BACKGROUND DOCUMENT

RESOURCE CONSERVATION AND RECOVERY ACT

SUBTITLE C - IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

§§261.31 and 261.32 - Listing of Hazardous Wastes (Finalization
                      of July 16, 1980 Hazardous Waste List)

U.S. ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF SOLID WASTE

January 12, 1981

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IN CHLORINE PRODUCTION WHERE SEPARATELY PREPURIFIED
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K106: WASTEWATER TREATMENT SLUDGE FROM THE MERCURY CELL
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I. SUMMARY OF BASIS FOR LISTING

The solid wastes of concern in this document are muds

from brine purification, and wastewater treatment sludges

from the mercury cell process in chlorine production. The

constituent of concern in these wastes is the toxic heavy

metal mercury.

The Administrator has determined that mercury-bearing

sludges and muds resulting from the mercury cell process in

chlorine production are solid wastes which may pose a substantial

present or potential hazard to human health or the environment

when improperly transported, treated, stored, disposed of or

otherwise managed, and which therefore should be subject to

appropriate management requirements under Subtitle C of

RCRA. This conclusion is based on the following considerations:

1. These wastes are generated in large quantities and
contain significant concentrations of mercury. At the
present time approximately 39,500 kkg of hazardous
mercury-bearing wastes are generated each year.
These wastes are calculated to contain about 154 kkg of
mercury. Large quantities of this highly toxic pollutant
are thus available for environmental release.

2. These wastes have been involved in a number of serious
damage incidents, demonstrating empirically that improper
waste management may result in substantial environmental
hazard.

II. SOURCES OF THE MERCURY AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

Twenty-seven facilities, located in 16 states, are engaged in chlorine and either sodium hydroxide or potassium hydroxide manufacture using the mercury cell process.[1,2,24] These facilities are identified in Tables 1 and 2. In 1980, their mercury cell production capacity was reported as ranging from 27,000 to 232,000 kkg per year.[24]

B. Manufacturing Process[1,3,22,24]

In the mercury cell process, rock or evaporated salt is dissolved in recycled brine or in fresh water in agitated tanks to form a saturated salt brine. In plants not using prepurified salt--most of the plants using this process--[*/] this brine is purified by adding soda ash and sodium hydroxide, and in some cases barium salts, precipitating barium sulfate, calcium carbonate and magnesium hydroxide. These filtered muds (A in Figure 1) are removed by settling and filtration, and constitute one of the wastes of concern. The purified brine is then fed to the electrolytic mercury cells, where it is decomposed by electrolysis to produce chlorine and

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[*/]Eight presently operating facilities (listed in Table 2) use evaporated rock salt already purified in on-site diaphragm cell operations; these plants do not perform significant purification, and therefore do not generate mercury-containing brine muds.

TABLE 1

FACILITIES PRODUCING MERCURY-BEARING BRINE PREPARATION/PURIFICATION MUDS.[24]

STATE	FACILITY	ROCK SALT SOURCE	CHLORINE CAPACITY 10^3 kkg/yr	HAZARDOUS BRINE MUDS TOTAL, DRY BASIS (kkg/year)
AL	Diamond Shamrock, Mobile	LA	38	981
	Diamond Shamrock, Mus.Sho.	LA [1]	132	2124
	Stauffer Chemical, LeMoyne	LA	70	1400
DL	Diamond Shamrock, Del.City	NY [1]	132	4750
GA	Olin Corporation, Augusta	LA	100	1818
IL	Monsanto Co., Sauget	LA [1]	40	600
KY	Convent Ch'l, Calvert City	LA	116	2914[3]
	Pennwalt Corp., Calvert City	LA	114	3147[3]
LA	Stauffer Chem., St.Gabriel	LA	170	2500
ME	Intl.Minerals, Orrington	NY	72	900
NJ	Linden Chemicals, Linden	NY	145	2900
NY	Hooker Sobin, Niag. Falls	Sask.KCl[2]	45	703[3]
	Olin Corp., Niag. Falls	NY	84	2325
NC	Linden Products, Acme	LA	54	540
OH	International Minerals, Ashtabula	Sask. KCl	33	800[3]
TN	Olin Corp., Charleston	TN	230	4230
WA	Georgia Pacific, Bellingham	Prepurif. evap.	76	336[3]
WI	Vulcan Materials, Pt.Edwards	MI	66	3360
			1717	36,328

1. Also use KCl for KOH production.
2. New York Rock salt also used prior to 1972.
3. Brine muds combined with all other mercury-containing wastes.

Table 2

FACILITIES WHICH DO NOT PRODUCE MERCURY-BEARING BRINE MUDS.[24]

STATE	FACILITY	MERCURY CELL CHLORINE CAPACITY 10^3 kkg/yr	SALT SOURCE
AL	Olin Corp., McIntosh	132	Solution mined.
GA	Linden Chemicals, Brunswick	92	Solar purified, evaporated, dissolved in recycle brine.
LA	BASF Wyandotte Corp., Geismar[b]	–	–
LA	PPG, Lake Charles[a]	232	Louisiana
NC	Linden Chemicals, Acme	46	European evap. salt, pre-purified.
NY	Linden Chemicals, Syracuse[d]	27	New York State
TX	Diamond Shamrock, Deer Park[a]	99	Texas
TX	Alcoa, Point Comfort[d]	150	Texas brine, pre-purified, evap., diss. in recycle brine.
WV	PPG, Natrium	60	West Virginia
WV	Linden Chemicals, Moundsville	76	Solution-mined, evap., diss. in recycle brine

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(a) These facilities use pure salt obtained from on-site diaphragm cell operations;

no hazardous brine preparation muds are generated.

(b) Facility closed in 1979.

(c) Prior to 1970 brine purification operations were conducted in the mercury cell circuits, therefore some of the accumulated wastes from this site may be hazardous.

(d) Prior to 1970 rock salt was used, and mercury-containing brine muds were generated.

RECYCLE (94% OF TOTAL OF DEPLETED BRINE)

AS APPROPRIATE { NaOH
Na$_2$CO$_3$
BaCl$_2$ }

VENT TO ATMOSPHERE

MAKE UP MERCURY & WATER

12 (8-18) 90% H$_2$SO$_4$

RAW SALT
1.7X10^{6}3 TON
NaCl WITH Mg,
Ca, SO$_4$ IMPURITIES

SATURATOR

BRINE PURIFICATION

ELECTROLYTIC CELL AND DENUDER

COOLING, DRYING
PURIFICATION AND COMPRESSION

1,000 Cl$_2$

16 (8-25) ACID BY-PRODUCT (70-80% H$_2$SO$_4$)

H$_2$

NaOH

FILTER

2240 CAUSTIC (50%)

28.6 HYDROGEN

BRINE PURIFICATION
MUDS (0.145)
CaCO$_3$, Mg (OH)$_2$
BaSO$_4$, NaCl, AND HgCl$_4$

5% OF DEPLETED BRINE

SPILLED MATERIALS

WASTE TREATMENT

TREATMENT SLUDGE
2 FILTER AID AND
MERCURY SULFIDE

WATER BORNE WASTE
DISCHARGED AS EFFLUENT TO NAVIGABLE WATERS
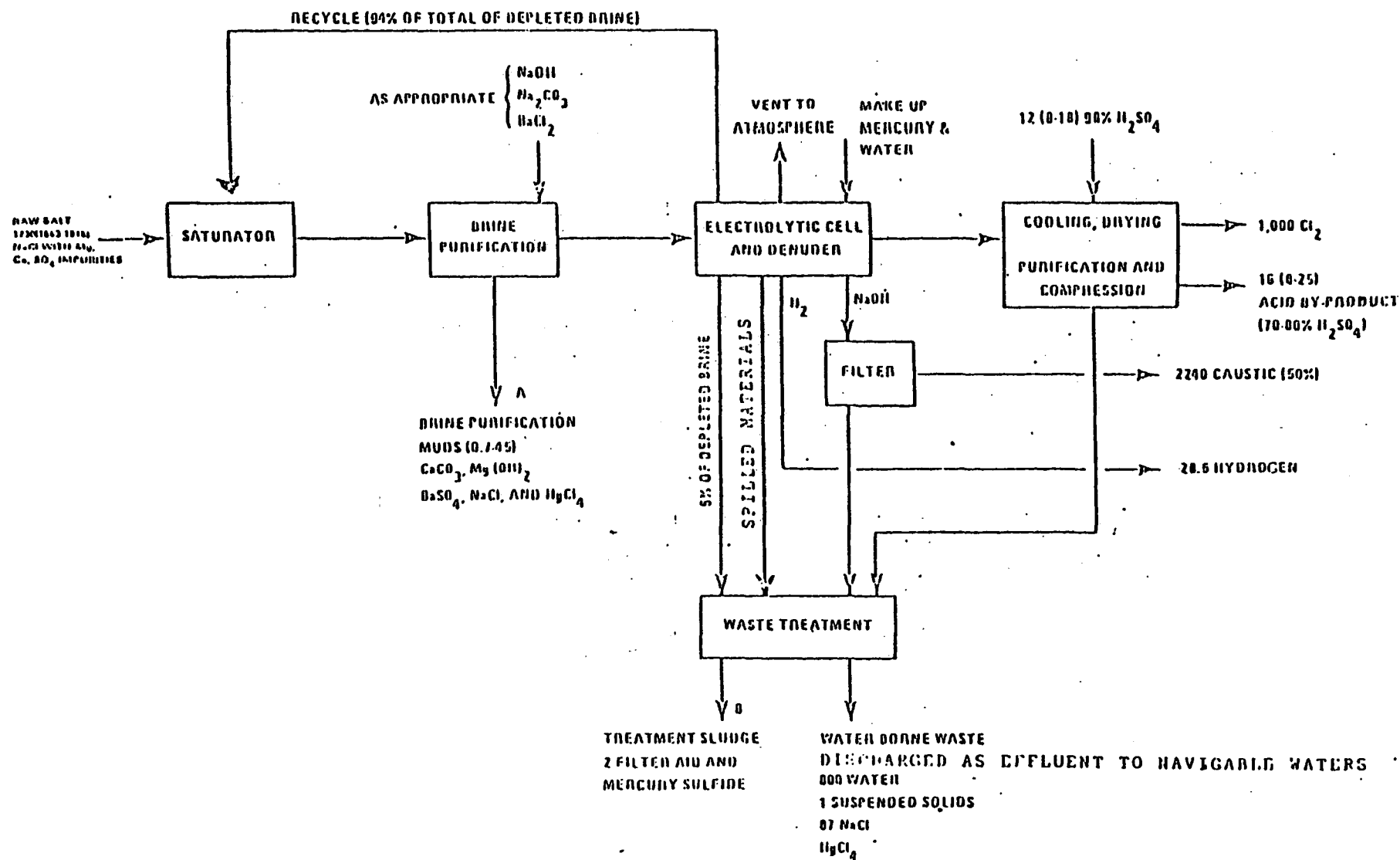000 WATER
1 SUSPENDED SOLIDS
07 NaCl
HgCl$_4$

FIGURE 1 CHLOR-ALKALI MANUFACTURING BY MERCURY (1)

sodium amalgam. The spent brine from the mercury cells is dechlorinated and approximately 94% is returned (recycled) to the initial brine make-up for resaturation; the remainder is discharged to wastewater treatment.

Since some of the feed of the brine purifier is a mercury-bearing recycle stream from the electrolytic cell, the muds (A in Figure 1) resulting from brine purification are contaminated with mercury. According to data provided by the Chlorine Institute, muds contain from 13-1000 ppm, averaging about 200 ppm of mercury.[24]

In all plants, the depleted purged brines from the electrolytic cell, together with two other waste streams generated from ancillary processes, are channeled to waste treatment. Wastewater treatment generates sludges (B in Figure 1) in amounts averaging 1.4 kg of sludge per kkg of chlorine product.[24] These wastes, contain about 0.2 to 15% of mercury, with an average concentration of 4.2% mercury[24], and constitute the second waste of concern.

The mercury leaving the cells in the form of sodium mercury amalgam is sent to denuders where the amalgam is decomposed at 80°C by the addition of deionized water. Water reacts with the sodium mercury amalgam to produce a 50 percent solution of sodium

hydroxide* essentially free of sodium chloride. This solu-
tion is filtered to recover entrained mercury. The waste
from the filtration step is sent to wastewater treatment,
where mercury precipitates into the treatment sludge (stream
B). Entrained mercury is removed from the hydrogen generated
in the denuders, and returned to the electrolytic process.
After removal of mercury, the hydrogen is either compressed
for sale, used on-site, or used as a fuel. The chlorine gas
collected in the electrolytic cells is cooled to condense out
excess water vapor. This stream, which is essentially free
of mercury, is sent to waste treatment. The partially dried
chlorine is then scrubbed with 98 percent sulfuric acid to
remove the rest of the entrained water vapor and is collected,
_compressed and liquified.

C. Waste Generation

The wastes of interest in this document are muds that
result from the treatment of rock salt and recycled depleted
brine, and sludges generated by the treatment of purged,
depleted brines and ancillary waste streams. Seventeen
facilities (see Table 1) generate both of these wastes.
Eight other operating facilities, (those which use prepurified
or evaporated salt - see Table 2) do not generate brine puri-
fication muds (waste A, Figure 1).[24]

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*Potassium hydroxide is produced in plants using potassium
chloride as raw material.

The source of mercury in the brine purification muds is the recycled brine from the electrolytic cell (which mercury is removed in the purification process step).

These brine preparation muds contain substantial concentrations of mercury, in elemental form, and as oxides, chlorides and the complex ion, $HgCl_4^=$. Earlier data indicated that the concentration of mercury in these muds ranges from 500[12] to 2000 ppm[13,14]. More recent data, however, indicate that the concentration of mercury in these muds ranges between 13-1000 ppm, with an average concentration of 200 ppm in samples from fifteen facilities.[24] Even at the new reported levels, the total potential mercury loadings are substantial: using the 1980 figure (ref. 24) the 36,000 kkg of hazardous brine _preparation and purification muds generated each year (Table 1) are therefore estimated to contain 7 kkg of mercury.

It should be noted that the amount of muds produced depends on the source of the salt used as raw material.[11,12] Facilities using salt from the Texas-Louisiana salt dome generate about 10 kg of brine mud per kkg of chlorine. Plants using other salt sources generate brine muds in amounts ranging from about 20 kg per kkg of chlorine (salt from Kansas and New York) to 45 kg per kkg chlorine (salt from Michigan and West Virginia deposits). All the above quoted figures are on a dry-weight basis.[1,10,11,12]

The sludges resulting from wastewater treatment consist mainly of mercuric sulfide. Approximately 3,500 kkg

of this waste is generated annually.[24] It contains mercury in concentrations ranging from 0.02 to 15%, with an average concentration of 4.2%.[24] Therefore 147 kkg of mercury are generated in the wastewater treatment sludges each year.

In total, therefore, of the approximately 39,500 kkg of hazardous mercury-bearing wastes from the mercury cell process for the production of chlorine, approximately 154 kkg of mercury are generated annually from the mercury cell process for the production of chlorine. A 1965 study[15] estimated that 846 kkg of mercury were lost to the environment from this industry as both water borne and solid wastes, and air emissions.

D. Waste Management (1,11,12)

Of the seventeen plants generating both listed waste streams, all but five combine their wastes prior to treatment. One plant retorts all mercury-containing wastes, eight others retort only the mercury-rich wastes, and of these eight, four store these wastes in drums until decisions are made on final disposal. One plant sends sludges to contractors for recovery. This latter disposal method is occasionally used by other facilities. Nine plants now use on-site pond storage of sludges, and seven use on-site landfill. Four plants send wastes to contractors for secured landfilling. Several plants employ combinations of these treatment and disposal techniques.*/

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*/ One plant utilizes a relatively new system for recovery of mercury from virtually all mercury bearing wastes. Treatment of contaminated wastes with sodium hypochlorite leaves wastes with a residual mercury content of less than 8 ppm.[24] The treated waste is then disposed of by landfilling. This waste recovery process is in theory capable of treating brine mud and of recycling recovered mercuric chloride. However, its applicability is limited by cell design and water balance considerations.

II. DISCUSSION OF BASIS FOR LISTING

A. Hazards Posed by the Waste

The two listed wastes are of regulatory concern because
of their contamination with the toxic metal mercury.
Brine preparation and purification muds are reported to contain
as much as 1000 ppm of mercury, and treatment sludges contain
about 4.2% mercury.[24] Moreover, very large amounts of these
wastes (39,500 kkg) are generated. Mercury is highly toxic
to a wide variety of organisms, including man, and can accu-
mulate in biological organisms in its various forms.

These wastes have been involved in a number of damage in-
cidents, demonstrating empirically that improper management
of these wastes may cause substantial harm. These damage
incidents are described below.

∘   The Olin 102nd Street Landfill, Niagara Falls, Niagara
     County, New York.(4)

          From mid 1948 to September, 1970 Olin Chemical Cor-
     poration utilized a landfill for the disposal of chemical
     wastes from its Niagara Falls plant. These wastes
     include brine sludge from a mercury cell chlor-alkali
     plant plus other wastes such as chlorinated organics,
     lime wastes, HTH wastes, fly ash, black cake wastes
     (sodium chloride, sodium chlorite, sodium chlorate,
     carbon, calcium carbonate, calcium hydroxide), graphite

     from electrolytic cells and concrete cell bodies, together

with a limited amount of research materials. This land-
fill is located in a suburban section of Niagara Falls,
New York, contiguous to the northern shore of the Niagara
River. When it was closed, the landfill was "secured" by
covering the waste with a soil cover, establishing vegetation,
and by constructing a dike along the Niagara River.

In 1978, a surface and groundwater sampling program was
initiated at the landfill site by RECRA Research Inc. and
WEHRAN Engineering Corporation[5] to provide both baseline
water quality data and sufficient information to assess the
impact of previous disposal operations at the site. The
program included the analysis of waters from the various
groundwater regimes encountered on-site, and of grab samples
of surface waters from the Niagara River. In view of the
fact that the EPA National Interim Primary Drinking Water
Standard for mercury is 2 ug/l, pertinent results indicated
serious mercury contamination:

1) On one of the two dates on which samples were

    taken, all mercury analyses for the six Niagara River

    surface grab samples (taken downstream from the

    furthest upriver point where the landfill borders

    the river) contravened the Drinking Water Standard

    in every case, with values ranging from 4.7 to 15

    ug/l. On the second date, there was no significant

difference in concentrations up- and down stream from the landfill site. On this date, stormy conditions prevailed, and the river flow was much above normal.

2) Water samples were taken from the fourteen piezo-meters located in the saturated water zone in the landfill. Soluble mercury readings ranged from non-detectable values to 40 ug/l, with the bulk of the readings ranging from 3.9 ug/l to 11 ug/l. Out of 14 samples taken, 13 contravened the Drinking Water Standard.

3) Contiguous to the saturated water zone of the land-fill is a semi-confined aquifer of alluvial deposits. Water samples were taken from piezometers located in the alluvial deposits aquifer. Soluble mercury readings ranged from non-detectable to 35 ug/l. These data are believed to indicate that leachate from the landfill has migrated to this zone.

° The Newco Solid Waste Management Facility Niagara Falls, New York (5,6)

At this disposal site, Olin is currently disposing of brine sludges emanating from its mercury chlor-alkali process. (This site has been used as a waste disposal area for over 80 years.) An evaluation was performed of the presence, movement, and quality of groundwater at this facility, and the data were incorporated in a Draft Environmental Impact Statement for the State of

New York.[5,6] Elevated levels of mercury (6.6 ug/l) have been found in the leachate of mercury-contaminated sludges that have been disposed of in the landfill.

In another damage incident[16] (involving an inactive chlor-alkali facility not otherwise identified in the literature), leaching of mercury from the solid wastes from the facility caused elevated levels of mercury in downstream water, suspended matter, and bottom sediment. About 39 kg of mercury are lost to water from this unlined lagoon each year. Concentration of mercury in water and suspended matter immediately downstream from the plant site are about 20 times higher than immediately upstream. The silt-clay fraction of bottom sediment immediately downstream of the plant site contains up to 200 times as much mercury as similar sediments collected immediately upstream from this facility.[16]

Contamination of Surface Water from an Alkali Processing Plant in Saltville, Virginia[21]:

In another damage incident involving the Olin Corporation, an alkali processing plant generating the wastes listed in this document (and other industrial waste) disposed of these wastes in a series of lagoons located on the North Fork of the Holston River in Saltville, Virginia. Although the site (presently owned by Olin) ceased operating in 1972, wastes continue to leach from the disposal lagoons. Mercury

continues to enter the Holston River both from the site of the chlorine plant and from disposal lagoons used for disposal of chlorine production wastes. The grounds where the cell building once stood are estimated to contain some 220,000 lbs. of mercury. Cleanup costs are estimated at $32-$40 million.

The incidents described demonstrate that mercury will migrate from mercury-bearing wastes in harmful concentrations and can cause substantial environmental harm unless proper management is assured.

There are also other factors which warrant listing these wastes as hazardous. Transportation of these wastes to off-site disposal facilities, a management practice utilized by several manufacturers, increases the likelihood of mismanagement of these hazardous wastes, for example, due to improper handling during transport, or failure to reach the intended destination. A transport manifest system, combined with designated standards for the management of these wastes will greatly reduce their availability to do harm to human beings and the environment.

The quantity of these wastes generated is an additional factor of concern. As indicated above, these wastes are generated in large quantities (39,500 kkg of waste per year, containing 154 kkg of mercury). Under improper disposal conditions large amounts of mercury are thus available for environmental release. The large quantities of this contaminant poses the danger of polluting large areas of ground and surface waters.

Contamination will also occur over long periods of time, since elemental mercury persists indefinitely. Since large amounts of pollutants are available for environmental loading, the attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutants available. All of these considerations increase the possibility of environmental exposure to the harmful constituent in the wastes.

B.   Health and Ecological Effects

The various forms of mercury are interconvertible under most environmental conditions. They are toxic to a wide variety of organisms, including man,[9] and are known to accumulate in biological organisms.[9] In humans, mercurials have been associated with neurological disorders, sensory impairment and tremors. Prenatal exposure can result in impaired brain development and psychomotor disorders. Organic mercury compounds inhibit fertility, and are more toxic than inorganic forms; 0.1 ug mercury/l is toxic to freshwater crayfish.[17] Mercury is bioconcentrated 63,000-fold in fathead minnows foraging under laboratory conditions resembling those in the field.[18] EPA estimates 200 ug/day as the acceptable daily intake and, in 1973, recommended 2 ug/l as a drinking water standard [20].

A World Health Organization expert group recommended 1 ug/l as an international standard for drinking water.[20]

For total recoverable mercury, the EPA has established criteria to protect aquatic life as 0.00057 ug/l and 0.025 ug/l for freshwater and saltwater species, respectively[26]. For the protection of human health from the toxic properties of mercury ingested through waster and contaminated aquatic organisms the ambient water criterion is 0.144 ug/l.[20] Additional information and specific references on the adverse effects of mercury on human health and the environment can be found in Appendix A.

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Response to Comments: Chlorine Production (Mercury Process) Waste.

1. Several commenters stated that the Agency's characterization of the industry and the quantity and quality of its wastes was inaccurate in several respects, and provided new data on siting, production capacity, source of raw materials and the mercury content of wastes of concern. The listing background document was modified to reflect this new information. Both the original and the new data were provided by the Chlorine Institute, thus, in both instances, the Agency relies in large part on the accuracy and timeliness of the trade association's figures.

2. several commenters indicated that brine muds and waste-water treatment sludges pose very different risks of environmental harm, and argued that these two wastes should be accordeddifferent regulatory treatment. In particular, it was argued that brine muds ordinarily contain lower con-centrations of mercury, and should not be considered irremediably hazrdous. It also was suggested that any of these wastes which pass the extraction procedure test should automatically not be regulated under subtitle C.

   The Agency agrees that the mercury content of these two wastes differs. However, we believe that mercury concentrations and potential mass loadings from brine muds alone are typically high enough to warrant listing.

Brine purification muds contain sufficient concentrations
(13 - 1000 ppm by industry figures) and volumes (7kkg
annually) of mercury to result in substantial environ-
mental harm if mismanaged. Even muds containing low
concentrations of mercury would need to leach only one
hundredth to one thousandth of their total mercury to exceed
the interim primary drinking water level of 0.002 ppm.

By listing these wastes the Agency is not precluding
possible site-specific delistings if individual wastes
do not meet the criteria for listing. Thus, facilities
that treat their brine purification muds to reduce
mercury concentrations could conceivably be able to delist
their wastes. EP leachate results are certainly relevant,
although not determinative, in making a delisting deter-
mination (see 45 FR 33111 - 33112, May 19, 1980). We
reiterate however, that we believe ample evidence exists
that the brine muds are typically hazardous, and therefore
intend to retain the listing for this waste stream.

3. Two commenters argued that the listing of mercury-
   bearing brine sludges as hazardous is contrary to
   the purposes of RCRA, because it discourages industry
   efforts to render these wastes less hazardous. We
   again disagree. As the commenter and the background
   document point out, these wastes can be treated
   to recover mercury and reduce the mercury content.
   We believe this listing strongly encourages such treatment.

Should the resulting residue in fact be non-hazardous,
the delisting mechanism allows individual facilities an
opportunity to avoid regulation. Further, even if
the resulting sludges are still hazardous wastes, it
it should be much easier to obtain final management
permits, again providing economic and managerial
incentives for generators to develop or make greater
use of technologies which can render such wastes non-
hazardous.

4. One commenter argued that no environmental hazard
has been shown to be associated specifically with
mercury-bearing brine purification muds. The commenter
pointed out that many varieties of mercury-bearing
wastes were deposited at the sites for which the Agency
documented mismanagement incidents. The Agency agrees
that the several damage incidents, documenting
contamination of water with mercury from landfills
in which solid wastes from chlorine production had
been disposed does not specifically implicate any
one of these residues as being the unique cause of
such contamination. Nor does the Agency deem it
necessary to make such unique identification. The
damage incidents and the published data concerning
leaching of soluble mercury in solid wastes from a

chlor-alkali plant reported in the listing background document illustrate that water contamination from such wastes _in toto_ does occur. Further, it appears probable that listed chlor-alkali wastes were responsible for at least some of the damage caused in these incidents. If the commenter were able to document the fact that mercury-bearing brine purification muds, when uniquely disposed for periods similar to those illustrated in the damage incidents, did not cause water contamination, this could constitute proof that such wastes might indeed not be hazardous. In the absence of such proof, however, the Agency will continue to list mercury-bearing brine purification muds as hazardous.

5. One commenter stated that, although poorly managed mercury-bearing wastes can result in environmental damage, such damage has resulted from wastes which were improperly managed in the past. The commenter felt it unreasonable to assume that such poor management practices would continue in the future.

It is the Agency's position that the fact that a waste is properly managed by particular generators or classes of generators does not render the waste non-hazardous. RCRA requires that EPA determine whether a waste is hazardous if substantial hazard

could result when wastes are improperly treated, stored, transported, disposed of, or otherwise managed. The potential of the waste to cause hazard is the key factor. This position is more fully explained at 45 FR 33113.

6. One commenter suggests that the EP toxicity test should be the sole criterion for determining whether these wastes are hazardous. While the Agency has determined that the EP is a valid and acceptable test for identifying wastes likely to leach toxic constituents into groundwater, it believes the EP to be a somewhat less precise instrument than the listing mechanism for determining hazard, inasmuch as the EP fails to take into account factors such as the concentration of toxicants in the waste, their chemical composition, and the quantity of waste generated, all of which have a bearing on the hazardousness of the waste. This position and the grounds for its determination are more fully discussed at 45 FR 33111. Therefore, the listing mechanism also may be used to bring wastes within the hazardous waste management system. Listing appears particularly appropriate here, where the wastes contain high concentrations of very toxic constituent, and are reliably believed to have caused substantial damage in acutal waste management practice.

LISTING BACKGROUND DOCUMENT

K073:   CHLORINATED HYDROCARBON WASTE FROM THE PURIFICATION STEP
        OF THE DIAPHRAGM CELL PROCESS USING GRAPHITE ANODES IN
        CHLORINE PRODUCTION (T)

I.   SUMMARY OF BASIS FOR LISTING

    Chlorinated hydrocarbons are generated during the pro-
duction of chlorine in diaphragm cells with graphite anodes.
Purification results in separation of the chlorinated
hydrocarbon waste from the product. The Administrator has
determined that this waste is a solid waste which may pose a
substantial hazard to human health and the environment when
improperly transported, treated, stored, disposed of or
otherwise managed, and which therefore should be subject to
appropriate management requirements under Subtitle C of RCRA.
This conclusion is based on the following considerations:

1.   The waste contains significant concentrations of the
     toxic compounds chloroform, carbon tetrachloride,
     hexachloroethane, trichloroethane, tetrachloroethylene,
     dichloroethylene, and 1,1,2,2-tetrachloroethane. The
     Agency's Carcinogenic Assessment Group has found that
     chloroform, carbon tetrachloride, tetrachloroethylene
     and 1,1,2,2-tetrachloroethane exhibit substantial
     evidence of carcinogenicity.

2.   Typical management practices include deep well injection
     and incineration. Landfilling has also been employed as
     a disposal method. If these practices are unregulated,
     hazardous substances could be released to the environ-
     ment. Improper construction or operation of a deep
     well could cause leakage of the waste from the well
     into usable aquifers; inadequate incineration can result
     in the generation of highly toxic combustion products
     such as phosgene. Uncontrolled landfilling may result
     in migration of hazardous substances to air and ground
     and surface waters.

3. Most of these compounds have significant migratory potential and have proven mobile and persistent in actual damage incidents caused by improper waste management.

II. SOURCES OF WASTE AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

Chlorine is produced by electrolysis of brine. It is used in the pulp and paper industry, plastics, water treatment and manufacture of organic and inorganic chemicals. About 75 percent of all chlorine manufactured in the United States is produced by the diaphragm cell process.( ) Approximately 32 plants use diaphragm cells; of these, six plants that utilize graphite anodes generate chlorinated hydrocarbon contaminants.*[1] Locations and production capacities of the six are given in Table 1.[2]

B. Manufacturing Process[1,3]

Brine is first purified by precipitation of metals before being sent to the diaphragm cell. Separation of solids during purification generates waste brine muds; the Agency has no data at this time to indicate that the brine muds are hazardous. The purified brine is heated, brought to saturation by the addition of salt and acidified. The saturated salt solution is then electrolyzed in the diaphragm cell to form chlorine, hydrogen and sodium hydroxide. Chlorine is liberated at the anode, and hydrogen and sodium hydroxide are produced at the cathode. Reaction of chlorine with

*Graphite anodes predominated in the past, but in recent years most plants have replaced them with metal anodes.

Table 1

FACILITIES GENERATING CHLORINATED HYDROCARBON BEARING WASTES[2]

PLANT/LOCATION	PRODUCTION CAPACITY 10^3 KKG/YR
ICI Americas Baton Rouge, LA	156
Dow Chemical Midland, Mich.	256
Vulcan Materials Denver City, Tex.	121
Champion Production Canton, N.C.	26
Pasedena, Tex	20
PPG Industries Barberton, Ohio	100

carbonaceous materials in the graphite anode results in
the presence of chlorinated hydrocarbon contaminants in the
chlorine product.

The hydrogen is purified and either sold, vented to the
atmosphere or burned. The salt solution, which has been
decomposed to approximately half its original concentration,
is partially evaporated to increase the sodium hydroxide
concentration. During evaporation, most of the sodium chloride
precipitates from the solution and is recovered in salt
separators. After filtration and washing, the salt is recycled
to initial brine preparation.

Chlorine is recovered from the cell and cooled to remove
water and other impurities. The condensates are discharged
or recycled to the brine purifier. After cooling, the chlorine
gas is scrubbed with acid to remove residual water vapor.
The gas is then compressed and cooled to -30°C to -45°C. At
these temperatures, the chlorine liquefies and is pumped to
steel storage tanks. Some further purification is performed
during the cooling and liquefaction process. The chlorinated
hydrocarbon waste of concern is liquefied from the chlorine
gas stream during purification. Figure 1 illustrates the
process.

The Agency is also concerned that wastewaters from
clean-out of the diaphragm cell and from caustic evaporation
and salt recovery operations and sludges resulting from
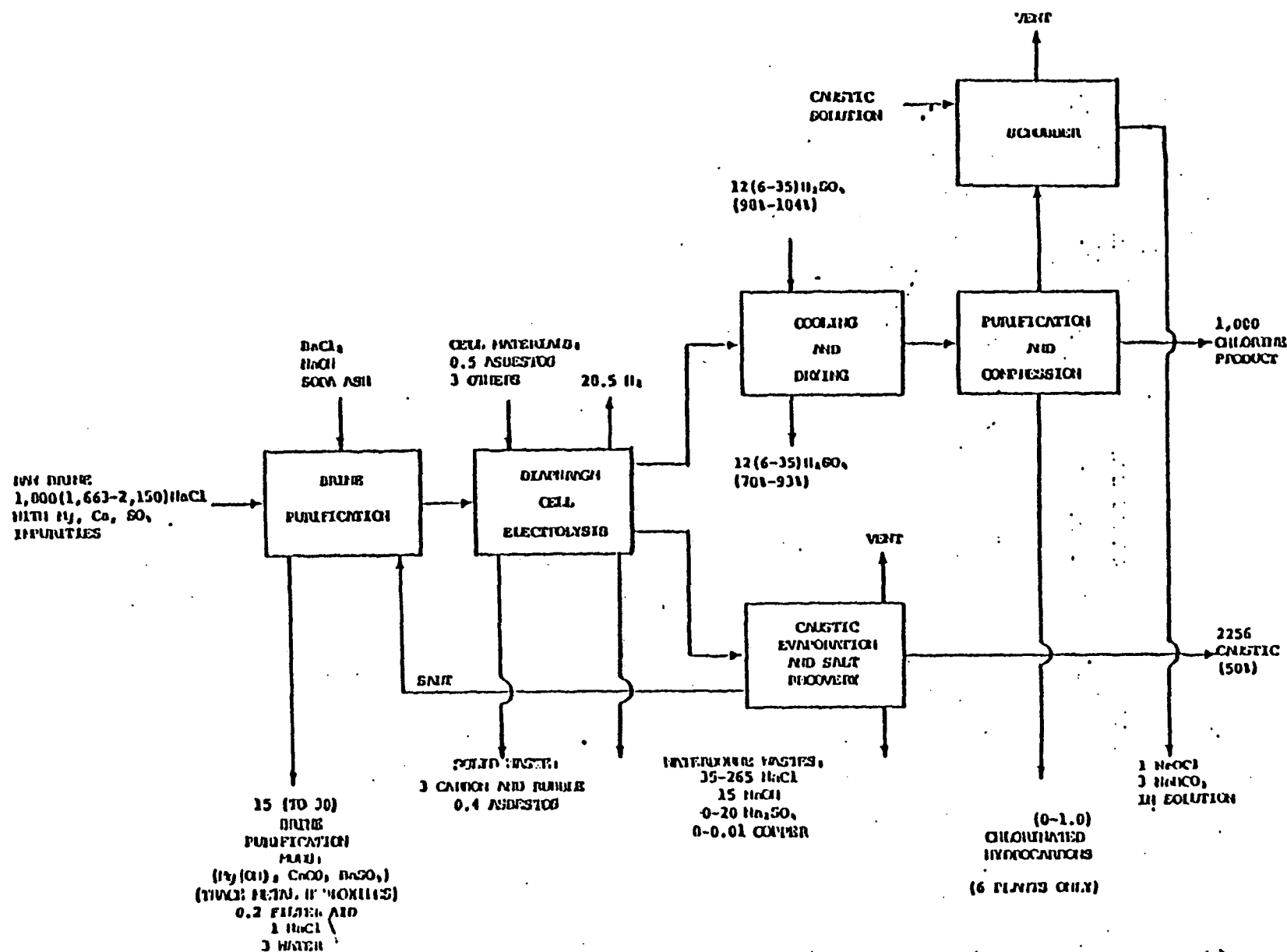treatment of these wastewaters may also be hazardous because

VENT

CAUSTIC
SOLUTION

DECARBER

12(6-35)H₂CO₄
(90%-104%)

BaCl₂
NaOH
SODA ASH

CELL MATERIALS:
0.5 ASBESTOS
3 OTHERS

20.5 H₂

COOLING
AND
DRYING

PURIFICATION
AND
COMPRESSION

1,000
CHLORINE
PRODUCT

RAW BRINE
1,000(1,663-2,150)NaCl
WITH Mg, Ca, SO₄
IMPURITIES

BRINE
PURIFICATION

DIAPHRAGM
CELL
ELECTROLYSIS

12(6-35)H₂SO₄
(70%-93%)

VENT

SALT

CAUSTIC
EVAPORATION
AND SALT
RECOVERY

2256
CAUSTIC
(50%)

SOLID WASTES:
3 CARBON AND RUBBER
0.4 ASBESTOS

WATERBORNE WASTES:
35-265 NaCl
15 NaOH
0-20 Na₂SO₄
0-0.01 COPPER

1 NaOCl
3 NaHCO₃
IN SOLUTION

15 (TO 30)
BRINE
PURIFICATION
MUDS:
(Mg(OH)₂, CaCO₃, BaSO₄)
(TRACE METAL HYDROXIDES)
0.2 FILTER AID
1 NaCl
3 WATER

(0-1.0)
CHLORINATED
HYDROCARBONS

(6 PLANTS ONLY)

FIGURE 1. CHLOR-ALKALI MANUFACTURE DIAPHRAGM CELL PROCESS /GRAPHITE ANODES (1).

they contain significant amounts of lead. The Agency currently does not have sufficient information on the concentrations and the migratory potential of the lead in these wastes, but they may be listed as hazardous at some time in the future. Generators, however, must determine whether this waste is hazardous pursuant to §§262.11 of the Subtitle C regulations.

C. Waste Generation and Management (4)

As mentioned previously, chlorinated hydrocarbon contaminants arise primarily from the reaction of chlorine with carbonaceous materials in the graphite anodes. Reaction of chlorine with oils and greases in the equipment and other hydrocarbons present in the system also contributes slightly to the generation of these contaminants. Depending on such variables as the type of liquefaction, quality of anodes and other factors, the chlorinated hydrocarbon contaminants are liquified from the chlorine gas stream during purification in amounts up to 1 kg per kkg of chlorine product.

Management practices vary. Vulcan Materials Co. disposes of the chlorinated hydrocarbon waste by deep well injection, and ICI Americas Ltd. incinerates its waste. Champion International Corp. and PPG Industries, Inc., which landfilled part of their wastes in sealed drums prior to 1977, apparently do not remove the chlorinated hydrocarbon contaminants from the chlorine product at this time. Dow Chemical's management practices are not known.

III. DISCUSSION OF BASIS FOR LISTING

    A.   Hazards Pose by the Waste

        The constituents of the chlorinated hydrocarbon
waste include the following (1):

Compound Identified	Weight (%)
chloroform	73.7
carbon tetrachloride	10.8
hexachloroethane	8.0
pentachloroethane	1.3
trichloroethane	1.0
tetrachloroethylene	0.6
dichloroethylene	0.3
1,1,2,2-tetrachloroethane	0.5

Clearly, the waste contains substantial amounts of organic
compounds believed to be toxic and carcinogenic. Thus, in
light of these constituents' high migratory potential and
their ability to persist in the environment, improper
management of this waste is likely to lead to substantial
hazard.

        Many of the constituents of concern have high vapor
pressures and thus could pose a substantial hazard to human
health and the environment via an air exposure pathway if
the waste is improperly managed. Evidence available to
EPA's Carcinogen Assessment Group indicates that chloroform,
carbon tetrachloride, tetrachloroethylene, and 1,1,2,2-tetra-
chloroethane are carcinogenic. The Agency believes that the
severity of the adverse health effects associated with exposure
to these constituents provides a sound basis for listing the
waste as hazardous. The high concentration of chloroform

alone justifies the listing of this waste as hazardous, in the Agency's judgment. EPA's decision to list the waste is supported further by case histories which reveal that these hazardous constituents can migrate and persist in the environment.

Carbon tetrachloride, a major component of the waste, has been identified in school and basement air in the vicinity of Love Canal (8) and has been implicated in groundwater contamination incidents in Plainfield, Connecticut, where drinking water sources were adversely affected (9). Chloroform has been found in drinking water wells near a Jackson Township, New Jersey landfill in which chemical wastes were dumped, and is also known to have migrated from the Love Canal disposal site (10). Hexachloroethane, another major constituent of the waste of concern, has also migrated from at least one chemical waste disposal site (Table 7.2, Ref. 9). In addition, damage incidents compiled by EPA reveal numerous instances of environmental contamination due to migration of trichloroethane and tetrachloroethylene.(10)

An estimated 125 kkg of waste per year is disposed of in deep wells or by incineration* (2); either method may unfavorably affect human health and the environment by con-taminating ground and surface waters or polluting the atmosphere. A deep well injection system that is not properly designed

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*This number was derived by multiplying 90% of the plant
 nameplate capacity by 0.5, on the assumption that, on
 average, 0.5 kg of chlorinated hydrocarbon wastes are
 generated per kkg of chlorine.

or operated can release hazardous constituents from the well to aquifers used as drinking water sources. Improper incineration of chlorinated hydrocarbons can result in the generation and emission of highly toxic combustion products such as phosgene (5,6,7) and chronically toxic chlorinated aromatic compounds.[15] The remainder of these wastes (up to 180 kkg per year) is disposed of by means not known to the Agency. Landfilling of drummed waste has been practiced in the past. This disposal method presents obvious hazards; drums are likely to corrode in the landfill and release the waste to the surrounding area. Waste constituents could then volatilize and enter the atmosphere or migrate to ground and surface waters.

Health and Environmental Effects

Chloroform

Chloroform has been identified by the EPA Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Due to its highly volatile nature, (App. B), improper disposal of chloroform-containing wastes may pose an air pollution hazard. Long range exposures have caused both physical and neurological disorders in humans, with liver and kidney toxic responses representing the most prevalent physical pathology. FDA prohibits the use of chloroform in drugs, cosmetics or food contact material. Additional information and specific references on the adverse effects of chloroform can be found in Appendix A.

Carbon Tetrachloride

Carbon tetrachloride (tetrachloromethane) has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Its toxic effects include neurological damage and damage to the kidney and lungs. It is volatile and slightly soluble in water, and is therefore expected to migrate readily in the environment (11). Additional information and specific references on the adverse effects of carbon tetrachloride can be found in Appendix A.

Hexachloroethane

Hexachloroethane is moderately toxic to humans and is one of the more toxic chlorinated ethanes to aquatic species. It appears to have the potential to bioaccumulate (App. B). Humans exposed to hexachloroethane may suffer central nervous system depression and liver, kidney and heart degeneration. It has also been shown to be carcinogenic to laboratory animals. Little information is available on its environmental fate and transport, but, due to the nature of the adverse affects associated with exposure to this compound, the Agency believes that improper disposal of a waste containing a significant amount of hexachloroethane may pose a hazard to human health and the environment. Additional information and specific references on the adverse effects of hexachloroethane can be found in Appendix A.

Trichloroethane

The trichloroethanes (1,1,1-trichloroethane and 1,1,2-trichloroethane) are toxic to humans and animals, and have been shown or are suspected to be carcinogenic. Because of the toxic and/or carcinogenic effects of these compounds, the Agency believes that improper management of wastes which contain them may pose a hazard to human health and the environment. Additional information and specific references on the adverse effects of trichloroethanes can be found in Appendix A.

Dichloroethylenes

Exposure to dichloroethylenes can result in adverse human health effects. The three isomers appear to have similar toxic effects, including depression of the central nervous system and liver and kidney damage (App. A). Two isomers are mutagenic in bacterial sytems and one isomer has been shown to be carcinogenic in laboratory animals (App.A). Information on environmental fate and transport is scarce but, due to the nature of the health effects resulting from exposure to dichloroethylenes, the Agency has determined that improper management of wastes containing these compounds poses a hazard to human health and the enviroment. Additional information and specific references on the adverse effects of dichloroethylenes can be found in Appendix A.

Tetrachloroethylene

Tetrachloroethylene has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. In addition, repeated exposure to tetrachloroethylene is implicated in mammalian liver and kidney damage (App.A). Additional information and specific references on the adverse effects of tetrachloroethylene is given in Appendix A.

1,1,2,2-Tetrachloroethane

1,1,2,2-tetrachloroethane has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Occupational exposure has produced neurological symptoms, liver and kidney damage, pulmonary edema and fatty degeneration of the heart muscle. 1,1,2,2-tetrachloroethane is soluble in water (2900 ppm) and thus has high migratory potential (11). Although environmental fate and transport processes are not well-defined (microbial degradation appears to be the only known degredation mechanism (App. B), and this process is not likely to occur under the abiotic conditions prevailing in most aquifiers), the Agency believes that, due to the severity of the health effects associated with exposure to this compound, improper disposal of the wastes in which it is contained poses a substantial hazard. Additional information and specific references on the adverse effects of 1,1,2,2-tetrachloroethane can be found in Appendix A.

The waste also contains a significant amount of pentachloro-
ethane, a toxic chlorinated organic. At this time the Agency
has not compiled data on specific health effects or environmental
persistence and mobility; when the data are obtained, a
document will be prepared for Appendix A.

REFERENCES

K073: Chlorine Production: diaphragm cell process.

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3. U.S. EPA. Development document for effluent limitations guidelines and standards for the inorganic chemicals manufacturing point source category. EPA No. 440/1-80/007b. June, 1980.

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5. Edwards, J.B. Combustion formation and emission of trace species. Ann Arbor Science. 1977.

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10. U.S. EPA. Damages and threats caused by hazardous material sites. EPA No. 430/9-80/004. January 1980.

11. Verschueren, K. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Co., New York. 1977.

Response to Comments: Chlorine Production (Diaphragm Cell Process).

1. One commenter questioned the Agency's characterization
    of 1,1,1-trichloroethane as a carcinogen. The commenter
    argues that based on their evaluation of the available
    data, 1,1,1-trichloroethane has not been found to be
    carcinogenic (i.e., the commenter believes that the
    Agency has incorrectly assessed the data).

    The Agency disagrees with the commenter's claim.
    Although an NCI Bioassay Study on the carcinogenicity of
    1,1,1-trichloroethane referred to in the listing background
    document and an unpublished study are inconclusive,
    positive responses in two in vitro systems (a rat embryo
    cell transformation assay (Price et. al. 1978) and a
    bacterial mutation assay (Simmon et. al. 1977; McCann
    and Ames, 1976)) currently used to detect chemical
    carcinogens, indicate that 1,1,1-trichloroethane has the
    potential for carcinogenicity in animals. Additionally,
    a two year carcinogenesis animal bioassay is being
    repeated at the National Cancer Institute. Therefore,
    the Agency believes that there is ample evidence to
    consider 1,1,1-trichloroethane as a suspect carcinogen.*
    The listing background document on trichloroethane

    _____
    *It should be noted that the Agency recently determined
    to retain the listing of 1,1,1-trichloroethane as a toxic
    pollutant under §307(a) of the Clean Water Act. The
    reasons for that action are incorporated by reference
    herein.

production and the Health and Environmental Effects
Profile on 1,1,1-trichloroethane has been modified to
discuss these findings.

References

McCann, J. and B. Ames. Detection of Carcinogens as
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Price, P.J. et al. Transforming Activities of Trichloroethylen
and Proposed Industrial Alternatives. In Vitro 14:290:1978.

Simmon, V.F. et al. Mutagenic Activity of Chemicals
Identified in Drinking Water. In: Progress in Genetic
Toxicology. I.D. Scott, B.A. Bridges and F.H. Sobels, ed.
pp.249-258. Elsevier, N.Y., 1977.

LISTING BACKGROUND DOCUMENT

NITROBENZENE/ANILINE PRODUCTION

K083:   Distillation bottoms from aniline production (T)

K103:   Process residues from aniline extraction from the production
        of aniline (T).

K104:   Combined wastewater streams generated from nitrobenzene/
        aniline production (T).

I.   Summary of Basis for Listing

The first listed waste is the bottom residue generated

from the purification of aniline by distillation. The second

listed waste results from the extraction step in aniline production

and may or may not be combined with other process waters. This

listing covers the uncombined waste streams. The third

listed waste is the combined process wastewater streams from

the co-production of nitrobenzene and aniline. These waste

streams all contain toxic nitrogenous organic materials, and the

wastewater stream is likely to contain benzene as well.

The Administrator has determined that still bottoms from

aniline distillation, process residues from aniline extraction

(when generated as a separate waste stream and not combined

with other process wastewater streams), and wastewater generated

from nitrobenzene and aniline production are solid wastes

which may pose a substantial present or potential hazard to

human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1) The distillation bottoms contain aniline, diphenylamine, nitrobenzene, and phenylenediamine while the combined wastewater stream contains these constituents and usually contains benzene as well. The process residue from aniline extraction, if disposed of separately, contains aniline, nitrobenzene and phenylenediamine. All of these constituents are toxic. Benzene is a known human carcinogen. Aniline, diphenylamine and phenylenediamine are carcinogenic to laboratory animals. Diphenylamine is expected to bioaccumulate.

2) Total potential loadings of benzene and aniline in the wastewater stream from the production of nitrobenzene and aniline could be as high as 9.5 kkg and 150 kkg annually, quantities believed by the Agency to be quite significant in view of these compounds' adverse health effects.

3) Current disposal practices of these wastes are not well documented. However, there is a high potential for contaminating groundwater by leaching from waste treatment lagoons or landfills that are not properly designed or operated, since these constituents have high migratory potential, and some have proven mobile and persistent in actual waste management practice. In addition, under certain conditions, release to the atmosphere by volatilization poses a risk of inhalation of aniline and nitrobenzene.

4) In a damage incident involving improperly managed aniline distillation bottoms, waste oils were contaminated with nitrobenzene from the distillation residues and spread over roads, posing the risk of human exposure to dangerously high concentrations of nitrobenzene. This waste has thus proven capable of posing a substantial hazard in actual waste management practice.

5) The State of Texas regulates distillation bottoms from aniline production as a hazardous waste.

II. Sources of the Waste and Typical Disposal Practices

A. Profile of the Industry

Nitrobenzene and aniline are major chemical intermediates; the actual nameplate capacity was reported as 557,000 kkg[25] and 313,000 kkg, respectively.[2] The U.S. International Trade Commission lists aniline as the sixth largest volume intermediate in terms of 1978 production.[1] Table 1 lists the facilities producing nitrobenzene and aniline, and their production capacities. As is indicated, most facilities produce both nitrobenzene and aniline. In 1978 97% of nitrobenzene produced was used for the synthesis of aniline.[2,25] The balance is purified for use chiefly as a solvent, or in the manufacture of pharmaceuticals, dyes and photographic chemicals.

United States production of aniline is increasing. Production levels were 151,000 kkg in 1969, 186,000 kkg in 1972, 187,000 kkg in 1975,[3] and 270,000 kkg in 1978.[1] Aniline production capacity is anticipated to reach 450,000 kkg in 1980. Most aniline (about 40%) is used for the production of polymeric methylene phenylisocyanate, an intermediate used in the manufacture of urethanes; another 35% is used in the synthesis of rubber chemicals.[2] The remainder is mainly used in the manufacture of dyes and drugs.

Table 1

PRODUCER LOCATIONS AND PRODUCTION CAPACITIES

| MANUFACTURER	FACILITY	PRODUCTION CAPACITY (10^3kkg) 1978 Nitrobenzene[25]	1977 Aniline[2
American Cyanamid Co.	Bound Brook, NJ	48	27
American Cyanamid Co.	Willow Island	33	28
E. I. Dupont de Nemours & Company, Inc.	Beaumont, TX	140	104
E. I. Dupont de Nemours & Company, Inc.	Gibbstown, NJ	90	59
First Mississippi Corp.	Pascagoula, MS	151	45
Mallinkrodt Corp.	Raleigh, NC	0	10
Mobay Chemical Corp.	New Martinsville, WV	61	45
Rubicon Chemicals, Inc.	Geismar, LA	34	27
		557	340

B. Manufacturing Process[2]

1. Manufacture of Nitrobenzene

Nitrobenzene is made by the direct nitration of benzene using a sulfuric-nitric acid mixture. In the most common continuous phase process, benzene is nitrated with an aqueous mixture of sulfuric acid (53 to 60 mole percent) and nitric acid (32 to 39 mole percent) at atmospheric pressure and temperatures between 45 to 90°C. Yields are typically better than 98 percent. This process (see Figure 1) is carried out in vented stainless steel vessels equipped with high speed agitators and cooling coils. Average residence time is approximately 8 to 10 minutes. Nitrobenzene is continuously drawn from the side of the reactor and separated in a decanter. Once separated, this "crude" nitrobenzene is reportedly used directly in the manufacture of aniline.

If pure nitrobenzene is required, the product is washed first with water and subsequently with an alkaline solution (generally either a sodium carbonate or sodium hydroxide solution) in small vessels equipped with high speed mechanical agitators, and then distilled. The wastewater resulting from the washing operation (stream 3 in Figure 1), is one component of the waterborne waste stream of concern in this document.

FIGURE 1
SIGNIFICANT POLLUTANTS FROM
NITROBENZENE/ANILINE MANUFACTURE (MODIFIED FROM (2))
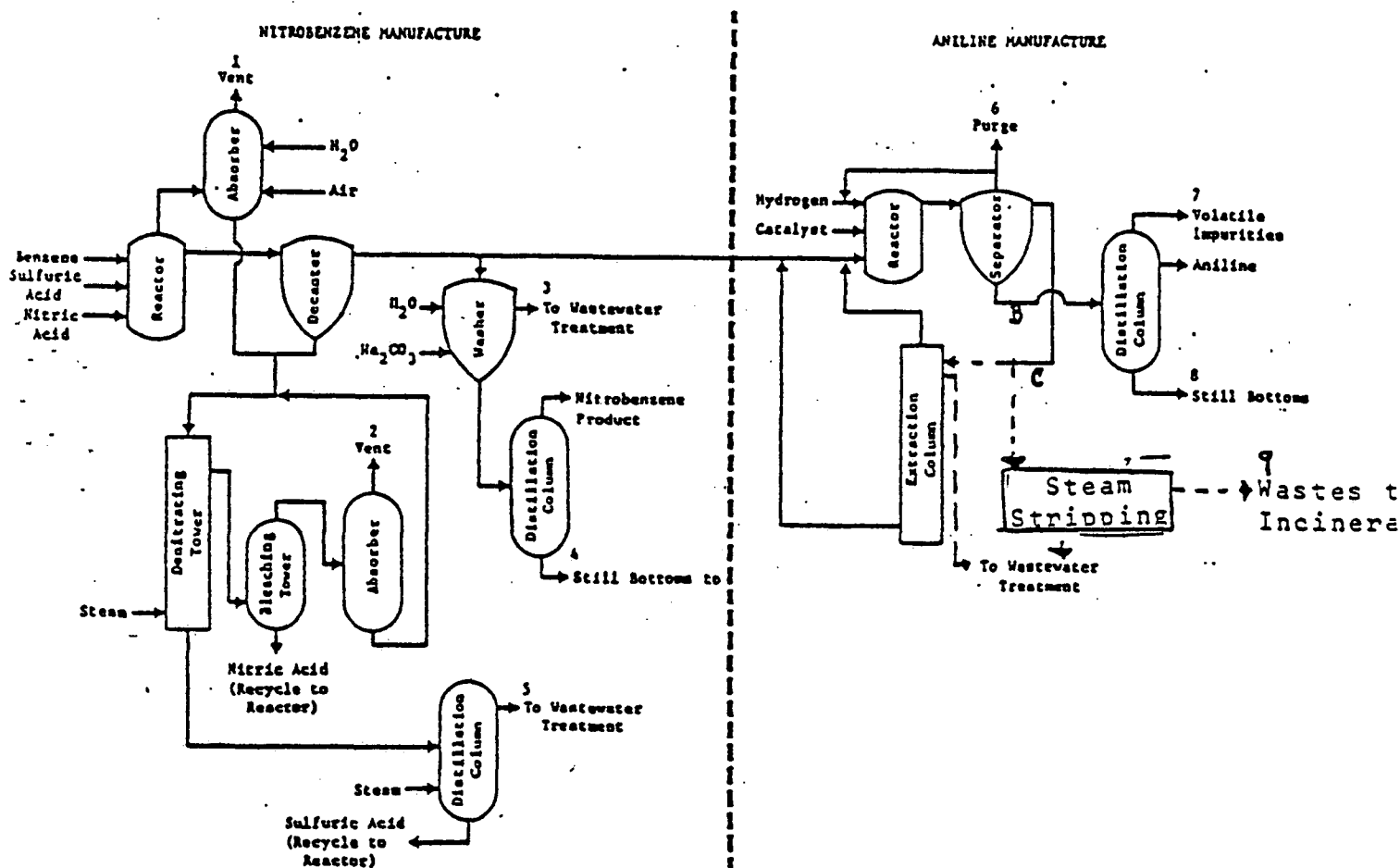
Point 1*
  Benzene, Nitroalkanes, Nitrobenzene, Nitrogen Oxides

Point 2*
  Benzene, Nitroalkanes, Nitrobenzene, Nitrogen Oxides

Point 3
  Benzene, Benzoic Acid, Carboxylic Acids, Nitrates, Nitrites,
  Nitrobenzene, Nitrophenol

Point 4**
  Dinitrobenzene, Nitrobenzene, Nitrophenol, Nitrogen Containing
  High Molecular Weight Polymers, Polycarboxylic Acid, Dinitro-
  toluene

FIGURE 1 CONTINUED

Point 5
  Benzene, Nitrobenzene, Nitrophenol, Polycarboxylic Acid, Nitrogen Containing High Molecular Weight Polymers

Point 6*
  Aniline, Carbon Monoxide, Hydrogen, Methane, Nitrobenzene

Point 7*
  Cyclohexylamine, Volatile Amines, Water

Point 8*
  Aminophenols, Azepins, Diphenylamine, Nitrobenzene, Phenylenediamine, Nitrogen Containing High Molecular Weight Polymers

Point 9
  Aminophenol, Aniline, Nitrobenzene, Phenylenediamine, Water Soluble Amines

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* Emitted to air and therefore not subject to RCRA.
**This waste was listed in the May 19, 1980 promulgation (see "Nitrobenzene Background Document" for details).

Recovery of spent acid is essential from the standpoint of economical operation. Generally, unreacted nitric acid is extracted from the spent acid by steam stripping (denitrating tower). The bottom product, dilute sulfuric acid (60 percent by weight), is then concentrated by distillation (sulfuric acid concentrator) and recycled to the reactor as shown, or used in other manufacturing operations. Nitric acid removed overhead from the denitrating tower is bleached with air to remove nitrogen oxide and subsequently recycled to the reactor. The overhead nitrogen oxides from the bleacher are scrubbed with water and recycled to the denitrating tower.*/ The waste resulting from acid recovery (number 5 in Figure 1) is another component of the aqueous waste stream of concern in this document.

2. Production of Aniline[2,3]

In the U.S., aniline production is based almost exclusively on vapor phase reduction of nitrobenzene in the presence of a copper catalyst. This process is also illustrated in Figure 1. With the exception of one facility (Mallinkrodt, Inc.), the nitrobenzene feedstock is produced on site.[2] The nitrobenzene is vaporized in a stream of hydrogen and introduced into the reactor. The crude product mixture (aniline, hydrogen and

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*Another approach to spent acid recovery uses benzene, rather than steam, to strip nitric acid from spent acid in the denitrating tower. The nitric acid is thus dissolved in the benzene and fed to the reactor. The remaining sulfuric acid is concentrated as before.

water) leaving the reactor is condensed and separated from
the gas stream. Most of this gas stream is compressed and
recycled to the reactor, but, to prevent build-up of gaseous
impurities in the reactor, some gas is purged. The two-phase
(aqueous and organic) reactor product mixture is separated.
The lower organic phase (stream B, Figure 1), consisting
principally of aniline, up to 5 percent nitrobenzene, and 5
percent water,[2] is purified by two stage distillation.
In the crude still, aniline and water are removed overhead,
while higher boiling organic impurities, such as nitrobenzene,
remain in the still bottoms (noted as 8, Figure 1). In a finishing
distillation step, the overhead product from the crude still
is purified to 99% specification, and the bottoms from
this finishing distillation step are combined with the crude
distillation bottoms. (This process is shown as a single
distillation in Figure 1.)[3]

Several methods are used to recover aniline from the
aqueous phase of the separator (C in Figure 1). Aniline may
for instance be concentrated from this stream by steam stripping.
The resulting enriched aniline/water mixture is then incinerated.
This latter waste stream is not included within the present
listing, although it may be listed in the future. The Agency
solicits information as to the composition of this waste and
risks associated with its improper disposal.

At some facilities aniline is recovered by countercurrent
extraction with nitrobenzene. Recovered aniline and nitrobenzene

are recycled to the reactor. In either case (i.e., if either

extraction or steam stripping is used), the residual waste

stream (9 in Figure 1) ordinarily is directed to wastewater

treatment with other process wastewater streams. This is

the third component of the waterborne waste stream of concern

in this document. In some facilities, the residues from the

extraction step are not combined with other process wastewaters.

In such cases, the listing includes the separate wastewater

stream from the extraction step.

C.   Waste Generation and Management

The listed wastes consist of still bottoms from the

distillation of aniline (Point 8, Figure 1) and the wastewater

streams generated from nitrobenzene/aniline manufacture

(points 3, 5 and 9 of Figure 1), which are most often combined

before wastewater treatment. (Wastes from the aniline extrac-

tion step are listed when disposed of separately, as discussed

above.)

On the basis of process chemistry assumptions set forth

in (2), the aniline distillation bottoms are expected to

contain nitrobenzene, nitrophenols, aniline, diphenylamine,

and phenylenediamine. While precise concentrations are

unknown, concentrations of nitrobenzene are expected to be

quite high, since the organic phase prior to distillation

consists of 5 percent nitrobenzene, most of which would be

expected to be (and is intended to be) removed by distillation,

leaving wastewater with low levels of nitrobenzene to go to

treatment.

The volume of aniline still bottoms and the present practices of the industry with regard to their disposal are not well defined. The most common disposal method for distillation bottoms is storage in drums in private landfills.[27] Some of these wastes are apparently utilized for their acid-neutralizing capacity in drilling operations.[4]

The wastewater stream components from nitrobenzene/aniline manufacture include: the nitrobenzene washwater (Point 3), the acid distillation column overhead (point 5) and the aniline recovery stream (point 9). Based on a knowledge of process chemistry, these streams are estimated to contain the pollutants indicated in Figure 1. Most manufacturers combine these wastewater streams prior to treatment.[2] Table 2 lists typical concentrations of selected pollutants found in combined nitrobenzene/aniline waste streams, as reported by two manufacturers.[2]

A variety of wastewater treatment methods are applied, and it is not known to what extent these are successful in removing the toxic chemicals from the listed waste. The following treatment methods have been reported:[2] steam stripping, carbon adsorption, aerated lagoon, biological contact stabilization, clarification, equalization, activated sludge, stabilization pond, land application, and subsurface disposal.

Table 2

Characterization of Raw Waste Loading From

Nitrobenzene/Aniline Manufacture[2]

| | kg/kkg aniline product | | | kkg/yr* |
	Avg.	Min.	Max.	Max.
Aniline	0.067	0.005	0.49	150
Benzene	0.005	0	0.031	9.5
Nitrobenzene	0.002	0	0.012	3.7

*Obtained by multiplying the maximal value by the 340,000
kkg by 90% of annual aniline nameplate production capacity
(since plants rarely operate at 100% of capacity).

In addition to the above pollutants whose identity was
quantitatively confirmed, animophenol, benzoic acid,
nitrophenol, and phenylene diamine as well as nitrates and
nitrites are estimated[2] to occur. Of these constituents
the wastewater loading data show that at least aniline,
benzene and nitrobenzene are present in substantial
concentrations, and generated in significant quantities
annually.

As noted above, the wastewaters from the extraction
step of aniline production are not always combined with other
process wastewater streams.

III. Discussion of Basis for Listing

    A.   Hazards Posed by the Waste

        On the basis of available information, it is apparent
that the listed wastes contain toxic organic materials, including
nitrobenzene, aniline, diphenylamine and phenylenediamine, and
(for the combined wastewaters) benzene. These constituents
are all toxic, and all but nitrobenzene are experimental or
(in the case of benzene) known carcinogens. All of these
constituents are projected to have migratory potential and
to be mobile and persistent in ground and surface water
- (Appendix B), so that they can create a substantial hazard
 if disposal facilities are not properly designed and operated.
Aniline, nitrobenzene and phenylenediamine are quite soluble
(solubility 34,000, 38,000 ppm and 1900 ppm respectively),[5]
and thus can easily migrate through dry sandy soils.
Diphenylamine is also significantly soluble for purposes of
risk of chronic exposure (300 ppm [6]). Furthermore, the
solubility of amines such as aniline, diphenylanime and
phenylendiamine increases significantly under conditions
which are more acidic than their acid dissociation constant
(pKa is 6.0 for phenylenediamine). Since the pH of the
rainfall in the United States presently ranges from 4.0 -
5.0[9,22], residues of aniline and phenylenediamine

can be expected to leach to surface and groundwater if these wastes are improperly transported, treated, stored, disposed of, or otherwise managed.

Present waste disposal practices may be inadequate to prevent waste migration. Certainly, improper management may result in release of harmful constituents, particularly in view of the properties of the waste constituents as described above. For instance, if this waste should be exposed to an environment subject to acid rainfall, disposed residues containing phenylenediamine contacted by acid rainfall can be expected to leach and to migrate to surface and groundwater.

Further, if this waste is treated in a lagoon, even under relatively mild environmental conditions, the harmful constituents can be expected to leach from the waste, as a result of their moderate to extreme water solubility properties if the lagoon is not properly designed or operated. Once released from the matrix of the waste, these constituents could migrate from the waste and contaminate groundwater. Nitrobenzene, for example, has proven mobile and persistent in two major damage incidents involving waste disposal at the Monsanto Chemical dump in East St. Louis and at the LaBounty dump in Charles City, Iowa.[10]

Another potential hazard associated with lagoon treatment of this waste would be the volatilization of compounds with appreciable vapor pressure such as benzene into the atmosphere, thus posing a hazard via inhalation. Benzene has proven

capable of migration and persistence via an air exposure
pathway in many actual damage incidents, Love Canal being the
most notorious.

If the wastes are landfilled, even in plastic-lined
drums, they can create a potential hazard. All drums have a
limited life span, for the exterior metal corrodes in the
presence of even small amounts of moisture. When this occurs,
the potential for groundwater contamination is high if the
landfill is not properly designed or operated. It should be
noted that many of the subject production facilities are
located in regions of significant rainfall (LA, NJ, WV), so
that ample percolating liquid is available for leachate
formation. (In any case, there is no reason to believe that
wastes will be containerized at all, since, absent Subtitle C
regulation, wastes could be landfilled in a variety of improper
ways.)

A special hazard posed by the subject wastes is the
possibility of the formation over time of highly carcinogenic
nitrosamines from some of their constituents.[2] Aniline and
other amines (most importantly secondary amines) as well as
nitrites are thought to be present in these wastes (Figure
1). These substances may react to form nitrosamines, especially
under acidic conditions. Such conditions might result as a
consequence of co-disposal of the listed wastes with acidic
wastes, or under conditions of continued acid rainfall.

Improperly managed aniline distillation bottoms have been involved in at least one damage incident.[23] From 1976 through November 1978, contaminated waste oils were used as dust suppressant on roads throughout East Texas. The chief source of contamination were aniline tars (still bottoms) from aniline production*, generated by Dupont's Beaumont facility. These still bottoms were sent to Browning-Ferris Industries Chemical Services, Inc., a state permitted waste management facility, which proceeded impermissibly to mix the wastes with waste oil, which oil was used indiscriminately as a road dust supressant. Nitrobenzene levels in contaminated soil varied, and were as high as 21,000 ppm. Most of the concentrations were deemed by state environmental officials as more than sufficient to cause substantial harm. The danger was discovered before occurence of known harm, and Browning-Ferris was ordered to remove approximately 10,000 cubic yards of contaminated material from one subdivision, and additional amounts of material from four additional subdivisions.[23]

This incident not only illustrates the potential for substantial harm if this waste is disposed of improperly, but also suggests strongly that the aniline distillation residues may contain very high concentrations of nitrobenzene, in light of the substantial concentrations found in the contaminated road oil. Furthermore, aniline distillation bottoms are

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* The waste oils were heavily contaminated with nitrobenzene, and the only source of nitrobenzene in wastes accepted by Browning-Ferris were aniline distillation wastes. (23 at p. 17.)

regulated as hazardous wastes (termed 'Class I wastes' under
the state waste management system) by the State of Texas
(23), another indication of their potential for hazard.

   B.   Health and Ecological Effects

   Benzene

   EPA's Carcinogen Assessment Group has designated benzene
as a human carcinogen (leukemogen). Acute exposure to high

   concentrations of benzene causes central nervous system
depression (euphoria, nausea, staggering gait and coma).
Inhalation of lower amounts produces dizziness, headache and
nausea. Benzene has demonstrated teratogenic effects in laboratory
animals. Chromosomal changes have also been demonstrated in
workers exposed to benzene.(28)

   For maximum protection of human health from the potential
carcinogenic effects of exposure to benzene through ingestion
the ambient water criterion is 0.80 ug/l(29).

   Because benzene is soluble in water, it could be leached
from the wastewater treatment sludge which would be generated
from treatment of the combined wastewaters, in a landfill
situation and pose a threat to groundwater supplies. Because
it is also volatile (vapor pressure = 100 mm at 26.1°C
(Appendix B.)), it may pose an inhalation hazard during
handling in transportation and disposal. Additional information
and specific references on the adverse health and environmental
effects of benzene can be found in Appendix A.

Nitrobenzene

Nitrobenzene has toxic reproductive effects: in rats it
delays embryogenesis, alters normal placentation, and produces
abnormal fetuses (14); changes in the tissues of the chorion
and placenta have been reported in women exposed to nitrobenzene
(15). Nitrobenzene has been listed as a Priority Pollutant
in accordance with §307(a) of the Clean Water Act of 1977.

With present data, it is not possible to fully estimate
its aquatic fate. Hydrolysis and volatilization from water
are considered unlikely (15). Adsorption onto humus and clay,
and subsequent production by weathering and biological action,
of (carcinogenic) benzidine and diphenylhydrazine could be
a major fate pathway (12) Nitrobenzene is neither stored
nor ecologically magnified, but is resistant to degradation
by soil microflora (11, 12). In mammalian systems nitrobenzene
is metabolized to aniline, nitrophenol, p-hydroxyaniline
and other metabolites, which are excreted in urine, but such
metabolism in man is slower by an order of magnitude than in
animals (13).

The criterion to protect freshwater aquatic life is 480
ug/l (24 hour average). The occupational exposure limit
(OSHA) is 5 mg/m^3 (skin, 8 hr TWA). The American Conference
of Governmental Industrial Hygienists (ACGIH) threshold
limit for industrial exposure to nitrobenzene is 1 ppm.[23]

Additional information and specific references on the adverse

health effects of nitrobenzene can be found in Appendix A.

Aniline

Aniline is an experimental carcinogen (16). Its absorption

causes anoxia due to the formation of methemoglobin, but

significant chronic problems (other than animal carcinogencity)

have not been demonstrated. Human exposure to vapor

concentrations of 7-50 mm has been observed to cause slight

symptoms.[30] Rapid absorption through the intact skin is

frequently the route of entry.[18,30] Cyanosis is the most

prominent outward symptom of aniline intoxication.[8] At

0.4 mg/l aniline is toxic to Daphnia (8). OSHA's PEL for

aniline is 19 mg/m^3 (skin, 8 hr TWA)(17). Additional information

and specific references on the adverse health effects of

aniline can be found in Appendix A.

Phenylenediamine

Phenylenediamine is a highly toxic substance, continued

exposure to which can cause liver injury (18). It is a

suspected carcinogen and teratogen (18). Of the three isomers,

the p-substituted compound is by far the more toxic (19).

The relative concentrations of the isomers in the listed

waste are not known. The oral toxicity for human beings is

high (LD_{10}= 50 mg/kg (19)), which, in combination with the

high water solubility of this compound is worrisome. Phenyl-

enediamine is listed by DOT as a hazardous substance (ORM-A),

and the OSHA PEL is 0.1 mg/m^3(8 hr TWA) (17).

Diphenylamine

Diphenylamine is an experimental carcinogen and teratogen
(19). Chronic exposure to diphenylamine induces cystic lesions
in the chicken[20] and the rat.[24] The American Conference
of Industrial Hygienists has established 10 mg/m^3 as an
acceptable TLV for occupational exposure (21). Diphenylamine
can also be expected to bioaccumulate, due to its high
octanol/water partion co-efficient of 2,200 (7).

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Response to Comments: Distillation Bottoms, Wastewater

Treatment Streams and Process Residues from Nitrobenzene/Aniline

Production.

One commenter, a manufacturer of these chemicals, objected
to the listing of wastewater streams from nitrobenzene/
aniline production, noting that they fully pre-treat
these wastewater streams, removing nitrobenzene, benzene
and aniline to extremely low levels, apparently taking
issue with the Agency's determination that these
wastes generally contain appreciable levels of these
(and other) toxic chemicals. The commenter went on to
state that the mismanagement incident (cited in the BD)
regarding distillation bottoms from the production of
nitrobenzene in fact involved waste nitrobenzene, rather
than the listed waste.

We are not persuaded by this comment that the listed
wastes typically and frequently contain inconsequential
levels of hazardous constituents. To the extent an individual
facility is able to remove or reduce the constituents of
concern by a treatment process, the May 19, 1980 regulations
provide explicit procedures which a generator may employ to
petition the Administrator to amend part 261 to exclude a
listed waste produced at a particular facility. (See §§ 261.20
and 260.22). a particular facility are set forth in §§261.20
and 260.22. The commenter can use these procedures to

petition for removal of the subject streams at its
facility. However, in the absence of proof regarding
error in its assumptions concerning the nature and concen-
tration of toxicants, and the amounts of these hazardous
wastes generated, the Agency will continue to list
these streams as hazardous wastes. It should also be noted
that two of the toxic constituents of concern (phenylene
diamine and diphenylamine) were not adressed by the
commenter, thus, no data was provided to refute their
prersence or potential for creating a hazard.

With regard to the demonstrated potential for
mismanagement of these wastes, the cited legal testimony
implicated aniline distillation wastes (ref. 23 of BD
at p. 17, citing aniline tars, not waste nitrobenzene,
as the waste mixed with the road oil).

The Agency therefore disagrees with the commenter,
and judges that, because of the toxic nature of many of
the components of these wastes, the large amount of
wastes generated, and the demonstrated potential
for mismanagement, these wastes may pose a substantial
present or potential hazard to human health or the
environment, and that they should be subject to appro-
priate management requirements.

LISTING BACKGROUND DOCUMENT
VETERINARY PHARMACEUTICALS

K084: Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

K101: Distillation tar residues from the distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

K102: Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

I. SUMMARY OF BASIS FOR LISTING.

Treatment of wastewater from the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds generates a wastewater treatment sludge containing arsenic or organo-arsenic compounds. The production of this class of veterinary pharmaceuticals also generates residues from the distillation of aniline-based compounds, and from the use of activated carbon for decolorization, which also contain arsenic or organo-arsenic compounds, wastes which are listed in this document.

The Administrator has determined that these wastewater treatment sludges and other arsenic-containing wastes from the production of veterinary pharmaceuticals are solid wastes which pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and, therefore, should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on

the following considerations:

1) These wastes have been shown to contain high concentrations of arsenic. Arsenic is highly toxic and has been identified by the Agency as a substance which has demonstrated substantial evidence of being carcinogenic. It is also a bacterial mutagen, and is teratogenic to laboratory animals.

2) Disposal of these wastes in improperly designed or operated landfills has resulted in arsenic contamination of ground and surface water, providing empirical proof that the arsenic in this waste is soluble and may migrate from disposal sites into soil, groundwater and surface water in concentrations sufficient to create a substantial hazard. Further, since arsenic is an element, and does not degrade with time, it persists, and any contamination caused by mismanagement of these wastes will be long-term.

3) These wastes are generated in large quantities, so that large amounts of arsenic are potentially available for environmental release, an additional hazard posed by this waste.

II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

A. Profile of the Industry

Three domestic companies currently produce veterinary pharmaceuticals containing arsenic: Salsbury Laboratories in Charles City, Iowa; Whitmoyer Laboratories in Meyerstown, Pennsylvania; and Fleming Laboratories in Charlotte, North Carolina.[1,2]

B. Manufacturing Process and Waste Generation

The manufacture of arsenic-containing pharmaceuticals requires the reaction of an organic compound with inorganic arsenic to form the organic arsenical product, and generates arsenic-containing solid wastes*/

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*/The Agency is aware that these wastes also contain other substances of concern. They contain large quantities of the toxic compounds 1,1,2 trichloroethane, phenol and nitrophenol, as well as o-nitro-aniline.[1] 26 organic compounds have been identified in the process waste water in substantial concentrations including 22 priority pollutants.[1] Upon further study and evaluation these wastes may be amended in the future to include these toxic constituents of concern, if this is deemed to be advisable.

Arsenic-containing solid wastes generated during the production

process include tars from the distillation of aniline-based

compounds, and residue from the use of activated carbon in the

decolorization of pharmaceuticals.[4,5] Whitmoyer reported

that it generates these wastes in annual quantities of one

hundred 55-gallon drums and more than six hundred 55-gallon drums,

respectively.[4] Salsbury Labs also generates arsenic-containing

tars from production processes.[5]

Production of veterinary pharmaceuticals from arsenic

compounds generates wastewaters which contain organic and

inorganic arsenic. Treatment of these wastewaters produce

arsenic-bearing sludges. Figure 1 is a simplified representation

of the wastewater treatment system of one manufacturer's facility:

Salsbury Laboratories, which produces organic arsenicals marketed

as feed additives for chickens, turkey and swine.[1] Process

wastewaters at Salsbury are partially segregated into two

sewer systems. The first sewer system (A in Figure 1) carries

waste acid washwater (approximately 10,000 gallons per day) from

the nitration processes; this washwater is neutralized and clarified.

Although this drain system is intended to receive non-arsenic

contaminated waste water, adequate separation of arsenic wastes has

not been achieved. The acid washwater stream contains approximately

4 kg of arsenic per day.[29] */ Since waste water treatment is claimed

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*/ In the July 16 version of this background document, the Agency
stated erroneously that the sludges resulting from treatment of the
acid process wastewaters were a separate waste stream, and did not
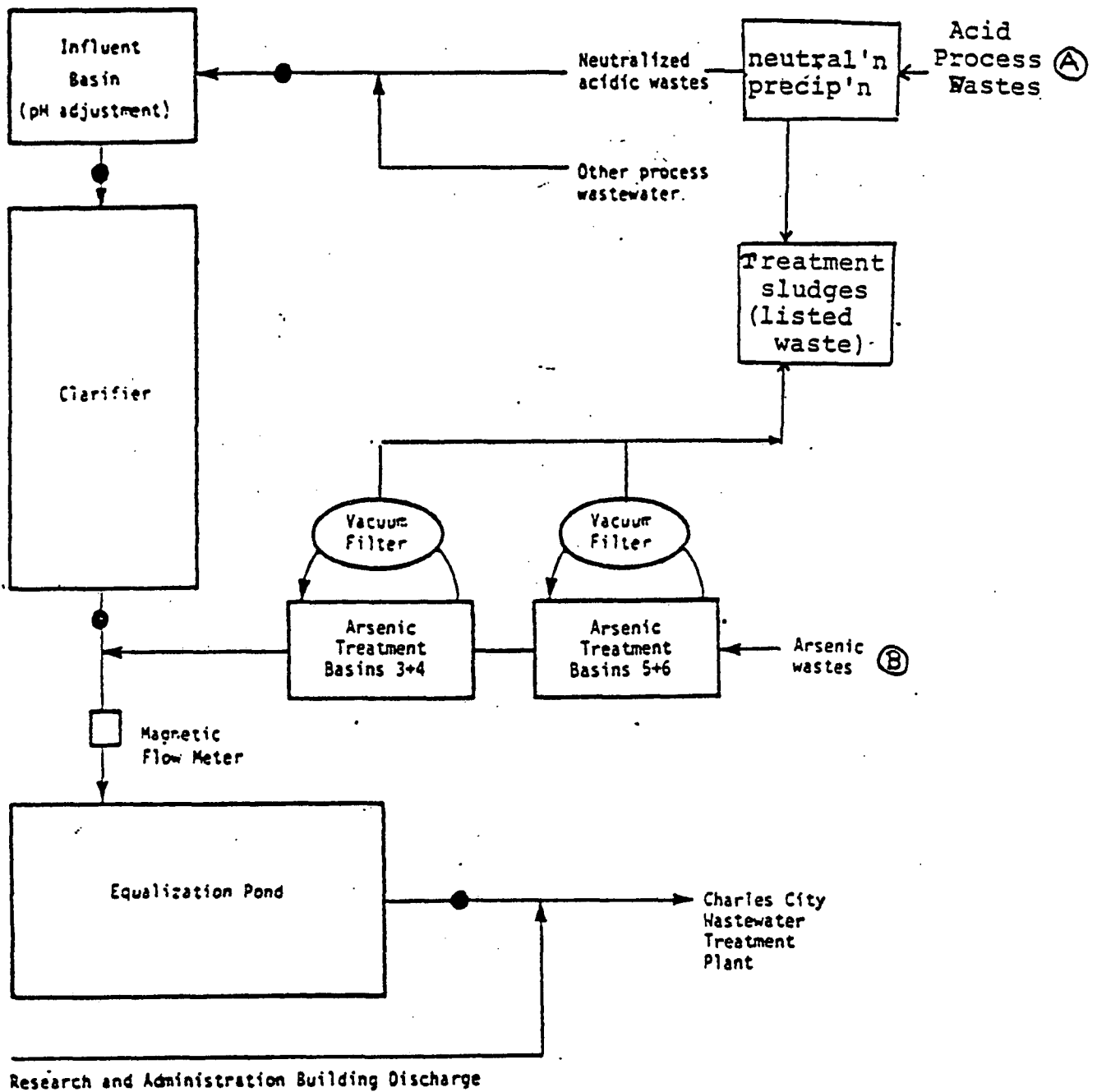contain significant concentrations of arsenic. This error is

FIGURE 1: Salsbury Wastewater Treatment Facility
(adapted from ref. 25).

to be 99% effective[27], the treatment sludges resulting from this

acid washwater will contain almost all of this arsenic loading.

The second sewer system (B in Figure 1), collects about

25,000 to 30,000 gallons per day of arsenic-containing process

wastewaters which originate from the manufacture of Salsbury's

arsenical compounds, such as 3-nitro-4-hydroxyphenylarsonic

acid and 4-nitrophenylarsonic acid. The treatment of this waste

stream is operated on a batch basis as a two stage process involving

neutralization with slaked lime, the addition of a flocculant,

treatment with $MnSO_4$, and two filtration steps. The resulting

sludges, containing about 1.6 kg of arsenic per day, are combined

with those formed from the treatment of waste stream A. The mixed

treatment sludges constitute the first listed waste of concern

in this document.

. ·The other manufacturers of arsenic-containing veterinary

pharmaceuticals also produce arsenic sludges. Whitmoyer

Laboratories generates approximately 1,260 drums per year of

sludge from the evaporation, volume reduction and centri-

fugation of waste salt solutions.[4] Fleming Laboratories

reported the production of arsenic sludges, but did not

describe the process by which they are generated (24).

The wastewater treatment sludges contain large amounts

of arsenic. One sample of fresh sludge from the Salsbury

Laboratories disposal site, the LaBounty landfill contained

28,000 ppm of arsenic (see below). In addition, the fact that

significant concentrations have been released from the waste

at the LaBounty site indicates that the contaminant is present
in these wastes in substantial amounts. Borings from soils
underlying the arsenic-containing solid waste deposits at the
landfill contain a mean arsenic concentration of 700 ppm, and
borings from surrounding soils exhibited a mean concentration
of 2200 ppm.[1] Samples obtained from a well located between
the site and the river showed an arsenic concentration of 590
ppm in groundwater.[1]

The Agency, at present, has no detailed flow process infor-
mation concerning the manner in which the other listed wastes
are generated. However the wastewater treatment sludges generated
at Whitmoyer's laboratories are reported to contain 1-7% arsenic.[4]

Arsenic concentrations in the other two listed wastes are also
substantial: distillation tars are reported to contain 10-15%
arsenic, and residues from activated carbon decolorization are
reported to contain 4-14% arsenic.[4]

C. Waste Management

From 1953 to December 1977, Salsbury Laboratories
disposed of its solid wastes in the LaBounty Dump, located
on the west bank of the Cedar River. (1) Prior to 1953,
solid wastes were disposed of across the river at the municipal
dump, but quantities are estimated to be relatively minor
compared to those at the LaBounty site. The wastewater treat-
ment sludge presently is stored in drums and shipped by rail

to Waste Management, Inc., a commercial disposal operation in Livingston, Alabama.[3]

Whitmoyer Laboratories' treatment sludges were stored in on-site lagoons until groundwater contamination was detected (this was also the disposal practice under prior ownership). Off-site disposal has been utilized since that time. Since 1975 Whitmoyer Laboratories has drummed all of its arsenic-containing wastes, and has shipped them to landfills specially designed to impede release of hazardous constituents to the environment.[4] The Agency has no information concerning the current disposal practices of Fleming laboratories.

III. DISCUSSION OF BASIS FOR LISTING

A. Hazards Posed by the Waste

These treatment sludges, distillation tars, and activated carbon residues contain high concentrations of arsenic, an extremely toxic substance. Arsenic and arsenic compounds have been identified by the Agency as a substance which has demonstrated substantial evidence of carcinogenicity. Arsenic is mutagenic to bacteria and teratogenic to laboratory animals. See Section B (Health and Ecological Effects) of this listing background document and Appendix A for further information.

It is quite obvious that improper management of these wastes can result in substantial hazard, since substantial harm has in fact occurred from their faulty management. The

most notorious example of this damage occured at the LaBounty
landfill.

Various wastes, including large amounts of arsenic sludges,
were disposed of at the LaBounty site. In January, 1978
approximately 7.5 cubic meters of arsenic sludge were disposed
per day. (1) At one time it was estimated that the site
contained more than six million pounds of arsenic[1]. The site
is located over a major aquifer. As noted above, substan-
tial arsenic contamination of soil and groundwater resulted
when the arsenic compounds leached from the waste site. As
a result of surface run-off and groundwater discharge, the
Cedar River picked up an average load of 53 kg of arsenic
per day in the vicinity of the LaBounty Site.(1) The Iowa
Department of Environmental Quality issued an order that
required Salsbury to cease disposal of wastes at the LaBounty
landfill. (77-DQ-01, Dec. 14, 1977). A report on this damage
incident concluded that arsenic in the wastewater treatment
sludge is "fairly easily solubilized even if it is precipitated
with calcium as the arsenate".[5] The presence of arsenic in
ground and surface waters in the vicinity of the LaBounty Site
likewise clearly indicates that, once released from the waste,
it is highly mobile and persistent.

The migratory potential of the arsenic contained in these
wastes is also substantiated by the groundwater contamination

resulting from the storage of the listed waste and similar
wastes by Whitmoyer Laboratories in holding lagoons (4).
When the groundwater contamination was discovered in the
late 1960's, the company began disposing of the sludges at a
number of different sites; presently, these wastes are transported
by truck to hazardous waste landfills or a specially designed
vault disposal operation (4). Again, this demonstrates the
potential hazard posed by the migration of waste constituents
from a disposal site and the generator's subsequent recognition
of this hazard.

An additional demonstration of the necessity for proper
management occurred when Salsbury Laboratories, as a result
of a cease order, began disposing of solid wastes in a temporary
-on-site holding basin.(1) This disposal method was quickly
terminated because leachate was detected in the underdrain
system within 24-hours after disposal.(1) The 1977 court
action, coupled with the present management of these wastes
in chemical waste landfills, substantiates the concern by
both the state and the generator for the proper management
and disposal of this hazardous waste.

These damage incidents show that arsenic may easily
migrate from these wastes and persist in the environment
upon release. Indeed, because arsenic is an element, and
does not degrade with the passage of time, it will persist
in some form virtually indefinitely.

There are a number of additional reasons to impose

hazardous waste status on this waste. Unregulated transportation of this waste to off-site disposal facilities increases the likelihood of harmful exposure to human beings and the environment. Without proper means to track the waste from the point of generation to its ultimate destination, the waste might not reach its designated destination at all, thus making it available to do harm elsewhere.

Furthermore, as previously indicated, arsenic sludges from the production of veterinary pharmaceuticals are generated in very substantial quantitites (in January 1978, approximately 7.5 m^3/day were generated at the Salsbury plant alone (1)). Large amounts of arsenic are thus available for potential environmental release, posing the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of this pollutant are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or exhausted due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to this harmful constituent.

B. Health and Ecological Effects

Health Effects

Arsenic is acutely toxic to animals and humans (6). Death in humans has occurred following ingestion of very small amounts (5mg/kg) (7). Several epidemiological studies have associated cancers with occupational exposure to arsenic (8-10), including

those of the lung, lymphatics and blood (11,12). Skin cancer has been associated with the presence of arsenic in drinking water (13), while liver cancer has developed in several cases following ingestion of arsenic (14). The human carcinogenic potential of arsenic is supported by animal studies. arsenic and its compounds have been identified by the Agency as demonstrating substantial evidence of carcinogenicity.

Occupational exposure to arsenic has also resulted in chromosomal damage (15), and several different arsenic compounds have demonstrated positive mutagenic effects in laboratory studies (16-18). The teratogenicity of arsenic and arsenic compounds is well established (19-21); observed defects include those of the skull, brain, kidneys, gonads, eyes, ribs and genitourinary system.

The effects of chronic arsenic exposure include skin diseases progressing to gangrene, liver damage, neurological disturbances (22), disturbances in red blood cell production and cardiovascular disease (8).

Additional information and specific reference on adverse effects of arsenic can be found in Appendix A.

Ecological Effects

The data base for the toxicity of arsenic to aquatic organisms is more complete for freshwater organisms; concentrations as low as 128 ug/l are acutely toxic to freshwater fish. Based on one chronic life cycle test using Daphnia magna, a chronic value for arsenic was estimated at 853 ug/l (21).

Regulatory Recognition of Hazard

OSHA has set a standard 8-hr air TWA in air of 0.5 mg/m^3 for occupational arsenic exposure. 0.05 mg/m^3 has been proposed for arsenic trioxide (23). DOT requires a "poison" warning label.

EPA's Office of Toxic Substances under FIFRA has issued a pre-RPAR. Arsenic is designated as a priority pollutant under Section 307(a) of the CWA. The Office of Drinking Water has regulated arsenic under the Safe Drinking Water Act and the Office of Air Quality Planning and Standards has begun a preregulatory assessment of arsenic based on its suspected carcinogenic effects. The Office of Water Planning and Standards under Section 304 (a) of the Clean Water Act has begun development of a regulation based on health effects other than oncogenicity and environmental effects. Finally, the Office of Toxic Substances has completed a Phase I assessment of arsenic under the Toxic Substances Control Act.

Industrial Recognition of Hazard

Arsenic administered by either the intra-muscular or subcutaneous routes is rated as highly toxic in Sax, Dangerous Properties of Industrial Materials (22). Arsenic is also rated as highly toxic through ingestion, inhalation, and percutaneous routes in Patty, Industrial Hygiene and Toxicology.

A ten-fold reduction (to 0.005 mg/m^3) of the present OSHA standard for arsenic trioxide has been proposed (23).

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HAZARDOUS WASTE LISTING BACKGROUND DOCUMENT

K085:   Distillation or Fractionating Column Bottoms from the
        Production of Chlorobenzenes (T).

K105:   Separated Aqueous Stream from the Reactor Product Washing
        Step in the Production of Chlorobenzenes (T).*/

        Distillation or fractionation column bottoms from the
                                    **/
production of chlorobenzenes, and the separated aqueous

waste stream from the reactor product washing step in the

batch production of chlorobenzenes, are composed of a vary-

ing mixture of chlorobenzenes (dichlorobenzene through hexa-

chlorobenzene) and benzyl chloride, and may also contain

benzene and monochlorobenzene. The Administrator has deter-

mined that these waste streams are solid wastes and as solid

wastes may pose a substantial present or potential hazard to

human health or the environment when improperly treated,

stored, disposed of, transported or otherwise managed. There-

fore, these wastes should be subject to appropriate management

requirements under Subtitle C of RCRA. This conclusion is

based on the following considerations:

        1. Distillation or fractionating column bottoms from
            chlorobenzene production are likely to contain sig-
            nificant concentrations of dichlorobenzenes, tri-
            chlorobenzenes, tetrachlorobenzene, pentachloroben-

*/In response to comment, we have revised this listing descrip-
  tion to indicate that a wastewater stream may be generated
  from both batch and continuous processes. (See response to
  comment #4.)

**/Throughout this background document, the terms 'chloroben-
   zene(s)' and 'chlorinated benzene(s)' are used synonomously
   to denote the group of substituted benzene compounds in
   which one to six hydrogen atoms of benzene are replaced by
   chlorine atoms, with no ring substituents present other
   than chlorine or hydrogen.

zene and hexachlorobenzene. Benzyl chloride is
expected to be present in significant concen-
trations. Benzene and monochlorobenzene may also
be present in lesser concentrations depending on the
efficiency of distillation . The dichlorobenzenes,
trichlorobenzenes and tetrachlorobenzenes are all
toxic. Pentachlorobenzene has been reported to
induce cancers in some animal species. Hexachloro-
benzene and benzene have been identified by EPA's
Carcinogen Assessment Group (CAG) as having substantial
evidence of carcinogenicity. Benzyl chloride is
reportedly carcinogenic. Monochlorobenzene is
toxic. All of the chlorobenzenes bioaccumulate.*/

2. The separated aqueous waste stream from the batch
production of chlorobenzenes is believed to contain
significant concentrations of benzene, several chloro
benzenes, and 2,4,6-trichlorophenol, all of which
present chronic toxicity hazards. Benzene and 2,4,6-
trichlorophenol have been identified by CAG as having
substantial evidence of carcinogenicity.

3. These waste constituents are capable of migration,
mobility and environmental persistence if managed
improperly, and have caused substantial hazard in
actual damage incidents. Disposal of these distil-
lation bottoms and the aqueous waste in uncontrolled
landfills, therefore, could allow migration of con-
taminants to ground and surface waters and release
of volatile toxicants to the air, while improper
incineration may result in the generation of ex-
tremely hazardous compounds such as phosgene.

I. Industry Characterization and Manufacturing Process

A. Profile of the Industry

Twelve chlorinated benzene compounds can be formed

during the chlorination of benzene including monochlorobenzene,

three isomers of dichlorobenzene, three of trichlorobenzene,

_____

*/Certain of these wastes (particularly where the higher chlorinated
benzenes are being produced) may contain polychlorinated biphenyls.
(See Petition for Exemption under §6(e)(3)(b) of the Toxic Substances
Control Act of Olin Corporation, dated June 28, 1979, noting concen-
trations of up to 8000 ppm PCB's in distillation residues from the
production of pentachlorobenzene). The Agency is not presently listing
PCB's as a waste constituent of concern pending integration of the
RCRA Subtitle C and TSCA PCB regulations. The regulated community
and permit writers should be aware, however, of the possibility
of hazardous levels of PCB's in these wastes.

pentachlorobenzene and hexachlorobenzene; their structures
and physical properties are illustrated in Figure 1 and
Table 1. In 1979 chlorobenzene production totalled about
204,000 kkg, or about half of the available capacity (56).
Most of the production is of mono-and dichlorobenzenes.
Monochlorobenzene is the dominant commercial product; in
1978, production was approximately 134,000 kkg.(1) Production
of ortho- and para-dichlorobenzene was estimated at 10,000
kkg each for that same year.(1) Production of 1,2,4-trichloro-
benzene was 13,000 metric tons in 1973. It is estimated
that approximately the same amount was produced in 1977.(1)
Annual production of the commercially important tri- and
tetrachlorobenzenes and of pentachlorobenzenes ranges from
1,000 - 50,000 kkg. Major producers of chlorobenzenes in
the United States include: Allied Chemical Corporation
(Syracuse, New York); Dow Chemical Company (Midland, Michigan);
Monsanto Company (Sauget, Illinois); Montrose Chemical
Corporation of California (Henderson, Nevada); PPG Industries,
Inc. (Natrium, West Virginia); Specialty Organics, Inc.
(Irwindale, California); and Standard Chlorine Chemical
Company, Inc. (Delaware City, Delaware).(2)   Certain companies,
including the Olin Corporation, produce chlorobenzenes as
intermediates rather than as end products. Distillation
residues and aqueous waste streams from the chlorobenzene
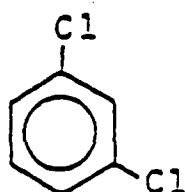manufacturing phase of such processes are included in the
present listing.

Figure 1.   Chemical Structures of the Chlorinated Benzenes
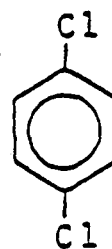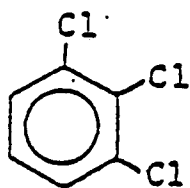

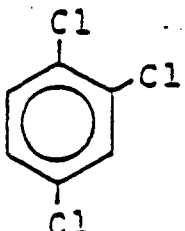Monochlorobenzene
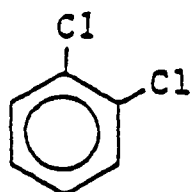
1,2-Dichlorobenzene
o-Dichlorobenzene

1,3-Dichlorobenzene
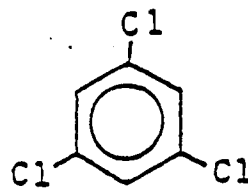m-Dichlorobenzene

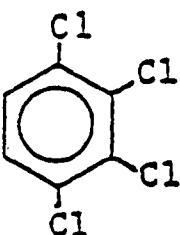1,4-Dichlorobenzene
p-Dichlorobenzene
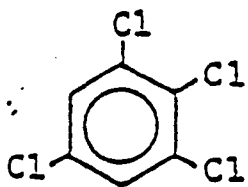

1,2,3-Trichlorobenzene
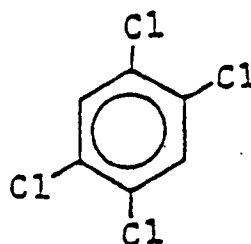

1,2,4-Trichlorobenzene

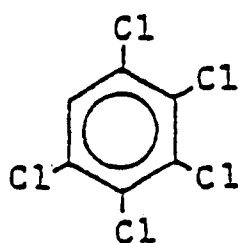

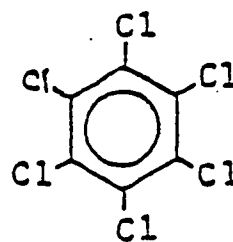1,3,5-Trichlorobenzene

1,2,3,4-Tetrachlorobenzene

1,2,3,5-Tetrachlorobenzene

1,2,4,5-Tetrachlorobenzene

Pentachlorobenzene

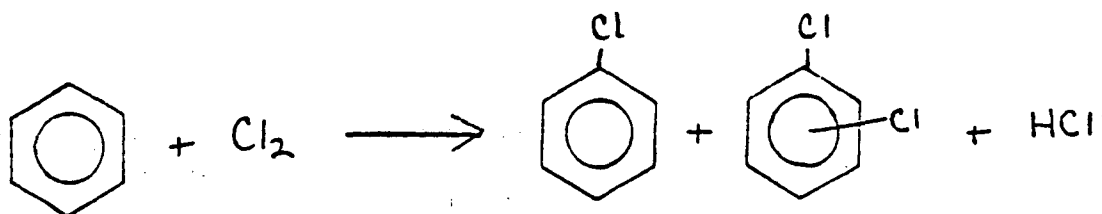Hexachlorobenzene

TABLE 1. PHYSICAL PROPERTIES OF CHLORINATED BENZENES[a]

Compound Name	CAS No.	Empirical formula	Mol. Wt.	M.p., °C	B.p.[b] °C	Vapor Press.	Density[c]	Water Solubility (mg/L)[d]	log P_oct
Monochlorobenzene	100-90-7	C_6H_5Cl	112.56	-45.6°	132°	10mm/22°	1.1050	500[e]	2.84[f]
1,2-Dichlorobenzene	95-50-1	$C_6H_4Cl_2$	147.01	-17.0°	180.5°	1mm/20°	1.3048	140[e]	3.38[f]
1,3-Dichlorobenzene	541-73-1	$C_6H_4Cl_2$	147.01	-24.7°	173°	1mm/12°	1.2884	123[g]	3.38[f]
1,4-Dichlorobenzene	106-46-7	$C_6H_4Cl_2$	147.01	53.1°	174°	0.4mm/25°	1.2475	79[e]	3.39[f]
1,2,3-Trichlorobenzene	87-61-6	$C_6H_3Cl_3$	181.45	54°	219°	1mm/40°			4.1[g,h]
1,2,4-Trichlorobenzene	120-82-1	$C_6H_3Cl_3$	181.45	17°	213.5°	1mm/38°	1.4542	30[i]	
1,3,5-Trichlorobenzene	108-70-3	$C_6H_3Cl_3$	181.45	64°	208°[j]	10mm/78°			
1,2,3,4-Tetrachlorobenzene	634-66-2	$C_6H_2Cl_4$	215.90	47.5°	254?	1mm/68°		0.36[e]	
1,2,3,5-Tetrachlorobenzene	634-90-2	$C_6H_2Cl_4$	215.90	54.5°[i]	246°	1mm/58°			
1,2,4,5-Tetrachlorobenzene	95-94-3	$C_6H_2Cl_4$	215.90	140.5°	246°	40mm/146°	1.858(22?)		
Pentachlorobenzene	608-93-5	C_6HCl_5	250.34	86°	277°	1mm/99°	1.8342(16°)		
Hexachlorobenzene[k]	118-74-1	C_6Cl_6	284.79	230°	322°	1mm/114°	1.5691(24°)	0.020[l]	5.8[g]

(a) From Ref. 56; Data are from standard reference sources, except partition coefficient and solubility data, for which references are cited. (b) At i atm. (c) At 20C except as noted. (d) At 25C. (e) Ref. 11. (f) Ref. 20. (g) Ref. 22. (h) isomer unspecified. (i) Ref. 28. (j) At 763 mm. (k) Ref. 51.

B. Manufacturing Process

Chlorobenzene, dichlorobenzenes, and higher chlorinated benzenes are produced in batch and in continuous processes by chlorination of benzene in the presence of a Friedel Crafts catalyst, such as ferric chloride, as shown in the following reaction*/for monochlorobenzene:

$$\text{C}_6\text{H}_6 + \text{Cl}_2 \longrightarrow \text{C}_6\text{H}_5\text{Cl} + \text{C}_6\text{H}_4\text{Cl}_2 + \text{HCl}$$

Because higher chlorinated benzenes always result from the direct chlorination of benzene, chlorobenzene production is a multiple product operation, i.e. a range of chlorinated benzenes may be produced. Product ratios are influenced by temperature, mole ratios of the feedstocks, residence time, and catalyst. The crude reaction product of a continuous process may be recycled to the process to achieve the desired final product mixture. Depending on the final product mixture, chlorobenzenes are purified by fractional distillation and/or crystallization. Continuous chlorination processes, in contrast to batch processes, minimize the amount of higher chlorinated products, thereby maximizing monochlorobenzene yields.

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*/ 1,3-Dichlorobenzene, 1,3,5-trichlorobenzene and 1,2,3,5-tetrachlorobenzene are not produced by the method discussed below.

1. Production of Monochlorobenzene

    a) Continuous Process (modified from references 1,6, and 7)

    As shown in Figure 2, in a typical continuous process
for the production of chlorobenzenes, anhydrous benzene and
chlorine are introduced into a reactor operating at a bottom
temperature of 90-125°C and a top temperature of about 80°C.
Benzene is introduced near the top of the column, and an
equimolar amount of chlorine is introduced near the midpoint
of the reactor. A variety of catalysts may be used, usually
iron or ferric chloride impregnated on a suitable carrier.

    The overhead reactor effluent consisting of hydrogen
chloride and benzene passes through a condenser which condenses
the benzene for recycle. Hydrogen chloride is recovered by
passing the uncondensed gas through a scrubber tower contain-
ing a chlorination catalyst, thereby removing unreacted
chlorine. The mixture is then passed through one or more
towers in which chlorobenzenes are used to remove organic
contaminants. The resultant hydrogen chloride is then recov-
ered as either an anhydrous product or as a 30-40% aqueous
solution. (If the hydrogen chloride must meet a low organic
specification, a carbon column may be used prior to or after
the water absorption tower.)

    The bottom effluent from the reactor comprises an
equilibrium mixture of benzene and mixed chlorobenzenes. To
maximize monochlorobenzene production, a high recycle rate of
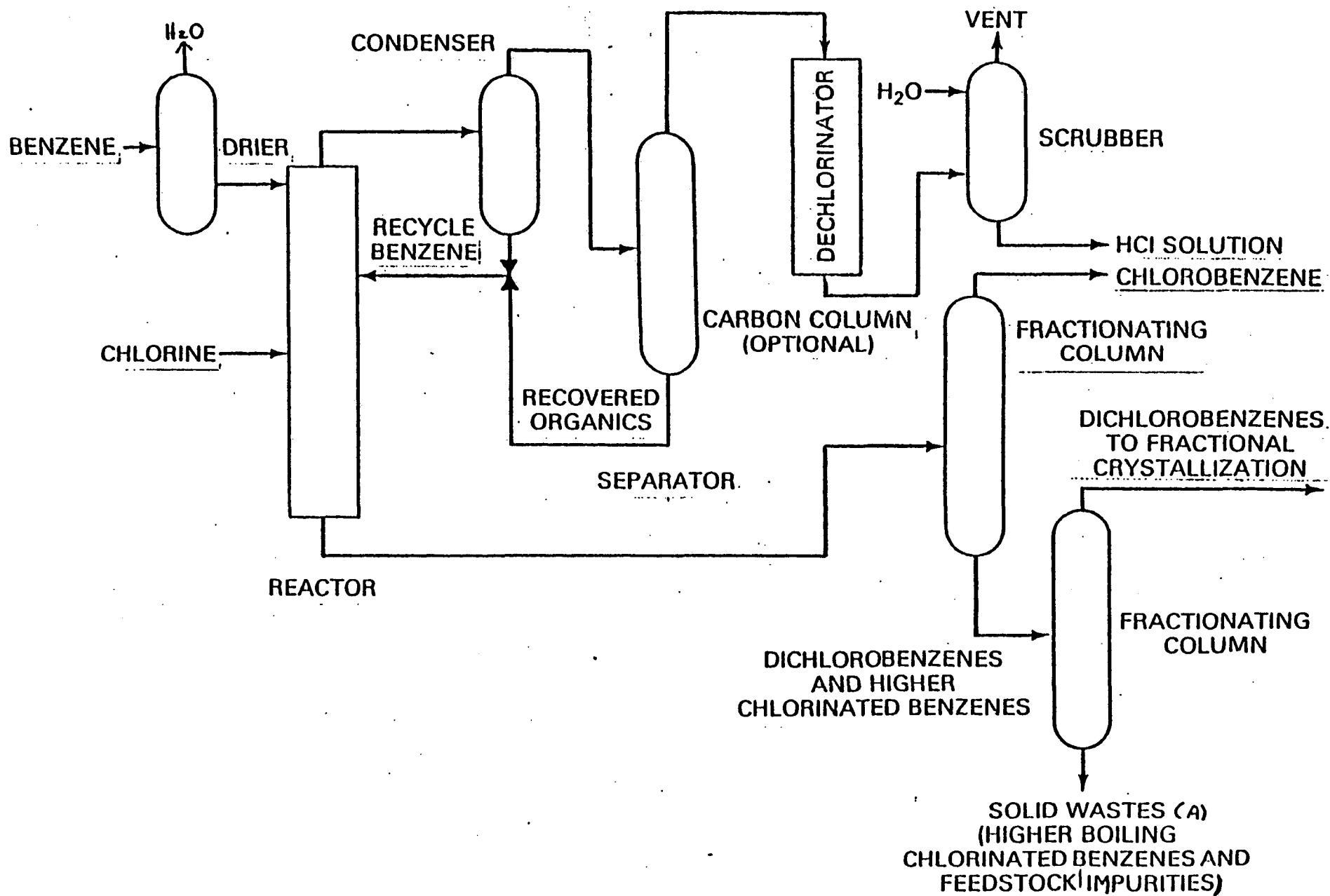benzene is maintained (20:1). Chlorobenzene is withdrawn at

FIGURE 2
CONTINUOUS PRODUCTION OF CHLOROBENZENE (MODIFIED FROM 7)

a rate equal to that at which benzene is fed and chlorinated, and flows to a fractionating column which operates at a bottom temperature of aproximately 190°C and top temperature of 140°C. The higher boiling bottom products (mostly dichlorobenzenes) are continuously bled at approximately 2% of the product feed to a fractionating column for recovery of the di- and trichlorobenzenes. The wastes of concern (waste A in Figure 2) are the bottoms from the two fractionating columns.*/

b) Batch Process

Chlorobenzenes may also be manufactured by a batch process as shown in Figure 3. Dry benzene is charged into an agitated glass-lined or iron (steel) reactor. Either iron turnings or anhydrous ferric chloride are used as a catalyst and remain in the chlorinator after each product batch is withdrawn. The desired product mix is achieved by adjustment of chlorine concentration and reactor temperature. If monochlorobenzene is the desired product, about 60 percent of the stoichiometeric requirement of chlorine is used, and the reaction temperature is maintained in the range of 20° to 30°C for 10 to 16 hours. If poly-substituted chlorobenzenes (generally dichlorobenzenes) are desired in addition to monochlorobenzene, the reaction is run at a temperature of 55° to 60°C for approximately six hours.

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*/ In some processes, the further fractionating steps for recovery of higher chlorobenzenes is not employed, in which case the waste of concern is the column bottoms from the first fractionating column.
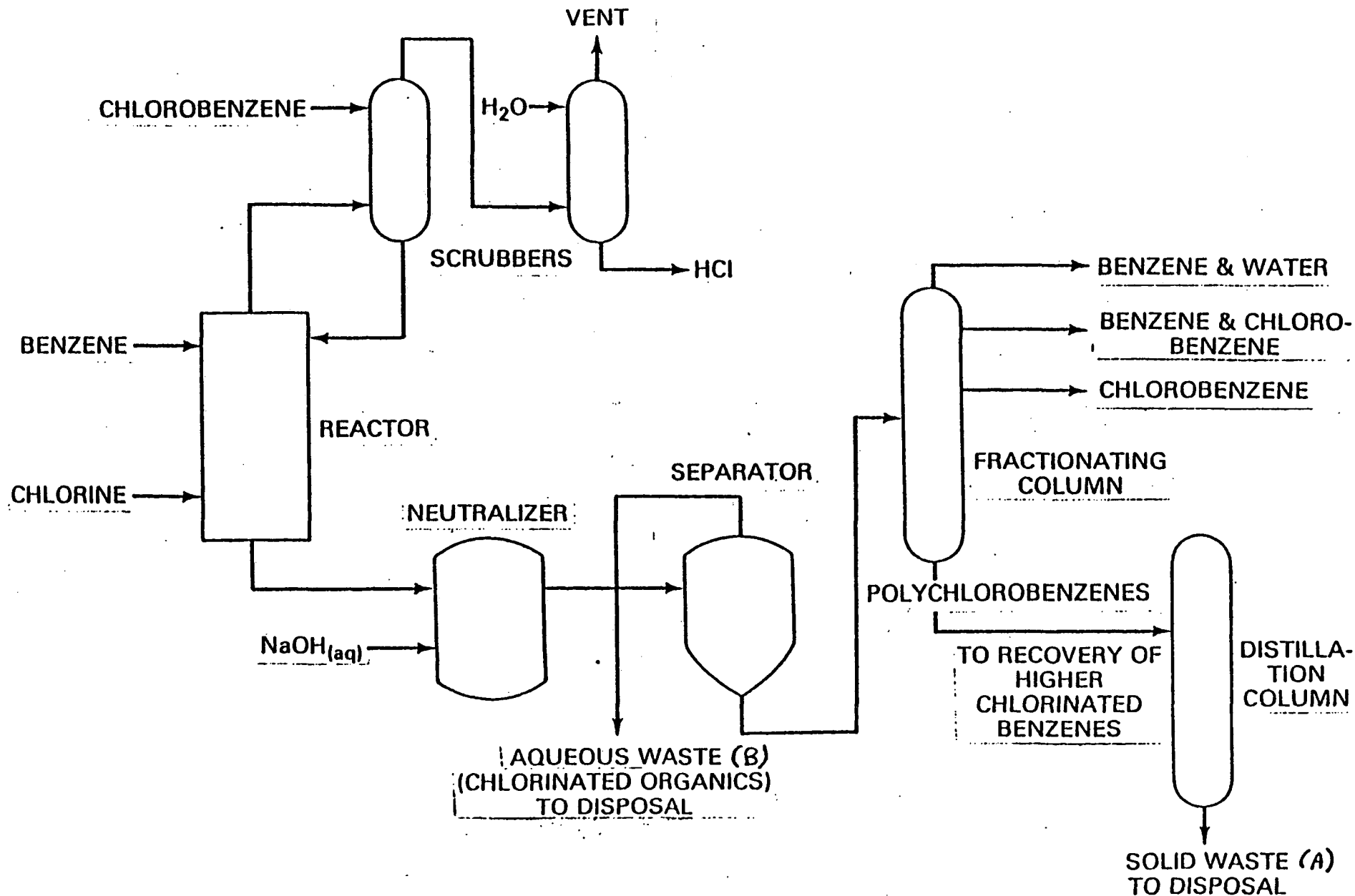
FIGURE 3
BATCH PRODUCTION OF CHLOROBENZENES (MODIFIED FROM 6)

Hydrogen chloride is recovered in a manner similar to that of continuous processes by scrubbing with chlorobenzene to remove organic contaminants and absorbing the product gas in water to give hydrochloric acid. The chlorobenzene product is washed in an agitated reactor with an aqueous solution of sodium hydroxide (10 percent by weight). The separated aqueous layer (waste B in Figure 3) is a separate waste, and is the second waste included in this listing.*/

After the neutralized organic layer is separated, it is sent to a fractionation column for product separation. As is the case in the continuous chlorination process, waste A (distillation or fractionation column bottoms are also generated). Table 2 illustrates the estimated product distribution for a fully chlorinated batch for which 100 percent of the theoretical amount of the chlorine requirement for monochlorobenzene was consumed.[6]

TABLE 2

PRODUCT DISTRIBUTION OF A CHLOROBENZENE BATCH REACTION (6)

Distillate Fraction	Component	% by weight
1	Benzene and water	3
2	Benzene and chlorobenzene	10
3	Chlorobenzene	75
4	Chlorobenzene and dichlorobenzene	10
5	Tar (trichlorobenzene and higher)	2

*/This aqueous stream is not expected to be present in most continuous processes, since during the stripping step in the continuous process (see Fig. 2) the temperature at the bottom of the condenser column is such that residual hydrogen chloride and benzene are removed, making a product washing step unnecessary. However, comments indicated that an aqueous waste stream is generated from at least one continuous manufacturing process. We therefore have revised the listing description of this waste to indicate that it is hazardous irrespective of the type of manufacturing process.

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87 90

Most batch processes include further distillation steps to
to separate higher chlorinated benzenes, particularly o- and
p-dichlorobenzene and trichlorobenzene.*/ The chlorobenzene
and dichlorobenzene fraction (No. 4) is usually further
distilled to recover p-dichlorobenzene and o-dichlorobenzene.
Trichlorobenzene may also be recovered. The tarry residue
(Table 2, Fraction 5, waste A in Figures 2 and 3, the solid
waste of concern) consists chiefly of trichloro- and higher
chlorinated benzenes.

2.   Production of Polychlorobenzenes

As noted previously, aromatic chlorination is a multiple
product process; most polychlorobenzenes can be produced via
processes similar to those described above. Reaction conditions
are, however, likely to be somewhat different. Higher reaction
temperatures, longer reaction times and higher chlorine to
benzene ratios are likely modifications. A process configu-
ration for production of dichlorobenzenes is shown in Figure 4.

Dichlorobenzenes[56]

o-Dichlorobenzene and p-dichlorobenzene are produced by
chlorinating benzene or monochlorobenzene at 150°C-190°C over
a ferric chloride (FeCl₃) catalyst. An orienting catalyst
such as benzensulfonic acid or p-dichlorobenzene may also be
employed. The isomers can be separated by fractional distillation,
or by crystallizing the p-dichlorobenzene. Another method of
obtaining the para isomer is by chlorination of crude dichloro-

*/Table 2 is a product mix prior to this second distillation

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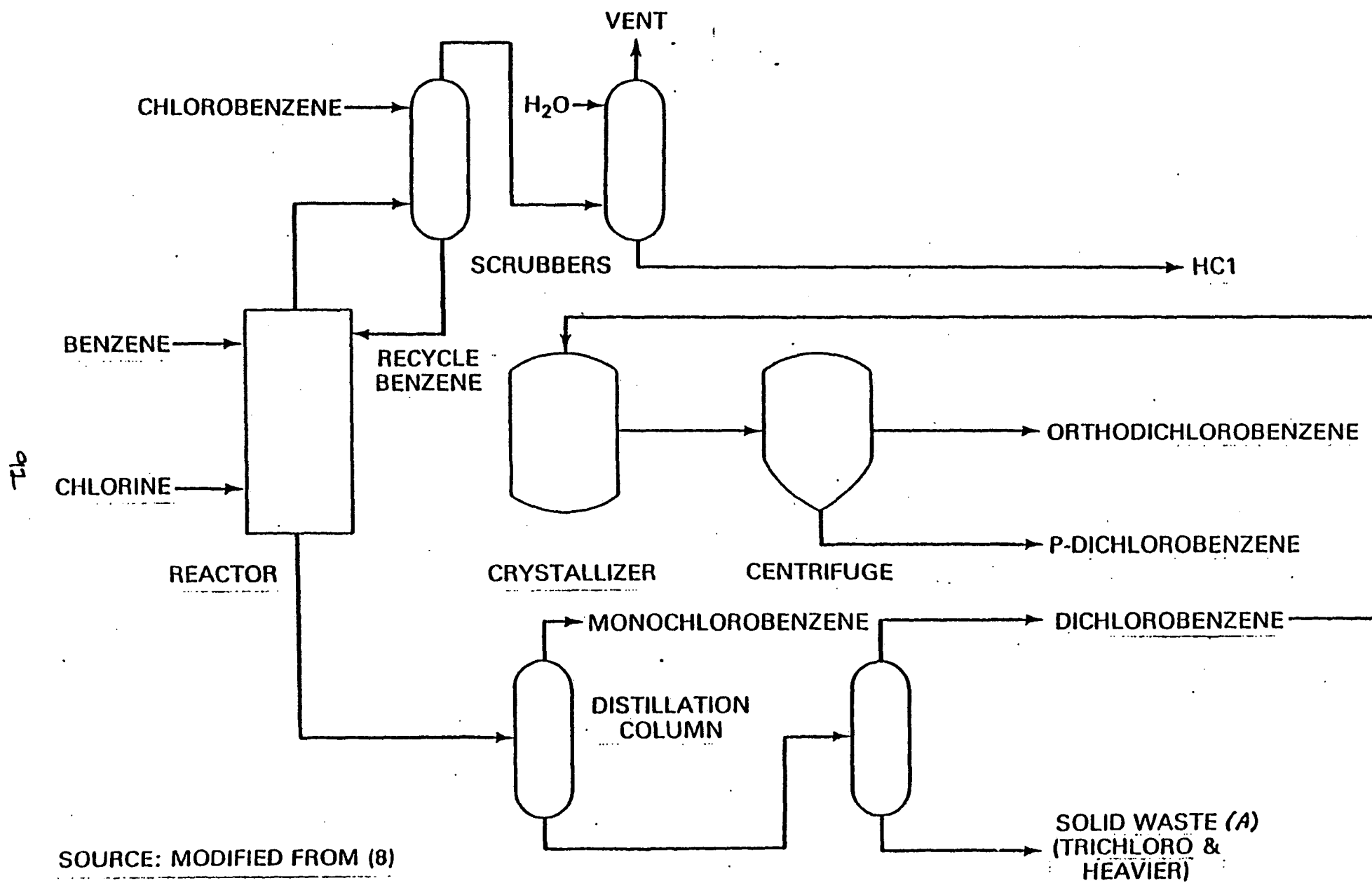
FIGURE 4
PRODUCTION OF HIGHER CHLOROBENZENES

benzene over FeCl₃, whereby the more reactive ortho isomer is converted to 1,2,4-trichlorobenzene. p-Dichlorobenzene can then be separated by distillation. The purified grade of o-dichlorobenzene is obtained by efficient redistillation of the technical product. m-Dichlorobenzene can be prepared by isomerization of o-dichlorobenzene and p-dichlorobenzene with heat under pressure in the presence of a catalyst.

Trichlorobenzenes.[56]

1,2,4-Trichlorobenzene is produced along with 1,2,3-trichlorobenzene by chlorination of o-dichlorobenzene at 25 to 30 °C in the presence of ferric chloride, then separated from the 1,2,3-trichlorobenzene by distillation. 1,3,5-Trichlorobenzene can be produced readily only by special methods such as by the diazotization of 2,4,6-trichloroaniline followed by treatment with alcohol. Additional methods of synthesis for trichlorobenzenes are reviewed in the report by Ware and West.[57]

Tetrachlorobenzenes.[56,57]

1,2,3,4-Tetrachlorobenzene can be produced by chlorinating 1,2,3-trichlorobenzene in the presence of a catalyst. 1,2,4,5-Tetrachlorobenzene is manufactured by chlorination of 1,2,4-trichlorobenzene over aluminum amalgam. To produce 1,2,3,5-tetrachlorobenzene, 1,3,5-trichlorobenzene can be chlorinated over aluminum amalgam. In practice, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene are produced only as by-products in the manufacture of 1,2,4,5-tetrachlorobenzene.

Pentachlorobenzene and Hexachlorobenzene (8,9)

Pentachlorobenzenes is formed by the chlorination of benzene in the presence of ferric or aluminum chloride at temperatures of 150 to 200°C, or by the chlorination of any of the lower chlorobenzenes. It may also be formed in small amounts when trichloroethylene is heated to 700°C[56].

Hexachlorobenzene is reported not to be produced commercially via catalytic (ferric chloride) chlorination of benzene. When generated as a by-product of the processes described in this document, it is found in the fractionating column bottoms.

C. Commercial Uses of Chlorobenzenes[56]

Most (50-70%) monochlorobenzene is used as a chemical intermediate in the synthesis of chloronitrobenzenes, herbicides, diphenyloxide, and silicones. The remainder is used as a solvent for herbicides, for synthetic processes and for degreasing operations.

Sixty-five percent of the o-dichlorobenzene produced is used in organic synthesis, primarily as a pesticide intermediate. Fifteen percent is used as a solvent in the production of toluene diisocyanate. Miscellaneous solvent uses, such as for oxides of nonferrous metals, for soft carbon deposits, for tars and wool oils in the textile industry, and for degreasing leather and automobile and aircraft engine parts, account for most of the rest of the annual production of o-dichlorobenzene. It is also a solvent in formulated toilet

bowl cleaners and drain cleaners. Other uses in metal polishes, in industrial odor control, as a heat transfer fluid, and in rustproofing mixtures account for 4 percent of annual o-dichlorobenzene production. o-Dichlorobenzene is registered as a fumigant and insecticide against termites, beetles, bacteria, slime, and fungi.

Eighty percent of the annual production of p-dichlorobenzene goes to home and industrial use: as a moth control agent (30 percent) and as a space odorant (50 percent), especially in toilets and rest rooms.

Miscellaneous uses as a dye intermediate, insecticide, extreme pressure lubricant, forming agent for grinding wheels, disintegrating paste for molding concrete and stoneware, and as an intermediate in the manufacture of 2,5-dichloroaniline and polyphenylenesulfide resins account for the remaining 10-20% of the consumption of p-dichlorobenzene. No uses were identified for m-dichlorobenzene apart from its conversion to higher chlorobenzenes.

The most widely used isomer of tetrachlorobenzene is 1,2,4,5-tetrachlorobenzene, which is used primarily as an intermediate in chemical synthesis. Of the approximately 8,000 kkg consumed in 1973, 2,700 kkg were used to produce the fungicide and bactericide 2,4,5-trichlorophenol, 4,500 kkg were used in the production of the herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), and the remainder went to miscellaneous uses. 1,2,4,5-Tetrachlorobenzene may

also be used as an impregnant for moisture resistance, as

electrical insulation and as temporary packing protection.

According to a recent review, 1,2,4,5-tetrachlorobenzene is

now used exclusively to make 2,4,5-T and its esters, however,

it is a component of the transformer fluid, Iralec©. Thus,

the use pattern for this material appears to be in flux.

EPA has no information on uses of 1,2,3,4- and 1,2,3,5-tetra-

chlorobenzenes except that the former, as a mixture with the

1,2,4,5-isomer, is an intermediate in the synthesis of the

fungicide pentachloronitrobenzene.

II. Waste Composition and Management

   1. Fractionation Bottoms

The distillation or fractionation bottoms from the

production of monochlorobenzene consist primarily of the

higher polychlorinated benzenes (trichlorobenzenes and higher),

benzyl chloride and chlorotoluenes[*] resulting from the chloro-

nation of toluene impurities in benzene feedstock, and lesser

concentrations of feedstock benzene, product chlorobenzene,

and dichlorobenzenes (depending on the efficiency of the

fractionating step). The relative concentrations of the

various chlorobenzenes in these wastes vary according to

reaction conditions and the efficiency of fractionation. In

general, when monochlorobenzene is the favored by-product,

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[*]Both o- and p-chlorotoluene are expected to be present.
These constituents are not considered to be of regulatory
concern because of their low chronic toxicity. Further
information as to the validity of this conclusion is solicited,
however.

dichlorobenzene will probably be the most prevalent of the chlorinated benzenes in the distillation residue (and in the waste if there is no subsequent distillation step to recover dichlorobenzenes as product) since benzene is being chlorinated for less time, so that smaller concentrations of tetra- to hexachlorobenzene are formed. If dichlorobenzenes are recovered as product, trichlorobenzenes represent the largest fraction in the waste. When the reaction is pushed in the direction of polychlorinated benzenes, there will be more trichloro through hexachlorobenzene in the waste stream.

Waste composition, and especially the concentrations of the various chlorinated benzenes, also will vary quantitatively, although not qualitatively, depending on whether a continuous or batch production process is used. Batch processes would tend to have somewhat higher concentrations of higher chlorinated benzenes, since benzene chlorination occurs for a longer period.

Table 2 gives an estimate of wastes resulting from a batch reaction favoring monochlorobenzene production. Distillation tars (Fraction 5), consisting principally of trichlorobenzenes and isomers of higher degree of chlorination are estimated to comprise roughly 2% by weight of the total reaction products.

Table 3 gives a second estimate of waste composition from a batch process favoring monochlorobenzene. Small amounts of unreacted benzene, hydrogen chloride and chloro-

benzenes are vented to the atmosphere; small concentrations
of these constituents are expected to remain in the distilla-
tion bottoms. The distillation residues (Table 3, Fraction 6),
the first-listed waste of concern in this document, comprise
about 80% of the wastes generated in this process.

Table 3[2]

ESTIMATED LOSS OF MATERIALS DURING CHLOROBENZENE MANUFACTURE
(BATCH PROCESS)

FRACTION	COMPOUND	SOURCE	QUANTITY (kg/kkg monochlorobenzene)
1	Hydrogen chloride	Hot scrubber vent	1.4
2	Monochlorobenzene	o-Dichlorobenzene column	.88
3	Dichlorobenzenes (isomers not specified)	do	3.7
4	Monochlorobenzene	Fractionating towers	4.0
5	Dichlorobenzenes	"	0.1
6	Polychlorinated benzenes	Distillation residues*	44.0

*waste A, Figures 2 and 3

A third reference[3] (shown in Table 4) taken from the
patent literature, and involving a continuous process, shows
monochlorobenzene present in fairly substantial concentrations
in the solid waste; the estimate for the production of heavier
chlorinated benzenes (31 kg/kkg of monochlorobenzene produced)
does not differ greatly from the estimate given in Table 2.

TABLE 4

ESTIMATED EMISSIONS FROM CHLOROBENZENE MANUFACTURE:
Chlorination of Benzene, Continuous Process[3]

Emission (kg/kkg)

Species	Solid
Benzene	trace
Monochlorobenzene	2.6
Polychlorinated benzenes	31
	33.6

The solid wastes (from both continuous and batch processes) are also expected to contain significant concentrations of benzyl chloride and o- and p-chlorotoluene resulting from chlorination of toluene impurities in benzene feedstock.*/ (As noted above, the chlorinated toluenes are not waste constituents of concern). The specific reaction pathways for these constituents are given below:

Toluene → (Catalyst, Cl$_2$) → Benzyl Chloride + HCl
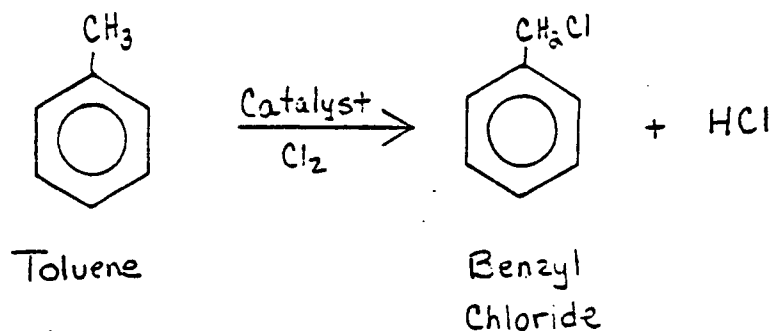
*/ Toluene is believed to be the most significant feedstock impurity. Benzene may typically contain up to 1% toluene[9]

The above side reactions are believed to be those most likely to occur under the usual conditions of benzene chlorination. Virtually all of these substances are expected to be present in the distillation bottoms since they are high boiling chemicals that the distillation process is designed to eliminate.

2. Separated Aqueous Stream from the Reactor Product Washing Step (batch process)

The aqueous stream from the reactor product washing step in the production of chlorinated benzenes will contain benzene, and all of the chlorinated benzenes in solution (along with water and caustic soda used in the washing operation). The concentrations of these constituents in the waste will depend on their concentration in the reaction product stream and their solubilities in the alkaline wash solution. While the Agency does not presently have precise information on these compounds' solubilities in basic solutions, they are not believed to differ significantly from their solubilities in water (if anything, solubilities would be slightly higher in basic solutions). Thus, the most soluble component, benzene (water solubility up to 1,780 ppm), would probably be the principal waste constituent, and monochlorobenzene and o- and p-dichlorobenzene would also be present in fairly significant levels (water solubilities from 79 ppm to 500 ppm, respectively)(See Table 1) would also be present in significant concentrations. The remaining chlorinated benzenes

are probably present at much lower levels, since their solu-

bilities (See Table 1) are quite low. Phenols could also be

formed if temperatures are sufficiently high to create hydrolysis

conditions, and a highly alkaline wash mixture is used.[58]

Chlorinated phenols could also be present from the phenolization

of the di- and tri-chlorobenzenes, although concentrations

of phenols and chlorinated phenols would probably be small.

Table 5 below shows organic contaminants found in the waste-
water stream from chlorobenzene manufacture at a Dow plant.

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TABLE 5

PRIORITY POLLUTANTS IDENTIFIED IN AQUEOUS WASTESTREAM FROM PRODUCT WASHING STEP IN PRODUCTION OF CHLOROBENZENES(29)

	Concentration mg/l		Loading kg/day
	sampling a	sampling b	(based on sampling a)
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*The underlined data are those obtained from proprietary reports
and data files.

3. Waste Management

Waste management practices for the distillation residues generally involve disposal in on-site and off-site landfills (1). Incineration is also practiced (2).

The separated aqueous stream generally is sent to wastewater treatment.(1) The most feasible treatment method is activated carbon preceded by sand filtration.(1) A wastewater treatment sludge is generated which is assumed to be hazardous unless generators show otherwise. (See §261.3(a)(2)(ii).)

III. Hazards Posed by the Waste

As noted above, the distillation wastes are expected to contain significant concentrations of tri- through hexachlorobenzene, and benzyl chloride, lesser concentrations of dichlorobenzenes, and some monochlorobenzene and benzene. Hexachlorobenzene and benzene have been identified by EPA's Carcinogen Assessment Group as having substantial evidence of carcinogenicity. Pentachlorobenzene is reported to induce cancers in some animal species. All the chlorobenzenes are toxic to the liver, kidney and central nervous system, in varying degree.(56) Benzyl chloride is reportedly carcinogenic. The remaining constituents present acute and chronic toxicity hazards. All are priority pollutants. In addition, all of the chlorinated benzenes are bioaccumulative (based on extremely high octanol/water partition coefficients), and so could pose an additional hazard even if exposure is only to small concentrations of the pollutant.

The aqueous waste stream contains benzene, chloroben-
zenes through trichlorobenzene, and (under certain conditions)
high chlorinated phenols (See Table 5). 2,4,6-Trichlorophenol
has been identified by the Carcinogen Assessment Group as
having substantial evidence of carcinogenicity. In addition,
it presents other chronic toxicity hazards, and is also mutagenic.

In light of the reported concentrations of these hazardous
constituents, these waste streams are clearly of regulatory
concern. Indeed, for the carcinogens in the wastes, there is no
known safe level of exposure, every exposure likely giving
rise to at least one cancer in a portion of the population,
regardless of exposure concentration.[10] The Agency thus requires
strong assurance that these waste constituents are incapable
of migration, mobility, and persistence in the event of improper
management to justify not listing this class of wastes. Such
assurance does not appear possible.

All of the waste constituents have proved capable of
migration, of mobility through soils, and of environmental
persistence in the course of actual waste management practice,
creating a substantial potential for hazard. Benzene and all
of the chlorinated benzenes through pentachlorobenzene have
been detected in air, basement sump and solid surface samples
collected in the vicinity of the Love Canal waste disposal
site in Niagara, New York.(5) Benzyl chloride has been
identified as leaching from Hooker's Hyde Park site in Niagara,
New York,[12] and has been shown to persist in the atmosphere

in the New Jersey area for considerable periods of time.[15]

Hexachlorobenzene has likewise been shown to migrate via air and groundwater pathways and to persist following migration. One damage incident involving hexachlorobenzene occured in Louisiana in the early 1970s. Inhalation exposure to hexachlorobenzene resulted from transport of hexachlorobenzene-contaminated wastes, resulting in dangerously elevated hexachlorobenzene concentrations in humans and animals along the route.[12] Hexachlorobenzene has also been detected in concentrations exceeding background levels in many groundwater monitoring samples taken at various locations at a chemical company dump. (Table 7.2. reference 1)

The higher chlorinated phenols present in the wastewater stream also are capable of migration, mobility, and persistence. Although they are subject to biodegradation (id.) by specifically adapted organisms, these compounds could persist for long periods of time in the abiotic conditions characteristic of most aquifers.[80] Migratory potential is thus substantial, and thus, if migration occurs, chlorinated phenols are mobile and persistent. For example, in a damage incident at Montebello, California, involving wastes from 2,4 dichlorophenol manufacture, 2,4-dichlorophenol and other phenolic compounds proved capable of passing through soils and causing longterm pollution of groundwater. Contamination of groundwater by 2,4-dichlorophenol and other hazardous compounds has also been reported

in East St. Louis, Ill. The source of the compounds was the Monsanto chemical dump.(12)

Since all of the waste constituents of concern have proven capable of migration, mobility, and environmental persistence, and have in fact caused substantial hazard in acutual waste management practice, the Agency believes that the waste constituents could migrate and reach environmental receptors if the wastes are improperly managed. Landfilling the waste without adequate cover could easily result in volatilization of hexachlorobenzene and benzene. Solubilization of hazardous compounds could occur if rainwater is allowed to percolate through the waste or run off the surface of exposed waste. Waste constituents could then be released if - landfills are improperly designed (built without leachate control in areas with permeable soil or located in areas where soils have low attenuative capacity), or managed. Improperly designed wastewater treatment ponds pose the same risk. In the case of improperly managed landfills, surface run-off might also transport compounds that have adsorbed to suspended particulates. Contaminant-bearing leachate and surface run-off may eventually enter ground and surface waters, polluting valuable water supplies and adversely affecting aquatic organisms.

Improper incineration of the distillation residues provides another means by which toxic compounds can be generated and introduced into the environment. If incineration is inade-

quate (for instance, if temperatures are insufficient or resi-
dence time incomplete), inadequate combustion can result in the
formation of substances (such as phosgene) that are even more
toxic than the original waste.(1) These contaminants can be
emitted from the incinerator to the atmosphere and dispersed
in the environment.

IV. Health and Ecological Effects

Health and ecological effects and potential transport
mechanisms for the constituents of concern that might be found
in the distillation bottoms and the separated aquaeous waste
stream from manufacture of chlorobenzenes are described below:

Benzene

Health Effects Benzene is a human carcinogen. Exposure
to benzene as a result of inhalation induces abnormalities
in the blood and causes leukemia.(31-33) Benzene administered
subcutaneously has been teratogenic in mice at extremely low
doses [3 ml/kg].(34) Chronic inhalation of this chemical in
low doses by rats has caused both inhibition and resorption
of embryos.(35) Benzene is also mutagenic when administered
orally to mice at extremely low doses [1 mg/kg].(36)

Exposure of humans to benzene has resulted in the reduction
of blood cells, aplastic anemia, impairment of the immunologic
system, and a variety of mutagenic effects in lymphocytes
and bone marrow.(37-42) Oral ingestion of benzene in small
amounts (50 mg/kg), or one-seventieth of the oral LD_{50} in
rats, has proven lethal to humans.(43)

Regulatory Recognition of Hazard - OSHA has set a PEL
for benzene at 10 ppm with a ceiling level of 30 ppm for
10 minutes. EPA's Office of Air Quality Planning and
Standards and Toxic Substances are performing a pre-regulatory
assessment of benzene based on its production volume, spill
reports and health and environmental effects. Additionally,
EPA's CAG has determined that there is substantial evidence
that benzene is a carcinogen. EPA has estimated 0.66 ug/l as
the concentration in ambient water which could result in a
10^{-6} additional risk for cancer from the consumption of
contaminated drinking water and contaminated aquatic organisms
(65). The Consumer Product Safety Commission requires benzene
to carry special labelling.

Benzene is a priority pollutant in accordance with §307
of the Clean Water Act of 1977 and is listed as a hazardous
waste or hazardous waste constituent in final or proposed
regulations of California, Maine, New Mexico and Oklahoma.

Industrial Recognition of Hazard - Benzene is designated
as highly toxic in industrial handbooks, and represents a
fire and moderate exposure hazard.

Additional information on the health and ecological
effects of benzene may be found in Appendix A.

Chlorobenzenes:[13] Chlorobenzenes have moderate acute
toxicity but, because they bioaccumulate to a significant
degree, chlorobenzenes may pose a substantial hazard if
chronic exposure occurs. They are relatively mobile in the

environment and likely to persist for long periods of time because biodegradation is slow.

Chlorobenzene (monochlorobenzene, MCB)

Health effects - Monochlorobenzene is a central nervous system depressant, with the typical anesthetic effect produced by most chlorinated benzenes (45,46); degeneration of the liver and kidney may develop on chronic exposure. Depending on dosage, acute inhalation produces narcosis, neuropathy and death.[46] The metabolism of monochlorobenzene may lead to the formation of carcinogenic active intermediates.(48) The weighted average bioconcentration factor for mono-chlorobenzene is calculated to be 10.3.[13]

Regulatory Recognition of Hazard - The OSHA PEL for chlorobenzene is a TWA of 75 ppm. EPA's Office of Water and Waste Management provides technical assistance data and regulation for chlorobenzene under Section 311 of the Clean Water Act. They are also involved with pre-regulatory assessment under the Safe Drinking Water Act. The Office of Air, Radiation and Noise and the Office of Research and Development are involved with preregulatory assessment under the Clean Air Act. The Office of Toxic Substances has developed test rule recommendations under Section 4(e) of the Toxic Substances Control Act.[56]

Monochlorobenzene is listed as a priority pollutant in accordance with §307 of the Clean Water Act of 1977, and final or proposed regulations of Maine, New Mexico, Oklahoma

and marine aquatic life.

p-Dichlorobenzene

Health Effects - p-dichlorobenzene is toxic in rats
(oral LD$_{50}$ = 500 mg/kg](53)), and is lethal to humans ingesting
similar amounts. (43) At smaller dose levels (300 mg/kg)
adverse effects are noted on liver and kidney.(43) This
chemical has induced growth depression, liver cell necrosis
and death in animals exposed by inhalation.(56)

Regulatory Recognition of Hazard - p-dichlorobenzene has
been designated as a priority pollutant under Section 307(a)
of the CWA. The OSHA PEL standard is 75 ppm (TWA). It is
listed as a hazardous waste or a component thereof in final
or proposed regulations of the states of California, New
Mexico, and Oklahoma. Additional information on the health and
ecological effects of dichlorobenzene can be found in Appendix A.

Trichlorobenzenes

Health Effects - 1,2,4-Trichlorobenzenes, as are the
other chlorinated benzenes, are metabolized to phenols by the
liver microsomal enzyme systems.(60) Trichlorobenzene
produces histological changes in the liver and kidney.(59)
This compound has slight to moderate acute toxicity for
various aquatic species.(13) Its bioconcentration factor
has been estimated as 182.(13)

Regulatory and Industrial Recognition of Hazard - The
ACGIH TLV for 1,2,4-trichlorobenzene is 5 ppm. Because of
the insufficiency of available information EPA could not
derive a water quality criterion using the guidelines in

and California list chlorobenzene as a hazardous waste or a component of hazardous waste.

Additional information on the health and ecological effects of monochlorobenzene may be found in Appendix A.

Dichlorobenzenes: The bioconcentration factors for three dichlorobenzenes range from 60-89.[13] Their bioaccumulative properties are therefore moderate.

o-Dichlorobenzene

Health Effects - O-dichlorobenzene is very toxic in rats [oral LD$_{50}$ = 500 mg/Kg].(49) Human death has also occurred at this level.(43) Chronic occupational exposure to this chemical and its isomer is toxic to the liver, central nervous system and respiratory system.(13) Chronic feeding of ortho-dichlorobenzene to rats in small doses causes anemia as well as liver damage and central nervous system depression.(52)

Regulatory Recognition of Hazard - o-dichlorobenzene has been designated as a priority pollutant under Section 307(a) of the CWA. The OSHA PEL for o-dichlorobenzene is 50 ppm for an 8-hour TWA. o-Dichlorobenzene was selected by NCI for Carcinogenesis Bioassay, September 1978, and is listed as a hazardous waste, or a component thereof, in final or proposed regulations of the States of California, New Mexico and Oklahoma. The U.S. EPA ambient water quality criterion for dichlorobenzenes (all isomers) is 400 ug/l. (13,65). U.S. EPA has also established criteria for freshwater

effect in 1980. Additional information and references on
the health and environmental effects of this substance can
be found in Appendix A.

Tetrachlorobenzene

Health Effects - Chronic exposure of rats and dogs to
tetrachlorobenzene affects the liver and the hemopoietic
system (19,56). Tetrachlorobenzene is not acutely toxic
to mammals, since its oral LD_{50} in the rat is 1500 mg/kg.(56)
It is reported to be acutely toxic in varying degrees to
some fresh- and saltwater organisms, and chronically toxic
to saltwater organisms.(19) The predominant mammalian dis-
position site for tetrachlorobenzene is in the lipid tissues
(16) of the body, and its bioconcentration factor was estimated
to be 1800.[13]

Tetrachlorobenzene was designated by Congress as a
priority pollutant under §307 of the Clean Water Act of
1977.

For the protection of human health from the toxic
properties 1,2,4,5-tetrachlorobenzene ingested through water
and contaminated aquatic organisms, the ambient water criterion
is determined to be 38 ug/1.[13]

Additional information on the health and ecological effects
of benzene can be found in Appendix A.

Pentachlorobenzene[56]

Health Effects - Pentachlorobenzene is reported to be
carcinogenic in mice, although not in rats or dogs. It

is also reported to have caused bone defects in the offspring of rats which were exposed to this compound during gestation.

Pentachlorobenzene is quite acutely toxic at low concentrations (ranging from 160 ug/l to 6,780 ug/l) to both salt- and freshwater organisms, including plants.

Pentachlorobenzene has an extremely high octanol/water partition coefficient of 154,000, indicating a dangerously high bioaccumulation potential.(14)

For the protection of human health from the toxic properties of pentachlorobenzene ingested through water and contaminated aquatic organisms, the ambient water criterion is determined to be 74 ug/l.[13]

Pentachlorobenzene is designated as a priority pollutant under §307 of the Clean Water Act.

Additonal information on the adverse health effects of pentachlorobenzene can be found in Appendix A.

Hexachlorobenzene

Health Effects - U.S. EPA's Carginogen Assessment Group (CAG) has evaluated hexachlorobenzene and has found sufficient evidence to indicate that it is carcinogenic. It is also fetotoxic to rats.(23) The distribution of hexachlorobenzene is apparently the same in the fetus and the adult, with the highest concentration accumulating in fatty tissue. (23) Its estimated bioconcentration factor is very high: 22,000.[13]

Chronic exposure of rats to hexachlorobenzene has caused histological changes in the liver and spleen (24), and in humans, causes porphyrinuria and other symptoms of porphyria cutanea tarda.[25,26]

For protection of human health from the potential carcinogenic effects of exposure to hexachlorobenzene through ingestion of contaminated water and contaminated aquatic organisms the ambient water quality criterion was set at 72 ug/1 (10^{-6} incremental cancer risk).[13]

Hexachlorobenzene is designated as a priority pollutant under §307 of the Clean Water Act.

Additional information on the adverse health effects of hexachlorobenzene can be found in Appendix A.

Benzyl Chloride

Health Effects - Benzyl chloride has been identified as a carcinogen (18), and is also mutagenic(27).

The OSHA TWA for benzyl chloride is 1 ppm. DOT requires labeling as a corrosive. The Office of Water and Waste Management, EPA, has regulated benzyl chloride under Section 311 of the Clean Water Act. Preregulatory assessment has been completed by the Office of Air, Radiation and Noise under the Clean Air Act. The Office of Toxic Substances has requested additional testing under Section 4 of the Toxic Substances Control Act.

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Benzyl chloride is listed in Sax's Dangerous_Properties_ of_Industrial_Materials as highly toxic via inhalation and moderately toxic via the oral route.

Additional information and specific references on the adverse effects of benzyl chloride can be found in Appendix A.

2,4,6-Trichlorophenol

Health_Effects - NCI has concluded that this compound is carcinogenic in mole F344 rats (inducing lymphomes and leukemias), and in both sexes of B_6, C_3, F_1, mice, inducing hepatocellular carcinogens and abensomas.[61] Accordingly, 2,4,6-trichlorophenol has also been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of carcinogenicity. 2,4,6-Trichlorophenol is lethal to humans by ingestion of 60% of the oral LD_{50} dose in rats [500 mg/kg].[43] This chemical is reportedly mutagenic[62] and adversely affects cell metabolism.[63,64] 2,4,6-Trichlorophenol has been designated a priority pollutant under 307(a) of the FWPCA.

Ecological_Effects[14] - Very small concentrations of 2,4,6-trichlorophenol are lethal to freshwater fish [LC_{50} = 175- 426 ug/l]; it is also lethal to freshwater invertebrates at very low concentrations.

Regulatory_Recognition_of_Hazard - 2,4,6-Trichlorophenol has been designated as a priority pollutant under Section 307(a) of the CWA. Based on carcinogenicity, EPA has recommended 1.2 ug/l as the ambient water quality criterion for

the ingestion of fish and water (10^{-6} excess cancer risk).[14]

Industrial Recognition of Hazard - Sax, in Dangerous Properties of Industrial Materials(45), lists 2,4,6-trichlorophenol as moderately toxic via ingestion.

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Response to comments column bottoms and aqueous stream from the production of chlorobenzenes (K085).

1. One commenter characterized the Agency's use of the terms "chlorobenzene" and "chlorinated benzene", and its occasional general references to chlorobenzenes with higher degree of chlorination as "polychlorinated benzenes" as "shoddy and ambiguous". The commenter went on to remark that these isomeric compounds differ in physical properties, production, waste management, health and environmental effects. The Agency deems the terms "chlorobenzene(s)" and "chlorinated benzene(s)" to be acceptable, widely used synonymous chemical terms. However, in order to leave no room for ambiguity as to the chemical nature of the chlorinated benzenes which are of concern in these wastes, and in order to facilitate a comparison of their relevant properties, a figure illustrating their chemical structure and a table delineating their physical properties have been added to the Background Document.

2. One commenter disagreed with the listing of the separated aqueous stream from the reactor product washing step as hazardous. The commenter disputed the Agency's determination that phenols and chlorinated phenols will be found in this waste stream, stating that the reported occurence of these compounds in the untreated wastewater is atypical.

The commenter went on to state that the aqueous waste,
in any case, contains pollutants at such low concentrations
(i.e., 3-135 ppm, averaging 56 ppm) that the waste should
be of no regulatory concern under RCRA.

The Agency disagrees with these comments. Phenol
and chlorinated phenols are likely to be found in this
waste in some concentration as stated in the background
document, because chlorinated benzenes are known to form
these compounds as a result of hydrolysis under alkaline
conditions and elevated temperatures, conditions present
during chlorobenzene manufacture.(58) The presence of
these compounds in the sampled wastewater stream confirms
this process assumption.

However, on further consideration, we have decided
that certain of these compounds are not present in
the waste in concentrations sufficient to warrant their
inclusion as toxic constituents of concern. Phenol,
2-chlorophenol, and 2,4-dichlorophenol are in this category.
Not only are the reported sampled concentrations already
low, but they may be greater than concentrations normally
present from processes involving only chlorobenzene
manufacture, since the sampled waste may have included
wastewater from chlorophenol manufacture.

We will continue to list the carcinogen 2,4,6-
trichlorophenol as a constituent of concern. Since the
reported concentration is many orders of magnitude above
the recently promulgated human health Ambient Water

Quality Criterion for this compound (45 FR 79329
November 7, 1980), we believe the value to indicate a
potential for hazard if the waste is mismanaged. We
also believe that benzene and chlorinated benzenes may
typically be present in substantial concentrations,
namely their limits of solubility, and so will continue
to list the waste for these constituents as well.

The commenter further argued that these constituents
are amenable to biological treatment, and so should not
be listed. The unstated thought is that although sludges
resulting from wastewater treatment are hazardous (see
§261.3), they may not contain appreciable concentrations
of the constituents of concern if biological treatment is
successful.

There are a number of answers to this comment. The
Agency, in its July 16 Background Document invited
commenters to show that their wastewater treatment sludges
are not hazardous. No data on this waste were submitted
by any commenter. Furthermore, the delisting mechanism
remains available to any facility wishing to demonstrate
that wastewater treatment sludges resulting from treatment
of wastewater from chlorobenzene manufacture is not
hazardous. Equally important, not all plants utilize
biological treatment, so that the hazardous constituents
could be present in some wastewater treatment sludges
in much higher concentration than in others.

Even where biological treatment is used, the Agency has
no assurance that the treatment is always successful in
removing hazardous constituents from the sludge, since
organisms must be specially adapted to degrade these
toxic constituents. We thus do not believe the comment
to be sufficiently persuasive to warrant deleting this
waste listing.

3. The same commenter also mentioned in passing that it
generates an aqueous waste stream from a continuous
chlorobenzene manufacturing process, even though the
background document indicated that this waste stream is
generated only from batch processes.

Available information continues to indicate that in
most cases, there will be no wastewater stream generated
from the continuous production of chlorobenzenes. In
response to the comment, however, we are revising the
listing description to include wastewater streams which
arise from continuous processes. Since raw materials are
the same and reaction processes are similar for both
processes, we expect any wastewater to be similar in
composition. The constituents and their concentrations
shown in reference 29, an analysis of wastewater from a
continuous process, is comparable to that predicted for
batch processes, confirming our assumption.

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4. One commenter criticized the Agency's characterization
    regarding the persistences, mobilities and toxicities of
    several chlorophenols. The commenter recommends that the
    Agency reassess the hazard of the aqueous process stream,
    since, in its view, phenols and chlorinated phenols are
    not hazardous constituents. Several of the comments
    raised are identical to those raised by the same manufacturer
    with respect to solid waste K043 (2,6-dichlorophenol
    waste from the production of 2,4-D). The Agency's reply
    to these comments were published on November 15, 1980
    (Response to Comments, page 635 of the BD dated November
    19, 1980). There is no need to repeat them here.

Based on the foregoing discussion, the Agency will continue
to list wastes K085 (distillation or fractionating column
bottoms from production of chlorobenzenes) and K105 (separated
aqueous stream from the reactor product washing step in the
batch production of chlorobenzenes) as hazardous.

K24
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LISTING BACKGROUND DOCUMENT

K086: SOLVENT WASHES AND SLUDGES, CAUSTIC WASHES AND SLUDGES
AND WATER WASHES AND SLUDGES FROM THE CLEANING OF TUBS
AND EQUIPMENT USED IN THE FORMULATION OF INK FROM PIGMENTS,
DRIERS, SOAPS AND STABILIZERS CONTAINING CHROMIUM AND LEAD
LEAD (T).

I. SUMMARY OF BASIS FOR LISTING*

Tubs and equipment used in ink formulation are washed by

solvents, caustics and/or water. The Administrator has deter-

mined that the spent washes and wash sludges generated after

ink formulation in which pigments, driers, soaps and stabili-

zers containing hexavalent chromium and lead are used may pose

a present or potential hazard to human health or the environ-

ment when improperly transported, treated, stored, disposed

of or otherwise managed and therefore should be subject to

appropriate management requirements under Subtitle C of RCRA.

This conclusion is based on the following considerations:

1. The washes and sludges typically contain significant
    concentrations of lead and hexavalent chromium. Lead
    is highly toxic to a variety of species and is reportedly
    carcinogenic in laboratory animals. Hexavalent chromium
    is also toxic; in addition, EPA's Cancer Assessment
    Group has found that CR^{+6} exhibits substantial
    evidence of carcinogenicity.

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*The Agency is investigating the potential hazards of organic
constituents of printing inks. We are, for instance, investi-
gating the possible conversion by heat, light or reducing agents
present in waste streams or the environment, of pigments derived
from 3,3'-dichlorobenzidine to the parent (carcinogenic) amine.
We are also concerned about wastes from the manufacture of jet
printing inks containing direct dyes derived from benzidine,
o-dianisidine and o-tolidine: such dyes could similarly be con-
verted to the carcinogenic parent amine.

Organic solvents likely to be used in these washes are covered
under listings F003, F004, and F005, §261.31, hazardous waste
from nonspecific sources (45 FR 74890, November 12, 1980).

2. Present management practices may be inadequate to prevent the migration of hexavalent chromium and lead from a disposal site. Disposal practices subject to RCRA include landfilling, impoundment and removal by contract haulers. Such practices, if uncontrolled, can result in contamination of ground and surface waters by lead and hexavalent chromium.

II. INDUSTRY DESCRIPTION AND MANUFACTURING PROCESS[1]

An EPA survey of the ink formulating industry indicates that there are approximately 460 ink manufacturers in the United States (excluding captive ink producers that manufacture ink in a printing plant solely for use in that plant). The distribution of ink manufacturing plants by state is given in Table 1. In 1972, total ink production was greater than one billion pounds.

The variety of inks used today is broad, ranging from ordinary writing inks to specialized magnetic inks. Inks manufactured for the printing industry, which utilizes a major portion of ink production, fall into four major categories: letterpress inks, lithographic inks, flexographic inks, and gravure inks.

Letterpress inks are viscous, tacky pastes using vehicles that are oil and varnish-based. They generally contain resins and dry by the oxidation of the vehicle.

Lithographic or off-set inks are viscous inks with a varnish-based vehicle, similar to the letterpress varnishes. The pigment content is higher in lithographic inks than letter-press ink because the ink is applied in thinner films.

Table 1 (1)

DISTRIBUTION OF INK MANUFACTURING PLANTS BY STATE

State	Number of Plants	Percent of Plants
California	47	10.2
Illinois	46	10.0
New Jersey	39	8.5
New York	34	7.4
Ohio	28	6.1
Pennsylvania	24	5.2
Texas	22	4.8
Massachusetts	21	4.6
Georgia	20	4.3
Missouri	16	3.5
Florida	14	3.0
Wisconsin	14	3.0
Michigan	13	2.8
Tennessee	13	2.8
North Carolina	10	2.2
Louisiana	9	2.0
Maryland	9	2.0
Minnesota	9	2.0
Virginia	9	2.0
Indiana	7	1.5
Oregon	7	1.5
All Others	49	10.7

Flexographic inks are liquid inks which dry by evaporation, absorption into the substrate, and decomposition. There are two main types of flexographic inks: water and solvent. Water inks are used on absorbent paper and the solvent inks are used on nonabsorbent surfaces.

Gravure inks are liquid inks which dry by solvent evaporation. The inks have a variety of uses ranging from printing publications to food package printing.

Inks are either water, oil or solvent-based. The "average" plant produces approximately 60 percent oil base ink, 25 percent solvent base ink and 5 percent water base ink.

In the manufacture of inks, the major ingredients (vehicles, pigments and driers) are mixed thoroughly to form an even dispersion of pigments within the vehicle. The mixing is accomplished with the use of high-speed mixers, ball mills, three-roll mills, sand mills, shot mills, and/or colloid mills.

Most inks are made in a batch process in tubs ranging in sizes from 19 liters (five gallons) to over 3,750 liters (1,000 gallons). The number of steps needed to complete the manufacture of the ink depends upon the dispersion characteristics of the ingredients. Most inks can be completely manufactured in one or two steps since many of the pigments used can be obtained predispersed in a paste or wetted form.

III. GENERATION AND MANAGEMENT OF HAZARDOUS WASTE[1]

Ink is manufactured by blending raw materials; chemical

reactions generally do not occur and no by-products are formed. When required, production tubs and manufacturing equipment are washed clean of residue from the formulation process. The spent cleaning solutions become contaminated with tank residue composed of the residual raw materials.

Four broad types of raw materials are used in ink manufacture:

- Pigments and dyes, flushes and dispersions
- Chemical specialties (including driers, plasticizers, soaps and stabilizers)
- Resins
- Solvents

Inorganic pigments are the primary source of (hexavalent) chromium and lead in ink industry wastewaters; chemical specialties are also reported to contain lead. Survey data obtained by EPA show that the ink formulation industry relies on inorganic pigments for about 40% of the total production. The two most widely used lead and chromium-containing pigments are chrome yellow and molybdate orange, although many other pigments are sources of lead and chromium in the waste. Chrome yellow is a compound consisting of lead, hexavalent chromium and oxygen; molybdate organge also contains lead and hexavalent chromium as well as molybdenum.

Particular chemical specialties are another significant source of lead and chromium in these wastes. For example, driers containing lead are used by approximately 30% of the

industry.* Stabilizers (some containing lead and phenol), metallic soaps, and flatting agents containing lead are also in use and are expected to contribute significant concentrations of lead to process wastes.**

Process wastewater from ink manufacturing plants results primarily from the rinsing of mixing tubs, roller mills, and other equipment. Some additional wastewater may come from floor and spill cleaning, laboratory and plant sinks, boiler and cooling water blowdown, air pollution control devices using water, and cleanout of raw material supply tank cars or trucks.

The ink industry commonly uses three methods of ink tub cleaning: (1) solvent-wash; (2) caustic-wash; and (3) water-wash.

(1) Solvent-Wash Wastes

Solvent-wash is used exclusively to clean tubs used for formulating solvent-based and oil-based ink. The dirty solvent generally is handled in one of three ways:

1. used in the next compatible batch of ink as part of the vehicle;

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* Examples are Shephard-lead tallates, lead linoleates, Rexogan, Aduasol and Catalox.[1]

**Industry survey data indicate that approximately 70% of the manufacturers use chromium-containing raw materials, and 55% use lead-containing raw materials. Thus, use of materials containing these pollutants is widespread in the industry.

2. collected and redistilled, either by the plant or by an outside contractor for subsequent resale or reuse; or

3. reused with or without settling to clean tubs and equipment until spent, and then drummed for disposal. If sludge is settled out it is also drummed. These spent solutions and sludges are usually disposed of by contract hauling.

(2) Wash-Water Wastes

Water-washing techniques are used in both the solvent-base and water-base segments of the ink industry. For solvent-base operations, water-washing usually follows caustic washing of solvent-base tanks. For water-base operations, water washes often constitute the only tub cleaning operation, although water-base ink tubs may be cleaned periodically with caustic.

Wastewater generated by rinsing tubs or equipment used for manufacturing water-base ink is usually handled in one of four ways:

1. reused in the next compatible batch of water-base ink as part of the vehicle;

2. reused either with or without treatment to clean tubs and equipment until spent and disposed. If sludge is settled out it is disposed by contract hauling;

3. discharged with or without treatment as wastewater; or

4. disposed of immediately by contract hauling.

The water rinse following a caustic-wash is rarely reused in a subsequent batch of ink. The most common methods for disposal of this rinse are:

1. recycling it back into the caustic as make-up water;

2. drumming it for contract hauling;

3. discharging it as wastewater, with or without pre-treatment. Combination with other wastewater prior to treatment or disposal is sometimes practiced. Discharge of this wastewater is currently prohibited by some states and municipalities and may be prohibited in other areas in the future.

(3) Caustic-Wash Wastes

Caustic wash techniques are used to clean both solvent-base and water-base ink manufacturing tanks. Plants using caustic rinse or washing systems usually rinse the caustic residue with water, although a few plants allow the caustic solution to evaporate in the tubs. There are several types of caustic systems commonly used by the ink industry. For periodic cleaning of fixed tubs two methods are popular:

1. maintaining the caustic in a holding tank (usually heated) and pumping through fixed piping or flexible hose to the tub to be cleaned. After cleaning, the caustic is returned to the holding tank; and

2. preparing the caustic solution in the tub to be cleaned, and soaking the tub until clean. The caustic solution is either transferred to the next tub to be cleaned, stored in drums or a tank for subsequent use, or is discarded.

For cleaning small portable tubs, three common methods are used by the ink industry:

1. pumping caustic from a holding tank (usually heated) to nozzles in a fixed or portable hood which is placed over the tub to be cleaned. The caustic drains to a floor drain or sump and is pumped back to the tank, or is pumped back directly from the tub;

2. maintaining an open top caustic holding tank. Small tubs are put into "strainers" and dipped into these tanks until clean; and

3. placing the tubs in a "dishwasher-like" device (which circulates hot caustic), and a subsequent water rinse. These devices can handle tubs up to about 1900 liters (500 gal).

Most plants using caustic, recycle the caustic solution until it loses some of its cleaning ability. The spent caustic is then disposed of either by contract hauling or as a wastewater, with or without neutralization or other treatment.

The most common methods of wastewater disposal are discharge to a sewer, contract hauling, evaporation, and land-fill or impoundment. Most contract haulers discharge the sludge to a landfill, although a few incinerate or reclaim it.[1]

Although precise figures on the amount of waste covered by this listing are not available, the quantity is expected to be significant, and, furthermore, is expected to increase in the future. Final regulations issued by EPA's Effluent Guidelines Division impose zero discharge requirements for certain pollutants on all ink manufacturers in the solvent wash category of the industry except existing pre-treaters; proposed regulations would impose zero discharge requirements on existing pre-treaters in the Solvent Wash category and all others in the Caustic and/or Water Wash category. Imple-mementation of these regulations will increase the amount of hazardous waste requiring disposal in accordance with the RCRA Subtitle C regulations.

V.   DISCUSSION OF BASIS FOR LISTING

A.   HAZARDS POSED BY THE WASTE

Solvent washes and sludges, caustic washes and
sludges and water washes and sludges from cleaning equipment
used in the formulation of ink from raw materials containing
lead and hexavalent chromium are listed as hazardous because
they typically contain significant concentrations of lead
and (presumably hexavalent) chromium.*

Lead is poisonous in all forms. It is one of the
most hazardous of the toxic metals because it accumulates in
many organisms and its deleterious effects are numerous and
severe. Epidemiology studies implicate occupational exposure
to hexavalent chromium in the induction of lung tumors.
Impairment of pulmonary function is also reported to result

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* Other toxic metals and various toxic organics are also
known to be present in some of the wash wastes, but sufficient
data are not yet available to list the wastes for those
contaminants. It also should be noted that the tub-cleaning
wastes can exhibit hazardous characteristics other than
toxicity; the Agency has information which indicates that
the listed wastes can be ignitable or corrosive (3,4,5,6).
In addition, a number of spent solvents are listed as hazardous
in §261.31 of the hazardous waste regulations published on
November 12, 1980 (45 FR 74890), and if these solvents are used
in ink formulation and are disposed of, they are considered
hazardous wastes under the earlier listing as well as the
present listing. Listed solvents presently in use by the
ink formulation industry include: toluene, 1,1,1-trichloroethane,
ethyl benzene methylene chloride and trichloroethylene.
Delisting petitions by ink formulators using these solvents must
address not only the presence of the spent solvent itself in the
waste, but the presence of lead and hexavalent chromium as
well.

from chronic exposure to hexavalent chromium. (For further information on Health and Ecological Effects of chromium and lead, see Section B (Health and Ecological Effects) in this background document, and Appendix A.

The following data substantiates the presence of significant concentrations of lead and chromium in the wash wastes:

- EPA has determined that the average concentrations of lead and chromium per day in ink industry caustic wash and water-wash wastewaters are 151 mg/l and 35 mg/l, respectively. Concentrations as high as 900 mg/l of lead and 200 mg/l of chromium were reported.[1]*

- A summary of industrial waste composition data taken from the manifests required by the State of California for transportation of hazardous wastes lists the following wastes from the manufacture of printing ink as hazardous:[2]

  1. Ink wastewater which contained 1000 ppm of lead.
  2. Equipment cleaning washwater which contained 10,000-20,000 ppm of lead chromate.

- "Special Waste Disposal Applications" were submitted to the State of Illinois for the following wastes from ink manufactures:[3]

  1. Solvent waste containing 120 ppm of chromium and 770 ppm of lead.
  2. Solvent waste containing 291 ppm of lead.

- A "Hazardous Waste Disposal Request" was submitted to the Missouri Department of Natural Resources for disposal of printing ink sludge (wash waste) containing 260 ppm of chromium and 1,340 ppm of lead.[4]

- The "Industrial Waste Surveys" file of the State of New Jersey contained a description of ink manufacturing wash water with 260 ppm of lead [7].

Clearly the concentrations of lead and chromium in the

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*These figures may be conservative in light of the higher concentrations contained in state manifests, given below.

wastes may be very substantial.

The presence of such high concentrations of toxic metals in a waste in and of itself raises regulatory concerns. Lead and hexavalent chromium have proven capable of migration, mobility and persistence in many waste management settings[28], raising the concern that, if these wastes are improperly managed, the lead and hexavalent chromium may be released from the waste in harmful concentrations and adversely effect human health and the environment. Because lead and chromium do not degrade with the passage of time, they will provide a potential source of long-term contamination if they are permitted to escape from the disposal site.

Current disposal methods do not appear adequate to prevent migration of these toxic metals from the waste into the environment. Toxic metal-bearing liquid wastes placed in an impoundment can release those hazardous constituents to the surrounding area if seepage and overflow are not controlled, or measures are not taken to prevent total washout. Without regulation, proper containment of the impounded wash wastes cannot be assured.

Clearly, if measures to retard migration of liquids from impoundments and landfills are not employed, ground and surface waters could easily become contaminated. Improper landfilling of sludges settled from the liquid wastes could also result in release of the hazardous constituents. The heavy metal compounds might already be solubilized or may

solubilize as a result of disposal conditions (co-disposal with acids, alkalis or decomposing organic matter, for instance) and could then migrate from the disposal site to ground and surface waters. As a result, ground and surface drinking water supplies may become contaminated, and wildlife and various aquatic species could be threatened by exposure to the toxic metals lead and hexavalent chromium.

Unregulated contract hauling of wastes by private disposal services, scavengers or purveyors in tank trucks -- a waste management method frequently used for these wastes -- creates additional hazards. There have been innumerable damage incidents involving unregulated contract hauling, resulting in substantial environmental harm. (Some examples are collected in Reference 28.) Thirty-one percent of the ink plants surveyed by EPA did not know what the contract hauler does with their waste.[1] There is obvious potential for abuse in this system since there is no way to determine whether these wastes are properly managed during transportation, treatment or disposal; irresponsible handling at any point could ultimately endanger human health and the environment. Therefore, it is essential that wastes of this nature be subject to regulation from "cradle to grave".

B.   Health and Ecological Effects

1.   Lead

Health Effects

Lead is poisonous in all forms. It is one of

the most hazardous of the toxic metals because it bioaccumulates in many species, and its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact. The hematopoietic system is the most sensitive target organ for lead in humans, although subtle neurobehavioral effects are suspected in children at similar levels of exposure.[8]

Lead exposure has been reported to decrease reproductive ability in men[9] and women.[10] It has also been shown to cause disturbances of blood chemistry,[11] neurological disorders,[12,13], kidney damage[14] and adverse cardiovascular effects.[15] Lead has been shown to be teratogenic in animals.[16] Although certain inorganic lead compounds are carcinogenic to some species of experimental animals, a clear association between lead exposure and cancer development has not been shown in human populations.

Additional information and specific references on adverse effects of lead can be found in Appendix A.

Ecological Effects

In the aquatic environment, lead has been reported to be acutely toxic to invertebrates at concentrations as low as 450 ug/l and chronically toxic at less than 100 ug/l.[17] The comparable figures for vertebrates are 900 ug/l for acute toxicity[18] and 7.6 ug/l for chronic toxicity.[19] Lead is bioconcentrated by all species tested - both marine

and freshwater - including fish, invertebrates and algae.
The mussel, Mytilus edulis, concentrated lead 2,568 times
that found in ambient water. Two species of algae concentrated
lead 900-1000 fold. Algae reportedly can concentrate lead in
their tissues to levels as much as 31,000 times ambient water
concentrations.[20] Lead does not degrade with the passage
of time and may be expected to persist indefinitely in the
environment in some form.

Regulatory Recognition of Hazard

As of February 1979, the U.S. Occupational Safety and
Health Administration has set the permissible occupational
exposure limit for lead and inorganic lead compounds at 0.05
mg/m^3 of air as an 8-hour time-weighted average. The U.S.
EPA (1979) has also established an ambient airborne lead
standard of 1.5 ug/m^3.

The U.S. EPA's Office of Water Regulations and Standards
has recommended an ambient water quality criterion for lead
to protect freshwater aquatic life of 0.75, 3.8, and 20
micrograms lead per liter (ug/l) corresponding to a water
hardness of 50, 100, and 200 mg/l calcium and carbonate. The
ambient water quality criterion for lead to protect human
health is recommended to be identical to the existing drinking
water standard of 50 ug/l.[21]

In addition, final or proposed regulations of the States
of California, Maine, Massachusettes, Minnesota, Missouri,
New Mexico, Oklahoma and Oregon define lead containing compounds

as hazardous wastes or components thereof.[22]

Industrial Recognition of Hazard

Lead is rated as highly toxic through ingestion, inhalation and skin absorption routes in Sax, _Dangerous Properties of Industrial Materials_.

Chromium

Health Effects

Hexavalent chromium is an animal carcinogen and there is evidence that it may be a human carcinogen as well.[23] EPA's Carcinogen Assessment Group has listed it as such. Mutagenic effects in bacteria have also been described. Cytogenetic effects in workers using hexavalent chromium compounds have been reported.[24]

Teratogenic effects of chromium have been reported in a single study and have not been confirmed.

Impairment of pulmonary function has been described in chrome electroplating workers subject to chronic chromium exposure.[25]

Additional information and specific references on the adverse effects of chromium can be found in Appendix A.

Ecological Effects

Hexavalent chromium, at low concentrations, is toxic to many aquatic species. For the most sensitive aquatic species, _Daphnia magna_, a final chronic no-effect level of less than 10 ug/l has been derived by the U.S. EPA.

Regulatory Recognition of Hazard

The U.S. EPA's Office of Water Regulations and Standard has recommended an ambient water quality criterion for hexavalent chromium to protect freshwater aquatic life of 0.29 ug/l as a 24-hour average. For protection of saltwater aquatic life, the criterion for hexavalent chromium is 18 ug/l. The ambient water quality criterion for hexavalent chromium to protect human health is recommended to be identical to the existing drinking water standard which is 50 ug/l.[27]

The OSHA time-weighted average exposure criterion for chromium (carcinogenic compounds) is 1 ug/m^3; for the "non-carcinogenic" classification of chromium compounds the criterion is 25 ug/^{3} TWA.

For the protection of aquatic species, proposed water criteria for both trivalent and hexavalent chromium in freshwater and marine environments have been prepared in accordance with the Guidelines for Deriving Water Quality Criteria.[27]

Industrial Recognition of Hazard

Sax, Dangerous Properties of Industrial Materials, 4th Ed. 1975, rates chromium as having a high pulmonary toxicity.

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K086: INK FORMULATION

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1.   One commenter stated that the proposed listing is

too broad and that all wash wastes should not be consid-

ered hazardous.

The listing of the above waste has been clarified.

After reviewing available information, the Agency has

narrowed the listing to cover wastes from the cleaning of

equipment used to formulate ink from raw materials containing

chromium and lead. Data show that raw materials containing

chromium and lead are widely used in the industry,

and the wash wastes generated when these raw materials

are used are likely to exhibit substantial concentrations

of these toxic metals. The Agency concluded that these

wash wastes present a potential hazard to human health

and the environment because improper disposal may result

in the contamination of ground and surface waters used

as drinking water sources (see the background document

for a more detailed discussion).

2. One commenter stated that wash wastes should not

be listed as corrosive since the corrosive waste streams

can be neutralized.

The fact that the wastes can be neutralized does not

mean that they are not hazardous when generated. In

order to make sure that corrosive wastes are managed

properly, corrosivity must be determined before treatment

by neutralization or any other means (see §261.3(b)(3).

For the final listing, the Agency has decided not to

characterize the wash wastes as corrosive because adequate

data are not available to indicate that the wastes are

typically corrosive as defined in §261.22. In addition,

the Agency believes that the corrosivity of the wastes

can easily be determined by the generator. Such a

determination is required for all wastes not included

in this listing, and for all wastes addressed by indivi-

dual petitions for delisting. (See §§ 262.11, 260.22.)

3. The commenter stated that classification of all wash

wastes as hazardous because some might contain toxic

organic substances is arbitrary.

The Agency has narrowed its proposed listing, although

the claims of the commenter are not particularly persuasive.

The revised listing does not at this time address toxic

organic substances in the waste. As additional data

becomes available, the Agency may include such substances

as toxic constituents of concern in these wastes. The Agency

for instance, concerned with the use of phthalates

used as plasticizers in ink formulation, and use of

phenols in chemical specialties. Information is solicited

as to concentrations of these materials in ink formulation

wastes, and potential mass loadings of these pollutants.

The Agency is particularly concerned over any potential
environmental degradation by heat, light, or chemical
reducing agents of the diarylide yellow pigments to the
parent amine, 3,3'dichlorobenzidine. Certain solvents
used in ink formulation are listed as hazardous wastes
under F002, F003, F004, and F005 (45 FR 33123, May 19,
1980).

LISTING BACKGROUND DOCUMENT

K087: Decanter Tank Tar sludge from coking operations* (T)

I. Summary of Basis for Listing

The spray cooling of coke oven gases during the by-product recovery process results in the generation of a decanter tank tar-sludge. The Administrator has determined that decanter tank tar-sludge may pose a present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1) The tank tar-sludge contains significant concentrations of phenol and naphthalene. Phenol and naphthalene are toxic to humans and aquatic life.

2) Phenol has leached in significant concentration from a waste sample tested in a distilled water extraction procedure. Although no leachate data is currently available for naphthalene, the Agency believes that, due to its presence in the tar in high concentrations and due to its relative solubility, naphthalene also may leach from the waste in harmful concentrations if the waste is improperly managed.

3) These tar-sludges are often land disposed in on-site landfills or dumped in the open. These methods may be inadequate to impede leachate migration and resulting groundwater contamination.

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*The listing description has been amended from that originally proposed on December 18, 1978 (43 FR 58959) which included two waste listings [i.e., Coking: Decanter tank tar and Coking: Decanter tank pitch/sludge]

Additional information substantiating the hazards associated with polynuclear aromatic hydrocarbon constituents in this waste will be evaluated in an expanded listing background document for an integrated by-product coke-making process.

II.   Waste Generation, Composition and Management

Coke, the residue from the destructive distillation of coal, serves as both a fuel and as a reducing agent in the making of iron and steel. Some coke plants recover by-products given off or created during the coke production process, and the recovery of by-products generates a sludge which is the listed waste in this document. There are 66 by-product coke plants, which generate an estimated 72,300 tons/yr of decanter tank tar-sludge. During the recovery of chemicals in the by-product coke production process, tar separates by condensation from coke oven gas and drains to a decanter tank. Recoverable oil fractions are decanted off the top and the tar sludge settles to the bottom.

Approximately 97% of this tar-sludge is elemental carbon. The remaining 3% consists of condensed tar materials. These condensed tar materials contain the waste constituents of concern, namely phenolic compounds and naphthalene, which are formed as a result of the destructive distillation of coal.

Based on a published reference, the condensed tar component contains, by weight, 2.2% naphthalene and 0.1% phenolic compounds[2]. With an estimated 2,169 tons/yr of condensed tar contained in the amount of tar-sludge generated annually (i.e., 3% of the 72,300 tons/yr of tar-sludge), approximately 47.7 tons of naphthalene and 2.2 tons of phenolic compounds will be contained in the waste generated each year[1,2].

Of the 66 coke plants generating decanter tank tar-sludge, 30 plants use the tar-sludge as a raw material in either the sintering process or open hearth furnace operation. The remaining 36 plants dispose of this waste in unsecure on-site landfills[1], or by dumping in the open[3].

III. Hazardous Properties of the Waste

Phenol and naphthalene are present in the tar component of this waste in significant concentrations: 0.1% by weight (1000 ppm) and 2.2% by weight (22,000 ppm), respectively[2]. Phenol and naphthalene are toxic to humans and aquatic life. Thus, the Agency believes that the concentrations of these materials in the waste are quite significant, in light of the constituents' known health hazards. Further, these waste constituents appear capable of migrating in significant concentrations if mismanaged, and are likely to be mobile and persistent so that waste mismanagement could result in a substantial human health or environmental hazard.

Phenol's potential for migration from this waste in significant concentrations has been demonstrated empirically. Phenol leached in significant concentration (approximately 500 ppm) from a decanter tar-sludge waste sample subjected to distilled water extraction procedure.[3] In addition, phenol is extremely soluble, about 67,000 ppm @ 25°C[5], indicating high potential for migration. Phenol biodegrades at a moderate rate in surface water and soil but moves very

readily (App. B). Even with a persistence of only a few day,

the rapid spreading of phenol could cause widespread contamina-

tion of the eco-system and contamination of potable water supplies.

The migratory potential of phenol and its ability to move

through soils is further confirmed by the fact that it has been

detected migrating from Hooker Corporation's S Area, Hyde Park,

and 102nd St. landfills in Niagara, New York (OSW Hazardous

Waste Division, Hazardous Waste Incidents, Open File, 1978).

The compound's persistence following migration is likewise

shown by these incidents.

Although no comparable leachate data is currently avail-

able for naphthalene, the Agency believes that this constituent

also may leach in harmful concentrations from the waste if not

properly managed. The water solubility of naphthalene has been

reported to range from 30 to 40 mg/l, depending on the salinity

of the dissolving medium (7). Naphthalene has been identified

in finished drinking water, lakes, and rivers, demonstrating its

persistence and mobility [4]. This information, naphthalene's

solubility in water, and its presence in the tar in such high

concentrations (22,000 ppm) make it likely that it will leach

from the waste in potentially harmful concentrations if the

waste is mismanaged, and will then be mobile and persistent, and

so poses the potential for causing substantial hazard to human

health and the environment.

Current practices of disposing of this waste in fact ap-

pear inadequate. Disposal of decanter tank tar-sludge in un-

secured landfills or by dumping in the open makes it likely

that the hazardous constituents in the waste will leach out and migrate into the environment, possibly reaching and contaminating drinking water sources. Siting of waste management facilities in areas with highly permeable soils could facilitate leachate migration. As demonstrated above, the waste constituents appear capable of migration, mobility and persistence. Thus, if disposal sites are improperly managed or designed (e.g., lack adequate leachate collection systems), waste constituents could leach into soils and contaminate groundwater.

Health and Ecological Effects

Phenol

Congress designated phenol a priority pollutant under §307(a) of the Clean Water Act.

Phenol is readily absorbed by all routes. It is rapidly distributed to mammalian tissues. This is illustrated by the fact that acutely toxic doses of phenol can produce symptoms within minutes of administration regardless of the route of entry. Repeated exposures to phenol at high concentrations have resulted in chronic liver damage in humans.[3] Chronic poisoning, following prolonged exposures to low concentrations of the vapor or mist, results in digestive disturbances (vomiting, difficulty in swallowing, excessive salivation, diarrhea), nervous disorders (headache, fainting, dizziness, mental disturbances), and skin eruptions[4].

Chronic poisoning may terminate fatally in some cases where there has been extensive damage to the kidneys or liver.

The Office of Water Regulations and Standards, U.S. EPA[6] has found that acute and chronic toxicity of phenol to freshwater aquatic life occur at concentrations as low as 10,200 and 2,560 ug/l, respectively, and would occur at lower concentrations in more sensitive species than those tested. The available data for phenol indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 5,800 ug/l and would occur a lower concentrations among species that are more sensitive than those tested. Based on available toxicity data, the ambient water quality criteria level for phenol to protect human health is 3.5 mg/l. The ambient water criteria level to control undesirable taste and odor qualities, the estimated level is 0.3 mg/l.

OSHA has set a TLV for phenol at 5 ppm. Phenol is listed in Sax's Dangerous Properties of Industrial Materials as highly toxic via an oral route.[4] Sax also describes phenol as a co-carcinogen and a demonstrated carcinogen via a dermal route in studies done with laboratory animals. Additional information and specific references on the adverse effects of phenol can be found in Appendix A.

Naphthalene

Naphthalene is designated as a priority pollutant under Section 307(a) of the CWA.

Systemic reaction to acute exposure to naphthalene in-
cludes nausea, headache, diaphoresis, hematuria, fever, anemia,
liver damage, convulsions and coma. Industrial exposure to
naphthalene appears to cause increased incidence of cataracts.
Also, hemolytic anemia with associated jaundice and occasion-
ally renal disease from precipitated hemoglobin has been des-
cribed in newborn infants, children, and adults after exposure
to naphthalene by ingestion, inhalation, or possibly by skin
contact.

The Office of Water Regulations and Standards, U.S.
EPA[7] has found that acute and chronic toxicity to freshwater
aquatic life occur at concentrations as low as 2,300 and 620
ug/l, respectively, and would occur at lower concentrations
among species that are more sensitive than those tested. The
available data for naphthalene indicate that acute toxicity
to saltwater aquatic life occurs at concentrations as low as
2,350 ug/l and would occur at lower concentrations among
species that are more sensitive than those tested. Using the
present guidelines, a satisfactory criterion for ambient
water quality could not be derived at this time because of
the insufficiency of data for naphthalene.

OSHA's standard for exposure to vapor for a time-weighted
industrial exposure is 50 mg/m^3.

Sax lists naphthalene as moderately toxic via the oral
route and warns that naphthalene is a demonstrated neoplastic

substance via the subcutaneous route in experiments done on laboratory animals[4]. Additional information and specific references on the adverse effects of naphthalene can be found in Appendix A.

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One commenter stated that the Agency has misstated the scientific evidence for the waste constituents phenol and naphthalene with respect to attributing potential carcinogenicity to these two constituents.

The Agency agrees with the commenter and has revised the listing background document in a manner consistent with the toxicological analyses contained in Appendix A – Health and Environmental Effects Profiles of Subtitle C – Identification and Listing of Hazardous Waste, RCRA. However, the Agency still believes that these contaminants exhibit sufficient toxicity to be of regulatory concern. More specifically, prolonged exposure to low concentrations of phenol can result in digestive disturbances, nervous and skin disorders. Similar exposure to naphthalene can cause liver and renal disease.