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Revision Memo

12/00 Added section on Incineration. Updated sections on Wet Air Oxidation and Biological Treatment. Removed sections on Crystallization and Resins. Removed 1995 budgetary estimates. Added Table 2, Figures 3, 21, and 24. Other minor updates and editorial revisions made.

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SCOPE

This section discusses the nature of spent caustic, ways to reduce production, current methods of disposal, and alternative methods of disposal. Although there are four major types of spent caustic (sulfidic, cresylic/phenolic, naphthenic, and sulfitic), this section will mainly focus on spent sulfidic caustic, since this is typically the largest and most difficult type to handle. A brief description, along with advantages and disadvantages, is provided for each management method. A comparative parameters table, a treatment selection flow sheet, and a relative cost comparison table are included to guide the user in the selection of the appropriate method of disposal for their site.

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BACKGROUND

Caustic soda (NaOH) solutions are used to remove acidic contaminants from refinery and chemical plant feed and product streams. These acidic contaminants: (hydrogen sulfide (H_2S), mercaptans, carbon dioxide, phenols, naphthenic acids, and sulfur dioxide) react with the caustic. The partially reacted caustic, along with the reaction products, is known as "spent caustic." Spent caustic can be classified as one of four types, depending on the composition: 1) sulfidic, 2) cresylic/phenolic, 3) naphthenic, and 4) sulfitic. Spent sulfidic caustic is generated from scrubbing LPG, virgin naphtha, gas oils, hydrofined products, and steam-cracked streams. The major contaminants of this stream are mercaptans and sulfides. Spent cresylic caustic is generated from cracked streams and as a waste stream from Merox units. Major contaminants include cresylic acids, phenols, mercaptans and sulfides. Due to the presence of high levels of phenols, this type is also referred to as phenolic caustic. Spent naphthenic caustic is derived from treating virgin naphthas, and kerosene from highly naphthenic crudes. Naphthenic acids, mercaptans, and sulfides are the major contaminants. Caustic produced from sulfuric acid alkylation units contains sulfate, and sulfites and is classified as sulfitic caustic. Sulfidic spent caustic represents the largest volume of spent caustic generated.

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BACKGROUND (Cont)

Spent caustic is considered a registered hazardous waste in Canada. Spent caustic sent for disposal in the US is also considered a hazardous waste due to its corrosivity (pH > 12.5) and reactivity (sulfide bearing waste). In order to dispose of spent caustic, the pH must be lowered and the sulfides must be deactivated by chemically converting the sulfide to a less reactive form (e.g. inert sulfur, insoluble metallic sulfide salts, soluble sulfates, etc.). Cresylic and naphthenic spent caustics reused as feedstock for the manufacture of cresylic or naphthenic acid are not considered a hazardous waste in the US.

With changes in environmental regulations and company philosophies concerning waste disposal, the current methods for disposal of spent caustic are being re-evaluated. A popular method involves sending spent caustic to companies such as Merichem or pulp and paper mills for caustic reuse or recovery of various constituents from the caustic. Sometimes this method provides a profit to the supplier. With the introduction of excess caustic in the market, reclamation companies may be reaching their limits. They have imposed stricter limits on the quality of caustic they will accept. If the caustic is below quality specifications, fees are incurred. These fees, coupled with transportation costs, sometimes exceed the sales price. Pulp and paper mills are also feeling the effects of stricter environmental regulations. In order to comply with government regulations, pulp and paper mills are changing their processes in order to reduce sulfur losses. This means their demand for spent sulfidic caustic is decreasing. Cost effective spent caustic management is a combination of existing process optimization, process modifications and treatment options, and review of disposal options, including direct sales opportunities. Because of the large amounts of spent caustic generated and possible hazardous waste implications, reducing amounts of spent caustic generated and reuse within the plant can be very attractive options.

Typical management methods used within ExxonMobil are listed in **Table 1**.

SELECTION OF A MANAGEMENT METHOD

Selection of a management method for caustic use and spent caustic reuse and/or disposal depends on characteristics of the site and the caustic. Many of the reuse options depend on units that are downstream of the spent caustic reuse / recycle point. For example, Slagen injects their spent caustic into the crude downstream of their desalter for pH control. This application is viable only for refineries that don't feed catalytic units with residuum due to possible catalyst poisoning from sodium. Spent caustic characteristics are very important in the selection of a management method. The major parameters that must be identified are COD, sulfides, mercaptans, and %NaOH. For example, COD is very important in the selection and sizing of wet air oxidation units. A medium pressure system can treat levels of COD in the 80,000 - 100,000 mg/l range and sulfides in the 10,000 - 40,000 mg/l range. High-pressure systems treat COD streams greater than 100,000 mg/l by diluting them with water to the 85,000 - 95,000 mg/l range. Sulfide levels are important for treatment methods such as chemical oxidation. Chemical oxidation is based on stoichiometric needs to oxidize the sulfides. Chemical oxidation may be an option for refineries or chemical plants that have a low COD and sulfide content whereas it is not economically feasible for high volume / high sulfide streams. Mercaptan levels can mean the difference between accepting a treatment method, accepting a method with modification and rejecting a method completely. Super critical water oxidation is not significantly affected by the presence of mercaptans, while wet air oxidation can treat mercaptans but may require raising the temperature to reduce foaming. Biotreatment currently cannot effectively treat mercaptan-containing streams. The degree to which caustic is spent prior to disposal or the level of NaOH present can also be a factor for choosing a management method. Spending caustic to a high level (< 1 - 3% caustic) can cause effluent pH in wet air oxidation to drop dramatically. This drop in pH will require neutralization to meet wastewater specs and careful selection of materials of construction to withstand dramatic pH swings. A list of common contaminants and their contribution to stream CODs is given in **Table 2**. "Typical" spent sulfidic caustic stream compositions are given in **Table 3**. These are for orientation purposes only, and it is essential to have an accurate characterization of spent caustic before selecting a technology or management method.

Figure 1 presents a hierarchy for spent caustic waste minimization/treatment. In order to determine what level a site is in the hierarchy, a flow sheet, **Figure 2**, presents a list of questions that will guide the user through the steps of spent caustic management. Because site and caustic characteristics are unique, **Table 4** is provided as a quick reference to narrow down possible options for a specific site. **Table 5** presents each option with a list of comparative parameters useful in determining the relative benefits and debits to each technology. These parameters include: pre-treatment, post-treatment, relative cost (H/M/L), applicability to all types of caustic, waste generated, material reuse, inherent problems in the process, and equipment involved. The specific caustic management tools available are discussed later in this document. **Figure 3** presents a methodology for conducting a site-wide caustic use optimization within refinery/petrochemical plants. Optimization encompasses the purchase, use, reuse, treatment, and/or disposal opportunities to reduce costs associated with the use of caustic in both onsite process units and offsite utility units (e.g., water and wastewater treatment facilities).

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MINIMIZATION OF SPENT CAUSTIC VOLUME

Minimization of spent caustic generation can be accomplished by two methods. Method 1 is to replace the caustic system with a system that will accomplish the same goal. Although this will eliminate the production of NaOH caustic, the alternative method may be more expensive such as the use of KOH or the method may produce a waste that is more difficult to handle such as a sponge iron system. While some of these methods are not as effective as caustic scrubbing, they can be coupled with caustic scrubbing to reduce the amount of caustic generated. The second method is to optimize the current caustic system. This can be achieved through techniques such as operator training and careful system monitoring.

H_2S REMOVAL BY AMINE PRE TREATMENT

Amine processes can be added as a pre-treatment in order to reduce the amount of spent caustic generated. This process removes relatively large quantities of H_2S but does not remove mercaptans. Amine processes typically use monoethanolamine (MEA) for refinery gas treating, although methyl-diethanol amine (MDEA) can also be used. Cold amine is injected into the top of an absorber while sour gas is injected counter currently. See **Figure 4**. The treated gas leaves the top of the absorber with typical H_2S concentrations of 10 - 15 ppm. The acid gases are absorbed into the amine stream and sent to a flash tank. In the flash tank, any dissolved or entrained hydrocarbons are vented from the system or skimmed from the amine. The stream is then heated and sent to a regeneration tower where the acid gases are steam stripped. The acid gases are sent to a sulfur recovery unit. Amine treating can offer spent caustic reductions of greater than 90% over caustic washing of H_2S without amine pre-treatment. Although the amine process requires additional capital expenditure, amine processes are currently installed in most plants owing to operating cost reductions. ExxonMobil licenses two solvents, FLEXSORB SE and FLEXSORB SE PLUS, which can be used in place of MDEA. Both these solvents have higher selectivity for H_2S, lower investment, lower solution recirculation rates and lower regeneration steam than MDEA. These solvents possess corrosion resistant and non-foaming properties.

UOP MEROX ® PROCESSES

UOP offers MEROX (MERcaptan OXidation) systems that reduce spent caustic generation by as much as 90%, as well as systems that utilize non-caustic alkalinity. Depending on the process employed and the product results desired, the Merox process is capable of treating feedstocks ranging from natural gas and LPG to distillate stocks with final boiling points as high as 650°F (340°C). The Merox process can be divided into two categories: extraction (mercaptan removal) and sweetening (mercaptan conversion).

Merox Liquid-Liquid Extraction

Merox liquid-liquid extraction systems are widely specified for the removal of mercaptans and sulfides from gas, LPG, light straight run and thermally cracked naphthas. The most common application of Merox liquid-liquid extraction is in the treatment of LPG, which typically has up to 5 wppm H_2S, in which a single, vertical, multistage, extraction column is typically specified. See **Figure 5**. In this process, the hydrocarbon stream enters the bottom of the tower. Caustic is introduced at the top and removes mercaptan as it flows counter currently. The product leaves the top and is virtually free of mercaptan and caustic. The caustic then flows to an oxidizer where the mercaptans are converted to disulfides and the caustic is regenerated. The effluent from the oxidizer goes to a disulfide separator where the disulfides are decanted and the regenerated caustic is sent back to the tower. The decanted disulfides can either be hydrotreated or sold. To reduce caustic spending on H_2S, LPG or gas caustic treatment is typically preceded by an amine system for bulk H_2S removal.

Mercaptan Conversion (Sweetening)

In this process, the mercaptans are converted to disulfides with no reduction of total sulfur in the hydrocarbon stream. It is typically used for heavy hydrocarbon streams such as gasoline and kerosene. There are two general categories of Merox sweetening, liquid-liquid and fixed-bed.

Liquid-liquid Sweetening

In this process, the hydrocarbon stream, catalyst containing caustic, and air are injected into the bottom of the tower. The catalyst in the presence of air, oxidizes the mercaptans to disulfides. Since mercaptan oxidation is essentially complete, the caustic phase does not carry mercaptans from the contactor and, therefore, does not require regeneration prior to recirculation. In earlier systems, the effluent was then sent to a separator to remove the caustic. However, in recent designs, the caustic is removed by a disengaging basket and the entire process can be accomplished in a single unit (see **Figure 6**). The major difference in liquid-liquid sweetening and liquid-liquid extraction is in sweetening, the mercaptans are converted to disulfides and are left in the hydrocarbon stream while in extraction, the mercaptans are first removed from the hydrocarbon stream before being converted to disulfides.

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MINIMIZATION OF SPENT CAUSTIC VOLUME (Cont)

Fixed-Bed Sweetening Processes

In this version of the Merox process, Merox catalyst is impregnated on a fixed bed of carbon. Sweetening is performed by passing a sour hydrocarbon stream containing dissolved atmospheric oxygen over the alkaline catalyst bed. All reaction chemistry is identical to the other Merox processes. There are two general classifications of fixed-bed sweetening systems, differentiated by the means of providing alkalinity to the system.

- **Conventional Fixed-Bed Sweetening**: In the basic, conventional fixed-bed sweetening process, a hydrocarbon stream, air, and caustic are mixed and introduced to a tower containing an alkaline catalyst bed (see **Figure 7**). As the mixture flows down over the bed, the mercaptans are oxidized to disulfides. The effluent is then sent to a caustic settler where the disulfides are decanted and either sent to a hydrotreater or sold. The caustic is recirculated for continued use. This process is well suited for treating jet fuel, kerosene, heavy naphtha, thermal gasolines, diesel, and distillate fuel oil. The process for jet fuel treating is slightly different from the basic process in order to meet product specifications (see **Figure 8**). A prewash is added to remove condensed water and naphthenic acids. Water removal is necessary to prevent dilution of caustic downstream. Naphthenic acids are removed to prevent the formation of sodium naphthenate salts, which foul and deactivate the catalyst bed. The reactor and caustic settler are the same as the basic system; however, in the jet fuel system, the reactor is followed by a post-treatment system. The post-treatment system consists of a water wash, salt filter, and clay filter to remove any water, oil-soluble surfactants, and organometallic compounds.
- **Minalk (MINimum ALKaline) Fixed-Bed Sweetening**: In the Minalk system, a very small stream of dilute caustic (several ppm) is continuously injected into the sour feed and withdrawn from the reactor bottom (see **Figure 9**). The effluent caustic is not only small in volume, but is largely neutralized both by the acidic compounds in the feedstock as well as by the air injected to supply oxygen. Thus, waste caustic disposal is both simple and direct (often directly to the wastewater treatment plant). Although, the caustic is not reused, the system uses less caustic than other systems due to the Minalk system's high efficiency. The Minalk process is typically used to treat FCC gasolines, natural gas liquids, and light straight run naphthas.

Caustic-Free Merox

UOP offers a “Caustic-Free Merox" system that uses a non-caustic alkaline. It offers the elimination of caustic consumption and disposal costs with a high-activity, non-caustic catalyst system, Merox No. 21 catalyst and Merox CF additive. The combination of this catalyst and additive enables weaker bases such as ammonia to achieve the alkalinity needed to direct the mercaptan reaction. The process is very similar to the Minalk process. The hydrocarbon stream is mixed with ammonia, Merox CF additive, and air (see **Figure 10**). The stream flows down the fixed bed containing Merox No. 21 catalyst and the mercaptans are oxidized to disulfides. The ammonia is easily separated from the hydrocarbon stream at the bottom of the reactor. The ammonia water stream can then be sent to the refinery sour water stripper. The advantage of this is that the spent alkaline solution is at roughly neutral pH, and so has low phenol levels (200 - 300 ppm). Where disposal of the spent caustic is a problem due to high phenol loading (COD), this alternative may be applied. Contemporary Minalk Merox units may be readily converted to caustic-free units if disposal requirements warrant. The caustic-free process has been applied to treatment of gasoline, kerosene, and jet fuel. Petro-Canada Inc.'s refinery in Oakville, Ont., near Toronto, converted its caustic-based UOP jet fuel Merox unit to a Caustic-Free Merox design in the mid-1990s to save on third party caustic disposal costs.

MERICHEM, INC. THIOLEX ®

Merichem Company offers their “Fiber-Film" technology adapted for caustic extraction of sulfidic compounds from gas, LPG, and virgin naphthas un containing Merox No. 21 catalyst **and the m**ercaptans are oxidized to disul**f**ides. The ammonia is easily separated from the hydrocarbon stream at the bottom of the reactor**.** The ammonia water stream can then be sent to the refinery sour water stripper. The advantage of this is that the spent alkaline solution is at roughly neutral pH, and so has low phenol levels (200 - 300 ppm the caustic strength. If the mercaptan sulfur content of the feed is high, extraction should be followed by a caustic regeneration system (“Regen") to allow the reuse of caustic (see **Figure 12**). This system catalytically oxidizes mercaptides to disulfide oils (DSO), which naturally separate (decant) from the regenerated caustic. The specific gravity difference between the DSO and caustic is slight, and traces of DSO may be back extracted to the hydrocarbon product stream. Where product sulfur specifications are very low, a naphtha wash at the DSO/caustic separator is recommended to reduce entrained sulfides to low ppm levels. Regenerated caustic is recirculated until the original caustic strength has been spent by approximately 10 - 20%. A small purge stream of spent caustic must continually be drawn off to allow for fresh caustic makeup. This spent caustic purge, containing only free caustic and sodium thiosulfate, may be used for H_2S removal where it can be spent up to 80%. As an example, a typical “Regen" unit treating some 440 gpm (980 m^3/hr) of light ends will require about 1 lb (0.45 kg) catalyst for 840k gal (3200 m^3) hydrocarbon treated, and will generate about 0.15 gpm (0.03 m^3/hr) of spent caustic, along with 100 - 200 SCFM (170 - 340 SCMH) of spent air that must be incinerated to convert organic sulfides to

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MINIMIZATION OF SPENT CAUSTIC VOLUME (Cont)

SO_2. Wash naphtha may be water washed and coalesced to obtain a material with less than 1 wppm of Na, which may be fed to a hydrotreater to convert the disulfides to H_2S and light ends. The primary treatment requirements for naphthas are that H_2S be removed virtually completely, while mercaptan sulfur must be below 10 wppm. The total sulfur specification will determine whether the mercaptans are extracted, or converted to disulfides by sweetening. Merichem offers their “Merifining" systems for mercaptan extraction to meet low total sulfur specs. “Mericat" sweetening systems are specified where total sulfur is less critical. Both systems have been designed to be caustic-regenerative.

OXIDATION OF H_2S TO ELEMENTAL SULFUR

Several different processes, such as Lo-Cat, Sulfa-check, Stretford Oxidation and sponge iron, convert H_2S to a solid form which can then be removed via settling or filtration. These processes do not remove CO_2; thus, in ethylene applications, a secondary treatment (i.e., caustic scrubbing) would be required. Lo-Cat uses an aqueous solution containing iron to absorb the H_2S from the hydrocarbon steam. The H_2S reacts with the oxidized iron to produce elemental sulfur. Stretford Oxidation, licensed by British Gas, selectively removes H_2S from gas streams with total sulfur recovery of > 99.9% and residual H_2S in the treated gas below 10 wppm. H_2S is removed with an alkaline solution, followed by the air oxidation of sulfides to elemental sulfur in the presence of a proprietary catalyst. Elemental sulfur is removed as a clean dry cake, the Stretford solution is regenerable, and an optional desalting unit can yield virtually zero liquid effluent from the process.

MOLECULAR SIEVES

Molecular sieves can be used in conjunction with amine systems or caustic scrubbing systems for removing hydrogen sulfide, mercaptans, carbonyl sulfides and moisture from light ends (C2 - C4). See **Figure 13**. Molecular sieves are porous inorganic solids that contain many micron-sized porous cubic zeolite (aluminosilicate) crystals. Because the pore-size is uniform and very precise, molecules can be separated by size. Molecular sieves remove sulfur compounds to extremely low levels but are not recommended for bulk removal of sulfur. High levels of sulfur exhaust the sieve quickly and, therefore, lead to short cycle times or a large sieve inventory. Neither option is attractive from an operating or economical standpoint. Recommended operating conditions are: feed rate 700 - 240,000 SCFM (1200 - 410,000 SCMH) pressure 315 - 1215 psi (20 - 80 atm), temperature 85 - 120°F (29 - 49°C), and H_2S content 0.022 - 5.5 lb/1000 SCF (0.35 - 88 kg/1000 SCM). Once sieves are spent, they can be regenerated by heating the sieves. During this process, sulfides and mercaptans are released in an off-gas which must be treated.

SWITCH FROM NaOH TO KOH

One alternative to eliminate the production of spent NaOH caustic involves switching from NaOH to KOH. This will not reduce the volume of spent caustic generated but it will now be in a form which can readily be reused as fertilizer. The chemistry involved with KOH is the same as NaOH. KOH is expected to remove CO_2 more completely than NaOH because it is less viscous than NaOH at a given molal concentration. KOH is 1.5 times more expensive than NaOH on a molal basis. Because the production of KOH, like NaOH, is tied to the manufacture of chlorine, KOH prices tend to rise and fall together with the price of NaOH. Spent KOH can be treated by neutralization with waste acid such as H_2SO_4 or HCl to produce K_2SO_4 or KCl, respectively. These salts, which act as fertilizers by supplying plants with potassium, could potentially be disposed of to the land. This allows sites not located on a saltwater body to dispose of their salts in an environmentally preferable manner.

CHANGES IN OPERATING PRACTICES

Optimization of Existing Processes

Optimizing the available hydroxide (causticity) left in the caustic is a low-cost option to minimize the volume of spent caustics. Often, significant reductions in caustic use and improvements in caustic exhaustion levels can be achieved simply through operator training, improved awareness, and attention to operating parameters. Inefficient contacting and inadequate contacting times will lead to non-optimum exhaustion of the available caustic alkalinity. Optimization will also produce spent caustic which contains larger concentrations of sulfides and acid gases. It is possible for high levels of constituents to reduce the quality of caustic below reuse or resale requirements; therefore, it is necessary to evaluate the optimum level of spending caustic.

The use of caustic titration (performed locally in a bench test, or with automatic on-line equipment) may be used to optimize caustic feed, and to ensure that excessive free alkalinity is not wasted when the caustic is purged. Consideration should also be given to increasing the strength of the fresh caustic stream used. This will reduce the volume of spent caustic production. However, higher concentrations may reduce contacting efficiency due to higher viscosity.

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MINIMIZATION OF SPENT CAUSTIC VOLUME (Cont)

Segregation of Spent Caustic

Since the reuse, treatment, and disposal options for a given spent caustic greatly depend on the concentration of residual free alkalinity in the waste caustic stream as well as composition, care should be taken when handling and storing spent caustics. Mixing of dissimilar caustics could limit treatment options, increase treatment and disposal costs, or degrade the reuse options or the resale value of spent caustics. For example, refineries that combine sulfidic caustic with cresylic caustic from Merox and Minalk units, could segregate these streams and possibly send the cresylic caustic to the wastewater treatment system. Currently, Rotterdam and Sriracha send their Merox and Minalk cresylic caustic to the wastewater treatment system. The combined stream cannot be treated at the wastewater facilities due to odors associated with sulfides and mercaptans in the sulfidic caustic.

CASCADED REUSE OF SPENT CAUSTIC

The strength, purity, and composition of caustic required for a given treatment, or generated by a treatment process varies widely. Quality of caustic will depend on both the product being treated and the type of treatment system being employed. An effective strategy to reduce the use of fresh caustic and minimize the generation of “end-of-pipe" spent caustics is to carefully match caustic treatment needs with available spent caustics being generated.

DIRECT REUSE FOR HYDROCARBON PRODUCT TREATMENT

Mercaptan removal depends on high free alkalinity dictating use of fresh caustic. Spent caustic from mercaptan treating is well suited for reuse in H_2S removal since it does not require as large an amount of free alkalinity. Spent mercaptan caustics should not generally be used for the removal of high-levels of hydrogen sulfide due to the low level of free alkalinity, but are very effective for low levels. Baton Rouge Refinery uses fresh caustic in several extraction towers, after amine treating for H_2S, to remove mercaptans from cat light ends. Spent caustic from these towers is used to remove mercaptans and sulfides from virgin light ends. However, reuse may reduce the resale value of a caustic. For example, cresylic sales for phenols recovery require low loads of sodium sulfide.

INJECTION INTO CRUDE

Spent caustic can be injected directly into the crude downstream of the desalter and upstream of the pipestill for pH control. Care must be taken to prevent sodium poisoning of catalyst for refineries with units such as Cat Crackers or Hydrofiners. Typically, US refineries have these units; therefore, this is not recommended for operations in the US. However, this is a possible option for a few selected non-US affiliate refineries. EMRE experts should be consulted to determine sodium limits for various catalyst operations. Slagen Refinery currently injects spent caustic into their crude.

pH CONTROL IN SOUR WATER STRIPPER

Spent caustics (sulfidic and cresylic spent caustics) containing low-molecular weight mercaptides, hydrogen sulfide and phenols may be sent to sour water strippers under certain conditions. Sour water strippers remove hydrogen sulfide and ammonia from sour waters and sour condensates. Stripped components are incinerated or sent for sulfur recovery, while the aqueous effluent is sent for further wastewater treatment (e.g., BIOX) prior to discharge. Acidic conditions favor the removal of H_2S, while alkaline conditions favor the stripping of ammonia. Thus, tower design and operating pH is determined by the feed compositions and the required effluent standards. Thus, the addition of spent sulfidic caustic could enhance ammonia strippers while caustic addition to H_2S strippers may decrease performance. Caustic can be added in one of two places, in the feed or between 6 - 8 actual trays. Spent caustic can only be substituted if it is added with the feed. Care must be taken when adding caustic to prevent overshooting the desired pH.

According to MEFA, mercaptans strip similarly to H_2S with no adverse effects on stripper performance. Phenols, though exhibiting weakly acidic properties, are also reported as having no adverse effect on performance. Spent caustic should not carry oils which can cause foaming or aromatics. Before adding spent caustic to the sour water stripper, EMRE experts should be consulted to evaluate feasibility and optimum pH and operating conditions. High dissolved salt levels attributed to spent caustic can lead to fouling and/or deposits within the stripper tower.

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CASCADED REUSE OF SPENT CAUSTIC (Cont)

pH CONTROL IN BIOLOGICAL OXIDATION (BIOX) UNIT

In a BIOX unit, oxidation of organics and (especially) ammonia reduces the alkalinity/pH of the system. pH levels below 6.5 are inhibitory to the microorganisms. Fresh caustic is typically used to maintain the optimum pH; however, spent sulfidic caustic can be substituted as a source of alkalinity. It should be noted, spent caustic must be applied to a BIOX unit at such a rate that mercaptides and sulfides present are biologically oxidized rather than released to the atmosphere. Spent caustic is characterized as having high BOD and COD levels, therefore, adequate aeration must be supplied to maintain a dissolved oxygen (DO) level of 2.0 mg/l or greater. Reduced sulfur compounds can result in filamentous bulking bacteria, which can negatively impact the performance of the BIOX system. Care must be taken when adding spent caustic in order to avoid "shocking" the BIOX system. Non-sulfidic caustics should not be used due to the presence of potentially toxic or inhibitory organic compounds and/or heavy metals. Antwerp, Bayway, Singapore and Slagen Refineries are examples of refineries using spent sulfidic caustic for BIOX pH control. Refer to the Biological Treatment section of this DP beginning on page 13.

pH CONTROL IN PIPESTILLS

Corrosion in pipestills is caused by HCl. Spent caustic can be injected into pipestills in order to neutralize the pH and reduce corrosion. Care must be taken to avoid the fouling of preheat heat exchangers, avoid pH swings, and comply with sodium specifications of pipestill residues. As mentioned above, EMRE experts should be consulted before adding spent caustic to avoid sodium poisoning of catalyst operations downstream. Spent caustic can cause upsets such as foaming in pipestills.

INJECTION OF SPENT CAUSTIC IN FCCU WET GAS SCRUBBERS

Wet gas scrubbers (WGS) are used to control particulate and gaseous emissions from FCCU (Fluidized-bed Catalytic Cracking Unit) regenerators. The WGS removes particulates by washing the flue gas stream with droplets of buffered scrubber liquid, while the SO_2 is removed by reaction with the solution. In order to increase the removal of SO_2 and to mitigate the corrosive effects, caustic or soda ash is continuously added to the recirculating scrubbing liquid to adjust its pH to the desired level (about 6.7). WGSs operate in an oxidizing atmosphere and at near-neutral pH. If spent sulfidic caustic is injected directly, conditions favor the release of mercaptides and sulfides as mercaptans and hydrogen sulfide gas, leading to emissions problems. Thus, it is necessary that sulfides and mercaptides be removed by a caustic scrubbing system or converted to thiosulfates and sulfates using a thermal oxidation system to facilitate the recycle/reuse of the caustic strength for pH control at the WGS. Baton Rouge and Baytown send oxidized spent caustic to the WGS.

REUSE AS FEEDSTOCK FOR OTHER INDUSTRIES

Once on-site reuse options have been exhausted, the next waste management option is to send the spent caustic to other industries to reuse in their processes. This option depends on the proximity to appropriate industries and their willingness to accept the stream.

PULP AND PAPER INDUSTRY

The paper industry uses the caustic and the sodium sulfide remaining in spent sulfidic caustic for the digestion of paper pulp in the Kraft pulping process. In the absence of spent caustic, paper mills begin with fresh caustic and salt cake to produce sodium sulfide. However, the outlook for this outlet for sulfidic caustic does not look promising. As environmental discharge restrictions on the paper industry have increased, chemical reuse within the industry has reduced the purchase of spent refinery caustic. Mills are switching to ClO_2 to replace sulfur in the pulping process. There is also environmental pressure to reduce the amount of chlorine used in the paper making process. If chlorine is totally eliminated from the bleaching process, demand for sulfidic spent caustic may begin to increase.

ALUMINA INDUSTRY

Baton Rouge Chemical Plant sends a portion of their spent caustic to Kaiser Gramercy for reuse in their alumina process. This is limited to spent caustic used to treat spent aluminum chloride catalyst. The spent stream is high in sodium aluminate. The Chem Plant receives a credit, but this outlet is very unstable. In addition to the viability of the alumina business being suspect, Kaiser has on several occasions, rejected caustic on the basis of odor and poor quality.

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REUSE AS FEEDSTOCK FOR OTHER INDUSTRIES (Cont)

CHEMICAL MANUFACTURING

Merichem

Merichem (Houston, Texas) handles all types of spent caustic. Mercaptans found in cresylic and naphthenic caustic are oxidized to form disulfides and are sold as a rubber solvent in the rubber industry and are also used as a raw material in the manufacture of sulfuric acid. The sodium cresylates found in cresylic spent caustic are used to produce cresylic acid products. Sodium naphthenate found in naphthenic spent caustic is used to produce naphthenic acid products. Sulfidic spent caustic is blended with other sulfidic caustic and sent to pulp and paper mills. Depending on the type and quality of caustic, refineries can either sell caustic at a profit (includes cresylic spent caustic and naphthenic spent caustic) or pay Merichem to take it (includes sulfidic spent caustic). However, it is necessary for the spent caustic to meet Merichem specifications.

Merisol, a joint venture between Merichem and SASOL, also reprocess spent cresylic caustics.

Americhem

Torrance Refinery sends spent caustic to Americhem in California for processing.

Hewchem

Hewchem, which is located on the coast of Mississippi, accepts only naphthenic caustic. Naphthenic caustic is used to produce naphthenic acid. Specifications were reported to include: no limit on BOD or COD and 5% minimum naphthenic acid in the stream.

CRI-MET

CRI-MET, located in Braithwaite, LA, accepts all types of spent caustic. Specifications for caustic are not fixed, and each spent caustic is evaluated individually. The spent caustic is used as a replacement for fresh caustic soda in the production of alumina trihydrate.

Penrice Soda Products

Adelaide Refinery ships spent caustic to Penrice Soda Products (Osborne, South Australia) for reuse.

TREATMENT AND REGENERATION

The next step in the hierarchy is treatment and regeneration. This involves regenerating the caustic partially or completely so that it may be used again in the gas treating process or another part of the refinery or chemical plant.

MEROX / MINALK

In addition to regenerating caustic, the Merox system offered by UOP also minimizes the production of spent caustic. A detailed description of this process can be found under the Minimization of Spent Caustic Volume section.

THIOLEX / REGEN

In addition to regenerating caustic, the Thiolex / Regen system offered by Merichem also minimizes the production of spent caustic. A detailed description of this process can be found under the Minimization of Spent Caustic Volume section.

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TREATMENT AND REGENERATION (Cont)

SHELL AIR OXIDATION

Baton Rouge and Baytown operate low-pressure oxidation systems offered by Shell for treating and partially regenerating sulfidic spent caustic. In Baton Rouge and Baytown, the oxidation unit treats both refinery and chemicals spent caustic. The oxidation unit, known as SCOLA, in Baton Rouge is located at and operated by Baton Rouge Chemical Plant. The unit treats caustic at a rate of 60 gpm (13.7 m^3/hr) consisting of 10 gpm (2.3 m^3/hr) Chemical Plant sulfidic caustic and 50 gpm (11.4 m^3/hr) Refinery caustic. Excess refinery caustic is sent to Merichem. In the SCOLA unit, caustic is mixed with air at a pressure of 90 psi (6 atm) and is heated to approximately 180°F (82°C). See **Figure 14**. Here, the sodium hydrosulfide and sulfide are converted to sodium thiosulfate and the mercaptans are converted to dimethyl disulfide or ethyl-methyl disulfide with partial regeneration of the NaOH as seen in the following equations:

$$2NaHS + 2O_2 \rightarrow Na_2S_2O_3 + H_2O \qquad \text{Eq. (1)}$$

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH \qquad \text{Eq. (2)}$$

$$Na_2S_2O_3 + 2NaOH + 2O_2 \rightarrow 2Na_2SO_4 + H_2O \qquad \text{Eq. (3)}$$

$$2CH_3SNa + \frac{1}{2} O_2 + H_2O \rightarrow CH_3 - S - S - CH_3 + 2NaOH \qquad \text{Eq. (4)}$$

$$CH_3CH_2SNa + CH_3SNa + \frac{1}{2} O_2 + H_2O \rightarrow CH_3CH_2 - S - S - CH_3 + 2NaOH \qquad \text{Eq. (5)}$$

Note that caustic is actually consumed in driving the thiosulfate to the sulfate form (**Eq. 3**). By limiting the conversion of sulfides predominantly to the thiosulfate form, the Shell Air Oxidation is a net producer of NaOH (**Eq. 2**). The partially regenerated caustic is reused for pH control in the Wet Gas Scrubber. The disulfides are very odorous and must be removed in order to prevent complaints. Baton Rouge has installed a thermal oxidizer to burn the disulfides to sulfur dioxide. The sulfur dioxide is removed from the gas stream with a caustic scrubber. The caustic scrubber effluent is sent to the wastewater treatment plant.

The oxidation unit (COU) at Baytown Refinery operates on the same principle, however, their tower operates at a pressure of 100 psi (7 atm) and temperature of 200°F (93°C) and a flow rate of 70 gpm (16 m^3/hr). Baytown also sends their regenerated caustic to the WGS for pH control. If the stream cannot be sent to the WGS, it must be neutralized before sending to the wastewater treatment plant. It should be noted that this stream will still have a high COD due to thiosulfates and may require further treatment if the WWTP cannot handle the COD level. If the WGS cannot take the caustic, Baytown sends the caustic to their Effluent Neutralization Unit (ENU) where it is used to neutralize spent acid wastewater from Rhone-Poulenc and subsequently to the sewer.

Fouling in the reactor is common in this system. Baton Rouge has installed a skimmer upstream of the SCOLA to remove hydrocarbons such as olefins which has helped reduce fouling. However, the system must still be taken off line every three months for cleaning. Fouling is more frequent if chemical plant caustic is increased and refinery caustic is backed out. Baytown also experiences fouling in their reactor to a lesser degree. Typically, the COU must be taken off line once a year for maintenance. Baytown has also found that olefins in the chemical plant caustic stream contribute to the fouling problem. In order to avoid odor problems, steam and air flowrates are adjusted. If this is not effective, the feed rate is reduced until the odor is eliminated.

Heritage Mobil has developed a catalytic low temperature / low pressure process for air oxidation of sulfidic spent caustic. The process employs a copper catalyst on a fixed carbon bed. Reaction conditions are 40 psi; 212°F; 1 liquid hour space velocity (LHSV); 2 ppm Cu^{++} co-feed; 600:1 volume/volume air:caustic for solutions containing 2-3 wt% sulfide; cocurrent air and caustic feed; and downflow operation. Limited conversion of sulfides to sulfate occurs. In high sulfide systems, the preferred route is thiosulfate formation due to both the availability of sulfides and oxygen mass transfer limitations. At high sulfides dilution is required. Sulfides are nominally non-detect in the treated effluent (> 99 % removal of sulfides; > 90 % removal Of RSH). Pilot studies have been conducted on Houston Olefin Plant spent caustic feed containing 0.25 wt% $S^=$, and on Beaumont Refinery spent caustic containing 2.3 wt.% $S^=$. No commercial applications have been installed.

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TREATMENT AND REGENERATION (Cont)

ELECTROLYTIC REGENERATION

The electrolytic regeneration process uses electrical current to dissociate molecules and ion selective membranes to separate, concentrate, and purify selected ions from the aqueous mixture. Several methods of electrolytic regeneration have been proposed. One method which was researched in 1978 by heritage Exxon, involves electrolysis. In this process a three-compartment (see **Figure 15**) or two-compartment system (see **Figure 16**) is used based on the method of pre-treatment. Pre-treatment is needed in order to eliminate pH changes and oxidation reactions that will inhibit current efficiency. Carbonated caustic is sent to a two-compartment electrolytic cell that contains a single membrane that is selectively permeable to cations (Na^+). The sodium carbonate enters the system and dissociates. The Na^+ ion migrates across the membrane to the cathode where it reacts with OH^- to form NaOH. This process produces a high-purity caustic, which is diluted to about 10% strength. On the anode side, the carbonic acid radical breaks down to form carbon dioxide and oxygen. A three-compartment cell containing an anionic and a cationic membrane is used for the neutralized caustic stream. In this process, the sodium sulfate enters the center compartment and is dissociated. The sulfate ion crosses the anionic membrane to the anode compartment and forms sulfuric acid. The sodium ion crosses the cationic membrane to the cathode and forms NaOH. In addition to forming reusable products, electrolytic regeneration is also beneficial to plants that must limit solids, specifically salts, in their effluent. Electrolytic regeneration are marketed by Huron Tech Corp. and by Ionsep Corporation. The technology has had some application in the metal plating industry; there have been no commercial applications within the petroleum industry.

Aqualytics, a division of Graver, uses a bipolar membrane to split water molecules into ions. These hydrogen (H^+) and hydroxyl (OH^-) ions combine with oppositely charged salt ions to form an acid and a base. This technology has not been applied to refinery and petrochemical spent caustic, although it has been used for the concentration of dilute base streams and the recovery of alkali from other industrial rinse waters. Theoretically, this process would produce sodium hydroxide and sulfuric acid. The spent caustic must be neutralized using fresh or waste acid before it can be used in the Aqualytics system. Untreated spent caustic cannot be regenerated in this system for three reasons: H_2S degradation of the membranes, reduced efficiency due to gas evolution, and potential of mercaptide salts to form elemental sulfur or disulfide oil. Aqualytics has indicated that based on their past experience with caustic streams, if spent caustic disposal presents a problem for a site and significant amounts are generated (> 2000 tons/yr (> 1800 tonnes/yr)), it is possible the process would be economically feasible. At present, Aqualytics has no plans to extend their technology to the spent caustic market. In order to determine if this option is technically and economically feasible, pilot testing would be necessary. Like the heritage Exxon electrolytic regeneration process, the Aqualytics system should be considered for plants that must limit solids in their effluents.

TREATMENT AND DISPOSAL

The final option to manage spent caustic is to treat the stream so that it can be readily disposed.

FLUE-GAS CARBONATION

Flue-gas carbonation is essentially a neutralization and stripping process. Carbon dioxide from a flue-gas source, such as the off-gas from a FCCU regenerator, neutralizes the sulfidic spent caustic, releasing H_2S and mercaptans to the off-gas. The off-gas concentrations of H_2S are too low to justify sulfur recovery and so are typically incinerated or sent to a sponge iron system. The carbonation process can be a batch or continuous process.

Nanticoke operates a batch operation. See **Figure 17**. In this process, 3000 - 4000 US gal (11 - 15 m^3) of spent caustic is contained in a vessel and flue gas is injected until the caustic achieves effluent standards. Sulfide levels and ammonia levels are each less than 50 ppm in caustic (< 10 ppm to WWTP). pH of the neutralized caustic is less than or equal to 9. The caustic is then slowly trickled into the sewer with water and off-gas is sent to their CO Boiler. This operation treats their alkylation caustic from the H_2SO_4 alkylation unit, phenolic caustic from the Merox system and sulfidic caustic from the light ends treating. There have been some operating problems with this unit, including corrosion in the tower, foaming in the system with the foam carrying over to the CO Boilers, entrainment, and glassy deposits in the CO Boiler. Improved metallurgy is expected to correct the corrosion problems while the foaming, entrainment, and deposits are not fully understood and are being studied.

Qenos (formerly Kemcor) uses a continuous carbonation process under license from Hyperno Pty., Ltd. (Australia) with four carbonation stages. See **Figure 18**. The process uses combustion gases drawn from the stacks of two boilers that burn natural gas and plant gas. The flue-gas is cooled in an air fin heat exchanger prior to being sucked into the first of a number of eductors where it and the spent caustic are intimately mixed. Flue-gas and spent caustic pass through the reaction stages in a counter-current fashion. The flue-gas flows from the top of one reactor to the section of the jet compressor on the next reactor while the spent caustic solution flows between the reactors under level control. The hydrogen sulfide and mercaptans in the off-gas reacts with Sulfatreat, which is an iron compound to form iron pyrite which is landfilled at a non-hazardous waste landfill. The residual tail gas is sent to an on-site furnace. Because the carbonation system is mild in terms of temperatures, pressures, and acid strength, the fouling problems experienced with sulfuric acid neutralization are not incurred.

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