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# **Catalytic Oxidation of Hydrogen Sulphide to Sulphur by Air**

A thesis submitted by

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Towards the Degree of  
Doctor of Philosophy



**University of St Andrews**  
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18<sup>th</sup> March 2003





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***Dedicated to my mother and father***

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## Abbreviations

ADA	Anthraquinone-2,6-disulfonic acid
Aero	Aerobic
An	Anaerobic
Bact	Bacterium
<sup>t</sup> BAQ	t-Butylanthraquinone
BBCAMP	Bis {[bis(carboxymethyl)amino]methyl}phosphinate
BC	2-Butoxyethanol
BCR	Biochemical catalyst regeneration
BE	2-Butoxyethanol
Bzac	Benzoylacetone
CHQ	2-Carboxy-8-hydroxyquinoline
CIMS	Chemical ionisation mass spectra
cm <sup>3</sup>	Cubic centimetre
cm <sup>-1</sup>	Wavenumber
CV	Cyclic voltammogram
DEGDE	Di-(ethylglycol)-diethylether
DEGME	Diethylglycolmonomethylether
DI	Deionised
DIPIA	2,6-Pyridinediacetic acid
DIPIC	2,6-Pyridinedicarboxylic acid
DMEA	<i>N,N</i> -Dimethylethanolamine DMEA
DMF	Dimethyl formamide

DMSO	Dimethylsulfoxide
DO	1,4-Dioxane
EA	Ethanolamine
ED3A	{Carboxymethyl-[2-(carboxymethyl-amino)-ethyl]-amino}-acetic acid
EDTA	Ethylenedinitrilotetraacetic acid
EDTA4P	Ethylenediaminetetramethylenephosphonic acid
EG	Ethylene glycol
EIMS	Electron ionisation mass spectra
Et	Ethyl, -C <sub>2</sub> H <sub>5</sub>
FA	Formamide
FAB	Fast atom bombardment
FABMS	Fast atom bombardment mass spectra
FT	Fourier transform (for NMR or IR)
GA	Glyoxylic acid
GLY	Glycine, NH <sub>2</sub> CH <sub>2</sub> COOH
H <sub>2</sub> BAQ	t-Butylanthrahydroquinone
HEDTA	<i>N</i> -(2-Hydroxyethyl)ethylenediamine- <i>N,N,N'</i> -triacetic acid
HGLY	<i>N</i> -(-Hydroxy-ethyl)-glycine
HIDA	<i>N</i> -(2-Hydroxyethyl)iminodiacetic acid
HMTA	Hexamethylenetetraamine
HPLC	High performance liquid chromatography
Hz	Hertz, sec <sup>-1</sup>

IR	Infra-red
IDA	Iminodiacetic acid
IRC	Fe(III)/Fe(II) redox couple
LRSR	Liquid redox sulphur recovery
Me	Methyl, -CH <sub>3</sub>
MeNTA2P	[(Methylphosphonomethylamino)methyl]phosphonic acid
MCF	Mass flow rate controller
MAA	Methyl-acetylacetonate
MP	Morpholine
m/z	Mass-to-charge ratio
NFMP	<i>N</i> -Formylmorpholine
NMP	<i>N</i> -Methylpyrrolidone
NMR	Nuclear magnetic resonance
NMS	<i>N</i> -Methylsuccinimide
NQS	Naphthoquinone sulfonate
NTA	Nitrilotriacetic acid
NTAP	[(Phosphonomethyl)imino]diacetic acid
NTA2P	(Bis-phosphonomethylamino)acetic acid
NTA3P	Nitrilo-trimethylenephosphonic acid
NTA6P	{[(2- {Bis-[2-(bis-phosphonomethyl-amino)-ethyl]-amino} -ethyl)- Phosphonomethyl-amino]-methyl} -phosphonic acid
OXA	Oxalate
PC	Propylene carbonate

2,6-PDPA	2,6-Pyridinediphosphonic-6-carboxylic acid
PEG	Polyethylene glycol
2PP6C	Pyridine-2-phosphonic-6-carboxylic acid
Ph	Phenyl, -C <sub>6</sub> H <sub>5</sub>
Ppm	Parts per milliom
SCE	Saturated calomel electrode
S-EDDA	<i>N,N</i> -Ethanediyl-bis-glycine
SULPHUR	We have used the industrial spelling as sulphur because this is conventional in that area
TCE	Trichloroethylene
TEA	Triethanolamine
TEPP	Triethylphosphate
THHT	1,3,5-Tri-(2-hydroxyethyl)hexahydro-[1,3,5]-triazine
UV	Ultraviolet

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## Abstract

Catalytic oxidation of H<sub>2</sub>S to sulphur with air has been widely used for the removal of H<sub>2</sub>S from gas streams. The aqueous Fe(III)/Fe(II)-nitrilotriacetic acid (NTA) system appears to be a currently prevailing commercial process. The limited lifetime of NTA is the most serious deficiency of this process. This project aims to improve the Fe(III)/Fe(II)-NTA system by selecting new ligands, new scavenger of free hydroxyl radical and alternative transition metals. Novel non-aqueous Fe(III)/Fe(II) systems have also been investigated for the sulphur recovery process.

Sixty-seven ligands with a variety of groups have been screened. [(Phosphonomethyl)imino]diacetic acid (NTAP) is found to be comparable with NTA on catalytic activity concerning the conversion of hydrogen sulphide to sulphur, half-life of ligand, consumption of ligand per kg of sulphur and so on; A series of inorganic and organic compounds have been tested as scavengers of hydroxyl radical. Two compounds are found to be more effective than Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and are very promising as alternatives of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> for the current Fe-NTA system. Attempts to replace Fe<sup>3+</sup>/Fe<sup>2+</sup> with Cu<sup>2+</sup>/Cu<sup>+</sup> or Co<sup>3+</sup>/Co<sup>2+</sup> for NTA and NTAP are not successful. Mn<sup>3+</sup> and Ru<sup>3+</sup> complexes of NTA and NTAP show low selectivity to sulphur and could not replace the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple. A series of Fe(III) salts and organic solvents have been screened to develop effective non-aqueous catalyst systems. A novel non-aqueous system containing only Fe salt and organic solvent is found to be highly efficient. The catalytic mechanisms and the influence of different iron salts on catalytic activity are also discussed.

# **Chapter 1**

## **Introduction**

Hydrogen sulphide (H<sub>2</sub>S) and other sulphur-containing volatile compounds such as methanethiol, dimethyl sulphide, and dimethyl disulphide are highly malodorous compounds and sources of pollution of air streams. They are found to be liberated in the production of natural gas and from combustible gases from coal, such as in coking operations, as well as being waste by-products in a number of chemical processes. These sulphur-containing compounds are also present in geothermal steam used in power generation plants and in natural gas itself. The removal of these sulphur-containing compounds from sour natural gas, bio-gas and other gaseous streams is necessary for health and safety reasons, and to prevent corrosion to equipment during their transmission and distribution.

The methods of gas desulphurization may be classified according to: (i) the degree of sulphur oxidation in the compounds produced, and (ii) the state of concentration which reactions take place.<sup>1,2</sup> Depending on demand, desulphurization processes are carried out in order to obtain such commercial products as sulphur, sulphuric acid, ammonium sulphate, copper sulphate or other sulphur compounds. In view of the concentration state the desulphurization methods can be divided into dry, semi-dry and wet methods.

"Dry" gas purification consists of adding a dry adsorbing agent while the adsorbent used does not change its concentration state. The processes of "semi-dry" purification depend on the adsorbent, which is added in the form of a solution or liquid. The chemical reaction takes place in the liquid phase while the temperature is

selected in such way that the adsorbent consumed can be removed in its solid state from the flowing tail gases. In the "wet" processes the reagent is added in the form of a liquid in which the impurities react with the solution. This results in wastes that are subjected to further treatment.

Each of these methods has its advantages and disadvantages. Current methods tend to depend on the demands of the degree of the purification of tail gases and the practical state of the waste such as the scale of waste gases and their concentration of the sulphur-containing components. Preference is given to methods whose final products are pure sulphur.

The gases subjected to desulphurization processes may be divided, according to their composition and suitability, into two basic groups: (i) Gases containing as their basic components hydrocarbons and other non-hydrocarbon combustible compounds, e.g. coke-oven gas, synthesis gas etc.; (ii) Tail gases, post-processed gases containing hydrogen sulphide, sulphur dioxide, mercaptans, carbon disulphide and other sulphur compounds diluted with nitrogen and carbon dioxide.

The methods for removing sulphur compounds from these basic groups of gases are completely different. When the first group of gases is desulphurized, it is necessary to use methods that do not disturb their basic gaseous components. These should be sensitive, selective methods that will make it possible to obtain a product completely freed of sulphur compounds. The second group of gases are technological wastes which should be subjected to treatment in such a way as to obtain commercial product or an inactive one that does not pollute the environment. The problem of desulphurization is of prime importance not only an account of the

protection of the environment but also in respect of the rational recovery of sulphur as a raw material for industrial use.

In this chapter, we will only review the evolution of the methods of purification of gases containing hydrogen sulphide.

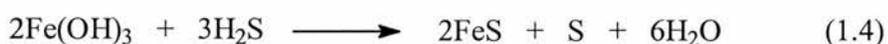
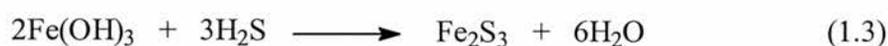
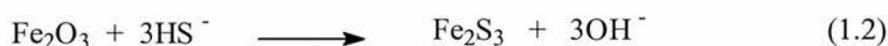
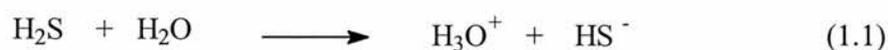
Traditional processes for removing  $H_2S$  from sour gases apply liquids to concentrate the  $H_2S$  by an absorption / desorption cycle in aqueous solutions of alkanolamine. The concentrated  $H_2S$  stream, often containing substantial amounts of  $CO_2$ , may then be treated in a second process step for conversion to elemental sulphur through partial oxidation of the  $H_2S$  stream by air in a thermal stage with one or more catalyst beds at high temperature.<sup>3</sup> This dry process has been developed since it was first patented in 1883 by C. F. Claus. Recent modifications include the use of highly selective catalysts, which enable a catalytic stage reaction to take place at low temperature, and thus to favour sulphur selective conversion.<sup>4-9</sup> Other developments such as the use of internally cooled and isothermal catalytic reactors may contribute to increasing sulphur yields.<sup>10,11</sup> However, the stability of the industrially used catalyst remains poor, hence its selectivity to sulphur is still lower than expected.<sup>12</sup> In addition, separation of  $H_2S$  in an alkanolamine system and subsequent gas phase sulphur recovery often appears to be difficult to control,<sup>13</sup> and these processes require big investments and ground space.<sup>3</sup>

Considering the disadvantages of the dry oxidation process, more efficient liquid redox sulphur recovery (LRSR) techniques ("wet" processes) were developed and applied as early as the beginning of last century. These processes mainly involve regenerative liquid phase redox cycle by air and will be reviewed as follows.

### 1.1 Early liquid redox sulphur recovery (LRSR) processes

Kohl and Riesenfeld reported the first LRSR application which was based on the ammonium sulphide / ammonium sulphate couple<sup>14</sup>. This process involved a number of ammonium polythionates. Feld<sup>15</sup> and Overdieck<sup>16</sup> described the details of the chemistry and the polythionate processes. However, as a result of the large number of side-reactions and undesired by-products, this concept never became a well established commercial application.

Another early LRSR example involved iron oxide particles suspended in alkaline Na<sub>2</sub>CO<sub>3</sub> solution, and is represented by the simplified set of reactions (1.1 - 1.7).



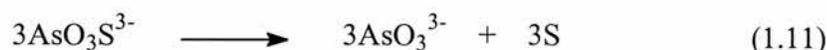
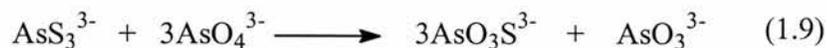
Subsequently suspensions of Fe(OH)<sub>3</sub> in aqueous Na<sub>2</sub>CO<sub>3</sub> solution were introduced. These process reactions were similar to reaction 1.1 - 1.7. Fe<sub>2</sub>O<sub>3</sub> and Fe(OH)<sub>3</sub> suspensions were applied in a few commercial processes, the most prominent being the American Ferrox process, the German Gluud process and the

British Manchester process. However, these processes appeared to be hampered by a number of side reactions in which the undesired sulphur compounds such as thiosulphate and sulphate are yielded.<sup>17</sup>

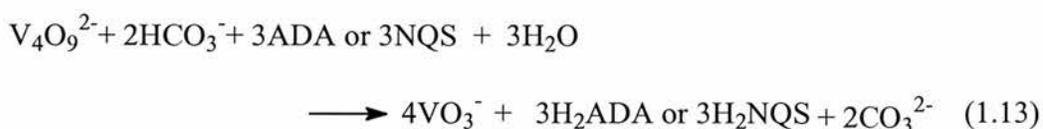
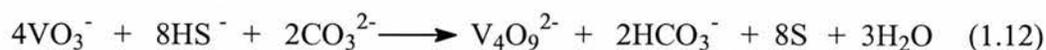
Fe(III)/Fe(II) redox couple technology further evolved through a hexacyanoferrate based system which is known as the Staatsmijnen-Otto process, and was described by Pieters and Van Krevelen.<sup>18</sup> The Staatsmijnen-Otto process appeared to be problematic because of the use of the toxic solution containing  $\text{Fe}(\text{CN})_6^{n-}$  ( $n = 3$  or  $4$ ) and ammonia, and the large number of side reactions.

The application of stable, aqueous, homogeneous and non-toxic iron chelates of ethylenediaminetetraacetic acid (EDTA), or related ligands, was the next development. A process based on this concept was first introduced by Humphreys and Glasgow.<sup>19</sup> However, it was soon discovered, due to severe losses of organic ligand, that this early application of iron chelates in gas purification failed to be economical. It was not until the 1970's that catalyst loss was sufficiently controlled, and iron chelates were re-introduced as LRSR couples, that is contemporary iron chelate processes, which will be discussed in more detail in **Section 1.2**.

Another redox couple used in LRSR applications is the As(V)/As(III) couple,  $\text{AsO}_3^{3-}/\text{AsO}_4^{3-}$  in the Giammarco-Vetrocoke process.<sup>20,21</sup> This process was said to be more efficient than the above processes. However because of the high toxicity of the As(V)/As(III) couples, this process gradually lost its significance during the 1950's. The process is represented by the simplified set of reactions (**1.8 - 1.11**):

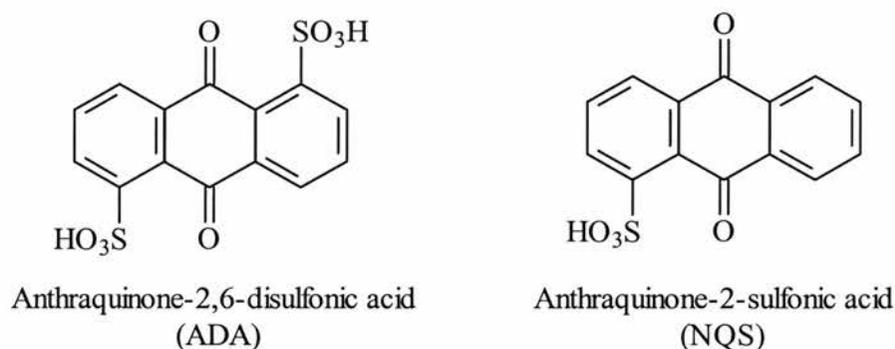


The first well established LRSR application developed during the 1950's, the Stretford process, employed the vanadium V(V)/V(IV)-redox couple.<sup>23,23</sup> There have been several patents involving modifications of these processes ever since.<sup>24</sup> The chemistry is represented by the simplified set of reactions:



The anthraquinone disulphonic acid (ADA) or naphthoquinone sulfonate (NQS) (see **Scheme 1.1**) is involved as a catalyst in the oxidation reaction. The reaction takes place in an alkaline  $\text{Na}_2\text{CO}_3$  buffer ( $\text{pH} = 9$ ) at a relatively low temperature ( $T = 323\text{K}$ ).<sup>25</sup> The Stretford process and the modified process have dominated the LRSR market during the 1980's and 1990's. There are several hundred Stretford process plants in operation in the late 1980's throughout the

world.<sup>24</sup> However, in these processes, several problems tend to increase the operating expenses, for example the degradation of catalysts, the undesired conversion of the absorbed hydrogen sulphide or the product sulphur to water-soluble sulphur-containing salts including sulphates, thiosulfates and polythionates, and increasingly strict environmental regulations to vanadium. Therefore, the Stretford process appeared to have lost its prominent position when the Fe(III)/Fe(II) redox couple LRSR process was introduced during 1980's and 1990's and is no longer chosen for new plants. However a large number of Stretford process plants remain in operation.



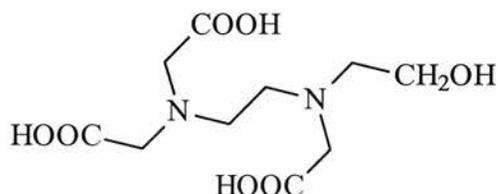
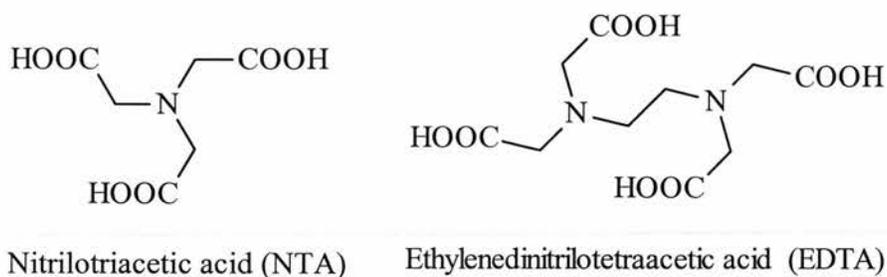
**Scheme 1.1** Catalysts used in the Stretford process

## 1.2 Contemporary LRSR processes

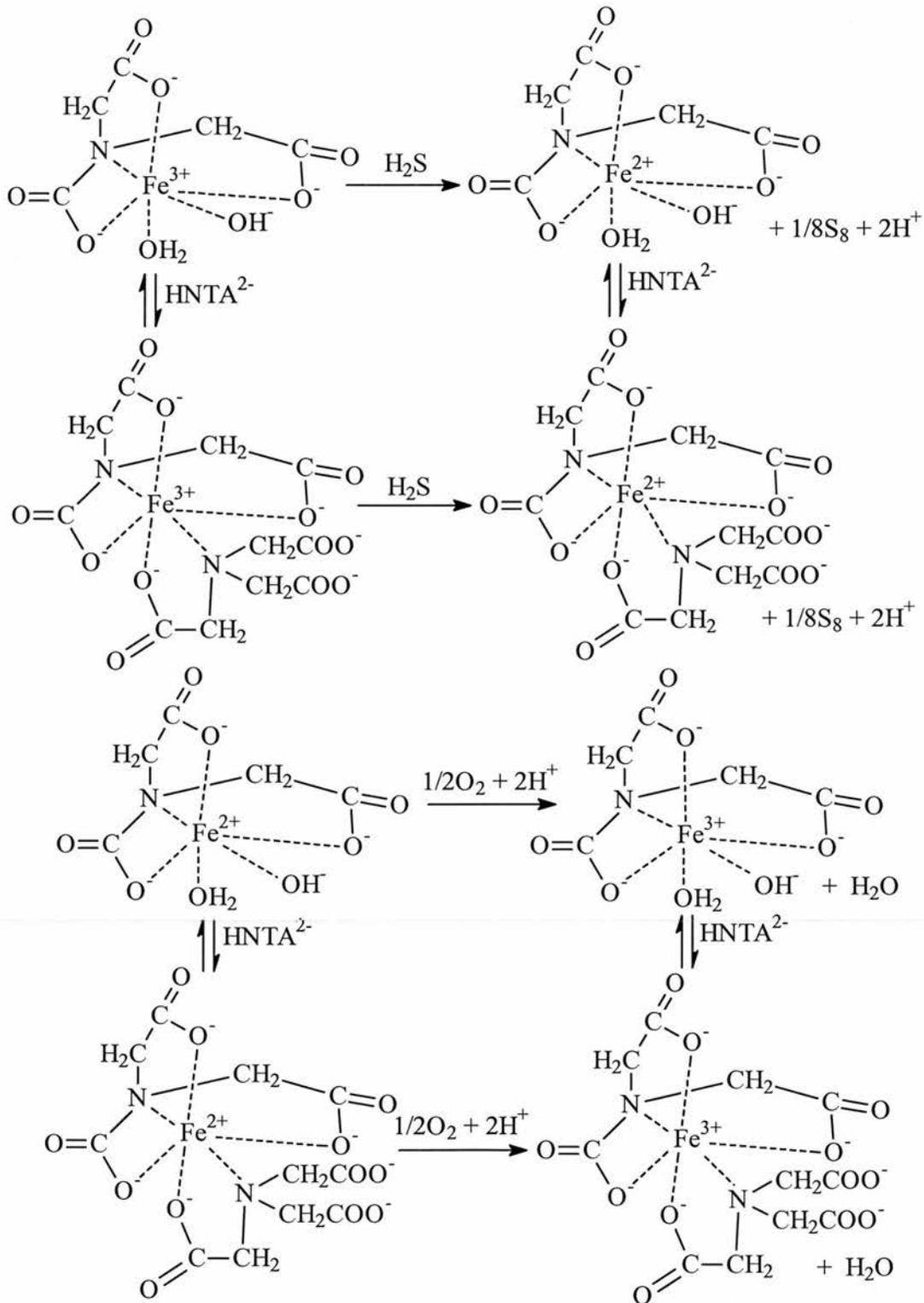
New, more efficient, economical and non-hazardous LRSR processes have become available and are replacing the application of the V(V)/V(IV) redox couple. Usually, these new generation processes involve a Fe(III)/Fe(II) redox couple. Other metal ion redox couple, organic redox couple and biochemical systems, biochemical systems in combination with an Fe(III)/Fe(II) redox couple are under development or in research, some are now commercial available.

### 1.2.1 Aqueous Fe(III)/Fe(II) redox couples

As mentioned above, aqueous chelated iron processes began in the early 1960's,<sup>26</sup> but because of the severe losses of ligand, no successful industrial operation emerged until small capacity systems were commissioned in the 1970's, and around 1980 the first large plants with sulphur productions up to  $1.5 \times 10^4$  kg/day became operational.<sup>27,28</sup> More recently, several aqueous and homogeneous chelated iron catalyst systems have been developed. The main chelate ligands are amino and polyaminopolyacetic acids, including nitrilotriacetic acid (NTA), ethylene dinitrilotetraacetic acid (EDTA) and *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N''*-triacetic acid (HEDTA) (See **Scheme 1.2**).<sup>29-33</sup>



**Scheme 1.2** Ligands used in the Fe(III)/Fe(II) redox couple systems

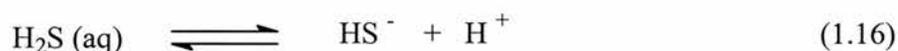
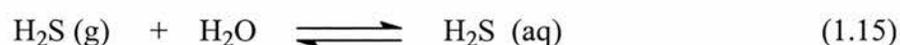


**Scheme 1.3** Redox of Fe(III)/Fe(II)-NTA for the oxidation of  $\text{H}_2\text{S}$  to S

Considering the ligand stability, the Fe(III)/Fe(II)-NTA systems are most widely commercially employed. The chemistry of this process is represented in **Scheme 1.3**. This system is further improved by addition of hexitol, sorbitol or mannitol [enantiomeric forms of  $[\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}]$  which deprotonate at high pH values and in the presence of Fe(III) form a very stable complex thereby preventing precipitation of Fe as  $\text{Fe}(\text{OH})_3$ ].<sup>29f,34</sup>

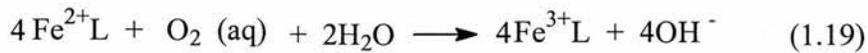
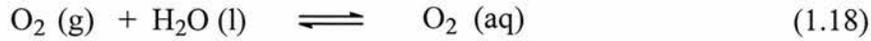
Chelated iron process plant configurations are somewhat varied,<sup>35-37</sup> but all incorporate the basic unit operations of  $\text{H}_2\text{S}$  absorption, Fe(II)L oxidation and sulphur removal.

In operation, the  $\text{H}_2\text{S}$  containing gas stream is contacted with an aqueous, mildly alkaline (pH 7-9) solution of Fe(III)L ( $[\text{Fe}] = 0.005$  to  $0.5$  M) in the absorber vessel where the following reactions take place:

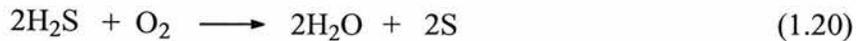


Absorbers are usually custom designed in order to accommodate the large range of sour gas stream compositions ( $[\text{H}_2\text{S}] = 50$  ppm to 100 %), pressures (atmospheric to over 7 MPa) and flow rates (up to  $65 \text{ m}^3\text{s}^{-1}$ ). Absorber devices include spray chambers, packed towers with a variety of packing, both fixed and mobile, static mixers, venturis or eductors and liquid filled columns. Precipitated sulphur is continuously removed by alternative methods including sedimentation, filtration or melting under pressure.<sup>38</sup>

The Fe(II)L formed in the absorber is oxidized by air in an oxidizing vessel or zone where the reactions are:



Thus, the overall reaction is:



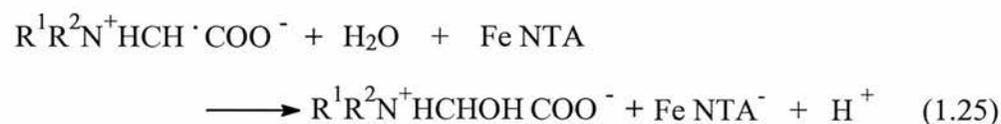
Now there are several successful iron chelates based processes known,<sup>3,39</sup> the most prominent being the LO-CAT/LO-CAT(II) process (US Filter) and the SulFerox process (Shell Oil Company, Dow Chemical Company).

The LO-CAT process has been available since 1980. The majority of plants operate under mildly alkaline conditions ( $7 \leq \text{pH} \leq 9$ ),<sup>27</sup> and iron concentrations are in the order of 0.02 M, temperatures may be within the range  $278 \leq T \leq 348$  K, usually  $T = 310$  K. In 1991 a second generation process, LO-CAT II was introduced which is more cost efficient.<sup>41,42</sup> The most important modification seems to be the use of the staged auto-circulation regenerator vessel which consists of multiple compartments for the regeneration reaction.<sup>43</sup>

The SulFerox process was established in 1987, and up to 1995 approximately 40 plants were licensed.<sup>44</sup> The process is very similar to the LO-CAT/LO-CAT II process apart from high iron concentrations ( $0.1 \leq C_{\text{Fe}} \leq 2.0$  M).<sup>31,35-37,41,42,45</sup> It is claimed that a high  $C_{\text{Fe}}$  reduces liquid circulation costs.

The Fe(III)/Fe(II)-NTA process has been applied in sweetening natural gas, direct oil refinery operations, enhanced oil recovery, marine vessel loading, underground oil shale retorting, landfill gas treating, waste water treating, plant odour control, bio-gas treating, geothermal electric power generation, coke oven gas treating, beverage quality carbon dioxide production and a large variety of chemical manufacturing operations like production of titanium dioxide.<sup>46,47</sup>

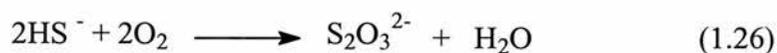
Despite the wide-spread application of these processes, the systems suffer from oxidation of the chelating ligand and eventual catalyst loss. The degradation of ligand may originate from the oxidation process of ferrous complex, which involves some strongly oxidising intermediates whose exact nature is still a subject of controversy.<sup>46,47</sup> Although there are some debates about the presence of free OH and H<sub>2</sub>O<sub>2</sub>, the following sequence of reactions is proposed to explain the degradation of Fe-NTA (1.21 to 1.25).<sup>48-52</sup>

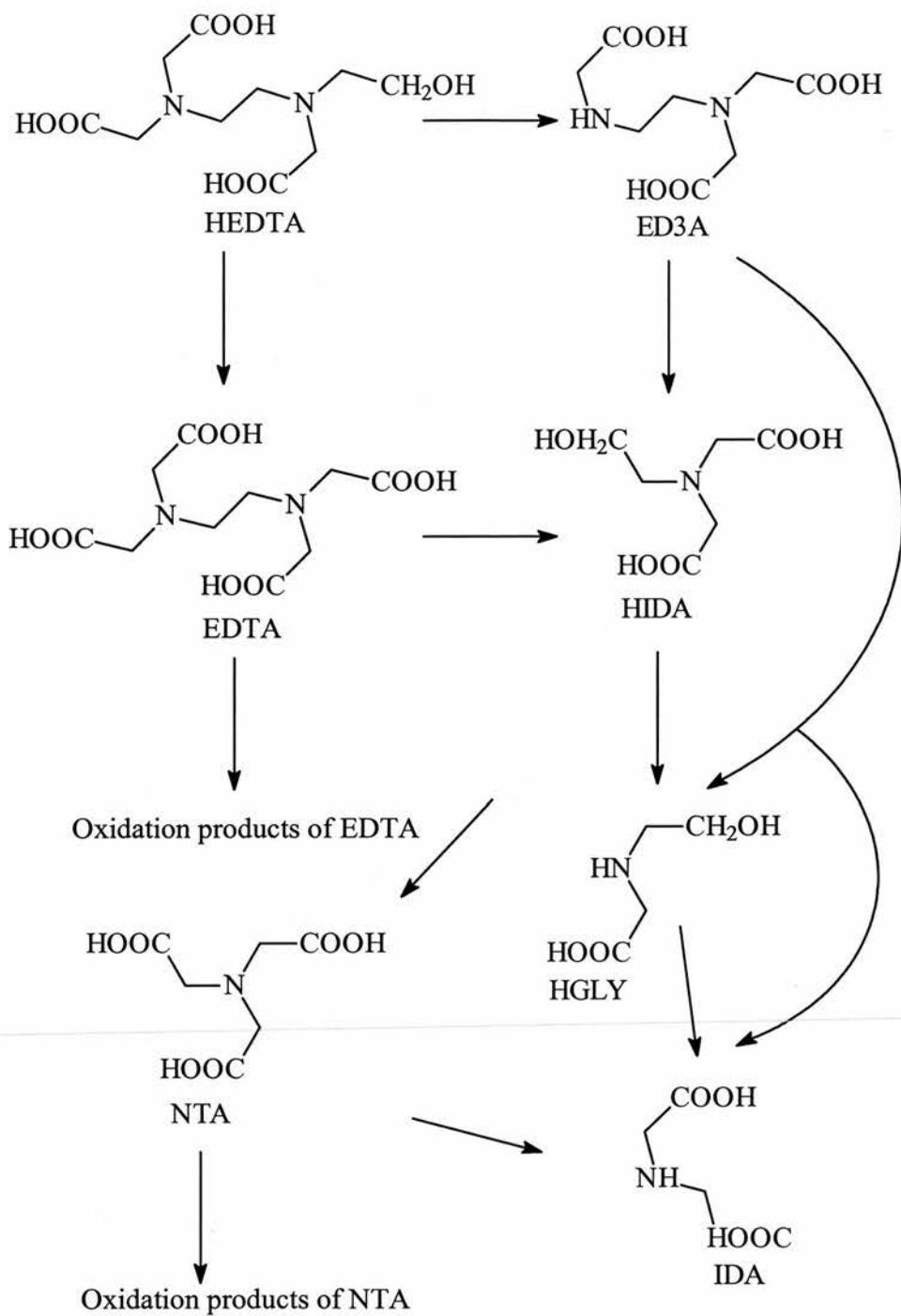


Other similar polyamino polycarboxylato iron chelates such as HEDTA and EDTA are presumed to degrade similarly in the process, the point of attack being the CH<sub>2</sub> group of the acetate chains. The degradation of these ligands can be shown by the following **Scheme 1.4 - 1.6**.<sup>17, 53 54</sup>

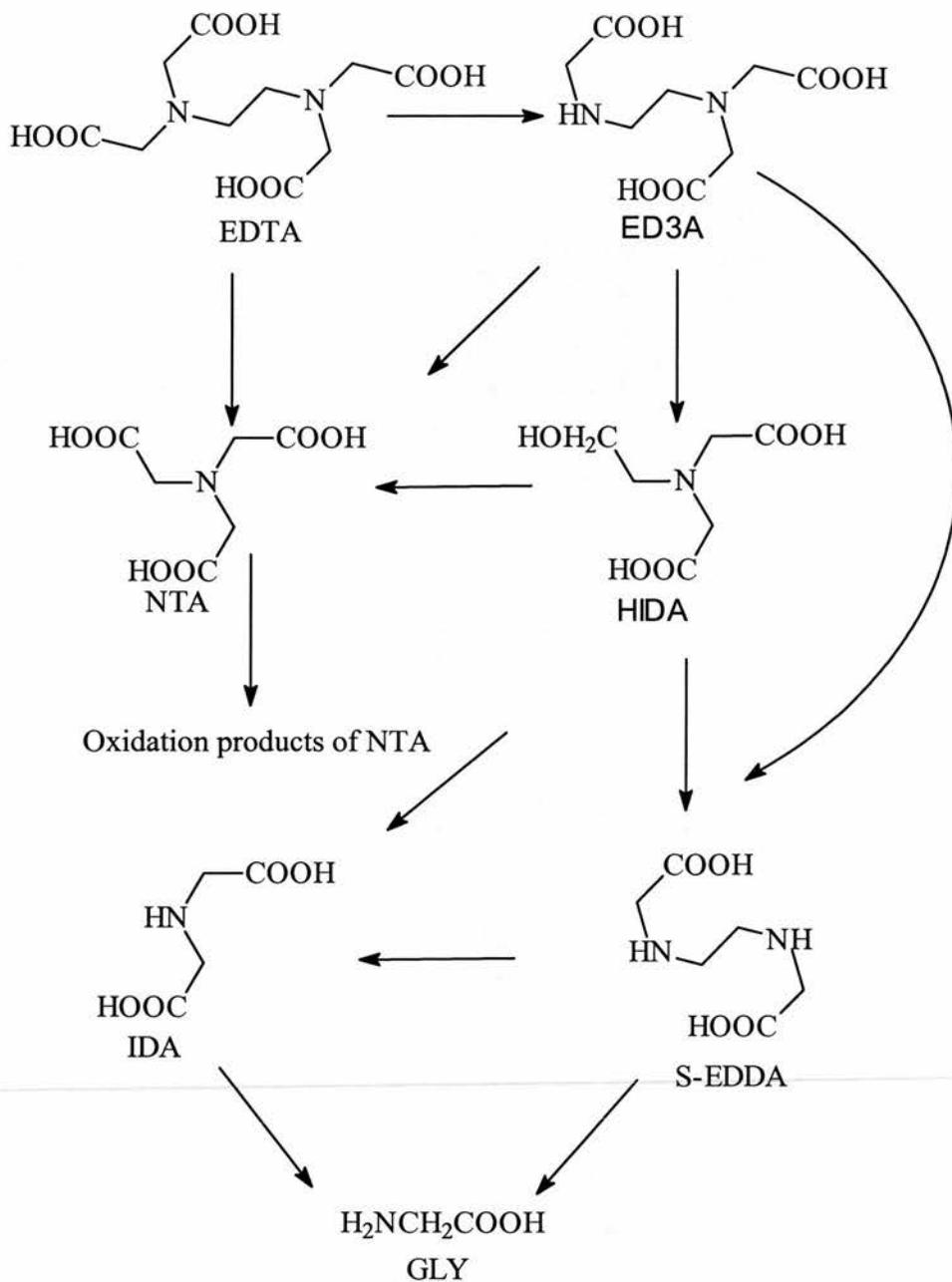
The fact that EDTA and HEDTA degrade faster than NTA makes NTA the preferable ligand.<sup>53,54</sup> However, the specific information is for the most part proprietary. Little information is available on actual loss of activity.

As a remedy for catalyst loss resulting from ligand degradation, some ligand-stabilizing agents which are considered as “radical scavengers”, such as t-butanol,<sup>35</sup> *N,N*-hydroxylamine, thiourea, thiosemicarbazide,<sup>32</sup> thioglycolic acid, 3,3-thiodipropionic acid,<sup>55</sup> sodium thiocyanate, dithionite<sup>56</sup> and anionic polymer JAYFLOC 803,<sup>57</sup> were added to prevent ligand degradation and to stabilize the catalyst system in the process. Thiosulfate is also an effective radical scavenger, which may be added to the iron chelate solution, and is also produced if H<sub>2</sub>S and O<sub>2</sub> are simultaneously present.<sup>29f</sup>

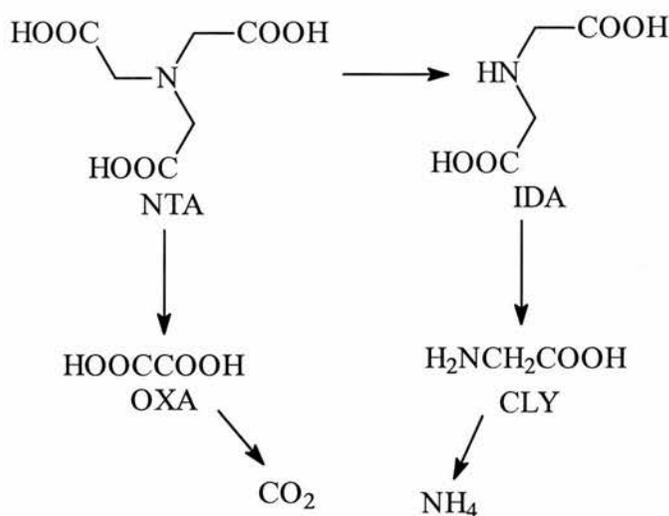




**Scheme 1.4** Proposed degradation scheme for HEDTA

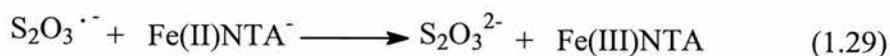
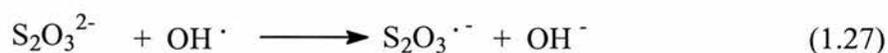


**Scheme 1.5** Proposed degradation scheme for EDTA

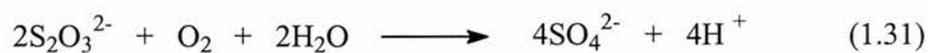


**Scheme 1.6** Proposed degradation scheme for NTA

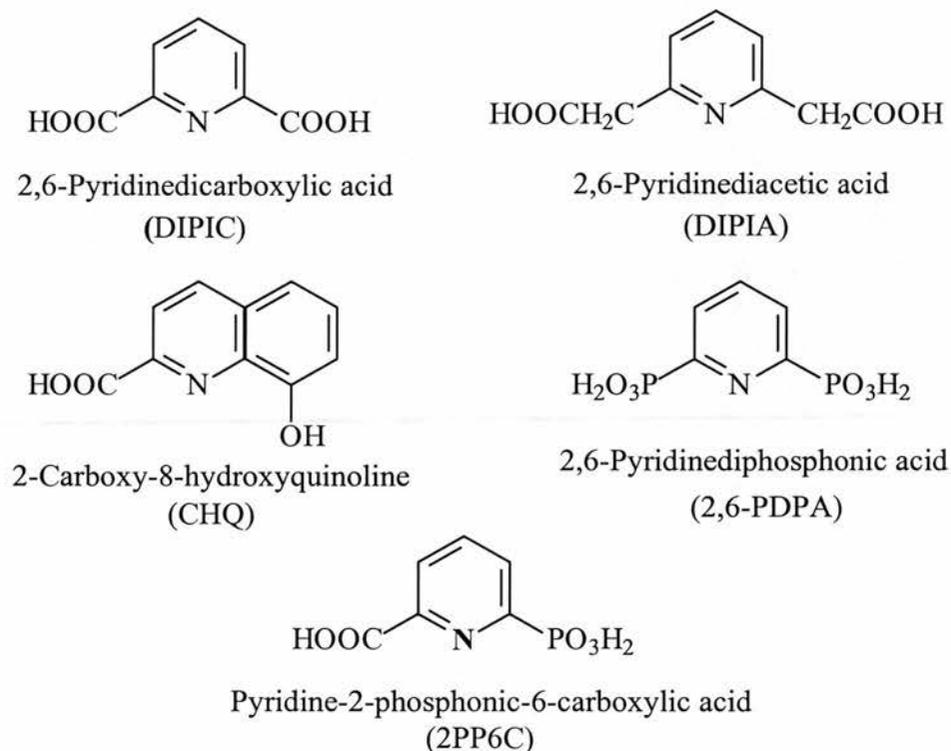
The possibility that thiosulfate ions can be regenerated in the process after reacting to scavenge hydroxyl radicals has been suggested<sup>58</sup> and is supported by earlier work involving pulsed radiolysis of aqueous thiosulfate.<sup>59</sup>



These additives, to a certain extent, are effective as ligand degradation reducing agents, reducing the catalyst loss in the process. But a key drawback of these additive agents is their consumption in the process,  $\text{S}_2\text{O}_3^{2-}$  is oxidized to  $\text{SO}_4^{2-}$  and  $\text{S}_4\text{O}_6^{2-}$ , resulting in inert salt accumulation which hampers the sulphur separation as well as the gas-liquid mass transfer.<sup>27</sup>



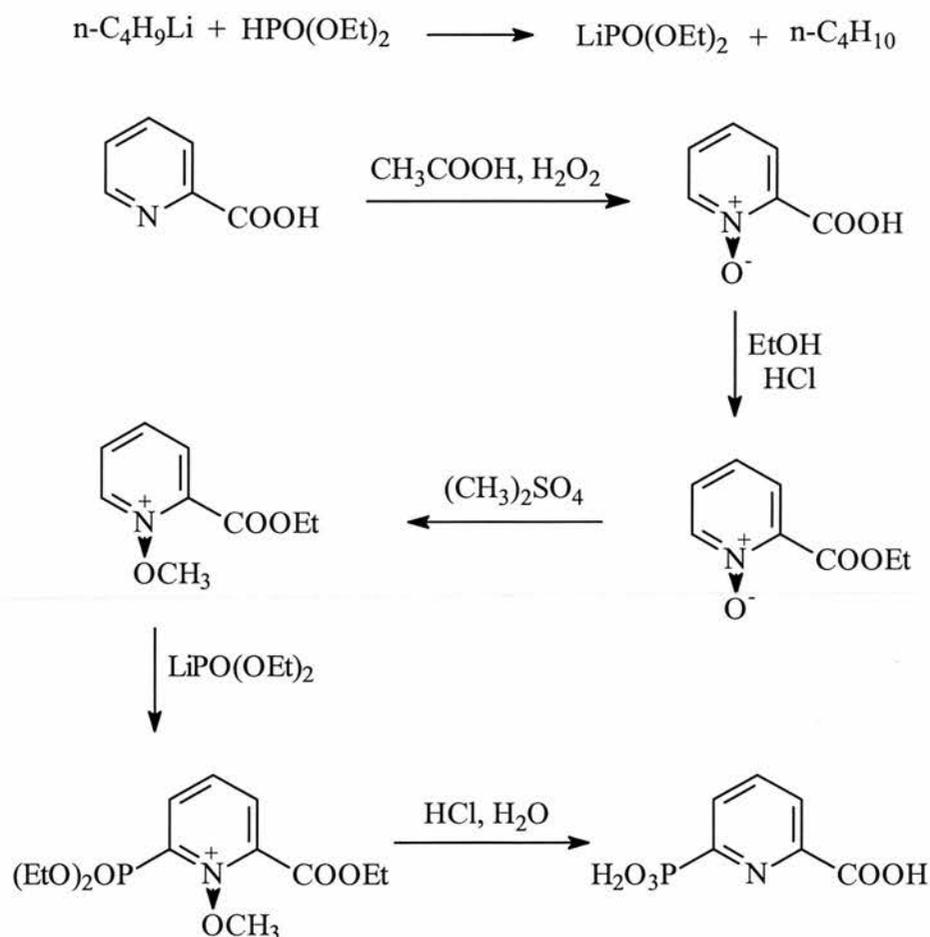
Due to the above reasons, further research aiming at improvement of ligands continues. An alternative ligand studied in some detail by Sawyer<sup>60</sup> and Chen et al<sup>54</sup> is 2,6-pyridinedicarboxylic acid (DIPIC, See **Scheme 1.7**). It was reported that no degradation was observed during a 100 hour test, but the stability of the Fe(III)-DIPIC is not high enough to prevent precipitation of Fe(OH)<sub>3</sub> at the required basic condition, even at high ligand to iron molar ratios.<sup>61-63</sup>



**Scheme 1.7** Some alternative ligands in aqueous Fe(III)/Fe(II) system

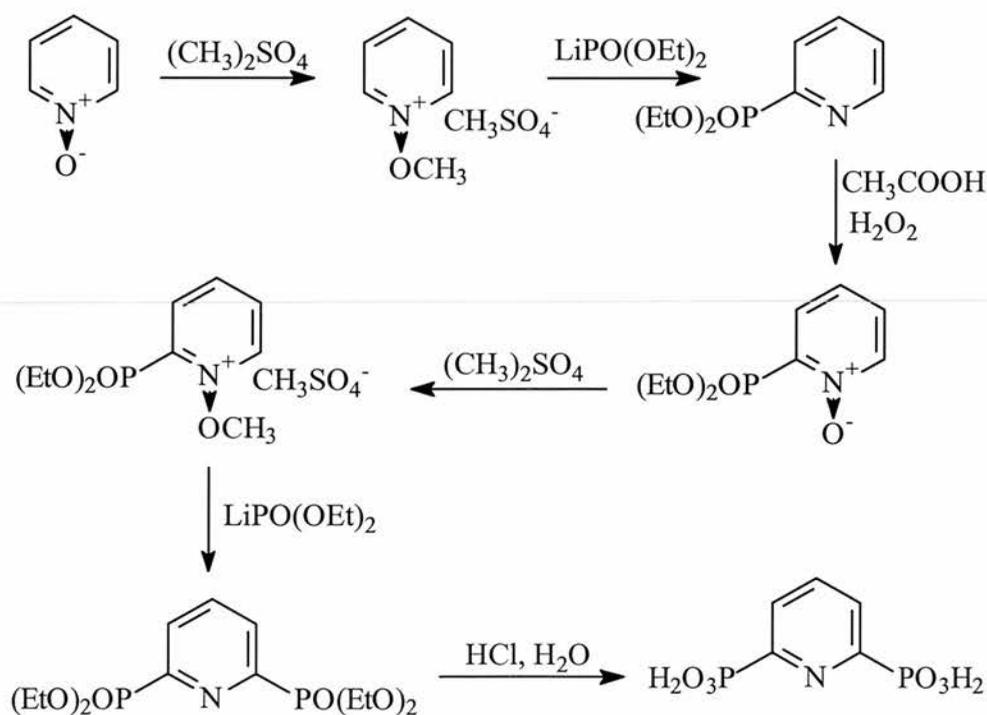
A closely related ligand, 2,6-pyridinediacetic acid (DIPIA) was also introduced,<sup>61</sup> but this ligand showed rapid degradation .

Using molecular mechanics, Hancock et al<sup>61,64</sup> selected 2-carboxy-8-hydroxyquinoline (CHQ) without methylene groups (-CH<sub>2</sub>) as an alternative ligand. It was found that even in the presence of thiosulfate as stabilising agent, CHQ degraded more rapidly than NTA. No details on the use of CHQ or related ligands are available as yet.



**Scheme 1.8** Synthesis of 2PP6C

Other interesting candidate ligands which were selected from molecular mechanics considerations are pyridine-2-phosphonic-6-carboxylic acid (2PP6C) and 2,6-pyridinediphosphonic acid (2,6-PDPA),<sup>61, 64-66</sup> which are closely related to DIPIC, ligands degradation were also reported to certain extent.<sup>62</sup> Obviously, the absence of easily oxidised  $\alpha$ -methylene group does not guarantee against the oxidative degradation of the ligand. However, a proper comparison with conventional ligands such as NTA, EDTA and HEDTA can not be made yet because no further information has been given. In fact, the synthesis cost of these ligands could be the major limiting factor for industrial development. The synthesis of some ligands involves the use of very toxic starting materials. **Scheme 1.8** and **1.9** show the syntheses of the phosphonate ligand 2PP6C and 2,6-PDPA.

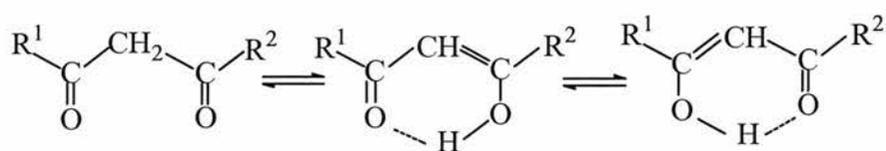


**Scheme 1.9** Synthesis of 2,6-PDPA

### 1.2.2 Non-aqueous LRSR processes

Peter <sup>67</sup> first patented the use of  $\beta$ -diketonate complexes of scandium, yttrium and some f-block elements in effectively scrubbing  $H_2S$  from a gas stream. However, no chemical reactions are described therein for the removal of impurities in the gas stream.

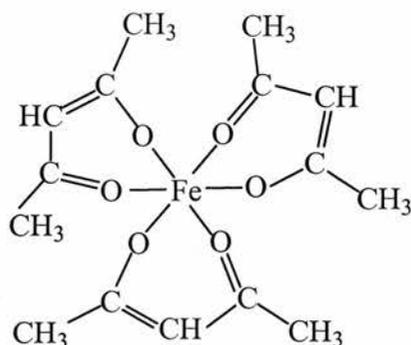
Recently, Ferm et al <sup>68</sup> and Eng et al <sup>69</sup> have reported in detail the application of non-aqueous liquid phase iron chelates in LRSR process, which employed  $\beta$ -diketonates such as acetylacetone, benzoylacetone, 1,1,1-trifluoro-2,4-pentanedione and 1-phenyl-4,4,4-trifluoro-1,3-butanedione (see **Scheme 8**) chelating iron in solvents or solvent mixtures including 1,4-dioxane, dimethyl sulfoxide, *N*-formylmorpholine, morpholine and *N*-methylpyrrolidone (NMP), ethanol and mixtures of the above.



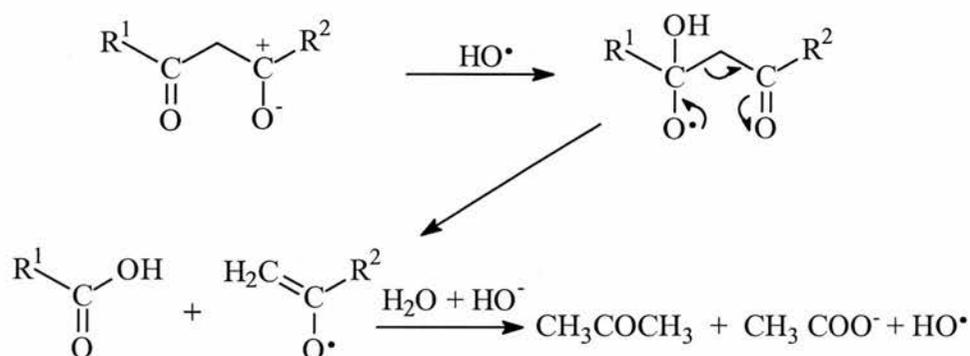
$R^1 = R^2 = H,$	acetylacetone (acac)
$R^1 = Ph, R^2 = H,$	benzoylacetone
$R^1 = CF_3, R^2 = CH_3,$	1,1,1-trifluoro-2,4-pentanedione
$R^1 = Ph, R^2 = CF_3,$	1-phenyl-4,4,4-trifluoro-1,3-butanedione

**Scheme 1.10** Tautomerization of  $\alpha$ -diketones

These ligands, existing in two tautomeric forms (**Scheme 1.10**), give sufficiently stable Fe(III)/Fe(II) complexes in the preferred solvent NMP from their keto-enol form (**Scheme 1.11**).<sup>68</sup>



**Scheme 1.11** Structure of tris-(acetylacetonato)iron(III)



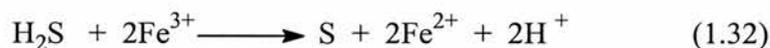
**Scheme 1.12** Proposed degradation scheme for acac

Eng et al investigated the degradation of the Fe(III)/Fe(II)-acetylacetonate (Fe(III)/Fe(II)-acac<sup>-</sup>) and Fe(III)/Fe(II)-benzoylacetate (Fe(III)/Fe(II)-bzac<sup>-</sup>) as catalysts in the oxidation of H<sub>2</sub>S in varied mixed solvent systems.<sup>70</sup> It was found that the rapid degradation of acac produces acetate and acetone in the re-oxidation of the Fe(II) complex to the Fe(III) complex, and a mechanism for the degradation of acac- was proposed which involves attack of the ligand by a hydroxyl radical (**Scheme 1.12**).

Advantages of the non-aqueous LRSR process include enhanced sulphur quality, reduced sulphur foaming and plugging. But a complication arising from the use of non-aqueous solvents is their high affinity for gaseous hydrocarbons, which requires several flash drums between absorber and regenerator. Also regenerator effluent air should be treated in an incinerator. Other disadvantages include water build-up, requiring a dehydration step, problems in pH control and possible oxidation of the organic solvent. Although the non-aqueous Fe(III)/Fe(II) chelate LRSR process appears to be a promising application, the process has not matured beyond laboratory scale and many of the above claims can't be verified yet.

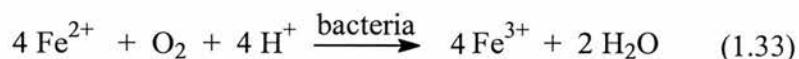
**1.2.3 The Fe(III)/Fe(II) redox couple in combination with biochemical catalyst regeneration LRSR processes ---- IRC - BCR processes**

In contrast to the Fe(III)/Fe(II) chelate processes discussed above, no organic ligands or inorganic ligand is used in these processes. To prevent precipitation of Fe(OH)<sub>3</sub> and FeS, the operating pH should be 1.5 ≤ pH ≤ 2.7. Similar to reaction (1.17), H<sub>2</sub>S is oxidized to elemental sulphur by Fe<sup>3+</sup>.



However, the rate of reaction (1.32) at the relative operational pH values appears to be lower than that for reaction (1.17).<sup>39,71-73</sup> Also in contrast to Fe(III)/Fe(II) chelate processes, which operate at ambient pH (7 ≤ pH ≤ 9)<sup>27</sup>, the dissociation of H<sub>2</sub>S at acidic condition is negligible.<sup>73</sup> Therefore, a larger absorber for H<sub>2</sub>S removal is likely to be necessary. In addition, in the absence of an organic or inorganic ligand, oxidation of the Fe(II) to Fe(III) proceeds too slowly for a

commercial process and therefore regeneration needs to be catalysed. Bacteria *Thiobacillus ferrooxidans*, immobilized on acid resistant materials (for instance glass wool) is used.<sup>74</sup> In these processes, bacteria may accelerate reaction (1.33) by a factor of  $2 \times 10^5$  depending on temperature and pH values.<sup>71,75,76</sup>

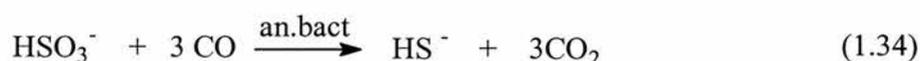


Despite the absence of costly organic or inorganic ligands, IRC - BCR processes show rather high operation costs relative to conventional Fe(III)/Fe(II) chelate processes.<sup>48</sup> However, Rehmat and Yoshizawa<sup>71</sup> questioned that the chemical costs of Fe(III)/Fe(II) chelate processes were underestimated. It is obvious that development activities are still ongoing.

Another LRSR application of bacteria in combination with the Fe(III)/Fe(II) redox couple involved aqueous solution of Fe(III)/Fe(II) chelates (proprietary LO-CAT liquid and Fe(III)/Fe(II) EDTA,  $7 \leq \text{pH} \leq 8.5$ ,  $303 \leq T \leq 318$ ,  $C_{\text{Fe}} \approx 0.02 \text{ M}$ ).<sup>77,78</sup> The rate of the regeneration reaction (1.33) can be substantially enhanced (50-150 %) by certain *Thiobacillus ferrooxidans* cultures, whereas ligand degradation is reduced down to undetectable limits. It was explained that ligand degradation results from strongly oxidizing intermediates, and certain enzymes produced by aerobic bacteria such as catalase and superoxide dismutase neutralize these intermediates resulting in reduced ligand degradation.<sup>79,80</sup> So far, the microbial/Fe(III)/Fe(II) chelate application has been tested by laboratory experiments only.

#### 1.2.4 Pure biological treatment processes

Buisman first disclosed a method for removing H<sub>2</sub>S or SO<sub>2</sub> from gas or waste streams using microorganisms (THIOPAQ process).<sup>81</sup> Gaseous streams are treated in a caustic scrubber (8 ≤ pH ≤ 9). The sulphur rich solution is then treated by microorganisms. If sulphur is present as SO<sub>2</sub>, anaerobic treatment by consuming an electron donor such as H<sub>2</sub> or CO or ethanol yields H<sub>2</sub>S, H<sub>2</sub>S formation maybe represented by the simplified reactions:



Preferred bacteria for this anaerobic process include the genera *Desulfovibrio*, *Desulfotomaculum*, *Desulfomonas*, *Desulfobulbus*, *Desulfobacter*, *Desulfococcus*, *Desulfomema*, *Desulfo Sarcina*, *Desulfobacterium* and *Desulforomas*.<sup>81</sup> The sulphide solution is subsequently treated in an aerobic reactor (1.37). Suitable bacteria for this aerobic reaction include the genera *Thiobacillus thioparus*,<sup>81-83</sup> *Thiobacillus concretivorus*,<sup>84-86</sup> *Thiobacillus ferrooxidans*,<sup>87,88</sup> *Chromatium vinosum*,<sup>89,90</sup> *Hyphomicrobium*,<sup>91</sup> *Xanthomonas*<sup>92</sup> and heterotrophic bacterium.<sup>93</sup> Undesired by-products appear to be overoxidized sulphur compounds such as sulfate.<sup>94</sup>



Pilot plant studies, initiated in 1993, show good technological prospects.<sup>95</sup> However, an independent economic evaluation mentions high circulation rates and a high blown down ratio as specific drawbacks.<sup>96</sup>

Successful H<sub>2</sub>S removal with microorganisms was also reported by Gadre and Sublette,<sup>97,98</sup> both dealing with bench scale studies. However, in these two cases, sulphate is the main product, not the elemental sulphur.

### ***1.2.5 Metal-phthalocyanine methods of removing hydrogen sulphide***

Metal-phthalocyanines were another type of catalysts used for removal / oxidation of hydrogen sulphide from gas streams.<sup>99-109</sup> Iron phthalocyanine,<sup>110,111</sup> cobalt phthalocyanine<sup>112-114</sup> and copper phthalocyanine<sup>115</sup> as well as alkalphthalocyanine<sup>116</sup> has been studied for this purpose. However, the main eventual product of H<sub>2</sub>S is S<sub>2</sub>O<sub>3</sub><sup>2-</sup> or SO<sub>4</sub><sup>2-</sup>, not sulphur.<sup>117</sup> The minor product, sulphur, due to the contamination of phthalocyanine complexes, the powerful dyes, is often green and very difficult to purify to yellow sulphur.

### ***1.2.6 Hydrogen recovery, alternative LRSR processes***

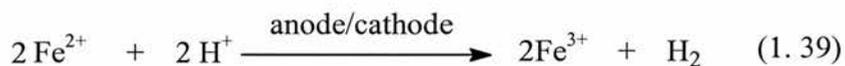
Another attractive idea is the recovery of both sulphur and hydrogen in the same process. Given the low standard enthalpy of formation as compared to water and methane, H<sub>2</sub>S seems a good potential source for hydrogen.<sup>118</sup> The recovery of H<sub>2</sub> from H<sub>2</sub>S according to reaction (1.38) has received attention since the 1930's.<sup>3,119,120</sup> However, this reaction is not practical under purely thermal conditions because it is thermodynamically unfavourable (e.g. at 298 K,  $\Delta H^{\circ} = 20 \text{ KJ mol}^{-1}$ ,  $\Delta S = -43 \text{ JK}^{-1} \text{ mol}^{-1}$ ), though the reaction has been accomplished thermally at high temperatures

(1000°C) and by various photo-, plasma- and electrochemical decomposition methods.<sup>121-127</sup>



The processes involving liquid redox cycles seem to have good prospects. These processes are known as IKC Hybrid and HySulf LRSR processes.

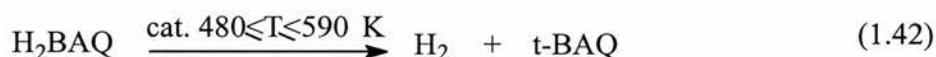
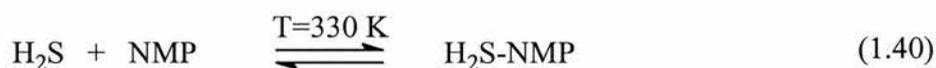
The IKC Hybrid process is based on the Fe(III)/Fe(II) couple, very similar to the above IRC - BCR process. The regeneration step takes place in an electrochemical cell, so the redox cycle may be represented as follows.<sup>128</sup>



Because of the undesired by-product of sulphuric acid and the high cost of electrical energy, as compared to thermal energy, the IKC Hybrid process will not be competitive with hydrogen production by, for instance, methane stream reforming. Therefore, the IKC Hybrid process should be considered as a sulphur recovery process, rather than an alternative method for H<sub>2</sub> production. Given the absence of organic ligands, the process may be an interesting alternative for Fe(III)/Fe(II) chelate processes, particularly if the produced H<sub>2</sub> can be used for chemical purposes.<sup>118</sup>

The Hysulf process uses an organic redox couple. The original process consisted of absorption of H<sub>2</sub>S into a polar organic solvent, for instance NMP,<sup>129</sup> then complexation to the solvent and subsequent reaction with t-butylanthraquinone (t-

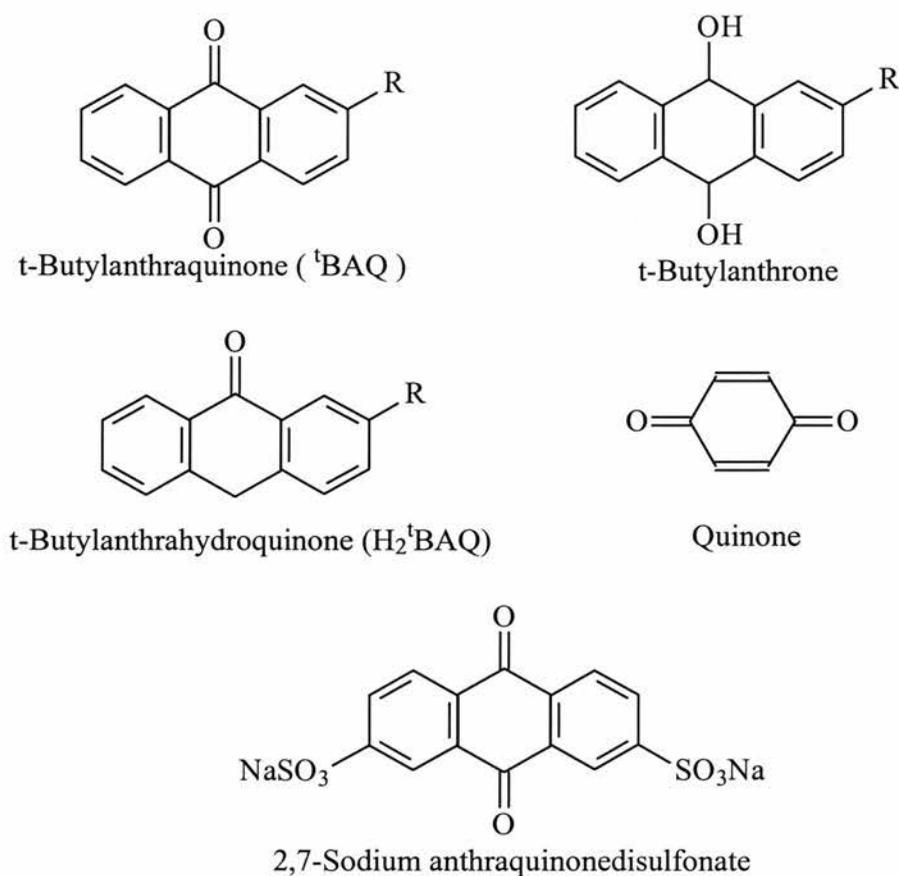
BAQ, see **Scheme 1.13**) to give sulphur, NMP and H<sub>2</sub>BAQ. In a second reactor, H<sub>2</sub>BAQ is dehydrogenated over a catalyst to yield H<sub>2</sub> and t-BAQ.<sup>130-132</sup>



In practice, reaction **(1.42)** produced undesired side product of t-butyl anthrone. Another drawback of the original process appeared to be the use of hazardous amide solvents.<sup>133</sup>

As an alternative, aqueous solutions of quinone / 2,7-sodium anthraquinone disulfonate together with a hydrogen sulphide complexing agent such as t-butylamine, a mixture of solvents, for instance, NMP with water as an additive (1-1.5 mole H<sub>2</sub>O per anthraquinone) is employed. This modification is claimed to yield better sulphur recovery as well as complete selectivity to anthraquinone.<sup>134</sup>

Other similar methods include using binuclear Pd-[bis(diphenylphosphino) methane] complexes or other transition metal-phosphine complexes for the conversion of H<sub>2</sub>S to a source of H<sub>2</sub> and elemental sulphur.<sup>135-147</sup> However, these researches have been limited to the bench only.



**Scheme 1.13** Catalysts used in the HySulf process

### 1.3 Conclusions

During the last century, there have been large numbers of publications and patents involving processes for sulphur recovery from H<sub>2</sub>S. Among them, the Gimmarco-Vetrocoke process using the As(V)/As(III) redox couple was quickly found to be unsuitable for the commercial market because of the environmental problem. The Stretford process employing the vanadium V(V)/V(IV) redox couple, which have dominated the 1980's and 1990's, is now being replaced by Fe(III)/Fe(II)

chelate systems, particularly the Fe(III)/Fe(II) NTA processes. However, even the prevailing Fe(III)/Fe(II) NTA processes are not perfect. Degradation of the organic ligands resulting in high chemical costs is the most serious deficiency in these processes. Other problems with Fe(III)/Fe(II) chelate processes include uncontrolled sulphur crystallization which lead to foaming and plugging as well as a poor sulphur quality. These problems call for research, aiming at reduced ligand degradation. Therefore, the use of non-degrading ligand or regeneration facilitated by microorganisms, either with or without organic ligands has appeared, and the latter has been applied on a pilot scale. Other processes, including the biological treatment without an auxiliary redox couple, metal-phthalocyanine methods and the combined sulphur / hydrogen recovery, are now being studied.

This project aims to improve the Fe(III)/Fe(II)-NTA system by selecting new ligands, new scavenger of free hydroxyl radical and alternative transition metals. A novel non-aqueous Fe(III)/Fe(II) redox couple has also been investigated for the sulphur recovery process.

## Chapter 2

# **Novel Aqueous Iron Chelating Agents as Catalysts for the Oxidation of Hydrogen Sulphide to Sulphur by Air**

### **2.1 Introduction**

As mentioned in **Chapter 1**, chelated-iron liquid redox processes are increasingly employed in a variety of industries to cocurrently absorb and to oxidise the hydrogen sulphide component of gas streams to elemental sulphur. In most cases the catalysts used commercially are Fe(III)/Fe(II) chelates and the chelating agent an aminopolycarboxylic acid such as NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid) or HEDTA (*N*-hydroxyethylethylenediamine-*N*, *N'*, *N''*-triacetic acid). In particular, the Fe(III)/Fe(II)-NTA system, which degrades more slowly than the other two ligands (EDTA and HEDTA) do in the process,<sup>29f</sup> has been widely applied. Nevertheless, the significant operating costs that are incurred in the process due to the oxidation and eventual loss of NTA has been the most serious deficiency, which obstructs the use of this system in large installation for the removal of hydrogen sulphide by catalytic oxidation. Although the rate of degradation can be slowed considerably by addition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, which is known as an quite effective scavenger for the hydroxyl radical, in fact, the problem involving the decomposition of NTA in-process is not resolved satisfactorily yet. The problem calls for research of novel or more robust ligands in place of NTA.

In this chapter, according to the general chemical criteria below for the selection of ideal ligand, we screened sixty-seven compounds which can be roughly

divided into ten types of ligands with a variety of functional groups. The solubilities and stabilities of Fe(III) complexes of the corresponding ligand in aqueous solution have been tested first. The catalytic activities of the Fe(III) complexes of the potential ligands were then tested preliminarily by a simple method using air to oxidise NaSH to sulphur. Further testing of the potential candidate was carried out in a 1-liter glass reactor provided by US Filter for the oxidation of hydrogen sulphide to sulphur by air. The testing results of the potential candidates were compared with that of the known Fe-NTA system with respect to efficiency and practicality under the same conditions. Several ligands and Fe(III) complexes have been characterised. The analytical methods involving the degradation of the promising ligands and confirmation of the side-products have been also established. In addition, the mechanism of the oxidative degradation of [(phosphonomethyl)imino]diacetic acid (NTAP) is proposed. The cyclic voltammograms of the Fe(III) complexes of several promising ligands are also discussed.

## **2.2 Criteria for the selection of ideal ligands**

An ideal ligand, which is used in aqueous iron complex catalysed hydrogen sulphide oxidation processes, must meet the chemical criteria below <sup>35</sup> and it is necessary to possess low toxicity, present no environmental limitations, and be available in commercial quantities at moderate cost.

- i) As gas to liquid mass transfer of H<sub>2</sub>S is much more efficient on aqueous systems at high pH value, the Fe(III)/Fe(II) complexes must possess sufficiently high thermodynamic stability to avoid precipitation of Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub> at pH up to 9 or more.

- ii) The stability of the Fe(II) complex must be great enough to prevent precipitation of FeS under the required mildly alkaline conditions.
- iii) The difference in stability of the Fe(III) and Fe(II) complexes must be low enough to allow reduction of the Fe(III) complex by H<sub>2</sub>S to the Fe(II) complex. If the Fe(III) complex is too stable, the complex will remain in the Fe(III) state and no oxidation of H<sub>2</sub>S will occur.
- iv) The stability of the Fe(III) complex must be greater than that of the Fe(II) complex for the oxidation of the Fe(II) complex by dissolved O<sub>2</sub> to be a highly favoured reaction. Ligands that stabilise Fe(II) over Fe(III) are not useful in the process.

## 2.3 The ligands that have been selected or prepared

### 2.3.1 Ligands with one sulphur donor



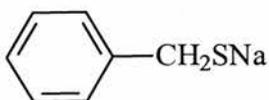
1

Ammonium thiocyanate



2

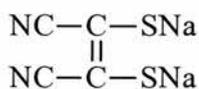
4-Methylbenzenethiol, sodium salt



3

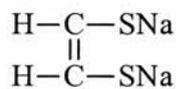
Benzylmercaptan, sodium salt

### 2.3.2 Dithiocarbamates and related ligands



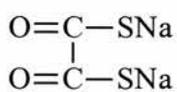
4

Disodium dimercaptomaleonitrile



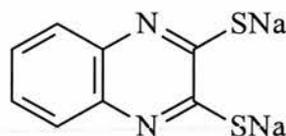
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Disodium ethylene-1,2-dithiol



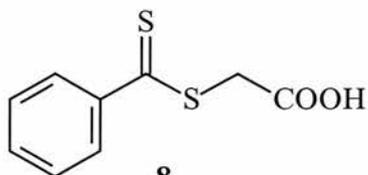
6

Disodium dithiooxalate



7

Quinoxaline-2,3-dithiol, sodium salt



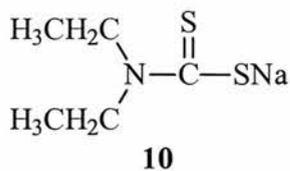
8

Thiobenzoylsulfanylacetic acid

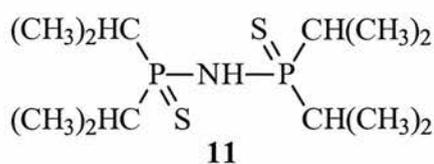


9

Hydrazine-*N,N*-dicarbothioic acid diamide

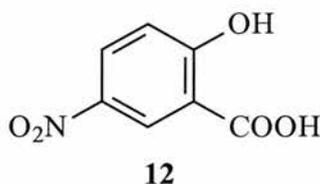


Sodium diethyldithiocarbamate

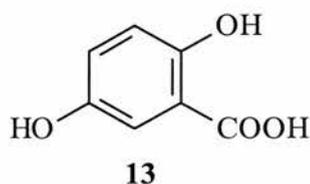


Diisopropyl-thiophosphinyl-amido-  
-diisopropyl-thiophosphinone

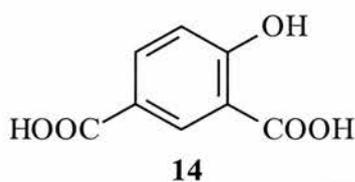
### 2.3.3 Ligands with only oxygen donor groups



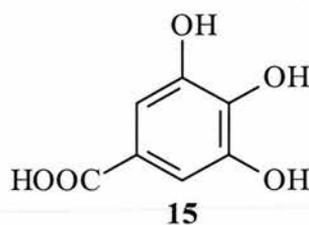
2-Hydroxy-5-nitrobenzoic acid



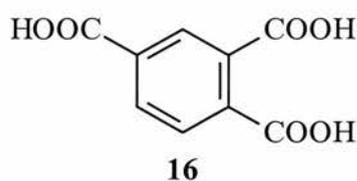
5-Hydroxysalicylic acid



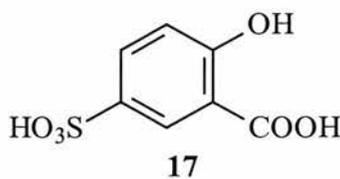
4-Hydroxyisophthalic acid



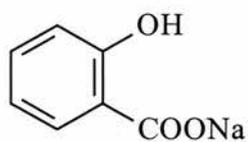
3,4,5-Trihydroxybenzoic acid



1,2,4-Benzenetricarboxylic acid



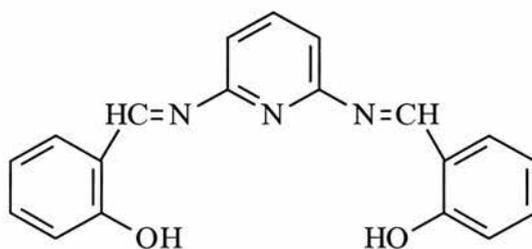
5-Sulfosalicylic acid



18

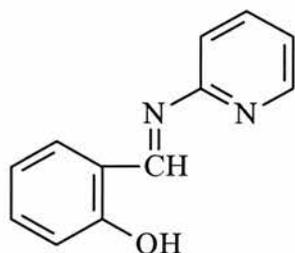
Sodium salicylate

### 2.3.4 Schiff base ligands



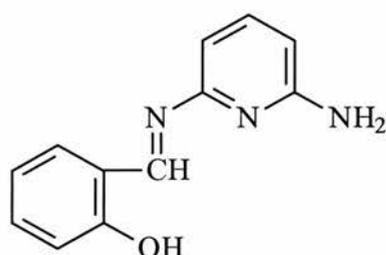
19

*N, N'*-2,6-Pyridinebis(salicylideneimine)



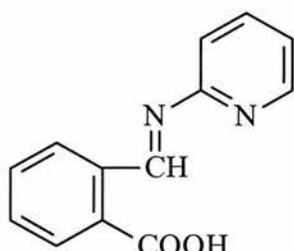
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2-Pyridinesalicylideneimine



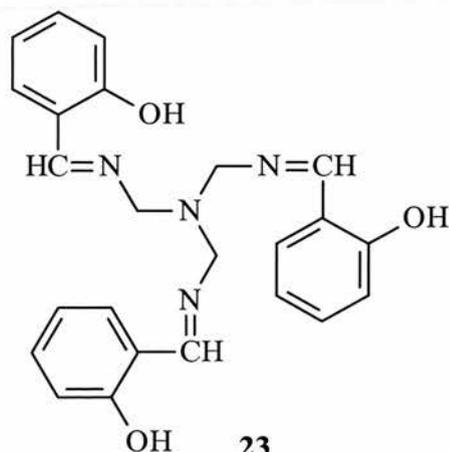
21

2-Amino-6-pyridinesalicylideneimine



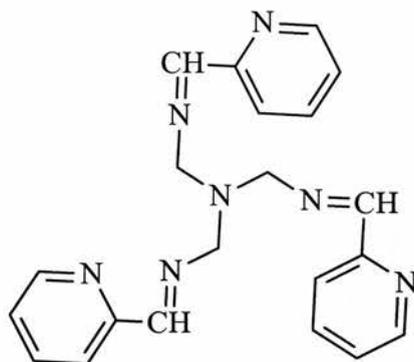
22

2-Pyridine-2'-carboxybenzylideneimine



23

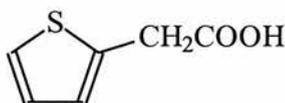
Tris-(2-salicylideneamino-ethyl)-amine



24

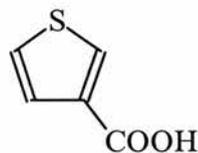
Tris[N-(2-pyridylmethyl)-2-iminoethyl]amine

### 2.3.5 Heterocyclic donor atom ligands



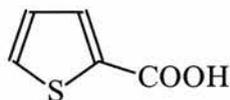
25

2-Thiopheneacetic acid



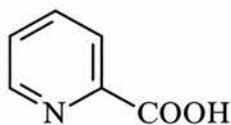
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Thiophene-3-carboxylic acid



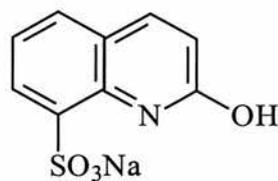
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Thiophene-2-carboxylic acid



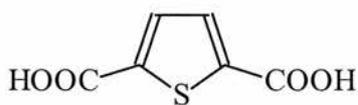
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2-Picolinic acid



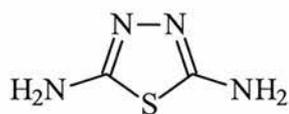
29

Sodium 2-hydroxyquinoline-8-sulfonate



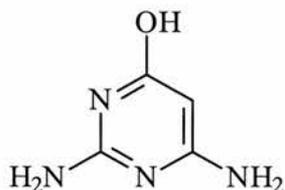
**30**

2,5-Thiophenedicarboxylic acid



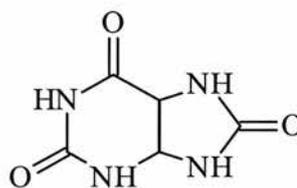
**31**

[1,3,4]-Thiadiazole-2,5-diamine



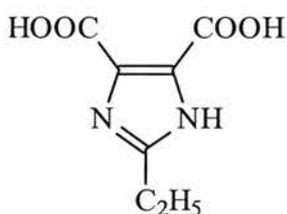
**32**

2,6-Diamino-3H-pyrimidin-4-one



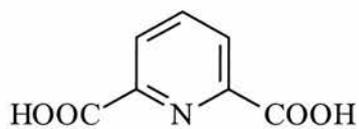
**33**

Uric acid



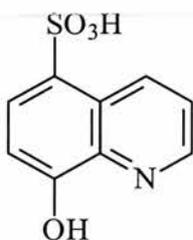
**34**

2-Ethyl-1H-imidazole-4,5-dicarboxylic acid



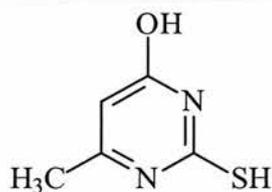
**35**

Pyridine-2,6-dicarboxylic acid



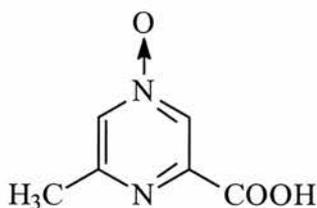
**36**

8-Hydroxyquinoline-5-sulfonic acid



**37**

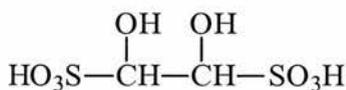
4-Hydroxy-2-mercapto-6-methylpyrimidine



38

5-Methyl-4-oxypyrazine-2-carboxylic acid

### 2.3.6 Ligands with one or two sulphonic acid groups



39

1,2-Dihydroxy-ethane-1,2-disulfonic acid



40

2,3-Dimercapto-1-propane-sulfonic acid

### 2.3.7 Ligands containing oxygen and sulphur atoms



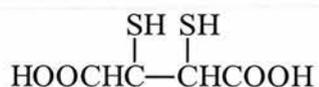
41

Disodium mercaptoacetate



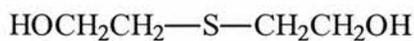
42

3-Mercaptopropionic acid



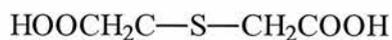
43

Meso-2,3-dimercaptosuccinic acid



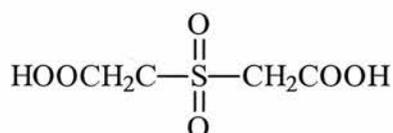
44

2,2'-Thiodiethanol



45

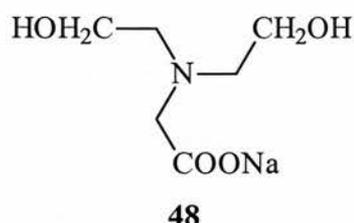
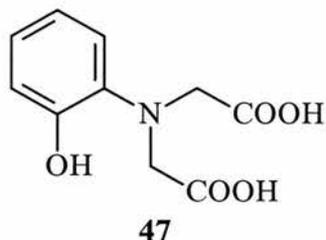
2,2'-Thiodiacetic acid



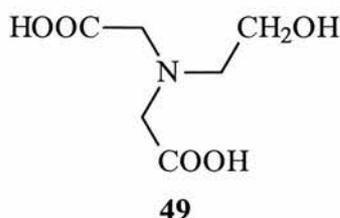
46

Sulfonyl-bis-acetic acid

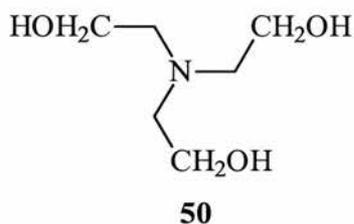
### 2.3.8 Analogues of NTA or EDTA



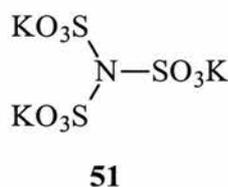
(2-Hydroxy-phenylimino)-di-acetic acid *N,N*-Di-(hydroxyethyl)glycine, sodium salt



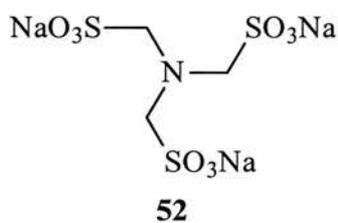
[carboxymethyl-(2-hydroxy-ethyl)-amino]-acetic acid



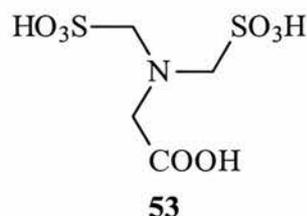
Triethanolamine



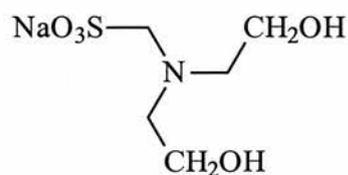
Potassium nitrosulphonate



Tris-sulphomethyl-amine, sodium salt

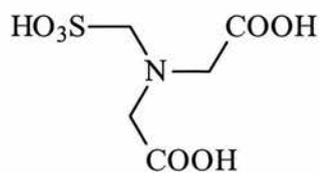


*N,N*-Bis-sulfomethyl-glycine



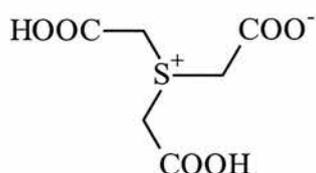
**54**

Sodium[bis(2-hydroxyethyl)amine]methanesulfonate



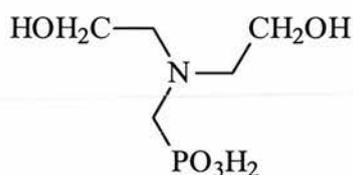
**55**

Sulfomethyliminodiacetic acid



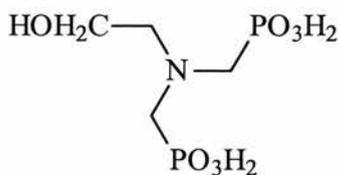
**56**

Tri-carboxymethylsulfonium-betaine



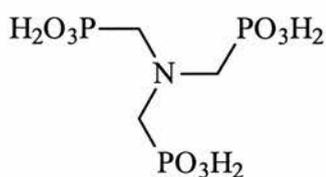
**57**

Bis-(hydroxy-ethyl)phosphono-methylamine



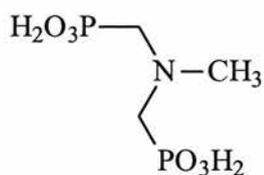
**58**

{[2-Hydroxyethyl]imino}bis(methylene)} bisphosphonic acid



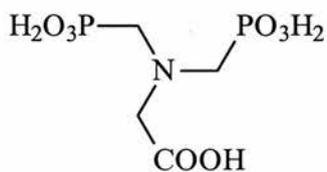
**59**

Nitrilo-trimethylenephosphonic acid (**NT3AP**)



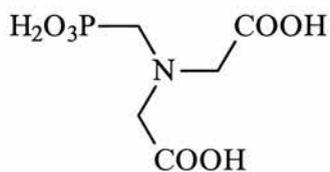
**60**

[(Methylphosphonomethylamino)methyl]phosphonic acid (**MeNTA2P**)



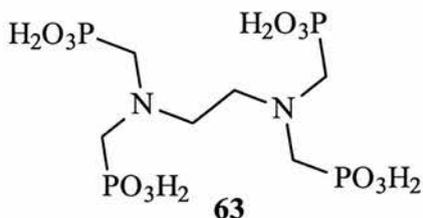
**61**

(Bis-phosphonomethylamino)acetic acid (**NTA2P**)

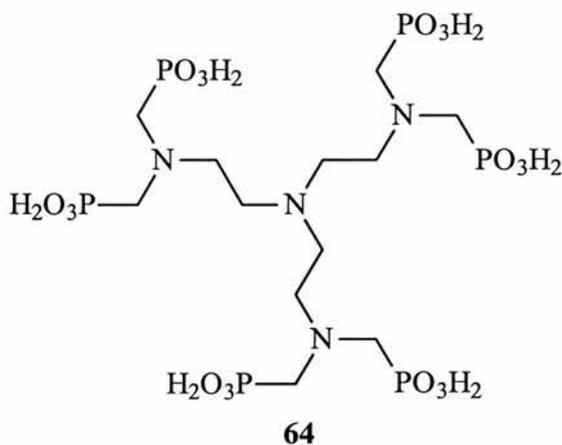


**62**

[(Phosphonomethyl)imino]diacetic acid (**NTAP**)

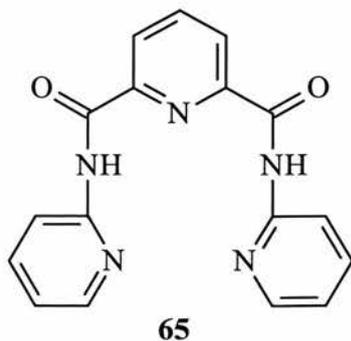


Ethylenediaminetetramethylenephosphonic acid (EDTA4P)

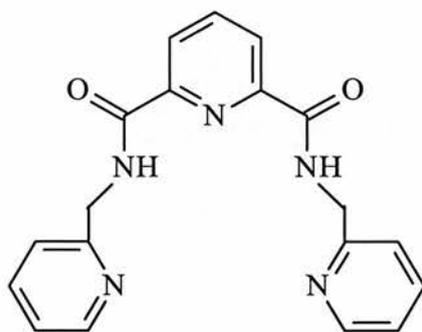


{[2- {Bis- [2- (bis-phosphonomethyl-amino)-ethyl]-amino }  
-ethyl)-phosphonomethyl-amino]-methyl}-phosphonic acid  
(NTA6P)

### 2.3.9 Carboxamide nitrogen ligands



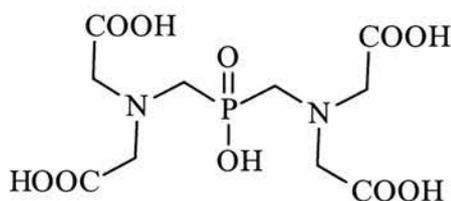
*N, N'*-Bis-(2-and 3-pyridine-2,6-pyridine dicarboxamide)



66

*N, N'*-Bis-[2-(2-pyridyl)methyl]pyridine-2,6-dicarboxamide

### 2.3.10 Ligand with amine phosphinate



67

Bis{[bis(carboxymethyl)amino]methyl} phosphinate (**BBCAMP**)

## ***Results and Discussion***

### ***2.4 Testing of the solubility and stability of Fe(III) complexes of ligands***

As an essential requirement for the aqueous alkaline Fe(III)/Fe(II) coordination processes, the complexes should dissolve in basic solution (pH 8.5 - 9.0) to form very stable solutions. Therefore the solubility and stability of Fe(III) complexes of ligands were first tested.

#### ***2.4.1 Fe(III) complexes of ligands containing one sulphur donor***

Fe(III) complexes of ligand **1** (ligand to iron molar ratio 3 : 1 and 6 : 1) only dissolved in acidic solution. When the solution was adjusted to pH  $\geq 7$ , a brown solid precipitated out immediately.

Fe(III) complexes of ligands **2** and **3** (ligand to iron molar ratio 3 : 1 and 6 : 1) are insoluble in either acidic solution or basic solution.

#### ***2.4.2 Fe(III) complexes of dithiocarbamates and related ligands***

There are a number of negatively charged ligands capable of coordinating *via* two sulphur atoms to a metal ion to form four, five or six-membered metal-complexes reported.<sup>148-152</sup> Ligands **4** - **11** are the typical representatives of this type of compounds. Their Fe(III) complexes are extensively studied largely because of their interesting magnetic properties.<sup>153-155</sup>

Fe(III) complexes of ligand **4** (ligand to iron molar ratio 2 : 1 and 3 : 1) are able to form brown solutions under the required basic condition (pH = 8.5 - 9.0). However, precipitates were found after storage at room temperature for one week. Sorbitol used as stabiliser did not improve the results. The cyano-group may have

limited the stabilities of Fe(III) complexes of ligand **4** in water, unfortunately, an attempt to convert the cyano group into carboxyl groups was unsuccessful.

Mixtures of Fe(III) and ligands **5 - 7** in 2 : 1 or 3 : 1 molar ratio only dissolved in an acidic medium to give slightly yellow solutions. As the pH was adjusted to the required basic condition (pH = 8.5 - 9.0), brown precipitates came out immediately.

The structure of ligand **8** is interesting. It contains two sulphur atoms and one carboxyl group, which tend to coordinate to transition metal ion to form stable complexes. However, Fe(III) complexes of ligand **8** (ligand to iron molar ratio 2 : 1 and 3 : 1) only dissolved in acidic medium, suspensions were obtained under basic condition (pH < 12). Surprisingly, when the pH values were adjusted to higher (pH ≥ 12), the suspension disappeared completely to form clear brown solutions. No precipitates were found when the solutions were re-adjusted to pH 8.5 - 9.0. However, brown solids were found to precipitate out from the solutions after storage at room temperature for one week. Addition of sorbitol did not improve the results.

Fe(III) complexes of ligands **9 - 10** (ligand to iron molar ratio 2 : 1 and 3 : 1) did not dissolve when pH ≤ 13. However, in stronger basic medium (pH > 13), the complexes gave stable and clear solutions. The solutions were still stable when re-adjusted to pH 8.5 - 9.0 and stored safely at room temperature.

Ligand **11** is known as a typical inorganic analogue of β-diketones.<sup>156</sup> Its Fe(III) complexes (ligand to iron molar ratio 2 : 1 and 3 : 1) did not dissolve in acidic medium. However, the complexes formed rather stable solutions in highly basic condition. Re-adjustment of the pH to 8.5 - 9.0 did not lead to any precipitation.

#### **2.4.3 Fe(III) complexes of ligands with only oxygen-donor groups**

Ligands containing oxygen donor atoms like the carboxylate group and the phenolate group are of interest for coordination chemistry in aqueous systems.<sup>157</sup> Ligands with several negatively charged oxygen donor groups, such as catecholates and phenolates, are also known to be a preferred ligands for Fe(III) in biological systems.<sup>158-161</sup> Fe(III) complexes of this type of ligands **12-18** (ligand to iron molar ratio 2 : 1 and 3 : 1) were found to form stable deep brown solutions in the required basic medium.

#### **2.4.4 Fe(III) complexes of Schiff Base ligands**

Condensation reactions of carbonyl compounds and primary amines have provided one of the most important and widely studied classes of chelating ligands -- Schiff base ligands. Gerlock has reported the preparation and isolation of the monomeric and dimeric of Fe(salen)<sub>n</sub>.<sup>162,163</sup>

Fe(III) complexes of ligands **19-24** (ligand to iron molar ratio 1 : 1, 2 : 1 and 3 : 1) were prepared. However, the complexes were absolutely insoluble in water. This precludes the possibility of the application of Schiff bases to aqueous desulphurization processes.

#### **2.4.5 Fe(III) complexes of heterocyclic donor atom ligands**

Ligands **25 - 28** look like good chelating agents. However, their Fe(III) complexes (ligand to iron molar ratio 2 : 1 and 3 : 1) only dissolved in highly acidic condition to form stable solutions. There were extensive precipitates when the pHs of the mixture solutions were raised to 4.0.

Ligand **29** was obtained from the hydrolysis of 2-hydroxyquinoline-8-sulphonyl chloride. Its Fe(III) complexes (ligand to iron molar ratio 2 : 1 and 3 : 1) only dissolved in highly acidic solution (pH less than 3).

Ligand **30** is closely similar in structure to that of 2,6-dicarboxypyridine. Its Fe(III) complexes (ligand to iron molar ratio 2 : 1 and 3 : 1) dissolved in basic condition. The higher the pH, the better the solubility. Their strong basic solutions (pH up to 14) were stored for one month without any precipitation.

Ligand **31** containing four nitrogen atoms and one mercapto group seems to be a good chelating agent. Actually, its Fe(III) complex (ligand to iron molar ratio 2 : 1 or 3 : 1) dissolved in strong acidic solution (pH less than 4.0). A yellow suspension appeared when the pH of the mixture was adjusted to 12. However, further increase of the pH value led to the re-dissolving of the suspensions once the pH was over 12. The solutions could be safely readjusted to pH 8.5 - 9.0 and stored for a long time.

Ligand **32** and Fe(III) (ligand to iron molar ratio 2 : 1 and 3 : 1) gave complexes which were soluble in pH  $\geq$  13 solution. The solutions could be safely re-adjusted to pH 8.5 - 9.0 without precipitation.

Fe(III) complexes of ligands **33** - **38** (ligand to iron molar ratio 2 : 1 and 3 : 1) only dissolved in acidic medium (pH less than 5.0).

#### **2.4.6 *Fe(III) complexes of ligands with one or two sulphonic acids groups***

Fe(III) complexes of ligand **39** (ligand to iron molar ratio 1 : 1 and 2 : 1) were stable in strong basic medium (pH  $\geq$  13). The solutions could be re-adjusted to pH 8.5 - 9.0 without precipitation.

Fe(II) complex of ligand **40** has been used as an absorbent to absorb NO efficiently in aqueous solution to form a very stable iron nitrosyl complex.<sup>164-166</sup> This prompted us to try the Fe(III)/Fe(II) complexes as catalysts for the oxidation of H<sub>2</sub>S to sulphur by air. Fe(III) complex of this ligand (ligand to iron molar ratio 1 : 1 and 2 : 1) dissolved perfectly in water in a wide range of pH value (pH 1-14) to give a stable black solutions.

#### ***2.4.7 Fe(III) complexes of containing oxygen and sulphur atoms***

Both **41** and **42** are bidentate ligands. Mixture of Fe(III) and ligands **41** or **42** (ligand to iron molar ratio 2 : 1 and 3 : 1) formed stable solutions in the required basic medium.

Ligand **43**, which contains two SH groups and two COOH groups, is a powerful chelating agent for transition metals. Its Fe(III) complexes (ligand to iron molar ratio 1 : 1 and 2 : 1) were highly soluble in a wide range of pH (1-14) to give stable deep dark solutions.

Compounds **44** and **45** are tridentate chelating agents. Fe(III) complexes of ligands **44** or **45** (ligand to iron molar ratio 2 : 1 and 3 : 1) were soluble in pH  $\geq$  13 solution. And it was safe to adjust the pH to 8.5 - 9.0 without any precipitation.

Ligand **46** was made from the oxidation of thiodiacetic acid. Fe(III) complexes of ligand **46** (ligand to iron molar ratio 2 : 1 and 3 : 1) dissolved in highly basic condition to form stable black solution. The mixture could be re-adjusted to pH 8.5 - 9.0 and stored for several months without precipitation.

#### 2.4.8 Fe(III) complexes of analogues of NTA or EDTA

Fe(III) complexes of ligands **47 - 50** (ligand to iron molar ratio 1 : 1 and 2 : 1) dissolved in the required pH 8.5 - 9.0 aqueous medium to give very stable red solutions.

Both ligands **51** and **52** contain three sulphonyl groups. Although the mixtures of Fe(III) and ligands **51** or **52** (ligand to iron molar ratio 1 : 1 and 2 : 1) did not dissolve in acidic medium, they dissolved in the required pH 8.5-9.0 aqueous medium to afford stable red solutions and are worthwhile for further testing.

Fe(III) complexes of ligands **53 - 55** (ligand to iron molar ratio 1 : 1 and 2 : 1) exhibited different solubilities at different pH values. They formed deep red solutions at  $\text{pH} \leq 8$ , brown suspensions in the range of pH 8.0 - 11.0, and dissolved again at high pH ( $\geq 11.0$ ). Readjustment of the highly basic solution to pH 8.5 - 9.0 gave the stable solution.

Fe(III) complexes of ligand **56** (ligand to iron molar ratio 2 : 1 and 3 : 1) dissolved at high pH value solutions. No precipitates were found when re-adjusted to pH 8.5 - 9.0.

Compounds **57 - 64** are the phosphonate ligands. Aminoalkylphosphonic acids are broadly defined as amino acid analogues in which the carboxylic function is replaced by one or poly-phosphonic functions or related function. Aminopolyphosphonic acids and their derivatives have also received considerable attention because of their interesting biological activity.<sup>167-169</sup> Metal aminophosphonate (aminopolyphosphonate) chemistry is attracting increasing interest because the variety of properties that can be introduced via the phosphonate

ligands. A number of studies have been reported on the complex formation of such *N*-bonded mixed acetic-methyl-phosphonic acids with the alkaline-earth metal ions such as  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  or  $Ba^{2+}$  and the divalent transition metal ions such as  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , or  $Cd^{2+}$ .<sup>170-184</sup>

Although metal complexes of aminophosphonic acids have been studied fairly extensively in solution,<sup>185-191</sup> Fe(III) complexes of this type of ligands have not been investigated as catalysts yet. In addition, the number of negative charge of these ligands is higher than that of the corresponding aminopolycarboxylates such as NTA or EDTA. Therefore, it would be interesting to try these Fe(III) / Fe(II) complexes as catalysts for the oxidation of hydrogen sulphide to sulphur by air.

All the Fe(III) complexes of ligands **57** - **62** (ligand to iron molar ratio 1 : 1 and 2 : 1), **63** and **64** (ligand to iron molar ratio 1 : 1) dissolved in the required pH 8.5 - 9.0 medium to give stable solutions.

#### **2.4.9 Fe(III) complexes of carboxamido nitrogens ligands**

Investigation of the coordination chemistry of Fe(III) with nonmacrocyclic chelating ligands containing pyridine amide functionality have received much attention in recent years.<sup>192-195</sup> For a long time, such coordination had been assumed to be improbable since Fe(III) precipitates out at pH values which are much lower than that required for the formation of the deprotonated carboxamido donor center.<sup>196</sup> However, during last decades, the stable Fe(III) complexes with coordinated carboxamido nitrogens have been characterized structurally.<sup>197-202</sup> It now appears that anionic carboxamido nitrogen donors are good donors for Fe(III)<sup>203</sup> and Fe(III)

complexes with even four such nitrogen donors can be synthesized quite readily.<sup>192,</sup>

202

Therefore, Fe(III) complexes of ligands **65** and **66** were synthesized by following the published procedure.<sup>193</sup> A solution of 36 mmol of ligand (11.46 g for ligand **65** and 13.05 g for ligand **66**) and 1.73 g (72 mmol) of NaH in 25 cm<sup>3</sup> of DMF was slowly added to a solution of 14.28 g (18 mmol) of [Fe(DMF)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> in 25 cm<sup>3</sup> of DMF. The resultant orange red solution was stirred for 3 hours, and then the solvent was removed under vacuum. The red solid, which was obtained without further washing, was dissolved in the strongly acidic medium to form a very stable deep red solution. However, a brown solid immediately precipitated out when the solution were adjusted to pH ≥ 6.0.

#### **2.4.10 Fe(III) complexes of ligand with amine phosphinate**

As part of a series of amine phosphinate compounds, ligand **67**, bis{[bis(carboxymethyl)amino]methyl}phosphinate (BBCAMP), was first synthesized by Maier.<sup>204</sup> Amine phosphinates are generally thought to be less coordinating at neutral pH than amine carboxylates or amine phosphonates because of the low basicity of the phosphinates.<sup>205,206</sup> However, BBCAMP does not form stable metal complexes in aqueous solution.<sup>207</sup> In a continuing quest for new chelating ligands, we rediscovered this old ligand whose close resemblance to EDTA demands attention. Interestingly, Fe(III) complex of ligand **67** (ligand to iron molar ratio 1 : 1) formed very stable and red solution in the required pH 8.5 - 9.0 medium.

## 2.5 Preliminary test of the catalytic activity

Based on the above observation of solubility and stability, the Fe(III) complexes of ligands **10 - 18**, **30 - 32**, **39 - 64** and **67**, which are stable in the required basic solution (pH 8.5 - 9.0), were tested by a simple method for the catalytic oxidation of sodium hydrogen sulphide to sulphur by air. The results are listed in **Table 2.1**.

As shown in **Table 2.1**, Fe(III) complexes of ligands **11**, **41** and **42** have no catalytic activities at all for the oxidation of sodium hydrogen sulphide to sulphur by air. For ligands **41** and **42**, the black suspensions of FeS, which were formed by addition of sodium hydrogen sulphide, did not disappear and no sulphur was found when air was bubbled into the mixture solution. Ligand **11** is a very tricky one. To a solution of Fe(III) complex of ligand **11** (pH = 8.5) was added NaSH to form a black suspension. When air was bubbled in, the dark suspension immediately disappeared and white solid precipitated out quickly, the solution became clear again. The white solid was initially presumed to be sulphur. However, analysis of the white solid by HPLC displayed no sulphur peak, and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum confirmed that it is the starting ligand **11** ( $\delta_{\text{p}}$  69 ppm). This means that its complex decomposed rapidly in this process and has no catalytic ability at all for the oxidation of  $\text{HS}^-$  to sulphur.

**Table 2.1** Catalytic activities of Fe(III) complexes for oxidation of NaSH to S

Ligand	L : Fe (molar ratio)	Added NaSH (g)	Sulphur Formation	Observation and Comments
<b>10</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Grey sulphur formed and blue suspension became clear
<b>11</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	No	White ligand precipitated out, solution became very clear
<b>12</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, the mixture became opaque, some dark solid precipitated together with sulphur, complex decomposed obviously
<b>13</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspensions solution disappeared, the mixture became opaque, some dark solid precipitated together with sulphur, complex decomposed visually
<b>14</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Deep dark suspension disappeared, the mixture became opaque, a lot of brown solid precipitated together with sulphur
<b>15</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, the mixture became opaque, a lot of dark solid precipitated together with sulphur
<b>16</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Dark suspension disappeared, the mixture became opaque, black solid precipitated together with sulphur

**Table 2.1** Catalytic activities of Fe(III) complexes for oxidation of NaSH to S  
(continued)

Ligand	L : Fe (molar ratio)	Added NaSH (g)	Sulphur Formation	Observations and Comments
<b>17</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Deep green suspension disappeared, the mixture became opaque, some black solid precipitated together with sulphur, complex decomposed obviously
<b>18</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, the mixture became opaque, some dark solid precipitated together with sulphur, complex decomposed obviously
<b>30</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, the mixture solution became clear
<b>31</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, the reactant solution became clear
<b>32</b>	2 : 1 or 3 : 1	0.37 <sup>a</sup>	Yes	Disappearance of black suspension too slow, and sulphur formation too few, the resultant solution became opaque
<b>39</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, solution became opaque, some black solid precipitated together with sulphur, complex obviously decomposed

**Table 2.1** Catalytic activities of Fe(III) complexes for oxidation of NaSH to S  
(continued)

Ligand	L : Fe (molar ratio)	Added NaSH (g)	Sulphur Formation	Observations and Comments
<b>40</b>	1 : 1 or 2 : 1	0.50 <sup>b</sup>	Yes	Black suspension disappeared, grey sulphur came out, and the reactant solution became clear
<b>41</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	No	Black suspension remained
<b>42</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	No	Black suspension remained
<b>43</b>	1 : 1 or 2 : 1	0.57 <sup>b</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>44</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>45</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>46</b>	2 : 1 or 3 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>47</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared very slowly. Some darkly stick solid came out together with grey sulphur. That means that complex decomposed

**Table 2.1** Catalytic activities of Fe(III) complexes for oxidation of NaSH to S  
(continued)

Ligand	L : Fe (molar ratio)	Added NaSH (g)	Sulphur Formation	Observations and Comments
<b>48</b>	1 : 1 or 2 : 1	0.51 <sup>b</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>49</b>	1 : 1 or 2 : 1	0.50 <sup>b</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>50</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared very slowly. Sulphur came out very slowly, too
<b>51</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>52</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>53</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>54</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>55</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear

**Table 2.1** Catalytic activities of Fe(III) complexes for oxidation of NaSH to S  
(continued)

Ligand	L : Fe (molar ratio)	Added NaSH (g)	Sulphur Formation	Observations and Comments
<b>56</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>57</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>58</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>59</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>60</b>	1 : 1 or 2 : 1	0.30 <sup>a</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>61</b>	1 : 1 or 2 : 1	1.20 <sup>d</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>62</b>	1 : 1 or 2 : 1	3.00 <sup>e</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>63</b>	1 : 1	0.90 <sup>c</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear

**Table 2.1** Catalytic activities of Fe(III) complexes for oxidation of NaSH to S  
(continued)

Ligand	L : Fe (molar ratio)	Added NaSH (g)	Sulphur Formation	Observations and Comments
<b>64</b>	1 : 1	1.20 <sup>d</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear
<b>67</b>	1 : 1	0.60 <sup>b</sup>	Yes	Black suspension disappeared, grey sulphur came out, and solution became clear

<sup>a</sup> Added in one portion; <sup>b</sup> Added in two portions; <sup>c</sup> Added in three portions; <sup>d</sup> Added in four portions; <sup>e</sup> Added in ten portions.

In the cases of Fe(III) complexes of ligands **12-18** and **39** there was sulphur found to some extent which were confirmed by HPLC, but meanwhile, the reactant solution became rather opaque, sometimes dark or brown solid other than sulphur precipitated out. This suggested that the complexes of Fe(III) are unsuitable for the catalytic oxidation of HS<sup>-</sup> to sulphur by air.

For ligands **32**, **47** and **50**, however, there were little sulphur found in the processes, the dark suspension disappeared rather slowly. It took a long time to recover its initial colour of the starting solution. This implies that Fe(III) complexes of these ligands do not show enough catalytic activities for the oxidation of HS<sup>-</sup> to sulphur.

Fe(III) complexes of ligands **10**, **30**, **31**, **40**, **43 - 46**, **48**, **49**, **51 - 64** and **67** look encouraging, further testing on these ligands was proceeded for the oxidation of H<sub>2</sub>S to sulphur by air in 1-liter reactor continuously.

## **2.6 Further testing of the catalytic activity for the oxidation of H<sub>2</sub>S to sulphur by air**

Further testings of catalytic activities of Fe(III) complexes of ligands **10, 30, 31, 40, 43 - 46, 48, 49, 51 - 64** and **67** have been carried out in a 1-liter reactor continuously. The results are listed in **Table 2.2**.

Although Fe(III) complexes of ligands **10, 30, 31, 40, 43 - 46, 48, 49, 51 - 58** and **63** exhibit catalytic activities to different extents, the rapid degradation of the ligands and the poor stabilities of the Fe(III) complexes in the processes are found to be the common setbacks. It is apparent that the Fe(III) complexes of these ligands are not suitable as catalysts for the oxidation of hydrogen sulphide to sulphur by air.

On the other hand, ligands **59, 60 - 62, 64** and **67** seem quite promising, all were consequently further investigated and compared with NTA.

**Table 2.2** Air oxidation of H<sub>2</sub>S to sulphur catalysed by Fe(III) complexes  
 ([Fe] = 18 mmol)

Ligand	L:Fe (molar ratio)	H <sub>2</sub> S Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	Air Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	pH	Test Time (h)	Results and Comments
10	2 : 1	2.00	700	8.5	5	Black suspension remained, little sulphur and severe tail gas
30	2 : 1	2.00	700	8.5	15.5	Yellow suspension, severe tail gas and little sulphur
31	2 : 1	2.00	700	8.5	5	Black suspension remained, severe tail gas and very little sulphur
40	2 : 1	2.00	700	8.5	15	Black suspension remained, severe tail gas and little sulphur
43	3 : 1	2.00	700	8.5	20	Milk suspension, severe tail gas and little sulphur
44	2 : 1	2.00	700	8.5	8	Reactant solution became suspension and the system lost activity
45	2 : 1	2.00	700	8.5	7	Reactant solution became suspension, complex decomposed quickly

**Table 2.2** Air oxidation of H<sub>2</sub>S to sulphur catalysed by Fe(III) complexes  
 ([Fe] = 18 mmol) (continued)

Ligand	L:Fe (molar ratio)	H <sub>2</sub> S Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	Air Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	pH	Test Time (h)	Results and Comments
<b>46</b>	2 : 1	2 : 1	700	8.5	8	The solution became opaque, the complex decomposed quickly
<b>48</b>	2 : 1	2.00	700	8.5	60	The system only worked for 60 hours. The reactant solution became deep dark and FeS was formed gradually
<b>49</b>	2 : 1	2.00	700	8.5	51.3	The complex was deactivated in 50 hours. The reactant solution became opaque and dark precipitate FeS was found. The complex degraded gradually
<b>51</b>	2 : 1	2.00	700	8.5	10.5	Brown suspension, severe tail gas and little sulphur
<b>52</b>	2 : 1	2.00	700	8.5	7	Brown suspension, severe tail gas and little sulphur
<b>53</b>	2 : 1	2.00	700	8.5	21.5	Deep brown solution, no sulphur. Severe tail gas was found in 21 hours

**Table 2.2** Air oxidation of H<sub>2</sub>S to sulphur catalysed by Fe(III) complexes  
 ([Fe] = 18 mmol) (continued)

Ligand	L:Fe (molar ratio)	H <sub>2</sub> S Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	Air Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	pH	Test Time (h)	Results and Comments
54	2 : 1	2.00	700	8.5	13	Deep brown became opaque, severe tail gas was found in 11 hours
55	2 : 1	2.00	700	8.5	22.5	Severe tail gas and black solution were found after 15 hour in the process. The complex decomposed very rapidly
56	2 : 1	2.00	700	8.5	20	Brown suspension, severe tail gas and little sulphur were found
57	2 : 1	2.00	700	8.5	20	Dark green solution, severe tail gas was found in 9 hours and the reactant solution became suspension
58	2 : 1	2.00	700	8.5	25.5	Very severe tail gas in 25 hour. The colour of the reactant solution became deep dark from brown
59	2 : 1	2.00	700	8.5	100	A lot of sulphur, trace tail gas

**Table 2.2** Air oxidation of H<sub>2</sub>S to sulphur catalysed by Fe(III) complexes  
([Fe] = 18 mmol) (continued)

Ligand	L:Fe (molar ratio)	H <sub>2</sub> S Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	Air Flow Rate (cm <sup>3</sup> min <sup>-1</sup> )	pH	Test Time (h)	Results and Comments
<b>60</b>	2 : 1	2.00	700	8.5	10 0	A lot of sulphur, trace tail gas
<b>61</b>	2 : 1	2.00	700	8.5	100	A lot of sulphur, trace tail gas
<b>62</b>	2 : 1	2.00	700	8.5	200	A lot of sulphur, no tail gas
<b>63</b>	1 : 1	2.00	700	8.5	4.5	Very severe tail gas and opaque black suspension
<b>64</b>	1 : 1	2.00	700	8.5	70	A lot of sulphur, trace tail gas
<b>67</b>	1 : 1	2.00	700	8.5	105	A lot of sulphur, no tail gas

### 2.7 Comparison investigation of the catalytic activities of iron complexes of ligands of 59 - 62, 64 and 67 against NTA

Since ligands **59 - 62, 64** and **67** show good results in the continuous test in 1-litre reactor, their Fe(III) complexes were further investigated in details concerning the conversion of hydrogen sulphide to sulphur, tail gas, the conversion of H<sub>2</sub>S to S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> and the half life and degradation of ligands. The results were compared with that of NTA.

Direct analyses of ligands **59 - 62, 64** and **67** with the absorbed solutions by  $^{31}\text{P}\{-^1\text{H}\}$  NMR were unsuccessful due to the paramagnetic properties of their Fe(III) complexes. Indirect analyses of ligands **59 - 62, 64** and **67** by  $^{31}\text{P}\{-^1\text{H}\}$  NMR by addition of excess boric acid and NaOH to the absorbed solutions to precipitate iron ions and to release the ligands and their related components of degradation has been developed successfully. The analyses of NTA and its corresponding degradation components were carried out directly according to the previous reported HPLC method.<sup>208</sup> The conversions of  $\text{H}_2\text{S}$  to S,  $\text{H}_2\text{S}$  to  $\text{CuS}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$ , and the loss rate of iron ion are defined as follows:

$$\text{Conversion of } \text{H}_2\text{S} \text{ to S} = \frac{[\text{H}_2\text{S}]_{\text{S}}}{[\text{H}_2\text{S}]_{\text{S}} + [\text{H}_2\text{S}]_{\text{S}_2\text{O}_3} + [\text{H}_2\text{S}]_{\text{SO}_4} + [\text{H}_2\text{S}]_{\text{CuS}}} \times 100 \%$$

$$\text{Conversion of } \text{H}_2\text{S} \text{ to } \text{S}_2\text{O}_3^{2-} = \frac{[\text{H}_2\text{S}]_{\text{S}_2\text{O}_3}}{[\text{H}_2\text{S}]_{\text{S}} + [\text{H}_2\text{S}]_{\text{S}_2\text{O}_3} + [\text{H}_2\text{S}]_{\text{SO}_4} + [\text{H}_2\text{S}]_{\text{CuS}}} \times 100 \%$$

$$\text{Conversion of } \text{H}_2\text{S} \text{ to } \text{SO}_4^{2-} = \frac{[\text{H}_2\text{S}]_{\text{SO}_4}}{[\text{H}_2\text{S}]_{\text{S}} + [\text{H}_2\text{S}]_{\text{S}_2\text{O}_3} + [\text{H}_2\text{S}]_{\text{SO}_4} + [\text{H}_2\text{S}]_{\text{CuS}}} \times 100 \%$$

$$\text{Conversion of } \text{H}_2\text{S} \text{ to } \text{CuS} = \frac{[\text{H}_2\text{S}]_{\text{CuS}}}{[\text{H}_2\text{S}]_{\text{S}} + [\text{H}_2\text{S}]_{\text{S}_2\text{O}_3} + [\text{H}_2\text{S}]_{\text{SO}_4} + [\text{H}_2\text{S}]_{\text{CuS}}} \times 100 \%$$

$$\text{Loss rate of iron} = \frac{[\text{Fe}]_{\text{starting solution}} - [\text{Fe}]_{\text{resulting solution}}}{[\text{Fe}]_{\text{starting solution}}} \quad (\text{mg} / \text{L} / \text{h})$$

Where  $[H_2S]_S + [H_2S]_{CuS} + [H_2S]_{S_2O_3} + [H_2S]_{SO_4}$  represents the total amounts of the consumption of  $H_2S$  which is converted into S, CuS,  $S_2O_3^{2-}$  and  $SO_4^{2-}$ .  $[Fe]$  represents the total concentration of  $Fe^{3+}$  ion and  $Fe^{2+}$  ion in the absorbed solution.

The  $\delta p$  of ligands **59 - 62**, **64** and **67** and their corresponding phosphorus-containing decomposition components are listed in **Table 2.3**. Since the  $\delta p$  of the ligands depends on the basicity of the aqueous solution, all the spectra were recorded at pH 13.

Signals were assigned to the proposed phosphorus-containing degradation compounds by comparing with known compounds. The quantitative calculations of the ligands and its corresponding phosphorus-containing degradation components were carried out by addition of an internal standard  $HOOCCH_2PO_3H_2$  to the sample solution before the removals of Fe(III) and Fe(II) ions. Peak area ratios of each ligand and its corresponding phosphorus-containing degradation components relative to the internal standard  $HOOCCH_2PO_3H_2$  were obtained as the values for quantitative calculation for each special sample which was taken from the absorbed solution with regular intervals of reaction time. The final calculations of the percent of the ligand and its phosphorus-containing degradation components for the same Fe(III) complex, which has been tested for hours, are based on the peak area ratio of the ligand of the starting solution relative to the internal standard  $HOOCCH_2PO_3H_2$ , which is assigned arbitrarily to be 100 %. The peak area ratio and the percent of the ligand and its phosphorus-containing degradation components are defined as follows:

$$\text{Peak area ratio (R)} = \frac{H_t}{H_s} \times \frac{C_s}{C_t}$$

$$\text{Percent of component (\%)} = \frac{R_t}{R_0} \times 100$$

Where R represents the peak area ratios of the ligands and their corresponding phosphorus-containing degradation components in the sample taken from the absorbed solution relative to the internal standard  $\text{HOOCCH}_2\text{PO}_3\text{H}_2$ .  $H_t$  and  $H_s$  are the practical peak area ( $\text{mm}^2$ ) of the  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR of the sample and the standard internal compound, respectively.  $C_s$  and  $C_t$  stand for the concentrations (mM) of the standard internal compound and the sample, respectively.  $R_0$  is the peak area ratio of the ligand of the starting solution relative to the internal standard  $\text{HOOCCH}_2\text{PO}_3\text{H}_2$ .

**Table 2.3**  $^{31}\text{P}\{-^1\text{H}\}$  NMR of ligands **59** - **62**, **64** and **67** as well as the decomposed compounds [a. in strong basic solution (pH = 13); b. the quantitative calculation peak; c. internal standard]

Compounds	Formula	Abbreviation	$^{31}\text{P}\{-^1\text{H}\}$ NMR ( $\delta_p$ , ppm)
<b>59</b>	$\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3$	NTA3P	17.8 <sup>a,b</sup>
<b>60</b>	$\text{MeN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$	MeNTA2P	14.1 <sup>a,b</sup>
<b>61</b>	$\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2\text{CH}_2\text{COOH}$	NTA2P	17.5 <sup>a,b</sup>
<b>62</b>	$\text{N}(\text{CH}_2\text{COOH})_2\text{CH}_2\text{PO}_3\text{H}_2$	NTAP	17.0 <sup>a,b</sup>
<b>64</b>	$\text{N}[(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2)_3]$	NTA6P	18.1 <sup>a,b</sup>
<b>67</b>	$(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{P}(\text{O})(\text{OH})\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$	BBCAMP	18.8 <sup>a,b</sup>
Decomposed component	$\text{HOOCCH}_2\text{NCH}_2\text{PO}_3\text{H}_2$		17.6 <sup>a</sup>
Decomposed component	$\text{H}_2\text{NCH}_2\text{PO}_3\text{H}_2$		20.2 <sup>a</sup>
Decomposed component	$\text{HOOCPO}_3\text{H}_2$		1.0 <sup>a</sup>
Decomposed component	$\text{H}_3\text{PO}_4$		5.4 <sup>a</sup>
Decomposed component	$\text{H}_3\text{PO}_3$		3.3 <sup>a</sup>
Internal standard	$\text{HOOCCH}_2\text{PO}_3\text{H}_2$ <sup>c</sup>		15.6 <sup>a</sup>

**Table 2.4** Catalytic activities of Fe(III) complexes of ligands **59** - **62**, **64** and **67** on the conversion of H<sub>2</sub>S to S and by products, compared with NTA

Ligand	NTA	59 NTA3P	60 MeNTA2P	61 NTA2P
Test time (h)	100	50	100	100.5
L : Fe (molar ratio)	2 : 1	2 : 1	3 : 1	2 : 1
Conversion of H <sub>2</sub> S to S (%)	92.8	67.4	71.3	76.6
Conversion of H <sub>2</sub> S to CuS (%)	0	0.1	1.2	13.6
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	1.8	17.9	5.4	4.1
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	5.4	14.6	22.0	5.7
Loss rate of iron (mg/L/h)	0.75	22.59	2.64	1.47
Half life of ligand (h)	39.8	27.8	49.4	57.1

**Table 2.4** Catalytic activities of Fe(III) complexes of ligands **59 - 62, 64** and **67** on the conversion of H<sub>2</sub>S to S and by products, compared with NTA (continued)

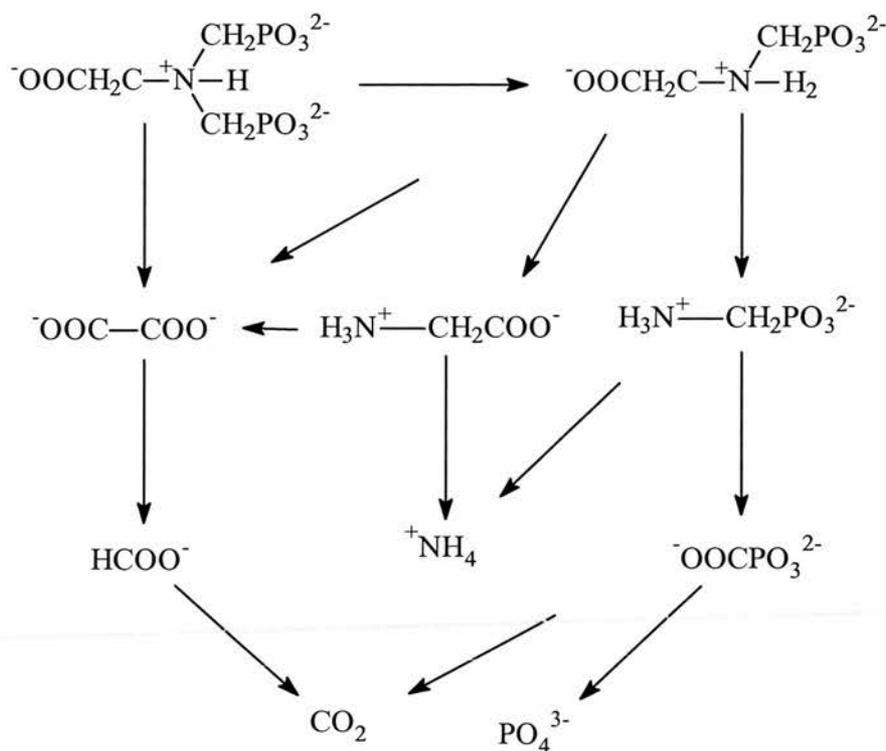
Ligand	NTA	62 NTAP	64 NTA6P	67 BBCAMP
Test time (h)	100	100	50	105
L : Fe (molar ratio)	2 : 1	2 : 1	1.1 : 1	1.1 : 1
Conversion of H <sub>2</sub> S to S (%)	92.8	93.4	79.8	80.9
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0.1	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	1.8	3.4	15.5	16.1
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	5.4	3.2	4.6	3.0
Loss rate of iron (mg/L/h)	0.75	0.90	0.44	0.33
Half life of ligand (h)	39.8	50.5	160.8	53.5

The comparative results on the catalytic activities of Fe(III) complexes of ligands **59** - **62**, **64** and **67** against NTA are listed in **Table 2.4**. Poor conversion rate of H<sub>2</sub>S to S and the extensive formation of by products are found for the Fe(III) complexes of all the potential ligands apart from ligand **62**. The severe iron ion loss and trace tail gas for the systems involving ligands **59** - **61** proved that the catalytic activities and the stabilities of the Fe(III) complexes of ligands **59**, **60** and **61** are worse than NTA. Even more loss of iron was found when ligand **59** was used. Although less loss of iron in the cases of ligands **64** and **67** than NTA is found, the catalytic activities proved to be poor. Surprisingly, ligand **62** shows highly efficient conversion of hydrogen sulphide to sulphur while rather low conversion of H<sub>2</sub>S to S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>. It also displays longer lifetime than NTA. All these factors make ligand **62** a potential alternative of NTA for the oxidation of hydrogen sulphide to sulphur by air.

### **2.8 Studies of degradation of the ligands**

The degradation rate and half-life of ligands **59** - **62**, **64**, **67** and NTA (only used as comparison) with different ligand to iron molar ratio are illustrated in **Table 2.5**. Monitoring by <sup>31</sup>P-<sup>1</sup>H} NMR revealed the continuous decrease of the ligand and progressive formation of degradation products during the process. For Fe(III) complexes of ligand **59** with ligand to iron molar ratio of 1 : 1 and 2 : 1, the half life of ligand is only 13.7 hours and 27.8 hours respectively, both shorter than the corresponding values of NTA (18.7 hours and 36.3 hours) under the same conditions. This means that ligand **59** decomposed more rapidly than NTA. The half-life of ligands **60** - **62**, **64** and **67** are longer than that of NTA under the same conditions.

In fact, the half-life of a ligand also depends upon ligand to iron molar ratio. Higher ligand to iron molar ratio shows longer half-life of a ligand. In addition, there is another interesting phenomenon worth mentioning, that is, the longer the testing runs, the longer the half life of the ligand is. This can be explained since longer running of the experiment testing produced more  $S_2O_3^{2-}$  which is known to be an effective scavenger of hydroxyl radical or other free radicals in the process.



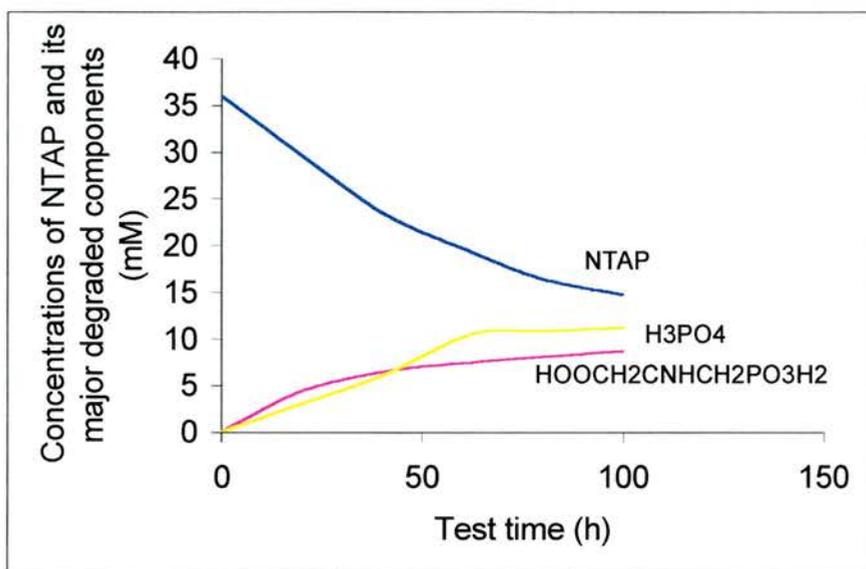
**Scheme 2.1** Proposed degradation scheme for ligand 62 NTAP

**Table 2.5** Relative degradation rates and half life of ligands

Ligand	Ligand to Iron Molar Ratio	Iron (mM)	Test Duration (h)	1 <sup>st</sup> Order Rate Constant of Ligand Degradation (h <sup>-1</sup> )	Half Life of Ligand (h)
NTA	1.1 : 1	18	50	0.0371	18.7
NTA	2.0 : 1	18	50	0.0191	36.3
NTA	2.0 : 1	18	100	0.0174	39.8
<b>59</b> NTA3P	2.0 : 1	18	50	0.0249	27.8
<b>59</b> NTA3P	1.1 : 1	18	50	0.0506	13.7
<b>60</b> MeNTA2P	2.0 : 1	18	50	0.0181	38.3
<b>60</b> MeNTA2P	3.0 : 1	18	50	0.0140	49.4
<b>60</b> MeNTA2P	3.0 : 1	18	100	0.0147	47.2
<b>61</b> NTA2P	1.1 : 1	18	50	0.0159	31.5
<b>61</b> NTA2P	2.0 : 1	18	100	0.0121	57.1
<b>62</b> NTAP	1.1 : 1	18	50	0.0182	38.0
<b>62</b> NTAP	2.0 : 1	18	100	0.0137	50.5
<b>64</b> NTA6P	1.1 : 1	18	50	0.0043	160.8
<b>67</b> BBCAMP	1.1 : 1	18	105	0.0130	53.5

Similar to the degradation of NTA, a mechanism of degradation of ligand **62** is proposed as in **Scheme 2.1**. The oxidation and cleavage of the acetate and the methylene phosphonate groups lead to the formation of a series of lower molecular weight compounds. However, only phosphorus-containing intermediates can be measured by  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR. The non-phosphorus-containing intermediates were not determined. The degradation products have also been reported as oxidation products when compound **62** was oxidised by molecular oxygen in the presence of manganese<sup>209</sup> and as biodegradation products when compound **62** was decomposed by micro-organisms from industrial activated sludge.<sup>210</sup>

**Fig. 2.1** and **Table 2.6** show the relationship between the concentration of NTAP and its major degradation products versus time in the absorption process. In the early stage of the testing,  $\text{HOOCCH}_2\text{N}(\text{H})\text{CH}_2\text{PO}_3\text{H}_2$ , the main degradation product, increased rapidly while NTAP decreased sharply. In about 70 hours, the increase of  $\text{HOOCCH}_2\text{N}(\text{H})\text{CH}_2\text{PO}_3\text{H}_2$  and the decrease of NTAP became steady. However, in the whole process the eventual degradation product,  $\text{H}_3\text{PO}_4$  increased progressively with the increase of the reaction time. The  $\text{HOOCCH}_2\text{N}(\text{H})\text{CH}_2\text{PO}_3\text{H}_2$  obviously decomposed further into smaller molecules until eventually to  $\text{H}_3\text{PO}_4$ ,  $\text{CO}_3^{2-}$  and  $\text{NH}_4^+$ .



**Fig. 2.1** Curves of the degradation of NTAP and the formation of its major degraded components in the Fe(III)-NTAP

**Table 2.6** Concentration of ligand **62** NTAP and its major decomposition products versus time

Time (h)	<b>62</b> NTAP (mM)	HOOCH <sub>2</sub> NHCH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub> (mM)	H <sub>3</sub> PO <sub>4</sub> (mM)
0	36.00	0	0
20	29.70	4.34	3.01
41	23.32	6.50	6.21
62.5	19.28	7.47	10.51
80	16.40	8.05	10.80
100	14.72	8.71	11.20

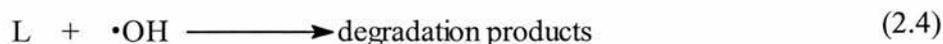
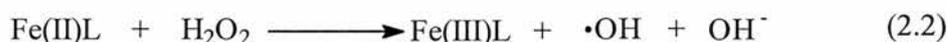
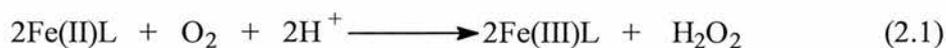
**Table 2.7** shows the detailed comparison of ligand **60 - 62** against NTA in terms of commercial practicality. Low consumption of ligand per kg sulphur recovery was found in the case of ligand **62** (394.3 g of NTAP / per kg of sulphur). This number was even lower than that of NTA (528.0 g of NTA per kg of sulphur). In addition, the conversion of H<sub>2</sub>S to sulphur for ligand **62** (93.3 %) is also comparable with NTA (92.9 %). If the commercial price of NTAP were close to that of NTA, NTAP would be a good alternative to NTA. However, NTAP is more expensive than NTA according to Aldrich (2002-2003) catalogue.

**Table 2.7** Comparison of ligands **60 - 62** against NTA without the scavenger Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

Ligand	<b>60</b> MeNTA2P	<b>61</b> NTA2P	<b>62</b> NTAP	NTA
Ligand : Fe (molar ratio)	3 : 1	2 : 1	2 : 1	2 : 1
Test time (h)	100	100.5	100	100
Conversion of H <sub>2</sub> S to S (%)	71.34	76.60	93.34	92.85
Conversion of H <sub>2</sub> S to CuS (%)	1.24	13.61	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	5.35	4.12	3.38	1.77
Half life (h)	47.2	57.1	50.5	39.9
Loss rate of Fe (mg/L/h)	2.64	1.47	0.90	0.75
Loss of ligand per kg of S (g)	781.51	614.18	394.25	528.01

## 2.9 Studies of iron chelate stabilisation

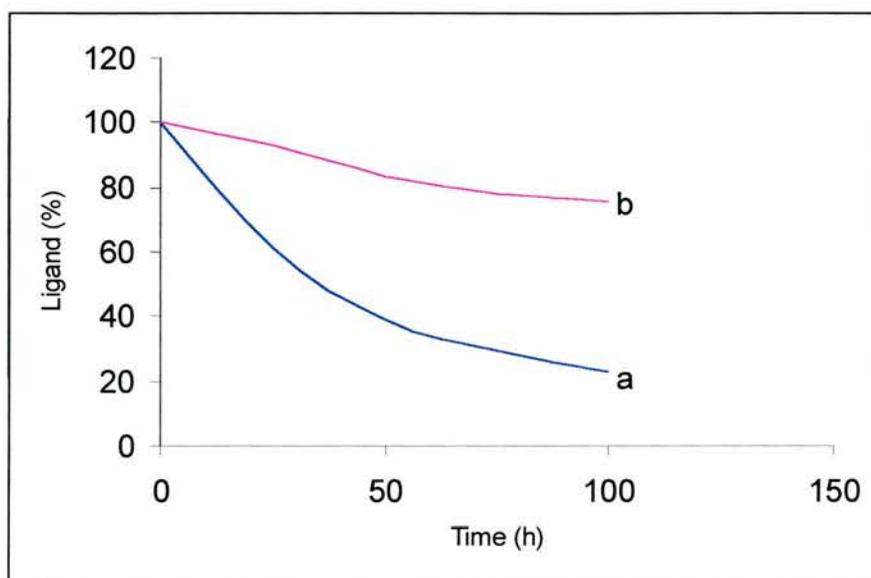
The degradation of a ligand is a complex process. Knowledge of the mechanism of NTA decomposition has enabled the inventors of the Fe-NTA system to control the degradation, which has become a key to using it in practice. Because NTA is usually very stable, and the degradation occurs during the re-oxidation of the ferrous-ligand system with air (molecular oxygen), it has been suggested that only free radicals have enough energy to decompose these chelating ligands. The reviews by Walling<sup>211</sup> and Wieckowska<sup>1</sup> indicate that the hydroxyl radical may be formed under the reaction conditions that prevail, leading to the decomposition of ligand.



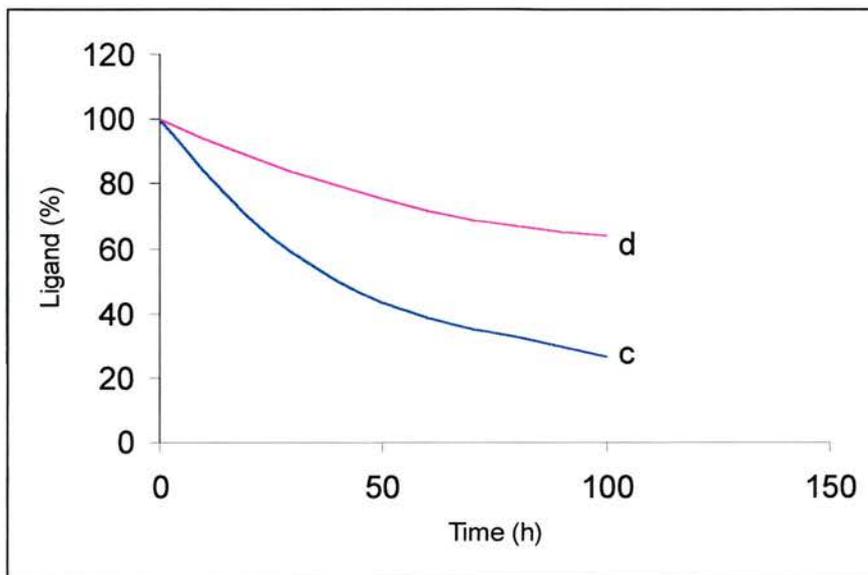
L stands for ligand

The stabilizing effect of thiosulphate for Fe(III)-NTA system, reported previously by McManus<sup>29f</sup>, as well as other stabilizers described by Diaz<sup>56,212</sup> and Bedell<sup>213</sup> could be understood since they have one property in common. They are all free radical scavengers, and reducing the degradation of ligands by decreasing the concentration of free radical on the reaction mixture. Thiosulphate has been demonstrated to remarkably increase the stability of NTA in the process.<sup>17</sup> Thiosulphate was selected as the agent of choice based on its low cost, chemical

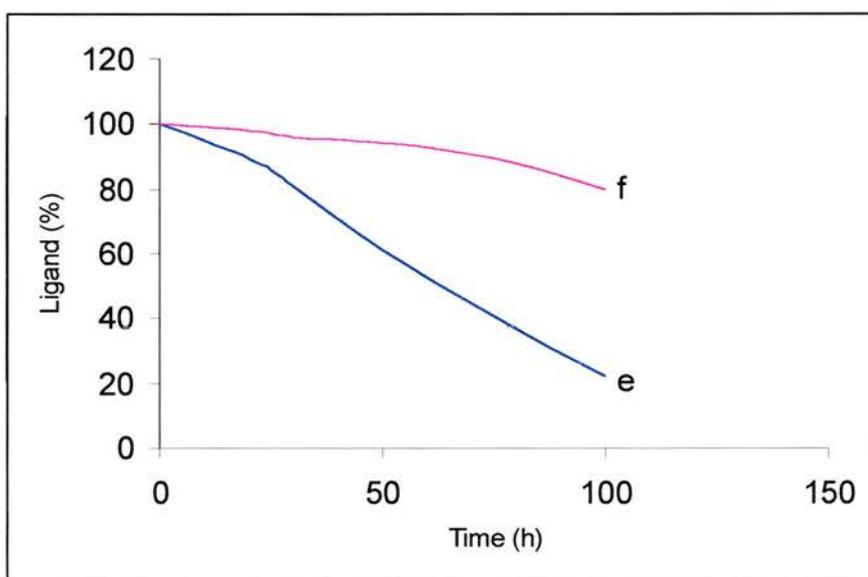
compatibility, low toxicity, good performance and the fact that it can be generated in-situ from  $H_2S$ . Naturally, we also applied thiosulphate to our experiments as a scavenger of hydroxyl radical in order to reduce the degradation of ligand in the process.



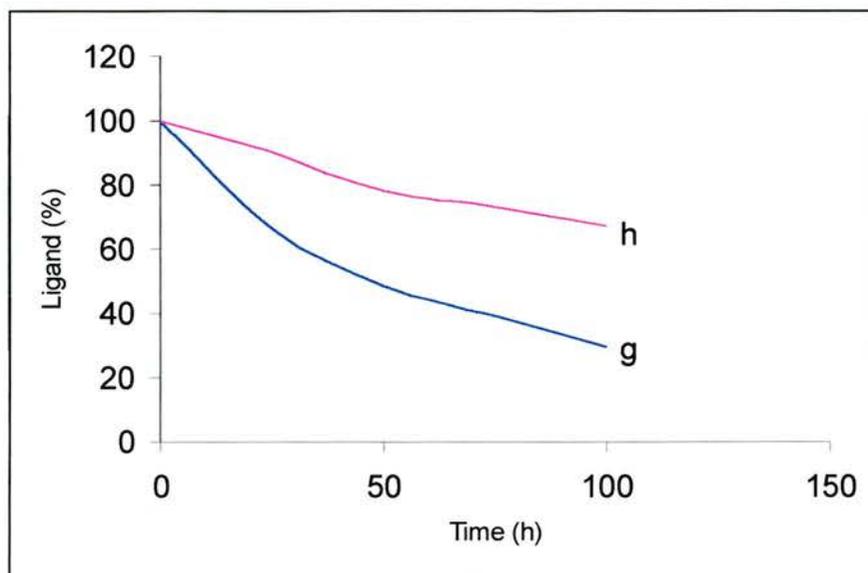
**Fig. 2.2** Degradation of Fe(III)-NTA at pH 8.5 (a, only NTA; b, NTA with 7 %  $Na_2S_2O_3$ )



**Fig. 2.3** Degradation of Fe(III)-MeNTA2P at pH 8.5 (c, only MeNTA2P; d, MeNTA2P with 7 %  $\text{Na}_2\text{S}_2\text{O}_3$ )



**Fig. 2.4** Degradation of Fe(III)-NTA2P at pH 8.5 (e, only NTA2P; f, NTA2P with 7 %  $\text{Na}_2\text{S}_2\text{O}_3$ )



**Fig. 2.5** Degradation of Fe(III)-NTAP at pH 8.5 (g, only NTAP; h, NTAP with 7 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)

**Fig. 2.2 - 2.5** and **Table 2.8** show that thiosulphate has slowed down the degradation of ligands **60 - 62** and **NTA** to a different extent. The presence of thiosulphate apparently enhances the selectivity of sulphur formation for all the cases. The application of thiosulphate as scavenger seems more suitable for **NTA** than for ligands **60 - 62**. Concerning the series of ligands **60 - 62**, thiosulphate is more effective for ligand **61** on the stabilisation of ligand or anti-oxidation of ligand in the process.

**Table 2.8** Comparison of ligands **60** - **62** against NTA in the presence of sodium thiosulphate (7 %)

Ligand	<b>60</b> MeNTA2P	<b>61</b> NTA2P	<b>62</b> NTAP	NTA
Ligand : Fe (molar ratio)	3 : 1	2 : 1	2 : 1	2 : 1
Test Time (h)	100	109	213	213
Conversion of H <sub>2</sub> S to S (%)	93.77	84.29	97.26	97.16
Conversion of H <sub>2</sub> S to CuS (%)	0	8.56	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	0.64	2.58	1.67	-1.54
Half Life (h)	127.3	473.5	170.5	246.6
Loss Rate of Fe (mg/L/h)	2.35	0.97	0.54	0.68
Loss of Ligand per kg of S (g)	291.00	149.30	155.83	135.38

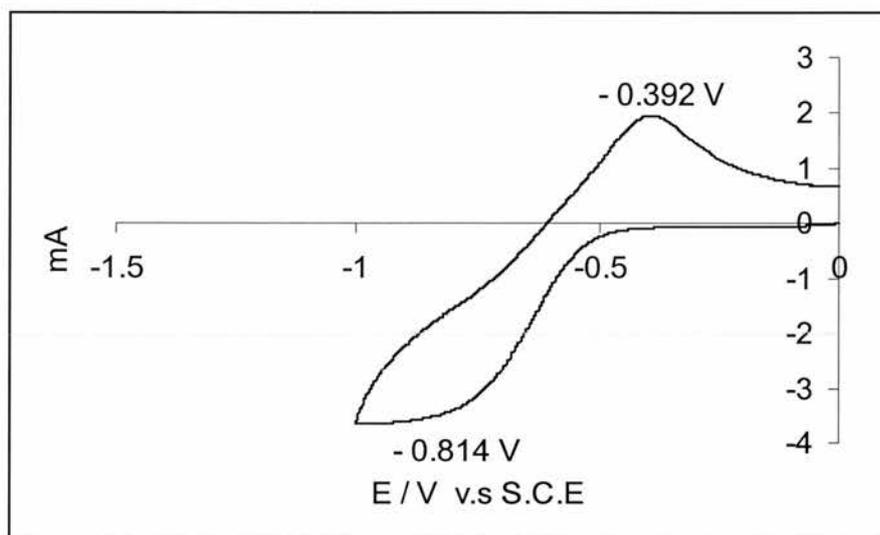
### 2.10 Cyclic voltammogram studies

It is known that the oxidation state +2 and +3 dominate in iron solution chemistry. The standard reduction potential  $E_0$  of ferric to ferrous ion under standard conditions is + 0.770 V.<sup>214</sup> Actually, the redox potential of Fe(III)/Fe(II) is largely dependent upon its coordination state and the medium in which it is measured.<sup>215, 216</sup> The cyclic voltammeteries of Fe(III)-NTA complexes at different conditions including solvent, pH value, molar ratio and so on have been previously studied.<sup>217-219</sup> The characteristic of the monomer-dimer equilibrium in the Fe(III)-NTA system at pH = 6.0 has been also established.<sup>220</sup> In order to explore the relationship between the

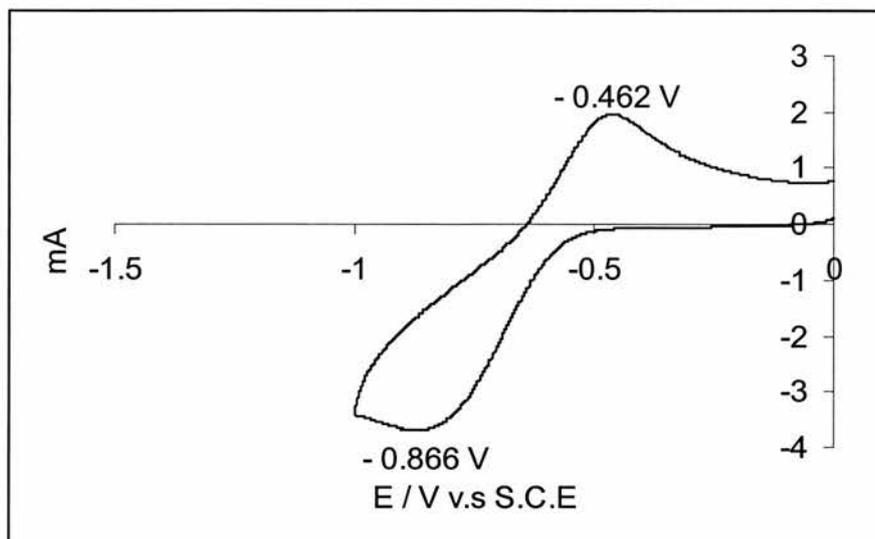
catalytic activities of the Fe(III) complexes of ligands **59** - **62** and their redox potential, their cyclic voltammograms have been acquired and compared with that of Fe(III)-NTA. All cyclic voltammograms were recorded in aqueous solutions at the same conditions: pH = 8.5, [Fe(III)] =  $20.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [ligand] =  $40.0 \times 10^{-3} \text{ mol dm}^{-3}$ . The results are listed in Fig. 2.6 - 2.10.

**Table 2.9** Half-wave potentials of Fe(III)-complexes of ligands **59** - **62** and NTA (V vs. saturated calomel electrode, SCE)

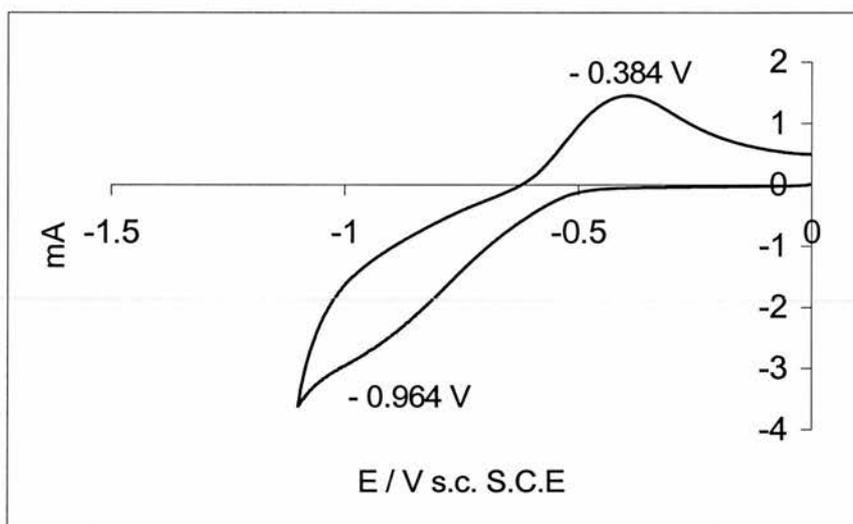
Ligand	<b>59</b> NTA3P	<b>60</b> MeNTA2P	<b>61</b> NTA2P	<b>62</b> NTAP	NTA
$E_{1/2}$ (V vs. SCE)	- 0.664	- 0.679	- 0.674	- 0.638	- 0.603



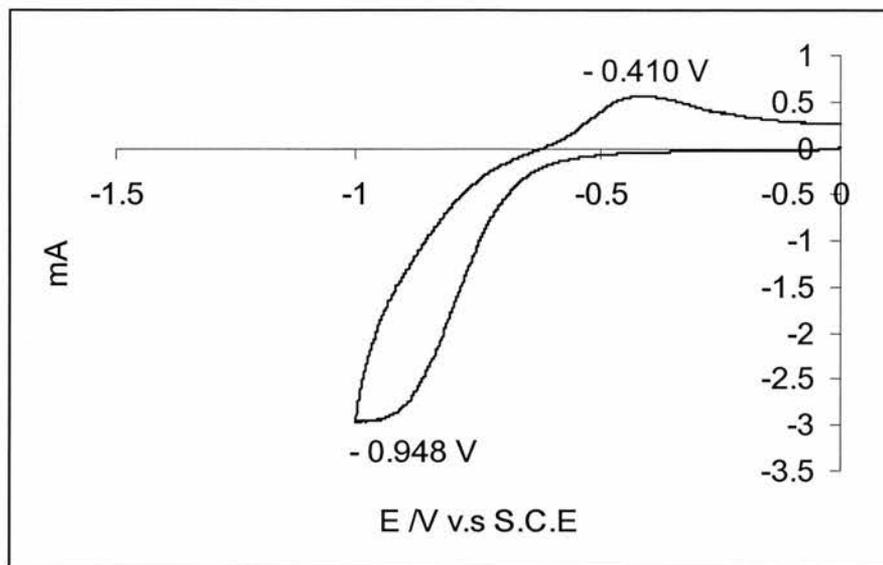
**Fig. 2.6** Cyclic voltammogram of Fe(III)-NTA in H<sub>2</sub>O (scan rate 50 mV s<sup>-1</sup>) at pH 8.5, [Fe(III)] =  $20.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [NTA] =  $40.0 \times 10^{-3} \text{ mol dm}^{-3}$



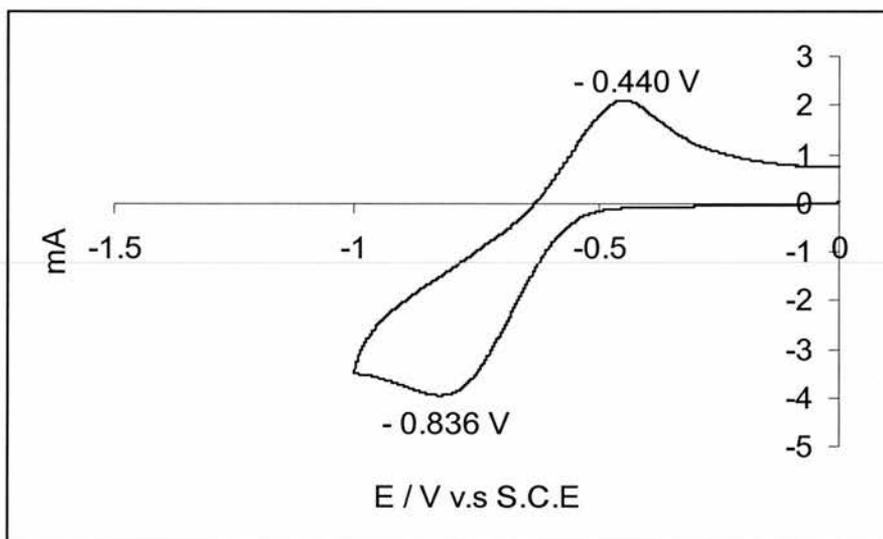
**Fig. 2.7** Cyclic voltammogram of Fe(III)-NTA3P in H<sub>2</sub>O (scan rate 50 mV s<sup>-1</sup>) at pH 8.5, [Fe(III)] = 20.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [NTA3P] = 40.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>



**Fig. 2.8** Cyclic voltammogram of Fe(III)-MeNT2P in H<sub>2</sub>O (scan rate 50 mV s<sup>-1</sup>) at pH 8.5, [Fe(III)] = 20.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [MeNTA2P] = 40.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>



**Fig. 2.9** Cyclic voltammogram of Fe(III)-NTA2P in H<sub>2</sub>O (scan rate 50 mV s<sup>-1</sup>) at pH 8.5, [Fe(III)] = 20.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [NTA2P] = 40.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>



**Fig. 2.10** Cyclic voltammogram of Fe(III)-NTAP in H<sub>2</sub>O (scan rate 50 mV s<sup>-1</sup>) at pH 8.5, [Fe(III)] = 20.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [NTAP] = 40.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>

The sensitivity of the Fe(III)/Fe(II) redox potential is neatly reflected in the electrochemical behaviour of these complexes when examined by cyclic voltammetry. The cathodic wave can be assigned to the reduction process, and anodic wave is due to complementary oxidation reaction. One-electron redox process in all cases can be expressed as the following equation (2.5).



L stands for NTA, NTAP, NTA2P, NTA3P and MeNTA2P, respectively

The half-wave potentials  $E_{1/2}$  for the above redox couples are calculated as the average of the cathodic potential ( $E_{pc}$ ) and anodic potential ( $E_{pa}$ ) and are collected in **Table 2.9**.

$$E_{1/2} = 1/2 (E_{pc} + E_{pa})$$

The half-wave potentials ( $E_{1/2}$ ) are influenced mainly by the ligand electronic properties arising from the donor atom types. The aminomethylphosphonate group tends to provide an extra stability to +3 oxidation-state of iron relative to the aminomethylcarboxylate group. It is readily noted that the highly negative reduction potentials (- 0.63 ~ - 0.70 V vs. SCE) for Fe(III) complexes of MeNTA2P, NTA3P, NTA2P and NTAP were obtained. These Fe(III) complexes comprise at least one methylphosphonate group around Fe(III) centre. The redox potentials of Fe(III) complexes tends to shift toward more negative values when the number of negatively charged methylphosphonic group of ligand is increased. It has been reported that methylphosphonate group stabilises the Fe(III) centre to a great extent than the

carboxylates and phenolates.<sup>221,222</sup> That the Fe(III) complexes of the methylphosphonate-containing ligands are more stable than Fe(III)-NTA could be accounted for from that the stability of Fe(III) centre arises from electrostatic effects of the negatively-charged donors.

The order of the half-wave potential of the Fe(III) shifting to more negative value compared to the standard redox potential is Fe(III)-MeNTA2P **60** > Fe(III)-NTA2P **61** > Fe(III)-NTA3P **59** > Fe(III)-NTAP **62** > Fe(III)-NTA, suggesting these Fe(III) complexes following the same order of stabilities. However, for a Fe(III) complex which is used as a catalyst for the catalytic oxidation of H<sub>2</sub>S to sulphur, high stability does not always mean high catalytic activity. Too high stability makes it difficult for H<sub>2</sub>S to reduce Fe(III) complex to Fe(II) complex. It seems that Fe(III)-NTA, Fe(II)-NTA, which show similar half-wave potential and stability to each other, are appropriate for the reduction with H<sub>2</sub>S. Fe(III)-NTAP proves slightly better than Fe(III)-NTA as catalyst for the oxidation of hydrogen sulphide to sulphur by air.

### **2.11 Conclusions**

Sixty-seven compounds, up to ten types, have been screened in order to find an alternative ligand to NTA for the catalytic oxidation of hydrogen sulphide to sulphur by air. Among them, forty-three ligands have been prepared and some have been characterised.

Fe(III) complexes of most of the compounds screened show poor solubility or stability in the required basic solution and low catalytic activity when applied as catalysts for removal of hydrogen sulphide. The analogues of NTA or EDTA looked promising on solubility or stability and catalytic activity of Fe(III) complexes.

Ligand **62**, **NTAP**, however, is comparable with **NTA** on the efficiency of catalytic activity such as the conversion of hydrogen sulphide to sulphur, half-life of the ligand, consumption of ligand per kg of ligand etc. **NTAP** was also subjected to the attack by free hydroxyl radical and degraded during the process. The addition of  $\text{Na}_2\text{S}_2\text{O}_3$  to the corresponding **Fe(III)** complex system could reduce the degradation of ligand to some different extent. The fact that ligand **62** is more expensive than **NTA** limits its commercial application in place of **NTA**.

Cyclic voltammograms of **Fe(III)** complexes of **NTAP**, **NTA2P**, **NTA3P** and **MeNTA2P** have been measured and compared with **Fe(III)-NTA** under the same conditions.

## ***Experimental***

### ***Materials and reagents***

The following materials were ordered from Aldrich or Lancaster and were used without further purification: nitrilotriacetic acid trisodium salt ( $\text{Na}_3\text{NTA}$ , 99.0 %); sorbitol (98.0 %); iron foil (99.99 %); iminodiacetic acid, disodium salt hydrate ( $\text{Na}_2\text{IDA}$ , 98.0 %); sodium oxalate (99.5 %); glacial acetic acid (99.99 %); methyl alcohol (HPLC grade); 1,10-phenanthroline (99.0 %); hydrogen sulphide (99.5 %); boric acid (99.5 %); Sulphur (99.99 %);  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (98.0 %);  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  (97.0 %);  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98.0 %);  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (98.0 %);  $\text{FeCl}_3$  (99.0 %);  $\text{FeCl}_2$  (99.0 %);  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (99.9 %);  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (98.0 %);  $\text{Cu}(\text{NO}_3)_2 \cdot 5/2\text{H}_2\text{O}$  (98.0 %);  $\text{NaSH} \cdot x\text{H}_2\text{O}$  (99.0 %);  $\text{CS}_2$  (99.9 %). Ligands **1 - 3**, **8**, **12 - 18**, **25 - 28**, **30**, **32 - 37**, **39 - 45**, **48 - 50**, **59** and **62** were obtained from Aldrich or Lancaster in the highest purity available and were applied without further purification.

Ligands **4**, **5**, **7**, **9 - 11**, **29**, **31** and **38** were prepared previously by our group.

Ligands **6**,<sup>223</sup> **14**,<sup>224</sup> **24**,<sup>225, 226</sup> **46**,<sup>227</sup> **47**,<sup>228</sup> **53**,<sup>229</sup> **54**,<sup>229</sup> **55**,<sup>230</sup> **56**,<sup>231</sup> **57**,<sup>232</sup> **58**,<sup>232</sup> **63**,<sup>233, 234</sup> **64**,<sup>232, 235</sup> and **66**,<sup>193</sup> were synthesised exactly according to previously described procedures.

The following Ligands have been prepared or synthesised by modified procedures of references.

***N, N'*-2,6-pyridinebis(salicylideneimine) 19.**<sup>236</sup> To a solution of 2,6-diaminopyridine (2.22 g, 20 mmol) in methanol (40 cm<sup>3</sup>) was added a solution of salicylaldehyde (5.08 g, 40 mmol) in methanol (10 cm<sup>3</sup>). Stirring and refluxing were continued for three hours. The reaction mixture was stood at room temperature overnight. The crude product was collected by suction filtration. Recrystallization from n-butanol gave brown crystals in a yield of 5.87 g (92.4 %). Microanalysis: Found: C, 71.02 %; H, 5.31 %; N, 13.38 %. C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> requires: C, 71.91 %; H, 4.76 %; N, 13.33 %. M.P. 220°C (dec.). IR (KBr disc., cm<sup>-1</sup>): 3464m, 3387m, 3052w, 2947w, 1614s, 1557m, 1481w, 1455vs, 1278m, 1230m, 1151m, 1118w, 754s. EIMS (m/z): 317 [M]<sup>+</sup>.

**2-pyridinesalicylideneimine 20.**<sup>237</sup> To a solution of salicylaldehyde (6.2 g, 50 mmol) in methanol (60 cm<sup>3</sup>) was added dropwise a solution of 2-aminopyridine (4.8 g, 50 mmol) in methanol (20 cm<sup>3</sup>). The reaction mixture was refluxed for one hour, concentrated to ca. 20 cm<sup>3</sup> and then stored at 0°C for 48 hours to give golden crystals, yield 8.3 g (83.7 %). M.P., 66 °C. Microanalysis: Found: C, 72.86 %; H, 4.87 %; N, 14.12 %. C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O requires: C, 72.71 %; H, 5.08 %; N, 14.13 %. <sup>1</sup>H

NMR ( $\delta_{\text{ppm}}$ ,  $\text{CD}_2\text{Cl}_2$ ): 14.41 (s, 1H, OH), 9.45 (s, 1H, CH=N), 8.68-6.92 (m, 8H, ArH). IR (KBr disc.,  $\text{cm}^{-1}$ ): 3427w, 1610vs, 1589vs, 1555vs, 1498m, 1467s, 1430s, 1346w, 1278m, 1186s, 1146m, 994m, 915m, 790m, 757s. EIMS (m/z): 198  $[\text{M}]^+$ , 181  $[\text{M}-\text{OH}]^+$ ; CIMS (m/z): 199  $[\text{M}+\text{H}]^+$ .

**2-amino-6-pyridinesalicylideneimine 21.**<sup>238</sup> To a solution of 2, 6-diamonopyridine (5.6 g, 50 mmol) in methanol (80  $\text{cm}^3$ ) was added salicylaldehyde (6.2 g, 50 mmol). The reaction mixture was refluxed for one hour and then was allowed to cooled at room temperature overnight. The brownish yellow product was obtained by suction filtration, washed with diethyl ether in a yield of 7.6 g (71.6 %). M.P., 204°C (dec.). Microanalysis: Found: C, 67.50 %; H, 5.35 %; N, 20.01 %.  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$  requires: C, 67.59 %; H, 5.20 %; N, 19.71 %. IR (KBr disc.,  $\text{cm}^{-1}$ ): 3417vs, 1617vs, 1481m, 1456s, 1386w, 1271w, 1243w, 755s. EIMS (m/z): 213  $[\text{M}]^+$ ; CIMS (m/z): 214  $[\text{M}+\text{H}]^+$ .

**2-pyridine-2'-carboxybenzylideneimine 22.** To a solution of 2-carboxybenzaldehyde (4.5 g, 20 mmol) in methanol (30  $\text{cm}^3$ ) was added dropwise 2-aminopyridine (3.1 g, 20 mmol) in methanol (10  $\text{cm}^3$ ). The reaction mixture was stirred at room temperature for one hour. A white solid deposited, which was presumed to be the salt of 2-carboxybenzaldehyde and 2-aminopyridine. The reaction mixture was refluxed until the solid disappeared (after ca. 5 hours) and then stored at room temperature for overnight. There are two kinds of precipitates separated mechanically or manually, one is colourless needle crystals, the expected

product, yield: 4.2 g (87.0 %). Microanalysis; Found: C, 69.05 %; H, 4.37 %; N, 12.46 %.  $C_{13}H_{10}N_2O_2$  requires: C, 69.05 %; H, 4.46 %; N, 12.39 %. IR (KBr disc.,  $cm^{-1}$ ): 3412w, 3223w, 3014w, 1766vs, 1612s, 1531m, 1481vs, 1423m, 1283m, 1146w, 1069s, 889s, 786m, 688w. EIMS (m/z): 227  $[M+H]^+$ ; CIMS (m/z): 453  $[2M+H]^+$ . The other (white solid) may be the salt.

**Tris-(2-salicylidenaïmo-ethyl)-amine 23.**<sup>239,240</sup> To a solution of tri(2-aminoethyl)amine (3.1 g, 20 mmol) in ethanol (100  $cm^3$ ) was added dropwise a solution of salicylaldehyde (7.4 g, 60 mmol) in ethanol (50  $cm^3$ ). The reaction mixture was stirred at room temperature for seven hours and then stood overnight. The orange crystal was obtained by suction filtration, washed three times with ether. Yield: 7.6 g (84 %). M. P: 90°C. Microanalysis: Found: C, 70.48 %; H, 6.68 %; N, 12.02 %.  $C_{27}H_{30}N_3O_3$  requires: C, 70.75 %; H, 6.60 %; N, 12.02 %. IR (KBr disc.,  $cm^{-1}$ ): 3456w, 2937w, 2884w, 2817m, 1633vs, 1611m, 1582m, 1459m, 1449m, 1430m, 1336m, 1279s, 774s, 764m, 756s.  $^1H$ NMR ( $CDCl_3$ , ppm): 13.75 (s, 3H, OH), 7.83 (s, 3H, N=CH), 7.26-6.13 (m, 12H, ArH), 3.53 (t, 6H,  $CH_2CH_2$ ), 2.84 (t, 6H,  $CH_2CH_2$ ). FABMS (m/z): 459  $[M+H]^+$ .

**Potassium nitrilosulphonate 51.**<sup>241</sup> A solution of potassium hydroxide (60.0 g, 1.05 mmol) in 100  $cm^3$  of water was saturated with  $SO_2$  which was produced by sodium bisulfite (105.0 g, 0.525 molar) reacting with 98 % sulphuric acid (30  $cm^3$ , 0.525 molar) in 60  $cm^3$  of water. A solution of potassium nitrite (22.5 g, 0.25 molar) in 60  $cm^3$  of water was added to the above hot solution with vigorous stirring. The liquid

soon became cloudy because of precipitation of fine needle crystals. The suspension was allowed to stand for one hour and the separated precipitate was re-dissolved by addition of 1000 cm<sup>3</sup> of hot KOH solution and heating. The solution had to be alkaline all the time. Then, the solution was allowed to cool to room temperature. The product is suction filtered, washed thoroughly with ice water, methanol and ether, and finally dried in vacuum. Yield of white solid N(SO<sub>3</sub>K)<sub>3</sub>·7H<sub>2</sub>O, 74.5 g (73.3 %) Microanalysis: Found: H, 3.15 %; N, 2.74 %. H<sub>14</sub>K<sub>3</sub>NO<sub>16</sub>S<sub>3</sub> requires: H, 3.46 %; N, 2.81 %. FABMS (m/z): 498 [M + 7 H<sub>2</sub>O]<sup>+</sup> and 426 [M + 2H<sub>2</sub>O]<sup>+</sup>.

**Tris-sulphomethylamine, sodium salt 52.**<sup>225</sup> To a solution of aminomethylenesulphonic acid (5.7 g, 50 mmol) in 40 cm<sup>3</sup> of water was added sodium hydroxide (6.0 g, 150 mmol). The mixture was stirred and then allowed to cool to room temperature. To this mixture was added a solution of 40 % formaldehyde (7.5 g, 100 mmol). The reactant solution was then bubbled in sulphur dioxide (6.4 g, 100 mmol) which was produced by reaction of sodium bisulfite (9.5 g, 50 mmol) with 98 % sulphuric acid (5.0 g, 50 mmol) in 10 cm<sup>3</sup> of water at room temperature over a period of 3 hours. The reaction mixture was heated to 70°C for another three hours under nitrogen. The product was precipitated out by addition of a little amount of methanol. Recrystallization from a water-methanol solution gave the product as colourless crystals N(CH<sub>2</sub>SO<sub>3</sub>Na)<sub>3</sub>·H<sub>2</sub>O, yield: 11.60 g (60.1 %). Microanalysis: Found: C, 9.23 %; H, 2.00 %; N, 3.40 %. C<sub>3</sub>H<sub>8</sub>NNa<sub>3</sub>O<sub>10</sub>S<sub>3</sub> requires: C, 9.35 %; H, 2.09 %; N, 3.80 %.

**[(Methylphosphonomethylamino)methyl]phosphonic acid (MPMP) 60.**<sup>232</sup> To a solution of 33 % methylamine in ethanol (9.4 g, 0.1 molar) and phosphorous acid (16.4 g, 0.2 molar) in water (20 cm<sup>3</sup>) was added dropwise a solution of 40 % formaldehyde (30 cm<sup>3</sup>, 0.4 molar) in concentrated hydrochloric acid (20 cm<sup>3</sup>). The reaction mixture was then heated to reflux for two hours. The reactant mixture was concentrated to *ca.* 25 cm<sup>3</sup> and subsequently added dropwise to hot ethanol. Upon cooling to room temperature, the crystallised white solid was collected by filtration. Yield: 20.8 g (95 %). Microanalysis: found: C, 16.50 %; H, 6.09 %; N, 6.41 %. C<sub>3</sub>H<sub>11</sub>NO<sub>6</sub>P<sub>2</sub> requires: C, 16.45 %; H, 5.06 %; N, 6.39 %. <sup>31</sup>P-<sup>1</sup>H NMR (D<sub>2</sub>O, ppm): δ<sub>p</sub> 8.86 (s). FABMS (m/z): 220 [M + H]<sup>+</sup>.

**(Bisphosphonomethylamino)acetic acid (BPMA) 61.**<sup>242</sup> To a solution of glycine hydrochloride (27.8 g, 0.25 molar) and phosphorous acid (41.5 g, 0.5 molar) was added dropwise with a syringe pump a solution of 40 % formaldehyde (75 cm<sup>3</sup>, 1.0 molar) and 50 cm<sup>3</sup> concentrated hydrochloric acid at reflux temperature for one hour. The mixture was refluxed for another hour and allowed to cool at room temperature, no crystal appeared. The solution was then concentrated to 100 cm<sup>3</sup>, ethanol was added to precipitate the white solid. Yield: 23.9 g (90 %). Microanalysis: found: C, 19.07 %; H, 2.62 %; N, 5.29 %. C<sub>4</sub>H<sub>11</sub>NO<sub>8</sub>P<sub>2</sub> requires: C, 18.46 %; H, 4.21 %; N, 5.32 %. IR (KBr disc., cm<sup>-1</sup>): 3012w, 2303m, 1730vs, 1413s, 1370m, 1342m, 1306m, 737w, 826m, 771m, 723m, 664s, 605s, 453s, 398m. <sup>31</sup>P-<sup>1</sup>H NMR (D<sub>2</sub>O, ppm): δ<sub>p</sub> 8.79 (s). FABMS (m/z): 264 [M + H]<sup>+</sup>.

***N,N'*-bis(2- and 3-pyridinyl)-2,6-pyridine dicarboxamide 65.**<sup>243</sup> 2,6-pyridinedicarboxylic acid (15.0 g, 0.09 mol) was suspended in pyridine (50 cm<sup>3</sup>), 2-aminopyridine (18.0 g, 0.19 mol) was added to the mixture, and the mixture was stirred for 30 min at 40°C. Initially a white precipitate formed, which finally formed an emulsion. To this was added triphenyl phosphite (50 cm<sup>3</sup>) in dropwise, the temperature of the reaction mixture was increased to 95°C, and the mixture was stirred for five hours. Stirring was continued at room temperature for overnight. After that, it was washed with water and an oil mud was obtained. Addition of methanol led to precipitation of white needles. This product was filtered off, washed with methanol, and dried in vacuum to give a yield of 93 % (12.5 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ ppm: 8.48 (t, 1H), 8.52 (d, 2H), 7.12 (m, 2H), CIMS (m/z): 319 [M+H]<sup>+</sup>.

**Bis{[bis(carboxymethyl)amino]methyl}phosphinate 67.**<sup>204,244,245</sup> Iminodiacetic acid (6.7 g, 50 mmol) and a 50 % solution of H<sub>3</sub>PO<sub>2</sub> (3.3 g, 25 mmol) were combined in 6 M HCl (10.0 cm<sup>3</sup>) and heated to reflux. An aqueous solution (40 %) of formaldehyde (8.0 g, 100 cm<sup>3</sup>) was added dropwise to the mixture and the reflux continued for five hours. A white precipitate formed during the process. The reaction mixture was cooled to room temperature and the precipitate was collected by filtration, washed with methanol, and dried under vacuum. The filtrate was concentrated, and a second crop of precipitate was harvested by filtration. The combined crude product was subsequently re-dissolved in a minimum amount of 6 M HCl, and the product was precipitated with methanol and similarly collected. Microanalysis, found: C, 29.91 %; H, 4.96 %; N, 6.73 %. C<sub>10</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>10.5</sub>P requires:

C, 29.90 %; H, 4.77 %; N, 6.97 %.  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ , ppm):  $\delta_{\text{P}}$  17.1.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , ppm):  $\delta$  4.2 (8H, s,  $\text{NCH}_2\text{COO}$ ), 3.6 (4H, d,  $\text{NCH}_2\text{P}$ ). Yield: 95.1 %.

#### ***Testing of Solubility and Stability of Fe(III)/Fe(II) Complexes***

A 100  $\text{cm}^3$  sample of iron complexes was prepared by dissolving 0.9 mmol  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  or 0.9 mmol  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and corresponding amount of ligand in distilled water. The pH of the mixture was adjusted to the required range by addition of 2 M NaOH or 2 M HCl solution. The solution was then stored at room temperature for visual observation of solubility and stability.

#### ***Simple testing of the catalytic activity of Fe(III) complexes with sodium hydrogen sulphide***

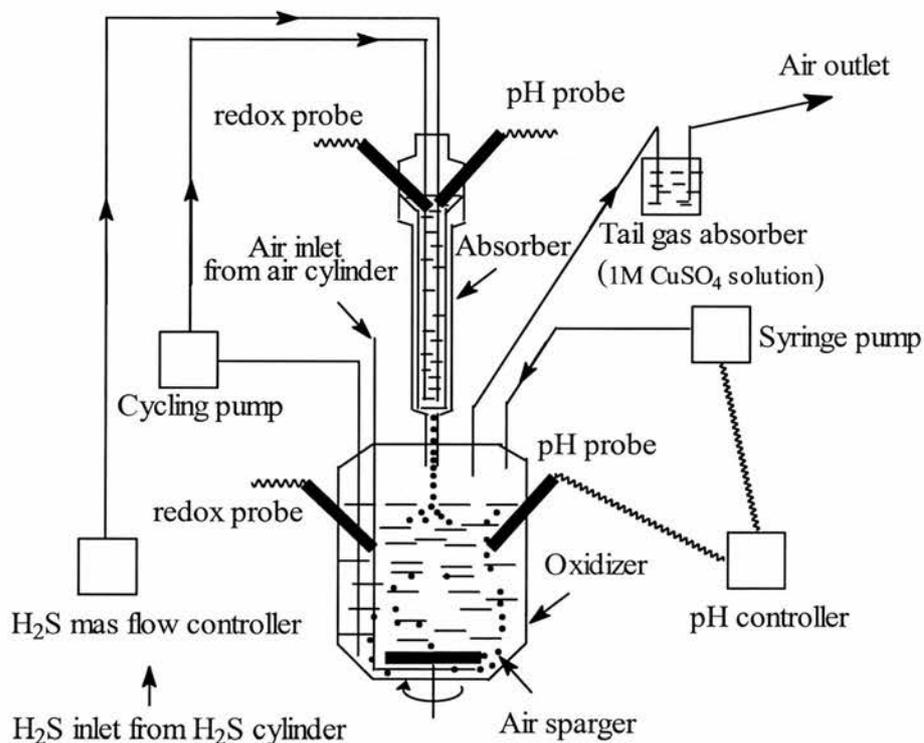
To the stable basic solution (100  $\text{cm}^3$ ) containing 1.8 mmol Fe(III) complex at pH 8.50 was added 0.3-3.0 g of sodium hydrogen sulphide (NaSH) (in one portion or in multiple portions). The pH of the mixture usually increased to some extent with such an addition and the solution became black suspension. The suspension was stirred and pH was re-adjusted to the required value by the addition of 2 M of NaOH or 2 M of HCl, air was then bubbled in at a rate of 20  $\text{cm}^3\text{min}^{-1}$ . If the Fe(III) complex is catalytic active, the dark suspension would gradually disappear, and grey sulphur (due to contamination with FeS) would come out, the solution became clear again. If not, the dark suspension would remain. Another case was that the colour of the black suspension gradually became lighter but no sulphur precipitated out, and the solution still remained opaque. This means that the ligand decomposed and the complex showed negative activity.

*Expanding testing of catalytic activity of Fe(III) complex in a 1-litre reactor with hydrogen sulphide*

**General procedure**

One litre of the Fe(III) complex solution was loaded in the oxidizer compartment. The liquid pump was then started and part of the solution was pumped into the absorber compartment with a flow rate of  $100 \text{ cm}^3 \text{ min}^{-1}$ . The pH and redox probes were then turned on. At this stage the air was bubbled into the oxidizer and the air flow was adjusted to the required value. The valve of the H<sub>2</sub>S cylinder was switched on and the H<sub>2</sub>S flow rate was adjusted to  $2.00 \text{ cm}^3 \text{ min}^{-1}$  by a H<sub>2</sub>S flow rate controller. The time of the start of the reaction was recorded, and the pH and redox probe readings were recorded from time to time. The pH was continuously controlled to 8.5 by the automatic addition of 2 M NaOH solution with a syringe pump. The sulphur was filtered at a 20 hours interval and  $5 \text{ cm}^3$  of sample was taken from the running system in at a regular time interval in order to monitor the degradation of ligand and the loss of Fe.

## Apparatus



**Scheme 2.2** 1 Liter glass reactor

## HPLC analysis and operating conditions

The analyses of NTA, IDA, oxalate and related ligands were measured by following the method of McManus.<sup>208</sup>

## Equipment

A Milton Roy pump No.043 024 equipped with a chromatography accessory, UV-visible spectromonitor 3000 (LDC analytical), and a chart recorder (Waters 746 Data Module) were used.

### **Operating conditions**

Analytical column: phenomenex IB-SIL 5  $\mu\text{m}$  C8, reverse phase,  $4.6 \times 250$  mm; column temperature: ambient; flow rate:  $2.0 \text{ cm}^3 \text{ min}^{-1}$ ; detector: UV absorption at 290 nm; sample: 10  $\mu\text{L}$ ; mobile phase: 0.001 M Copper nitrate, 40 % methyl alcohol, pH = 4.2; recorder: 10 mV full scale; chart speed:  $0.5 \text{ cmmin}^{-1}$ .

### **Preparation of mobile phase**

40  $\text{cm}^3$  of 0.05 M copper nitrate solution and 40  $\text{cm}^3$  of glacial acetic acid were mixed in 800  $\text{cm}^3$  of deionised water in 2000  $\text{cm}^3$  beaker. The pH value of the solution was adjusted to 4.2 with 4 M NaOH. The solution was transferred to 2000  $\text{cm}^3$  volumetric flask. 800  $\text{cm}^3$  of HPLC grade methyl alcohol was added and the solution was diluted to volume with deionised water. At this stage, 4.0 g of cetyltrimethylammonium bromide was added and the solution was filtered through a 0.45 mm micron filter to give the mobile phase.

### **Preparation of sample**

A 4.0 g of specimen was taken from the continuous reactor and placed in a 100-mL volumetric flask. To this was added 10  $\text{cm}^3$  0.05 M copper nitrate solution and the mixture were diluted to 100  $\text{cm}^3$  with water. The mixture was stored at room temperature for at least 15 min before analysis.

### **Calibration of HPLC analysis**

The quantitative calibrations for the HPLC analyses of all ligands and intermediates were carried out by varying amounts of known samples of these compounds. The peak areas at the indicated amplification settings were plotted vs. concentration of the species. The linear nature of these plots indicated accurate

HPLC determinations of these molecular species over a considerable range of concentration.

#### ***Analyses of IR, MS and microanalysis***

Infrared spectra were recorded (KBr discs) on a Perkin-Elmer system 2000 spectrometer. Microanalysis was performed by the University Service within this Department and bombardment mass spectra (FABMS), electron ionisation mass spectra (EIMS) and chemical ionisation mass spectra (CIMS) by the EPSRC Mass Spectrometer Service (Swansea, UK).

#### ***Cyclic voltammogram analysis***

##### **Method and procedure**

Cyclic voltammograms were recorded using an EG and G PARC 273 A potentiostat / galvanostat controlled by version 4.11 of the electrochemistry research software running on a PC. All the experiments were carried out in degassed solution containing iron complexes ( $2 \times 10^{-2}$  M) and tetrabutylammonium hexafluorophosphate (0.50 g for organic solvent) or lithium chloride (0.50 g for aqueous solution) as a supporting electrolyte. The measurement was carried out using a saturated calomel electrode (SCE) as the reference with a luggin capillary and a Pt wire as the counter electrode. The reference electrode, separated from the voltammetric cell by a salt bridge, was Ag / AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN). The electronic spectrum was recorded on Perkin-Elmer spectrometer by Lambda research software.

### **Preparation of sample**

The investigated mixtures were prepared by mixing defined volumes of solutions containing  $C_{\text{Fe}^{3+}} = 0.02 \text{ M}$ ,  $C_{\text{ligand}} = 0.04 \text{ M}$ . These solutions were all adjusted to the desired pH 8.50 by addition of  $\text{NH}_4\text{OH}$  (2 M) solution. The samples were deoxygenated for at least 10 min with  $\text{N}_2$ . The experiments were performed at room temperature.

### **Analysis of NMR**

$^1\text{H}$  NMR spectra (300 MHz) were recorded on a Varian Gemini 2000 spectrometer and on a JEOL GSX 270 spectrometer, and chemical shifts are reported in ppm relative to TMS.  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra at 121.4 MHz with  $\delta$  referenced to external 85 %  $\text{H}_3\text{PO}_4$ .

### **Quantitative analysis of $^{31}\text{P}\{-^1\text{H}\}$ NMR**

The quantitative determinations of the containing phosphorus ligands and the related compounds were based on addition of phosphonoacetic acid ( $\text{H}_2\text{O}_3\text{PCH}_2\text{COOH}$ ) as standard material. The quantitative calibrations for the  $^{31}\text{P}\{-^1\text{H}\}$  NMR analysis of all ligands and the related compounds were carried out varying amounts of known samples of these compounds. The peak areas at the indicated amplification settings were plotted vs. concentration of the species. The linear nature of these plots indicated accurate  $^{31}\text{P}\{-^1\text{H}\}$  NMR determinations of these molecular species over a considerable range of concentration.

### **Preparation of iron-free samples for $^{31}\text{P}\{-^1\text{H}\}$ NMR analysis**

To a 2.000 g of solution taken from the continuous reactor or the starting solution, 0.500 g of 0.144 M of phosphonoacetic acid (standard material) and 0.40 g

of NaOH and 0.15 g of boric acid (destabilisation) were added with stirring. The stirring was continuing for 15 min and the reaction mixture was allowed to stand at room temperature for 30 min. The  $\text{Fe}(\text{OH})_3$  that precipitated was filtered off with 0.45 mm micron filter. The solution was subjected to  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra. The resonance peaks were assigned by comparing with corresponding commercial standard materials in the same condition.

#### ***Determination of iron by UV-vis spectrophotometer***

UV-vis analysis of iron was performed on a PYE Unicam Pu 4025 UV detector. The concentration of iron was measured according to the following method. To a 100  $\mu\text{L}$  of solution taken from the continuous reactor or the starting solution was added 1  $\text{cm}^3$  of 10% hydroxylamine, 10  $\text{cm}^3$  of 1.2 M sodium acetate and 10  $\text{cm}^3$  of 1.0 g/L orthophenanthroline. The mixture was diluted with deionised water to 100  $\text{cm}^3$  and allowed to stand for 15 min. The solution was ready for UV-vis spectrophotometric analysis. The calibration of the UV-vis analysis of iron by this method results in Beer's Law behaviour up to  $2 \times 10^{-4}$  M.

#### ***Determination of $\text{S}_2\text{O}_3^{2-}$ by redox titrations***

To a solution of 20  $\text{cm}^3$  of sample and 100  $\text{cm}^3$  of water, to which was pre-bubbled air for 3 hours to oxidise all Fe(II) to Fe(III), was added 10  $\text{cm}^3$  of 1 % of starch solution (as indicator) and an excess of 0.1 N of  $\text{I}_2$  standard solution. The mixture became very dark. To this solution 0.0993 N of  $\text{Na}_2\text{S}_2\text{O}_3$  standard solution was added dropwise until the colour of the solution recovered to initial colour of the solution. The percentage of  $\text{S}_2\text{O}_3^{2-}$  in the sample was calculated based on the total consumption of  $\text{H}_2\text{S}$ .

### ***Determination of $SO_4^{2-}$ by gravimetry***

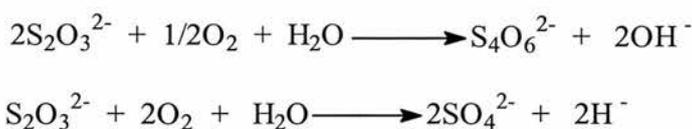
A 40 cm<sup>3</sup> of the sample solution and a 200 cm<sup>3</sup> of water were placed into 500 cm<sup>3</sup> beaker. The solution was then adjusted to pH < 1 with 2 N HCl solution. The solution was heated. To this hot solution, 20 cm<sup>3</sup> of 5 % of barium chloride solution (5 g BaCl<sub>2</sub>·2H<sub>2</sub>O in 100 cm<sup>3</sup> of water --- ca. 0.2 M) was added dropwise through a pipette with stirring. The solution was kept hot but not boiling for 5-6 hours to ensure precipitation of BaSO<sub>4</sub> was complete. Then the solution was cooled. The white solid (BaSO<sub>4</sub>) was filtered off through a 0.45 mm micron filter, washed three times with cold water, dried at 140°C for overnight, cooled in a desiccator and weighed to calculate the percentage of SO<sub>4</sub><sup>2-</sup> in the sample.

## Chapter 3

### **Improvement of the Fe-NTA System by Changing Scavenger of Hydroxyl Radical**

#### **3.1 Introduction**

As mentioned in **Chapter 1**, the degradation of NTA is a major deficiency in the Fe-NTA system for the oxidation of hydrogen sulphide to sulphur by air. NTA decomposes rapidly in the process, resulting in significant operating costs due to eventual loss of the chelating ligand, which then has to be continuously replenished. The rate of degradation of NTA can be slowed considerably down by the addition of  $\text{Na}_2\text{S}_2\text{O}_3$ , which can also be generated in the process. It has been found that  $\text{Na}_2\text{S}_2\text{O}_3$  is beneficial at concentration up to 0.5 mole in protecting the Fe-NTA from degradation by hydrogen radical attack. Higher concentration of thiosulphate provides little further improvement. On the contrary, further oxidation of  $\text{Na}_2\text{S}_2\text{O}_3$  to sulphate *via* tetrathiosulphate (see **Scheme 3.1**)<sup>55</sup> results in inert salt accumulation, which eventually hampers the sulphur separation as well as the gas-liquid mass transfer in the process.



**Scheme 3.1** Oxidation of thiosulfate by oxygen in the process

To circumvent the above problem, we have considered two approaches: (i) to develop some alternative ligands which are more robust than NTA and would be

resistant to hydroxyl radical attack; (ii) to find some more effective scavengers of the hydroxyl radical than  $\text{Na}_2\text{S}_2\text{O}_3$  to lengthen the lifetime of NTA.

Our work in **Chapter 2** has proved that it is very difficult, if not impossible, to find a better and more practical ligand than NTA. What is more, as reported by McManus and Martell in their research on the pyridine-type ligand such as pyridine-2-phosphonic-6-carboxylic acid (2PP6C), 2,6-pyridine-diphosphonic acid (2,6-PDPA), pyridine-2,6-dicarboxylic acid (DIPIC), and 2-carboxy-8-hydroxyquinoline (CHOX),<sup>61,65,66</sup> the absence of  $\alpha$ -methylene groups, which are known easily subjected to the attack and oxidation of free hydroxyl radical, does not guarantee against the oxidative degradation of the ligands. Therefore, finding more effective scavengers of free hydroxyl radical substituting  $\text{Na}_2\text{S}_2\text{O}_3$  appears to be a preferred option for the currently commercial Fe-NTA system. Although there are numerous radical scavengers or anti-oxidants that are related or applied to biological processes, few can be used directly on pure chemical processes, even less suitable for the aqueous Fe-NTA system. Traditional scavengers or inhibitors of free radical such as dibutylmethyl phenol, *N*-acetylcysteine, diisopropylphenol, allopurinol, indole-3-acetyl acid, butylalcohol, ascorbic acid and quinolinic acid et al,<sup>246-251</sup> are either insoluble in aqueous solution or too expensive to be used in the process for the conversion of  $\text{H}_2\text{S}$  to S. Ideally speaking, additives that not only remove the free radical but also can be regenerated automatically in the system are the best of choice. However this is not always available. Therefore, our screening was carried out with various reagents which could be oxidised by free hydroxyl radical. As long as the efficiency, cost and environmental factors are acceptable, it is worthwhile even if the

additives were consumed sacrificially for NTA. With this in mind, we have tested the following inorganic and organic compounds as scavengers or inhibitors of hydroxyl radical for the Fe-NTA system. The results are compared with that of  $\text{Na}_2\text{S}_2\text{O}_3$  concerning the half-life of NTA, the selectivity to sulphur, the loss of Fe ion and so on. Unless otherwise, all experiments were performed at conditions of  $\text{pH} = 8.50$ ,  $\text{H}_2\text{S}$  flow rate =  $2.00 \text{ cm}^3/\text{min}$ , air flow rate =  $700 \text{ cm}^3/\text{min}$ , circulation rate of absorption solution =  $100 \text{ cm}^3/\text{min}$ ,  $[\text{NTA}] = 36 \text{ mM}$ ,  $[\text{Fe(III)}] = 18 \text{ mM}$  and  $[\text{sorbitol}] = 9 \text{ mM}$ .

***Inorganic salts screened:***

1. Potassium iodide KI
2. Potassium bromide KBr
3. Potassium chloride KCl
4. Ammonium thiocyanate  $\text{NH}_4\text{SCN}$
5. Sodium nitrite  $\text{NaNO}_2$

***Organic compounds screened:***

6. Dimethylsulfoxide DMSO
7. Sorbitol
8. *N, N*-dimethylacetamide DMAA
9. Hexamethylenetetraamine HMTA
10. Triethanolamine TEA
11. Ethanolamine EA
12. 1,3,5-tri-(2-hydroxyethyl)hexahydro-[1,3,5]-triazine THHT
13. Ethylene glycol EG

14. Polyethylene glycol PEG
15. Glyoxylic acid GA
16. Glycerol
17. Glyoxal
18. Acrylamide
19. Furan
20. *N*-methylpyrrolidinone NMP

## ***Results and Discussions***

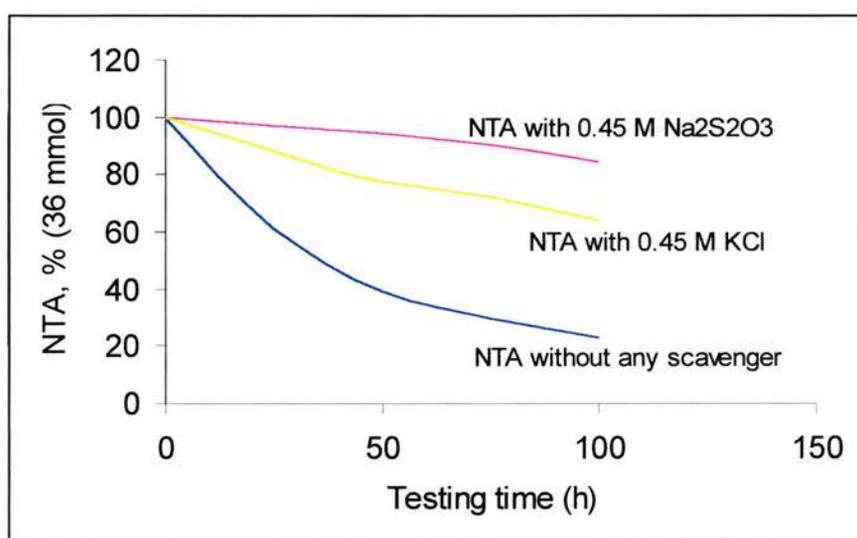
### ***3.2 General screening of scavengers***

All the above compounds are found to be able to diminish radical-induced oxidative degradation of NTA to some extent. Among them, potassium halides KCl, KBr and KI are the simplest examples. The addition of KCl, KBr and KI to the Fe-NTA system has producing four to nine fold increase in the half-life of NTA (**Fig. 3.1 - 3.3** and **Table 3.1**) compared with the system without any additives (*ca.* 40 hours). The function of Cl<sup>-</sup> or Br<sup>-</sup> or I<sup>-</sup> as radical scavenger in the process could be interpreted from the mechanism shown in **Scheme 3.2**: the X<sup>-</sup> anion reacted with the OH radical to yield Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup> and I<sub>2</sub><sup>-</sup> radicals, the latter then are reduced by Fe(II)-NTA to regenerate Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>.<sup>252</sup> The halides, however, were not as good as Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in both extending the half-life of NTA and yielding sulphur. When Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used, there was 14 % of extra sulphur formed over the calculated yield due to the decomposition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

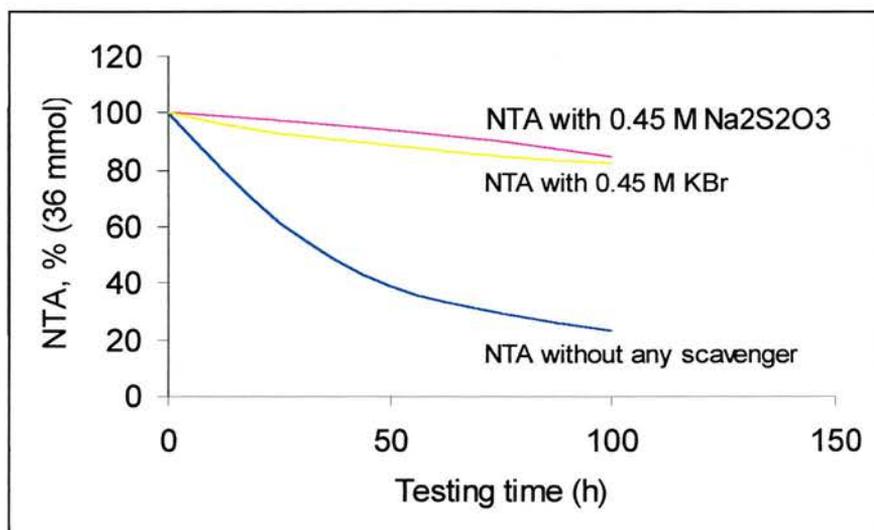


X = Cl, Br and I

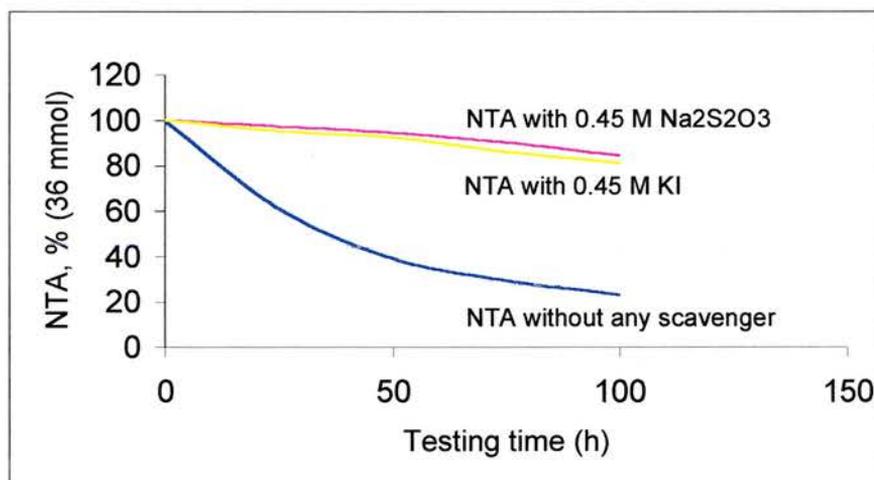
**Scheme 3.2** Proposed mechanism of  $X^-$  as scavengers of hydroxyl radical



**Fig. 3.1** Degradation of NTA in Fe(III)-NTA system without any additive and with 0.45 M KCl, 0.45 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



**Fig. 3.2** Degradation of NTA in Fe(III)-NTA system without any additive and with 0.45 M KBr, 0.45 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



**Fig. 3.3** Degradation of NTA in Fe(III)-NTA system without any additive and with 0.45 M KI, 0.45 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions

**Table 3.1** Scavenging and catalytic activities of the Fe-NTA with various additives

Scavenger	None	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Concentration (M)	0	0.45	0.45	0.45	0.45
Test time (h)	100	95	95	100	96
S <sub>8</sub> (g)	11.75	11.58	11.83	12.75	13.72 <sup>a</sup>
CuS (g)	0	0	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	10.10	4.15	4.40	3.58	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	8.25	4.39	3.54	6.21	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	43	28	29	31	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	92.80	96.61	96.77	95.75	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	1.80	2.22	2.31	1.75	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	5.40	1.18	0.92	1.51	*
Loss rate of Fe ion (mg/L/h)	0.75	1.30	0.42	0.57	0.65
Half life of NTA (h)	39.9	154.0	367.5	331.7	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	17.38	4.50	1.89	2.09	1.66

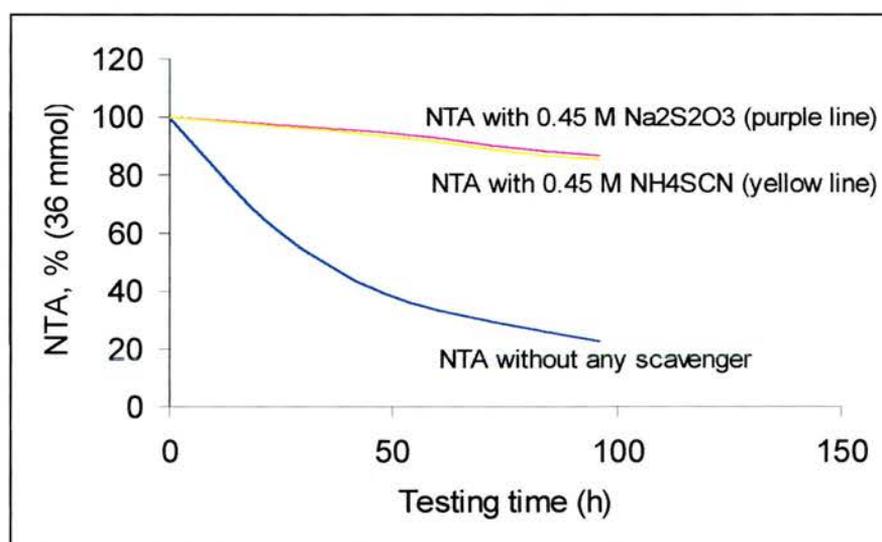
<sup>a</sup> Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

<sup>b</sup> Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate

As can be seen in **Fig. 3.4 - 3.13**, and **Table 3.2 - 3.6**, even more dramatically different effects can be achieved with ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ), sodium nitrite ( $\text{NaNO}_2$ ), dimethylsuloxide (DMSO), dimethylacetamide (DMAA), hexamethylenetetraamine (HMTA), triethanolamine (TEA), ethanolamine (EA), 1,3,5-tri(2-hydroxyethyl)hexahydro-[1,3,5]-triazine (THHT), acrylamide and furan.

The effect of ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) on enhancing the half lifetime of NTA is similar to that of  $\text{Na}_2\text{S}_2\text{O}_3$ . However, low yield of sulphur (86.07 %) and relatively high yield of side products (up to 14 %) were found in this system. The decomposition of  $\text{NH}_4\text{SCN}$  was also obvious in the process.

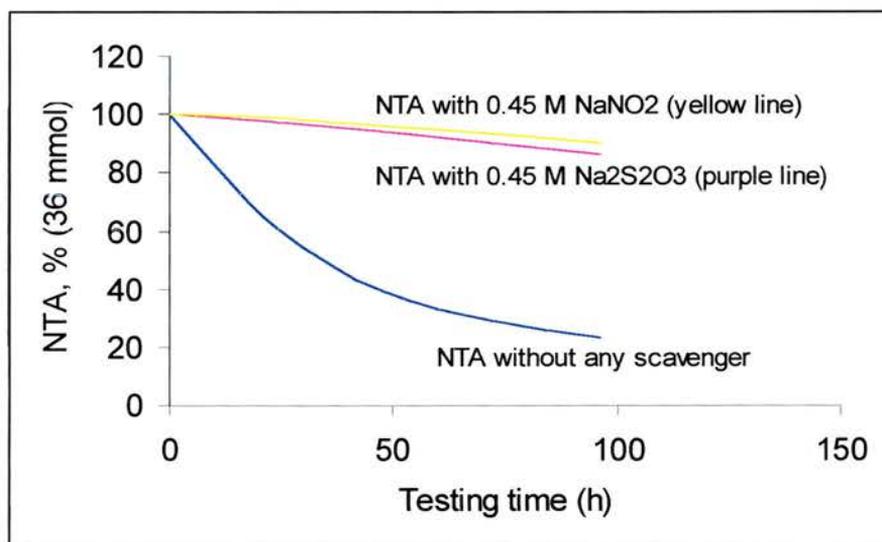


**Fig. 3.4** Degradation of NTA in the Fe(III)-NTA system without any additive and with 0.45 M  $\text{NH}_4\text{SCN}$ , 0.45 M  $\text{Na}_2\text{S}_2\text{O}_3$  under comparable conditions

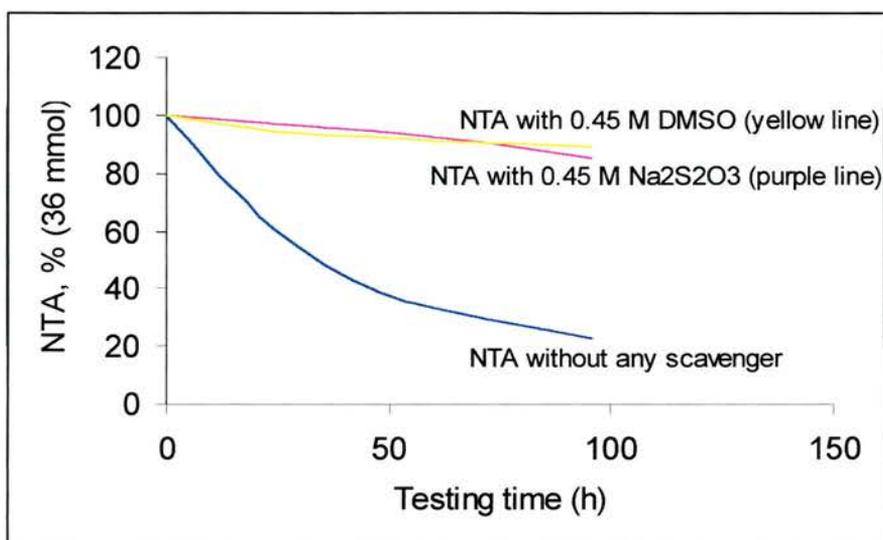
$\text{NaNO}_2$  is not only a gentle reducing agent but also a gentle oxidising agent in aqueous solution. Application of  $\text{NaNO}_2$  to Fe-NTA system has increased the half-life of NTA to 617.2 hours, suggesting the reducing function works to react with free

hydroxyl radical in the process as expected. However, the yield of sulphur (84.93 %) was not satisfactory. The concentration of  $\text{SO}_4^{2-}$  (up to 12.85 % in the resulting solution) was quite high, implying the action of the oxidative property of  $\text{NaNO}_2$ . In addition, severe loss of iron was also observed in this system.

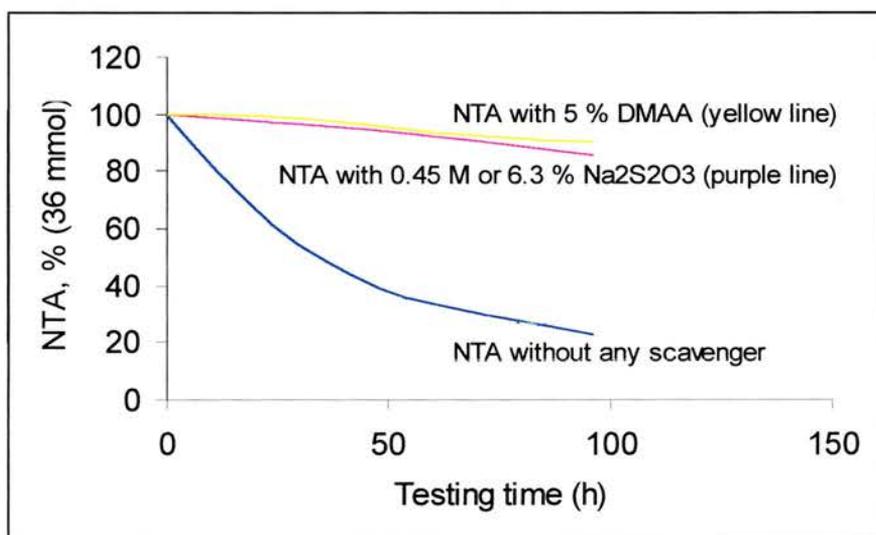
With ideal conversion of  $\text{H}_2\text{S}$  to sulphur (97.80 %), satisfactory half-life time of NTA (560.7 hours) and low formation of side products, DMSO seems a better scavenger of hydroxyl radical for the Fe-NTA system than  $\text{Na}_2\text{S}_2\text{O}_3$ . However, the high consumption of  $\text{NaOH}$  (2 N) (up to  $58 \text{ cm}^3$  for 95 hours running) means that DMSO was oxidised very rapidly by  $\text{O}_2$  or the hydroxyl radical in the process. In addition, that a notorious smell during the process was released due to the formation of methyl sulphone (the oxidised product of DMSO) thereby apparently limits its application as a scavenger of hydroxyl radical for the Fe-NTA system.



**Fig. 3.5** Degradation of NTA in the Fe(III)-NTA system without any additive and with 0.45 M  $\text{NaNO}_2$ , 0.45 M  $\text{Na}_2\text{S}_2\text{O}_3$  under comparable conditions



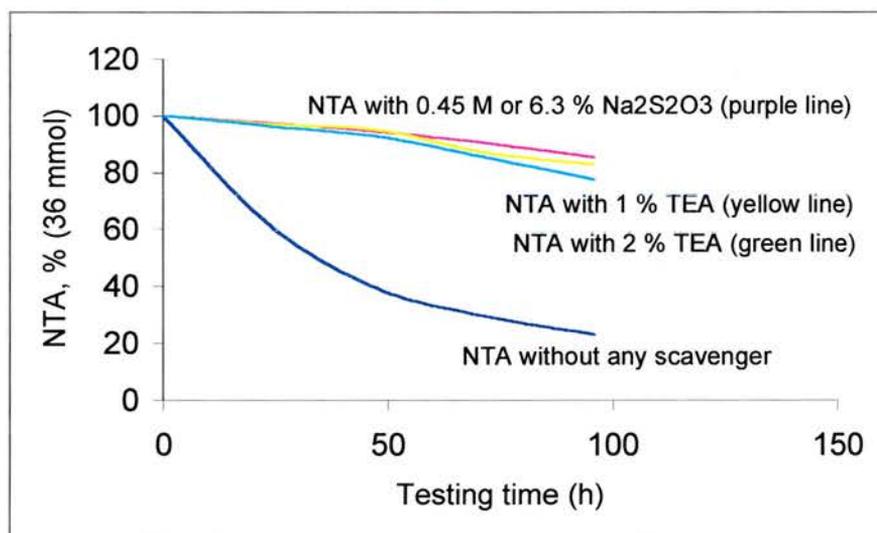
**Fig. 3.6** Degradation of NTA in the Fe(III)-NTA system without any additive and with 0.45 M DMSO, 0.45 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



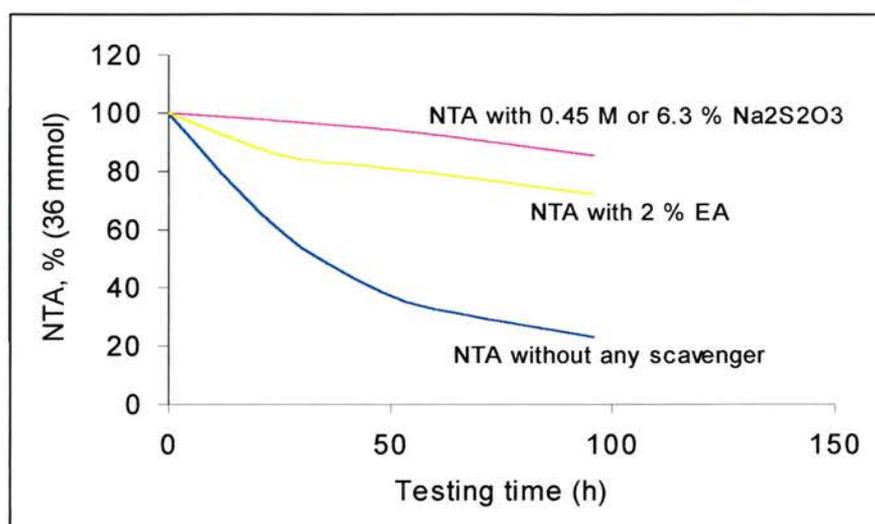
**Fig. 3.7** Degradation of NTA in the Fe(III)-NTA system without any additive and with 0.45 M dimethylacetamide (DMAA), 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions

Dimethylacetamide (DMAA) is found to be somewhat more effective in enhancing the half-life of NTA than  $\text{Na}_2\text{S}_2\text{O}_3$ . The lower conversion of hydrogen sulphide to sulphur (only 88.78 %), however, proves that it is not ideal scavenger for the Fe-NTA system, either.

Triethanolamine (TEA) reacts with Fe(III) or Fe(II) ion to form stable iron complexes which could prevent precipitation of iron hydroxide at up to pH 14.<sup>253</sup> Introduction of TEA to the Fe-NTA system led to little loss of iron in the process. However, only limited effect was found with TEA in extending the half-life of NTA (260 hours). The conversion of  $\text{H}_2\text{S}$  to sulphur (91.34 %) is not marked. TEA functions as a stabiliser for Fe(III) and Fe(II) ion better than a scavenger of hydroxyl radical for the Fe-NTA system.



**Fig. 3.8** Degradation of NTA in the Fe(III)-NTA system without any additive and with 1 % and 2 % triethanolamine (TEA), 0.45 M or 6.3 %  $\text{Na}_2\text{S}_2\text{O}_3$  under comparable conditions



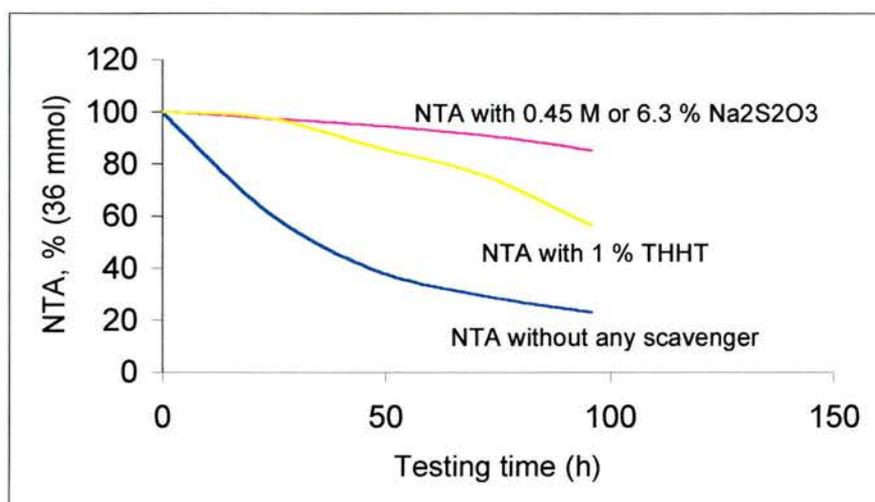
**Fig. 3-9** Degradation of NTA in the Fe(III)-NTA system without any additive and with 2 % ethanolamine (EA), 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions

In the case of EA, the same selectivity to sulphur as and a shorter half-life of NTA than that with TEA were observed. However, a marked consumption of NaOH (2 N) (58 cm<sup>3</sup> for the 96 hours running) and the extensive black solid precipitated at the outlet of H<sub>2</sub>S in Fe-NTA-EA system suggests that EA is not as good as TEA.

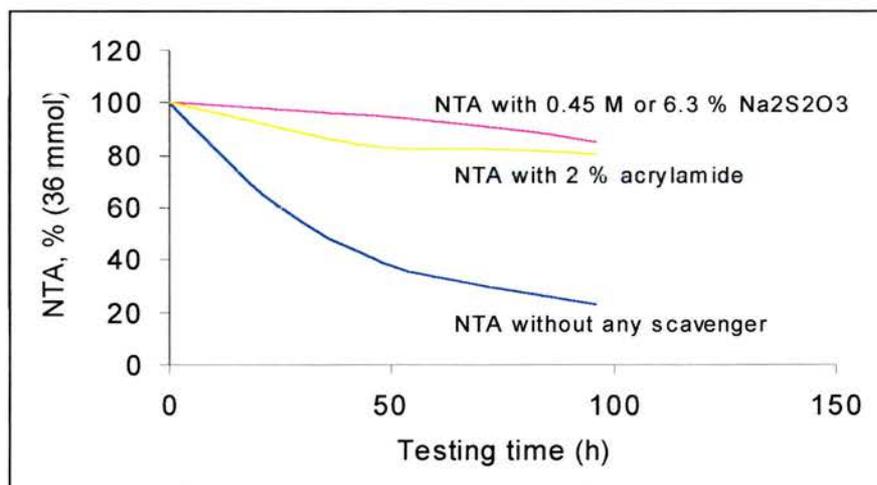
1,3,5-Tri-(2-hydroxyethyl)hexahydro-[1,3,5]-triazine (THHT) can be obtained by reacting ethanolamine (EA) with formaldehyde.<sup>254</sup> THHT was obviously unsuitable for improving the Fe-NTA system. Although the half-life of NTA (119 hours) is increased somewhat, the conversion of H<sub>2</sub>S to sulphur (88.43 %) was quite low due to the formation of further oxidised products. The loss of iron ion (up to 1.77 mg / L / h) was also remarkable.

The addition of acrylamide extended the half-life of NTA to 306 hours. The conversion of H<sub>2</sub>S to sulphur was not bad (93.66 %). However the accumulation of

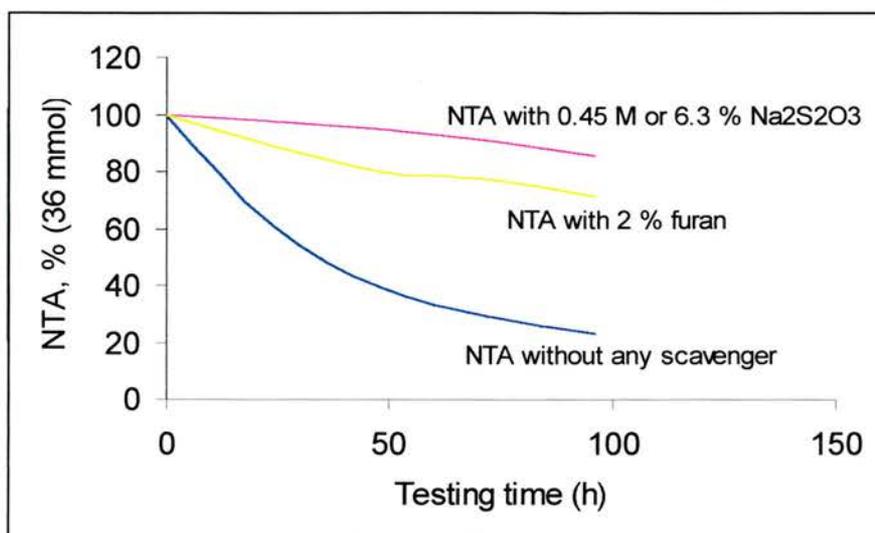
dark solid at the outlet of H<sub>2</sub>S suggested that the Fe-NTA-acrylamide system was not stable enough. Acrylamide seems to decompose easily in alkaline solution.



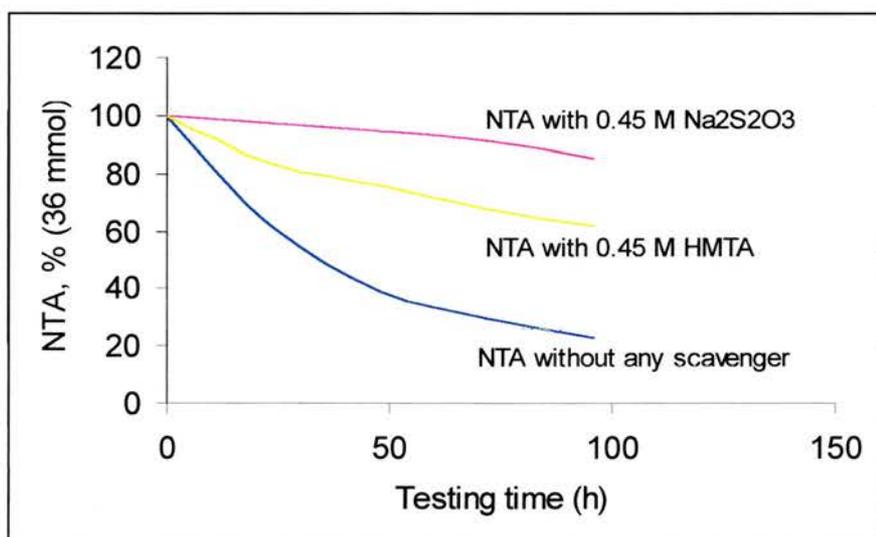
**Fig. 3.10** Degradation of NTA in the Fe(III)-NTA system without any additive and with 2 % 1,3,5-Tri-(2-hydroxyethyl)hexahydro-[1,3,5]-triazine (THHT), 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



**Fig. 3.11** Degradation of NTA in the Fe(III)-NTA system without any additive and with 2 % acrylamide, 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



**Fig. 3.12** Degradation of NTA in the Fe(III)-NTA system without any additive and with 2 % furan, 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



**Fig. 3.13** Degradation of NTA in the Fe(III)-NTA system without any additive and with 0.45 M HMTA, 0.45 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions

The presence of furan in the Fe-NTA system did not improve the lifetime of NTA apparently. The half-life of NTA is only 198.04 hours. The less impressive conversion of H<sub>2</sub>S to sulphur (91.76 %) and the relatively high concentration of by-products means that furan is not suitable as a scavenger of hydroxyl radical for the Fe-NTA system for the catalytic oxidation of H<sub>2</sub>S by air.

Hexamethylenetetraamine (HMTA) did not enhance the lifetime of NTA (145.8 hours) much longer, either. The marked loss rate of Fe ion (up to 3.35 mg / L / h) and relatively low conversion of H<sub>2</sub>S to sulphur (90.67 %) also preclude the possibility for HMTA to replace Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as hydroxyl radical scavenger in the Fe-NTA system.

So far, none of the above reagents are as effective as Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in extending the half-life of NTA and increasing the selectivity to sulphur. The thiosulphate anion is unreplaceable in stabilising the NTA ligand in Fe-NTA system.

However, the overriding effect of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was exceeded surprisingly by two cheap and simple compounds, ethylene glycol (EG) and *N*-methylpyrrolidinone (NMP). As shown in **Fig. 3.14 - 3.15** and **Table 3.7**, the effect of EG and NMP on extending the half-life of NTA was so profound that the half life of NTA has been increased by at least an order of magnitude. Furthermore, the Fe-NTA systems with EG or NMP show good to excellent selectivity to sulphur. EG afforded the most remarkable results, with sulphur yield  $\geq 99$  % and the longest half-life of NTA (about 30 times as the original Fe-NTA system). No tail gas was evolved, only trace amount of by-products and moderate loss of iron ion were observed in this system. As will be described below, the optimum concentration (20 %) of EG in Fe-NTA

system made the degradation of NTA negligible. EG proved to be the most powerful hydroxyl radical scavenger for the Fe-NTA system for the conversion of H<sub>2</sub>S to sulphur by air to date.

**Table 3.2** Catalytic activities of the Fe-NTA with various scavengers

Scavenger	NH <sub>4</sub> SCN	NaNO <sub>2</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Added amount	0.45 M	0.45 M	0.45 M
Test time (h)	95	95	96
S <sub>8</sub> (g)	10.64	10.51	13.72 <sup>a</sup>
CuS (g)	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	9.72	4.29	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	3.43	49.6	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	64	38	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	86.07	84.93	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	5.04	2.22	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	8.89	12.85	*
Loss rate of Fe ion (mg/L/h)	0.72	10.52	0.65
Half life of NTA (h)	415.7	617.2	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	1.67	1.12	1.66

<sup>a</sup> Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

<sup>b</sup> Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate

**Table 3.3** Catalytic activities of the Fe-NTA with various scavengers

Scavenger	DMSO	HATH	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Added amount	0.45 M	0.45 M	0.45 M
Test time (h)	95	102	96
S <sub>8</sub> (g)	11.15	11.72	13.72 <sup>a</sup>
CuS (g)	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	2.36	15.82	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	5.46	6.00	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	58	24	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	97.80	90.67	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	0.67	7.85	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	1.53	1.49	*
Loss rate of Fe ion (mg/L/h)	0.62	3.35	0.65
Half life of NTA (h)	560.7	145.8	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	1.24	4.75	1.66

<sup>a</sup> Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

<sup>b</sup> Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate

**Table 3.4** Catalytic activities of the Fe-NTA with various scavengers

Scavenger	TEA	TEA	EA	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Added amount (w/v, %)	1	2	2	6.3
Test time (h)	96	96	96	96
S <sub>8</sub> (g)	11.09	11.46	11.69	13.72 <sup>a</sup>
CuS (mM)	0	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	22.02	15.00	12.00	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	2.46	3.86	3.86	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	48	44	58	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	88.06	91.34	92.90	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	10.79	7.67	6.12	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.60	0.99	0.98	*
Loss rate of Fe ion (mg/L/h)	0.56	0.31	0.85	0.65
Half life of NTA (h)	352.6	260.6	204.7	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	1.97	2.66	3.39	1.66

a Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

b Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate

**Table 3.5** Catalytic activities of the Fe-NTA with various scavengers

Scavenger	DMAA	THHT	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Added amount (w/v, %)	5	1	6.3
Test time (h)	96	98	96
S <sub>8</sub> (g)	10.78	11.19	13.72 <sup>a</sup>
CuS (mM)	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	19.91	18.60	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	3.00	8.46	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	38	44	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	88.71	88.43	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	10.51	9.43	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.79	2.14	*
Loss rate of Fe ion (mg/L/h)	0.28	1.77	0.65
Half life of NTA (h)	647.8	119.0	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	1.07	5.83	1.66

a Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

b Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate

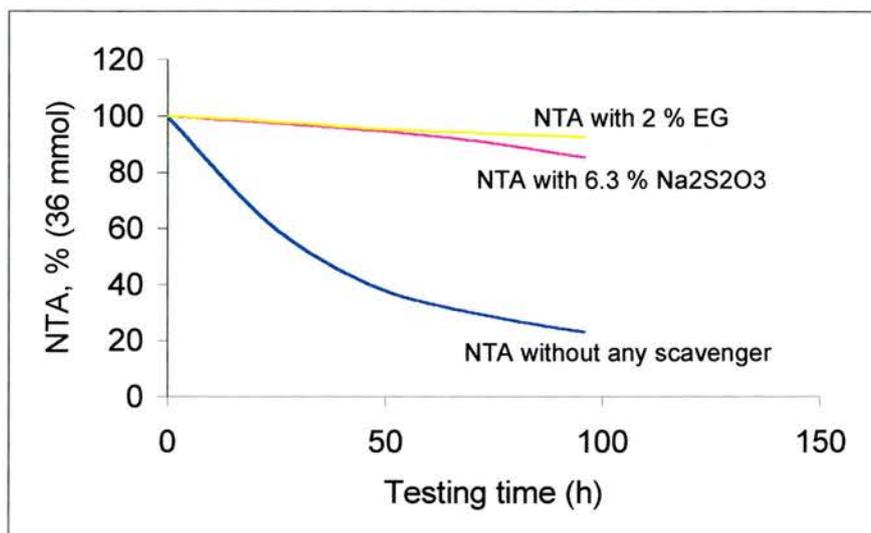
**Table 3.6** Catalytic activities of the Fe-NTA with various scavengers

Scavenger	Furan	Acrylamide	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Added amount (w/v, %)	2	2	6.3
Test time (h)	96	96	96
S <sub>8</sub> (g)	11.43	11.56	13.72 <sup>a</sup>
CuS (g)	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	14.30	11.50	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	3.43	1.39	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	32	42	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	91.76	93.66	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	7.36	5.98	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.88	0.37	*
Loss rate of Fe ion (mg/L/h)	0.51	0.46	0.65
Half life of NTA (h)	198.0	306.0	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	3.50	2.27	1.66

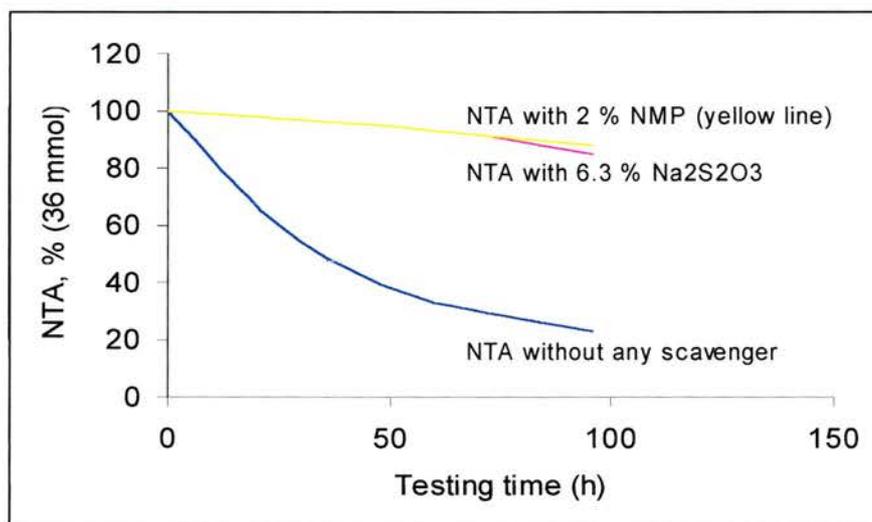
a Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

b Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate



**Fig. 3.14** Degradation of NTA in the Fe(III)-NTA system without any additive and with 2 % ethylene glycol (EG), 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions



**Fig. 3-15** Degradation of NTA in the Fe(III)-NTA system without any additive and with 2 % *N*-methylpyrrolidinone NMP, 0.45 M or 6.3 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> under comparable conditions

**Table 3.7** Catalytic activities of the Fe-NTA with 2 % EG and 2 % NMP

Scavenger	EG	NMP	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Added amount (w/v, %)	2	2	6.3
Test time (h)	96	96	96
S <sub>8</sub> (g)	12.37	11.6243	13.72 <sup>a</sup>
CuS (g)	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	4.96	4.19	368.21
SO <sub>4</sub> <sup>2-</sup> (mM)	1.18	3.00	44.13
Consumed NaOH or NH <sub>4</sub> OH (2 N) (cm <sup>3</sup> )	44	36	37
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)	99.38	96.96	114.23 <sup>b</sup>
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	0.31	2.24	*
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.31	0.80	*
Loss rate of Fe ion (mg/L/h)	0.47	0.55	0.65
Half life of NTA (h)	875.4	518.2	417.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	0.79	1.34	1.66

a Including that produced from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

b Calculation based on consumed H<sub>2</sub>S

\* Difficulty to calculate

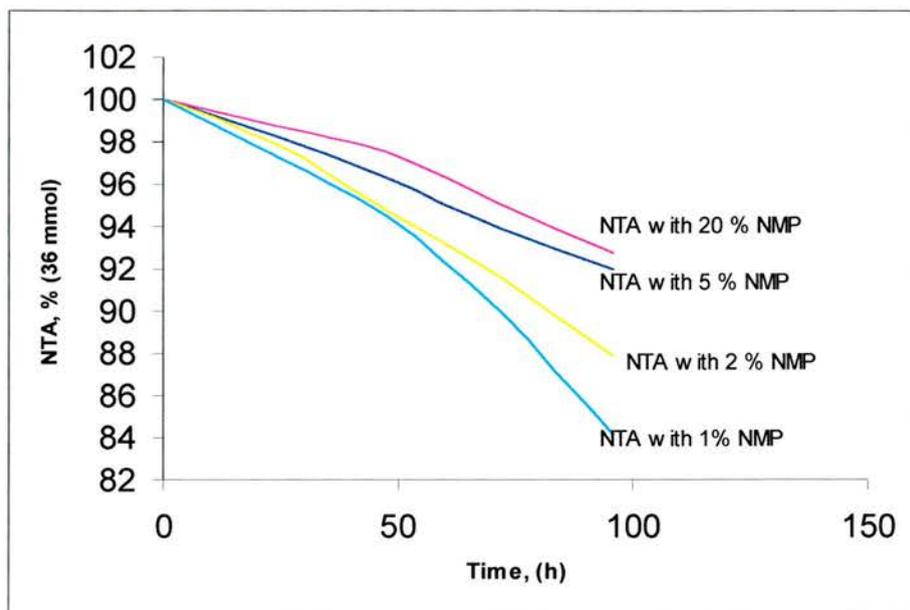
### 3.3 *Influence of concentration on the efficiency of a scavenger*

As described above, various additives show various effects in improving the Fe-NTA system. Even for the same additive (for instance TEA), different activity was observed at different concentration (**Table 3.4**). EG and NMP at the concentration of 2 % shows much better effect than  $\text{Na}_2\text{S}_2\text{O}_3$  (0.45 M or 6.3 %). Is it possible to lengthen the half-life of NTA and improve the selectivity to sulphur further by increasing the concentration of the additives? Experiments with NMP and EG have proved that increasing the concentration of an additive within a certain range does improve the performance of the Fe-NTA system, however, further increasing of the concentration of EG and NTA is not really beneficial.

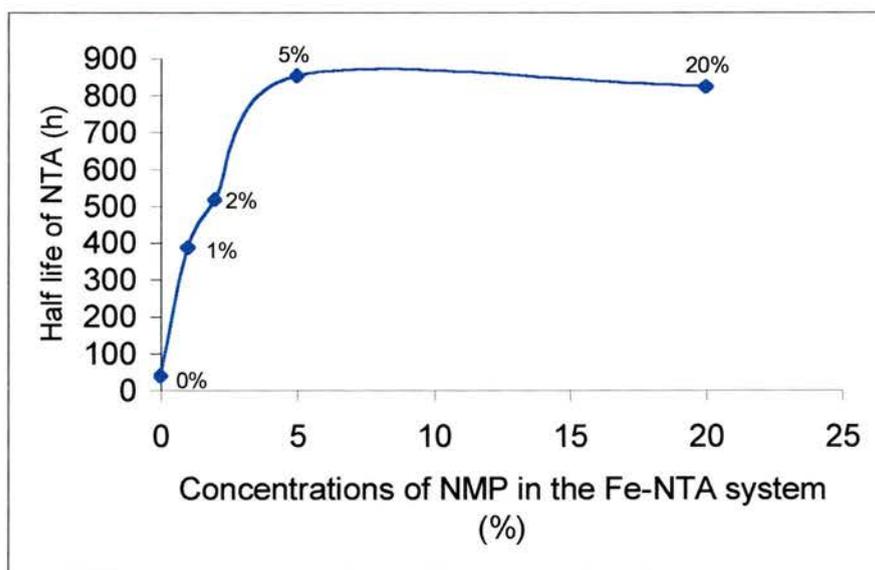
First, the maximum solubility of NMP in the aqueous Fe-NTA system was measured. Massive brown solid immediately precipitated out when the concentration of NMP was beyond 30 w/v. %. Brown precipitate was formed gradually with the Fe-NTA solution consisting of 20 w/v. % - 30 w/v. % of NMP while stored at room temperature for more than a month. Therefore, the addition of NMP to the Fe-NTA system was limited below 20 w/v %. **Table 3.8** and **Fig. 3.16** and **3.17** displayed the results with different concentration of NMP. The conversion of  $\text{H}_2\text{S}$  to sulphur and the half-life of NTA are found to increase with increasing of NMP. The half-life increases with increasing of concentration of NMP from 0 to 5 w/v %. However, further increase of the concentration of NMP does not improve the half-life of NTA any more (**Fig. 3.17**).

**Table 3.8** Catalytic activities of the Fe-NTA with various concentrations of NMP under same conditions

Added Concentration (w/v, %)	1	2	5	20
Test time (h)	96	96	100	98
S <sub>8</sub> (g)	11.60	11.62	11.34	11.82
CuS (g)	0	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	4.53	4.19	1.22	1.17
SO <sub>4</sub> <sup>2-</sup> (mM)	3.43	3.00	2.40	0.09
Consumed NaOH (2 N) (cm <sup>3</sup> )	36	36	39	
Conversion of H <sub>2</sub> S to S (%)	96.66	96.96	98.63	99.14
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0	0
	2.42	2.24	0.68	0.63
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.92	0.80	0.69	0.23
Loss rate of iron ion (mg/L/h)	0.86	0.55	0.11	0.25
Half life of NTA (h)	387.5	518.2	852.6	823.6
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	1.79	1.34	0.81	0.88

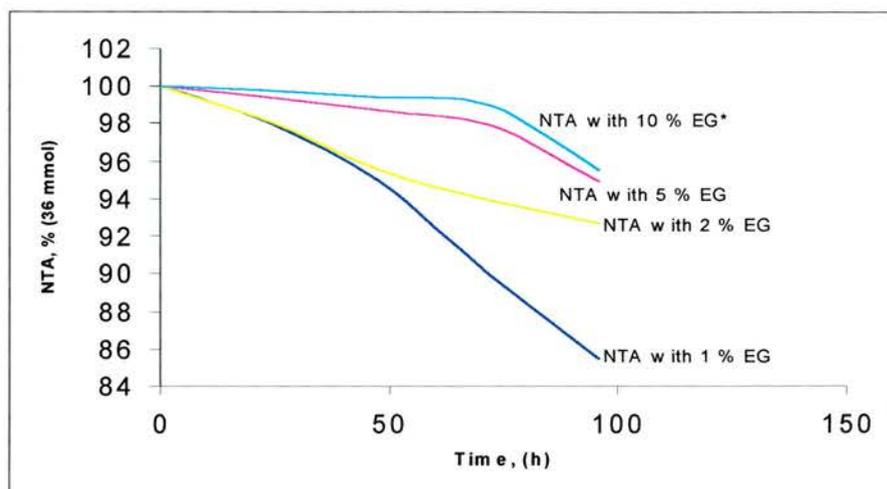


**Fig. 3.16** Degradation curves of NTA in the Fe(III)-NTA system at pH 8.5 with 1 %, 2 %, 5 % and 20 % NMP under comparable conditions

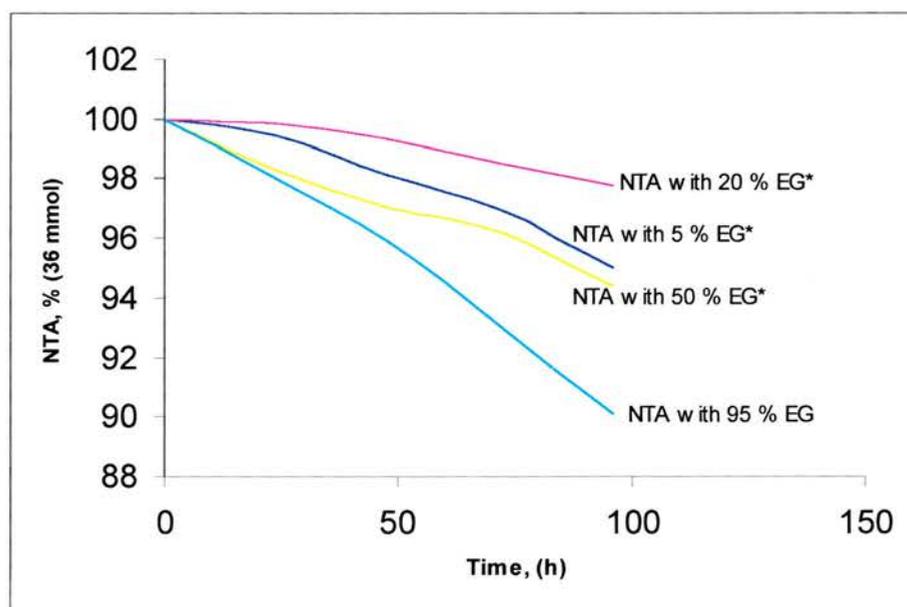


**Fig.3.17** Half-life time of NTA in the Fe-NTA with various concentrations of NMP in the Fe-NTA (Test time: 96 hours)

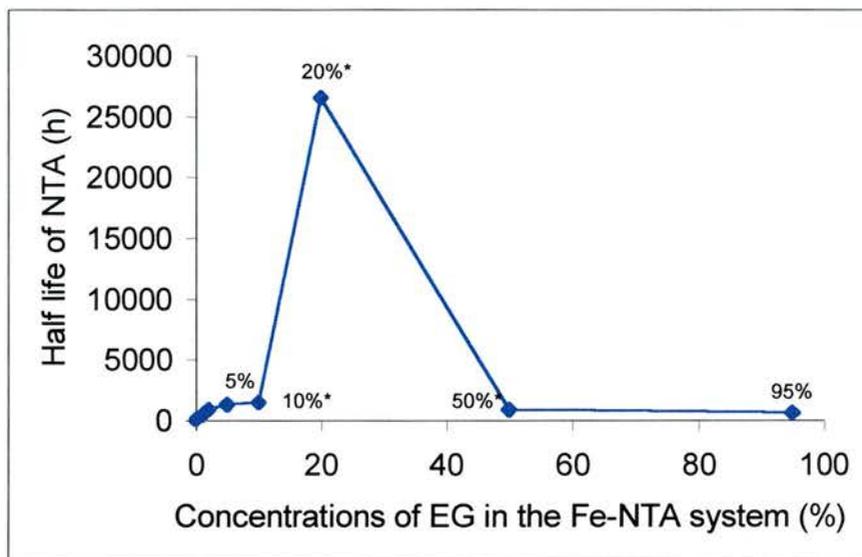
EG is almost completely soluble (up to 95 %) in the aqueous Fe-NTA (pH 8.5 - 9.0) to give a stable homogeneous solution, with or without sorbitol. As can be seen in **Fig. 3.18 - 3.20**, in the range of 1 % - 20 %, the increase of the concentration of EG increasingly extends the half-life of NTA. At the optimum concentration (20 % of EG), the degradation of NTA is negligible. However, if the concentration of EG is beyond 20 %, the half-life of NTA is found to decrease with the increase of concentration of EG. The use of highly concentrated EG-Fe-NTA (EG concentration up to 95 %) was even less effective than 2 % of EG. Obviously, the massive amount of EG can stabilise the iron under basic condition as effective as sorbitol. The systems without sorbitol show similar Fe ion loss to that with sorbitol. However, the addition of sorbitol is favourable for the selectivity to sulphur. With the same addition of EG (5 %), the experiment with sorbitol gave 99.22 % yield of sulphur and 1320 hours half-life of NTA, while that without sorbitol afforded 93.64 % conversion of sulphur from H<sub>2</sub>S and 1289 hours of half-life of NTA.



**Fig. 3.18** Degradation of NTA in the Fe(III)-NTA system with 1 %, 2 %, 5 % and 10 %\* EG under comparable conditions (without sorbitol)



**Fig. 3.19** Degradation of NTA in the Fe(III)-NTA system with 5 %\*, 20 %\*, 50 %\* and 95 % EG under comparable conditions (\* without sorbitol)



**Fig.3.20** Half-life time of NTA in the Fe-NTA with various concentrations of EG in the Fe-NTA (Test time: 96 hours)

**Table 3.9** Catalytic activities of the Fe-NTA with various concentrations of EG

Added Concentration (w/v, %)	1	2	5	5*
Test time (h)	96	96	98	96
S <sub>8</sub> (g)	11.66	12.37	12.38	11.77
CuS (g)	0	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	10.64	4.96	1.08	9.00
SO <sub>4</sub> <sup>2-</sup> (mM)	2.36	1.18	0.96	6.27
Consumed NaOH (2 N) (cm <sup>3</sup> )	34	44	55	47
Conversion of H <sub>2</sub> S to S (%)	93.90	97.30	99.22	93.64
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	5.49	2.40	0.55	4.61
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.61	0.30	0.23	1.60
Loss rate of iron ion (mg/L/h)	0.86	0.47	0.58	0.44
Half life of NTA (h)	424	875	1320	1289
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	1.63	0.79	0.52	0.54

\* Without Sorbitol

**Table 3.10** Catalytic activities of the Fe-NTA with various concentrations of EG

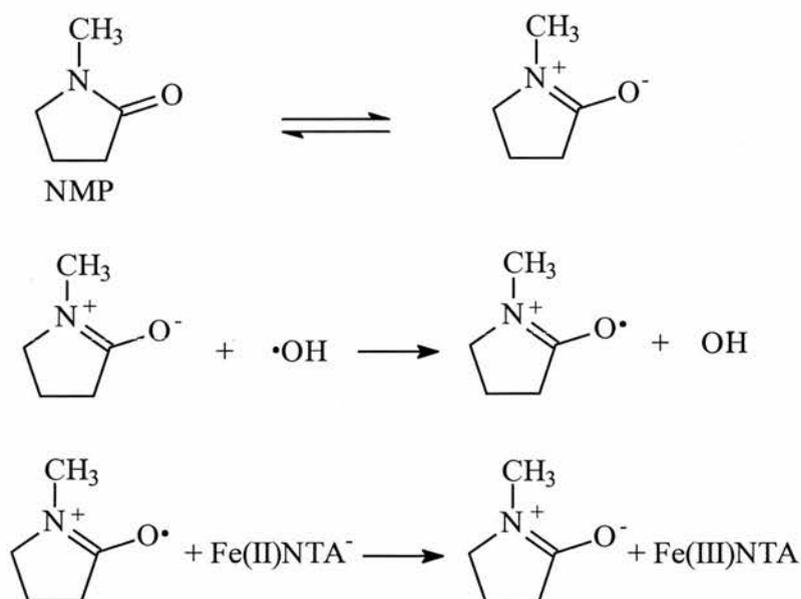
Added concentration (w/v, %)	10*	20*	50*	95
Test time (h)	96	96	166	208
S <sub>8</sub> (g)	11.91	11.68	21.19	22.44
CuS (g)	0	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	7.41	9.94	17.05	10.00
SO <sub>4</sub> <sup>2-</sup> (mM)	3.53	5.03	4.71	7.49
Consumed NaOH (2 N) (cm <sup>3</sup> )	50	21	143	72
Conversion of H <sub>2</sub> S to S (%)	95.30	93.58	94.47	96.53
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	3.80	5.31	4.86	2.52
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.90	1.29	0.67	0.95
Loss rate of iron ion (mg/L/h)	0.13	0.21	0.45	0.25
Half life of NTA (h)	1459	26583	867	630
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	0.48	0.26	0.80	1.10

\* Without sorbitol

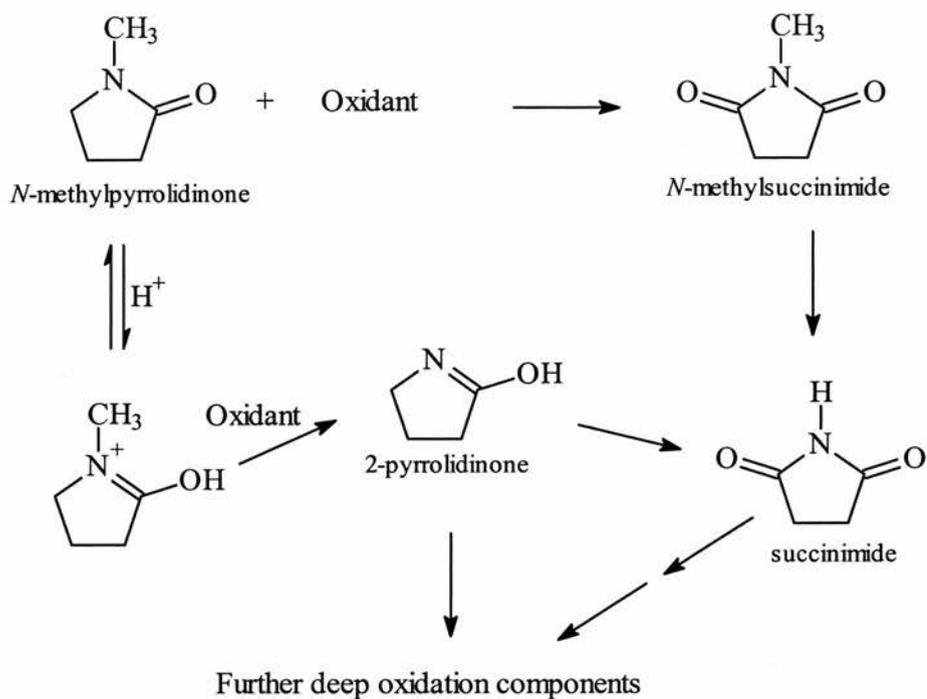
### 3.4 Possible mechanisms of NMP and EG in removing the hydroxyl radical in Fe-NTA system

It has been shown that many additives, inorganic or organic, can decrease the degradation of NTA to some extent. This may result from the competitive reaction of the free hydroxyl radical with the additive and with NTA or Fe-NTA. The additives

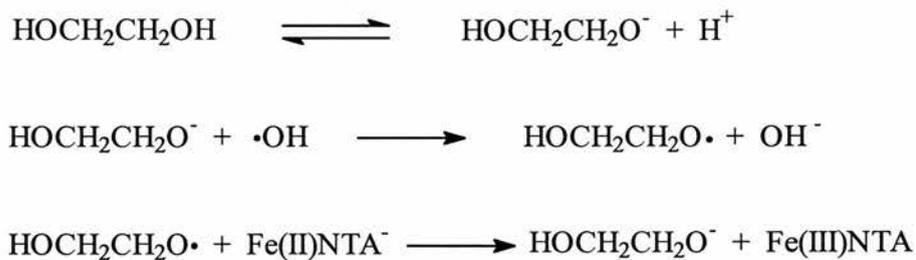
can be either permanently decomposed/consumed/regenerated from the system, or more commonly, partly consumed and partly regenerated. **Scheme 3.3** and **3.4** show the possible mechanism of NMP in removing the free hydroxyl radical and the possible degradation products of NMP, respectively. While in **Scheme 3.5** and **3.6**, the possible approach of the reaction of the free hydroxyl radical with EG and the corresponding decomposed compounds were displayed. However, it is not easy to find detailed evidence in such a complicated system, which consists of many components including iron ions, sorbitol, NTA, and the scavenger itself as well as the degradation products.



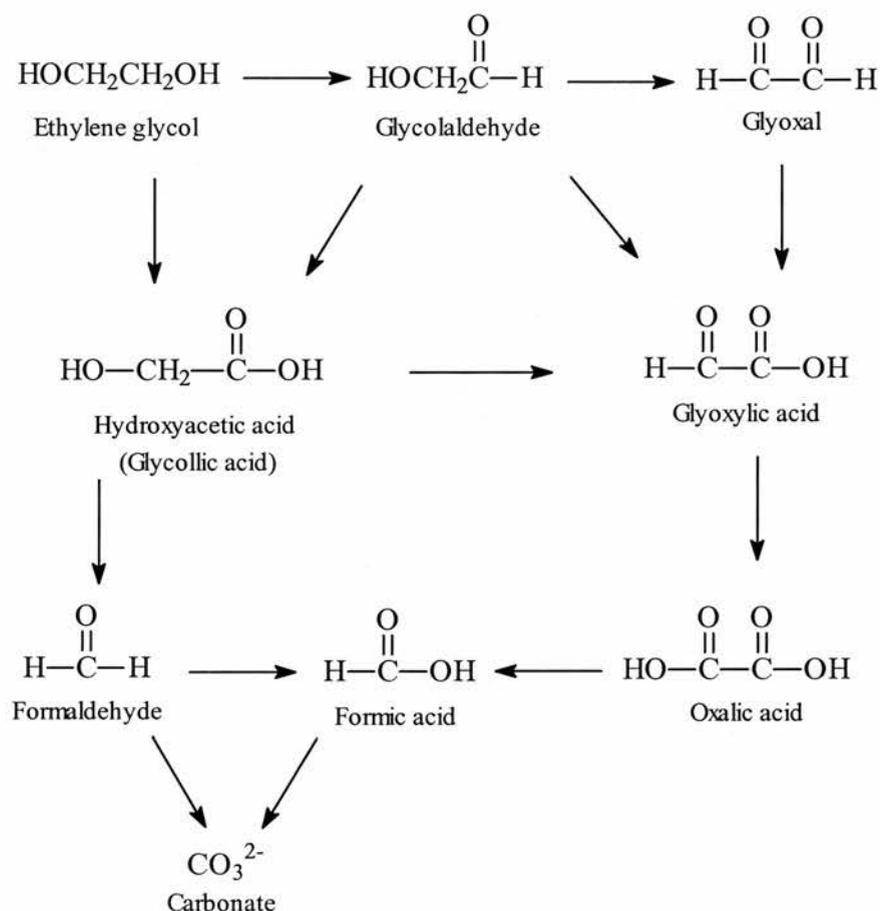
**Scheme 3.3** Suggested mechanism of scavenging hydroxyl radical of NMP



**Scheme 3.4** Proposed oxidation pathway of NMP<sup>257</sup>



**Scheme 3.5** Suggested mechanism of scavenging hydroxyl radicals of EG



**Scheme 3.6** Proposed oxidation pathway of EG

### 3.5 *Function of NMP in scavenging the free hydroxyl radical*

NMP has been used to replace more volatile and toxic organic solvents in paint coating and cleaning applications. The NMP contaminated process water was oxidized harshly with ozone and hydrogen peroxide in a semicontinuous advanced oxidation reactor to reduce the organic concentration.<sup>255</sup> The oxidative by-products of NMP were identified by GC/MS as methylsuccinimide, succinimide, 2-

pyrrolidione, acetaldehyde, etc. (**Scheme 3.4**). The oxidation of H<sub>2</sub>S to S by air catalyzed by Fe-NTA-NMP system, though far milder than the O<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> process, would also lead to the similar degradation of NMP as a consequence of free hydroxyl radical attack. We have successfully monitored the concentration change of NMP in the absorption-oxidation process when NMP was used as scavenger of Fe-NTA system and detected the decomposed species *N*-methylsuccinimide by HPLC (**Table 3.11**). However, other degradation components of NMP, if there were any as shown in **Scheme 3.4**, were not found using this method.

As determined by HPLC (**Table 3.11**), NMP is consumed to some extent in the process. The consumption of NMP is proportional to the starting concentration of NMP in the starting solution, while the accumulation of *N*-methylsuccinimide (NMS) is proportional to the consumption of NMP. For all experiments with NMP as additive to the Fe-NTA system, the presumed eventual oxidised product, CO<sub>3</sub><sup>2-</sup>, has not been found in the resulting solution by gravity method. This means that NMP degrades rather slowly through NMS etc. during the process. It may also be possible that *N*-methyl-pyrrolidinone (NMP) be regenerated in the process subsequent to reacting with scavenge radicals (**Scheme 3.4**). The effective performance of NMP in extending the half-life of NTA suggests that NMP maybe more vulnerable to the attack of the free hydroxyl radical or other oxidant than NTA.

**Table 3.11** Concentration of NMP and its oxidation components in the Fe-NTA-NMP

Concentration of NMP (w/v, %)	1	2	5	20
Concentration of NMP of the starting solution (g / L)	10.105	20.252	49.619	196.451
Concentration of NMP of the resulting solution (g / L)	9.640	19.092	45.382	167.200
The difference of the concentration, $\Delta C$ (g / L)	0.462	1.160	4.237	29.251
The loss rate of NMP (g / L / h) $\times 10^{-2}$	0.48	1.21	4.32	30.47
Concentration of NMS* of the resulting solution (g / L)	0.283	0.763	3.902	5.752

NMS: *N*-methylsuccinimide

### 3.6 *EG in scavenging the hydroxyl radical*

We have attempted to propose the mechanism of EG in scavenging the free hydroxyl radical (**Scheme 3.5**) and outlined the possible degradation products of EG (**Scheme 3.6**) based on general organic chemistry. However, it proved to be very difficult to measure the oxidative products of EG apart from oxalic acid by HPLC and  $\text{CO}_3^{2-}$  by gravimetric method (**Table 3.12**). It should be pointed out that oxalate and carbonate are also the degradation products of NTA.

**Table 3.12** Concentrations of oxalate in the resulting solution when various concentrations of EG are used as scavengers of hydroxyl radicals in the Fe-NTA system (Test time: 96 hours)

Concentration of EG (w/v, %)	0	1	2	5	10	50
Concentration of oxalate (g / L)	0.04	0.79	0.82	1.33	0.78	0.53
Concentration of carbonate (g / L)	0	0	0	0	0	0

As shown in **Table 3.12**, no carbonate is found in the resulting solution. The concentration of oxalate, the actually ultimate degradation product, in the resulting solution (0.04-1.33 g / L) increases with the initial concentration of EG in the range of 0-5 %. When the initial concentration of EG reaches up to 10 %, the total degradation of EG proceeds less. The formation of the ultimate degradation product oxalate tends to decrease.

The absence of the evidence of other intermediates does not affect our understanding that most of the intermediates of EG degradation are still oxidizable and can also function as hydroxyl radical scavenger, rendering EG extra efficacy in removing or inhibiting the free hydroxyl radical in Fe-NTA system. To confirm our assumption, comparative experiments were carried out with glyoxylic acid (GA) and glyoxal (**Table 3.13**), the supposed degradation intermediates of EG in the Fe-NTA system.

It turns out that both glyoxylic acid and glyoxal are effective in extending the half-life of NTA. Glyoxylic acid not only gives comparable results with EG on the half-life of NTA and reasonable yield of sulphur but also leads to less loss of iron ion

than EG. Even so, it is still not economical to use glyoxylic acid as additives commercially, since glyoxylic acid is much more expensive than EG. However, the results support our proposal: the overriding effect of EG in extending the half-life of NTA not only arise from itself (**Scheme 3.5**), but also from its successive oxidation derivatives (**Scheme 3.6**), which also show appreciable activity towards the free hydroxyl radical.

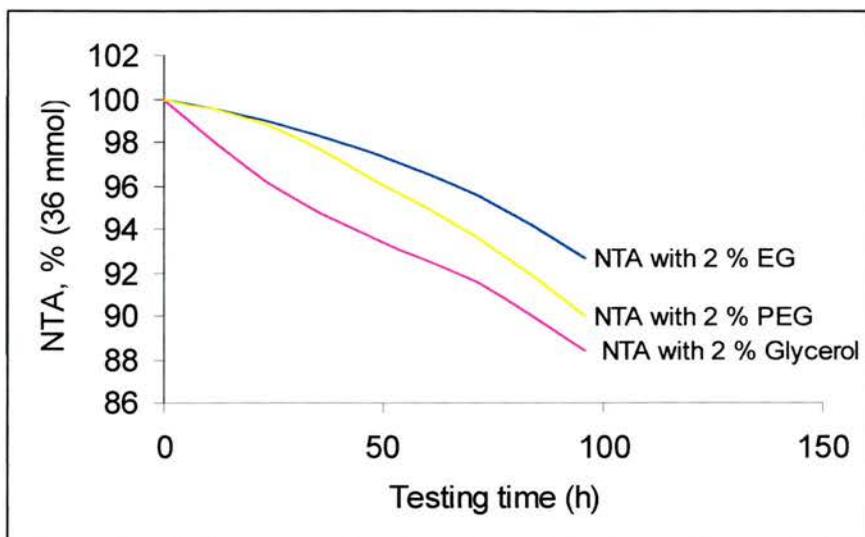
**Table 3.13** Catalytic activities of the possible degradation products of EG: glyoxylic acid (GA), glyoxal and EG under the same conditions

Scavenger	EG	Glyoxal	Glyoxylic acid
Added concentration (w/v, %)	2	2	2
Test time (h)	96	96	96
S <sub>8</sub> (g)	12.37	10.91	11.66
CuS (g)	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	4.06	23.00	12.25
SO <sub>4</sub> <sup>2-</sup> (mM)	1.18	3.00	4.18
Consumed NaOH (2 N) (cm <sup>3</sup> )	44	211	51
Conversion of H <sub>2</sub> S to S (%)	97.30	87.41	92.69
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	2.40	11.83	6.25
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.30	0.77	1.06
Loss rate of iron ion (mg/L/h)	0.47	0.52	0.21
Half life of NTA (h)	875.4	273.9	739.0
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	0.79	2.53	0.94

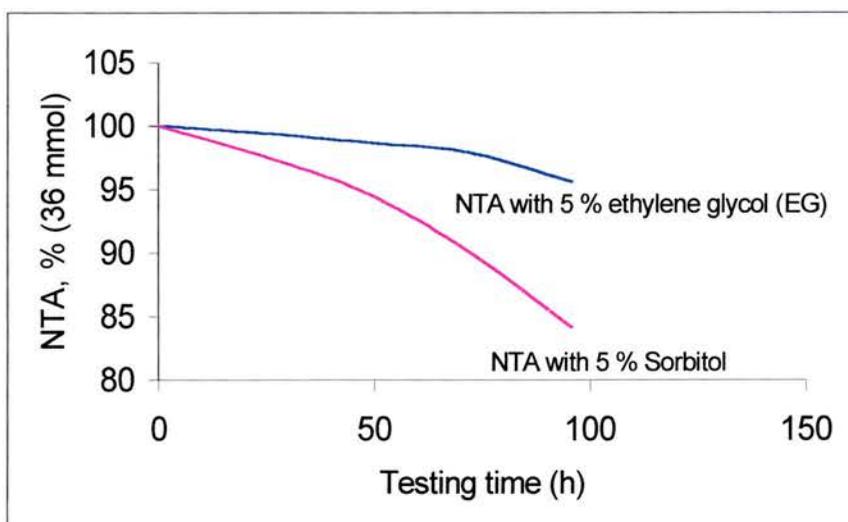
### 3.7 Comparative studies of the analogues of EG

Sorbitol has been able to form a number of stable complexes with some transition metal ions including Fe(III) and Fe(II) by displacement of protons from the hydroxyl groups of the ligand.<sup>256-258</sup> This coordination has been used successfully to stabilise the Fe(III) and Fe(II) ion from the precipitation of Fe(OH)<sub>2</sub> and Fe(OH)<sub>3</sub> in the basic solution (pH 8.5-9.0) of the commercial Fe(III)/Fe(II)-NTA process for the conversion of H<sub>2</sub>S to S and through all of our experiment. The excellent performance of sorbitol in stabilising Fe(III)/Fe(II) ion in basic condition and its structural similarity to EG (with multi-hydroxyl groups) prompts us to consider it as both a iron stabiliser and a scavenger of the free hydroxyl radical at the same time in the Fe-NTA system. Excessive addition 5 % of sorbitol (compared with 9 mmol for normal stabilisation of Fe iron) did exert further effect in stabilising Fe(III)/Fe(II) ion, leading to the least loss of iron among all the related experiments. The selectivity to sulphur is good (94.9 %). The half-life of NTA (385.1 hours), however, is slightly shorter than when Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was employed. Obviously, sorbitol behaves better as a Fe(III)/Fe(II) stabilizer than a scavenger of hydroxyl radical.

Polyethylene glycol (PEG) and glycerol, closer analogues of EG in structure than sorbitol, have also been tested (**Fig. 3.21 - 3.22** and **Table 3.14**). At the concentration of 2 %, PEG and glycerol are found to be more effective than Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> but less efficient than EG in extending the half-life of NTA (539 hours and 630 hours respectively), though increase of concentration of PEG to 5 % does not increase the half-life of NTA (316.5 hours) further.



**Fig. 3.21** Comparative degradation of NTA in the Fe(III)-NTA system with 2 % EG, 2 % PEG and 2 % Glycerol under the same conditions



**Fig. 3.22** Comparative degradation of NTA in the Fe(III)-NTA system with 5 % EG and 5 % Sorbitol under the same conditions

**Table 3.14** Catalytic activities of Fe-NTA with the analogues of EG

Scavenger	EG	glycerol	PEG	EG	Sorbitol
Added concentration (w/v, %)	2	2	2	5	5
Test time (h)	96	96	96	98	96
S <sub>8</sub> (g)	12.37	11.70	11.77	12.38	10.85
CuS (g)	0	0	0	0	0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	4.06	12.35	12.50	1.08	12.05
SO <sub>4</sub> <sup>2-</sup> (mM)	1.18	1.18	1.93	0.96	2.03
Consumed NaOH (2 N) (cm <sup>3</sup> )	44	58	69	55	53
Conversion of H <sub>2</sub> S to S (%)	97.30	93.38	93.10	99.22	92.82
Conversion of H <sub>2</sub> S to CuS (%)	0	0	0	0	0
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	2.40	6.32	6.40	0.55	6.61
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	0.30	0.30	0.50	0.23	0.56
Loss rate of iron ion (mg/L/h)	0.47	0.74	0.25	0.58	0.15
Half life time of NTA (h)	875	630	539	1320	380
1 <sup>st</sup> order rate constant of NTA degradation (h <sup>-1</sup> ) × 10 <sup>-3</sup>	0.79	1.10	1.28	0.52	1.82

### 3.8 Conclusions

A series of inorganic and organic compounds have been tested as scavengers or inhibitors of hydroxyl radical for the Fe-NTA system. Among them, *N*-methylpyrrolidinone (NMP) and ethylene glycol (EG) were found to be more effective than  $\text{Na}_2\text{S}_2\text{O}_3$ . Ethylene glycol (EG) appears to be a promising alternative of  $\text{Na}_2\text{S}_2\text{O}_3$  for the current Fe-NTA system. In the ideal instance of Fe-NTA with 20 % of EG, the degradation of NTA is negligible. The mechanisms of EG and NMP in scavenging free hydroxyl radical and their possible degradation approaches have been proposed.

The analogues of ethylene glycol (EG) including glycerol, polyethylene glycol (PEG) and sorbitol have also been tested as free hydroxyl radical for Fe-NTA system. These additives, generally speaking, are better than  $\text{Na}_2\text{S}_2\text{O}_3$  but less effective than EG in improving the Fe-NTA system.

## Experimental

### Materials and reagents

The following materials and solvents were ordered from Aldrich or Lancaster and were used directly without further purification: nitrilotriacetic acid trisodium salt  $\text{Na}_3\text{NTA}$  (99.0 %); sorbitol (98.0 %);  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  (97.0 %);  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (98.0 %); sodium oxalate (99.5 %); glacial acetic acid (99.99 %); methyl alcohol (HPLC grade); 1, 10-phenanthroline (99.0 %); hydrogen sulphide (99.5 %);  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; acetonitrile (HPLC grade); potassium iodide KI (99.0 %); potassium bromide KBr (99.9 %); potassium chloride KCl (99.0 %); ammonium thiocyanate  $\text{NH}_4\text{SCN}$  (98.0 %); sodium nitrite  $\text{NaNO}_2$  (97.0 %); sodium tetraborate  $\text{NaBF}_4$  (99.0 %); sodium

thiosulphate  $\text{Na}_2\text{S}_2\text{O}_3$  (99.0 %); methylsulfoxide DMSO (99.9 %); sorbitol (99.0 %); *N,N*-dimethylacetamide DMAA (99.5 %); hexamethylenetetraamine HMTA (99.0 %); triethanolamine TEA (99.0 %); ethanolamine EA (99.0 %); ethylene glycol EG (99.0 %); polyethylene glycol PEG (99.0 %); glyoxylic acid GA (99.0 %); glycerol (99.0 %); glyoxal (99.0 %); acyamide (98.5 %); furan (99.5 %); *N*-methylpyrrolidinone NMP (99.0 %).

1,3,5-tri(2-hydroxyethyl)hexahydro-[1,3,5]-triazine THHT (99.0 %) was provided by US Filter and used directly.

### ***Testing of scavenging activity of Fe-NTA with various scavengers***

#### **General procedure**

To the oxidizer compartment of 1-litre reactor (**Scheme 2.2**) was added the aqueous Fe(III)-NTA solution with 9 mM of sorbitol and appropriate amount of scavenger of hydroxyl radicals at pH 8.50. The liquid pump was then started and some of the solution was pumped into the absorber compartment with a flow rate of  $100 \text{ cm}^3 \text{ min}^{-1}$ . The pH and redox probes were then turned on. At this stage the air was bubbled into the oxidizer and the air flow rate was adjusted to the required value. The valve of the  $\text{H}_2\text{S}$  cylinder was switched on and the  $\text{H}_2\text{S}$  flow rate was adjusted to  $2.00 \text{ cm}^3 \text{ min}^{-1}$ . The start time of the reaction was recorded, and the pH and redox probe readings were recorded from time to time. The pH was continuously controlled to 8.50 by the addition of 2 M of NaOH solution with a syringe pump. The sulphur was filtered off with every *ca.* 50 hours interval and  $5 \text{ cm}^3$  of sample was taken from the running system every 24 hours in order to monitor the degradation of NTA and the loss of iron.

### ***HPLC analysis and operating conditions***

#### ***Analyses of NMP and its related composition species***

A Milton Roy Pump No.043 024 equipped with a chromatography accessory, UV-visible spectromonitor 3000 (LDC analytical) and a chart recorder (*Waters 746 Dato Module*) were used.

Analytical column: *Spherisorb ODS II* 5  $\mu\text{m}$  4.6 mm  $\times$  250 mm; column mobile phase; acetonitrile : water = 5 : 95; flow rate: 1.0  $\text{cm}^3\text{min}^{-1}$ ; temperature: ambient; detector: UV absorption at 220 nm; injection sample: 10  $\mu\text{L}$ ; recorder: 10 mV full scale; chart speed: 0.5  $\text{cm min}^{-1}$ .

#### ***Preparation of sample***

0.04 g of the reaction mixture was taken from the oxidizer compartment of the 1-liter continuous reactor and placed in a 100- $\text{cm}^3$  volumetric flask. This sample was diluted to 100  $\text{cm}^3$  with water and then filtered through a 0.45  $\mu\text{m}$  micron filter before analysis.

#### ***Calibration of HPLC analysis***

Quantitative analyses of NMP and its degradation intermediates were based on the calibration curve established by varying the concentration of the corresponding known samples. Peak heights at the indicated amplification settings were plotted vs. concentration of the species. The linear nature of these plots indicated precise HPLC determinations of these molecular species over a considerable range of concentration.

***Analyses of NTA and its related degradation products, iron ion,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  are the same as that in Chapter 2.***

## Chapter 4

### **Novel Non-Aqueous Fe(III)/Fe(II) Redox Couple Sulphur Recovery Process**

#### **4.1 Introduction**

Iron complex catalytic solutions for removing hydrogen sulphide contained in a wide range of industrial gas streams have been used for over a century and a half as redox catalysts. Current systems using aqueous aminopolycarboxylate chelate iron redox catalyst solution was introduced around 1962.<sup>26</sup> Since then, numerous improvements in both process equipment, plant configuration and process chemistry have been made. As described in **Chapter 3**, we have successfully improved the Fe-NTA process by increasing the half-life time of NTA three fold relative to the current commercial Fe-NTA- $\text{Na}_2\text{S}_2\text{O}_3$  system.

Actually, the gas streams containing hydrogen sulphide are usually also contaminated with carbon dioxide ( $\text{CO}_2$ ) or other contaminating gases which need to be cleaned out from gas streams. Consequently gas streams are generally first contacted with an alkanolamine to remove  $\text{H}_2\text{S}$  &  $\text{CO}_2$  then dehydrated with glycol. The alkanolamine is thermally regenerated liberating the  $\text{H}_2\text{S}$  &  $\text{CO}_2$ . This secondary acid gas stream is desulfurized by Fe-NTA redox system and the  $\text{CO}_2$  is directly released to atmosphere.<sup>259</sup>

Considering the economical and practicable reasons, it is necessary to develop a more efficient process that can remove not only sulphur contaminants, but

also carbon dioxide and water in a single process while producing or recovering a high quality of solid elemental sulphur. The non-aqueous catalyst system could be a unique possibility to sort out the above problems in a single process because a specific organic solvent employed, for example NMP, is able to absorb all the contaminants gas including water.

However, most of the conventional aqueous catalysts such as the Fe(II) and Fe(III) complexes of EDTA, HEDTA, NTA are inadequately soluble in the organic solvents, as are the phosphorus analogues NTAP, NTA2P, MeNTA2P and NTA3P employed in **Chapter 2**. Up to now, only the  $\beta$ -diketone  $[R_1C(O)CH_2C(O)R_2]$  chelate complexes are feasible as catalysts in non-aqueous process for the removal of hydrogen sulphide from natural gas streams. The metals patented as  $\beta$ -diketone chelates for this purpose include polyvalent iron, copper, cobalt, vanadium, nickel and manganese,<sup>260,261</sup> as well as scandium, yttrium or the elements in lanthanide and actinium groups.<sup>67</sup> Among them the Fe(III) chelate of acetylacetonone (2, 4-pentanedione) in NMP, water free or with a water content of less than or equal to 5 w/v %, was the most successful catalyst system. The substantially non-aqueous process was claimed to desulphurise, decarbonate (i.e. remove or absorb carbon dioxide) and dehydrate a gas stream simultaneously. However, a key deficiency in this system is found to be substantial loss of ligand,  $\beta$ -diketone that eventually led to deactivation of the catalyst system in the process.<sup>68</sup>

Accordingly, attempts to further improve current non-aqueous catalyst system by selecting more robust ligands in place of easily degraded  $\beta$ -diketone and to seek suitable organic solvents are our initial object. However, it is rather difficult

to find a suitable iron complex which is both highly soluble in organic solvent and comparable to the iron complex of  $\beta$ -diketone in price and practicality under the required conditions (pH = 8.50). Is it possible to oxidise  $H_2S$  to S directly with plain iron(III) salts in organic solvent?

The simplest idea provides us surprising and fantastic results. The preliminary experiment with  $FeCl_3$ -NMP catalyst system without any ligand did work unexpectedly well for the conversion of hydrogen sulphide to sulphur. This triggered our following investigation for different iron salts in various organic solvents.

## ***Results and Discussion***

### ***4.2 Selection of organic solvents***

About twenty common organic solvents were screened based upon the solubility and stability of  $FeCl_3$  in the solvent (either water-free or with 5 w/v % of water) without pH control. If  $FeCl_3$  dissolves well in a solvent to give a stable homogeneous solution (water-free or with 5 w/v. % of water), the solution is then loaded in the 1-litre reactor for preliminary test on catalytic activity toward the oxidation of  $H_2S$  to sulphur by air. The catalytic experiments were performed at conditions of  $H_2S = 2.0 \text{ cm}^3 / \text{min}$ , air =  $700 \text{ cm}^3 / \text{min}$ , circulation rate of absorption solution =  $100 \text{ cm}^3 / \text{min}$ , initial pH value and room temperature. **Table 4.1** lists the qualitatively testing results of different  $FeCl_3$  / organic solvent systems based on visual observations.

Furan, sulfolane, trichloroethylene (TCE), morpholine (MP) and *N*-formylmorpholine (NFMP) (water-free or with 5 w/v % of water) could not dissolve  $\text{FeCl}_3$  properly. Therefore these solvents were not further tested.

$\text{FeCl}_3$  is soluble in a variety of other organic solvents, either water-free or with 5 w/v % of water, to give corresponding stable homogeneous solution. The solvents include formamide (FA), *N*-methylpyrrolidinone (NMP), *N,N*-dimethylethanolamine (DMEA), dimethyl sulfoxide (DMSO), dimethyl formamide (DMFA), propylene carbonate (PC), 1,4-dioxane (DO), diethylglycolmonomethylether (DEGME), di-(ethylglycol)-diethylether (DEGDE), triethylphosphate (TEPP), methyl-acetoacetate (MAA), triethanolamine (TEA), acrylic acid and ethanol. However, as displayed in **Table 4.1**, only the  $\text{FeCl}_3$  / NMP system, our initial discovery, was found to have catalytic activity towards the oxidation of hydrogen sulphide to sulphur by air.  $\text{FeCl}_3$  in other organic solvents showed little catalytic activity. Therefore, NMP becomes our solvent of choice for further studies.

**Table 4.1** Screening of organic solvents for FeCl<sub>3</sub> catalytic conversion of H<sub>2</sub>S to S by air

Solvent	Catalyst Composition	Stability	Test Time (h)	Results & Comments
Propylene carbonate (PC)	FeCl <sub>3</sub> ([Fe] = 90 mM) / 95 % PC / 5 % water	Stable	5	~ Severe tail gas ~ Poor catalytic activity
Methyl-acetoacetate (MAA)	FeCl <sub>3</sub> ([Fe] = 90 mM) / 95 % MAA / 5 % water	Stable	3	~ Bad smell ~ Severe tail gas ~ Poor catalytic activity
Diethylglycolmono methylether (DEGME)	FeCl <sub>3</sub> ([Fe] = 90 mM) / 95 % DEGME / 5 % water	Very stable	19.5	~ Colour of the reaction solution deepened ~ Severe tail gas ~ Poor catalytic activity
Diethylglycoldiethyl ether (DEGDE)	FeCl <sub>3</sub> ([Fe] = 90 mM) / 95 % DEGDE / 5 % water	Stable	1.3	~ A lot of tail gas ~ Very poor catalytic activity
Triethylphosphate (TEPP)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % TEPP / 5 % water	Stable	7	~ A lot of tail gas ~ Very poor catalytic activity
Formamide (FA)	FeCl <sub>3</sub> ([Fe] = 90 mM) / 95 % FA / 5 % water	Stable	5	~ Grey solid precipitated out ~ Severe tail gas ~ Very poor catalytic activity

**Table 4.1** Screening of organic solvents for FeCl<sub>3</sub> catalytic conversion of H<sub>2</sub>S to S by air (continued)

Solvent	Catalyst Composition	Stability	Test Time (h)	Results & Comments
<i>N,N</i> -Dimethylethanamine (DMEA)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % DMEA / 5 % water	Stable	5	~ Severe tail gas ~ Very poor catalytic activity
Acrylic acid	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % Acrylic acid / 5% water	Stable	15	~ A lot of tail gas ~ Very poor catalytic activity
Furan	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % Furan / 5 % water	Unstable		
Sulfolane	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % Sulfolane / 5 % water	Unstable		
Ethanol	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % Ethanol / 5 % water	Stable	0.5	~ A lot of tail gas ~ Very poor catalytic activity
2-butoxyethanol (BE)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % BE / 5 % water	Stable	17	~ Severe tail gas ~ Poor catalytic activity
Trichloroethylene (TCE)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % TCE / 5 % water	Unstable		

**Table 4.1** Screening of organic solvents for FeCl<sub>3</sub> catalytic conversion of H<sub>2</sub>S to S by air (continued)

Solvent	Catalyst Composition	Stability	Test Time (h)	Results & Comments
Triethanolamine (TEA)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % TEA / 5 % water	Stable	3	~ A lot of tail gas ~ Very poor catalytic activity
1,4- dioxane (DO)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % DO / 5 % water	Stable	10	~ A lot of tail gas ~ Very poor catalytic activity
Dimethyl formamide (DMFA)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % DMFA / 5 % water	Stable	15	~ Grey suspension found ~ A lot of tail gas ~ Very poor catalytic activity ~ Very poor catalytic activity
Dimethyl sulfoxide (DMSO)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % DMSO / 5 % water	Stable	4	~ A lot of tail gas ~ Very poor catalytic activity
Morpholine (MP)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % MP / 5 % water	Unstable		

**Table 4.1** Screening of organic solvents for FeCl<sub>3</sub> catalytic conversion of H<sub>2</sub>S to S by air (continued)

Solvent	Catalyst Composition	Stability	Test Time (h)	Results & Comments
<i>N</i> -formylmorpholine (NFMP)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % NFMP / 5 % water	Unstable		
<i>N</i> -methylpyrrolidinone (NMP)	FeCl <sub>3</sub> ([Fe] = 36 mM) / 95 % NMP / 5 % water	Stable	300	~ Trace of tail gas ~ Bright yellow crystalline sulphur

Actually, *N*-methylpyrrolidinone (NMP) has been widely applied in industrial scale gas purification,<sup>262-264</sup> for example in the Purisol<sup>®</sup> process for the physical removal of H<sub>2</sub>S and CO<sub>2</sub> from gas streams.<sup>265</sup> In addition, it has also been widely used to remove adhesives (especial cyanoacrylate-based) from plastic, glass, metal, ceramic, stone and fiber surfaces and also from human skin and to clear surfaces of a plastic, esp. poly(lauryl methacrylate)<sup>266</sup> and to dehydrate gas streams.<sup>267</sup> As can be seen from **Table 4.2**, the inexpensive and environmental acceptable NMP can be a perfect organic media for the conversion of hydrogen sulphide to sulphur with its ideal high boiling point, low freezing point, large change in sulphur solubility with temperature, low toxicity, high H<sub>2</sub>S and CO<sub>2</sub> solubility and completely miscibility with water.

**Table 4.2.** Property of *N*-pyrrolidinone (NMP) <sup>68</sup>

Property	
High boiling point	202°C
Low freezing point	-24 °C, -12 °F
Low specific heat	0.4 cal / g. °C
Low toxicity	LD50.7 g / kg rat
TSCA listed	Yes
Biodegradable	Yes
Low viscosity	1.65 cp at 25 °C
High flash point	95 °C, 204 °F
High auto ignition temperature	346 °C, 655 °F
Complete miscibility with water	Yes
Inexpensive	£ 0.94 / 1b
Assured availability	Yes, from 1,4-butanediol
In-process stability	Early work is favourable
Dissolve sulphur	Readily
Steep sulphur solubility gradient	0.4 % at 20 °C; 9 % at 130 °C
High H <sub>2</sub> S solubility	48 L / L NMP at 20 °C, 1 atm.
Good O <sub>2</sub> solubility	55 cm <sup>3</sup> / L NMP at 20 °C, 1 atm.
High H <sub>2</sub> S over CO <sub>2</sub> selectivity	Yes

### 4.3 Selection of ferric salts

Now that  $\text{FeCl}_3$  in NMP exhibited efficient catalytic activity toward the oxidation of  $\text{H}_2\text{S}$  to S, other iron salts may also have similar activity in the same solvent for the same conversion. Therefore, a number of ferric salts were tried in water-free NMP or 95 % of NMP / 5 % of water in the same procedure. The ferric salts used in this study include ferric citrate, ferric oxalate  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ , ferric carbonate  $\text{Fe}_2(\text{CO}_3)_3$ , ferric acetylacetonate  $[\text{CH}_3\text{C}(\text{O})\text{CH}=\text{C}(\text{O}^-)\text{CH}_3]_3\text{Fe}$ , ferric hydroxyl acetate  $\text{Fe}(\text{OH})(\text{CH}_3\text{CO}_2)_2$ , ferric sulphate  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , ferric nitrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}(\text{H}_2\text{PO}_2)_3$ . The results are listed in **Table 4.3** and compared with that of  $\text{FeCl}_3$ .

Ferric citrate, ferric oxalate and ferric carbonate dissolved in neither pure NMP nor 95 % of NMP / 5 % of  $\text{H}_2\text{O}$  nor any other organic solvents mentioned in **Section 4.2**.

Ferric acetylacetonate,  $\text{Fe}(\text{H}_2\text{PO}_2)_3$  and ferric hydroxy acetate  $\text{Fe}(\text{OH})(\text{CH}_3\text{CO}_2)_2$  are partly soluble in 95 % of NMP / 5 % of water to give slight suspension. The suspensions showed low catalytic activities when employed as catalysts for the oxidation of hydrogen sulphide to sulphur. The same unsatisfactory results are obtained when other organic solvents were used to substitute for pure NMP or 95 % of NMP / 5 % of  $\text{H}_2\text{O}$ .

Both ferric sulphate and ferric nitrate dissolved in pure NMP very slowly. In 95 % of NMP / 5 % of water, however, the two salts dissolved readily to give stable solution with concentration up to 360 mmol / L. The pH value of the resulting solution, lower than 1, was slightly different between two salts and various

concentration. Catalytic experiments were performed with samples of 90 mmol of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  in 95 % of NMP / 5 % of water and 90 mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 95 % of NMP / 5 % of water with both uncontrolled pH or controlled pH value (to 1 by addition of 2 N NaOH). Both salts displayed catalytic activities for the catalytic oxidation of hydrogen sulphide to sulphur to some extent. However, their catalytic activities were found to decrease gradually with the increase of the running time. The catalysts were completely deactivated eventually. High proportion of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (more than 90 %) was found in the resultant solution for both catalyst systems. Obviously, the  $\text{Fe}^{2+}$  formed during the process is hard to re-oxidize to  $\text{Fe}^{3+}$ . In both instances, the tail gas became gradually severer with the running of experiment. In one case of 90 mmol of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  in 95 % of NMP / 5 % of water whose pH value has been previously adjusted to the same as that of corresponding  $\text{FeCl}_3$  solution with 2 N  $\text{H}_2\text{SO}_4$ , an unknown water-soluble solid was found to precipitate out which was shown not to be sulphur by HPLC analysis. The concentration of iron ion reduced dramatically in the process.

In clear contrast, 90 mmol of ferric chloride in 95 % of NMP / 5 % of water showed fantastic efficiency for the catalytic oxidation of  $\text{H}_2\text{S}$  to sulphur by air. The system works perfectly with high selectivity to sulphur 98.72 %, low conversion to  $\text{S}_2\text{O}_3^{2-}$ , 0.02 % and  $\text{SO}_4^{2-}$ , 0.09 %. No tail gas was observed in 300 hours running.

**Table 4.3** Screening of ferric salts in 95 % NMP / 5 % water for the catalytic oxidation\* of hydrogen sulphide by air

Ferric Salt	Concentration (mmol/L) of Fe(III)	Test Time (h)	Results & Comments
Iron(III) acetylacetonate	90	5	<p>~ Iron salt partly dissolved, suspension</p> <p>~ Dark solid formed</p> <p>~ Colour deepened</p> <p>~ Trace of tail gas observed</p> <p>~ Poor catalytic activity</p>
Fe(OH)(OAc) <sub>2</sub>	36	78.5	<p>~ Iron salt partly dissolved to give suspension</p> <p>~ No tail gas observed</p> <p>~ Grey S<sub>8</sub> (3.727 g mixed with unknown dark solid) and residual of S<sub>8</sub> 4.70 g in the filtration (analysis by HPLC)</p> <p>~ Severe loss of iron ion: Fe ion concentration changed from 2084 to 944 mg / L</p> <p>~ Not ideal catalytic system</p>
Fe(H <sub>2</sub> PO <sub>2</sub> ) <sub>3</sub>	90	3	<p>~ Iron salt partly dissolved, suspension</p> <p>~ Dark solid formed</p> <p>~ Colour deepened</p> <p>~ Severe tail gas</p> <p>~ Poor catalytic activity</p>

**Table 4.3** Screening of ferric salts in 95 % NMP / 5 % water for the catalytic oxidation\* of hydrogen sulphide by air (continued)

Ferric salt	Concentration of Fe(III) (mmol/L)	Test Time (h)	Results & Comments
Ferric nitrate $\text{Fe}(\text{NO}_3)_3$	90 * (Initial pH value without any control pH in the process)	24	~ Low yield of $\text{S}_8$ : 63.03 % ~ High conversion to $\text{SO}_3^{2-}$ : 28.56 % ~ High conversion to $\text{SO}_4^{2-}$ : 1.05 % ~ Severe tail gas in the process ~ Poor catalytic activity
Ferric nitrate $\text{Fe}(\text{NO}_3)_3$	90 *(pH controlled to 1.00 by addition of 2 N of NaOH in the process)	10.5	~ Severe tail gas found in 9.5 hours ~ High ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ : 94.42 % ~ Poor catalytic activity
Ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$	90 * (Initial pH value and does not control pH in the process)	80.5	~ Moderate yield of $\text{S}_8$ : 88.00 % ~ Severe tail gas: CuS 10.17 % ~ Low conversion to $\text{SO}_3^{2-}$ : 1.42 % ~ Low conversion to $\text{SO}_4^{2-}$ : 0.41 % ~ High loss of iron: 34.21 mg/L/h ~ Poor catalytic activity
Ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$	90 * (pH of the starting solution was adjusted to the same as that of 90 mmol $\text{FeCl}_3$ / 95 % NMP / 5 % water. No further control during the process)	14	~ Severe tail gas in 10 hours. ~ Low yield of $\text{S}_8$ : 48.49 % ~ Unknown water-soluble precipitate ~ Severe loss of iron: 288 mg / L / h ~ Poor catalytic activity

**Table 4.3** Screening of ferric salts in Fe(III) salt / 95 % NMP / 5 % water for the catalytic oxidation\* of hydrogen sulphide by air (continued)

Ferric Salt	Concentration of Fe(III) (mmol/L)	Test Time (h)	Results & Comments
Ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$	90 * (pH controlled to 1.00 by addition of 2 N of NaOH in the process)	9.5	~ Severe tail gas in 9 hours ~ High ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ : 92.33 % ~ Poor catalytic activity
Ferric chloride $\text{FeCl}_3$	90 * (Initial pH value without any control pH in the process)	300	~ High quality of $\text{S}_8$ : yellow crystalline ~ High yield of $\text{S}_8$ : 98.72 % ~ Low yield of $\text{SO}_3^{2-}$ : 0.19 % ~ Low yield of $\text{SO}_4^{2-}$ : 0.09 % ~ No iron loss ~ No tail gas ~ Perfect catalytic system

#### 4.4 Influence of concentration of $\text{FeCl}_3$ on catalytic activity

While other organic solvents and iron salts show negative or poor results for the catalytic oxidation of  $\text{H}_2\text{S}$  to S by air, the combination of  $\text{FeCl}_3$  with NMP provides a perfect catalyst for this conversion. **Table 4.4** has shown the influence of  $\text{FeCl}_3$  concentration on the catalytic activity in pure NMP and 95 % of NMP / 5 % of water.

As usual, the maximum solubility of  $\text{FeCl}_3$  in pure NMP or 95 % of NMP / 5 %  $\text{H}_2\text{O}$  was firstly determined. Also tested was  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Both anhydrous  $\text{FeCl}_3$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  mixed with pure NMP or 95 % of NMP / 5 % of water to give

stable solution, though the latter dissolved in pure NMP rather slowly. The maximum concentration of  $\text{FeCl}_3$  anhydrous is 270 mmol / L in pure NMP and 180 mmol / L in 95 % of NMP / 5 % of water. While that of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 95 % of NMP / 5 % of water is 180 mmol / L. Experiments were carried out with concentration of  $\text{FeCl}_3$  varying in the range of 18 to 90 mmol.

When 18 mmol of  $\text{FeCl}_3$  in pure NMP was tested for the conversion of  $\text{H}_2\text{S}$  to sulphur by air, no tail gas was observed within the first 17 hours. Longer running of the experiment led to the disclosure of trace tail gas. This can be explained from the shortage of  $\text{Fe}^{3+}$  ion in the process. At the initial stage of experiment, there was enough  $\text{Fe}^{3+}$  ion in the system to oxidise hydrogen sulphide. As the redox process continued, the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions reached to equilibrium, at which the content of  $\text{Fe}^{3+}$  was insufficient to convert hydrogen sulphide completely to sulphur, as a consequence, the excess of hydrogen sulphide was released in the form of tail gas. Even so, the absorption of hydrogen sulphide was still very impressive. The formation of relatively high concentration of by-products  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  might result from the direct oxidation of  $\text{H}_2\text{S}$  by the oxygen (air) in the oxidiser zone.

Doubling the concentration of  $\text{FeCl}_3$  to 36 mmol in pure NMP led to the enhancement of selectivity to sulphur from 90.3 % to 95.2 %. The concentration of the over-oxidized components  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  decreased. The loss of  $\text{H}_2\text{S}$  in tail gas (0.12 %), though lower than in the case of 18 mmol (0.46 %), was still observed, suggesting that the  $\text{Fe}^{3+}$  ion in the equilibrium was still not abundant. Increase of  $\text{FeCl}_3$  to 90 mmol in 100 % of NMP sorted out the loss of  $\text{H}_2\text{S}$  in tail gas completely in spite of the fact that the yield of sulphur has not been further improved (95.84 %).

The slight increase of the side product  $\text{SO}_4^{2-}$  implied that the concentration of iron ion might be a little bit higher than required.

Further improvement for the selectivity to sulphur was achieved by slight modification of the solvent with addition of 5 w/v % of water. As shown in **Table 4.4**, 90 mmol / L ferric chloride in 95 % of NMP / 5 w/v % of water afforded 98.72 % yield of sulphur, while the concentration of side products  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  slightly decreased. Actually, the presence of 5 w/v % of  $\text{H}_2\text{O}$  in NMP somewhat reduced the solubility or residential time of  $\text{H}_2\text{S}$  in the absorption solution and might have increased the rate of the conversion of  $\text{H}_2\text{S}$  to sulphur. There was less residual  $\text{H}_2\text{S}$  in 95 % of NMP than in water-free NMP.

90 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 95 % NMP / 5 % of water showed closely similar results to its anhydrous counterpart in spite of the slight increase of  $\text{H}_2\text{O}$  content in the reaction solution. However, if the content of water in the catalyst system reached up to 20 %, the catalytic activity was found to reduce sharply -- severe tail gas re-appeared in the process.

All experiments listed in **Table 4.4** gave high quality of bright yellow crystalline sulphur, which is in clear contrast to the grey sulphur contaminated with more or less of  $\text{FeS}$  from Fe-NTA system. In addition to the crystalline sulphur, there is still considerable amount of sulphur dissolved in the solution. Work-up with addition of  $\text{H}_2\text{O}$  precipitated the sulphur out as yellow solid, also in high quality. The solvent can be recycled by evaporation of the excess of water.

No iron loss was observed in the process. For the catalyst system with 90 mmol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{FeCl}_3$  in 95 % of NMP, the total iron concentration in the

**Table 4.4** Catalytic activity of FeCl<sub>3</sub> / NMP or 95 % of NMP / 5 % of water system

Solvent System	100 % NMP	100 % NMP	100 % NMP	95 % NMP/5 % H <sub>2</sub> O	95 % NMP/5 % H <sub>2</sub> O
Ferric salt	FeCl <sub>3</sub>	FeCl <sub>3</sub>	FeCl <sub>3</sub>	FeCl <sub>3</sub>	FeCl <sub>3</sub> ·6H <sub>2</sub> O
Concentration iron salt (mmol/L)	18	36	90	90	90
Test time (h)	100	300	313	300	198
Crystalline S <sub>8</sub> (g)	11.846	34.010	37.780	46.968	19.296
Residual S <sub>8</sub> in the filtrate (g)	0.226	1.077	0.819	7.167	3.491
Tail gas (CuS) (g)	0.184	0.135	0	0	0
C <sub>SO<sub>3</sub><sup>2-</sup></sub> (mM) in the resulting solution	4.91	4.12	4.56	0.20	3.00
C <sub>SO<sub>4</sub><sup>2-</sup></sub> (mM) in the resulting solution	3.66	4.34	11.03	1.50	2.89
Residual H <sub>2</sub> S (M) in the resulting solution	13.33	18.50	16.06	4.13	1.00
Conversion of H <sub>2</sub> S to S <sub>8</sub> (%)*	90.32	95.15	95.84	98.72	98.49
Conversion of H <sub>2</sub> S to CuS (%)*	0.46	0.12	0	0	0
Conversion of H <sub>2</sub> S to SO <sub>3</sub> <sup>2-</sup> (%)*	2.36	0.72	0.73	0.02	0.83
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)*	0.46	0.12	0.88	0.09	0.40
Residual H <sub>2</sub> S (%)	6.40	3.26	2.56	1.17	0.28

**Table 4.4** Catalytic activity of FeCl<sub>3</sub> / NMP or 95 % of NMP / 5 % of water system  
(continued)

Solvent System	100 % NMP	100 % NMP	100 % NMP	95 % NMP/5 % H <sub>2</sub> O	95 % NMP/5 % H <sub>2</sub> O
Iron content of the starting solution (mg/L)	1002.21	1999.55	5033.55	5042.57	5152.75
Iron content of the resulting solution (mg/L)	1004.95	2006.10	5035.91	5104.17	5279.79
H <sub>2</sub> O content of the starting solution (g/L)	0	0	0	50.06	49.65
H <sub>2</sub> O content of the resulting solution (g/L)	1.32	4.01	4.10	42.37	43.13
Fe <sup>2+</sup> / Fe <sup>3+</sup> in the process (%)	40.20	45.55	50.10	44.86	44.05

\*Calculation based on the amount of all components-containing sulphur, which is supposed to be 100 %.

resulting solution was a little bit higher than that in the starting solution. This may arise from the evaporation of H<sub>2</sub>O in the process, leading to the slightly condensed reactant solution. The degradation of NMP, which will be discussed below in details, may also be responsible for the condensation of solvent during the process.

#### 4.5 *Effect of the anion of the ferric salt in water*

Due to the drastic different effect of various iron salts on the catalytic activity for the conversion of H<sub>2</sub>S to S in NMP, we decided to investigate the same iron salts in water for the same conversion. Surprisingly, the aqueous FeCl<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and

Fe(NO<sub>3</sub>)<sub>3</sub> show extreme similarity to each other with very low catalytic activity (Table 4.5). Actually, the similar irreversibility of Fe<sup>3+</sup> to Fe<sup>2+</sup> has been reported before. When FeCl<sub>3</sub> or Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or Fe(NO<sub>3</sub>)<sub>3</sub> dissolved in water, a series of hydroxylated ferric ions, which formed by hydrolysing of Fe(III) ion, have been found to dominate in the solution.<sup>268-290</sup> Asai et al have used a stirred cell reactor for

**Table 4.5** Catalytic activities of the various ferric salts in H<sub>2</sub>O

Catalyst Composition	Test Conditions	Test Time (min)	Results and Comments
FeCl <sub>3</sub> ([Fe] = 90 mM)/ 100 % H <sub>2</sub> O	*H <sub>2</sub> S = 2.00 cm <sup>3</sup> /min. *Air = 700 cm <sup>3</sup> /min. *Without any control of pH during the process.	700	~ Initial pH = 0.44 ~ Resulting pH = 0.20 ~ No tail gas with the first 600 min. ~ Conversion of H <sub>2</sub> S to S <sub>8</sub> (grey): 58.03 % (1.08 g of sulphur). ~ CuS: 0.29 g ~ No iron ion loss. ~ High Fe <sup>2+</sup> /Fe <sup>3+</sup> in the resulting solution: 95.51 % ~ Positive activity observed within the first 600 min, but it gradually dwindled away due to hard conversion of Fe <sup>2+</sup> to Fe <sup>3+</sup> in the process.

**Table 4.5** Catalytic activities of the various ferric salts in H<sub>2</sub>O (continued)

Catalyst Composition	Test Conditions	Test Time (min)	Results and Comments
Fe(NO <sub>3</sub> ) <sub>3</sub> ([Fe] = 90mM)/ 100 % H <sub>2</sub> O	~ H <sub>2</sub> S = 2.00 cm <sup>3</sup> /min. ~ Air = 700 cm <sup>3</sup> /min. ~ pH of the solution controlled to 1.00 by addition of 2 N NaOH during the process.	630	~ Initial pH = 0.95 ~ No tail gas with the first 570 min. ~ Conversion of H <sub>2</sub> S to S <sub>8</sub> (grey): 81.24 % (1.36 g of sulphur). ~ CuS: 0.07 g ~ No iron ion loss. ~ High Fe <sup>2+</sup> /Fe <sup>3+</sup> in the resulting solution: 94.42 % ~ Positive activity observed within the first 630 min, but it gradually dwindled away due to hard conversion of Fe <sup>2+</sup> to Fe <sup>3+</sup> in the process.
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ([Fe] = 90mM)/ 100 % H <sub>2</sub> O	~ H <sub>2</sub> S = 2.00 cm <sup>3</sup> /min. ~ Air = 700 cm <sup>3</sup> /min. ~ Control pH of solution to 1.00 by addition of 2 N NaOH during the process.	555	~ Initial pH = 1.07 ~ No tail gas at all in the first 550 min. ~ Conversion of H <sub>2</sub> S to S <sub>8</sub> (grey): 80.00 % (1.18g of sulphur). ~ CuS: 0.07g ~ No iron ion loss. ~ High Fe <sup>2+</sup> /Fe <sup>3+</sup> in the resulting solution: 92.33 % ~ Positive activity was observed on the first 630 min, but it gradually dwindled away due to hard conversion of Fe <sup>2+</sup> to Fe <sup>3+</sup>

absorption of hydrogen sulphide into aqueous solution of ferric sulphate and ferric chloride respectively in the absence of any organic ligands, the hydroxylated ferric ion  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  was concluded to be the actual reactive species in the processes,<sup>291</sup> and the hydrated ferrous ion  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  was the major form of  $\text{Fe}^{2+}$  in the solution which was found hard to oxidise to  $\text{Fe}^{3+}$  by air. That is, in the aqueous solution, the hydrated  $\text{Fe}^{2+}$  is very stable and difficult to be oxidised to hydrated or hydroxylated  $\text{Fe}^{3+}$  ion. As a consequence, the influence of anion in iron salt on the catalytic activity, which could be ignored in practice, is far lower than that of solvent water molecule itself.

#### 4.6 Possible catalytic mechanism of iron salts in NMP

However, changing solvent from water to pure NMP or 95 % NMP / 5 %  $\text{H}_2\text{O}$ , the effect of anion on the catalytic activity of iron salt becomes vital, implying that the reactive species in the catalytic cycle must be an anion-containing complex. This is not difficult to understand. The NMP is far less polar than water. Iron salts thus have less possibility for ionization in NMP. Therefore the solution can not be dominated by total solvated iron as that in water. The complexes for  $\text{FeCl}_3$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  in NMP or 95 % NMP / 5 %  $\text{H}_2\text{O}$  can be expressed actually as  $[\text{Fe}(\text{NMP})_{6-x}\text{Cl}_x]^{(3-x)+}$ ,  $[\text{Fe}(\text{NMP})_{6-x-y}(\text{H}_2\text{O})_y\text{Z}_x]^{(3-x)+}$  ( $\text{Z} = \text{Cl}^-, \text{NO}_3^-$ ) and  $\sim[\text{Fe}(\text{NMP})_{5-2x-y}(\text{SO}_4)_x(\text{H}_2\text{O})_y]^{(2-2x)+}$ , respectively. The following are the mechanisms we have tentatively proposed for the iron catalytic conversion of  $\text{H}_2\text{S}$  to sulphur by air in NMP (**Scheme 4.1- 4.3**).

As shown in **Scheme 4.1- 4.3**, iron salts in NMP or in 95 % NMP / 5 %  $\text{H}_2\text{O}$  could initially form partly solvated  $\text{Fe}^{3+}$  ions or complexes [step (1)]. Hydrogen

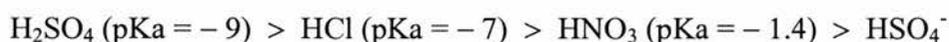
sulphide then dissolves in a solution containing iron salt and NMP to afford new complexes containing sulphur by ligand exchange or substitution reaction in step (2) - (4) in which the anion ion such as  $\text{Cl}^-$  or  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  is substituted by  $\text{HS}^-$ . One NMP molecule may pop out and in during the process. Electron transfers between the sulphide and  $\text{Fe}^{3+}$  within the Fe complex sulphur-containing take place in step (5) and step (6). The free radical of sulphur-containing complex, which is formed in step (5), readily decomposes to release the elemental sulphur, and to dissociate a  $\text{Fe}^{2+}$  solvated ion in step (6). Re-generation reaction of catalyst is carried out in step (6) and step (7).

In **Scheme 4.1A** or **Scheme 4.1B**, Step (2) can be rate determining, because the step that release a free radical needs higher active energy. Addition of appropriate amount of water (5 %) to the  $\text{FeCl}_3$  / NMP system reduces the residential time of  $\text{H}_2\text{S}$  in solution to some extent and decrease the possibility for further oxidation, and therefore is beneficial to the selectivity to sulphur. A limited number of  $\text{H}_2\text{O}$  may also coordinate with iron in the reactive species in shown in **Scheme 4.1B**, **4.2** and **4.3**. The active energy in step (2) in **Scheme 4.1B** which contains water maybe lower than in **Scheme 4.1A**, so the formation of sulphur is quicker in the present of water. However, if the water content reaches up to 20 %, water molecules would compete with NMP or the anion ligands to co-ordinate with iron, especially with  $\text{Fe}^{2+}$  to give totally hydrated iron, which is as in aqueous system, loses its catalytic activity sharply.

In **Scheme 4.2** and **Scheme 4.3** water is considered as part of coordinated ligands, step (7) is vital for the whole cycle as suggested by the high proportion of

$\text{Fe}^{2+} / \text{Fe}^{3+}$  (up to 94.4 %) in the resulting solution (see **Section 4.3**). Like the hydrated  $\text{Fe}^{2+}$  in aqueous system, the nitrate or sulphate-containing Fe(II) species in **Scheme 4.2** and **Scheme 4.3** are quite stable and very difficult to oxidize into corresponding Fe(III) counterparts by air. Therefore, the catalytic cycle were blocked in step (7) for  $\text{Fe}_2(\text{SO}_4)_3 / \text{NMP}$  and  $\text{Fe}(\text{NO}_3)_3 / \text{NMP}$  systems, the diminishing of  $\text{Fe}^{3+}$  in the system directly leads to the gradual loss of catalytic activity of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Fe}(\text{NO}_3)_3$  in NMP for the conversion of  $\text{H}_2\text{S}$  to S by air.

But how can the stability of Fe(II) species of chloride, nitrate and sulphate or hydrogen sulphate be so different? Firstly, according to the Lewis theory of acid and base,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  are the corresponding conjugate bases of HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$ , respectively.<sup>293</sup> The acidity of the above acids and basicity of the conjugate bases are found to follow the order shown below:



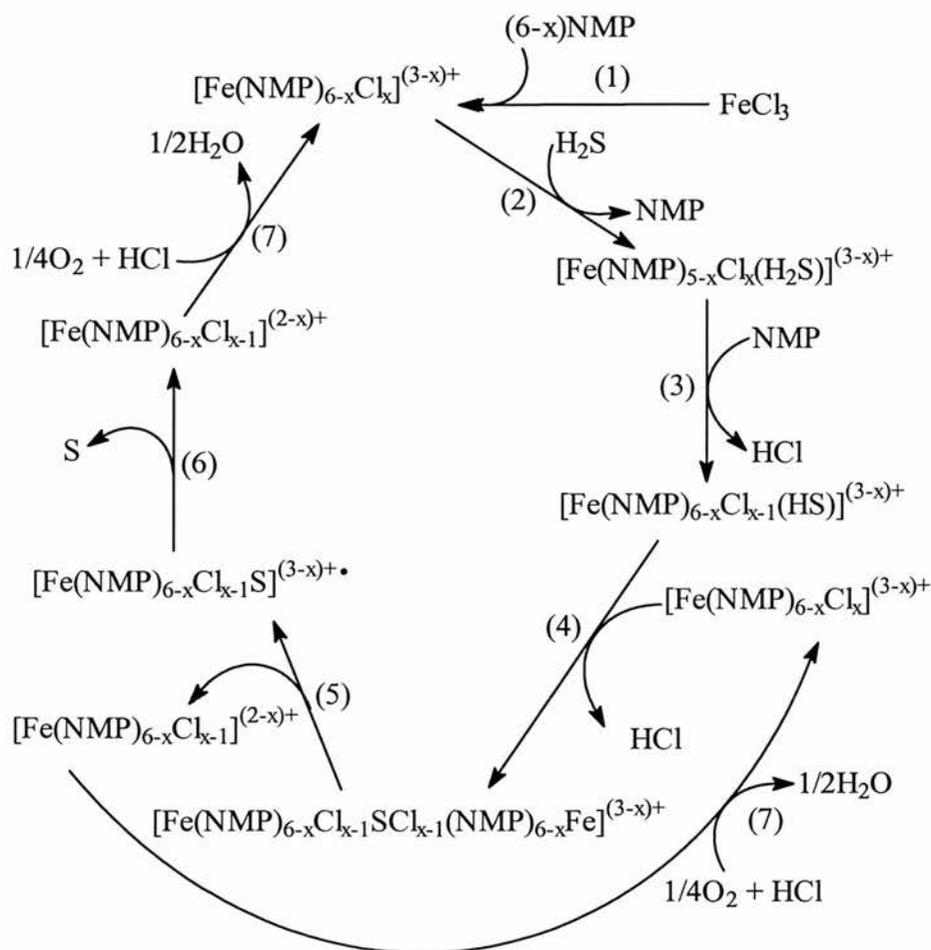
Increasing acid strength ←—————



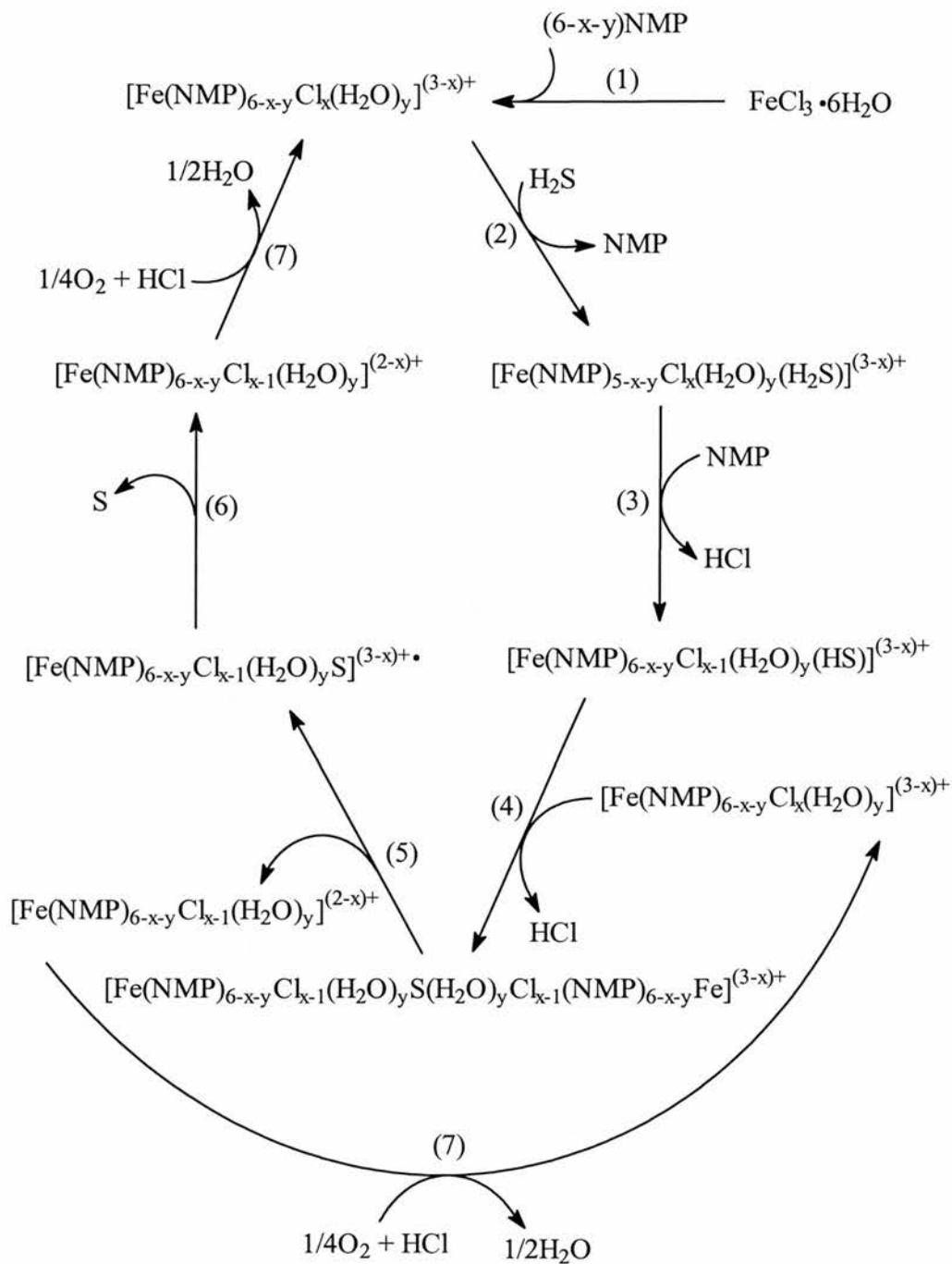
Increasing strength ←—————

This means that the basicities of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are stronger than  $\text{Cl}^-$ .  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are therefore believed to have slightly higher affinity for Fe ions than  $\text{Cl}^-$ . Secondly,  $\text{Cl}^-$  is a typical weak monodentate ligand while  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  can be regarded as weak bidentate ligands due to their special resonance structures. Therefore it is reasonable that iron chloride species are better solvated or replaced by solvent than iron nitrate and iron sulphate species in NMP. Furthermore,  $\text{Fe}^{3+}$  is

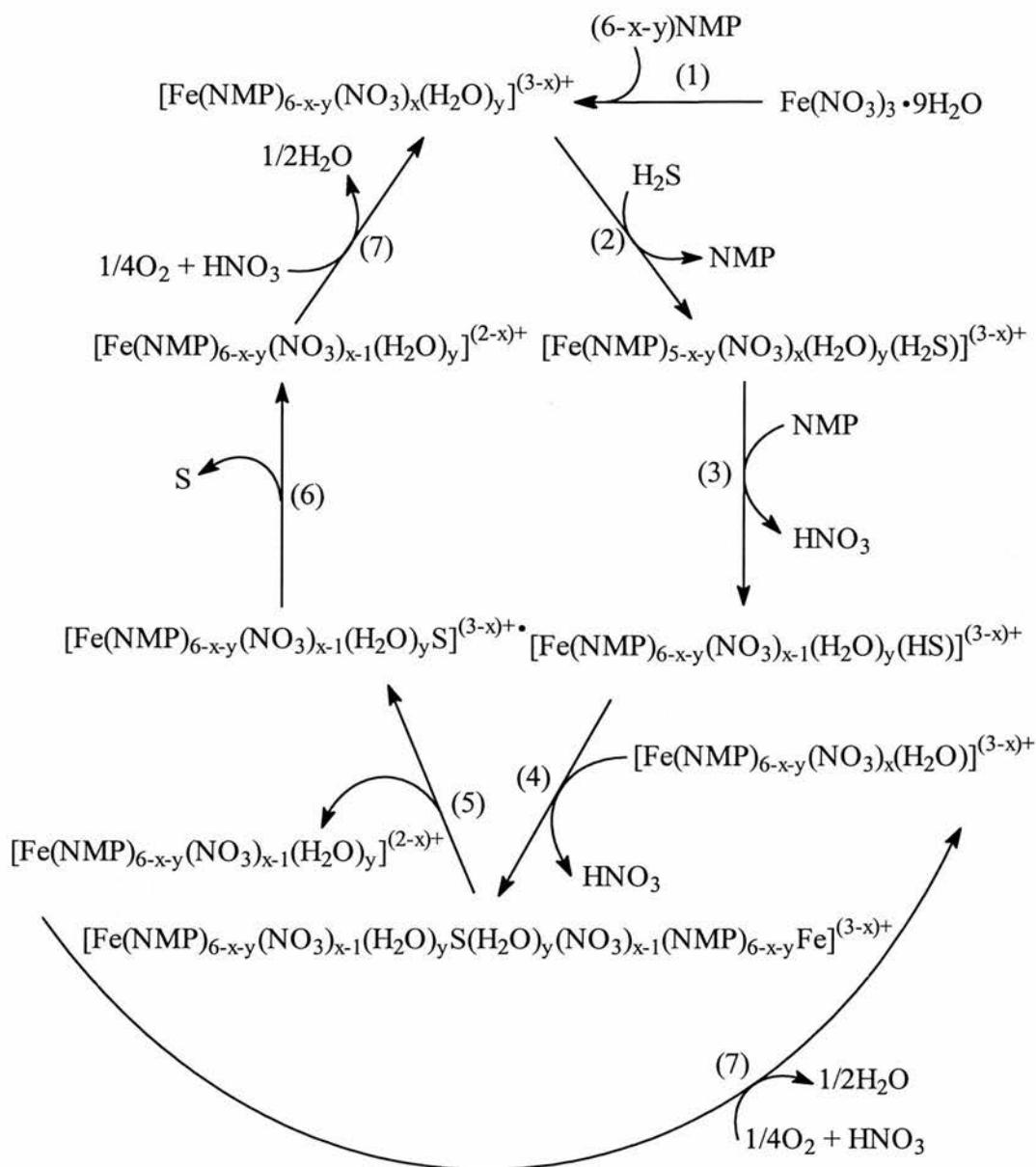
generally believed to prefer to coordinate nitrogen-containing ligand rather than oxygen-containing ligand to form stable complex. On the contrary,  $\text{Fe}^{2+}$  tends to coordinate oxygen-containing rather than nitrogen-containing ligand. Therefore, the more *N*-donor ligand NMP molecules coordinated with the iron ion, the easier the  $\text{Fe}^{3+}$  regeneration and the more active of the iron species for the catalysis. A similar



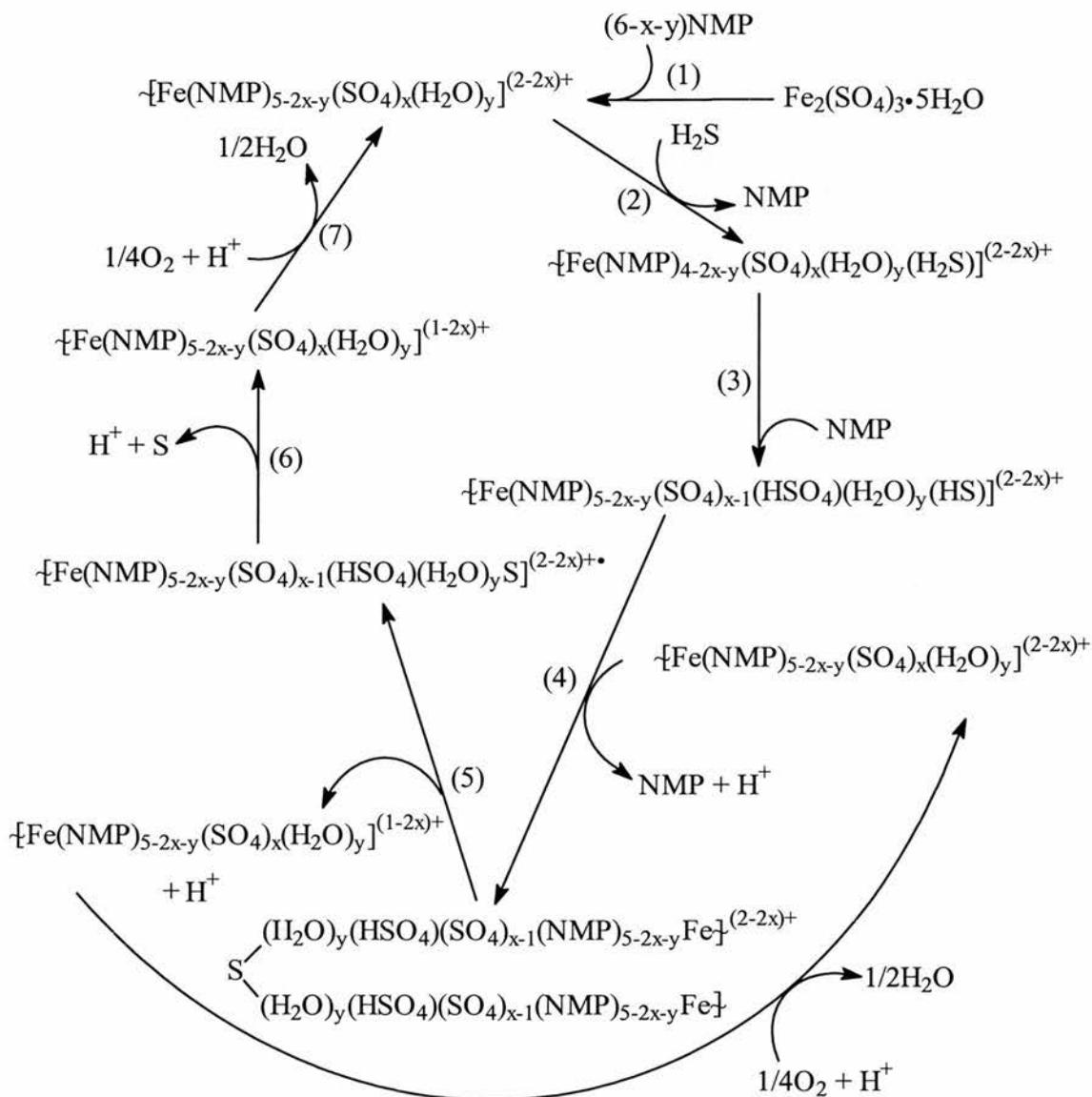
**Scheme 4.1A** A suggested catalytic cycle in non-aqueous catalyst system of  $\text{FeCl}_3$  / NMP for the conversion of  $\text{H}_2\text{S}$  to  $\text{S}$



**Scheme 4.1B** A suggested catalytic cycle in non-aqueous catalyst system of  $\text{FeCl}_3$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  / NMP or 95 % NMP / 5 %  $\text{H}_2\text{O}$  for the conversion of  $\text{H}_2\text{S}$  to S



**Scheme 4.2** A suggested catalytic cycle in non-aqueous catalyst system of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  / 95 % NMP / 5 %  $\text{H}_2\text{O}$  for the conversion of  $\text{H}_2\text{S}$  to S

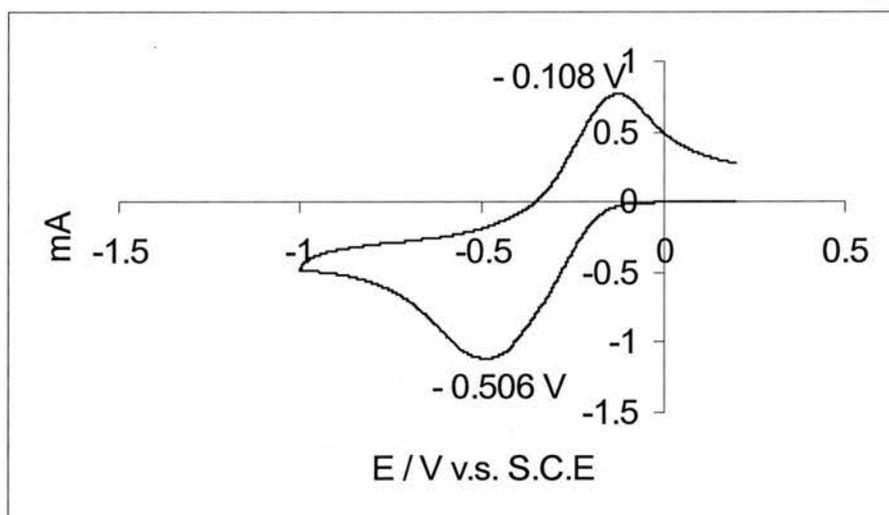


**Scheme 4.3** A suggested catalytic cycle in non-aqueous catalyst system of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  / 95 % NMP / 5 %  $\text{H}_2\text{O}$  for the conversion of  $\text{H}_2\text{S}$  to S

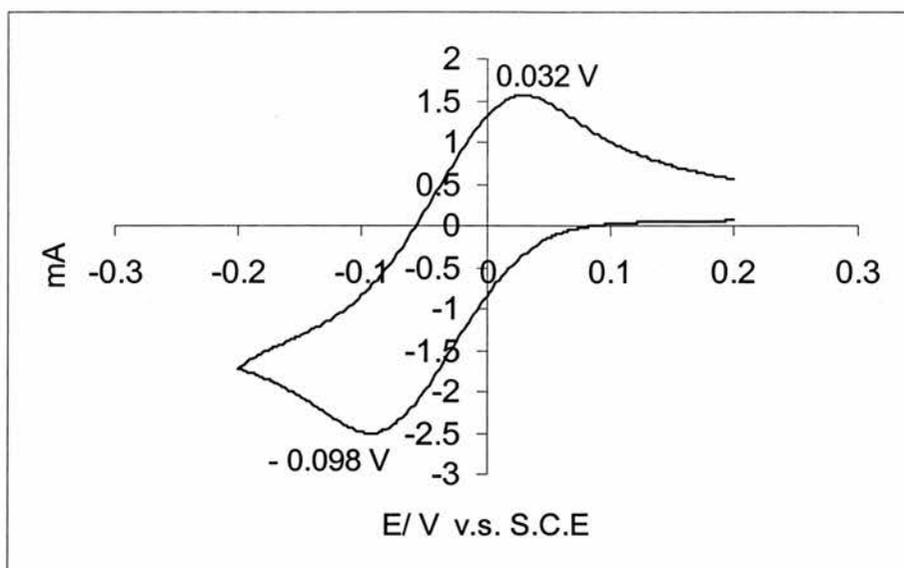
point of view has also been reported before.<sup>299</sup> The  $\text{Fe}^{2+}$  species in  $\text{Fe}(\text{NO}_3)_3 / \text{NMP}$  or  $\text{Fe}_2(\text{SO}_4)_3 / \text{NMP}$  system must have been stabilised by oxygen-donor sulphate or nitrate ligand. They proved to be very difficult to oxidise into  $\text{Fe}^{3+}$  by air.

#### 4.7 Cyclic Voltammogram study of non-aqueous catalyst system

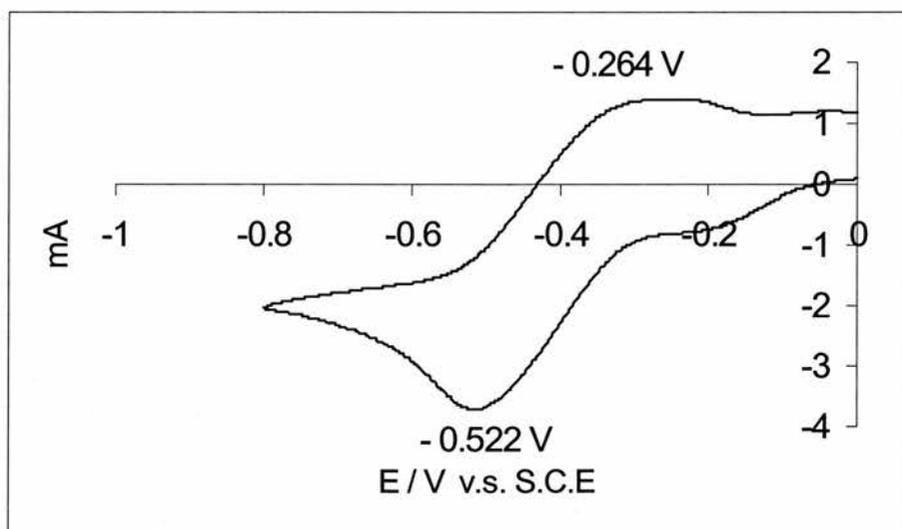
In order to further explore the difference of the catalytic activities between  $\text{Fe}(\text{NO}_3)_3 / \text{NMP}$ ,  $\text{Fe}_2(\text{SO}_4)_3 / \text{NMP}$  and  $\text{FeCl}_3 / \text{NMP}$  for the catalytic oxidation of hydrogen sulphide to sulphur, their cyclic voltammometries were measured. The following cyclic voltammograms were recorded at initial pH value and 0.02 M  $\text{Fe}(\text{III}) / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  shown in the following **Fig. 4.1 - 4.3**.



**Fig. 4.1** Cyclic voltammogram of  $\text{Fe}(\text{NO}_3)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  ( $[\text{Fe}(\text{III})] = 0.02 \text{ M}$ , initial pH value)



**Fig. 4.2** Cyclic voltammogram of  $\text{Fe}_2(\text{SO}_4)_3$  / 95 % NMP / 5 %  $\text{H}_2\text{O}$  ( $[\text{Fe}(\text{III})] = 0.02$  M, initial pH value)



**Fig. 4.3** Cyclic voltammogram of  $\text{FeCl}_3$  / 95 % NMP / 5 %  $\text{H}_2\text{O}$  ( $[\text{Fe}(\text{III})] = 0.02$  M, initial pH value)

The cathodic wave can be assigned to the reduction process, and anodic wave to complementary oxidation reaction. The half wave potentials of  $\text{FeCl}_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  are listed in **Table 4.6**.

**Table 4.6** Half-wave potentials (V vs. saturated calomel electrode, SCE)  
([Fe] = 0.02 M, initial pH value)

System	$\text{FeCl}_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$	$\text{Fe}_2(\text{SO}_4)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$
$E_{1/2}$ (V vs. SCE)	- 0.393	- 0.307	- 0.066

For the  $\text{Fe}^{3+} / \text{Fe}^{2+}$  redox couple, the standard potential  $E_o$  of ferric ion to the ferrous ion is + 0.770 V under standard condition. As shown in **Table 4.6**, the half wave potentials  $E_{1/2}$  of  $\text{Fe}^{3+} / \text{Fe}^{2+}$  in non-aqueous system, which depend on the nature of anion ion, are all much more negative than the standard potential  $E_o$ . Though it is still difficult to correlate the wave potentials to the catalytic activity of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple directly, there is indeed an obvious difference between the wave potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  of the catalytic active  $\text{FeCl}_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  system and the poor catalytic system of  $\text{Fe}(\text{NO}_3)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$ . Further studies are needed for establishing the relationship between the half wave potential  $E_{1/2}$  of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and the actual catalytic activity.

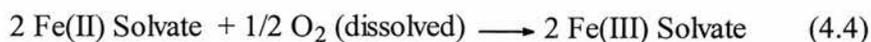
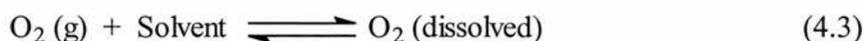
#### 4.8 Process chemistry

The process chemistry for the air oxidation of H<sub>2</sub>S to sulphur catalysed by non-aqueous system is, actually, closely similar to that in aqueous systems. The H<sub>2</sub>S is induced into a circulating catalyst solution in the absorber zone where it is solvated and physically removed; simultaneously, the solvated H<sub>2</sub>S reacts with the Fe(III) solvate forming elemental sulphur which does not precipitate but remains in solution in the organic solvent-NMP or 95 % NMP / 5 % H<sub>2</sub>O in the early stage. The Fe(III) solvate is cocurrently reduced to the Fe(II) solvate state. Reactions occurring in the absorber are represented as follow.

In the laboratory, the sulphur produced dissolved continuously in the organic solvent. Once the organic solvent is saturated by dissolved sulphur, the yellow crystalline sulphur precipitates gradually in both absorber zone and oxidiser zone. In industry, the whole process can be operated at higher temperature (60 - 70°C) to increase the solubility of sulphur. Crystal sulphur product can be harvested by cooling the reaction mixture in a specific zone to simplify removal.



The combined oxidiser-crystallizer provides sufficient residence time for the regeneration of the active Fe(III) solvate and crystallization of dissolved sulphur. The process can be represented by the following equations.



The overall process can be represented by the following equation.



Yields of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  in the  $\text{FeCl}_3$  / NMP were very low indeed (< 0.1 %) compared with the aqueous process.

#### 4.9 *Comparison with aqueous processes*

As mentioned above, the absorbed solution also serves to remove  $\text{CO}_2$  and water, if they present in a practical industrial process, by absorption into the solvent. Hence the process can simultaneously desulphurize, decarbonate and dehydrate sub-quality natural gas in a single operation while giving high quality of sulphur. This is in marked contrast to the traditional combination of amine plant, glycol dehydrator and sulphur recovery unit. The advantages of this novel non-aqueous process as indicated by Ferm<sup>68</sup> over aqueous redox processes have been listed in **Table 4.7**.

**Table 4.7** Advantages of non-aqueous FeCl<sub>3</sub>/ NMP liquid redox sulphur recovery process versus the aqueous chelated iron redox sulphur recovery process <sup>68</sup>

Consideration	<b>Aqueous System</b>	<b>Novel non-aqueous System</b>
Components of catalyst	Fe(III) complex / stabiliser / H <sub>2</sub> O	FeCl <sub>3</sub> / NMP / H <sub>2</sub> O
Organic ligand	Required a robust ligand A key deficiency was the rapid degradation of the ligand in the process	No other ligand involved. The NMP functions as both the organic solvent and organic ligand
Sulphur product	Grey amorphous precipitate, fouls equipment especially gas/liquid contactor and gas spargers Precludes use of efficient porous metal spargers It is difficult to obtain all the product sulphur by filtration	Bright yellow crystalline sulphur is obtained by cooling the circulating solution in certain zones. No solid sulphur is deposited elsewhere Sulphur can be washed with neat solvent then water to recover valuable chemicals. High efficiency gas spargers and packed absorber towers can be used It is very easy to get crystalline product sulphur by filtration
Scavenger or inhibitor	A constant concentration of scavenger or inhibitor of the hydroxyl radical or other free radicals was required to prevent the degradation of ligand	No need, but some NMP oxidizes
H <sub>2</sub> O removal	Produced sweet gas is saturated with glycol at about 44 °C. Dehydration requirements can be increased	Dehydration to pipe-line specification is achieved by the hygroscopic solvent

**Table 4.7** Advantages of non-aqueous FeCl<sub>3</sub>/ NMP liquid redox sulphur recovery process versus the aqueous chelated iron redox sulphur recovery process  
(continued)

Consideration	Aqueous System	Novel non-aqueous System
Carbon dioxide removal	Only minimal CO <sub>2</sub> removal is achieved Amine plants are needed if the sour gas contains more than 2 % CO <sub>2</sub>	Complete removal of CO <sub>2</sub> is possible. As H <sub>2</sub> S is oxidised to sulphur, recovery of CO <sub>2</sub> as a resource is possible Market size for the process is expanded considerably
Carbonyl sulphide removal	Inert, could not remove	Converts to crystalline sulphur
Presumed space requirements	Relative large, especially if an amine plant and a glycol dehydration unit are also required	Considerably more compact and therefore cheaper. Much more suited to smaller, remote wells. Attractive for off shore platform applications O <sub>2</sub> solubility in NMP is greater than in water. 48L of H <sub>2</sub> S dissolve in 1L NMP
Corrosion	Stainless steel equipment required	Special materials equipment required because of the acidity of the absorbed solution and the likely corrosion of Cl <sup>-</sup> to equipment
Surfactant application	Needed to wet and sink sulphur	No need
Antifoam addition	Occasionally required	Probably no need
Biocide addition	Normally used	Probably unnecessary

**Table 4.7** Advantages of non-aqueous FeCl<sub>3</sub>/ NMP liquid redox sulphur recovery  
(continued)

Consideration	Aqueous System	Novel non-aqueous System
Chelate stabiliser addition	Required in initial catalyst fill, subsequent additions are sometimes required	May not be needed

#### 4.10 Degradation of NMP

NMP used in non-aqueous Fe(III)/Fe(II) redox process for the conversion of H<sub>2</sub>S to S acts as both ligand and solvent, that is, NMP involves both physical and chemical processes during the absorption and conversion of H<sub>2</sub>S to sulphur. Though under the acidic condition (in contrast with the basic condition in Fe chelate aqueous process), there is less opportunity for free hydroxyl radicals surviving, it can still be expected that NMP may experience degradation to some extent. HPLC analysis did confirm this slight decomposition of NMP.

The decomposition pathway should be similar to that described in **Scheme 3.6** in **Chapter 3**. **Table 4.8** shows the changing of organic components of FeCl<sub>3</sub> / NMP and FeCl<sub>3</sub> / 95 % NMP / 5 % H<sub>2</sub>O system after running for *ca.* 300 hours by HPLC. As mentioned in **Table 4.4**, appropriate amount (*ca.* 5 %) of water is beneficial to the selectivity to sulphur. However, water also accelerates the oxidative degradation of NMP due to the increase of opportunity of H<sub>2</sub>O<sub>2</sub> formation.

**Table 4.8** Results of HPLC analyses of the non-aqueous catalyst systems

Type of the sample	Component	FeCl <sub>3</sub> ([Fe] = 90 mmol) / 100 % NMP (Test time: 313 hours)	FeCl <sub>3</sub> ([Fe] = 90 mmol) / 95 % NMP / 5 % H <sub>2</sub> O (Test time: 300 hours)
Starting solution	NMS	0	0
	NMP	100 %	100 %
Resulting solution	NMS	2.78 %	10.78 %
	NMP	96.99 %	88.77 %

#### 4.11 Conclusions

A series of Fe(III) salts and organic solvents have been screened to develop novel non-aqueous catalyst for the conversion of H<sub>2</sub>S to sulphur. FeCl<sub>3</sub> / 95 % NMP / 5 % H<sub>2</sub>O proved to be the most efficient non-aqueous system.

The influence of concentration of iron ion has been investigated simply. Satisfactory results were obtained with 90 mM of FeCl<sub>3</sub> in NMP or 95 % NMP / 5 % H<sub>2</sub>O.

NMP could function as both solvent and coordinating agent to form a series of anion-containing solvated complexes of Fe(III) and Fe(II). In the case of FeCl<sub>3</sub>, due to the loose coordination of Cl<sup>-</sup> ion to Fe ion, it was believed the Fe ions are highly solvated, Fe(II) ion can be easily oxidised to Fe(III) ion by air, so the catalytic cycle proceeds smoothly. In the cases of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>, however, due to the higher affinity of oxygen donor sulphate and nitrate and their stabilising effect to Fe(II) ion, the catalytic cycle was blocked at the regeneration step of Fe(III) ion with air. Therefore, only FeCl<sub>3</sub> / NMP or FeCl<sub>3</sub> / 95 % NMP / 5 % H<sub>2</sub>O is catalytic active system for the conversion of H<sub>2</sub>S to sulphur.

The influence of the anion of Fe(III) salt is also reflected in cyclic voltammograms of the  $\text{FeCl}_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  which were measured at initial pH value and  $[\text{Fe}] = 20 \text{ mM}$ . The  $\text{FeCl}_3 / 95\% \text{ NMP} / 5\% \text{ H}_2\text{O}$  showed the most negative half wave potential and was the most stable system as catalyst for the removal of  $\text{H}_2\text{S}$ .

Briefly, 90 mM of  $\text{FeCl}_3$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 95 % NMP / 5 %  $\text{H}_2\text{O}$  proved to be highly efficient catalyst for air oxidation of hydrogen sulphide to sulphur to give high quality of sulphur. In spite of the fact that there are a lot of advantages to the  $\text{FeCl}_3 / \text{NMP}$  catalyst system over the aqueous iron complexes catalyst system, the concern of the corrosivity of  $\text{Cl}^-$  requires careful selection of materials of construction to avoid limiting its commercial applications.

## ***Experimental***

### ***Materials and agents***

The following solvents and compounds were obtained from Aldrich or Lancaster and were used directly without further purification: formamide (FA, 99.5+ %), *N*-methylpyrrolidinone (NMP, 98.0 % and 99.0+ %), *N*-formylmorpholine (NFMP, 99.0 %), *N, N*-dimethylethanolamine (DMEA, 99.0 %), morpholine (MP, 99.0+ %), dimethyl sulfoxide (DMSO, 99.0 %), dimethyl formamide (DMFA, 99.8 %), propylene carbonate (PC, 99.7 %), 1,4- dioxane (DO, 99.0+ %), diethylglycolmonomethylether (DEGME, 99.0 %), di-(ethylglyco)-diethylether (DEGDE, 99.0 %), triethylphosphate (TEPP, 99.0+ %), methyl-acetoacetate (MAA, 99.5 %), triethanolamine (TEA, 98.0 %), trichloroethylene (TCE, 99.0+ %), 2-

butoxyethanol (BE, 99.0 %), sulfolane (96.0 %), acrylic acid (99.0 %), furan (99.0+ %), ethanol (100 %), ferric citrate (98.0 %), ferric oxalate (99.0 %), ferric carbonate (99.0 %), ferric acetylacetonate (99.9+ %), ferric acetate (98.0 %), ferric sulphate (97.0 %), ferric nitrate (99.0 %), iron(III) chloride (97.0 %), iron(III) chloride, hexahydrate (98.0 %),  $\text{Fe}(\text{H}_2\text{PO}_2)_3$  (98.0 %),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (98.0 %), barium chloride 99.8 %), acetonitrile (HPLC grade), *N*-methylsuccinimide (NMS, 99.0 %), succinimide (99.0 %), 2-pyrrolidinone (99.0 %).

### ***Testing of the catalytic activity of the iron salts - organic solvents***

#### **Apparatus**

All redox reactions were carried out in a two-chambered glass apparatus, 1-liter reactor provided by US Filter (see ***Scheme 2.2***). The pH and redox potential in the absorber and oxidizer were not monitored due to the corrosive reason. The  $\text{H}_2\text{S}$  inlet was controlled by a mass flow rate controller (MFC) and air was gauged by a rotometer. The tail gas was adducted to a  $\text{CuSO}_4$  (1.0 M) absorber. All experiments were accomplished at room temperature.

#### **General procedure**

1000  $\text{cm}^3$  of iron(III) salt in organic solvent or 95 % of organic solvent / 5 %  $\text{H}_2\text{O}$  solution was placed in the oxidizer compartment. The liquid pump was then started and part of the solution was pumped into absorber compartment with a flow rate of 100  $\text{cm}^3 \text{min}^{-1}$ . At this stage the air was bubbled into the oxidizer and the flow rate of the air was adjusted to the required value. The valve of the  $\text{H}_2\text{S}$  cylinder was turned on and the  $\text{H}_2\text{S}$  flow rate was adjusted to 2.00  $\text{cm}^3 \text{min}^{-1}$ . The time of the start of the reaction was recorded. The produced sulphur was filtered at a 50 hours

interval and 5 cm<sup>3</sup> of sample was taken from the running system at set time intervals in order to monitor the process change like the change of iron ion concentration and the oxidative degradation of organic solvent etc.

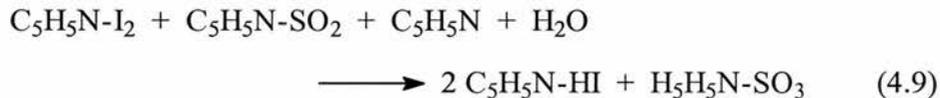
### ***HPLC analysis of the NMP***

(The same as part of *Analysis of the NMP* in **Chapter 3**)

### ***Determination of water by Karl Fisher reagent***

#### **Principle of determination**

Karl Fisher Reagent is composed of iodine, sulphur dioxide, pyridine, and methanol. The commercially available reagent consists of Karl Fisher Reagent A and Karl Fisher Reagent B which contain the above components, respectively. The mixture of A and B reacts with water according to the following equations.



Only the first step involves the oxidation of sulphur dioxide by iodine to give sulphur trioxide and hydrogen iodide and consumes water. In the presence of a large amount of pyridine, C<sub>5</sub>H<sub>5</sub>N, all reagents and products exist as complexes, as indicated in the equations. The second step, which occurs when an excess of methanol is present, is important to the success of the titration because a large excess of methanol prevents the following reaction.



The end point in a Karl Fisher titration is signalled by the appearance of the first excess of the pyridine / iodine complex when all water has been consumed. The colour of the reagent is intense enough for visual end point, the change is from the yellow of the reaction products to brown of the excess reagent.

**Practical procedure**

10 cm<sup>3</sup> of Karl Fisher Reagent A (1 cm<sup>3</sup>  $\leftrightarrow$  3 mg of water) and 10 cm<sup>3</sup> Karl Fisher Reagent B (1 cm<sup>3</sup>  $\leftrightarrow$  3 mg of water) were mixed under the presence of dry N<sub>2</sub>. The mixture solution was then added dropwise to the sample while stirring until the colour of the mixture solution changed from deep brown to bright yellow.

***Determination of SO<sub>3</sub><sup>2-</sup> by redox titration***

Determination of SO<sub>3</sub><sup>2-</sup> is similar to the measure of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (Cf. **Chapter 2**).

***Determinations of iron ion, SO<sub>4</sub><sup>2-</sup> ion, and the Cyclic Voltammograms analyses***

(The same as the related parts of **Chapter 2**)

## Chapter 5

### **Catalytic Activities of Non-Iron Metal Complexes for the Oxidation of H<sub>2</sub>S to Sulphur by Air**

#### **5.1 Introduction**

As we have seen in **Chapter 2**, the limited lifetime of NTA used to coordinate the iron centres is a major problem in current Fe-NTA system. It is generally recognised that hydroxyl radical, which is formed in the re-oxidation of Fe<sup>2+</sup> with O<sub>2</sub> to Fe<sup>3+</sup> and usually associated with 'Fentons Reagent', is responsible for the degradation of ligand. This led us to consider using alternative metals to prevent the formation of hydroxyl radicals / peroxide in the process. To the best of our knowledge, the redox couples Cu<sup>2+</sup>/Cu<sup>+</sup>, Mn<sup>3+</sup>/Mn<sup>2+</sup>, Co<sup>3+</sup>/Co<sup>2+</sup> and Ru<sup>3+</sup>/Ru<sup>2+</sup> have not been reported as catalysts for the oxidation of hydrogen sulphide to sulphur by air. Herein, the complexes of transition metal Cu<sup>2+</sup>, Mn<sup>3+</sup>, Co<sup>3+</sup> and Ru<sup>3+</sup> of nitrilotriacetic acid (NTA) and [(phosphonomethyl)imino]diacetic acid (NTAP) have been tested as catalysts for the removal of H<sub>2</sub>S.

#### **Results and Discussion**

##### **5.2 Catalytic activities of the Cu and Co complexes of NTA and NTAP**

Nitrilotriacetic acid (NTA) (36 mM) or [(phosphonomethyl)imino]diacetic acid (NTAP) (36 mM) reacts with copper (II) acetate monohydrate (18 mM) in water

in the presence of sorbitol (9 mM) to afford a bright blue solution at pH = 8.5. No precipitate was found when the solutions were stored at room temperature for more than one month. Unfortunately, no catalytic activity was found when they were tried as catalysts for the catalytic oxidation of hydrogen sulphide to sulphur by air, either. Both Cu-NTA and Cu-NTAP systems showed severe tail gas and a lot of black solid in the absorbed solution. The black solid should be CuS, since no sulphur was formed as determined by HPLC. It is obvious that  $\text{Cu}^{2+}/\text{Cu}^{+}$ -NTA chelate complex is not as stable as CuS. This redox couple is not suitable for replacing  $\text{Fe}^{3+}/\text{Fe}^{2+}$  as the coordinating centre ion.

NTAP (36 mM) or NTA (36 mM) was added to the aqueous solution of cobalt(III) chloride (18 mM), which was obtained by pre-oxidation of cobalt(II) chloride (18 mM) with equivalent molar amount of  $\text{H}_2\text{O}_2$ , to give a violet solution in the presence of sorbitol at pH = 8.5. No precipitate was found when both solutions of Co-NTAP and Co-NTA were stored at room temperature for more than one month. The solutions were loaded on 1-litre reactor for the catalytic conversion of  $\text{H}_2\text{S}$  to S. Massive dark solid formed and severe tail gas was observed in both processes. In addition, a lot of foam formed during the process in the case of Co-NTA.

### **5.3 Catalytic activities of Mn complexes of NTA and NTAP**

NTAP (36 mM) reacted with manganese(III) acetate dihydrate (18 mM) in the presence of sorbitol at pH = 8.5 to give a colourless solution. The solution can be adjusted to pH = 14 safely. Both solutions with pH = 8.5 and pH = 14 were stored at room temperature for more than one month without the formation of precipitate. However, poor catalytic activity was observed when the solution (pH = 8.5) was

used to absorb hydrogen sulphide. Although no black solid was found in the process, there is severe tail gas.

NTA (36 mM) mixed with manganese(III) acetate dihydrate (18 mM) in the presence of sorbitol (9 mM) at pH = 8.5 to give a colourless solution. Increase of the concentration of NTA to 180 mM, manganese(III) acetate dihydrate to 90 mM and sorbitol to 45 mM at the same pH value led to a brown solution. Both solutions are stable when stored at room temperature for more than one month.

As shown in **Table 5.1**, Mn(III)-NTA possesses obvious catalytic activity for the oxidation of hydrogen sulphide by air, though the selectivity to sulphur was unsatisfactory and the formation of side products such as  $S_2O_3^{2-}$  and  $SO_4^{2-}$  was obvious. Unexpectedly, higher concentration of catalyst did not improve either the effects of the absorption or the conversion of hydrogen sulphide. The amount of tail gas almost kept the same regardless of the increase of Mn ion concentration. The conversion of  $H_2S$  to sulphur did not benefit from the increase of the Mn concentration, on the other hand, higher concentration of catalyst obviously increased the formation of the further oxidised products  $S_2O_3^{2-}$  and  $SO_4^{2-}$ . The half-life of NTA in Mn-NTA system, however, was much longer than in the Fe(III)-NTA process. Interestingly, the half-life of NTA is in proportion to the concentration of Mn(III)-NTA. Higher concentration of catalyst seems good for preventing NTA from oxidative degradation. The general degrading mechanism is still not clear yet.

**Table 5.1** Catalytic activity of Mn(III)-NTA for the oxidation of H<sub>2</sub>S to S by air

Catalyst	T <sub>I</sub>	T <sub>II</sub>
Catalyst composition	Mn/NTA = 1/2	Mn/NTA = 1/2
Mn(III) concentration (mM)	18	90
pH of absorbed solution	8.50	8.50
H <sub>2</sub> S flow rate (cm <sup>3</sup> /min)	2.00	2.00
Air flow rate (cm <sup>3</sup> /min)	800	800
Cycling rate of liquid (cm <sup>3</sup> /min)	100	100
Test time (h)	30	66
Amount of consumed NaOH (2 M) (cm <sup>3</sup> )	21.5	36.0
Product sulphur (g)	2.13	5.86
CuS (tail gas) (g)	0.137	0.490
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	12.00	34.77
SO <sub>4</sub> <sup>2-</sup> (mM)	5.03	83.77
Conversion of H <sub>2</sub> S to S (%)	68.58	53.57
Conversion of H <sub>2</sub> S to CuS (tail gas) (%)	1.48	1.50
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	24.76	20.38
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	5.18	24.55
Half life of NTA (h)	122.5	679.0
1 <sup>st</sup> order rate constant of ligand degradation (h <sup>-1</sup> ) x 10 <sup>-3</sup>	5.66	1.21

In summary, it is impossible for Cu, Co and Mn to replace Fe as coordinating centre of NTA for the catalytic oxidation of hydrogen sulphide to sulphur by air.

#### **5.4 Catalytic activities of the Ru complexes of NTA and NTAP**

The formation and catalytic activity of ( $\mu$ -peroxo) ruthenium (III) complexes with amino polycarboxylic acids have also been reported.<sup>294-301</sup> For example, the oxidation of saturated and unsaturated substrates catalyzed by  $K[Ru(III)(EDTA-H)Cl]$  (EDTA-H = protonated ethylenediaminetetraacetate) and  $K[Ru(III)(PDTA-H)Cl]$  (PDTA-H = protonated propylenediaminetetraacetate) in the presence of NaOCl as a cheap oxidant, which has successfully been used as an oxidant for the epoxidation of olefins by manganese porphyrins.<sup>302-304</sup> However, no report has been found so far that the complex of Ru(III) was applied as a catalyst for the catalytic oxidation of hydrogen sulphide in the presence of molecular oxygen (air).

NTAP (36 mM) reacted with ruthenium (III) chloride hydrate (18 mM) in  $H_2O$  in the presence of sorbitol (9 mM) at the pH = 8.5 to afford a dark green solution. The mixture solution is still stable even its pH value was adjusted to up to 13. No precipitate was found when the solution was stored at room temperature for more than two months.

NTA (36 mM) mixed with ruthenium (III) chloride hydrate (18 mM) in water in the presence of sorbitol (9 mM) at the pH = 8.5 to form a black solution. No precipitate was discovered in the mixture solution when stored at room temperature for more than two months.

Both Ru(III)-NTA and Ru(III)-NTAP exhibit catalytic activities to different extent for the oxidation of H<sub>2</sub>S to S. The results are listed in **Table 5.2**. As shown in **Table 5.2**, catalytic abilities of both Ru(III)-NTA and Ru(III)-NTAP are much lower than that of the corresponding Fe(III) complexes under the required conditions. More than 40 % of H<sub>2</sub>S was found to be further oxidised to S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> and tiny tail gas was observed in the both systems. However, it is obvious that degradation of ligands in the Ru(III) complex system is slower than that in the corresponding Fe(III) complex system, especially the half life of NTAP is extended by twenty times when Ru(III)-NTAP was applied. It seems that the Ru(III) / Ru(II) redox couple can inhibit the formation of hydroxyl radical and prevent degradation of NTA or NTAP in the process. However, the low selectivity of hydrogen sulphide to sulphur and the high yield of side products limit the application of Ru(III)-NTAP or Ru(III)-NTA as catalyst for the removal of hydrogen sulphide.

### 5.5 Conclusions

The Cu<sup>2+</sup>/Cu<sup>+</sup> or Co<sup>3+</sup>/Co<sup>2+</sup> complexes of NTA and NTAP proved useless for the catalytic oxidation of hydrogen sulphide to sulphur. Mn<sup>3+</sup> and Ru<sup>3+</sup> complexes of NTA and NTAP did display some catalytic activities for this process, however, the selectivity to sulphur was low and the absorption of hydrogen sulphide was incomplete. This precludes the possibility of Mn<sup>3+</sup>/Mn<sup>2+</sup> and Ru<sup>3+</sup>/Ru<sup>2+</sup> in replacing Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple for the catalytic oxidation of hydrogen sulphide to sulphur.

**Table 5.2** Catalytic activities of Ru(III)-NTA and Ru(III)-NTAP  
for the catalytic oxidation of H<sub>2</sub>S to S by air

Catalyst	Ru(III)-NTA	Ru(III)-NTAP
Catalyst composition	Ru/NTA = 1/2	Ru/NTAP = 1/2
Ru(III) concentration (mM)	18	18
Concentration of ligand (mM)	36	36
pH of absorbed solution	8.50	8.50
H <sub>2</sub> S flow rate (cm <sup>3</sup> /min)	2.00	2.00
Air flow rate (cm <sup>3</sup> /min)	700	700
Cycling rate of liquid (cm <sup>3</sup> /min)	100	100
Test time (h)	100	100
Product sulphur (g)	9.29	9.36
CuS (tail gas) (g)	0.35	0.55
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mM)	91.90	83.00
SO <sub>4</sub> <sup>2-</sup> (mM)	20.20	33.80
Conversion of H <sub>2</sub> S to S (%)	58.26	58.69
Conversion of H <sub>2</sub> S to CuS (tail gas) (%)	0.73	1.15
Conversion of H <sub>2</sub> S to S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (%)	36.95	33.37
Conversion of H <sub>2</sub> S to SO <sub>4</sub> <sup>2-</sup> (%)	4.06	6.79
Half life of NTA (h)	340.3	819.3
1 <sup>st</sup> order rate constant of Ligand degradation (h <sup>-1</sup> ) x 10 <sup>-3</sup>	2.04	0.85

## ***Experimental***

### ***Reagents and materials***

The following materials were ordered from Aldrich or Lancaster and were used without further purification: nitrilotriacetic acid trisodium salt ( $\text{Na}_3\text{NTA}$ , 99.0 %); sorbitol (98.0 %); iminodiacetic acid, disodium salt hydrate ( $\text{Na}_2\text{IDA}$ , 98.0 %); sodium oxalate (99.5 %); glacial acetic acid (99.99 %); methyl alcohol (HPLC grade); hydrogen sulphide (99.5 %); boric acid (99.5 %);  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (98.0 %);  $\text{CuNO}_3 \cdot 5/2\text{H}_2\text{O}$  (98.0 %); copper monohydrate (99.0 %); cobalt(II) chloride (99.0 %); manganese(III) acetate dihydrate (98.5 %); Ruthenium(III) chloride hydrate (97.0 %).

**Apparatus and general procedure of testing, determinations of NTA by HPLC, NTA2P by  $^{31}\text{P}$  - $\{^1\text{H}\}$  NMR,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_4^{2-}$  see Chapter 2.**

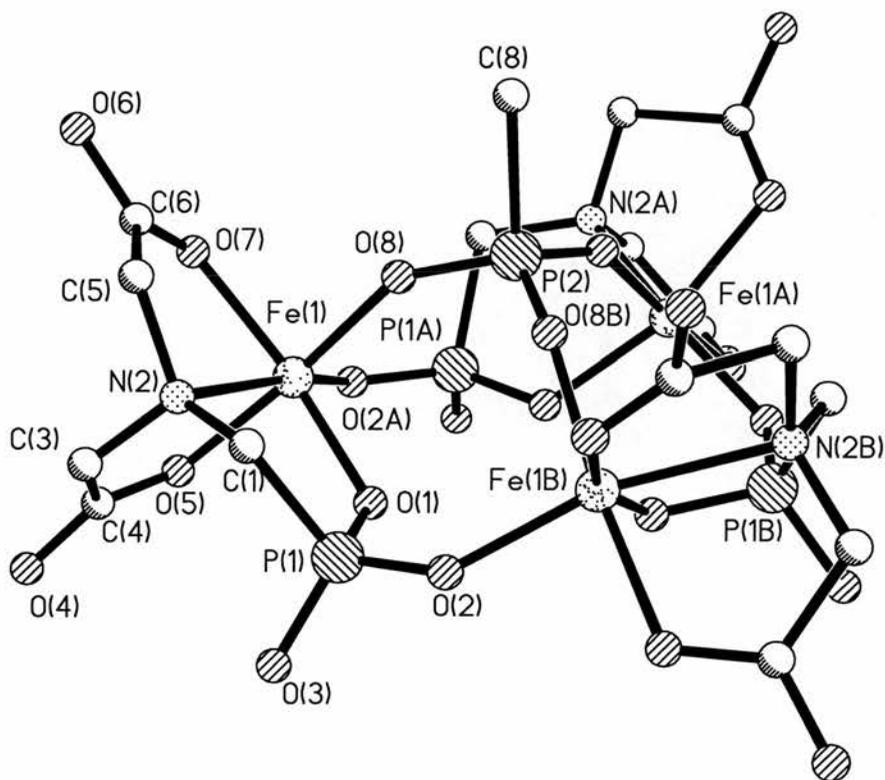
## Appendix

### 6.1 *The crystal structure of Fe(III)-NTAP*

The acid H<sub>4</sub>NTAP (1.14 g, 5 mmol) was dissolved in 0.3 N of sodium hydroxide solution (0.8 g, 20 mmol). This solution was added slowly to a solution of anhydrous iron(III) chloride (0.81 g, 5 mmol) in distilled water (50 cm<sup>3</sup>) while stirring. The pH was adjusted to 5.0 by 2 N NaOH. Slow evaporation of the aqueous solution gave brown crystals of [Na{Fe<sub>3</sub>[N(CH<sub>2</sub>COO)<sub>2</sub>(CH<sub>2</sub>PO<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>PO<sub>3</sub>)<sub>2</sub>}(3NaOH) 9H<sub>2</sub>O}]<sup>4+</sup> suitable for X-ray analysis.

Details of the X-ray data collection and refinement are given in **Table 6.1**, selected bond lengths and angles in **Table 6.2**. Again, the final R factor is not satisfactory. However, as shown in **Fig. 6.1**, the trimeric unit structure is undoubtable. In each trimeric unit three chemically and crystallographically equivalent iron(III) ions are bridged by four groups of O-P-O. The ligand (NTAP) occupies five coordination sites, N(2), O(1), O(2A), O(5) and O(7), and the sixth by a coordinated O(8), from the impurity CH<sub>3</sub>PO<sub>3</sub><sup>2-</sup>, which also coordinated to other two iron(III) ions. The geometry around the iron shows large deviations from idealized octahedral geometry with *cis* angles ranging from 78.8(6)° to 99.9(6)° and *trans* angle from 161.8(6)° to 173.9(6)°. The Fe-O (phosphate) bonds [1.957(12)-1.967(15) Å] are significantly shorter than the Fe-O (carboxylate) bonds [2.019(15)-2.020(14) Å]. The Fe(1)-O(2A), Fe(1)-O(1) (phosphate from ligand NTAP) and Fe(1)-O(8) (in the bridging phosphate from impurity CH<sub>3</sub>PO<sub>3</sub>H<sub>2</sub>) bond distances are equivalent. In Fe-NTAP Fe-O (carboxylate) and Fe-N bond lengths are comparable

with those found for the Fe-NTA complex.<sup>305-307</sup> The Fe(1)-N(2) bond distance of 2.235(15) Å is significantly longer than the Fe-O bond lengths [1.957(12)-2.020(14) Å]. This is attributed to the greater affinity of iron for oxygen than for nitrogen and has been observed for other complexes of mixed N-O donating ligands.<sup>305, 308-310</sup> The structure co-crystallised with nine molecules of water, three molecules of sodium hydroxide and one sodium ion.



**Fig. 6.1** The crystal structure of Fe(III)-NTAP

**Table 6.1** Details of the X-ray data collections and refinements for Fe(III)-NTAP complex

Empirical formula	C <sub>16</sub> H <sub>42</sub> Fe <sub>3</sub> N <sub>3</sub> Na <sub>4</sub> O <sub>36</sub> P <sub>4</sub>
Formula weight	1235.92
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal size (mm <sup>3</sup> )	0.15 x 0.1 x 0.1
Crystal system	Hexagonal
Space group	P6cc
a/Å	17.1066(12)
b/Å	17.1066(12)
c/Å	26.066(4)
α/°	90°
β/°	90°
γ/°	120°
U/Å <sup>3</sup>	6605.8(11)
Z	4
Dc/g cm <sup>3</sup>	1.243
U/mm <sup>-1</sup>	0.849
F(000)	2516
Measured reflections	26027
Independent reflections	2610 [R(int) = 0.2566]
Final R indices [I>2σ(I)]	R1 = 0.1189, wR2 = 0.2763

**Table 6.2** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for Fe(III)-NTAP complex

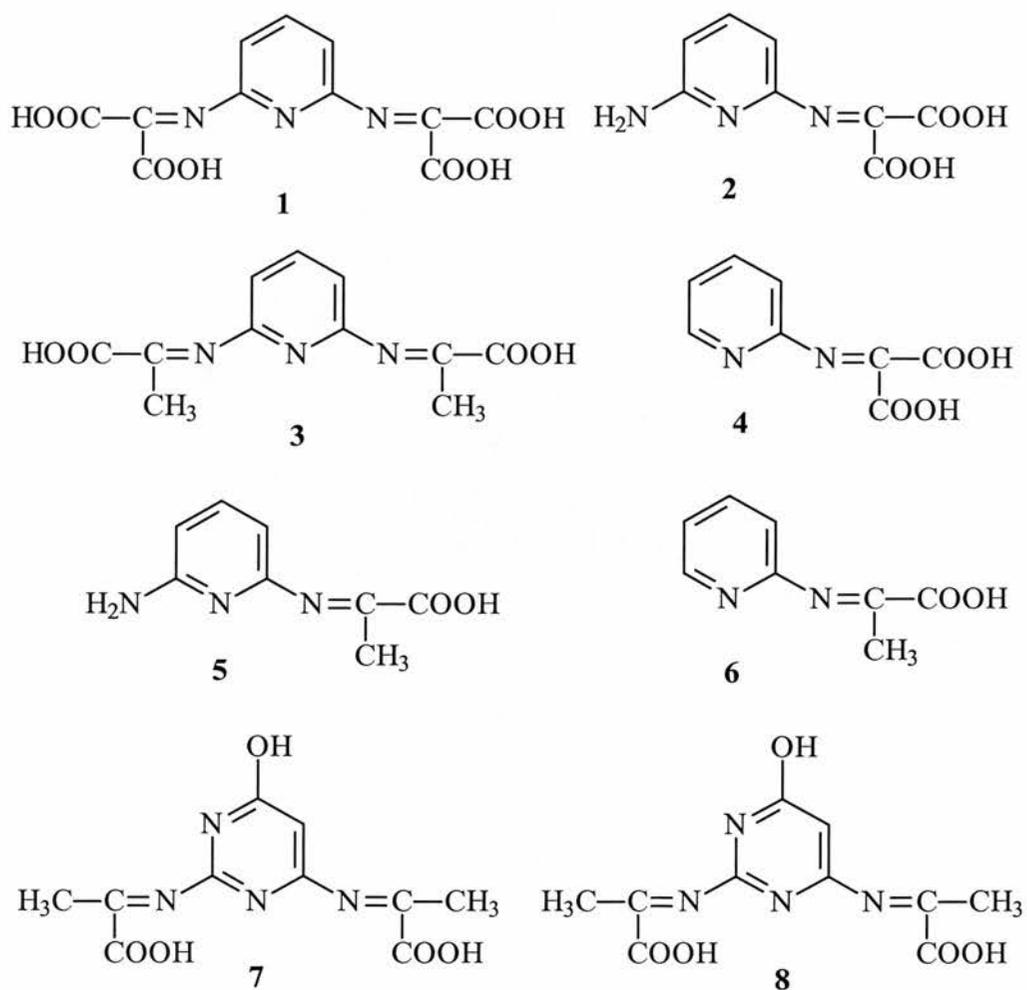
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Fe(1)-O(2A)	1.957(12)	N(2)-C(5)	1.52(3)
Fe(1)-O(1)	1.961(12)	C(3)-C(4)	1.50(4)
Fe(1)-O(8)	1.967(15)	C(4)-O(5)	1.25(3)
Fe(1)-O(7)	2.019(15)	C(4)-O(4)	1.28(3)
Fe(1)-O(5)	2.020(14)	C(5)-C(6)	1.60(3)
Fe(1)-N(2)	2.235(15)	C(6)-O(7)	1.17(3)
O(1)-P(1)	1.542(12)	C(6)-O(6)	1.31(4)
O(2)-P(1)	1.489(12)	P(2)-O(8B)	1.508(14)
O(3)-P(1)	1.485(14)	P(2)-O(8A)	1.508(15)
P(1)-C(1)	1.82(2)	P(2)-O(8)	1.508(14)
C(1)-N(2)	1.46(2)	P(2)-C(8)	2.04(11)
N(2)-C(3)	1.42(3)		
O(2A)-Fe(1)-O(1)	99.9(6)	O(2A)-Fe(1)-N(2)	163.5(6)
O(2A)-Fe(1)-O(8)	101.1(6)	O(1)-Fe(1)-N(2)	83.4(5)
O(1)-Fe(1)-O(8)	90.0(5)	O(8)-Fe(1)-N(2)	95.1(6)
O(2A)-Fe(1)-O(7)	98.2(6)	O(7)-Fe(1)-N(2)	78.8(6)
O(1)-Fe(1)-O(7)	161.8(6)	O(5)-Fe(1)-N(2)	79.4(6)
O(8)-Fe(1)-O(7)	87.9(6)	P(1)-O(1)-Fe(1)	122.1(8)
O(2A)-Fe(1)-O(5)	84.3(6)	C(3)-N(2)-Fe(1)	107.2(13)
O(1)-Fe(1)-O(5)	91.9(6)	C(1)-N(2)-Fe(1)	106.0(11)
O(8)-Fe(1)-O(5)	173.9(6)	C(5)-N(2)-Fe(1)	104.6(11)
O(7)-Fe(1)-O(5)	88.5(6)	C(4)-O(5)-Fe(1)	119.3(16)

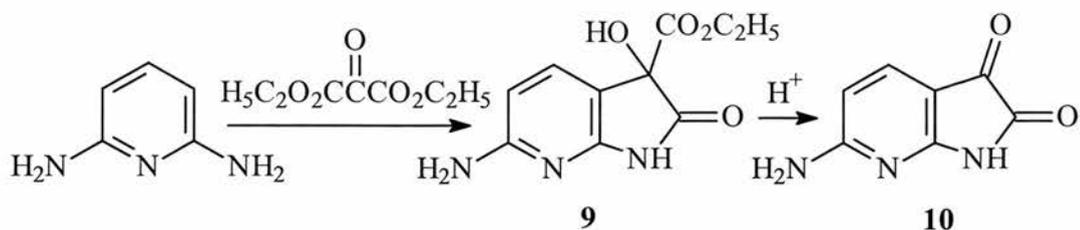
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## 6.2 Preparation of multidentate Schiff base ligands

According to our original plan, preparation of a series of multidentate Schiff base ligands was tried. Unfortunately, attempts to synthesise the following ligands were unsuccessful.



The common problem in the preparation of the above ligands is cyclization. For example, an attempt to get ligand 1 led to the formation of compound 9 and compound 10.

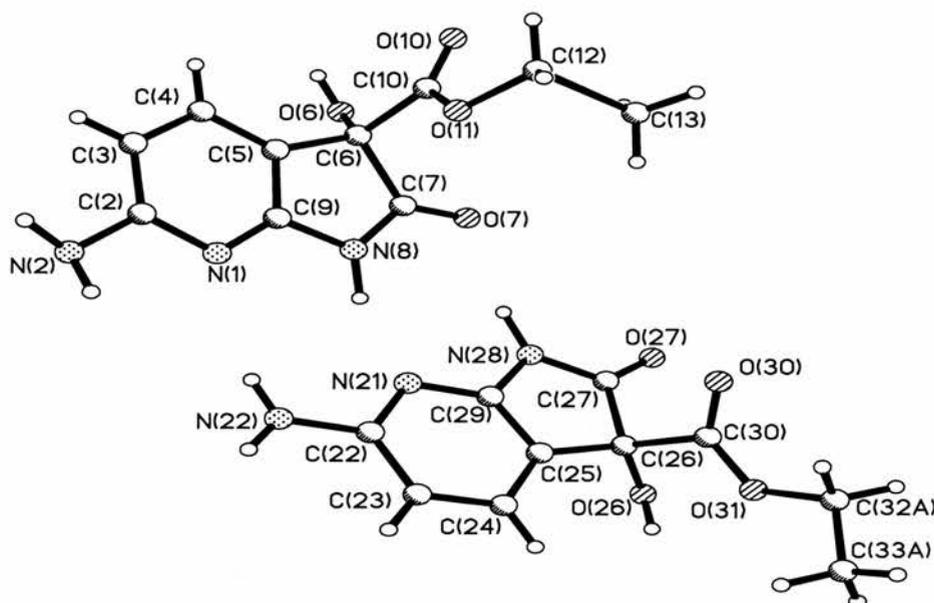


Compound **9**. Orange crystal. Microanalysis: Found, C, 50.54 %; H, 4.76 %; N, 17.56 %. C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub> requires: C, 50.63 %; H, 4.76 %; N, 17.71 %. M.P., 203 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm): 10.74 (s, 1H, OH), 7.13 (d, 1H, CH, <sup>3</sup>J<sub>CHCH</sub> = 7.9 Hz), 6.79 (s, 1H, NH), 6.17 (s, 2H, NH<sub>2</sub>), 5.99 (d, 1H, CH, <sup>3</sup>J<sub>CHCH</sub> = 8.2 Hz), 4.05 (m, 2H, CH<sub>2</sub>), 1.04 (t, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>CHCH</sub> = 7.2 Hz). IR (KBr disc, cm<sup>-1</sup>): 3393m, 3343m, 3304s, 3220br m, 2981w, 2758w, 1753vs, 1702s, 1630s, 1595s, 1455m, 1419w, 1234m, 1181m, 1135m, 1089w, 1018m, 831w, 791w, 726w. EIMS (m/z): 237 [M]<sup>+</sup>, 164 [M-CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>. CIMS (m/z): 238 [M+H]<sup>+</sup>, 255 [M+H<sub>2</sub>O]<sup>+</sup>.

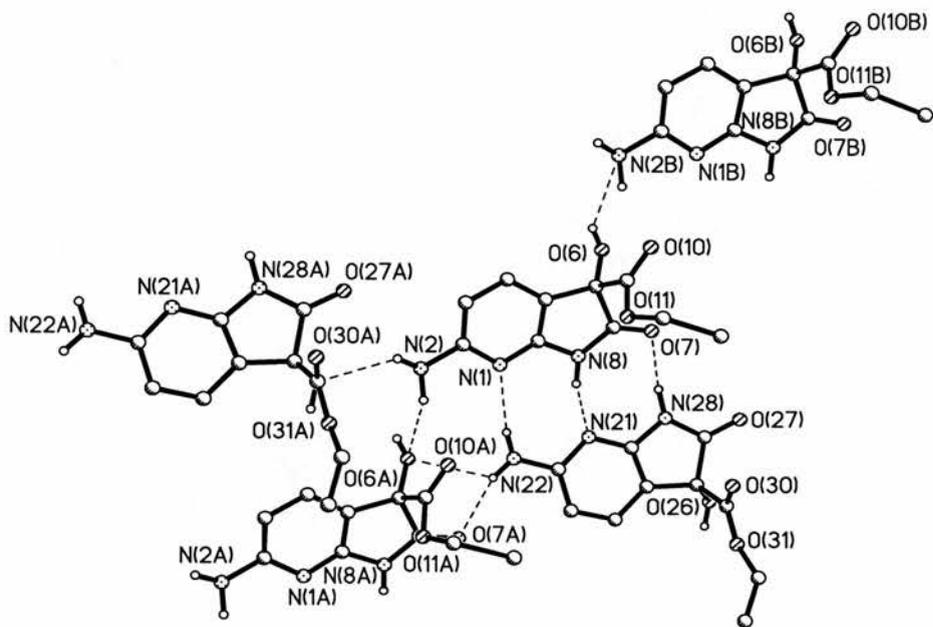
Compound **10**. Pale red solid. Microanalysis: Found: C, 51.17 %; H, 3.15 %; N, 25.12 %. C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub> requires: C, 51.53 %; H, 3.09 %; N, 25.76 %. IR (KBr disc, cm<sup>-1</sup>): 3385s (ν<sub>N-H</sub>), 1752m (ν<sub>C=O</sub>), 1695w (ν<sub>C=O</sub>), 1595s, 1437m, 1118w. EIMS: 163 [M]<sup>+</sup>. CIMS 164 [M+H]<sup>+</sup>.

Tiny crystals of **9** were obtained by slow evaporation of methanol solution. The crystal structure of compound **9** is shown in **Fig. 6.2**. Details of the X-ray data collection and refinement are given in **Table 6.3**. Though the resolution is not satisfactory (R1 = 0.0983), the bond lengths and angles in **Table 6.4** are in the reasonable range. As shown in **Fig. 6.2(b)**, hydrogen bonding plays a predominant role in the stabilisation of the structure. Hydrogen bonds occur between adjacent

molecules through interactions of the NH of pyrrolidine moiety and the oxygen of carbonyl [N(28)-H(28A)...O(7), d(D...A) 3.017(6) Å, d(H...A) 2.048(5) Å,  $\angle$ (DHA) 169.3(10) $^\circ$ ]; NH of pyrrolidine moiety and the N atom of pyridine moiety N(8)-H(8A)...N(21), d(D...A) 2.790(6) Å, d(H...A) 1.840(6) Å,  $\angle$ (DHA) 162.6(9) $^\circ$ ; NH<sub>2</sub> and the N atom of the pyridine moiety N(22)-H(22A)...N(1), d(D...A) 3.281(8) Å, d(H...A) 2.47 Å,  $\angle$ (DHA) 158.2 $^\circ$ ; NH<sub>2</sub> and the oxygen atom of the carbonyl N(22)-H(22B)...O(7A), d(D...A) 2.976(7) Å, d(H...A) 2.15 Å,  $\angle$ (DHA) 161.9 $^\circ$ ; NH<sub>2</sub> and OH group [N(2)-H(2B)...O(6), d(D...A) 3.066(5) Å, d(H...A) 2.291(5) Å,  $\angle$ (DHA) 135.4(4) $^\circ$ ; O(6)-H(6A)...N(2), d(D...A) 3.066(5) Å, d(H...A) 2.39 Å,  $\angle$ (DHA) 139.9 $^\circ$ ]. Minor interactions between NH<sub>2</sub> and OH were also observed [N(2)-H(2A)...O(26), d(D...A) 2.996(5) Å, d(H...A) 2.358(10) Å,  $\angle$ (DHA) 122.1(7) $^\circ$ ; N(22)-H(22B)...O(6), d(D...A) 3.167(6) Å, d(H...A) 2.65 Å,  $\angle$ (DHA) 120 $^\circ$ ].



**Fig. 6.2(a)** Crystal structure of the compound 9



**Fig. 6.2(b)** Crystal structure of the compound **9** showing hydrogen bonds

**Table 6.3** Details of the X-ray data collections and refinements for compound **9**

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Empirical formula	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub>
Formula weight	237.22
Temperature (K)	293(2)
Wavelength (Å)	1.54178
Crystal size (mm <sup>3</sup> )	0.13 x 0.1 x 0.03
Crystal system	Triclinic
Space group	P <sup>-1</sup>
a/Å	8.5722(17)
b/Å	11.201(2)
c/Å	12.954(3)
α/°	98.46(3)
β/°	108.88(3)
γ/°	98.45(3)
U/Å <sup>3</sup>	1138.8(4)
Z	4
Dc/g cm <sup>3</sup>	1.384
U/mm <sup>-1</sup>	0.928
F(000)	496
Measured reflections	3482
Independent reflections	3290 [R(int) = 0.0690]
Final R indices [I>2σ(I)]	R1 = 0.0983, wR2 = 0.2560

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**Table 6.4** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for compound **9**

N(1)-C(9)	1.314(7)	C(6)-C(10)	1.512(9)
N(1)-C(2)	1.362(7)	C(6)-C(7)	1.572(9)
C(2)-C(3)	1.366(9)	C(7)-O(7)	1.225(6)
C(2)-N(2)	1.393(6)	C(7)-N(8)	1.345(7)
C(3)-C(4)	1.368(9)	N(8)-C(9)	1.400(5)
C(4)-C(5)	1.372(7)	C(10)-O(10)	1.205(9)
C(5)-C(9)	1.378(9)	C(10)-O(11)	1.304(8)
C(5)-C(6)	1.507(7)	O(11)-C(12)	1.470(15)
C(6)-O(6)	1.393(7)	C(12)-C(13)	1.90(3)
C(9)-N(1)-C(2)	113.5(5)	O(6)-C(6)-C(7)	110.6(4)
N(1)-C(2)-C(3)	122.9(5)	C(5)-C(6)-C(7)	100.8(5)
N(1)-C(2)-N(2)	114.6(5)	C(10)-C(6)-C(7)	107.6(5)
C(3)-C(2)-N(2)	122.5(4)	O(7)-C(7)-N(8)	126.5(6)
C(2)-C(3)-C(4)	120.9(5)	O(7)-C(7)-C(6)	125.2(6)
C(3)-C(4)-C(5)	118.0(6)	N(8)-C(7)-C(6)	108.3(4)
C(4)-C(5)-C(9)	116.4(5)	C(7)-N(8)-C(9)	111.2(4)
C(4)-C(5)-C(6)	134.5(6)	N(1)-C(9)-C(5)	128.2(5)
C(9)-C(5)-C(6)	109.1(5)	N(1)-C(9)-N(8)	121.1(5)
O(6)-C(6)-C(5)	117.4(5)	C(5)-C(9)-N(8)	110.6(4)
O(6)-C(6)-C(10)	107.5(5)	O(10)-C(10)-O(11)	125.2(6)
C(5)-C(6)-C(10)	112.4(4)	O(10)-C(10)-C(6)	123.2(6)

## Publications

1. The evolution, chemistry and applications of homogeneous liquid redox sulphur recovery techniques

G. X. Hua, D. McManus, J. D. Woollins

*Comments Inorg. Biol.*, 2001, **22**(5), 327-351

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