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Citation for published version:

Wylde, JJ, Taylor, GN, Sorbie, KS & Samaniego, WN 2020, 'Formation, Chemical Characterization, and Oxidative Dissolution of Amorphous Polymeric Dithiazine (apDTZ) during the Use of the H₂S Scavenger Monoethanolamine-Triazine', *Energy and Fuels*, vol. 34, no. 8, pp. 9923–9931. ²
<https://doi.org/10.1021/acs.energyfuels.0c01402>

Digital Object Identifier (DOI):

[10.1021/acs.energyfuels.0c01402](https://doi.org/10.1021/acs.energyfuels.0c01402)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

Energy and Fuels

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The Formation, Chemical Characterization and Oxidative Dissolution of Amorphous Polymeric Dithiazine (apDTZ) During the Use of the H₂S Scavenger MEA-Triazine

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ABSTRACT

Hexa-1,3,5-hydrotriazines form the main product class used for chemical hydrogen sulphide (H₂S) scavenging. The reaction mechanism between these triazine species and H₂S is discussed in detail with emphasis laid upon the reaction products and their fate. The paper goes on to then describe a novel method of oxidative dissolution of these reaction products including a full analysis of the resultant species and a mechanistic postulation. The single reaction product of MEA-triazine (1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine) has been repeatedly found by the authors to be initially monomeric 5-(2-hydroxyethyl)-hexahydro-1,3,5-dithiazine which, when separated out of aqueous solution, invariably polymerizes an insoluble, solid polymeric species. This solid product is referred to as amorphous polymeric 5-(2-hydroxyethyl)-hexahydro-1,3,5-dithiazine, abbreviated as apDTZ. The occurrence of this material in oil production systems causes heavy deposits or fouling in pipelines, valves, chokes and turbine blades. Its removal by any means other than physical intervention is extremely challenging. The current work shows how the presence of a terminal hydroxyl functionality is critical in enabling the dithiazine to polymerize to form the apDTZ.

This work goes onto dispel previous misconceptions in the industry and the literature regarding this process which is finally systematically addressed. Specifically, two very important issues are dealt with in this work which were previously unresolved in the literature. An explanation why the thiadiazine reaction product (1st sulphur molecule substitution) from tris(2-hydroxyethyl) triazine (MEA-triazine) is never observed. Following upon the above an explanation why the dithiazine (2nd sulphur molecule substitution) in all cases never progress to the trithiane (3rd sulphur molecule substitution). This is probably the greater misconception in the industry and literature regarding triazine and H₂S reactions. Despite the widespread occurrence of apDTZ in the oil and gas industry, there are very few studies of effective methods for its removal. This study presents such a process.

1. INTRODUCTION TO H₂S IN THE OIL AND GAS INDUSTRY

Hydrogen sulphide is a prevalent and undesirable chemical species that occurs during oil and gas production. It can be present not only in produced gas but also in the produced hydrocarbon liquid and water phases. H₂S is highly toxic and often accumulates in lethal concentrations. In addition, it is highly corrosive to many common materials of construction used by the industry, e.g. carbon and stainless steels. Furthermore, H₂S produces highly corrosive and damaging combustion products (SO_x) if not reduced to an acceptable level. Therefore, there are often strict fiscal and technical limits placed on upstream oil and gas producers by the midstream (pipeline) and downstream (refinery) sectors of the industry. H₂S occurs in oil and gas production operations from just a few ppmv to 20 up to approx. 30% vol. However, the range of concentrations that may be treated by chemical H₂S scavengers, the subject of the current review, are typically up to approx. 5,000 ppmv.^{1,2} Concentrations higher than this require different technologies to be economically feasible.³ These include sequestering systems such as recycling amine units, which temporarily lock up the H₂S along with other acid gases such as CO₂ in the form of a relatively labile ammonium salts (hydrosulphide or bicarbonate). The spent amine is then regenerated, and the gases released in a separate part of the process. Typically, monoethanolamine (MEA) and other small

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3 molecular weight amines are used for this purpose.⁴ H₂S levels can, in some regions, reach extremely high
4 levels to the point where there is in fact more H₂S in the produced gas than methane. In these cases, the
5 H₂S can be the more valuable component and is typically converted into elemental sulphur by the Claus
6 process and then to sulphuric acid and ammonium sulphate for agrochemical purposes.⁵
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9 In this paper, we focus on several crucial aspects regarding the use of organic H₂S scavengers. It
10 is well known that chemical scavengers react with H₂S in an irreversible process to form an organic
11 sulphide, in which a new carbon sulphur bond is formed.^{6,7,8} The byproducts of the scavenging process are
12 of vital importance and their nature and properties can have an important bearing on the selection of the
13 correct molecular species for H₂S scavenging. It is the fate and further reaction of these species that is the
14 subject matter and focus of this paper. This work aims to dispel the ambiguity that exists in the industry
15 and literature regarding the formation of the byproducts and will provide a systematically and definitive
16 benchmark in the literature for this process. Specifically, two issues are addressed as they currently
17 remain unresolved in the literature: (i) why the thiadiazine reaction product from tris(2-hydroxyethyl)
18 triazine is never observed; and (ii) why dithiazine never progress to trithiane.
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21 In addition, this study makes several detailed observations and proposes some novel reactive
22 processes which can dissolve or more correctly chemically remove this apDTZ material once formed. This
23 provides the basis of an alternative chemical means of removal of the apDTZ rather than the physical
24 removal performed today, which is costly, time consuming and potentially hazardous. The use of the
25 strongly oxidizing per(oxy)acetic acid is proposed and the reaction is studied in detail and characterized
26 using a range of analytical methods.
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30 **2. REACTION OF TRIAZINES AND H₂S: CRITICAL REVIEW**

31 **2.1 Triazine Chemistry Introduction and Common Myths**

32 The majority of H₂S scavengers used today in the oil and gas industry are organic molecular
33 species. Within this broad category, 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine is by far the most
34 widely used chemical; the structure of this species (I) is shown in Figure 1 and it is commonly known as
35 MEA-triazine, or sometimes even just *triazine*, such is its prevalence.^{1,9,10} MEA-triazine is relatively
36 inexpensive, kinetically superior to many other chemistries and has a high capacity for H₂S removal. The
37 stoichiometry of reaction is between 2:1 to 4:1 moles H₂S to chemical depending upon the presence or
38 absence of other acid gases. The produced amine will react with any acidic gas present and be salted out.
39 If CO₂ is very minimal that acid gas will be H₂S thus forming the bisulphide salt (4:1 stoichiometry) if CO₂
40 is in high concentration it will CO₂ thus forming the bicarbonate (2:1 stoichiometry). The next most
41 prominent H₂S scavenger is another hexahydrotriazine, 1,3,5-trimethylhexahydro-s-triazine, shown as
42 structure V in Figure 1. This is commonly known as MMA-triazine and has certain advantages (but also
43 shortcomings) in comparison with MEA-triazine.^{11,12,13,14,15,16,17}
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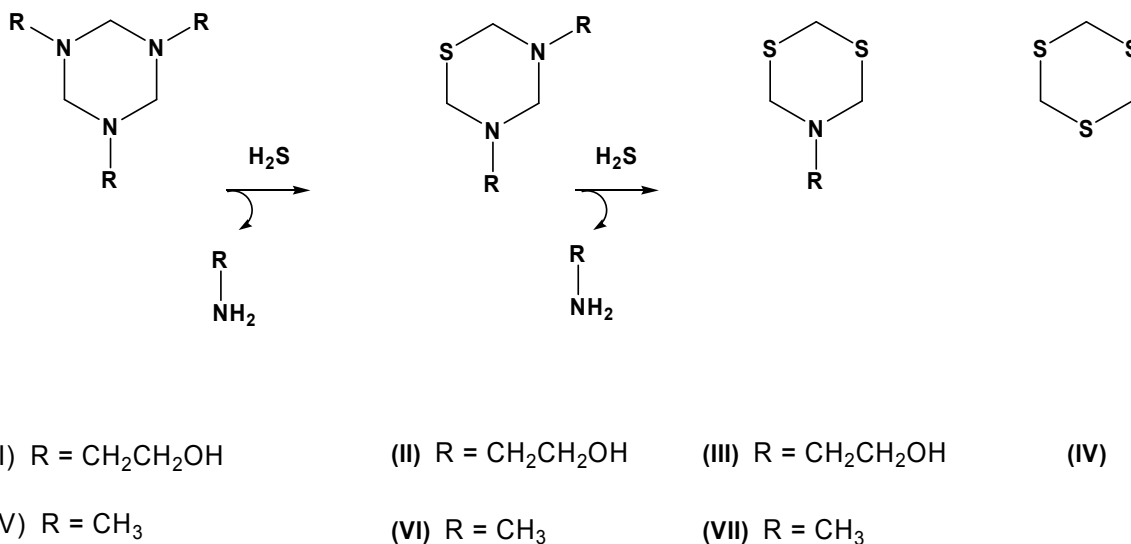


Figure 1 – Structure of (I) 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine (MEA-triazine); and (V) 1,3,5-trimethylhexahydro-s-triazine (MMA-triazine) and their subsequent reaction with H₂S¹⁸

MEA-triazine has been established as the primary H₂S scavenger in the oil and gas industry for decades in accordance with the patent literature. Historically, it was the subject and teaching of an early patent by Dillon¹⁹ but in fact, it is suspected that it was formed inadvertently in an earlier patent by Baize²⁰ when formalin and amine buffers were mixed. The Dillon patent teaches the use of various amines and aldehydes and their reaction products as mixtures of MEA-triazine and the corresponding bis-oxazolidine structure.¹⁹ Work by Gatlin²¹ also describes and covered the use of MEA-triazine and improved upon the methodology first proposed by Dillon.¹⁹ While the bis-oxazolidine structure can form, the procedure is normally carried out with a reaction stoichiometry of approximately 1:1. This favors the formation of the desired cyclic trimer structure or hexahydrotriazine. Bis-oxazolidines are favored by higher proportions of formaldehyde and dehydrating conditions, typically used to synthesize the 5,5'-bisoxazolidine.

While there is no such thing as the perfect H₂S scavenger, the chemical class of hexahydrotriazines comes closer than any other to fitting this ambitious description. However, there are several well established drawbacks with this chemical, with perhaps the most frequently encountered being the formation of heavy and insoluble deposits from the initial byproducts.^{22,23,24,25,26} It is critical to understand the chemistry of this process before any attempt to remediate the effect can be undertaken. The first goal of this work is to provide a critical summary and review of the exact chemical nature of these byproducts and their mechanism of formation. The second goal of this work is to then understand their remediation using a novel chemical method.

It is also very important to dispel some of the inaccurate information which has appeared in the literature over the years about this process. One prominent misconception is that this solid fouling deposit is the so-called “over-spent” condition of triazines which results in the formation of 1,3,5-trithiane (Structure IV in Figure 1). There are many earlier studies that incorrectly assign this species as a reaction product.^{13,16,17,27,28} In fact, as this review will show, the reaction of all triazines terminate at dithiazine (the 2nd sulphur molecule substitution) and 1,3,5-trithiane (IV) is *not* formed in any significant quantity. It is therefore the dithiazine which causes the observed deposits/fouling. Based on the analysis of this paper, we propose a practical chemical solution to deal with this fouling challenge as an alternative to using time consuming and costly physical interventions.

2.2 State of the Art Triazine Reaction Mechanism Understanding

The reaction mechanism of MEA-triazine with H_2S has been known in outline since its origin, but only recently have the details been fully clarified.^{23,24,25} Initially, it was thought that MEA-triazine could react with up to 6 moles of H_2S and ultimately form the three-sulphur molecule 1,3,5-s-trithiane.²⁹ This was believed to occur in what was rather misleadingly called an “over-spent” condition. Trithiane can be synthesized by an elegant process described in the organic synthesis literature where formalin is dissolved in concentrated sulphuric acid and H_2S passed through the solution causing trithiane to precipitate.³⁰ Trithiane can also be synthesized by the vacuum sublimation of polymethylene sulphide presumably by a process of depolymerization to the highly transient species thioformaldehyde followed by immediate trimerization.³¹ This process is analogous to the depolymerization, or thermal cracking process, of paraformaldehyde. As noted above, the reaction process of MEA-triazine with H_2S does *not* proceed to trithiane. Initially then, it involves two double $\text{S}_\text{N}2$ reactions to form the highly transient thiadiazine and then the ultimate reaction product dithiazine as shown in Figures 2 and 3 respectively.

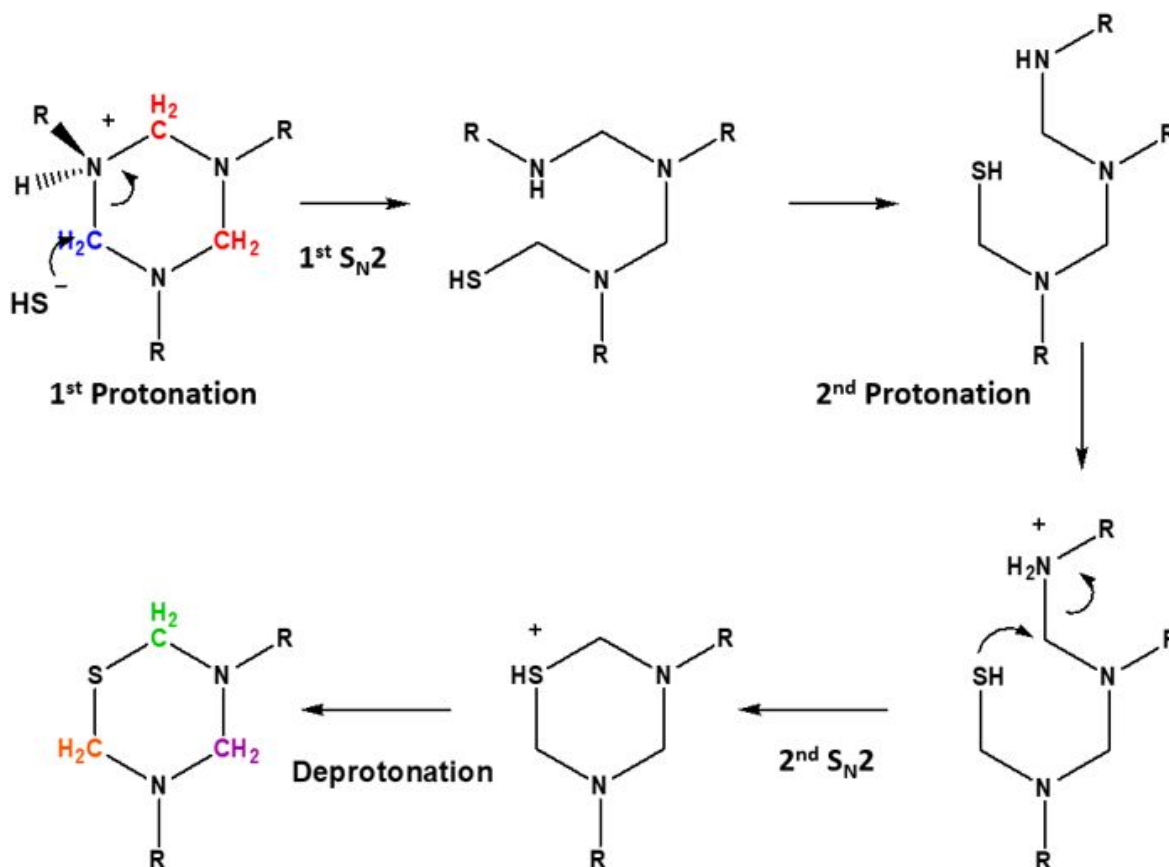


Figure 2 – 1st double $\text{S}_\text{N}2$ reaction and substitution of the first nitrogen atom with sulphur to yield the formation of thiadiazine³²

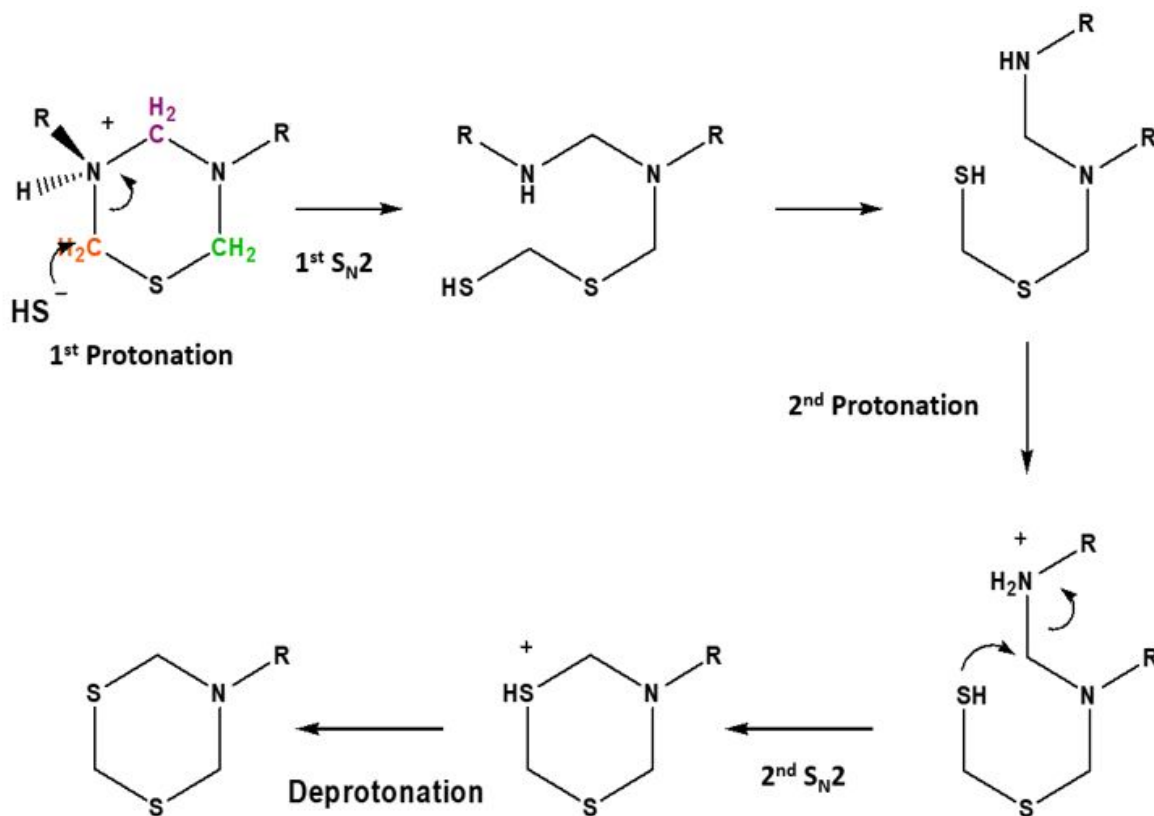


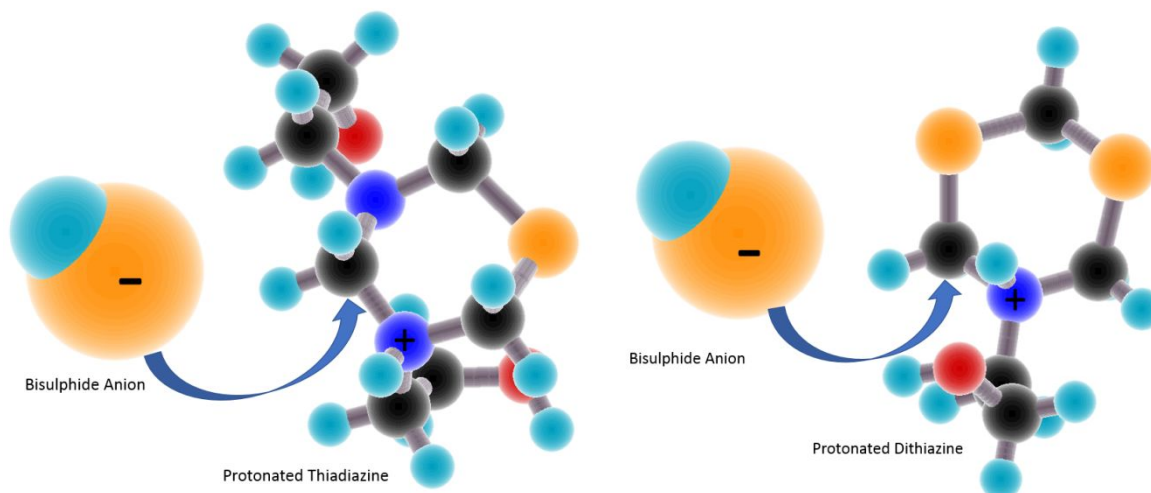
Figure 3 – 2nd double S_N2 reaction and substitution of the second nitrogen atom with sulphur to yield the formation of dithiazine³²

2.3 Triazine Reaction Mechanism – Myths Explained

Several aspects of this reaction are at present uncertain and are open to speculation. In all reactions carried out between MEA-triazine and H₂S, only two components are observed by conventional analytical methods such as GCMS; namely, unreacted MEA-triazine and dithiazine. The thiadiazine, while it must be formed, is clearly more reactive with H₂S than MEA-triazine and will immediately be converted into dithiazine. By way of contrast to the above, when one compares the reaction of MEA-triazine with H₂S to that of 1,3,5-trimethylhexahydrotriazine (MMA-triazine), the latter *does* form a more stable thiadiazine (Figure 1, structure VI) and this molecule is easily observed in the reaction sequence. In a typical partial reaction profile all three of the components, unreacted triazine, thiadiazine and dithiazine, are observable,¹¹ but again the trithiane species is not observed.

Further, the dithiazine must be resistant to further reaction with H₂S and does not form the trithiane as stated earlier. No satisfactory explanation as to why the dithiazine does *not* react further to form the trithiane has been proposed to date. One plausible proposal is that thiadiazine has a nucleophilic carbon center flanked by two nitrogen atoms and the *p*K_a of those nitrogen atoms allows sufficient protonation at the normal pH of these H₂S reactions such that a facile leaving group can exist, and thus the carbon-nitrogen bond breaks when the nucleophilic carbon is attacked by the bisulphide nucleophile; see Figure 4. It is suggested that the *p*K_a for the two thiadiazine nitrogen atoms would be in the range

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3 ideal for this type of S_N2 reaction, even more so than the parent hexahydrotriazine. This would explain
4 why the thiadiazine is even more reactive to H_2S than the hexahydrotriazine and that it is not isolated in
5 partially reacted mixtures.
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25 **Figure 4 – (left) bisulphide anion nucleophilic attack on thiadiazine resulting in the C-N bond breaking;**
26 **and, (right) bisulphide anion nucleophilic attack on dithiazine which is ineffective and, in this instance,**
27 **cannot break the C-N bond**
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30 The dithiazine does not possess a nucleophilic carbon atom flanked by two nitrogen atoms and the pK_a of the remaining nitrogen atom, probably also influenced by the presence of two sulphur atoms instead of one, is insufficiently basic to render this nitrogen moiety a good leaving group. As a result, the bisulphide nucleophile cannot effectively attack the carbon atom and break the carbon nitrogen bond (shown on the right-hand side of Figure 4).
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37 When considered from a charge density perspective conformers of these molecules were minimized using the MMFF94 force field, and then a Molecular Electrostatic Potential (MEP) for each configuration was calculated.³³ The positive density is higher (0.54) when there is a nitrogen rather than a sulphur atom (0.50) on each alpha position of the reactive carbon. The observation is also consistent with the fact that nitrogen has a higher electronegativity (3.04) than sulphur (2.58). The high negative charge of the sulphur atom is reflected on the MEP surface, probably rejecting the approach of bisulphide nucleophile due to repulsion forces as well as steric hindrance (Figure 5). This would explain the lack of reactivity for a third bisulphide moiety and hence the absence of (IV) trithiane.
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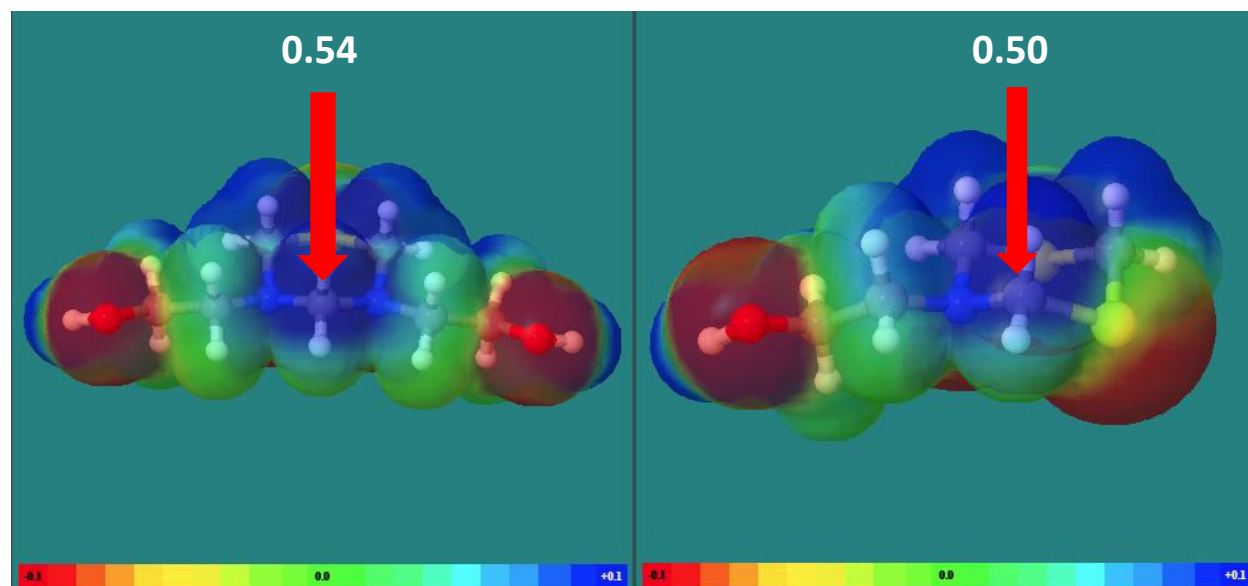


Figure 5 – MEP surfaces for (left) thiadiazine and (right) dithiazine with nucleophilic center and carbon positive density indicated

To further investigate the difference between the S_N2 reactions and determine why one is very favourable (to the point of not observing the thiadiazine while the other is essentially blocked) was out of scope of this study as it required advanced computational studies. However, we postulate that it involves the energy barrier presented by the transition states of these two processes, represented in Figure 6. Here we illustrate the ring fracture for the first of the S_N2 reactions in each case which progresses through the pentavalent carbon configuration. There is some discussion as to whether this reaction goes through a true pentavalent state in which case there could be a slight dip and energy minimum on top of the activation profile. Either way it is likely though currently only conjecture, that the difference in these two transitional processes account for the large difference in facility of these two sulphur inclusion reactions for a) either electron density reasons and the basicity of the nitrogen leaving group or b) a steric ring conformation effect dictated by the two ring sulphur atoms as opposed to a nitrogen and sulphur situation.

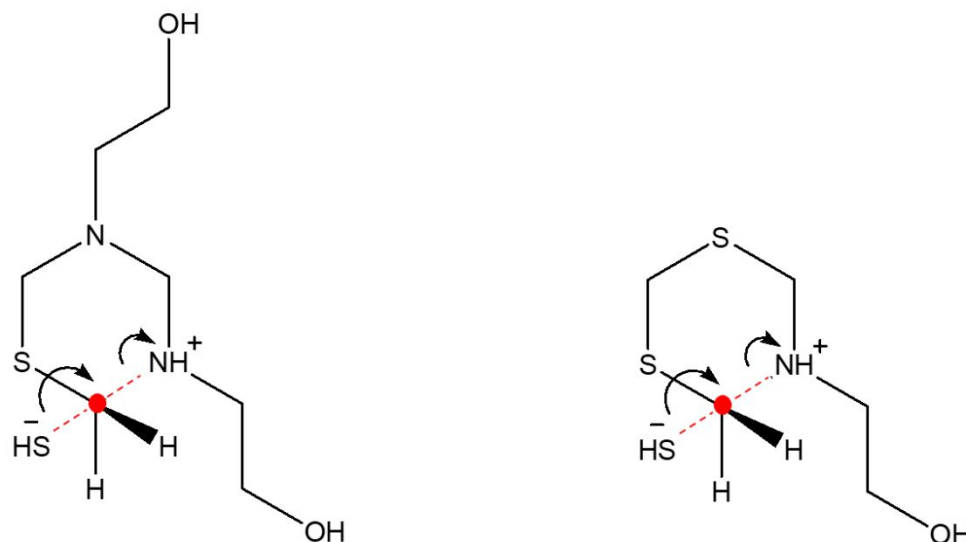


Figure 6 – Transition states for S_N2 ring opening of thiazine and dithiazine molecular species, nucleophilic carbon center is show in red

Whatever the interpretation of the behavior described above; the final reaction products that result in the observed apDTZ solids manifest themselves initially as a saturated dithiazine layer that separates from the aqueous phase as a lower, highly dense, liquid layer (specific gravity of approximately 1.3 g cm^{-3}). This is seen ubiquitously when MEA-triazine is used at the typical commercial concentrations of 35 wt.% to 60 wt.% of active triazine. In laboratory studies this lower dithiazine layer is typically colorless but in field operations it often has a bright yellow coloration. This observed two-phase condition is relatively short lived and remains for only a few hours and, in the absence of any further H_2S , will form a solid mass within 24 hours. This process is the formation of the amorphous polymeric dithiazine, apDTZ, and cannot be arrested. The exact mechanism of this process is somewhat obscure, but there are multiple lines of evidence that support the postulated mechanism displayed in Figure 7, supported by several other works.^{15,25,26}

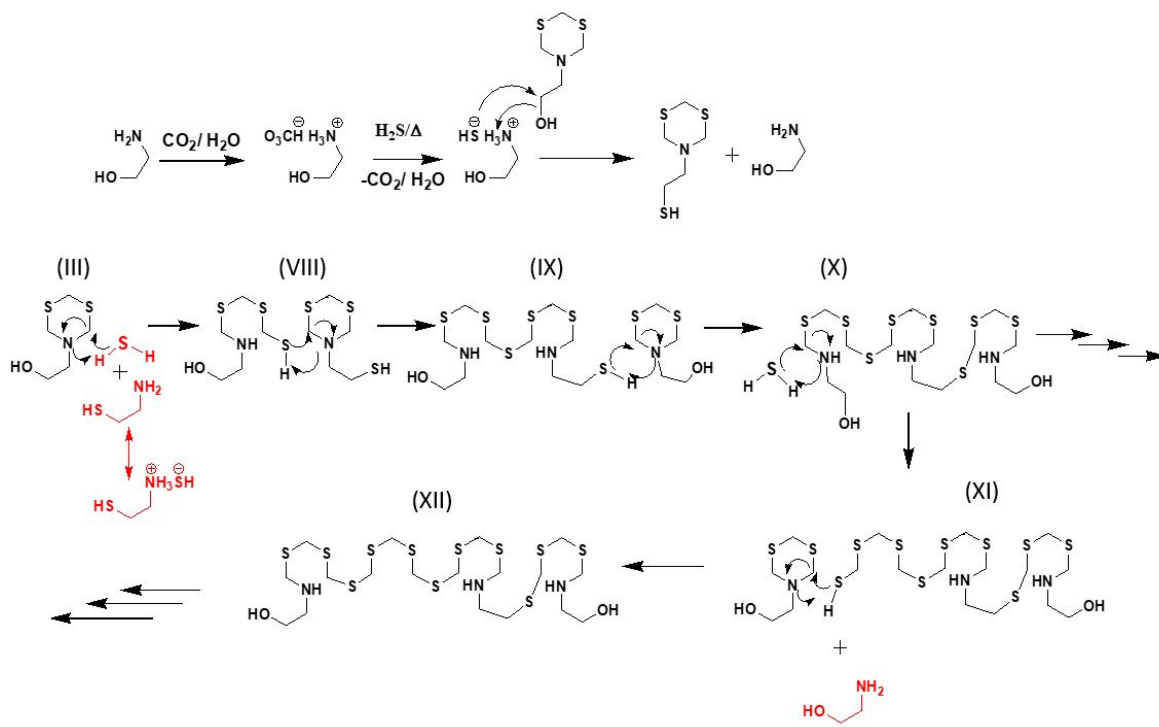


Figure 7 – Postulated mechanism for formation of amorphous polymeric dithiazine from the dithiazine starting point that does not result in trithiane formation²⁵

The mechanism in Figure 7 was based on several observations of the properties of apDTZ both from synthetic material prepared in the lab and field samples, as follows:

- (i) A rigorous elemental analysis of the purified and dried samples clearly indicated that the material contained more carbon, hydrogen and sulphur than monomeric dithiazine
- (ii) The apDTZ samples contained nitrogen and oxygen, the latter being determined directly rather than by difference
- (iii) ^{13}C NMR analysis for apDTZ (VIII – XII) clearly shows a highly complex multiple resonance appearance which is entirely consistent with a polymeric structure when compared with the monomeric molecular structure (III). Certainly, ^{13}C NMR did not support the evidence of trithiane since this would result in one singlet signal. These data are presented and discussed in detail in previous literature.²⁴
- (iv) Elimination of ethanolamine from the growing polymeric structure was confirmed by a FAIMS study of the two-phase fluid before and after solidification yielding increased levels of ethanolamine in the aqueous supernatant.³⁴

It is critical to understand the observation that apDTZ forms only with triazine scavengers whose substituent groups have a terminal hydroxyl functionality.²⁴ Neither trimethyl triazine nor 3-methoxypropyltriazine produce the polymer. However, MEA-triazine and 3-hydroxypropyl triazine both readily form the polymer within 24-hours in an over-spent condition.²⁴ It is this observation that leads to the conjecture that the first critical feature of the mechanism involves reaction at the hydroxyl group with conversion into a thiol. In the laboratory, when a hydroxyl-terminated triazine was fully spent with a gas

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3 mixture containing both H₂S and CO₂, the liquid layer remained, and the polymer would not form. In the
4 presence of only H₂S gas, the polymer readily forms indicating the presence of CO₂ has an impact upon
5 the ratio of amine bisulphide to amine bicarbonate. It is the presence of amine bicarbonate that inhibits
6 the reaction of the bisulphide anion with the hydroxyl terminus, thus preventing the formation of the
7 polymer.
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10 Intriguingly, this restriction is not replicated in field operations. H₂S almost always occurs in the
11 presence of large quantities of CO₂ and yet the polymerization of liquid dithiazine is a very common and
12 problematic aspect of using MEA-triazine as a scavenger.^{8,35} The authors have tried and failed to ever
13 produce crystalline dithiazine by any means other than the crystallization of field derived samples of pure
14 liquid dithiazine, typically obtained from heavily spent fluids from a static gas contact tower. The material
15 is exemplified by large very pale yellow highly crystalline material which has a very defined x-ray
16 diffraction pattern typical of a crystalline structure, and a well-defined, low melting point of 55°C. An
17 example is contained in Figure 8 along with the monomeric dithiazine (lower layer) precursor.
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37 **Figure 8 – (left) example of amorphous polymeric dithiazine deposition in field installations, note the**
38 **very pervasive and solid form; and, (right) crystallization of monomeric dithiazine which will remain in**
39 **this form for only a few hours before spontaneously polymerizing to form apDTZ³⁶**
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43 **3. REMEDIATION AND ANALYSIS OF THE apDTZ DIGEST PRODUCTS**

44 **3.1 Introduction and Literature Review**

45 The chemical removal of apDTZ deposits has not been well covered in the literature. We know
46 that apDTZ is exceptionally insoluble and has been observed in many oil and gas processing systems often
47 in substantial quantities. These deposits can precipitate and collect in aggregates that form blockages in
48 process equipment and cause the fouling of heat exchangers, tubulars, tank trucks, water disposal wells,
49 scrubbers, compressors, etc. Remedial action is required and typically involves taking the affected
50 equipment offline so that manual cleaning operations can be performed. Typically, this involves jetting
51 and can be very time consuming and challenging.³⁷
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54 There have been reports concerning inhibition of this process using various cosolvents,³⁸ but
55 overall the literature is sparse on this topic. The cosolvent approach probably provides additional solubility
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of dithiazine in the aqueous medium, and thus delays the onset of phase separation. Owens described the use of triethylene glycol in a triazine formulation to delay or inhibit the formation of amorphous dithiazine.³⁹ These efforts met with limited success (based upon unpublished laboratory work by the authors) and the problem of amorphous dithiazine, which is practically insoluble, has remained very pervasive in the industry. The only published studies that directly deal with this topic come from the patent literature.^{37,40} Taylor teaches the reactive dissolution of apDTZ using hydrogen peroxide alone but at elevated temperatures; typically 65°C to 70°C is used.⁴⁰ The process involved the use of hydrogen peroxide which oxidized the sulphide species to sulphone or sulphoxide thus rendering them insoluble. The oxidative dissolution required elevated temperatures (65°C to 70°C) and, due to its limited effects (Table 1), is likely to be only of theoretical interest.

Peroxides alone are very aggressive to oil and gas assets and cannot be used without the necessary additives designed to mitigate these negative effects. An extension of the work by Taylor has recently been described in the form of a more aggressive and facile oxidative dissolution of amorphous dithiazine using per(oxy)acetic acid.³⁷ The extension from hydrogen peroxide to per(oxy)acetic acid was initially made by reasoning that, since the latter is an organic acid, the initial solubility and thus inception of the dissolution process, would be facilitated but at a slightly higher solubility. Per(oxy)acetic acid was shown to be far more effective than hydrogen peroxide and it is this reaction with apDTZ that has been elucidated for the first time in this paper and a mechanism proposed.³⁷

3.2 Per(oxy)acetic Acid Dissolution Experiments

Reactive or digestive dissolution (here after simply referred to as dissolution) data for apDTZ in H₂O₂ and per(oxy)acetic acid is shown in Table 1. These static dissolution tests were performed using 10 grams of dissolver solution and 0.5 grams of amorphous dithiazine sample. All tests were performed at either 20°C or 65°C (if 20°C tests were ineffective) and were run for 6 hours. The apDTZ was carefully pre-weighed and then after the test, was dried, prepared and reweighed thus calculating a weight loss and therefore a dissolution percentage. The aggressive nature of per(oxy)acetic acid dissolution of apDTZ is evident when one adds the two substances together and a violently exothermic process begins liberating copious gas and typically causing a thick and pervasive foam. The results in Table 1 show that the per(oxy)acetic acid has a remarkable capacity to dissolve the solid apDTZ. However, while per(oxy)acetic acid is a very powerful apDTZ dissolver, it is also a very corrosive entity and corrosion inhibition must be addressed. In order to test the corrosivity of peracetic acid on carbon steel (C1018) and stainless steel (SS316L) standard ASTM methods (ASTM G31-72 and ASTM D471) were employed. Tests were run for 24 hours in a static jar test at 40°C and the results are presented in Table 2. These results show that per(oxy)acetic acid is extremely corrosive, but that its corrosivity may be controlled to some extent by commercially available corrosion inhibitors which have no adverse effects on the dissolution process.

Table 1 – Dissolution Data comparing hydrogen peroxide and per(oxy)acetic acid showing the far superior dissolution power of the latter^{37,40}

Dissolver Formulation	apDTZ Laboratory Generated (wt.% loss)	apDTZ Field Sample (wt.% loss)	Temperature (°C)
H ₂ O ₂ 34%	5.6±0.06	5.6±0.06	65
H ₂ O ₂ 17%	4.5 to 5.0±0.05	4.5 to 5.0±0.05	65
H ₂ O ₂ 8.5%	3.0±0.03	N/A	65
Per(oxy)acetic acid 15%	100.0±1.0	100.0±1.0	20

Table 2 – Corrosion inhibition of dissolution agents; note Corrosion Inhibitor 1 = phosphate ester inhibitor, Corrosion inhibitor 2 = commercial blend of quinoline quat., an alkyl thioamide and an oxyalkylated phenol)³⁷

Dissolver Formulation	C1018 Corrosivity (mpy)	SS316L Corrosivity (mpy)
Hydrogen peroxide	>2,000±20	>2,000±20
Per(oxy)acetic acid	>2,000±20	>2,000±20
Per(oxy)acetic acid + 5000 ppm Corrosion Inhibitor 1	1.82±0.02	2.92±0.03
Per(oxy)acetic acid + 5000 ppm Corrosion Inhibitor 2	2.92±0.03	4.67±0.05

3.3 Reaction Product Characterization and Mechanism of Per(oxy)acetic Acid Oxidation

It is recognized that the dissolution of amorphous dithiazine by per(oxy)acetic acid is not simply a dissolution process but involves an aggressive oxidative chemical reaction. Numerous unpublished studies by the authors have been undertaken on various samples of amorphous dithiazine both of field and lab origin. Per(oxy)acetic acid is typically supplied as either a 15% or 35% active solution and both concentrations have been used successfully. An early observation on this system was that, since per(oxy)acetic acid is typically refrigerated in storage, it is important to allow it to reach room temperature for optimum reaction. A second important observation was made during this study regarding the storage of the powdered apDTZ. When the apDTZ was freshly separated from a heavily spent scavenger fluid, washed and dried, its activity towards this dissolution process was very aggressive and highly exothermic. However, if the polymeric powder was stored for any significant time, the activity markedly decreased to the point where almost no reaction occurred. This observation was thought to be due to surface oxidation by air of the very finely divided polymer particles such that a protective layer of partially oxidized polymer coats the particles. This was further verified by taking an aged sample and grinding it to a finer powder with a pestle and mortar and this process significantly restored the activity towards per(oxy)acetic acid approaching, but to an extent not quite equaling that of the freshly isolated polymer. This dissolution process is very aggressive and liberates a significant amount of heat as well as gas and previously described and shown in Figure 9. The released gas is probably oxygen being liberated from the heated excess per(oxy)acetic acid, but it may also include carbon dioxide from exhaustive oxidation of the polymer. To identify the fate of sulphur in the polymer, three analyses were carried out, as described below.

3.3.1 GCMS Analysis of the Polymer Digest

The digested solution was concentrated as much as possible on a vacuum rotary evaporator and the resulting residue treated with (trimethylsilyl)diazomethane in methanol. The resulting solution was analyzed, and the total ion current chromatogram is shown in Figure 10. While not all components could be identified and are likely larger fragments from the polymer digest, a prominent peak is observed at Rt 5.1 mins. The mass spectrum of the material in this peak is shown inset in Figure 10 and was identified as dimethyl sulphate. This indicates that the sulphur in the polymer is fully oxidized to a VI valence state as sulphate which, upon reaction with methanol, produces the dimethyl ester.

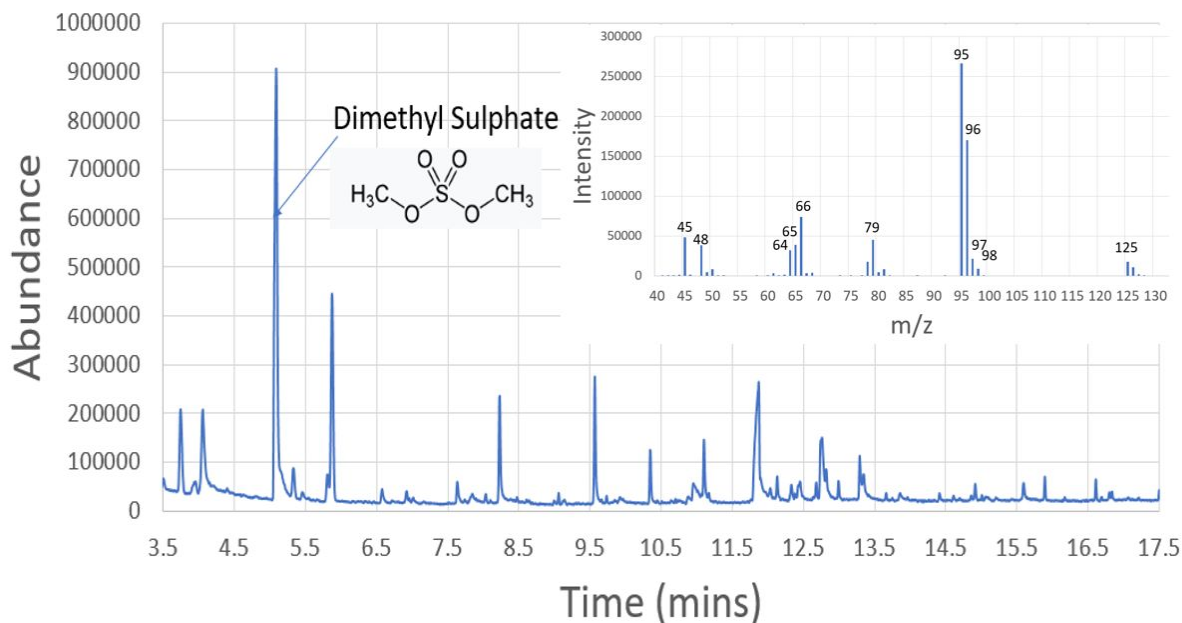


Figure 10 – Digested amorphous polymeric dithiazine (apDTZ) solution – total ion current chromatogram of reaction residue treated with (trimethylsilyl)diazomethane in methanol and (inset top right) – Mass Spectrum of Component at T = 5.1 minutes showing a dominance of dimethyl sulfate as the ultimate reaction product

Further identification of the oxidative breakdown products of the polymer, and specifically the fate of the carbon in the polymer backbone, was carried out using GCMS. The digested polymer slurry was treated with methanol in order to form methyl esters of any acids present. Clearly, a large quantity of methyl acetate would be expected from the degraded per(oxy)acetic acid and indeed this was observed by the GCMS detection of a molecular ion at 74 amu in the electron impact spectrum. Also very clearly observed, with a shorter retention time than methyl acetate, was methyl formate with a molecular ion at 60 amu. As further verification, when the digest was treated with isopropanol the formation of isopropyl formate at 88 amu was observed in the mixture of components for the corresponding GCMS analysis as shown in Figure 11.

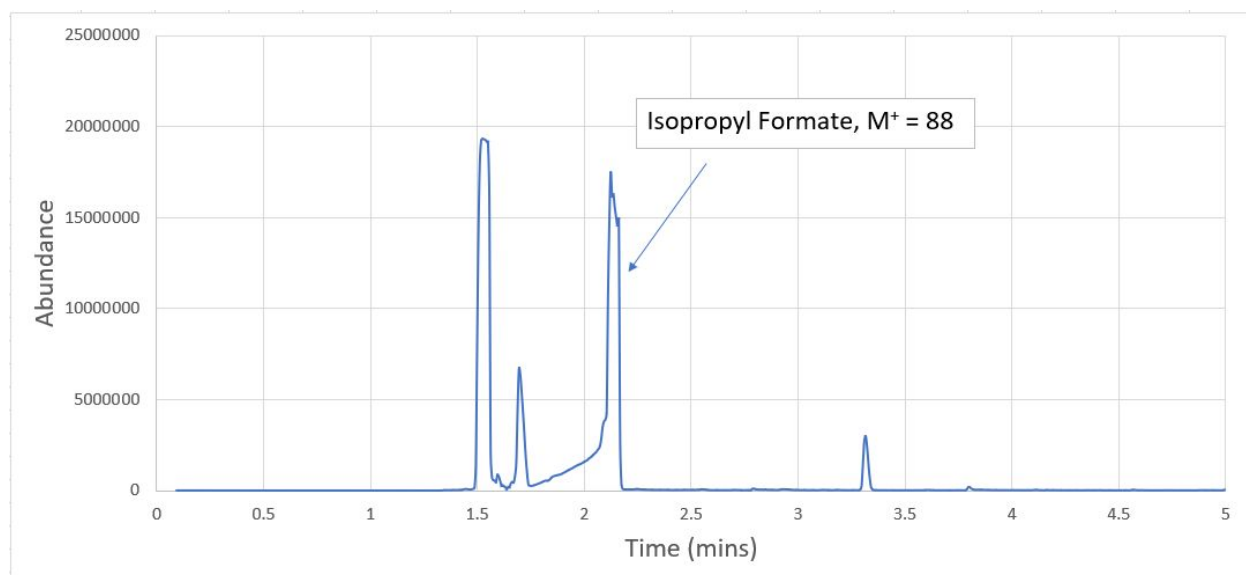


Figure 11 – apDTZ digest esterified with isopropanol

This is good evidence that the carbon back bone was fully degraded down to single units, with not only sulphur residues becoming sulphate, but also with carbon residues becoming formic acid/formate. Since a very powerful evolution of gas was observed when the dry polymer was treated with per(oxy)acetic acid, further studies were undertaken to establish if either sulphur or carbon residues were liberated into the gas phase as either sulphur trioxide or dioxide and/or carbon dioxide.

3.3.2 Barium Chloride Precipitation Analysis of the Polymer Digest

Since the earlier experiments indicated sulphuric acid/sulphate was the final reaction product, in order to corroborate the GCMS results, a further amorphous dithiazine digest was undertaken and the solution centrifuged. The clear supernatant was transferred to a fresh centrifuge tube and an aliquot of barium chloride solution added. An immediate white precipitate was formed which was centrifuged and examined by X-ray Diffraction, shown in Figure 12 and was confirmed to be barium sulphate although other (contaminant) material is present. To confirm this finding, a second more extensive quantitative experiment was carried out and it was established that approximately 79% by mass of the sulphur present in the amorphous dithiazine was converted to barium sulphate.

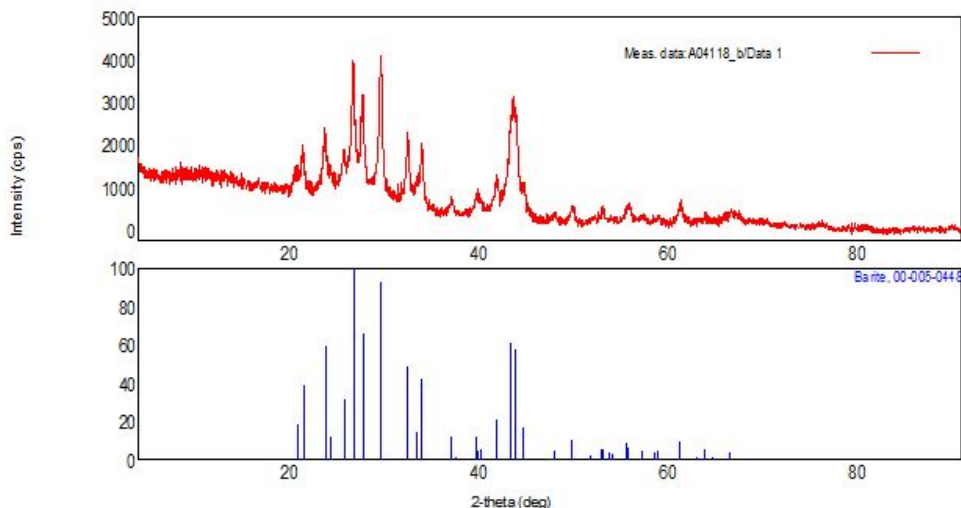


Figure 12 – Powder XRD (top) recovered precipitate and (bottom) barium sulphate reference. More detailed experimentation showed 79 wt.% of the sulphur was converted to BaSO₄

3.3.3 Analysis of Gas By-products from Polymer Digest

To further understand the precise chemistry of the apDTZ digest by per(oxy)acetic acid, an experimental apparatus was designed and deployed. Under a stream of flowing nitrogen in a 3-necked flask fitted with septum caps, a sample of freshly filtered and dried apDTZ was accurately weighed into the bottom of the flask and was degassed and all oxygen and carbon dioxide from the atmosphere removed. Per(oxy)acetic acid (32wt.%) was added dropwise and the gaseous byproducts purged under a stream of nitrogen into a freshly prepared and filtered lime water (pH = 12.6) and dilute a solution of barium chloride. This experiment was carried out to confirm whether either carbon dioxide or sulphur dioxide/trioxide was liberated into the gas phase by the very vigorous boiling which is invariably observed. In all cases the solution remained completely clear confirming that neither CO₂, SO₂ or SO₃ were liberated during the reaction. The apparent gaseous evolution that is clearly seen in this experiment is thus attributed to (a) thermal breakdown of the per(oxy)acetic acid to liberate oxygen and/or (b) the physical boiling of the acid aqueous solution given that per(oxy)acetic acid boils within a few degrees of water. Further evidence for this is that following the addition of the per(oxy)acetic acid after the initial large gas evolution, an immediate negative pressure and possibly suck back (if steps were not taken to prevent this) was observed. This is consistent with a fluid boiling initially then condensing in a cooler part of the flask, thus creating a negative pressure.

4. SUMMARY AND CONCLUSIONS

The dominant and final reaction product of MEA-triazine is a highly insoluble, solid polymeric species that we have referred to as amorphous polymeric 5-(2-hydroxyethyl)-hexahydro-1,3,5-dithiazine, abbreviated as apDTZ. In this paper, we have presented a critical review of the issue of the formation and remediation of apDTZ, which is an undesirable deposit which leads to considerable fouling in oil production systems. The chemistry of the formation of apDTZ and potential mechanisms and reaction routes to its formation are reviewed and discussed, as these offer critical information which helps greatly with its remediation. The presence of a terminal hydroxyl functionality is critical to enable the corresponding dithiazine to readily undergo polymerization. Two important issues are which have not

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3 previously been satisfactorily addressed in the literature, are resolved here: viz. we explain (i) why the
4 thiadiazine reaction product from tris(2-hydroxyethyl) triazine (MEA triazine) is never observed, and (ii)
5 why the dithiazine never progresses to the trithiane.
6

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8 A reactive oxidation procedure using per (oxy) acetic acid is proposed for digesting the polymeric
9 insoluble apDTZ deposits. The digestion products for this process have been analyzed using a range of
10 analytical methods. The fate of the sulphur (S) in the apDTZ is shown to be sulphate (oxidation state +6)
11 and the carbon (C) backbone is oxidized to formic acid and formates.
12

13 The remaining challenge to overcome is the practical deployment of this chemical method into a
14 useable and safe application to deal with apDTZ in the field. The reaction is extremely aggressive and
15 highly exothermic. It is important to attenuate this reaction enabling its practical application on a larger,
16 industrial scale in oil and gas facilities. A reduction in concentration and careful choice of cosolvents will
17 probably be key factors in this task. The exact condition of the deposit is also extremely important; for
18 example, are there significant contaminants, is the apDTZ deposit oil wet or water wet, etc. While it is
19 recognized that there are currently commercially available products which claim to a) inhibit the initial
20 formation of apDTZ when used as an additive for commercial MEA triazine or b) dissolve apDTZ when
21 formulated in various solvents, to date none has proven to be completely successful. Powerful oxidizing
22 agents are not preferred in oil and gas operations and thus a very judicious approach, involving careful
23 risk assessment, will be required. However, the basic elements of the oxidative apDTZ digestive process
24 have been established in this work, and it remains now to bring this technology to a useful conclusion and
25 value to oil and gas producers.
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41 **Notes**

42 The authors declare no competing financial interest.
43
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46 **ACKNOWLEDGEMENTS**

47 The authors thank Clariant for allowing this work to be published.
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