June 1989

DEEP WELL INJECTION CHEMICAL WASTES DISPOSED AND THEIR SUBSURFACE REACTIONS

Regina M. Capuano and Charles W. Kreitler

assisted by Andrew Donnelly

Bureau of Economic Geology

The University of Texas at Austin

Austin, Texas 78713

Prepared for

U. S. Environmental Protection Agency

Office of Drinking Water

Cooperative Agreement: CR-814056-01-0

Robert Smith, Project Officer

QAe5622

ABSTRACT

More than half the liquid hazardous waste disposed of annually in the United States is disposed of by deep well injection. Little is known, however, about the chemical compositions of these wastes or about the subsurface reactions that could degrade hazardous compounds within them. This study presents the compositions of waste streams disposed of into Class I wells in Texas and their degradation processes. These Texas waste streams, which constitute 60 percent of the industrial waste disposed of annually by deep well injection in the United States, are probably representative of such injection nationwide. Phenols, chlorinated organics, cyanide, nickel, nitriles, and ketones-aldehydes compose 92 to 95 percent of the acute hazardous and toxic wastes disposed of annually.

Biodegradation, if it occurs in deep injection aquifers, is probably the most effective degradation process because it causes nearly complete consumption of the organic nutrient and can degrade the widest range of hazardous organic compounds. Hydrolysis, chemical interactions, sorption, and oxidation-reduction are other possible degradation processes. Degradation in the deep subsurface probably changes with distance from the well bore. Oxidation and hydrolysis are likely near the well bore, where solutions are oxidized and have extremely low or high pH values, whereas anaerobic microbial activity probably dominates in an outer zone where toxic compounds are more dilute, the solution is reduced, and pH conditions are near neutral.

All compounds in the waste solution must be considered when waste degradation processes are predicted. For example, generally nonhazardous carboxylic acids and their derivatives, present in 30 of the 98 waste streams studied, are highly reactive, and their presence in solution significantly affects the solution pH and hydrolysis and sorption reactions of hazardous compounds. Because carboxylic acids are generally favored as a primary substrate, their presence may either inhibit biodegradation of other primary substrates in the waste solution or enhance degradation of secondary substrates. Another common component in the organic waste streams, cyanide, is generally toxic to microbes and therefore inhibits biodegradation of other hazardous compounds. Field experiments backed up by laboratory experiments and numerical simulations are the best method for verification of waste degradation reactions. Waste-stream compositions could be altered before injection to enhance degradation and discourage unfavorable reactions using the relationships predicted from this type of experiment.

This report was submitted in fulfillment of Cooperative Agreement CR-814056-01-0 by the Bureau of Economic Geology under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from August 1, 1987, to July 31, 1988, and work was completed as of July 31, 1988.

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INTRODUCTION

More than 32.6 billion liters (8.6 billion gallons) of liquid industrial waste is disposed of by deep well injection each year (Mankin and Moffett, 1987). This constitutes more than half of the approximately 56.8 billion liters (15 billion gallons) of liquid hazardous waste that must be disposed of. In recent years the proportion of waste managed by deep well injection has increased because of limitations on other methods of disposal, such as landfills, surface impoundments, and mixing with surface soil. Therefore, until methods of waste minimization adequately limit the production of liquid hazardous waste, deep well injection is a much-needed disposal method.

Recent legislation limits deep well injection unless the injector demonstrates that the injected fluid will not migrate within 10,000 years vertically upward out of the injection zone or laterally within the injection zone to a point of discharge or interface with an underground source of drinking water (U.S. Federal Register 40CFR, part 148, subpart C, July 26, 1988). Or it must be shown that before the injected fluids migrate out of the injection zone or to a point of discharge or interface with an underground source of drinking water, the fluid will no longer be hazardous because of attenuation, transformation, or immobilization of hazardous constituents within the injection zone by hydrolysis, chemical interactions, or other means (U.S. Federal Register 40CFR, part 148, subpart C, July 26, 1988). It is unlikely that fluids are immobile in deep Texas aquifers, as evidenced by the large gradients in fluid potential produced around injection zones (Kreitler and others, 1988). In addition, improperly sealed abandoned wells and deep growth faults, both of which are common in the Gulf Coast, can provide unexpected pathways to the surface. What is needed, therefore, is to show that the hazardous chemicals will be immobilized through reactions with the sediments or transformed to nonhazardous substances.

At present little is known of the chemical compositions of waste streams disposed of by deep well injection or of the chemical reactions that limit the mobility and degradation of hazardous materials in these complex waste streams (see, for example, Strycker and Collins, 1987; appendices I and II). Most previous research on waste degradation was conducted on chemical compounds that are contaminants because of surface and near-surface usage and disposal, such as pesticides, solvents, and metals. Most studies that include chemicals commonly disposed of by deep well injection only involve surface or shallow aquifer conditions of ambient temperature, atmospheric pressure, and oxygenated fluids with aerobic microbial activity. In addition, these studies generally deal with reactions in simple waste solutions containing only the compound of interest and not the effects of other constituents commonly present in the waste solution that could control aqueous reactions or the effect of interactions with the aquifer material.

This report is a compilation of the compositions of industrial waste injected into the 98 active on-site Class I industrial waste-disposal wells in Texas. These Texas waste streams were selected for this compilation because they represent 60 percent of the industrial wastes disposed of by deep well injection in the United States and, therefore, are representative of the majority of wastes disposed of nationally. Data on compositions and injection volumes of Texas waste streams were obtained from the Underground Injection Control (UIC) files of the Texas Water Commission.

From the compilation of waste-stream compositions, the more significant hazardous chemicals and chemical groups injected (by weight) and their potential for degradation and sorption in the deep subsurface are determined. The chemical environment of subsurface injection is presented in the context of reactions and mixing with formation fluid and reactions with the aquifer material, and the degradation of significant hazardous materials in this environment is discussed. Results of experimental and numerical simulations of this environment are contrasted with field experimentation, and suggestions for future research are given.

CHEMICAL WASTES INJECTED INTO CLASS I HAZARDOUS WASTE DISPOSAL WELLS IN TEXAS

Hundreds of chemicals, both hazardous and nonhazardous, are disposed of by deep well injection each year. To augment a study of the chemical reactions of injected wastes in the subsurface the authors compiled data that include the compositions of 98 Texas waste streams, calculations of yearly injection masses, and comparisons of the chemical character of these wastes so as to determine the more significant wastes and waste groups. This section reviews the data used to select these significant wastes and waste groups.

WASTE-STREAM COMPOSITIONS

The chemical compositions of liquid-waste streams injected into all the active on-site Class I industrial waste disposal wells in Texas are compiled in appendix III. The U.S. Environmental Protection Agency (EPA) Office of Drinking Water (ODW) compiled a partial list of waste compositions (D. Morganwalp, personal communication, 1987) that includes 68 of the 98 Texas Class I injection wells compiled in appendix III. The more complete compilation of waste-stream compositions listed in appendix III was determined necessary because the waste stream compositions reported for several of the 68 Texas waste streams included in the EPA-ODW list did not include a complete list of both hazardous and nonhazardous organic compounds injected, and because the majority of the 30 Texas waste streams excluded from the preliminary EPA listing contain toxic organic wastes.

Complete lists of waste compositions are important in the regulation of hazardous waste, especially since numerous organic compounds that are currently injected have not yet been evaluated as potential hazardous wastes. In addition, knowledge of complete chemical compositions of waste streams is necessary to predict degradation reactions because degradation of hazardous components in a waste stream can be affected by all the chemical constituents in solution.

Class I waste disposal wells inject hazardous waste into a formation that is below the deepest underground source of drinking water within 0.4 km (0.25 mi) of the disposal well. This category includes disposal wells operated in conjunction with uranium-mining activities. On-site wells are used by the company that generates the hazardous waste to inject material produced at the disposal site, and off-site (commercial) waste-disposal wells are used by operators of hazardous-waste management facilities to dispose of waste brought to the site by the waste generator. Off-site waste-disposal wells are excluded from this compilation because the compositions of the waste streams injected into these wells change daily, depending on which generators submit waste for disposal on any given day. There are currently only seven active off-site Class I wells in Texas.

DATA RETRIEVAL

Data on the chemical compositions of wastes injected into Class I injection wells in Texas are from the Underground Injection Control (UIC) files of the Texas Water Commission. The Texas UIC files include copies of the original permit application and supporting data reports, annual permit reports, permit amendments, correspondence between the disposal company and members of the Texas UIC staff, and repermit reports as required by recent EPA regulations.

Compositions of the waste streams reported by disposal companies in the Texas UIC files are often generalized and incomplete, listed as containing only the selected elements and compounds that were analyzed. This analytic selectivity is particularly true of organic compositions. Often the compositions and concentrations of organic compounds that should have been present in the waste (given the nature of the manufacturing process or as indicated by a total organic carbon analysis) have not been reported (for example, WDW 16, 28, and 111 in appendix III). Analytic methods used to determine the chemical concentration have not been reported, and most of the reported waste compositions represent analyses of a single sample, usually that collected and analyzed at the time of initial permitting. This single initial analysis appears to have been then included repeatedly as the total waste composition to fulfill annual reporting and repermitting requirements.

The records show that chemical pretreatment of the waste stream by the addition of a scale inhibitor to increase formation compatibility, or by addition of an acid or base to adjust the pH to within limits set by the Texas UIC permit, is common. None of the injectors, however, listed the composition of the scale inhibitor used, and few listed the composition of the chemicals used to adjust the pH. In addition, the reports generally do not indicate whether the waste sample analyzed was collected before or after chemical pretreatment.

Concentrations of chemical components in the waste stream are reported in the data base as minimum and maximum values, but waste compositions as reported by the disposal company generally do not include minimum and maximum values. In those cases, a representative minimum and maximum concentration for each chemical constituent has been selected from all waste analyses listed for that well in the Texas UIC files. When only one concentration was reported for an element or compound, even if it was reported as an average concentration, that single value has been used in the data base as both the minimum and the maximum concentration. When both average and maximum concentrations were provided by the injector, the average concentration reported by the injector appears in the data base as the minimum concentration, and the maximum concentration is listed in the data base as the maximum concentration. If several waste analyses were provided by the injector, then the minimum and maximum concentrations as reported have been used as such in the data base.

Several injectors reported analyses for multiple waste streams but have not provided an analysis of the combined injection stream, nor have they provided the ratio at which the streams are mixed. For mixed streams, the minimum and maximum values reported in the data base are based on the assumption that waste streams are either singular or fully combined.

Often the concentrations in solution have been reported by the injector as less than the lower limit of analytic detection. Moreover, if the only analysis reported by the injector for a chemical constituent was less than the analytic detection limit, then the detection limit was used as the maximum concentration and zero as the minimum concentration in the data base. When multiple analyses were available and at least one of the analyses was above the detection limit and one below, the highest concentration reported by the injector has been included in the data base as the maximum concentration, and half the detection limit reported by the injector has been included in the data base as the minimum concentration.

On the basis of limited and inconsistent data in the Texas UIC permit reports, we recommend that the requirements of the U.S. EPA and UIC regulations to provide chemical analyses of waste be more explicit as to the types of analyses to be provided, the sampling methods, and analytic methods.

ANNUAL INJECTION VOLUMES AND WASTE PRODUCTION

A brief description of the waste-producing processes and the waste streams for the 98 wells included in this report is listed in table 1, as well as the volume of waste injected into each well in 1985 and 1986. The 1985 list of waste volumes injected is nearly complete, injection volumes being included for all but 1 of the 98 wells. The 1986 list of gallons of waste injected, however, is relatively incomplete: injection volumes have been included for only 43 of the 98 wells. Injection volumes in 1986 for the remaining 55 wells were not available at the time of this compilation. Comparison of the volumes of waste injected into the 42 wells having injection volumes available for both 1985 and 1986 yields a correlation coefficient of 0.9. This close correlation suggests that similar volumes of waste were injected in both years. Thus, 1985 injection volumes are probably representative of what was injected in 1986, and possibly of what will be injected in the future. The more complete 1985 data, therefore, have been used in the following discussion of injection volumes and masses.

The data in table 1 indicate that 19.3 billion liters (5.10 billion gallons) of hazardous industrial waste is injected annually into the 98 active on-site industrial waste disposal wells in Texas. Annual injection in Texas represents 59 percent of the 32.6 billion liters (8.6 billion gallons) of industrial waste disposed of annually by deep well injection in the United States, and Texas' wells represent half of the United States' 187 active industrial hazardous-waste disposal wells (U.S. General Accounting Office, 1987). Thus, the majority of waste disposed of in the United States is disposed of in Texas.

TABLE 1. WASTE-PRODUCTION PROCESS, GENERAL WASTE DESCRIPTION, AND GALLONS OF WASTE INJECTED IN 1985 AND 1986 FOR ACTIVE CLASS-I ON-SITE WASTE-DISPOSAL WELLS IN TEXAS.[a]

No.	Company	Plant	WDW	Process	Waste	1985 (gal)	1986 (gal)
1	Amoco	Texas City	80	refinery operation	organic, brine, caustic	13540330	33790
2	Amoco	Texas City	12	refinery operation	organic, brine, caustic	148105360	nd[b]
3	Amoco	Texas City	128	refinery operation	organic, brine, caustic	45947780	nd
4	ARCO	Channelview	36	manufacture of synthetic organic chemicals	organic	0	24750327
5	ARCO	Channelview	14	manufacture of synthetic organic chemicals	organic	77240689	nd
6	ARCO	Channelview	162	manufacture of synthetic organic chemicals	organi	44	nd
7	Asarco	Amarillo Copper	129	electrolytic refining of Cu	acid, metals	69743814	nd
8	Badische	Freeport	51	manufacture of cyclohexanone and caprolactam	organic	33780000	38287000
9	Badische	Freeport	99	manufacture of cyclohexanone and caprolactam	organic	0	0
10	Caithness Mining	Hebbronville	185	in situ mining leach for uranium and aquifer restoration	low level radioactive (Ra^{226}-U)	44302504	nd
11	Celanese	Bay City	14	chemical manufacturing	organic	57803040	66307680
12	Celanese	Bay City	32	chemical manufacturing	organic	53062560	37015200
13	Celanese	Bay City	49	chemical manufacturing	organic	5402560	34165440
14	Celanese	Bay City	110	chemical manufacturing	acid, organic	56823840	89974080
15	Celanese	Bishop	211	chemical manufacturing	organic	93793000	nd
16	Celanese	Bishop	212	chemical manufacturing	organic	12355000	nd
17	Celanese	Clear Lake	33	chemical manufacturing	organic	120029200	123720240
18	Celanese	Clear Lake	45	chemical manufacturing	organic	0	319800
19	Chevron	Palangana Dome	134	in situ leach mining for U	Ra^{226}	15046100	nd
20	Cominco Chem	Borger	115	manufacture of anhydrous ammonia and urea	alkaline ammonia-sulfate	148765918	182640372
21	Conoco	Trevino Mine	189	in situ leach mining for U	Ra^{226}	63084765	nd
22	Corpus Christi Petro	Olefins	152	manufacture of olefinic hydrocarbons	sulfide waste water from refinery	18017580	nd
23	Corpus Christi Petro	Olefins	153	manufacture of olefinic hydrocarbons	sulfide waste water from refinery	121680	nd
24	Diamond Shamrock	McKee	20	petroleum refinery, natural gas processing, NH_3 plant	ammonia, organic	82549300	nd
25	Diamond Shamrock	McKee	102	petroleum refinery, natural gas processing, NH_3 plant	ammonia, organic	11973690	11721940
26	Diamond Shamrock	McKee	192	petroleum refinery, natural gas processing, NH_3 plant	ammonia, organic	78110500	nd
27	Dupont	Beaumont	100	chemical manufacturing	organic, ammonium sulfate	80600000	80800000
28	Dupont	Beaumont	101	chemical manufacturing	organic, ammonium sulfate	145900000	143900000
29	Dupont	Ingleside	109	manufacture of chlorocarbons and freon	freon alkaline waste	0	154490
30	Dupont	Ingleside	121	manufacture of chlorocarbons and freon	freon alkaline waste	7881120	6830820
31	Dupont	LaPorte	82	manufacture of polyvinyl alcohol and vinyl acetate	acid, organic	48667900	64076118
32	Dupont	LaPorte	83	manufacture of polyvinyl alcohol and vinyl acetate	acid, organic	51258300	62969487

(continued)

TABLE 1 (continued)

No.	Company	Plant	WDW	Process	Waste	1985 (gal)	1986 (gal)
33	Dupont	LaPorte	149	manufacture of polyvinyl alcohol and vinyl acetate	acid, organic	50861400	nd
34	Dupont	Sabine River	54	manufacture of adiponitrile	organic	147576000	134877000
35	Dupont	Sabine River	55	manufacture of adiponitrile	organic	0	0
36	Dupont	Sabine River	56	manufacture of adiponitrile	organic	16137000	28086000
37	Dupont	Sabine River	57	manufacture of adiponitrile	organic	1955000	3473000
38	Dupont	Sabine River	132	manufacture of adipic acid	organic, acid	0	0
39	Dupont	Sabine River	191	manufacture of adiponitrile	organic	26708000	nd
40	Dupont	Sabine River	207	manufacture of adipic acid	organic, acid	138140000	nd
41	Dupont	Victoria	4	manufacture of adiponitrile, hexamethylenediamine	organic, cyanide, metals, alkaline	26729280	586704
42	Dupont	Victoria	28	manufacture of adipic acid, dodecanedioic acid, nitric acid	nitric acid, organic, metals	138520000	152447780
43	Dupont	Victoria	29	manufacture of adipic acid, dodecanedioic acid, nitric acid	nitric acid, organic, metals	131222340	138422500
44	Dupont	Victoria	30	manufacture of adipic acid, dodecanedioic acid, nitric acid	nitric acid, organic, metal	132608400	136931220
45	Dupont	Victoria	105	manufacture of adiponitrile, hexamethylenediamine	organic, cyanide, metals, alkaline	12722400	41194080
46	Dupont	Victoria	106	manufacture of adiponitrile, hexamethylenediamine	organic, cyanide, metals, alkaline	40907520	28335600
47	Dupont	Victoria	142	manufacture of adiponitrile, hexamethylenediamine	organic, cyanide, metals, alkaline	72298080	nd
48	Dupont	Victoria	143	manufacture of adiponitrile, hexamethylenediamine	organic, cyanide, metals, alkaline	85126509	nd
49	Dupont	Victoria	144	manf. adiponitrile, hexamethylenediamine; tritotylphosphite degradation	organic, cyanide, metals, alkaline	35848800	nd
50	Dupont	Victoria	145	manufacture of adipic acid, dodecanedioic acid, nitric acid	nitric acid, organic, metals	137275800	nd
51	El Paso Prod	Odessa Petro	16	chemical manufacturing	organic	nd	75300000
52	El Paso Prod	Odessa Petro	88	chemical manufacturing	organic	74419000	88509000
53	El Paso Prod	Odessa Petro	126	chemical manufacturing	organic	99962000	nd
54	El Paso Prod	Odessa Petro	154	chemical manufacturing	organic	37305000	nd
55	Everest Mineral	Hobson Mine	168	in situ leach mining for U and yellow cake extraction	Ra^{226}	21216830	nd
56	Everest Mineral	Las Palmas Mine	187	in situ leach mining for U	Ra^{226}	41380709	nd
57	GAF Corp	Texas City	34	organic chemical synthesis; aceteline industrial chemicals	organic	89670000	75370000
58	GAF Corp	Texas City	113	organic chemical synthesis; aceteline industrial chemicals	organic	0	16240000
59	GAF Corp	Texas City	114	organic chemical synthesis; aceteline industrial chemicals	organic	57960000	30800000
60	IEC	Three Rivers	159	in situ solution mining for U and aquifer restoration	Ra^{226}	22383821	nd
61	Iowa Beef Proc.	Amarillo Hide	120	hide processing	NaCl brine	4232702	4281406
62	Jetco	Amine	117	manufacture of nitriles and quaternary ammonium chloride	ammonia, ammonium chloride	26204283	23076808
63	Lundberg Ind	Dumas	3	potassium sulfate production	HCl	74632	53332
64	Merichem	Houston	147	hydrocarbon extraction from refinery waste	caustic, organic	85910390	nd

(continued)

TABLE 1 (continued)

No.	Company	Plant	WDW	Process	Waste	1985 (gal)	1986 (gal)
65	Mobil	Corpus Christi	150	in situ solution mining for U	Ra^{226}	29434896	nd
66	Mobil	Corpus Christi	151	in situ solution mining for U	Ra^{226}	53875008	nd
67	Mobil	Corpus Christi	197	in situ solution mining for U	Ra^{226}	68787648	nd
68	Monsanto	Chocolate Bayou	13	organic chemical production	organic	362851000	330004000
69	Monsanto	Texas City	91	chemical manufacturing	organic	74150000	7247
70	Monsanto	Texas City	196	chemical manufacturing	organic	179970000	nd
71	Penwalt	Crosby	122	organic peroxide, nitrogen compound manf.	petrochemical waste, organic	32374078	nd
72	Phillips	Borger	67	Rubber Chemical Complex	organic	4666500	1135500
73	Phillips	Borger	68	manufacture of polyphenylene sulfide (Ryton)	organic	64225000	62050000
74	Sandoz-Velsicol	Beaumont	125	organic chemical manufacturing	organic	64426834	nd
75	Sandoz-Velsicol	Beaumont	155	organic chemical manufacturing	organic	63217883	nd
76	Shell	Deer Park	172	manufacture of resins, intermediate products, solvents	organic	45232000	nd
77	Shell	Deer Park	173	manufacture of resins, intermediate products, solvents	organic	60889822	nd
78	Standard Oil-Vistron	Port Lavaca	163	petrochemical manufacturing	organic, cyanide	45275153	nd
79	Standard Oil-Vistron	Port Lavaca	164	petrochemical manufacturing	organic, cyanide	62384101	nd
80	Standard Oil-Vistron	Port Lavaca	165	petrochemical manufacturing	organic, cyanide	63412519	nd
81	Tenneco Uranium	Bruni Mine	195	in situ solution mining for U	Ra^{226}	6290923	nd
82	Tex Tin-Gulf	Texas City	237	smelting and refining	acid inorganic	2312503	nd
83	Texaco	Amarillo	135	gasoline, diesel fuel manufacturing	inorganic sulfate-chloride brine	35802890	nd
84	Texaco	Amarillo	136	gasoline, diesel fuel manufacturing	inorganic sulfate-chloride brine	54590323	nd
85	US Steel	George West	123	in situ solution mining for U	Ra^{226}	12283269	nd
86	US Steel	George West	124	in situ solution mining for U	Ra^{226}	66306226	nd
87	US Steel	George West	130	in situ solution mining for U	Ra^{226}	58606642	nd
88	US Steel	George West	140	in situ solution mining for U	Ra^{226}	10328192	nd
89	US Steel	George West	141	in situ solution mining for U	Ra^{226}	68738708	nd
90	US Steel	George West	174	in situ solution mining for U	Ra^{226}	87861744	nd
91	W R Grace	Deer Park	222	manufacture of nitroparafins	organic	0	nd
92	W R Grace	Deer Park	223	manufacture of nitroparafins	organic	11422200	nd
93	Westinghouse	Bruni Mine	170	in situ solution mining for U	Ra^{226}	16463084	nd
94	Witco	Houston	111	chemical manufacturing	organic	3365900	14846830
95	Witco	Houston	139	chemical manufacturing	organic	33442400	nd
96	Witco	Marshall	107	manufacture of organic peroxide materials	organic	92000	0
97	Witco	Marshall	180	manufacture of organic peroxide materials	organic	13856000	nd
98	Wyoming Minerals	Three Rivers	156	in situ solution mining for U	Ra^{226}	1075950	nd
				TOTAL GALLONS OF WASTE INJECTED YEARLY:		5,097,273,866	2,353,694,791[c]

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[a] Data compiled from Underground Injection Control files at the Texas Water Commission, Austin, Texas.
[b] nd = total gallons of waste injected for that year not available at the time of this compilation.
[c] The total gallons of waste injected in 1986 is well below the actual amount because of the large number of injection volumes not available.

Waste streams containing organic compounds derived predominantly from chemical manufacturing are injected into 71 of the 98 waste streams and comprise 4.09 billion (80 percent) of the 19.3 billion liters (5.10 billion gallons) injected each year (table 1). The remaining waste streams lack organic compounds, 14 percent (2.6 billion liters, or 0.69 billion gallons) of which is composed of low-level radioactive waste from uranium in situ mining operations, and which is injected into 18 wells; and 6 percent (1.3 billion liters, or 0.34 billion gallons) of which is composed of inorganic waste containing metals, chloride brine, acid, or ammonia, and which is injected into 8 wells.

WASTE GROUPS

The yearly minimum and maximum mass of each chemical constituent injected into each well (table 2) was calculated as the product of the minimum or maximum concentration of the constituent (appendix III) times the yearly injection volume for the well (table 1) (adjusting the units by assuming a fluid density of 1 g/cm^3). The total mass of each constituent injected annually was then calculated as the sum of the mass injection into each individual well annually. Annual injection masses of the waste-stream components are calculated and used in this study to determine the relative magnitude of disposal of each chemical constituent. This type of comparison permits selection of the more significant waste groups on the basis of the relative annual injection masses.

The chemicals listed in table 2 are by no means all the chemicals that are injected as constituents or the total mass of each chemical injected. The annual injection masses calculated in this study are minimum values because, as discussed earlier, most of the waste-stream analyses available in the Texas UIC files are incomplete, containing only the selected elements and compounds the injector has analyzed. Therefore, annual injection masses reported in table 2 generally have an accuracy no greater than that represented by two or three significant digits, and the reporting of a greater number of significant digits in table 2 is an artifact of the data-base program used to calculate these values.

Hazardous chemicals are noted in table 2 by superscripts that indicate whether the chemical is an acute hazard, a toxic waste only because of ignitability, or a toxic waste for reasons other than ignitability (U.S. Federal Register 40CFR, part 261, subpart D, July 1, 1987). Hazardous constituents of concern (U.S. Federal Register 40CFR, part 261, appendix VIII, July 1, 1987) are also indicated by superscripts in table 2, as are extraction procedure (EP) toxic wastes (U.S. Federal Register 40CFR, part 261, subpart C, July 1, 1987). The U.S. Federal Register lists maximum concentrations of contaminants for the characteristic of EP toxicity (table 1 in 40CFR, part 261, subpart C, July 1, 1987), and which are listed in parentheses in table 2 after the element of concern.

TABLE 2. MASS OF ALL CHEMICALS INJECTED IN 1985 AND 1986[a]

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
INORGANIC				
Na	76747308.	171358138.	28557813.	64932221.
K	2258534.	3454078.	9410.	113612.
Ca	1774374.	3438674.	483197.	520052.
Mg	298285.	542896.	83771.	86601.
Fe	283417.	465495.	33038.	42458.
Si	36215.	159386.	5595.	16234.
Al	4575.	5308.	350.	1002.
Cl	95804769.	198328813.	22642248.	84735476.
CO_3	7072922.	62959666.	1062981.	2637619.
HCO_3	13805726.	21934393.	2419103.	4532835.
ammonia	3735694.	129750862.	2486344.	114271842.
nitrate	15574145.	44604067.	8097020.	26704137.
nitrogen	17085767.	23325743.	7296114.	13480671.
phosphate	201580.	1921160.	35741.	3028136.
sulfide	628220.	23514853.	29584.	828590.
sulfate	94490593.	185736249.	56680342.	131622048.
sulfite	4714491.	9489277.	798.	3476.
B	105723.	150358.	27008.	65001.
F	26540.	303256.	21152.	264393.
I	454.	6632.	469.	6854.
Sn	80.	297.	0	0
Bi	77.	140.	0	0
Zn	4919.	701410.	2254.	1202064.
V	33853.	54335.	16194.	32408.
Mo	21092.	162399.	3997.	34104.
Mn	2327.	9975.	548.	5212.
Co	261.	2776.	246.	2898.
Cu	552532.	607478.	33058.	72956.
U	9140.	93510.	0	0
TOXIC				
CN^- (cyanide)[b,c]	5289199.	7509429.	2405308	4437993.
Ni[e]	555893.	5559119.	195724.	6360775.
Pb[c] (5.0mg/l)[d]	76135.	77419.	79.	142.
As[c] (5.0 mg/l)[d]	1153.	76157.	33.	66118.
Ba[c] (100 mg/l)[d]	18017.	20713.	748.	1053.
Cr[c] (5.0mg/l)[d]	5057.	10596.	2195.	4693.
Se[c] (1.0mg/l)[d]	33.	5637.	2.	16.
Cd[c] (1.0 mg/l)[d]	4766.	4788.	39.	53.
Hg[f] (0.2 mg/l)[d]	197.	1728.	258.	2240.
Sb[e]	113.	131.	0	4.
Ag[c] (5.0 mg/l)[d]	55.	91.	2.	23.
Inorganics Total	341,224,231	896,347,432	132,632,763	460,116,010
Inorganics Total Toxic	5,950,618	13,265,808	2,604,388	10,873,110

(continued)

TABLE 2 (continued)

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
ORGANIC COMPOUNDS				
ALKANES				
Straight-chain alkanes				
propane	0	12050132.	0	0
Cycolalkanes				
cyclohexane[i]	131030.	452260.	172189.	548116.
TOTAL	131,030	12,502,392	172,189	548,116
TOTAL TOXIC - ignitable[i]	131,030	452,260	172,189	548,116
ALCOHOLS				
Aliphatic having single carbon-carbon bonds				
methyl alcohol (methanol)[i]	1541679.	18637324.	1310101.	13713809.
ethyl alcohol (ethanol)	0	196545.	0	258283.
propyl alcohol (propanol)	0	196545.	0	258283.
butyl alcohol (butanol)[i]	207872.	502796.	20093.	278141.
pentyl alcohol (pentanol, amyl alcohol)	0	589,636.	0	774,850.
hexanol	0	655153.	0	860945.
Aliphatic having a double carbon-carbon bond				
allyl alcohol[b]	0	46165.	0	9367.
Alkyne (acetylene) alcohols - alliphatic having triple carbon-carbon bond				
hydroxymethylacetylene (propargyle alcohol)[b]	111755.	558779.	80370.	401853.
butynediol	111755.	558779.	80370.	401853.
Cyclic (nonaromatic)				
cyclohexanol (cyclohexyl alcohol)	127857.	460286.	144916.	521698.
Diols				
Vicinal diols				
ethylene glycol (ethanediol)	454310.	4543105.	469491.	4694915.
diethylene glycol	45431.	4543105.	46949.	4694915.
triethylene glycol	45431.	2271552.	46949.	2347457.
propylene glycol (propanediol)	5082769.	6310759.	1031416.	1280605.
butylene glycol (butanediol)	241591.	1205949.	74004.	803707.
ethyl propalene glycol (ethyl propanediol)	0	194456.	0	0
neopentyl glycol	52230.	52230.	0	0
Triols				
glycerol (glycerine, propanetriol)	2169023.	20083554.	0	0
Pentaerythritols				
pentaerythritol	80755.	848940.	0	0
di pentaerythritol	8437.	8437.	0	0
Oxirane-ether alcohol (heterocyclic nonaromatic)				
glycidol	52217.	52217.	0	0
Other nonaromatic alcohols				
trimethylol propane	15669.	613503.	0	0
ditrimethylol propane	0	1607.	0	0
trimethylol propane mono cyclic formal	10847.	660108.	0	0
bis-trimethylol propane mono layer formal	6026.	18079.	0	0
chlorinated				
chlorohydrin (mono-, di- and epi-)	140584.	140584.	0	0
Phenol-alcohol				
α-methyl benzyl alcohol	1214140.	1671174.	246378.	339121.
TOTAL	11,720,378	65,621,367	3,551,037	31,639,802
TOTAL TOXIC - ignitable	1,749,551	19,140,120	1,330,194	13,991,950
TOTAL TOXIC - nonignitable[h]	111,755	604,944	80,370	411,220

(continued)

TABLE 2 (continued)

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
ETHERS - HETEROCYCLIC NONAROMATIC				
tetrahydrofuran (THF)[i]	55877.	558779.	40185.	401853.
bisdioxane[f]	281169.	281169.	0	0
trioxane (metaformaldehyde)	136601.	136601.	0	0
tetroxane	30132.	30132.	0	0
TOTAL	503,779	1,006,681	40,185	401,853
TOTAL TOXIC - ignitable	55,877	558,779	40,185	401,853
TOTAL TOXIC - nonignitable	281,169	281,169	0	0
BENZENE AND BENZENE DERIVATIVES				
benzene[f]	111755.	947335.	80370.	1008475.
ethyl benzene	0	46165.	0	9367.
styrene (vinyl benzene)	0	18466.	0	3747.
anisole (methoxybenzene)	1449.	1449.	0	0
phenyl borates	6214196.	7249895.	1592343.	1857733.
trichlorobenzene[e]	483.	3381.	0	0
dichloroanisoles (dichloromethoxybenzene)[e]	11112.	11112.	0	0
TOTAL	6,338,995	8,277,803	1,672,713	2,879,322
TOTAL TOXIC - nonignitable	123,350	961,828	80,370	1,008,475
PHENOLS				
phenols (group)[g]	358923.	19074232.	8351.	13748269.
phenol[f] 1780902.	15185964.	198569.	2750711.	
cresol (cresylic acid)[f]	0	6724024.	0	5973077.
hydroquinone (1,4 benzenediol)	0	114146.	0	96173.
tertiary butyl catechol	0	883135.	0	214893.
triphenyl borane	27137.	54275.	0	0
dichlorophenol[f,e]	31886.	188422.	0	0
TOTAL	2,198,848	42,224,198	206,920	22,783,123
TOTAL TOXIC - nonignitable	2,171,711	41,172,642	206,920	22,472,057

(continued)

TABLE 2 (continued)

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
KETONES-ALDEHYDES				
Ketones				
Aliphatic				
butanone (methyl ethyl ketone)[f]	8235.	8235.	0	0
acetone (dimethyl ketone)[i]	80334.	803342.	0	0
Cyclic				
cyclohexanone[i]	12785.	127857.	14491.	144916.
Aromatic (benzene derivative)				
acetophenone (methyl phenyl ketone)[f]	101563.	286223.	20609.	58081.
Aldehydes				
aldehydes	228394.	324650.	0	0
formaldehyde (methanal)[f]	1308550.	1755573.	135230.	456713.
acetaldehyde (ethanal)[i]	492132.	2510487.	517578.	2647885.
acrolein (propenal)[b]	28290.	28290.	28066.	28066.
Chlorinated				
chloroaldehyde	454310.	4543105.	469491.	4694915.
dichloroaldehyde	454310.	4543105.	469491.	4694915.
trichloroaldehyde	454310.	2271552.	469491.	2347457.
TOTAL	3,623,213	17,202,419	2,124,447	15,072,948
TOTAL TOXIC - ignitable	585,251	3,441,686	532,069	2,792,801
TOTAL TOXIC - nonignitable	1,446,638	2,078,321	183,905	542,860
CARBOXYLIC ACIDS				
organic acids (monobasic acid, carboxylic acid)	0	20600865.	0	18735977.
formic acid (methanoic acid)[f]	63928.	1111274.	72458.	1436334.
acetic acid (ethanoic acid)	4777887.	19474744.	3106507.	18131142.
propionic acid (propanoic acid)[i]	848218.	1894876.	72458.	1436334.
butyric acid (butanoic acid)	1632508.	2679166.	72458.	1436334.
valeric acid (pentanoic acid)	952790.	13890177.	72458.	14913549.
caproic acid (hexanoic acid)	108371.	5158735.	72458.	5796651.
acrylic acid (2-propenoic acid)[i]	2645071.	2645072.	754322.	754322.
hydroxycaproic acid	3196432.	38357190.	3622907.	43474888.
TOTAL	14,225,205	105,812,099	7,846,026	106,115,531
TOTAL TOXIC - ignitable	3,493,289	4,539,948	826,780	2,190,656
TOTAL TOXIC - nonignitable	63,928	1,111,274	72,458	1,436,334
DICARBOXYLIC ACIDS				
malonic acid	1278573.	3452147.	1449162.	3912739.
succinic acid	3004010.	5505161.	1449162.	4343212.
glutaric acid	4990878.	5318454.	1449162.	1879635.
adipic acid	5404298.	7010448.	4347488.	6227124.
TOTAL	14,677,759	21,286,210	8,694,974	16,362,710
TOTAL TOXIC	0	0	0	0

(continued)

TABLE 2 (continued)

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
AROMATIC CARBOXYLIC ACIDS (BENZOIC ACID DERIVATIVES)				
Chlorinated				
2,5-dichlorobenzoic acid	109689.	1096893.	89023.	890232.
dichlorosalicylic acid (dichlorohydroxybenzoic acid)	3381.	3381.	0	0
Banvel (methylated dichlorohydroxybenzoic acid)	3865.	72470.	0	0
Dicamba (3,6-dichloro-2-methoxybenzoic acid)	4348.	42032.	0	0
Chlorinated and Nitrated				
dichloronitrobenzoic acids	1447898.	20840967.	1175106.	16914408.
TOTAL	1,569,181	22,055,743	1,264,129	17,804,640
TOTAL TOXIC	0	0	0	0
NITRILES (N derivative of carboxylic acid)				
organic nitrile compounds	2175185.	16884004.	255254.	10210188.
dinitrile 0	66423873.	0	115867290.	
acetonitrile (ethanenitrile)[f]	969336.	1368839.	355303.	751631.
acrylonitrile[f]	634488.	876247.	177966.	417804.
succinonitrile	2665995.	2665995.	2032897.	2032897.
maleonitrile	1295384.	1295384.	1285089.	1285089.
fumaronitrile	2343566.	2343566.	1747025.	1747025.
phthalonitrile	54867.	54867.	54431.	54431.
nicotinonitrile	351494.	351494.	348700.	348700.
TOTAL	10,490,315	92,264,269	6,256,665	132,715,055
TOTAL TOXIC - nonignitable	1,603,824	2,245,086	533,269	1,169,435
ESTERS (carboxylic-acid derivatives)				
methyl acetate (methyl ethanoate)	171219.	1141462.	144260.	961735.
ethyl acetate (ethyl ethanoate)[f]	0	57072.	0	48087.
butyl acetate (butyl ethanoate)	0	57072.	0	48087.
vinyl acetate (vinyl ethanoate)	308081.	3983745.	263908.	3790060.
dimethyl phthalate (phthalic acid dimethyl ester)[f]	58.	58.	0	0
Banvel methyl esters(dichlorohydroxybenzoic acid methyl ester)	4831.	4831.	0	0
sodium acetate	1025041.	4100166.	950359.	3801436.
potassium acetate	0	34243.	0	28852.
Cyclic Esters (LACTONES, deriv. of carboxylic acid)				
butyrolactone(4-hydroxybutanoic acid lactone)	111755.	558779.	80370.	401853.
TOTAL	1,620,985	9,937,428	1,438,897	9,080,110
TOTAL TOXIC - ignitable	0	57,072	0	48,087
TOTAL TOXIC - nonignitable	58	58	0	0

(continued)

TABLE 2 (continued)

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
AMIDES				
acrylamide (primary aliphatic amide)[f]	625198.	637200.	178294.	190201.
LACTAMES (heterocyclic nonaromatic amides)				
caprolactam (aminohexanoic acid lactam)	0	639286.	0	724581.
UREAS				
urea (diamide of carbonic acid)	96184.	101804.	27429.	27429.
AMINES				
Tertiary amines				
tertiary butylamine	96184.	96184.	27429.	27429.
Quaternary ammonium salts				
quarternary ammonium chloride	0	7006302.	0	6170101.
tetra ethylamine (composition of salt not indicated)	10446.	10446.	0	0
Heterocyclic aromatic amines				
pyridine[f]	0	12002.	0	11906.
methyl pyridine[f]	0	12002.	0	11906.
cyanopyridine	721383.	721383.	205724.	205724.
pyrrolidone (2-pyrrolidone)	111755.	1117559.	80370.	803706.
N-methyl pyrrolidone	923731.	2513501.	885549.	2400780.
vinyl pyrrolidone	111755.	1117559.	80370.	803706.
TOTAL	6,212,982	12,606,938	1,279,442	10,435,258
TOTAL TOXIC - nonignitable	0	24,004	0	23,812
IMINES (nitrogen ketones)				
hexamethylene imine	917214.	917214.	1205323.	1205323.
POLYMERS				
Hydropilic				
polyvinyl alcohol (PVA)	5707.	171219.	4808.	144260.
polyglycerols (an alcohol)	1205013.	1205013.	0	0
Condensation				
polyesters	0	10867870.	0	12317885.
TOTAL	1,210,720	12,244,102	4,808	12,462,145
TOTAL TOXIC	0	0	0	0
ORGANO HALOGENS				
chlorinated organics[g]	577359.	1858831.	912594.	2872153.
chlorinated hydrocarbons[g]	2008355.	6025066.	0	0
Alkyl halides				
freon 113 (a fluorinated alkyl halide)	0	2983.	0	2643.
carbon tetrachloride[f]	0	596.	0	528.
Vinyl halides				
tetrachloroethylene[f]	0	59.	0	52.
Aryl halides				
polychlorinated biphenyl (PCB)[e]	0	59.	0	52.
TOTAL	2,585,714	7,887,594	912,594	2,875,428
TOTAL TOXIC - nonignitable	2,585,714	7,884,611	912,594	2,872,785

(continued)

TABLE 2 (continued)

	1985 Minimum (kg)	1985 Maximum (kg)	1986 Minimum (kg)	1986 Maximum (kg)
ORGANIC SULFUR COMPOUNDS:				
mercaptans	0	3142965.	0	511.
beta mercaptoethanol	0	189611.	0	183190.
sulfonated organics	0	1278573.	0	1449162.
Sulfolane	0	232152.	0	224290.
Sulfolene	9.	54695.	9.	52843.
carbonyl-bisulfite adduct	0	15218025.	0	0
volatile sulfur compounds	0	13733910.	0	12490651.
TOTAL	9	33,849,931	9	14,400,647
ORGANIC PHOSPHOROUS COMPOUNDS[j]	0	6847822.	0	11945081.
OTHER ORGANICS[j]				
H-10 Defoamer	0	28536.	0	24043.
Versenex 80	0	28536.	0	24043.
TOTAL	0	57,072	0	48,086
ORGANICS : **TOTAL**	78,700,000	474,000,000	36,900,000	409,000,000
TOTAL TOXIC	15,020,000	85,200,000	5,150,000	50,100,000
TOTAL TOXIC - ignitable	6,010,000	28,200,000	2,900,000	20,000,000
TOTAL TOXIC - nonignitable	9,010,000	57,000,000	2,250,000	30,100,000

[a] The yearly minimum and maximum masses injected are calculated from the waste stream compositions taken from the Underground Injection Control files of the Texas Water Commission which are compiled in Appendix III.Hazardous wastes are indicated by superscripts which note the toxic character as listed in the Federal Register 40CFR Part 261, July 1, 1987.

[b] Acute hazard as indicated by a "P" listing or an (H) notation in the "U" listing in 40CFR261 subpart D.

[c] Compounds of this element are also considered hazardous as indicated in 40CFR261 Appendix VIII.

[d] EP toxicity with concentrations for the characteristic of EP toxicity in parenthesis as listed in Table 1 from 40CFR261 subpart C.

[e] A member of a general class of compounds that are hazardous as indicated in 40CFR261 Appendix VIII.

[f] Toxic waste as indicated by a "U" listing ub 40CFR261 subpart D.

[g] Group considered hazardous because contains common hazardous constituents in 40CFR261 subpart D in"U" or "P" listings or in 40CFR261 Appendix VIII.

[h] This total includes all wastes in the group that are toxic for reasons other than just ignitability

[i] Toxic waste only because of ignitability, 40CFR261 subpart D.

[j] For compositions of these compounds see Appendix III.

(continued)

The chemical constituents listed in table 2 are subdivided into inorganic and organic compounds. Organic compounds are separated into their primary functional groups for this study because compounds within the same functional group generally have similar chemical properties, behave similarly in chemical reactions, and often exhibit a regular gradation in physical properties with increasing molecular weight (March, 1977). These functional groups are in some cases further subdivided into structural groups for those situations in which the molecule attached to the functional group influences reactions great enough to change the style. Within a given subgroup, while the styles of reactions will be the same for all compounds, the rates and equilibrium concentrations will usually differ for different molecules. This grouping of organic compounds allows information on the reactions of individual compounds within a group to be inferred as being representative of possible reactions of other compounds within that same group. Studying the reactions of organic compounds in groups rather than individually cannot account for all reactions; however, this grouping allows comparison of the different styles of reactions that can be expected to degrade the most commonly injected chemical subgroups of organic compounds.

Of the compounds analyzed for in these waste streams, 40 are inorganic and 125 are organic. The total mass of all inorganic constituents injected annually, ranging from 341 to 896 million kg/yr, is approximately twice as great as the total mass of organic compounds injected annually, ranging from 79 to 474 million kg/yr. When the hazardous component of inorganic versus organic injection is assessed, however, this relationship is reversed. The mass of hazardous organic compounds injected annually, ranging from 15 to 85 million kg/yr, is two to six times greater, or more, than the mass of hazardous inorganics injected annually, which ranges from 6 to 13 million kg/yr. Thus, hazardous organic compounds actually comprise 71 to 87 percent of the hazardous compounds injected annually.

Of the 40 inorganic constituents disposed of, 11 are EPA-listed hazardous wastes. Seven of these hazardous inorganics have EP toxicity, two (nickel and antimony) are members of a general class of compounds considered hazardous, and one (cyanide) is an acute hazardous waste. Of the hazardous inorganics, two have injection masses in excess of 1 million kg/yr: cyanide (5 to 8 million kg/yr), and nickel (0.5 to 5 million kg/yr).

The 125 organic compounds present in waste streams are organized into 21 chemical subgroups. Twenty-six organic compounds are hazardous for reasons other than ignitability and 10 are hazardous only because of their ignitability. The hazardous wastes of greatest concern in this report are those that are hazardous for reasons other than their ignitability (referred to as "nonignitable" in table 2). The presence of compounds in subsurface aquifers that are considered hazardous only because they are ignitable is considered less important than the presence of wastes that are hazardous because of their potential toxicity. Furthermore, the ignitability of these wastes is reduced when the waste stream is diluted upon mixing with ground water. The remainder of this text will refer only to nonignitable hazardous organic compounds.

Five organic waste groups that have an annual injection of nonignitable hazardous compounds in excess of 1 million kg/yr in order of magnitude include:

phenols	2 to 41 million kg/yr,
organo halogens	3 to 8 million kg/yr,
nitriles	2 million kg/yr,
ketones-aldehydes	1 to 2 million kg/yr,

and

carboxylic acids	0.1 to 1 million kg/yr.

Of the individual nonignitable hazardous organics, six have injection masses of more than 1 million kg/yr, the two with higher masses being phenols,

phenol	2 to 15.2 million kg/yr,
cresol	0 to 6.7 million kg/yr,

followed in mass by

butanone	0.5 to 2.3 million kg/yr (a ketone),
formaldehyde	1.3 to 1.8 million kg/yr (an aldehyde),
acetonitrile	1.0 to 1.4 million kg/yr (a nitrile),

and

formic acid	0.1 to 1.1 million kg/yr (a carboxylic acid).

For comparison between injection volumes of nonignitable and ignitable wastes, note that the injection masses of two ignitable hazardous organics,

methyl alcohol	1.5 to 18.6 million kg/yr

and

butyl alcohol	0.4 to 23.2 million kg/yr,

exceed the masses of all of the above-listed nonignitable wastes.

As is discussed in the latter part of this study, nonhazardous constituents present in the waste streams might also be important in that they can limit or alter the style of hazardous waste degradation reactions. Numerous nonhazardous constituents are disposed of in much higher amounts than are hazardous constituents. Of the nonhazardous inorganic elements injected,

chloride	96 to 198 million kg/yr,

and

sodium	77 to 171 million kg/yr,

are injected in amounts in excess of 100 million kg/yr, as are the sulfur compounds,

sulfate	95 to 186 million kg/yr,
sulfide	0.6 to 24 million kg/yr,
and	
sulfite	5 to 9 million kg/yr,

and nitrogen compounds,

ammonia	4 to 130 million kg/yr,
nitrate	16 to 45 million kg/yr,
and	
nitrogen	17 to 23 million kg/yr.

The groups of organic compounds having the greater mass of hazardous and nonhazardous compounds injected include:

carboxylic acids	14 to 106 million kg/yr,
nitriles	10 to 92 million kg/yr,
and	
alcohols	12 to 66 million kg/yr.

The compositions, relative injection masses, hazardous character, and reactions of each group, which are determined as major based on their annual injection masses, are discussed and compared in the following section, and the more significant wastes and waste groups are selected.

CHEMICAL PROPERTIES OF INJECTED WASTES AND WASTE GROUPS

Hazardous chemicals injected into subsurface aquifers can be transformed into nonhazardous substances through chemical reactions. In addition, however, nonhazardous chemicals also present in the waste streams can influence the reactions of hazardous compounds and can sometimes be transformed into hazardous constituents themselves. Controls on the chemical compositions, structures, and reactions of the more significant hazardous and nonhazardous compounds injected will be briefly reviewed. Organic compounds are the focus of this discussion because they compose the greatest proportion (71 to 87 percent) of hazardous chemicals injected annually.

Formulas for organic compounds are usually written in their structural form. For a generalized representation of structural groups an R is used to indicate an alkyl (carbon chain) or aryl (aromatic ring) group, and an Ar indicates only an aryl group. Sources of information on the structure and reactivity of organic compounds to be discussed are from March (1977), Meislich and others (1977), and Wade (1987).

SIGNIFICANT HAZARDOUS WASTE GROUPS

Phenols (13-58 percent of hazardous compounds)

Phenols are benzene derivatives having a hydroxyl group (OH) bound directly to a carbon atom in the benzene ring. Phenols are more acidic than normal alcohols because of the influence of the aromatic ring.

phenol: (toxic waste) C_6H_5 OH. Phenol is a benzene ring having one of the hydrogens replaced by OH. Phenol is acidic in character, and under the proper conditions it can ionize in water as follows:

$$C_6H_5OH = C_6H_5O^- + H^+$$

cresols (methylphenol, cresylic acid): (toxic waste) $OH\text{-}C_6H_4\text{-}CH_3$. Cresols have a methyl group and hydroxyl group bound directly to a benzene ring. There are three possible cresols depending on the positions of the methyl and hydroxyl groups.

dichlorophenol: (toxic waste) $Cl_2\text{-}C_6H_3\text{-}OH$. Dichlorophenol is a benzene ring having every other hydrogen ion replaced by either a chloride or an OH group.

triphenylborane: three phenyl groups attached to a boron atom.

hydroquinone (1,4 benzenediol; 1,2 dihydroxybenzene): $OH\text{-}C_6H_4\text{-}OH$. Hydroquinone is a benzene ring having two opposing hydrogens replaced by -OH groups.

tertiary butyl cathecol: $CH_3(CH_2)_3\text{-}C_6H_3\text{-}(OH)_2$. This compound is composed of a butyl group ($CH_3(CH_2)_3$) and two hydroxyl groups (OH) replacing hydrogen ions on a benzene ring.

Phenols are given primary consideration in the study of hazardous degradation reactions because they constitute the group with the largest mass (13 to 58 percent) of hazardous material injected each year. In addition, phenol and cresol each individually constitute the larger annual injection mass of all other nonignitable hazardous wastes.

Cyanide (11-33 percent of hazardous compounds)

Cyanide (CN^-) is studied as a significant hazardous waste because of its large injection mass and acute hazardous character. The CN^- group resembles both inorganic halogens and organic nitrile compounds in reactions and, therefore, is included in the study of organic reactions.

Organo Halogens (11-20 percent of hazardous compounds)

The reactions of the alkyl, vinyl, and aryl halides differ from one another because their bonding and hybridization are different.

Alkyl Halides--

Alkyl halides have a halogen atom bonded to an alkyl group. Halogen atoms are the functional group. Reactions with this group are a result of the polarization of the carbon-halogen bond. The halogen atom can be eliminated or replaced by a wide variety of functional groups.

Freon 113: (fluorinated alkyl halide), a refrigerant

Carbon tetrachloride: (toxic waste) CCl_4, a halo methane, a solvent

Vinyl Halides--

Vinyl halides have a halogen atom bonded to one of the carbon atoms of an alkene.

Tetrachloroethylene: (toxic waste) $Cl_2C{=}CCl_2$

Aryl Halides--

Aryl halides have a halogen atom bonded to one of the carbon atoms of an aromatic ring.

Polychlorinated biphenyl (PCB): member of a group of compounds considered hazardous.

Organo halogens are the third largest mass of hazardous material injected annually. More than 99.9 percent of the mass of this organo halogen group, however, is reported as chlorinated organics or chlorinated hydrocarbons rather than as individual compounds. In contrast to the other organic subgroups, organo halogen reactions differ widely from one another depending on the structure and composition of the compound. Reactions of each organo halogen, therefore, ought to be considered individually. On the other hand, because the individual compositions of these organo halogens are unavailable, organo halogens have not been included in this study of waste degradation despite their large mass and potentially hazardous character.

Nitriles (3-13 percent of hazardous compounds injected)

Nitriles ($R\text{-}C{\equiv}N$) contain the cyano group, $\text{-}C{\equiv}N$. Nitriles, although they do not contain the carbonyl group of carboxylic acids, are considered derivatives of carboxylic acids because they hydrolyze to carboxylic acids as follows:

$$\underset{\text{nitrile}}{R\text{-}C{\equiv}N} + H_2O = \underset{\text{primary amide}}{R\text{-}CO\text{-}NH_2}$$

under basic conditions followed by

$$\underset{\text{primary amide}}{R\text{-}CO\text{-}NH_2} + H_2O = \underset{\text{carboxylate ion}}{R\text{-}CO\text{-}O^-} + NH_3 + H^+$$

or under acid conditions followed by

$$\underset{\text{primary amide}}{R\text{-}CO\text{-}NH_2} + H_2O = \underset{\text{carboxylic acid}}{R\text{-}CO\text{-}OH} + NH_4^+$$

As with other carboxylic acid derivatives, nitriles are generally insoluble in water, the smaller nitriles being somewhat soluble, and they are generally highly polar solvents. Nitriles are not very basic despite a lone pair of electrons on the nitrogen and, therefore, they do not protonate readily, which makes them good organic solvents.

dinitrile (dicyano compounds): $N{\equiv}C\text{-}R\text{-}C{\equiv}N$. (R is an aryl chain.)

acetonitrile (ethanenitrile): (toxic waste) $CH_3\text{-}C{\equiv}N$. Acetonitrile is only 10 percent water soluble at 25°C and is a highly polar solvent that solvates ions almost as well as water does, having relatively unreactive O-H and N-H groups that will not donate protons or act as nucleophiles. Deprotonation of acetonitrile produces the carbanion

$$\underset{\text{acetonitrile}}{CH_3\text{-}C{\equiv}N} = \underset{\text{carbanion}}{{}^-CH_2\text{-}C{\equiv}N} + H^+$$

acrylonitrile: (toxic waste) $CH_2{=}CH\text{-}CN$

succinonitrile: $COOH\text{-}(CH_2)_2\text{-}C{\equiv}N$

maleonitrile: $COOH\text{-}CH{=}CH\text{-}C{\equiv}N$

fumaronitrile: $COOH\text{-}CH{=}CH\text{-}C{\equiv}N$

phthalonitrile: $1,2\text{-}C_6H_4\text{-}(COOH)\text{-}CN$

nicotinonitrile: $C_6H_5N\text{-}C{\equiv}N$

Nitriles are significant as a hazardous waste group because they are the fourth largest mass of hazardous compounds injected. Nitriles are also significant for their possible effect on reactions of other hazardous compounds in solution, because they compose the second largest mass of nonhazardous organic compounds injected annually. In addition, because they are carboxylic acid derivatives (and therefore readily transform to carboxylic acids in aqueous reactions) they could have an effect on reactions in solutions in which they are contained (see discussion on carboxylic acid reactions that follows).

Ketones-Aldehydes (3-7 percent of hazardous compounds)

A ketone contains a carbonyl group (C=O) that has the carbon attached to two alkyl groups (RCOR'), and an aldehyde contains a carbonyl group attached to an alkyl group and a hydrogen atom (RCOH). Ketones and aldehydes react similarly, whether aliphatic, cyclic, or aromatic (benzene derivatives), because it is the oxygen atom of the carbonyl group that reacts and it is the bond between the oxygen and carbon atom in the carbonyl group that is most readily distorted and broken. The alkyl groups attached to the carbonyl group are less reactive.

KETONES:

butanone (methyl ethyl ketone): (toxic waste) $CH_3CH_2\text{-}CO\text{-}CH_3$
acetone (dimethyl ketone): (hazard because of ignitability) $CH_3\text{-}CO\text{-}CH_3$
Cyclic Ketone
cyclohexanone: (toxic waste) C_6H_8O
Aromatic (benzene derivative) Ketone
acetophenone (methyl phenyl ketone): (toxic waste) $CH_3\text{-}CO\text{-}C_6H_5$

ALDEHYDES:

formaldehyde (methanal): (toxic waste) H-CO-H
acetaldehyde (ethanal, "aldehyde"): (ignitable hazard) $CH_3\text{-}CO\text{-}H$
acrolein (propenal): (acute hazard) $CH_2{=}CH\text{-}CO\text{-}H$
Chlorinated Aldehydes
chloroaldehyde: $ClCH_2CHO$
dichloroaldehyde: Cl_2CHCHO
trichloroaldehyde: Cl_3CH_2HO

Ketones-aldehydes are given secondary consideration in the determination of the degradation of hazardous compounds because they are the fifth largest mass of hazardous material injected. In addition, this group includes butanone and formaldehyde, which are two of the six toxic wastes having yearly injection masses of more than 1 million kg/yr, and acrolein, which is one of the four acute toxic wastes injected in Texas.

Nickel (3-7 percent of hazardous compounds)

Nickel is the hazardous inorganic compound having the second largest annual injection mass. The general class of nickel compounds is listed as hazardous in the Federal Register 40CFR, part 261, July 1, 1987, rather than elemental nickel. The only analyses for nickel provided in the Texas UIC files, however, are for elemental nickel. Without the compositions of nickel compounds, although a discussion of the immobilization of nickel through interaction with sediments is feasible, one concerning the transformations of nickel compounds is not.

WASTE GROUPS SIGNIFICANT FOR LARGE MASSES OF NONHAZARDOUS COMPOUNDS AND THEIR REACTIVE CHARACTER

Carboxylic acids (18-22 percent of total organics)

Carboxylic acids have the carboxyl group COOH attached to an alkyl or aryl group (R-COOH or Ar-COOH). The carboxyl group is composed of an oxygen attached to the carbon by a double bond (C=O) and an OH group that has the oxygen attached to the carbon by a single bond (C-OH).

All of the carboxylic acids injected into Texas waste streams are straight-chain carboxylic acids. The majority have only single carbon-carbon bonds, the alkyl (R) group in RCOOH having one (formic acid), two (acetic acid), three (propionic acid), four (butyric acid), five (valeric acid), and six (caproic acid) carbon atoms. Hydroxycaproic acid contains an alkyl group having six carbons bound by single carbon-carbon bonds, one of the hydrogens on the aryl group being substituted with OH. Acrylic acid has two carbon atoms in the alkyl group bound by a double carbon-carbon bond. Only carboxylic acids containing five or fewer carbon atoms are highly soluble in water.

The H on the carboxyl group (CO OH) is acidic. Acid carboxylation of carboxylic acids (R-CO OH) in aqueous solution produces carboxylate ions ($RCOO^-$):

$$RCOOH = RCOO^- + H^+.$$

Salts of carboxylate ions are relatively stable, that is,

$$RCOO^- + K^+ = RCOOK.$$

Additionally, Na, K, Li, and NH_4 salts are water soluble, whereas most other salts, particularly Ca, Mg, and Fe, are generally insoluble and will deposit from solution (for example, soap scum that forms in the bathtub).

Carboxylic acids are more acidic than alcohols (ROH), and the relative strengths of acids can be accounted for in terms of their conjugate bases. The weaker (more stable base) has the stronger acid. Since the electron density in the carboxyl ion ($RCOO^-$) is dispersed to both oxygens, $RCOO^-$ is more stable and a weaker base than RO^-, whose charge is localized on only one oxygen.

Although carboxylic acids compose only the fifth largest group of hazardous organic compounds injected annually, they compose the largest group of hazardous and nonhazardous organic compounds disposed of. Degradation of hazardous carboxylic acids is, therefore, given minor consideration in the study of waste reactions. In contrast, the effects of carboxylic acids on the degradation of hazardous compounds in other waste groups are given primary consideration because of the large mass and the acidity of injected carboxylic acids. The importance of carboxylic acids in hazardous-waste reactions is further marked by their occurrence in 17 of the 71 organic waste streams injected in Texas. In addition, the presence of carboxylic acids in a waste solution is even greater than that predicted by the injection composition, because the decomposition of dicarboxylic acids and carboxylic acid derivatives results in the formation of carboxylic acids.

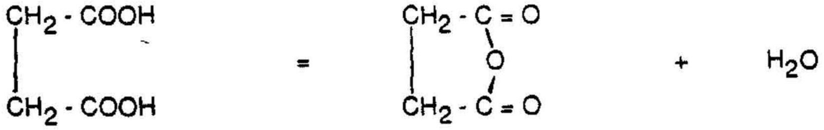
Dicarboxylic Acids--

Heating of short-chain carboxylic acids containing three or fewer carbons causes them to undergo decarboxylation to carboxylic acids and CO_2 (Meislich and others, 1977).

$$\text{malonic acid: } HOOC\text{-}CH_2\text{-}COOH = CO_2 + CH_3COOH$$

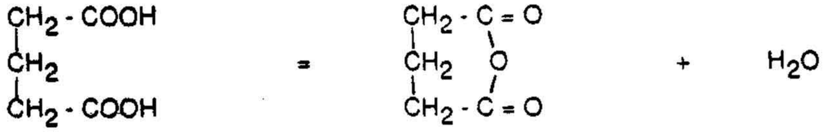
Dicarboxylic acids containing four to five carbons undergo intramolecular dehydration and ring formation to an anhydride:

succinic acid:



succinic acid succinic anhydride

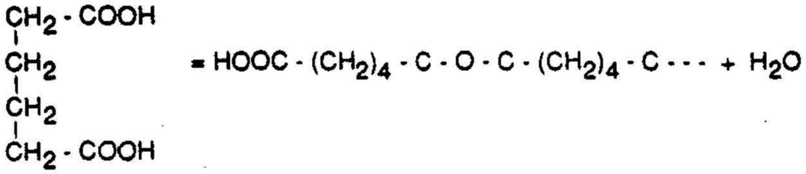
glutaric acid:



glutaric acid glutaric anhydride

Longer chain dicarboxylic acids undergo intermolecular dehydration on heating to form long-chain polymeric anhydrides.

adipic acid:



$$\begin{array}{l} CH_2 - COOH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 - COOH \end{array} = HOOC - (CH_2)_4 - C - O - C - (CH_2)_4 - C \cdots + H_2O$$

Reactivities of dicarboxylic acids are considered only because they can react similarly to carboxylic acids and decompose to form carboxylic acids. As discussed previously, the presence of carboxylic acids in solution can significantly affect the degradation and mobility of hazardous materials.

Carboxylic-acid derivatives--

Esters, amides and nitriles are carboxylic-acid derivatives that have been disposed of by deep well injection. Carboxylic acid derivatives contain a functional group that converts to a carboxylic acid by simple acidic or basic hydrolysis. Hydrolysis of carboxylic-acid derivatives generally occurs in high-temperature acid or basic aqueous solutions. The presence of carboxylic-acid derivatives in waste streams, therefore, is important because of the possible role of carboxyl ions in solution. Carboxylic-acid derivatives are generally insoluble in water, unless they have very short chains, and act as good polar solvents.

<u>Esters</u>--Esters are composed of a carboxylic acid and an alcohol with the loss of a molecule of water (R-CO-O-R'). In an acidic aqueous solution, esters hydrolyze to a carboxylic acid and an alcohol. Esters will not be considered in the study of degradation reactions because their injection mass of both hazardous and nonhazardous organic compounds is relatively low. The importance of esters is their ability to transform to a carboxylic acid.

<u>Amides</u>--Amides are composed of a carboxylic acid and an amine and have an NH and an alkyl group replacing the OH of the carboxyl (R-CO-NH-R'). Amides are a carboxylic-acid derivative; thus they are converted to a carboxylic acid and an amine by means of simple acidic or basic hydrolysis. Amides are only weakly basic and are considered neutral functional groups. A concentrated acid is needed to protonate an amide, and when the amide is protonated, the protonation occurs on the carbonyl oxygen rather than on the nitrogen atom.

acrylamide: (toxic waste) $CH_2=CH-CO-NH_2$ is a primary aliphatic amide composed of acrylic acid and an amine.

Degradation reactions of hazardous amides are not studied because the amides, like esters, constitute such a small group. The importance of amides, as with esters, is their potential to transform into a carboxylic acid and thereby contribute carboxylate ions to solution.

Nitriles (see also the discussion in "Significant Hazardous Compounds," above.) (13-19 percent of total organics)

Nitriles are important both for their large mass of hazardous and nonhazardous compounds injected annually and for their reactive character.

Alcohols (14-15 percent of total organics)

The molecular structure of an alcohol resembles that of water, an alkyl group replacing one of the hydrogen atoms of water. There is a wide variety of alcohols, the only common characteristic being that each has at least one hydroxyl group (-OH) bonded to one of its carbon atoms. Each alcohol is classified by the type of carbon atom that is bonded to the -OH group. Primary alcohols have the -OH bonded to a carbon atom that is attached to only one other carbon atom, secondary alcohols have the -OH group bonded to a carbon atom that is attached to two other carbon atoms, and tertiary alcohols have the -OH group bonded to a carbon atom that is attached to three other carbon atoms. Primary, secondary, and tertiary alcohols each react differently.

Aliphatic Alcohol Having Single Carbon-Carbon Bonds--

methyl alcohol: CH_3OH - (toxic waste because of ignitability)
ethyl alcohol: CH_3CH_2OH
propyl alcohol: $CH_3(CH_2)_2OH$ (1° or 2°)
butyl alcohol: $CH_3(CH_2)_3OH$ (1° or 2°) (toxic waste because of ignitability)
pentyl alcohol: $CH_3(CH_2)_4OH$ (1°)
hexanol: $CH_3(CH_2)_5OH$ (1°)

The compositions of propyl and butyl alcohols are reported by permit requests in the Texas UIC files without a designation as to whether they are primary (1°) or secondary (2°). Pentyl alcohol and hexanol are inferred to be primary from how they are reported. None of these alcohols were injected with the tertiary structure.

The electron pair on the oxygen makes alcohols into Lewis bases; thus it is the oxygen and the hydrogen on the OH that dominate reactions. However, the larger the R group on the alcohols (ROH) the more the alcohol begins to resemble the hydrocarbon in reactions rather than the alcohol. Hydrogen bonding occurs when alcohols have C/OH ratios less than or equal to four, making them generally soluble in water. In contrast, the hydrogen bonding with alcohols that have C/OH ratios greater than four is insignificant by comparison, making them less soluble in water.

The hydrogen of OH is weakly acidic. The order of decreasing acidity is (Meislich and others, 1977)

$H_2O > ROH(1°) > ROH(2°) > ROH(3°) > RC{\equiv}CH >> RCH_3$.

A strong base (B^-) can remove the hydroxyl proton of an alcohol to give an alkoxide ion:

$R\text{-}O\text{-}H$ (alcohol) + B^- = $R\text{-}O^-$ (alkoxide ion) + $B\text{-}H$;

that is,

$CH_3\text{-}O\text{-}H$(methanol) + B^- = $CH_3\text{-}O^-$(methoxide ion) + $B\text{-}H$.

The acidity of alcohols varies according to their structure, but generally ranges from as acidic as water for primary alcohols to three orders of magnitude less acidic for tertiary alcohols. The more highly substituted alkyl group inhibits solvation of the alkoxide ion, thereby inhibiting dissociation of the alcohol. The 1° and 2° alcohols have at least one hydrogen on the carbinol carbon and are oxidizable to carbonyl compounds.

Aliphatic Alcohol Having Double Carbon-Carbon Bond--

Allyl alcohol: $H_2C{=}CH\text{-}CH_2OH$ (acute hazard)

Alkyne (Acetylene) Alcohol (Aliphatic Having Triple Carbon-Carbon Bond)--

The acetylene alcohols listed below are straight-chain alkynes in that they have a triple carbon-carbon bond in the aryl group and are alcohols that have an OH group replacing a hydrogen on the main carbon chain. Although these wastes are alkynes, they are listed with the alcohols because the OH group on the alkyne chain is expected to have properties similar to those of the OH group on alcohols. Also similar to other alcohols, the smaller the R group the less the compound acts like an alkyne in reactions. The two alkyne alcohol wastes listed have low C/OH ratios of three and four.

Hydroxymethylacetylene (propargyle alcohol): $H\text{-}C{\equiv}C\text{-}CH_2OH$ (acute hazard)

Butynediol: is structurally either $CH_3\text{-}CHOH\text{-}C{\equiv}C\text{-}H$, which reacts like a secondary alcohol, or

$HOCH_2\text{-}CH_2\text{-}C{=}C\text{-}H$, which reacts like a primary alcohol.

The most distinctive property of the alkyne chain is its acidity, which results from the nature of the $\equiv C\text{-}H$ bond. Deprotonation of alkynes forms acetylide ions ($R\text{-}C{\equiv}C\text{-}^-$), and terminal alkynes, those having the triple bond at the end of the carbon chain, are the most readily deprotonated. Both the alkyne wastes listed below are terminal. The acetylenic proton is removed by a very strong base, but hydroxide and alkoxide ions are not strong enough to do this at low temperatures. Acetylide ions are strong nucleophiles, and therefore form alkyne salt, which can be a cation (such as sodium or in some cases metals such as Ag^+ and Cu^+). Metal salts of alkynes are relatively insoluble and in most solutions form precipitates. Alkynes having physical properties similar to those of the corresponding alkanes and alkenes are relatively nonpolar and thus insoluble in water. Alkynes are soluble in most organic solvents.

Cyclic (nonaromatic)--

Cyclohexanol: cyclo-$C_6H_{11}OH$

Diols--

Diols are alcohols having two -OH groups. Vicinal diols (glycols) are 1,2 diols, containing the two hydroxyl groups on adjacent carbon atoms. None of the vicinal diols are listed as hazardous.

Triols--

Triols are alcohols having three -OH groups.

Glycerol

Pentaerythritols--

Pentaerythritol

Dipentaerythritol

Oxirane-ether alcohol (heterocyclic nonaromatic)--

Glycidol (oxiranemethanol) - H_2C-O-$CHCH_2OH$

Other nonaromatic alcohols--

Trimethylol propane

Ditrimethylol propane

Trimethylol propane mono cyclic formal

Bis-trimethylol propane mono layer formal

Phenol alcohols--

Alcohols having the -OH group bonded directly to a carbon atom in a benzene ring are phenols. Some phenol alcohols have properties similar to those of other alcohols, whereas other properties are derived from their aromatic character. Phenols can be more acidic than other alcohols because of the influence of the aromatic ring. In this section, the alcohol-like properties of phenols are considered. In the section on benzene derivatives, the aromatic properties of the phenols are discussed and other nonalcohol phenol wastes are listed. The only phenol alcohol disposed is α-methy benzyl alcohol (CH_3-C_6H_4-CH_2OH).

Alcohols (other than phenols) compose 14 percent of the annual injection of organic compounds, which makes them the third largest group of nonhazardous organic compounds injected annually. In contrast, hazardous alcohols compose approximately 1 percent of the nonignitable hazardous organics injected annually. Most of the alcohols injected are aliphatic, diol, and triol alcohols. All of the hazardous alcohols are aliphatic and include the nonignitable acute-hazardous compounds allyl alcohol and hydroxymethylacetylene. Alcohols that are hazardous only because of their ignitability include methyl and butyl alcohols, which are the hazardous compounds having the largest injection masses. As discussed earlier, these ignitable hazardous compounds are omitted from the compilation of hazardous compounds because of their relatively small injection masses. Alcohols are instead considered to be significant because of their reactive character and large injection masses and for their possible effect on the degradation reactions of other hazardous compounds in solution.

Inorganic Nitrogen Compounds (11-23 percent of total inorganics)

Inorganic nitrogen compounds as a group compose the fourth largest mass of inorganic compounds injected annually. This group includes the acutely hazardous compound cyanide (CN^-), which has the highest injection mass of all hazardous inorganic compounds and is only second in injection mass to the hazardous organic compounds, phenols and chlorinated organics. Ammonium (NH_4^+), nitrate (NO_3^-), and nitrogen, which are also included in this group, are not listed as hazardous in the Federal Register 40CFR, part 261, July 1, 1987. Nitrate concentrations in excess of 10 mg/L, however, are considered to be unacceptable in drinking water (Federal Register 40CFR, part 141, subpart B, July 1, 1987). Microbes commonly use nitrogen for nutrients; therefore, the injection of these nitrogen compounds into the subsurface could possibly enhance microbiologic reactions and degradation. Thus, the presence of these nitrogen compounds and their possible effects on hazardous-waste reactions are discussed.

CHEMICAL PROPERTIES OF OTHER SELECTED ORGANIC COMPOUNDS NOT DETERMINED SIGNIFICANT

Alkanes

Alkanes are hydrocarbons in which the carbons are connected by single bonds; both cyclic and straight-chain alkanes are extremely weak acids. They are considered to be the least reactive class of organic compounds because they do not react with strong acids or bases or with most other reagents. As a result of their nonpolar and unreactive nature, alkanes are used as solvents, fuels, and lubricants. Alkanes are referred to as hydrophobic because they do not dissolve in water. Alkanes are less dense than water, having densities on the order of 0.7 g/cm^3 at 20°C compared with the density of water of 1.0 g/cm^3 at the same temperature. Insoluble alkanes injected with water, therefore, will generally rise relative to the water once in the formation.

Straight-chain (normal) and cyclic alkanes resemble one another in their properties and chemistry. Cycloalkanes are also nonpolar and relatively inert compounds. Cycloalkanes are held in a more compact cyclic shape than aliphatic alkanes and therefore have physical properties more similar to the compact, branched alkanes.

Most alkane reactions take place under high-temperature conditions. Thermal cracking of large hydrocarbons results in smaller hydrocarbons in the form of alkanes and alkenes. In the presence of water, hydrocracking at high temperatures yields saturated hydrocarbons. Given the proper high-temperature conditions, alkanes can halogenate through reactions with halogens to form alkyl halides.

Straight-chain alkanes--

Propane: $CH_3CH_2CH_3$

Cycloalkanes--

Cyclohexane: C_6H_{12} - (toxic waste because of ignitability)

Alkanes are not considered significant for inclusion in the study of waste-degradation reactions because they are relatively unreactive and they compose less than 3 percent of the organic compounds and less than 1 percent of the hazardous organics disposed of annually.

Ethers

Like alcohols (R-O-H), ethers (R-O-R') are relatives of H_2O (H-O-H), alkyl or aryl (benzene ring) groups (R) replacing the hydrogens. Although ethers are quite polar and have large molecular dipole moments, they are relatively unreactive. Ethers lack the OH of alcohols; instead the oxygen has nonbonding electrons that act as a solvate pair. The oxygen of ethers is able to undergo hydrogen bonding with the hydrogen of H_2O. Ethers are very volatile because of the absence of intermolecular hydrogen bonding. Ethers are basic because of the unshared electron pair on the oxygen; they are also extremely flammable.

Heterocyclic Nonaromatic Ethers--

Tetrahydrofuran (toxic waste because of ignitability) and dioxane (toxic waste) are polar, nonhydrous solvents that are miscible in water. These compounds have one oxygen substituted for a carbon in a five-carbon ring (single bonds) and two oxygens substituted for two carbons in a six-carbon ring (single bonds), respectively. Trioxane is a metaformaldehyde, an oxygen substituted for every other carbon in a six-carbon ring. Tetroxane has four oxygens substituted on a six-carbon ring.

Ethers are relatively unreactive and compose only a small component of both the hazardous and nonhazardous organic wastes injected and, therefore, are not considered a significant waste group.

Benzene and Benzene Derivatives

Electrophilic aromatic substitution is the most important mechanism involved in the reactions of aromatic compounds. Substitutions on the ring influence its reactivity toward electrophilic aromatic substitution and the positional orientations found in the products. The overall reaction is the substitution of an electrophile for a proton (H^+) on the aromatic ring. This is the process of halogenation to ArBr (bromination), ArCl (chlorination), and ArI (iodination), nitration to $ArNO_2$, sulfonation to $ArSO_3H$ (benzene sulfonic acid), and others. Ar in the structural formulas indicates the aryl group (an aromatic ring), which in this discussion is always a phenyl group (benzene ring).

Benzene: C_6H_6 (toxic waste), the benzene ring, is unusually stable, being marked by its inability to undergo typical alkene reactions.

Benzene derivatives are composed of a benzene ring having one or more hydrogens substituted with a functional group

ethyl benzene: C_6H_5-CH_2-CH_3

styrene (vinyl benzene): C_6H_5-$CH=CH_2$

anisole (methoxybenzene): C_6H_5-O-CH_3

phenyl borate: The phenyl group is an aryl group composed of a benzene ring having one hydrogen atom replaced so as to attach the ring to any one of a wide range of compounds containing boron, hydrogen and oxygen (such as $B(OH)_4^-$ or BO_3).

trichlorobenzene: (member of a general class of hazardous compounds) $C_6H_3Cl_3$, composed of a benzene ring having every other hydrogen replaced by a chloride.

dichloroanisole (dicholoromethoxybenzene): (member of a general class of hazardous compounds) Cl_2-C_6H_3-O-CH_3, composed of a benzene ring having every other hydrogen replaced twice by a chloride ion and a third by -O-CH_3.

Benzene and benzene derivatives comprise only a small fraction of nonhazardous (2 to 8 percent) and hazardous (2 percent) compounds injected annually and, therefore, are not one of the significant waste groups.

Lactames

Lactames are heterocyclic nonaromatic amides. They are formed from amino acids, in which the amino group and the carboxyl group have joined to form an amide. Caprolactam is an aminohexanoic acid lactam. Lactams compose only a small proportion of the organic wastes injected, and caprolactam is not hazardous; therefore, lactams will not be considered in the study of degradation reactions.

Amines

Amines are derivatives of ammonia having one or more alkyl or aryl group bonded to the nitrogen atom. Amines encourage biological activity by providing a food source. Amines react differently depening on whether they are one, two, three, or four substituted.

tertiary butylamine: $(CH_3)_3$-C-NH_2

quaternary ammonium salts: have four alkyl or aryl groups replacing the hydrogens on the NH_4^+ ion, with the addition of a halogen to create a neutral compound.

pyridines: C_5H_5-N have a benzene ring that has nitrogen substituted for a carbon on the ring. Pyridine protonates to pyridinium ion in acid solutions, a hydrogen attaching to the nitrogen on the ring and yielding an aromatic, positively charged ion (C_5H_5-NH^+).

pyrrolidones: O=C_4H_8-NH are five-member heterocyclic rings having a nitrogen substituted for one of the carbons on the ring and an oxygen replacing the two hydrogens bound to one of the carbons on the ring.

Amines form only a small fraction of both the hazardous and nonhazardous organic compounds injected and therefore are not a focus of the study of degradation reactions. But because amides may be used as a food source they may contribute to microbiologic reactions and therefore are considered in that context.

Polymers

A polymer is a large molecule composed of many smaller repeating units (the monomers) bonded together. Polymers are not considered a significant waste group because they compose only a small fraction (1-2 percent) of the mass of nonhazardous organics injected annually and no hazardous compounds.

SELECTION OF SIGNIFICANT WASTE GROUPS

Waste groups can be subdivided into two on the basis of their significance for the future study of their subsurface chemical reactions after injection. The first subdivision is those that are significant because they are hazardous and a large percentage is injected annually. The second subdivision is those significant not because they are hazardous but because they are very reactive and have a large annual injection mass. The nonhazardous but reactive wastes can strongly influence the reactions of hazardous wastes in the solution, as well as reactions between the solution and the enclosing sediments.

Of the waste groups that are significant because they include a large mass of injected hazardous compounds, the phenol group is the most significant, followed by organo halogen, cyanide, nickel, nitriles, and ketones-aldehydes. Of these significant hazardous waste groups, organo halogens and nickel are not considered in the discussion of waste reactions that follows because, although individual compounds in these groups react differently from one another, information on the compositions of individual compounds within these groups was unavailable.

Of the waste groups selected not because of the hazardous component but because of large injection masses and because of their possible influence on reactions in the solution in which they are contained, carboxylic acids are the most significant. Nitrogen compounds, which include nitriles and cyanide, are also significant for reasons other than their hazardous character, particularly because of their ability to influence microbiologic reactions. Alcohols, having the third largest mass of nonhazardous organic compounds injected annually, are much less reactive than carboxylic acids and are given lower priority.

REACTIONS OF SIGNIFICANT WASTE GROUPS

The transformation and sorption reactions of the significant hazardous and nonhazardous waste groups are discussed below. Consideration is given to interactions of hazardous wastes with other compounds present in the waste solution, such as other hazardous or nonhazardous compounds that are commonly injected and highly reactive. Attention is also given to reactions in aqueous sodium-chloride solutions at elevated temperatures (50 to 80°C) and hydrostatic pressures (2.5 to 4.5 kbar), common in injection aquifers. The full pH range is considered because the pH of the waste streams injected ranges from 0.3 to 13.5 (appendix III).

HAZARDOUS WASTE REACTIONS

Phenols

Phenols can undergo reactions that involve the benzene ring or the functional group (OH). Electrophylic substitution of phenols is common in which a halogen, nitrate, sulfate, or other ion is substituted for a hydrogen on the benzene ring. This can result in the formation of halogenated phenols, which in some cases are more toxic or more resistant to degradation than is the nonhalogenated form.

Dissociation--

The acid dissociation constant, pK_a, for phenol dissociation

$$ArOH \Leftrightarrow ArO^- + H^+$$

equals

$$pK_a = [ArO^-][H^+]$$

where $[ArO^-]$ and $[H^+]$ are the activities of the ions in solution. At $pH > pK_a$ the dissociated phenoxyl ion $[ArO^-]$ is dominant in solution over the undissociated parent phenol compound. The pK_a of the phenol group compounds is generally above 7 at ambient temperatures, having values of 9.8 for cresol and 9.8 and 13 for the two phenolic groups in catechol (Thurman, 1985). The chlorinated phenols have much lower pK_a values at ambient temperatures ranging from 4.75 to 9, the higher chlorinated phenols having lower values (Schwarzenbach and Westall, 1985). For example, $pK_a = 4.75$ for pentachlorophenol, 5.40 for 2,3,4,6 tetrachlorophenol, 6.35 for 2,3,4,5-tetrachlorophenol, and 6.94 for 2,4,5-trichlorophenol. Phenol ionization can result in phenol reactions such as sorption being dependent on pH and solution ionic strength.

Sorption--

Phenol mobility in subsurface aquifers is inhibited by sorption on clays and organic surfaces. Ionization of phenols, as is true of other ionizable (anionic) hydrophobic compounds such as amines and carboxylic acids, reduces their sorption onto natural organic carbon in sediments (Schwarzenbach and Westall, 1985). In low pH solutions, in which phenol is present in its unionized form, sorption is highest and decreases with increased pH over a pH range of $pH - pK_a = 0$ to $pH - pK_a = 2$. Sorption is lowest in solutions with $pH - pK_a > 2$, in which phenoxy ions dominate. In these basic solutions sorption becomes ionic strength dependent (increased sorption being in higher-ionic-strength solutions).

Phenol sorption on Frio sandstone samples collected from Gulf Coast sediments at a depth commonly used for deep well injection, 2.18 m (7,155 ft), was tested by Collins and Crocker (1988). These phenol sorption tests were conducted at temperatures of 38° and 60°C and at pressures equivalent to hydrostatic at the depth from which the samples were collected. The sorbant in the Frio sand was the kaolinite that was present as 3 weight percent of the sediment. Flow-through experimental results indicate that phenol sorption increases with increased phenol concentration in solution and decreases with increased temperature. One kilogram of the Frio sandstone having 36 percent porosity could adsorb 13 percent (at 38°C) to 7 percent (at 60°C) of the phenol from pore fluid containing 500 mg/L phenol, and 22 percent (at 38°C) and 19 percent (at 60°C) of the phenol from pore fluid containing 10,000 mg/L phenol. The pH of the solutions in these flow-through experiments started at 5.7 and shifted to a final pH of 8.1 during the experiment. The pH dependence of phenol sorption on clay minerals was not considered in the experiments of Collins and Crocker (1988). Over the pH range of their experiments phenol was probably unionized and so the results represent maximum phenol sorption.

A flow-through experiment conducted to test the desorption of phenol sorbed by the Frio sandstone showed phenol not to be desorbed by a dilute sodium chloride solution (Collins and Crocker, 1988). This desorption experiment, however, did not test for the possible desorption of phenol by more complex solutions.

Results of these experiments on the sorption of phenolic compounds by clay minerals and organic material indicate that sorption can act to retard phenolic compound mobility in the deep subsurface and that the lack of phenolic desorption suggests that this retardation may be permanent. The efficiency of this process depends on the amount of sorbing surface, temperature, pH, ionic strength, the concentration of the phenolic compound in solution, and the absence of other aqueous compounds that might be preferentially sorbed.

Oxidation--

Phenols oxidize readily, and since the hydroxyl (OH) group in phenols is attached to a benzene ring rather than a hydrocarbon chain as in alcohols, phenols oxidize more readily than do alcohols (Rinehart, 1973). Although there are many products of the oxidation of phenols, phenols commonly oxidize to the corresponding quinone.

$$\underset{\text{phenol}}{C_6H_5\text{-}OH} + O_2 \Rightarrow \underset{\text{quinone}}{O{=}C_6H_4{=}O} + H^+ + e^-$$

Quinones exist as a redox couple, phenols existing at a redox potential of approximately -0.7 volts (Thurman, 1985). Given the relationship between Eh and pH at 25°C for this coupling, the equation

$Eh = E^\circ + 0.059\ pH$ (see Garrels and Christ, 1965)

indicates that the oxidation of phenols to generally nonhazardous quinones is favored in shallow, oxidized ground waters. Equilibrium relationships at the high temperatures present in the formations of deep well injection were not determined because of the lack of available thermochemical data for these calculations. It is possible, however, that phenol oxidation to quinones could proceed in an injected waste stream at least until the solution becomes reduced by reactions with the aquifer material and mixing with the reduced formation fluid. Information on the rate of phenol oxidation was not located but, in general, oxidation reactions proceed more rapidly in the presence of bacteria. Thus, phenol degradation by aerobic bacteria and oxidation could possibly be enhanced by the introduction of oxygen into the disposal formation. The effects of added oxygen on other reactions, however (such as the formation of gypsum as a result of the transformation of sulfide to sulfate and subsequent sealing of the formation), must be considered.

Microbial Degradation--

Microbial degradation of phenolic compounds in waste-treatment water and water in surficial and near-surface environments is well studied (appendix I). From this work it is well established that phenolic compounds are readily degraded by aerobic bacteria (Chapman, 1972). Microbial degradation is a favored method of hazardous-waste treatment of phenolic compounds because the common products of microbiologic degradation of phenolic compounds are generally nonhazardous carboxylic acids and catechols.

The potential for anaerobic degradation is greater than for aerobic degradation in the deep well injection environment because of the general lack of oxygen in deep subsurface aquifers. Recent experiments on the anaerobic degradation of phenolic compounds suggest that phenols could be successfully degraded by methanogenesis and sulfate reduction under anaerobic conditions in subsurface aquifers (Healy and Young, 1978; Suflita and others, 1988). This work indicates that upon introduction of the phenolic compounds to the subsurface environment there is an acclimation period of

10 days to 1 year before anaerobic biodegradation begins. The success of methanogenesis has been found to be dependent on pH and temperature (Beeman and Suflita, in press). Over a pH range of 5 to 9 and temperature range from 5 to 45°C, the optimum conditions for methanogenic degradation of phenolic compounds are pH 8 and 35°C. Batch experiments of the anaerobic degradation of pentachlorophenol were conducted on ground water collected from pentachlorophenol-contaminated sediments at a depth of 7.3 m (24 ft). These experiments suggest that low concentrations of pentachlorophenol, 0.1 mg/L, are microbially degraded in the shallow subsurface at a rate of 10 to 15 percent a week (Lee and others, 1984).

Whereas phenols in low concentrations can be consumed by microbial populations, in elevated concentrations phenols can be toxic to the same microbes (Gaudy and Gaudy, 1980). Anaerobes have been shown to acclimate with time so as to tolerate concentrations of pentachlorophenol as high as 250 mg/L. Furthermore, while these high concentrations were tolerated the microbes did not consume the pentachlorophenol as a substrate. In waste-treatment plants, either phenolic compounds are removed before microbial digestion of the waste or care is taken not to shock the microbial population by changing the concentration of the phenolic compounds during treatment processes (Gaudy and Gaudy, 1980). Similar measures may be necessary for the deep well injection of wastes containing phenols, if microbial degradation is the desired method of subsurface decomposition of the phenol or of other contaminants in the solution.

Anaerobic consumption and sorption are the most likely methods of purifying phenolic waste solutions. Oxidation and aerobic activity are less favored under the generally reducing subsurface conditions in the injection aquifer, except possibly at the point of injection. The experimental work discussed previously suggests that both phenol biodegradation and sorption can be enhanced by adjustment of the solution pH, temperature, and composition. Phenolic biodegradation may be most successful when the waste stream is introduced slowly, allowing the bacterial population to acclimate. Once bacteria are acclimated, the waste should then be injected continuously and at a uniform composition to maintain the bacterial population.

Cyanide

Cyanide, CN^-, is a negatively charged ion that is a prototype of the cyano group, -CN (Rappaport, 1970), and, therefore, its reactivity is in part related to that of the nitriles. Cyanide forms hydrogen cyanide in acidic aqueous solutions with pK_a's of 9.63, 9.21, and 8.88 at 10, 25, and 40°C, respectively (Sharpe, 1976). The cyanide ion acts similarly to halogen ions, such as Cl^-, in solution, readily forming complexes with cations, particularly those of the transition metals (Sharpe, 1976). Addition of cyanide to a complex waste stream, therefore, can increase the mobility of hazardous metals by forming complexes that inhibit their sorption.

Hydrolysis--

Cyanide hydrolyzes to formamide and then to formic acid. The rate of cyanide hydrolysis at 30°C, calculated by Scrivner and others (1986), is most rapid in basic solutions, $pH > 9$, having a half life of approximately 3 years. In lower pH solutions this half life decreases to a low of 270,000 years at a pH of 4. A further reduction in pH increases this half life to 1,000 years at a pH of 2. An increase in temperature increases the rate of cyanide hydrolysis by a factor of 2 for every 10 to 15°C increase (Scrivner and others, 1986). At temperatures at the depths commonly used for deep well injection along the Texas Gulf Coast of 60 to 80°C, the half life of cyanide hydrolysis would be less than 1 year in basic solutions having an approximate pH of greater than 9 and on the order of 300 yrs at a pH of 7, while hydrolysis rates in more acidic solutions would remain slow, having half lives on the order of thousands of years. Cyanide hydrolysis could be a significant degradation process if the waste stream were to maintain a neutral to basic pH and temperatures on the order of 60°C or greater in the aquifer. Otherwise, under more acidic conditions or cooler temperatures, hydrolysis rates may be too slow to result in adequate degradation within the timeframe of concern. Cyanide hydrolysis could be enhanced by injection of the waste into deeper, higher temperature aquifers than currently used. The half life of cyanide hydrolysis at pH 7 could be reduced from 1,000 years at 30°C to approximately 10 years at 100°C.

Oxidation--

Oxidation of cyanide to cyanogen (C_2N_2) or cyanate (OCN^-) is favored under oxidized conditions at ambient temperatures (Sharpe, 1976). Oxidation in the reduced injection environment, however, is unlikely.

Chemical Interactions--

Cyanide transformation to hydroxynitriles is favored upon injection with a ketone-aldehyde organic waste stream (Rappaport, 1970). This reaction, $R\text{-}CO\text{-}R' + CN^- + H^+ \Leftrightarrow R\text{-}COHCN\text{-}R'$, is favored in acid solutions. Hydrolysis of these hydroxynitriles to ammonium and the corresponding hydroxy-carboxylic acid is then favored.

Microbial Degradation and Toxicity--

The presence of cyanide in solution has been found in laboratory experiments to inhibit the anaerobic degradation of the alcohols, methanol and propanol, the carboxylic acid, acetic acid, and phenol (Lewandowski, 1984). It is the inhibition of acetic acid biodegradation by cyanide that ultimately limits the anaerobic degradation of phenolic compounds. However, anaerobic biodegradation of phenolic compounds does take place in the presence of cyanide, although the greater the presence of cyanide in solution the slower the phenolic degradation (Fedorak and others, 1986). In the process of anaerobic degradation of phenols, a first group of microbes degrades the phenolic compound to acetic acid and a second group of methanogenic bacteria converts the acetate to methane. The first step, the degradation of phenolic compounds, occurs uninhibited in the presence of cyanide. However, the second step, methanogenic degradation of the acetic acid product, was inhibited by the presence of cyanide. Phenolic biodegradation was, therefore, slowed in the presence of cyanide because of the accumulation of the acetic acid by product in solution.

In contrast, the denitrification of ketones and aldehydes is made possible by the presence of cyanide and results in the removal of both the ketone-aldehyde and cyanide. Ketone-aldehyde biodegradation in the presence of cyanide is displayed in experimental work on acetone degradation in cyanide-contaminated solutions (Lewandowski, 1984). In this work, acetone-cyanide reactions to produce hydroxynitriles are credited with permitting the biologic degradation of ketones, despite the toxic effects of cyanide, and with the removal of cyanide from the solution. Biodegradation of acetone in the presence of cyanide was also found to be pH dependent because of the pH dependence both of hydroxynitrile formation from acetone-cyanide reactions and of the hydrolysis of the resulting hydroxynitrile. Biodegradation of acetone by denitrifying bacteria in the presence of cyanide was favored in more acid solutions, pH < 7.9 at 25°C, in which the reaction of acetone with cyanide to form a hydroxynitrile and hydroxynitrile hydrolysis are favored. In basic solutions acetone biodegradation was unsuccessful.

The effects of cyanide concentrations of approximately 8 mg/L on nitrile biodegradation also were found to be minimal, as evidenced by a field study of subsurface nitrile degradation (Ehrlich and others, 1979; Vecchioli and others, 1984). In this study not only did the acrylonitrile waste completely degrade from concentrations of 26 mg/L, but a reduction in cyanide in backflush samples indicates that cyanide also degraded. Acetone concentrations in backflush samples of 1.5 mg/L were equivalent to the injection concentration, suggesting that acetone was not degrading. The persistence of acetone may have been caused by the solution being basic and having a pH ranging from 7.9 to 8.2, in which case acetone-cyanide reactions are inhibited. Another possible reason for the persistence of acetone is that nitrile degradation is favored over ketone degradation in the presence of cyanide. Although these reactions were attributed to biodegradation, the reported transformation could have been the result of cyanide/nitrile reactions producing a hydroxynitrile (as indicated above), which then degraded by hydrolysis or biodegradation.

The toxic effects of cyanide in surface treatment plants have been well studied (Gaudy and Gaudy, 1980). Similar to phenolic-waste toxicities, microbial populations that tolerate cyanide concentrations of as much as 20 mg/L can be developed if the cyanide is introduced into the system slowly, so as not to shock the microbes, and is injected continuously so as to support the population's resistance, once developed. With increases in cyanide levels from 5 to 10 to 15 to 20 mg/L, the microbial populations took from 2 to 4 weeks to adapt and return to initial levels of organic and cyanide consumption. In these cyanide systems, a small portion of the microbial population is believed to metabolize cyanide, with the majority of the population having a selective resistance to cyanide's inhibitory effects.

These results suggest that cyanide degradation is minimal unless cyanide is injected with organic compounds such as ketones, aldehydes, or nitriles, which can include cyanide in their degradation reactions, or is injected in basic solutions having a pH $>$ 9, in which case cyanide will hydrolyze to formamide and ultimately formic acid. On the other hand, cyanide could inhibit its biodegradation and that of organic compounds because of its toxicity if it is not injected in a solution that results in its transformation. To counteract this inhibitory effect, the aquifer could be pretreated, allowing a microbe population to develop that has a resistance to the cyanide levels and that consumes cyanide. Once this population is developed, waste injection needs to be continuous, maintaining uniform levels of cyanide, and thus maintaining the population's resistance. If subsurface degradation of hazardous industrial wastes is planned as a method of waste mediation, then cyanide toxicity is a problem that should be addressed, particularly since cyanide is a component in 26 of the 98 industrial-waste streams injected into Texas aquifers. In addition, undegraded cyanide can complex with metals in the waste stream and increase their mobility.

Nitriles

Hydrolysis--

During hydrolysis the nitriles initially convert to an amide, which then hydrolyzes to a carboxylic acid and ammonia (March, 1977). The rate of acetonitrile hydrolysis at 30°C was calculated by Scrivner and others (1986), who found that acetonitrile hydrolysis is fastest in basic solutions having a half life of less than 1 year at a pH of 12. With decreased pH the half life of acetonitrile hydrolysis decreases rapidly to a half life of more than 1,000 years at a pH of 9 to a maximum half life of more than 1 million years at a pH of 6. In more acidic solutions acetonitrile half lives decrease to approximately 1,000 years at a pH of 2. In a way similar to that of cyanide, the hydrolysis half life for acetonitrile drops by a factor of 2 for every 10 to 15°C increase. Between the common injection aquifer temperatures of 60 to 80°C the acetonitrile half life should be on the order of 100 years or less at a pH of 9 or greater, or a pH of 2 or less, and 1,000 years at pH's of 8 and 3. For the pH range between 8 and 3, the hydrolysis half life should remain very slow, ranging from thousands to hundreds of thousands of years. In a way similar to that of cyanide, injection of the waste into deeper and higher temperature aquifers would favor degradation by hydrolysis. At 100°C the half life of approximately 1 million years at pH 7 might be reduced to about 10,000 years.

The presence of the acetate ion in solution has been found to accelerate the rate of hydrolysis and in some cases catalyze the process (Wade, 1987). Nitrile hydrolysis may be reversed, ammonia and carboxylic acids reacting to form nitriles at elevated temperatures (March, 1977). It is possible, therefore, that hazardous nitriles may develop in ammonia-rich carboxylic acid solutions subjected to elevated temperatures in the injection aquifer. Both ammonia and carboxylic acids are commonly present in the waste streams injected.

Sorption--

Information on sorption at the elevated temperatures of the deep well injection environment is limited. However, it is known that sorption of nitriles onto clay minerals or organic material in aqueous solutions is not significant at low temperatures (Callahan and others, 1979). Short chain n-alkyl nitriles in concentrations of 5,000 mg/L in a 2-ml n-hexane solution were 40 to 85 percent sorbed by 1 g of montmorillonite after 1 week of contact at 60°C (Charlesworth, 1986). It is possible, therefore, that nitrile sorption could reduce nitrile mobility in deep aquifers.

Biodegradation--

Aerobic degradation of nitriles is well documented (see, for example, Smith and Cullimore, 1974; DiGeronimo and Antoine, 1976); however, little experimental work has been done on anaerobic nitrile degradation. Subsurface degradation (at 400 m) of acetonitrile by denitrifying bacteria under anaerobic conditions was documented in a backflush experiment at the American Cyanamid Company's waste-injection site outside Pensacola, Florida (Ehrlich and others, 1979). Acetonitrile concentrations were reduced by half in the 4.5 days that the waste solution remained in the aquifer. Flow-through tests conducted at the same site showed that having a longer residence time, up to 2.5 years, the acetonitrile was completely degraded, along with nitrate and alcohol, which also were in the waste stream (Vecchioli and others, 1984). Cyanide injected into this waste stream degraded and appeared not to prevent the activity of denitrifying bacteria.

Nitrile biodegradation followed by sorption and hydrolysis are possible mechanisms for removing hazardous nitriles from deep-aquifer fluids. The contribution of hydrolysis to nitrile degradation is dependent on the pH and temperature of the solutions. The subsequent shift in the pH of the waste solution toward neutral after injection decreases the rate of nitrile hydrolysis, whereas the increase in temperature increases the hydrolysis rate, although to a lesser degree.

Ketones-Aldehydes

Chemical Interactions--

Ketones and aldehydes can react as both acids and bases (Wade, 1987). The carbonyl oxygen, -COH, which is double-bonded to the carbon atom and has two nonbonding pairs of electrons, can act as a base and attack either a proton or an electrophile to form a new bond. Otherwise, the carbonyl acts as an acid having a strong nucleophile attached to the carbon, which leaves a negative charge on the oxygen atom of the carbonyl group. Despite the potential reactive character of ketones and aldehydes in aqueous solution, the effects of these reactions in deep injection aquifers on the degradation of hazardous ketones and aldehydes generally have not been studied.

Sorption--

Sorption of ketones and aldehydes by both clays and organic material in sediments can be a significant retardant to the mobility of these compounds, provided that the sediments contain sufficient amounts of the sorbing material (Donaldson and others, 1975; Khan and others, 1979; Briggs, 1981; Southworth and Keller, 1986). Experiments on the sorption of formaldehyde (an aldehyde) at 25°C, from an acidic waste solution (pH = 4) that also contained several carboxylic acids, showed that formaldehyde did not sorb onto sandstone aquifer material (Leenheer and others, 1976b). The carboxylic acids instead of the formaldehyde, were strongly sorbed from the solution.

Biodegradation--

Most research on biodegradation of ketones and aldehydes covers aerobic rather than anaerobic activity (see, for example, Grula and Grula, 1975). Anaerobic denitrification of ketones and aldehydes in the presence of cyanide has been documented by Lewandowski (1984). However, in two studies (Ehrlich and others, 1979; Vecchioli and others, 1984) it was found that acetone (a ketone) injected into a subsurface aquifer in a nitrate-nitrile-cyanide waste stream was not consumed by denitrifying bacteria that consumed the nitrate, nitrile, and cyanide. Heptaldehyde (an aldehyde) injected in a waste stream that did not include nitriles or cyanide into a subsurface aquifer, where anaerobic conditions prevailed

(Roberts and others, 1978), was found to biodegrade by 69 percent in the 12 hours it took the injected fluid to reach a nearby monitor well (Rittmann and others, 1980). Roberts and others (1978) concluded that the heptaldehyde was used as a secondary substrate by the bacteria, which accounted for the incomplete degradation.

Laboratory experiments were conducted on an aqueous solution containing formaldehyde (in concentrations of less than 18 mg/L), acetic acid, methanol, nitrate, and phosphate as a waste stream (Elkan and Horvath, 1977). It was found that anaerobic activity degraded the carboxylic acid and acetic acid but not the formaldehyde. Changes in concentrations of other constituents in the solution were not reported in these experiments. In this same waste stream, moreover, an increase in the formaldehyde concentration to greater than 18 mg/L was found to cause it to be toxic to the microbes, and the increase resulted in a cessation of microbial degradation of the carboxylic acids. Thus, biodegradation of ketones and aldehydes in complex waste streams or in the absence of cyanide is uncertain. It appears that ketones and aldehydes may compete unsuccessfully for microbial attention when injected with other chemical compounds, such as those containing carboxylic acids or nitrogen compounds, which may be more favored by subsurface microbes for nutrition.

A reduction of the concentrations of hazardous ketones and aldehydes in deep-subsurface-aquifer fluids is possible through chemical transformations and sorption, and possibly through biodegradation. To enhance degradation reactions, the concentrations of ketones-aldehydes should be increased gradually to allow the microbial population to acclimate; compounds such as cyanide that may chemically transform the ketone-aldehyde to a form not toxic to microbes should be added to the waste stream; and compounds such as carboxylic acids that may be preferentially consumed by the microbes should be removed from the waste stream prior to injection.

NONHAZARDOUS WASTE REACTIONS

Carboxylic Acids

Comprehensive study of subsurface reactions of a carboxylic-acid-laden waste injected (by Hercules, Inc.) into a sandstone aquifer near Wilmington, North Carolina, (Leenheer and others, 1976a, 1976b) indicates that carboxylic and dicarboxylic acids in a waste solution result in significant waste/rock reactions and microbial activity. Upon injection, the waste solution, which was initially acid (having a pH of 4), dissolved carbonate and silicate material in the formation, which resulted in an increase in calcium, production of carbon dioxide gas, and neutralization of the pH. Beyond this inner zone of active water/rock reactions, dilution of the waste by formation fluid reduced organic concentrations to those tolerated by the microbial population. In this diluted zone, carboxylic acids contributed to waste reactions by acting as a primary substrate for microbial activity. Calculations by Drez (1988) of fluid/mineral reactions between a carboxylic-acid-laden waste stream and a sandstone aquifer confirm that the inorganic reactions that result in carbonate and silicate dissolution near the injection well would cause changes in the chemical character of the solution similar to those documented in the Wilmington field test.

In determining the possible degradation of hazardous materials disposed of in a waste stream containing carboxylic acids, the following must be taken into consideration: (1) the neutralization of the acid pH common to carboxylic acid wastes by rapid waste-rock reactions, in calculating rates of hydrolysis, sorption coefficients, and the progress of other chemical transformation reactions that are pH dependent; (2) the importance of carboxylic acids as a microbial substrate and thus the possibility that carboxylic acids will be consumed in preference to the hazardous material that must be degraded; (3) the sorptive properties of carboxylic acids that allow them to be preferentially sorbed, as was the case when they were present in a solution with ketone-aldehydes; (4) the presence of carboxylic acids in the ionic form in neutral to basic solutions that allows them to form complexes with hazardous metals and thereby increase metal mobilities (see, for example, Loch and Lagas, 1985).

Carboxylic-Acid Derivatives as a Source of Carboxylic Acids

A potentially significant source of carboxylic acids in waste streams is the hydrolysis of carboxylic-acid derivatives. How this hydrolysis is controlled is therefore important.

Aliphatic esters hydrolyze to give alcohols and carboxylic acids,

$$RCOOR' + H_2O \Rightarrow RCOOH + R'OH,$$

at 25°C and pH 7. The hydrolysis half life for the simple aliphatic esters ranges from 1 to 10 years (Mabey and Mill, 1978). Since the esters injected into Texas aquifers are all aliphatic, carboxylic acid and alcohol production as a result of hydrolysis will proceed rapidly enough to be considered a source of carboxylic acids for waste degradation reactions.

All esters injected into Texas aquifers are acetate esters and therefore produce acetic acid, a nonhazardous carboxylic acid, upon hydrolysis, as well as methyl, ethyl, propyl, butyl, and vinyl alcohols. Of these alcohols, methyl and butyl are listed as hazardous only for their ignitability, and the remaining three are not listed as hazardous. The contribution of alcohols to solution could also affect aqueous complexing and thereby chemical reactions.

Amides hydrolyze to carboxylic acids and amines--

$$RCONR'R'' + H_2O \Rightarrow RCOOH + R'R''NH \,.$$

Most amides, except for a few halogenated acetamides, hydrolyze to carboxylic acids extremely slowly at 25°C and pH 7, half lives measuring in centuries, from more than 4,000 to 11,000 years (Mabey and Mill, 1978). Acrylamide, a toxic waste and the only amide injected into Texas aquifers, hydrolyzes to acrylic acid and ammonia--

$$\underset{\text{acrylamide}}{CH_2{=}CH\text{-}CO\text{-}NH_2} + H_2O \Rightarrow \underset{\text{acrylic acid}}{CH_2{=}CH\text{-}COOH} + NH_3.$$

Acrylic acid is listed as a hazardous waste only because of its ignitability; ammonia is not listed. Slow acrylamide hydrolysis will not produce carboxylic acid rapidly enough to affect other reactions in the waste stream.

Nitriles also hydrolyze to a carboxylic acid and ammonia. Half lives for nitrile hydrolysis under injection aquifer conditions are on the order of 1,000 to more than 10,000 years. Because of the slow hydrolysis rates, nitrile hydrolysis is probably only a minor source of carboxylic acids.

Alcohols

Alcohols are less acidic than carboxylic acids, which causes them to be less reactive in aqueous solutions. Alcohols are potentially important contributors in waste reactions because they are so often injected and because of their acidity. Experimental studies on the reactions of the hazardous compound in question in the presence of alcohol-rich aqueous solutions, however, were not found in the literature, and are therefore not considered in this report. Alcohols are potentially important contributors in the waste streams, however, so their contribution to waste reactions should ultimately be assessed.

Inorganic Nitrogen Compounds

Nitrate is generally needed as a substrate to permit microbial consumption of nonnitrogen organic compounds. For example, acetic acid consumption by microbial attack was found to be limited in solutions having low nitrate concentrations, but the introduction of excess substrate, in the form of nitrate and phosphate, induced a microbial attack that resulted in nearly complete destruction of acetic acid at levels of 100 mg/L in about 30 days (Elkan and Horvath, 1977). Therefore, the high levels of inorganic nitrogen compounds in injection waste streams could be favorable for microbial degradation. In some cases it may even be necessary to introduce a suitable substrate such as nitrate to injected solutions to encourage microbial activity.

SUMMARY

This review of the possible degradation pathways of the significant waste groups disposed of by deep well injection makes it apparent that subsurface degradation of the hazardous compounds in question could in some cases be enhanced by pretreatment of the aquifer or the waste stream. Unfortunately, the preferred pathway for each waste group appears to differ from that of the others. For example, nitriles and possibly ketone-aldehydes are degraded by denitrifying bacteria, whereas phenols are favored by methanogenic and sulfate-reducing bacteria. Hydrolysis reactions can transform nitriles and cyanide, chemical interactions can transform ketones and aldehydes, particularly in the presence of cyanide, and oxidation can transform phenols and cyanide. Sorption can reduce the mobility of phenols, nitriles, and, to a lesser extent, ketone-aldehydes.

The injection of complex waste streams results in the interaction of hazardous and nonhazardous compounds that can either enhance or inhibit degradation. For example, the presence of phenol, cyanide, or formaldehyde in an organic waste stream can inhibit microbial degradation of hazardous compounds because of its toxic character. Ketone-aldehydes present in a cyanide waste stream, however, can react with the cyanide and transform it into a hydroxynitrile, which is then susceptible to microbial attack. The presence of carboxylic acids in a hazardous organic waste stream could result in more rapid hydrolysis of nitriles, while having an adverse effect on the sorption of a hazardous compound, such as a ketone-aldehyde, because it is strongly favored for sorption sites.

Additional laboratory and field experiments and thermochemical calculations are needed to determine the conditions necessary for optimization of waste degradation. Some of the conditions that could be altered to enhance degradation include temperature, pH, waste-stream composition, composition of the aquifer material, and composition of the microbial population. Possible effects of these changing conditions on degradation of the compounds of interest are discussed in forthcoming pages.

DEGRADATION PROCESSES

Five processes can reduce the concentrations of hazardous compounds most often disposed of by deep well injection: microbial activity, sorption, hydrolysis, oxidation, and chemical interaction. Controls and limitations on these processes and their possible effectiveness in the injection environment require examination.

MICROBIAL ACTIVITY

Biodegradation is possibly the most active method of subsurface degradation of the significant hazardous compounds. Moreover, of the significant organic waste groups studied, all contain compounds that can be transformed by microbial activity, and since the majority of hazardous compounds injected annually are organic, microbial degradation becomes even more important.

Biodegradation includes several distinct processes (Alexander, 1980). For instance, microbial decomposition of organic compounds can occur as mineralization (metabolism) or cometabolism. Mineralization, however, is the most favored type of microbial activity. During mineralization microbes consume the organic as a nutrient, and because the presence of the nutrient allows the selected microbial population to flourish, degradation increases. Mineralization also is favored because it generally results in the transformation of the organic compound to a nonhazardous inorganic such as CO_2. Metabolism is particularly favored as a method of waste degradation because, once the microbial population is developed, metabolism will cause near complete destruction of the compound down to the minimum concentration necessary to support metabolism. This minimum concentration is generally on the order of 0.1 to 1 mg/L (Bouwer and McCarty, 1984).

In contrast, in cometabolism, although the microbe transforms the organic during metabolism, it does not use the organic compound as a source of nutrition.. Thus, in cometabolism the population density of the responsible species does not increase with the presence of the compound being transformed because the compound is not a nutrient and therefore does not give the favored microbe a selective advantage. Therefore, without an increase in the population of the responsible species, cometabolism does not result in an increase in degradation as the chemical increases in the environment. Instead, an advantage of cometabolism over mineralization is that while degradation of a compound by metabolism is limited by a minimum concentration, on the order of 0.1 to 1 mg/L, cometabolism can continue in much lower concentrations, less than 0.01 g/L, and can eventually result in near-destruction of the compound to below the limits of analytic detection (Bouwer and McCarty, 1984).

A serious disadvantage of cometabolism concerns its by-products. Cometabolism does not break down the organic compound to an inorganic form such as CO_2, but instead transforms it into another organic molecule, which in some cases is more toxic and resistant to degradation than the original compound. One such example that applies to wastes disposed of by deep well injection is the conversion by cometabolism of organic molecules to nitrosamines (RR'N-N=O) (Alexander, 1980), which are carcinogenic, mutagenic, and teratogenic. The immediate precursors of nitrosamines are secondary amines and nitrite. Secondary amines are commonly injected and can also form microbiologically from primary, tertiary, and quaternary amines, all hazardous wastes disposed of by deep well injection. Nitrite, on the other hand, which is not commonly injected with organic waste streams, is formed from oxidation of ammonia or reduction of nitrate, common components of the organic-waste streams studied. This example underscores the need for studies of the presence of nonhazardous substances in the injection solution along with hazardous-waste degradation because of their potential influence on subsurface reactions and possible transformation to hazardous materials.

Most studies of biodegradation of hazardous waste include only the reactions of aerobic bacteria (see, for example, Stryker and Collins, 1987). It is only in the last decade that anaerobic degradation has been recognized as a mechanism that can contribute significantly to contaminant transformations (see, for example, Bouwer and others, 1981; Kobayashi and Rittmann, 1982; Young, 1984). Reduced conditions in the deep subsurface, furthermore, favor anaerobic activity.

For biologic oxidation of organic compounds by anaerobic bacteria under oxygen-poor conditions, aqueous complexes of nitrate, sulfate, or carbonate are used as oxygen sources (Young, 1984). Recent work by Suflita and others (1988) suggests that oxygen in water is also used in anaerobic degradation reactions. In deep Gulf Coast aquifer fluids (at the depth of deep well injection) nitrogen is generally present in the reduced form as ammonia, whereas sulfate concentrations range from 0 to 1,000 mg/L, and carbonate from 100 to 2,000 mg/L (Kreitler and Richter, 1986). Under these conditions anaerobic degradation in Gulf Coast sediments can involve sulfate reduction, methanogenesis, or transformation of water. Sulfate reduction and methanogenesis can occur simultaneously, but when they do sulfate reduction predominates (Oremland and Taylor, 1978).

The presence and activity of microbes in the deep subsurface are still in question. Populations of sulfate-reducing and fermentative (enteric) bacteria have been found in sediments at depths of as much as 410 m (1,350 ft) by White and others (1985), and 300 m (1,000 ft) in the Tuscaloosa aquifer of South Carolina (Wobber, 1986). The sulfate-reducing and enteric bacteria populations present 1,000 ft down in the Tuscaloosa aquifer showed a general decrease in the population density as depth increased, the highest numbers appearing in the permeable sandstone and the lowest numbers in the less permeable clays at a given depth (Wobber, 1986). Evidence of microbiologic degradation of organic compounds at depths of as much as 7,000 ft in Gulf Coast sediments has been indicated by the presence of biodegraded oils and lack of organic acids in formation fluids (Kreitler and others, 1988).

The toxic waste stream disposed of by deep well injection often contains organic compounds in high concentrations that can be toxic to microbial populations. Microbes, however, that are feeding (metabolism) on the hazardous material become resistant to its toxic effects and eventually become more active in the presence of the toxic material. This suggests that if microbial degradation is the method of waste degradation, then introduction of a waste stream of the same composition over long periods of time is preferred over the injection of multiple waste-stream compositions (as is the case for commercial injection wells). For example, the zoning of microbial activity as seen at the Wilmington, North Carolina, injection site indicates that an inner zone of high waste concentration can remain toxic to microbial activity, an outer zone of diluted waste being the location of the greatest microbial activity (Leenheer and others, 1976b).

Microbial activity appears to be pH and temperature dependent. Experimental work conducted over a pH range from 5 to 9 and temperature range from 5 to 45°C indicates that the optimum conditions for methanogenesis are pH 8 and 35°C (Beeman and Suflita, in press). In general most bacteria have the most rapid growth in near-neutral pH solutions, ranging from 5 to 9, although some bacteria can flourish over an extremely wide pH range.

SORPTION

Sorption is probably secondary in importance to microbial activity in the mitigation of wastes disposed of by deep well injection. It can limit the mobility of phenols, and possibly, to a lesser extent, ketone-aldehydes and nitriles. Sorption is limited by several factors: (1) the presence and amount of sorbing material in the aquifer, (2) the presence of other possible sorbants in the waste stream that could be sorbed in preference to the hazardous compound in question, (3) the subsurface temperature and pressure, and (4) the presence of solution pH and ion concentrations, but only if the compound in question dissociates to the ionic form.

Gulf Coast sandstones probably cannot sorb large quantities of hazardous material because they contain only small amounts of sorbing material, at most a few percent clay and little or no organic material (Loucks and others, 1979). Thus, since the sorbing material is so limited, it is probable that the sorbed sites in the vicinity of the injection well will fill, and, with continued injection sorption, will decrease, which in turn will result in increased mobility of the contaminants. Clay-rich shale units that bound the sandstone aquifers in the Gulf Coast are, however, better retardants of waste mobility. These shale units, which can comprise as much as 90 percent of Gulf Coast Basin sediments, are composed of mostly clay and average 0.6 weight percent organic material (Siebert and others, 1984). Sorption by shales, therefore, can act to retard vertical migration of wastes.

Elevated temperatures in the injection aquifers can limit sorption because sorption generally decreases with temperatures (above approximately 40°C). Additionally, for compounds that are present in the ionic form in solution, such as phenols, sorption will be affected by the solution pH and ion concentrations, sorption being lowest in basic solutions having low ion concentrations. The effect of other compounds in the waste stream on sorption can also significantly decrease the potential for sorption of hazardous compounds. For example, carboxylic acids, which are common nonhazardous components in waste streams, are highly sorbing and have been found to sorb in preference to ketone-aldehydes.

Sorbed compounds can later desorb when chemical conditions in the aquifer change. When desorption does occur, sorption, although having been temporary, provides additional time for degradation reactions to take place prior to the compounds moving out of the vicinity of the well bore.

HYDROLYSIS

Many organic compounds hydrolyze in aqueous solutions to simpler compounds. Hydrolysis, therefore, is an important mechanism in the degradation of hazardous organic compounds. Unfortunately hydrolysis in some cases results in the transformation of a nonhazardous compound into a hazardous one. However, of the significant hazardous compounds disposed of in Texas, nitriles and cyanide are the only groups that degrade by hydrolysis.

Hydrolysis of organic compounds usually results in the exchange of a leaving group (X) for a hydroxyl group (OH).

$$RX + H_2O \Rightarrow ROH + HX$$

Rates of hydrolysis can vary widely, ranging from half lives of a few seconds to thousands of years (Mabey and Mill, 1978), and are dependent on pH, temperature, and ion concentrations in solutions. First, hydrolysis of an organic compound is generally fastest at the extremes of acidity and basicity, the rate of hydrolysis decreasing to a minimum at some intermediate pH. Second, hydrolysis rates increase with increased temperature. Third, elevated concentrations of non-nucleophilic salts (for example, NaCl, LiBr) in solution can act either to increase or decrease the rates of hydrolysis, although high concentrations change the rate constant by no more than 30 or 40 percent (Mabey and Mill, 1978). The addition of nucleophilic anions (acetate, phosphate) to solution accelerates the rate of hydrolysis and in some cases catalyzes the process by displacing the leaving group (X) more rapidly than does water

$$RX + A^- \Rightarrow RA + X^-,$$

$$RA + H_2O \Rightarrow ROH + HA$$

where,

$$(HA + X^- \Leftrightarrow A^- + HX).$$

Because hydrolysis products and rates are dependent on the solution pH and temperature, it can also be expected that hydrolysis reactions will change with distance from the point of injection.

Hydrolysis rates can be expected to decrease, and reactions change, as the generally acidic or basic waste plume is neutralized as distance from the injection well increases. In contrast, hydrolysis rates can be expected to increase as distance from the injection well increases because of heating of the generally ambient temperature waste. This subsurface zoning should be considered in calculations of subsurface hydrolysis reactions and rates.

OXIDATION

Oxidation is of only limited importance in subsurface degradation. It has the potential of degrading phenols and possibly cyanide. There are generally only small amounts of oxygen available for oxidation in the subsurface aquifer. Injection of waste into deep aquifers, however, may increase oxygen in the aquifer in the vicinity of the injection well. Industrial-waste streams which are generally exposed to the atmosphere will be oxidized unless a reduced phase has been added to the solution during production. Conversely, fluids in deep aquifers are already reducing and minerals in the deep sediments contain elements in their reduced form. Introduction of the oxidized waste stream into the reduced subsurface environment will act to reduce the waste stream. Numerous field examples document this subsurface reduction of the injection solution (see, for example, Ragone and others, 1973; Leenheer and others, 1976b; Ehrlich and others, 1979). It is expected, therefore, that oxidation reactions will occur only near the injection well, whereas reduction predominates beyond the inner plume environment.

CHEMICAL INTERACTIONS

Chemical interactions between compounds (1) within the waste stream, (2)within the waste stream and formation fluid, or between compounds in the waste and those in the rock could contribute to degradation of hazardous compounds. The reactions between ketone-aldehydes and cyanide are one example of favorable subsurface interactions. Few data are available, however, on the interactions that could occur in the complex waste streams injected at the elevated temperatures and pressures common in the disposal aquifers.

Summary

Apparently, pH, temperature, and the oxidation state of the disposed-of fluid will govern the types and extent of degradation of hazardous compounds in the deep subsurface. In addition, the continuum of reactions and chemical changes that take place from the point of injection out to the limits of the contaminant plume should result in multiple processes that in turn should result in degradation and in a physical and temporal zonation of these processes.

HYDROGEOLOGY OF INJECTION

FORMATION FLUID AND AQUIFER MATERIAL

Most injection operators in Texas use porous, saline sandstone aquifers along the Gulf Coast, namely the Frio, Yegua, Catahoula, Oakville, Wilcox, and undifferentiated Miocene sandstones (Kreitler and Richter, 1986). Sediments in the Gulf Coast are predominantly shale, the sandstone component being as little as 15 volume percent (Boles and Franks, 1979). Injection occurs within a depth range of 610 to 2600 m (2,000 to 8,500 ft) below land surface, mostly within a range of (1,200 to 2,100 m) (4,000 to 7,000 ft). At these depths, water in sandstone aquifers of the Gulf Coast contains sodium chloride and dissolved solids ranging from 30,000 to 80,000 mg/L (Kreitler and Richter, 1986). This pore water is generally anoxic and reducing; it also has a pH of near neutral to slightly acidic, a temperature ranging from 50 to 80°C (over the depth range of 1,200 to 2,100 m [4,000 to 7,000 ft] and a thermal gradient ranging from 20 to 30°C/km), and a pressure less than or nearly equal to hydrostatic (Hanor, 1979; Kharaka, 1979; Capuano, 1988; Kreitler and others, 1988).

The mineralogy of Tertiary units along the Gulf Coast is surprisingly uniform. Quartz is the major component, constituting as much as 95 volume percent, followed by feldspar and rock fragments, which generally make up 5 to 50 volume percent of the total rock (Loucks and others, 1979). As depth increases in the sedimentary column, the sandstone-clay content increases and the clay composition changes, smectite giving way to illite at depths nearing 2,700 m (9,000 ft) (Loucks and others, 1979). Thus, smectite is the dominant clay mineral in sandstones at the depths of deep well injection. Carbonate cementation also is common and occurs predominantly as calcite at the depths of deep well injection (Boles, 1978; Land, 1984) in Gulf Coast sandstones. Calcite cement within the Frio sandstone, a common disposal aquifer, averages 5 volume percent (Land, 1984). Organic material is generally present in the clay-rich shale units and averages 0.6 weight percent (Siebert and others, 1984).

INJECTION AQUIFER

Upon injection of the waste solution, increases in temperature and pressure and chemical transformations resulting from waste/rock and waste/formation-fluid interactions should cause changes in the types of chemical and biological reactions that may degrade or immobilize hazardous compounds. Thermal and chemical zonation between the point of injection and the sediments containing original formation fluid results in a zonation of chemical degradation reactions. The injection solution is generally cooler and more oxidizing than the formation fluid, and it has extreme pH values that are lower or higher than the near-neutral pH of the formation fluid. The zone of mixing of these two chemically distinct fluids in a porous medium does not produce a sharp contact but generally occurs over a measurable distance, one end member changing gradationally in composition to that of the other. This gradational change is documented by the passage of a mixed waste/formation fluid past a monitor well and takes from several hours to a few days (see, for example, Ehrlich and others, 1979).

Introduction of the waste stream into the formation also results in reactions with the aquifer material that ultimately chemically neutralize and reduce the waste stream. In turn, the aquifer material in the vicinity of the well bore becomes altered through the process of waste solution reduction, resulting in the dissolution of mineral phases containing elements in their reduced state, such as pyrite and biotite, and the precipitation of minerals containing these elements in their oxidized form, such as hematite or magnetite. Reactions of acidic-waste solutions with the arkosic sandstones commonly used for disposal result in the dissolution of minerals, such as feldspars and carbonates, and ultimately in an increase in the solution pH to near neutral (see, for example, Capuano, 1977; Roy and others, 1988). Reactions of alkaline waste solution with these sandstones result in the dissolution of silica grains, which compose a large fraction of the sediment but which do not result in the reduction of the pH to near neutral (see, for example, Roy and others, 1988). In addition, the waste plume is heated to subsurface temperatures as it gains heat conductively from the formation and through mixing with the formation fluid that is higher in temperature.

All these processes act to create three chemically distinct environments in which degradation or immobilization of hazardous chemicals can take place: (1) oxidized, lower temperature conditions characteristic of the original waste stream in the immediate vicinity of the well bore that expands as injection increases, (2) a mixed zone in which the waste plume and formation fluid are mixing, and (3) an outer zone of formation fluid that contains diluted waste but has a chemical character that is more similar to that of the original formation fluid. The presence of these different environments and their effects on inorganic and organic reactions are documented in deep well injection field experiments, laboratory experiments, and numerical simulations, as will be discussed.

OTHER ENVIRONMENTS

There are two other subsurface processes in connection with which the degradation and retention of hazardous compounds should be considered: (1) the mobility of waste fluid in the overlying shale beds and (2) waste fluid mobility in faults that are hydrologically connected to shallow aquifers. Unfortunately, studies of the effects of these hydrologic conditions on waste degradation were unavailable.

Shale units overlying disposal aquifers are generally rich in clays and organic material and act as imperfect seals that retard the vertical mobility of fluids. The clay and organic material in these sediments can also act as sorbants to retard waste mobility. In addition, the chemical environment in the shale units differs from that in the injection aquifer and thus could encourage additional degradation reactions.

The degradation or retardation of waste that escapes the disposal aquifer through faults is difficult to document. The pressure and temperature decrease attending upward fluid flow could result in the precipitation of mineral phases that either seal these faults or incorporate the hazardous material. However, these favorable processes possibly may be encouraged through chemical pretreatment of the waste stream.

APPROACHES FOR PREDICTION AND VALIDATION OF SUBSURFACE WASTE REACTIONS

NUMERICAL SIMULATION

In the proposed research, geochemical modeling was to be completed using existing data bases. Thermodynamic data bases and programs that permit the calculation of inorganic fluid/mineral equilibria and water/rock reactions in multicomponent systems under the conditions of elevated temperature and pressure present in aquifers used for deep well injection have been available for the past decade (Helgeson, 1969; Helgeson and others, 1970, 1978; Wolery, 1983, 1984). Available thermochemical data bases, however, lack data on organic compounds and ions, other than a few naturally occurring carboxylic acids, such as acetic acid. Prior to the compilation of waste-stream-composition data provided in this study, it was not apparent from information in the literature that the majority of the waste streams disposed of were complex mixtures of organic and inorganic compounds. Thus, without a thermochemical data base containing organic compounds and species it was impossible to model subsurface reactions in waste streams containing the compounds determined to be injected most often.

The lack of an internally consistent thermochemical data base containing data on both inorganic and organic species is a severe limitation for future work that might include numerical simulations of subsurface waste reactions. Compilation of this type of data base is a sizable but greatly needed task for the numerical simulation of transformations of organic compounds in the multicomponent organic-waste solutions most often disposed of by deep well injection. Recent work by Shock (1987) provided the equations and thermochemical constants needed to compile such a data base for many of the naturally occurring organic compounds, but it, too, lacks information on many of the products of chemical manufacturing that are disposed of by deep well injection.

Little work has been done by other researchers on the calculation of organic transformations and organic-waste/rock reactions in the subsurface, particularly on the complex organic-inorganic waste streams most often injected. The effects of a carboxylic acid waste stream on mineral precipitation and dissolution in the injection aquifer were calculated by Drez (1988) after metal-acetate complexes were added to the preexisting thermochemical data base for the reaction pathway code EQ3/6 (Wolery, 1983, 1984). The results of Drez's calculations, as discussed in the previous section on the effects of carboxylic acids on waste reactions, appear to agree with the transformations that occurred when a sandstone aquifer near Wilmington, North Carolina, was injected with a carboxylic-acid-laden waste stream, as described by Leenheer and others (1976a, 1976b). Upon injection of the carboxylic acid waste stream, a "fast reaction zone" developed, in which the pH of the originally acidic waste stream was neutralized, calcium increased, and carbon dioxide evolved, as carbonate and silicate minerals dissolved.

Another limitation is that most computer codes used for calculation of chemical transformations in solution and fluid/mineral reactions do not calculate adsorption reactions or biologic transformations, both of which are important in the degradation of hazardous materials and in the retardation of their mobility. There are numerical models available for the calculation of the results of adsorption (see, for example, Morel and others, 1981), of biologic transformations using a model of biofilm kinetics (Rittmann and McCarty, 1980a, 1980b), and of combined inorganic reactions and denitrification (Sorek and Braester, in review). Similar to the water/rock reaction codes, sorption reaction codes generally contain data only for inorganic species and, therefore, have not been tested to predict sorption of the hazardous materials of concern in this study. The numerical models for predicting biologic transformation have nevertheless been used successfully to simulate the results of laboratory flow-through experiments (Bouwer and McCarty, 1984), as discussed in detail in the following section.

An in-depth review and comparison of computer codes for calculating inorganic chemical equilibrium and fluid/mineral reactions was completed by Kincaid and others (1984) and Morrey and others (1986). They found EQ3/6 (Wolery, 1983, 1984) to be the most comprehensive code for conducting these types of calculations. An added benefit of EQ3/6 is that it is in public domain and is continually being updated. A laboratory experiment was conducted to validate a simulation by EQ3/6 of the aqueous concentrations of elements that would dissolve from a mixture of copper carbonate, lead carbonate, iron hydroxide, calcium sulfate, and aluminum hydroxide minerals. For most elements the results of the numerical simulation were comparable (within a few percentage points) to those of the experiment. These researchers found that EQ3/6 had several limitations: it is extremely difficult to use, the thermochemical data base for some elements is inadequate, and rate and sorption processes are not considered. A precursor to EQ3/6, PATHI (Helgeson and others, 1970), has been used successfully to simulate inorganic reactions between formation fluids and sediments under the temperature, pressure, and chemical conditions that can be expected in disposal aquifers (see, for example, Sverjensky, 1984) and to simulate chemical changes and mineral deposition that occur when an oxygenated fluid is introduced into a reduced aquifer environment (see, for example, Capuano, 1977).

Another limitation of EQ3/6 and all other chemical equilibrium codes is the inadequacy of the thermodynamic equations used in solving for solution equilibria in the high ionic strength solutions that compose many waste streams and injection-aquifer fluids. Some equations exist that can take into account concentrated solutions in EQ3/6; however, those available in the code to date can calculate equilibrium in only simple carbonate-sulfate solutions. The capability of calculating equilibrium in more complex concentrated solutions is expected to increase as EQ3/6 is developed.

Another computer code for calculating subsurface waste reactions, ECES, has been developed by researchers at E.I. du Pont de Nemours (Scrivner and others, 1986). This code is described as an electrolyte solution equilibrium program with kinetics and flow. However, because this code is currently proprietary, the validity of its output cannot yet be compared with that of other equilibrium codes, so the thermodynamic assumptions and data base cannot be evaluated. This code has been used to predict the hydrolysis of cyanide in a high pH (near 12.5) solution (Scrivner and others, 1986); cyanide hydrolysis is very rapid at a pH greater than 9, with a tenfold reduction in cyanide every 14 years. Scrivner and others also indicated that ammonia in the input solution would buffer the pH and keep it near 11. The pH remaining so high for 14 years may be unrealistic; however, the reaction mineralogy must have been limited if only silica was considered. Reactions of the waste with feldspars and carbonate minerals, common in sandstone units, can considerably alter the pH in the waste solution, just as could mixing of the waste with the formation fluid. Without additional information on the assumptions and methodology used in the calculations, the reliability of the predictions made is uncertain.

Summary of Limitations and Advantages

Although reaction codes have not yet been tested in the prediction of subsurface waste transformations and waste/rock reactions for complex inorganic- and organic-waste streams, their ability to simulate experimental results and to predict reaction path sequences found in natural systems suggests that they are useful tools for predicting waste degradation. A limiting factor, however, appears to be the quality of thermochemical data used in the calculations and the ready availability of this data in an internally consistent data base that contains all the inorganic and organic elements and compounds that can contribute to reactions in the complex waste stream of interest. In addition, reaction kinetics for slower reactions, such as organic-hydrolysis reactions, must be considered, although a code containing equations that consider reaction kinetics, sorption, biologic reactions, and high ionic strength solutions does not exist.

Despite these limitations, however, chemical equilibrium calculations can provide useful information about the physical and chemical controls on reactions if used in conjunction with field or laboratory experiments. Furthermore, another benefit of thermochemical calculations is their ability to provide generic characterizations of degradation processes, characterizations that can be applied to numerous sites. A thermochemical analysis of laboratory or field experimental results could permit an understanding of the processes that occur, which could then be more readily extended to predictions of the reactions that could occur at other locations or under changed conditions.

NATURAL AND ARTIFICIAL ANALOGS

Because of the great depth of deep well injection aquifers, it is generally impossible to study subsurface degradation firsthand. Nor is the use of monitor wells to document reactions always advisable because drilling is expensive and because monitor wells increase the possibility of waste leaking into shallower aquifers. In addition, it is impossible to determine long-term degradation because deep well injection has been used to dispose of many hazardous organic compounds only during the last 10 to 20 years. Natural and artificial analogs of subsurface waste reactions would, therefore, be useful in the prediction of the geochemical processes active in deep injection aquifers and in the degradation pathways that can be expected. Natural analog environments might include diagenetic sediments and marine sediments, and artificial analog environments might include landfills or injections into a shallow aquifer.

The trait common between landfill and marine-sediment environments and deep well injection environments is that in all three, oxygenated fluid is introduced to an anoxic environment. The chemical environments around a landfill and in marine sediments and the similarities between the environments were described by Baedecker and Back (1979a, 1979b). These workers found that the lateral zonation of aqueous species in landfills is similar to the vertical zonation in marine sediments, and they attributed this similarity to a reaction sequence that includes initial oxidation of the sediments at the source of the foreign fluid and then a reduction of the fluid as it migrates from its source into the sediments. Fluid reduction is initially indicated by the reduction of nitrate and sulfate, and later by the presence of methane and ammonia being produced during the microbial consumption of organic compounds. The pH in the reaction zones is buffered at near-neutral in both environments. This zonation in oxidation potential of the solutions is similar to the zonation described in the injection environment present in aquifers around wells used for deep well injection. The presence of an aerated zone around an injection well in aquifer sediments is further documented by a study of the injection of tertiary-treated sewage 127 to 146 m (418 to 480 ft) into a sandstone aquifer on Long Island, New York (Ragone and others, 1973). Waste fluid collected from a series of monitor wells showed evidence of pyrite oxidation in the sandstone and subsequent deposition of ferric hydroxide minerals.

The sequence in chemical species described by Baedecker and Back (1979a, 1979b) in landfills and marine sediments also suggests a zonation in microbial activity similar to that expected around injection wells as described by Bouwer and McCarty (1984). This sequence includes a progression from aerobic heterotrophic respiration in the vicinity of the injection well to a zone of denitrification, then sulfate respiration, and finally methanogenesis on the outer margins.

There are dissimilarities between landfill and marine sediment environments and that of deep well injection, however. The most important is the elevated temperature and pressure common in deep well injection aquifers, which the other environments do not share. In addition, fluids in landfills and marine sediments generally lack the organic compounds that are significant hazardous wastes disposed of by deep well injection. Or, if the landfill and marine sediment fluids do contain these compounds, they have concentrations that are at least an order of magnitude lower than injection concentrations (see, for example, appendices I and II; Moore and Ramamoorthy, 1984; Thurman, 1985).

Shallow well injection is more similar to deep well injection, although the temperature and pressure of shallow aquifers are lower. These thermal and pressure differences, however, can influence the rate and magnitude of organic transformations, sorption and water/rock reactions, and the activity and composition of bacterial populations (see, for example, Wobber, 1986).

Diagenesis of sediments at the depths, temperatures, and pressures of deep well injection aquifers is another possibility for finding information on likely degradation reactions. Chemical and microbial transformations of sedimentary organic compounds released from the thermal decomposition of sedimentary organic material during diagenesis can be determined through examination of the present-day mineral alteration suites and pore fluids. Organic compounds present in natural pore fluids exposed to thermally degraded organic material are generally not the same hazardous organic compounds as those that are deep well injected. Natural organic compounds, however, are sometimes from organic chemical groups similar to those of the hazardous organics injected and, therefore, may react similarly. One instance in which natural diagenetic reactions were used to derive information about reactions in aquifers used for deep well injection is that in which Kreitler and others (1988) used the presence of degraded hydrocarbons and the lack of organic acids in pore fluids as evidence of microbial degradation at 2,134 m (7,000 ft) in Gulf Coast aquifers. The diagenetic environment is not clearly analogous to that of deep well injection because deep well injection is the introduction of oxygenated fluids that are clearly out of equilibrium with the subsurface environment that then mix with pore fluids that have a distinctly different composition. Diagenesis, therefore, is similar to the other situations in that it gives only partial information on possible deep well injection reactions.

Summary of Limitations and Advantages

This review of the processes controlling reactions in each of the environments possibly analogous to deep well injection environments indicates that, although each of these analogs represents some aspects of the deep well injection geochemical environment, none of these analogs represents that environment fully. Each analog lacks a key element such as elevated temperature, pressure, or, for the natural analogs, presence of the contaminants in question. This shortcoming, although it allows the use of analogs as tools for defining some of the controls on degradation reactions, does not fully represent the types and rates of degradation reactions or sorption that will occur in the deep well injection environment. Nevertheless, an advantage of using analogs despite this limitation is that an analog can provide information on the mobility and transformations of compounds over much longer time periods, such as the 10,000-year limitation set on mobility by recent legislation. Analogs would therefore be particularly useful in the study of the degradation of compounds that degrade by reactions, such as hydrolysis, that can proceed extremely slowly, or in the study of the degradation of compounds that have only recently become candidates for deep well disposal. In addition, analogs can be useful when field data from backflush and monitor wells are not available to confirm experimentally or thermochemically derived degradation pathways, and when these types of derivations are impossible.

LABORATORY EXPERIMENTS

Batch and flow-through experiments of waste degradation have been used extensively to predict sorption, biodegradation, and the effects of waste/rock reactions. Comparison of the number of laboratory experimental studies with the number of field experiments and numerical simulations listed in appendix II reveals that to date laboratory experiments, particularly batch experiments, are the most-used method of studying degradation reactions.

Numerous problems are inherent in the simulation of subsurface conditions in the laboratory, and they must be accounted for. For example, batch experiments reflect natural aquifer conditions much less than flow-through experiments do. Batch experiments, however, can be useful in providing information on reaction paths and are used extensively to study microbial activity and, to a lesser extent, organic and inorganic reactions (see, for example, appendices I and II). Results from both batch and flow-through experiments used in the study of biodegradation of hazardous wastes (microcosm studies), however, indicate that prediction of subsurface biodegradation of compounds must be verified by direct experimentation for each compound and each site of interest (Wilson and others, 1985).

Batch experiments conducted by Roy and others (1988) on the effects of inorganic acid and alkaline waste streams reacting with a sandstone, a siltstone, and a dolomite were successful in predicting (1) the neutralization of the acid-waste solution, the reduction of Eh, and the dissolution of carbonate minerals and (2) that the alkaline-waste solution would dissolve silica and result in Eh reduction but would not be neutralized. Their batch experiments were run at temperatures that ranged from 25 to 55°C at hydrostatic pressures for the depth at which those temperatures are achieved. Although the researchers did not confirm their experimental results through comparison with an actual site, they did simulate their reactions using the fluid/mineral equilibria computer codes WATEQ2 and SOLMNEQF. They concluded that the calculations of fluid/mineral reactions, although unsuccessful in exactly duplicating the experimental results, were a useful tool when used in conjunction with the experimental results to determine the controls on reactions.

Flow-through experiments, although used much less extensively, duplicate natural conditions more accurately than do batch experiments. The protocol for designing flow-through experiments to study subsurface inorganic-organic reactions at the temperatures and pressures of injection aquifers was presented by Collins and Crocker (1988). In their experimental setup, however, they did not indicate that the core should be sterilized to prevent biodegradation reactions, they did not test the possibility of sorption on the rubber lining material, and they did not test their experimental results against the results from a natural system.

Flow-through experiments for testing microbial activity were performed at low temperatures and pressures by Wilson and others (1985). Their work indicates that for a laboratory study of subsurface microbial degradation it is important to have a sample from the subsurface that contains the native flora. In their flow-through experiments they did not test for reactions other than the loss of the hazardous wastes in question. Studies using a flow-through experimental apparatus of biodegradation at high temperature and pressure were not available.

Summary of Limitations and Advantages

Limitations of laboratory experiments are (1) their inability to duplicate the deep aquifer environment accurately and (2) the impracticality of running experiments for long periods of time. It is nearly impossible, given the current lack of knowledge of deep microbial activity, to introduce microbes that could be present. Technology does not yet allow collection of live microbes from the high-pressure environment of the deep wells used for injection. And even if they exist, these deep microbes are certain to have different nutritional preferences than microbes collected from near-surface environments. Laboratory experiments, therefore, offer as their greatest advantage the ability to simulate and predict abiotic reactions. Experiments allow the stepwise testing of reactions and can be particularly useful, therefore, in predicting reaction pathways, in developing new methodologies that enhance degradation, and in determining the controls on degradation documented by backflush and flow-through experiments.

FIELD STUDIES

Field tests can prove invaluable in predicting the sequence, types, and rates of transformations of hazardous organics in the subsurface. Several field studies have been conducted to test subsurface degradation reactions (see Case Studies in appendix II). Most of these were conducted at active injection sites, rather than having been designed specifically for the study of degradation reactions.

Field-test information can be derived by either the backflushing of the injection well or the sampling of nearby monitor wells. A combination is ideal. Both backflush and flow-through experiments were conducted at the Pensacola, Florida, waste-disposal site, where an organonitrile waste stream was injected by the American Cyanamid Company at a depth of 400 m (1,300 ft) into a limestone aquifer (Ehrlich and others, 1979; Vecchioli and others, 1984). The results of these tests indicate that unique data are derived from each type of test. The backflush experiment, for instance, was the most useful in documenting reactions in the immediate vicinity of the injection well, which were completed by the time the fluid reached the monitor well only 132 m (433 ft) away. Also, biologic reactions appeared to proceed more rapidly than the waste/rock reactions and, therefore, biologic reactions were characterized from backflush data and waste/rock reactions were characterized from monitor well data.

Backflush and flow-through data were also collected at the Wilmington, North Carolina, waste-disposal site, where a carboxylic-acid waste stream was injected into a sandstone aquifer by Hercules Chemical, Inc. (Leenheer and Malcom, 1973; Leenheer and others, 1976a, 1976b). Again the results from both types of tests were useful in determining waste reactions in all the transition zones from the waste plume to the unaltered formation fluid (Leenheer and others, 1976a, 1976b). In contrast to the American Cyanamid test case, however, the backflush data from the Wilmington test case provided information on waste/rock reactions and the monitor well data provided information on microbial degradation.

Although field experiments are the most reliable method of determining subsurface waste transformations, thermochemical calculations and laboratory experiments are needed to support these results. Without the generic understanding of the processes and controls on degradation derived from thermochemical and laboratory experiments, field tests would have to be conducted at each geologically distinct site for every combination of waste solution, formation-fluid composition, and reservoir temperature and pressure in order to predict degradation reactions.

Summary of Limitations and Advantages

Field experiments that include data from both backflush and monitor wells that grid the area of the injection plume are the best method of studying degradation reactions within a particular waste stream composition and injection environment. Although these optimum conditions are unlikely ever to exist at even a single deep well injection site, field data (even when limited to data from a single backflush of the disposal well) are a great advantage over laboratory experiments in understanding degradation reactions. Field data provide information that can be used to confirm thermochemical and laboratory results, and they are particularly useful in documenting microbial pathways that cannot currently be predicted by thermochemical calculations and laboratory experiments. A drawback to using field data would occur only if the samples were improperly collected. For example, if gases are not collected, chemical constituents are not adequately preserved, or if a complete analysis of all constituents is not provided, information might be presented that could be misleading or contradict experimental and thermochemical predictions.

THEORETICAL, LABORATORY, AND FIELD VALIDATION OF EXPECTED GEOCHEMICAL REACTIONS

Subsurface degradation of hazardous materials results from chemical reactions within the waste stream responding to temperature, pressure, oxidation-reduction, pH and other chemical changes as the waste stream mixes with the aquifer fluid, interacts with the sediments, and provides nutrients for microbial activity. The significant hazardous waste groups disposed of by deep well injection are all organic compounds, except for cyanide, which in some cases reacts similarly to the organic nitrile compounds. Organic and microbiologic reactions, therefore, are the focus of this discussion of degradation reactions.

A number of review studies address the mobility of contaminants in ground water (see, for example, appendices I and II). Most of these studies, however, focus on the problems of the mobility of contaminants under near-surface conditions resulting from the infiltration of toxins into the ground-water system from surface disposal (see, for example, Cherry and others, 1984) or from shallow disposal to depths below approximately 400 m (1,300 ft). Many of these review studies also focus on the mobility of metals, rather than organic compounds, which have been shown in this report to be the dominant component of hazardous material disposed of by deep well injection, or focus on pesticides (halogenated organics), fertilizers, and other organics that are common surface contaminants (appendices I and II) rather than on the industrial contaminants that are the concern of this study. In addition, these studies generally report on the chemical reactivity of the hazardous material in question but do not address how other contaminants in solution might effect its mobility.

Several studies, however, include sufficient information on the composition of the injected and recovered solution to permit an evaluation of subsurface reactions. Three of these studies--(1) Bouwer and McCarty's (1984) biofilm simulation, (2) Leenheer and Malcom's (1973) and Leenheer and others' (1976a, 1976b) study of the Hercules Chemical site and (3) Erlich and others' (1979) and Vecchioli and others' (1984) study of the American Cyanamid site--were selected for inclusion in this report because they discuss waste streams whose compositions are similar to those typical of a waste disposed of by deep well injection. These studies represent shallow aquifer conditions to 300 m (1,000 ft), rather than the deeper conditions present in Texas injection aquifers of 610 to 2,600 m (2,000 to 8,500 ft).

BIOFILM SIMULATION - THEORETICAL AND LABORATORY EXPERIMENTS

Production of zones of changing microbiologic degradation processes in the subsurface are predicted by Bouwer and McCarty (1984) through the calculation of subsurface biotransformations for which they used a model of steady-state biofilm kinetics (Rittmann and McCarty, 1980a, 1980b) combined with the results of laboratory flow-through column experiments. It is apparent from their work that a progression in subsurface biologic activity can develop from the point where a contaminant plume is introduced into the formation. Biologic activity will progress from aerobic heterotrophic respiration in the vicinity of the injection well where waste fluids still maintain oxygenated conditions, to a zone of denitrification, then to a zone of sulfate respiration, and finally to a zone of methanogenesis on the outer margins. Methanogenesis and sulfate reduction can occur on the outer margins of the mixed zone where sulfate and carbon dioxide available in the formation fluid can drive the activity.

Zoning in the concentration of inorganics in the waste and waste/formation-fluid mixture was also found to accompany this biologic zoning (Bouwer and McCarty, 1984). The oxidation potential of the waste stream is decreased with increased distance into the formation with the consumption of available oxygen in the zone of aerobic respiration, to the consumption of nitrate in the zone of denitrification, to the consumption of sulfate in the zone of sulfate respiration. This biologic activity can also shift the pH of the solution, particularly from the production of carbon dioxide if the outer methanogenic zone is active.

There is a threshold on the concentration of the primary substrate (nutrient), approximately 0.01 mg/L, below which biologic activity ceases (Bouwer and McCarty, 1984). Thus biologic activity generally will not proceed beyond the zone of primary mixing and will not completely consume the organic compounds being degraded. Organic compounds used as the secondary substrate (cometabolism), however, can be consumed at much lower concentrations but at a much slower rate. Therefore, they can also persist beyond the zone of biologic activity (Bouwer and McCarty, 1984).

The presence of a primary substrate that is favored by microorganisms such as a carboxylic acid could result in increased microbial activity and thereby increase the degradation of compounds that are preferentially consumed by organisms as a secondary substrate, such as halogenated organics (Bouwer and McCarty, 1984). The primary substrate acetic acid injected in a concentration of as much as 100 mg/L was found to degrade by 99 percent within 2 days to 0.05 mg/L, the probable lower limit for nutrient activity. Halogenated organics consumed as secondary substrates during the acetic-acid consumption were also degraded up to 99 percent, their concentrations decreasing from about 0.1 mg/L to less than 1 x 10^{-3} mg/L. This process contrasts with the effect a primary substrate such as a carboxylic acid can have in a solution containing another primary substrate that is less favored by microbes for nutrition. In this case the presence of two compounds that are both generally consumed as primary substrates could result in the preferential consumption of the favored compound and the reduced consumption of the other.

Numerical simulations of the biologic activity that included a model of steady-state biofilm kinetics resulted in good agreement with the experimental results. The efficiency of microbial decomposition of the primary and especially the secondary substrates was found to be dependent not only on the initial concentration of the compounds and the density of the microbial population but also on the rate at which the injectate would flow through the zone of microbial activity. Increased fluid flow rates result in decreased microbial degradation efficiency. Upon the injection of an organic waste, microbial zones should develop that include an initial (inside) zone of aerobic respiration, followed by one of denitrification, then a zone of sulfate reduction, and, finally, a zone of methanogenesis. The chemical character of the solution and degradation of organic compounds are predicted to change within each of these zones.

HERCULES CHEMICAL SITE, WILMINGTON, NORTH CAROLINA

An acid (pH = 4) waste stream containing predominantly carboxylic acids, formaldehyde, methanol, and aromatic dicarboxylic acids was injected from May 1968 to December 1972 into a sandstone aquifer at approximately 260 to 300 m (850 to 1,000 ft) in depth near Wilmington, North Carolina, by Hercules Chemical, Inc. (now called Hercofina) (Leenheer and Malcom, 1973; Leenheer and others, 1976a, 1976b). Fluid samples collected from observation wells confirmed the passage of a front containing evidence of chemical zonation induced by waste/rock reactions and biological activity. These observation wells were located 427 to 823 m (1,400 to 2,700 ft) from the point of injection, and waste fluid sampled from these wells was predicted to have a post-injection residence time of 2 to 4 years.

Leenheer and others (1976b) defined several reactions zones between the waste plume and the waste front. The outermost zone, referred to as the dilute zone, contains waste in concentrations too dilute to support microbiologic activity, and also lacks evidence of any waste transformations.

The zone inside the dilute waste zone is referred to as the microbial zone, and from the data presented by Leenheer and others (1976a and 1976b) this microbial zone can be further subdivided. In the Leenheer study the outermost zone of microbiologic activity encountered showed evidence of methanogenesis as marked by the presence of methane gas and reduction in dissolved organic carbon (DOC). The next zone of microbial activity showed evidence of sulfate reduction in the formation of black sulfide precipitates and the presence of hydrogen sulfide gas, suggested by the researchers to be evidence of microbiologic sulfate reduction. Methanogenesis was still evident in this second zone. Fluids in the innermost zone of microbial activity have increased concentrations of nitrogen gas and decreased methane production, possibly marking a zone of denitrification. Analyses of the organic carbon fraction of fluids sampled from these three microbial zones indicated that acetic acid was measurably degraded, whereas formic acid had undergone little degradation.

Inside the microbial zone is the transition zone (Leenheer and others, 1976), in which the concentrations of organic compounds are toxic to microbial activity and in which formation-fluid nitrogen, which is needed for the microbial activity, is absent. In this transition zone the waste solution has already been neutralized by waste/rock reactions that occurred closer to the injection well, and as a result there are limited chemical transformations in this zone.

Inside the transition zone is the fast reaction zone, where waste/rock reactions result in significant chemical changes in the inorganic composition of the waste fluid (Leenheer and others, 1976b). In the fast reaction zone the pH of the acid-waste solution is neutralized, calcium in solution is increased, and carbon dioxide is evolved into silicate while carbonate minerals are dissolved. Inside the fast reaction zone is a slow reaction zone, where sediments have been altered to near equilibrium with the waste plume. This innermost zone contains essentially pure waste.

The above reactions were documented by Leenheer and others (1976b) through analyses of pH, oxidation potential, and gaseous concentrations in fluids collected from several monitor wells. Analyses of organic compounds in recovered solutions were limited. Organic analyses were limited to analyses of only organic acids in samples from three of the monitor wells. Because of the analytic data, it is difficult to ascertain the organic reactions that were taking place. The available organic acid analyses indicate considerable degradation of acetic acid from 800 to less than 50 mg/L and formic acid from 4 mg/L to undetectable concentrations. Microbial attack was credited with reduction of these carboxylic acids, while sorption was credited with the reduction of dicarboxylic acids in the same solution from about 16 to 1 mg/L. Leenheer and others' (1976b) conclusion of microbial degradation is consistent with the experimental work of Elkan and Horvath (1977) on solutions and sediments from the Hercules site. Furthermore, the work of Elkan and Horvath (1977) showed the same waste solution to be toxic in concentrations of greater than 1 percent in the ground water because of toxic formaldehyde levels. This is consistent with Leenheer and others' (1976b) observation of an innermost zone of concentrated waste where microbial activity does not take place.

In the extrapolation of the reactions that are described at the Hercules site to what could be expected in other injection aquifers, it is apparent that if a waste does not contain toxic compounds, such as the formaldehyde in the Hercules waste, then microbial activity could begin within the inner zone. Thus the zones of microbial and rapid waste/rock reactions could then overlap.

The reaction zones described above were developed during the approximately 4.5 years that waste was injected at the Hercules site. Microbes were able to exist on fluids after approximately a 90 percent dilution to acetate concentrations below 800 mg/L, an order of magnitude lower than the initial injection concentration of approximately 9,500 mg/L. The less diluted waste solution was thought to be toxic to microbial activity, probably because of high initial formaldehyde concentrations. Microbial activity appeared not to remove all of the acetic acid; as much as 50 mg/L remained in solution when it left the zone of microbial attack. This is consistent with Elkan and Horvath's (1977) experimental results, which suggested that for nearly complete consumption of the acetic acid from this waste solution, either microbes or a substrate such as nitrate needs to be added to the waste fluid to encourage microbial growth. In addition, the presence of the toxicant formaldehyde in the waste solution may have affected the ability of the microbial population to develop adequately so as to completely consume the available acetic acid. The spatial sequence of microbial activity present in the microbial zone at the Hercules site, which includes an inner zone of denitrification, a center zone of sulfate reduction, and an outside zone of methanogenesis, duplicates the microbial zoning predicted by Bower and McCarty (1984) in the biofilm simulation and in the flow-through experiments presented previously.

AMERICAN CYANAMID SITE, PENSACOLA, FLORIDA

Degradation reactions in an organic waste stream injected 400 m (1,300 ft) deep into a limestone aquifer by American Cyanamid near Pensacola, Florida, from June 1975 to the sampling date of August 1978, were determined from fluid samples collected from injection well backflush tests (Ehrlich and others, 1979; Vecchioli and others, 1984). Fluid samples collected from a monitor well located 132 m (433 ft) away from the injection well were also used. The waste stream was acidic (pH ~ 5.8) and contained several compounds of concern in this study, namely nitrate, acrylonitrile, cyanide, methyl alcohol, and acetone. The temperature of subsurface reactions was probably 32°C, the temperature measured in backflush samples.

Fluids sampled from backflushing of the monitor well showed signs of denitrification, as evidenced by a 59 to 63 percent decrease in nitrate from an injection concentration of 210 to 235 mg/L to a backflush concentration of 87 mg/L and a corresponding increase in two by-products characteristic of denitrification nitrate, nitrous oxide and elemental nitrogen (Payne, 1973). Other changes believed to be a result of this denitrification were a pH increase to about 8 and a reduction of the hazardous compounds acrylonitrile from an initial concentration ranging from 26 to 31 mg/L to 8 mg/L and cyanide from 8 to 3 mg/L. These reactions took place during the aquifer residence time of the backflush fluid of 107 hours. The Eh of the backflush fluid dropped from +40 to -80 within 20 hours of residence time and remained at that level throughout the remainder of backflushing. Both methyl alcohol at 5 mg/L and acetone at 1.5 mg/L were undegraded in the backflush solution. It is uncertain if waste/rock reactions were taking place inside this zone of denitrification because analyses of inorganic compounds such as Ca and Mg, which would have permitted an estimation of waste/rock reactions, were not provided.

Fluid samples were collected from a monitor well located 130 m (430 ft) from the injection well during the initial 900 days of injection. Between day 260 and day 800 of injection, a front of waste diluted with formation fluid passed by the monitor well. Chemical reactions in this mixed waste/formation fluid were evidenced by the occurrence of elevated bicarbonate and reduced pH between day 400 and day 600 of injection (figure 6, Ehrlich and others, 1979), with organic nitrogen concentrations (figure 7, Ehrlich and others, 1979) below those expected if simple mixing had occurred. These reactions suggest that denitrification had been active in the mixed waste/formation fluid. After 800 days, unmixed but chemically altered waste reached the monitor well. The complete removal of all of the injected nitrate, the absence of nitrite and nitrous oxide, transient intermediate species of denitrification, and elevated dissolved nitrogen gas concentrations of 145 mg/L led Vecchioli and others (1984) to conclude that denitrification had been completed in fluids that reaching the monitor well.

Wastes recovered from this monitor well were devoid of acrylonitrile and methyl alcohol, suggesting complete degradation. Acetone was not tested in the monitor well fluid, so its ultimate fate is uncertain. High dissolved organic carbon concentrations in the monitor well fluid, of which 58 mg/L are unaccounted for by analyses for compounds injected, suggest that new organic compounds may have formed as products of the degradation of those injected (Ehrlich and others, 1979).

Methane was found in gases sampled at all the monitor wells but not in the backflush solution. It is possible that this methane is a product of a zone of methanogenesis that occurred beyond the zone of denitrification. This could explain a narrow zone of probable methanogenic activity present in the mixed waste zone during 450 and 600 days of backflush, in which there was a sharp drop in pH to 7.5 accompanied by a peak in bicarbonate concentrations, the possible result of CO_2 released during methanogenesis.

The degradation reactions and geochemical zones described in the American Cyanamid site study are consistent with those described at the Hercules site. Cyanide was described as toxic to microbes in the Hercules injection aquifer. It was suggested that nitrile injection with cyanide at the Hercules site permits both cyanide and the nitrile to degrade as a result of denitrification. This is consistent with the reactions described from the American Cyanamid study, in which cyanide and acrylonitrile both degraded in the zone of denitrification.

Comparison of the zones present in the Hercules carboxylic acid/aldehyde waste stream with those produced by the American Cyanamid nitrile/cyanide waste stream suggests that the zones present at the Hercules site, if present at the American Cyanamid site, are compressed. In the American Cyanamid nitrile/cyanide waste stream, the zone of microbial activity appears to overlap the inner zone of rapid waste/rock interactions and neutralization (the fast reaction zone) described at the Hercules site. This overlapping of zones is probably a result of the slower reactivity of components such as alcohol in the nitrile/cyanide waste stream with the carbonates in the formation to neutralize the solution, compared to the greater reactivity of the carboxylic acids in the Hercules waste. In addition, the microbiologic activity in the American Cyanamid nitrile/cyanide waste stream was denitrification, which occurs closer to the source of injection than does methanogenesis (Bouwer and McCarty, 1984), the dominant form of microbial activity in the Hercules carboxylic acid/aldehyde waste stream. In addition, the cyanide concentration of 8 mg/L at the American Cyanamid site may have been low enough to not have been toxic to the microbial population, permitting microbial degradation in the undiluted waste closest to the injection well. In contrast, formadehyde in the Hercules waste stream was present in toxic concentrations in the undiluted waste while preventing microbial activity in the inner reaction zones.

Nitrile, cyanide, and alcohol compounds injected into a limestone aquifer at the Hercules Site at a depth of 400 m (1,300 ft) were completely degraded within 800 days of injection. The temperature of these reactions approximated the 32°C reservoir temperature. The zone of microbial degradation appeared to either coincide with or to be contained within the zone of rapid waste/rock reactions. The relationship between these two zones is the opposite of that found at the Hercules site, where a fast reaction zone of rapid waste/rock reactions was well within the zone of microbial activity. Differences between these two sites are probably the result of carboxylic acids at the Hercules site being more reactive and resulting in more rapid waste/rock reactions than American Cyanamid waste, and because of the presence of formaldehyde in the Hercules waste, which would be toxic to microbial activity in the inner zone and would allow microbes to thrive only after the waste was adequately diluted on the margins of the plume while the American Cyanamid waste contained no microbial toxins.

Summary

Results of these three field, laboratory, and numerical simulation studies indicate that biologic and chemical zones may develop in the injection aquifer. Biologic activity appears to occur in zones that follow a sequence (starting from the inside) of aerobic oxidation, denitrification, sulfate reduction, and methanogenesis. All or part of this zoning sequence may be present depending on the composition of the waste stream, formation fluid, and sediments. For example: (1) a zone of sulfate reduction was not found at the American Cyanamid site, possibly because the abundance of nitrogen compounds injected permitted denitrification to dominate, and (2) in the biofilm experiment, where acetone was the only primary substrate in the injectate, only aerobic respiration and methanogenic zones developed.

The location of the zone of biologic activity also depends on the composition of the waste stream, the formation fluid, and the sediments. Biologic activity may have begun in the immediate vicinity of the injection well, when all of the compounds injected at the American Cyanamid site were below toxic levels. In contrast, the biologic zone developed hundreds of feet from the injection well at the Hercules site only after formaldehyde, which was injected in toxic concentrations, was adequately diluted by the formation fluid so as to be nontoxic to the microbes.

Chemical zoning is governed by the combined effects of water/rock reactions, mixing with the formation fluid and biologic activity. In general, the zoning expected is that of oxygenated and either basic or acid fluid inside the waste plume to reduced and neutralized on the outer margins of the plume. Oxygenation and pH shifts do not necessarily occur simultaneously but are dependent on reactions in the aquifer. The chemical character of the fluid in the zone of biologic activity can influence the solution composition, particularly pH and oxidation potential, which may be altered by gases produced during respiration, particularly CO_2 or CH_4, or by metabolization of components such as oxygen or sulfate. Biologic activity generally results in reduction of the solution, whereas the consequences of biologic activity on the solution pH depend on the chemical system. A shift in pH is governed not only by the depletion or addition of components to the waste stream but also by shifts in aqueous speciation, which are governed by overall composition of the solution.

Results of the field studies, laboratory experiments, and calculations of subsurface reactions reveal that interactions of the waste solution with the reservoir rock, formation fluid, and microbes produce a complex series of reactions that are specific to the composition of the waste solution and to a lesser extent to the composition of the reservoir rock. Three processes--waste/rock reactions, microbial activity, and waste/formation fluid mixing--play a role in the types and extent of the reactions that will occur.

All constituents in the injected solution must be considered in evaluating waste rock reactions because all compounds in solution can possibly limit or alter the degradation paths of the hazardous compound of concern. Examples of these interrelationships are (1) the presence of the toxicant formaldehyde in the Hercules waste stream, which may have shifted the zone of biologic activity and inhibited microbial growth, resulting in incomplete microbial consumption of other compounds in solution; (2) carboxylic acids resulting in the development of an inner zone of rapid waste/rock reactions at the Hercules site (although this zone did not develop at the American Cyanamid site, in which carboxylic acids were absent from the waste stream), and (3) carboxylic acids enhancing the microbial degradation of compounds consumed as secondary substrates by acting as a nutrient in the biofilm simulation study.

In both of the field studies, microbial degradation was described as the mechanism responsible for transformation of the organic compounds disposed. Wastes in these studies had interacted in the formation for periods ranging from days to 4.5 years, producing degradation efficiencies as high as 94 and 100 percent. This suggests that in the short term if microbial activity is not inhibited it is the preferred method for degradation of organic compounds. Chemical reactions needed to permit the degradation of cyanide and other compounds in the cyanide solution also occurred during this short time. Chemical transformations, therefore, might also be an efficient method of waste mitigation. To ascertain the processes that resulted in the waste transformations described above, more complete analyses of the monitor well and backflush fluid samples, formation fluid, and aquifer material, from both the field and laboratory experiments, are needed.

RECOMMENDATIONS

Waste degradation in deep aquifers as a mechanism for waste mitigation needs further investigation. Organic wastes represent the largest types of waste injected into Gulf Coast saline formations. The toxic waste groups that should be tested are the phenols, the ketone-aldehydes, cyanide, and nitriles, both as separate waste streams and as admixtures with nontoxic organics such as carboxylic acids and alcohols. Because these chemical groups represent the largest mass of hazardous organic wastes that are injected, study of degradation reactions should focus on these organic wastes. Biodegradation appears to be an important reaction in the natural geologic setting, and, if it is occurring or could occur, then biotic reactions for organic waste degradation may be faster or far more important than abiotic degradation.

Investigating the potential for degradation should be a multifaceted program. Initially, subsurface brines in this potentially biologically active zone in the hydrostatic section should be tested for the presence of bacteria and other indicators of biologic activity. Next, an injection well needs to be tested to determine if degradation of wastes is occurring and to determine whether there are bacterial populations associated with the injection process. Bacterial populations for both studies need to be tested so that types and population densities can be determined. Then, laboratory experiments need to be designed to evaluate this potential for deep subsurface biodegradation of organic wastes and to determine whether the process can be enhanced. Finally, computer geochemical models should be used as predictive and diagnostic tools. Another recommended area of study is injection of wastes into high-temperature, high-pressure zones of the geopressured section of the Gulf Coast sediments. The high temperatures and pressures should accelerate reaction rates of abiotic degradation of organics.

The following sections discuss the different approaches for testing waste degradation.

FIELD TESTING

Field testing is the most important element for testing waste degradation. Three elements need to be tested: (1) Are there naturally occurring bacteria in the Gulf Coast formations at depths used for injection, (2) Is biodegradation occurring within active injection wells, and (3) If degradation is occurring, can we enhance the degradation process.

(a) Natural occurring bacteria. Wells drilled into the saline hydrostatic section need to be tested for bacterial populations. Some previously studied wells that show evidence of the degradation of naturally occurring organics would be good candidates for study.

(b) Waste degradation. An experimental facility for in situ testing of injected wastes is needed. It could be operated either as a test well with monitor wells or as a single well that could be backflushed.

(i) Several different waste streams could also be tested by testing wells at different waste disposal facilities. This approach would be the most cost effective. The difficulty with this approach is that a waste plume may be complexly zoned, with a biologically active zone at an intermediate distance away from the injection well. A short backflush may not pull waters from this biologic zone back to the well bore.

(ii) Testing for degradation at an injection well with monitor wells would provide the best scientific data. Known chemicals could be injected and monitored as the waste migrates away from the well. Although this approach is limited by the expense of this type of facility and the amount of time necessary for monitoring possible degradation, perhaps monitor wells could be drilled near operating injection wells. It would also be of value to core through an injection plume to study degradation by-products that may have been in the ground for many years.

(c) Enhanced degradation. If degradation is occurring between wastes and the deep geologic environment, these reactions may be enhanced with the addition of specific bacteria or the addition of nutrients. Specific reducing bacteria (denitrifiers, sulfate reducers, etc.), addition of oxygen sources (NO_3 or SO_4), or pH control may accelerate reaction rates. Wastes and additives may need to be injected into the formation as separate pulses to prevent formation clogging around the well bore by rapid biologic growth. The problem of enhancing degradation could be studied with a dedicated field test facility.

(d) Types of chemical analyses. Geochemical processes are interrelated, such that a shift in equilibrium in solution affects all components in solution. All aqueous species that could indicate the results of reactions or affect other reactions in solution should be analyzed for and studied. That includes all major and minor inorganic and organic compounds, gases, and microbial populations in fluid samples collected from laboratory and field experiments. Isotopic analysis could also prove useful in predicting reaction mechanisms. Analysis for only the hazardous compound of interest and a couple of major cations and anions does not permit prediction of chemical transformations, waste/rock reactions, microbial activity, and sorption. Reporting of complete chemical analyses permits predictions of chemical interactions from the field testing conducted on the carboxylic waste stream injected near Wilmington, North Carolina (Leenheer and others, 1976a, 1976b). In that study of the carboxylic waste reactions, for example, without complete chemical analyses it would have been difficult to discern waste losses from chemical transformation, microbial activity and sorption, and the source of gases as being from either waste/rock reactions or microbial activity. Most of the experimental work on waste transformations reported in the literature lacks complete chemical data sets and, therefore, the reported conclusions as to waste transformations are in many cases inferred and not verifiable by the data reported.

LABORATORY EXPERIMENTATION

Continued laboratory experimentation is needed. High-temperature and high-pressure conditions (that is, above surface temperatures and pressures) are needed to simulate typical injection conditions. Biodegradation may be enhanced or retarded under higher temperatures and pressures of the deep subsurface environment. Geochemical reactions (particularly those with a gas phase) are dependent upon temperature and pressure. Laboratory experimentation should be oriented toward testing biotic rather than abiotic processes. Laboratory experimentation allows several experiments to be conducted simultaneously; batch experiments, rather than flow-through experiments, will permit a greater number of degradation experiments to be run for the same cost.

THERMOCHEMICAL CALCULATIONS

Chemical equilibrium and reactions in mixed organic-inorganic waste solutions are interrelated and, therefore, thermochemical calculations can be used to predict the results of these reactions or to interpret reactions documented by experimental results from individual waste streams and injection environments. Although programs for doing these types of calculations are available, a thermochemical data base including all chemical species in solution that could affect reaction pathways is needed. A data base is already available for inorganic species and precipitates (Helgeson and others, 1978), but organic species of interest to industrial waste disposal problems need to be added to that data base. This is a major task because (1) much of the data on aqueous organic ions and compounds is unavailable and needs to be calculated from other available data (see for example, Shock, 1987), and (2) data available or calculated must be evaluated and adjusted to ensure internal consistency within the data base (for example, all experiments and calculations used the same standard states). Therefore, a thermochemical data base containing equilibrium constants for the dissociation reactions for organic compounds and ions commonly disposed of by deep well injection and their product phases in conjunction with already available data for inorganic species needs to be compiled.

INTEGRATED STUDIES

Integrated investigations to predict subsurface waste reactions include theoretical studies with coupled thermochemical calculations and numerical simulation of chemical and biological reactions, batch and flow-through laboratory experiments, and injection-backflow and flow-through field tests.

Thermochemical calculations alone cannot adequately predict hazardous waste reactions at subsurface conditions, particularly for the most commonly injected waste stream, which consists of a concentrated solution enriched in a suite of organic compounds and in some cases trace metals. Thermochemical data necessary for calculation of organic, organic-inorganic, and biochemical reactions that control degradation in complex waste streams are unavailable. In addition, ion interaction models for calculation of the behavior of organic compounds and trace metals in high-ionic-strength solutions, common to both the injectate and formation fluids, have not yet been developed. Thermochemical calculations alone that are limited to those chemical constituents for which thermochemical data are available may not adequately predict degradation reactions because chemical reactions in solution are affected by all components in the solution.

Laboratory experiments also have problems preventing adequate prediction of waste degradation reactions without being augmented with thermochemical calculations and field verification. An important limitation on laboratory experiments is the unknown contribution of microbiologic activity on waste degradation. Although preliminary data suggest that microbes are present and active at the depths of deep well injection (Wobber, 1986), not enough information is available to duplicate this microbial activity in the laboratory. If subsurface conditions are not closely duplicated, controls on degradation reactions could be misrepresented.

The favored approach is to combine field testing of a tracer-laden waste stream with monitor well samples, and injection well backflush samples, with thermochemical calculations to document inorganic and organic reactions augmented by laboratory experiments to document microbial activity, and organic reactions and sorption where thermochemical data are lacking.

REPORTING OF WASTE-STREAM COMPOSITIONS

To assist in future studies of waste degradation, it would be helpful to require more detailed waste stream descriptions in UIC permit reports. Most injectors responded to the broad requirement of a chemical analysis of the waste stream by reporting an incomplete list of major inorganic and organic constituents in solution. Rather than requiring a chemical analysis in general, specific analysis should be requested, and in some cases the preferred analytic methods should be stated. The injector should be required to ascertain that all major and minor constituents are analyzed for by using standard inorganic and organic wet chemical procedures, such as comparing the total anion and cation concentrations to the analysis of total dissolved solids, and total organic and inorganic carbon analyses to the total reported concentrations of organic compounds and alkalinity.

Information on the significant waste degradation processes and the chemical and physical limitations of these processes can be used to transform deep well injection into a method of waste mitigation rather than storage. Simple procedures exist that could be used to enhance the degradation of currently disposed solutions. For example, waste streams containing hazardous compounds for which biodegradation is the favored method of degradation are best disposed of under the following restrictions: (1) that the well be dedicated to disposal of that waste stream alone, (2) the waste stream composition be kept uniform, and (3) injection be continuous. This type of injection program will allow the microbial population that would preferentially consume the organic compounds injected to flourish with a constant food supply. Injection of a uniform composition waste prevents injection of toxic concentrations or concentrations too low to support the population. Injection of other waste streams should be prevented because those wastes may be toxic to the microbes already developed, or they may be inadequate to support the microbial population.

Another example is the case in which chemical transformations are the favored methods of degradation. Injection of multiple waste stream compositions in this situation could be used to encourage degradation by changing the solution pH or oxidation potential or by clearing sorption sites for the hazardous compound of concern. On the down side, multiple waste stream compositions might result in later desorption of hazardous compounds sorbed from a previous waste stream.

DISCUSSION AND CONCLUSIONS

CRITICAL ELEMENTS FOR DEGRADATION

Material to be Degraded

The compilation of waste stream compositions included in this report indicates that most of the wastes and hazardous materials injected are organic compounds and that they contain an array of toxic and nontoxic organic compounds and trace metals. Three of the more significant hazardous waste groups are organic, phenols, ketones-aldehydes and nitriles, and one inorganic, cyanide. The most significant nonhazardous waste groups include carboxylic acids and alcohols.

Methods of Degradation

Although microbial degradation is generally the most desired method of subsurface waste degradation, little is known of this process in the deep subsurface. Sorption can act to retard the mobility of most of the significant hazardous wastes; however, these wastes may be desorbed later when chemical conditions change in the aquifer such as might occur when injection ends. Sorption is also limited by the generally small amounts of organic material, less than 0.6 weight percent, and clay, only as grain coatings, present in the aquifer. Chemical transformations such as hydrolysis, oxidation, and chemical interactions also result in degradation, but affect only a limited number of waste groups, and each requires specific chemical conditions.

Timing of Degradation

Biodegradation can result in nearly complete degradation of organic compounds within as little as 2 days or as much as 5 years. Sorption is relatively rapid, requiring only days to occur. Chemical reactions that result in degradation, such as the transformation of cyanide by nitriles, appear to be immediate.

Hydrolysis is generally slower than biodegradation, sorption, and chemical reactions. Hydrolysis rates vary widely with pH and temperature, the fastest rates being in basic solutions at elevated temperatures. At temperatures in excess of 30°C and a pH of 9 or greater, cyanide hydrolysis could result in a 90 percent reduction in about 14 years; at 60°C, this same reduction would occur in about 3 years. In lower pH solutions, cyanide hydrolysis becomes extremely slow (on the order of thousands to hundreds of thousands of years). Nitrile hydrolysis, although somewhat slower than that of cyanide, responds similarly to pH and temperature changes.

Efficiency of Degradation

Biodegradation may be the most efficient degradation process. If a compound is metabolized as a primary substrate, biodegradation can result in consumption of concentrations of thousands of mg/L within several years. A minimum concentration of 0.01 mg/L, below which microbial activity cannot be supported, however, will remain in solution. If a compound is cometabolized as a secondary substrate, biodegradation is less efficient in that it can transform much lower amounts (tens of mg/L) of the compound. The advantage of cometabolism is that the secondary substrate concentrations, if present in small amounts (10 mg/L), can be essentially completely transformed.

The efficiencies of hydrolysis, chemical transformation, and oxidation will be governed by the equilibrium concentrations of the parent and product compounds, if the kinetics of the reaction are rapid enough so that equilibrium is achieved. Sorption efficiency is governed by the amount of sorbing material in the aquifer and the amount of sorbing compounds injected. For some compounds, such as phenols, sorption efficiency is also governed by the solution pH. Sorption probably has a relatively low efficiency in Gulf Coast injection aquifers because of the small amounts of organic material and clay present in the sandstone aquifers.

Effects of Waste Composition on Degradation

Waste Interactions--

In multicomponent waste streams, hazardous compounds can affect one another's degradation and nonhazardous compounds can affect the degradation of hazardous compounds. These interactions can be either beneficial or detrimental to hazardous waste degradation. A few of these relationships are described below.

1. Sorption interferences - Carboxylic acids are highly sorbing and have been found to be favored for sorption sites over ketone-aldehydes.

2. Metal complexing - In basic solutions, carboxylic acids and cyanide are present in the ionic form, in which state they can increase the mobility of hazardous metals by forming complexes.

3. Bacterial toxicity - Cyanide, formaldehyde, and phenols can be toxic to microbes in concentrations of 10 to 200 mg/L or greater. Their inclusion in waste streams without a compound to transform them to a nontoxic form results in delayed development of the biologic zone to the outer, diluted margins of the waste stream. Their presence also decreases the efficiency of microbial activity.

4. Enhanced cometabolism - Carboxylic acids can increase the degradation of compounds that are cometabolized as a secondary substrate by acting as a nutrient for the desired microbial population.

5. Chemical interactions - When injected with a compound that can interact with it (such as a ketone-aldehyde of a nitrile), cyanide is rendered nontoxic to microbial populations. Furthermore, cyanide injection with a ketone-aldehyde not only results in cyanide degradation but also enhances the degradation of the ketone-aldehyde.

Uniform Injection--

Biodegradation can be enhanced by following certain injection procedures. An adequate nutrient source needs to be provided continuously, as should nitrate and phosphate, which are needed for all metabolism. The waste stream should initially be introduced to the aquifer in low concentrations, allowing the microbial population to acclimate to the solution. This acclimation stage is particularly important if compounds that are toxic to microbes are in the waste stream. Solutions having microbial toxicant concentrations in excess of 10 mg/L should either be pretreated to remove some of the toxicant or have compounds added to solution to chemically transform the toxicant (such as the addition of a ketone-aldehyde to a cyanide-rich waste stream, which results in the transformation of the cyanide and permits microbial activity to persist). The worst case for microbial degradation is an injection schedule that results in intermittent injection and that includes waste streams that change in concentration or composition.

Bacterial Activity at the Depths of Deep Well Injection

Bacterial activity has to date been confirmed only to a depth of approximately 300 m (1,000 ft). Most wastes, however, are disposed of at greater depths, with Gulf Coast disposal at depths generally ranging from 610 to 2,400 m (2,000 to 8,000 ft). There is indirect evidence, however, of microbial activity to depths of 2,100 m (7,000 ft) within the Gulf Coast. It is recommended that a deep disposal aquifer that has a history of receiving a waste stream with a composition that favored microbial activity be tested for evidence of microbial activity.

Zoning in the Waste Plume

Biologic and chemical zones can develop within an injection aquifer. The biologic zones are predicted to follow a sequence starting near the injection well with aerobic oxidation, denitrification, sulfate reduction, and methanogenesis. The location of these zones and whether one or all of these zones are present depends on the waste, formation fluid, and sediment composition. Chemical changes in the injection aquifer are a product of the combined effects of microbial activity, waste/rock reactions, and mixing with the formation fluid. Oxidation and pH in the injection plume generally grade from oxygenated fluid with either an acid or basic pH near the well bore, to reduced fluid with a near neutral pH on the margins of the plume. Shifts in the oxidation potential and pH in the plume do not necessarily coincide, and pH changes in the microbial zone could result in zones of anomalous pH conditions.

Temporal Changes in the Waste Plume

Degradation reactions should change with time. In the early stages prior to development of an adequate micobial population, chemical reactions will control degradation. Once the microbial population has had a chance to acclimate and grow, biodegradation may dominate reactions. After injection is discontinued and there is no longer a source of nutrients for biodegradation, chemical reactions may again become dominant.

Subsurface degradation of wastes is generally accomplished by several processes that can be controlled by different solution components. Interactions of the waste solution with the reservoir rock, formation fluid, and microbes produce a complex series of reactions that are specific to the composition of the waste solution and to a lesser extent to the composition of the reservoir rock. In addition, all three processes--waste/rock reactions, microbial activity and waste/formation fluid mixing--play a role in the types and extent of the reactions that will occur.

A sequence of reactions develops, starting at the point of injection and progressing out into the formation. Chemical zoning includes shifts from oxidized to reduced conditions, a zone of biologic activity and waste/rock reactions. In studies of subsurface disposal aquifers, each of these processes is generally active in a disposal aquifer, but they can overlap, their order of occurrence being dependent on the waste composition and aquifer conditions. Nonhazardous components in the waste stream, such as carboxylic acids, can have effects on subsurface reactions and, therefore, the presence of all reactive species in the waste stream should also be considered in the prediction of toxic waste degradation.

In the study of subsurface waste reactions a number of approaches have been taken, notably laboratory experiments and field testing. Because of the deficiencies in thermochemical data for complex organic systems and the inherent problems of laboratory experiments in duplicating deep subsurface microbial activity, field testing is still necessary to determine the complex suite of reactions occurring upon subsurface degradation. The preferred field test would include samples from backflushing of the injection well and samples from monitor wells and would be augmented by supplemental laboratory experiments and thermochemical calculations.

Based on the potential importance of microbial degradation and lack of understanding of this mechanism at depths of over 300 m (1,000 ft), the recommendation for future work should include a field test of an injection aquifer on the order of 610 m (2,000 ft) deep, or greater, that receives a waste solution that contains compounds that would favor microbial activity, such as carboxylic acids, nitrate and phosphate. If a site with monitor wells is unavailable, backflush samples should be adequate to identify the inner microbial zones and waste/rock reactions. Care should be taken not to inject anything that would inhibit microbial growth, as this could push the microbial active zone out into the formation. After injection of the waste there should be an acclimation period prior to backflushing to allow the microbial population to grow and the zones of chemical and microbial degradation to develop.

The hazardous compounds most often disposed of by deep well injection could possibly be degraded in the subsurface and thereby prevent their long-term contamination of ground water. At present, however, disposal practices, waste-stream compositions, and waste pretreatment measures are probably inadequate for maximum subsurface degradation. Before specific recommendations for individual waste streams can be made, documentation of their reactions in the subsurface must be undertaken. Thermochemical calculations and laboratory and field verification of subsurface waste degradation reactions can possibly be used to design injection procedures that enhance waste transformations and ensure that the greatest possible degradation is taking place.

ACKNOWLEDGMENTS

Funding for this research was provided by the U.S. Environmental Protection Agency under Cooperative Agreement ID. No. CR-814056-01-0. We thank Robert Smith, Project Officer for the U.S. Environmental Protection Agency, Office of Drinking Water, Washington, D.C., Ben Knape, Tom Roth, Sam Pole, and Sheldon Seidel of the Texas Water Commission, Daniel McKaskill of Celanese, and M. T. Swoboda and M. L. Payne of E.I. Du Pont de Nemours & Co. for providing us access to information on waste compositions; David Morganwalp and Robert Smith of the U.S. Environmental Protection Agency Office of Drinking Water, Washington, D. C., for their interest in the project and for providing us with the data base compiled by the EPA-ODW; Joseph Suflita and Ralph Beeman of The University of Oklahoma for providing us with unpublished work on the anaerobic degradation of phenolic compounds; and Shaul Sorek of Technion, Haifa, Israel, for providing unpublished work on a mathematical model for ground-water denitrification. We are also grateful to Andrew Donnelly of the Bureau of Economic Geology for compiling appendices I and II, and Kelly Webb, formerly of the Bureau of Economic Geology, for assistance in compiling appendix III. This report benefited from technical reviews by Robert Smith, U.S. EPA-ODW, Kris Kamath, U.S. EPA Region 5, Frank W. Schwartz, Ohio State University, and David Koppenaal, Pacific Northwest Lab, who reviewed an earlier version of the report, and from editorial reviews by Lana Dieterich and Amanda Masterson, Bureau of Economic Geology.

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Appendix I.

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Appendix II.

Compilation of Research on Degradation and Sorption Reactions for Hazardous Waste (references listed in Appendix I)

Chemical	Environment	Degradation	References	Notes
		ORGANICS		
		Biological Processes		
Phenols				
Creosote and pentachlorophenol	Unconfined, shallow, sandy aquifer. A spill created a plume in the aquifer.	Biodegradation	Borden et al., 1986	Plume of contaminants was smaller than the Cl plume, indicating retardation. Model was used and simulated this fairly well.
p-nitrophenol	Laboratory study on soil samples	Biodegradation	Raymond and Alexander, 1971	Degraded to 4-nitrocatechol in approximately 48 hours if soil was treated with chloroform (about 20-30% degraded). If the soil was not treated with chloroform, about 50% degraded to nitrite in 4 hours.
n-nitrophenol	Laboratory study on soil samples	Cometabolism	Raymond and Alexander, 1971	Degraded to nitrohydroquinone in 60-72 hours. 50% reduction.
3,5-dinitro-o-cresol	Laboratory study on a pure culture	Biodegradation	Tewfik and Evans, 1966	Showed that biodegradation occurred in a pure culture in the laboratory.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
m, o, p- cresols	Laboratory study on shallow, anoxic sand aquifer material	Biodegradation (anaerobic)	Smolenski and Suflita, 1987	All cresols degraded. Cresols degraded at a more rapid rate under sulfate reducing conditions. If sulfate was added, the rate of degradation increased. Lag times of 10 to 100 days of p, m, o- cresols.
Phenolic compounds	Laboratory study with cyanide present	Biodegradation (methanogenic bacteria)	Fedorak et al., 1986	The presence of cyanide slowed the degradation on the phenols because it inhibits the methanogenic bacteria that degrade acetate (a product of phenol degradation) to methane. An increase in cyanide will decrease the rate of phenol degradation.
o- cresol	Laboratory study on phenol acclimated activated sludge	Biodegradation	Masunaga et al., 1986	Cresol disappeared in 1.5 hours. Went to three different dihydroxytoluenes.
Pentachlorophenol	Laboratory study	Biodegradation (anaerobic)	Guthrie et al., 1984	Pentachlorophenol (PCP) is anaerobically biodegraded. Acclimation achieved only if the PCP concentration is low during the initial exposure. Removal is complete, and sorption is only a minor removal mechanism. Anaerobic degradation is characterized as "extensive."
Ketone-Aldehydes				
Heptaldehyde, naphthalene	Injection into a shallow well in a sandy aquifer	Biodegradation/adsorption	Rittman et al., 1980	Biofilm theory. Bacteria live in thin film on the individual grains in the aquifer. Heptaldehyde was degraded to 31% of its original concentration, but unclear whether it was due to biodegradation or sorption processes. Naphthalene degraded to less than 10%.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Nitriles				
Bromoxynil (a nitrile)	Laboratory study in a basal medium (final pH= 6.6)	Biodegradation	Smith and Cullimore, 1974	After 5 weeks only 5% of the original concentration was left. There was no loss in a sterile experiment.
2,6-dichlorophenylacetonitrile	Laboratory study on surface and subsurface soils	Biodegradation	Briggs and Dawson, 1970	Rate of disappearance was 23 times faster in non-sterile soils than in sterile soils.
Acetonitrile, propionitrile, acrylonitrile, butenenitrile, hydroacrylonitrile, succinonitrile, benzonitrile	Laboratory study	Biodegradation	DiGeronimo and Antoine, 1976	All but benzonitrile supported bacterial growth. Acetonitrile degraded completely in 15 minutes sequentially to acetamide, acetic acid, and ammonia. Propionitrile degraded to approximately 10% original concentration in 100 hours to propionic acid and ammonia.
Carboxylic Acids				
Carboxylic acids	Landfill polluting an aquifer 100-200 ft below land surface	Biodegradation	Baedecker and Back, 1979a	Acid concentration decreased downgradient, and so did CH_4 concentration produced by the biodegradation of acetic acid. Note: products of biodegradation may be more harmful than the original chemicals.
Alcohols				
Methanol	Laboratory microcosm study on soil samples	Biodegradation	Novak et al., 1985	Degraded quickly with a concentration of 500-1000 mg/L totally gone in about 200 days. Anaerobic degradation occurs, but it is slower.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Methanol and higher alcohols	Laboratory study	Biodegradation (anaerobic)	Lettinga et al., 1981	Higher alcohols degraded immediately and after a lag time of a few days so did the methanol. Process may be very unstable and upset by the presence of one or more trace elements.
Tertiary butyl alcohols	Laboratory microcosm study on soil samples	Biodegradation	Novak et al., 1985	200+ days for the tertiary butyl alcohols to degrade. The degradation rate increased as the initial concentration increased.
Other and Mixed Organics				
Chlorinated hydrocarbons (tetrachloroethylene, and 1,4-dichlorobenzene)	Surface (natural infiltration of river water) Batch and column studies also conducted	Biodegradation, sorption	Schwarzenbach and Giger, 1985	Retardation depends on the size fraction of the aquifer material. 85% of the sorption occurs at size fraction $\phi < 125\ \mu$. Biological processes appear to remove many chlorinated hydrocarbons as the water infiltrates.
Monochlorobiphenyl and biphenyl	Laboratory study on river water (die-away study)	Biodegradation	Bailey et al., 1983	Both chemicals biodegraded, but the biphenyl degraded faster than the monochlor. Both reduced to 50% of the original concentration in less than 5 days. Rate of biodegradation decreased as the concentration of the chemical increased. The rate of biodegradation increased with time.
Dimethylamine, diethylamine, dithanolamine	Laboratory study using trace concentrations (ng level) in stream water	Biodegradation	Boethling and Alexander, 1979	At trace levels biodegradation decreases. This is because at low levels the bacteria cannot grow and increase in population. Important because natural conditions are often at low levels like this. Density of bacteria is important because if the chemical is present at low concentrations, no more bacteria can grow.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Trihalomethanes, chloroform	Batch laboratory experiments, aerobic and anaerobic conditions	Biodegradation	Bouwer et al., 1981	No aerobic degradation occurred. The trihalomethanes biodegraded almost completely in less than 2 weeks. Chloroform also degraded, but at a significantly slower rate.
m-chlorobenzoate and 2,3,6-trichlorobenzoate	Laboratory study	Cometabolism	Horvath and Alexander, 1970	The two were completely converted to other organics (4-chlorocatechol, 3,5-dichlorocatechol)
Naphthalene, fluorene, dibenzofuran, anthracene, and pentachlorophenol	Study in ground-water samples and laboratory study on subsurface soil samples from approximately 24 ft down	Biodegradation	Lee et al., 1984	Naphthalene degraded the most quickly (up to 100%/week), then dibenzofuran and fluorene. Anthracene and pentachlorophenol degraded the most slowly. An increased initial concentration did not seem to have an effect on the rate of biodegradation. In both contaminated and uncontaminated soil samples the pollutants removed at approximately 3.5% per week.
Trichloroethylene	Field site with ground-water contamination by organics; 1.2-m-thick sand aquifer about 4-5 m below ground surface	Biodegradation by methane consuming bacteria, sorption	Semprini et al., 1988	Retardation factors for trichloroethylene and trichloroethane estimated at 3 and 7.5 respectively. Trichloroethylene biodegraded 30% in a test case at a field site. Methane and trichloroethylene were added to the aquifer in pulses.
Toluene, styrene, chlorobenzene	Samples used in laboratory study taken from above and below the water table (2-5 m depth) at 2 sites	Biodegradation	Wilson et al., 1983	Toluene degraded 1-3%/week Styrene degraded 2.5-12%/week Chlorobenzene degraded 1-2%/week

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Naphthalene, 1-methylnaphthalene	Laboratory study done with soil samples (a sandy loam)	Biodegradation	Sims et al., 1988	Half lives were about 2 days. Degradation was characterized as "extensive."
Chlorinated methane, ethane, and ethenes	Spilling on ground that infiltrates to a shallow aquifer (200'-300')	Biodegradation	Wood et al., 1985	This paper deals with volatile organics in ground water. Many of the highly volatile compounds present are due to the biodegradation of tri- and tetrachloroethylene. All parent and daughter compounds studied were susceptible to biodegradation.
Toluene and styrene	Surface and subsurface environments were simulated in microcosm (batch and column) experiments in the laboratory.	Biodegradation	Wilson et al., 1985	Study shows that the amount of biodegradation varies from site to site and is different in different environments. Concluded that biodegradation in the subsurface cannot be determined by the behavior at the surface.
Naphthalene	Injection into a shallow well in a sandy aquifer	Adsorbed, then biodegraded	Rittman et al., 1980	Naphthalene degraded to <10% of its original concentration in less than 12 hours. It was retarded and then biodegraded by bacteria in biofilm.
Toluene	Unconsolidated sediments (0-10 m). Two sites were used, a pristine site in OK, and a site contaminated by a disposal lagoon for wood-creosoting wastes.	Biodegradation	Wilson et al., 1986	Study relates amount of ATP present in the organic to the amount of biodegradation that occurs. As ATP increases in the toluene it becomes more susceptible to biodegradation.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Alkylated and chlorinated benzenes	Field study. Looked at river water infiltrating into ground water.	Biodegradation	Schwarzenbach et al., 1983	The volatile organics were not adsorbed at all and therefore dispersed if they were not biodegraded. Biodegradation did not occur for chloroform, 1,1,1-trichloroethane, trichloroethylene, or tetrachloroethylene. 1,4-dichlorobenzene biodegraded only in aerobic conditions. Biodegradation occurred for all alkylated benzenes, naphthalenes, and methylnaphthalenes. Eliminated in the first few meters of infiltration and at 5°C. 1,4-dichlorobenzene biodegraded at a rate slower than the others.
Alkylpyridines	Ground water	Biodegradation (anaerobic and aerobic)	Rogers et al., 1985	Aerobic degradation reduced concentrations to zero in 10-31 days. Anaerobic degradation reduced concentrations 40-80% in 33 days, notably more slowly.
Methanol, propanol, sodium acetate, glucose, acetone, cyanide	Laboratory study	Biodegradation	Lewandowski, 1984	Cyanide inhibits denitrification of methanol, propanol and sodium acetate. Doesn't inhibit glucose or acetone degradation because the cyanide reacts to form cyanohydrins, and therefore removes the toxic effect.
Carboxylic acids, alcohols, phenols, ketone-aldehydes, nitriles	Laboratory study at high temperatures and pressures	Biodegradation (aerobic)	Grula and Grula, 1976	Simulated deep well conditions; unfortunately did not do anaerobic degradation. Determined that many wastes did degrade, but under conditions existing in deep wells they will not degrade and therefore that biodegradation should not be relied on.
Alkylbenzenes and halogenated aliphatic hydrocarbons	Laboratory microcosm study	Biodegradation (anaerobic)	Wilson, Smith, and Rees, 1986	Biodegradation did occur, but often with a long lag time (many weeks). Alkylbenzenes are not expected to degrade in anoxic waters.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Halogenated organics	Laboratory column studies and a batch model	Biodegradation (aerobic and methanogenic)	Bouwer and McCarty, 1984	Biofilm model developed to model the secondary utilization of trace pollutants. This occurs when a trace compound is biodegraded by bacteria biodegrading the primary substrate. Study showed up to 95%+ removal.
Nitriloacetic acid	River sediment	Biodegradation	Loch and Lagas, 1985	Nitriloacetic acid rapidly disappears owing to biodegradation. There is no difference between anoxic and oxic conditions. Complete degradation occurred within 8 days if organisms were present at the start of the experiment, but took one month if bacteria had to be acclimated. Nitriloacetic acid did not affect metal concentrations.
		Sorptive Processes		
Phenols				
Phenol	Laboratory study-flow through model (at 60^{o}C and 38^{o}C)	Adsorption	Collins and Crocker, 1988	More phenol was adsorbed at 38^{o} C than at 60^{o} C. There was also a larger percent adsorbed at a higher initial concentration. No desorption occurred. No degradation seemed to occur.
Chlorinated phenols (and ionizable hydrophobic compounds: phenols, amines, carboxylic acids)	River sediments	Sorption	Schwarzenbach and Westall, 1985	Sorption increased as pH decreased owing to decreased ionization.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Chlorinated phenols	Laboratory study	Sorption	Schellenberg et al., 1984	As pH decreased, sorption increased. There was a correlation between K_{ow} and percent organic carbon in the sorbent. If percent organic carbon decreased then there were small distribution ratios for chlorinated phenols. For some, phenolate sorption is very important, and the degree of sorption depends on the ionic strength of the aqueous solution.
Chlorinated phenols	Laboratory study	Sorption	Westall et al., 1985	Organic-inorganic pairs can be very important in the non-aqueous phase. As the pH and ionic strength increase, chlorophenolate ions in association with K^+ were the dominant species. Distribution of chlorinated phenols between aqueous and non-aqueous phases was shown to depend on pH and ionic strength.
Acetophenone, benzophenone, phenol, 2,4-dichlorophenol	Laboratory	Sorption (and chemical reactions)	Briggs, 1981	Laboratory work determined: Phenol K_{ow}= 1.46 Acetophenone K_{ow}= 1.58 Benzophenone K_{ow}= 3.18 2,4-dichlorophenol K_{ow}= 2.80 and R_f= 0.30
Ketone-Aldehydes				
Camphor, fenchone (ketones)	Waste dump	Sorption	Zoetman et al., 1981	Half lives of camphor and fenchone are 0.3 and 0.6 years. Half life estimates for many more compounds are available in this paper.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Acetophenone	Laboratory study on sediments and soils	Sorption	Khan et al., 1979	K_p (partition coefficients) increase with increasing organic carbon percent in the sediments. If the total organic carbon is low then an increase in montmorillonite causes K_p to increase. As the amount of acetophenone increases the amount adsorbed increases.
Nitriles				
n-butyronitrile, pyridine,2,6-dimethylpyridine, 2,5-dimethylpyrrole, quinoline, inodole, stearonitrile	Petroleum reservoir, studying natural organics (no anthropogenic pollutants). Laboratory work done on clays.	Ion exchange, adsorption onto clays	Charlesworth, 1986	Neutral and especially basic nitrogen compounds are removed by clay adsorption. Based on the ion exchange capacity of the clays.
2,6-dichlorobenzonitrile	Laboratory study on surface and subsurface soils	Sorption	Briggs and Dawson, 1970	Partition coefficients correlated with the organic matter content. The amount of clay in the sorbent had no effect. There was no difference between the sterile and non-sterile experiments. Half lives were at least 5 months in this closed system.
Other and Mixed Organics				
Chlorobenzene, chloroform, ammonia trihalomethanes	Shallow aquifer (30'-50')	Sorption	Roberts et al., 1985	Very few details. Shows that chlorobenzene is retarded the most, then bromoform, and the least retarded in the study is chloroform. Retardation is attributed to sorption.
di-, tri-, and tetrachlorophenyls	Shallow (<50 cm) marine sediments, polluted by PCB rich harbor waters	Sorption to organic colloids; possible biodegradation	Brownawell and Farrington, 1986	Di-, tri-, and tetrachlorobiphenyls were sorbed to organic colloids and may also have been biodegraded.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Benzene, naphthalene, anthracene	Natural estuarine colloids studied in the laboratory	Sorption	Wijayaratne and Means, 1984	Sorption was by an order of magnitude greater than that reported for pond sediments. Suggests that hydrophobic compounds are more strongly bonded to estuarine colloid organic material. K_d's are 920, 4060, and 510000 for benzene, naphthalene, and anthracene.
Pyrene, methoxychlor	Laboratory study--studied bottom sediments in different sediment size fractions	Sorption	Karickoff et al., 1979	Sorption increases with increasing organic carbon content and with a smaller size fraction ($< 50\ \mu$). Knowing K_{ow} can help in getting a good estimate of the K_{oc} of the sediments.
Nonpolar organics- halogenated alkenes and benzenes	Column and batch experiments	Sorption	Schwarzenbach and Westall, 1981	These are volatile solutes. There is a correlation between the organic carbon content of the sorbent and the K_p of the compounds if the organic carbon content of the sediments is greater than 0.1%. Compounds are very mobile (low K_p) in "organic poor" media. Sorption is reversible for natural conditions.
Pyrene, 7,12-dimethylbenz[α]anthracene, 3-methylcholanthracene, dibenzanthracene	Laboratory study--11 sediments and 3 soils	Sorption	Means et al., 1980	An increase in the mass of the compound does not control the sorptive properties. The effective chain length does (increase chain length, increase sorption). Pyrene < 7,12-dimeth. < 3,methyl. < dibenz. in sorption.
Naphthalene, anthracene, fluoranthene	Laboratory, modeling	Sorption	Grenney et al., 1987	A model was developed to simulate movement of a hazardous substance in the unsaturated zone. Lab work done with three polynuclear aromatic hydrocarbons shows that the model closely simulated the fate and behavior of the three compounds.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Nonionic organic compounds	Laboratory study on a silt loam soil	Sorption	Chiou et al., 1983	Found that the insolubility of the solute in water is the main factor in estimating the octanol-water partition coefficient. The percent organic carbon in the soil is important, but secondary.
1-butanol, phenol, crotonaldehyde, pyridine, 2-butanone, 1,2-dichloroethane, n-hexyamine, 1-nitropropane, propylproponate	Laboratory study on sandstone core	Sorption	Donaldson et al., 1975	Adsorption increased as initial concentration increased and as temperature decreased. Adsorption controlled by the bulk and internal pore diffusion.
1,4-dioxane, benzene, carbon tetrachloride, diethyl ether, tetrahydrofuran, 1,2-dichloroethane	Landfill leachate in a shallow (approximately 20 ft below the surface) aquifer	Sorption	Patterson et al, 1985	Plumes were different sizes; all were smaller than the chloride plume. Retardation factors were estimated to be from 1.6 to 23, with carbon tetrachloride being the most retarded, but also severely retarded was benzene and 1,2-dichloroethane.
Phenols, ketones, alcohols	Laboratory study on three soils	Sorption	Southworth and Keller, 1986	No real correlation was found between the amount of sorption and the hydrophobicity. Any estimate of the sorption coefficient is probably imprecise.
		Other Processes		
Cholesterol, 2,2',5,5'-tetrachlorobiphenyl (PCB)	River water	Association with organics	Hassett and Anderson, 1979; 1982	Association of cholesterol and PCB with dissolved organic matter inhibits adsorption of these chemicals.
Hydrogen	Study in sediments	Methanogenesis and sulfate reduction	Oremland and Taylor, 1978	Methanogenesis and sulfate reduction are not mutually exclusive.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Acidic waste and alkaline waste	Sandstone and dolomite samples studied in the lab	Neutralization	Roy et al., 1988	The acidic waste reacted with the carbonate and was neutralized. It was only partially neutralized by the sandstone. The alkaline waste remained hazardous after it reacted with the rocks.
Ammonia, chloroform, chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene	Injection of reclaimed water into an aquifer approximately 185 ft below the surface.	Biological or chemical reactions	Roberts et al., 1978	Ammonia travels at approximately one-fortieth as fast as the front's rate. 1,3- and 1,4-dichlorobenzene were retarded somewhat.
1,1-dichloroethane, chloroform, 1,1,1-trichloroethane	Samples studied in the laboratory on soil samples taken from above and below the water table (2-5-m depth) at two sites	Lack of biodegradation	Wilson et al., 1981	These compounds did not degrade.
Monohalogenated alkanes	Surface (leaking waste water tank). Batch and column studies also conducted.	Hydrolysis (esp. important for tertiary halides)	Schwarzenbach and Giger, 1985	Hydrolysis seems to be important, especially for the tertiary halides. Hydrolysis depends on the constitution of the compound. Study shows that under anaerobic conditions the alkylhalides can undergo other reactions, such as nucleophobic substitution reactions.

Case Studies of Deep Well Injection

Wilmington, NC

Chemical	Environment	Degradation	References	Notes
Carboxylic and dicarboxylic acids, formaldehyde, methanol	Deep well injection (850-1000 ft) into unconsolidated sediments (sand and clay) with some interbedded limestones	Biodegradation, chemical reactions, neutralization, adsorption. Produced CH_4, CO_2, and H_2S. Biodegradation, however at a fairly low efficiency	Leenheer and Malcolm, 1973; DiTommaso et al., 1973; Leenheer et al., 1976a, 1976b	Wilmington, NC, case study. Study showed that four different types of reactions occurred as the waste front moved into the aquifer: dilution, biodegradation, chemical reactions, and then neutralization. As the waste front arrived the number of microorganisms in the aquifer increased tremendously, indicating microbial activity. Low efficiency system.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
				Waste front also appears to cause changes that harm the bacteria. Acid first reacts with the aquifer to form CO_2. Also dissolves the aluminosilicates, Fe sesquioxide coatings. Fe complex (complexed with phthalic acid) precipitates. Biodegradation produces methane. There appears to be a retention of the waste due to adsorption and anion exchange.
Pensacola, FL- Monsato Co.				
Organic acids, nitric acid, amines, ketones	Deep well injection into a limestone aquifer (1000+ ft deep)	Chemical reactions	Goolsby, 1971, Barraclough, 1966 for background and operations	Nitrate reduction occurs. Also neutralization, but not from dissolving $CaCO_3$; rather it is thought to be due to nitric acid reaction with alcohols and ketones. About ten months after injection began, the Ca concentration increased at an observation well 1300 feet away. This was thought to be due to the dissolution of calcite in the limestone.
Alcohols, ketones, acids, esters, nitriles	Deep well injection into a limestone aquifer (1000+ ft deep)	Neutralization and denitrification	Goolsby, 1972	Acidic waste is thought to dissolve the limestone and is therefore neutralized. Denitrification was shown to occur in a backflushing experiment.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Pensacola, FL- American Cyanamid				
Organonitriles, nitrate, cyanide, acetone	Deep well injection into a limestone aquifer (approximately 1300 ft deep)	Biodegradation	Ehrlich et al., 1979 Vecchioli et al., 1984	The organonitriles and nitrate degraded. Back flow test showed that the degradation was complete within 100 meters of the point of injection. Confirmed by monitoring well. Denitrifying bacteria (anaerobic) present. Cyanide also appears to decrease, although this is not covered in the report.
Other Studies				
Iron	Deep well injection of reclaimed water into a sand aquifer 420 to 480 ft deep	Redox reactions	Ragone et al., 1973	Change in the redox conditions caused by the waste causes pyrite to dissolve, and therefore the Fe in solution increases. Eventually a ferric hydroxide precipitates, and the Fe in solution decreases.
Injected waste (especially acetate)	Deep well injection	Complexing, destabilization of mineral phases	Drez, 1988	Waste can affect formation minerals, especially the organic acids. Acetate is good at complexing some metals and can affect mineral stability, including aluminosilicate minerals.

Other Case Studies

Chemical	Environment	Degradation	References	Notes
Palo Alto, CA				
Fresh water	Aquifer approximately 45 to 55 ft below the surface	Dilution, dissolution	Hamlin, 1987	As injected fresh water gets into the aquifer, dilution of the formation water occurs. Calcite becomes undersaturated and dissolves.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
Injected water	Aquifer approximately 45 to 55 ft below the surface	Ion exchange	Valocchi et al., 1981	Computer simulation closely agreed with field simulation of fronts of injected ions. Indicates that laboratory-determined chemical parameter values can be used in field scale simulations.
Chloroform, chlorobenzene, trihalomethanes, naphthalene	Aquifer approximately 45 to 55 ft below the surface	Biodegradation	Roberts et al., 1982 Roberts and Valocchi, 1981	Trihalomethanes biodegrade very quickly. Chloroform degrades slightly.
Chlorobenzene, chloroform, bromoform	Aquifer approximately 45 to 55 ft below the surface	Sorption	Roberts et al., 1982 Roberts and Valocchi, 1981	Chlorobenzene is greatly retarded, followed by bromoform and chloroform, which are retarded only slightly. The bulk of the organics are not retarded.
Other Studies				
Butyric acid, phenol, chlorophenol, dimethyl phthalate	Injection into an aquifer 16 to 20 ft below the surface	Biodegradation	Sutton and Barker, 1985	No sorption occurs. The organic carbon content in the sand is 0.15%. Biodegradation does appear to be occurring. Degrades in the order: Butyric acid >> phenol > chlorophenol > dimethyl phthalate
NH_4^+, CH_4, Fe, Mn	Marine sediments as a natural analog to a landfill	Biodegradation	Baedecker and Back, 1979b	Concluded that it is a good analog. Found three biochemical zones: an anaerobic zone, a transition zone, and an aerobic zone. The boundaries are controlled by dilution and self-purification processes.

Appendix II (continued).

Chemical	Environment	Degradation	References	Notes
		INORGANICS		
Sr^{90}, Cs^{137}	Basaltic aquifer, approximately 500 ft beneath surface	Sorption, which has a large influence	Robertson and Barraclough, 1973	All radionuclides. Ground-water motion and mass transport model was developed for this problem, and this proved to be useful, by successfully simulating *distribution* and transport history of chloride and tritium.

Appendix III.

Chemical Compositions of Hazardous Waste Streams Injected into Noncommercial Class I Industrial Waste Disposal Wells in Texas.

Company: Amoco
Plant: Texas City
UIC No.: WDW-80

Waste: organic, brine, caustic
Process: refinery operation

Gallons of waste injected in 1985:	13540330
Gallons of waste injected in 1986:	33790
Injection temperature (centigrade):	
Specific gravity: 1.00-1.14	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.6	7.6
total dissolved solids	1820	16619
Na	520	520
K	0.2	0.2
Mg	0.01	0.01
Cl	760	1843
HCO_3	12070	12070
sulfide	0.1	1117
sulfate	78	78
sulfite	6000	6000
F	1.2	1.2
ammonia	0.1	985
nitrate	36	36
nitrogen	12000	12000
Zn	0.11	0.11
As	0.16	0.16
Cu	600	600
Cr	0.08	0.08
Se	0.01	0.01
Pb	96	96
Cd	6	6
Ba	0	0.8
Ag	0.02	0.02
CN (cyanide)	0.01	0.01
ORGANIC COMPOUNDS		
total organic carbon	16	13650
chemical oxygen demand	31	74130
biochemical oxygen demand	64	21116
oil and grease	4	4
phenols (group)	420	872
cresol (cresylic acid)	0	4200
mercaptans	0	4000

NOTES:
Type of waste: sour water, ammonia-rich water, amine solutions, brines, spent caustic. The same waste is injected into WDW-127 and 128.

Company: Amoco
Plant: Texas City
UIC No.: WDW-127

Waste: organic, brine, caustic
Process: refinery operation

Gallons of waste injected in 1985:	148105360
Gallons of wste injected in 1986:	no data
Injection temperature (centigrade):	
Specific gravity: 1.00-1.14	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.6	7.6
total dissolved solids	1820	16619
Na	520	520
K	0.2	0.2
Mg	0.01	0.01
Cl	760	1843
HCO_3	12070	12070
sulfide	0.1	1117
sulfate	78	78
sulfite	6000	6000
F	1.2	1.2
ammonia	0.1	985
nitrate	36	36
nitrogen	12000	12000
Zn	0.11	0.11
As	0.16	0.16
Cu	600	600
Cr	0.08	0.08
Se	0.01	0.01
Pb	96	96
Cd	6	6
Ba	0	0.8
Ag	0.02	0.02
CN (cyanide)	0.01	0.01
ORGANIC COMPOUNDS		
total organic carbon	16	13650
chemical oxygen demand	31	74130
biochemical oxygen demand	64	21116
oil and grease	4	4
phenols (group)	420	872
cresol (cresylic acid)	0	4200
mercaptans	0	4000

NOTES:
Type of waste: sour water, ammonia-rich water, amine solutions, brines, spent caustic. The same waste is injected into WDW-80 and 128.

Company: Amoco
Plant: Texas City
UIC No.: WDW-128

Waste: organic, brine, caustic
Process: refinery operation

Gallons of waste injected in 1985:	45947780
Gallons of waste injected in 1986:	no data
Injection temperature (centigrade):	
Specific gravity: 1.00-1.14	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.6	7.6
total dissolved solids	1820	16619
Na	520	520
K	0.2	0.2
Mg	0.01	0.01
Cl	760	1843
HCO_3	12070	12070
sulfide	0.1	1117
sulfate	78	78
sulfite	6000	6000
F	1.2	1.2
ammonia	0.1	985
nitrate	36	36
nitrogen	12000	12000
Zn	0.11	0.11
As	0.16	0.16
Cu	600	600
Cr	0.08	0.08
Se	0.01	0.01
Pb	96	96
Cd	6	6
Ba	0	0.8
Ag	0.02	0.02
CN (cyanide)	0.01	0.01
ORGANIC COMPOUNDS		
total organic carbon	16	13650
chemical oxygen demand	31	74130
biochemical oxygen demand	64	21116
oil and grease	4	4
phenols (group)	420	872
cresol (cresylic acid)	0	4200
mercaptans	0	4000

NOTES:
Type of waste: sour water, ammonia-rich water, amine solutions, brines, spent caustic. The same waste is injected into WDW-80 and 127.

Company: Arco
Plant: Channelview
UIC No.: WDW-36

Waste: organic
Process: manufacture of synthetic organic chemicals

Gallons of waste injected in 1985:	no data
Gallons of waste injected in 1986:	24750327
Injection temperature (centigrade): ambient	
Specific gravity: 1.03-1.06	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	11	13
total dissolved solids	60500	86100
Na	11650	25450
CO_3	9550	13750
sulfide	50	8550
nitrogen	5	21
Hg	0	0.02
ORGANIC COMPOUNDS		
total organic carbon	22900	46000
chemical oxygen demand	75000	133000
alpha-methyl benzyl alcohol	2630	3620
propylene glycol (propanediol)	11010	13670
benzene	0	100
ethyl benzene	0	100
styrene (vinyl benzene)	0	40
acetophenone (methyl phenyl ketone-benzene deriv)	220	620
phenol	2100	3800
allyl alcohol	0	100

NOTES:
Chemical pretreatment: pH adjusted
WASTE produced from manufacture of: methyl ethyl ketone by butylene hydrolysis, isopropyl alcohol by catalytic hydrogenation of acetone, poly butadiene by polymerization, ethylene and propylene by pyrolysis of naphthe and/or gas and oil, styrene maleic anhydride by esterification of styrene, and maleic anhydride.
Type of waste: 4 waste streams
1. caustic wastewater
2. oxidation heavies
3. formaldehyde
4. misc. wastewaters

Permit reports suggest that the same waste stream is injected into WDW-148 and 162.

Company: Arco
Plant: Channelview
UIC No.: WDW-148

Waste: organic
Process: manufacture of synthetic organic chemicals

Gallons of waste injected in 1985:	77240689
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity: 1.03-1.06

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	11	13
total dissolved solids	60500	86100
Na	11650	25450
CO_3	9550	13750
sulfide	50	8550
nitrogen	5	21
Hg	0	0.02
ORGANIC COMPOUNDS		
total organic carbon	22900	46000
chemical oxygen demand	75000	133000
alpha-methyl benzyl alcohol	2630	3620
propylene glycol (propanediol)	11010	13670
benzene	0	100
ethyl benzene	0	100
styrene (vinyl benzene)	0	40
acetophenone (methyl phenyl ketone-benzene deriv)	220	620
phenol	2100	3800
allyl alcohol	0	100

NOTES:
Chemical pretreatment: pH adjusted
See memo WDW-36

Company: Arco
Plant: Channelview
UIC No.: WDW-162

Waste: organic
Process: manufacture of synthetic organic chemicals

Gallons of waste injected in 1985:	44
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity: 1.03-1.06

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	11	13
total dissolved solids	60500	86100
Na	11650	25450
CO_3	9550	13750
sulfide	50	8550
nitrogen	5	21
Hg	0	0.02
ORGANIC COMPOUNDS		
total organic carbon	22900	46000
chemical oxygen demand	75000	133000
alpha-methyl benzyl alcohol	2630	3620
propylene glycol (propanediol)	11010	13670
benzene	0	100
ethyl benzene	0	100
styrene (vinyl benzene)	0	40
acetophenone (methyl phenyl ketone-benzene deriv)	220	620
phenol	2100	3800
allyl alcohol	0	100

NOTES:
Chemical pretreatment: pH adjusted
See memo WDW-36

Company: Asarco
Plant: Amarillo Copper
UIC No.: WDW-129

Waste: acid, metals
Process: electrolytic refining of Cu

Gallons of waste injected in 1985:	69743814
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1.5	1.5
total dissolved solids	13520	13520
Na	1700	1700
Mg	51	51
Cl	827	827
H_2SO_4	4900	4900
nitrate	1700	1700

NOTES:
Chemical pretreatment: pH neutralized
Other chemicals reported as present without concentrations: SiO_2, K, Al, Fe
Also trace metal compounds = 382 mg/L

Company: Badische
Plant: Freeport
UIC No.: WDW-51

Waste: organic
Process: manufacture of cyclohexanone and caprolactam

Gallons of waste injected in 1985:	33780000
Gallons of waste injected in 1986:	38287000

Injection temperature (centigrade): ambient
Specific gravity: 1.16

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	7.5
total dissolved solids	50000	100000
Na	100000	125000
Ca	0	1
Mg	0	1
Fe	0	2.6
Si	0	73
Al	0	4.5
Cl	0	2500
B	0	15
sulfate	0	30000
ammonia	0	3000
Zn	0	5
Cu	0	0.1
Ni	0	1.2
Mn	0	0.1
Cr	0	0.16
Co	1.7	20
ORGANIC COMPOUNDS		
cyclohexane	0	2000
cyclohexanol (cyclohexyl alcohol)	1000	3600
cyclohexanone	100	1000
formic acid	500	1000
acetic acid (ethanoic)	500	1000
propionic acid (propanoic)	500	1000
butyric acid (butanoic)	500	1000
valeric acid (pentanoic)	500	94000
caproic acid (hexanoic)	500	40000
hydroxycaproic acid	25000	300000
malonic acid	10000	27000
succinic acid	10000	27000
glutaric acid	10000	10000
adipic acid	30000	40000
caprolactam (aminohexanoic acid lactam)	0	5000
polyesters	0	85000
sulfonated organics	0	10000

NOTES:
Generalized description of waste stream: A combination of varying amounts of extraction tower bottoms, caustic water, and acid water. The same waste is injected into WDW-99.

Company: Badische
Plant: Freeport
UIC No.: WDW-99

Waste: organic
Process: manufacture of cyclohexanone and caprolactam

Gallons of waste injected in 1985: 0
Gallons of waste injected in 1986: 0
Injection temperature (centigrade): ambient
Specific gravity: 1.16

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	7.5
total dissolved solids	50000	100000
Na	100000	125000
Ca	0	1
Mg	0	1
Fe	0	2.6
Si	0	73
Al	0	4.5
Cl	0	2500
B	0	15
sulfate	0	30000
ammonia	0	3000
Zn	0	5
Cu	0	0.1
Ni	0	1.2
Mn	0	0.1
Cr	0	0.16
Co	1.7	20
ORGANIC COMPOUNDS		
cyclohexane	0	2000
cyclohexanol (cyclohexyl alcohol)	1000	3600
cyclohexanone	100	1000
formic acid	500	1000
acetic acid (ethanoic)	500	1000
propionic acid (propanoic)	500	1000
butyric acid (butanoic)	500	1000
valeric acid (pentanoic)	500	94000
caproic acid (hexanoic)	500	40000
hydroxycaproic acid	25000	300000
malonic acid	10000	27000
succinic acid	10000	27000
glutaric acid	10000	10000
adipic acid	30000	40000
caprolactam (aminohexanoic acid lactam)	0	5000
polyesters	0	85000
sulfonated organics	0	10000

NOTES:
See WDW-51

Company: Caithness Mining
Plant: Hebbronville
UIC No.: WDW-185

Waste: low level radioactive (Ra^{226}-U)
Process: In situ leach for uranium and aquifer restoration

Gallons of waste injected in 1985: 44302504
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.0-1.1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	7.5
total dissolved solids	1000	42000
Na	500	10000
K	0	100
Ca	100	3000
Mg	0	200
Cl	500	10000
CO_3	100	3000
HCO_3	100	5000
sulfate	100	5000
Mo	0	100
U	0	100
Ra^{226} (pCi/liter)	200	1000

Company: Celanese
Plant: Bay City
UIC No.: WDW-14

Waste: organic
Process: chemical manufacturing (see memo)

Gallons of waste injected in 1985: 57803040
Gallons of waste injected in 1986: 66307680
Injection temperature (centigrade): 29-35
Specific gravity: 1.002

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.9	6.6
total dissolved solids	366	948
ammonia	500	500
nitrate	0.6	1.5
Zn	0.15	0.42
V	0.001	0.032
As	0.001	0.006
Cu	0.07	0.14
Ni	1	3.45
Mn	0.1	0.61
Cr	0.011	0.26
Se	0.001	0.006
Pb	0.001	0.017
Cd	0.001	0.002
Ba	0.002	0.093
Hg	0.3	2.6
CN (cyanide)	0	10
ORGANIC COMPOUNDS		
total organic carbon	1430	2591
cyclohexane	200	300
methyl alcohol (methanol)	0	300
ethyl alcohol (ethanol)	0	300
propyl alcohol (propanol)	0	300
butyl alcohol (butanol)	0	300
pentyl alcohol (pentanol)	0	300
hexanol	0	1000
amyl alcohol	0	600
phenols (group)	0.10	0.33
formic acid	0	1500
acetic acid (ethanoic)	0	1500
propionic acid (propanoic)	0	1500
butyric acid (butanoic)	0	1500
valeric acid (pentanoic)	0	1500
succinic acid	0	500
glutaric acid	0	500
adipic acid	0	500
hexamethylene imine	1400	1400
chlorinated organics	9	403

NOTES:
Chemical pretreatment: pH adjusted with NH_3 and NaOH.
Waste from manufacture of: acetaldehyde, vinyl acetate, n-butyl alcohol, n-propyl alcohol, iso-butyl alcohol, heptanoic acid, nonanoic acid hydrogen, systhesis gas, C7 and C9 aldehydes, propionic acid, and fatty alcohols. The same waste is injected into WDW-32 and 49.

Company: Celanese
Plant: Bay City
UIC No.: WDW-32

Waste: organic
Process: chemical manufacturing (see WDW-14)

Gallons of waste injected in 1985: 53062560
Gallons of waste injected in 1986: 37015200
Injection temperature (centigrade): 29-35
Specific gravity: 1.002

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.9	6.6
total dissolved solids	366	948
ammonia	500	500
nitrate	0.6	1.5
Zn	0.15	0.42
V	0.001	0.032
As	0.001	0.006
Cu	0.07	0.14
Ni	1	3.45
Mn	0.10	0.61
Cr	0.011	0.26
Se	0.001	0.006
Pb	0.001	0.017
Cd	0.001	0.002
Ba	0.002	0.093
Hg	0.3	2.6
CN (cyanide)	0	10
ORGANIC COMPOUNDS		
total organic carbon	1430	2591
cyclohexane	200	300
methyl alcohol (methanol)	0	300
ethyl alcohol (ethanol)	0	300
propyl alcohol (propanol)	0	300
butyl alcohol (butanol)	0	300
pentyl alcohol (pentanol)	0	300
hexanol	0	1000
amyl alcohol	0	600
phenols (group)	0.10	0.33
formic acid	0	1500
acetic acid (ethanoic)	0	1500
propionic acid (propanoic)	0	1500
butyric acid (butanoic)	0	1500
valeric acid (pentanoic)	0	1500
succinic acid	0	500
glutaric acid	0	500
adipic acid	0	500
hexamethylene imine	1400	1400
chlorinated organics	9	403

NOTES:
Chemical pretreatment: pH adjusted with NH_3 and NaOH. See notes for WDW 14.

Company: Celanese
Plant: Bay City
UIC No.: WDW-49

Waste: organic
Process: chemical manufacturing (see WDW-14)

Gallons of waste injected in 1985: 5402560
Gallons of waste injected in 1986: 34165440
Injection temperature (centigrade): 29-35
Specific gravity: 1.002

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.9	6.6
total dissolved solids	366	948
ammonia	500	500
nitrate	0.6	1.5
Zn	0.15	0.42
V	0.001	0.032
As	0.001	0.006
Cu	0.07	0.14
Ni	1	3.45
Mn	0.10	0.61
Cr	0.011	0.26
Se	0.001	0.006
Pb	0.001	0.017
Cd	0.001	0.002
Ba	0.002	0.093
Hg	0.3	2.6
CN (cyanide)	0	10
ORGANIC COMPOUNDS		
total organic carbon	1430	2591
cyclohexane	200	300
methyl alcohol (methanol)	0	300
ethyl alcohol (ethanol)	0	300
propyl alcohol (propanol)	0	300
butyl alcohol (butanol)	0	300
pentyl alcohol (pentanol)	0	300
hexanol	0	1000
amyl alcohol	0	600
phenols (group)	0.10	0.33
formic acid	0	1500
acetic acid (ethanoic)	0	1500
propionic acid (propanoic)	0	1500
butyric acid (butanoic)	0	1500
valeric acid (pentanoic)	0	1500
succinic acid	0	500
glutaric acid	0	500
adipic acid	0	500
hexamethylene imine	1400	1400
chlorinated organics	9	403

NOTES:
Chemical pretreatment: pH adjusted with NH_3 and NaOH. See note for WDW-14.

Company: Celanese
Plant: Bay City
UIC No.: WDW-110

Waste: acid, organic
Process: chemical manufacturing (see memo)

Gallons of waste injected in 1985: 56823840
Gallons of waste injected in 1986: 89974080
Injection temperature (centigrade): 49-54
Specific gravity: 1.001

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	2.6	2.9
total dissolved solids	380	423
nitrate	1.5	2.5
Zn	0.01	0.04
V	0.004	0.008
As	0.001	0.003
Cu	0.19	0.35
Ni	0.01	0.03
Mn	0.01	0.04
Cr	0.001	0.003
Se	0.002	0.008
Pb	0	0.036
Cd	0	0.002
Ba	0.042	0.09
Hg	0.3	2.6
ORGANIC COMPOUNDS		
total organic carbon	3697	4460
chemical oxygen demand	4310	12298
cyclohexane	200	300
methyl alcohol (methanol)	0	300
ethyl alcohol (ethanol)	0	300
propyl alcohol (propanol)	0	300
butyl alcohol (butanol)	0	300
pentyl alcohol (pentanol)	0	300
hexanol	0	1000
amyl alcohol	0	600
phenols (group)	0.05	0.12
formic acid	0	1500
acetic acid (ethanoic)	0	1500
propionic acid (propanoic)	0	1500
butyric acid (butanoic)	0	1500
valeric acid (pentanoic)	0	1500
succinic acid	0	500
glutaric acid	0	500
adipic acid	0	500
hexamethylene imine	1400	1400
chlorinated organics	2666	7818

NOTES:
Chemical pretreatment: pH adjusted to 2-4 by adding NH_3 and/or NaOH. Waste produced from manufacture of: acetaldehyde, acetic acid, n-butyl alcohol, n-propyl alcohol, isobutyl alcohol, vinyl acetate.
An analysis of the organic composition of the WDW-110 waste stream was not provided. Waste production for WDW 110, however, is the result of processes similar to waste production processes for waste injected into WDW-14, 34, and 49, which are located

WDW-110 (continued)
at the same site as WDW-110. Therefore, the organic waste analysis from WDW-14, 34, and 49 injection stream were included in the composition of WDW-110's waste stream as a best estimate.

Company: Celanese
Plant: Bishop
UIC No.: WDW-211

Waste: organic
Process: chemical manufacturing (see memo)

Gallons of waste injected in 1985: 93793000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 18-29
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4.5	5.5
total dissolved solids	500	10000
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	331	900
butyl alcohol (butanol)	65	106
trimethylol propane	39	1527
ditrimethylol propane	0	4
trimethylol propane mono cyclic formal	27	1643
bis-trimethylol propane mono layer formal	15	45
pentaerythritol	201	2113
di pentaerythritol	21	21
trioxane (metaformaldehyde)	340	340
tetroxane	75	75
tetra ethylamine	26	26
formaldehyde	2500	2500
butylene glycol (butanediol)	45	220
ethyl propalene glycol (ethyl propanediol)	0	484
neopetyl glycol	130	130

NOTES:
Chemical pretreatment: pH adjusted to 5
Waste produced from manufacture of: formaldehyde, methanol oxidation, methanol synthesis, paraformaldehyde, nylon production, compounding of polybutylene terephthalate, pentaerythol, diacetone, alcohol, butyraldehyde, butanol, methylal, and butyl acetate.

Company: Celanese
Plant: Bishop
UIC No.: WDW-212

Waste: organic
Process: chemical manufacturing (see memo)

Gallons of waste injected in 1985: 12355000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 18-25
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4.5	5.5
total dissolved solids	500	1000
ORGANIC COMPOUNDS		
trimethylol propane	39	1527
ditrimethylol propane	0	4
trimethylol propane mono cyclic formal	27	1643
bis-trimethylol propane mono layer formal	15	45
pentaerythritol	201	2113
di pentaerythritol	21	21
trioxane (metaformaldehyde)	340	340
tetroxane	75	75
tetra ethylamine	26	26
formaldehyde	2500	2500
butylene glycol (butanediol)	45	220
ethyl propalene glycol (ethyl propanediol)	0	484
neopetyl glycol	130	130

NOTES:
Chemical pretreatment: pH adjusted to 5.
Waste produced from the manufacture of the same group of chemicals as WDW-211 in addition to: propyl acetate, 1,3,butylene glycol, trimethylol propane, trioxane, and polyacetal copolymer.
Despite the additional chemicals manufactured in the production of the waste injected into WDW-212, the organic compositions of the WDW-211 and WDW-212 waste streams are the same.

Company: Celanese
Plant: Clear Lake
UIC No.: WDW-33

Waste: organic
Process: chemical manufacture (see memo)

Gallons of waste injected in 1985: 120029200
Gallons of waste injected in 1986: 123720240
Injection temperature (centigrade): ambient
Specific gravity: 1.002

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	3	5
total dissolved solids	1901	2629
Na	200	1000
K	5	20
B	1	20
CO_3	250	2500
HCO_3	250	2500
I	1	14.6
Zn	1	3
Cu	1	10
Mn	1	10
Cr	1	5
CN (cyanide)	0.08	0.2
ORGANIC COMPOUNDS		
total organic carbon	5000	25000
methyl alcohol (methanol)	500	10000
ethylene glycol (ethanediol)	1000	10000
diethylene glycol	100	10000
triethylene glycol	100	5000
acetaldehyde (ethanal)	1000	5000
chloroaldehyde	1000	10000
dichloroaldehyde	1000	10000
trichloroaldehyde	1000	5000
acetic acid (ethanoic)	5000	30000
vinyl acetate (vinyl ethanoate)	50	5000
sodium acetate	1000	4000

NOTES:
Chemical pretreatment: pH adjusted to about 5 by addition of caustic. Waste produced from manufacture of: acetaldehyde, acetic acid, vinyl acetate, methyl alcohol, carbon monoxide, acrylic acid, acrylic esters, ethylene oxide, ethylene glycol, diethylene glycol, and triethylene glycol. The same waste is injected into WDW-45.

Company: Celanese
Plant: Clear Lake
UIC No.: WDW-45

Waste: organic
Process: chemical manufacture (see memo WDW 33)

Gallons of waste injected in 1985: 0
Gallons of waste injected in 1986: 319800
Injection temperature (centigrade): ambient
Specific gravity: 1.002

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	3	5
total dissolved solids	1901	2629
Na	200	1000
K	5	20
B	1	20
CO_3	250	2500
HCO_3	250	2500
I	1	14.6
Zn	1	3
Cu	1	10
Mn	1	10
Cr	1	5
CN (cyanide)	0.08	0.2
ORGANIC COMPOUNDS		
total organic carbon	5000	25000
methyl alcohol (methanol)	500	10000
ethylene glycol (ethanediol)	1000	10000
diethylene glycol	100	10000
triethylene glycol	100	5000
acetaldehyde (ethanal)	1000	5000
chloroaldehyde	1000	10000
dichloroaldehyde	1000	10000
trichloroaldehyde	1000	5000
acetic acid (ethanoic)	5000	30000
vinyl acetate (vinyl ethanoate)	50	5000
sodium acetate	1000	4000

NOTES:
Chemical pretreatment: pH adjusted to about 5 by addition of caustic.
WDW-33 and 45 have the same waste stream composition.

Company: Chevron
Plant: Palangana Dome
UIC No.: WDW-134

Waste: Ra^{226}
Process: in situ leach mining for U

Gallons of waste injected in 1985: 15046100
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 16-27
Specific gravity: 1.003

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	7.96
total dissolved solids	6299	233204
Na	160	82361
Ca	20	6800
Mg	47.7	1215
Fe	22	22
Cl	732	141830
HCO_3	273	1674
sulfate	839	1870
ammonia	449	2969
Mo	18.3	292
Ba	0.106	29.6
Ra^{226} (pCi/liter)	122	1168

NOTES:
Chemical pretreatment: pH to 6.5 with HCl.

Company: Cominco Chem
Plant: Burger
UIC No.: WDW-115

Waste: alkaline ammonia-sulfate
Process: manfacture of anhydrous ammonia and urea

Gallons of waste injected in 1985:	148765918
Gallons of waste injected in 1986:	182640372

Injection temperature (centigrade): 16
Specific gravity: 1.00-1.02

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7	8.5
total dissolved solids	1653	3960
Na	740	740
Ca	112	160
Mg	61	61
Si	8	8
Al	0.5	0.5
Cl	314	559
HCO_3	1220	2190
sulfate	612	1080
ammonia	323	600
ORGANIC COMPOUNDS		
chemical oxygen demand	292	687
biochemical oxygen demand	186	186

Company: Conoco
Plant: Trevino Mine
UIC No.: WDW-189

Waste: Ra^{226}
Process: in situ leach mining for U (see memo)

Gallons of waste injected in 1985:	63084765
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 16
Specific gravity: 1.007

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4	5
total dissolved solids	5840	9670
Na	790	2610
K	31	36
Ca	267	1025
Mg	113	247
Fe	0.04	0.09
Si	33	37
Cl	1349	3200
B	2.4	2.4
HCO_3	34	332
sulfate	2004	3177
F	0.39	1
ammonia	0.1	0.24
nitrate	0.16	0.16
Mo	0.16	1.3
Zn	0.04	0.04
V	0	0.02
As	0.012	0.074
Cu	0	0.02
Ni	0	0.02
Mn	0.26	0.29
Cr	0	0.006
Se	0.06	0.175
Pb	0.001	0.001
Ba	0	0.14
Hg	0	0.001
U	5.09	12.7
Ra^{226} (pCi/liter)	27	140

NOTES:
Chemical pretreatment: pH to 4-5 with HCl.
Lixiviant is either $NaHCO_3$ or NH_4 based.

Company: Corpus Christi Petro
Plant: Olefins
UIC No.: WDW-152

Waste: sulfide contaminated wastewater from refinery
Process: manufacture of olefinic hydrocarbons

Gallons of waste injected in 1985: 18017580
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 32
Specific gravity: 1.01-1.14

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	12.8	13.5
total dissolved solids	22000	173000
Na	25000	44240
K	64.7	75
Ca	13.2	196
Mg	0.1	2.2
Fe	0	7.1
Cl	4	456
CO_3	20000	20981
sulfide	3700	35000
sulfate	100	135
sulfite	0	69500
Ba	0	0.1
ORGANIC COMPOUNDS		
total organic carbon	1080	35000
oil and grease	11	126
phenols (group)	0.03	15

NOTES:
The same waste is injected into WDW-153.

Company: Corpus Christi Petro
Plant: Olefins
UIC No.: WDW-153

Waste: sulfide contaminated wastewater from refinery
Process: manufacture of olefinic hydrocarbons

Gallons of waste injected in 1985: 121680
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 32
Specific gravity: 1.01-1.14

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	12.8	13.5
total dissolved solids	22000	173000
Na	25000	44240
K	64.7	75
Ca	13.2	196
Mg	0.1	2.2
Fe	0	7.1
Cl	4	456
CO_3	20000	20981
sulfide	3700	35000
sulfate	100	135
sulfite	0	69500
ORGANIC COMPOUNDS		
total organic carbon	1080	35000
oil and grease	11	126
phenols (group)	0.03	15

Company: Diamond Shamrock
Plant: McKee
UIC No.: WDW-20

Waste: process: petroleum refinery, natural gas processing, NH_3 plant

Gallons of waste injected in 1985: 82549300
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8.5	8.5
total dissolved solids	4339	4339
Na	880	880
K	50	50
Ca	106	106
Mg	56	56
Fe	1.7	1.7
Cl	875	875
PO_4	0.3	0.3
HCO_3	230	230
sulfide	0.12	0.12
sulfate	1150	1150
ammonia	53	53
nitrate	0.12	0.12
nitrogen	86	86
Zn	0.23	0.23
As	0	0.01
Cu	0.12	0.12
Ni	0.16	0.16
Mn	0.12	0.12
Cr	0.08	0.08
Se	0	0.01
Pb	0	0.01
Cd	0.01	0.01
Ba	16.5	16.5
Hg	0	0.005
ORGANIC COMPOUNDS		
total organic carbon	74	74
chemical oxygen demand	326	326
biochemical oxygen demand	192	192
oil and grease	30	30
phenol	10.25	10.25

NOTES:
Chemical pretreatment: pH adjusted.
The same waste is injected into WDW-102 and 192.

Company: Diamond Shamrock
Plant: McKee
UIC No.: WDW-102

Waste: process: petroleum refinery, natural gas processing, NH_3 plant

Gallons of waste injected in 1985: 11973690
Gallons of waste injected in 1986: 11721940
Injection temperature (centigrade): 38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8.5	8.5
total dissolved solids	4339	4339
Na	880	880
K	50	50
Ca	106	106
Mg	56	56
Fe	1.7	1.7
Cl	875	875
PO_4	0.3	0.3
HCO_3	230	230
sulfide	0.12	0.12
sulfate	1150	1150
ammonia	53	53
nitrate	0.12	0.12
nitrogen	86	86
Zn	0.23	0.23
As	0	0.01
Cu	0.12	0.12
Ni	0.16	0.16
Mn	0.12	0.12
Cr	0.08	0.08
Se	0	0.01
Pb	0	0.01
Cd	0.01	0.01
Ba	16.5	16.5
Hg	0	0.005
ORGANIC COMPOUNDS		
total organic carbon	74	74
chemical oxygen demand	326	326
biochemical oxygen demand	192	192
oil and grease	30	30
phenol	10.25	10.25

NOTES:
Chemical pretreatment: pH adjusted.

Company: Diamond Shamrock
Plant: McKee
UIC No.: WDW-192

Waste: Process: petroleum refinery, natural gas processing, NH_3 plant

Gallons of waste injected in 1985: 78110500
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8.5	8.5
total dissolved solids	4339	4339
Na	880	880
K	50	50
Ca	106	106
Mg	56	56
Fe	1.7	1.7
Cl	875	875
PO_4	0.3	0.3
HCO_3	230	230
sulfide	0.12	0.12
sulfate	1150	1150
ammonia	53	53
nitrate	0.12	0.12
nitrogen	86	86
Zn	0.23	0.23
As	0	0.01
Cu	0.12	0.12
Ni	0.16	0.16
Mn	0.12	0.12
Cr	0.08	0.08
Se	0	0.01
Pb	0	0.01
Cd	0.01	0.01
Ba	16.5	16.5
Hg	0	0.005
ORGANIC COMPOUNDS		
total organic carbon	74	74
chemical oxygen demand	326	326
biochemical oxygen demand	192	192
oil and grease	30	30
phenol	10.25	10.25

NOTES:
Chemical pretreatment: pH adjusted.

Company: Dupont
Plant: Beaumont
UIC No.: WDW-100

Waste: organic, ammonium sulfate
Process: chemical manufacture (see memo)

Gallons of waste injected in 1985: 80600000
Gallons of waste injected in 1986: 80800000
Injection temperature (centigrade): 45
Specific gravity: 1.02-1.06

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	8.1
total dissolved solids	41045	68836
Na	0	5329
Fe	2.27	5.9
PO_4	1.8	3
sulfate	12070	43510
ammonia	1615	4965
nitrogen	8459	15729
Mo	4.7	40.1
Zn	0.06	0.28
As	0.007	0.017
Cu	0.02	0.03
Ni	3.20	3.54
Cr	0.04	0.24
CN	174	547
HCN	2000	3000
ORGANIC COMPOUNDS		
total organic carbon	13763	16543
chemical oxygen demand	17827	29691
biochemical oxygen demand	6353	9517
acetaldehyde (ethanal)	0	14
acrolein (propenal)	33	33
phenol	1.63	6.18
pyridine	0	14
methyl pyridine	0	14
acetonitrile (ethanenitrile)	192	658
acrylonitrile	177	459
fumaronitrile	1780	1780
nicotinonitrile	410	410
succinonitrile	2100	2100
phthalonitrile	64	64
maleonitrile	1511	1511
acrylamide	0	14

NOTES:
Chemical pretreatment: pH adjusted. Waste produced from manufacture of: animal feed supplement, chlorosulfonated synthetic rubber, hydrocarbon synthetic rubber, ammonia, amethonal, acrylonitrile, and blending of tetraethyl lead. The same waste is injected into WDW-101 and ultimately into WDW-188, which is not yet in service.

Company: Dupont
Plant: Beaumont
UIC No.: WDW-101

Waste: organic, ammonium sulfate
Process: chemical manufacture (see memo WDW-100)

Gallons of waste injected in 1985: 145900000
Gallons of waste injected in 1986: 143900000
Injection temperature (centigrade): 45
Specific gravity: 1.02-1.06

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	8.1
total dissolved solids	41045	68836
Na	0	5329
Fe	2.27	5.9
PO_4	1.8	3
sulfate	12070	43510
ammonia	1615	4965
nitrogen	8459	15729
Mo	4.7	40.1
Zn	0.06	0.28
As	0.007	0.017
Cu	0.02	0.03
Ni	3.20	3.54
Cr	0.04	0.24
CN	174	547
HCN	2000	3000
ORGANIC COMPOUNDS		
total organic carbon	13763	16543
chemical oxygen demand	17827	29691
biochemical oxygen demand	6353	9517
acetaldehyde (ethanal)	0	14
acrolein (propenal)	33	33
phenol	1.63	6.18
pyridine	0	14
methyl pyridine	0	14
acetonitrile (ethanenitrile)	192	658
acrylonitrile	177	459
fumaronitrile	1780	1780
nicotinonitrile	410	410
succinonitrile	2100	2100
phthalonitrile	64	64
maleonitrile	1511	1511
acrylamide	0	14

NOTES:
Chemical pretreatment: pH adjusted.

Company: Dupont
Plant: Ingleside
UIC No.: WDW-109

Waste: freon* alkaline waste
Process: manufacture of chlorocarbons and freon*

Gallons of waste injected in 1985: 0
Gallons of waste injected in 1986: 154490
Injection temperature (centigrade): ambient
Specific gravity: 1.07-1.09

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	10	13.8
total dissolved solids	70000	100000
Na	500	75000
K	50	60
Ca	10	20
Mg	6	7
Fe	1.5	3
Cl	250	50000
HCO_3	11000	18000
sulfate	80	200
sulfite	0	100
F	800	10000
As	1	2500
Cu	0.15	0.2
ORGANIC COMPOUNDS		
carbon tetrachloride	0	20
polychlorinated biphenyl (PCB)	0	2
tetrachloroethylene	0	2
freon 113* (a fluorinated haloalkane)	0	100

NOTES:
Chemical pretreatment: sodium sulfite or H_2O_2 added to destroy sodium hypochlorite. The same waste is injected into WDW-121.

Company: Dupont
Plant: Ingleside
UIC No.: WDW-121

Waste: freon* alkaline waste
Process: manufacture of chlorocarbons and freon*

Gallons of waste injected in 1985: 7881120
Gallons of waste injected in 1986: 6830820
Injection temperature (centigrade): ambient
Specific gravity: 1.07-1.09

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	10	13.8
total dissolved solids	70000	100000
Na	500	75000
K	50	60
Ca	10	20
Mg	6	7
Fe	1.5	3
Cl	250	50000
HCO_3	11000	18000
sulfate	80	200
sulfite	0	100
F	800	10000
As	1	2500
Cu	0.15	0.2
ORGANIC COMPOUNDS		
carbon tetrachloride	0	20
polychlorinated biphenyl (PCB)	0	2
tetrachloroethylene	0	2
freon 113* (a fluorinated haloalkane)	0	100

NOTES:
Chemical pretreatment: sodium sulfite and H_2O_2 added to destroy sodium hypochlorite.

Company: Dupont
Plant: LaPorte
UIC No.: WDW-82

Waste: acid, organic
Process: manufacture of polyvinyl alcohol and vinyl acetate

Gallons of waste injected in 1985: 48667900
Gallons of waste injected in 1986: 64076118
Injection temperature (centigrade): 50
Specific gravity: .9-1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	2	7
total dissolved solids	1000	5000
K	0	200
CO_3	0	200
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	1000	4000
acetaldehyde (ethanal)	100	600
hydroquinone (1,4 benzenediol)	0	200
acetic acid (ethanoic)	1000	5000
methyl acetate (methyl ethanoate)	300	2000
ethyl acetate (ethyl ethanoate)	0	100
butyl acetate (butyl ethanoate)	0	100
vinyl acetate (vinyl ethanoate)	500	3000
sodium acetate	1000	4000
potassium acetate	0	60
polyvinyl alcohol (PVA)	10	300
H 10 Defoamer (see notes)	0	50
Versenex 80 (see notes)	0	50

NOTES:
The same waste is injected into WDW-83 and 149.
Versenex 80 is:
- 52% water
- 38% pentasodium diethylene triaminepentacetate
- 4% tetrasodium diethylene triaminepentacetate
- 1% trisodium diethylene triaminepentacetate
- 1% trisodium nitrile acetate

H 10 Defoamer is Dow Corning antifoam H10 emulsion, a silicon emulsion

Company: Dupont
Plant: LaPorte
UIC No.: WDW-83

Waste: acid, organic
Process: manufacture of polyvinyl alcohol and vinyl acetate

Gallons of waste injected in 1985:	51258300
Gallons of waste injected in 1986:	62969487

Injection temperature (centigrade): 50
Specific gravity: .9-1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	2	7
total dissolved solids	1000	5000
K	0	200
CO_3	0	200
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	1000	4000
acetaldehyde (ethanal)	100	600
hydroquinone (1,4 benzenediol)	0	200
acetic acid (ethanoic)	1000	5000
methyl acetate (methyl ethanoate)	300	2000
ethyl acetate (ethyl ethanoate)	0	100
butyl acetate (butyl ethanoate)	0	100
vinyl acetate (vinyl ethanoate)	500	3000
sodium acetate	1000	4000
potassium acetate	0	60
polyvinyl alcohol (PVA)	10	300
H 10 Defoamer (see notes)	0	50
Versenex 80 (see notes)	0	50

NOTES:
The same waste is injected into WDW-82 and 149.
Versenex 80 is:
52% water
38% pentasodium diethylene triaminepentacetate
4% tetrasodium diethylene triaminepentacetate
1% trisodium diethylene triaminepentacetate
1% trisodium nitrile acetate
H 10 Defoamer is Dow Corning antifoam H10 emulsion, a silicon emulsion

Company: Dupont
Plant: LaPorte
UIC No.: WDW-149

Waste: acid, organic
Process: manufacture of polyvinyl alcohol and vinyl acetate

Gallons of waste injected in 1985:	50861400
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 50
Specific gravity: .9-1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	2	7
total dissolved solids	1000	5000
K	0	200
CO_3	0	200
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	1000	4000
aldehydes	100	600
hydroquinone (1,4 benzenediol)	0	200
acetic acid (ethanoic)	1000	5000
methyl acetate (methyl ethanoate)	300	2000
ethyl acetate (ethyl ethanoate)	0	100
butyl acetate (butyl ethanoate)	0	100
vinyl acetate (vinyl ethanoate)	500	3000
sodium acetate	1000	4000
potassium acetate	0	60
polyvinyl alcohol (PVA)	10	300
H 10 Defoamer (see notes)	0	50
Versenex 80 (see notes)	0	50

NOTES:
The same waste is injected into WDW-82 and 83.
Versenex 80 is:
52% water
38% pentasodium diethylene triaminepentacetate
4% tetrasodium diethylene triaminepentacetate
1% trisodium diethylene triaminepentacetate
1% trisodium nitrile acetate
H 10 Defoamer is Dow Corning antifoam H10 emulsion, a silicon emulsion

Company: Dupont
Plant: Sabine River
UIC No.: WDW-54

Waste: organic
Process: manufacture of adiponitrile

Gallons of waste injected in 1985: 147576000
Gallons of waste injected in 1986: 134877000
Injection temperature (centigrade):
Specific gravity: 1.00-1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
Fe	0	5
Cl	50	300
PO_4	15	25
B	0	50
H_2SO_4	1000	5000
ammonia	10	500
Zn	0	5
Cu	0	5
Ni	0	4000
CN	50	1000
ORGANIC COMPOUNDS		
organic nitrile compounds (see notes)	500	20000

NOTES:
The same waste is injected into WDW-55 and 191. The organic nitrile compounds are a combination of (personal communication, M.T. Swoboda, 1989):

adiponitrile
decenedinitrile
2-methyl-glutaronitrile
ethyl succinonitrile
meta [and para] tolunitrile
cis (and trans) 2-pentenenitrile
cis (and trans) 2-methyl 2-butenenitrile
cis (and trans) 3-pentenenitrile

Company: Dupont
Plant: Sabine River
UIC No.: WDW-55

Waste: organic
Process: manufacture of adiponitrile

Gallons of waste injected in 1985: 0
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity: 1.00-1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
Fe	0	5
Cl	50	300
PO_4	15	25
B	0	50
H_2SO_4	1000	5000
ammonia	10	500
Zn	0	5
Cu	0	5
Ni	0	4000
CN (cyanide)	50	1000
ORGANIC COMPOUNDS		
organic nitrile compounds (see notes)	500	20000

NOTES:
The same waste is injected into WDW-54 and 191. The organic nitrile compounds are a combination of (personal communication, M.T. Swoboda, 1989):

adiponitrile
decenedinitrile
2-methyl-glutaronitrile
ethyl succinonitrile
meta [and para] tolunitrile
cis (and trans) 2-pentenenitrile
cis (and trans) 2-methyl 2-butenenitrile
cis (and trans) 3-pentenenitrile

Company: Dupont
Plant: Sabine River
UIC No.: WDW-56

Waste: organic
Process: manufacture of adiponitrile

Gallons of waste injected in 1985:	16137000
Gallons of waste injected in 1986:	28086000
Injection temperature (centigrade):	
Specific gravity: .95-1.15	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7	14
Na	15000	125000
Cl	16000	60000
PO_4	0	25000
B	0	11.5
Zn	0	10000
Ni	500	35000
ORGANIC COMPOUNDS		
benzene	0	5000
phenol	0	20000
cresol (cresylic acid)	0	50000
dinitrile	0	970000
organic phosphorous compounds (see note)	0	100000

NOTES:
The same waste is injected into WDW-57. Two waste stream compositions were reported, but no mixing ratio was given. The range in waste stream composition listed here was determined assuming that 100% of either stream could be injected at any time.
The organic phosphorous compounds can be any combination of (personal communication, M.T. Swoboda, 1989) :

- ditolyl cis(or trans) 2 butenylphosphonate
- ditolyltolyl phosphonate/tritolyl phosphate mixture
- tritolyl phosphate
- tetrakis-[tritolyl-phosphite] nickel o
- tritolyl phosphite

Company: Dupont
Plant: Sabine River
UIC No.: WDW-57

Waste: organic
Process: manufacture of adiponitrile

Gallons of waste injected in 1985:	1955000
Gallons of waste injected in 1986:	3473000
Injection temperature (centigrade):	
Specific gravity: .95-1.15	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7	14
Na	15000	125000
Cl	16000	60000
PO_4	0	25000
B	0	11.5
Zn	0	10000
Ni	500	35000
ORGANIC COMPOUNDS		
benzene	0	5000
phenol	0	20000
cresol (cresylic acid)	0	50000
dinitrile	0	970000
organic phosphorous compounds (see notes)	0	100000

NOTES:
The same waste is injected into WDW-56. See memo WDW-56.
The organic phosphorous compounds can be any combination of (personal communication, M.T. Swoboda, 1989) :

- ditolyl cis(or trans) 2 butenylphosphonate
- ditolyltolyl phosphonate/tritolyl phosphate mixture
- tritolyl phosphate
- tetrakis-[tritolyl-phosphite] nickel o
- tritolyl phosphite

Company: Dupont
Plant: Sabine River
UIC No.: WDW-132

Waste: organic acid
Process: manufacture of adipic acid

Gallons of waste injected in 1985:	no data
Gallons of waste injected in 1986:	no data
Injection temperature (centigrade): 25-35	
Specific gravity: 1.02	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	0.3	3
nitrate	9000	9000
V	25	25
Cu	74	74
ORGANIC COMPOUNDS		
butyl alcohol (butanol)	300	300
aldehydes	400	400
acetic acid (ethanoic)	2200	2200
propionic acid (propanoic)	1500	1500
butyric acid (butanoic)	3000	3000
valeric acid (pentanoic)	1700	1700
caproic acid (hexanoic)	85	85
succinic acid	3300	3300
glutaric acid	7100	7100
adipic acid	3000	3000
organic acids (monobasic acid, carboxylic acid)	2000	5000
dicarboxylic acids (dibasic acids)	10000	15000

NOTES:
The same waste is injected into WDW-207.

Company: Dupont
Plant: Sabine River
UIC No.: WDW-191

Waste: organic
Process: manufacture of adiponitrile

Gallons of waste injected in 1985:	26708000
Gallons of waste injected in 1986:	no data
Injection temperature (centigrade):	
Specific gravity: 1.00-1.04	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
Fe	0	5
Cl	50	300
PO_4	15	25
B	0	50
H_2SO_4	1000	5000
ammonia	10	500
Zn	0	5
Cu	0	5
Ni	0	4000
CN	50	1000
ORGANIC COMPOUNDS		
organic nitrile compounds (see notes)	500	20000

NOTES:
The same waste is injected into WDW-54 and 55.
The organic nitrile compounds are a combination of (personal communication, M.T. Swoboda, 1989):

adiponitrile
decenedinitrile
2-methyl-glutaronitrile
ethyl succinonitrile
meta [and para] tolunitrile
cis (and trans) 2-pentenenitrile
cis (and trans) 2-methyl 2-butenenitrile
cis (and trans) 3-pentenenitrile

Company: Dupont
Plant: Sabine River
UIC No.: WDW-207

Waste: organic, acid
Process: manufacture of adipic acid

Gallons of waste injected in 1985: 138140000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 25-35
Specific gravity: 1.02

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	0.3	3
nitrate	9000	9000
V	25	25
Cu	74	74
ORGANIC COMPOUNDS		
butyl alcohol (butanol)	300	300
aldehydes	400	400
acetic acid (ethanoic)	2200	2200
propionic acid (propanoic)	1500	1500
butyric acid (butanoic)	3000	3000
valeric acid (pentanoic)	1700	1700
caproic acid (hexanoic)	85	85
succinic acid	3300	3300
glutaric acid	7100	7100
adipic acid	3000	3000

NOTES:
The same waste stream is injected into WDW-132.

Company: Dupont
Plant: Victoria
UIC No.: WDW-4

Waste: organics, salts, cyanide, metals–alkaline
Process: manufacture of adiponitrile, hexamethylenediamine

Gallons of waste injected in 1985: 26729280
Gallons of waste injected in 1986: 586704
Injection temperature (centigrade): 40-60
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	12
total dissolved solids	40000	60000
Na	18000	22000
Fe	100	100
Cl	18000	22000
PO_4	100	100
B	100	100
sulfate	1000	1000
ammonia	400	400
Ni	500	500
CN	2000	2000
ORGANIC COMPOUNDS		
total organic carbon	4000	5000
chemical oxygen demand	9170	12000
oil and grease	300	700
phenyl borates	6000	7000

NOTES:
The same waste is injected into WDW-105, 106, 142, and 143.
Additional waste components:
hydroxides = 200 mg/L
miscellaneous trace metals = 200 mg/L

Company: Dupont
Plant: Victoria
UIC No.: WDW-28

Waste: nitric acid, organic acid, organics, metals
Process: manufacture of adipic acid, dodecanedioic acid, nitric acid

Gallons of waste injected in 1985: 138520000
Gallons of waste injected in 1986: 152447780
Injection temperature (centigrade): 40-60
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
total dissolved solids	5000	10000
Fe	1	3
Cl	20	40
ammonia	25	75
nitrate	5000	15000
Zn	1	1
V	10	20
Cu	20	40
Cr	1	1
ORGANIC COMPOUNDS		
total organic carbon	5000	8000
chemical oxygen demand	15000	20000

NOTES:
The same waste is injected into WDW-29, 30, and 145.

Company: Dupont
Plant: Victoria
UIC No.: WDW-29

Waste: nitric acid, organic acid, organics, metals
Process: manufacture of adipic acid, dodecanedioic acid, nitric acid

Gallons of waste injected in 1985: 131222340
Gallons of waste injected in 1986: 138422500
Injection temperature (centigrade): 40-60
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
total dissolved solids	5000	10000
Fe	1	3
Cl	20	40
ammonia	25	75
nitrate	5000	15000
Zn	1	1
V	10	20
Cu	20	40
Cr	1	1
ORGANIC COMPOUNDS		
total organic carbon	5000	8000
chemical oxygen demand	15000	20000

NOTES:
The same waste is injected into WDW-28, 30, and 145.

Company: Dupont
Plant: Victoria
UIC No.: WDW-30

Waste: nitric acid, organic acid, organics, metals
Process: manufacture of adipic acid, dodecanedioic acid, nitric acid

Gallons of waste injected in 1985: 132608400
Gallons of waste injected in 1986: 136931220
Injection temperature (centigrade): 40-60
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
total dissolved solids	5000	10000
Fe	1	3
Cl	20	40
ammonia	25	75
nitrate	5000	15000
Zn	1	1
V	10	20
Cu	20	40
Cr	1	1
ORGANIC COMPOUNDS		
total organic carbon	5000	8000
chemical oxygen demand	15000	20000

NOTES:
The same waste is injected into WDW-28, 29, and 145.

Company: Dupont
Plant: Victoria
UIC No.: WDW-105

Waste: organics, salts, cyanide, metals--alkaline
Process: manufacture of adiponitrile, hexamethylenediamine

Gallons of waste injected in 1985: 12722400
Gallons of waste injected in 1986: 41194080
Injection temperature (centigrade): 40-60
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	12
total dissolved solids	40000	60000
Na	18000	22000
Fe	100	100
Cl	18000	22000
PO_4	100	100
B	100	100
sulfate	0	1000
ammonia	400	400
Ni	500	500
CN	2000	2000
ORGANIC COMPOUNDS		
total organic carbon	4000	5000
chemical oxygen demand	9170	12000
oil and grease	300	700
phenyl borates	6000	7000

NOTES:
The same waste is injected into WDW-4, 106, 142, and 143.
See note WDW-4.

Company: Dupont
Plant: Victoria
UIC No.: WDW-106

Waste: organics, salts, cyanide, metals--alkaline
Process: manufacture of adiponitrile, hexamethylenediamnie

Gallons of waste injected in 1985: 40907520
Gallons of waste injected in 1986: 28335600
Injection temperature (centigrade): 40-60
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	12
total dissolved solids	40000	60000
Na	18000	22000
Fe	100	100
Cl	18000	22000
PO_4	100	100
B	100	100
sulfate	0	1000
ammonia	400	400
Ni	500	500
CN	2000	2000
ORGANIC COMPOUNDS		
total organic carbon	4000	5000
chemical oxygen demand	9170	12000
oil and grease	300	700
phenyl borates	6000	7000

NOTES:
The same waste is injected into WDW-4, 105, 142, and 143.
See note WDW-4.

Company: Dupont
Plant: Victoria
UIC No.: WDW-142

Waste: organics, salts, cyanide, metals--alkaline
Process: manufacture of adiponitrile, hexamethylenediamine

Gallons of waste injected in 1985: 72298080
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 40-60
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	12
total dissolved solids	40000	60000
Na	18000	22000
Fe	100	100
Cl	18000	22000
PO_4	100	100
B	100	100
sulfate	1000	1000
ammonia	400	400
Ni	500	500
CN	2000	2000
ORGANIC COMPOUNDS		
total organic carbon	4000	5000
chemical oxygen demand	9170	12000
oil and grease	300	700
phenyl borates	6000	7000

NOTES:
The same waste is injected into WDW-4, 105, 106, and 143.
See note WDW-4.

Company: Dupont
Plant: Victoria
UIC No.: WDW-143

Waste: organics, salts, cyanide, metals--alkaline
Process: manufacture of adiponitrile, hexamethylenediamine

Gallons of waste injected in 1985: 85126509
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 40-60
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	12
total dissolved solids	40000	60000
Na	18000	22000
Fe	100	100
Cl	18000	22000
PO_4	100	100
B	100	100
sulfate	1000	1000
ammonia	400	400
Ni	500	500
CN	2000	2000
ORGANIC COMPOUNDS		
total organic carbon	4000	5000
chemical oxygen demand	9170	12000
oil and grease	300	700
phenyl borates	6000	7000

NOTES:
The same waste is injected into WDW-4, 105, 106, and 142. See note WDW-4.

Company: Dupont
Plant: Victoria
UIC No.: WDW-144

Waste: organics, salts, cyanide, metals--alkaline
Process: manf. adiponitrile, hexamethylenediamine; tritotylphosphite degradation

Gallons of waste injected in 1985: 35848800
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 40-60
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	12
total dissolved solids	40000	60000
Na	18000	22000
Fe	100	100
Cl	18000	22000
PO_4	100	100
B	100	100
sulfate	1000	1000
ammonia	400	400
Ni	500	500
CN	2000	2000
ORGANIC COMPOUNDS		
total organic carbon	4000	5000
chemical oxygen demand	9170	12000
oil and grease	300	700
phenyl borates	6000	7000
triphenyl borane	200	400
organic nitrile compounds (see notes)	13600	27200

NOTES:
The waste stream injected into WDW-144 is similar to that injected into WDW-4, 105, 106, 142, and 143 with the addition of tritotylphosphite degradation products equivalent to 6000-12000 mg/L. See note WDW-4.
The organic nitrile compounds are a combination of (personal communication, M.T. Swoboda, 1989):

- adiponitrile
- decenedinitrile
- 2-methyl-glutaronitrile
- ethyl succinonitrile
- meta [and para] tolunitrile
- cis (and trans) 2-pentenenitrile
- cis (and trans) 2-methyl 2-butenenitrile
- cis (and trans) 3-pentenenitrile

Company: Dupont
Plant: Victoria
UIC No.: WDW-145

Waste: nitric acid, organic acid, organics, metals
Process: manufacture of adipic acid, dodecanedioic acid, nitric acid

Gallons of waste injected in 1985:	137275800
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 40-60
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	1	3
total dissolved solids	5000	10000
Fe	1	3
Cl	20	40
ammonia	25	75
nitrate	5000	15000
Zn	1	1
V	10	20
Cu	20	40
Cr	1	1
ORGANIC COMPOUNDS		
total organic carbon	5000	8000
chemical oxygen demand	15000	20000

NOTES:
The same waste is injected into WDW-28, 29, and 30.

Company: El Paso Prod
Plant: Odessa Petro
UIC No.: WDW-16

Waste: organic
Process: chemical manufacture (see memo)

Gallons of waste injected in 1985:	no data
Gallons of waste injected in 1986:	75300000

Injection temperature (centigrade): 27-38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.5	8.5
total dissolved solids	10500	10500
Na	2700	2700
Ca	418	418
Mg	17	17
Cl	5460	5460
HCO_3	650	650
sulfate	690	690
Zn	0	1
Cu	0	1

NOTES:
Chemical pretreatment: pH adjusted to 7.5-8.5 by addition of HCl.
Waste produced from manufacture of:
- olefins
- polyolefins
- styrene
- ammonia
- 1,3-butadiene

Same waste injected into WDW-88,126,154. (Except 2,4 dintrophenol is injected only into WDW-16. Amount injected not reported.)
Note: this should be an organic waste but no organic analyses were reported.

Company: El Paso Prod
Plant: Odessa Petro
UIC No.: WDW-88

Waste: organic
Process: chemical manufacture (see WDW-16)

Gallons of waste injected in 1985: 74419000
Gallons of waste injected in 1986: 88509000
Injection temperature (centigrade): 27-38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.5	8.5
total dissolved solids	10500	10500
Na	2700	2700
Ca	418	418
Mg	17	17
Cl	5460	5460
HCO_3	650	650
sulfate	690	690
Zn	0	1
Cu	0	1

NOTES:
Chemical pretreatment: pH adjusted to 7.5-8.5 by addition of HCl.
The same waste is injected into WDW-16, 126, and 154.

Company: El Paso Prod
Plant: Odessa Petro
UIC No.: WDW-126

Waste: organic
Process: chemical manufacture (see WDW-16)

Gallons of waste injected in 1985: 99962000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 27-38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.5	8.5
total dissolved solids	10500	10500
Na	2700	2700
Ca	418	418
Mg	17	17
Cl	5460	5460
HCO_3	650	650
sulfate	690	690
Zn	0	1
Cu	0	1

NOTES:
Chemical pretreatment: pH adjusted to 7.5-8.5 by addition of HCl.
The same waste is injected into WDW-16, 88, and 154.

Company: El Paso Prod
Plant: Odessa Petro
UIC No.: WDW-154

Waste: organic
Process: chemical manufacture (see WDW-16)

Gallons of waste injected in 1985: 37305000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 27-38
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.5	8.5
total dissolved solids	10500	10500
Na	2700	2700
Ca	418	418
Mg	17	17
Cl	5460	5460
HCO_3	650	650
sulfate	690	690
Zn	0	1
Cu	0	1

NOTES:
Chemical pretreatment: pH adjusted to 7.5-8.5 by addition of HCl.
The same waste is injected into WDW-16, 88, and 126.

Company: Everest Mineral
Plant: Hobson Mine
UIC No.: WDW-168

Waste: Ra^{226}
Process: in situ leach mining for U and yellow cake extraction

Gallons of waste injected in 1985: 21216830
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity:

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.59	7.6
total dissolved solids	5840	47100
Na	1210	16660
K	37	250
Ca	169	800
Mg	19	158
Fe	52	52
Si	46	75
Cl	1810	27120
B	14	14
HCO_3	346	615
sulfate	23	2030
F	0.41	0.41
ammonia	29	245
nitrate	0	0.01
Mo	0.02	10.2
Zn	0.06	0.06
V	0.03	0.03
As	0.025	0.68
Cu	0.06	0.06
Ni	0	0.01
Mn	0.84	0.84
Cr	0.032	0.032
Se	0	0.06
Pb	0.029	0.029
Cd	0.001	0.001
Ba	88	88
U	0	11
Ra^{226} (pCi/liter)	177	670
Pb^{210} (pCi/liter)	202	254

Company: Everest Mineral
Plant: Las Palmas Mine
UIC No.: WDW-187

Waste: Ra^{226}
Process: in situ leach mining for U

Gallons of waste injected in 1985:	41380709
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity: 1.0-1.1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4.5	6.5
total dissolved solids	9500	9500
Na	1200	1200
K	15	15
Ca	2040	2040
Mg	50	50
Fe	5	5
Si	50	50
Cl	1800	1800
PO$_4$	1	1
HCO$_3$	860	860
sulfate	2030	2030
F	1	1
ammonia	245	245
nitrate	0.5	0.5
Mo	30	30
Zn	2	2
As	0.6	0.6
Cu	0.1	0.1
Ni	0.05	0.05
Se	0.05	0.05
Pb	0.2	0.2
Cd	0.01	0.01
Ba	0.5	0.5
U	12	12
Ra^{226} (pCi/liter)	2500	2500

Company: GAF Corp
Plant: Texas City
UIC No.: WDW-34

Waste: organic
Process: organic chemical synthesis; aceteline industrial chemicals (see note)

Gallons of waste injected in 1985:	89670000
Gallons of waste injected in 1986:	75370000

Injection temperature (centigrade): ambient
Specific gravity: 1.05-1.15

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	8.5
Na	100	1900
Cl	100	1000
sulfate	1620	8100
ammonia	500	5000
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	1000	4000
butyl alcohol (butanol)	50	200
butylene glycol (butanediol)	400	2000
tetrahydrofuran	100	1000
formaldehyde (methanal)	200	1000
hydroxymethylacetylene (propargyle alcohol)	200	1000
butynediol	200	1000
benzene	200	1000
pyrrolidone (2-pyrrolidone)	200	2000
N-methyl pyrrolidone	50	200
vinyl pyrrolidone	200	2000
butyrolactone (4-hydroxybutanoic acid lactone)	200	1000

NOTES:
Chemical pretreatment: pH adjusted to 6.5-8.5.
Waste produced from manufacture of:
- 1,4-butynediol
- propargyl alcohol
- 1,4-butenediol
- 1,4-butanediol
- 2 butyrolactone
- 2-pyrrolidone
- N-vinyl-2-pyrrolidone
- N-methyl-2-pyrrolidone
- polyvinylpyrrolidone
- polyvinylpyrrolidone/polyvinyl acetate copolymers
- amiben

WDW 34 waste is different from WDW 114. WDW 34 waste is sent to WDW 113 if necessary.

Company: GAF Corp
Plant: Texas City
UIC No.: WDW-113

Waste: organic
Process: organic chemical synthesis; aceteline industrial chemicals (see WDW-34)

Gallons of waste injected in 1985: no data
Gallons of waste injected in 1986: 16240000
Injection temperature (centigrade): ambient
Specific gravity: 1.05-1.15

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	8.5
Na	3800	50000
Cl	10000	50000
sulfate	19620	81000
Zn	0.13	0.85
Ni	0.29	1.5
Mn	0.1	0.9
Cr	0.29	1.8
Se	0.007	0.008
Pb	0.04	0.2
Hg	0	0.002
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	3000	30000
2,5-dichlorobenzoic acid	500	5000
dichloronitrobenzoic acids	6600	95000

NOTES:
Chemical pretreatment: pH adjusted to 6.5-8.5.
WDW 113 waste is different from that of WDW 34.
WDW 113 waste sent to WDW 114 if necessary.

Company: GAF Corp
Plant: Texas City
UIC No.: WDW-114

Waste: organic
Process: organic chemical synthesis; aceteline industrial chemicals (see WDW-34)

Gallons of waste injected in 1985: 57960000
Gallons of waste injected in 1986: 30800000
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.15

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.5	8.5
Na	100	50000
Cl	100	50000
sulfate	1620	81000
ammonia	500	5000
Zn	0.13	0.85
Ni	0.29	1.5
Mn	0.1	0.9
Cr	0.29	1.8
Se	0.007	0.008
Pb	0.04	0.2
Hg	0	0.002
ORGANIC COMPOUNDS		
methyl alcohol (methanol)	1000	30000
butyl alcohol (butanol)	50	200
butylene glycol (butanediol)	400	2000
tetrahydrofuran	100	1000
formaldehyde (methanal)	200	1000
hydroxymethylacetylene (propargyle alcohol)	200	1000
butynediol	200	1000
benzene	200	1000
pyrrolidone (2-pyrrolidone)	200	2000
N-methyl pyrrolidone	50	200
vinyl pyrrolidone	200	2000
butyrolactone (4-hydroxybutanoic acid lactone)	200	1000
2,5-dichlorobenzoic acid	500	5000
dichloronitrobenzoic acids	6600	95000

NOTES:
Chemical pretreatment: pH adjusted to 6.5-8.5.
WDW-114 is used as a standby well for WDW-34 and 113. See note WDW-34.

Company: IEC
Plant: Three Rivers
UIC No.: WDW-159

Waste: Ra^{226}
Process: in situ solution mining for U and aquifer restoration

Gallons of waste injected in 1985: 22383821
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 23
Specific gravity: 1.02

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7	7
total dissolved solids	160	54073
Na	13	8648
K	1.4	132
Ca	3.2	245
Mg	0.5	173
Fe	0	2.72
Si	1.8	169
Cl	52	12748
B	0.02	3.74
HCO_3	60	14316
sulfate	20	15620
F	0.16	14
ammonia	0.09	9436
nitrate	0.7	19
Mo	0	377
Zn	0.01	28.77
V	0.002	0.24
As	0.01	2.25
Cu	0	0.44
Ni	0	0.25
Mn	0.01	0.21
Cr	0	0.22
Se	0.01	65.22
Pb	0	0.004
Cd	0	0.004
Ba	0.01	0.38
Ag	0	0.16
Hg	0	0.074
U	1.2	114
Ra^{226} (pCi/liter)	5.5	4096

NOTES:
Chemical pretreatment: pH adjusted with HCl.

Company: Iowa Beef Proc.
Plant: Amarillo Hide
UIC No.: WDW-120

Waste: NaCl brine
Process: hide processing

Gallons of waste injected in 1985: 4232702
Gallons of waste injected in 1986: 4281406
Injection temperature (centigrade): 21
Specific gravity: 1.158

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.5	5.5
total dissolved solids	249000	249000
Na	77000	77000
Ca	7960	7960
Mg	1540	1540
Fe	27	27
Si	4	4
Al	0.3	0.3
Cl	143000	143000
HCO_3	1340	1340
sulfate	1600	1600

Company: Jetco
Plant: Amine
UIC No.: WDW-117

Waste: ammonia, ammonium chloride
Process: manufacture of nitriles, and quaternary ammonium chloride

Gallons of waste injected in 1985:	26204283
Gallons of waste injected in 1986:	23076808
Injection temperature (centigrade):	
Specific gravity:	

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.95	10.7
Cl	38	1610
sulfate	58	7900
As	0	0.01
Cr	0.02	0.02
Se	0	0.1
Pb	0.06	0.06
Cd	0	0.01
Ba	0	0.08

ORGANIC COMPOUNDS		
chemical oxygen demand	3650	238000
biochemical oxygen demand	300	320
oil and grease	0.9	1740
quarternary ammonium chloride	0	70640

Company: Lundberg Ind
Plant: Dumas
UIC No.: WDW-3

Waste: HCl
Process: potassium sulfate production

Gallons of waste injected in 1985:	74632
Gallons of waste injected in 1986:	53332

Injection temperature (centigrade): ambient
Specific gravity: 1.13-1.16

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	0.02	1
total dissolved solids	815	860
Fe	36	44
Cl	270000	310000
sulfate	300	350
sulfite	155	325
As	0	0.1
Cu	0	1
Pb	0.88	0.88

Company: Merichem
Plant: Houston
UIC No.: WDW-147

Waste: caustic, organic
Process: hydrocarbon extraction from refinery waste

Gallons of waste injected in 1985: 85910390
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.147

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	12	12
total dissolved solids	80000	80000
Na	20000	80000
CO_3	0	160000
sulfide	1000	50000
ORGANIC COMPOUNDS		
phenols (group)	0	10000

Company: Mobil
Plant: Corpus Christi
UIC No.: WDW-150

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 29434896
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 7-27
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4	10
total dissolved solids	3050	22900
Na	942	12950
K	26	100
Ca	150	520
Mg	37	97
Fe	0.19	8.3
Si	21	188
Cl	804	20720
HCO_3	0	638
sulfate	0	2006
F	0.43	2.1
ammonia	0.14	11
nitrate	0.48	3.7
Mo	0.02	5.2
As	0.001	0.125
Mn	0.14	1.7
Se	0	0.045
Pb	0.003	0.041
Cd	0	0.005
Hg	0	0.001
U	0	43
Ra^{226} (pCi/liter)	29	311

NOTES:
The same waste is injected into WDW-151 and 197.

Company: Mobil
Plant: Corpus Christi
UIC No.: WDW-151

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 53875008
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 7-27
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4	10
total dissolved solids	3050	22900
Na	942	12950
K	26	100
Ca	150	520
Mg	37	97
Fe	0.19	8.3
Si	21	188
Cl	804	20720
HCO_3	0	638
sulfate	0	2006
F	0.43	2.1
ammonia	0.14	11
nitrate	0.48	3.7
Mo	0.02	5.2
As	0.001	0.125
Mn	0.14	1.7
Se	0	0.045
Pb	0.003	0.041
Cd	0	0.005
Hg	0	0.001
U	0	43
Ra^{226} (pCi/liter)	29	311

NOTES:
The same waste is injected into WDW-150 and 197.

Company: Mobil
Plant: Corpus Christi
UIC No.: WDW-197

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 68787648
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 7-27
Specific gravity: 1.04

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4	10
total dissolved solids	3050	22900
Na	942	12950
K	26	100
Ca	150	520
Mg	37	97
Fe	0.19	8.3
Si	21	188
Cl	804	20720
HCO_3	0	638
sulfate	0	2006
F	0.43	2.1
ammonia	0.14	11
nitrate	0.48	3.7
Mo	0.02	5.2
As	0.001	0.125
Mn	0.14	1.7
Se	0	0.045
Pb	0.003	0.041
Cd	0	0.005
Hg	0	0.001
U	0	43
Ra^{226} (pCi/liter)	29	311

NOTES:
The same waste is injected into WDW-150 and 151.

Company: Monsanto
Plant: Chocolate Bayou
UIC No.: WDW-13

Waste: organic
Process: organic chemical production

Gallons of waste injected in 1985: 362851000
Gallons of waste injected in 1986: 330004000
Injection temperature (centigrade): 25-60
Specific gravity: 1.00-1.05

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6	9.5
total dissolved solids	25000	200000
Cl	100	35000
sulfate	25000	45500
ammonia	0	85000
CN	0	300
ORGANIC COMPOUNDS		
chemical oxygen demand	2500	50000
phenols (group)	0	11000
organic acids (monobasic acid, carboxylic acid)	0	15000
volatile sulfur compounds	0	10000

NOTES:
Waste produced from manufacture of:
- phenol
- diphenyl
- oxide
- acrylonitrile
- solf alkyl benzene
- nitrilotriacetic acid
- methionine hydroxy analog
- sorbic acid
- formalin

Company: Monsanto
Plant: Texas City
UIC No.: WDW-91

Waste: organic
Process: chemical manufacturing (see note)

Gallons of waste injected in 1985: 74150000
Gallons of waste injected in 1986: 7247
Injection temperature (centigrade):
Specific gravity: 1.05-1.12

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4.5	7.5
total dissolved solids	104560	104560
Cl	20400	20400
sulfate	41840	41840
ammonia	1000	1000
nitrate	0	8800
nitrogen	350	350
ORGANIC COMPOUNDS		
total organic carbon	13500	13500
chemical oxygen demand	22400	22400
biochemical oxygen demand	8600	8600
methyl alcohol (methanol)	30	30
formaldehyde (methanal)	200	200
phenols (group)	30	30
cyanopyridine	750	750
acetic acid (ethanoic)	750	750
acrylic acid (2-propenoic acid)	2750	2750
acetonitrile (ethanenitrile)	700	700
acrylonitrile	100	100
fumaronitrile	850	850
succinonitrile	900	900
acrylamide	650	650
urea	100	100
tertiary butylamine	100	100

NOTES:
Chemical pretreatment: pH control
Waste produced from manufacture of: acrylonitrile, HCN, tert-butylamine, lactic acid, acetone cyanohydrin, iminodiacetic acid, styrene monomer, and process wastewaters from other manufacturing areas generally high in organics and inorganics. The same waste is injected into WDW-196.

Company: Monsanto
Plant: Texas City
UIC No.: WDW-196

Waste: organic
Process: chemical manufacturing (see WDW-91)

Gallons of waste injected in 1985: 179970000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity: 1.05-1.12

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4.5	7.5
total dissolved solids	104560	104560
Cl	20400	20400
sulfate	41840	41840
ammonia	1000	1000
nitrate	0	8800
nitrogen	350	350
ORGANIC COMPOUNDS		
total organic carbon	13500	13500
chemical oxygen demand	22400	22400
biochemical oxygen demand	8600	8600
methyl alcohol (methanol)	30	30
formaldehyde (methanal)	200	200
phenols (group)	30	30
cyanopyridine	750	750
acetic acid (ethanoic)	750	750
acrylic acid (2-propenoic acid)	2750	2750
acetonitrile (ethanenitrile)	700	700
acrylonitrile	100	100
fumaronitrile	850	850
succinonitrile	900	900
acrylamide	650	650
urea	100	100
tertiary butylamine	100	100

NOTES:
Chemical pretreatment: pH control.
The same waste is injected into WDW-91.

Company: Penwalt
Plant: Crosby
UIC No.: WDW-122

Waste: petrochemical waste, organic
Process: organic peroxide, nitrogen compound manf.

Gallons of waste injected in 1985: 32374078
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity:

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.5	7.5
total dissolved solids	26000	26000
Na	5200	5200
K	3700	3700
Ca	7	7
Mg	28	28
Cl	6000	6000
PO_4	150	150
HCO_3	4700	4700
sulfate	1300	1300
nitrate	0.1	0.1
nitrogen	80	80
As	0.1	0.1
Cr	0.1	0.1
Pb	0.6	0.6
Cd	0.001	0.001
Ba	0.1	0.1
Ag	0.08	0.08
Hg	0.001	0.001
ORGANIC COMPOUNDS		
chemical oxygen demand	2500	2500

NOTES:
Organic analyses not reported, although COD of 2500 ppm suggests the presence of organic compounds.

Company: Phillips
Plant: Borger
UIC No.: WDW-67

Waste: organic
Process: Rubber Chemical Complex

Gallons of waste injected in 1985: 4666500
Gallons of waste injected in 1986: 1135500
Injection temperature (centigrade): 38-49
Specific gravity: 1.03

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	10	11.5
total dissolved solids	0	250000
Na	0	125000
K	0	4
Ca	0	650
Mg	0	400
Fe	0	1.4
Si	0	14
Cl	0	125000
HCO_3	0	55
sulfate	0	325
ammonia	0	1.5
V	0	1
Cu	0	0.07
Mn	0	1.4
Sb	0	1
ORGANIC COMPOUNDS		
total organic carbon	0	378
chemical oxygen demand	0	2440
biochemical oxygen demand	0	330
oil and grease	0	8.7
tertiary butyl catechol	0	50000

NOTES:
Report suggests that different waste is injected into WDW 67 and 68. But elsewhere in the report it is suggested that WDW 68 is used as backup for WDW 67. Reported here as different waste streams injected into each well.

Company: Phillips
Plant: Borger
UIC No.: WDW-68

Waste: organic
Process: manufacturing of polyphenylene sulfide (Ryton)

Gallons of waste injected in 1985: 64225000
Gallons of waste injected in 1986: 62050000
Injection temperature (centigrade): 38-49
Specific gravity: 1.03

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	10	11.5
total dissolved solids	33258	42383
Na	10462	13324
K	15	18
Ca	28	30
Mg	13	17
Fe	1.8	2.3
Cl	14861	18962
CO_3	217	339
HCO_3	3011	3869
sulfide	106	117
sulfate	928	1140
nitrate	0.19	1
Cr	0.04	0.16
Pb	0.23	0.29
Cd	0.16	0.21
Ba	0.004	1
Ag	0.01	0.1
ORGANIC COMPOUNDS		
chemical oxygen demand	2373	2795
biochemical oxygen demand	550	707
methyl alcohol (methanol)	0	1475
N-methyl pyrrolidone	3685	9880
beta mercaptoethanol	0	780
Sulfolane	0	955.
Solfolene	0.04	225.

Company: Sandoz-Velsicol
Plant: Beaumont
UIC No.: WDW-125

Waste: organic
Process: organic chemical manufacturing (see memo)
Gallons of waste injected in 1985: 64426834
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 41
Specific gravity: 1.025

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	2.3	6.5
total dissolved solids	34106	48890
Na	3627	14500
K	3444	5350
Fe	0.6	1.15
Cl	20815	30000
sulfate	27	128
Zn	0.1	5.96
Cr	1	1.7
ORGANIC COMPOUNDS		
total organic carbon	1214	2593
oil and grease	23	409
methyl alcohol (methanol)	80	6145
anisole (methoxybenzene)	3	3
trichlorobenzene	1	7
dichloroanisoles (dichloromethoxybenzene)	23	23
dichlorophenol	66	390
dichlorosalicylic acid (dichlorohydroxybenzoic acid)	7	7
Banvel (methylated dichlorosalicylic acid)	8	150
Banvel methyl esters	10	10
Dicamba (3,6-dichloro-2-methoxybenzoic acid)	9	87

NOTES:
Process that produces waste: conversion of 1,2,4-trichlorobenzene to 3.6-dichloro-o-anisic acid. Wastes for WDW 125 and 155 are the same.

Company: Sandoz-Velsicol
Plant: Beaumont
UIC No.: WDW-155

Waste: organic
Process: organic chemical manufacturing (see memo 155)

Gallons of waste injected in 1985: 63217883
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 41
Specific gravity: 1.025

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	2.3	6.5
total dissolved solids	34106	48890
Na	3627	14500
K	3444	5350
Fe	0.6	1.15
Cl	20815	30000
sulfate	27	128
Zn	0.1	5.96
Cr	1	1.7
ORGANIC COMPOUNDS		
total organic carbon	1214	2593
oil and grease	23	409
methyl alcohol (methanol)	80	6145
anisole (methoxybenzene)	3	3
trichlorobenzene	1	7
dichloroanisoles (dichloromethoxybenzene)	23	23
dichlorophenol	66	390
dichlorosalicylic acid (dichlorohydroxybenzoic acid)	7	7
Banvel (methylated dichlorosalicylic acid)	8	150
Banvel methyl esters	10	10
Dicamba (3,6-dichloro-2-methoxybenzoic acid)	9	87

NOTES:
Wastes for WDW 125 and 155 are the same.

Company: Shell
Plant: Deer Park
UIC No.: WDW-172

Waste: organic
Process: manufacture of resins, intermediate products, solvents (see note)

Gallons of waste injected in 1985:	45232000
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 25-66
Specific gravity: 1.0-1.2

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4	8
total dissolved solids	56750	172000
Na	40000	60000
K	100	200
Ca	1	3
Mg	0.5	1
Fe	0.1	5.6
Al	0	0.24
Cl	60000	80000
CO_3	500	1000
HCO_3	1000	8000
sulfate	20	50
Zn	0.2	1
As	0	0.06
Cu	0.2	1.2
Ni	0.1	0.5
Mn	0.2	2
Cr	0.1	0.2
Co	0	0.35
Pb	0.04	1
Ba	0.06	0.1
Hg	0.001	0.005
ORGANIC COMPOUNDS		
propane	0	30000
glycerol (glycerine, propanetriol)	5400	50000
polyglycerols	3000	3000
glycidol	130	130
bisdioxane	700	700
acetone (dimethyl ketone)	200	2000
phenol	2000	30000
chlorinated hydrocarbons	5000	15000
chlorohydrin (mono-, di- and epi-)	350	350

NOTES:
Chemical pretreatment: pH 4 to 8 with HCl. Waste from: epon resin water cuts, bisphenol of acetone brine, epichlorohydrin water cuts, and intermittent miscellaneous aqueous Shell manufacturing wastes. The same waste is injected into WDW-173.

Company: Shell
Plant: Deer Park
UIC No.: WDW-173

Waste: organic
Process: manufacture of resins, intermediate products, solvents (see WDW-172)

Gallons of waste injected in 1985:	60889822
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 25-66
Specific gravity: 1.0-1.2

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4	8
total dissolved solids	56750	172000
Na	40000	60000
K	100	200
Ca	1	3
Mg	0.5	1
Fe	0.1	5.6
Al	0	0.24
Cl	60000	80000
CO_3	500	1000
HCO_3	1000	8000
sulfate	20	50
Zn	0.2	1
As	0	0.06
Cu	0.2	1.2
Ni	0.1	0.5
Mn	0.2	2
Cr	0.1	0.2
Co	0	0.35
Pb	0.04	1
Ba	0.06	0.1
Hg	0.001	0.005
ORGANIC COMPOUNDS		
propane	0	30000
glycerol (glycerine, propanetriol)	5400	50000
polyglycerols	3000	3000
glycidol	130	130
bisdioxane	700	700
acetone (dimethyl ketone)	200	2000
phenol	2000	30000
chlorinated hydrocarbons	5000	15000
chlorohydrin (mono-, di- and epi-)	350	350

NOTES:
Chemical pretreatment: pH 4 to 8 with HCl. The same waste is injected into WDW-173.

Company: Standard Oil-Vistron
Plant: Port Lavaca
UIC No.: WDW-163

Waste: organic, cyanide
Process: petrochemical manufacture

Gallons of waste injected in 1985: 45275153
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity: 1.042

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.2	6.2
total dissolved solids	109000	109000
CN	2038	2038
ORGANIC COMPOUNDS		
acetonitrile (ethanenitrile)	203	203
acrylonitrile	597	597

NOTES:
The same waste is injected into WDW-164 and 165.

Company: Standard Oil-Vistron
Plant: Port Lavaca
UIC No.: WDW-164

Waste: organic, cyanide
Process: petrochemical manufacture

Gallons of waste injected in 1985: 62384101
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity: 1.042

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.2	6.2
total dissolved solids	109000	109000
CN	2038	2038
ORGANIC COMPOUNDS		
acetonitrile (ethanenitrile)	203	203
acrylonitrile	597	597

NOTES:
The same waste is injected into WDW-163 and 165.

Company: Standard Oil-Vistron
Plant: Port Lavaca
UIC No.: WDW-165

Waste: organic, cyanide
Process: petrochemical manufacture

Gallons of waste injected in 1985:	63412519
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade):
Specific gravity: 1.042

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.2	6.2
total dissolved solids	109000	109000
CN	2038	2038
ORGANIC COMPOUNDS		
acetonitrile (ethanenitrile)	203	203
acrylonitrile	597	597

NOTES:
The same waste is injected into WDW-163 and 164.

Company: Tenneco Uranium
Plant: Bruni Mine
UIC No.: WDW-195

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985:	6290923
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity:

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.8	9.5
total dissolved solids	22700	22700
Na	5570	5570
K	330	330
Ca	470	470
Mg	400	400
Cl	5800	5800
CO_3	880	880
HCO_3	5300	5300
sulfate	3400	3400
F	50	50
nitrate	440	440
Mo	425	425
V	10	10
As	20	20
U	50	50
Ra^{226} (pCi/liter)	1000	1000

Company: Tex Tin-Gulf
Plant: Texas City
UIC No.: WDW-237

Waste: acid inorganic
Process: smelting and refining

Gallons of waste injected in 1985:	2312503
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 21
Specific gravity: 1.06-1.11

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	0.6	1
total dissolved solids	139896	139896
Ca	6078	6078
Mg	205	205
Fe	18500	35800
Al	490	497
Cl	53100	92631
CO_3	0	0.5
HCO_3	0	0.5
sulfate	150	150
Zn	180	180
As	46	56
Cu	87	392
Ni	46	56
Mn	164	332
Cr	54	358
Co	5.1	9
Se	0.02	0.1
Pb	58	150
Sn	9.2	34
Cd	0.5	1
Ba	4.2	4.2
Bi	8.8	16
Ag	3.2	3.2
Sb	13	13
Hg	0.007	0.28
ORGANIC COMPOUNDS		
chemical oxygen demand	0	1800
biochemical oxygen demand	0	42

Company: Texaco
Plant: Amarillo
UIC No.: WDW-135

Waste: inorganic sulfate-chloride brine
Process: gasoline, diesel fuel manufacturing

Gallons of waste injected in 1985:	35802890
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): 38
Specific gravity: 1.006

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.94	7.94
total dissolved solids	11367	11367
Na	3784	3784
Ca	218	218
Mg	67.5	67.5
Fe	0	0.02
Cl	4065	4065
HCO_3	219	219
sulfate	3014	3014

NOTES:
The same waste is injected into WDW-136.

Company: Texaco
Plant: Amarillo
UIC No.: WDW-136

Waste: inorganic sulfate-chloride brine
Process: gasoline, diesel fuel manufacturing

Gallons of waste injected in 1985: 54590323
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): 38
Specific gravity: 1.006

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	7.94	7.94
total dissolved solids	11367	11367
Na	3784	3784
Ca	218	218
Mg	67.5	67.5
Fe	0	0.02
Cl	4065	4065
HCO_3	219	219
sulfate	3014	3014

NOTES:
The same waste is injected into WDW-135.

Company: US Steel
Plant: George West
UIC No.: WDW-123

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 12283269
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.6	7.2
total dissolved solids	3530	9078
Na	392	2130
K	18	38
Ca	418	656
Mg	62	100
Fe	0.24	10.45
Cl	850	1890
HCO_3	249	910
sulfate	1008	5250
ammonia	0.5	1030
Mo	1	38
V	0.1	0.1
Cu	0.05	2.4
U	4	30
Ra^{226} (pCi/liter)	800	800

NOTES:
Chemical pretreatment: corrosion and scale inhibitor.
The same waste is injected into WDW-124, 130, 140, 141, and 174.

Company: US Steel
Plant: George West
UIC No.: WDW-124

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 66306226
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.6	7.2
total dissolved solids	3530	9078
Na	392	2130
K	18	38
Ca	418	656
Mg	62	100
Fe	0.24	10.45
Cl	850	1890
HCO_3	249	910
sulfate	1008	5250
ammonia	0.5	1030
Mo	1	38
V	0.1	0.1
Cu	0.05	2.4
U	4	30
Ra^{226} (pCi/liter)	800	800

NOTES:
Chemical pretreatment: corrosion and scale inhibitor.
The same waste is injected into WDW-123, 130, 140, 141, and 174.

Company: US Steel
Plant: George West
UIC No.: WDW-130

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 58606642
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.6	7.2
total dissolved solids	3530	9078
Na	392	2310
K	18	38
Ca	418	656
Mg	62	100
Fe	0.24	10.45
Cl	850	1890
HCO_3	249	910
sulfate	1008	5250
ammonia	0.5	1030
Mo	1	38
V	0.1	0.1
Cu	0.05	2.4
U	4	30
Ra^{226} (pCi/liter)	800	800

NOTES:
Chemical pretreatment: corrosion and scale inhibitor.
The same waste is injected into WDW-123, 124, 140, 141, and 174.

Company: US Steel
Plant: George West
UIC No.: WDW-140

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 10328192
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.6	7.2
total dissolved solids	3530	9078
Na	392	2130
K	18	38
Ca	418	656
Mg	62	100
Fe	0.24	10.45
Cl	850	1890
HCO_3	249	910
sulfate	1008	5250
ammonia	0.5	1030
Mo	1	38
V	0.1	0.1
Cu	0.05	2.4
U	4	30
Ra^{226} (pCi/liter)	800	800

NOTES:
Chemical pretreatment: corrosion and scale inhibitor.
The same waste is injected into WDW-123, 124, 130, 141, and 174.

Company: US Steel
Plant: George West
UIC No.: WDW-141

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 68738708
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.6	7.2
total dissolved solids	3530	9078
Na	392	2130
K	18	38
Ca	418	656
Mg	62	100
Fe	0.24	10.45
Cl	850	1890
HCO_3	249	910
sulfate	1008	5250
ammonia	0.5	1030
Mo	1	38
V	0.1	0.1
Cu	0.05	2.4
U	4	30
Ra^{226} (pCi/liter)	800	800

NOTES:
Chemical pretreatment: corrosion and scale inhibitor.
The same waste is injected into WDW-123, 124, 130, 140, and 174.

Company: US Steel
Plant: George West
UIC No.: WDW-174

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 87861744
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.00-1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	6.6	7.2
total dissolved solids	3530	9078
Na	392	2130
K	18	38
Ca	418	656
Mg	62	100
Fe	0.24	10.45
Cl	850	1890
HCO_3	249	910
sulfate	1008	5250
ammonia	0.5	1030
Mo	1	38
V	0.1	0.1
Cu	0.05	2.4
U	4	30
Ra^{226} (pCi/liter)	800	800

NOTES:
Chemical pretreatment: corrosion and scale inhibitor.
The same waste is injected into WDW-123, 124, 130, 140, and 141.

Company: W R Grace
Plant: Deer Park
UIC No.: WDW-222

Waste: organic
Process: manufacture of nitroparafins

Gallons of waste injected in 1985: no data
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	3	3
total dissolved solids	4424	4424
Na	97	97
Ca	0.8	0.8
Mg	2.1	2.1
Fe	1.9	1.9
Cl	20	20
HCO_3	0	1
sulfide	0.25	0.25
sulfate	60	60
sulfite	0	2
ammonia	1108	1108
nitrate	129	129
Zn	0.12	0.12
CN	31.9	31.9
HNO3	3740	6900
ORGANIC COMPOUNDS		
total organic carbon	93020	93020
formic acid	0	15.9
acetic acid (ethanoic)	0	220
urea	0	130
carbonyl-bisulfite adduct	0	352000

NOTES:
Chemical pretreatment: pH adjusted.
The same waste is injected into WDW-223.

Company: W R Grace
Plant: Deer Park
UIC No.: WDW-223

Waste: organic
Process: manufacture of nitroparafins

Gallons of waste injected in 1985:	11422200
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity: 1

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	3	3
total dissolved solids	4424	4424
Na	97	97
Ca	0.8	0.8
Mg	2.1	2.1
Fe	1.9	1.9
Cl	20	20
HCO_3	0	1
sulfide	0.25	0.25
sulfate	60	60
sulfite	0	2
ammonia	1108	1108
nitrate	129	129
Zn	0.12	0.12
CN	31.9	31.9
HNO3	3740	6900
ORGANIC COMPOUNDS		
total organic carbon	93020	93020
formic acid	0	15.9
acetic acid (ethanoic)	0	220
urea	0	130
carbonyl-bisulfite adduct	0	352000

NOTES:
Chemical pretreatment: pH adjusted.
The same waste is injected into WDW-222.

Company: Westinghouse
Plant: Bruni Mine
UIC No.: WDW-170

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985:	16463084
Gallons of waste injected in 1986:	no data

Injection temperature (centigrade): ambient
Specific gravity: 1.01

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	4.5	7.5
Ca	460	460
Cl	4886	4886
HCO_3	467	467
sulfate	967	967
ammonia	943	943
U	0.5	11.1
Ra^{226} (pCi/liter)	424	777

NOTES:
Chemical pretreatment: pH adjusted to 5-6

Company: Witco
Plant: Houston
UIC No.: WDW-111

Waste: organic
Process: chemical manfacturing (see note)

Gallons of waste injected in 1985: 3365900
Gallons of waste injected in 1986: 14846830
Injection temperature (centigrade): ambient
Specific gravity: 1.005

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.5	6.5
total dissolved solids	5690	5690
Na	1700	1700
Ca	108	108
Mg	7.3	7.3
Fe	35	35
Cl	109	109
HCO_3	425	425
sulfate	3350	3350

NOTES:
Chemical pretreatment: pH adjusted.
The same waste is injected into WDW-139.
Waste producing processes: Sulfonation, oxylation, neutralization, esterification, amidification, phosphation, phenol-formaldehyde resins, blending, and solvents.
The waste is a water solution of sulfonated organics and their salts consisting of oxylated organic compounds, fatty acid esters and amides, phenol-formaldehyde resins, aromatic and aliphatic solvents.
The organic compounds listed below were reported as percent of total organic fraction but the total concentration of organics in solution was not given.

ethoxylated C10-C12 alcohols	22%
propaxylated diols and triols	20%
ethoxylated alkyl phenols	15%
ethoxylated phenolic resins	12%
esters of polyols and dibasic acids	12%
phenolic resins	5%
Ca salts of alkyl benzene sulfonic acid	5%
phosphate esters	2%
amine salts of alkyl benzene sulfonic acid	1%
diethanolamides	1%
alkyl benzene sulfonic acids, alcohol ether sulfates and sodium salts of each	1%
ethoxylated fatty and resin amines	0.5%
quartanery ammonium compounds	0.5%

Company: Witco
Plant: Houston
UIC No.: WDW-139

Waste: organic
Process: chemical manfacturing (see WDW-111)

Gallons of waste injected in 1985: 33442400
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity: 1.005

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	5.5	6.5
total dissolved solids	5690	5690
Na	1700	1700
Ca	108	108
Mg	7.3	7.3
Fe	35	35
Cl	109	109
HCO_3	425	425
sulfate	3350	3350

NOTES:
Chemical pretreatment: pH adjusted.
The same waste is injected into WDW-111.

Company: Witco
Plant: Marshall
UIC No.: WDW-107

Waste: organic
Process: manfacture of organic peroxide materials

Gallons of waste injected in 1985: 92000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity: 1.043

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	13	13
total dissolved solids	65500	65500
Na	20000	20000
Ca	11.3	11.3
Mg	1.02	1.02
Cl	4400	4400
PO_4	1285	1285
CO_3	16785	16785
sulfate	600	600
Cr	25	25
ORGANIC COMPOUNDS		
total organic carbon	7000	7000
chemical oxygen demand	17000	17000
oil and grease	16	16
butanone (methyl ethyl ketone)	156	156
dimethyl phthalate (phthalic acid dimethyl ester)	1.1	1.1

NOTES:
The same waste is injected into WDW-180.
Waste: A mixture of sodium-chloride and sodium sulfate brines with varying amounts of water-soluble organic acids, peroxides and ketones.
Process: The plant produces a variety of organic peroxide materials by semi-continuous and batch methods.

Company: Witco
Plant: Marshall
UIC No.: WDW-180

Waste: organic
Process: manfacture of organic peroxide materials

Gallons of waste injected in 1985: 13856000
Gallons of waste injected in 1986: no data
Injection temperature (centigrade):
Specific gravity: 1.043

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	13	13
total dissolved solids	65500	65500
Na	20000	20000
Ca	11.3	11.3
Mg	1.02	1.02
Cl	4400	4400
PO_4	1285	1285
CO_3	16785	16785
sulfate	600	600
Cr	25	25
ORGANIC COMPOUNDS		
total organic carbon	7000	7000
chemical oxygen demand	17000	17000
oil and grease	16	16
butanone (methyl ethyl ketone)	156	156
dimethyl phthalate (phthalic acid dimethyl ester)	1.1	1.1

NOTES:
The same waste is injected into WDW-107.

Company: Wyoming Minerals
Plant: Three Rivers
UIC No.: WDW-156

Waste: Ra^{226}
Process: in situ solution mining for U

Gallons of waste injected in 1985: 1075950
Gallons of waste injected in 1986: no data
Injection temperature (centigrade): ambient
Specific gravity:

WASTE COMPOSITION	MINIMUM (mg/L)	MAXIMUM (mg/L)
pH	8	8
total dissolved solids	19700	19700
Na	250	250
Ca	1100	1100
Mg	310	310
Cl	12560	12560
HCO_3	1720	1720
sulfate	4190	4190
ammonia	6810	6810
U	29	29
Ra^{226} (pCi/liter)	671	671