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We greatly appreciate the cooperation of the individual companies that permitted their plants to be sampled and that submitted detailed information to the U.S. EPA on treatment of these wastes.

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1. INTRODUCTION

Pursuant to section 3004(m) of the Resource Conservation and Recovery Act, as enacted by the Hazardous and Solid Waste Amendments on November 8, 1984, the Environmental Protection Agency (EPA) is establishing treatment standards based on the best demonstrated available technology (BDAT) for nonwastewater forms of the wastes generated from the production of acrylonitrile. These wastes are identified in 40 CFR 261.32 as KO11, KO13, and KO14. Compliance with these BDAT treatment standards is a prerequisite for the placement of these wastes in units designated as land disposal facilities according to 40 CFR Part 268. The effective date of these nonwastewater treatment standards is June 8, 1989. The applicability of the restrictions for KO11, KO13, and KO14 wastewaters and the effective date are discussed in the preamble to the final rule for the Second Third wastes.

This background document presents the Agency's technical support for selecting and developing the treatment standards for the constituents to be regulated in the acrylonitrile nonwastewaters. This document also contains some information relevant to the acrylonitrile wastewaters. The EPA will summarize any additional information used to develop performance standards for the wastewaters from acrylonitrile production in an addendum to this background document. Section 2 presents waste-specific information--the number and location of facilities affected by the land disposal restrictions, the waste generating process, and waste characterization data. The technologies used to treat the waste (or similar wastes) are

discussed in Section 3. All the available performance data, including data on which the treatment standards are based, are presented in Section 4. Section 5 explains EPA's determinations of BDAT, and Section 6 discusses the selection of constituents to be regulated. The treatment standards are determined in Section 7.

EPA wishes to point out that, because of facility claims of confidentiality, this document does not contain all of the data that EPA used in its regulatory decision-making process. Under 40 CFR Part 2, Subpart B, facilities may claim any or all of the data that are submitted to EPA as confidential. EPA will make determinations regarding the validity of the facility's claim of confidential business information (CBI) according to 40 CFR Part 2, Subpart B. In the meantime, the Agency will treat the data as CBI. Additionally, the Agency would like to emphasize that it evaluated all available data (including CBI data) in developing the BDAT treatment standards for KOII/KOI3/KOI4 nonwastewaters.

The BDAT program and EPA's promulgated methodology are more thoroughly described in two additional documents: Methodology for Developing BDAT Treatment Standards (USEPA 1988a) and Generic Quality Assurance Project Plan for Land Disposal Restrictions Program (BDAT) (USEPA 1987). The petition process to be followed in requesting a variance from the BDAT treatment standards is discussed in the methodology document.

The Agency has information indicating that generators of the KOll, KOl3, and KOl4 listed wastes currently mix them together before treatment and disposal. Consequently, EPA has developed treatment standards for

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these wastes as KO11/KO13/KO14 mixed nonwastewaters. However, each individual waste, if disposed of separately, must also meet the treatment standards. (For the purpose of determining the applicability of the treatment standards, wastewaters are defined as wastes containing less than 1 percent (weight basis) total suspended solids^{*} and less than 1 percent (weight basis) total organic carbon (TOC). Waste not meeting this definition must comply with the treatment standards for nonwastewaters.)

The acrylonitrile wastes contain cyanide and BDAT list organic constituents. Rotary kiln incineration was determined to be the BDAT for both the organics and cyanides in the KOll/KOl3/KOl4 nonwastewaters. The Agency is regulating four organic constituents and cyanide in nonwastewater forms of the acrylonitrile wastes. For the BDAT list organics and cyanide, the treatment standards reflect total waste concentration. The units for total waste concentration are mg/kg (parts per million on a weight-by-weight basis). Because the Agency is not regulating any BDAT list metal constituents, there are no treatment standards based on the metal concentrations in the leachate from the toxicity characteristics

[&]quot;The term "total suspended solids" (TSS) clarified EPA's previously used terminology of "total solids" and "filterable solids." Specifically, total suspended solids is measured by Method 209c. (Total Suspended Solids Dried at 103 to 105°C) in Standard Methods for the Examination of Water and Wastewater, 16th Edition (APHA, AWWA, and WPCF 1985).

leaching procedure (TCLP). Testing procedures for all sample analyses performed for the regulated constituents are specifically identified in Appendix A of this background document.

The treatment standards for the KOll/KOl3/KOl4 nonwastewater forms are shown in Table 1-1. Nonwastewaters that, as generated, contain the regulated constituents at concentrations that do not exceed the treatment standards are not prohibited from land disposal units untreated.

In the January II. 1989, proposed rule (54 FR 1066-1071), the Agency proposed wastewater treatment standards based on the performance of wet air oxidation followed by biological treatment for amenable cyanides, total cyanides, and organic constituents, and chemical precipitation, settling, and filtration for metal constituents. The Agency received many comments concerned with EPA's rationale for transferring performance data for the cyanide constituents from wet air oxidation of F007 wastes, and for organic constituents from the effluent limitations for facilities in the Organic Chemical Plastics and Synthetic Fibers (OCPSF) industry for biological treatment. Because of these comments and the additional treatment data that are being compiled by the Ad Hoc Acrylonitrile Producers UIC Group, the Agency believes that additional data collection and analysis is necessary prior to promulgation of these treatment standards.

Therefore, the Second Third land disposal restriction rule does not promulgate treatment standards for the wastewater forms of KOII, KOI3 and KOI4. These wastes were originally scheduled for regulation in the First

Third, with a statutory deadline of August 8, 1988. Since the Agency still has not promulgated standards for the wastewater forms of KO11, KO13 and KO14, land disposal of these wastewaters shall continue to be regulated by the "soft hammer" provisions in 40 CFR 268.8. EPA intends to promulgate concentration-based treatment standards for cyanides, organics, and metals constituents for these wastes prior to May 8, 1990.

Table 1-1 BDAT Treatment Standards

Constituent	Maximum for any single grab sample				
	Total composition (mg/kg)	n TCLP (mg/l)			
Acetonitrile	1.8	Not Applicable			
Acrylonitrile	1.4	Not Applicable			
Acrylamide	23	Not Applicable			
Benzene	0.03	Not Applicable			
Cyanides (Total)	57	Not Applicable			

BDAT Treatment Standards for KO11/KO13/KO14 Nonwastewaters

BDAT Treatment Standards for KO11/KO13/KO14 Wastewaters

	Maximum for any	
	single_grab_sample	
	Total composition	
Constituent	(mg/1)	

(EPA intends to propose and promulgate KO11/KO13/KO14 wastewater treatment standards prior to May 8, 1990.)

2. INDUSTRY AFFECTED AND WASTE CHARACTERIZATION

This section includes a description of the industry affected by the land disposal restrictions for waste codes KOll, KOl3, and KOl4 and the production processes employed in this industry. Also included is a discussion of how KOll. KOl3, and KOl4 wastes are generated as well as characterization of both the individual KOl1, KOl3, and KOl4 wastes and the KOl1/KOl3/KOl4 mixed wastes. This section concludes with a discussion of the basis for combining listed acrylonitrile waste codes into one treatability group.

The full list of hazardous waste codes from specific sources is given in 40 CFR 261.32. Within this list, three specific hazardous waste codes are generated by acrylonitrile manufacturers:

- KOII: Bottom stream from the wastewater stripper in the production of acrylonitrile.
- K013: Bottom stream from the acetonitrile column in the production of acrylonitrile.
- K014: Bottoms from the acetonitrile purification column in the production of acrylonitrile.

2.1 Industry Affected and Process Description

The four-digit standard industrial classification (SIC) code reported for the acrylonitrile industry is 2869. The Agency has identified six facilities in the United States that actively manufacture acrylonitrile and could generate KO11, KO13, and KO14 listed wastes (Standford Research Institute 1988). Of the six acrylonitrile manufacturers, one is located in Ohio (EPA Region V), one in Louisiana (EPA Region VI), and four in Texas (EPA Region VI).

Acrylonitrile is manufactured in the United States by the Sohio Process. This process involves vapor-phase catalytic air oxidation of propylene and ammonia, also known as ammoxidation, to yield acrylonitrile. The principal byproducts of the process are hydrogen cyanide, acetonitrile, and acrylamide. The process flow diagram is illustrated in Figure 2-1. Approximate stoichiometric quantities of propylene, ammonia, and oxygen (as air) are reacted in a fluidized bed reactor to yield acrylonitrile and other byproducts. The gaseous effluents from the reactor are quenched and scrubbed in a quenching column using sulfuric acid solution. Unreacted ammonia is converted to soluble ammonium sulfate in the presence of sulfuric acid. Liquid effluents from the quench column are treated in a wastewater stripping column to recover the low boiling point organics. The bottom stream from the stripping column constitutes one of the listed wastes (KOll). Typical generation rates for this waste stream vary from 100 to 200 gallons per minute.

Gaseous effluents from the quench column are sent to an absorber, where the acrylonitrile and byproducts are absorbed in water. The aqueous solution from the absorber is treated in an acrylonitrile recovery column to obtain acrylonitrile and hydrogen cyanide (HCN) as the overhead products. The overhead products are treated further in a heads column to recover hydrogen cyanide. The acrylonitrile bottom stream from the heads column is dried and purified further to yield polymer-grade acrylonitrile.

The bottom stream from the recovery column consists of a dilute aqueous solution of acetonitrile, which is treated in a steam stripping column to obtain acetonitrile and hydrogen cyanide as the overhead



FIGURE 2-1. SCHEMATIC FLOW DIAGRAM OF THE SOHIO PROCESS FOR PRODUCTION OF ACRYLONITRILE

products. The bottom stream from this column constitutes a listed waste stream (K013). Typical generation rates for this stream vary from 100 to 200 gallons per minute. Depending upon the demand for acetonitrile, some acrylonitrile production plants treat the crude acetonitrile stream in a purification column to obtain commercial-grade acetonitrile. The bottoms from the acetonitrile purification column represents the third listed waste stream (K014). Typical generation rates for this stream vary from 4 to 14 gallons per minute. In acrylonitrile production facilities where the acetonitrile is not refined, the crude acetonitrile stream is usually incinerated in an off-gas incinerator, thus eliminating the generation of K014.

2.2 <u>Waste Characterization</u>

The waste streams are identified in Figure 2-1. The listing constituents for KO11, KO13. and KO14 include acrylonitrile, acetonitrile, and hydrocyanic acid. The approximate percent concentrations of major constituents making up individual KO11, KO13, and KO14 listed wastes, KO11/KO13/KO14 wastewater mixtures, and KO11/KO13/KO14 nonwastewater mixtures are summarized in Table 2-1 at the end of this section. (For the purposes of this rule, the Agency's definition of a wastewater is a waste that contains less than 1 percent (weight basis) total suspended solids and less than 1 percent (weight basis) total organic carbon (TOC). Wastes not meeting this definition are defined as nonwastewaters.)

Typically, the KOll waste stream contains about 100 to 4,000 ppm of cyanide, 40 to 3,000 ppm of acetonitrile, 0.2 to 8,000 ppm of acrylonitrile, 1,000 to 2,000 ppm of acrylamide, and less than 200 ppm of

acrolein. In addition to the primary contaminants listed above, this stream also contains approximately 4 percent suspended solids. The suspended solids consist largely of spent, inorganic catalyst particles and polymeric acrylonitrile. Also, the KOI1 stream contains about 10 percent dissolved sulfates. Waste characterization data for KOI1 are presented in Table 2-2. These data indicate that KOI1 is a nonwastewater by definition.

The KO13 waste stream typically is 99 percent water and contains about 26 to 60 ppm of cyanide, less than 35 ppm of acetonitrile, less than 10 ppm of acrylonitrile, less than 120 ppm of acrylamide, and less than 1 ppm of acrolein. Waste characterization data for KO13 are presented in Table 2-3. These data indicate that KO13 is a wastewater by definition.

Primary pollutants in the KO14 waste stream are acetonitrile and cyanide. Generally, the KO14 waste stream contains 1,000 to 60,000 ppm of acetonitrile and up to 10,000 ppm of ethyl cyanide and is 83 to 99 percent water. Waste characterization data for KO14 are presented in Table 2-4. These data indicate that KO14 is a nonwastewater by definition.

It is current practice to mix the waste streams in settling ponds/ tanks where the suspended solids are separated as a sludge that is generally land disposed or incinerated and a liquid that is usually injected into a deep well. Waste characterization data for mixed KO11/KO13/KO14 wastewaters and mixed KO11/KO13/KO14 nonwastewaters are presented in Table 2-5.

2.3 Determination of Waste Treatability Group

In cases where EPA believes that constituents present in different listed wastes can be treated to similar concentrations by using the same technologies, the Agency may combine the listed wastes into one treatability group.

The Agency has determined that the acrylonitrile waste codes (KOll, KOl3, and KOl4) represent a single waste treatability group. This determination was made because these wastes originate from the same industry and similar processes and have similar chemical characteristics. Although concentrations of specific constituents will vary from one listed waste to another, all of the above wastes contain similar constituents and are expected to be treatable to similar levels using the same technology. Furthermore, in a typical production facility, the acrylonitrile waste streams (KOll, KOl3, and possibly KOl4) are commingled prior to their ultimate disposal. The mixed waste is sent to settling ponds/tanks, where the suspended solids are removed as an underflow sludge and the liquid is disposed of in deep wells.

The Agency is aware that all acrylonitrile production facilities generate KOll and KOl3 waste streams and only those facilities that purify the crude acetonitrile generate the KOl4 waste stream. However, the Agency believes the KOl1/KOl3/KOl4 waste matrix is more difficult to treat than the KOl1/KOl3 matrix, hence, the KOl1/KOl3 waste mixture can be treated to the same levels as the KOl1/KOl3/KOl4 waste mixture. This assumption is based on the characterization data for the individual

wastes showing KO14 typically has the highest concentrations of the regulated BDAT constituents among these wastes. Consequently, EPA examined the characteristics of the KO11/KO13/KO14 mixed wastes, applicable treatment technologies, and treatment performance levels attainable in order to support a single regulatory approach for the three wastes as a KO11/KO13/KO14 nonwastewater mixture and a KO11/KO13/KO14 wastewater mixture.

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Table 2	-1 Ma	jor Ço	nstitueni	Analysis o	f Untreated
	KOII,	K013,	and K014	Listed Vas	tes

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	Concentration (wt X)							
Major constituents	KOII	K013	K014	Nixed KO11/KO13/KO14 wastewater	Mixed K011/K013/K014 nonwastewater			
Ammonium sulfate	10	-		1.0	-			
BDAT list volatile constituents (including acrolein, acetonitrile, acrylonitrile, benzene, ethyl cyanide)	0.5	<0.1	6	. 0.9	4			
Cyanide	0.5	<0.1	ব	0.1	16			
Inert solids (including silicon, molybdenum, iron, aluminum oxides)	4	0.8	-	<1.0	50			
Vater	85	99	93	97	30			

- = No analysis performed.

	Untreated KOII waste characterization (mg/kg)										
Ana lys i s	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(i)	
BDAl_List_Volatiles:						•					
Acrolein	200			-	-	30.1	-	60-120	-	-	
Acetonitrile	3,000		-	-	3,000	2,300	-	40-2,800	1,100	-	
Acry lamide	1,000	-		-	-	2,040	-	-	-	-	
lory lon itri le	>500	-	-	<0.2	< 500	5,420	-	100-2,500	8,000		
lenzene	-	-	-	-	-		-	-	100		
thyl cyanide	-	-	-	-	-		-	-	47		
Pyr idine	-	-	-	-	-			-	300		
ADAT List Semivolatiles:											
'heno l	-	-	-	<0.03	-	-	-	-	0.13		
IDAT List Metals:											
Int imony	-	-	-	-	-	-	-	-	0.20	-	
rsenic	-	-	-	-	-	-	-	-	0.21	-	
larium -	· –	-	-	-	-	-	-	-	0.004	-	
lickel	-	-	-	-	-	-	-	-	0.59	-	
ead	-	• -	-	-	-	-	-	-	0.04	-	
linc	-	-	-	-	-	-	-	-	0.02		
<u>)ther BDAT List Inorganic</u>	<u>cs</u> :										
Cyan ide	-	270	700	100	-	1,240	-	-	3,700	-	
iyanide (as											
hydrogen cyanide)	4,000	-	-	<0.2	7,000	-	-	-	-	-	
luor ide	-	-	-	-	-	۲.	-	-	47	-	
<u>ithers</u> :											
iceta Idehyde	1,000	-	-	-	-	-	-	-	-	-	
cetic acid	2.000	-	-	-	-	-	-	-	-		
crylic acid	300	-	-	-	-	-	-	-	-	-	
crylonitrile polymer	-	-		-	-	-	-	-	-		
mmori i a	16,500	19,000	24,000	9,300	15,000	-	-	-	-	-	
mmonia sulfate	-	-	-	-	-	-	100,000			100,000-120.0	
ish content		1,000	-	-	-	-				-	

Table 2-2 BDAT Constituent Composition and Other Data for K011

	Untreated KO11 waste characterization (mg/kg)										
Ana lys is	(a)	(b)	(c)	(d)	(e)	(f)	(9)	(h)	(i)	(i)	
thers (continued):											
00	-	-	-	-	-	46,300	-	-	-	-	
oron	-	-	-	0.4	-	-	-	-	-	-	
tu content (Btu/lb)	-	-	-	-	-	-	-	-	524	-	
00	-	-	-	-	-	65,500	-		-	-	
umaronitrile	500	-	-	-	-	-	-	-		-	
ydrogen sulfide	-	-	-	-	-		-	-	6	-	
itri les	2,800	-	-	-	-	-	-	-	-	-	
itrogen (as amide)	3,100	-	-	-	-	-	-			-	
itrogen (as ammonia)	13,700	-	-	-	-	-	-	-		-	
itrogen (as nitrate)	61	-	-	-	-	-	-	-	-	-	
itrogen (as nitrile)	4,200	-	-	-	-	-	-	-	-	-	
itrogen (as nitrite)	540	-	-	-	-	-	-			-	
H	4.9-5.0	-	-	-	-	-	-	-	-	-	
hosphorous	-	-	-	0.4	-	-	-	-	-	-	
olymeric material	60,000	-	-	-	-	-	-	-	-	-	
ulfates	32,000	74,000	86,000	90,000	32,000	-	-	-	-	-	
ulfur	-	-	-	-	-	-	-	-	1.4		
uspended solids	-	-	-	-	40,000	-	-	-	-	-	
DC	-	-	-	-	-	26,000	-	-	-	-	
ater (%)	-	-	-	-	-	-	90	-	90	-	

Table 2-2 (continued)

- = No analysis performed.

(a) Reference: USEPA 1986a.

- (b) Reference: USEPA 1986a.
- (c) Reference: USEPA 1986a.
- (d) Reference: USEPA 1986a.
- (e) Reference: USEPA 1980.

(f) Reference: Nemorandum from Samuell. Hayes, EER Laboratory Manager, to Lisa Brown, HWERL Project Officer, on November 25, 1987, concerning sample results.

(g) Reference: Memorandum from Radha Krishman, PEI, to Ron Turner, EPA-ORD, on October 23, 1987, concerning telephone conversation with Steve Lang, Environmental Superintendent for the Sobio Lima Plant.

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(h) Reference: Memorandum frum Duane Parker, Dyanamac, to Yvunne Garbe, £PA-OSW, on January 2, 1987.

(i) Reference: USEPA 1988a.

(j) Reference: Memorandum from Radha Krishman, PEL, to Ron Turner, LPA-OKD, on December 9, 1987, concerning site visit to Schio Chemical.

-			Untreate	d KO13 waste char	acterization	mg/kg)		
Analysis	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
DAI List Volatiles:								
cetone	-	-	-	-	-	-	_	0.45
cetonitrile	35	-	-	-	35	26.5	_	6.8
rolein	-	-	-	0.8	-	0.34	-	-
crylamide	-	-	-	-	-	120	-	
crylonitrile	<10	-	-	2.5	<10	1.61	-	2.1
DA <u>l List Semivolatiles</u> :								
neno 1	-	-	-	<0.01		-	-	-
DAT List Metals:								
rsenic	-	-	-	-	-	-	-	0.01
n ium	-	-	-	-	-	-	-	0.03
ickel	-	-	-	-	-	-	-	0.02
ead	-	-	-	-	-	-	-	0.003
inc	-	-	-	-	-	· –	-	0.02
ther BDAT List Inorganics:								
yan ide	-	35	26	60	-	34	-	31
yanide (as hydrogen cyanide)	225	-	-	-	225	-	-	-
<u>lhers</u> :								
cetic acid	120	-	-	-	-	-	-	-
monia	220	143	500	300	-	-	-	-
h	-	4,000	-	-	-	-	-	-
ND	-	-	-	-	-	46,300	-	-
bron		-	-	0.2	-	-	-	-
u content (Btu/1b)	-	-	-	-	-	-	-	103
	-	-	-	-	-	15,800	-	-
itri les	6,700	-	-		-	-	-	-
		6.7		5.2	-	-	-	
osphorous	-	-	-	19	-	-	-	-
ulfates	500	153	-	36	-	-	-	-
DC	-	-	-	-	-	4,810	1,000	4,800
ater (%)		-	-	-	-	-	99	99.5

Table 2-3 BDAT Constituent Composition and Other Data for KO13

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- = Nu analysis performed.
- (a) Reference: USEPA 1986a.
- (b) Reference: USEPA 1986a.
- (c) Reference: USLPA 1986a.
- (d) Reference: USLPA 1986a.
- (e) Reference: USEPA 1980.

(f) Reference: Memorandum from Samuel L. Hayes, EER Laboratory Manager, to Lisa Brown, HMERL Project Officer, on November 25, 1987, concerning sample results.

(g) Reference: Momorandum from Radha Krishman, PEI, to Ron Turner, EPA-ORD, on October 23, 1987, concerning telephone conversation with Steve Lang, Environmental Superintendent for the Sobio Lima Plant.

(h) Reference: USEPA 1988b.

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		Untreated KO14 waste characterization (mg/kg)						
Ana lys i s	(a)	(b)	(c)	(ป)	(e)			
DAT List Volatiles:								
cetone	-	-	-		4.3			
ceton itri le	1,000-2,000	-	22,000	60,000	3,000			
ichlorodifluoromethane	-	-	-		9.1			
thyl cyanide	-	-	-	10,000	130			
yridine	-		-	1,700	99			
NAI List Somiuolatiles								
-Picoline	-	-	-	120	-			
DAT List Netals:								
nt imony	-	-	<0.85	0.05	<0.034			
arium	••	-	<0.05	0.01	0.00			
adm i um		-	<0.10	0.006	0.02			
hromium	-	-	<0.18	0.03	0.01			
opper	-	-	<0.15	0.05	0.03			
icke 1	-	-	<0.38	0.04	0.02			
ead		-	<0.05	0.011	0.04			
inc	-	-	0.07	0.03	0.04			
ther BDAT List Inorganic	<u>s</u> :							
yan ide	5,000	-	4.3	300	4,500			
thers:								
tu content (Btu/lb)	-	-	1,589	718	435			
н	2.0-2.5	-	-	-	-			
00	-	1,000	-	-	-			
ater (X)	-	99	83.4	93.2	96			

Table 2-4 BDAT Constituent Composition and Other Data for KO14

- = No analysis performed.

(a) Buttoms from the acetonitrile purification column in the production of acrylonitrile (Reference: USEPA 1985).

(b) Reference: Memorandum from Radha Krishman, PEI, to Ron Turner EPA-ORD, on October 23, 1987, concerning Telephone conversation with Steve Lang, Environmental Superintendent for the Sobio Lima Plant.

(c) Reference: USEPA 1988b.

(d) Reference: USEPA 1988b.

(e) Reference: USEPA 1988b.

	Untreated mixed K011/K013/K014 waste characterization (mg/kg)					
Ana lys is	(a)	(b)	(c)	(d)	(e)	
<u>BDAY List Volatiles:</u>						
Acetonitrile	0.68-2./	177	500-50,000	420-490	575	
Acetone	0.04 0.095	-	-	-	24.4	
Acrylamide	2.4-2.9	-	-	-	270	
Acrylonitrile	0.41-0.95	217	-	<5-65	-	
Benzene	48-61	-	-	-	-	
Ch loroform	0.030-0.042	-	-	-	-	
Nethylene chloride	0.023 0.042	-	-		-	
1,1,1-Trichloroethane	0.026-0.045	-	-	-		
Trichloroethene	0.014-0.019	-	-	-	-	
<u>Other volatiles</u>						
St yrene	14-19	-	-	-	-	
<u>BDAT List Semivolatiles</u> :						
Pheno I	-	4.2	-	-	-	
BDAT List Metals:						
Arsenic	2.7-6.2	0.02	-	-	<0.05	
Barium	82-200	-	-	-	15.4	
Cadmium	2.0-2.9	-	-	-	<0.04	
Chromium	95-200	0.17		-	0.38	
lead	35-41	-	-	-	0.012	
Nickel	280-470	3.2		-	1.08	
Zinc	140-210	0.28		-	8.1	
<u>Other BDAT List Inorganics</u> :						
Cyan ide	5,000-5,200	391	500-50,000	240-350	1,277	
Cyanide (as hydrogen cyanide)	-	-	20,000 250,000	-	-	
Fluoride	56-73	-	-	-	-	

Table 2-5 BDA1 Constituent Composition and Other Data for K011/K013/K014 Wixed Wastes

	Untreated mixed K011/K013/K014 waste characterization (mg/kg)					
Ana tys is	(a)	(b)	(c)	(d)	(e)	
Other:						
Acrylonitrile polymer	-	-	20,000-250,000	-	-	
Aluminum	500-1,100	-	-	`		
Aluminum oxide		-	20,000-500,000	-	-	
Ammonia	-	4,000	-	-	-	
80D (biological oxygen demand)	-	-	-	-	7,207	
COD (chemical oxygen demand)	-	-	-	6,440-26,100	37,900	
Copper	12-22	-	-		0.20	
Iron	2,000-4,000	5.9	20,000 500,000	-	-	
to lybdenum	8,300 17,000	40.1	20,000-500,000	-	73.6	
H	-	-	-	-	8.1	
Phosphorous	-	2.4		-	-	
Silicon	45-200	-	-	-	-	
Sulfațe	33,000-36,000	12,000 `	20,000-500,000	29,000-45,000	-	
lotal solids	-	-	100,000-400,000	-	91,000	
IDS (total dissolved solids)	-	-	-	53,000-75,000	-	
IOC (% carbon)	17-31	-	-	-	-	
dater (X)	-	97	10-30	-	-	

Table 2-5 (continued)

- = No value reported.

- (a) Nonwastewater spent catalyst from the bottom of a surface impoundment containing KOI1, KOI3, and KOI4. (Reference: USEPA 1988a.)
- (b) Combined K011, K013, and K014 wastewater. Aqueous waste includes plant washdown water, transport vehicle flush water, and rainwater runoff from the manufacturing unit. (Reference: USEPA 1985.)
- (c) Combined KOII, KOI3, and KOI4 nonwastewater. (Reference: USEPA 1985.)
- (d) Combined K011, K013, and K014 wastewaters. (Reference: Memorandum to Ronald Turner, EPA-OSV, from Radha Krishnan, PEI, on February 1, 1988.)
- (e) Combined K011, K013, and K014 wastewaters. (Reference: Memorandum to James Berlow, EPA-OSW, from Ronald Turner, EPA-ORD, on June 21, 1988, concerning the results of wet air oxidation bench-scale tests of K011, K013, and K014 mixed sludge.)

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3. APPLICABLE AND DEMONSTRATED TECHNOLOGIES

Section 2 established one treatability group for the management of KO11, KO13, and KO14 nonwastewaters. This section identifies the treatment technologies that are applicable to this group and determines which, if any, of the applicable technologies can be considered demonstrated for the purposes of establishing BDAT.

To be applicable, a technology must be theoretically capable of treating the waste in question or of treating a waste that is similar in terms of the parameters that affect treatment selection. The applicable technologies are discussed in Appendix B and Appendix C. To be demonstrated, the technology must be employed in full-scale operation for the treatment of the waste in question or a similar waste. Technologies that are available only at pilot- and bench-scale operations are <u>not</u> considered in identifying demonstrated technologies.

3.1 <u>Applicable Treatment Technologies</u>

Initial data gathering on the treatment of KOII, KOI3, and KOI4 wastes included phone contacts with industry, review of the technical literature, and contacts with the EPA Office of Research and Development.

Characterization data presented in Section 2 show that the KO11, KO13, and KO14 listed wastes contain treatable quantities of BDAT list organics and cyanide. By definition, the KO11 and KO14 listed wastes are nonwastewaters and KO13 is a wastewater; however, most generators of the acrylonitrile wastes mix them together in a settling pond/tank, which

generally results in a KOll/KOl3/KOl4 wastewater and nonwastewater. The treatment technologies considered applicable for the nonwastewater forms are those that destroy or recover BDAT list organic compounds and cyanide.

The applicable technologies that the Agency has identified for treatment of BDAT list organics and cyanide present in KO11/KO13/KO14 nonwastewater are rotary kiln incineration and wet air oxidation.

Incineration is a technology that destroys the cyanide and organic components in the waste. Wet air oxidation is a technology used to treat aqueous wastes that contain certain organics and oxidizable inorganics such as cyanide. Wet air oxidation reduces but typically does not totally destroy the organic concentrations in the treatment residuals (i.e., wastewater effluent and reactor still bottoms). That is, these residues may still contain quantities of BDAT list organic and cyanide concentrations that may require further treatment prior to disposal.

3.2 <u>Demonstrated Treatment Technologies</u>

The Agency believes that incineration is demonstrated to treat the BDAT list organics and cyanide present in the KO11/KO13/KO14 nonwastewaters. The Agency has identified one facility performing pilot-scale incineration tests on the KO11/KO13 nonwastewaters. Incineration of the KO11/KO13/KO14 nonwastewaters has also been tested at an EPA test facility. Furthermore, incineration is a proven full-scale technology for destroying organics and cyanides in numerous hazardous waste streams. Hence, the Agency believes that incineration is demonstrated for KO11/KO13/KO14 nonwastewaters.

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Wet air oxidation is demonstrated to treat KO11/KO13/KO14 nonwastewaters. EPA has identified one facility that is currently performing pilot-scale tests on the KO11/KO13/KO14 nonwastewaters. In addition, wet air oxidation is a proven full-scale technology for treating organics and cyanides in numerous hazardous wastes. Thus, the Agency considers wet air oxidation to be demonstrated for KO11/KO13/KO14 nonwastewaters.

Detailed discussions of incineration, and wet air oxidation are presented in Appendix B and Appendix C.

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4. TREATMENT PERFORMANCE DATA BASE

This section presents the data available to EPA on the performance of demonstrated technologies in treating the KOll, KOl3, and KOl4 listed wastes. These data are used elsewhere in this document for determining which technologies represent BDAT (Section 5), for selecting constituents to be regulated (Section 6), and for developing treatment standards (Section 7). In addition to full-scale demonstration data, the data used to develop treatment standards may include data developed at research facilities or obtained through other applications at less than full-scale operation, as long as the technology is demonstrated in full-scale operation 5.

Performance data, to the extent that they are available to EPA, include the untreated and treated waste concentrations for a given constituent, values of operating parameters that were measured at the time the waste was being treated, values of relevant design parameters for the treatment technology, and data on waste characteristics that affect performance of the treatment technology.

Where data are not available on the treatment of the specific wastes of concern, the Agency may elect to transfer data on the treatment of a similar waste or wastes, using a demonstrated technology. To transfer data from another waste category, EPA must find that the wastes covered by this background document are no more difficult to treat (based on the waste characteristics that affect performance of the demonstrated treatment technology) than the treated wastes from which treatment performance levels are being transferred.

4.1 <u>Nonwastewaters</u>

EPA tested incineration to demonstrate the actual performance achievable by this technology for treatment of the BDAT list organics and cyanide present in the KO11/KO13/KO14 nonwastewaters. Since EPA is not aware of any generator or treatment, storage, and disposal (TSD) facility currently using full-scale incineration for treatment of KO11, KO13, and KO14 listed wastes, the KO11/KO13/KO14 nonwastewaters were collected from a generator and incinerated using a pilot-scale unit at a commercial facility, John Zink Company in Tulsa, Oklahoma.

The Agency has received incineration performance data from an industrial source testing incineration as a treatment for KOll/KOl3 nonwastewaters; however, no BDAT list constituent concentrations for the treatment residuals (i.e., scrubber water, ash) were reported.

EPA has collected untreated and treated data for KO11/KO13/KO14 nonwastewaters using rotary kiln incineration at the commercial facility. These data are shown in Table 4-1 at the end of this section. Four of the data sets show significant treatment for two organics (i.e., benzene, styrene) and cyanide detected in the untreated KO11/KO13/KO14 nonwastewaters. (For a discussion on significant treatment, see Section 5.) The treated data represent total waste concentration found in the scrubber water and ash residuals. Operating data and design data collected during the test are also shown in Table 4-1. These data indicate that the system was operated within the design specifications.

The Agency has received wet air oxidation performance data from an industrial source. These data show reductions for some of the organics

and cyanide concentrations in the treatment residuals. However, these data and all treatment process information have been classified as confidential business information and cannot be presented in the KOll/KOl3/KOl4 background document. These data are located in the RCRA CBI docket.

4.2 <u>Wastewaters</u>

Treatment performance data specifically for the KOll/KOl3/KOl4 wastewaters are being compiled by the Ad Hoc Acrylonitrile Producers UIC Group. These data will be presented in an addendum to this background document.

5. IDENTIFICATION OF BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT)

This section presents the Agency's rationale for determining the best demonstrated available technology (BDAT) for KOll/KOl3/KOl4 nonwastewaters. Based on the lack of available data specifically for treatment of acrylonitrile wastewaters as described in Section 4, the Agency intends to collect additional data on treatment of KOll/KOl3/KOl4 wastewaters and to identify the BDAT by May 8, 1990.

To determine BDAT, the Agency examines all available performance data on technologies that are identified as demonstrated to determine (using statistical techniques) whether one or more of the technologies performs significantly better than the others. All performance data used for determination of best technology must first be adjusted for accuracy, as discussed in EPA's publication, Methodology for Developing BDAT Treatment Standards. (Accuracy adjustment accounts for the ability of an analytical technique to recover a particular constituent from the waste in a particular test. The recovery of a constituent is usually determined by spiking a sample with a known amount of the target constituent and then comparing the spiked sample amounts with results from unspiked samples.) The accuracy-corrected performance data for the KO11/KO13/KO14 wastes are presented in Table 5-1 at the end of this section. BDAT must be specifically defined for all streams associated with the management of the listed waste or wastes; this pertains to the original waste as well as to any residual waste streams created by the treatment process.

The technology that performs best on a particular waste or waste treatment is then evaluated to determine whether it is "available." To be available, the technology must (1) be commercially available to any generator and (2) provide "substantial" treatment of the waste, as determined through evaluation of accuracy-adjusted data. In determining whether treatment is substantial, EPA may consider data on the performance of a waste similar to the waste in question, provided the similar waste is at least as difficult to treat. If the best technology is found to be not available, then the next best technology is evaluated, and so on.

5.1 BDAT for Nonwastewaters

As mentioned in Section 2, the KOll/KOl3/KOl4 nonwastewaters contain BDAT list organics and cyanide. These wastes can have a total organic carbon content of greater than 1 percent and a total suspended solids content of greater than 1 percent.

The two demonstrated technologies identified for organics and cyanide treatment of KOI1/KOI3/KOI4 nonwastewaters for which the Agency has data are rotary kiln incineration and wet air oxidation. Operating data collected during both the incineration and wet air oxidation tests show that both data sets represent the performance of systems operating within the design specifications. Therefore, all data were used in the selection of BDAT.

Next, the Agency examined both data sets to determine whether incineration performs better than wet air oxidation. The results of the comparison of incineration and wet air oxidation indicate that incineration provides better treatment for the organics and cyanide in the KO11/KO13/KO14

nonwastewaters. Because the wet air oxidation data are confidential, reasons for this decision are presented as confidential business information and are located in the RCRA CBI docket.

Using the incineration performance data, EPA's determination of substantial treatment for organics is based on the reduction of BDAT list organic constituents from levels as high as 61 mg/kg to nondetectable levels of less than 0.01 mg/kg in the ash residual. EPA's determination of substantial treatment for cyanide is based on the reduction of total cyanide from levels as high as 2,000 mg/kg to levels of less than 38 mg/kg in the ash. The concentrations of cyanide in the ash residual may actually be lower than the values reported, but the complex ash residual matrix caused a higher than desired detection limit.

The Agency has determined that these reductions are substantial and that incineration is available to treat organics and cyanide present in KO11/KO13/KO14 nonwastewaters because it is commercially available. Therefore, incineration represents BDAT for the organics and cyanide present in the KO11/KO13/KO14 nonwastewaters.

5.2 BDAT for Wastewaters

The characterization data presented in Section 2 reveal that the KO11/KO13/KO14 wastewaters contain BDAT list organics and cyanide. The wastewaters usually contain less than 1 percent total organic carbon and less than 1 percent total suspended solids.

The Agency received several comments on the proposed rule indicating that treatability studies on actual KO11/KO13/KO14 wastewaters will be available in the future. EPA has decided to review these additional data

before establishing BDAT for the KO11/KO13/KO14 wastewaters, since the Agency believes that these treatability tests may show better treatment than the available data.

Table 5-1 Summary of Accuracy Adjustment of Performance Data for Incineration of KO11/KO13/KO14 Nonwastewater

<u>Analytical Data</u> Constituents	BDAT_list_constituent_concentrations							
	Sample Set #1							
			Percent					
	Mixed KOll/KOl3/KOl4 nonwastewaters (mg/kg)	Ash (mg/kg)	for matrix spike test	Accuracy correction factor	Accuracy- adjusted concentration (mg/kg)			
BDAT list volatiles								
Acetonitrile	0.870	<0.5	7 9	1.266	<0.63			
Acrylonitrile	0.410	<0.5	100	1.0	<0.5			
Acrylamide	2.8	<6.5	79	1.266	<8.2			
Acetone	<0.04	<0.25	100	1.0	<0.25			
Benzene	57	<0.01	100	1.0	<0.01			
Chloroform	0.032	<0.01	100	1.0	<0.01			
Methylene chloride	0.034	<0.25	100	1.0	<0.25			
I,1,1-Trichloroethane	0.045	<0.01	100	1.0	<0.01			
Trichlorpethene	0.016	<0.01	100	1.0	<0.01			
Other volatiles								
Styrene	16	<0.01	100	1.0	<0.01			
BDAT list inorganics			•					
Cyanide (total)	1200	10	58	1.724	17			

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Analytical Data	BDAT list constituent concentrations							
	Sample Set #2							
	·	Percent						
	Hivari		for		Accuracy-			
	K011/K013/K014		matrix	Accuracy	adjusted			
	nonwastewaters	Ash	spike	correct ion	concentration			
Constituents	(nog/kg)	(mag/kg)	test	factor	(mag/kg)			
BDAT_list_volatiles								
Acetonitrile	0.68	<0.5	79	1.266	<0.63			
Acrylonitrile	0.52	<0.5	100	1.0	<0.5			
Acrylanide	2.4	<6.5	79	1.266	<8.2			
Acetone	<0.04	<0.25	100	1.0	<0.25			
Benzene	61	<0.01	100	. 1.0	<0.01			
Chloroform	0.39	<0.01	100	1.0	<0.01			
Methylene chloride	0.023	<0.25	100	1.0	<0.25			
1,1,1-Trichloroethane	0.026	<0.01	100	1.0	<0.01			
Trichloroethene	0.019	<0.01	100	1.0	<0.01			
Other volatiles								
Styrene	19	<0.01	100	1.0	<0.01			
BOAT list inorganics								
Cyanide (total)	1400	5.8	58	1.724	10			

Analytical Data	BDAT list constituent concentrations						
	Sample Set #3						
Constituents	Hixed K011/K013/K014 nonwastewaters (mg/kg)	Ash (mg/kg)	Percent recovery for matrix spike test	Accuracy correction factor	Accuracy- adjusted concentration (mg/kg)		
BDAT list volatiles							
Acetonitrile	1.2	-	-	-	-		
Acrylonitrile	0.54	-	-	-	-		
Acrylamide	2.6	-	-		-		
Acetone	0.095	-	-	-	-		
Benzene	48	-	-	-	-		
Chloroform	0.030	-	-	-	-		
Methylene chloride	0.24	-	-	-	-		
1,1,1-Trichloroethane	0.029	-	-	-	-		
Trichloroethene	0.014	-	-	-	-		
Other volatiles							
Styrene	15	-	-	-	-		
BOAT list inorganics							
Cyanide (total)	2000	-	-	-	-		

- = No value available because no analysis performed on treatment residuals.

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<u>Analytical Data</u>	BDAT list constituent concentrations							
	Sample Set #4							
		Parcent						
	41		recovery		A			
	Mixed K011/K013/K014		TOP Batrix	Accuracy	Accuracy- adjusted			
	nonwastewaters	Ash	spike	correction	concentration			
Constituents	(mg/kg)	(ang/kg)	test	factor	(ang/kg)			
BOAT_list_volatiles								
Acetonitrile	1.9	<0.5	79	1.265	<0.63			
Acrylonitrile	0.63	<0.5	100	1.0	<0.5			
Acrylaside	2.7	<6.5	79	1.266	<8.2			
Acetone	<0.04	<0.25	100	1.0	<0.25			
Benzene .	59	<0.01	100	1.0	<0.01			
Ch lorofo ra	0.034	<0.01	100	1.0	<0.01			
Methylene chloride	0.041	<0.25	100	1.0	<0.25			
1,1,1-Trichloroethane	0.02	<0.01	100	1.0	<0.01			
Trichloroethene	0.017	<0.01	1 00	1.0	<0.01			
<u>Other_volatiles</u>								
Sty rene	16	<0.01	100	1.0	<0.01			
BOAT list inorganics								
Cyanide (total)	1300	22	58	1.724	38			

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Analytical Data	BDAT list constituent concentrations						
	Sample Set #5						
	Percent						
			recovery				
	M1xed		tor	Accuracy	Accuracy-		
	normastematers	Ash	spike	correction	concentration		
Constituents	(mag/kg)	(mg/kg)	test	factor	(ang/kg)		
BOAT_list_volatiles				-			
Acetonitrile	2.7	<0.5	79	1.266	<0.63		
Acrylonitrile	0.95	<0.5	100	1.0	<0.5		
Acrylamide	2.9	<6.5	79	1.255	<8.2		
Acetone	0.081	<0.25	100	1.0	<0.25		
Benzene	55	<0.01	100	1.0	<0.01		
Chlorofarm	0.042	<0.01	100	1.0	<0.01		
Methylene chloride	0.21	<0.25	100	1.0	<0.25		
1,1,1-Trichloroethane	0.032	<0.01	100	• 1.0	<0.01		
Trich loroethene	0.018	<0.01	100	1.0	<0.01		
Other volatiles							
Styrene	18	<0.01	100	1.0	<0.01		
BOAT list inorganics							
Cyanide (total)	1500	4.8	58	1.724	8.3		

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Analytical Data	BDAT list constituent concentrations						
	Sample Set 16						
Constituents	Nixed KO11/KO13/KO14 nonwastewaters (mg/kg)	Ash (mg/kg)	Percent recovery far matrix spike test	Accuracy correction factor	Accuracy- adjusted concentration (mg/kg)		
BDAT list volatiles							
Acetonitrile	-	-	-	- ,	-		
Acrylonitrile	-	-	-	-	-		
Acrylamide	-	-	-	-	-		
Acetone	-	-	-	-	-		
Benzene	-	-	-	-	-		
Ch lorof ora	-	-	-	-	-		
Methylene chlaride	-	-	-	-	-		
1,1,1-Trichloroethane	-	-	-	-	-		
Trichloroethene	-	-	-	-	-		
Other volatiles							
Styrene	-	-	-	-	-		
BDAT list inorganics			•				
Cyanide (total)	-	9.0	58	1.724	16		

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- = No value available because no analysis performed on untreated waste or treatment residuals.

Table 5-1 (continued)

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<u>Analytica] Data</u>	BDAT list constituent concentrations						
	Sample Set #7						
Constituents	Mixed KD11/KO13/KO14 nonwastewaters (mg/kg)	Ash (æg/kg)	Percent recovery for matrix spike test	Accuracy correction factor	Accuracy- adjusted concentration (mg/kg)		
BDAT list_volatiles							
Acetonitrile	-	-	-	-	-		
Acrylonitrile	-	-	-	-	-		
Acrylamide	-	-	-	-	-		
Acetone	-	-	-	-	-		
Benzene	•	-	-	-	• ·		
Chloroform	-	-	-	-	-		
Methylene chloride	-	-	-	-	-		
1,1,1-Trichloroethane	-	-	-		-		
Irichloroethene	•	-	-	-	-		
Other volatiles							
Styrene	-	-	-	-	-		
BDAT_list_inorganics							
Cyanide (total)	•	12	58	1.724	21		

- = No value available because no analysis performed on untreated waste or treament residuals.

Reference: USEPA 1988a.

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5. SELECTION OF REGULATED CONSTITUENTS

This section presents the rationale for the selection of regulated constituents for the treatment of KO11/KO13/KO14 nonwastewaters. The Agency will determine regulated constituents for KO11/KO13/KO14 wastewater forms prior to May 8, 1990.

Constituents selected for regulation must satisfy the following criteria:

- They must be on the BDAT list of regulated constituents. (Presence on the BDAT list implies the existence of approved techniques for analyzing the constituent in treated waste matrices.)
- 2. They must be present in, or be suspected of being present in, the untreated waste. For example, in some cases, analytical difficulties (such as masking) may prevent a constituent from being identified in the untreated waste, but its identification in a treatment residual may lead the Agency to conclude that it is present in the untreated waste.
- 3. Where performance data are transferred, the selected constituents must be easier to treat than the waste constituent(s) from which performance data are transferred. Factors for assessing ease of treatment vary according to the technology of concern. For instance, for incineration the factors include bond dissociation energy, thermal conductivity, and boiling point.

From the group of constituents that are eligible to be regulated, EPA may select a subset of constituents as representative of the broader group. For example, out of a group of constituents that react similarly to treatment, the Agency might name only those that are the most difficult to treat as regulated constituents for the purpose of setting a standard.

6.1 <u>Identification of Constituents in the Untreated Waste and Waste</u> <u>Residuals</u>

The first step in selecting candidate constituents to be regulated is to identify the BDAT list constituents present in the KO11/KO13/KO14

wastes in quantities treatable by the selected BDAT. Table 6-1 (at the end of this section) shows which of the 231 BDAT list constituents were detected, not detected, and not analyzed for in the KO11/KO13/KO14 nonwastewaters and incinerator ash residual. In addition to reviewing the constituents detected in the nonwastewater streams as summarized in Table 6-1, the Agency evaluated all available characterization data presented in Section 2 and the waste-generating process to identify constituents that are generally present in the nonwastewater. Table 6-2 presents all constituents known to be present in any KO11/KO13/KO14 nonwastewater and treatment residuals.

6.2 Determination of Significant Treatment from BDAT

The next step in selecting the constituents to be regulated is to identify those constituents in the waste that were significantly treated by the technology designated as BDAT. The determined BDAT for organic and cyanide treatment of KO11/KO13/KO14 nonwastewaters is rotary kiln incineration.

6.2.1 BDAT List Organic Constituents and Inorganics Other Than Metals

The incineration data presented in Table 4-1 demonstrate significant treatment for cyanides, and benzene. The concentrations of the other BDAT list organics in the untreated wastes are too low to demonstrate significant reduction. However, as discussed in the incineration write-up presented in Appendix B, the Agency is using theoretical bond energies as a surrogate for measuring combustibility. In general, the higher the bond energy for a constituent, the more difficult it is to combust. Of all the organics determined to be present in KO11/KO13/KO14 wastes (as shown

in the waste characterization data in Section 2 and the performance data in Section 4), styrene and benzene rank as the most difficult to treat based on their high bond energy (see Table 6-3). Since these constituents were significantly treated to nondetectable concentrations in the treatment residuals, EPA believes that the other organic constituents can also be significantly treated to nondetectable levels if they are present in high concentrations in the untreated waste. Therefore, all BDAT list organic constituents expected to be present in the KO11/KO13/KO14 nonwastewaters will be considered for regulation. (Table 6-3 shows the calculated bond energies for the candidate organic constituents.)

Fluoride and sulfide were detected in the KOll/KOl3/KOl4 nonwastewater untreated waste and treated waste streams. Since fluoride and sulfide were detected in the incineration treatment residuals, it does not appear that incineration is BDAT for sulfide and fluoride. Therefore, these two constituents are not being regulated at this time as the Agency currently has not completed its evaluation of treatment information for sulfide and fluoride.

6.2.2 BDAT List Metals

EPA reviewed information on the possible origin of the BDAT list metals in the EPA-tested KO11/KO13/KO14 nonwastewaters, such as the metal catalyst used to improve process efficiency and reduce the amount of byproducts, and concluded that the catalyst is the source of the high iron and molybdenum but not the BDAT list metal concentrations. Therefore, EPA is not regulating any BDAT list metals because the Agency has insufficient data that indicate that arsenic, barium, cadmium, chromium, copper, lead,

nickel, and zinc are present in treatable quantities in most KO11/KO13/ KO14 nonwastewaters. If additional treatment performance and characterization data for nickel becomes available, the Agency is not precluded from regulating nickel as a nonwastewater treatment standard for KO11, KO13, and KO14 wastes.

6.3 <u>Rationale for Selection of Regulated Constituents</u>

Table 6-2 presents all of the candidate constituents that were detected in the untreated waste and nonwastewater treatment residual generated from treatment with the identified BDAT.

The Agency selected acrylonitrile, acetonitrile, acrylamide, and benzene as the BDAT organic constituents for regulation. These organic constituents were present in the untreated waste in large quantities relative to the presence of the other constituents. Cyanide has been selected for regulation because of its high concentration in the untreated KO11/KO13/KO14 wastes.

The Agency believes that regulation of the constituents selected will ensure that treatment occurs for the remaining BDAT list organic candidates since BDAT treatment of the selected constituents will, at the same time, effectively treat those constituents not selected. Table 6-2 presents the selected regulated constituents for the KO11/KO13/KO14 wastes.

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BDAT			K011/K013/K014	Incinerator
no.	Parameter	CAS no.	nonwastewater	residua]
	Volatile Organics			
222	Acetone	67-64-1	D	ND
1	Acetonitrile	75-05-8	0	ND
2	Acrolein	107-02-8	ND	ND
	Acrylamide	79-06-1	D	ND
3	Acrylonitrile	107-13-1	D	ND
4	Benzene	71-43-2	0	ND
5	Bramodichloromethane	75-27-4	ND	ND
6	Bromomethane	74-83-9	NÐ	ND
223	n-Butyl alcohol	71-36-3	ND	ND
7	Carbon tetrachloride	56-23-5	ND	ND
8	Carbon disulfide	75-15-0	ND	ND
9	Chlorobenzene	108-90-7	ND	ND
10	2-Chloro-1,3-butadiene	108-90-7	ND	ND
11	Chlorodibromomethane	108-90-7	ND	ND
12	Chloroethane	75-00-3	ND	ND
13	2-Chloroethyl vinyl ether	110-75-8	ND	ND
14	Chloroform	67- 66-3	D	ND
15	Chloromethane	74-87-3	ND	ND
16	3-Chloropropene	107-05-1	ND	ND
17	1,2-Dibromo-3-chiloropropane	96-12-8	ND	ND
18	1,2-Dibromoethane	106-93-4	ND	ND
19	Dibromomethane	74-95-3	ND	ND
20	Trans-1,4-Dichloro-2-butene	11 0-57-6	ND	ND
21	Dichlorodifluoromethane	75-71-8	ND	ND
22	1,1-Dichloroethane	75-35-3	ND	ND
23	1,2-Dichloroethane	105-06-2	ND	ND
24	1,1-Dichloroethylene	75-35-4	ND	ND
25	Trans-1,2-Dichloroethene	156-60-5	ND	ND
26	1,2-Dichloropropane	78-87-5	ND	ND
27	Trans-1.3-Dichloropropene	10061-02-6	ND	ND
28	cis-1,3-Dichloropropene	10061-01-5	ND	ND
29	1.4-Dioxane	123-91-1	ND	ND
224	2-Ethoxyethanol	110-80-5	ND	ND
225	Ethyl acetate	141-78-6	ND	ND
226	Ethyl benzene	100-41-4	ND	ND

Table 6-1 BDAT Constituents Detected or Not Detected in the K011/K013/K014 Wastes and Waste Residuals

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Table 6-1 (continued)

BDAT				Incinerator
reference			K011/K013/K014	ash
no.	Parameter	CAS no.	nonwastewater	residual
	<u>Volatile Organics</u> (continued)			
30	Ethyl cyanide	10712-0	ND	ND
227	Ethyl ether	60-29-7	ND	ND
31	Ethyl methacrylate	97-63-2	ND	DK
214	Ethylene oxide	75-21-8	ND	ND
32	loaomethane	74-88-4	ND	ND
33	Isobutyl alcohol	78-83-1	ND	ND
228	Methano 1	67-56-1	ND	ND
34	Methyl ethyl ketone	78-93-3	ND	ND
229	Methyl isobutyl ketone	108-10-1	ND	ND
35	Methyl methacrylate	80-62-5	ND	ND
36	Methyl methanesulfonate	66-27-3	ND	ND
37	Methylacrylonitrile	126-98-7	ND	ND
38	Methylene chloride	75-09-2	0	ND
230	2-Nitropropane	79-46-9	ND	NÐ
39	Pyridine	110-86-1	KD	ND
40	1,1,1,2-Tetrachloroethane	630-20-6	ND	ND
41	1,1,2,2-Tetrachloroethane	7 9-34-5	ND	ND
42	Tetrachloroethene	127-18-4	ND	MD
43	Toluene	108-88-3	ND	ND
44	Tribromomethane	75-25-2	ND	ND
45	1,1,1-Trichloroethane	71-55-6	D	ND
46	1,1,2-Trichloroethane	79-00-5	ND	ND
47	Trichloroethene	79-01-6	0	ND
48	Trichloromonofluoromethane	75-69-4	ND	ND
49	1,2,3-Trichloropropane	96-18-4	ND	ND
231	1.1.2-Trichloro-1.2.2-			
	trifluoroethane	76-13-1	ND	ND
50	Vinyl chloride	75-01-4	ND	ND
215	1,2-Xy lene	97-47-6	ND	ND
215	1, 3-Xy lene	108-38-3	ND	ND
217	1,4-Xylene	106-44-5	ND	ND
	<u>Semivolatiles</u>			
51	Acenaphtha lene	208-95-8	MD	ND
52	Acenaphthene	83-32-9	ND	MÐ

Table 6-1 (continued)

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BDAT				Incinerator
reference			K011/K013/K014	ash
no.	Parameter	CAS no.	nonwastewater	residual
	<u>Semivolatiles</u> (continued)			
53	Acetophenone	96-86-2	ND	ND
54	2-Acetylaminofluorene	53-96-3	ND	ND
55	4-Aminobipheny1	92-67-1	ND	ND
56	Aniline	62-53-3	ND	ND
57	Anthracene	120-12-7	ND	ND
58	Aramite	140-57-8	NÛ	ND
59	Benz(a)anthracene	56-55-3	ND	ND
218	Benzal chloride	98-87-3	ND	ND
60	Benzal chloride	98-87-3	ND	ND
61	Benzenethiol	1 08-98 -5	ND	ND
62	Benzo(a)pyrene	50-32-8	ND	ND
63	Benzo(b)fluoranthene	205-99-2	ND	ND
64	Benzo(ghi)perylene	191-24-2	ND	ND
ô5	Benzo(k)fluoranthene	207-08-9	ND	ND
66	p-Benzoquinone	106-51-4	ND	ND
67	Bis(2-chloroethoxy)methane	111-91-1	NO	ND
68	Bis(2-chloroethyl)ether	111-44-4	ND	ND
69	Bis{2-chloroisopropyl)ether	39638-32-9	ND I	ND
70	Bis(2-ethylhexyl)phthalate	117-81-7	ND	ND
71	4-Bromophenyl phenyl ether	101-55-3	NO	ND
72	Butyl benzyl phthalate	85- 68 -7	· ND	ND
73	2-sec-Buty1-4,6-dimitrophenol	88-85-7	ND	ND
74	p-Chloroaniline	106-47-8	ND	ND
75	Chlorobenzilate	510-15-6	ND	ND
76	p-Chloro-m-cresol	59-50-7	· ND	NÔ
77	2-Chloronaphthalene	91-58-7	ND	ND
78	2-Ch loropheno l	95-57-8	ND	ND
79	3-Chloropropionitrile	542-76-7	ND	ND
80	Chrysene	218-01-9	ND	ND
81	ortho-Cresol	95-48-7	ND	ND
82	para-Creso}	106-44-5	ND	NÐ
232	Cyc lohexanone	108-94-1	ND	ND
83	Dibenz(a,h)anthracene	53-70-3	ND	ND
84	Dibenzo(a,e)pyr ene	192-65-4	ND	ND
85	Dibenzo(a,i)pyrene	189-55-9	ND	ND
86	m-Oichlorobenzene	541-73-1	ND	ND
87	o-Dichlorobenzene	95-50-1	ND	ND

Table 6-1 (continued)

BOAT				Incinerator
reference			K011/K013/K014	ash
no.	Parameter	CAS no.	nonwastemater	residua l
	Semivolatiles (continued)			
88	p-Dichlorobenzene	106-46-7	ND	ND
89	3,3'-Dichlorobenzidine	91-94-1	ND	ND
90	2,4-Dichlorophenol	120-83-2	ND	ND
91	2,6-Dichlorophenol	87~65-0	ND	ND
92	Diethyl phthalate	84-66-2	ND	NO
93	3,3'-Dimethoxybenzidine	119-90-4	ND	ND
94	p-Dimethylaminoazobenzene	60-11-7	ND	ND
95	3,3'-Dimethylbenzidine	119-93-7	NO	ND
96	2,4-Dimethylphenol	105-67-9	ND	ND
97	Dimethyl phthalate	131-11-3	NO	ND
98	Di-n-butyl phthalate	84-74-2	ND	ND
99	1,4-Dinitrobenzene	100-25-4	ND	ND
100	4,6-Dinitro-o-cresol	534-52-1	ND	ND
101	2,4-Dinitrophenol	51-28-5	ND	ND
102	2.4-Dinitrotoluene	121-14-2	ND	ND
103	2,6-Dinitrotoluene	606-20-2	ND	ND
104	Di-n-octyl phthalate	117-84-0	ND	ND
105	Di-n-propylnitrosamine	621 -64 -7	ND	ND
106	Diphenylamine	122-39-4	NO	ND
219	Diphenylnitrosamıne	86-30-6	ND	ND
107	1,2-Diphenylhydrazine	122-66-7	ND	ND
108	Fluoranthene	206-44-0	ND	ND
109	Fluorene	86-73-7	NO	ND
110	Hexach lorobenzene	118-74-1	ND	ND
111	Hexach lorobutad iene	87-68-3	ND	ND
112	Hexach lorocyc lopentadiene	77-47-4	ND	ND
113	Hexach loroethane	67-72-1	ND	ND
114	Hexach lorophene	70-30-4	ND	ND
115	Indeno(1,2,3-cd)pyrene	193-39-5	ND	ND
116	Isosafrole	120-58-1	ND	ND
117	Methapyrilene	91-80-5	ND	ND
118	3-Methylcholanthrene	56-49-5	ND	ND
119	4,4'-Nethylenebis		ND	ND
120 -	(2-chloroaniline)	101-14-4	ND	ND
121	Naphtha lene	91-20-3	ND	ND
122	L,4-Naphthoquinone	130-15-4	ND	NO
123	1-Naphthy lamine	134-32-7	ND	ND

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Table 6-1 (continued)

BDAT			×011 /×013 /×014	Incinerator
reterence	_		KU11/KU13/KU14	asn
no.	Parameter	CAS no.	nommastemater	residua i
	Semivolatiles (continued)			
124	2-Naphthylamine	91-59-8	ND	ND
125	p-Nitroaniline	100-01-6	ND	ND
126	Nitrobenzene	98-95-3	ND	ND
127	4-Nitrophenol	100-02-7	ND	ND
128	N-Nitrosodi-n-butylamine	924-16-3	ND	ND
129	N-Nitrosodiethylamine	55-18-5	ND	, ND
130	N-Nitrosodimethylamine	62-75-9	ND	ND
131	N-Nitrosomethylethylamine	10595-95-6	ND	ND
132	N-Nitrosomorpholine	59-89-2	ND	ND
133	N-Nitrosopiperidine	100-75-4	ND	ND
134	n-Nitrosopyrrolidine	930-55-2	ND	ND
135	5-Nitro-o-toluidine	99-65-8	ND	ND
135	Pentach lorobenzene	608-93-5	ND	ND
137	Pentach loroethane	76-01-7	ND	ND
138	Pentachloronitrobenzene	82-68-8	ND	ND
139	Pentachlorophenol	87-86-5	ND	ND
140	Phenacetin	62-44-2	ND	ND
141	Phenanthrene	85-01-8	ND	ND
142	Pheno 1	108-95-2	ND	ND
220	Phthalic anhydride	85-44-9	ND	ND
143	2-Picoline	109-06-8	ND	ND
144	Pronamide	23950-58-5	ND	ND
145	Pyrene	129-00-0	ND	ND
145	Resorcinol	108-46-3	ND	ND
147	Safrole	94-59-7	· ND	ND
148	1,2,4,5-Tetrachlorobenzene	95-94-3	ND	ND
149	2,3,4,6-Tetrachlorophenol	58-90-2	ND	ND
150	1,2,4-Trichlorobenzene	120-82-1	ND	ND
151	2,4,5-Trichlarophenol	95-95-4	ND	ND
152	2,4,6-Trichlorophenol	88-06-2	ND	ND
153	Tris(2,3-dibromopropyl)			
	phosphate	126-72-7	ND	ND
	<u>Metals</u>			
154	Antimony	7440-36-0	ND	KA
155	Arsenic	7440-38-2	D	D

Table 6-1 (continued)

BDAT reference			KD11/KD13/KO14	Incinerator ash
no .	Parameter	CAS no.	nonwastewater	residual
	<u>Metals</u> (continued)			
156	Barium	7440-39-3	D	D
157	Beryllium	7440-41-7	ND	NA
158	Cadmium	7440-43-9	D	ND
159	Chromium	7440-47-32	D	0
160	Copper	7440-50-8	D	D
221	Hexavalent Chromium	NA	KA	NA
161	Lead	7439-92-1	D	D
162	Nercury	7439-97-6	ND	ND
163	Nickel	7440-02-0	D	D
164	Selenium	7782-49-2	ND	D
165	Silver	7440-22-4	ND	D
166	Thallium	7440-28-0	ND	NA
167	Vanadium	7440-62-2	ND	NA
168	Zinc	7440-66-6	D	D
	Inorganics			
169	Cyanide	57-12-5	D	ND
170	Fluorade	16964-48-8	D	D
171	Sulfide	8496-25-8	ND	D
	Organochlorine Pesticides			
172	Aldrin	309-00-2	ND	ND
173	a Ipha-BHC	319-84-6	ND	ND
174	beta-BHC	319-85-7	ND	ND
175	delta-BHC	319-86-8	ND	ND
176	ganna-8HC	58-89-9	ND	ND
177	Ch lordane	57-74-9	ND	ND
178	000	72-54-8	ND	ND
179	DDE	72-55-9	ND	ND
180	DOT	50-29-3	ND	ND
181	Dieldrin	60-57-1	ND	ND
182	Endosulfan I	939- 98 -8	ND	ND
183	Endosulfan II	33213-6-5	жD	ND
184	Endrin	72-20-8	ND	ND
185	Endrin aldehyde	7421-93-4	MD	ND

Table 6-1 (continued)

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BDAT reference no.	Parameter	CAS no.	K011/K013/K014 nonwastewater	Incinerator ash residual
	Organochlorine Pesticides (continu	ed)		
		~~,		
186	Heptachlor	76-44-8	ND	ND
187	Heptachlor epoxide	1024-57-3	ND	ND
188	lsodrin	465-73-6	ND	ND
189	Kepone	143-50-0	ND	ND
190	Hethoxyclor	72-43-5	ND	ND
191	Toxaphene	8001-35-2	` ₩D	ND
	Phenoxyacetic Acid Herbicides			
192	2,4-Dichlorophenoxyacetic acid	94-75-7	ND	ND
193	Silvex	93-72-1	ND	ND
194	2,4,5-T	93-76-5	MD	ND
	Organophosphorous Insecticides			
195	Disulfoton	298-04-4	ND	ND
196	Famphur	52-85-7	ND	ND
1 97	Hethyl parathion	298-00-0	D	ND
198	Parathion	56-38-2	ND	ND
199	Phorate	298-02-2	D	ND
	PCBs			
200	Aroclar 1016	12674-11-2	ND	ND
201	Aroclar 1221	11104-28-2	ND	ND
202	Aroclor 1232	11141-16-5	ND	ND
2 03	Araclar 1242	53469-21-9	ND	ND
204	Aroclor 1248	12672-29-6	ND	ND
205	Aroclor 1254	11097-69-1	ND	ND
206	Aroc lor 1260	11096-82-5	ND ND	ND
	Dioxins and Furans			
207	Hexach lorodibenzo-p-diox ins	KA.	ND	ND
208	Hexach lorod ibenzofuran	NA	ND	ND
209	Pentachlorodibenzo-p-dioxins	NA	ND	ND
210	Pentach lorod i benzofuran	MA	10	KD.

BDAI eference no.	Parameter	CAS no.	KO11/KD13/KO14 normastemater	Incinerator ash r es idual
	Dioxins and Furans (continued)			
2 11	Tetrach lorod i benzo-p-diox ins	NA	ND	ND
211 212	Tetrachlorodibenzo-p-dioxins Tetrachlorodibenzofuran	NA NA	ND ND	ND ND

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NL = Not on list at the time of analysis

ND = Not detected

D = Detected

NA = Not applicable

Reference: USEPA 1988h.

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Candidate BDAT list		
constituents determined		
to be present in KO11/	Eliminated based	Se lected
K013/K014 nonwastewaters	on treatability ^a	constituents
<u>Volatiles</u>		
Acetone		
Acetonitrile		X
Acrolein		
Acrylonitrile		X
Acrylamide		X
Benzene		X
Chloroform		
Dichlorodifluoromethane		
Ethyl cyanide		
Methylene chloride		
Pyridine		
1,1,1-Trichloroethane		
Trichloroethene		
<u>Semivolatiles</u>		
Pheno 1		
2-Picoline		
Inorganics Other Than Metals		
Cyanide		X
Fluoride	x	
Sulfide	X	
<u>Metals</u>		
Arsenic	x	
Barium	x	
Cadmium	X	
Chromium	X	
Copper	X	
Lead	X	
Nickel	X	
Selenium	X	
Silver	X	
Zinc	· X	

^aConstituents eliminated because they were determined not to be present in treatable quantities in most K011/K013/K014 nonwastewaters and/or cannot be significantly treated by the technologies designated as BOAT.

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Constituent	Calculated bond energy ^d (Kcal/mol)
Acetone	945
Acrolein	805
Acetonitrile	590
Acrylamide	985
Acrylonitrile	860
Benzene	1320
Ch loroform	340
lichlorodifluoromethane	390
Ethyl cyanide	880
Hethylane chloride	355
Pyridine	1210
Phenol	1421
L, 1, 1-Trichloroethane	625
richloroethene	485
Styrene	1750

Table 6-3 Calculated Bond Energies for the Organic Constituents

^a Calculations are based on information in Sanderson 1971.

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7. DEVELOPMENT OF THE BOAT TREATMENT STANDARDS

The Agency bases the treatment standards for the regulated constituents on the performance of well-designed and well-operated BDAT treatment systems. These standards must account for analytical limitations in available performance data and must be adjusted for variabilities related to treatment, sampling, and analytical techniques and procedures.

The BDAT standards are determined for each constituent by multiplying the arithmetic mean of accuracy-adjusted constituent concentrations detected in treated waste by a "variability factor" specific to each treatment technology defined as BDAT. Accuracy adjustment of performance data was discussed in Section 5 in relation to defining "substantial treatment." Variability factors correct for normal variations in the performance of a particular technology over time. They are designed to reflect the 99th percentile level of performance that the technology achieves in commercial operation. For more information on the principles of calculating variability factors, see EPA's publication, Methodology for Developing BDAT Treatment Standards.

The calculations of the organic and cyanide standards are presented in Table 7-1. The Agency is establishing the treatment standards as shown in Table 7-2 for KO11, KO13, and KO14 nonwastewaters. For nonwastewater forms of these wastes, the BDAT list organic and cyanide treatment standards are based on the performance of incineration.

	Unadjusted concentration (mg/kg) <u>Sample Set No.</u>				Acci	racy-co	rrect	ed conce	entrati	ion (I	ng/kg)			Treatmen				
				Correction	n	Sample Set No.						Nean	Variability	standard				
Constituent	1	2	3	4	5	6	7	factor	1	2	3	4	5	6	7	(mg/kg)	factor	(mg/kg)
BDAT List Volatile	Organics	<u>6</u>																
Acetonitrile	0.5	0.5	-	0.5	0.5	-	-	1.266	0.63	0.63	-	0.63	0.63	-	-	0.63	2.8	1.8
Acrylonitrile	0.5	0.5	-	0.5	0.5	-	-	1.000	0.5	0.5	-	0.5	0.5	-	-	0.5	2.8	1.4
Acrylamide	6.5	6.5		6.5	6.5	-	-	1.266	8.2	8.2	-	8.2	8.2	-	-	8.2	2.8	23.
Benzene	0.01	0.01	-	0.01	0.01	-	-	1.000	0.01	0.01	-	0.01	0.01	-	-	0.01	2.8	0.03
<u>BDAT List Inorganic</u> Other Than Netals	<u>3</u>																	
Cyanide (total)	10	5.8	-	22	4.8	9.0	12	1.724	17	10	-	38	8.3	16	21	18.3	3.1	57

Table 7-1 Calculation of the Proposed Nonwastewater Organic and Cyanide Treatment Standards for the Regulated Constituents Based on Rotary Kiln Incineration Performance Data

- = No value available.

Table 7-2 BDAT Treatment Standards

	Maximum for any single grab sample		
Total composition Constituent	TCLP (mg/kg)	(mg/1)	
Acetonitrile Acrylonitrile Acrylamide Benzene (vanides (Total)	1.8 1.4 23 0.03 57	Not Applicable Not Applicable Not Applicable Not Applicable Not Applicable	

BDAT Treatment Standards for K011/K013/K014 Nonwastewaters

BDAT Treatment Standards for KO11/KO13/KO14 Wastewaters

••••••••••••••••••••••••••••••••••••••	Maximum for any single grab sample	
Constituent	Total composition (mg/l)	

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(EPA intends to propose and promulgate K011/K013/K014 wastewater treatment standards prior to May 8, 1990.)

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APPENDIX A

Analytical QA/QC

The analytical methods used for analysis of the regulated constituents identified in Section 6 are listed in Table A-1. SW-846 methods (EPA's Test Methods for Evaluation of Solid Waste; Physical/Chemical Methods, SW-846, Third Edition, November 1986) were used in most cases for determining total constituent concentrations.

In some instances SW-846 allows for the use of alternative or equivalent procedures or equipment. Table A-2 presents the specific procedures or equipment used in extraction of organic compounds. The specific procedures or equipment used for analysis of organic compounds are shown in Table A-3.

As stated in the introduction, all concentrations for the regulated constituents will be corrected to account for analytical interference associated with the chemical makeup of the waste matrix. The correction factor for a constituent is based on the matrix spike recovery values. Table A-4 presents the organic matrix spike recoveries used to determine the correction factor for the nonwastewater organic and cyanide data.

A-1

Regulated constituents	Extraction method	Nethod number	Analytical method	Nethod number	
Volatile					
Acetonitrile	Purge and trap	5030	Gas Chromatography/Mass Spectrometry	8240	
Acrylonitrile	Purge and trap	5030	Gas Chromatography/Mass Spectrumetry	8240	
Acrylamide	Purge and trap	5030	Gas Chromatography/Nass Spectrumetry*	8015	
Benzene	Purge and trap	5030	Gas Chromatography/Mass Spectrometry	8240	
Inorganics Other Than M	let a ls				
Cyanide (total)	Specified in analytical metho	d	Color Imetric	9012	

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Table A.L. Analytical Nethods for Regulated Constituents in KO11/KO13/KO14 Wastes

*A high-performance liquid chromatography (HPLC) method has also been used to perform acrylamide analysis.

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References: (1)USEPA 1986b.

Ana lys is	SW-846 method	Sample aliquot	Alternatives or equivalents allowed by SV-846 methods	Specific procedures or equipment used
Purge and trap	5030	5 milliliters of liquid	 The purge and trap device to be used is specified in the method in Figure 1, the desorber to be used is described in Figures 2 and 3, and the packing materials are described in Section 4.10.2 of SV-846. The method allows equivalents of this equipment or these materials to be used. The method specifies that the trap must be at least 25 cm long and have an invide diameter of at 	The purge and trap equipment and the desorber used were as specified in SW-846. The purge and trap equipment is a Teckmar LSC 2 with standard purging chambers (Supelco cat. 2-0293). The packing materials for the traps were 1/3 silica gel and 2/3 2,6-diphenylene. The length of the trap was 30 cm and the diameter was 0.105 cm.
			 The surrogates recommended are A brown filmentees are 	The surrogates were added as
			toluene-d8,4-bromofluorobenzene, and 1,2-dichloroethane-d4. The recommended concentration level is 50 µp/1	specified in SV-846.

Table A-2 Specific Procedures or Equipment Used in Extraction of Organic Compounds When Alternatives or Equivalents Are Allowed in the SV-846 Methods

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References: USEPA 1988a. USEPA 1986b.

SV-8 Analysis Neth		Sample preparation method	Alternatives o allowed in equipment or	r equivalents SV-846 for In procedure	Specific equipment or procedures used .			
<u>Organic Compounds</u>		·	Recommended GC/MS operating co	nd i tions :	Actual GC/NS operating condition	ns :		
Gas Chromatography/ Mass Spectrometry for volatile organics	8240	5030	Electron energy: Nass range: Scan time: Initial column temperature:	70 ev (nominal) 35-260 amu lo give 5 scans/peak but not to exceed 7 sec/scan 45°C	flectron energy: Mass range: Scan time: Initial column temperature:	70 ev 35-260 amu 2.5 sec/sçan 38°C		
₽ - ₽			Initial column holding time: Column temperature program: Final column temperature: Final column holding time: Injector temperature: Source temperature:	3 min 8°C/min 200°C 15 min 200-225°C According to manufacturer's	Initial column holding time: Column temperature program: Final column temperature: Final column holding time: Injector temperature: Source temperature:	2 min 10°C/min 225°C 30 min or xylene elutes 225°C Manufacturer's recommended		
			Transfer line temperature: Carrier gas:	specification 250-300°C Hydrogen at 50 cm/sec or helium at 30 cm/sec	Transfer line temperature: Carrier gas:	value of 100°C 275°C Helium at 30 cm/min cm/sec		
					 Additional Information on Equipment: Finnegan Model Data system: SUPERINCOS A Mode: Electron impact NBS library available Interface to MS - Jet sepa 	Actual System Used: 5100 GC/MS/DS system autoquan rator		
			 The column should be 6 ft x packed with 1% SP-1000 on Ca an equivalent. 	0.1 in 1.D. glass; rbopack B (60/80 mesh) or	 The column used was an 8 f packed with 1X SP-1000 on 	t x 0.1 in L.D. glass, Carbopack 8 (60/80 mesh).		
			 Samples may be analyzed by p or by direct injection. 	urge and trap technique	 The samples were analyzed technique. 	using the purge and trap		

Ana lys is	SV 846 method	Sample preparation method	Alternatives or equivalents allowed in SW-846 for equipment or in procedure	Specific equipment or procedures used
<u>lotal and Amenable</u> <u>Cyanide</u>	9012	500 m1	Pretreatment with bismuth nitrate may be necessary if sulfides are present.	Pretreatment was not necessary.
Colorimetric			Pretreatment with sulfamic acid may be necessary if nitrites/nitrates are present.	Pretreatment was not necessary.
			A Fisher-Mulligan absorber or equivalent should be used.	An ACE smog bubbler absorber was used.
				A Bausch and Lomb Model Spectronic 21 was used.
			A spectrophotometer suitable for measurements	
			at 578 nm with a 1.0-cm cell or larger is required.	

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References: USEPA 1986b. USEPA 1988a.

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BDAF list constituent	Original amount found (µg/g)	Anount spiked (µg/g)	Sample		Duplicate		Accuracy-
			Spike result (µg/g)	Percent recovery ^a	Spik e result (µg/g)	Percent recovery ^a	correction factor ^b
Acetonitrile	ND	125	3 9	79	100	80	1.266
Acrolein	ND	125	100	80	38	47	2.128
Acrylonitrile	ND	125	138	110	119	108	1.000
Benzene	ND	25	35	141	206	146	1.000
Ch lorobenzene	ND	25	27	107	115	107	1.000
1,1-Dichloroethene	ND	25	24.8	99	103	104	1.010
To luene	ND	25	28	- 113	132	117	1.000
Ir ich loroethene	ND	25	26	<u>104</u>	109	<u>105</u>	1.000
Average				104		102	1.000
Acrylamide	ND	56	45	81	44	79	1.266
Cyanide (total)	ND	4.9	0	0	2.8	58	1.724

Table A 4 Matrix Spike Recoveries Used to Calculate Correction factors for K011/K013/K014 Nonwastewater Organic and Cyanide Concentrations

^aPercent recovery = [[spike result - original amount]/spike added].

^bAccuracy-correction factor = 100/percent recovery (using the lowest percent recovery values).

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Reference: USEPA 1988a.

APPENDIX B

TECHNOLOGY - INCINERATION

This section addresses the commonly used incineration tech liquid injection, rotary kiln, fluidized bed, and fixed hearth. appropriate, the subsections are divided by type of incineration u

Applicability

Liquid Injection

Liquid injection is applicable to wastes that have viscosity values low enough that the waste can be atomized in the combustion chamber. A range of maximum viscosity values are reported in the literature, with the low being 100 Saybolt Seconds Universal (SSU) and the high being 10,000 SSU. It is important to note that viscosity is temperature dependent so that while liquid injection may not be applicable to a waste at ambient conditions, it may be applicable when the waste is heated. Other factors that affect the use of liquid injection are the presence of suspended solids and particle size. Both of these can cause plugging of the burner nozzle.

Rotary Kiln/Fluidized Bed/Fixed Hearth

These incineration technologies are applicable to a wide range of hazardous wastes. They can be used on wastes that contain high or low total organic content, high or low filterable solids, various viscosity ranges, and a range of other waste parameters. EPA has not found these technologies to be demonstrated on most wastes that are composed essentially of metals with low organic concentrations. In addition, the Agency expects that the incineration of some of the high metal content

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wastes may not be compatible with existing and future air emission limits without emission controls far more extensive than those currently in use.

<u>Underlying Principles of Operation</u>

Liquid Injection

The basic operating principle of this incineration technology is that incoming liquid wastes are volatilized and then additional heat is supplied to the waste to destabilize the chemical bonds. Once the chemical bonds are broken, these constituents react with oxygen to form carbon dioxide and water vapor. The energy needed to destabilize the bonds is referred to as the energy of activation.

Rotary Kiln and Fixed Hearth

There are two distinct principles of operation for these incineration technologies, one for each of the two chambers involved. In the primary chamber, energy, in the form of heat, is transferred to the waste to achieve volatilization of the various organic waste constituents. During this volatilization process some of the organic constituent bonds destabilize and oxidize to carbon dioxide and water vapor. In the secondary chamber, additional heat is supplied to overcome the energy requirements needed to destabilize the remaining chemical bonds and allow the constituents to react with excess oxygen to form carbon dioxide and water vapor. The principle of operation for the secondary chamber is similar to that of liquid injection.

Fluidized Bed

The principle of operation for this incinerator technology is somewhat different from that for rotary kiln and fixed hearth

incineration, in that there is only one chamber, which contains the fluidizing sand and a freeboard section above the sand. The purpose of the fluidized bed is to both volatilize the waste and combust the waste. Destruction of the waste organics can be accomplished to a better degree in this chamber than in the primary chamber of the rotary kiln and fixed hearth because of (a) improved heat transfer from fluidization of the waste using forced air and (b) the fact that the fluidization process provides sufficient oxygen and turbulence to convert the organics to carbon dioxide and water vapor. The freeboard volume generally does not include an afterburner; however, additional time is provided for conversion of the organic constituents to carbon dioxide and water vapor (and hydrochloric acid if chlorine is present in the waste).

Description of Incineration Technologies

Liquid Injection

The liquid injection system is capable of incinerating a wide range of gases and liquids. The combustion system has a simple design with virtually no moving parts. A burner or nozzle atomizes the liquid waste and injects it into the combustion chamber, where it burns in the presence of air or oxygen. A forced draft system supplies the combustion chamber with air to provide oxygen for combustion and turbulence for mixing. The combustion chamber is usually a cylinder lined with refractory (i.e., heat-resistant) brick, and it can be fired horizontally, vertically upward, or vertically downward. Figure I illustrates a liquid injection incineration system.

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FIGURE 1 LIQUID INJECTION INCINERATOR

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Rotary Kiln

A rotary kiln is a slowly rotating, refractory-lined cylinder that is mounted at a slight incline from the horizontal (see Figure 2). Solid wastes enter at the high end of the kiln, and liquid or gaseous wastes enter through atomizing nozzles in the kiln or afterburner section. Rotation of the kiln exposes the solids to the heat, vaporizes them, and allows them to combust by mixing with air. The rotation also causes the ash to move to the lower end of the kiln, where it can be removed. Rotary kiln systems usually have a secondary combustion chamber or afterburner following the kiln for further combustion of the volatilized components of solid wastes.

Fluidized Bed

A fluidized bed incinerator consists of a column containing inert particles such as sand, which is referred to as the bed. Air, driven by a blower, enters the bottom of the bed to fluidize the sand. Air passage through the bed promotes rapid and uniform mixing of the injected waste material within the fluidized bed. The fluidized bed has an extremely high heat capacity (approximately three times that of flue gas at the same temperature), thereby providing a large heat reservoir. The injected waste reaches ignition temperature quickly in the hot fluidized bed. Continued bed agitation by the fluidizing air allows larger particles to remain suspended in the combustion zone. (See Figure 3)

Fixed Hearth

Fixed hearth incinerators, versions of which are also called controlled air or starved air incinerators, are another major technology

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FIGURE 2 ROTARY KILN INCINERATOR

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FIGURE 3 FLUIDIZED BED INCINERATOR

used for hazardous waste incineration. Fixed hearth incineration is a two-stage combustion process (see Figure 4). Waste is fed into the first stage, or primary chamber, and usually burned at less than stoichiometric conditions (less than the theoretically required amount of air). The resultant smoke and pyrolysis products, consisting primarily of volatile hydrocarbons and carbon monoxide, along with the normal products of combustion, pass to the secondary chamber. Here, additional air is usually injected to complete the combustion. This two-stage process generally yields low stack particulate and carbon monoxide (CO) emissions. The primary chamber combustion reactions and combustion gas volumes are maintained at low levels by the starved air conditions so that particulate entrainment and carryover are minimized.

Air Pollution Controls

Following incineration of hazardous wastes, combustion gases are generally further treated in an air pollution control system. The presence of chlorine or other halogens in some waste requires a scrubbing or absorption step to remove hydrogen chloride (HCl) and other halo-acids from the combustion gases. Ash in the waste is not destroyed in the combustion process. Depending on its composition, ash will exit either as bottom ash, at the discharge end of a kiln or hearth for example, or as particulate matter (fly ash) suspended in the combustion gas stream. Particulate emissions from most hazardous waste combustion systems generally have particle diameters of less than 1 micron and require high-efficiency collection devices to minimize air emissions. In

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FIGURE 4 FIXED HEARTH INCINERATOR

addition, scrubber systems provide an additional buffer against accidental releases of incompletely destroyed waste products resulting from poor combustion efficiency or combustion upsets.

Waste Characteristics Affecting Performance (WCAPs)

Liquid Injection

In determining whether liquid injection will achieve the same level of performance on an untested waste as on a previously tested waste, and whether performance levels can be transferred, EPA examines the dissociation bond energies of the constituents in the untested and tested wastes. This parameter is being used as a surrogate indicator of activation energy which, as discussed previously, destabilizes molecular bonds. In theory, the bond dissociation energy would be equal to the activation energy; however, in practice this is not always the case. Other energy effects (e.g., vibrational effects, the formation of intermediates, and interactions between different molecular bonds) may have a significant influence on activation energy.

Because of the shortcomings of bond energy calculations in estimating activation energy, EPA analyzed other waste characteristic parameters to determine whether these parameters would provide a better basis for transferring treatment standards from an untested waste to a tested waste. These parameters include heat of combustion, heat of formation, use of available kinetic data to predict activation energies, and general structural class. All of these were rejected for the reasons provided below.

The heat of combustion measures only the difference in energy of the products and reactants; it does not provide information on the transition state (i.e., the energy input needed to initiate the reaction). Heat of formation is used as a tool to predict whether reactions are likely to proceed; however, there are a significant number of hazardous constituents for which these data are not available. The use of kinetic data was rejected because these data are limited and could not be used to calculate dissociation requirements for the wide range of hazardous constituents. Finally, EPA decided not to use structural classes because the Agency believes that evaluation of bond dissociation energies allows for a more direct determination of whether a constituent will be destabilized.

Rotary Kiln/Fluidized Bed/Fixed Hearth

Unlike liquid injection, these incineration technologies always generate a residual ash. Accordingly, in determining whether these technologies will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics that affect volatilization of organics from the waste, as well as destruction of the organics once volatilized. Relative to volatilization, EPA examines the thermal conductivity of the entire waste and the boiling points of the various constituents. As with liquid injection, EPA examines bond energies in determining whether treatment standards for scrubber water residuals can be transferred from a tested waste to an

untested waste. Below is a discussion of how EPA arrived at thermal conductivity and boiling point as the best means to assess volatilization of organics from the waste; the discussion relative to bond energies is the same for these technologies as for liquid injection and is therefore not repeated.

(1) <u>Thermal conductivity</u>. Consistent with the underlying principles of incineration, a major factor with regard to whether a particular constituent will volatilize is the transfer of heat through the waste. In the case of rotary kiln, fluidized bed, and fixed hearth incineration, heat is transferred through the waste by three mechanisms: radiation, convection, and conduction. For a given incinerator, heat transferred through various wastes by radiation is more a function of the design and type of incinerator than of the waste being treated. Accordingly, the type of waste treated has a minimal impact on the amount of heat transferred by radiation. With regard to convection, EPA also believes that the type of heat transfer is generally more a function of the type and design of incinerator than of the waste itself. However, EPA is examining particle size as a waste characteristic that may significantly impact the amount of heat transferred to a waste by convection and thus may impact volatilization of the various organic compounds. The final type of heat transfer, conduction, is the one that EPA believes has the greatest impact on volatilization of organic constituents. To measure this characteristic, EPA uses thermal conductivity; an explanation of this parameter, as well as how it can be measured, is provided below.

Heat flow by conduction is proportional to the temperature gradient across the material. The proportionality constant is a property of the material and is referred to as the thermal conductivity. (Note: The analytical method that EPA has identified for measurement of thermal conductivity is described in Section 5, High Temperature Metals Recovery in the Treatment Technology Background Document (USEPA 1989)). In theory, thermal conductivity would always provide a good indication of whether a constituent in an untested waste would be treated to the same extent in the primary incinerator chamber as the same constituent in a previously tested waste.

In practice, thermal conductivity has some limitations in assessing the transferability of treatment standards; however, EPA has not identified a parameter that can provide a better indication of heat transfer characteristics of a waste. Below is a discussion of the limitations associated with thermal conductivity, as well as other parameters considered.

Thermal conductivity measurements, as part of a treatability comparison of two different wastes to be treated by a single incinerator, are most meaningful when applied to wastes that are homogeneous (i.e., uniform throughout). As wastes exhibit greater degrees of nonhomogeneity (e.g., significant concentration of metals in soil), thermal conductivity becomes less accurate in predicting treatability because the measurement essentially reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste.

Btu value, specific heat, and ash content were also considered for predicting heat transfer characteristics. These parameters can no better account for nonhomogeneity than can thermal conductivity; additionally, they are not directly related to heat transfer characteristics. Therefore, these parameters do not provide a better indication of the heat transfer that will occur in any specific waste.

(2) <u>Boiling point</u>. Once heat is transferred to a constituent within a waste, removal of this constituent from the waste depends on its volatility. As a surrogate for volatility, EPA is using the boiling point of the constituent. Compounds with lower boiling points have higher vapor pressures and, therefore, would be more likely to volatilize. The Agency recognizes that this parameter does not take into consideration the impact of other compounds in the waste on the boiling point of a constituent in a mixture; however, the Agency is not aware of a better measure of volatility that can easily be determined.

Design and Operating Parameters

Liquid Injection

For a liquid injection unit, EPA's analysis of whether the unit is well designed focuses on both the likelihood that sufficient energy is provided to the waste to overcome the activation level for breaking molecular bonds and whether sufficient oxygen is present to convert the waste constituents to carbon dioxide and water vapor. In assessing the effectiveness of the design and operaton of a liquid injection unit, EPA examines the following parameters: (a) the temperature, (b) the excess

oxygen concentration, (c) the carbon monoxide concentration, and (d) the waste feed rate. Below is a discussion of why EPA believes that these parameters are important, as well as a discussion of how these parameters are monitored during operation.

It is important to point out, relative to the development of land disposal restriction standards, that since liquid injection generally does not produce bottom ash, EPA is concerned with these design parameters only when a quench water or scrubber water residual is generated from treatment of a particular waste. If treatment of a particular waste in a liquid injection unit would not generate a wastewater stream, then the Agency, for purposes of land disposal treatment standards, would be concerned only with the waste characteristics that affect selection of the unit, not with the above-mentioned design parameters.

(1) <u>Temperature</u>. Temperature provides an indirect measure of the energy available (i.e., Btu/hr) to overcome the activation energy of waste constituents. As the design temperature increases, it becomes more likely that the molecular bonds will be destabilized and the reaction completed.

The temperature is normally controlled automatically through the use of instrumentation that senses the temperature and automatically adjusts the amount of fuel and/or waste being fed. The temperature signal transmitted to the controller can be simultaneously transmitted to a recording device and thereby continuously recorded. To fully assess the

operation of the unit, it is important to know not only the exact location in the incinerator at which the temperature is being monitored but also the location of the design temperature.

(2) <u>Excess oxygen concentration</u>. It is important that the incinerator contain oxygen in excess of the stoichiometric amount necessary to convert the organic compounds to carbon dioxide and water vapor. If insufficient oxygen is present, then destabilized waste constituents could recombine to form the same or other BDAT list organic compounds and potentially cause the scrubber water to contain higher concentrations of BDAT list constituents than would be the case for a well-operated unit.

In practice, the amount of oxygen fed to the incinerator is controlled by continuous sampling and analysis of the stack gas. If the amount of oxygen drops below the design value, then the analyzer transmits a signal to the valve or damper controlling the air supply and thereby increases the flow of oxygen. The analyzer simultaneously transmits a signal to a recording device so that the amount of excess oxygen can be continuously recorded. Again, as with temperature, it is important to know the location from which the combustion gas is being sampled.

(3) <u>Carbon monoxide concentration</u>. The carbon monoxide concentration is an important operating parameter because it provides an indication of the extent to which the waste organic constituents are being converted to carbon dioxide and water vapor. An increase in the carbon monoxide level indicates that greater amounts of organic waste

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constituents are unreacted or partially reacted. Increased carbon monoxide levels can result from insufficient oxygen, too much oxygen (causing cooling), insufficient turbulence in the combustion zone, or insufficient residence time of combustion gases.

(4) Waste feed rate. It is important to monitor the waste feed rate because it is correlated to the residence time. The residence time is associated with a specific Btu energy value of the feed and a specific volume of combustion gas generated. Prior to incineration, the Btu value of the waste is determined through the use of a laboratory device known as a bomb calorimeter. The volume of combustion gas generated from the waste to be incinerated is determined from a waste analysis referred to as an ultimate analysis. This analysis determines the amount of elemental constituents present, which include carbon, hydrogen, sulfur, oxygen, nitrogen, and halogens. Using this analysis plus the total amount of air added, the volume of combustion gas can be calculated. After both the Btu content and the expected combustion gas volume have been determined, the feed rate can be fixed at the desired combustion gas residence time. Continuous monitoring of the feed rate determines whether the unit was operated at a rate corresponding to the designed residence time.

Rotary Kiln

For this incineration technology, EPA examines both the primary and secondary chamber in evaluating the design of a particular incinerator.

Relative to the primary chamber, EPA's assessment of design focuses on whether it is likely that enough energy is provided to the waste to volatilize the waste constituents. For the secondary chamber, analogous to the sole liquid injection incineration chamber, EPA examines the same parameters discussed previously under liquid injection incineration. (These parameters will not be discussed again here.)

In assessing the effectiveness of the design and operation of the primary chamber, EPA examines the following parameters: (a) the kiln temperature, (b) the residence time of the waste solids, and (c) the revolutions per minute. Below is a discussion of why EPA believes that these parameters are important, as well as a discussion of how these parameters are monitored during operation.

(1) <u>Temperature</u>. The primary chamber temperature is important because it provides an indirect measure of the energy input (i.e., Btu/hr) available for heating the waste. The higher the design temperature in a given kiln, the more likely it is that the constituents will volatilize. As discussed earlier in the Liquid Injection summary, temperature should be continuously monitored and recorded. Additionally, it is important to know the location of the temperature sensing device in the kiln.

(2) <u>Residence time of the waste solids</u>. This parameter is important in that it affects whether sufficient heat is transferred to a particular constituent for volatilization to occur. As the time that the waste is in the kiln is increased, a greater quantity of heat is transferred to

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the hazardous waste constituents. The residence time is a function of the specific configuration of the rotary kiln, including the length and diameter of the kiln, the waste feed rate, and the rate of rotation.

(3) <u>Revolutions per minute (RPM)</u>. This parameter provides an indication of the turbulence that occurs in the primary chamber of a rotary kiln. As the turbulence increases, the quantity of heat transferred to the waste would also be expected to increase. However, as the RPM value increases, the residence time of waste solids decreases, resulting in a reduction of the quantity of heat transferred to the waste. This parameter needs to be carefully evaluated because it provides a balance between turbulence and residence time.

Fluidized Bed

As discussed previously, the primary chamber accounts for almost all of the conversion of organic wastes to carbon dioxide and water vapor (and acid gas if halogens are present). The freeboard volume will generally provide additional residence time for combustion gases for thermal oxidation of the waste constituents. Relative to the primary chamber, the parameters that EPA examines in assessing the effectiveness of the design are temperature, residence time, and bed pressure differential. The first two were included in the rotary kiln discussion and will not be discussed here. The last, bed pressure differential, is important in that it provides an indication of the amount of turbulence and, therefore, indirectly the amount of heat supplied to the waste. In general, as the pressure drop increases, both the turbulence and heat

supplied increase. The pressure drop through the bed should be continuously monitored and recorded to ensure that the designed valued is achieved.

Fixed Hearth

The design considerations for this incineration unit are similar to those for a rotary kiln with the exception that rate of rotation (i.e., RPMs) is not an applicable design parameter. For the primary chamber of this unit, the parameters that EPA examines in assessing how well the unit is designed are the same as those discussed under Rotary Kiln; for the secondary chamber (i.e., afterburner), the design and operating parameters of concern are the same as those discussed under Liquid Injection.

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APPENDIX C

TECHNOLOGY - WET AIR OXIDATION

Applicability

Wet air oxidation is a treatment technology applicable to wastewaters containing organics and oxidizable inorganics such as cyanide. The process is typically used to oxidize sewage sludge, regenerate spent activated carbon, and treat process wastewaters. Wastewaters treated using this technology include pesticide wastes, petrochemical process wastes, cyanide-containing metal finishing wastes, spent caustic wastewaters containing phenolic compounds, and some organic chemical production wastewaters.

This technology differs from other treatment technologies generally used to treat wastewaters containing organics in several ways. First, wet air oxidation can be used to treat wastewaters that have higher organic concentrations than are normally handled by biological treatment, carbon adsorption, and chemical oxidation, but may be too dilute to be effectively treated by thermal processes such as incineration. Wet air oxidation is most applicable for waste streams containing dissolved or suspended organics in the 500 to 15,000 mg/l range. Below 500 mg/l, the rates of wet air oxidation of most organic constituents are too slow for efficient application of this technology. For these more dilute waste streams, biological treatment, carbon adsorption, or chemical oxidation may be more applicable. For more concentrated waste streams (above 15,000 mg/l), thermal processes such as incineration may be more

applicable. Second, wet air oxidation can be applied to wastes that have significant concentrations of metals (roughly 2 percent), whereas biological treatment, carbon adsorption, and chemical oxidation may have difficulty in treating such wastes.

It is important to point out that wet air oxidation proceeds by a series of reaction steps and the intermediate products formed are not always as readily oxidized as are the original constituents. Therefore, the process does not always achieve complete oxidation of the organic constituents. Accordingly, in applying this technology it is important to assess potential products of incomplete oxidation to determine whether further treatment is necessary or whether this technology is appropriate at all.

Studies of the wet air oxidation of different compounds have led to the following empirical observations concerning a compound's susceptibility to wet air oxidation based on its chemical structure:

- Aliphatic compounds, even with multiple halogen atoms, can be destroyed within conventional wet air oxidation conditions. Oxygenated compounds (such as low molecular weight alcohols, aldehydes, ketones, and carboxylic acids) are formed, but these compounds are readily biotreatable.
- Aromatic hydrocarbons, such as toluene, acenaphthene, or pyrene, are easily oxidized.
- Halogenated aromatic compounds can be oxidized provided there is at least one nonhalogen functional group present on the ring (e.g., pentachlorophenol (-OH) or 2,4,6-trichloroaniline (-NH₂)).
- 4. Halogenated aromatic compounds, such as 1,2-dichlorobenzene, and PCBs, such as Aroclor 1254, are resistant to wet air oxidation under conventional conditions.

- 5. Halogenated ring compounds, such as the pesticides aldrin, dieldrin, and endrin, are expected to be resistant to conventional wet air oxidation.
- 6. DDT can be oxidized, but results in the formation of intractable oils in conventional wet air oxidation.
- 7. Heterocyclic compounds containing oxygen, nitrogen, or sulfur are expected to be destroyed by wet air oxidation because the O, N, or S atoms provide a point of attack for oxidation reactions to occur.

Underlying Principles of Operation

The wet air oxidation of aqueous wastes occurs at high temperatures and pressures. The typical operating temperature for the treatment process ranges from 175 to 325°C (347 to 617°F). The pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase at the operating temperature, generally between 300 and 3000 psi. At these elevated temperatures and pressures, the solubility of oxygen in water is dramatically increased, thus providing a strong driving force for the oxidation. The reaction must take place in the aqueous phase because the chemical reactions involve both oxygen (oxidation) and water (hydrolysis). The wet air oxidation process for a specific organic compound generally involves a number of oxidation and hydrolysis reactions in series, which degrade the initial compound by steps into a series of compounds of simpler structure. Complete wet air oxidation results in the conversion of hazardous compounds into carbon dioxide, water vapor, ammonia (for nitrogen-containing wastes), sulfate (for sulfur-containing wastes), and halogen acids (for halogenated wastes).

However, treatable quantities of partial degradation products may remain in the treated wastewaters from wet air oxidation. Therefore, effluents from wet air oxidation processes may be given subsequent treatment including biological treatment, carbon adsorption, or chemical oxidation before being discharged.

Description of Wet Air Oxidation Process

A conventional wet air oxidation system consists of a high-pressure liquid feed pump, an oxygen source (air compressor or liquid oxygen vaporizer), a reactor, heat exchangers, a vapor-liquid separator, and process regulators. A basic flow diagram is shown in Figure 1.

A typical batch wet air oxidation process proceeds as follows. First, a copper catalyst solution may be mixed with the aqueous waste stream if preliminary testing indicates that a catalyst is necessary. The waste is then pumped into the reaction chamber. The aqueous waste is pressurized and heated to the design pressure and temperature, respectively. After reaction conditions have been established, air is fed to the reactor for the duration of the design reaction time. At the completion of the wet air oxidation process, suspended solids or gases are removed and the remaining treated aqueous waste is either discharged directly or fed to a biological treatment, carbon adsorption, or chemical oxidation treatment system if further treatment is necessary prior to discharge.



FIGURE 1 WET AIR OXIDATION PROCESS FLOW DIAGRAM.

Wet air oxidation can also be operated in a continuous process. In continuous operation, the waste is pressurized, mixed with pressurized air or oxygen, preheated in a series of heat exchangers by the hot reactor effluent and steam, and fed to the reactor. The waste feed flow rate controls the reactor residence time. Steam is fed into the reactor column to adjust the column temperature. The treated waste is separated in a gas-liquid separator, with the gases treated in an air pollution control system and/or discharged to the atmosphere, and the liquids either further treated, as mentioned above, and/or discharged to disposal.

Waste Characteristics Affecting Performance (WCAPs)

In determining whether wet air oxidation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the chemical oxygen demand and (b) the concentration of interfering substances.

Chemical Oxygen Demand

The chemical oxygen demand (COD) of the waste is a measure of the oxygen required for complete oxidation of the oxidizable waste constituents. The limit to the amount of oxygen that can be supplied to the waste is dependent on the solubility of oxygen in the aqueous waste and the rate of dissolution of oxygen from the gas phase to the liquid phase. This sets an upper limit on the amount of oxidizable compounds that can be treated by wet air oxidation. Thus, high-COD wastes may

require dilution for effective treatment to occur. If the COD of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Pretreatment of the waste or dilution as part of treatment may be needed to reduce the COD.to within levels treatable by the dissolved oxygen concentration and to achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

Concentration of Interfering Substances

In some cases, addition of a water-soluble copper salt catalyst to the waste before processing is necessary for efficient oxidation treatment (for example, for oxidation of some halogenated organics). Other metals have been tested and have been found to be less effective. Interfering substances for the wet air oxidation process are essentially those that cause the formation of insoluble copper salts when copper catalysts are used. To be effective in catalyzing the oxidation reaction, the copper ions must be dissolved in solution. Sulfide, carbonate, and other negative ions that form insoluble copper salts may interfere with treatment effectiveness if they are present in significant concentrations in wastes for which copper catalysts are necessary for effective treatment. If an untested waste for which a copper catalyst is necessary for effective treatment has a concentration of interfering substances (including sulfide, carbonate, or other anions that form

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insoluble copper salts) significantly higher than that in a tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

Design and Operating Parameters

In assessing the effectiveness of the design and operation of a wet air oxidation system, EPA examines the following parameters: (a) the oxidation temperature, (b) the residence time, (c) the excess oxygen concentration, (d) the oxidation pressure, and (e) the amount and type of catalyst.

Oxidation Temperature

Temperature is the most important parameter affecting the system. The design temperature must be high enough to allow the oxidation reactions to proceed at acceptable rates. Raising the temperature increases the wet air oxidation rate by enhancing oxygen solubility and oxygen diffusivity. The process is normally operated in the temperature range of 175 to 325°C (347 to 617°F), depending on the hazardous constituent(s) to be treated. EPA monitors the oxidation temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

Residence Time

The residence time impacts the extent of oxidation of waste contaminants. For a batch system, the residence time is controlled

directly by adjusting the treatment time in the reaction tank. For a continuous system, the waste feed rate is controlled to make sure that the system is operated at the appropriate design residence time. Generally, the reaction rates are relatively fast for the first 30 minutes and become slow after 60 minutes. Typical residence times, therefore, are approximately 1 hour. EPA monitors the residence time to ensure that sufficient time is provided to effectively oxidize the waste.

Excess Oxygen Concentration

The system must be designed to supply adequate amounts of oxygen for the compounds to be oxidized. An estimate of the amount of oxygen needed can be made based on the COD content of the untreated waste; excess oxygen should be supplied to ensure complete oxidation. The source of oxygen is compressed air or a high-pressure pure oxygen stream. EPA monitors the excess oxygen concentration (the concentration of oxygen in the gas leaving the reactor) continuously, if possible, by sampling the vent gas from the gas-liquid separator to ensure that an effective amount of oxygen or air is being supplied to the waste.

Oxidation Pressure

The design pressure must be high enough to prevent excessive evaporation of water and volatile organics at the design temperature. This allows the oxidation reaction to occur in the aqueous phase, thereby improving treatment effectiveness. EPA monitors the oxidation pressure continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

Amount and Type of Catalyst

Adding a catalyst that promotes oxygen transfer and thus enhances oxidation has the effect of lowering the necessary reactor temperature and/or improving the level of destruction of oxidizable compounds. For waste constituents that are more difficult to oxidize, the addition of a catalyst may be necessary to effectively destroy the constituent(s) of concern. Catalysts typically used for this purpose include copper bromide and copper nitrate. If a catalyst is required, EPA examines the amount and type added, as well as the method of addition of the catalyst to the waste, to ensure that effective oxidation is achieved. - · -

References

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