# Novel non-aqueous Fe(III)/Fe(II) redox couple for the catalytic oxidation of hydrogen sulfide to sulfur by air

Guoxiong Hua,<sup>a</sup> Qingzhi Zhang,<sup>a</sup> Derek McManus,<sup>b</sup> Alexandra M. Z. Slawin<sup>a</sup> and J. Derek Woollins<sup>\*a</sup>

Received 21st September 2005, Accepted 7th December 2005 First published as an Advance Article on the web 19th December 2005 DOI: 10.1039/b513384j

A series of Fe(III) salts and organic solvents have been screened to develop novel non-aqueous catalysts for the conversion of  $H_2S$  to sulfur. FeCl<sub>3</sub>/95% *N*-methylpyrrolidinone/5%  $H_2O$  was found to be a most efficient non-aqueous system. The process chemistry, the proposed mechanism of catalytic oxidation of  $H_2S$ , and the CV are discussed.

# Introduction

Iron complex catalytic solutions for removing hydrogen sulfide contained in a wide range of industrial gas streams have been used for over a century and a half as redox catalysts. Current systems to use aqueous aminopolycarboxylate chelate iron redox catalyst solutions were introduced around 1962.1Since then, numerous improvements in process equipment, plant configuration and process chemistry have been made.<sup>2</sup> Actually, the treated gas streams containing hydrogen sulfide are usually contaminated with carbon dioxide (CO<sub>2</sub>) or other contaminating gases which still need to be cleaned out from gas streams. The currently applied Fe-NTA (nitrilotriacetic acid) system consists of two separate processes, which use an aqueous catalyst system to convert H<sub>2</sub>S to S and a non-aqueous phase to absorb CO<sub>2</sub>, H<sub>2</sub>O and other organic contaminants. That is, CO2, H2O and other organic contaminants are absorbed using an organic solvent such as *N*-methylpyrrolidinone (NMP),  $H_2S$  is catalytically converted to sulfur by using an aqueous catalyst solution of Fe(III) complex.

Considering the economical and practicable reasons, it is necessary to develop a more efficient process that can remove not only sulfur contaminants, but also carbon dioxide and water in a single process while producing or recovering a high quality of solid elemental sulfur. A non-aqueous catalyst system could be a unique possibility to solve the above problems in a single process because a specific organic solvent employed, for example NMP, could also absorb all the contaminant gas including water.

However, most of the conventional aqueous catalysts such as the Fe(II) and Fe(III) complexes of NTA, EDTA (ethylenedinitrilote-tracetic acid) and HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid) are not adequately soluble in organic solvents, nor are that of the phosphorus-containing analogues of NTA or EDTA. Up to now, only the  $\beta$ -diketone (R<sub>1</sub>–CO–CH<sub>2</sub>–CO–R<sub>2</sub>) chelate complexes are feasible as catalysts in non-aqueous processes for the removal of hydrogen sulfide from natural gas. The metals patented as  $\beta$ -diketone chelates for this purpose include polyvalent iron, copper, cobalt, vanadium, nickel and manganese,<sup>3</sup> as well as scandium, yttrium or the elements in the lanthanide and actinide groups. Among them the Fe(III)

<sup>a</sup>School of Chemistry, University St Andrews, St Andrews, Fife, UK KY16 9ST. E-mail: jdw3@st-and.ac.uk <sup>b</sup>US Filter Corporation. Inc. Plainfield, II, 60544, US 4

<sup>b</sup>US Filter Corporation, Inc., Plainfield, IL, 60544, USA

chelate of acetylacetone (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 desulfurise, 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>4</sup>

Accordingly, attempts to further improve current non-aqueous catalyst systems by selecting more robust ligands in place of easily degraded  $\beta$ -diketones and to seek suitable organic solvents were our initial objective. However, it is rather difficult to find a suitable iron complex which is both soluble in organic solvents and comparable to the iron complex of  $\beta$ -diketone in price and practicality under the required conditions (pH = 8.5). We decided to test if it is possible to oxidize H<sub>2</sub>S to S directly with simple iron(III) salts in an organic solvent. The simplest idea provided us with surprising and excellent results. The preliminary experiment with the FeCl<sub>3</sub>–NMP catalyst system without any ligand did work unexpectedly well for the conversion of hydrogen sulfide to sulfur. This triggered further investigation of different iron salts in various organic solvents.

## **Results and discussion**

## Selection of organic solvents

About twenty common organic solvents were screened based upon the solubility and stability of FeCl<sub>3</sub> in the solvent (either water-free or with 5 w/v% of water) without pH control. If FeCl<sub>3</sub> dissolves well in a solvent to give a stable homogeneous solution (waterfree or with 5 w/v.% of water), the solution was then loaded on the 1-litre reactor for preliminarily tests on catalytic activity for the oxidation of H<sub>2</sub>S to sulfur by air. The catalytic experiments were performed under conditions of H<sub>2</sub>S = 2.0 cm<sup>3</sup> min<sup>-1</sup>, air = 700 cm<sup>3</sup> min<sup>-1</sup>, circulation rate of absorption solution = 100 cm<sup>3</sup> min<sup>-1</sup>, initial pH value and room temperature. Table 1 lists the qualitatively tested results of different FeCl<sub>3</sub>/organic solvent systems based on visual observations.

Furan, sulfolane, trichloroethylene, morpholine and *N*-formylmorpholine (water-free or with 5 w/v% of water) do not dissolve FeCl<sub>3</sub> properly. Therefore these solvents were not tested further.

:17:58.	
2014 15	
n 27/10/	
kingston o	
University - I	
Queens 1	
Downloaded by (	
cember 2005. J	
19 Dec	
ned on	
Publis	

 Table 1
 Screening of organic solvents for FeCl, catalytic conversion of H<sub>2</sub>S to S by air

and comments
tail gas and poor catalytic activity eelt, severe tail gas and poor catalytic activity of the reaction solution deepened, severe tail gas and poor catalytic activity f tail gas, very poor catalytic activity olid precipitated, severe tail gas and very poor catalytic activity f tail gas and very poor catalytic activity
and comments tail gas and poor catalytic activity well, severe tail gas and poor catalytic of the reaction solution deepened, fail gas, very poor catalytic activit fail gas and very poor catalytic activit fail gas and very poor catalytic activity fail gas activity fail gas activity

View	Article	Online
view	Alucie	Onnie

 Table 2
 Properties of N-pyrrolidinone (NMP)<sup>7</sup>

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

FeCl<sub>3</sub> is soluble in a variety of other organic solvents, either water-free or with 5 w/v% of water, to give stable homogeneous solutions. The solvents include formamide (FA), *N*-methylpyrrolidinone (NMP), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), propylene carbonate (PC), 1,4-dioxane (DO), diethylglycolmonomethyl ether (DEGE), di-(ethylglyco)-diethyl ether (DEGDE), triethylphosphate (TEPP), methyl-acetoacetate (MAA), triethanolamine (TEA), 2-butoxyethanol (BE), acetamide and ethanol. However, as displayed in Table 1, only the FeCl<sub>3</sub>/NMP system, our initial discovery, was found to have catalytic activity for the oxidation of hydrogen sulfide to sulfur by air. FeCl<sub>3</sub> in other organic solvents showed little catalytic activity. Therefore, NMP became our solvent of choice for further studies.

Actually, *N*-methylpyrrolidinone (NMP) has been widely applied in industrial scale gas purification,<sup>5</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. 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 plastic, especially poly(lauryl methacrylate)<sup>6</sup> and to dehydrate.<sup>7</sup> As can be seen from Table 2, the inexpensive and environmentally acceptable NMP can be a perfect organic media for the conversion of hydrogen sulfide to sulfur with its ideal high boiling point, low freezing point, low toxicity, high H<sub>2</sub>S and CO<sub>2</sub> solubility and complete miscibility with water.

#### Selection of ferric salts

Since FeCl<sub>3</sub> in NMP exhibits efficient catalytic activity toward the oxidation of H<sub>2</sub>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% NMP/5% water in the same procedure. The ferric salts used in this study include ferric citrate, ferric oxalate (Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>), ferric carbonate (Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>), ferric acetylacetonate( [CH<sub>3</sub>C(O)CH=C(O<sup>-</sup>)CH<sub>3</sub>]<sub>3</sub>Fe), ferric hydroxyl acetate (Fe(OH)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>), ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O), ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and Fe(H<sub>2</sub>PO<sub>2</sub>)<sub>3</sub>. The results are listed in Table 3 and compared with that of FeCl<sub>3</sub>.

Table 3	Screening of ferric salts in 95% NMP/5	% water for the catalytic oxidation of hydrogen sulfide by air
	Concentration of	Test

Ferric salt	Fe(III)/mmol L <sup>-1</sup>	time/h	Results and comments
Iron(III) acetylacetonate,	90	5	Iron salt partly dissolved to give a suspension, dark solid formed, trace of tail gas observed and poor catalytic activity
Fe(OH)(OAc) <sub>2</sub>	36	78.5	Iron salt partly dissolved to give a suspension, no tail gas observed, grey $S_8$ (3.727 g mixed with unknown dark solid) and residue of $S_8$ 4.70 g in the filtration (analysis by HPLC), severe loss of iron ion: Fe ion concentration changed from 2084 to 944 mg L <sup>-1</sup> and not ideal catalytic system
$Fe(H_2PO_2)_3$	90	3	Iron salt partly dissolved to give a suspension, dark solid formed, severe tail gas and poor catalytic activity
Ferric nitrate (Fe(NO <sub>3</sub> ) <sub>3</sub> )	90 <sup><i>a</i></sup>	24	Low yield of $S_8$ : 63.03%, high conversion to $SO_3^{2-}$ (28.56%) and to $SO_4^{2-}$ (1.05%), severe tail gas in the process and poor catalytic activity
Ferric nitrate (Fe(NO <sub>3</sub> ) <sub>3</sub> )	90 <sup>b</sup>	10.5	Severe tail gas found in 9.5 hours, high ratio of Fe <sup>2+</sup> /Fe <sup>3+</sup> : 94.42% and poor catalytic activity
Ferric sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	90 <sup>c</sup>	80.5	Moderate yield of $S_8$ : 88.50%, severe tail gas: CuS 10.77%, low conversion to $SO_3^{2-}$ : 1.92%, low conversion to $SO_4^{2-}$ , high loss of iron: 34.21 mg L <sup>-1</sup> h <sup>-1</sup> and poor catalytic activity
Ferric sulfate $(Fe_2(SO_4)_3)$	90 <sup>d</sup>	14	Severe tail gas in 10 hours, low yield of $S_8$ : 48.49%, unknown water-soluble precipitate, severe loss of iron: 288 mg L <sup>-1</sup> h <sup>-1</sup> and poor catalytic activity
Ferric sulfate $(Fe_2(SO_4)_3)$	90 <sup>e</sup>	9.5	Severe tail gas in 9 hours, high ratio of $Fe^{2+}/Fe^{3+}$ (92.33%) and poor catalytic activity
Ferric chloride (FeCl <sub>3</sub> )	90 <sup>c</sup>	300	High quality of $S_8$ : yellow crystalline, high yield of $S_8$ : 98.72%, low yield of $SO_3^{2-}$ : 0.02%, low yield of $SO_4^{2-}$ : 0.09%, no iron loss, no tail gas and perfect catalytic system

<sup>*a*</sup> Initial pH value without any pH control during the process. <sup>*b*</sup> pH controlled to 1.00 during the process. <sup>*c*</sup> Initial pH value and does not control pH during the process. <sup>*d*</sup> The pH of the starting solution was adjusted to the same as that of 90 mmol FeCl<sub>3</sub>/95% NMP/5% water. No further control of pH during the process. <sup>*e*</sup> pH controlled to 1.00 by addition of 2 N of NaOH during the process.

Ferric acetylacetonate, Fe(H<sub>2</sub>PO<sub>2</sub>)<sub>3</sub> and ferric hydroxyl acetate (Fe(OH)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>) are partly soluble in 95% NMP/5% water to give a slight suspension. The suspensions showed low catalytic activities when employed as catalysts for the oxidation of hydrogen sulfide to sulfur. The same unsatisfactory results are obtained when other organic solvents were used to substitute for pure NMP or 95% NMP/5% H<sub>2</sub>O.

Both ferric sulfate and ferric nitrate dissolve in pure NMP very slowly. In 95% NMP/5% water, however, the two salts dissolved readily to give a stable solution with concentrations up to 360 mmol L<sup>-1</sup>. The pH value of the resulting solution, lower than 1, was slightly different between the two salts and the various concentrations. Catalytic experiments were performed with samples of 90 mmol of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O in 95% NMP/5% water and 90 mmol of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 95% NMP/5% water with both uncontrolled pH or controlled pH (to 1 by addition of 2 N NaOH). Both salts displayed catalytic activities for the catalytic oxidation of hydrogen sulfide to sulfur to some extent. However, their catalytic activities were found to decrease gradually with an increase in the running time. The catalysts were completely deactivated eventually. A high proportion of Fe<sup>2+</sup>/Fe<sup>3+</sup> (more than 90%) was found in the resultant solution for both catalyst systems. Obviously, the Fe<sup>2+</sup> formed during the process is hard to re-oxidize to Fe<sup>3+</sup>. In both instances, the tail gas became gradually more severe with running of the experiment. In one case of 90 mmol of Fe2(SO4)3.5H2O in 95% NMP/5% water whose pH value has been previously adjusted to the same as that of the corresponding FeCl<sub>3</sub> solution with 2 N H<sub>2</sub>SO<sub>4</sub>, an unknown water-soluble solid was found to precipitate out. The concentration of iron ion was reduced dramatically during the process.

In clear contrast, 90 mmol of ferric chloride in 95% NMP/5% water showed excellent efficiency for the catalytic oxidation of  $H_2S$  to sulfur by air. The system works perfectly with high selectivity

for sulfur (98.7%), low conversion to  $S_2O_3^{2-}$  (0.02%) and  $SO_4^{2-}$  (0.09%). No tail gas was observed after 300 hours of running.

## Influence of concentration of FeCl<sub>3</sub> on catalytic activity

While other organic solvents and iron salts show negative or poor results for the catalytic oxidation of  $H_2S$  to S by air, the combination of FeCl<sub>3</sub> with NMP provides a perfect catalyst for this conversion. Table 4 shows the influence of FeCl<sub>3</sub> concentration on the catalytic activity in pure NMP and 95% NMP/5% water.

The maximum solubility of FeCl<sub>3</sub> in pure NMP or 95% NMP/5% H<sub>2</sub>O was determined. Also tested was FeCl<sub>3</sub>·6H<sub>2</sub>O. Both anhydrous FeCl<sub>3</sub> and FeCl<sub>3</sub>·6H<sub>2</sub>O mixed with pure NMP or 95% NMP/5% water to give a stable solution, although the latter dissolved in pure NMP rather slowly. The maximum concentration of FeCl<sub>3</sub> anhydrous is 270 mmol L<sup>-1</sup> in pure NMP and 180 mmol L<sup>-1</sup> in 95% NMP/5% water. While that of FeCl<sub>3</sub>·6H<sub>2</sub>O in 95% NMP/5% water is 180 mmol L<sup>-1</sup>. Experiments were carried out with concentrations of FeCl<sub>3</sub> varying in the range of 18 to 90 mmol.

When 18 mmol of FeCl<sub>3</sub> in pure NMP was tested for the conversion of H<sub>2</sub>S to sulfur 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 by the shortage of the Fe<sup>3+</sup> ion in the process. In the initial stages of the experiment, there was enough Fe<sup>3+</sup> in the system to oxidize hydrogen sulfide. As the redox process continued, the Fe<sup>3+</sup> and Fe<sup>2+</sup> ions reached equilibrium, at which point the content of Fe<sup>3+</sup> was insufficient to convert hydrogen sulfide completely to sulfur, as a consequence, the excess of hydrogen sulfide was released in the tail gas. Even so, the absorption of hydrogen sulfide was still very impressive. The formation of relatively high concentrations of by-products SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> might result from the direct oxidation of H<sub>2</sub>S by the oxygen (air) in the oxidizer zone.

stem

Solvent system	100% NMP	100% NMP	100% NMP	$95\%NMP/5\%H_2O$	95% NMP/5% H <sub>2</sub> O
Ferric salt	FeCl <sub>3</sub> .6H <sub>2</sub> O				
Iron salt/mmol L <sup>-1</sup>	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 $S_8$ in filtrate/g	0.226	1.077	0.819	7.167	3.491
Tail gas (CuS)/g	0.184	0.135	0	0	0
$C_{SO3}^{2-}$ in the resulting solution/mM	4.91	4.12	4.56	0.20	3.00
$C_{SO4}^{2-}$ in the resulting solution/mM	3.66	4.34	11.03	1.50	2.89
Residual $H_2S$ in the resulting solution/M	13.33	18.50	16.06	4.13	1.00
Conversion of $H_2S$ to $S_8^{a}$ (%)	90.32	95.15	95.84	98.72	98.49
Conversion of $H_2S$ to $CuS^a$ (%)	0.46	0.12	0	0	0
Conversion of $H_2^{TS}$ to $SO_3^{2-a}$ (%)	2.36	0.72	0.73	0.02	0.83
Conversion of $H_2S$ to $SO4^{2-a}$ (%)	0.46	0.12	0.88	0.09	0.40
Residual $H_2S(\%)$	6.40	3.26	2.56	1.17	0.28
Iron content of the starting solution/mg $L^{-1}$	1002.21	1999.55	5033.55	5042.57	5152.75
Iron content of the resulting solution/mg $L^{-1}$	1004.95	2006.10	5035.91	5104.17	5279.79
$H_2O$ content of the starting solution/g $L^{-1}$	0	0	0	50.06	49.65
$H_2O$ content of the resulting solution/g $L^{-1}$				42.37	43.13
$Fe^{2+}/Fe^{3+}$ in the process (%)	40.20	45.55	50.10	44.86	44.05

Doubling the concentration of FeCl<sub>3</sub> to 36 mmol in pure NMP led to the enhancement of selectivity to sulfur from 90.3% to 95.2%. The concentration of the over-oxidized components  $SO_3^{2-}$  and  $SO_4^{2-}$  decreased. The loss of H<sub>2</sub>S in the tail gas (0.12%), though lower than in the case of 18 mmol (0.46%), was still observed, suggesting that the Fe<sup>3+</sup> ion in the equilibrium was still not abundant. An increase in FeCl<sub>3</sub> concentration to 90 mmol in 100% of NMP stopped the loss of H<sub>2</sub>S in the tail gas completely in spite of the fact that the yield of sulfur was not further improved (95.84%). A slight increase in the side product  $SO_4^{2-}$  implied that the concentration of iron ion might be a little bit higher than required.

Further improvement for the selectivity to sulfur was achieved by a slight modification of the solvent with the addition of 5 w/v%of water. As shown in Table 4, 90 mmol L<sup>-1</sup> ferric chloride in 95% NMP/5% water afforded 98.7% yield of sulfur, while the concentration of side products SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> slightly decreased. Actually, the presence of 5 w/v% of H<sub>2</sub>O in NMP somewhat reduced the solubility or residential time of H<sub>2</sub>S in the absorption solution and might have increased the rate of the conversion of H<sub>2</sub>S to sulfur. There was less residual H<sub>2</sub>S in 95% of NMP than in water-free NMP.

90 mmol of FeCl<sub>3</sub>· $6H_2O$  in 95% NMP/5% water showed closely similar results to its anhydrous counterpart in spite of the slight increase of  $H_2O$  content in the reaction solution. However, if the content of water in the catalyst system reached 20%, the catalytic activity was found to reduce sharply—severe tail gas re-appeared in the process.

All the experiments listed in Table 4 gave high quality bright yellow crystalline sulfur, which is in clear contrast to the grey sulfur contaminated with FeS from the Fe–NTA system. In addition to the crystalline sulfur, there is still a considerable amount of sulfur dissolved in the solution. Work-up by addition of  $H_2O$  precipitated the sulfur out as a yellow solid, also in high quality. The solvent can be recycled by evaporation of the excess water.

No iron loss was observed in the process. For the catalyst system with 90 mmol FeCl<sub>3</sub>. $6H_2O$  or FeCl<sub>3</sub> in 95% of NMP, the total iron concentration in the resulting solution was a little bit higher than

that in the starting solution. This may arise from the evaporation of  $H_2O$  in the process, leading to the slightly condensed reactant solution. The degradation of NMP, which will be discussed below in detail, may also be responsible for the condensation of solvent during the process.

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

Due to the drastic different effects 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 5). Actually, this 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> are dissolved in water, a series of hydroxylated ferric ions, which form by hydrolysis of the Fe(III) ion, have been found to dominate in solution.<sup>8-16</sup> When a stirred cell reactor for absorption of hydrogen sulfide into aqueous solutions of ferric sulfate and ferric chloride respectively in the absence of any organic ligands, the hydroxylated ferric ion [Fe(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup> was found to be the actual reactive species in the processes,<sup>17</sup> and the hydrated ferrous ion [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> was the major form of Fe<sup>2+</sup> in the solution which was found to be hard to oxidize to Fe<sup>3+</sup> in air. That is, in the aqueous solution, the hydrated Fe<sup>2+</sup> is very stable and difficult to oxidize to hydrated or hydroxylated Fe<sup>3+</sup> ion. As a consequence, the influence of the anion in the iron salt on the aqueous catalytic activity, which could be ignored in practice, is far lower than that of the solvent water molecule itself.

## The possible catalytic mechanism of iron salts in NMP

On changing the solvent from water to pure NMP or 95% NMP/5% H<sub>2</sub>O, the effect of the anion on the catalytic activity of the 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

Catalyst composition	Testing conditions	Testing time/min	Results and comments
$FeCl_3$ ([Fe] = 90 mM)/100% H <sub>2</sub> O	H <sub>2</sub> S: 2.00 cm <sup>3</sup> min <sup>-1</sup> ; air = 700 cm <sup>3</sup> min <sup>-1</sup> ; without any control of pH during the process	700	pH 0.44 changed to resulting pH 0.20, no tail gas found in the first 600 min, conversion of H <sub>2</sub> S to S <sub>8</sub> (58.03%), CuS: 0.29 g and no iron ion loss, high Fe <sup>2+</sup> /Fe <sup>3+</sup> in the resulting solution: 95.51%, and 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> during the process
$Fe_2(SO_4)_3 ([Fe] = 90 \text{ mM})/100\% \text{ H}_2\text{O}$	$H_2S: 2.00 \text{ cm}^3 \text{ min}^{-1}; \text{ air:}$ 700 cm <sup>3</sup> min <sup>-1</sup> ; control pH of solution to 1.00 by addition of 2 N NaOH during the process	555	Initial pH = 1.07, no tail gas found in the first 550 min, conversion of H <sub>2</sub> S to S <sub>8</sub> (1.18 g, 80%), CuS (0.07 g) and no iron ion loss, high Fe <sup>2+</sup> /Fe <sup>3+</sup> in the resulting solution: 92.33%, and positive activity was observed in the first 630 min, but it gradually dwindled away due to hard conversion of Fe <sup>2+</sup> to Fe <sup>3+</sup>
$Fe(NO_3)_3 ([Fe] = 90 \text{ mM})/100\% \text{ H}_2\text{O}$	$H_2S: 2.00 \text{ cm}^3 \text{ min}^{-1}$ ; air: 700 cm <sup>3</sup> min <sup>-1</sup> ; 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 found in the first 570 min, conversion of H <sub>2</sub> S to S <sub>8</sub> (1.36 g, 81%), CuS (0.07 g) and 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

salts thus have less possibility for ionization in NMP. Therefore the solution is not dominated by totally solvated iron as in the aqueous system. The complexes FeCl<sub>3</sub> or FeCl<sub>3</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O in NMP or 95% NMP/5% H<sub>2</sub>O can be represented as [Fe(NMP)<sub>6-x</sub>Cl<sub>x</sub>]<sup>(3-x)+</sup>, [Fe(NMP)<sub>6-x-y</sub>(H<sub>2</sub>O)<sub>y</sub>Z<sub>x</sub>]<sup>(3-x)+</sup>, respectively. The following are the mechanisms we have tentatively proposed for the iron catalytic conversion of H<sub>2</sub>S to sulfur by air in NMP.

As shown in Schemes 1–4, iron salts in NMP or in 95% NMP/5% H<sub>2</sub>O could initially form partly solvated Fe<sup>3+</sup> ions or complexes [step (1)]. Hydrogen sulfide then dissolves in a solution containing the iron salt and NMP to afford new complexes



 $\label{eq:Scheme1} \begin{array}{l} A \mbox{ suggested catalytic cycle in the non-aqueous catalyst system} \\ of \mbox{ FeCl}_3/NMP \mbox{ for the conversion of $H_2S$ to $S$.} \end{array}$ 



Scheme 2 A suggested catalytic cycle in the non-aqueous catalyst system of FeCl<sub>3</sub> or FeCl<sub>3</sub>. $6H_2O/NMP$  or 95% NMP/5% H<sub>2</sub>O for the conversion of H<sub>2</sub>S to S.

containing sulfur by ligand exchange or substitution reaction in steps (2)–(4) in which the anion ion such as  $Cl^-$  or  $NO_3^-$  or  $SO_4^{2^-}$  is substituted by HS<sup>-</sup>. One NMP molecule may be displaced during the process. Electron transfer between the sulfide and Fe<sup>3+</sup> within the sulfur-containing Fe complex takes place in step (5) and step (6). The free radical of sulfur-containing complex, which is formed



Scheme 3 A suggested catalytic cycle in the non-aqueous catalyst system of  $Fe(NO_3)_3$ ·9H<sub>2</sub>O/95% NMP/5% H<sub>2</sub>O for the conversion of H<sub>2</sub>S to S.



Scheme 4 A suggested catalytic cycle in the non-aqueous catalyst system of  $Fe_2(SO_4)_3$ - $5H_2O/95\%$  NMP/5%  $H_2O$  for the conversion of  $H_2S$  to S.

in step (5), readily decomposes to release the elemental sulfur, and to dissociate a  $Fe^{2+}$  solvated ion in step (6). A regeneration of the catalyst is carried out in step (6) and step (7).

In Scheme 1 or Scheme 2, step (2) can be rate determining, because the step that releases a free radical needs higher activation

energy. Addition of the appropriate amount of water (5%) to the FeCl<sub>3</sub>/NMP system reduces the residence time of H<sub>2</sub>S in solution to some extent and decreases the possibility for further oxidation, and therefore is beneficial to the selectivity to sulfur. A limited number of H<sub>2</sub>O molecules may also be coordinated to the iron in the reactive species as shown in Schemes 2, 3 and 4. The active energy in Scheme 1, so the formation of sulfur is quicker in the presence of water. However, if the water content reaches 20%, water molecules would compete with NMP or the anion ligands to co-ordinate with iron, especially with Fe<sup>2+</sup> to give totally hydrated iron, which as in the aqueous system, loses its catalytic activity sharply.

In Schemes 3 and 4 water is considered as part of the coordinated ligands, step (7) is vital for the whole cycle as suggested by the high proportion of  $Fe^{2+}/Fe^{3+}$  (up to 94.4%) in the resulting solution. Like the hydrated  $Fe^{2+}$  in the aqueous system, the nitrate or sulfate-containing Fe(II) species in Schemes 3 and 4 are quite stable and very difficult to oxidize into their corresponding Fe(III) counterparts with air. Therefore, the catalytic cycles were blocked in step (7) for the  $Fe_2(SO_4)_3/NMP$  and  $Fe(NO_3)_3/NMP$  systems, the diminishing  $Fe^{3+}$  in the system directly leading to the gradual loss of catalytic activity of  $Fe_2(SO_4)_3$  and  $Fe(NO_3)_3$  in NMP for the conversion of  $H_2S$  to S with air.

How can the stability of the Fe(II) species of chloride, nitrate and sulfate or hydrogen sulfate be so different? Firstly, according to the Lewis theory of acids and bases, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are the corresponding conjugate bases of HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HSO<sub>4</sub><sup>-</sup>, respectively.<sup>18</sup> The acidity of the above acids and basicity of the conjugate bases are found to follow the order shown below:

$$H_2SO_4 (pK_a = -9) > HCl (pK_a = -7) > HNO_3 (pK_a = -1.4) > HSO_4^-$$

Increasing acid strength  $\leftarrow$ 

 $SO_4^{2-} > Cl^- > NO_3^- > HSO_4^-$ 

#### Increasing base strength $\leftarrow$

Cl<sup>-</sup> is a typical weak monodentate ligand while SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> 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 sulfate species in NMP. Furthermore, Fe<sup>3+</sup> is generally believed to prefer to coordinate nitrogen-containing ligands rather than oxygen-containing ligands to form stable complexes. On the contrary, Fe<sup>2+</sup> tends to coordinate oxygen-containing rather than nitrogen-containing ligands. Therefore, the more N-donor ligand NMP molecules coordinated to the iron ion, the easier the Fe<sup>3+</sup> regeneration and the more active the iron species is for catalysis. A similar point of view has also been previously reported before.<sup>18</sup> We believed that the Fe<sup>2+</sup> species in the  $Fe(NO_3)_3/NMP$  or  $Fe_2(SO_4)_3/NMP$  systems must be stabilized by oxygen-donor sulfate or nitrate ligands and this has proved to be very difficult to oxidize to Fe<sup>3+</sup> with air.

Table 6	Half-wave potentials (V vs. saturated calomel electrode, SCE) ([Fe] = 0.02 M, initial pH value)					
	System         FeCl <sub>3</sub> /95% NMP/5% H <sub>2</sub> O         Fe(NO <sub>3</sub> ) <sub>3</sub> /95% NMP/5% H <sub>2</sub> O         Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> /95% NMP/5% H <sub>2</sub> O					
	$E_{1/2}$ /V vs. SCE	-0.393	-0.307	-0.066		

#### Cyclic voltrammogram study of non-aqueous catalyst systems

In order to further explore the difference in the catalytic activities between Fe(NO<sub>3</sub>)<sub>3</sub>/NMP, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/NMP and FeCl<sub>3</sub>/NMP for the catalytic oxidation of hydrogen sulfide to sulfur, their CVs were measured. The cathode wave in Fig. 1–3 can be assigned to the reduction process, and the anodic wave to a complementary oxidation reaction. The half wave potentials of FeCl<sub>3</sub>/95% NMP/5% H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>/95% NMP/5% H<sub>2</sub>O and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/95% NMP/5% H<sub>2</sub>O are listed in Table 6.



Fig. 1 Cyclic voltammogram of  $Fe(NO_3)_3/95\%$  NMP/5% H<sub>2</sub>O ([Fe(III)] = 0.02 M, initial pH value).



Fig. 2 Cyclic voltammogram of  $Fe_2(SO_4)_3/95\%$  NMP/5% H<sub>2</sub>O ([Fe(III)] = 0.02 M, initial pH value).



Fig. 3 Cyclic voltammogram of FeCl<sub>3</sub>/95% NMP/5%  $H_2O$  ([Fe(III)] = 0.02 M, initial pH value).

For the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple, the standard potential  $E_0$  for the reduction of the ferric ion to the ferrous ion is +0.770 V under standard conditions. As shown in Table 6, the half wave potentials  $E_{1/2}$  of Fe<sup>3+</sup>/Fe<sup>2+</sup> in a non-aqueous system, which depends on the nature of the anion ion, are all much more negative than the standard potential  $E_0$ . Though it is still difficult to correlate the wave potentials to the catalytic activity of the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple directly, there is indeed an obvious difference between the wave potential of Fe<sup>3+</sup>/Fe<sup>2+</sup> of the catalytically active FeCl<sub>3</sub>/95% NMP/5% H<sub>2</sub>O system and the poor catalytic system of Fe(NO<sub>3</sub>)<sub>3</sub>/95% NMP/5% H<sub>2</sub>O and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/95% NMP/5% H<sub>2</sub>O. Further studies are needed to establish the relationship between the half wave potential  $E_{1/2}$  of Fe<sup>3+</sup>/Fe<sup>2+</sup> and the actual catalytic activity.

### Process chemistry

The process chemistry for the air oxidation of  $H_2S$  to sulfur catalysed by the non-aqueous system is, actually, closely similar to that in the aqueous systems. The  $H_2S$  is induced into a circulating catalyst solution in the absorber zone where it is solvated and physically removed, simultaneously, the solvated  $H_2S$  reacts with the Fe(III) solvate forming elemental sulfur which does not precipitate but remains in the organic solvent—NMP or 95% NMP/5%  $H_2O$ —in the early stages. The Fe(III) solvate is concurrently reduced to the Fe(II) solvate state. Reactions occurring in the absorber are represented as follows.

The sulfur produced dissolved continuously in the organic solvent. Once the organic solvent is saturated with dissolved sulfur, the yellow crystalline sulfur precipitates gradually in both absorber zone and oxidizer zone. In industry, the whole process can be operated at higher temperatures (60–70 °C) to increase the solubility of sulfur. Crystalline sulfur product can be harvested by cooling the reaction mixture.

 $H_2S + Solvent \rightleftharpoons H_2S$  (dissolved)

 $H_2S$  (dissolved) + 2 Fe(III) Solvate  $\rightarrow$  S (dissolved) + 2 Fe(II)

The combined oxidizer–crystallizer provides sufficient residence time for the regeneration of the active Fe(III) solvate and crystallizaton of dissolved sulfur. The process can be represented by the following equations.

$$O_2(g) + Solvent \rightleftharpoons O_2 \text{ (dissolved)}$$

2 Fe(II) Solvate +  $1/2 O_2$  (dissolved)  $\rightarrow$  2 Fe(III) Solvate

 $S \text{ (dissolved)} \rightarrow S \text{ (s)}$ 

The overall process can be represented by the following equation.

$$H_2S(g) + 1/2 O_2(g) \rightarrow S(s) + H_2O_2(g)$$

Table 7	Advantages of non-aqueous	s FeCl <sub>3</sub> /NMP liquid redox	sulfur recovery process vers	sus the aqueous chelated ir	on redox sulfur recovery process7
---------	---------------------------	---------------------------------------	------------------------------	-----------------------------	-----------------------------------

Consideration	Aqueous system	Novel non-aqueous system
Components of catalyst Organic ligand Sulfur product	Fe(III) complex/stabilizer/H <sub>2</sub> O Required a robust ligand. A key deficiency was the rapid degradation of the ligand in the process Grey amorphous precipitate, fouls equipment especially gas/liquid contactor and gas spargers. Precludes use of efficient porous metal spargers. It is difficult to obtain the product sulfur by filtration	FeCl <sub>3</sub> /NMP/H <sub>2</sub> O Needs no special ligand. The NMP functions as both the organic solvent and organic ligand Bright yellow crystalline sulfur is obtained by cooling the circulating solution in certain zones. No solid sulfur is deposited elsewhere. Sulfur 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 sulfur 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
H <sub>2</sub> O removal	Produced sweet gas is saturated with water at about 44 °C. Dehydration requirements can be increased	Dehydration to pipe-line specification is achieved by the hygroscopic solvent
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 $CO_2$ is possible. As $H_2S$ is oxidized to sulfur, recovery of $CO_2$ as a resource is possible. Market size for the process is expanded considerably
Carbonyl sulfide removal	Inert, could not remove	Converts to crystalline sulfur
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. 48 L of H <sub>2</sub> S dissolve in 1 L NMP
Corrosion	Stainless steel equipment required	Special materials equipment required because of the acidity of the absorbed solution and the likely corrosion of equipment by Cl <sup>-</sup>
Surfactant application	Needed to wet and sink sulfur	No need
Antifoam addition	Occasionally required	Probably no need
Biocide addition	Normally used	Probably unnecessary
Chelate stabilizer addition	Required in initial catalyst fill, subsequent additions are sometimes required	May not be needed

The processes of formation of the side products can be represented by the following equations.

 $2 \text{ H}_2\text{S} + 3 \text{ O}_2 \rightarrow 2 \text{ SO}_3{}^{2-} + 4 \text{ H}^+$ 

$$H_2S + 2 O_2 \rightarrow SO_4^{2-} + 2 H^4$$

#### Comparison with aqueous processes

As mentioned above, the absorbed solution also serves to remove  $CO_2$  and water, if they are present in a real industrial process, by absorption into the solvent. Hence the process can simultaneously desulfurize, decarbonate and dehydrate sub-quality natural gas in a single operation while giving high quality sulfur. This is in marked contrast to the traditional combination of amine plant, glycol dehydrator and sulfur recovery unit. The advantages of this novel non-aqueous process, as indicated by Ferm,<sup>4</sup> over aqueous redox processes have been listed in Table 7.

#### **Degradation of NMP**

NMP used in non-aqueous Fe(III)/Fe(II) redox processes for the conversion of  $H_2S$  to S acts as both ligand and solvent, that is, NMP involves both physical and chemical processes during the absorption and conversion of  $H_2S$  to sulfur. Although under acidic conditions (in contrast to the basic conditions used in the Fe chelate aqueous process), there is less opportunity for the free hydroxyl radicals to survive, it can still be expected that NMP may experience degradation to some extent. HPLC analysis did confirm this slight decomposition of NMP.

Table 8 shows the change in the organic components of the FeCl<sub>3</sub>/NMP and FeCl<sub>3</sub>/95% NMP/5% H<sub>2</sub>O systems after running for *ca*. 300 hours as determined by HPLC. As mentioned in Table 4, an appropriate amount (*ca*. 5%) of water is beneficial to the selectivity to sulfur. However, water also accelerates the oxidative degradation of NMP due to the increased opportunity of H<sub>2</sub>O<sub>2</sub> formation.

Table 8	Results of HPLC analyses	of the non-aqueous cat	alyst systems:
---------	--------------------------	------------------------	----------------

Туре с	of sample Componen	$FeCl_3 ([Fe] = 90 \text{ mmol})/10$ t NMP (test time: 313 hours	$\begin{array}{l} 00\% & \text{FeCl}_3 \ ([\text{Fe}] = 90 \ \text{mmol}) / 95\% \ \text{NMP} / \\ \text{s}) & 5\% \ \text{H}_2 \text{O} \ (\text{test time: 300 hours}) \end{array}$	
Startin	ng solution NMS NMP	0 100%	0 100%	
Result	ing solution NMS NMP	2.78% 96.99%	10.78% 88.77%	

## Conclusions

A series of Fe(III) salts and organic solvents have been screened to develop novel non-aqueous catalyst for the conversion of  $H_2S$  to sulfur. FeCl<sub>3</sub>/95% NMP/5%  $H_2O$  proved to be the most efficient non-aqueous system.

The influence of concentration of iron ions 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 functions 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 the Cl<sup>-</sup> ion to the Fe ion, it is believed that the Fe ion is highly solvated; Fe(II) ions can be easily oxidized to Fe(III) ions with 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 sulfate and nitrate and their stabilizing effect on Fe(II), the catalytic cycle is blocked at the regeneration step of Fe(III) with air. Therefore, only FeCl<sub>3</sub>/NMP or FeCl<sub>3</sub>/95% NMP/5% H<sub>2</sub>O are catalytically active systems for the conversion of H<sub>2</sub>S to sulfur.

The influence of the anion of the Fe(III) salt is also reflected in cyclic voltrammograms of the FeCl<sub>3</sub>/95% NMP/5% H<sub>2</sub>O, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/95% NMP/5% H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>/95% NMP/5% H<sub>2</sub>O systems which were measured at initial pH value and [Fe] = 20 mM. FeCl<sub>3</sub>/95% NMP/5% H<sub>2</sub>O showed the most negative half wave potential and was the most useful system as catalyst for the removal of H<sub>2</sub>S.

Briefly, 90 mM of FeCl<sub>3</sub> or FeCl<sub>3</sub>· $6H_2O$  in 95% NMP/5%  $H_2O$  proved to be a highly efficient catalyst for air oxidation of hydrogen sulfide to sulfur to give high quality sulfur. However, in spite of the fact that there are a lot of advantages to the FeCl<sub>3</sub>/NMP catalyst system over the aqueous iron complexes catalyst system, the concern over the corrosive nature of Cl<sup>-</sup> might limit its commercial applications.

#### Experimental

#### Materials and agents

Unless otherwise stated, all chemicals were obtained from Aldrich or Lancaster and were used directly without further purification: formamide (FA), *N*-methylpyrrolidinone (NMP), *N*formylmorpholine (NFMP), morpholine (MP), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), propylene carbonate (PC), 1,4-dioxane (DO), diethylglycolmonomethyl ether (DEGE), di(ethylglyco)diethyl ether (DEGDE), triethylphosphate (TEPP), 2,4-pentanedione (ACAC), triethanolamine (TEA), trichloroethylene (TCE), 2-butoxyethanol (BE), sulfolane, acetamide, furan, ethanol, ferric citrate, ferric oxalate, ferric carbonate, ferric acetylacetonate, ferric acetate, ferric sulfate, ferric nitrate, iron(III) chloride, iron(III) chloride hexahydrate, copper sulfate pentahydrate, barium chloride, acetonitrile (HPLC grade), *N*-methylsuccinimide (NMS), succinimde, 2-pyrrolidinone.

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

All redox reactions were carried out in a two-chambered glass apparatus, 1-liter reactor provided by US Filter. The pH and redox

potential in the absorber and oxidizer were not monitored. The  $H_2S$  inlet was controlled by a mass flow rate controller (MFC) and air was gauged by a rotometer. The tail gas was passed through to a CuSO<sub>4</sub> (1.0 M) absorber. All experiments were accomplished at room temperature.

1000 cm<sup>3</sup> of iron(III) salt in organic solvent or 95% organic solvent/5% H<sub>2</sub>O solution was placed 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 cm<sup>3</sup> min<sup>-1</sup>. At this stage air was bubbled into the oxidizer and the flow rate of the air was adjusted to the required value. The valve of the H<sub>2</sub>S cylinder was turned on and the H<sub>2</sub>S flow rate was adjusted to 2.00 cm<sup>3</sup> min<sup>-1</sup>. The time of the start of the reaction was recorded. The produced sulfur was filtered off at 50 hour intervals and 5 cm<sup>3</sup> of sample was taken from the running system at set time intervals in order to monitor the changes in the process, *i.e.* the change of iron ion concentration and the oxidative degradation of organic solvent *etc*.

#### HPLC 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 (Water 746 Dato Module) were used.

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

0.04 g of the reaction mixture was taken from the oxidizer compartment of the 1-liter continuous reactor and placed in a 100-mL volumetric flask. This sample was diluted to 100 cm<sup>3</sup> with water and then filtered through a 0.45  $\mu$ m micron filter before 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 concentration range.

#### Determination of water by Karl Fisher reagent

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 dry N<sub>2</sub>. The solution was then added dropwise to the sample while stirring until the colour of the solution changed from deep brown to bright yellow.

Determinations of  $SO_3^{2-}$ , iron ion,  $SO_4^{2-}$  ion, and the cyclic voltammograms are carried out according to literature methods.<sup>8</sup>

#### Acknowledgements

We are grateful to US Filter for financial support and Dr J. A. Crayston (University of St Andrews) for assistance with the cyclic voltammetric analysis.

#### References

- 1 G. X. Hua, D. McManus and J. D. Woollins, *Comments Inorg. Chem.*, 2001, 22, 327.
- 2 J. Wieckowska, Catal. Today, 1995, 24, 405.
- 3 F. C. Boston and M. L. Schneider, *Proceedings, Gas Conditioning Conference*, University of Oklahoma, Norman, OK, April 1971.
- 4 B. Ferm, W. A. Freivald, D. McManus and M. Reicher, Sulfur Recovery Using Non-Aqueous, Chelated Iron, Redox Catalyst Solution, in *Sulfur Recovery Conference*, GRI, London, UK, 1997, vol. 8.
- 5 Q. Feng and H. Qaki, Polyhedron, 1988, 7, 291.
- 6 W. C. Bray and A. V. Hershey, J. Am. Chem. Soc., 1934, 56, 1889.
- 7 R. S. Sapieszko, R. C. Patel and E. Matilevic, J. Phys. Chem., 1977, 81, 1061.

- 8 P. Hemmes, L. D. Rich, D. V. Cole and E. M. Eyring, J. Phys. Chem., 1971, 75, 929.
- 9 G. H. Khoe and R. G. Robins, J. Chem. Soc., Dalton Trans., 1988, 2015.
- 10 B. B. Hasinoff, Can. J. Chem., 1976, 54, 1820.
- 11 T. Sekine and T. Tetsuka, Bull. Chem. Soc. Jpn., 1972, 45, 1620.
- 12 R. D. Hancock and F. Marsicano, Inorg. Chem., 1980, 19, 2709.
- 13 C. Brandt and R. van Eldik, Chem. Rev., 1995, 95, 119.
- 14 M. Taqui Khan and G. Ramachandraiah, Inorg. Chem., 1982, 21, 2109.
- 15 M. M. Taqui Khan, Pure Appl. Chem., 1983, 55, 159.
- 16 M. M. Taqui Khan, A. Hussain, K. V. Subramanian and G. Ramachandraiah, J. Mol. Catal., 1988, 44, 117.
- 17 M. M. Taqui Khan and R. S. Shukla, J. Mol. Catal., 1986, 37, 269.
- 18 M. M. Taqui Khan, R. S. Shukla and A. P. Rao, J. Mol. Catal., 1986, 39, 237.