SOLUBILITY AND TOXICITY OF POTENTIAL POLLUTANTS IN SOLID COAL WASTES

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Abstract

Chemical and mineralogical characteristics of a LURGI gasification ash and an H-Coal liquefaction residue from the Illinois Herrin (No. 6) Coal Member are related to chemical solubility at several pH's and to biological toxicity of aqueous supernatant solutions. Chemical analyses were performed for some 60 constituents. The major constituents in the solid residues were Al, Ca, Fe, K, and Si. Large quantities of Mg, Mn, Na, S, and Ti and significant quantities (10-1000 ppm) of trace metals were also present.

The minerals detected in the liquefaction solid wastes included quartz, pyrrhotite, sphalerite, calcite, anhydrite, wollastonite, and clay minerals. A small amount of quartz and calcite reacted to form wollastonite, and nearly all the pyrite present in the feed coal was converted to pyrrhotite during conversion. The minerals detected in the LURGI ash included quartz, mullite, plagioclase feldspar, and hematite. Nearly all the pyrite present in the feed coal was converted to hematite during gasification. Clays were converted to mullite, and other accessory minerals were apparently converted to feldspars.

Of the approximately 60 chemical constituents measured in the raw LURGI ash, only 15 were found to be soluble enough to excede recommended water quality levels, even at pH values as low as 3. Six of these constituents—Al, Cr, Co, Cu, Fe, and Zn—exceeded the recommended values for natural waters only when the pH was quite acid. Over the pH range 3-10, the remaining nine—B, Ca, Cd, K, Mn, NH_4, Pb, SO_4, and Sb—exceeded the recommended levels in all solutions. These 9 are thought to pose the highest potential pollution hazard.

The results of 96-hour static bioassays indicated that the water-soluble constituents in equilibrium with the wastes were not acutely toxic to young fathead minnows at near-neutral pH's (7.0-8.5); however, in both the high- and low-pH solutions all the minnows died. Mortality may have been the combined result of pH and total ion content. Further studies of the causes of the fathead minnow mortality are being conducted.

INTRODUCTION

The potential need for development of a coal gasification and liquefaction industry in the United States has been dramatically demonstrated by the widespread shortages of natural gas and fuel oil during the winter of 1977. Because the production of clean fuel from coal is not without environmental impacts, assessment of potential impacts of coal conversion plants is underway (e.g., Sather et al., 1975; Forney et al., 1975; and Jahnig and Bertrand, 1976). Such studies have emphasized the effects of coal conversion upon air pollution. Although these problems are serious, they have tended to overshadow another important matter—the potential pollution of water resources.

Solid Coal Wastes As Sources of Pollutants

One by-product of coal conversion is the generation of solid wastes For example, a commercial coal gasification plant with a capacity of 250 million cubic feet of gas per day will use about 8 million tons of coal and will generate about 2.3 million tons of ash and dry refuse per year (Sather et al., 1975). The amount of residue generated by a single coal gasification plant has been estimated to occupy an area of 625 acre feet per year and in 20 years would cover 1250 acres to a depth of 10 feet (Seay et al., 1972, and Asburg and Hoglund, 1974). The disposal of these huge amounts of solid waste is unprecedented, and successful commercial production of synthetic gas by these processes will depend, in part, on the environmental acceptability of disposal of the solid-waste residues.

Interest in the potential pollution hazard from the accessory elements contained in the solid wastes is increasing. About 60 of these elements are found in concentrations of less than 1 ppm to several percent (Gluskoter et al., 1977). These accessory elements in the coal are either retained in the gasifier ash or are removed by downstream scrubbing of the raw gases. The ultimate disposal of the ash and downstream processing wastes will probably be in tailings ponds and landfills. The types and quantities of solid wastes from several proposed gasification processes are given in Table 1.

Consideration must be given to undesirable accessory elements that might be leached from the wastes during handling in water slurries. Even those wastes handled dry will ultimately be exposed to leaching by ground water when landfilled. Potentially severe contamination from accessory elements contained in the ash may also result from the disposal of refuse from the cleaning of coal prior to gasification or liquefaction. It is well-known that iron sulfates and acids are produced from the oxidation of pyritic minerals contained in the refuse when exposed to air (e.g., Singer and Stumm, 1969; Smith et al., 1969; and Jones and Ruggeri, 1969). Garrels and Thompson (1960) concluded that the rate of oxidation was chiefly a function of oxidation-reduction potential (Eh) and was independent of total Fe content. Similarly, Bell and Escher (1969) found that production of acidic iron salt from pyrite was an almost immediate response to the atmospheric gas composition in contact with the water. Reversing the gases from air to nitrogen caused the acid formation to decrease, and reversal from nitrogen to air caused the acid formation to increase. There is also some evidence that oxygenation of Fe (II) can be affected by the catalytic responses of trace constituents such as copper (Stauffer and Lovell, 1969).

TABLE 1

SOLID WASTES PRODUCED BY SEVERAL COAL GASIFICATION PROCESSES

Process	Type of Solid Waste	Quantity of Solid[a] (lb/hr)
BI-GAS	Water quenched Slag	68,400
CO_2 Acceptor	Water cool, Char/Spent Acceptor	496,800
HYGAS	Water cool, lock hoppers Ash/Char	138,900
Koppers-Totzek	Water quenched Slag	111,500
LURGI	Water cool, ash locks Ash	314,000
SYNTHANE	Dry let-down, fluid bed Char	362,200
U-GAS	Water cool, venturi throat Char	86,400
Winkler	Water-cooled screw conveyor Char	372,500

SOURCE: Magee, 1976.

[a] If individual values are used, Magee (1976) should be consulted to determine the original basis of computation.

These results have far-reaching implications for those proposals that recommend the use of alkaline gasification ashes to neutralize acid mine refuse or disposal of the ash and refuse together as landfill in strip mines. It is likely that accessory elements in the ash and refuse will be extracted by the acid solution and that these trace elements may actually catalyze the further formation of acid.

The chemical form of the accessory elements in gasification ashes and slags is important but has not been investigated thoroughly. Data on fly ashes and slags produced in coal-fired furnaces may not be pertinent because the gasification ashes and liquefaction residues are produced under different conditions, namely, at high temperatures and pressures and usually in a reducing atmosphere rather than in an oxidizing one. Significant alterations in mineralogy and chemical form of the feed coal may affect the solubility of accessory elements in the ash and thus affect their potential as pollutants.

Solid Coal Wastes As Resources

Another problem facing the United States is a minerals deficit that will exceed the energy deficit by the year 2000. The U.S. Department of the Interior estimates the trade deficit in minerals to be $100 billion within 25 years. The United States is almost completely dependent on foreign sources for 22 of the 74 nonenergy minerals considered essential for a modern industrial society. Of the 12 considered crucial, 7 are imported in large quantities (>50 percent of use) (Malhotra, 1976).

Previous studies (Ruch, Gluskoter, and Shimp, 1974, and Gluskoter et al., 1975) have shown that certain minor and trace elements are concentrated in coal ash. For example, zinc occurred in certain coal ashes in concentrations as high as those mined as commercial sources. Thus, the high quantities of solid waste generated from coal gasification and liquefaction processes may be used as ore in the future. It is conceivable that the acid mine waters may be used to extract recoverable amounts of copper, nickel, zinc, iron, and other minerals from the solid wastes. Although some studies have been made in this general area (EPA, 1971), much more work is necessary to predict both the positive and negative potential environmental effects of coal conversion processes.

CURRENT STUDIES OF ACCESSORY ELEMENTS IN COAL GASIFICATION AND LIQUEFACTION RESIDUES

Obtaining data concerning the accessory element content, mineralogy, solubility, and toxicity of leachates from coal solid wastes is a necessary first step in assessing the environmental aspects of coal utilization; it has not always been among the first steps taken, however (DiGioia et al., 1974). The project reported here grew out of an ongoing research effort at the Illinois State Geological Survey involving the characterization of coal and coal residues.

Data on the chemical analyses and summaries of the geological significance of over 170 coals have been published by the Illinois State Geological Survey (Ruch, Gluskoter, and Kennedy, 1971; Ruch, Gluskoter, and Shimp, 1973; Ruch, Gluskoter, and Shimp, 1974; Gluskoter et al., 1977). Current investigations are expanding these studies to include the feed coals and residues from coal conversion processes. Complete chemical, physical, and mineralogical characterizations of slags, ashes, chars, cleaning wastes, and residues from various coal gasification and liquefaction processes are being made. These chemical and mineralogical characteristics are then being related to chemical solubilities at several pH's and to biological toxicity of aqueous extracts of the solid-waste residues. This report presents some recent data obtained from a LURGI gasification ash and an H-Coal liquefaction residue from an Illinois No. 6 Coal.

Sources of Gasification Ash and Liquefaction Residue

During 1973 and 1974, the American Gas Association and the Office of Coal Research studied the performance and suitability of various American coals for gasification by the LURGI process. Four different coals were sent to Scotland, where they were gasified in the LURGI plant at Westfield. Among the four coals were 5000 tons of Herrin (No. 6) coal from Illinois that was gasified; the unquenched waste ash was then sent back to the United States for analyses. The sample of LURGI ash from the No. 6 Coal, for which data is reported here, was supplied by Peabody Coal Company's Central Laboratory at Freeburg, Illinois.

The coal liquefaction residue was obtained from Hydrocarbon Research, Inc., Trenton, New Jersey. The residue comprised the vacuum still bottoms generated during production of a fuel oil product using an Illinois No. 6 Coal and the H-Coal^R PDU at the HRI Trenton Lab on May 3, 1976.

Chemical and Mineralogical Characterization

The chemical composition of the H-Coal residue and the LURGI ash has been determined for approximately 60 constituents and is summarized in Tables 2 and 3. The major constituents found were Al, Ca, Fe, K, and Si. Large quantities of Mg, Mn, Na, S, and Ti and significant quantities (10-1000 ppm) of trace metals were also present.

The minerals detected in the LURGI ashes by X-ray diffraction included quartz, mullite, hematite, and plagioclase feldspar. Nearly all

TABLE 2

CHEMICAL COMPOSITION OF LURGI ASH AND SLURRY SUPERNATANT SOLUTIONS OF THE ASH FROM AN ILLINOIS NO. 6 COAL AT SEVERAL pH'S

	Chemical Composition of 10% Slurry Supernatant (mg/l)									
Constituents	Air				Argon				Recommended Water Quality Levels (mg/l)	Solid Ash Content (mg/kg)
pH	7.55[a]	5.10	3.82	2.68	8.82[a]	7.20	5.35	3.79	6.0 - 9.0	-
Ag	-	-	-	-	-	-	-	-	.05	<.4
Al	ND[b]	2	14	132	ND	ND	ND	92	.1	108,121
Au	-	-	-	-	-	-	-	-	-	<.001
As	ND	ND	ND	ND	ND	ND	ND	ND	.1	3
B	4.0	4.5	4.5	5.5	4.5	3.0	4.5	8.0	.75	355
Ba	ND	ND	ND	ND	ND	ND	ND	ND	1.0	950
Be	ND	ND	.01	.03	ND	ND	ND	.01	.1	12
Br	-	-	-	-	-	-	-	-	-	<1.0
Ca	290	480	400	570	440	370	430	500	50	16,652
Cd	.02	.03	.03	.06	.01	ND	.02	.05	.01	<1.6
Ce	-	-	-	-	-	-	-	-	-	140
Cl	ND	ND	ND	ND	ND	ND	ND	ND	250	100
COD[c]	2	2	2	81	2	2	16	140	50	-
MCE[d]	28	28	0	23	10	3	6	4	-	-
Cr	ND	.02	.05	.12	.01	.01	.06	.16	.05	212
Co	ND	.05	.08	.19	ND	ND	ND	.17	.05	34
Cu	.01	.02	.13	.73	.01	.05	.01	.05	.2	57
Cs	-	-	-	-	-	-	-	-	-	11
Eu	-	-	-	-	-	-	-	-	-	1.9
F	.31	.30	.09	.04	.51	.34	.16	.02	1.0	<10
Fe_{Total}	.06	.19	.24	560	.06	.11	101	880	.3	143,780
Fe^{+2}	.03	.11	.10	533	.13	.05	110	865	-	-
Ga	-	-	-	-	-	-	-	-	-	26
Ge	-	-	-	-	-	-	-	-	-	7.0
Hf	-	-	-	-	-	-	-	-	-	6.1
Hg	ND	ND	ND	ND	ND	ND	ND	ND	.0002	.05
K	42	49	51	26	39	43	48	61	5	14,611
La	-	-	-	-	-	-	-	-	-	47
Li	1.8	1.9	2.0	2.0	1.6	1.8	1.9	2.1	2.5	42
Lu	-	-	-	-	-	-	-	-	-	1.5
Mg	10.5	14	15	22	9.5	11	13.5	23	50	3,739
Mn	.45	1.94	2.7	3.8	.11	.90	2.3	3.7	.05	1,859
Mo	ND	ND	ND	ND	ND	ND	ND	ND	.01	30
Na	34	37	38	40	32	37	37	40	20[e]	1,929
NH_4	17	8	12	11	10	10	10	17	.02	-
Ni	.03	.13	.23	.50	ND	.04	.14	.42	1.	89
Pb	.1	.1	.1	.2	ND	ND	.1	.2	.03	45
P	-	-	-	-	-	-	-	-	-	87
PO_4	ND	ND	ND	ND	ND	ND	ND	ND	.05	-
Rb	-	-	-	-	-	-	-	-	-	162
S_{Total}	-	-	-	-	-	-	-	-	-	6,100
S^{-2}	ND	ND	ND	ND	ND	ND	ND	ND	.002	1,500
SO_4	820	943	808	338	730	735	700	710	250	8,100
Sb	.2	.3	.3	.6	.3	.3	.3	.5	.05	4.2

TABLE 2 (Continued)

Sc	-	-	-	-	-	-	-	-	-	29
Se	-	-	-	-	-	-	-	-	.01	< 1
Si	5	29	60	130	4	9	27	120	-	229,946
Sm	-	-	-	-	-	-	-	-	-	10
Sn	ND	ND	ND	ND	ND	ND	ND	ND	-	-
Sr	1.8	1.9	2.1	2.9	1.5	1.7	1.9	2.6	50.	370
Ta	-	-	-	-	-	-	-	-	-	1.1
Te	ND	ND	ND	ND	ND	ND	ND	ND	-	-
Th	-	-	-	-	-	-	-	-	-	21
Ti	ND	ND	ND	ND	ND	ND	ND	ND	-	6,295
Tl	ND	ND	ND	ND	ND	ND	ND	ND	-	4.6
U	-	-	-	-	-	-	-	-	-	17
V	-	-	-	-	-	-	-	-	0.1	184
W	-	-	-	-	-	-	-	-	-	1.5
Yb	-	-	-	-	-	-	-	-	-	2.9
Zn	.12	5.5	12	17	.01	.11	6.5	20	.2	400
Zr	-	-	-	-	-	-	-	-	-	170
EC (mmhos/cm)	1.17	1.50	1.95	5.60	1.20	1.39	1.80	5.20	18	-
Eh (electrode mv)	+223	+246	+407	+349	+109	+161	+102	+243	-	-

[a] Natural pH of supernatant [b] Not detectable [c] Chemical oxygen demand [d] Methylene chloride extractable [e] For low Na diet; 250 ppm for taste

TABLE 3

CHEMICAL COMPOSITION OF H-COAL LIQUEFACTION WASTE AND SLURRY SUPERNATANT SOLUTIONS OF THE WASTE AT SEVERAL pH'S

Constituents	Solid Ash Content (mg/kg)	Chemical Composition of 10% Slurry Supernatant (mg/l)								Recommended Water Quality Levels (mg/l)
		Air				Argon				
pH	—	8.83[a]	8.16	5.01	3.14	11.31[a]	8.50	5.53	2.30	6.0 - 9.0
Ag	0.16	—	—	—	—	—	—	—	—	.05
Al	17,253	3.0	<.5	<.5	5.5	1.5	<.5	1.5	5.7	.1
Au	—	—	—	—	—	—	—	—	—	—
As	1.5	<1	<1	<1	<1	<1	<1	<1	<1	.1
B	300	11.0	13.0	11.6	13.6	11.0	12.2	12.9	15.0	.75
Ba	40	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0
Be	1.8	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	.1
Br	6.7	—	—	—	—	—	—	—	—	—
Ca	7862	110	175	380	497	133	155	425	487	50
Cd	<.4	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03	.01
Ce	16	—	—	—	—	—	—	—	—	—
Cl	1000	75	71	67	75	78	70	75	64	250
COD[b]	—	15	9	7	15	24	8	2	24	50
Cr	27.5	<.02	<.02	<.02	.03	<.02	<.02	<.02	.05	.05

TABLE 3 (Continued)

Co	4.45	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	.05
Cu	14	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05	.2
Cs	1.7	—	—	—	—	—	—	—	—	—
Eu	0.69	—	—	—	—	—	—	—	—	—
F	100	1.00	1.15	0.60	0.86	0.70	1.20	0.85	0.84	1.0
Fe_{Total}	23,662	<.1	<.1	14	31.5	<.1	<.1	6.5	90	.3
Fe^{+2}	—	<.1	<.1	11	29.5	<.1	<.1	.9	90	—
Ga	4.6	—	—	—	—	—	—	—	—	—
Ge	4.9	—	—	—	—	—	—	—	—	—
Hf	0.86	—	—	—	—	—	—	—	—	—
Hg	—	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	.0002
K	2490	1.4	1.4	2.1	2.8	1.2	1.5	2.0	2.5	5
La	9.8	—	—	—	—	—	—	—	—	—
Li	—	<.01	.01	.02	.02	<.01	.01	.02	.02	2.5
Lu	.024	—	—	—	—	—	—	—	—	—
Mg	844	0.5	0.6	2.7	4.0	0.6	0.8	3.0	4.0	50
Mn	77	<.02	.04	1.67	2.68	<.02	0.10	1.83	2.52	.05
Mo	6.4	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2	.01
Na	619	6.7	7.0	7.5	9.3	6.5	6.8	109[c]	9.0	20[d]
NH_4	—	9	6	8	8	8	5	7	5	.02
Ni	21	<.07	<.07	<.07	<.07	<.07	<.07	<.07	.25	1.0
Pb	32	<0.1	<.1	.2	.25	<.1	<.1	.15	.2	.03
P	44	—	—	—	—	—	—	—	—	—
PO_4	—	<.025	<.025	<.025	<.025	<.025	<.025	<.025	0.1	.05
Rb	16	—	—	—	—	—	—	—	—	—
S_{Total}	18,000	—	—	—	—	—	—	—	—	—
S^{-2}	300	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2	.002
SO_4	600	65.5	68.5	148.5	96.5	65.5	66.0	70.5	73.5	250
Sb	1.2	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4	.05
Sc	4.1	—	—	—	—	—	—	—	—	—
Se	—	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	.01
Si	39,641	<1	<1	<1	3	<1	<1	<1	3	—
Sm	2.3	—	—	—	—	—	—	—	—	—
Sn	0.6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	—
Sr	30	.20	.24	.34	.50	.20	.26	.38	.48	50
Ta	0.17	—	—	—	—	—	—	—	—	—
Te	<0.1	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	—
Th	3.5	—	—	—	—	—	—	—	—	—
Ti	1019	<.6	<.6	<.6	<.6	<.6	<.6	<.6	<.6	—
Tl	1.7	<.4	<.4	<.4	<.4	<.4	<.4	<.4	<.4	—
U	5.7	—	—	—	—	—	—	—	—	—
V	33	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	0.1
W	4.4	—	—	—	—	—	—	—	—	—
Yb	1.0	—	—	—	—	—	—	—	—	—
Zn	71	.01	.01	.06	.27	.02	.02	.12	.76	.2
Zr	41	—	—	—	—	—	—	—	—	—
EC (mmhos/cm)	—	0.05	0.87	2.18	2.83	0.68	1.00	2.51	3.49	18
Eh (electrode mv)	—	+202.8	+235	+295.1	+419.6	+13.9	+178.9	+233.7	—	—

[a] Natural pH of supernatant [b] Chemical oxygen demand [c] NaOH added for pH adjustment [d] For low Na diet; 250 ppm for taste

the pyrite present in the feed coal was converted to hematite during gasification. The clay minerals present in the feed coals were not detected in the ash and were apparently converted to mullite, a high-temperature-phase aluminosilicate. The other accessory minerals were apparently converted to a feldspar.

The minerals detected in the H-Coal residue samples by X-ray diffraction included quartz, pyrrhotite, sphalerite, calcite, anhydrite, illite, kaolinite, and some expandable clay minerals. Wallastonite ($CaSiO_3$), undetected by X-ray diffraction, was found by the scanning electron microscope with the energy-dispersive X-ray analyzer in polished and etched samples of heavy minerals from the H-Coal residues.

Several minerals participate in chemical reactions during coal conversion processes. For example, in the H-Coal process, a small amount of quartz and calcite reacted to form wollastonite. More importantly, nearly all the pyrite present in the feed coal was converted to pyrrhotite in the solid waste. This occurred at temperatures lower than would be expected from comparisons with published data on reactions of pure iron sulfides at equilibrium conditions. These reactions could have occurred in the slurry preheaters or in the liquefaction process reactors. The pyrite-to-pyrrhotite conversion might have been a result of the cobalt-molybdate catalyst, which is used for conversion of organic constituents to a fuel oil product in the H-Coal process, but the effect of the catalyst on the mineral interactions is not known. We have also studied other liquefaction process residues and the change from pyrite to pyrrhotite also occurred without the aid of the catalyst in the Solvent Refined Coal (SRC) process. The SRC process does not use a catalyst. In the three liquefaction processes studied (H-Coal, SRC, and SYNTHOIL), nearly all pyrite in the feed coals was converted to pyrrhotite in the solid residues. This conversion may be the result of intimate association of the hydrogen in the liquefaction system with the pyrite in the coal slurry. Established phase relationships in closed systems cannot be directly applied to mineral matter in the liquefaction processes because of the undefined interactions of the components and the removal of vapor from the system during reactions. Therefore, mineral reactions must be deduced from a thorough study of the coal mineral matter before and after coal conversion.

Aqueous Solubility

Probably the single most important factor affecting the solubility of the accessory elements in coal solid wastes is pH. Many coal wastes contain sulfide minerals that can acidify upon exposure to air. In terms of heavy metals, solid wastes disposed of in acidic strip or underground mines are potentially more soluble than wastes disposed of under neutral or alkaline conditions.

The oxidation potential (Eh) is also an important factor affecting the solubility of minerals (Garrels and Christ, 1965). When solid wastes are buried underground or in water-saturated materials, anaerobic (oxygen deficient) conditions usually develop. Studies of the effect of Eh and pH on the solubilities of coal solid wastes could produce data that would allow prediction of potential pollution hazards or, on the other hand, prediction of optimum conditions for extraction of the potentially valuable elements contained in the wastes.

The current experimental design involved making 10% aqueous slurries of each of the solid wastes studied. The slurries were set up in series that had been adjusted to four individual pH values over the range 2 to 11. The pH values of the slurries were monitored daily and readjusted to the specified value if necessary. Chemical equilibrium was assumed when the pH values remained constant. This process took approximately 3 months; however, studies with LURGI ashes from three different coals showed that chemical equilibrium was more than 90 percent complete in one week.

Duplicate sets of slurries were used. One set was equilibrated under an argon (oxygen and CO_2 free) atmosphere and the second set was equilibrated under an air (oxidizing) atmosphere. The results for a LURGI ash and an H-Coal residue obtained from an Illinois No. 6 Coal are reported in Tables 2 and 3. Tables 2 and 3 contain the measurements for some 63 chemical constituents measured in the solid ash and in the aqueous supernatant solutions. Also included in the tables is a summary of recommended water quality levels (EPA, 1973) for as many constituents for which data could be found. This was done for comparison with the water solubility levels found under conditions given in Tables 2 and 3.

Potential Pollutants

Of the approximately 60 chemical constituents measured in the raw LURGI ash and H-Coal residue (Tables 2 and 3), about 31 were found to be present at concentrations that could present a potential hazard. The remainder were present at such low levels that, even if completely soluble, they would pose no particular problem. Of the 31 that were a potential problem, 16 were found to be in forms soluble enough to exceed recommended water quality levels in some samples at pH values between 3 and 8. These 16 constituents are listed in Table 4. Seven of the constituents—Al, Cr, Co, Cu, F, Fe, and Zn—exceeded the recommended levels in water only under certain pH conditions, generally when the pH was quite acid. The other nine constituents—B, Ca, Cd, K, Mn, NH_4, Pb, SO_4, and Sb—exceeded the recommended levels in all LURGI ash solutions over the pH range 3 to 9. These nine constituents are thought to represent the highest potential pollution hazard. Discharges of the 16 constituents listed in Table 4 at the levels found in this study could cause some environmental degradation and require some form of wastewater treatment.

Toxicity Studies

The acute toxicities of the water-soluble con-

TABLE 4

ELEMENTS EXCEEDING RECOMMENDED WATER QUALITY LEVELS

	LURGI Ash Solubility		H-Coal Residue Solubility		
Constituent	pH 3 (mg/l)	pH 8 (mg/l)	pH 3 (mg/l)	pH 8 (mg/l)	Recommended Levels (mg/l)
Al	132.	<0.5	5.5	<0.5	0.10
B[a]	5.5	4.0	13.6	13.0	0.75
Ca[a]	570.	290.	497.	175.	50.
Cd[a]	0.06	0.02	—	—	.01
Cr	0.12	<0.02	—	—	0.05
Co	0.19	<0.10	—	—	0.05
Cu	0.75	0.01	—	—	0.20
F	—	—	0.86	1.15	1.00
Fe	560.	0.06	31.50	<0.10	0.30
K[a]	26.	42.	—	—	5.00
Mn[a]	3.80	0.45	2.68	0.04	0.05
NH_4[a]	11.	17.	8.	6.	0.02
Pb[a]	0.20	0.10	0.25	<0.10	0.03
SO_4[a]	338.	820.	—	—	250.
Sb[a]	0.60	0.20	—	—	0.05
Zn	17.00	0.12	0.27	0.01	0.20

[a] Highest pollution potential

stituents in the solid-waste leachates from coal conversion were assayed, used fathead minnows, *Pimephales promelas*. Three-to-six-day-old free-swimming fatheads were used for the 96-hour static bioassays. These studies were performed under controlled conditions in an environmental chamber, using procedures suggested by the Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). All bioassays were replicated one or more times.

The toxicities of the water-soluble compounds in equilibrium with the H-Coal liquefaction residue and the LURGI gasification ash at various pH values are shown in Figure 1. The waste leachates do not appear acutely toxic to young fathead minnows at near-neutral pH's (7.0-8.5); however, 100 percent mortality occurred in both the high- and low-pH solutions (Figure 1). To test only the pH effect on the mortality of the fathead minnows, bioassays were conducted using buffered solutions of reconstituted water ranging in pH from 5.0 to 11.0. The results of these bioassays (Figure 1) were similar to those found for the waste leachates. It is possible that most of the mortality observed was the result of pH values. However, the higher mortality observed in the alkaline range for the H-Coal leachate than for the reconstituted water indicates a toxicity that is not accounted for by pH values.

Attempts were made to decrease the mortality due to pH effects by neutralizing some of the acidic leachate solutions with NaOH. In all cases 100 percent mortality occurred even though the pH was neutral. All the neutralized solutions had specific conductance values greater than 7.00 mmhos/cm. We hypothesized that the high total ion concentration resulted in ionic shock and was responsible for the mortality in the neutralized solutions. This conclusion was verified by a study in which the specific conductance of several solutions of reconstituted water was varied by the addition of NaCl. The results are shown in Figure 2.

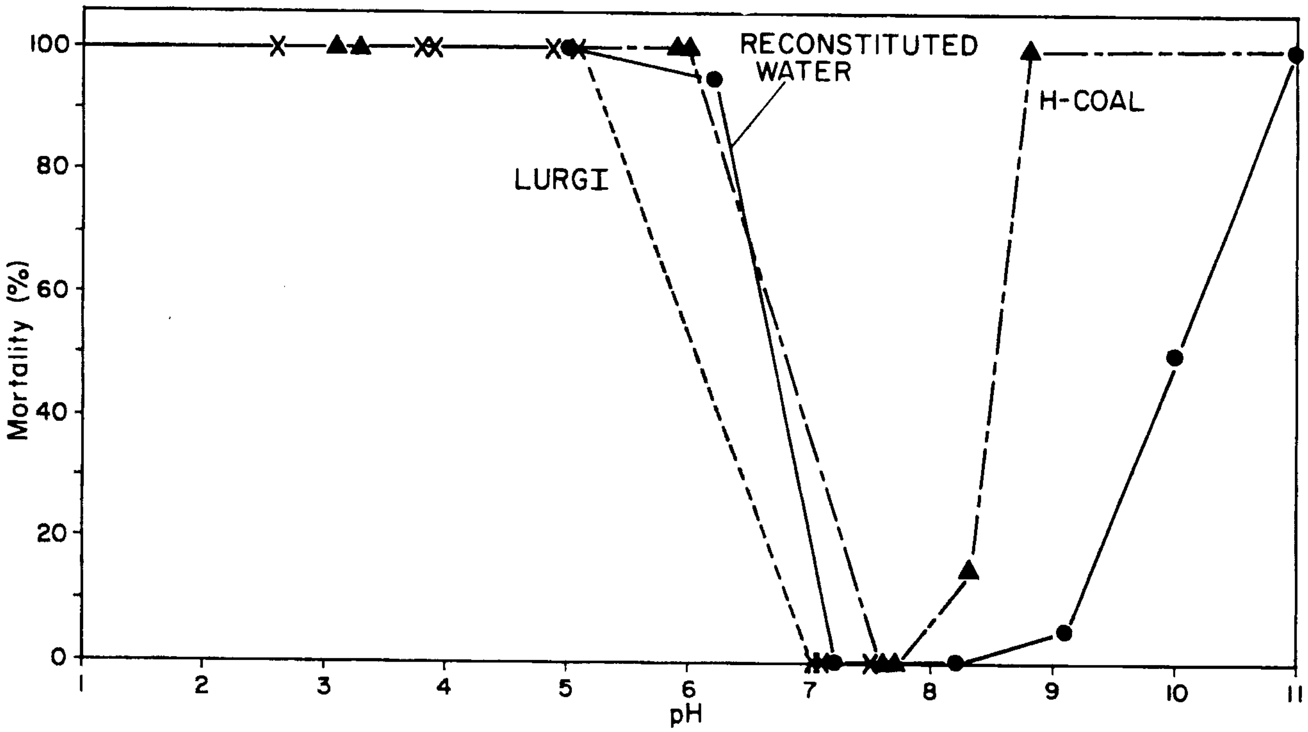

Figure 1. **Effect of pH on the mortality of fathead minnows in LURGI ash leachate, H-Coal residue leachate, and reconstituted water.**

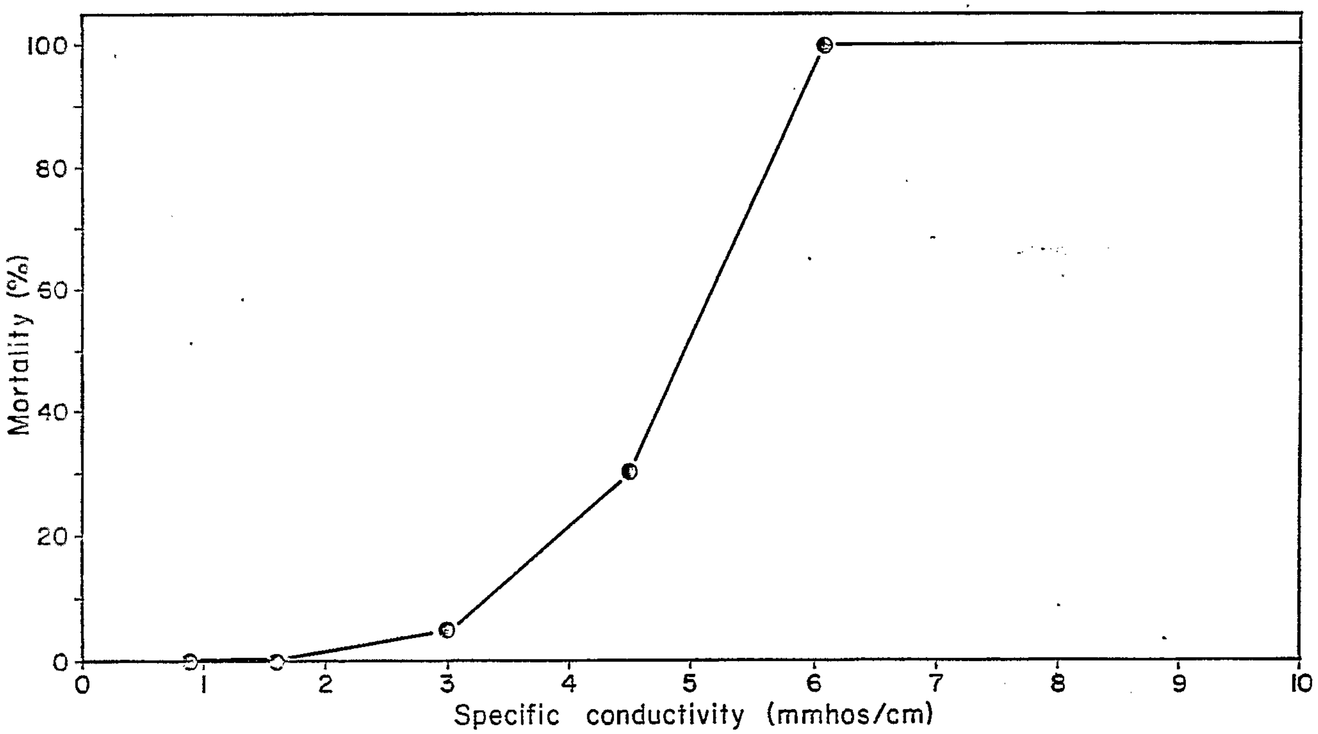

Figure 2. Effect of specific conductance on the mortality of fathead minnows in reconstituted water.

Solutions with a specific conductance greater than 6.10 mmhos/cm caused 100 percent mortality.

The LC-50's were determined for the waste leachates and are presented in Table 5. The LC-50 is the number of milliliters of waste material per 100 milliliters of total volume that results in the death of 50 percent of the test organisms during 96 hours. For example, if the LC-50 is 5.0 ml/100ml, then a solution of 5.0 ml of waste leachate and 95.0 ml of reconstituted water will kill 50 percent of the fathead minnows. If the LC-50 is greater than 100ml/100ml, a solution of undiluted leachate will not kill 50 percent of the minnows. The approximate LC-50 values for the H-Coal and LURGI ash leachates of various pH's are listed in Table 5. Very acidic solutions (pH <4.0) must be diluted 20 or more times to decrease mortality to 50 percent, whereas full-strength near-neutral solutions were not toxic.

These studies indicate that the water-soluble constituents in equilibrium with wastes at near-neutral pH's (7.0-8.5) are not acutely toxic to young fathead minnows. Both pH and total salt concentration do appear to be important factors that affect the observed mortality of the young minnows. Further studies are being conducted to determine the interactions of pH, total ion concentration, and toxic compounds extracted from the wastes.

RECOMMENDATIONS

The potential environmental and economic consequences associated with the disposal of the solid wastes generated by even a single large-scale coal conversion facility is impressive because of the sheer magnitude of the wastes generated. The major solid wastes are the refuse from coal cleaning; ashes, slags, and chars from the conversion process; and sludges from water cleanup. Clearly, careful planning is required to mitigate adverse en-

TABLE 5

PERCENTAGE MORTALITY AND APPROXIMATE LC-50'S FROM BIOASSAYS OF FATHEAD MINNOWS FOR LURGI ASH AND H-COAL LEACHATES

LURGI			H-COAL		
pH	Mortality (%)	LC-50 (ml/100 ml)	pH	Mortality (%)	LC-50 (ml/100 ml)
7.5	0	>100	8.8	100	50-100
7.1	0	> 100	8.3	15	>100
7.1	0	> 100	7.7	0	> 100
5.1	100	25-50	7.6	0	> 100
4.9	100	5-25	6.0	100	50-100
3.9	100	5-25	5.9	100	50-100
3.8	100	<5	3.3	100	<5
2.6	100	<5	3.1	100	<5

vironmental impacts; however, planning can be effective only when an adequate data base is available.

Specific research needs include the qualitative and quantitative characterization of coal conversion solid wastes:

1. Quantitative determination of the accessory elements contained in the wastes
2. Determination of the solubility of the accessory elements under a variety of environmental conditions
3. Establishment of the effects of coal characteristics and process operating variables on the character of the solid wastes generated by a given process
4. Determination of methods for recovering valuable metals from the solid wastes
5. Determination of the ultimate fate of waterborne pollutants resulting from solid-waste materials
6. Characterization and quantification of both the acute and chronic biological toxicity and public health hazard associated with pollutants from coal solid wastes
7. Pursuit of research to establish environmental standards that will maintain the integrity of the environment within realistic bounds

The energy demands of the nation are such that construction of large-scale coal gasification and liquefaction plants will be undertaken. The process designs are at the pilot plant stage of development and demonstration plants will undoubtedly be built within the next decade. There are few precedents with which to predict the environmental impact of the disposal of waste products on a scale this large. It is expected that valuable trace elements can be recovered from many wastes if proper planning is provided. Basic and applied research is needed to develop the technical information necessary to formulate those strategies and disposal options necessary to avoid serious problems that could appear suddenly in large-scale operations. Further, the research must be begun soon so that the data will be available for the planning of the initial large-scale coal conversion facilities.

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