

Coke Oven Gas Condensate Hazardous Waste Issues

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INTRODUCTION

What is a hazardous waste?^a A hazardous waste is a solid waste, or combination of solid waste, that because of its quantity, concentration, or physical, chemical, or infectious characteristics may (1) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (2) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed. This broad definition provides a general indication of which wastes Congress intended to regulate as hazardous, but it does not provide the clear distinctions necessary for industrial waste handlers to determine whether their wastes pose a sufficient threat to warrant regulation or not. In order to develop a regulatory framework capable of ensuring adequate protection under the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) has developed artfully crafted (some might say arcane and convoluted) definitions, criteria, and methodologies for determining what is a hazardous waste and for determining which waste management standards are to be applied. Proper characterization, classification, and determination are paramount because only those wastes that have specific attributes are subject to regulation as a hazardous waste. Making this determination is a complex task and it is a central component of the hazardous waste management regulations. To complicate the determination as to whether or not a material is a hazardous waste, EPA provides conditional exclusions and exemptions for certain wastes when they are recycled in certain ways. Over the years, there has been substantial confusion and continuing controversy regarding appropriate classification and management of waste streams associated with the manufacture of coke and coke oven gas by-products. The refinement and manufacturing of these coke by-products generate several materials that are recycled; absent recycling, these materials would be classified as solid wastes and they may be regulated as listed and/or characteristically hazardous waste streams depending on the physical and chemical characteristics, the nature of the generating process, and the solid waste management techniques employed. The focus of this paper is coke oven gas condensate.

Coke and coke by-products, including coke oven gas, are produced by the pyrolysis (heating in the absence of air) of suitable grades of coal. The process also includes the processing of coke oven gas to remove tar, ammonia, naphthalene, light oil, and sulfur before the gas is used as fuel. In the coke-making process, coal is fed (usually after processing operations to control the size

^a The information provided herein is believed to be accurate and correct. This information is provided to promote discussion and understanding. The information may be used by third parties only if the user agrees that such information shall be used at the risk of the third party user without legal recourse against Environmental Quality Management, Inc. (EQ), its parents, subsidiaries, employees, officers, or directors. CFR data is current as of July 27, 2006.

and quality of the feed) into a series of ovens that are sealed and heated at high temperatures in the absence of oxygen, typically in cycles lasting 12 to 36 hours. The hot solid carbon remaining in the oven is coke. After hot coke is pushed from the oven into a quench car, the quench car travels by rail to a quench tower. Wet quenching involves spraying a large quantity of water onto the hot coke for 90 to 120 seconds. Modern quenching operations use a recirculating system by which quench water is reused and makeup water is added to replenish the loss due to evaporation. The water cools the coke and the resulting steam is discharged through baffles and mist eliminators into the atmosphere. After the coke is cooled, it is dewatered, screened, and sent to a blast furnace or to storage.

Makeup water is typically derived from a nearby river or lake, but has included process waters such as scrubber blow-down and/or wastewater from the by-product recovery plant. Water quality may have a significant effect on emissions from quenching because dissolved solids may be emitted in the form of particulate and because organic contaminants can become airborne either by vaporization or entrainment in water droplets. These gaseous emissions are not regulated under RCRA, but they are regulated under the Clean Air Act (CAA).

During the coking cycle, volatile matter, 25 to 35% by weight of the initial coal charge, is driven from the coal mass into a common horizontal steel duct, called the collecting main, as coke oven gas. The gas contains hydrogen and methane, ammonia, carbon monoxide, carbon dioxide, ethane, ethylene, benzene, oxygen and nitrogen, hydrogen sulfide, water vapor, cyclopentadiene, toluene, naphthalene, hydrogen cyanide, cyanogen, and nitric oxide. Coke oven gas is initially cleaned with a weak ammonia liquor spray that condenses water, tar, ammonia, and other chemicals (e.g., cyanide, phenol, etc.) from the gas. Some of the collected liquid is used as makeup in the weak ammonia spray, and the excess is pumped to treatment. There are many variations in the by-product recovery plant used to treat the coke oven gas. Historically, many chemicals were derived from the gas because of their market value. The economics have shifted to where many plants now leave various components in the gas. The ultimate example is the non-recovery ovens where the raw gas is combusted inside the oven chamber. When the gas leaves the tar extractor, it carries approximately 75% of the ammonia and 95% of the light oil (primarily benzene, toluene, and xylene) originally present in the raw coke oven gas. The ammonia can be recovered either as an aqueous solution by water absorption or as ammonium sulfate salt. The gas is taken to final coolers or condensers where it is typically cooled by indirect heat exchange to approximately 24°C (75°F). The cooled gas may be passed through light oil or benzol scrubber by using a counter-current circulated heavy petroleum fraction called wash oil that serves as the absorbent medium. The recovered light oil may be sold as crude or distilled to recover benzene, toluene, xylene, and solvent naphtha. After tar, ammonia, and light oil removal, the gas may undergo a final desulphurization process to remove H₂S before being used as fuel. The coke oven gas has a rather high heating value, on the order of 550 Btu/scf. Typically, 35 to 40% of the gas is returned to fuel the coke oven combustion system, and the remainder is used for other heating needs, or is sold or flared.

Major wastewater streams are generated from the cooling of the coke oven gas and the processing of ammonia, tar, naphthalene, phenol, and light oil. Process wastewater may contain benzene, biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, phenols, polycyclic aromatic hydrocarbons (PAH), ammonia, cyanides, and others.

Additional liquid condensates are formed when the pressure and temperature conditions in the coke oven gas transport lines decrease to points that are below the moisture and vapor phase organic compound dew points. The liquid condensate flows through the transport line until it reaches a knock-out pot/settling tank and/or is removed from the main line via bleed-off valves. These liquid condensates are periodically removed because they are heavier than the coke oven gas, subject to freezing, and may prevent the free flow of the coke oven gases. Historical management practices within the industry pertaining to this condensate have included: localized discharge to the ground and/or surface drainage systems, container and tank collection, truck transport to on- and/or off-site wastewater treatment system, tank storage and piping networks to recycle the condensate to the by-product fractionators and recovery system, and reuse as makeup water in the quench systems (coke quench and primary coolers). The physical and chemical characteristics of these condensed liquids may vary significantly from plant to plant, location to location within a plant, and over time. The quantity of and the physical and chemical characteristics of the condensate are affected by the efficiency of the upstream condensers and by-product recovery systems, the amount of insulation on the transport lines, atmospheric temperature, system operating temperature and pressure, and frequency of liquid removal. It should be noted that because of the benzene concentrations, there are several National Emission Standards for Hazardous Air Pollutants (NESHAPS) that may restrict and limit how the condensate is managed or used.^b For example, Part 63 Subpart CCCCC defines acceptable makeup water for the coke quenching systems as surface water from a river, lake, or stream; water meeting drinking water standards; storm water runoff and production area cleanup water except for water from the by-product recovery plant area; process wastewater treated to meet effluent limitation guidelines in 40 CFR Part 420; water from any of these sources that has been used only for non-contact cooling or in water seals; or water from scrubbers used to control pushing emissions. Hence, using the coke oven gas condensate as makeup water for the coke quenching system is limited by the contaminant and pollutant concentrations.

In order for a material to be classified as a hazardous waste, it must first be a solid waste. Therefore, the first step in the hazardous waste identification process is determining if a material is a solid waste. The statutory definition points out that whether a material is a solid waste is not based on the physical form of the material (i.e., whether or not it is a solid as opposed to a liquid or gas), but rather that the material is a waste. The regulations further define solid waste as any material that is discarded by being either abandoned, inherently waste-like, certain military munitions, or recycled. There are 21 exclusions from the definition of solid waste. Some of these are directly applicable to the characterization, classification and determination of the applicable management standards for coke oven gas condensates.

Materials that are recycled are a special subset of the solid waste universe. When recycled, some materials are not solid wastes and therefore are not hazardous wastes. Other recycled materials are solid and hazardous waste, but are subject to less-stringent regulatory controls. The level of regulation that applies to recycled materials depends on the material and the type of recycling. Because some types of recycling pose threats to human health and the environment, RCRA does

^b Including but not limited to: 40 CFR Part 63 Subpart CCCCC – coke ovens, pushing, quenching, and battery stacks; 40 CFR Part 61 Subpart L – benzene emissions from coke by-product recovery plants; 40 CFR Part 61 Subpart J – equipment leaks (fugitive emission sources) of benzene; 40 CFR Part 61 Subpart Y – emissions from benzene storage vessels; 40 CFR Part 61 Subpart BB – benzene emissions from benzene transfer operations; and 40 CFR Part 61 Subparts FF – benzene waste operations.

not exempt all recycled materials from the definition of solid waste. As a result, the manner in which a material is recycled will determine whether or not the material is a solid waste and therefore potentially regulated as a hazardous waste. In order to encourage waste recycling, RCRA exempts three types of wastes from the definition of solid waste:

- Waste Used as an Ingredient — if a material is directly used as an ingredient in a production process without first being reclaimed, then that material is not a solid waste.
- Waste Used as a Product Substitute — if a material is directly used as an effective substitute for a commercial product (without first being reclaimed), it is exempt from the definition of solid waste.
- Wastes Returned to the Production Process — when a material is returned directly to the production process (without first being reclaimed) for use as a feedstock or raw material, it is not a solid waste.

As noted above, the quantity and physical and chemical characteristics of the coke oven gas condensate may vary from plant to plant and perhaps even over time within a plant. Hence, if a company decides that condensate is not a solid waste because it is either an ingredient, product substitute, or was returned to the production process as a feed stock, the company must be prepared to defend the decision with contemporaneous records. The criteria used in making this determination must include a demonstration that the condensate is used without reclamation, beneficiation, and/or treatment; that it is effective; that other product consumption is reduced; that it is not used in an amount that is more than necessary to meet production purposes; and that the facility has maintained records documenting these determinations. There is often uncertainty about when a reclamation process is complete and when the recycled material is a final product rather than a partially reclaimed material. Sometimes a product must be further purified to be sold or used, and this is viewed as refining or purification of the product, and not reclamation. Reducing the moisture content of the coke oven gas via condensation is a purification process. Returning the coke oven gas condensate directly to the production process without reclamation is manufacturing and not wastes management.

Not all materials can be directly used or reused without reclamation. A material is reclaimed if it is processed to recover a usable product (e.g., smelting a waste to recover valuable metal constituents), or if it is regenerated through processing to remove contaminants in a way that restores them to their usable condition (e.g., distilling dirty spent solvents to produce clean solvents). If secondary materials are reclaimed before use, their regulatory status depends on the type of material. For this solid waste determination process, EPA groups all secondary materials into five categories:

- Spent materials are materials that have been used and can no longer serve the purpose for which they were produced without processing. Spent materials are regulated as solid wastes and potentially as hazardous waste while they are in storage and transport. Spent materials that are recycled, however, are no longer regulated as a solid waste while they are being processed or remanufactured and after they are reclaimed or manufactured.
- Sludges are any solid, semisolid, or liquid wastes generated from a wastewater treatment plant, water supply treatment plant, or air pollution control device (e.g., filters,

condensers, spray driers, and/or bag house dust). Sludges from specific industrial processes or sources (known as listed sludges) are solid wastes when reclaimed; used in a manner constituting disposal; burned for energy recovery, used to produce a fuel, or contained in fuels; or accumulated speculatively. On the other hand, characteristic sludges (which are sludges that exhibit certain physical or chemical properties) are not solid wastes when reclaimed. The scrubbers, condensers, fractionators, and precipitators that are used to recover and manufacture the by-products are integral components of the by-product manufacturing processes, and they are not air pollution control devices or wastewater treatment systems; hence, coke oven gas condensate is not sludge.

- By-products are materials that are not one of the primary products of a production process and are not solely or separately produced by the production process. An example is the sediment remaining at the bottom of a distillation column. Another example is the blow-down water from a solvent distillation column. Listed by-products are solid wastes when reclaimed; used in a manner constituting disposal; burned for energy recovery, used to produce a fuel, or contained in fuels; or accumulated speculatively. On the other hand, characteristic by-products are not solid wastes when reclaimed, unless they are used in a manner constituting disposal; burned for energy recovery, used to produce a fuel, or contained in fuels; or accumulated speculatively. Coke oven gas condensate is a by-product of a production process. Coke oven gas is not a listed by-product. Condensate that exhibits the characteristic of a hazardous waste is exempt from the definition of solid waste when destined for recycling. In order to ensure these materials are actually recycled, EPA has established a provision in §261.2 that penalizes facilities that recycle insufficient amounts of these materials. This provision designates as solid wastes certain materials that are accumulated speculatively. A material is accumulated speculatively if it has no viable market or if the person accumulating the material cannot demonstrate that 75 percent or more of the material is recycled in a calendar year, commencing on January 1.
- Commercial chemical products (CCP) are unused or off-specification chemicals (e.g., chemicals that have exceeded their shelf life), spill or container residues, and other unused manufactured products that are not typically considered chemicals. Coke oven gas condensate is not a commercial chemical product.
- Scrap metal is worn or extra bits and pieces of metal parts, such as scrap piping and wire, or worn metal items, such as scrap automobile parts and radiators. Scrap metal that is recycled is exempt from RCRA hazardous waste regulation. Coke oven gas condensate is not scrap metal.

For all recycling activities, the above rules are based on the premise that legitimate reclamation or reuse is taking place. EPA rewards facilities recycling some wastes by exempting them from regulation, or by subjecting them to lesser regulation. Some facilities, however, may claim that they are recycling a material in order to avoid being subject to RCRA regulation, when in fact the activity is not legitimate recycling. EPA has established guidelines for what is legitimate recycling and for activities it considers to be illegitimate or sham recycling. Considerations in making this determination include whether the secondary material is effective for the claimed

use, if the secondary material is used in excess of the amount necessary, and whether or not the facility has maintained records of the recycling transactions. Hence, if a company decides that condensate is not a solid waste or is conditionally excluded from regulation as a hazardous waste, the company must be prepared to defend the decision with contemporaneous records. A company claiming that a waste is not a solid waste or that a waste is conditionally exempt from regulation because it is recycled must be prepared to demonstrate that the conditions for the exclusion are being met.

After a facility determines its waste is a solid waste, it must determine if it is a hazardous waste. This entails determining if the waste is listed and/or has the characteristics of a hazardous waste. A hazardous waste listing is a narrative description of a specific type of waste that EPA considers dangerous enough to warrant regulation. Hazardous waste listings describe wastes from various industrial processes, wastes from specific sectors of industry, or wastes in the form of specific chemical formulations. These wastes are described or listed on four different lists that are found in the regulations.

- The F list is known as wastes from nonspecific sources.
- The K list is known as waste from specific sources.
- The P list and the U list are known as off-specification commercial chemical products.

Characteristic wastes are hazardous because they possess one of four unique and measurable properties. The four characteristics of hazardous waste are:

- ignitability
- corrosivity
- reactivity
- toxicity

Determining whether a waste exhibits the characteristic of a hazardous waste requires one to apply process knowledge or to use the methodologies and procedures described in the regulations to measure the chemical and physical properties and to compare the results of the sample against the established regulatory levels. When a waste generator conducts testing to determine if the waste exhibits any of the four characteristics of a hazardous waste, he or she must obtain a representative sample. For compliance purposes, no sample of the waste stream should exhibit a characteristic that exceeds the characteristic criteria. When using a statistical approach to demonstrate that a waste stream's ignitability and toxicity characteristics are such that the waste is not a hazardous waste, there is a finite possibility that an incorrect determination will be made and non-compliance can occur. The statistical approach reviews the history of data associated with the waste and provides an indication of continued compliance at a certain level of confidence. At any time, a single data point could be received that, when used to calculate the waste characteristic, causes an exceedance of a concentration or ignitability limit.

Coke manufacturing is one of the 13 different industrial or manufacturing categories that generate listed hazardous waste. The following listed waste codes are uniquely generated by the coke manufacturing industry:

- K060 Ammonia still lime sludge from coking operations
- K087 Decanter tank tar sludge from coking operations
- K141 Process residues from the recovery of coal tar, including, but not limited to, collecting sump residues from the production of coke from coal or the recovery of coke by-products produced from coal
- K142 Tar storage tank residues from the production of coke from coal or from the recovery of coke by-products produced from coal
- K143 Process residues from the recovery of light oil, including, but not limited to, those generated in stills, decanters, and wash oil recovery units from the recovery of coke by-products produced from coal
- K144 Wastewater sump residues from light oil refining, including, but not limited to, intercepting or contamination sump sludges from the recovery of coke by-products produced from coal
- K145 Residues from naphthalene collection and recovery operations from the recovery of coke by-products produced from coal
- K147 Tar storage tank residues from coal tar refining
- K148 Residues from coal tar distillation, including, but not limited to, still bottoms

In June 1992, EPA granted a conditional exclusion from the hazardous waste management requirements for K087, K141, K142, K143, K144, K145, K147, and K148 listed wastes, *and any other coke by-product wastes* that exhibit the toxicity characteristic if they are contained and not placed directly on the land and they are recycled in one of the following ways:

- returned to the coke oven as a feedstock to produce coke, or
- returned to the tar recovery process as a feedstock to produce coal tar, or
- mixed with coal tar prior to coal tar refining or sale as a product

It is the opinion of this author that coke oven gas condensate is not a “K,” “F,” “P,” or “U” listed hazardous waste.^c As noted above, the physical and chemical properties of coke oven gas condensate may vary considerably. This variability may affect the feasibility and economics of recycling the condensate, which in turn affects whether it is a solid waste; it is not a factor, however, in determining whether it is or is not a listed hazardous waste.

Once a facility generates a hazardous waste, the waste may become mixed with other wastes, be treated and produce residues, or even be spilled. RCRA provides special regulatory provisions to address the regulatory status of hazardous wastes in these situations. The mixture rule regulates a combination of any amount of a non-hazardous solid waste and any amount of a listed hazardous waste as a listed hazardous waste. Even if a small vial of listed waste is mixed with a large quantity of non-hazardous waste, the resulting mixture bears the same waste code and regulatory status as the original listed component of the mixture, unless the generator obtains a

^c It should be noted that the administrative record associated with a February 1998 EPA administrative law ruling (Final Decision - Docket No. RCRA-111-080-CA) indicates that inspectors employed by the West Virginia Department of Natural Resources observed “K087 drippings from the coke oven gas line.” The administrative law judge found that soil and/or groundwater contamination was caused in part by releases of hazardous waste in the form of drips, spills, and leaks and the burial of K087 and he subsequently ruled in favor of EPA. The original dispute concerned EPA authority and jurisdiction to unilaterally require the facility to undertake responsibility for implementing a RCRA corrective action program.

delisting. Hence, if coke oven gas condensate were to be mixed with a solid hazardous waste having one of the K waste codes shown above, the entire mixture would be regulated as a K waste. The mixture rule applies differently to characteristic wastes. A mixture involving characteristic wastes is hazardous only if the mixture itself exhibits a characteristic. Once a characteristic waste no longer exhibits one of the four properties, it is no longer regulated. Thus, a characteristic waste can be made non-hazardous by treating it to remove its hazardous property. Additionally, any wastes that were listed solely for exhibiting the characteristic of ignitability, corrosivity, and/or reactivity are not regulated as hazardous wastes once the mixture no longer exhibits this characteristic. Coke oven gas condensate that is characteristically hazardous because of toxicity and/or ignitability and that is subsequently mixed with wastewater or other forms of solid waste in such proportions that the mixture is no longer characteristically hazardous are not regulated under RCRA, but may be regulated under the CAA and/or the CWA.

SUMMARY

Hazardous wastes generated in raw material, product storage, or process (e.g., manufacturing) units are exempt from hazardous waste regulation while the waste remains in such units. These units include tanks, pipelines, vehicles, and vessels used either in the manufacturing process or for storing raw materials or products, but specifically do not include surface impoundments. Once the waste is removed from the unit or when a unit temporarily or permanently ceases operation for 90 days, the waste is considered generated and is subject to regulation. Coke oven condensate that remains in the pipe line are exempt from hazardous waste regulation until such time that it is removed from the pipe line in which it was generated or until and unless the coke oven gas manufacturing process ceases operation for more than 90 days.

With careful and diligent management, coke oven gas condensate may:

- be excluded from the realm of solid waste management
- be exempt from the realm of hazardous waste management
- be characteristically hazardous waste
- be subject to numerous NESHAPS