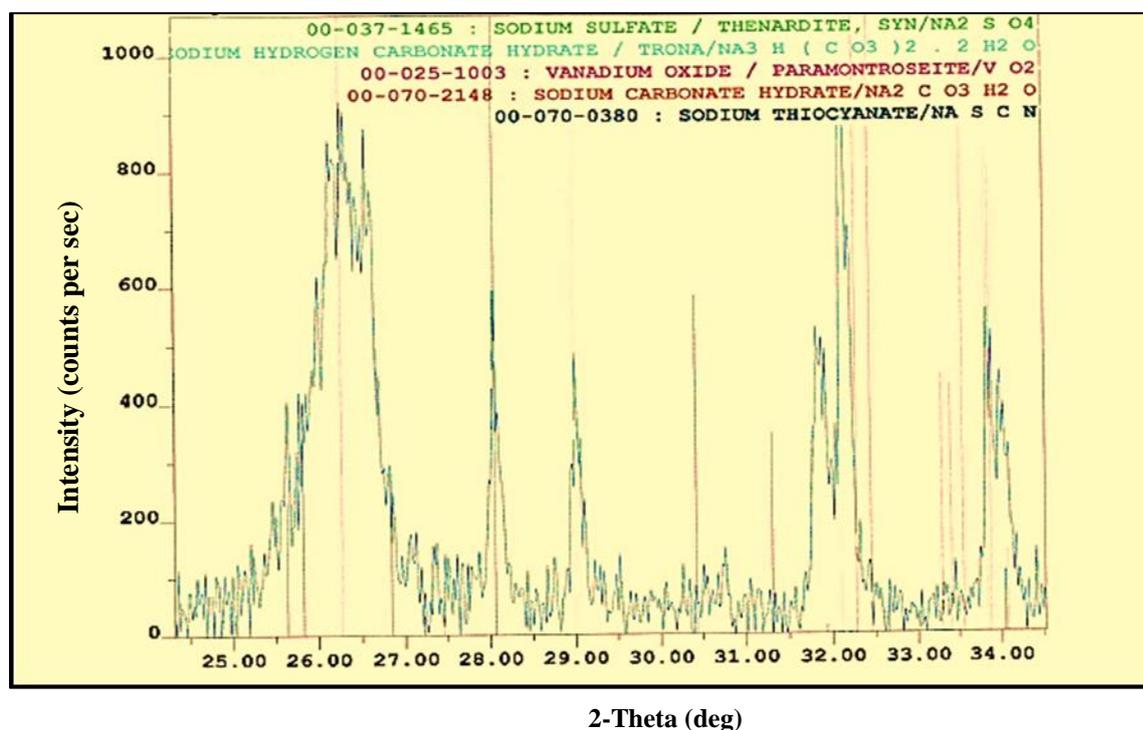


Figure 4.8: X-ray diffraction pattern for the solid product formed from the evaporation experiment of $1.97 \text{ mol.dm}^{-3} \text{ NaSCN} + 3.32 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$.

Table 4.2: XRD results of the solid samples that were formed from the evaporation experiments of aqueous NaSCN and slurry samples of NaSCN solution and H₂O₂.

Mineral	Sample Identification			
	7	8	9	10
Sodium Sulphate (Na₂SO₄)	Major	Major	Major	Major
Sodium Thiocyanate (NaSCN)	Major	Major	Major	Major
Trona (Na₂CO₃NaHCO₃(H₂O)₂)	-	Minor	Minor	Minor
Sulphur Oxide (SO₂)	-	-	Trace	Trace
Sodium Cyanide Hydrate (NaCN(H₂O)₂)	-	-	Trace	Trace
Sulphur Amide (S₄(NH)₄)	-	-	Trace	Trace
Sulphur Imide (S₆(NH)₂)	-	-	Trace	Trace
High amorphous content	Major	Major	Major	Major

Note:

7. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 0.83 mol.dm⁻³ H₂O₂
8. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 1.66 mol.dm⁻³ H₂O₂
9. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 2.49 mol.dm⁻³ H₂O₂
10. Solid sample was formed from the evaporation experiment of 1.97 mol.dm⁻³ NaSCN + 3.32 mol.dm⁻³ H₂O₂

4.2. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.3 using hydrogen peroxide

The procedure for the oxidation of NaSCN is outlined in Section 3.1.2. The chemical analyses results for the various sodium based salts, pH, vanadium salts and Na₂[ADA] for Stretford aqueous liquor A are shown in Figure 4.9 and Figure 4.10 respectively. The results indicate that as the concentration of H₂O₂ increased, there was an impact on the total alkalinity concentration, pH values, and the concentration of Na₂SO₄. The total alkalinity decreased from 0.28 mol.dm⁻³ in solution 11 (Stretford aqueous liquor A + 0 mol.dm⁻³ H₂O₂) to 0.04 mol.dm⁻³ in solution 15 (Stretford aqueous liquor A + 4.98 mol.dm⁻³ H₂O₂) (see Figure 4.9 and Figure 4.11). Hydrogen peroxide reacted with sodium carbonate to evolve carbon dioxide gas. The loss of total alkalinity concentration in the Stretford

aqueous liquor sample impacted the pH values directly and hence a reduction in pH was observed as the concentration of H_2O_2 that was added to Stretford aqueous liquor A was increased.

The concentration of NaSCN decreased while the concentration of Na_2SO_4 increased as the concentration of H_2O_2 was increased. This implies that NaSCN in the Stretford aqueous liquor sample is being oxidised to form Na_2SO_4 upon addition of H_2O_2 . The oxidation of thiocyanate by hydrogen peroxide proceeds through an intermediate hypothiocyanite complex. Depending on the pH of the solution, this intermediate complex undergoes a series of reactions and is further oxidised to sulphate, ammonia and bicarbonate (HCO_3^-) [Cristy and Edgeberg, 2000].

Upon the addition of $0.83 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ to Stretford aqueous liquor A, the initial concentration of $0.93 \text{ mol.dm}^{-3} \text{ NaSCN}$ decreased to 0.73 mol.dm^{-3} and the initial concentration of $0.86 \text{ mol.dm}^{-3} \text{ Na}_2\text{SO}_4$ increased to 1.08 mol.dm^{-3} . As the concentration H_2O_2 in Stretford aqueous liquor A was increased to 4.98 mol.dm^{-3} , the initial concentration of $0.93 \text{ mol.dm}^{-3} \text{ NaSCN}$ decreased to 0.00 mol.dm^{-3} and the initial concentration of $0.86 \text{ mol.dm}^{-3} \text{ Na}_2\text{SO}_4$ subsequently increased to 1.49 mol.dm^{-3} . At a concentration of $3.32 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ complete oxidation of NaSCN to Na_2SO_4 was observed in Stretford aqueous liquor A. The % oxidation at a concentration of $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ was 100%. This could be attributed to the fact that H_2O_2 present in excess concentrations will facilitate the formation of Na_2SO_4 at faster reaction rates [Cristy and Edgeberg, 2000]. Due to a noticeable decrease in the pH from approximately 8 to 6, it can be deduced that H_2O_2 is present in excess concentrations in solutions 14 (Stretford aqueous liquor A + $3.32 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$) and 15 (Stretford aqueous liquor A + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$) (see Figure 4.9) hence confirming the complete oxidation of NaSCN to Na_2SO_4 .

The results and observations are verified by the XRF and XRD results in Table 4.3 and Table 4.4 respectively.

The $\text{Na}_2[\text{ADA}]$ concentration slightly decreased from $0.00078 \text{ mol.dm}^{-3}$ to $0.00061 \text{ mol.dm}^{-3}$ as the concentration of H_2O_2 in the solution sample increased (Figure 4.10). This occurred as a result of the Stretford aqueous liquor being diluted with dissolved oxygen (DO) in the form of hydrogen peroxide during the stipulated addition of $\text{Na}_2[\text{ADA}]$ to the Stretford aqueous liquor. $\text{Na}_2[\text{ADA}]$ is classified as a stable compound and therefore suitable for use in Stretford aqueous solution samples. But $\text{Na}_3[\text{HADA}]$ can react with oxygen and water to form hydrogen peroxide, sodium hydroxide and $\text{Na}_2[\text{ADA}]$ (Gamage, et al, 1991; Trofe, 1987). $\text{Na}_2[\text{ADA}]$ is responsible for the re-oxidation of V^{4+} to V^{5+} [Kohl and Riesenfeld, 1974]. Although $\text{Na}_2[\text{ADA}]$ does undergo a slight decomposition, it can be used for long periods of time [Nicklin, et al, 1961]. It can therefore be concluded that the concentration of $\text{Na}_2[\text{ADA}]$ will decrease slightly during the hydrogen peroxide oxidation process.

The total vanadium concentration will also be slightly affected however the concentration of V^{5+} decreased. This implies that the V^{4+} concentration increased slightly. At high pH, V^{5+} is the most

stable form of vanadium in aqueous solution, whereas at low pH, V^{4+} is the more favoured species [Crans, *et al*, 2004; Tracey and Crans, 1998]. This is consistent with the pH obtained during the experiments. As the pH dropped from 8.29 to 6.34, the V^{5+} slightly decreased from 0.023 to 0.014 $\text{mol}\cdot\text{dm}^{-3}$ (Figure 4.10), indicating that V^{4+} and V^{3+} species are present in higher concentrations than V^{5+} at lower pH values.

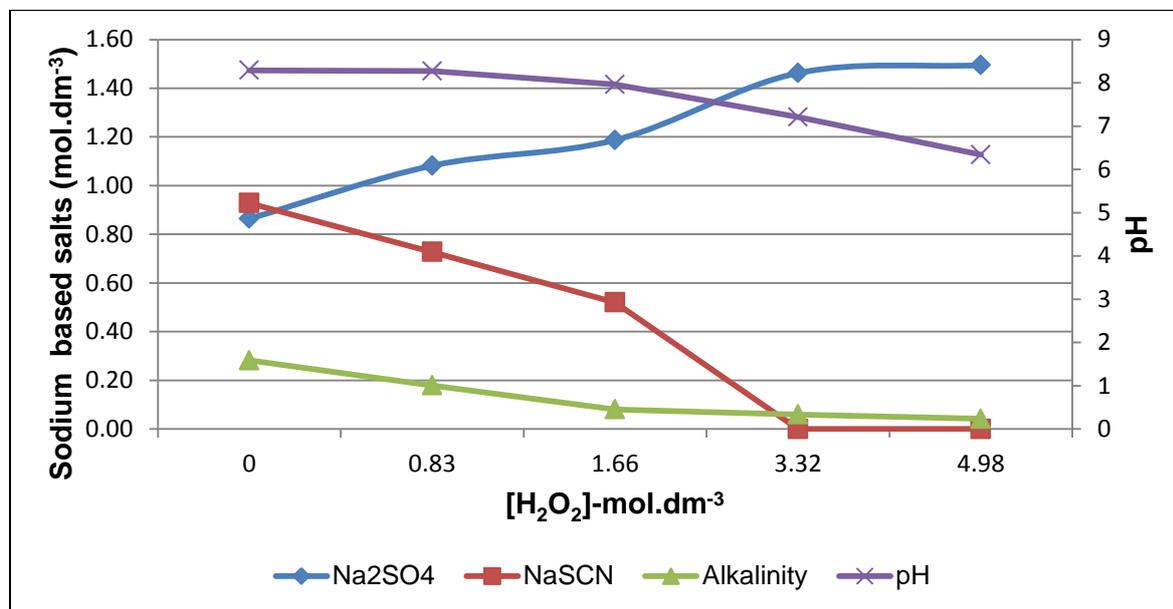


Figure 4.9: Concentrations of sodium based salts and pH values in Stretford aqueous liquor A before and after the addition of H_2O_2 .

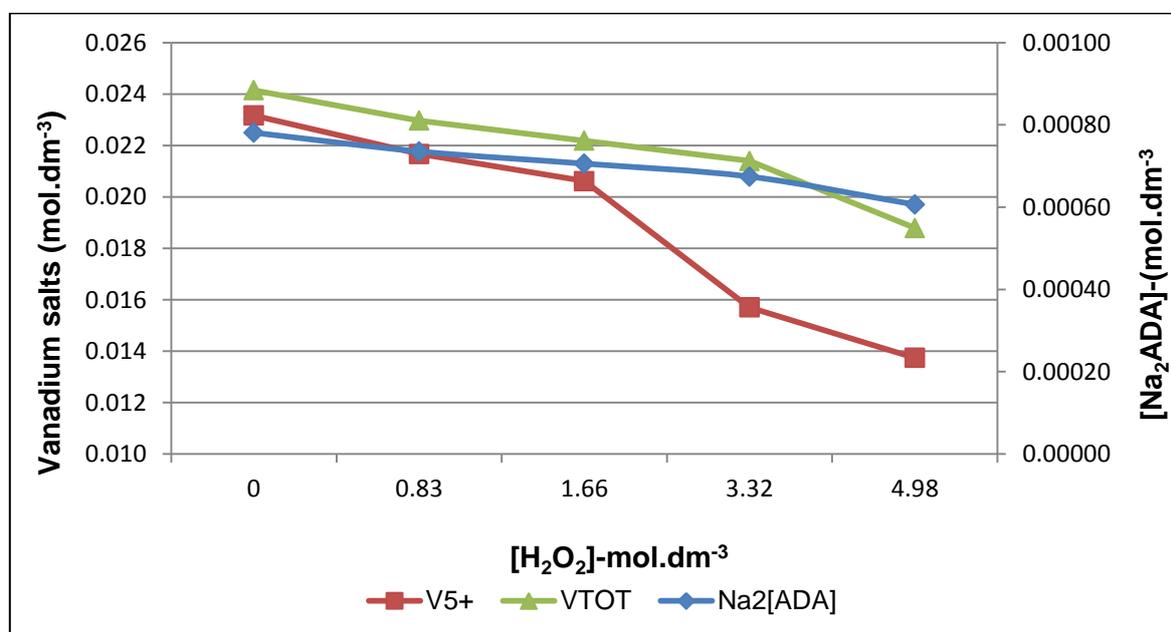


Figure 4.10: Concentrations of V^{5+} , total vanadium, and $\text{Na}_2[\text{ADA}]$ in Stretford aqueous liquor A before and after the addition of H_2O_2 .

Note: V^{TOT} = Total vanadium concentration



Figure 4.11: Stretford aqueous liquor A sample (11) and Stretford aqueous liquor A samples (12 to 15) with increasing $[H_2O_2]$.

Note:

- a) **Solution sample 11:** Stretford aqueous liquor A + $0 \text{ mol.dm}^{-3} H_2O_2$
- b) **Solution sample 12:** Stretford aqueous liquor A + $0.83 \text{ mol.dm}^{-3} H_2O_2$
- c) **Solution sample 13:** Stretford aqueous liquor A + $1.66 \text{ mol.dm}^{-3} H_2O_2$
- d) **Solution sample 14:** Stretford aqueous liquor A + $3.32 \text{ mol.dm}^{-3} H_2O_2$
- e) **Solution sample 15:** Stretford aqueous liquor A + $4.98 \text{ mol.dm}^{-3} H_2O_2$

The XRF and XRD analyses results that are given in Tables 4.3 and 4.4 indicate that the concentrations of sodium and sulphur-containing compounds in the solid samples analysed dominated the concentrations of other inorganic elements and compounds. The concentrations of the Na and S in the solid samples are expressed as the elemental oxides (Na_2O) and sulphur oxide (SO_3) respectively (Table 4.3). The presence of significant sodium and sulphur compounds and sodium sulphate crystals confirmed that some sodium thiocyanate species in the high ionic strength Stretford liquor (Stretford aqueous liquor A) oxidised to sodium sulphate salts during the addition of H_2O_2 to the Stretford aqueous liquor samples. The XRF analysis results for Stretford aqueous liquor A are in good agreement with the XRD analysis results for the solid samples formed after evaporation of the Stretford aqueous liquor A samples and Stretford aqueous liquor samples containing H_2O_2 .

The XRD results (Table 4.4) confirmed the presence of sodium sulphate as the dominating component in the solid samples produced after evaporation of the Stretford aqueous liquor A sample and Stretford aqueous liquor samples containing H_2O_2 . The concentrations of sodium thiocyanate in the solid

samples produced after the addition of H_2O_2 to the Stretford aqueous liquor samples decreased. The less dominant constituents are trona ($\text{Na}_2\text{CO}_3\text{NaHCO}_3(\text{H}_2\text{O})_2$), vanadium (V) oxide (V_2O_5), burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$), sodium hydrogen sulphate (NaHSO_4) and mascagnite ($(\text{NH}_4)_2\text{SO}_4$). As the concentration of H_2O_2 was increased to $3.32 \text{ mol}\cdot\text{dm}^{-3}$, NaSCN was not detected by XRD, also confirming complete oxidation of NaSCN to Na_2SO_4 , NaHSO_4 , ammonium sulphate and other possible OSCN species at concentrations in excess of $3.32 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{O}_2$. At high alkaline pH values, all of the elemental sulphur particles present in the Stretford solutions will be oxidised to sulphates (see reaction 32) [Jones, 1999]. The presence of sulphates in the solids obtained after evaporation is evident from the XRD analysis.

Table 4.3: XRF analyses results for the solid samples that were formed after evaporation of the Stretford aqueous liquor A sample and Stretford aqueous liquor A samples containing H_2O_2 .

Mass %	Sample Identification				
	11	12	13	14	15
Fe₂O₃	0.01	0.01	0.03	<0.01	0.01
MnO	<0.01	<0.01	<0.01	<0.01	<0.01
Cr₂O₃	0.10	0.11	0.13	0.14	0.13
V₂O₅	0.78	1.17	1.66	1.66	1.37
TiO₂	<0.01	<0.01	<0.01	<0.01	<0.01
CaO	<0.01	<0.01	<0.01	<0.01	<0.01
K₂O	0.03	0.04	0.05	0.05	0.04
P₂O₅	ND	ND	0.0058	0.0093	0.011
SiO₂	<0.01	<0.10	<0.10	<0.10	<0.10
Al₂O₃	<0.01	<0.10	<0.10	<0.10	<0.10
MgO	0.53	0.53	0.52	0.55	0.55
Na₂O	43.41	42.86	39.57	39.1	39.38
Cl	0.004	0.008	0.016	0.008	0.006
SO₃	54.32	55.38	58.03	58.49	58.51

Note:

11. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + $0 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{O}_2$
12. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + $0.83 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{O}_2$
13. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + $1.66 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{O}_2$
14. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + $3.32 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{O}_2$
15. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + $4.98 \text{ mol}\cdot\text{dm}^{-3} \text{ H}_2\text{O}_2$

Table 4.4: XRD analyses results for the solid samples that were formed after evaporation of the Stretford aqueous liquor A sample and Stretford aqueous liquor A samples containing H₂O₂.

Mineral	Sample Identification				
	11	12	13	14	15
Sodium Sulfate (Na₂SO₄)	Major	Major	Major	Major	Major
Sodium Thiocyanate (NaSCN)	Major	Major	Minor	-	-
Vanadium (V) Oxide (V₂O₅)	Minor	Minor	Minor	Minor	Minor
Burkeite (Na₆(CO₃)(SO₄)₂)	Minor	Minor	Minor	Minor	Minor
Sodium Hydrogen Sulfate (NaHSO₄)	Trace	Trace	Trace	Trace	Trace
Trona (Na₂CO₃NaHCO₃(H₂O)₂)	-	Minor	Minor	Minor	Minor
Mascagnite ((NH₄)₂SO₄)	-	Minor	Minor	Minor	Minor

Note:

11. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + 0 mol.dm⁻³ H₂O₂
12. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + 0.83 mol.dm⁻³ H₂O₂
13. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + 1.66 mol.dm⁻³ H₂O₂
14. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + 3.32 mol.dm⁻³ H₂O₂
15. Solid sample that was formed during the evaporation of Stretford aqueous liquor A + 4.98 mol.dm⁻³ H₂O₂

As was mentioned previously in Section 3.1.2, the oxidation experiments were also carried out in Stretford aqueous liquor B containing a higher concentration of NaSCN. Stretford aqueous liquor B also contains different concentrations of NaSCN, Na₂SO₄, Na₂CO₃, vanadium and Na₂[ADA].

This was done to observe the extent of oxidation using H₂O₂ when the concentration of NaSCN is considerably higher. The results of the sodium based salts and pH is summarised in Figure 4.12 and trends for the vanadium salts and Na₂[ADA] are given in Figure 4.13.

Figure 4.14 is a visual representation of the colour changes observed as the concentration of H₂O₂ was increased from 0 mol.dm⁻³ in bottle 16 (Stretford aqueous liquor B + 0 mol.dm⁻³ H₂O₂) to 4.98 mol.dm⁻³ in bottle 20 (Stretford aqueous liquor B + 4.98 mol.dm⁻³ H₂O₂). A similar phenomenon was observed as with Stretford aqueous liquor A, however complete oxidation of the NaSCN was not observed with Stretford aqueous liquor B. This can be attributed to the high concentration of NaSCN in Stretford aqueous liquor B, which needs a significant amount of H₂O₂ for complete oxidation of

NaSCN. The pH value decreased from 8.26 to 2.07, while the total alkalinity decreased from 0.33 mol.dm⁻³ to 0.00 mol.dm⁻³.

Upon the addition of 0.83 mol.dm⁻³ H₂O₂ to Stretford aqueous liquor B, the initial concentration of 1.90 mol.dm⁻³ NaSCN slightly decreased to 1.54 mol.dm⁻³ and the initial concentration of 0.61 mol.dm⁻³ Na₂SO₄ slightly increased to 0.75 mol.dm⁻³. As the H₂O₂ concentration in the Stretford aqueous liquor B was increased to 4.98 mol.dm⁻³, the initial concentration of 1.90 mol.dm⁻³ NaSCN considerably decreased to 0.56 mol.dm⁻³ and the initial concentration of 0.61 mol.dm⁻³ Na₂SO₄ greatly increased to 1.48 mol.dm⁻³. The % oxidation at a concentration of 4.98 mol.dm⁻³ H₂O₂ is 70.53%. The results and observation are in good agreement with the XRF and XRD results in Table 4.5 and Table 4.6 respectively. This implies that H₂O₂ added to the Stretford aqueous liquor B sample oxidised some sodium thiocyanate species to sodium sulphate species.

The Na₂[ADA] concentration decreased from 0.0012 mol.dm⁻³ to 0.00093 mol.dm⁻³ as the concentration of H₂O₂ increased (Figure 4.13). This occurred as a result of the Stretford aqueous liquor being diluted with peroxide during the stipulated additions. As previously stated Na₂[ADA] is classified as a stable compound and therefore suitable for use in Stretford solutions. [Nicklin, *et al*, 1961]. Na₂[ADA] is a catalyst in the oxidation of V⁴⁺ to V⁵⁺ [Kellsall and Thompson, 1993b]. Due to the slight decomposition of Na₂[ADA], the re-oxidation of V⁴⁺ to V⁵⁺ is impacted. A decrease in the concentration of V⁵⁺ is therefore observed whereas the V⁴⁺ concentration increases.

The total vanadium concentration in the Stretford aqueous liquor samples was not significantly affected however the concentration of V⁵⁺ slightly decreased (Figure 4.13). This implies that the V⁴⁺ concentration increased. As stated above, at high pH values, V⁵⁺ is the most stable form of vanadium in aqueous solution, whereas at low pH, V⁴⁺ is the more favoured species and some V⁴⁺ species can precipitate in the form of black V⁴⁺ salts [Crans, *et al*, 2004, Tracey and Crans, 1998]. This is consistent with the pH obtained during the experiments. As the pH dropped from 8.26 to 2.07 (Figure 4.12), the V⁵⁺ decreased from 0.025 mol.dm⁻³ to 0.012 mol.dm⁻³, indicating that V⁴⁺ is present in higher concentrations than V⁵⁺ at lower pH values. The green colour displayed in solution 20 (Stretford aqueous liquor B + 4.98 mol.dm⁻³ H₂O₂) in Figure 4.14 indicates the presence of V³⁺ species. This is confirmed by literature, that at pH values between 2 to 3, V³⁺ compounds are stable and more dominant in solution [Crans, *et al*, 2004].

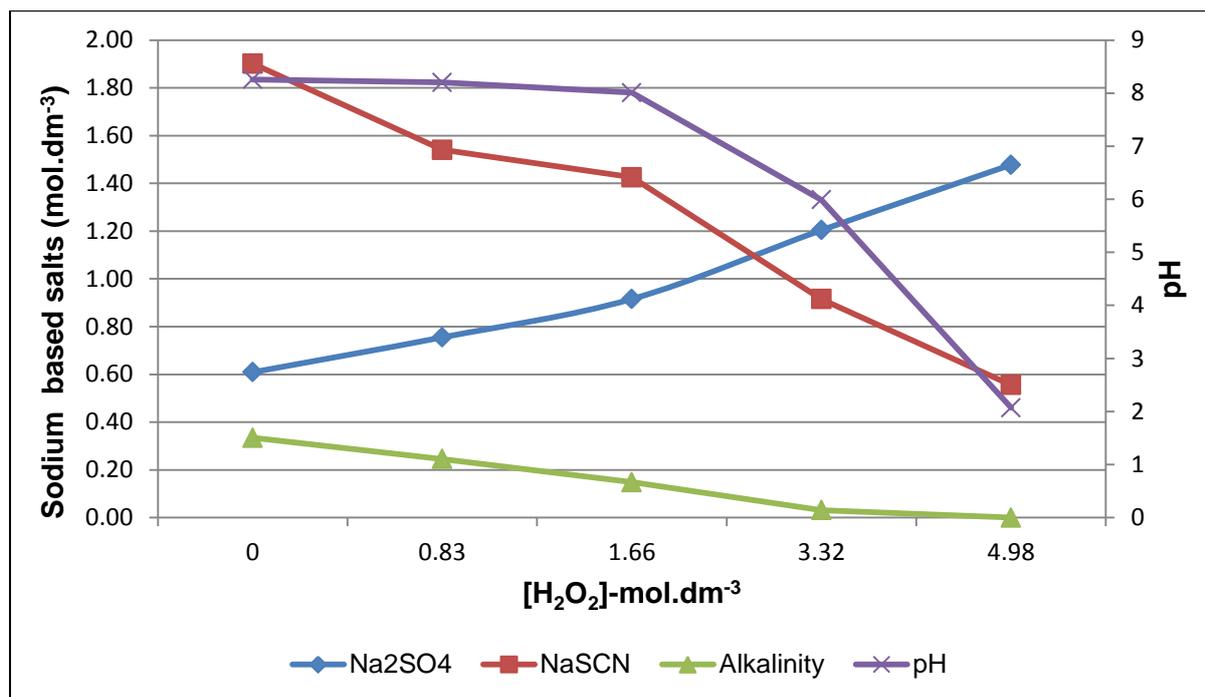


Figure 4.12: Concentrations of sodium based salts and pH values in Stretford aqueous liquor B before and after the addition of H₂O₂.

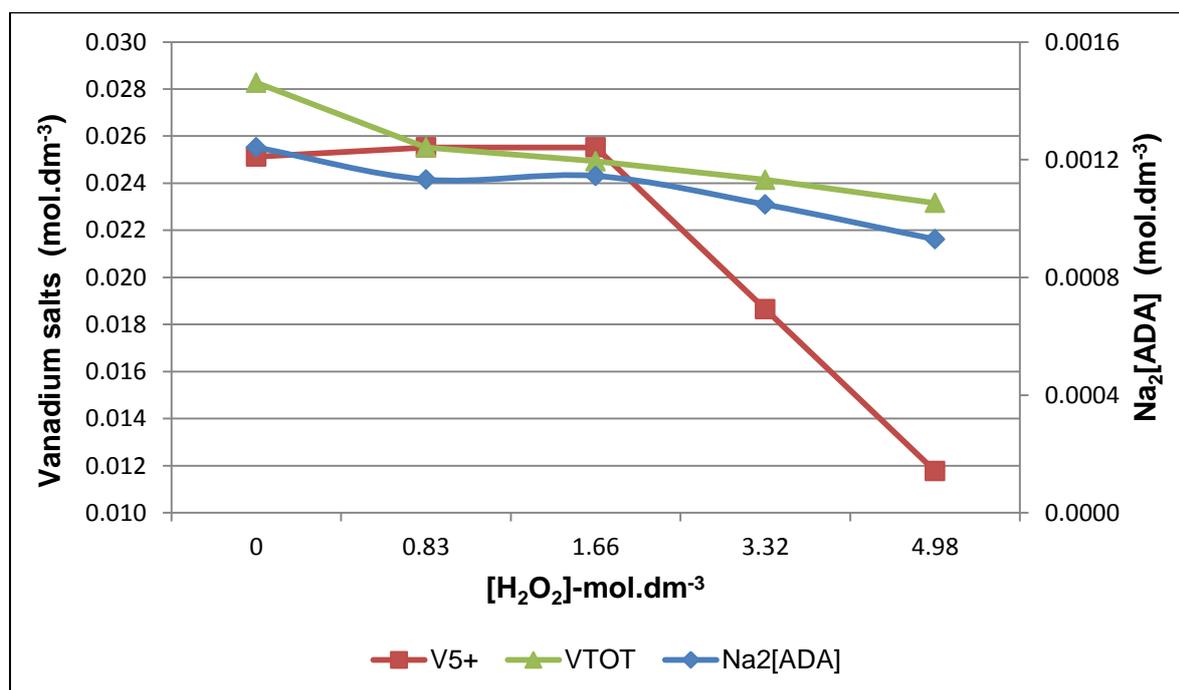


Figure 4.13: Concentrations of V⁵⁺, total vanadium, and Na₂[ADA] in Stretford aqueous liquor B before and after the addition of H₂O₂.

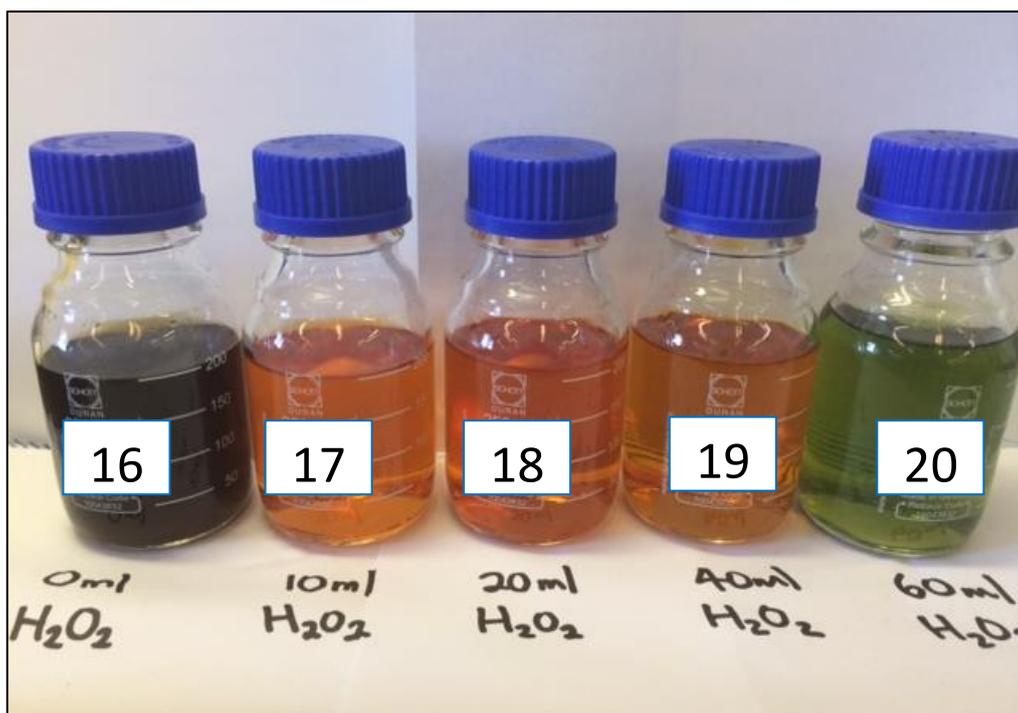


Figure 4.14: Stretford aqueous liquor B samples (17 to 20) with increasing amounts of H_2O_2

Note:

- a) **Solution sample 16:** Stretford aqueous liquor B + $0 \text{ mol.dm}^{-3} \text{H}_2\text{O}_2$
- b) **Solution sample 17:** Stretford aqueous liquor B + $0.83 \text{ mol.dm}^{-3} \text{H}_2\text{O}_2$
- c) **Solution sample 18:** Stretford aqueous liquor B + $1.66 \text{ mol.dm}^{-3} \text{H}_2\text{O}_2$
- d) **Solution sample 19:** Stretford aqueous liquor B + $3.32 \text{ mol.dm}^{-3} \text{H}_2\text{O}_2$
- e) **Solution sample 20:** Stretford aqueous liquor B + $4.98 \text{ mol.dm}^{-3} \text{H}_2\text{O}_2$

The XRF results that are shown in Table 4.5 indicate that sodium and sulphur elements dominate in the solid samples produced from the Stretford aqueous liquor B. The concentrations of Na and S species that are expressed as the sodium oxide (Na_2O) and sulphur oxide (SO_3) in the solid samples from evaporation of Stretford aqueous liquor B are 49.79 - 53.94% and 44.61 - 48.32% respectively.

The XRD results in Table 4.6 confirmed the presence of sodium sulphate as major component in the solid samples produced from the Stretford aqueous liquor B. Solids formed from evaporation of sample 19 contained NaSCN as a major component, while solids formed from the evaporation of sample 20 has NaSCN as a minor component (See Table 4.6). The minor constituents are trona ($\text{Na}_2\text{CO}_3\text{NaHCO}_3(\text{H}_2\text{O})_2$), vanadium(V)oxide (V_2O_5), burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$), sodium hydrogen sulphate (NaHSO_4) and mascagnite ($(\text{NH}_4)_2\text{SO}_4$). It is evident from reactions 38-40 in Chapter 2, that ammonium ions, sulphate and carbonate are major soluble by-products from the oxidation of SCN^- [Kalmár, *et al*, 2013; Wilson and Harris, 1960; Orban, 1986; Barnett and Stanbury, 2002 and Nagy, *et al*, 2006]. These ions were predominantly found in the solids from evaporation following XRF and XRD analyses. Elemental sulphur was found to be present in the solid samples formed from the

evaporation of solutions 19 (Stretford aqueous liquor B + 3.32 mol.dm⁻³ H₂O₂) and 20 (Stretford aqueous liquor B + 3.32mol.dm⁻³ H₂O₂) (Table 4.6). At acidic and neutral pH values or pH 8-9, most of H₂S and HS⁻ species present in Stretford aqueous liquors can be oxidised to elemental sulphur in the presence of H₂O₂ (see reactions 30 and 31) [Jones 1999].

The XRD results obtained from this study indicated clearly that the solid samples produced from Stretford aqueous liquor A and B samples contained double salts such as burkeite and trona. Double salts are crystalline salts that have the composition of two simple salts (i.e. contain more than one cation or anion) with independent crystal structures from each other [<http://www.chemicalforums.com/index.php>].

Table 4.5: XRF analyses results for the solid samples that were formed after evaporation of the Stretford aqueous liquor B sample and Stretford aqueous liquor B samples containing H₂O₂.

Mass %	Sample Identification				
	16	17	18	19	20
Fe ₂ O ₃	<0.01	<0.01	<0.01	0.07	0.04
MnO	<0.01	<0.01	<0.01	<0.01	<0.01
Cr ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01
V ₂ O ₅	0.78	1.09	1.46	0.43	0.78
TiO ₂	<0.01	<0.01	<0.01	<0.01	<0.01
CaO	0.16	0.14	0.16	0.11	0.14
K ₂ O	0.07	0.13	0.13	0.01	0.04
P ₂ O ₅	0.03	0.04	0.06	0.04	0.07
SiO ₂	0.32	0.1	<0.1	<0.1	0.32
Al ₂ O ₃	<0.10	<0.10	<0.10	<0.10	<0.10
MgO	<0.10	<0.10	<0.10	<0.10	<0.10
Na ₂ O	53.94	50.22	49.79	51.03	52.12
Cl	0.08	0.13	0.15	0.01	0.03
SO ₃	44.61	48.15	48.26	48.32	46.45

Note:

- 16. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 0 mol.dm⁻³ H₂O₂
- 17. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 0.83 mol.dm⁻³ H₂O₂
- 18. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 1.66 mol.dm⁻³ H₂O₂
- 19. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 3.32 mol.dm⁻³ H₂O₂
- 20. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 4.98 mol.dm⁻³ H₂O₂

Table 4.6: XRD analyses results for the solid samples that were formed after evaporation of the Stretford aqueous liquor B sample and Stretford aqueous liquor B samples containing H₂O₂.

Mineral	Sample Identification				
	16	17	18	19	20
Sodium Sulfate (Na₂SO₄)	Major	Major	Major	Minor	Major
Sodium Thiocyanate (NaSCN)	Major	Major	Major	Major	Minor
Vanadium (V) Oxide (V₂O₅)	Minor	Minor	Minor	Minor	Minor
Burkeite (Na₆(CO₃)(SO₄)₂)	Minor	Minor	Minor	-	-
Sodium Hydrogen Sulfate (NaHSO₄)	Trace	Trace	Trace	Trace	Trace
Trona (Na₂CO₃NaHCO₃(H₂O)₂)	-	Minor	Minor	Minor	Minor
Mascagnite ((NH₄)₂SO₄)	-	-	-	Minor	Minor
Elemental Sulphur (S)	-	-	-	Major	Major

Note:

16. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 0 mol.dm⁻³ H₂O₂
17. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 0.83 mol.dm⁻³ H₂O₂
18. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 1.66 mol.dm⁻³ H₂O₂
19. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 3.32 mol.dm⁻³ H₂O₂
20. Solid sample that was formed during the evaporation of Stretford aqueous liquor B + 4.98 mol.dm⁻³ H₂O₂

4.3. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 7.0 using HCl

The oxidation of NaSCN was tested at a pH of 7.0 using hydrochloric acid as a possible oxidising agent. The steps outlined in Section 3.1.3 were followed. All the results obtained for the analyses of Na₂SO₄, NaSCN, Na₂[ADA], V⁵⁺, total vanadium, alkalinity and pH for Stretford aqueous liquors A and B before and after pH adjustment are presented in Table 4.7. All chemical parameters with the exception of total alkalinity measured as Na₂CO₃ and pH remained relatively unchanged. Any changes in these parameters can be attributed to dilutions as a result of HCl addition to the Stretford aqueous liquors A and B.

The total alkalinity concentration dropped from 0.26 mol.dm^{-3} to 0.22 mol.dm^{-3} in Stretford aqueous liquor A and from 0.33 mol.dm^{-3} to 0.28 mol.dm^{-3} in Stretford aqueous liquor B (Table 4.7). This can be attributed to an acid-base reaction between Na_2CO_3 and HCl in the two solution samples.

The reaction between Na_2CO_3 and HCl forms carbonic acid and sodium chloride. Carbonic acid which is a weak and unstable acid rapidly breaks down to form carbon dioxide and water [Skoog, *et al.*, 1997]. This results in the formation of a neutral solution and explains the drop in the total alkalinity concentration from 0.26 mol.dm^{-3} to 0.22 mol.dm^{-3} in Stretford aqueous liquors A and from 0.33 mol.dm^{-3} to 0.28 mol.dm^{-3} in Stretford aqueous liquors B. The acid base reaction is the dominating reaction; hence there is little evidence available that lower pH ranges affect the oxidation of NaSCN .

Table 4.7: Concentrations of sodium sulphate, sodium thiocyanate, $\text{Na}_2[\text{ADA}]$, total vanadium, total alkalinity and pH in the two working Stretford aqueous liquors A and B after HCl addition.

Chemical concentrations and pH	Stretford aqueous liquor A -Before pH adjustment	Stretford aqueous liquor A -After pH adjustment	Stretford aqueous liquor B -Before pH adjustment	Stretford aqueous liquor B -After pH adjustment
Na_2SO_4	0.87	0.86	0.61	0.60
NaSCN	0.97	0.95	1.90	1.88
$\text{Na}_2[\text{ADA}]$	0.0010	0.0010	0.0012	0.0012
V^{5+}	0.023	0.023	0.025	0.025
Total Vanadium	0.028	0.027	0.028	0.027
Total alkalinity (Na_2CO_3)	0.26	0.22	0.33	0.28
pH	8.29	7.03	8.26	7.01

4.4. Oxidation of NaSCN in Stretford aqueous liquors samples at a pH of 9.0 using NaOH

The oxidation of NaSCN was tested at a pH of 9.0 using sodium hydroxide as a possible oxidising agent. The steps that are outlined in Section 3.1.4 were followed. All the results obtained for the analyses of Na_2SO_4 , NaSCN , $\text{Na}_2[\text{ADA}]$, V^{5+} , total vanadium, total alkalinity and pH for Stretford aqueous liquor A and B before and after pH adjustment are presented in Table 4.8.

The total alkalinity content was increased from 0.26 mol.dm^{-3} to 0.32 mol.dm^{-3} in Stretford aqueous liquor A and from 0.33 mol.dm^{-3} to 0.42 mol.dm^{-3} in Stretford aqueous liquor B (Table 4.8). This can be attributed to the addition of more NaOH which results in the pH increasing as well as an associated total alkalinity increase. As expected, the pH increased as a result of an increased in $[\text{OH}^-]$ which

derived from the additional NaOH which was added to the Stretford aqueous liquor (refer 2.2.4 b). With the exception of the pH values and total alkalinity concentrations, other parameter concentrations changed slightly.

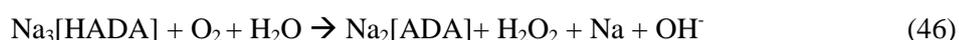
Table 4.8: Concentrations of sodium sulphate, sodium thiocyanate, Na₂[ADA], total vanadium, total alkalinity and pH in the two working Stretford aqueous liquors A and B after NaOH addition.

Chemical concentrations and pH	Stretford aqueous liquor A -Before pH adjustment	Stretford aqueous liquor A -After pH adjustment	Stretford aqueous liquor B -Before pH adjustment	Stretford aqueous liquor B -After pH adjustment
Na ₂ SO ₄	0.87	0.87	0.61	0.60
NaSCN	0.97	0.95	1.90	1.89
Na ₂ [ADA]	0.0010	0.0010	0.0012	0.0012
V ⁵⁺	0.023	0.023	0.025	0.022
Total Vanadium	0.028	0.027	0.028	0.028
Total alkalinity	0.26	0.32	0.33	0.42
pH	8.29	9.07	8.26	9.04

4.5. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.40 using increased concentrations of Na₂[ADA]

The oxidation of NaSCN in Stretford aqueous liquor was also tested by varying the concentration of Na₂[ADA]. This was done by varying the concentration of Na₂[ADA] that was added to Stretford aqueous liquor. The detailed steps are outlined in Section 3.1.5 were followed and the results obtained for the experimental procedure are shown in Figures 4.15 and 4.16.

As the concentration of Na₂[ADA] increased, there was very little or no impact on the other sodium based salts (Na₂SO₄, NaSCN and Na₂CO₃) concentrations. The pH values slightly dropped from 8.51 to 8.33 as the Na₂[ADA] concentrations were increased from 0.0010 mol.dm⁻³ to 0.049 mol.dm⁻³. This phenomenon probably occurs as a results of the liberation of H₂O₂ during the re-oxidation of H₂ADA²⁻ to Na₂[ADA] (Gamage, *et al*, 1991). Similar to other hydroquinones, H₂ADA²⁻ and HADA³⁻ will react with oxygen (air) back to ADA⁴⁻. The reaction is very important shown below, since it is responsible for the formation of H₂O₂ under certain conditions [Kelsall, *et al*, 1993].



Although small amount of H₂O₂ is generated during the re-oxidation process, it may not be present in significant concentrations so as to facilitate the oxidation of all NaSCN species to Na₂SO₄ and other undesirable salts. The stable concentrations of total alkalinity and sodium sulphate in the process aqueous liquor also confirmed low concentrations of H₂O₂ generated during the re-oxidation process.

In addition, high H_2O_2 generation would impact the pH by lowering it significantly. Slight changes in the pH values from 8.51 to 8.33 were noted and this confirms that the liberation of H_2O_2 is not substantial.

The total vanadium content and V^{5+} are almost equivalent to each other (Figure 4.16). Slight differences may be noted and can be attributed to uncertainties in the method. The relative equivalence of total vanadium to V^{5+} is due to $\text{Na}_2[\text{ADA}]$ being present in significant quantities and acting as a catalyst in the oxidation of V^{4+} to V^{5+} [Kellsall and Thompson, 1993b]. Also as stated above, H_2O_2 is formed when $\text{H}_2\text{ADA}^{2-}$ and HADA^{3-} will react with oxygen (air) back to $\text{H}_2\text{ADA}^{2-}$. H_2O_2 is a strong oxidant and a weak acid in water. As a result of its oxidising properties, it also facilitates V^{4+} being rapidly oxidised back to V^{5+} [Trofe, *et al*, 1993].

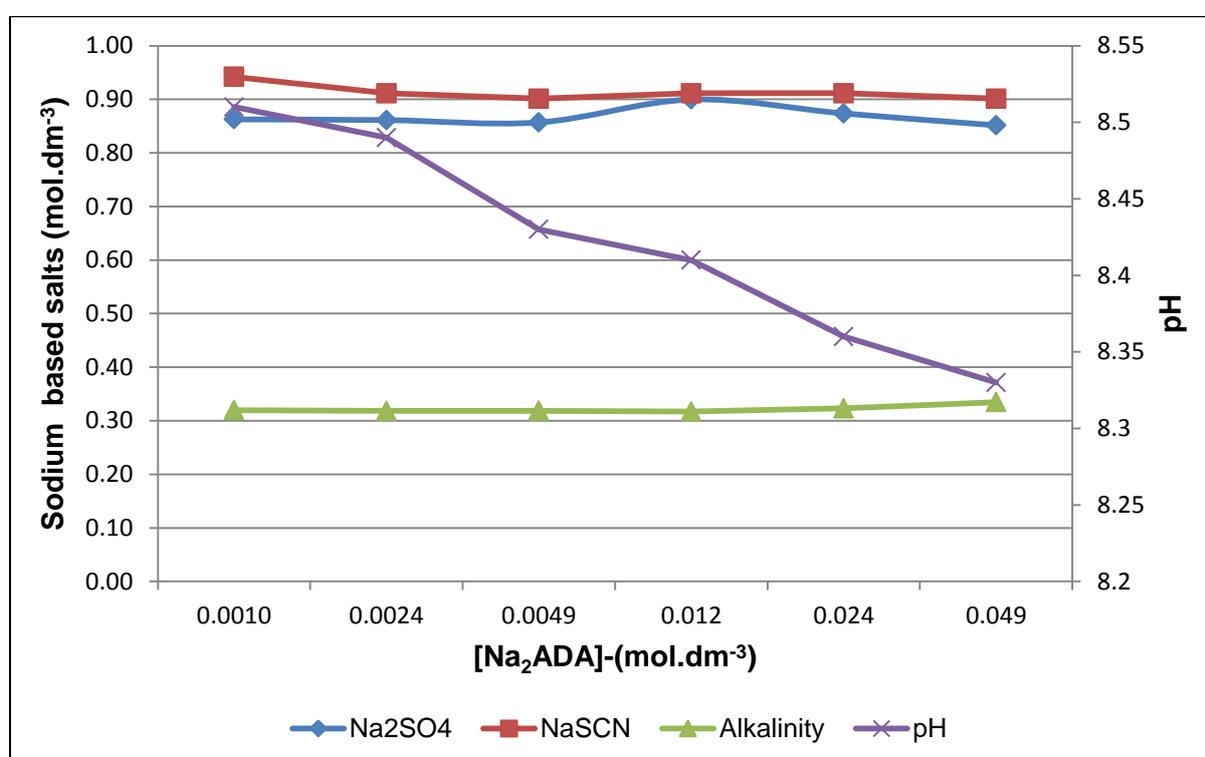


Figure 4.15: Concentrations of sodium based salts and pH values with increasing $[\text{Na}_2[\text{ADA}]]$ in Stretford aqueous liquor.

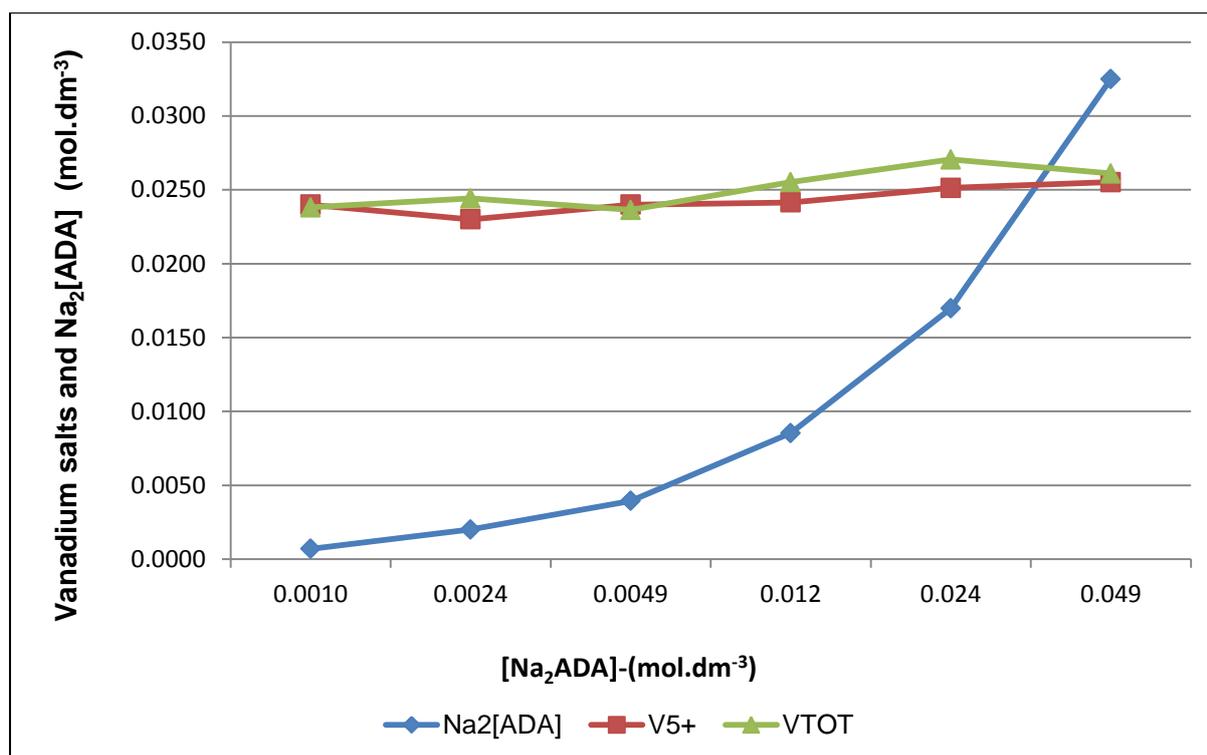


Figure 4.16: Concentrations of Na₂[ADA], V⁵⁺ and total vanadium with increasing [Na₂[ADA]] in Stretford aqueous liquor.

4.6. Oxidation of NaSCN in Stretford aqueous solutions at a pH of 8.40 using sodium ammonium vanadate (SAV)

The influence of sodium ammonium vanadate on the oxidation of NaSCN was also tested. This was done by varying the concentration of SAV that was added to Stretford aqueous liquor. The procedure for the SAV additions is outlined under Section 3.1.6. The results are presented in Figures 4.17 and 4.18 respectively.

As the concentration of SAV was increased from 0.028 mol.dm⁻³ to 0.39 mol.dm⁻³, no significant changes are evident in the concentrations of sodium based salts such as Na₂SO₄, NaSCN and total alkalinity however the concentration of V⁵⁺ in the solution was increased (Figures 4.17 and 4.18).

There was a slight decrease in the pH from 8.40 to 7.81 which is possibly attributed to the re-oxidation of dinuclear anion HV₂O₇³⁻ to form H₂O₂ and other V³⁺ and V⁴⁺ compounds which started to dominate as the pH dropped (Figure 4.17). Due to the fact that mononuclear and various polynuclear anions exist in equilibrium with each other, the chemistry of V⁵⁺ becomes very complex. The pH value, temperature and ion strength influence the equilibria. There is information on the pH value and concentration dependence on the equilibria; however ion strength using NaSCN and Na₂SO₄ has not

been studied. In the presence of sulphate, the formation of V(III) compounds increases [Crans, *et al*, 2004; Tracey and Crans, 1998].

The trends confirmed that the V^{5+} concentrations were increasing as the pH decreased also confirming the formation of intermediate H_2O_2 from the oxidation of $HV_2O_7^{3-}$. The $Na_2[ADA]$ content remains stable at approximately $0.00070 \text{ mol.dm}^{-3}$.

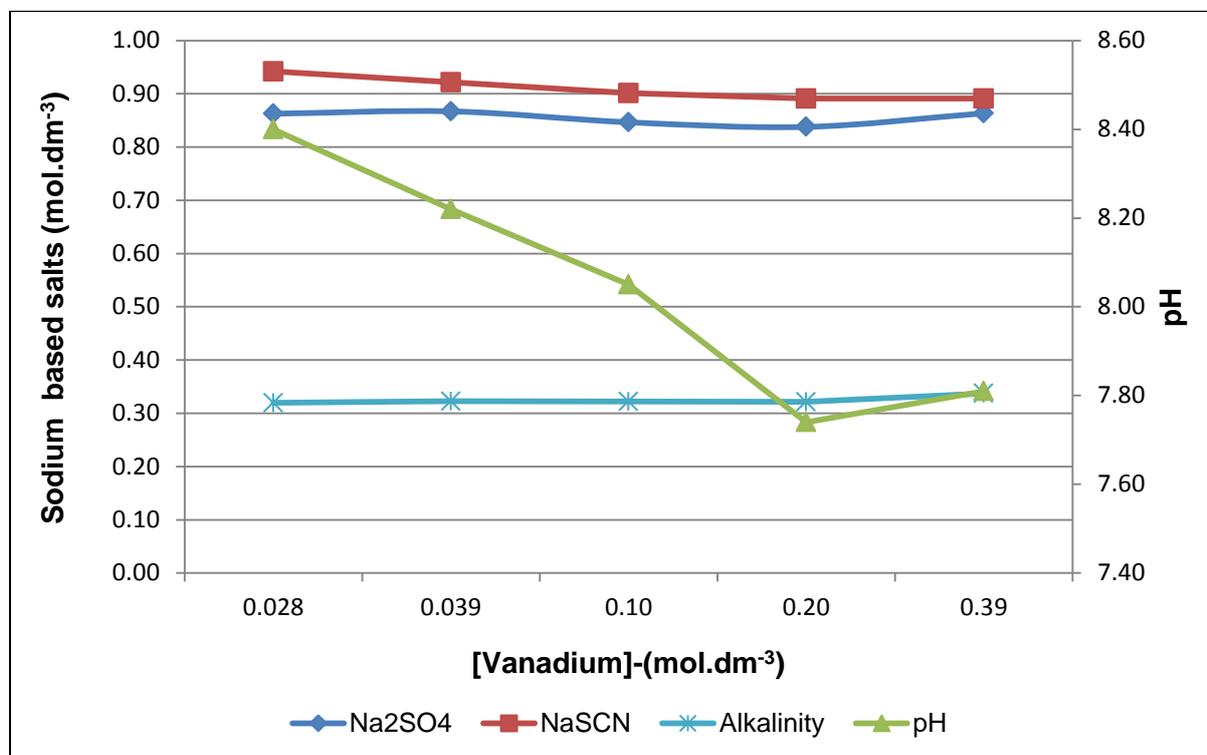


Figure 4.17: Concentrations of sodium based salts and pH values with increasing [total vanadium] in Stretford aqueous liquor.

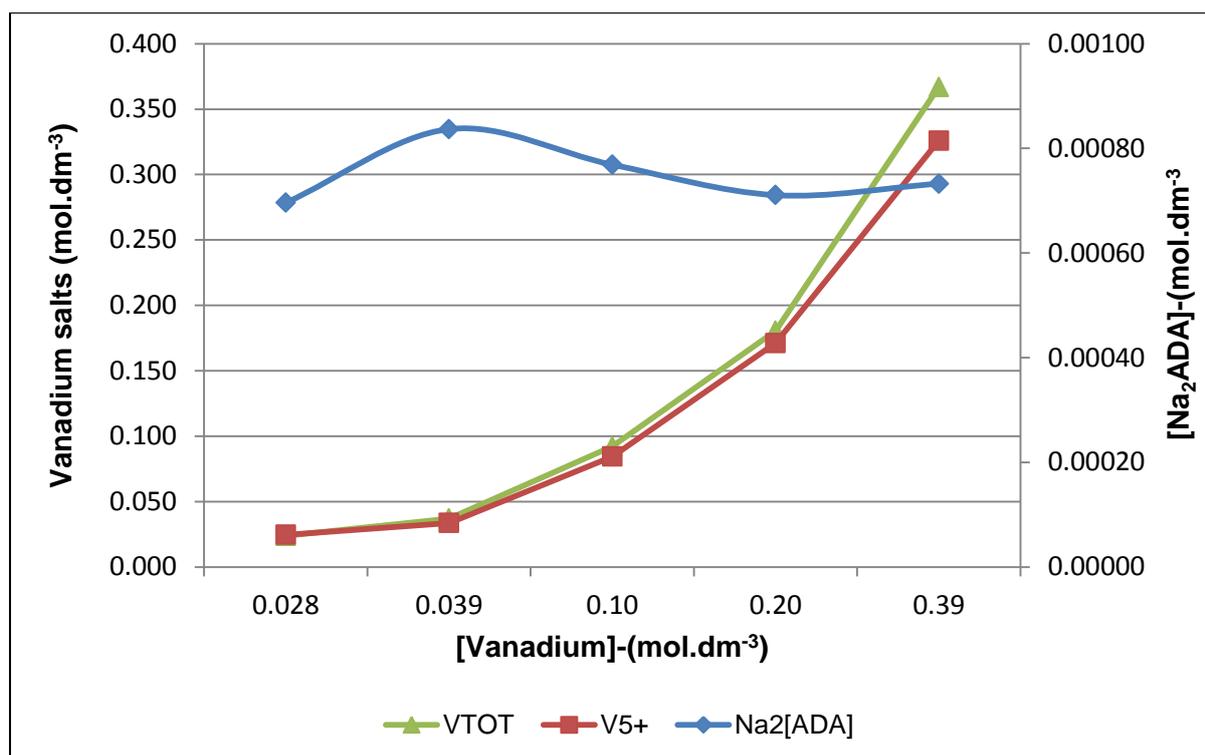


Figure 4.18: Concentrations of total vanadium, V⁵⁺ and Na₂[ADA] with increasing [total vanadium] in Stretford aqueous liquor.

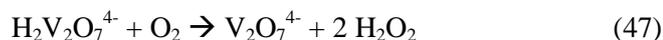
4.7. Air Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.3

a. Air and without air oxidations of Stretford aqueous liquor sample C

The aim of these experiments was to test the oxidation of NaSCN using air as an oxidising agent. The steps for this investigation are outlined in Section 3.1.7. The results for the oxidation of NaSCN in Stretford aqueous liquor C are shown in Figure 4.19 and Figure 4.20.

Figure 4.19 illustrates the behaviour of the sodium based salts while Figure 4.20 shows the trends for vanadium salts and Na₂[ADA]. As the air oxidation time was increased from 2 hours to 24 hours, an increase in the Na₂SO₄ concentration was observed and a decrease in the NaSCN concentration was noted. The concentration of NaSCN slightly decreased from 0.99 mol.dm⁻³ under oxidising condition without air bubbling to 0.88 mol.dm⁻³ after 24 hours of oxidation with air. In Stretford aqueous liquor C the concentration of Na₂SO₄ slightly increased from 0.87 mol.dm⁻³ to 0.95 mol.dm⁻³ under oxidising condition without air bubbling and 24 hours of air oxidation respectively. A decrease in total alkalinity and pH was also observed.

During the oxidation process, intermediate H_2O_2 is formed as a result of the equation below.



It has been previously stated that H_2O_2 is a weak acid and a strong oxidising agent and this liberated H_2O_2 is probably the reason for the decrease in pH that was observed [Gamage, *et al*, 1991]. The $\text{Na}_2[\text{ADA}]$ concentration showed a slight increase in the trend from 0.0012 to 0.0013 $\text{mol}\cdot\text{dm}^{-3}$. $\text{H}_2\text{ADA}^{2-}$ and $\text{Na}_3[\text{HADA}]$ that cannot be detected by the $\text{Na}_2[\text{ADA}]$ analysis are known to react with molecular oxygen (air) back to $\text{Na}_2[\text{ADA}]$. An intermediate H_2O_2 is liberated under certain conditions (see reaction 21) [Kelsall, *et al*, 1993]. From Figure 4.20, the V^{5+} concentration shows a noticeable increase and this is due to oxidation of V^{4+} to V^{5+} during the oxidation process and can also be as a result of the increase in the concentration of $\text{Na}_2[\text{ADA}]$. $\text{Na}_2[\text{ADA}]$ promotes the re-oxidation of V^{4+} to V^{5+} [Trofe, *et al*, 1993]. The concentration of total vanadium in the solution was expected to be constant but it was slightly increased. This could possibly be due to the analytical errors.

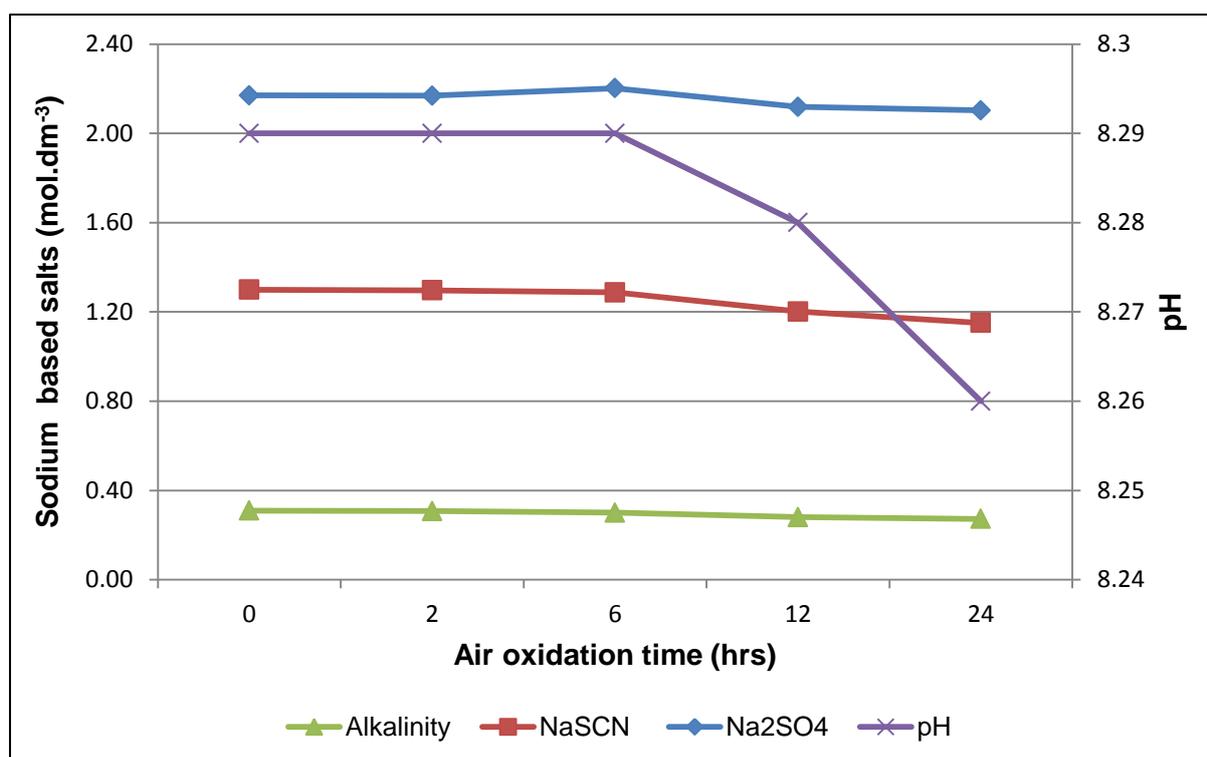


Figure 4.19: Concentrations of sodium based salts and pH in Stretford aqueous liquor C sample with and without air oxidation using bubbling.

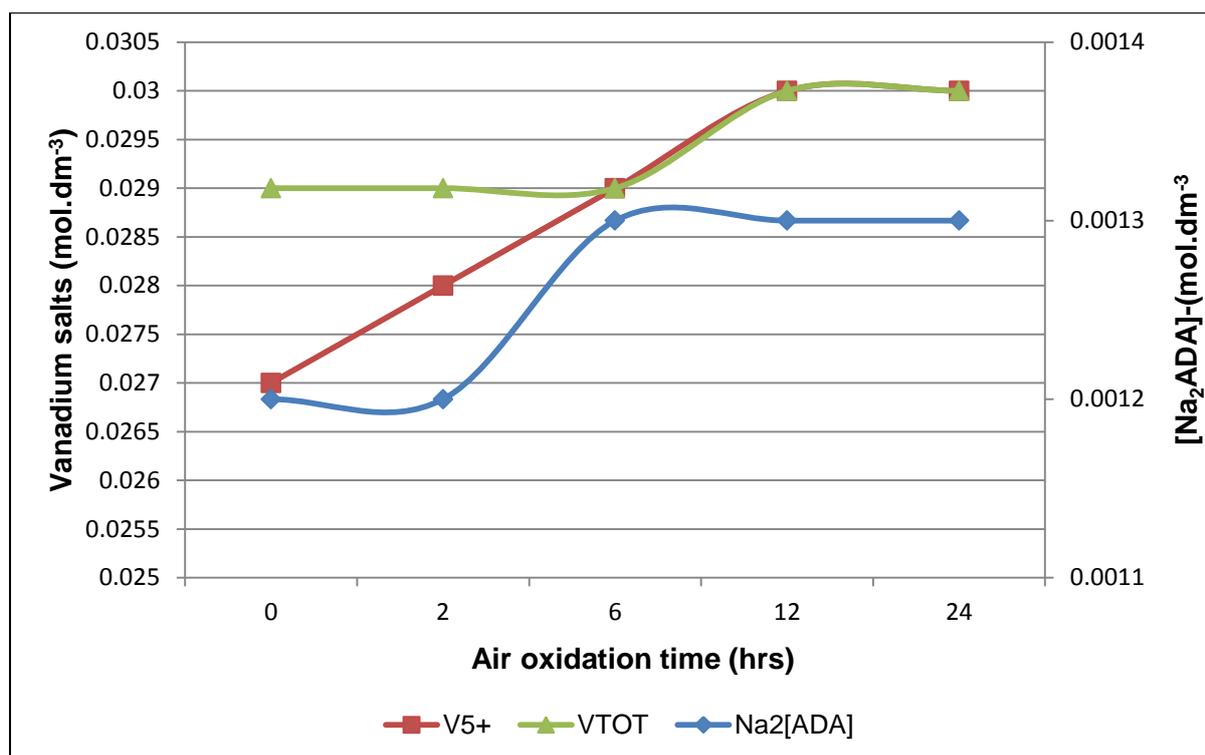


Figure 4.20: Concentrations of V⁵⁺, total vanadium and Na₂[ADA] in Stretford aqueous liquor C sample with and without air oxidation using bubbling.

b. Air and without air oxidations of Stretford aqueous liquor sample D

The results for the oxidation of NaSCN in Stretford aqueous liquor D are shown in Figure 4.21 and Figure 4.22. The behaviour of sodium based salts is shown in Figure 4.21 while results for the vanadium salts and Na₂[ADA] are shown in Figure 4.22. As the oxidation with air was increased from 2 hours to 24 hours, an increase in the Na₂SO₄ concentration was observed and a decrease in the NaSCN concentration was noted.

The concentration of NaSCN decreased from 1.74 mol.dm⁻³ under oxidising condition without air bubbling to 1.60 mol.dm⁻³ after 24 hours of oxidation with air. In Stretford aqueous liquor D, the concentration of Na₂SO₄ was increased significantly from 0.57 mol.dm⁻³ to 0.75 mol.dm⁻³ with no air bubbling and 24 hours of air bubbling oxidation respectively. This indicates that there is definitely oxidation of NaSCN to Na₂SO₄ using air as an oxidant. The increase in Na₂SO₄ concentration is more predominant in Stretford aqueous liquor D compared to Stretford aqueous liquor C. This implies that the higher the NaSCN concentration in the Stretford aqueous liquor, the higher the formation of Na₂SO₄ will be under oxidising conditions.

A decrease in total alkalinity and pH was also observed. It is important to note that evaporation occurred during the oxidation process as a result of maintaining the temperature at 40°C using a hotplate. All concentration factors were taken into consideration before presenting the data.

As previously mentioned in this section, the $\text{Na}_2[\text{ADA}]$ concentration showed a slight increase from 0.00097 to 0.0011 $\text{mol}\cdot\text{dm}^{-3}$. $\text{H}_2\text{ADA}^{2-}$ and $\text{Na}_3[\text{HADA}]$, that cannot be detected by the $\text{Na}_2[\text{ADA}]$ analysis, are known to react with molecular oxygen (air) back to $\text{Na}_2[\text{ADA}]$. From Figure 4.22 it is clear that the V^{5+} concentration showed a noticeable increase and this is due to oxidation of V^{4+} to V^{5+} during the oxidation process and can also be as a result of the increase in the concentration of $\text{Na}_2[\text{ADA}]$. [Trofe, *et al*, 1993]. The concentration of total vanadium in the solution was gradually increasing due to the possible analytical error occurred during the determination of the concentration of V^{5+} in the sample.

This phenomenon is explained above as the same trends were observed when oxidising Stretford aqueous liquor C with air.

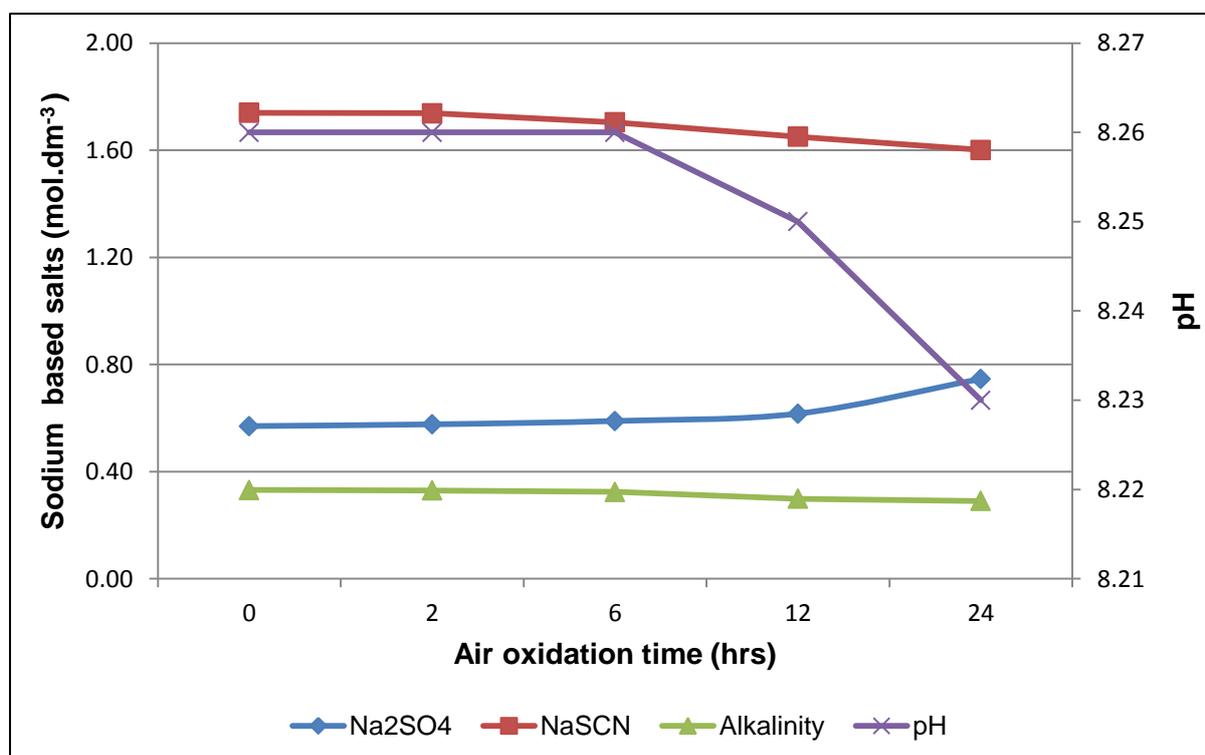


Figure 4.21: Concentrations of sodium based salts and pH in Stretford aqueous liquor D sample with and without air oxidation using bubbling.

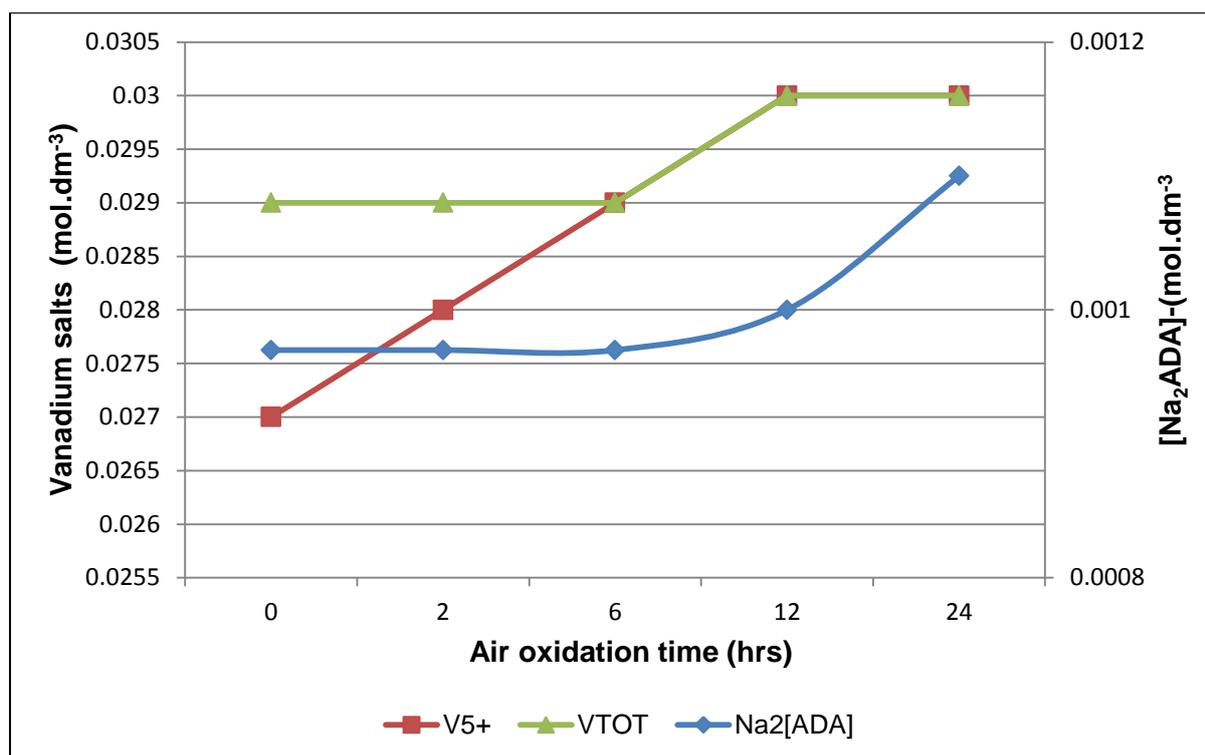


Figure 4.22: Concentrations of V⁵⁺, total vanadium and Na₂[ADA] in Stretford aqueous liquor D sample with and without air oxidation using bubbling.

4.8. Evolution of gases during the oxidation of NaSCN in the Stretford aqueous samples using hydrogen peroxide

During the oxidation of NaSCN in Stretford aqueous solutions using hydrogen peroxide, there was evolution of gases. For safety purposes, it is important to understand what gases are evolved during the experiments. Approximately 3.32 mol.dm⁻³ of H₂O₂ was added to 200 ml of Stretford aqueous liquor. During the addition, a vigorous reaction was observed and gases evolved. The evolved gases were trapped in syringe and injected on a Gas Chromatography-Mass Spectrometry (GC-MS) immediately to identify and qualify which gases were most predominant. The profiles from the injection can be seen in Figure 4.23 and Figure 4.24.

Hydrogen cyanide gas was positively identified from the analysis. Carbon dioxide was also evolved however it eluted with the huge air peak and cannot be differentiated as is seen in Figure 4.24.

The presence of HCN in the feed gas to the Stretford aqueous liquor results in the formation of NaSCN during the addition of H₂O₂ and total dissolved salts (TDS) and these lead to substantial increase in Stretford purge requirements to control increases in total dissolved solids [Kohl and Riesenfeld, 1974].

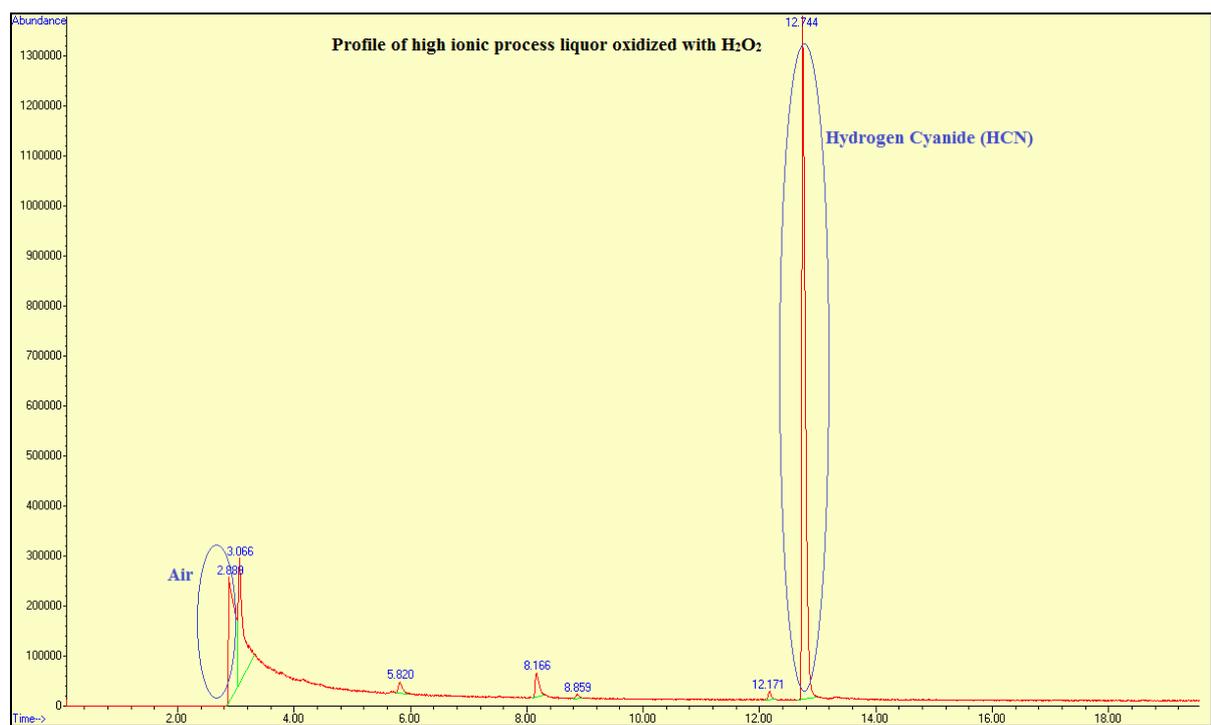


Figure 4.23: GC-MS profile of gases evolved during oxidation of Stretford aqueous liquor using H₂O₂.

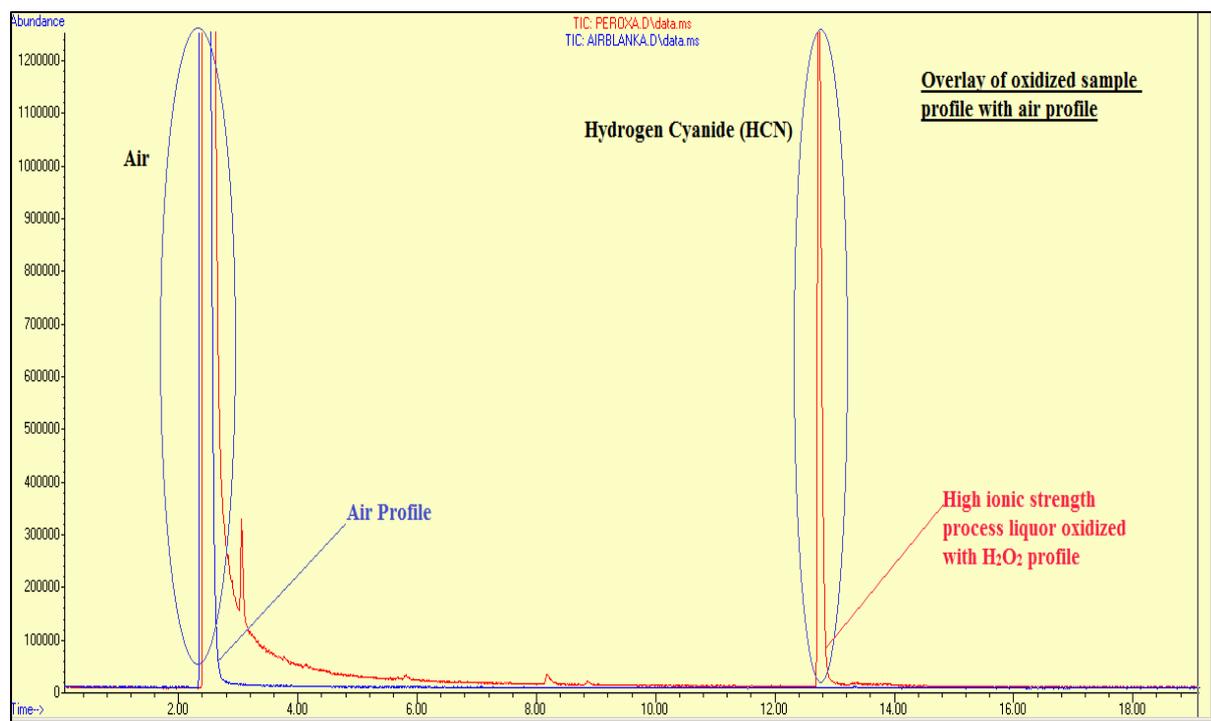


Figure 4.24: GC-MS profile overlay of air injection and gases evolved during oxidation of Stretford aqueous liquor using H₂O₂.

4.9. Determination of the concentration of the unwanted by-product sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) in the Stretford aqueous liquor samples

Sodium thiosulphate forms in the Stretford liquor from an unwanted side reaction. The oxidation of sodium thiosulphate to sodium sulphate in the Stretford process liquors is catalysed by sodium thiocyanate [Weber, 1985].

The concentration of $\text{Na}_2\text{S}_2\text{O}_3$ was determined in Stretford aqueous liquor A, Stretford aqueous liquor B, Stretford aqueous liquor A + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$, Stretford aqueous liquor B + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$, Stretford aqueous liquor C, Stretford aqueous liquor D, Stretford aqueous liquor C-oxidised with air for 24 hours and Stretford aqueous liquor D-oxidised with air for 24 hours. The results for the $\text{Na}_2\text{S}_2\text{O}_3$ determination are found in Table 4.9. The chromatograms for Stretford aqueous liquors A and B are shown in Figure 4.25 and Figure 4.26 respectively. Stretford aqueous liquors C and D are very similar in composition to Stretford aqueous liquors A and B, hence the chromatograms were not shown. The $\text{Na}_2\text{S}_2\text{O}_3$ concentration could not be detected in Stretford aqueous liquor A + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ and Stretford aqueous liquor B + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$. This can be attributed to the fact that thiosulphate is subject to greater rates of oxidation due to the presence of H_2O_2 . The oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ to Na_2SO_4 is presumed to occur according to the reaction stated below: [Kohl and Riesenfeld, 1974].



The reaction above also confirms the drop in pH observed in these two scenarios due to the formation of carbonic acid which forms carbon dioxide and water. According to Kohl and Riesenfeld, 1974, the rate of thiosulphate oxidation increases with increasing pH and increasing temperature. At pH ranges exceeding approximately 9.5°C and temperatures exceeding 65°C, the formation of thiosulphate is known to increase exponentially [Kohl and Riesenfeld, 1974]. The experiments were carried out at 40°C and observed pH values were 6.34 for the Stretford aqueous liquor A + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$ and 2.07 for the Stretford aqueous liquor B + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$, implying that conditions were not favourable for the formation of thiosulphate. During the oxidation of thiosulphates by H_2O_2 , a series of reactions occurs, whereby tetrathionates, are formed first followed by trithionates, sulphites and sulphates [Jones, 1999]. The reason for thiosulphates not being detected in these solutions is confirmed by the oxidation of thiosulphates to sulphates.

The concentrations of sodium thiosulphate for the Stretford aqueous liquor C -oxidised with air for 24 hours and Stretford aqueous liquor D -oxidised with air for 24 hours were $0.088 \text{ mol.dm}^{-3}$ and $0.096 \text{ mol.dm}^{-3}$ respectively. The air oxidation did not impact the concentration of sodium thiosulphate significantly. This is due to the fact that sodium thiocyanate ions in excess of the prescribed concentration of 0.25 mol.dm^{-3} were present in the Stretford solutions on which experiments were done [Weber, 1985]. The concentration of NaSCN in Stretford aqueous liquor C -oxidised with air for

24 hours and Stretford aqueous liquor D -oxidised with air for 24 hours was 0.99 mol.dm^{-3} and 1.74 mol.dm^{-3} respectively. Technically, the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ should increase due to the presence of molecular oxygen according to the reaction below but there is no increase as a result of the presence of excess concentrations of NaSCN.



The presence of NaSCN in the scrubbing solution suppresses the formation of $\text{Na}_2\text{S}_2\text{O}_3$ hence there are no significant increases or decreases of $\text{Na}_2\text{S}_2\text{O}_3$ under these conditions [Weber, 1985]. The pH of the (Stretford aqueous liquor C -oxidised with air for 24 hours) and (Stretford aqueous liquor D -oxidised with air for 24 hours) was 8.26 and 8.23 respectively. The experiments were also controlled at 40°C thus implying that the conditions were not favourable for the formation of thiosulphate in this scenario.

Table 4.9: Concentrations of sodium thiosulphate in working and oxidised Stretford aqueous liquors.

Sample Identification	$[\text{Na}_2\text{S}_2\text{O}_3]\text{-mol.dm}^{-3}$
Stretford aqueous liquor A	0.086
Stretford aqueous liquor B	0.093
Stretford aqueous liquor A + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$	ND*
Stretford aqueous liquor B + $4.98 \text{ mol.dm}^{-3} \text{ H}_2\text{O}_2$	ND*
Stretford aqueous liquor C	0.085
Stretford aqueous liquor D	0.094
Stretford aqueous liquor C -oxidised with air for 24 hours	0.080
Stretford aqueous liquor D -oxidised with air for 24 hours	0.088

*ND- Not Detected

It is important to note that the concentration of $\text{S}_2\text{O}_3^{2-}$ in the analysed Stretford liquor is quite low. It would be preferable to inject the solutions on the ion chromatograph (IC) for $\text{S}_2\text{O}_3^{2-}$ with a smaller dilution (serial dilutions of 10 000X were used in this study), however this is not possible as the sulphates have to be diluted significantly to prevent sulphate overload on the column. If the $\text{S}_2\text{O}_3^{2-}$ concentration is lower than $0.074 \text{ mol.dm}^{-3}$, it will be very difficult to integrate the $\text{S}_2\text{O}_3^{2-}$ peak. An example of how small the $\text{S}_2\text{O}_3^{2-}$ peaks are is illustrated in Figures 4.25 and 4.26.

To obtain more accurate results, it would be preferable to use an IC with UV detection.

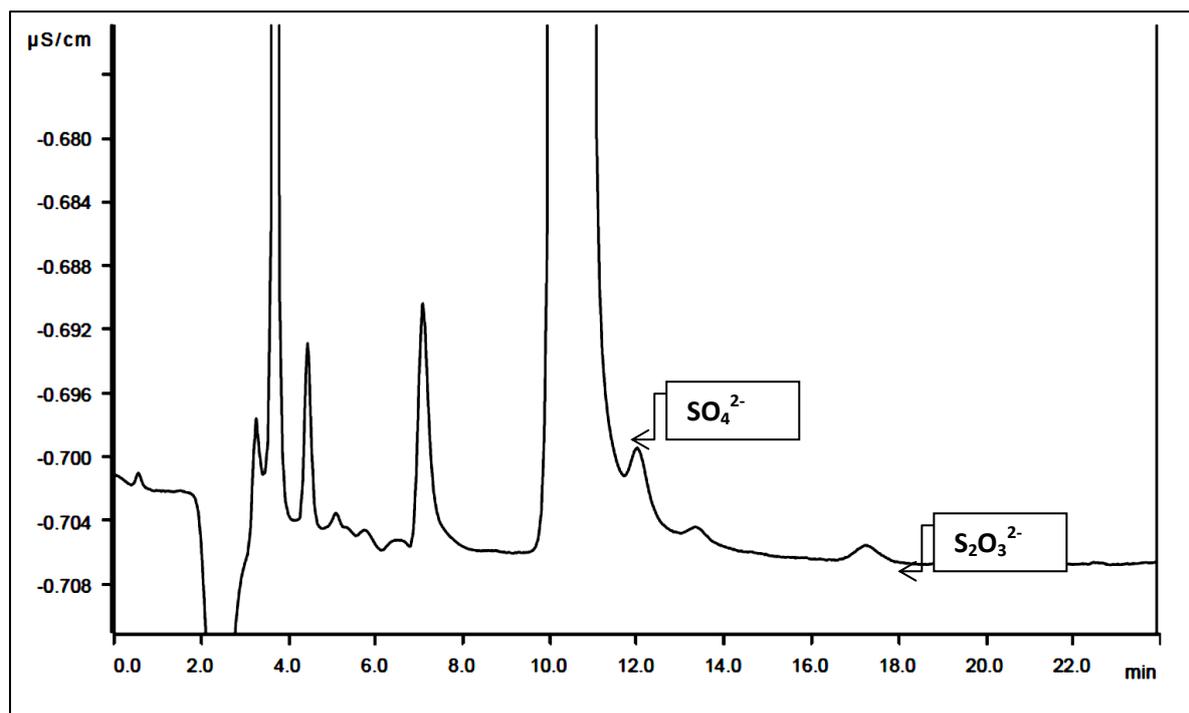


Figure 4.25: Ion Chromatography profile for Stretford aqueous liquor A.

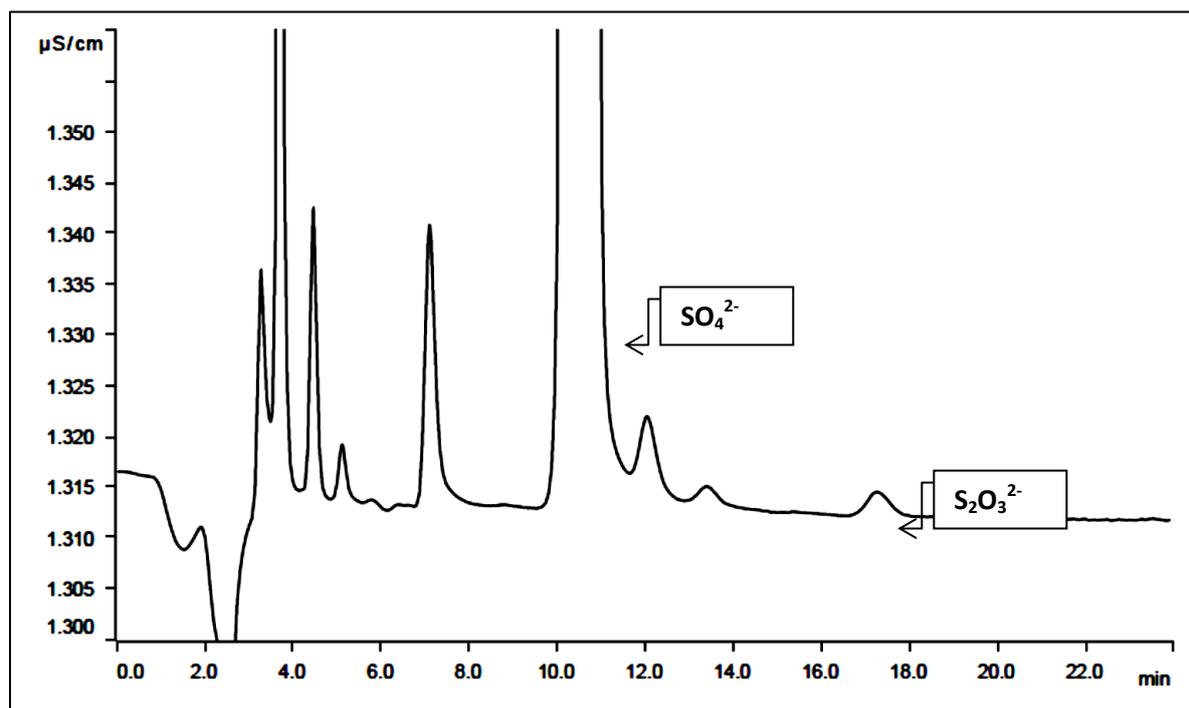


Figure 4.26: Ion Chromatography profile for Stretford aqueous liquor B.

Note:

The SO_4^{2-} peaks shown in Figures 4.25 and 4.26 are not fully displayed and cannot fit into the ion chromatography profiles, due to high concentrations of sulphates and the need to emphasise the $\text{S}_2\text{O}_3^{2-}$ peak.

Chapter 5

Conclusions and Recommendations

The objectives of this study were to determine the degree of oxidation of NaSCN in aqueous solution samples using oxidants such as hydrogen peroxide (H_2O_2), air, intermediate H_2O_2 from sodium ammonium vanadate (SAV) and sodium anthraquinone 2,7-disulphonate ($\text{Na}_2[\text{ADA}]$). The general conclusions derived from this study are summarised in this chapter. All recommendations from the research study are also highlighted and these can give direction to future related studies.

5.1. Conclusions

5.1.1. Oxidation of NaSCN in de-ionised water using H_2O_2 as an oxidising agent

The degree of oxidation of NaSCN between a 0.99 mol.dm^{-3} NaSCN solution and a 1.97 mol.dm^{-3} NaSCN solution using H_2O_2 varied. Complete oxidation to Na_2SO_4 was obtained when the 0.99 mol.dm^{-3} NaSCN solution was oxidised with 3.32 mol.dm^{-3} H_2O_2 , whereas partial oxidation of NaSCN was observed using the 1.97 mol.dm^{-3} NaSCN solution. A yellow amorphous or colloidal precipitate which was formed during the oxidation of sodium thiocyanate in an aqueous NaSCN with H_2O_2 as an oxidising agent in this study is a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$.

At high concentration of H_2O_2 , the yellow precipitate species was re-dissolved in the aqueous solution and this solution was subsequently converted or changed to the colourless aqueous solution containing major sodium sulphate. The presence of a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ precipitate after the oxidative process was confirmed using FTIR, XRD and elemental analysis.

5.1.2. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.3 using hydrogen peroxide

The chemistry of Stretford aqueous liquor samples proved to be very complex. Stretford aqueous liquor samples with varying concentrations of NaSCN were used under H_2O_2 oxidative conditions. It was proved that NaSCN was oxidised to Na_2SO_4 primarily when H_2O_2 was used as an oxidising agent. The formation of other double salts (burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$), trona ($\text{Na}_2\text{CO}_3\text{NaHCO}_3(\text{H}_2\text{O})_2$) and as well as mascagnite ($(\text{NH}_4)_2\text{SO}_4$, sodium carbonate and sodium bicarbonate was also observed.

As the H_2O_2 concentration was increased, loss of total alkalinity, reflected in lower pH values was obtained. It was also found that specific pH values determine the type of salt formed during oxidation of sodium thiocyanate species in an aqueous solution. The 3.32 mol.dm^{-3} H_2O_2 solution oxidised all the NaSCN in Stretford aqueous liquor A (0.93 mol.dm^{-3} NaSCN) to Na_2SO_4 , whereas the same concentration of H_2O_2 only resulted in partial oxidation of Stretford aqueous liquor B (1.90 mol.dm^{-3}

NaSCN) to Na_2SO_4 . The $\text{Na}_2[\text{ADA}]$ concentration slightly decreased for both solutions and this is consistent with literature that states that a slight decomposition of $\text{Na}_2[\text{ADA}]$ occurs in the presence of H_2O_2 . The V^{5+} concentration also decreased as a result of lower $\text{Na}_2[\text{ADA}]$ to catalyse the oxidation of V^{4+} to V^{5+} .

Sodium thiocyanate and sodium sulphate are major and minor components in the other solid samples produced from oxidised Stretford aqueous liquors A and B. Other minor constituents are trona ($\text{Na}_2\text{CO}_3\text{NaHCO}_3(\text{H}_2\text{O})_2$), Vanadium (V) Oxide (V_2O_5), burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$) and mascagnite ($(\text{NH}_4)_2\text{SO}_4$). Sodium Hydrogen Sulphate (NaHSO_4) was found in trace amounts in the solids.

5.1.3. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 7.0 using HCl

With the exception of the concentration of total alkalinity, the concentrations of all other chemical parameters (i.e. Na_2SO_4 , NaSCN, $\text{Na}_2[\text{ADA}]$, V^{5+} , total vanadium) in the Stretford aqueous liquor sample remained mostly unaffected when the oxidation of NaSCN was tested at a pH of approximately 7.0 using HCl. The total alkalinity concentration decreased due to the acid base reaction between Na_2CO_3 and HCl. It was concluded that lower pH values do not impact the oxidation of NaSCN to other sodium based salts because HCl is not an oxidising agent.

5.1.4. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 9.0 using NaOH

With the exception of the concentration of total alkalinity, concentrations of all other chemical parameters (i.e. Na_2SO_4 , NaSCN, $\text{Na}_2[\text{ADA}]$, V^{5+} , total vanadium) in the Stretford aqueous liquor samples remained mostly unaffected when the oxidation of NaSCN was tested at a pH of approximately 9.0 using NaOH. The total alkalinity concentration increased due to the increase in the concentration of OH^- ions. It was concluded that higher pH values do not impact the oxidation of NaSCN to other sodium based salts because sodium hydroxide is not an oxidising agent.

5.1.5. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.40 using increased concentrations of $\text{Na}_2[\text{ADA}]$

Increased concentrations of $\text{Na}_2[\text{ADA}]$ have little or no impact on the concentrations of sodium based salts namely Na_2SO_4 , NaSCN and Na_2CO_3 . A decrease in the pH was noted as the concentration of $\text{Na}_2[\text{ADA}]$ was increased. This phenomenon is explained by the fact that a small amount of H_2O_2 is liberated during the re-oxidation of $\text{Na}_2[\text{H}_2\text{ADA}]$ to $\text{Na}_2[\text{ADA}]$. Other experiments indicated that H_2O_2 facilitates the oxidation of NaSCN to Na_2SO_4 and other sodium based salts, however it does not seem to be present in significant concentrations in this experiment so as to facilitate the oxidation of

NaSCN to form Na_2SO_4 . A small amount of liberated H_2O_2 and increased $\text{Na}_2[\text{ADA}]$ also catalysed the oxidation of V^{4+} to V^{5+} .

5.1.6. Oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.40 using sodium ammonium vanadate (SAV)

Increased concentrations of sodium ammonium vanadate have little or no impact on the concentrations of sodium based salts namely Na_2SO_4 , NaSCN and Na_2CO_3 . The pH decreased as the concentration of sodium ammonium vanadate increased and this could be as a result of H_2O_2 being formed as a result of the re-oxidation of the dinuclear anion $\text{HV}_2\text{O}_7^{3-}$. The concentration of V^{5+} decreased while V^{4+} increased due to the fact that pH and low concentrations of $\text{Na}_2[\text{ADA}]$ affected vanadium speciation.

5.1.7. Air oxidation of NaSCN in Stretford aqueous liquor samples at a pH of 8.3

The Stretford aqueous liquor samples were bubbled with air from 2 hours to 24 hours. As the time increased, to 24 hours, the concentration of NaSCN in Stretford aqueous liquor A and Stretford aqueous liquor B decreased while the concentration of Na_2SO_4 increased. The concentration of $\text{Na}_2[\text{ADA}]$ increased in both solution samples due to the reaction of $\text{Na}_2[\text{H}_2\text{ADA}]$ and $\text{Na}_3[\text{HADA}]$ that cannot be detected by the $\text{Na}_2[\text{ADA}]$ analysis with molecular oxygen to form $\text{Na}_2[\text{ADA}]$. The concentration of V^{5+} also increased and is consistent with the literature that V^{4+} is oxidised back to V^{5+} in the presence of increased concentrations of $\text{Na}_2[\text{ADA}]$ which acts as a catalyst.

5.1.8. Evolution of gases during the oxidation of NaSCN in the Stretford aqueous liquor samples using hydrogen peroxide

Gases evolved during the oxidation of NaSCN in Stretford aqueous liquor using a 3.32 mol.dm^{-3} of H_2O_2 were qualified using GC-MS. The main gas that was identified was HCN. The evolved HCN can dissolve into the Stretford aqueous liquor and react with sodium sulphide ($\text{Na}_2\text{S}_{n+1}$) and Na_2CO_3 to form NaSCN and NaHCO_3 . This resulted in the formation of higher concentrations of Total Dissolved salts (TDS) and increased the purging requirements in order to prevent unwanted salt build-up. Such solution purges resulted in plant downtime as well as increased cost to optimise Stretford process chemicals before start-up.

5.1.9. Determination of the concentration of the unwanted by-product sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) in the Stretford aqueous liquor samples

The formation of $\text{Na}_2\text{S}_2\text{O}_3$ is promoted with increasing pH and temperature therefore $\text{Na}_2\text{S}_2\text{O}_3$ was not detected during the oxidation of Stretford aqueous liquor A and Stretford aqueous liquor B with 4.98 mol.dm^{-3} H_2O_2 since the pH at which oxidation occurs is less than a pH value of 9 which promotes

$\text{Na}_2\text{S}_2\text{O}_3$ formation. The concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ in Stretford aqueous liquor C and Stretford aqueous liquor D were not affected significantly during the oxidation of Stretford aqueous liquor samples with air.

5.2. Achievement of objectives and aims

It can be successfully concluded that oxidants such as hydrogen peroxide (H_2O_2) and air are responsible for oxidising NaSCN in Stretford process aqueous liquors to form Na_2SO_4 and other salts such as burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$) and mascagnite ($(\text{NH}_4)_2\text{SO}_4$). Hydrogen peroxide can react with sodium thiocyanate in the aqueous phase to form a mixture of $(\text{NaSCN})_x$ and amorphous polymeric $(\text{SCN})_x$ which is known as thiocyanogens.

Hydrogen peroxide, formed as an intermediate from catalysts such as sodium ammonium vanadate (SAV) and sodium anthraquinone 2,7-disulphonate ($\text{Na}_2[\text{ADA}]$) present in the Stretford process liquors, did not contribute to significant oxidation of NaSCN to Na_2SO_4 and other salts. The reason for this is due to the fact that the liberated H_2O_2 from the catalysts are not present in high enough concentrations so as to facilitate a high degree of NaSCN oxidation.

As stated in previous chapters NaSCN crystals in the Stretford process liquors are very important for microbial control and for reducing the consumption of anthraquinone 2,7-disulphonate ($\text{Na}_2[\text{ADA}]$). NaSCN crystals are very expensive, and it is critical to ensure that NaSCN does not oxidise under operating conditions, or as a result of increased concentrations of dissolved oxygen from air and hydrogen peroxide formed from catalysts such as sodium ammonium vanadate (SAV) and sodium anthraquinone 2,7-disulphonate ($\text{Na}_2[\text{ADA}]$).

The oxidation of NaSCN under the above-mentioned conditions lead to high concentrations of Na_2SO_4 and other sulphate salts that facilitate crystallisation, which results in serious blockages of plant equipment. The unwanted high salt concentrations can only be solved by the expensive process of purging. These blockages result in increased plant downtime as well as increased costs to replace the oxidised NaSCN and other expensive chemicals that are lost during the purging process.

The crystallisation of Na_2SO_4 changes the critical chemical parameters of the Stretford process liquors and adversely affects the absorption of hydrogen sulphide into the solution to be converted to elemental sulphur.

The various research objectives were completed successfully and used to draw the final conclusions mentioned. The experimental work and results can also be used in conjunction with process changes to optimise plant parameters and critical chemical concentrations.

5.3. Recommendations

5.3.1. Stretford process liquor optimisation

Immediate action must be taken to prevent salt crystallization from increasing. Such action can include Stretford process liquor exchange between Stretford process liquors containing high concentrations of NaSCN and Stretford process liquor, where the NaSCN concentration have decreased and the Na_2SO_4 concentration have increased. This will result in a blend of liquids that will balance all critical concentrations such as NaSCN and Na_2SO_4 and alter total dissolved solids to acceptable concentrations for high efficiency operation. It is also important to note that NaSCN crystals should not be added into the Stretford process solutions when the flow rate of air is high.

5.3.2. NaSCN to be tested for suppressing $\text{Na}_2\text{S}_2\text{O}_3$ formation in Stretford aqueous liquor

Many citations indicate that NaSCN suppresses the formation of $\text{Na}_2\text{S}_2\text{O}_3$ in the Stretford aqueous liquor samples. It is therefore recommended that detailed studies be performed on the Stretford aqueous liquor samples used in this study to determine the mechanism that results in the suppressed formation of $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of high concentrations of NaSCN.

5.3.3. NaSCN to be tested for reducing the consumption of $\text{Na}_2[\text{ADA}]$ and enhancing the dissolution of vanadium salts in Stretford aqueous liquor

U.S. Patent 4 017 594 has stated that NaSCN reduces high consumption of $\text{Na}_2[\text{ADA}]$ and may also enhance dissolution of vanadium salts in aqueous phases. Further studies will reveal whether this is true and the results can be directly used in Stretford processes to reduce chemicals added to the absorber solution to maintain optimum absorption of H_2S into the Stretford aqueous liquor samples. This will have advantages in industry in terms of cost saving.

5.3.4. Study of the speciation and quantification of OSCN^-

During this study, OSCN^- featured in many reactions and literature as the transient species that forms while NaSCN is being oxidised to Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, NH_4HCO_3 and NaHSO_4 [Kalmar, *et al*, 2013]. It is cited as being formed and used up in the reactions at high rates. A study of the speciation will provide insight on its actual formation and kinetics during the oxidation process. Some of the transient species such as CN^- , OCN^- and OSCN^- may actually be the active bacteriostatic species from NaSCN. Identification of these components can add value to understanding the Stretford process better.

Chapter 6

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