U.S. EPA HPV Challenge Program

Category Assessment Document for

Acids and Caustics from Petroleum Refining Category

- Tar acids, cresylic, sodium salts, caustic solutions (CAS No. 68815-21-4);
- Neutralizing agents (petroleum), spent sodium hydroxide (CAS No. 064742-40-1);
- Phenols, sodium salts, mixed with sulfur comp; gasoline alky scrubber residues (CAS No. 68988-99-8);
- Sludges (petroleum), acid (CAS No. 064742-24-1).

Submitted by:
American Petroleum Institute
Petroleum HPV Testing Group

American Petroleum Institute
1220 L Street NW
Washington, DC 20005

Consortium Registration # 1100997

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CATEGORY ASSESSMENT DOCUMENT
Acids and Caustics from Petroleum Refining

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Plain Language Summary

An assessment was performed to evaluate the adequacy of existing information on four materials in the acids and caustics reclaimed substances category. Data pertaining to the composition, physical properties, environmental fate, ecotoxicity, and health effects were each evaluated to determine if additional studies were needed to more fully characterize the fate and hazards of these materials. Information was collected from textbooks, government reports, peer reviewed publications and product literature to get a collective picture of these substance, their primary sources, and their potential to cause harm. The assessment indicates that additional testing of the substances in this category is unnecessary in each of the focus areas examined. It is concluded that further testing of these substances would be an ineffective use of resources and would yield ambiguous results.

All four materials have a long association with the refining of petroleum, and more specifically with the extraction of constituents from petroleum products such as fuel gases, kerosene, and gasoline. The four substances in this category are not used in consumer products and are not a source of human exposure or environment release. The substances are all highly corrosive with three of the solutions containing high concentrations of sodium hydroxide and one solution containing high levels of sulfuric acid. Although these substances have traditionally been thought of as waste streams, many of the key organic and inorganic components are often recovered and reused. Those portions of the waste stream not reclaimed are treated and disposed of in an appropriate manner that can include oxidation and discharge to a waste water treatment plant or incineration.

The three caustic substances in this category are generated when different petroleum streams are purified or "sweetened" to remove undesirable constituents such phenols, cresols and mercaptans. The forth substance, acidic sludge, is a byproduct of petroleum alkylation and contains a high percentage of sulfuric acid along with various hydrocarbons and suspended sediment. One of the substances, a caustic tar solution, is a highly valuable waste product that can be processed into cresylic acid. Because of the extremely corrosive nature of these substances, they are handled and disposed of with particular care and diligence.

Available information shows these materials to be a highly heterogeneous group of materials whose composition can very dramatically depending on their specific source and the particular types of crude oil being processed. Given these characteristics and the fact that their physical properties are directly dependant upon the dissolved constituents they contain, there are no unique sets of chemical or physical properties that can be ascribed to these materials. Likewise, because the substances exist as aqueous liquids with low vapor pressure, they will not volatilization to air and their distribution will be limited to water and soil. Many of the individual constituents will biodegrade in the environment if there is sufficient buffering capacity to neutralize the excess acid or base in the mother liquor. Because each of the four substances can contain dozens of individual organic chemicals that can occur in myriad of different combinations, testing a particular sample will not be predictive of the entire class and will likely over or under predict the behavior of other samples. Consequently, additional property testing is not likely to yield any new or valuable information. This is in agreement with an earlier decision

by the EPA that found testing of substances in the acid and caustics category to be pointless and impractical (Hernandez, 2004).

Table 1. Matrix of Available Data

HPV Endpoint	Caustic Streams			Acidic Stream
	68815-21-4	64742-40-1	68988-99-8	64742-24-1
Physical-Chemical Properties Melting Point Boiling Point Vapor Pressure Partition Coefficient Water Solubility	These substances are highly variable, corrosive, aqueous mixtures that exist in a liquid phase at relevant environmental conditions. Measuring the physical-chemical endpoints for these substances would not reveal meaningful data due to their complex and variable nature.			
Ecotoxicity Acute Freshwater Fish Chronic Freshwater Fish Acute Freshwater Invertebrate Algal Growth Inhibition	The ecotoxicity of these substances will reflect their extreme pH and corrosivity. Testing of aquatic organisms is not appropriate for these substances and would not provide meaningful data. Potential hazards should be assessed in accordance with the information available for the main corrosive components: sodium hydroxide and sulfuric acid. No testing of these category members is necessary.			
Environmental Fate Biodegradation Stability in Water Photo degradation Transport and Distribution	Environmental fate characteristics for these substances will be defined by the individual components within the mixtures. In the environment, components will partition, distribute, and degrade independently of one another in accordance with their own properties.			
Mammalian Toxicity Acute Repeat-dose Reproductive/Developmental Genotoxicity, *in-vitro* Genotoxicity*, in-vivo*	The mammalian toxicity of these substances will reflect their extreme pH and corrosivity. Animal or genotoxicity testing is not appropriate for these substances and would not provide meaningful data. Potential hazards should be assessed in accordance with the information available for the main corrosive components: sodium hydroxide and sulfuric acid. No testing of these category members is necessary.			

The ecotoxicity and health effects of the acidic and basic substances in this category are dominated by the corrosiveness of the mother liquor. It is a well accepted and documented fact

that strongly acidic and caustic solutions are highly toxic to all manner of plants and animals. It is this property that dominates any consideration of additional testing for these materials. Although each of these acidic and basic substances contains organic compounds that possess their own intrinsic hazard potential, any toxicity testing of the constituents would require neutralization to remove the excess acid or base. This "springing" of the dissolved organics would result in the creation of an immiscible liquid layer that would not be representative of the chemical mix in the original sample. As summarized in Table 1, given these considerations and others centering on animal welfare and sample variability, no further testing is necessary for any of the substances in this category.

1. Introduction

Four separate types of reclaimed substances have been grouped together in this category assessment and review. All four substances are a product of petroleum refining and are extremely corrosive with a highly variable organic composition. Three of the solutions are caustic and contain high levels of sodium hydroxide; whereas a single solution is an acidic mixture with high levels of sulfuric acid. Each substance contains a wide variety and an ever varying amount of organic constituents extracted from individual petroleum fractions. The most commonly encountered chemicals are contained in four classes that include the phenols, cresols, xylenols, and mercaptans. The materials are all acidic substances that are easily extracted as their sodium salts by washing with a strong basic solution. This process can be depicted by the following reaction equations, where R represents a short chain alkyl group and Ar an aromatic ring.

$$RSH \ + \ NaOH \ \rightarrow \ NaSR \ + \ H_2O$$

$$ArOH + NaOH \ \rightarrow \ ArONa + H_2O$$
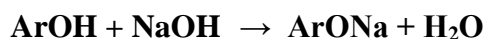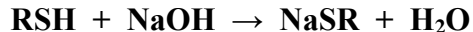
Acidic and caustic treatment of hydrocarbon streams is essential to the production of petroleum products. Solutions of sodium hydroxide and concentrated sulfuric acid are used in large volumes in most modern refinery operations to accomplish several important enrichment or purification steps. These acidic and basic mixtures are largely recovered and reused in a continuous cycle, but as the strength of the solution weakens, small amounts are removed from the circulation so that the solutions can be recharged and replenished with fresh reagent. Three of the four substances in this category review are spent materials; whereas the forth is a caustic extract used to initially purify petroleum feedstocks. The four materials that are topic of this category review include:

1. *Caustic tar acids* - Tar acids, cresylic, sodium salts, caustic solutions (CAS No. 68815-21-4);

2. *Sulfidic caustics* - Neutralizing agents (petroleum), spent sodium hydroxide (CAS No. 064742-40-1);

3. *Phenolic caustics* - Phenols, sodium salts, mixed with sulfur comp; gasoline alky scrubber residues (CAS No. 68988-99-8);

4. *Acidic sludges* - Sludges (petroleum), acid (CAS No. 064742-24-1).

The substances in this category have traditionally been thought of as waste streams with no inherent value. This is no longer the case, however, and a large percentage of the materials in this category are recycled. The substances, however, have no value in their native state and are not sold for use in any commercial product. Today, spent caustics can be recycled to recover the sodium hydroxide and the individual organic constituents, which can be used as feedstocks for the manufacture of phenolic resins, herbicides, enamel solvents, antioxidants, wood preservatives, paint and ink driers, and fuel additives (Merichem, 2007).

Table 2. Chemical Characteristics of Spent Caustic Solutions

Property	Typical	Lowest	Highest
Chemical Oxygen Demand (COD mg/L)	10,000 to 100,000	3,000	200,000
Biochemical Oxygen Demand (BOD mg/L)	5,000 to 50,000	1000	10000
Total Organic Carbon (TOC mg/L)	1,000 to 5,000	300	10000
Sulfides (mg/L)	5,000 to 35,000	500	72000
Acid Oils* (% w/w)	0.5 to 8	0.5	34
Phenol (mg/L)	0 to 2,500	BDL[#]	80000
Cresols (mg/L)	0 to 2,500	BDL[#]	80000
Naphthenates (ng/L)	100 to 2,000	BDL[#]	5000
Volatiles (mg/L)	50 to 1,000	100	5000
Semi-Volatiles (mg/L)	500 to 2,500	100	80000
Heavy Metals (mg/L)	BDL to 5	BDL[#]	25
Residual Caustic (%)	3 to 8	0.5	22

[#]   BDL below detection limit of 0.5 mg/L
*   values observed when the measurements are above the detection limit of 0.5 % v/v

Table 2 shows the most salient properties of two types of spent caustics: sulfidic and phenolic (TTC, 2009). The solutions typically have a high chemical and biochemical oxygen demand as a result of all the dissolved organics. These include the chemical classes mentioned earlier as well as appreciable quantities of volatile hydrocarbons and semi-volatile materials that can include xylenols and other high molecular weight phenols. Although the compositions of

these solutions can be quite complex their most dominating feature is the high alkalinity and corrosivity. Ultimately, it is this feature that overrides all others when considering the actual health and environmental hazards that these materials possess.

The complete list of on-site management options for the acids and caustics in this category include: i) treatment of the caustic with subsequent disposal; ii) reuse of the caustic as a neutralizing agent for acidic wastewater streams; iii) recycle of particular spent caustic streams for use elsewhere in the refinery; iv) disposal "as-is", and; v) storage. In practice, spent caustic may be managed by several different methods within a facility and throughout the industry (Heritage, 1992).

An appreciable amount of caustic waste is generated inside refineries where Merox® units are used for sweetening the petroleum streams. The Merox unit uses a basic solution of caustic soda as an extracting solvent, which is recycled and reused in a continuous loop following each use (Dziabis, 2004). These units can be used to extract phenolic as well as sulfidic materials. The mercaptans from Merox units can be oxidized to disulfides, which are separated from the caustic soda solution. The final disulfide oil is then either disposed of on site or processed as: i) an internal fuel; ii) a feedstock for sulfuric acid production; or iii) an agent for conditioning refinery catalysts.

EPA has reviewed the production, handling, and recycling of these substances under its Hazardous Waste Management System (EPA 1998). EPA had "… previously excluded from the definition of solid waste spent sulfuric acid used to produce virgin sulfuric acid (40 CFR 261.4(a)(7)). The Agency reexamined this exclusion as it pertains to sulfuric acid used as a catalyst in refinery alkylation processes and found no reason to change the existing regulatory structure."   In that same notice, EPA finalized "… the exclusion proposed for spent caustic solutions from petroleum refining when used as feedstocks to produce cresylic or naphthenic acid." This new exclusion was added at 40 CFR 261.4(a)(19).

2. Category Description

The four reclaimed substances in this category include three caustic solutions and a single acidic mixture. Each contains a host of constituents that are always present and typify the material class. The most commonly encountered chemicals include alkyl mercaptans and simple phenolics along with hydrogen sulfide and various hydrocarbons from mixed chemical classes. The amount of each individual chemical is highly variable with the levels showing little batch to batch consistency, except in broad categorical terms. Although the four substances are not pure materials, they have been grouped together into a single category for purposes of this review because they share several physical, chemical, or toxicological characteristics that justify their examination as a group of materials with a common level of concern. These properties include the following characteristics:

  i)   each of the substances is highly corrosive due their high acid or base concentration and corresponding extremes in pH;

  ii)   the substances are all complex mixtures with a highly variable composition that cannot be reliably or consistently defined;

iii)   the substances are amorphous and do not posses a unique set of physical properties that can be reliably determined;

iv)   the solutions and their solutes are known by experience to be highly toxic to both humans and aquatic species;

v)   the materials are all reclaimable substances that are produced at a particular stage of the refining process, then either recycled on site, sold for recovery, or treated for disposal.

vi)   There are no consumer uses or sales to children of these substances.

A typical spent caustic solution from a petroleum refinery is extremely corrosive and may contain up to 15% (w/w) sodium hydroxide with varying but appreciable quantities of organic compounds such as mercaptans, sulfidic oils, naphthenic acids, cresylic acids and their derivatives (Heritage, 1992). In addition, the spent solution may contain may contain approximately 5% to 20% of a heterogeneous oil mixture. Long ago, a majority of these spent solutions were considered to be useless waste streams requiring significant processing before final disposal. The modern approach to spent caustic disposal has incorporated the principle of resource recovery and has taken advantage of the monetary value in the isolatable chemicals.

The acids and caustics examined in this category review serve multiple purposes in the refining of petroleum products, the most import of which are acid neutralization, desulfuration, and alkylation. Figure 1 shows an idealized petroleum refining operations and depicts several of the more important operations where corrosive waste solutions are generated. To understand and fully appreciate the implicit hazards and fates of the corrosives covered in this assessment, it is instructive to first review the refining process and to examine the generation and use of acids and caustics in different operation (EPA, 1996a).

3. Substance Descriptions and their Sources

This section provides a more detailed discussion of the four acidic or basic substances in this category review. The description provides a more comprehensive picture of the sources and ultimate fates of these materials and allows a greater appreciation of the complexity and variability that is the hallmark of these materials.

A.   Caustic Tar Acid Streams (CAS No. 68815-21-4)

Tar acid is a generic term that refers to a mixture of phenols and cresols that can be extracted from any of a variety of hydrocarbon feedstocks, including coal tar distillate, crude oil, or coal gasification products (Strunk and Wells, 1999). The phenolic compounds in tar acids are weak acids, which require a relatively strong aqueous caustic solution for extraction. The tar acid extracts from crude oil are generally derived from the treatment of cracked naptha streams with caustic concentrations of 10% or greater (Gallo *et al*., 1952). Caustic tar acid recovery streams are a valuable commodity that can be shipped off site if necessary for recovery and purification of the cresylic acid constitutions. The recovered cresylates have a variety of important commercial

uses as disinfectants, wood preservatives, chemical intermediates, or in the manufacture of wiring insulation.

Crude tar acids are produced after acid neutralization of the caustic tar acid solutions (Betts, 1997). These materials are not manufactured or sponsored by the Petroleum HPV Testing Group. The exact composition of a tar acid mixture can vary considerably depending on the hydrocarbon feedstock and the manner of handling. In general, however, cresylic tar acids are composed of phenol, the three isomers of cresol, and the six isomers of xylenol (dimethyl phenol). Tar acids are distinctly different from tar bases, which contain basic nitrogen compounds such as aniline and pyridine.

Figure 1. The Processing of Middle Oil from a Coal Tar Distillation Plant to Yield Individual Tar Acid Chemicals
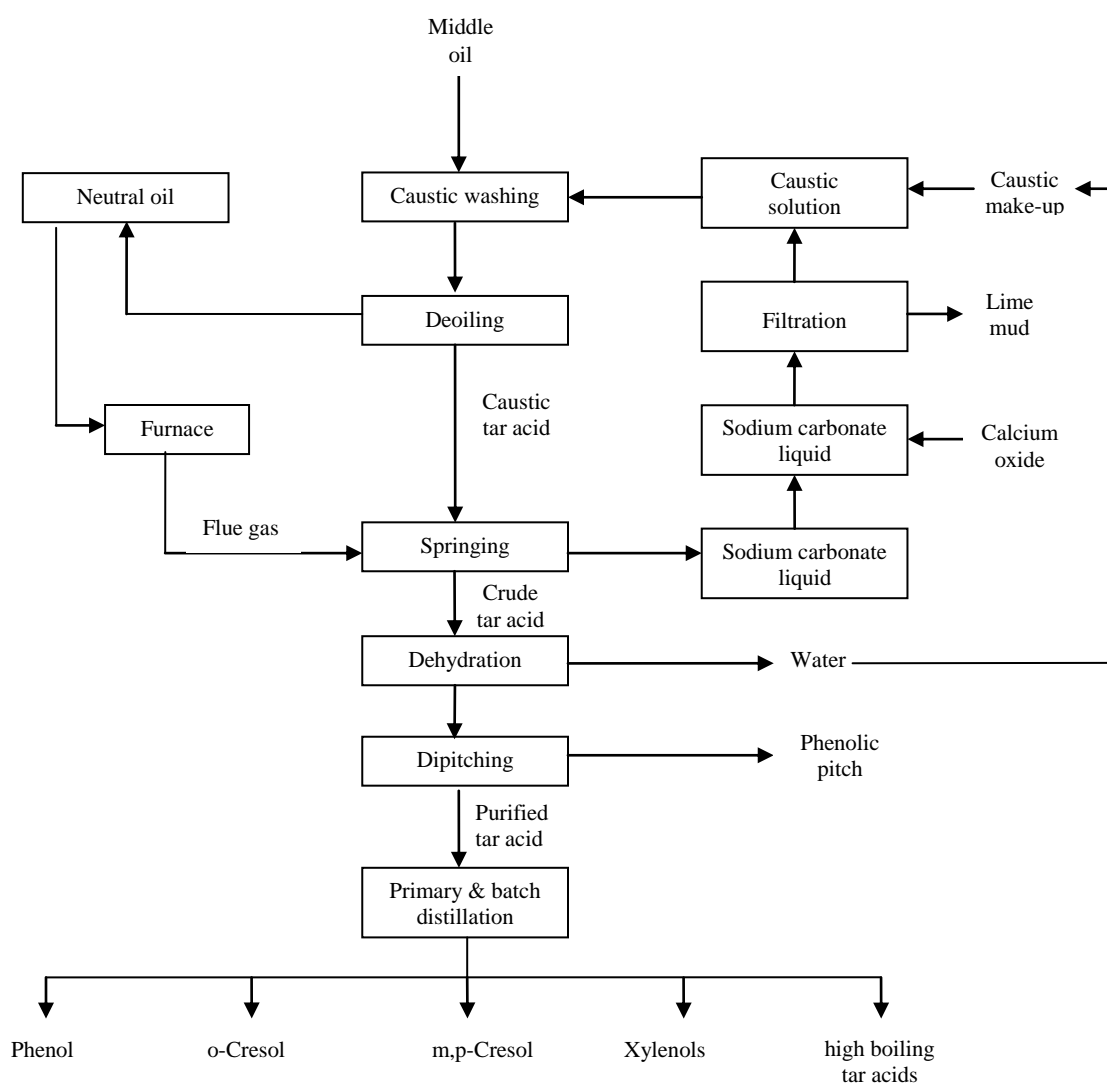
The majority of tar acids are derived from coal tar with petroleum refining contribution only about 25% of the worldwide total (Skunk and Wells, 1999). Coal tar contains far greater

quantities of tar acids than petroleum feedstocks with many coal liquids containing a 5-15% tar acid content (Speight, 1994). Tar acids are generally removed from petroleum early in the refinery process since they tend to poison the catalysts used in later stages (Young, 1922). Cresylic acid was historically isolated from the caustic waste streams used to reduce hydrogen sulfide and mercaptans levels in light distillates streams. The use of more modern refining techniques such as hydrodesulfurized has resulted in caustic waste streams that are not a practical source of cresylic acids. Cresylic acid is still obtained to some degree from petroleum fractions, especially cracked gasoline fractions, which contain a higher percentage of phenolics. As shown in Figure 2, cresylates are also extracted from the tar acids obtained from coal liquids (Tiwari *et al*., 1998). These tar acids are isolated from the middle oil portion of a coal tar distillation by extraction with strongly basic solutions of caustic soda. The composition of cresylic acid varies according to the source of the coal. The high boiling tar acids contain C_3, C_4, and C_5 alkyl-phenols, as well as 4- and 5-indanols, as the main components.

When a caustic solution of tar acid is neutralized with an acidic solution, the ionized phenolics are converted back to their insoluble and unionized form. The phenols and cresols liberated from solution in this fashion are said to have been "sprung" with two immiscible layers resulting. The oily top layer contains the cresylic acid mixture which is further refined and the lower spent aqueous layer is sent to waste water treatment for disposal. The cresylic acid tar residue remaining after the recovery of the phenolic components has been delisted and no longer meets the designation criteria as an HPV (Penberthy, 2004).

B.   Sulfidic Caustic Petroleum Streams (CAS No. 64742-40-1)

Caustics, primarily sodium hydroxide, are used within the petroleum refineries to treat various petroleum streams containing sulfidic constituents or organic acids (Carlos and Maugans, 2000). As depicted in Figure 3, sulfidic caustic streams are generated when light petroleum fractions are treated with a dilute 10% caustic solution to convert odorous or objectionable chemical constituents to their salt forms, which are then soluble in aqueous solution (EU, 2001). This caustic extraction is done to improve color, odor, and oxidation stability of the petroleum product. Caustic is typically re-used, but as extractable constituents accumulate in the caustic solution, residues are removed and fresh caustic is added. Spent sulfidic caustic represents that portion removed from the circulating caustic solution. Extraction of mercaptans from a petroleum stream depends on the type, amount, and concentration of the base used to prepare the extracting solution. Lower boiling mercaptans, which are more common in cracked gasoline fractions, are more easily extracted than the higher boiling mercaptans, which are not as soluble in the caustic solution.

Spent caustic liquors typically come from the production of fuel gases, cracked gasoline, or chemical feedstocks such as propylene. The chemical streams are scrubbed with aqueous sodium hydroxide to extract acidic constituents, such as hydrogen sulfide and low molecular weight mercaptans. Additional mercaptan removal can take place in a separate sweetening operation involving a Merox® unit, which can be designed to operate with any of a variety of petroleum streams including liquefied petroleum gas (LPG), naphtha, or any other hydrocarbon fraction. The Merox unit uses a concentrated solution of caustic soda which is removed, recycled and reused in a continuous loop. Once removed from circulation, the dissolved mercaptans are oxidized to disulfides, which are separated from the caustic soda solution. The final disulfide oil

is then either disposed of on site or processed as: i) an internal fuel, ii) a feedstock for sulfuric acid production, or iii) an agent for conditioning refinery catalysts.

Figure 2. Major Sources of Sulfidic and Phenolic Spent Caustics
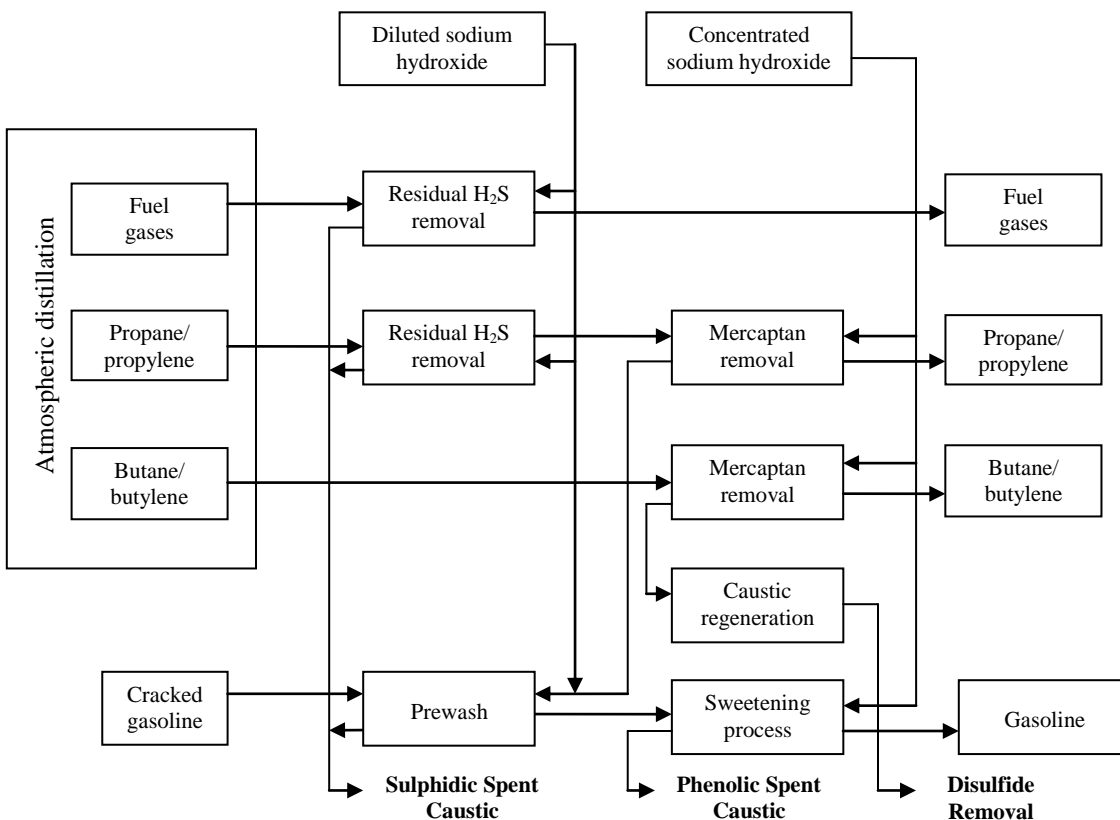
Spent sulfidic caustics generated by refineries can either be: i) sent off-site to a commercial recovery operation for beneficial reuse; ii) injected into deep wells for disposal; iii) incinerated; or iv) managed on-site. Changes in the environmental regulations and classification of such streams as hazardous waste have motivated the industry to minimize deep-well injection. On site treatment includes oxidation prior to discharge to a biological waste water treatment plant. The chemical oxygen demand (COD) of spent caustics is typically very high because of the presence of constituents such as sodium sulfides, mercaptans, phenols, and emulsified hydrocarbons. Initial oxidation reduces the COD and improves the operating efficiency of the waste water treatment facility. The preferred method of treatment involves wet oxidation, which involves oxidation of the soluble or suspended components using oxygen as the oxidizing agent (Ellis, 1998). Depending upon specific constituents and treatment objectives, spent caustic wet air oxidation systems can be divided into three ranges of operation. When air is used as the source of oxygen, the process is referred to as wet air oxidation. The oxidation reactions occur at temperatures of 150 °C to 320 °C and pressures from 150 to 3200 psig. Temperatures less than 150 °C achieves partial oxidation of the sulfides to both sulfate and thiosulfate, which is acceptable for dilute solutions when thiosulfate is not a concern for downstream treatment facilities. A medium temperature of about 200 °C achieves complete oxidation of sulfides to sulfate and also destroys any mercaptans that are present. A high temperature of about 260 °C

achieves complete oxidation of sulfides and mercaptans, plus destruction of any other organic constituents such as cresylic acids.

C.   Phenolic Caustic Petroleum Streams (CAS No. 68988-99-8)

Phenolic spent caustic is one of three spent caustics streams originating in oil refineries (Suarez, 1996). The first type, sulfidic caustics, was discussed in the previous section, whereas the third type of spent caustic, naphthenic, is outside the scope of this category review. Spent phenolic caustic, also called cresylic caustic, results when concentrated sodium hydroxide solutions are used to purify cracked gasoline. The phenolic content of spent caustic can be up to 10-25%, which is high enough to make phenolic recovery a profitable option. A more diluted version of phenolic caustic is generated in those refineries were mercaptan oxidation is performed without extraction to "sweeten" the cracked gasoline. The majority of phenols present in refinery spent caustic solutions originate from the processing of heavy cracked naptha streams. Thermal cracking processes include visbreakers, delayed coking, and steam crackers, which produce ethylene, propylene, and petrochemicals, can also result in the production of spent phenolic caustics.

Table 3. Phenolics from Different Types of Crude Oil Refining

Refinery Type	No. of Refineries	Total Crude Capacity (Bbl)	Phenolic Yield (lbs/Bbl)	Phenolic Output (lbs/day)
Crude distillation	13	204,900	0.03	1809
Cracking	71	3,448,900	1.54	16620
Cracking and petrochemicals	27	3,416,830	4.02	27668
Cracking and lubes	11	1,068,450	2.18	4317
Cracking, lubes, and petrochemicals	13	3,354,470	2.67	18430

In 1972, EPA and API conducted a survey of refinery waste loads to assess the amounts and types of raw aqueous wastes that were generated by the refining industry (Short *et al*., 1974). Raw wastes were defined to be those wastes which received no treatment other than gravity separation. The amount of phenolics produced by each class of refinery surveyed is listed according to the API refinery classification system utilized in the study. Generally, as the refinery class goes from distillation through the cracking of lubes and petrochemicals, the complexity of the refinery increases. As shown in Table 3, crude distillation refineries with no cracking produced only 0.03 lbs of phenolics per 1000 barrels refined; whereas, those refineries where cracking was included saw much higher phenolic yields.

D.   Acidic Sludge Streams (CAS No. 64742-24-1)

Acid sludge is a waste product from the alkylation process employed in petroleum refining. Through alkylation, light olefins (e.g., propylene, butylenes, amylene, pentylene, pentenes) are chemically reacted with isobutane to create a mixture of saturated hydrocarbons (Graves, 2004). The resulting mixture contains a group of low molecular weight hydrocarbons, an excess of isobutane, and a fraction termed alkylate. Each fraction is isolated and used in various products or processes. Propane may be used to produce liquefied petroleum gas (LPG), *n*-butane may be used in LPG or gasoline, and the excess isobutane can be recycled back to the alkylation reactor. The alkylate fraction consists mostly of C_7-C_9 branched, saturated, hydrocarbons with a low vapor pressure and high octane value (Energetics, 1998). These characteristics make alkylate highly desirable as a blending stock for premium grades of gasoline. Additionally, because alkylate contains no olefins, aromatics, or sulfur, it is highly valued as a blending stock for reformulated gasoline. Approximately 13–30 pounds of spent acid are generated per barrel of alkylate produced.

The alkylation reaction is catalyzed by the presence of strong sulfuric acid (Energetics, 1998). In the reactor, the olefin and isobutane feedstock reacts in the presence of the acid catalyst. The reactor product is sent to a settler where hydrocarbons are separated from the acid, which is then recycled back to the reactor. The concentration of sulfuric acid is a key operating parameter for the reaction process. Acid strength is maintained at 88-94% by the continuous addition of fresh acid and the continuous withdrawal of spent acid. When the sulfuric acid becomes less than approximately 88%, a portion of the acid must be removed and replaced with stronger acid (Energetics, 1998). The acid that is removed is considered "spent" and must be regenerated in a sulfuric acid manufacturing plant. Feed impurities can affect the amount of sulfuric acid required for the process (Graves, 1998). Many of these impurities form acid-soluble compounds that will increase acid make-up requirements and must therefore be purged along with the spent acid. Mercaptan sulfur is one example of a feed impurity. Approximately 40 pounds of additional make-up acid are needed for each pound of mercaptan that enters with the feed. For this reason, caustic treating facilities are used in the refinery to remove sulfur from the olefin feed prior to alkylation. Butadiene is another feed impurity that tends to polymerize and form acid-soluble oils and increase acid make-up requirements. Nearly all the spent acid generated at refineries is regenerated and recycled (API, 1997).

4. Chemical Composition of Reclaimed Substances

Because of their chemical complexity, there is no single analytical method that can be used to quantitate the acidic or caustic materials described in this category. Ancillary information is, however, available from a variety of sources that provide a general picture of the chemical classes that can be found in each of the four substances. Table 4 provides an initial indication of the types of chemicals can be encountered in each reclaimed substance.

Table 4. General Chemical Characteristics of the Acidic and Basic Materials in the Reclaimed Substances Category

Reclaimed	Caustic	Sulfidic	Phenolic	Acidic
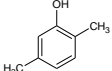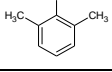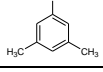
Substance	tar acids	caustics	caustics	Sludges
Residual acid/base (wt %)	10	0.7 – 14.0	10 – 15	89 – 91
Oil (ppm)	4500	0 – 11160	---	$\approx$ 100000
Total sulfide as H_2S (ppm)	---	272- 86200	0 – 10000	---
Mercaptans as S (ppm)	---	30 – 30000	0 – 40000	---
Phenolics (ppm)	76000	0 – 8000	100000 – 250000	---
Reference	Tiwari *et al*., 1998	Heritage, 1992	Duesel *et al*., 2007	Bider and Hunt, 1982

The corrosive nature of these materials as evidenced by the extremes in pH and the high acid/base strength is their most distinguishing chemical characteristic. Notable quantities of oil can also be present in various chemical forms including olefins, paraffins, or aliphatic hydrocarbons. Likewise, numerous low molecular weight sulfur compounds, other than mercaptans, can be found in several spent caustics. The majority of these sulfurous chemicals are extracted from the naptha streams as hydrogen sulfide analogs. The phenolic chemicals are widely distributed in most of the reclaimed substances, but are most commonly found in the caustic tar acids and the phenolic caustics.

A.   Composition of Caustic Tar Acid Streams

Strong alkaline solutions are necessary to extract the cresylates from tar acid sources such as petroleum. The chemical composition of these caustic extracts is dependant upon the extracting conditions and the source of the feedstock. Caustic extracts of petroleum fractions have yielded tar acid concentrations of 10 – 50% with thiocresol levels ranging from 1-20% (Jones and Neuworth, 1963). Solvent extraction of a neutralized petroleum feed of this type resulted in tar acid levels of 82.2%, thiocresol levels of 16.3 %, and neutral oil concentrations of 1.5%. The distribution of cresylates from the tar acids generated in coal carbonization or coal coking operation reveal of cresol and xylenol content that can be up to 3-4 times higher than the level of phenol.

Table 5. Phenolic Chemicals Derived from a Purified Tar Acid

Chemical	Chemical Structure	CAS Number	Refined Tar Acid Composition (%)
Phenol		108-95-2	8.8
o-cresol		95-48-7	10.8
m-cresol		108-39-4	13.3
p-cresol		106-44-5	12.9
2,3-xylenol		526-75-0	3.1
2,4-xylenol		105-67-9	---
2,5-xylenol		95-87-4	---
2,6-xylenol		576-26-1	1.4
3,4-xylenol		95-65-8	2.7
3,5-xylenol		108-68-9	9.1
2-ethylphenol		90-00-6	5.0
Catechol		120-80-9	2.6
Resorcinol		108-46-3	3.9
other monohydric phenols	---	---	2.5
other dihydric phenols	---	---	9.6

Tar acids from coal gasification or coal carbonization units are generally processed on site, whereas the caustic tar acid solutions from petroleum refineries are often sent off site to a company specializing in the recovery and purification cresylic caustics (Merichem, 2007). The

purification process can be used to isolate the phenolic chemicals identified in Table 5 (Tiwari *et al*., 1998). The composition is somewhat dominated by the presence of lower molecular weight phenol and cresols rather than the more highly substituted xylenols. Unlike the distribution observed with the tar acids from coal, none of the individual cresylates are recovered at levels exceeding 15% of the total.

B.   Composition of Spent Sulfidic Caustic Streams

The predominant extracted species in spent caustic streams depends on the refinery stream being considered (Beychok, 1967). For example, light refinery streams (e.g., refinery gases, liquefied petroleum gases, and light naphthas) contain sulfur mostly as hydrogen sulfide, carbonyl sulfide, and mercaptans. (Suarez, 1996). When treated with a dilute caustic solution to remove the sulfur, the waste generated contains a predominance of inorganic sulfidic species (e.g., sodium sulfide and sodium hydrosulfide).

Table 6. Mercaptans from Caustic Extraction of Different Petroleum Feedstocks

Chemical	Chemical Structure	CAS Number	Virgin Naptha Feedstock (%)	Cracked Naptha Feedstock (%)
hydrogen sulfide	H_2S	7783-06-4	---	---
methyl mercaptan	H_3C—SH	74-93-1	4	19
ethyl mercaptan	H_3C—CH_2 \ SH	75-08-1	6	34
propyl mercaptan	H_3C—CH_2 \ CH_2 SH	107-03-9	13	18
butyl mercaptan	H_3C—CH_2 \ $CH_2$$CH_2$ \ SH	109-79-5	19	15
amyl mercaptan	H_3C \ $CH_2$$CH_2$ \ $CH_2$$CH_2$ \ SH	110-66-7	18	9
hexyl mercaptan[#]	H_3C—CH_2 \ $CH_2$$CH_2$ \ $CH_2$$CH_2$ \ SH	111-31-9	40	5

[#] hexyl mercaptans and higher

Spent sulfidic caustic is obtained when hydrocarbon streams are treated for mercaptan removal at the sweetening unit. Much of the waste caustic comes from a Merox regeneration unit

used to oxidize and remove the extracted sulfur compounds as disulfides. These regeneration units return most of the caustic to the treatment unit, but a portion is periodically removed to keep the sulfides from concentrating to the point where the regenerated caustic is no longer useful. The spent solution contains relatively high amounts of sodium sulfide and sodium mercaptides. Approximately 400,000 lb/yr of the sulfidic caustic that is generated is re-used in the paper and pulp industry.

Depending on the source, spent sulfidic caustic may also contain phenols, amines, and other organic compounds that are soluble or emulsified in the caustic. The levels of these chemicals, however, are generally much lower than the mercaptan levels. The most commonly identified mercaptans in spent sulfidic caustic are depicted in Table 6 along with the relative amounts from virgin and cracked naptha streams (Hengstebeck, 1959). Not surprisingly, the cracking process can be seen to convert the higher molecular weight mercaptans into more easily handled methyl and ethyl mercaptan.

C.   Composition of Spent Phenolic Caustic Streams

The primary difference between phenolic and sulfidic caustic is quantitative rather then qualitative. As the name implies, phenolic spent caustic contains a higher percentage of phenolic materials and a lower percentage of mercaptans. This shift in composition is accompanied by changes in caustic concentration and pH as well. The compositional variation in sulfidic and phenolic spent caustic is best illustrated in Table 7, which compares spent caustic generated from treating petroleum gases and light naphtha streams (sulfidic caustic streams) versus heavy naphtha, jet fuel/kerosene/diesel, and heavy cracked naphtha streams (phenolic caustic streams) (Suarez, 1996).

Table 7. Characteristics of Typical Refinery Spent Caustic Streams

Property	Sulfidic Caustic Streams	Phenolic Caustic Streams
sodium hydroxide (wt%)	2 – 10	10 – 15
inorganic sulfides as S (wt%)	0.5 – 4	0 – 1
mercaptide as S (wt%)	0.1 – 4	0 – 4
carbonate as CO_3 (wt%)	0 – 4	0 – 0.5
cresylic acids (wt%)	---	10 – 25
pH	13 – 14	12 – 14
total sodium (wt%)	4 – 10	---
Ammonia	---	trace

The various phenolic chemicals isolated from spent caustic solutions generated at a Mexican refinery are presented in Table 8 (Olmos *et al*., 2004). The phenolic concentrations generally ranged from 2-40 g/L with phenol being the most commonly encountered chemical in

the group. It is important to recognize that the types of phenols and their relative amounts can vary across refineries depending on the types of operations employed. For instance, fluidized catalytic cracking can produce a different array of phenolic materials than steam cracking (Berné and Cordonner, 1995). Likewise, the types and amounts of cresols and xylenols are subject to considerable variation (Field *et al*., 1940). Whereas, most spent phenolic caustic is put through a recovery operation, small amounts can be sold for use in other downstream manufacturing operations. For instance, approximately 200,000 lb/yr of phenolic caustic is used in metal smelting. This, however, represents a very small fraction of the total amount produced. Excess caustic of any type is not sold off site for use in any commercial products.

Table 8. Phenolic Compounds Isolated from a Spent Caustic Solution

Chemical	Average Concentration (g/L)	Standard Deviation (g/L)
phenol	30.6	27.4
o-cresol	6.0	3.2
m-cresol	---	---
p-cresol	17.9	6.0
2,5-xylenol	2.9	0.3
3,4-xylenol	1.4	0.6
2-ethylphenol	0	---

D.   Composition of Acidic Sludge Streams

Most spent acid sludge is derived from alkylation units. The concentration of sulfuric acid in the spent solutions from petroleum plants has been reported to be 87% with another 10% composed of mixed hydrocarbons, and a water content of just 3% (Anon, 1954). Whereas the sulfuric acid is mostly recovered for reuse, the sludges are combusted in furnaces used to reclaim the sulfuric acid first as sulfur dioxide gas then as sulfur trioxide, which is the anhydrous form of sulfuric acid. The hydrocarbon content of the sludge can also be quite high depending on the source; however, most is removed prior to recovery.

The EPA described acid sludge from alkylation reactor tanks as containing sulfuric acid and other hydrocarbon constituents (EPA, 1996b). In contrast, the Chemical Abstract Service termed petroleum acid sludge as "a complex combination of sulfuric and sulfonic acids, water, esters and high molecular weight organic compounds such as polymers of olefinic hydrocarbons". The hydrocarbon fraction also contains conjunct polymers, or alternatively, acid-soluble polymers

or "red oil" (Albright, 1988). The conjunct polymers are minor byproducts formed during the alkylation reaction. They have molecular weights in the range $300 - 500$ amu, contain C_5 and perhaps C_6 ring groups, and are highly unsaturated with both conjugated and nonconjugated double bonds. Spent acid typically contains $4 - 6\%$ conjunct polymers. Refineries may adopt a procedure to minimize the oil portion of the spent acid. This is done by mixing some alkylate with the acid discharge from the settler. The heavy hydrocarbons absorb light hydrocarbons and carry them to the hydrocarbon layer in a secondary settler. This significantly reduces the portion of hydrocarbons entrained in the spent acid and allows all of the hydrocarbons to be captured and reused as fuel gas.

5. Physical Chemical Properties

The single most important characteristic of the substances in this category is their high corrosivity, which should dominate any discussion of the safe handling and disposal of these materials. Each of the four substances is a complex heterogeneous mixture with an indefinable number of major and minor components. All four substances are liquids at room temperature with highly variable solution densities and viscosities. Because of these characteristics, specific physical and chemical properties can not be reliably determined or meaningfully assigned to any of the substances in this category. It is, however, possible to examine some rather general characteristics of these substances for the purposes of comparison. As shown in Table 9, all of the acid and caustic substances show extremes of pH with relatively high concentrations of either sodium hydroxide or sulfuric acid. In addition, the materials are all darkly colored and have a distinct, oftentimes, offensive odor.

Table 9. Key Properties of the Four Substances in Acid and Caustic Category

Abbreviated Description	Appearance	Character	pH Range	Corrosive Agent	Acid/base Strength
caustic tar acid	dark-brown oily liquid	strongly basic	$12 - 14$	sodium hydroxide	$\approx 10\%$
sulfidic caustic	pungent smelling reddish liquid	strongly basic	$13 - 14$	sodium hydroxide	2 - 10%
phenolic caustic	brown liquid with a tar -like odor	strongly basic	$12 - 14$	sodium hydroxide	10 - 15%
acidic sludge	black viscous liquid	strongly acidic	≈ 1	sulfuric acid	89 - 91%

Despite their highly variable composition and foul appearance, these substances are not simply wastes. As the name suggests, reclaimed substances contain identifiable chemicals that can be profitably recovered and reused (Bider and Hunt, 1982). These recoverable chemicals tend to occur at higher concentrations than many of the minor components and their relative amounts can impact the properties of the mixture. As described in the previous section, these substances also contain an assortment of mineral species (e.g., sulfur in various forms) in a

suspended or dissolved state and a smaller petroleum component. The melting point and boiling point characteristics are strongly related to the aqueous character of these substances. Therefore, at relevant environmental conditions, these substances will exist in liquid form and boil at temperatures in accordance with their water content and the concentrations of ionic components. Vapor pressure, octanol/water partition coefficient, and water solubility will also be related to the individual constituents in the mixtures.

In the interest of completeness, the chemical and physical properties for several of the most relevant isolatable chemicals from the substances in this category are described in Table 10. The physical and environmental properties for the individual phenols and mercaptans were compiled using EPA's EPI Suite software package (EPA, 2007). For comparative purposes, the actual or estimated values for sodium hydroxide and sulfuric acid have also been included. A range of values can be seen in each of the five measurement categories with no apparent pattern or consist relationship that would allow for the development of any general property statements. These results indicate that specific physical or chemical properties measurements would not provide any meaningful data due to the complex and variable nature of these substances
.

Conclusions
Additional physical property testing is unlikely to yield any meaningful information that can be generally applied to the materials in each category. The substances are far too heterogeneous for any set of test results to be applicable beyond the range of solutions being tested.

Table 10. Chemical/Physical Properties of Constituents in Acid and Caustic Category†

Phenolic or Sulfidic Component	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (mmHg 25 °C)	Octanol/Water Partition Coeff. (log K_{ow})	Water Solubility (g/L)
sodium hydroxide	318.0	730.3*	1.8×10^{-21}	-3.88*	1000*
sulfuric acid	10.3	290.0	5.9×10^{-5}	-2.20	1000
Phenol	40.9	181.8	0.35	1.46	82.8
o-cresol	29.8	191.0	0.17	1.95	25.9
m-cresol	11.8	202.2	0.11	1.96	22.7
p-cresol	35.5	201.9	0.11	1.94	21.5
2,3-dimethylphenol	72.8	216.9	0.09	2.48	4.57
2,4-dimethylphenol	24.5	210.9	0.10	2.30	7.87
2,5-dimethylphenol	74.8	211.1	0.15	2.33	3.54
2,6-dimethylphenol	45.7	201.0	0.17	2.36	6.05
3,4-dimethylphenol	60.8	227.0	0.04	2.23	4.76
3,5-dimethylphenol	63.6	221.7	0.04	2.35	4.88
2-ethylphenol	18	204.5	0.15	2.47	5.34
hydrogen sulfide	3.8	101.4	20.6	-1.38	482.0
methyl mercaptan	-123.0	5.9	1510	0.78*	15.4
ethyl mercaptan	-147.8	35.1	529	1.27*	15.6
propyl mercaptan	-113.3	67.8	154	1.81	1.9
butyl mercaptan	-115.7	98.5	45.5	2.28	0.6
pentyl mercaptan	-75.7	126.6	13.8	2.74*	0.16
hexyl mercaptan	-81.0	151.0	4.2	3.23*	0.08*

* - estimated value
† - measured values taken from Syracuse Research Corp. PhysProp Database (SRC, 2009)

6. Environmental Fate

The acidic and basic substances in this category are primarily composed of inorganic materials with no appreciable vapor pressure. The two main chemicals of concern in this category, sodium hydroxide and sulfuric acid, exist in their native state as a solid and a liquid, respectively (HSDB, 1998; 1999). Both substances are highly soluble in water and will not distribute into the air to any significant degree. It is important to note, however, that sulfuric acid can form atmospheric aerosols that can be taken up aqueous cloud droplets and distributed for long distances. Process controls and regulatory oversight of the emissions from acid recycling facilities reduce the potential for aerosol release from these operations.

The phenolates, mercaptides, and other soluble organics found in the three caustics substances discussed above will be largely ionized in solution. In the ionized form, these organics will be entirely water soluble without any appreciable vapor pressure or potential for volatilization. Even after evaporation of the water, the phenolates and mercaptides will precipitate from solution as their respective sodium salts, which are solids rather than volatile liquids or gases at room temperature. The native phenols and mercaptans are only recoverable in their unionized form when the solutions are first neutralized to a pH of 7 with a strong acid, whereupon they will separate from solution as an oily layer. When this operation is performed the spent caustic solution is said to have been "sprung". Methods for the effective biological treatment of unaltered spent caustics materials continue to be developed and evaluated as alternative technologies become available (Sipma *et al*., 2004).

The strength of an acid or base and its tendency to ionize in aqueous solution is dictated by its acid or base dissociation constant, also known as the K_a or K_b, respectively. The reaction can be described chemically as follows for an acid:

$$HA \rightleftharpoons A^- + H^+$$

or, alternatively, in the case of a basic substance as:

$$BOH \rightleftharpoons B^+ + OH^-$$
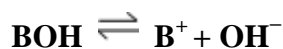
where HA is a generic acid and BOH is a generic base. Each of these materials dissociates in solution by splitting into A^-, known as the conjugate base of the acid, and B^+, known as the congate acid of the base. Each acid and base has its own unique K_a an K_b value, which describe the strength of the dissociation, and the corresponding corrosiveness of the solution. Because K_a or K_b values can span many orders of magnitude, a logarithmic measure of the dissociation constants is commonly used. The pK_a and pK_b value are equal to $-\log 10$ of the K_a and K_b. The pK_a value for sulfuric acid is -2 and the pK_b value for sodium hydroxide is 0.2. Values less than 2 describe strong acids and bases and indicate complete ionization in solution.

The primary concern associated with the release of acids and bases into the environment is related to the effects of pH on soil, sediment, or water. Hydroxyl and sulfate anions resulting from the dissociation of sodium hydroxide and sulfuric acid will completely distribute throughout the water and soil columns once released into the environment. The rate and degree of oxidation and biodegradation of inorganic anions is not a practical issue, since the ions are not capable of further chemical breakdown. Sodium hydroxide is not expected to contaminate ground water or accumulate in the food chain (EPA, 2007). Sulfuric acid aerosols in the form of acid rain are capable of concentrating in cold mountain lakes and excessively acidifying the water (OECD, 2001).

Like many complex mixtures, the fate characteristics of these substances are defined by the individual components within the mixtures. In the environment, the components will partition, distribute, and degrade independently of one another in accordance with their own chemical properties. Because the substances in this category are aqueous solutions, releases to the aquatic compartment would result in dilution and dispersal of the dissolved components. Suspended materials also may dissolve, disperse, or become incorporated into the sediment compartment. Releases to the terrestrial environment may result in soil absorption in accordance with soil permeability. As noted above, the mineral fraction in aqueous solution would not be expected to biodegrade; however, these substances may form new compounds, colloids, or ionic species in accordance with their thermodynamic properties. Residual hydrocarbons in the waste solutions would be expected to float, volatilize or disperse according to individual compound characteristics. The abiotic and biotic degradability of these oil fractions can be estimated, but because of the highly variable composition, the results would only be applicable to the sample being studied and are not applicable to other chemical combinations or to the range of possible compositional combinations.

Conclusions

If released to the environment, the constituents within these complex mixtures will partition, distribute, and degrade in accordance with their own chemical properties. Because the substances in this category are aqueous solutions, releases to water bodies will result in dilution and dispersion of the dissolved components. Releases to terrestrial environments will result in absorption into the soil. Mineral fractions may transform and reach equilibrium with other ionic species, while the residual hydrocarbons will degrade through abiotic and biotic pathways. Because of the complex and variable nature of these substances, further evaluation of the environmental fate and distribution of the acidic and basic substances in this category will not yield any meaningful information that can be used to assess environmental persistence.

7. Ecotoxicity

The aquatic effects of the four corrosive materials in this category have not been assessed. Testing of these solutions is complicated by the fact that each substance is a highly heterogeneous mixture that can vary tremendously in composition from one refinery to the next based on the operations employed and on the source of the crude oil being refined. Likewise, since the dissolved materials are generally waste or recovery streams that can contain a variable quantity of residual acid or base, any ecological testing will produce inconsistent results that will vary according to the chemical content and acid/base strength.

Perhaps more importantly, it is expected that any evaluation of the ecotoxicity of these reclaimed substances will be dominated by their corrosiveness and their propensity for causing lethality simply on the basis of the pH change that can occur. All ecotoxicity endpoints would need to be tested within a narrow pH range (6.5 to 8.5) to ensure the viability of the test organisms. Due to the pH extremes for the substances in this category, neutralization to raise or lower the pH of the test solution would be necessary to conduct a valid test on the contents of each reclaimed substance (Abernathy and Westlake, 1991). Sample neutralization will result in the formation of precipitates, sediments, and suspended solids that will have a variable impact on the assay results depending on the exact nature of the sample being examined. It is quite probable that the results obtained with a neutralized sulfidic spent caustic sample could vary over an order of magnitude depending on the refinery where it was produced. In addition, potential degradation and decomposition could result in the formation of new contaminants, force chemical adsorption on suspended sediment, or generally alter the relative ratio of the sprung components. All of these potential changes call into question the representativeness of a particular test sample and its actual relationship to the native unadjusted substance.

Another aspect of testing that needs to be considered is the relative aquatic toxicity of some key components in these substances. A substantial number of the phenolic compounds and many of the sulfides found in these substances have been examined in the HPV reviews and test plans submitted by other organizations (EPA, 2009). Aquatic testing would only serve to confirm what is implicitly recognized; that the substances in this category should be treated as highly hazardous to aquatic organisms.

Conclusions

The ecotoxicity of these substances will reflect their extreme pH and corrosivity. Direct testing of aquatic organisms is not appropriate for these substances and would not provide meaningful data. Potential hazards should be assessed in accordance with the information available for the main corrosive components: sodium hydroxide and sulfuric acid. As an aid to this evaluation, the SIDS (Screening Information Data Set) dossiers for sodium hydroxide and sulfur acid have been attached as Annexes to this report.

8. Health Effects

The four acidic and basic substances in this category are all highly corrosive to human tissue by virtue of their extremes in pH. Although the materials are actually complex mixtures containing a variety of potentially hazardous phenols and mercaptans, their corrosive properties should dominate any evaluation of the potential health effects from these materials. Whereas, toxicity studies could be performed with neutralized supernatants or extracts of these corrosive mixtures, the results could yield conflicting or unanticipated results that could grossly understate the magnitude of the hazard. Likewise, any alteration or manipulation of the original substance for the purpose of testing could result in chemical or physical transformations of the components that would confound the interpretation of the results. All hazards should be assessed in accordance with the information available for the main corrosive components: sodium hydroxide and sulfuric acid. As an aid to this evaluation of potential health effects, the SIDS dossiers for sodium hydroxide and sulfur acid have been attached as Annexes to this report.

There is a plethora of information available from Poison Control Centers documenting the severe gastrointestinal and esophageal injuries associated with ingestion of the corrosive acids and bases found in household products (Ramasamy and Gumaste, 2003; Zargar *et al*., 1989). A particularly dramatic example of the overwhelming corrosive effects of sodium hydroxide appeared in a case report for a small Texas town whose municipal water source was accidentally contaminated with sodium hydroxide. The highly alkaline water with a pH greater than 12 resulted in the hospitalization of 248 people for skin and gastrointestinal problems (Bender *et al*., 1998). Oral, dermal, ocular, and inhalation (aerosol) contact with sodium hydroxide and sulfuric acid is capable of causing severe irreversible injury after brief contact.

Depending on the concentration, solutions of sodium hydroxide can be non-irritating, irritating or corrosive to the skin, eyes, and gastrointestinal tracts. Four factors determine the corrosive potency of a sodium hydroxide solution: pH, viscosity, concentration, and titratable alkalinity (Vancura *et al*., 1980). Human case studies revealed that concentrations of 0.5 - 4.0% were irritating to the skin, whereas higher concentrations were lethal following dermal contact. As the pH gets closer to 14, the destructiveness of the caustic solution becomes greater (Bryson, 1996). Solutions with a pH greater than 12.5 will cause esophageal stricture and ulceration. In laboratory animals, a sodium hydroxide concentration of 8.0% or greater was corrosive for the skin (OECD, 2002). Eye irritation was not evident at levels of 0.2 - 1.0%, whereas corrosive ocular injury was present at a concentration was 1.2% or higher. Lethality has been reported for animals treated orally at doses of 240 and 400 mg/kg. No valid repeat dose toxicity studies are available for sodium hydroxide by any route including oral, dermal, or inhalation.

Under normal conditions, neither the concentration of sodium in the blood nor the pH of the blood will be affected by a casual exposure to a non-irritating solution of sodium hydroxide. Sodium hydroxide is not expected to be systemically available in the body and therefore it is not expected to impact male and female reproduction or affect the developing fetus. Consequently, there would be no expected increase in risk for reproductive damage or developmental toxicity from an exposure to the hydroxyl ions. Both *in vitro* and *in vivo* genetic toxicity tests show no evidence for mutagenic activity.

Similar to sodium hydroxide, sulfuric acid is corrosive, irritating, and causes direct local effects on the skin, eyes and gastrointestinal tracts after exposure to sufficiently high concentrations (OECD, 2001). Small droplets of sulfuric acid aerosol can also be inhaled and elicit local effects on the respiratory tract. The severity of damage from inhaled sulfuric acid aerosols depends on the exposure concentrations, the duration of exposure, and the size of the aerosol particles, which determines the site of deposition in the respiratory tract. The effects of sulfuric acid are the result of hydrogen ion formation and the resulting change in pH, rather than alteration caused by the formation and distribution of the sulfate ion (ATSDR, 1998). Sulfuric acid is not absorbed or distributed in the body as an intact molecule. The acid rapidly dissociates and the anion will enter the body electrolyte pool and will not play a specific toxicological role. The body pool of this sulfate anion is large, and it is therefore unlikely that minor aerosol exposures will significantly modify the normal body load.

The low LC_{50} values for sulfuric acid aerosol are a consequence of the corrosive effect of this chemical (OECD, 2001). Depending on the duration of exposure, the LC_{50} ranges from 0.37 to 0.42 mg/L in rats, 0.6 to 0.85 mg/L in mice and 1.47 to 1.61 mg/L in rabbits. Only one acute oral toxicity study has been performed and it resulted in an LD_{50} of 2140 mg/kg in the rat. Sulfuric acid is corrosive to the skin, eyes, and mucous membranes, but solution concentrations of 10% or less are not irritating to the skin of difference species. Variable results were obtained in ocular irritation studies with 10% sulfuric acid with the results dependant on the test protocol employed.

Numerous repeated exposure studies with inhaled sulfuric acid aerosol have shown that the toxicity is confined to changes in the structure and function of the respiratory tract. The observed changes were related to the irritant properties of the chemical. Sulfuric acid was not mutagenic in genetic toxicity studies performed *in vitro* with prokaryotes, but it has been shown to cause chromosomal aberrations in a non-bacterial test *in vitro*. The chromosomal effects are known to be a consequence of the low pH that accompanies the testing of a strong acid. No chronic health effects were observed in carcinogenicity studies performed in three different animal species that inhaled sulfuric acid aerosol.

It is generally acknowledged that substances with a pH greater than 11.5 or less than 2 are highly corrosive to skin and mucous membranes and should not be the subject of acute animal testing (Stitzel, 2002). This is in agreement with decisions EPA disseminated in their initial examination of the acid and caustics category submission (Hernandez, 2004). Likewise, the OECD evaluation of the SIDS databases for sodium hydroxide and sulfuric acid concluded that no further testing was necessary for these highly corrosive materials, despite the fact that a minimal amount acute testing had actually been performed. It was generally agreed that extensive testing of such highly corrosive materials was at variance with the intentions of the program and that the effects would be mediated by physical rather than the chemical properties of these materials.

Conclusions
The corrosive substances in this category are all known by experience to be highly damaging to living tissue, regardless of the exposure route or the length of contact. Potential hazards should be assessed in accordance with the information available for the main corrosive components: sodium hydroxide and sulfuric acid. As an aid to this evaluation of potential health effects, the SIDS (Screening Information Data Set) dossiers for sodium hydroxide and sulfur acid have been attached as Annexes to this report.

9. Conclusions

The category analysis has provided strong and reasonable support for the use of existing health and information for the two primary components of these solutions: sodium hydroxide and sulfuric acid. Although appreciable quantities of phenols, cresols, xylenols, mercaptans, and hydrocarbons can be found in these acidic and caustic substances, the evidence suggests that the health and environmental effects of the constituents play a relatively minor role in overall toxic hazard. Therefore, on the basis of this analysis, no further testing or analysis is recommended for the materials in this category. The potential harm associated with the release and contact of these

materials should be judged on the basis of existing information on the corrosivity of the mother liquor, or, if necessary, using available data on the organic chemicals dissolved in solution. These substances are not sold to consumers and members of the general public, including children and the elderly, are not exposed in any fashion.

EPA has reviewed the production, handling, and recycling of these substances under its Hazardous Waste Management System (EPA 1998). EPA had "… previously excluded from the definition of solid waste spent sulfuric acid used to produce virgin sulfuric acid (40 CFR 261.4(a)(7)). The Agency reexamined this exclusion as it pertains to sulfuric acid used as a catalyst in refinery alkylation processes and found no reason to change the existing regulatory structure."   In that same notice, EPA finalized "… the exclusion proposed for spent caustic solutions from petroleum refining when used as feedstocks to produce cresylic or naphthenic acid." This new exclusion was added at 40 CFR 261.4(a)(19).

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