

Ammonium Thiosulfate Production at Refineries

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Abstract

Ammonium thiosulfate (ATS) production can be profitable, especially in recent years. This paper reviews fundamentals of ATS production processes and their use to treat Claus tail gas, to process or consume sour water stripper gas, to remove H₂S from specialized hydrotreating facilities focused on making marine fuels, etc. The paper reviews some of the history of the process and some historical applications that have been documented. The paper also reviews ATS production, value, uses, and quality issues. The paper draws upon Trimeric's direct experience consulting with ATS process operators and ATS technology licensors.

1 Introduction

The disposal of sulfur and nitrogen species from refinery waste streams historically has been a costly and troublesome problem for oil refiners. Improving the efficiency and reducing the cost of sulfur recovery and disposal is the driving force behind the Brimstone Symposia series. Converting sulfur- and nitrogen-containing components in refinery waste streams to aqueous ammonium thiosulfate [ATS, (NH₄)₂S₂O₃] solution has the potential to improve the economics by the sale of a valuable byproduct. This paper considers the production of ATS from refinery streams that contain hydrogen sulfide (H₂S), sulfur dioxide (SO₂), and ammonia (NH₃), with supplemental feedstocks as necessary to balance the stoichiometry.

The primary sources of the refinery streams that can be used for ATS production are shown graphically in Figure 1 and include the following:

- H₂S: Sour water stripper (SWS) gas; Amine acid gas (e.g., from hydrotreater gas cleanup)
- SO₂: Claus tail gas
- NH₃: Sour water stripper gas

- And sometimes, elemental sulfur (S): Claus product

This paper is not meant to be a comprehensive review of ATS technologies and refinery applications. The intent is to bring attention to ATS production as a potential revenue source for refineries to offset the cost of treatment. There have been relatively few recent public presentations on ATS production in refineries, so much of the technical content in this paper was obtained from patents and academic literature.

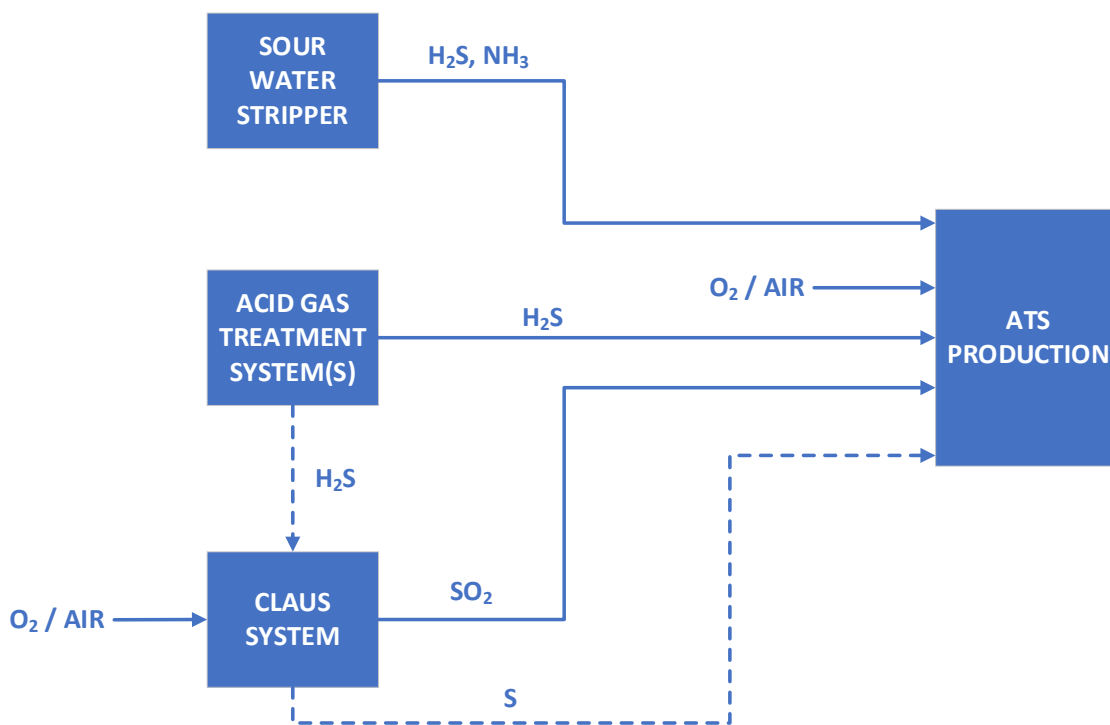


Figure 1. Refinery Block Flow Diagram – Sources of ATS Production Feedstocks.

2 ATS Applications and Markets

This section is an overview of applications and potential markets for ATS.

2.1 Industrial

An early industrial application for ATS was as a photographic fixer. There are numerous patents from the 1940s and later that are related to photographic applications. Use of ATS as a fixing agent requires that the solution be free of elemental sulfur [1] and presumably other contaminants. ATS and other related sodium thiosulfate chemicals were noted to be expensive compared to the conventional alternatives (especially sodium thiosulfate). Additionally, the

market for photographic chemicals was limited from the beginning and has shrunken further with the rise of digital photography.

ATS has been used as a leaching agent for gold, silver, and/or copper in mining processes. The first patents and academic literature that Trimeric could find were from the early 2000s [2, 3]. ATS has the potential to replace the more hazardous cyanide leaching agents that are used in the conventional metals recovery processes.

2.2 Agriculture

Sulfur dioxide (SO₂) emissions from power plants and industrial facilities in the Industrial Age led to the formation of acid rain. An unintended positive consequence of acid rain was the addition of sulfur to the soil that was a net benefit for agriculture. The mitigation of atmospheric SO₂ emissions over multiple generations has significantly reduced the atmospheric contribution of sulfur to the soil. Farmers now must add sulfur to make up for the lost deposition from the atmosphere. ATS and the closely related ammonium sulfate [AMS, (NH₄)₂SO₄] both are used as fertilizers. ATS is known by the fertilizer description 12-0-0-26S, which has 12wt% nitrogen, 0% phosphorous, 0% potassium, and 26wt% sulfur on a wet basis when applied as a 60wt% ATS aqueous solution.¹ The alternative AMS is more typically applied as a dry solid.

One of the reported advantages of ATS over ammonium sulfate is that the second sulfur in ATS is not readily available to the plants and slowly converts to the active form to provide an extended benefit but more quickly than elemental sulfur [4]. Thiosulfate initially is converted to tetrathionate (S₄O₆²⁻) and eventually to the active sulfate form over a period of weeks [5]. ATS also is reported to reduce the rate of ammonia conversion to nitrate, which can slow nitrate loss to the atmosphere and surface water [5]. ATS can damage foliage and roots if applied improperly [4].

Aqueous solutions of ATS at nominally 60wt% used for fertilizer begin to form solids at or slightly below 45 °F [6]. Proper heat trace and insulation is required for the solutions to remain pumpable in cold weather. The ATS is produced continuously in a refinery but is used seasonally for fertilizer applications. The low temperature properties of ATS solutions and seasonality of demand have important implications for the design of storage and handling equipment in refineries.

ATS fertilizer is marketed in North America by several distributors and brokers, including but not limited to the following:

- Tessenderlo Kerley (sold as Thio-Sul®, also Jupiter Sulphur joint venture with Phillips 66)
- Brandt

¹ Fertilizers typically are rated by a three number code N-P-K representing the weight percent of nitrogen, phosphorous, and potassium. A fourth number can be added if there are non-standard components like sulfur.

- CHS
- Koch Fertilizer
- Hydrite (sold as ATS™)
- Kugler

2.3 ATS Market Size and Perspective

Publicly available market estimates put the global market for ATS at around 462,000 ton/yr [7] and 831,000 ton/yr [8], both assumed to be of 60wt% ATS solution, the customary article of commerce.

However, a source with about 4 decades experience in the fertilizer market and more than 2 decades experience with ATS markets reported that ATS is historically undercounted and unreliable in such public market estimates, due to the addition of ATS to other liquid fertilizers (M. Ray, personal communication, 4 September 2024). For example, when ATS is added to UAN, it is then reported as part of the UAN market and not part of the ATS market. This source noted that most of the ATS that is produced is blended with UAN. ATS is also said to be the feedstock for conversion to other products, such as potassium thiosulfate (KTS) and ABS, which may also skew the publicly reported ATS market size. This source estimated the North American market to be roughly in the range of 1,300,000-1,500,000 tons/yr of 60wt% ATS.

For perspective, consider a 200 LTPD Claus sulfur recovery unit (SRU) with 96% sulfur recovery. The tail gas would contain nominally 8 LTPD of total sulfur. Assuming that i] this 8 LTPD total sulfur is combusted to SO₂ on the front end of an ATS-based tail gas unit (TGU), and ii] H₂S is separately fed to the ATS unit in the proper ratio to react with that SO₂ (an additional 4 LTPD elemental sulfur equivalent) along with sufficient ammonia, then iii] the amount of 60wt% ATS that would be produced is on the order of 19,000 ton/yr on a 365 day/yr basis.

3 ATS Properties, Production Methods, and Chemistry

This section describes the key properties and chemistry for ATS.

3.1 ATS Properties

The public literature on physical and transport properties of ATS is thin except for the basic information for the fertilizer-grade solutions. The properties of nominal 60wt% ATS

aqueous solution that is the standard 12-0-0-26S fertilizer are summarized in Table 1. ATS is only slightly hazardous with no flammability or reactivity risk [9].

Table 1. 60wt% ATS Aqueous Solution Properties [10].

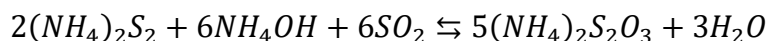
Property	Typical Value
Density	82.4-84.2 lb/ft ³ @ 77 °F
pH	6.5-8.5
Viscosity	5-10 cP @ 77 °F
Heat Capacity	1.06 Btu/lb-°F
Thermal Conductivity	0.30 Btu/hr-ft-°F
Solids Formation Temperature	39 °F

3.2 ATS Production Methods and Chemistry

This section summarizes publicly available ATS production processes and the applicable chemistry. It is not intended to be an exhaustive summary of all commercial ATS processes but to highlight a few representative process concepts and the evolution of the production methods.

3.2.1 Early Concepts

One of the early patents for ATS production involved the reaction of ammonium sulfide or polysulfide with SO₂ in the presence of aqueous ammonia [11]:



The potential feedstocks for ATS production in a refinery environment include ammonia (NH₃), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), elemental sulfur (S), and oxygen (O₂). The ATS contains equimolar nitrogen and sulfur, so streams that contain both NH₃ and H₂S, such as sour water stripper gas, theoretically are candidates for ATS production with minimal external feedstocks. ATS solution produced in refineries can contain up to several weight percent of ammonium sulfate and / or ammonium sulfite or bisulfite produced through side reactions that may or may not be included in the nominal 60wt% ATS concentration.

3.2.2 Refinery Integration

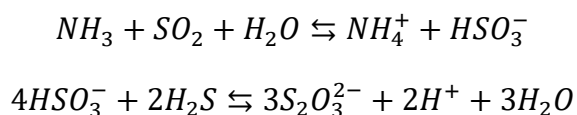
An ATS production unit may be integrated with a refinery operation in several ways, depending on the ratio of sulfur species and NH₃ available. Sour water stripper gas, amine acid gas, and Claus tail gas streams are prime candidates for producing ATS because ATS can be

more valuable than the other primary product from these streams - elemental sulfur. The economics of using externally sourced anhydrous or aqueous ammonia as a feedstock to supplement what is available in SWS gas will depend on local conditions, but it is likely that the higher value of ATS relative to NH₃ would justify the cost in most cases. One advantage of ATS production from SWS gas is that the NH₃, which consumes a large volume of air in the Claus unit, can be diverted directly to ATS production, freeing up Claus capacity to process non-NH₃-containing streams. ATS production potentially is a lower-cost option for treating sulfur-containing waste gases than expansion of or installation of a new Claus unit.

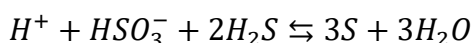
There may be special cases for which ATS production is economical with only H₂S feedstock generated in the facility. The NH₃ and either SO₂ or ABS solution are purchased and fed to a one-step process to convert the H₂S. Trimeric knows of a couple ATS-producing units that operate in this mode.

3.2.3 Early Refinery Applications

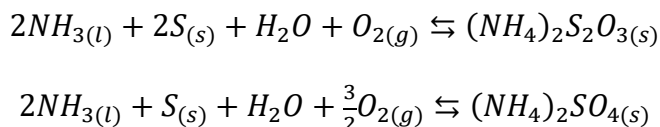
Patents for ATS production related to refinery operations started appearing in the 1960s. One of the early patents was by Union Oil Company of California [12]. The Union Oil Co. concept was a two-step process with bisulfite intermediate in a preferred temperature range of 35-70 °C (95-158 °F) and presumably in the presence of sufficient ammonia to maintain the required stoichiometry:



The Union Oil concept included a subsequent step to produce elemental sulfur using the bisulfite solution if the feedstock contains excess H₂S:

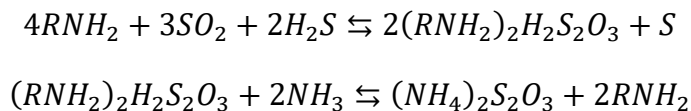


Continental Oil Company (Conoco) was actively developing ATS processes in the late 1960s and early 1970s. One scheme produced mixtures of solid ATS and AMS by reaction in liquid NH₃ [13]:



A second Continental Oil process to produce ATS and AMS mixtures by contacting SO₂ with aqueous ammonia containing dissolved sulfur, followed by conversion of the resulting ammonium bisulfite solution by additional NH₃, S, and SO₂ [14].

A third Continental Oil process used a primary amine to facilitate the production of ATS from SO₂, H₂S, and NH₃ [15]:

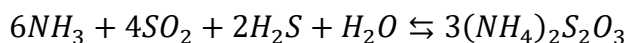


where R is an alkyl or mononuclear aryl group.

Other processes that used various combinations of elemental sulfur, bisulfite solution, and ammonia (for example, the process developed by Goldschmidt A.G. [16]).

UOP in the 1970s developed several refinery-focused waste treatment processes that had ATS as an intermediate but not as a target salable product (for example, U.S. Patents 3,531,395; 3,644,087; 3,672,837; 3,728,433; 3,728,439, etc.).

The Colorado Interstate Gas Company (CIGS) and Wycon Chemical Company formed a joint venture at the CIGS Table Rock Plant for a nominal 60 ton per day ATS system fed by Claus unit tail gas [17]. The Table Rock ATS system was developed and designed by Pritchard and started up in 1980. The Table Rock system had a quench column for the inlet tail gas, three SO₂ absorption towers in series, and a stirred reactor to convert ABS to ATS by reaction with H₂S. An evaporator package was provided to increase the ATS concentration to approximately 60wt% if the reactor product was too dilute. The overall chemistry of the ATS production is the following:



Ott developed a process to produce aqueous ATS from elemental sulfur or H₂S and aqueous ammonia feedstocks [18]. Ott's patent claimed to improve on the existing processes by solving the problem of sulfide fog and formation of sulfur particles by the Claus side reaction (H₂S + SO₂) that caused plugging problems. The elemental sulfur and/or H₂S is combusted to generate SO₂ that is absorbed in a solution containing ammonium sulfite [AMS or (NH₄)₂SO₃] and ammonium bisulfite (ABS or NH₄HSO₃).

3.2.4 Haldor Topsoe

Haldor Topsoe's process is representative of the typical two- or three-column systems in use at refineries [19], [20], [21]. A simplified process flow diagram for the Haldor Topsoe process is provided in Figure 2 and representative reactions are summarized below. SO₂ is contacted with an aqueous ammonia solution at pH 5-6 in a one- or two-stage absorber at 10-50

°C (50-122 °F) to generate ammonium hydrogen sulfite² (AHS, or NH_4HSO_3). The AHS is reacted with H_2S and additional NH_3 in a second absorber to produce aqueous ATS. Haldor Topsoe specifically mentions sour water stripper gas containing both H_2S and NH_3 , but no SO_2 , as a preferred feed gas to the second absorber. Some or all the SO_2 may be generated by combustion of H_2S if required to maintain the target stoichiometry. Haldor Topsoe claims 99.99% capture of sulfur species.

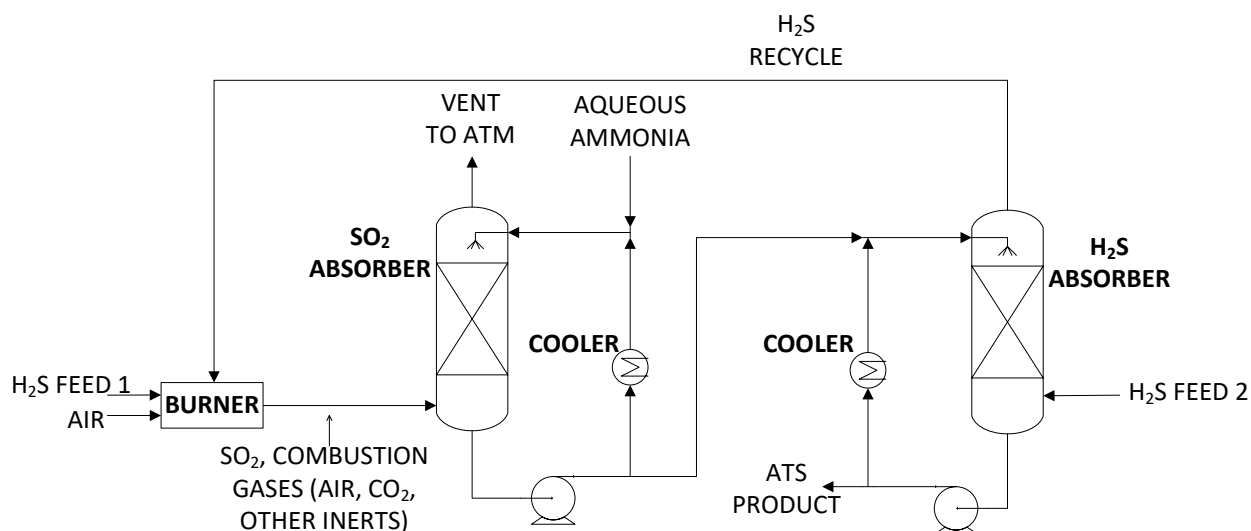
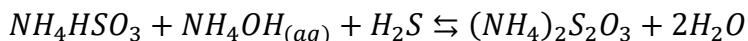
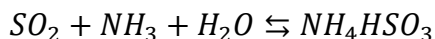


Figure 2. Simplified PFD for Haldor Topsoe ATS Production Process.

3.2.5 ThioSolv SWAATS

The ThioSolv Sour Water Ammonia to Ammonium ThioSulfate (SWAATS) process was developed specifically to remove H_2S and/or NH_3 from sour water stripper gas or other gas streams containing CO_2 [22], [23], [24], [25]. A simplified process flow diagram for the most basic SWAATS process is provided in Figure 3. There are SWAATS variations with additional absorption/reaction steps. The chemistry of the SWAATS process is similar to the Haldor Topsoe process but with the order of the H_2S and SO_2 absorbers reversed. A solution containing ammonium sulfite and ammonium bisulfite (ABS) absorbs and reacts with H_2S in the feed gas. CO_2 in the feed gas does not react with the solution and so is picked up by the solution only by physical absorption, which is minimal at low pressures. No preferred temperature range for the absorption steps is provided in the patents but presumably the temperatures are maintained below

² Ammonium hydrogen sulfite (AHS) is called ammonium bisulfite (ABS) by others. We use the terminology in the respective patents. It should be noted that AHS and ABS are the same compound, NH_4HSO_3 .

the boiling point of water for the solution composition. The overall chemistry is the following (like the Table Rock chemistry summarized in Section 3.2.3):

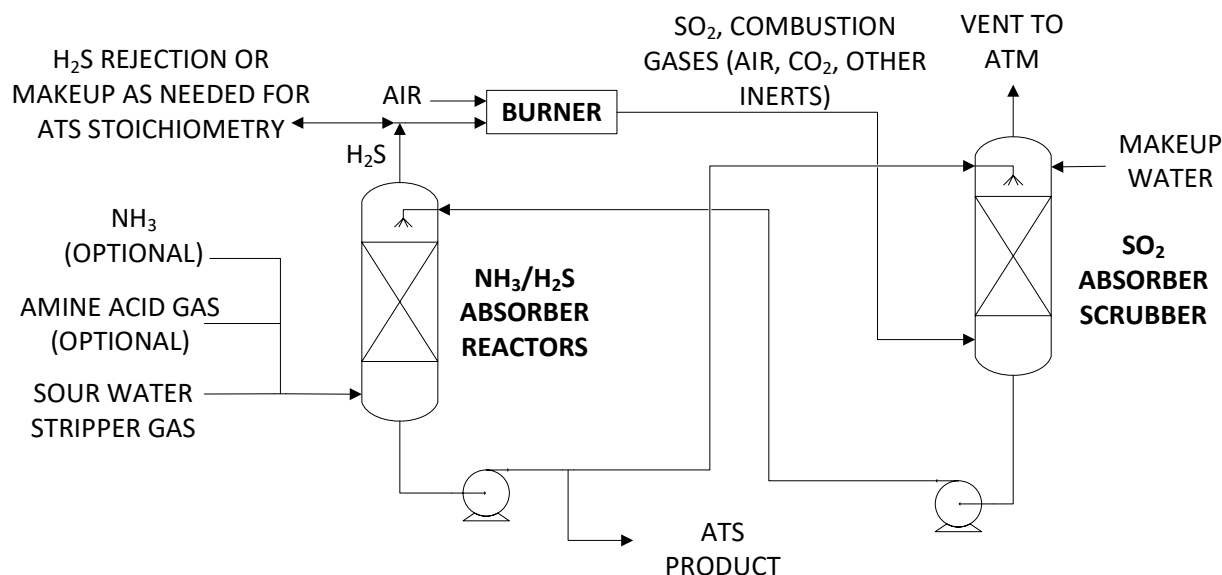
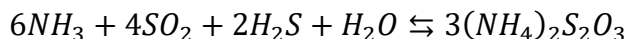


Figure 3. Simplified PFD for ThioSolv SWAATS ATS Production Process.

3.3 Process Modeling of ATS Systems

This section provides general guidance on process modeling of ATS systems. The typical 60wt% ATS product and intermediate solutions in the reaction pathway have high ionic strength and exhibit highly non-ideal behavior. An electrolyte activity coefficient model is required for the ATS production processes in the common process modeling software packages. Modelers should not expect to simply accept the default chemistry and thermodynamic packages without careful checking of the results against the literature. ATS may need to be added as a hypothetical component if it is not in the default property package.

Trimeric has used common process software to model ATS production systems with reasonable success. The reaction chemistry and product composition in the models has been matched to several refinery ATS systems. The one parameter that was poorly modeled is the density of the concentrated ATS and intermediate solutions. Trimeric's recent process models have significantly underestimated the solution densities. In some cases, Trimeric has used the ACAPP electrolyte software (a Trimeric-internal aqueous electrolyte software) to check the process models or to evaluate side operations that are difficult to model in the standard modeling packages.

4 ATS Production at Refineries

This section summarizes the publicly available information about refinery based ATS production. There is not a lot of public information about the process details and plant capacities. In general, the refinery operators do not provide detailed information on process configuration and capacity in permitting and other public documents.

The Phillips 66 refineries in Billings, MT [26] and Ponca City, OK [27] have a joint venture with Tessengerlo Kerley called Jupiter Sulphur to produce ATS from gas streams originating in the refinery in a fence-line arrangement. The Billings ATS Plant, which has a Claus-style thermal reactor (followed presumably by a sulfur condenser) followed by a combustor, was constructed in c. 1990 and has capacity for elemental sulfur plus ATS combined of 110 long tons per day (LTPD) elemental sulfur equivalent. The Ponca City Jupiter Sulphur facility recently announced 30 years of operation with no lost time injuries [28].

Flint Hills Resources announced the startup of an ATS production unit in 2019 with 100,000 short tons per year ATS capacity (or about 63 LTPD elemental sulfur equivalent), which is stated to be “one of the world’s largest” [29]. Flint Hills Resources distributes the ATS through the affiliated company Koch Fertilizer [30].

CHS produces ATS at its refinery in McPherson, KS [31] and possibly also at its Laurel, MT refinery [32]. CHS also distributes the ATS for use as fertilizer through its Agronomy business.

The now closed Marathon refinery in Gallup, NM (formerly Tesoro and Western Refining, among other owners) has an ATS production unit [33]. No details on the ATS plant capacity or process design were found in the state permit documents.

An ATS unit was reported in 2010 to be planned at Wyoming Refining Company in Newcastle, WY [34] and a SWAATS unit was listed among the units in a 2024 web posting [35].

As a result of its work with ATS systems, Trimeric also knows of other ATS units in the U.S. that remove H₂S from hydrotreater gas streams at facilities focused on making marine fuels and which import both NH₃ and SO₂ (or ABS) to react with the H₂S. However, no public references were available for these units for this paper.

In addition to the facilities in the U.S., there are several ATS facilities publicly announced in Europe. There may be others that are not listed here. An ATS production facility in Slovakia using ThioSolv’s process was announced in 2018 [36]. The ATS plant operator, Stercorat, announced a plant capacity of 30,000 metric tons per year (or about 19 LTPD elemental sulfur equivalent) [37]. Tessengerlo Kerley announced plans in 2021 for an ATS facility in The Netherlands with a target startup date 2024 [38]. Trimeric was not able to confirm

that the facility was built. The Klesch Group (former Equinor) Kalundborg Refinery near Copenhagen installed a Haldor Topose ATS unit in 1999/2000 with a projected capacity of 15,000-27,000 metric tonnes per year (or about 9.5-17 LTPD elemental sulfur equivalent) [39], [40]. It appears that the ATS system is still in operation.

5 ATS Product Quality Issues and Potential Solutions

5.1 Water Balance

The desired ATS product is 60wt% ATS. Thus, it is necessary to manage the water balance. Water balance issues are mentioned by ATS operators as a potential quality issue, especially when using or considering the use of SWS gas directly. Water spray is often used as a polishing step to absorb the last bit of SO₂ and/or NH₃ before the treated gas is vented to the atmosphere, which can result in tradeoffs between performance and water balance. As a result of Trimeric's work with ATS plants, Trimeric is aware of ATS plants that use un-combusted SWS gas in an ATS column while making ATS product that meets concentration specifications. Trimeric's own simulations of ATS plants running at near-design conditions have also shown that the water balance can be managed. Thus, it is possible to manage the water balance with most or all ATS plant designs, including those that use SWS gas as a direct, un-combusted feedstock.

However, in Trimeric's experience, we also know that some plants that successfully manage water balance at near-design conditions report that it is very difficult to maintain concentration specifications in off-design conditions, such as low rates. Careful design that considers extended turndown conditions and careful control may be needed if a plant will operate for significant time at low rates.

5.2 Other Product Quality Issues (e.g. black flecks and odor)

Other product quality issues (e.g., black flecks and odor) have been reported at ATS plants, especially perhaps when using un-combusted SWS gas as a feed to ATS units. The exact nature of the black flecks is debatable and may depend on the specific plant, but thienyl compounds are one possibility (generally large molecular weight molecules into which are incorporated 5-membered aromatic rings with one of the 5 ring members being S – a thienyl ring).

Some observations about black flecks and odor problems:

- Black flecks and odor tend to be associated (often occur together).

- Black flecks and odor problems tend to be associated with startup conditions and low-load conditions.
- Black flecks can tend to settle in quiet areas (e.g., in low velocity piping and in tanks) and may re-appear if stirred up.

Trimeric's experience is that black flecks and odor problems can be addressed in several ways:

- ATS product tends to be better if the streams fed to the ATS unit are cleaner.
 - If an ATS unit is using un-combusted SWS gas, then making improvements in the sour water system upstream of the SWS in order to improve the quality of the SWS gas will likely result in major improvements in ATS quality with respect to black flecks and odor.
 - Example SWS improvements that can help ATS quality.
 - Improvements in upstream units to limit dumping hydrocarbon into the sour water system.
 - Improvements in hydrocarbon separations unit operations within the sour water system.
 - Improvements to hydrocarbon separations from SWS tanks.
 - Addition of final SWS cleanup systems prior to the SWS tower, for example filtration and liquid-liquid coalescers.
 - Similarly, the general concept of improving ATS-plant feed quality by taking action upstream to prevent contaminant ingress should result in better ATS quality in any ATS plant, even if they do not accept SWS gas directly.
- Good product filtration may be effective at removing the black flecks prior to railcar or tank car loading.
 - Short of preventing ingress of material that causes black flecks and/or operating in a way that doesn't produce black flecks, a very good product filtration system may allow a plant to make on-spec product at times when doing so would be difficult or impossible without good filtration.
 - Product filtration may be overlooked or under maintained.

While there can be significant product quality issues with ATS produced in refineries, good design, improvements upstream to clean up streams feeding the ATS plant, and good product filtration can limit product quality issues.

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