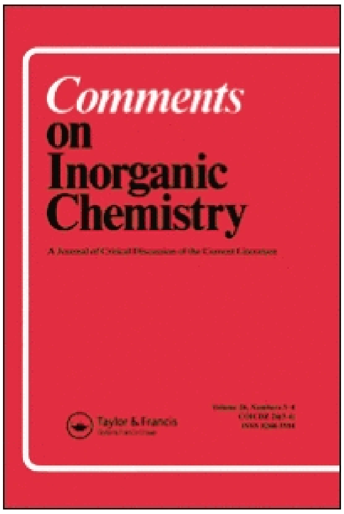

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Guo Xiong Hua[a]; Derek McManus[b]; J. Derek Woollins[a]
[a] School of Chemistry, University of St Andrews, Scotland, UK [b] US Filter Corporation, Inc., Plainfield, IL, USA

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The Evolution, Chemistry and Applications of Homogeneous Liquid Redox Sulfur Recovery Techniques

GUO XIONG HUA[a], DEREK McMANUS[b] and
J. DEREK WOOLLINS[a]*

[a]*School of Chemistry,*
University of St Andrews,
St Andrews, Fife KY16 9ST Scotland, UK and
[b]*US Filter Corporation, Inc.,*
Plainfield, IL 60544, USA

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Hydrogen sulfide is a highly undesirable component of natural gas and other gaseous streams. Its removal from sour natural gas streams is necessary for health and safety reasons and to prevent corrosion of equipment during its transmission and distribution. Herein an overview of desulfurization processes mainly concerning liquid redox sulfur recovery (LRSR) techniques is given. Three successful commercial applications of LRSR processes are the Stretford process, the LO-CAT process and the SulFerox process. The first using V(V)/V(IV) redox couple has dominated the 1980's, but now stopped spreading because of the chemical degradation and environmental problems with vanadium. The iron based processes employing Fe(III)/Fe(II) chelate systems, particularly the Fe(III)/Fe(II)-NTA system, is gradually replacing V(V)/V(IV) systems. However, the degradation of the chelating ligand in Fe(III)/Fe(II)-NTA system results in high chemical costs, which obviously obstructs the use of this system in large installations for the removal of H_2S by homogeneous catalytic oxidation. Although the rate of degradation can

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* Corresponding Author.

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be slowed considerably by addition of $Na_2S_2O_3$, which is known as an effective scavenger for the hydroxyl radical, it seems that the problem involving the degradation of NTA in-process is not resolved completely yet. The serious deficiency calls for research or selection of robust ligands. Therefore, Processes using of non-degrading ligands or regeneration facilitated by microorganisms, either with or without organic ligand have appeared, some of them have been applied on a pilot scale. Other processes, Such as the biological treatment without an auxiliary redox couple and the combined sulfur/hydrogen recovery, are now being developed.

Keywords: *hydrogen sulfide; sulfur; sulfur recovery; desulfurization process; Stretford process; LO-CAT process; SulFerox process; Claus process; homogeneous redox; Fe(III)/(II) redox couple; V(V)/V(IV) redox couple; nitrilotriacetic acid; ethylenedinitrilotetraacetic acid; 2,6-pyridinedicarboxylic acid; 2-carboxy-8-hydroxyquinoline; 2, 6-pyridinediphosphonic acid*

1 INTRODUCTION

Hydrogen sulfide (H_2S) and other sulfur-containing volatile compounds such as methanethiol, dimethyl sulfide, and dimethyl disulfide are highly malodorous compounds and sources of pollution of air streams. They are found to be liberated in the production of natural gas and of combustible gases from coal, such as in coking operations, as well as being waste by-products in a number of chemical processes. These sulfur-containing compounds are also present in geothermal steam used in power generation plants and in natural gas itself. Its removal from sour natural gas, bio-gas and other gaseous streams is necessary for health and safety reasons, and to prevent corrosion to equipment during its transmission and distribution.

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 sulfur through partial oxidation of the H_2S stream by air in a thermal stage with one or more catalyst beds at high temperature[1]. This dry process, the Claus 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 sulfur selective conversion[2]-[7]. Other developments such as the use of internally cooled, isothermal catalytic reactors may contribute to increasing sulfur yields[8,9]. In addition, separation of H_2S in an alkanolamine system and subsequent gas phase sulfur recovery often appears to be difficult to control[10, 11], and these processes require big investments and ground space[1].

Considering the disadvantages of the dry oxidation process, more efficient liquid redox sulfur recovery (LRSR) techniques 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.

2 EARLY LIQUID REDOX SULFUR RECOVERY (LRSR) PROCESSES

Kohl and Riesenfeld reported the first LRSR application which was based on the ammonium sulfide / ammonium sulfate couple[12]. This process involved a number of ammonium polythionates. Feld[13] and Overdieck[14] 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_2CO_3 solution, and is represented by the simplified set of reactions (**1**, **2** and **3**).

$$H_2S + H_2O \rightarrow H_3O^+ + HS^- \qquad (1)$$

$$Fe_2O_3 + 3HS^- \rightarrow Fe_2S_3 + 3\ OH^- \qquad (2)$$

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S \qquad (3)$$

Subsequently suspensions of $Fe(OH)_3$ in aqueous Na_2CO_3 solution were introduced. These process reactions were similar to reaction **1**, **2** and **3**. Fe_2O_3 and $Fe(OH)_3$ 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 which yield undesired sulfur compounds such as thiosulfate and sulfate[15].

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[16]. The Staatsmijnen-Otto process appeared to be problematic because of the use of the toxic solution containing $Fe(CN)_6^{n-}$ (n = 3 or 4) and ammonia, and the large number of side reactions.

The application of 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[17]. However, as it was soon discovered, due to severe losses of organic ligand, this early application of iron chelates in gas purification failed to be economical. It was not until the early 1980's that catalyst loss was sufficiently controlled, and iron chelates were re-introduced as LRSR couples, that is the contemporary iron chelate processes, which will be discussed in more detail in **Section 3**.

Another redox couple used in LRSR applications is the As(V)/As(III) couple, AsO_3^{3-}/AsO_4^{3-} in the Giammarco-Vetrocoke process[18,19]. This process is 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.

$$AsO_3^{3-} + 3H_2S = AsS_3^{3-} + 3H_2O \qquad (4)$$

$$AsS_3^{3-} + 3AsO_4^{3-} = 3AsO_3S^{3-} + AsO_3^{3-} \qquad (5)$$

$$3AsO_3S^{3-} = 3AsO_3^{3-} + 3S \qquad (6)$$

$$AsO_3^{3-} + 1/2\ O_2 = AsO_4^{3-} \qquad (7)$$

The first well established LRSR application developed during the 1950's, the Stretford process, employed the vanadium V(V)/V(IV)-redox couple[20,21]. There have been several patents involving modifications of these processes[22]. The chemistry is represented by the simplified set of reactions:

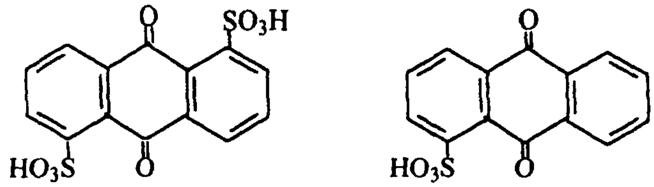
$$4VO_3^- + 8HS^- + CO_3^{2-} = V_4O_9^{2-} + 2HCO_3^- + 8S + 3H_2O \quad (8)$$

$$\begin{aligned} &V_4O_9^{2-} + 2HCO_3^- + 3ADA \text{ or } 3NQS + 3H_2O \\ &\quad = 4VO_3^- + 3H_2ADA \text{ or } 3H_2NQS + 2CO_3^{2-} \end{aligned} \qquad (9)$$

$$2H_2ADA \text{ or } 2H_2NQS + O_2 = 2ADA \text{ or } 2NQS + 2H_2O \qquad (10)$$

The anthraquinone disulphonic acid (ADA) or naphthoquinone sulfonate (NQS) (see **Scheme 1**) is involved as a catalyst in the oxidation reaction. The reaction takes place in an alkaline Na_2CO_3 buffer (pH = 9) at a relatively low temperature (T = 323K)[23]. The Stretford processes and the modified processes 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[22]. However, in these processes, several problems tend to increase the operating expenses, for example the degradation of ADA, the undesired conversion of the absorbed hydrogen sulfide /or the product sulfur to water-soluble sulfur-containing salts including sulfates, 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 not often chosen for new plants. However a large number of Stretford process plants remain in operation.



Anthraquinone-2,6-disulfonic acid (ADA) **Anthraquinone-2-sulfonic acid (NQS)**

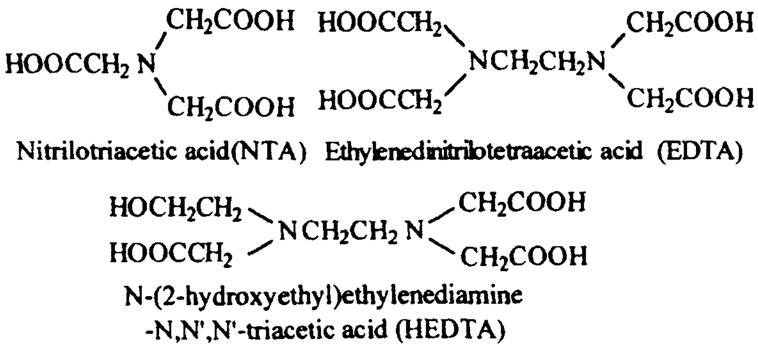
SCHEME 1 Catalysts used in the Stretford process

3 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.

3.1 AQUEOUS Fe(III)/Fe(II) REDOX COUPLES

As mentioned above, aqueous chelated iron processes began in the early 1960's[24], 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 sulfur productions up to 1.5 × 10^4 kg/day became operational[25, 26]. More recently, several aqueous and homogeneous chelated iron catalyst systems have been developed. The main chelate ligands are amino and polyaminopolyacetic acid, including nitrilotriacetic acid (NTA), ethylene dinitrilotetracetic acid (EDTA) and N-(2-hydroxyethyl)ethylenediamine-N,N',N'triacetic acid (HEDTA) (See **Scheme 2**) [27]-[31].



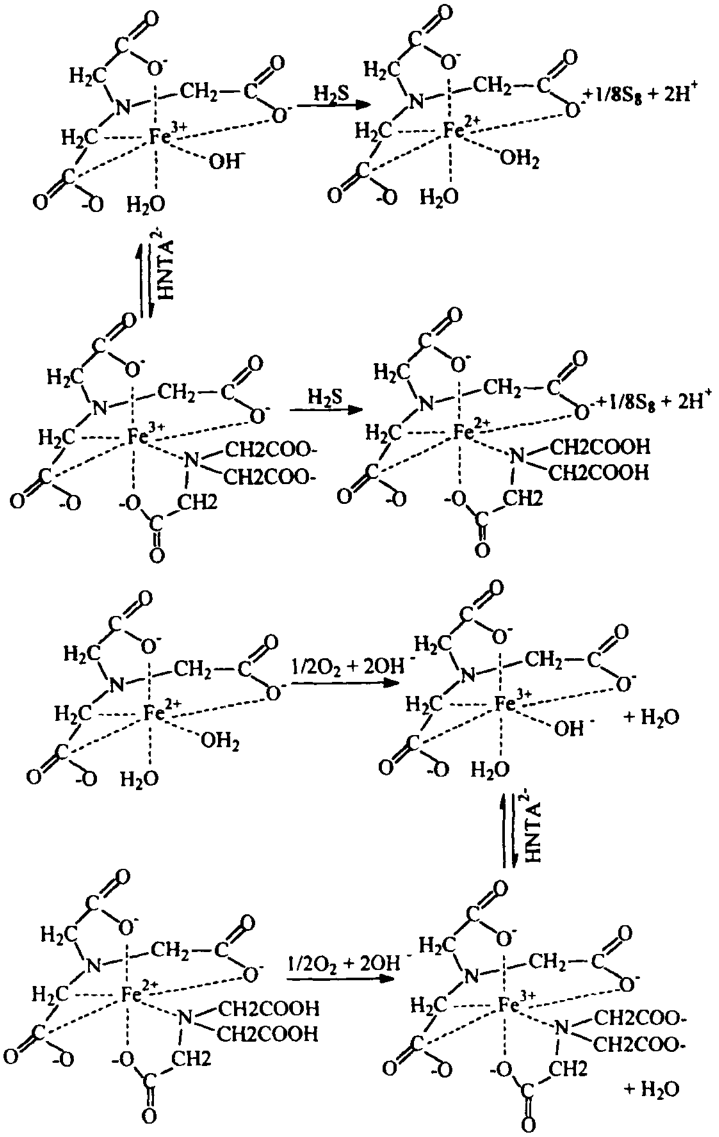
SCHEME 2 Ligands used in the Fe(III)/(II) redox couple systems

Considering the ligand stability and overall economics, the Fe(III)/Fe(II)-NTA systems are most widely commercially employed. The chemistry of this process is represented in **Scheme 3**. This system is further improved by addition of a hexitol [enantiomeric forms of $CH_2OH(CHOH)_4CH_2OH$] which deprotonates at high pH values and in the presence of Fe(III) forms a very stable complex thereby preventing precipitation of Fe as $Fe(OH)_3$][27, 32].

Chelated iron process plant configurations are somewhat varied[33, 34, 35], but all incorporate the basic unit operations of H_2S absorption, Fe(II)L oxidation and sulfur removal.

In operation, the H_2S containing gas stream is contacted with an aqueous, mildly alkaline (pH 7–9) solution of Fe(III)L ([Fe] = 0.005 M to 0.5 M) in the absorber vessel where the following reactions take place:

$$H_2S\ (g) + H_2O \rightleftharpoons H_2S\ (aq) \tag{11}$$



SCHEME 3 Reaction for the oxidation of H_2S to S with the Fe(III)/Fe(II)-NTA system as catalyst

$$H_2S\ (aq) \rightleftharpoons HS^- + H^+ \tag{12}$$

$$2Fe^{3+}L + HS^- \longrightarrow 2\ Fe^{2+}L + S \tag{13}$$

Absorbers are usually custom designed in order to accommodate the large range of sour gas stream compositions ($[H_2S]$ = 50 ppm to 100%), pressures (atmospheric to over 7 MPa) and flow rates (up to 65 m^3s^{-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 sulfur is continuously removed by alternative methods including sedimentation, filtration or melting under pressure[38].

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

$$O_2\ (g) + H_2O\ (l) \rightleftharpoons O_2\ (aq) \tag{14}$$

$$2Fe^{2+}L + 1/2\ O_2\ (aq) + H_2O \longrightarrow 2Fe^{3+}L + 2OH^- \tag{15}$$

Thus, the overall reaction is:

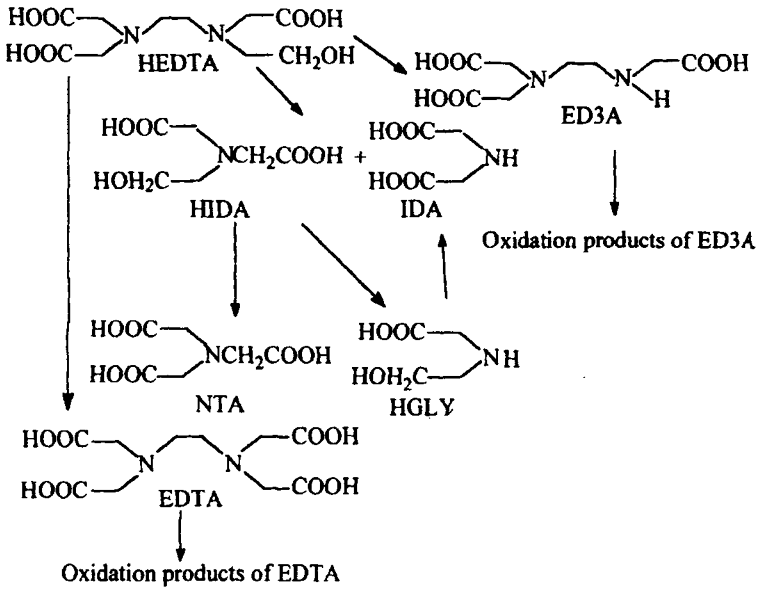
$$H_2S + 1/2\ O_2 \longrightarrow H_2O + S \tag{16}$$

Now there are several successful iron chelate based processes known[1, 39], the most prominent being the LO-CAT process (US Filter) and the SulFerox process (Shell Oil Company, the Dow Chemical Company).

The LO-CAT process has been available since the late 1970's. The majority of plants operate under mildly alkaline conditions ($7 \leq pH \leq 9$)[25], 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[39, 40]. 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[41].

The SulFerox process was established in 1987, and up to 1995 approximately 40 plants were licensed[42]. The process is very similar to the LO-CAT process apart from high iron concentrations ($0.1 \leq C_{Fe} \leq 2.0$ M)[29, 33, 34, 35, 39, 40, 43]. It is claimed that a high C_{Fe} reduces liquid circulation costs[41].

The Fe(III)/Fe(II)-NTA process has been applied in sweeting natural gas, oil refinery operations, enhanced oil recovery, marine vessel load-



SCHEME 4 Proposed degradation route of HEDTA

ing, 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[44, 45].

Despite the wide-spread application of these processes, the systems suffer from oxidation of the chelating ligands and eventual catalyst loss. The degradation of ligands may originate from the oxidation process of ferrous complex, which involves some strongly oxidising intermediates whose exact nature is still a subject of controversy[44, 45]. Although there are some debates about the presence of free OH· and H_2O_2, the following sequence of reactions is proposed to explain the degradation of Fe-NTA (**17** to **21**)[[46]-[50]].

$$\mathrm{FeNTA^- + O_2 + H_2O \longrightarrow Fe\ NTA + H_2O_2 + 2OH^-} \quad (17)$$

$$\mathrm{FeNTA^- + H_2O_2 \longrightarrow Fe\ NTA + OH^- + OH^\cdot} \quad (18)$$

$$R^1R^2N^+HCH_2COO^- + OH^- \longrightarrow R^1R^2N^+HCH_2COO^\cdot + OH^\cdot \quad (19)$$

$$R^1R^2N^+HCH_2COO^\cdot \rightleftharpoons R^1R^2N^+HCH^\cdot COO^- + H^+ \quad (20)$$

$$R^1R^2N^+HCH^\cdot COO^- + H_2O + Fe\ NTA \longrightarrow R^1R^2N^+HCHOH\ COO^- + Fe\ NTA^- + H^+ \quad (21)$$

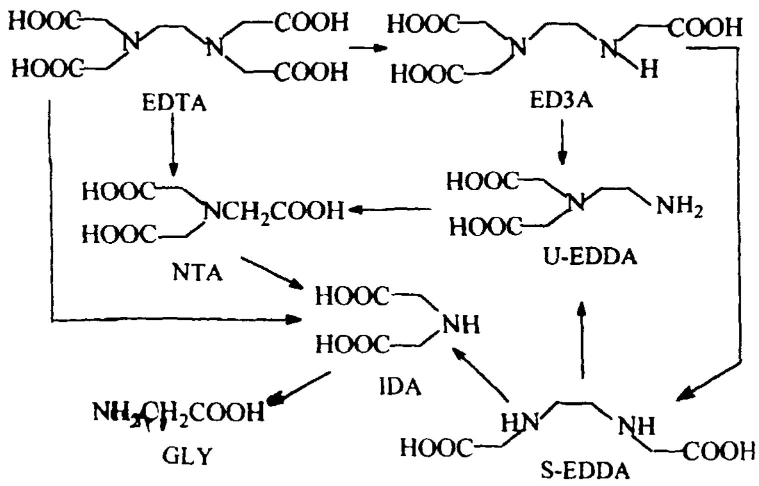
in which

$R^1 = R^2 = CH_2COO^-$, NTA

$R^1 = CH_2COO^-$, $R^2 = H$, IDA

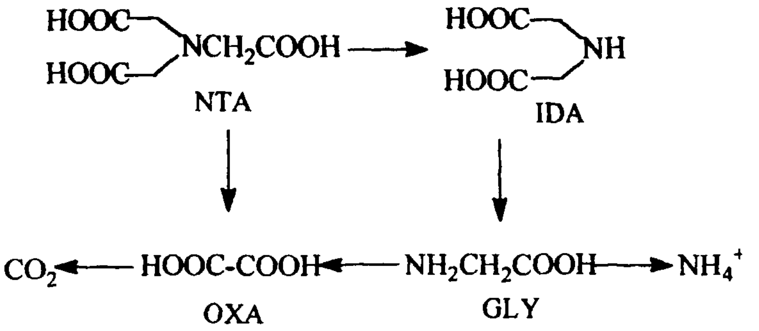
$R^1 = R^2 = H$, GLY

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_2 group of the acetate chains. The degradation of these ligands can be shown by the following Schemes **4–6**[15, 51, 52].



SCHEME 5 Proposed degradation route of EDTA

The fact that EDTA and HEDTA degrade faster than NTA makes NTA the preferable ligand[51, 52]. However, the relative information is for the most part proprietary. Little information is available on actual loss of activity.



SCHEME 6 Proposed degradation route of NTA

As a remedy for catalyst loss resulting from ligand degradation, some ligand-stabilizing agents which are considered as "radical scavenger", such as t-butanol, ethylene glycol[33], N,N-hydroxylamine, thiourea, thiosemicarbazide[30], thioglycolic acid, 3,3-thiodipropionic acid[53], sodium thiocyanate, dithionite[54] and anionic polymer JAYFLOC 803[55], 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_2S and $O_2$are simultaneously present[27].

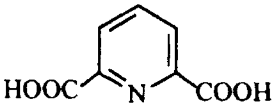
$$2HS^- + 2O_2 \longrightarrow S_2O_3^{2-} + H_2O \qquad (22)$$

The possibility that thiosulfate ions can be regenerated in the process after reacting to scavenge hydroxyl radicals has been suggested[56] and is supported by earlier work involving pulsed radiolysis [57].

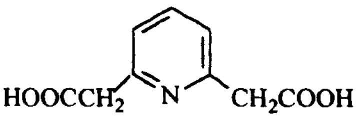
$$S_2O_3^{2-} + OH^{\cdot} \longrightarrow S_2O_3^{\cdot -} + OH^- \qquad (23)$$

$$2\ S_2O_3^{\cdot -} \longrightarrow S_4O_6^{2-} \qquad (24)$$

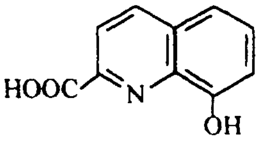
$$S_2O_3^{\cdot -} + Fe(II)NTA^- \longrightarrow S_2O_3^{2-} + Fe(III)NTA \qquad (25)$$



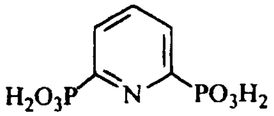
2,6-pyridinedicarboxylic acid
(DIPIC)



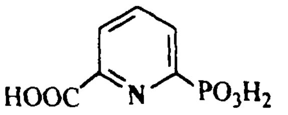
2,6-pyridinediacetic acid
(DIPIA)



2-carboxy-8-hydroxyquinoline
(CHQ)



2,6-pyridinediphosphonic acid
(2,6-PDPA)



pyridine-2-phosphonic-6-carboxylic acid
(2PP6C)

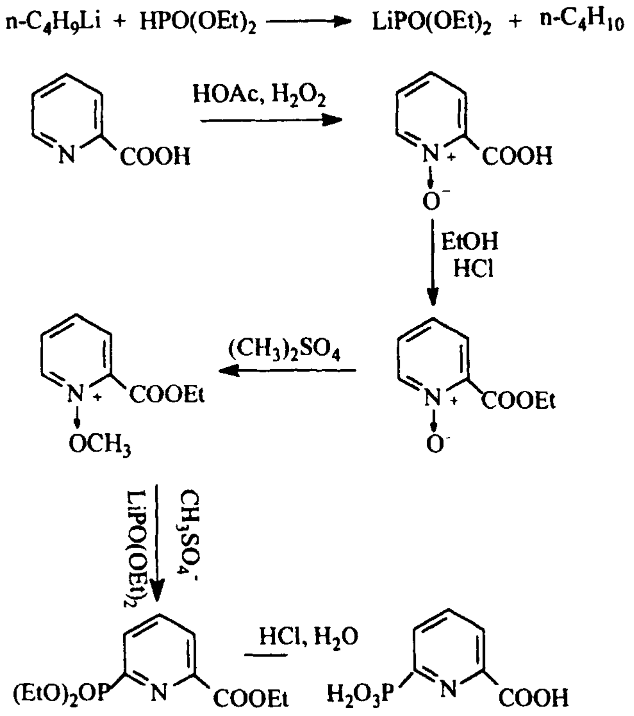
SCHEME 7 Some alternative ligands in aqeuous Fe(III)/Fe(II) system

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, $S_2O_3^{2-}$ can be oxidized to SO_4^{2-} and $S_4O_6^{2-}$, resulting in inert salt accumulation which eventually builds sufficiently to hamper the sulfur separation as well as the gas-liquid mass transfer[25].

$$2\ S_2O_3^{2-} + 1/2\ O_2 + H_2O \longrightarrow S_4O_6^{2-} + 2OH- \qquad (26)$$

$$S_2O_3^{2-} + 1/2O_2 + H_2O \longrightarrow 2SO_4^{2-} + 2H^+ \qquad (27)$$

Due to the above reasons, further research aiming at further improvement of ligands continues. An alternative ligand studied in some detail by Sawyer[58] and Chen et al[52] is 2,6-pyridinedicarboxylic acid (DIPIC, See **Scheme 7**). It was reported that no degradation was observed during a 100 hour test, but the stability of the Fe(III)-DIPIC is



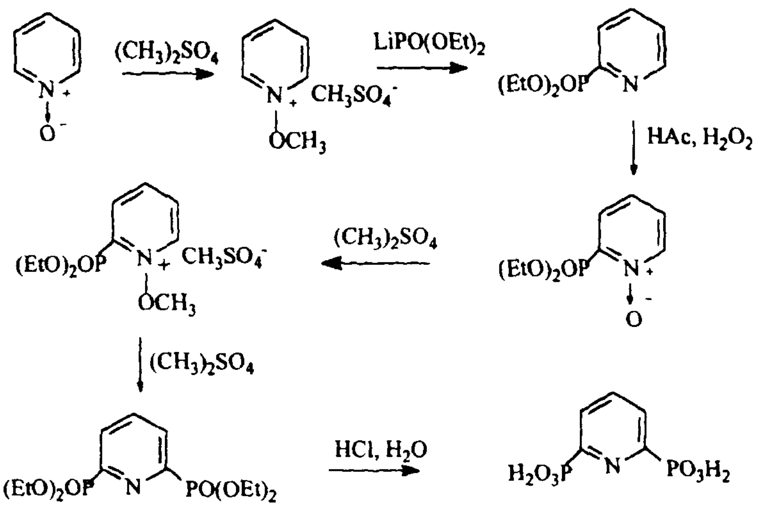
SCHEME 8 Synthesis of 2PP6C

not high enough to prevent precipitation of $Fe(OH)_3$ at the required basic condition[59, 60, 61].

A closely related ligand, 2,6-pyridinediacetic acid (DIPIA) was also introduced[59], but this ligand showed rapid degradation.

Using molecular mechanics, Hancock et al[59, 62] selected 2-carboxy-8-hydroxyquinoline (CHQ) without methylene groups ($-CH_2$) 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.

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)[59, 62, 63, 64]. Both are closely related to DIPIC, ligand degradation was also



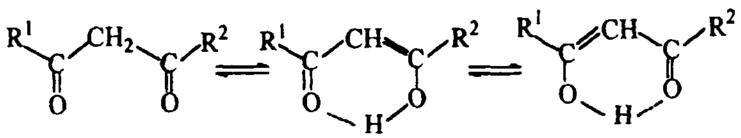
SCHEME 9 Synthesis of 2,6 PDPA

reported to certain extent[60]. Obviously, the absence of easily oxidised α-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 8** and **9** show the synthesis of the phosphonate ligand 2PP6C and 2,6-PDPA.

3.2 NON-AQUEOUS LRSR PROCESSES

Peter[65] first patented the use of β-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[66] and Eng et al[67] have reported in detail the application of non-aqueous liquid phase iron chelates in LRSR process,



$R^1 = R^2 = CH_3$,	**acetylacetone (acac)**
R^1 = Ph, $R^2 = CH_3$,	**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-butanedio**

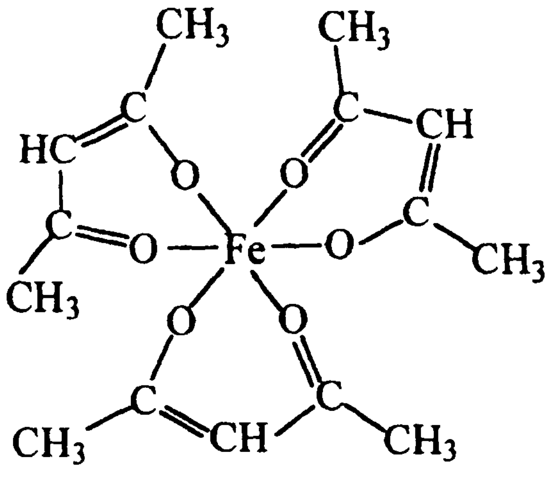
SCHEME 10 Tautomerization of α-diketones

which employed β-diketonates such as acetylacetone, benzoylacetone, 1,1,1-trifluoro-2,4-pentaneadione and 1-phenyl-4,4,4-trifluoro-1,3-butanedione(see **scheme 10**) 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.

These ligands, existing in two tautomeric forms, give sufficiently stable Fe(III)/Fe(II) complexes in the prefered solvent NMP from their keto-enol form **(Scheme 11)**[66].

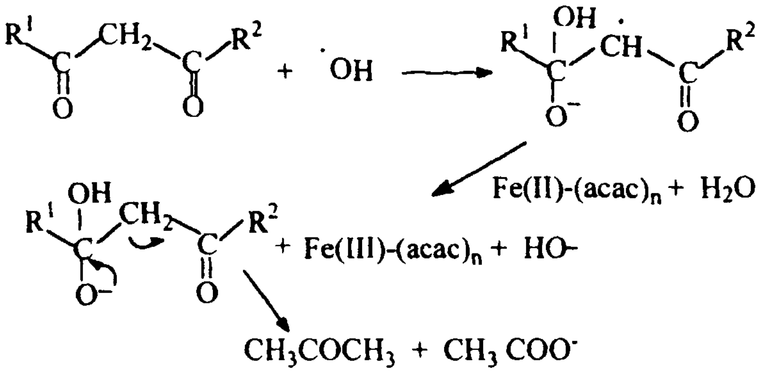
Eng et al investigated the degradation of the Fe(III)/Fe(II)-acetylacetonate (Fe(III)/Fe(II)-acac$^-$) and Fe(III)/Fe(II)-benzoylacetonate (Fe(III)/Fe(II)-bzac$^-$) as catalysts in the oxidation of H_2S in varied mixed solvent systems[68]. It was found that the rapid degradation of acac produces acetate and acetone in the re-oxidation of the Fe(II) complex to the Fe(III) complex, and a mechanism for the degradation of acac- is proposed which involves attack of the ligand by a hydroxyl radical (See **scheme 12**).

Advantages of the non-aqueous LRSR process include enhanced sulfur quality, reduced sulfur 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



SCHEME 11 Structure of tris-(acetylacetonato)iron(III)

process appears to be a promising application, the process has not matured beyond laboratory scale and many of the above claims can not be verified yet.



SCHEME 12 Mechnism of degradation of acac

3.3 THE Fe(III)/Fe(II) REDOX COUPLE IN COMBINATION WITH BIOCHEMICAL CATALYST REGENERATION LRSR PROCESSES----IRC-BCR PROCESSES

Different from the Fe(III)/Fe(II) chelate processes discussed above, no organic ligands or inorganic ligand are used in these processes. To prevent precipitation of $Fe(OH)_3$ and FeS, the operating pH should be $1.5 \leq pH \leq 2.68$. Similar to reaction **(13)**, H_2S is oxidized to elemental sulfur by Fe^{3+}.

$$H_2S + 2Fe^{3+} \longrightarrow S + 2Fe^{2+} + 2H^+ \qquad (28)$$

However, the rate of reaction **(28)** at the relative operational pH values appears to be lower than that for reaction **(13)**[69]-[72]. Also in contrast to Fe(III)/Fe(II) chelate processes, which operate at ambient pH ($7 \leq pH \leq 9$)[25], the dissociation of H_2S at acidic condition is negligible[72]. Therefore, a larger absorber for H_2S 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 ferroxidans*, immobilized on acid resistant materials (for instance glass wool) is used[73]. In these processes, bacteria may accelerate reaction **(29)** by a factor of 2×10^5 depending on temperature and pH values[69, 74, 75].

$$4\ Fe^{2+} + O_2 + 4\ H^+ \xrightarrow{\text{bacteria}} 4\ Fe^{3+} + 2\ H_2O \qquad (29)$$

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[46]. However, Rehmat and Yoshizawa[69] 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, $7 \leq pH \leq 8.5$, $303 \leq T \leq 318$, $C_{Fe} \approx 0.02$ M)[76, 77] The rate of the regeneration reaction **(29)** can be substantially enhanced (50–150%) by certain *Thiobacillus ferrooxidans* cultures, whereas ligand degradation is claimed to be reduced. 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[78, 79]. So far, the microbial/Fe(III)/Fe(II) chelate application has been tested by laboratory experiments only.

3.4 PURE BIOLOGICAL TREATMENT PROCESSES

Buisman first disclosed a method for removing H_2S or $SO_2$from gas or waste streams using microorganisms(THIOPAQ process)[80]. Gaseous streams are treated in a caustic scrubber ($8 \leq pH \leq 9$). The sulfur rich solution is then treated by microorganisms. If sulfur is present as SO_2, anaerobic treatment by consuming an electron donor such as H_2 or CO or ethanol yields H_2S, H_2S formation maybe represented by the simplified reactions:

$$HSO_3^- + 3\ CO \xrightarrow{\text{an.bact}} HS^- + 3CO_2 \qquad (30)$$

$$HSO_3^- + 3\ H_2 \xrightarrow{\text{an.bact}} HS^- + 3\ H_2O \qquad (31)$$

$$HSO_3^- + C_2H_5OH \xrightarrow{\text{an.bact}} 2HS^- + 3\ H_2O + 2\ CO_2 \qquad (32)$$

Prefered bacteria for this anaerobic process include the genera *Desulfovibrio, Desulfotomaculum, Desulfomonas, Desulfobulbus, Desulfobacter, Desulfococcus, Desulfomema, Desulfo Sarcina, Desulfobacterium* and *Desulforomas*[80]. The sulfide solution is subsequently treated in an aerobic reactor (**33**). Suitable bacteria for this aerobic reaction include the genera *Thiobacillus thioparus*[80, 81, 82], *Thiobacillus concretivorus*[83, 84, 85], *Thiobacillus ferrooxidans*[86, 87], *Chromatium vinosum*[88, 89], *Hyphomicrobium*[90], *Xanthomonus*[91] and heterotrophic bacterium[92]. Undesired by-products appear to be overoxidized sulfur compounds such as sulfate[93].

$$2HS^- + O_2 \xrightarrow{\text{aero.bact.}} 2S + 2\ OH^- \qquad (33)$$

Pilot plant studies, initiated in 1993, show good technological prospects[94]. However an independent economic evaluation mentions high circulation rates and a high blown down ratio as specific drawbacks[95].

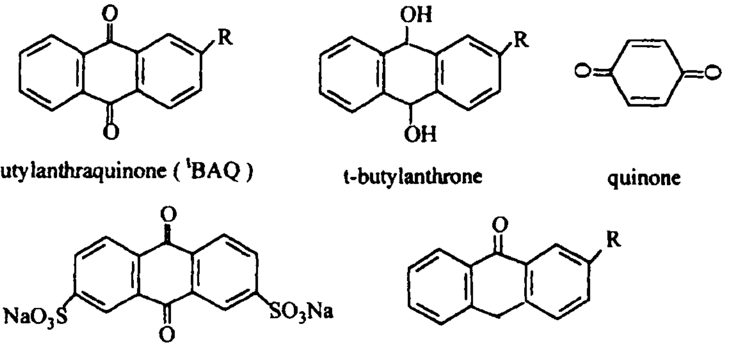
Successful H_2S removal with microorganisms was also reported by Gadre and Sublette[96, 97], both dealing with bench scale studies. However, in these two cases, sulfate is the main product, not the elemental sulfur.

3.5 HYDROGEN RECOVERY, ALTERNATIVE LRSR PROCESSES

Another attractive idea is the recovery of both sulfur and hydrogen in the same process. Given the low standard enthalpy of formation as compared to water and methane, H_2S seems a good potential source for hydrogen[98]. The recovery of H_2 from H_2S according to reaction **(34)** has received attention since the 1930's[1, 99, 100]. However, this reaction is not practical under purely thermal conditions because it is thermodynamically unfavourable (e.g. at 298 K, $\Delta H^o = 20\ kJmol^{-1}$, $\Delta S = -43\ JK^{-1}mol^{-1}$)[108], though the reaction has been accomplished thermally at high temperatures (1000°C) and by various photo-, plasma- and electrochemical decomposition methods[101]-[107].

$$H_2S \longrightarrow H_2 + S \qquad (34)$$

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



t-butylanthraquinone (^tBAQ) **t-butylanthrone** **quinone**

2,7-sodium anthraquinonedisulfonate **t-butylanthrahydroquinone ($H_2{}^tBAQ$)**

SCHEME 13 Catalysts used in the HySulf process

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[108].

$$2Fe^{2+} + 2\,H^{+} \xrightarrow{\text{anode/cathode}} 2Fe^{3+} + H_2 \qquad (35)$$

Because of the undesired by product of sulfuric 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 steam reforming. Therefore, the IKC Hybrid process should be considered as a sulfur recovery process, rather than an alternative method for H_2 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_2 can be used for chemical purposes[98]. The Hysulf process uses an organic redox couple. The original process consisted of absorption of H_2S into a polar organic solvent, for instance NMP, then complexation to the solvent and subsequent reaction with t-butylanthraquinone (tBAQ, see **Scheme 13**) to give sulfur, NMP and H_2BAQ. In a second reactor, H_2BAQ is dehydrogenated over a catalyst to yield H_2 and t-BAQ[110, 111, 112].

$$H_2S + NMP \overset{T=330\ K}{\rightleftharpoons} H_2S\text{-}NMP \qquad (36)$$

$$H_2S\text{-}NMP + t\text{-}BAQ \xrightarrow{T=330\ K} S + NMP_{+}H_2BAQ \qquad (37)$$

$$H_2BAQ \xrightarrow{cat.480 \leq T \leq 590\ K} H_2 + t\text{-}BAQ \qquad (38)$$

In practice, reaction **(38)** produced undesired side product of t-butyl anthrone. Another drawback of the original process appeared to be the use of hazardous amide solvents[113].

As an alternative, aqueous solutions of quinone/ 2,7-sodium anthraquinone disulfonate together with a hydrogen sulfide complexing agent such as t-butylamine, a mixture of solvents, for instance, NMP with water as an additive (1–1.5 mole H_2O per anthraquinone) is employed. This modification is claimed to yield better sulfur recovery as well as complete selectivity to anthraquinone[114].

Other involving sulfur abstraction and generation of H_2, catalytic conversions of H_2S to H_2, using some reaction of H_2S with solutions of transition metal complexes such as Pd-, Ru- and Pt-phosphine complexes[115]-[122], carbonyl complexes of metallocenes of Ti and Zr{123}, W-phosphine complexes[124], and homo- and heterobimetallic complexes of Ir, Rh, and Re containing μ-dpm($dpm=Ph_2PCH_2PPh_2$) ligands[125]-[127] are well studied. However, these researches have been limited to the bench only.

4 CONCLUSIONS

During the last century, there have been large numbers of publications and patents involving processes for sulfur recovery from H_2S. 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, are 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 sulfur crystallization which lead to foaming and plugging as well as relatively poor sulfur 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 and the combined sulfur/hydrogen recovery, are now being studied.

Acknowledgements

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References

[1] Kohl, A. L.; Riesenfeld, F. C. *Gas Purification*, Gulf Publishing Company, Houston, TX, 4 edition **1985**.

[2] Lagas, J. A.; Borboom, J.; Berben, P. H.; Geus, J. W. *Europen Patent Application* **1985**, 02 42006.

[3] Berben, P. H. *Thesis*, Utrecht, the NetheLands **1992**.

[4] Lapersrix, E.; Costentin, G.; Guyen, N. N.; Saur, O.; Lavalley, J. C. *J. Catalysis* **1999**, 187, 385.

[5] Kensell, W.; Leppin, D. *Review of the H_2S Direct Oxidation Process*. In GRI Sulfur Recovery Conference, Austin, Texas **1995**.

[6] Gowdy, H. W.; Bertram, R. V.; Sahlin, R. K. *Review of the H_2S Direct Oxidation Process*. In GRI Sulfur Recovery Conference, Austin, Texas **1995**.

[7] Adachi et al, *US Patent* **1976**, 3957691. Thompson, *US Patent* **1984**, 4440874. Kim et al, *US Patent* **1986**, 4591580. Wan et al, *US Patent* **1988**, 4738947. Joy et al, *US Patent* **1988**, 4760044. Kim et al, *US Patent*, **1988**, 4780447. Rieek et al, *US Patent* **1990**, 4916105.

[8] Heisel, M.; Marold, J.F.; Gwinner, M. *CLINSULF- Do for Sulfur Recovery from* H_2S *Containing Gas*, Linde Reports on Science and Technology **1994**, 53, 15.

[9] Heisel, M. P.; Schwarz, C.; Schreiner, B. *CLINSULF-Do for Sulfur Recovery from Gasification Gas.* In GRI Sulfur Recovery Conference, Austin, Texas **1995**.

[10] Quinlan, M. P. *Technical and Economic Analysis of the Iron-Based Redox Process, In Proc.* Annual G. P. A. Convention **1992**, 215.

[11] Leppin, D.; Wessels, J. *Overview Liquid Redox Sulfur Recovery and* H_2S *Scavenging Processes*, In GRI Sulfur Recovery Conference **1995**.

[12] Kohl, A. L.; Riesenfeld, F. C. *Gas Purification*, Mcgraw-Hill, New York **1960**.

[13] Feld, W. *Uber die Bildung von Eidenbisufid in Losugen und die Entstehung der Naturlichen Pyritlager, Zeitschrift fur Angewanste Chemie* **1911**, 24, 97.

[14] Overdieck, F. *Eine neue Technische Ausfuhrungstorm des Walter Feldschen* Polythionateverfahrens, Zeitschrift fur Angewandte Chemie **1930**, 43, 1048.

[15] McManus, D., Martell, A. E. *J. Molecular Catalysis, A: Chemical* **1997**, **117**, 289.

[16] Pieters, H. A. J.; Krevelen, D. W. *The Wet Purification of Coal Gas and Similar Gases by the Staatsmijnen-Otto-Process*, Elsevier **1946**.

[17] Hartley, W.; Craig, R. S.; Sapiro, R. H. *British Patent* **1960**, BP 855421.

[18] Gollmar, H.A. *Ind. Eng. Chem.* **1934**, 26, 130.

[19] Jenett, E. *Oil & Gas Journal* **1962**, 60, 72.

[20] Dalrymple, D. A.; Trofe, T. W. *Chem. Eng. Prog.* **1989**, 85, 43.

[21] Dalrymple, D. A.; Trofe, T. W.; Leppin, D. *Oil & Gas Journal* **1994**, 92, 54.

[22] Gollmar, *US Patent* **1939**, 2163169. Matheson, *US Patent* **1941**, 2259901. Fetterly, *US Patent* **1949**, 2472473. Patton, *US Patent* **1958**, 2819950. Szombathy, *US Patent* **1959**, 2911438. Hag, *US Patent* **1963**, 3087793. Lida et al, *US Patent* **1969**, 3459495. Redmer, *US Patent* **1973**, 3764548. Nicklin, *US Patent* **1974**, 3810833. Landrun et al, *US Patent* **1974**, 3812243. Schulz, *US Patent* **1975**, 3928535. Hasebe, *US Patent* **1976**, 3937795. Espenscheid et al, *US Patent* **1976**, 3959452. Fenton et al, *US Patent* 1976, 3972989. Frame, *US Patent* **1976**, 3978137. Toyama et al, *US Paten* **1976**, 3989810. Sonda et al, *US Patent* **1977**, 4009251. Fenton et al, *US Patent* **1977**, 4017594. Nicklin et al, *US Patent* **1977**, 4049776. Fenton et al, *US Patent* **1977**, 4060594. Fenton et al, *US Patent* **1978**, 4083945. Sano et al, *US Patent* **1978**, 4118467. Kawoda et al, *US Patent* **1980**, 4199553. Fenton et al, *US Patent* **1980**, 4206194. Marshall, *US Patent* **1981**, 4251492. Gowdy et al, *US Patent* **1984**, 4432962.

[23] Wilson, B. M.; Newell, R. D. *Chem. Eng. Prog.* **1984**, 313.

[24] Hartley, W.; Craig, R. S.; Sapiro, R. H. *US Patent 1962*, 3068065.

[25] McManus, D.; Martell, A. E. *The Evolution, Chemistry an Application of Chelated Iron Hydrogen Sulfide Removal and Oxidation Processes*, In 6th International Symposium on the Activation of Dioxygen and Homogeneous Oxidation, Noordwijkerhout, the Netherlands **1996**.

[26] Cabodi, A. et al, *Oil & Gas Joural* **1982**, 5.

[27] Thompson, *US Patent* **1980**, 4189462. Hardison, *US Patent* **1992**, 5139753. Hardison, *US Patent* **1992**, 5160714. Naraghi, *US Patent* **1989**, 4880609. Honna et al, *US Patent* **1995**, 5391278. McManus, D.; Kin, F. R. *US Patent* **1986**, 4622212. Klecka, M. E. *US Patent* **1985**, 4518577.

[28] Martell, A. E.; Motekaitis, R. J.; Chen, D.; Hancock, R. D.; McManus, D. *Can. J. Chem.* **1996**, 74, 1872.

[29] Nagl, G. J. *Gas Research Institutes (Chicago), In 7th Sulfur Recovery Conferenc-e*September **1995**, Austin, TX, USA.

[30] Diaz, Z. *US Patent* **1983**, 4400368.

[31] Bedell, S. *International Patent* **1990**, 90/01984.

[32] Thompon, R.B. *US Patent* **1980**, 4218342.

[33] McManus, D.; Reicher, M. *AIChE Spring National Meeting*, Houston, TX, USA **1995**, 54a.

[34] McManus, D.; Niemiec, W. J. *AIChE Spring National Meeting*, New Orleans, LA, USA **1996**, 46b.

[35] McManus, D. *AIChE Spring National Meeting*, Atlanta, GA, USA **1994**, 276.

[36] McManus, D. Gas Research Institutes (Chicago), *In 7th Sulfur Recovery Conference*September **1995**, Austin, TX, USA.

[37] Wubs, H. J.; Beenackers, A. A. C. M. *AIChE J.* **1994**, 40, 433.

[38] Hardison, L.C. *LO-CA T-II: A Big Step forward in Iron Redox Chemistry, In GRI Liquid Redox Sulfur Recovery Conference*, GRI **1991**.

[39] Hardison, L. C.; McManus, D. *Chelon Degradation Mechanisms in Chelated Iron Redox Processes for H_2S Removal*, Annual Meeting AIChE, Miami Beach, Florida, AIChE **1992**.

[40] Hardison, L. C. *US Patent* **1992**, 5139753.

[41] Cantrall, R. *LO-CAT and LO-CAT II Application of Technology Update, In Sulfur Recovery Conference*, GRI **1997**.

[42] Oostwouder, S. P.; Hodge, V. B. *Sulferox Process Technology and Application Update, In Sulfur Recovery Conference*, GRI **1995**.

[43] Nagl, G. J. *Chem. Eng.* **1997**, 125.

[44] Nagl, G. J. *Gas Reseach Institutes (Chicago), In 7th Sulfur Recovery Conference*, Austin, TX, USA September, **1995**.

[45] McManus, D.; Niemiec, W. J. *Application of Homogeneous, Catalytic, Chelated Iron Hydrogen Sulfide Advanced Oxidation Processes to Titanium Dioxide Manufacture, 1998 Pan-American Workshop on Commericallization of Advanced Oxidation Technologies* June 28, **1998**.

[46] Quinlan, M. P. *Technical and Economic Analysis of the Iron-Based Redox* Proc*esss, In Proc.* Annual GPA, Covention **1992**, 215.

[47] Quinlan, M. P.; Echterhoff, L. W. *Technical and Economic Comparison of LO-CAT II with Other Iron-Based Liquid Redox Processes, In Sulfur Recovery Conference*, GRI **1992**.

[48] Liu, X.; Sawyer, D. T.; Bedell, S. A. Worley, C. M. *Gas Research Institutes (Chicago), In 7th Sulfur Recovery Conference* September **1995**, Austin, TX, USA.

[49] DeBerry, D. W.; McManus, D. *Private Communication.*

[50] Klein, G. W.; Bhatia, K.; Madhawan, V.; Schuler, R. H. *J. Phys. Chem.* **1975**, 79, 1767.

[51] Chen. D.; Motekaitis, R. J.; Martell, A. E.; McManus, D. *Can. J. Chem.* **1993**, 71, 1524.

[52] Chen, D.; Martell, A. E.; McManus, D. *Can. J. Chem.* **1995**, 73, 264.

[53] McManus, D.; Martell, A. E. *unpublished work.*

[54] Diaz, Z. *US Patent* **1983**, 4388293.

[55] Diaz, Z. *US Patent* **1983**, 4382918.

[56] DeBerry, D. W. *AIChE Spring National Meeting*, New Orleans, LA, USA **1996**, 46b.

[57] Mehnert, R.; Brede, O.; Janovsky, I. *Radiat. Phys. Chem.* **1984**, 23, 463.

[58] Sawyer et al, *US Patent* **1993**, 5273734.

[59] Hancock, R. D.; Martell, A. E.; Chen, D. *Can. J. Chem.* **1997**, 75, 591.

[60] Martell, A. E.; Motekaitis, R. J.; Chen, D.; Hancock, R. D.; McManus, D. *New Fe(III)/Fe(II) Chelating Agents as Catalysts for the Oxidation of Hydrogen Sulfide to Sulfur by Air*, AIChE Spring National Meeting **1996**.

[61] Hancock, R. D.; Martell, A. E.; Chen, D.; McManus, D. *Design of Ligands For Complexation of Fe(III)/Fe(II) in the Catalytic Oxidation of Hydrogen Sulfide to*

Sulfur, In AIChE Spring National Meeting, Sulfur Recovery from Gas Streams, New Orleans, LA **1996**.

[62] McManus, D. et al, *US Patent* **1997**, 5686613.

[63] McManus, D. et al. *US Patent* **1997**, 5591419.

[64] Chen, D.; Martell, A. E.; Motekaitis, R. J.; McManus, D. *Can. J. Chem.* **1998**, 76, 445–451.

[65] Peter, S. *US Patent* **1990**, 4892718.

[66] Ferm, B.; Freivald, W. A.; McManus, D,; Reicher, M. *Sulfur Recovery Using Non-Aqueous, Chelated Iron, Redox Catalyst Solution, In Sulfur Recovery Conference*, Volume 8, GRI **1997**.

[67] Eng, S. J.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem. Acta* **1998**, 278, 170.

[68] Eng, R. J.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem. Acta* **2000**, 299, 9.

[69] Rehmat, A.; Yoshizawa, J. *Bio-SR Technology Update*, In GRI Sulfur Recovery Conference, Austin, Texas, GRI **1995**.

[70] Wubs, H. J.; Beenackers, A. A. C. M. *AIChE. J.* **1994**, 40, 433.

[71] DeBerry, D. W. *Environ. Prog.* **1997**, 16, 193.

[72] Tsonopoulos, C.; Coulson, D. M.; Inman, J. B. *J. Chem. Eng Data* **1976**, 21, 190.

[73] Sonta, H.; Shiratori, T. *US Patent* **1990**, 4931262.

[74] Pagella, C.; Perego, P.; Zilli, M. *Chem. Eng. Tech.* **1996**, 19, 79.

[75] Pagella, C.; Zambelli, L.; Spilvestri, P.; Faveri, D. M. *Chem. Eng. Tech.* **1996**, 19, 378.

[76] Rai, C.; Taylor, M. *Improving Liquid Redox Processes by Microbial Redox Solution Reoxidation Rate Enhancement, In sulfur Recovery Conference*, Volume 8, GRI **1997**.

[77] Rai, C. *US Patent* **1996**, 5508014.

[78] McManus, D. *Biologically Enhanced Redox Solution Oxidation: Evaluation in a LO-CAT Process Simulation Reactor, Gas Research Institutes Project Advisors Group Meeting*, Chicago, IL September 10, **1998**.

[79] Rai, C.; McManus, D. *Biologically Enhanced Liquid Redox Process: Evaluation in Process Simulation Reactors, Gas Research Institutes, In Sulfur ecovery Conference*, San Antonio, TX October **1999**.

[80] Buisman, C. J. N. *Europen Patent* **1991**, EP 451922B1.

[81] Tanji, Y.; Kanagawa, T.; Mikami, E. *J. Ferment. Bioeng.* **1989**, 67, 280.

[82] Cho, K.S.; Hirai, M.; Shoda, M. *J. Ferment. Bioeng.* **1991**, 71, 384.

[83] Moriarty, D. J. W.; Nicholas, D. J. D. *Biochem. Biophs. Acta* **1969**, 184, 114.

[84] Moriarty, D. J. W.; Nicholas, D. J. D. *Biochem. Biophs. Acta* **1970**, 197, 143.

[85] Moriarty, D. J. W.; Nicholas, D. J. D. *Biochem. Biophs. Acta* **1970**, 216, 130.

[86] Sugio, T.; Mizunashi, W.; Inagaki, K.; Tano, T. *J. Nacteriol.* **1987**, 169, 4916.

[87] Sugio, T.; Suzuki, H.; Oto, A.; Inagaki, K.; Tano, T. *Agric. Biol. Chem.* **1991**, 55, 2091.

[88] Kusai, K.; Yamanaka, T. *Biochem. Biophys. Acta* **1973**, 325, 304.

[89] Fukumori, Y.; Yamanaka, T. *J. Biochem.* **1979**, 85, 1405.

[90] Zhang, L.; Hirai, M.; Shoda, M. *J. Ferment. Bioeng.* **1991**, 72, 392.

[91] Cho, K. S.; Hirai, M.; Shoda, M. *Appl. Environ. Microbiol.* **1992**, 58, 1183.

[92] Nakada, Y.; Ohta, Y. *J. Biosci. Bioeng.* **1999**, 87, 452.

[93] Buisman, C. J. N.; Geraats, B. G.; Ijspeert, P.; Lettinga, G. *Biotech. Bioeng.* **1990**, 35, 50.

[94] Buisman, C. J. N.; Vegt, A. L. *Thiopaq Bioscrubber: An Innovative Technology to Remove Hydrogen Sulfide from Air and Gaseous Streams*, In Liguid Sulfur Recovery Conference, Austin, Texas, GRI **1995**.

[95] Quinlan, M. P.; Echterhoff, L. W. *Onshore/Offshore Sulfur Recovery Process Evaluation, In Sulfur Recovery Conference*, Volume 8 GRI **1997**.

[96] Gadre, R. V. *Biotech. Bioeng.* **1989**, 34, 410.

[97] Cadenherd, P.; Sublette, K. L. *Biotech. Bioeng.* **1990**, 35, 1150.

[98] Luinstra, E. *Sulfur* **1996**, 37.

[99] Mizuta, S.; Kondo, W.; Fuji, K. *Ind. Eng. Chem. Res.* **1991**, 30, 1601.

[100] Luinstra, E. *Hydrogen from H_2S: A Review of the Leading Processes, In GRI Sulfur Recovery Conference*, Austin,Texas **1995**.

[101] Mark, H. F.; McKetta Jr, J. J.; Othmer, D. F. *In Kirk-Othmer Encyclopedia of Chemical Technology* **1983**, 3rd edn. Vol. 22, P267.

[102] Kaloidas, V. E.; Papayannakos, N. G. *Chem. Eng. Sci.* **1989**, 44, 2493.

[103] Kaloidas, V.E.; Papayannakos, N.G. *Int. J. Hydrogen Energy* **1987, 12**, 403.

[104] Linkous, C. A.; Mingo, T. E.; Muradov, N. Z. *Int. J. Hydrogen Energy* **1994**, 19, 203.

[105] Traus, I.; Suhr, H. *Plasma Chem. Plasma Process* **1992**, 12, 275.

[106] Alexander, S.R.; Winnick, J. *AIChE. J.* **1994**, 40, 613.

[107] Mao, Z.; Anani, A. A.; White, R. E.; Srinivasan, S.; Appleby, A. J. *J. Electrochem. Soc.* **1991**, 137, 1299.

[108] Honna, K.; Noguehi, H.; Goto, M. *Europen Patent* **1994**, EP 612556.

[109] Sonta, H.; Shiratori, T. *US Patent* **1990**, 4931262.

[110] Plummer, M. A.; Beazly, P. M. *US Patent* **1986**, 4592905.

[111] Plummer, M. A. *Hydrocarbon Processing* **1987**, 38.

[112] Plummer, M. A.; Cowley, S. W. *Hydrogen Sulfide Decomposition into Hydrogen and Sulfur by Quinone Cycles, Gas Reseach Institute Final Report, Technical Report*P2/0400, GRI **1993**.

[113] Plummer, M.A. *US Patent* **1993**, 5180572.

[114] Plummer, M. A. *Int. Patent* **1994**, Wo. 94/12431.

[115] James, B. R. *Pure & Appl. Chem.* **1997**, 69, 2213.

[116] Lee, C. L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175.

[117] Shaver, A.; El-khateeb, M.; Lebuis, A. M. *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 2362.

[118] Wong, T. Y. H.; Barnabas, A. F.; Sallin, D.; James, B. R. *Inorg. Chem.* **1995**, 34, 2278.

[119] Osakada, K.; Yamamoto, T.; Yamamoto, Y. *Inorg. Chim. Acta* **1984**, 90, L5.

[120] Kuehn, G. C.; Taube, H. *J. Am. Chem. Soc.* **1976**, 98, 689.

[121] Morelli, D.; Segre, A.; Ugo, R.; Cenini, S.; Conti, F.; Bonti, F. *J. Chem. Soc., Chem. Commun.* **1967**, 524.

[122] Ugo, R.; Monica. G. L.; Cenini, S.; Segre, A.; Conti, F. *J. Chem. Soc. A.* **1971**, 522.

[123] Howard, W.A.; Parkin, G. *Organometallics* **1993**, 12, 2363.

[124] Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, 113, 5904.

[125] McDonald, R.; Cowie, M. *Inorg. Chem.* **1993**, 32, 1671.

[126] Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, 29, 3339.

[127] Mueting, A. M.; Boyle, P. D.; Pignolet, L. H. *Inorg. Chem.* **1981**, 23, 44.