pt 2

Previous work done by Dr. James Hoffman (professor of Geology at UW-Oshkosh and member of Wisconsin's Metallic Mining Council and the Legislative Council's Special Committee on Groundwater Quality Management) and published under the title "Geochemistry of Acid Mine Drainage on the Aquifers of Southwestern Wisconsin and Regulatory Implications" indicates knowledge by state agencies of area groundwater quality deterioration after closure of the Bearhole and Shullsburg Mines in 1978 and 1979, respectively. This understanding, however, did not include heavy metal and arsenic contamination as these parameters were not anticipated or sampled.

The groundwater contamination was discovered when the pumps were shut down in these mines and the groundwater table was allowed to return to normal. Area residents near these mines experienced contaminated wells nine months after the mine pumps were shut down. Several dairy farmers with impacted wells experienced a significant drop in milk production in their herds. Drinking the water is reported to have produced strong cathartic effects in both humans and dairy cows (Hoffman, 1984).

Dr. Hoffman indicates that presence of the sulfur-eating bacteria, Thiobacillus ferrooxidans, probably catalyzes the process of sulfide oxidation in exposed underground deposits and he provides an excellent summary of the geochemical aspects of sulfide mineral oxidation. He proposes an interesting hypothesis of thiosulfate reactions to help explain why elevated levels of metals can be found in mine waters with pH levels greater than 7. Hoffman also presents a very clear and accurate description of the hydrogeological parameters and controls encountered in the Southwestern Wisconsin Zinc-Lead Mining District.

Another interesting study was done by De Geoffroy (1969) entitled Geochemical Prospecting by Spring Sampling in the Southwest Wisconsin Zinc Mining Area. This study was designed to discover zinc concentration highs in the groundwater in order to detect new and profitable mining areas in the district. High concentrations of zinc in De Geoffry's study and map match quite well with Heyl's (1959) district map (Figure 2-Map of Regional Zoning of Zinc-Lead Mineralization) showing regional variation of elements in the mineral deposits.

Arsenic contamination of groundwater due to mining and leaching of arsenical sulfides is not unique to Wisconsin's Zinc-Lead mining district. Numerous studies of recent publication can be cited. For example: Arsenic Contamination of Water Wells in Nova Scotia (1977) by Grantham and Jones; Arsenic in Nova Scotian Groundwater (1984) by Meranger and Subramanian and Arsenic Speciation and Quality of Groundwater in a Lead-Zinc Mine, Idaho (1988) by Mok, Riley and Wai.

Heavy metals contamination of mine-related groundwaters has also received recent publicity in technical publications such as Determining Heavy Metal Leaching and Transport from Abandoned Mine Waste and Subsequent Attenuation (1989) by Lambeth et al.; Undoing the Damage: Wetlands Treat Groundwater Contaminated by Mine Drainage-Naturally (1993) by Godsey; Mining and Groundwater; Can They Coexist? (1993) by Swanson and Abandoned Mine Holds Water Quality Problems (1993) by Ross.

These are a few of many peer-reviewed technical papers concerning arsenic and heavy metals environmental contamination caused by mining of sulfide deposits that are currently available through the American Geological Institute's GEO-REF database.

High heavy metal concentrations in groundwater are not always caused by mine activity. Sometimes mineral deposits are exposed at the earth's surface and bacteria begins the acid leaching process. Other times, highly soluble (but undisturbed) minerals can and have been leached by groundwater such as might have occurred with the high arsenic levels in groundwater recently detected in two separate areas of east-central and northeastern Wisconsin. See the article Metals in Water: Determining Natural Background Concentrations in Mineralized Areas (1992) by Runnels, Shepard and Angino. See also the November 19, 1993, newspaper article by Todd Haefer on "Arsenic in Algoma?" in the Oshkosh Northwestern. Also refer to Evaluation of N.U.R.E. Hydrogeochemical Data for use in Wisconsin Groundwater Studies (1993) by Mudrey and Bradbury.

In summary of this section of the data results, it is evident that groundwater is being negatively impacted by heavy and toxic elements in quantities that sometimes grossly exceed maximum contaminant levels. MCL's are established to protect human and environmental health. Another interesting detail to note is that mine waters with a neutral (7.0) pH are still able to carry considerable concentrations of heavy metals in solution.

One also has to review what is not known from these sample results. The first unknown is the district wide extent of groundwater contamination due to infiltration of these mine related groundwaters into the surrounding local aquifers. As was pointed out in Appendix A, over 400 zinc mines and thousands of lead mines are located throughout the counties of Dane, Iowa, Grant, Lafayette, and Green Counties and some of these mines had bore holes drilled into lower parts of the local dolomitic limestone aquifer which would act like gravity sumps and would drain and spread contaminants into lower parts of the aquifer. As Hoffman and others (Mok, Reily and Wai, 1988; Runnells, Shepherd and Angino, 1992) point out, the local geologic structures (which include joint and fracture systems that may conduct surface waters with high dissolved oxygen values down into mined openings; folds, faults and the strike and dip of beds) contribute to the degree of acid mine drainage production with corresponding heavy metal leaching as well as contaminant plume flow direction.

It is known that private water wells have, in the past, been completed into mine shafts and mine tunnels because large quantities of water are encountered at a shallow depth and are cheaper to exploit. Some farms still use capped spring houses (which may be an old mine seep or spring) as a source of drinking and livestock water. This is a potential health hazard since it is not customary for private wells to be tested for arsenic and heavy metals. These private wells and spring houses should be identified, sampled and, if found contaminated, abandoned. In light of the previously presented evidence, it is not unreasonable to recommend that private water wells in the mining district be routinely screened for arsenic and a few of the more toxic and soluble heavy metals.

Health checks of local persons with impacted wells might also be prudent along with a check of the morbidity and mortality records for cancer-types and rates in the mining district counties. Specific cancers (including skin cancer) have been strongly linked to arsenic exposure in an 11 year study of a human population exposed to natural arsenic in drinking water wells on the island of Taiwan (see Ecological Correlation Between Arsenic Level in Well Water and Age-Adjusted Mortality from Malignant Neoplasms by Chien Jen-Chen and Chih-Jen Wang; Arsenic in Drinking Water--Bigger Cancer Threat by Raloff; Arsenic--Recommended Public Health Level for Drinking Water by Brown and Fan; Arsenic in Drinking Water by California EPA; Toxicological Profile for Arsenic, Final Update, 1993, Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Social Services).

### *Public and Private Water Supply Sample Results*

Three public water supply samples were taken to see if any arsenic or heavy metals could be detected in the deeper St. Peter Sandstone aquifer in the vicinity of known zinc mines. Five private well samples were submitted simultaneously to the Wisconsin State Laboratory of Hygiene for analysis but only two samples were analyzed and reported. The other three samples were lost with no record of their existence.

The three missing samples were from wells that were known to be completed into or closely adjacent to mines. Therefore, the reader must be aware that this section is incomplete and cannot properly represent private well water quality in and around the mines. Further representative sampling should be under taken.

<u>Sample MW-1R</u> was taken to represent point-of-use water quality of the public water supply in Shullsburg, Wisconsin. The sample was collected from a restaurant rest room. Arsenic was detected at 1.4 ppb (0.0014 ppm), barium was detected at 53 ppb (0.053 ppm), cadmium was detected at 0.08 ppb (0.00008 ppm), copper was detected at 13 ppb (0.013 ppm), lead was detected at 4.5 ppb (0.0045 ppm), nickel was detected at 19 ppb (0.019 ppm).

<u>Sample MW-2</u> was taken at the newest Shullsburg Municipal Well; located up on a hill (up gradient) and a few blocks away from the Badger Mine. This well is reported as being completed into the St. Peter Sandstone. Arsenic was detected at 1.9 ppb (0.0019 ppm), barium was detected at 65 ppb (0.065 ppm), cadmium was detected at 0.06 ppb (0.00006 ppm), copper was detected at 3.3 ppb (0.0033 ppm), iron was detected at 360 ppb (0.36 ppm), lead was detected at 2.2 ppb (0.0022 ppm), nickel was detected at 15 ppb (0.015 ppm), zinc was detected at 23 ppb (0.023 ppm).

<u>Sample MW-3</u> was taken at the Benton Municipal Well. The well is completed into the Platteville Formation (dolomitic limestone) and is up gradient from an intensively mined area to the west-northwest. Barium was detected at 65 ppb (0.065 ppm), cadmium was detected at 0.12 ppb (0.00012 ppm), nickel was detected at 48 ppb (0.048 ppm).

<u>Sample HW-001</u> was taken at a private residence near the Etna and Corr Mines. Sampling was done in the house from a sampling hydrant before the well water entered the pressure tank and water softener. Depth of well, depth of casing and local geologic structure are unknown. Sampling was performed after an extended dry period in late summer. Arsenic was detected at 1.2 ppb (0.0012 ppm), cadmium was less than 0.04 ppb (0.00004 ppm), lead was less than 1 ppb (0.001 ppm), zinc was detected at 25 ppb (0.025 ppm).

Sample CW-001 was taken at a private residence near the Etna Mine. Sampling was done in the house from a sampling hydrant before the well water entered the pressure tank and water softener. Depth of well, depth of casing and local geologic structure are unknown. Sampling was performed after an extended dry period in late summer. Arsenic was detected at 1.0 ppb (0.001 ppm), cadmium was detected at 0.05 ppb (0.00005 ppm), lead was less than 1 ppb (0.001 ppm) and zinc was detected at 140 ppb (0.14 ppm).

For a complete review of data; see Table 2-Public and Private Water Supply Samples.

TABLE 2

Public and Private Water Supply Samples
(ug/L)(ppb)

| | MCL | MW-2 | MW-1R | MW-3 | HW-001 | CW-001 |
|---|---|---|---|---|---|---|
| Arsenic | 50 | 1.9 | 1.4 | <1 | 1.2 | 1.0 |
| Barium | 1000 | 65 | 53 | 65 | - | - |
| Cadmium | 10 | 0.06 | 0.08 | 0.12 | <0.04 | 0.05 |
| Chromium | 50 | <1 | <1 | <1 | - | - |
| Cobalt | - | <10 | <10 | <10 | - | - |
| Copper | 1300 | 3.3 | 13 | <1 | - | - |
| Iron | 300 | 360 | <50 | <50 | - | - |
| Lead | 50 | 2.2 | 4.5 | <1 | <1 | <1 |
| Manganese | 50 | <40 | <40 | <40 | - | - |
| Nickel | 100 | 15 | 19 | <10 | - | - |
| Zinc | 5000 | 23 | <10 | 48 | 25 | 140 |
| pH (s.u.) | - | - | - | 7.2 | - | - |

| | |
|---|---|
| MW-1R | Shullsburg Restaurant |
| MW-2 | Shullsburg Municipal Well |
| MW-3 | Benton Municipal Well |
| HW-001 | Private Well near Etna & Corr Mines |
| CW-001 | Private Well near Etna Mine |

Note: There is a pending change in the MCL for arsenic from the current concentration of 50 ug/L to 2 or 3 ug/L.

These samples do not show any immediate reason for concern. The Shullsburg Municipal Well sample may be showing metals concentrations that correlate to leakage and dilution of contaminated groundwater from the upper dolomitic aquifer, through fracture flow, down into the St. Peter Sandstone aquifer since the only reported sulfides of any significance in the St. Peter Sandstone occurs near Centerville, Wisconsin (Heyl, 1959). This may further imply that the St. Peter Sandstone aquifer is vulnerable to contamination through the upper rock formations and may necessitate a review of groundwater and aquifer protection strategies in the mining district so that contamination of the St. Peter Sandstone is minimized. If contamination through fracture flow is occurring, then contamination from land spreading of various ag chemicals and wastes along with leakage from septic systems may be hidden problems to be considered. In the extreme, it may eventually imply that private water wells should be drilled and cased down into the deeper Cambrian sandstone aquifer if the upper St. Peter Sandstone becomes heavily contaminated.

Private wells should be actively screened for some of the more toxic metals and arsenic that were encountered in this study in order to ascertain and certify the safety of the private well water supply in the entire mining district (see discussion in previous section). Reason for concern lies in the fact that most private wells in this study area are completed into the same geologic horizons (Platteville and Decorah Formations) in which the mines and ore deposits are located. Mine related groundwaters are showing definite contamination and have a history of impacting nearby private wells (Hoffman, 1984).

Efforts also should be made to log the precise coordinates (when possible) for known mines (and mine related structures) and make that information public so lending institutions, landowners, homeowners, real estate developers, well drillers, county sanitarians, etc. can know and avoid building homes and larger load-bearing buildings over, drilling wells into, and constructing septic systems over these subsurface structures.

### *Surface Water Sample Results*

Five surface water samples were taken. These include mine spring water samples 001 and 004 which were previously described under mine related groundwater samples because these waters discharge to the Shullsburg Branch and the New Diggings Branch of the Fever (Galena) River, respectively. The water quality of these samples is widely variable with zinc being consistently high in all samples. One sample- 006 -had a high lead concentration.

<u>Sample 001</u> is described in the previous Mine Related Groundwater section. Arsenic was detected at 110 ppb (0.11 ppm), barium concentration was less than 40 ppb (0.04 ppm), cadmium was detected at 180 ppb (0.18 ppm), cobalt was detected at 36 ppb (0.036 ppm), copper was detected at 360 ppb (0.36 ppm), lead was detected at 480 ppb (0.48 ppm), manganese was detected at 3600 ppb (3.6 ppm), molybdenum concentration was less than 40 ppb (0.04 ppm), nickel was detected at 91 ppb (0.091 ppm), silver concentration was less than 0.5 ppb (0.0005 ppm), zinc was detected at 91,000 ppb (91 ppm) and the pH was 2.3.

Sample 002 was taken from the County Highway W concrete culvert over a feeder stream of the New Diggings Branch downstream from the roaster pile located there. Arsenic concentration was less than 10 ppb (0.01 ppm), barium concentration was less than 40 ppb (0.04 ppm), cadmium was detected at 1.2 ppb (0.0012 ppm), cobalt concentration was less than 10 ppb (0.01 ppm), copper concentration was less than 3 ppb (0.003 ppm), lead was detected at 10 ppb (0.01 ppm), manganese was detected at 110 ppb (0.11 ppm), nickel was detected at 13 ppb (0.013 ppm), silver concentration was less than 0.5 ppb (0.005 ppm), zinc was detected at 1400 ppb (1.4 ppm).

Sample 003 was taken 20 yards downstream from the sampling point for sample 002. Arsenic concentration was less than 10 ppb (0.01 ppm), barium was detected at 41 ppb (0.041 ppm), cadmium was detected at 0.9 ppb (0.0009 ppm), cobalt concentration was less than 10 ppb (0.01 ppm), copper concentration was less than 3 ppb (0.003 ppm), lead concentration was less than 3 ppb (0.003 ppm), manganese was detected at 110 ppb (0.11 ppm), nickel concentration was less than 10 ppb (0.01 ppm), silver concentration was less than 0.5 ppb (0.0005 ppm), zinc was detected at 1400 ppb (1.4 ppm).

Sample 004 is described in the previous Mine Related Groundwater section. Arsenic was detected at 22 ppb (0.022 ppm), barium concentration was less than 40 ppb (0.04 ppm), cobalt was detected at 190 ppb (0.19 ppm), copper was detected at 18 ppb (0.018 ppm), lead was detected at 260 ppb (0.26 ppm), manganese was detected at 7400 ppb (7.4 ppm), molybdenum concentration was less than 40 ppb (0.04 ppm), nickel was detected at 140 ppb (0.14 ppm), silver concentration was less than 0.5 ppb (0.0005 ppm), zinc was detected at 33,000 ppb (33 ppm).

Sample 006 was a sample of roadside storm water run-off collected 3 miles north of Lead Mine, Wisconsin on Knee Deep Road during a severe storm. Sample was red and sediment-filled. Arsenic concentration was less than 10 ppb (0.01 ppm), barium was detected at 880 ppb (0.88 ppm), cadmium was detected at 2.0 ppb (0.002 ppm), cobalt was detected at 31 ppb (0.031 ppm), copper was detected at 33 ppb (0.033 ppm), lead was detected at 8,500 ppb (8.5 ppm), manganese was detected at 4,200 ppb (4.2 ppm), nickel was detected at 85 ppb (0.085 ppm), silver was detected at 1.1 ppb (0.0011 ppm), zinc was detected at 16,000 ppb (16 ppm).

For further detailed sample data information; see Table 3-Surface Water Sample Results.

TABLE 3

Surface Water Sample Data
(ug/L)(ppb)

| | 001 | 002 | 003 | 004 | 006 |
|---|---|---|---|---|---|
| Arsenic | 110 | < 10 | < 10 | 22 | < 10 |
| Barium | < 40 | < 40 | 41 | < 40 | 880 |
| Cadmium | 180 | 1.2 | 0.9 | 29 | 2.0 |
| Chromium | [1] | [1] | [1] | [1] | [1] |
| Cobalt | 36 | < 10 | < 10 | 190 | 31 |
| Copper | 360 | < 3 | < 3 | 18 | 33 |
| Iron | [1] | [1] | [1] | [1] | [1] |
| Lead | 480 | 10 | < 3 | 260 | 8500 |
| Manganese | 3600 | 110 | 110 | 7400 | 4200 |
| Molybdenu | < 40 | < 40 | < 40 | < 40 | < 40 |
| Nickel | 91 | 13 | < 10 | 140 | 85 |
| Silver | < 0.5 | < 0.5 | < 0.5 | < 0.5 | 1.1 |
| Zinc | 91000 | 1400 | 1400 | 33000 | 16000 |
| pH (s.u.) | 2.3[2] | - | - | - | - |

[1] Not Analyzed

[2] Tested at site 2 months after original sampling

| | |
|---|---|
| 001 | Etna Mine Spring |
| 002 | Stream near roaster pile on "W" |
| 003 | Stream near roaster pile on "W" - 20 yds downstream from 002 sample point |
| 004 | Penna-Benton Mine Spring |
| 006 | Roadside storm water runoff 3 miles north of Lead Mine on Knee Deep Rd. - red & sediment filled |

One can readily see that the sampled surface waters are impacted by arsenic and heavy metals. Samples 001, 004 and 006 may be unsuitable as drinking water sources for wildlife and livestock.

Further study should be made to ascertain the extent to which stream sediments have been rendered toxic since distribution of heavy metal and arsenic laden sediment has been observed in other zinc-lead sulfide mining districts. See Characterization of Heavy Metal Contamination in the Lateral Lakes of the Lower Coeur d'Alene River Valley, Northern Idaho by Hoffman et al., 1992; Relationships between Particle Size and Metal Concentrations in Contaminated Bed Sediment of the Clark Fork River, Western Montana by Brook and Moore, 1987; Distribution of Metal Contamination in the Floodplain Sediments of the Clark Fork River, near Deer Lodge, Montana by Brook and Moore, 1987; Heavy Metal Contamination of a Greenland Fjord System by Mine Wastes, by Loring and Asmund, 1989; Lead and Zinc Pollution for Marine Dumping of Waste Rock from Lead-Zinc Mining, by Asmund, 1992; Heavy Metal Contamination in the Tanat Valley, North Wales, by Fuge et al., 1989; Impact of Industrial and Mine Drainage Wastes on the Heavy Metal Distribution in the Drainage Basin and Estuary of the Sado River (Portugal), by Quevauviller et al, 1989; Environmental Impact of Base Metal Mining in the Himalaya; a case study with special reference to Rangpo ore field, Sikkim, India, by Rai and Rao, 1987. Also see Toxicity of Sediment-Associated Metals to Freshwater Organisms: Biomonitoring Procedures, by Birge et al., 1984; Acid Volatile Sulfide Predicts the Acute Toxicity of Cadmium and Nickel in Sediments, by Di Toro et al., 1992 and EPA Sediment Classification Methods Compendium, by U.S. EPA, 1992.

The reader should bear in mind that sulfur-eating bacteria are present in some if not all of the study surface waters (Siderococcus was identified by the State Lab of Hygiene in sample 001) and their activity may liberate more heavy metal from the sediments than can be accounted for in the sediment partitioning model.

### *Roaster Pile Sample Results*

These results were first reported from the State Laboratory of Hygiene to the DNR as "provisional" meaning they had experienced some technical difficulty in analyzing these samples because of the high iron and manganese concentrations in the samples and needed to do further replicate analyses to check reported concentrations. Later, the State Lab rejected the results (with the exception of the identification and concentrations of silver and gold) of their own analyses because the quantitation results were not reproducible within their quality assurance parameters. Manganese and iron interferences in the sample peak recoveries caused problems with quantification but not identification of the elements of interest. Quality control data indicate that the values reported are less than the true values present in the samples.

Sample STA-001 was taken at the toe of the New Diggings (Skinner Roaster Plant) roaster pile. Arsenic was detected at 405,000 ppb (405 ppm), barium was detected at 14,600 ppb (14.6 ppm), cadmium was detected at 16,600 ppb (16.6 ppm), chromium was detected at 2,680 ppb (2.68 ppm), cobalt was detected at 18,600 ppb (18.6 ppm), copper was detected at 14,800 ppb (14.8 ppm), iron was detected at 326,000,000 ppb (326,000 ppm), lead was detected at 4,500,000 ppb (4,500 ppm), mercury was detected at 210 ppb (0.21 ppm), nickel was detected at 41,700 ppb (41.7 ppm), zinc was detected at 1,260,000 ppb (1,260 ppm). The pH of New Diggings Branch at the base of the pile was 3.4.

Sample STA-003 was taken from a rotary roasted jig tailings pile located on the north side of County Highway W, east of New Diggings, Wisconsin. Arsenic was detected at 67,200 ppb (67.2 ppm), barium was detected at 48,600 ppb (48.6 ppm), cadmium was detected at 12,000 ppb (12.0 ppm), chromium was detected at 2,800 ppb (2.8 ppm), cobalt was detected at 12,800 ppb (12.8 ppm), copper was detected at 8,040 ppb (8.04 ppm), iron was detected at 244,000,000 ppb (244000 ppm), lead was detected at 200,000 ppb (200 ppm), manganese was detected at 421,000 ppb (421 ppm), mercury was detected at 30 ppb (0.03 ppm), nickel was detected at 31,500 ppb (31.5 ppm), zinc was detected at 15,000,000 ppb (15,000 ppm). The pH of the feeder stream at the side of the pile was 7.5.

Sample STA-004 was taken from the roaster pile on the north side of State Highway 11, east of Lead Mine, Wisconsin. Arsenic was detected at 45,800 ppb (45.8 ppm), barium was detected at 122,000 ppb (122 ppm), cadmium was detected at 3,680 ppb (3.68 ppm), chromium was detected at 9,160 ppb (9.16 ppm), cobalt was detected at 3,460 ppb (3.46 ppm), copper was detected at 9,740 ppb (9.74 ppm), iron was detected at 216,000,000 ppb (216,000 ppm), lead was detected at 309,000 ppb (309 ppm), manganese was detected at 95,400 ppb (95.4 ppm), mercury was detected at 50 ppb (0.05 ppm), nickel was detected at 5,890 ppb (5.98 ppm) and zinc was detected at 1,560,000 ppb (1,560 ppm).

Sample STA-004A was a sample of stream sediment taken from the base of the previously described roaster pile. Arsenic was detected at 42,600 ppb (42.6 ppm), barium was detected at 35,900 ppb (35.9 ppm), cadmium was detected at 5,490 ppb (5.49 ppm), chromium was detected at 8,380 ppb (8.38 ppm), cobalt was detected at 3,010 ppb (3.01 ppm), copper was detected at 8,500 ppb (8.50 ppm), iron was detected at 307,000,000 ppb (307,000 ppm, manganese was detected at 26,900 ppb (26.9 ppm), nickel was detected at 6,990 ppb (6.99 ppm) and zinc was detected at 1,120,000 ppb (1,120 ppm).

Sample STA-004B was a sample taken from a leachate puddle at the base of the roaster pile described in sample STA-004. Arsenic was detected at 4,680 ppb (4.68 ppm), barium was found to be less than 40 ppb, cadmium was detected at 12,000 ppb (12 ppm), chromium was detected at 270 ppb (0.270 ppm), cobalt was detected at 7,000 ppb (7 ppm), copper was detected at 3,100 ppb (3.1 ppm), gold was detected at 3,500 ppb (3.5 ppm), iron was detected at 36,000,000 ppb (36,000 ppm), manganese was detected at 1,600 ppb (1.6 ppm), nickel was detected at 10,000 ppb (10 ppm), silver was detected at 44.81 ppb (0.045 ppm) and zinc was detected at 4,600,000 ppb (4,600 ppm). The pH was taken at the time of sampling and was found to be 1.8.

For a complete review of the data; see Table 4-Roaster Pile Sample Results.

TABLE 4

Roaster Pile Survey Data

| | STA-001[a] mg/kg(ppm) | STA-003[a] mg/kg(ppm) | STA-004[a] mg/kg(ppm) | STA-004A[a] mg/kg(ppm) | STA-004B[a] ug/l(ppb) |
|---|---|---|---|---|---|
| Arsenic | 405 | 67.2 | 45.8 | 42.6 | 4680 |
| Barium | 14.6 | 48.6 | 122 | 35.9 | <40 |
| Cadmium | 16.6 | 12.0 | 3.68 | 5.49 | 12000 |
| Chromium | 2.68 | 2.8 | 9.16 | 8.38 | 270 |
| Cobalt | 18.6 | 12.8 | 3.46 | 3.01 | 7000 |
| Copper | 14.8 | 8.04 | 9.74 | 8.50 | 3100 |
| Iron | 326000 | 244000 | 216000 | 307000 | 36000000 |
| Lead | 4500 | 200 | 309 | 95.0 | 1600 |
| Manganese | [b] | 421 | 95.4 | 26.9 | 380000 |
| Mercury | 0.21 | 0.03 | 0.05 | - | - |
| Nickel | 41.7 | 31.5 | 5.98 | 6.99 | 10000 |
| Zinc | 1260 | 15000 | 1560 | 1120 | 4600000 |
| pH (s.u.) | 3.4[c] | 7.5[d] | - | - | 1.8 |

[a] Values should be considered estimates due to QC exceedances. Low spike recoveries indicate that actual concentrations are higher.
[b] Unable to quantify due to severe interferences.
[c] pH of New Diggings Branch at base of pile.
[d] pH of feeder stream at side of pile.
*Also detected gold at 3500 ppb and silver at 44.8 ppb in STA-004B sample.

| | |
|---|---|
| STA-001 | New Diggings(Skinner Roaster Plant) roaster pile |
| STA-003 | Mixed fine grounds and roaster spoil on north side of County Highway W |
| STA-004 | Roaster pile on Highway 11 |
| STA-004A | Stream sediment near base of roaster pile at STA-004 |
| STA-004B | Leachate puddle at base of roaster pile at STA-004 |

The potential toxicity of these wastes is immediately apparent except that mining wastes,specifically, are excepted from definition as a toxic and hazardous waste in NR 605. Some attempt should be made to identify, locate and prioritize the severity of environmental impact caused by these wastes within the district. Proximity to private residences and accessibility by humans and livestock must be assessed as well as impact to nearby streams and water wells. Burial of these wastes is not the preferred method of disposal as they may continue to leach into groundwater. The arsenic, chromium and mercury may change valence state and become even more mobile and toxic under acidic and reducing conditions (Fetter, 1993; EPA - Subsurface Contamination Reference Guide, 19 ). The mobility of these elements is well covered by Fetter in his section on geochemical zonation beneath landfills and solid waste disposal sites. Perhaps the metals content could be carefully quantified (assayed) for each pile and the wastes be reclaimed for their metal content since all of the elements including arsenic and sulfur have value due to their industrial demand and uses (Fetter, 1993, p. 7-8).

There are many recent studies in the literature that will demonstrate to the reader how widespread (and widely identified) this type of mine waste problem is. See Metalliferous Mine Spoil in Wales: A Toxic and Hazardous Waste, by Davies, Jones and Peterson, 1983; Lead, Cadmium and Zinc Contamination in Southwest Missouri, by Clevenger et al., 1991; Identification and Management of Acid Generating Mining Wastes in Australasia, by Miller et al., 1990; Solubility of Heavy Metals in Lead Mine Spoil Extracts, by Shaw, Rorison and Baker, 1984; Determining Heavy Metal Leaching and Transport from Abandoned Mine Waste and Subsequent Attenuation, by Lambeth et al., 1989.

# STUDY CONCLUSIONS AND RECOMMENDATIONS

It is readily seen that this study has uncovered mine waste problems of some magnitude. Mine related groundwaters show definite exceedances of State and Federal designated drinking water action limits and maximum contaminant levels. Public and private water supplies have not been adequately sampled to draw any concrete conclusions about mine related groundwater impacts to them. Further representative sampling is desirable. Surface waters show definite impacts from mine waste leachate and mine related groundwaters and mine springs. Some of the surface water has been made unsuitable for watering livestock and inhospitable to aquatic life. Roaster wastes and rotary roasted jig tailings show extreme concentration of potentially toxic arsenicals and heavy metals.

## PRIMARY RECOMMENDATIONS

1. Conduct a fully funded study to determine the mining district-wide extent of groundwater contamination due to infiltration of mine related groundwaters into the surrounding local aquifers and natural leaching of un-mined mineral deposits. Make the results available to the public so they may share in the decisions about further remedial actions.

2. Establish routine screening of private and public water supplies in the mining district for arsenic and selected, more soluble heavy metals in order to insure the safety of the drinking water supply. Properly abandon wells found to be drilled into mine tunnels and shafts as well as capped spring houses. Establish safe minimum setback distances away from underground mine structures for water well constructors if found to be feasible and necessary. Ban well construction into known mine workings. Well construction regulation may be necessary in order to shift well construction from the Platteville and Decorah Formations down into the St. Peter Sandstone for private water wells. These wells may require casing and grouting down into the top of this sandstone.

3. Locate, identify and prioritize the severity of environmental impacts caused by the mine wastes in this mining district for the purpose of State funded mitigation and reclamation of these waste piles and the damaged lands and surface waters (including stream sediment toxicity and contamination) surrounding them. This process should include consideration of proximity to private residences, accessibility by humans and livestock and potential impacts to nearby streams and wells.

4. Review groundwater and aquifer protection strategies for the St. Peter Sandstone aquifer in the mining district since there appears to be some evidence of infiltration of surface waters down into the subsurface through fracture flow. This should include renewed oversight of landspreading practices for various ag chemicals as well as municipal and industrial wastes.

5. Detailed mapping of the physical location and orientation of known mine workings, shafts and exploration bore holes should be added to the computerized land data base for rapid review and correlation with proposed surface land uses. By doing this, an important improvement in pollution prevention may be achieved.

## SECONDARY RECOMMENDATIONS:

1. Contact State Toxicologist for risk assessment and the Wisconsin Division of Health for health checks of individuals and families with impacted wells. A record search of the morbidity and mortality types and rates should be conducted for the southwestern counties with past mining activity to ascertain whether or not there is a statistically higher rate of incidence of certain types of cancer in the mining district.

2. Enact legislation to require mining companies to make full mandatory public disclosure of all minerals in any sulfide deposits currently being mined or to be mined in the future. Mining companies should then be required by law to treat wastes and prevent environmental contamination based on the elemental analysis of the mined ores and wastes produced in the course of the mining venture.

3. Make a thorough review of all current mine waste handling and treatment technologies to determine their efficacy. Perhaps, specific treatment methods or standards should be stipulated as part of future mining permits.

4. Make locational information for mines and mined land readily accessible to the general public for the use of banks and lending institutions, land purchasers and home owners, real estate developers, county sanitarians, and well drillers, etc., so that informed decisions can be made as to desirability of land and appropriate land use.

# APPENDIX A: MINING AND METHODS HISTORY WITH CONNECTION TO WASTE TYPES

Mining activities in the Southwestern Wisconsin Zinc-Lead District reach back nearly three and a half centuries to the early 1630's according to Jean Nicolet. Nicolas Perrot also reported Native Americans engaged in mining during his explorations of the region in 1683 (Thwaites, 1931). Lead mining, and later zinc mining, fluctuated through periodic boom and bust cycles in the metals markets (Heyl, 1959) until October of 1979 ". . . when Eagle-Picher Industries, Inc., auctioned off its mine and mill equipment at Shullsburg and Linden in southwestern Wisconsin's zinc-lead district. The Shullsburg Mine in Lafayette County . . . [was] the last operating underground metal mine in the State . . ." (Hill and Evans, 1980).

The Wisconsin mining district is only part of a greater tri-state mining district that includes eastern Iowa and northwestern Illinois and covers roughly 4,000 square miles (see Figure 1-Map of Mining District). Heyl reports in The Geology of the Upper Mississippi Valley Zinc-Lead District that as of 1959, in the Wisconsin mining district, there had been "Thousands of small lead mines, about 400 zinc mines, and a few small copper, iron and barite mines . . . " in addition to several known iron sulfide mines which mined rich concentrations of iron sulfides for sulfuric acid production (Heyl, 1959, p79).

FIGURE 1.
Map of the Mississippi Valley Zinc-Lead District After Heyl, 1959.

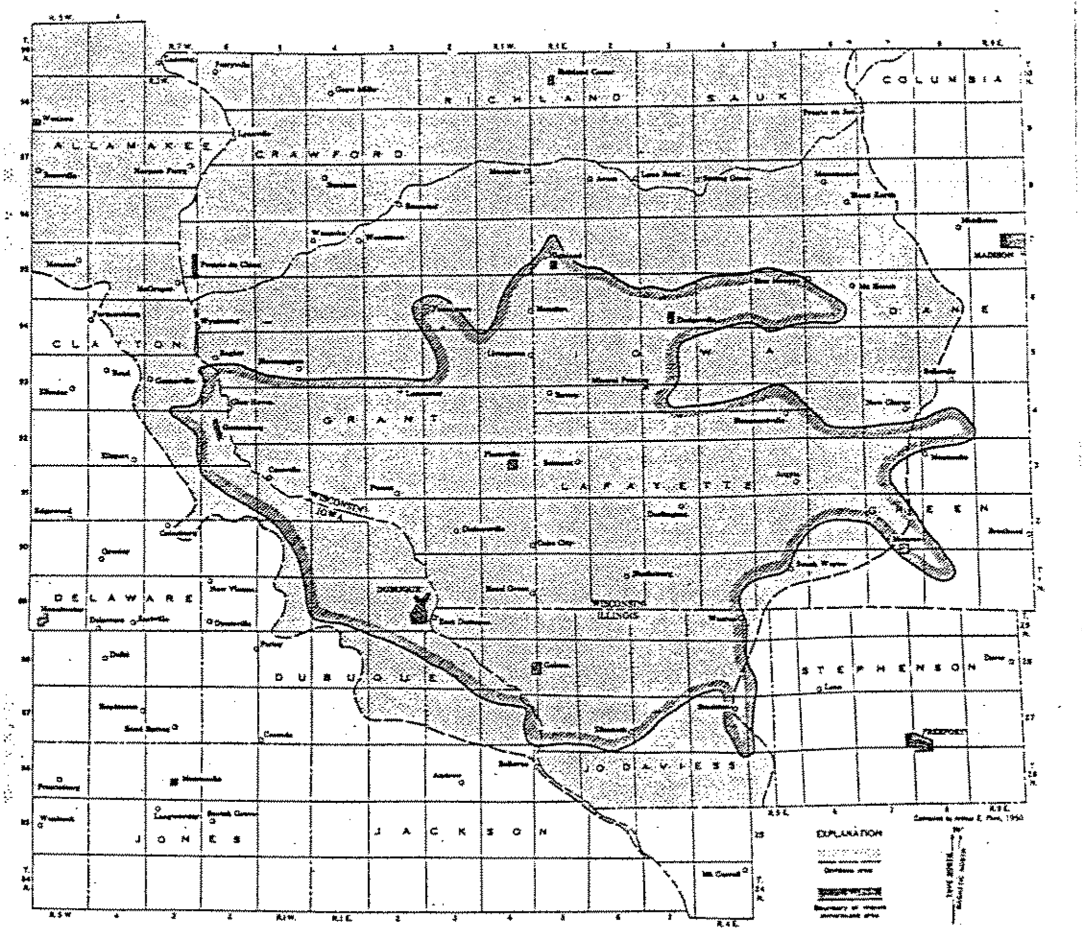

FIGURE 1—Map of the Driftless Area of the upper Mississippi Valley zinc-lead district.

Mining activities by the Native Americans prior to the arrival of the Europeans were conducted on a relatively small scale. Systematic mining of the ore deposits, in the Wisconsin mining district, is recorded to have commenced in the early 1700's by a group of Frenchmen. Mining operations were continued by the Spanish when they took over possession of Louisiana which included the Wisconsin mining district (Clark, 1955). Local human populations associated with mining activities were surprisingly numerous. By 1800 some 6000 Europeans and slaves were known to be engaged in mining in the district (Clark, 1955). This population estimate did not include Native Americans. The population quickly swelled to 16,615 in the July, 1836 census and 28,000 by 1850 (Roe, 1991). Published maps from 1829 show widespread and intense mining of surface lead digs extending from the Galena, Illinois vicinity, northeast over to Blue Mounds, Wisconsin, roughly paralleling the Wisconsin River over to the Highland, Wisconsin area and west-southwest to the Cassville, Wisconsin area, then crossing the Mississippi River to include Dubuque's Mines of Spain (Heyl, 1959, Plate 9; Clark, 1955).

The first metal to be mined in the district was lead ore; a lead sulfide formally named "galena." The majority of the lead ore mined in the southwestern Wisconsin mining district was mined before 1871 (Heyl, 1959). The "lead" was first found as weathering and erosion products at the bases of hills and in stream beds. Later, the ore was traced back to the shallow deposits called "gash veins" which were essentially mineralized vertical joints in the bedrock. The ore was dug from shallow surface pits that followed the vein 50 to 60 feet downward until the water table was encountered and the miner could not safely dig further (Clark, 1955; Roe, 1991; Heyl, 1959). The arrival in the early 1830's of the Cornish miners, with their considerable mining skills honed in the mines of Cornwall, brought further improvements to mine stabilization and safety. Their underground mining techniques were soon universally adopted (Clark, 1955; Roe, 1991). For a better understanding of the level of surprising technological sophistication of the mining methods used at this time, please see De Re Metallica by Georgius Agricola and translated by Herbert C. Hoover. Also see The Cornish Mining Industry-a brief history by J.A. Buckley.

The century between the early 1700's and the early 1830's saw some technological progress in regard to lead ore mining and processing techniques. Until the arrival of the Cornish, ore was for the most part surface collected and surface pit mined. Underground mining in this mining district essentially began with the Cornish (Roe, 1991). Several descriptions exist as to how the ore was sorted and dressed in order to remove the nonmineralized and unprofitably mineralized gangue rock. The gangue contained minerals like iron sulfides, zinc carbonate, zinc sulfide and calcium carbonate which would be enriched (with other minerals) in surface and underground waste piles from this period.

Local sources of water have always played an integral part in ore processing (Clark, 1955; Holland, 1983; Fatzinger, 1971). Stanley Holland (also Roe, 1991), in A History of Mining in Iowa County, talks about washing or "cradling" lead ore in dammed pools in the creeks before smelting. This would wash the dirt and clay off of the galena masses and into the streams. The clay commonly found in these mineralized deposits is recorded as being sauconite clay. This is a clay that runs roughly 20 percent zinc by weight (Heyl, 1959). The miners would then hand "cobb" the ore by using a hammer and knocking off the gangue.

The concentrated lead ore was subsequently heated to burn off the sulfur and render metallic lead. At first, this was accomplished by use of a crude log smelting furnace (Roe, 1991; Holland, 1983; Heyl, 1959). During this time period, this meant that a smelting site was selected in a ravine to take advantage of natural air currents which were formed and controlled by the surrounding hills. A solid (roughly 15' by 15') flat-bedded limestone slab was laid down and channels to a bowl (also carved into the slab) were carved in the slab surface. Alternating layers of wood and lead ore were ricked on the slab and set on fire. The sulfur was burned off and the metallic lead was collected in the carved bowl (Roe, 1991; Holland, 1983; Heyl, 1959; Clark, 1955). The cooled 70 pound circular "plat" or "pig" represented only a portion of the total recoverable metal (Heyl, 1955; Holland, 1983). This left piles of heavy metal enriched slag, some of which were later re-smelted at a profit (Heyl, 1959; Holland, 1983), exposed to surface weathering and leaching. Heyl indicates that, in 1959, many of these piles were still visible.

Later improvements occurred with the utilization of water wheel-powered, bellows driven Cupola and Scotch Hearth furnaces as replacements of the crude log smelter furnaces. These were commonly located near a flowing stream to capitalize on the available water power and also implies that their slag wastes were mounded near these surface waters. The Cupola furnace, which recovered between 65 to 75 percent of the recoverable lead (again leaving a heavy metal enriched slag), came into use in the 1820's (Heyl, 1959; Clark, 1955). The Scotch Hearth arrived later in 1835 (Heyl, 1959). These stone or brick furnaces, at first, utilized local wood, then locally produced charcoal, and finally bituminous coal from the Illinois coal fields that was shipped in by rail (Fatzinger, 1971; Strong, 1877).

Fifty-two government licensed and bonded lead smelters, which collectively produced 13,343,150 pounds of metallic lead (in 1829), were recorded as being in Wisconsin in 1829 (Roe, 1991). Numerous private (and unrecorded) lead smelting facilities were in use. Most mines illegally smelted their own lead ore to avoid paying 10 percent of their ore as mine lease fees to the federal superintendent of mines at the government smelters (Heyl, 1959; Clark, 1955). Since almost all lead produced in the mining district was shipped as refined metal (Heyl, 1959; Roe, 1991), the refined product could easily slip past government agents who were only responsible for monitoring the licensed and bonded smelters for the Army's Bureau of Ordinance. This lease payment schedule was so unsuccessful that the 1807 law mandating it was stricken down in 1846 when the government ceased leasing the land for mining and sold it for settlement (Roe, 1991; Heyl, 1959). Thus, one can see the implications for the possibility of wide spread occurrence of buried and surface deposits of lead slag waste in the district. For a partial listing of lead mines and smelters in operation in the district between January, 1862 and October, 1876, see Moses Strong in Geology of Wisconsin, Volume 2. (See also Roe, 1991; Holland, 1983; Heyl, 1959).

Further improvements in ore dressing and concentrating were seen in the district with the introduction and use of gravity separation methods (Roe, 1991; Holland, 1983). The ore processing scheme had progressed to embrace an ore quality grading procedure which was done at the mine mill. The premium grade ore consisted of large hand-dressed pieces which were shipped directly to the smelter furnace. The second grade ore was "contaminated" with undesirable minerals that were unacceptable to the smelter, who would charge a penalty fee in order to process the material (Heyl, 1959). Therefore, further crushing, washing and "jigging" were required in order to separate the iron sulfides and other undesirable minerals from the desirable ore materials. The last grade of ore was the fine particulate "mud" left over from the crushing, washing and jigging process that was heavily contaminated with iron sulfides and other minerals not being sought for profit. This last grade was referred to as "smittems" (Fatzinger, 1971).

The processing of mine dirt entailed hoisting the ore from underground, sorting out the premium grade ore, dumping the balance of the second grade ore into the crushers and sorter screens, and sending the crushed material (1/8 inch pea gravel and smaller) to the "shaker tables" or "jigs" in order to concentrate and separate the valuable mineral from the gangue (Fatzinger, 1971). Early crushers may have included mechanical devices called "Cornish Stamp Mills" which were invented in the mines of Cornwall (Fountain, 1992). Agricola mentions mechanisms, similar to these stamp mills, being used a few centuries before the Cornish in the mid-1500's. Some of the later mechanical rock crushers of the 1880's were capable of crushing one ton of ore per minute (Fountain, 1992).

The shakers or jigs, in the early 1800's were manually operated either dry or wet. When water was available, the process resembled panning and flume methods used by amateur gold miners of today; the only difference being the scale of the operation. The shakers and jigs were the miners' early gravity separation method used to isolate the denser, heavier mineral material from the lighter material (Roe, 1991). Mechanical steam driven Hartz-type Cooley jigs replaced the manual jigs later in the century and could continuously process hundreds of pounds of material at a time. Some could process nearly 100 tons per 10 hour shift (Roe, 1991; Fatzinger, 1971; Heyl, 1959, p71).

The Cooley jigs used a minimum of 700 to 1200 gallons per minute of water which was often pumped from the mine or the nearest creek. The water was re-used many times after passing through the mill settling ponds which collected the waste fines or smittems (Fatzinger, 1971; Roe, 1991). Later, this mud laden wastewater was occasionally pumped back into the old or abandoned parts of the mine as fill material. These early methods of gravity separation were so inefficient that only 45 to 48 percent of the ore was recovered (Holland, 1983) and the tailings piles left at the site were rich in both iron sulfides and zinc ore as well as other minerals such as lead, cobalt and arsenic bearing sulfides and cadmium sulfides.

Mining, milling and smelting techniques changed little during the 1800's (Fatzinger, 1971, p. 165). The same techniques were used when zinc became the predominant metal mined in the mining district around 1860 while lead ore continued to be produced in lesser amounts (Fatzinger, 1971; Heyl, 1959).

The main ore of interest to miners changed as the result of a visit by two German chemists, Matthiessen and Hegeler, to Southwestern Wisconsin in 1852 (Heyl, 1959; Fatzinger, 1971; Strong, 1877). They saw the abundance of zinc carbonate on the lead mine waste piles, developed a new method for smelting zinc and constructed a zinc smelter in La Salle, Illinois. La Salle was selected because of its close proximity to the coal fields in southern Illinois. The invention of these two chemists, along with the demand in the eastern U.S. for zinc oxide provided the economic impetus for zinc carbonate recovery from the lead mining tailings piles. Another smelter was constructed and used briefly in Mineral Point, Wisconsin by a Mr. George but the venture was short-lived (Heyl, 1959). Within a short period, the zinc smelting technology spread throughout the district and was not confined solely to La Salle.

Production of zinc ores is recorded as commencing in 1860 (Strong, 1877). All of the zinc ore produced between 1860 and 1876 in the mining district was shipped to La Salle for final processing. The majority of ore shipped during this time was "dry bone" or smithsonite (zinc carbonate). Dry bone was first roasted or calcined in the vicinity of the mine and then shipped to La Salle. The calcining was typically done in a small furnace like a lime-kiln which, at the time, was designed to hold sixty tons of raw ore. The furnace could roast twenty-five tons of ore in twenty-four hours with the combined labor of six men per eight hour shift (three shifts). Eighty to one hundred tons of bituminous coal were required for each ton of ore processed (Strong, 1877). Again, a heavy metal enriched clinker would be a waste product and was usually abandoned at the site of the kiln.

Both Heyl and Fatzinger report that iron oxide was intimately associated with the dry bone and was considered an impurity to be removed. In the southwest Wisconsin mining district, zinc sulfide (sphalerite; the other zinc ore that was mined in the district after the dry bone became scarce) was also intimately mixed with iron sulfides which were also undesirable at the smelter. (Heyl, 1959; Fatzinger, 1971; Grant, 1903, 1906). This accounted for the slow development of the mining district's zinc industry. Some mines tried burning their zinc ores to remove the iron contaminants prior to the late 1890's. The process proved ineffective and left piles of roaster waste to dot the landscape.

By the 1880's, major ore processing (or roaster) plants began to emerge which produced multiple products and by-products of the district's zinc and lead ores. It was during this time that the Mineral Point Zinc Works began producing zinc oxide, "spelter" (roasted, impure metallic zinc), white lead and iron pigment. Later in 1899, sulfuric acid production was added to the by-product line.

For a more detailed accounting of these major ore processing plants, which include the Platteville Separator, the Campbell and National Separators, the Skinner Roaster, the Mineral Point Zinc Works and the Galena Roasters, see Fatzinger, 1971; Grant, 1903, 1906; Heyl, 1959.

The wastes generated by these large ore processing plants are well known. Fatzinger notes that in the process of heating the zinc ore to produce zinc oxide, some three and one half percent of the zinc particulate was blown through the stacks. Most likely the airborne particulates included lead and cadmium coupled with arsine and sulfur gases because those elements are found closely associated with the zinc ore. The effects of these airborne emissions were well documented. In 1916 the Skinner Roaster fumes had " . . . poisoned cattle, killed vegetation, rotted wire fences and screen doors, and poisoned water in the creek" (Fatzinger, 1971). Fatzinger explains that the airborne emissions affected the agricultural land use around these plants for many years. The roaster piles around these large ore processing facilities also serve as a reminder of past activities. Rich in sulfurous compounds and heavy metals, they remain for the most part, devoid of vegetative cover and are vulnerable to erosive rainfalls and wind re-distribution.

The 1890's marked the period when iron sulfides were first recognized as being profitable for sulfuric acid production and therefore were removed, to a certain extent, from the mine mill waste solids. Ore processing technology was changing at this time with the introduction in 1892 of William P. Blake's furnace and roasting technique which desulfurized the iron sulfides and allowed a more efficient gravity separation of zinc and lead ores from the iron sulfides at the mine mill (Fatzinger, 1971). The only drawback to this method was the loss of the now profitable sulfur which was beginning to be used for sulfuric acid production. This problem was further solved by modification of the technique to the "rotary roasting and magnetic separation" process. This entailed lightly roasting the milled ore in the long steel-fire brick lined-cylindrical furnace until only one third of the sulfur was driven off and the iron oxide coated iron sulfide particles were rendered magnetic on their surface. The roasted ore was then run through electro-magnets which separated the magnetic iron sulfides from the zinc and lead ores.

The separated and concentrated ore was shipped to a smelter or one of the larger district roaster plants such as Mineral Point or Skinner. The method still lost a great deal of fine zinc ore to the tailings piles (Grant, 1903). Various sources indicate that the large roaster plants also did custom rotary roasting for the smaller mines that could not afford to process their own ore.

There is some conflict in the literature as to the extent that mine mills used rotary roasting during the early 1900's. Fatzinger insists that the practice was not extensive and only sixteen had roasters. Yet both Fatzinger and Grant cite the profitability of treating the ore with the rotary roasting process. Rotary roasted jig tailings can be found, today, in locations where there is no record of a rotary roaster-mill and it can be seen that the waste pile still lies where it was first generated. Fatzinger does state that after 1915, more mills with rotary roasters were constructed to handle the new higher production levels of the mines. No number estimate is cited.

In 1906 seventy-three mines were recorded as being in operation and only thirty-nine had mills. By 1908, all mines had mills and some fifteen additional mills were constructed. Mines were also known to have mills constructed on skids so that they could be moved to a more advantageous position over the mine tunnel. Some mills were completely deconstructed and reconstructed elsewhere while retaining the original name. It was also common for these mills to process over 100 tons of ore in a ten hour shift. For a partial listing of mines and mills in operation during the early 1900's, see Grant, Heyl, Holland and Jewell as well as the mining history records in the Linden, Dodgeville, Mineral Point, Platteville, and Shullsburg public library or historical society archives. Most towns and villages in the mining district retain mining records and documents in archives held by local historians or the local newspapers. Mine lease and mineral lease records are still archived in the Register of Deeds offices in Dane, Iowa, Grant, Lafayette, and Green Counties.

Dewatering of the mines was a constant problem throughout the history of the mining district. Heyl lists pumping rates for individual mines. Some of them exceeded 1000 gallons per minute. Hoffmann, in Geochemistry of Acid Mine Drainage on the Aquifers of Southwestern Wisconsin and Regulatory Implications, cites Evans et al. (1983) as saying that the Shullsburg Mine pumped 20 million gallons of groundwater per day during its initial development phases and flows of 8000 gallons per day occurred when new fractures were intersected in the process of mining.

Heyl indicates and cites specific mines that drove slanting adits so that groundwaters in the mine would drain by gravity directly into the local streams. Many continue to do so. Strong also states that some mines sank drill holes, in low portions of the tunnels, down into the next more porous or fractured layers of limestone. These drill holes acted like gravity sumps and conducted mine waters down into lower layers of the aquifer.

These drainage waters were notorious for having high levels of soluble and suspended solids from the ore deposit being worked and blasted in the mine. Discharging mine waters of the Little Benny Mining Company of New Diggings, Wisconsin were sampled by District Sanitary Engineer - George F. Bernauer in August of 1943 at the request of State Sanitary Engineer - L.F. Warrick. DNR records show total solids in the 2700 parts per million range and that the New Diggings Creek received 6,000 pounds of suspended solids (just from this operation) in a 16 hour work day. Records also state the New Diggings Creek had no fish except a very few minnows near its confluence with the Fever (Galena) River in 1943. Land holders interviewed by Bernauer said fish used to be in the creek years ago but had disappeared with the mining activity.

The last innovation in the southwestern Wisconsin mining district was the advent of floatation separation of finely ground ore using sodium cyanide as the foaming agent. This process was introduced in the 1920's(?) and remained in use in the district until the Shullsburg Mine shut down in 1979. This method recovered 70 to 74 percent of the ore. This method also employed the use of self-building tailings ponds where the waste slurry of water, foaming agent and fine particulate was pumped out on the land. The fluid would drain away and the left-over mud would form a berm. The slurry hose would then be moved to extend these berms as they were formed. The waste products would include some residual heavy metals in the sludge and sodium cyanide leachate. A recent paper on the subject is Cyanide Contamination Near Elk City, Idaho: The Regulatory Implications by Murrey and Moeller.

The mines themselves harbor residual wastes and waste by-products. Jewell (1990) and others mention that some of the smaller mines were only operated part-time when the metals prices were sufficiently high. Some of the owners were known to blast ore down in the mine and leave it stock piled until the metals prices rose. Some ore was abandoned in this manner when the metals market collapsed and was left underground in contact with groundwater. Also, preliminary sorting of ore occurred underground where large chunks and boulders of gangue material, including iron sulfides, were left as tunnel back-fill and roof support "cribbing". Oak logs were longitudinally stacked to form a square, four-side structure which was built up to the mine roof, filled with waste rock and had an appearance much like a corn-crib (see Bevans Mine-Platteville Mining Museum). The logs tended to decay and collapse.

Jewell notes that during the Great Depression, out-of-work miners often supported themselves by opening and mining old mines. They found these oak logs had been crushed to half their original diameters and that they had decayed. This rendered portions of the mine roof unstable and evolved explosive methane gas. Pockets of carbon dioxide gas (called "dead air" by miners) were also found as a product of the log decay. Hydrogen sulfide (another poisonous gas) evolved as part of the decomposition of the sulfides underground.

Work by the curator of Pendarvis House, while excavating the Merry Christmas Mine for tourist use, found a variety of machines, tools and animal carcasses (some of which were mules and ponies used in underground ore cart tramming). Others (students and DNR employees) have found cases of unstable dynamite, canisters of pelleted sodium cyanide (November, 1993 wastewater staff meeting presentation by Bill Weber) and trash of various sorts that was dumped because the mine shaft or tunnel was a handy garbage pit.

Millions of tons of rock have been processed for metals recovery in southwestern Wisconsin. Both Heyl and Strong give good production figures for individual mines and the district as a whole. For all the past mining activity, comparatively little of the original waste rock tailings remain. Much of it has gone into road construction, concrete block manufacture and fill for construction projects. Still, enough remains in the form of roaster wastes, jig tailings and smittems to cause localized environmental impacts to soils, sediments, surface waters and groundwaters.

*We do not truly know the extent to which the remaining wastes are distributed. We do not know to what extent these waste products have impacted soils, sediments, surface waters and groundwaters within the Southwestern Wisconsin Zinc-Lead Mining District as a whole nor do we know how these wastes have impacted our human and animal populations.*

# APPENDIX B: REPORTED MINERALS IN THE SW WISCONSIN MINING DISTRICT

According to Heyl, in the Geology of the Upper Mississippi Valley Zinc-Lead District, the following list of minerals have been observed in the Southwestern Wisconsin ore deposits. They are presented in the order designated by the Dana system. Chemical composition of the more environmentally important minerals on this list are shown in Appendix C.

Minerals of the Wisconsin-Illinois-Iowa zinc-lead district

## Primary Minerals

- Gold
- Galena
- Sphalerite
- Wurtzite
- Pyrrhotite
- Millerite
- Chalcopyrite
- Pyrite
- Cobaltite or Safflorite
- Marcasite
- Calcite
- Dolomite
- Ankerite
- Quartz
- Muscovite (var. Sericite)
- Barite

## Secondary Minerals

- Sulfur
- Copper
- Chalcocite
- Covellite
- Greenockite
- Bornite
- Bravoite
- Violarite
- Cuprite
- Tenorite
- Hematite
- Pyrolusite
- Honessite
- Limonite
- Psilomelane
- Smithsonite
- Aragonite
- Cerussite
- Malachite
- Azurite
- Aurichalcite
- Hydrozincite
- Hemimorphite
- Sauconite
- Zincian Montmorillonite
- Pyromorphite
- Vivianite
- Erythrite
- Anglesite
- Gypsum
- Epsomite
- Goslarite
- Melanterite
- Copiapite

**Miscellaneous Minerals**

*deposited under conditions unrelated to ore deposition

Hematite
Limonite
Psilomelane
Calcite (var. Travertine)
Glauconite and Celadonite
Dolomite
Aragonite
Quartz
Opal (var. Hyalite)

(After Heyl, 1959, p84)

Many previously unreported minerals may yet be found in these mineral deposits if some of the more common minerals were to be subjected to x-ray crystallographic analysis. More detailed inspection of current collections using reflected light microscopy could shed additional light upon mineral species, textures and intergrowths. Some of the primary and secondary minerals represent end members of geochemical solution series which, upon closer inspection, could show intermediate gradational mineral species, as well.

# APPENDIX C: CHEMICAL COMPOSITION OF KEY SULFIDE MINERALS IN THE DISTRICT

The following section is based upon Dana's Textbook of Mineralogy which is recognized as a primary reference on this topic. Other references will be cited where appropriate.

Galena: a member of the Galena group, the local ore for lead, chemical formula is $PbS$, often contains silver, selenium, zinc, cadmium, antimony, bismuth, and copper bound up as sulfides; sometimes contains native silver and gold. Uytenbogaardt and Burke (1985, p 64) also list tellurium as a possible contaminant. Sometimes mined as a silver ore.

Sphalerite: a member of the Sphalerite group, the local ore for zinc, chemical formula $ZnS$, colorless when pure, contains iron, manganese, cadmium, mercury, lead, tin, indium, gallium and thallium through isomorphous replacement (p 354); may also carry silver and gold; is the chief ore of gallium, indium and cadmium according to Pough (1960, p 93). Wurtzite is a high temperature zinc sulfide ($ZnS$) and forms a solid solution with cadmium sulfide (Greenockite, $CdS$).

Pyrrhotite: a member of Cinnabar-Wurtzite-Millerite group; chemical formula varies between $Fe_5S_6$ and $Fe_{16}S_{17}$; generally contains sulfur in excess; often contains nickel due to included grains of pentlandite; also can carry cobalt, chromium and manganese.

Millerite: a member of the Cinnabar-Wurtzite-Millerite group; classed as a capillary pyrite; chemical formula is $NiS$; shows traces of copper, iron, cobalt, and silver.

Chalcopyrite: copper pyrite; has a chemical formula of $CuFeS_2$; can contain silver, gold, selenium, thallium, iridium, bismuth, barium; is the world's major ore of copper.

Pyrite: member of the Pyrite group; chemical formula is $FeS_2$; can contain nickel, cobalt, thallium, copper, selenium, gold; very rarely contains arsenic. Crystals intergrown with marcasite and arsenopyrite (Uytenbogaardt, 1985, pp 204-207, 190-191). More will be said about the chemical interrelationship between pyrite, marcasite and arsenopyrite at the end of this section.

Marcasite: member of the Marcasite group; chemical formula is $FeS_2$; can contain arsenic in small amounts due to intergrowths of arsenopyrite in the crystal lattice. Thought to be deposited in temperatures below 450°C and from acid solutions. As the solution becomes more alkaline the crystal lattice arrangement switches over to that of pyrite, also an iron sulfide ($FeS_2$).

Cobaltite: member of the Pyrite group; chemical formula is $CoAsS$ or $CoS_2{*}CoAs_2$; resembles pyrite in crystal form; associated with nickel, copper and silver ores; also molybdenum.

Safflorite: member of the Marcasite group; chemical formula is $CoAs_2$; contains iron and nickel.

Barite: member of the Barite group; chemical formula is $BaSO_4$ can contain minor amounts of strontium.

Chalcocite: member of the Chalcocite group; chemical formula is $Cu_2S$.

Covellite: member of the Cinnabar-Wurtzite-Millerite group; chemical formula is $CuS$.

Greenockite: member of the Cinnabar-Wurtzite-Millerite group; chemical formula is $CdS$; forms a solid solution series with wurtzite ($ZnS$); ore of cadmium.

Bornite: related to chalcopyrite; chemical formula is $Cu_5FeS_4$.

Bravoite: member of the Pyrite group; chemical formula is $(Fe,Ni)S_2$; can be associated with vanadium.

Violarite: related to bornite and chalcopyrite; chemical formula either $NiS_2$ $(Ni,Fe)_3S_4$ or $(Ni,Fe)_3S_4$.

Arsenopyrite ($FeS_2*FeAS_2$) was also tentatively identified, by this study group, using microscopic and chemical methods from collected and donated hand specimens. The specimens consist of weathered crusts found in some abundance on waste piles in the Shullsburg-New Diggings vicinity and donated fresh specimens from private mineral collectors who specialize in the iron sulfide minerals of this mining district. It must be noted that "...Because arsenopyrite resembles pyrite and contains arsenic, the word arsenopyrite was coined as a contraction of arsenical pyrites..." (Chesterman and Lowe, 1985).

Heyl (p. 87) comments on the analyses run on marcasite specimens from the Benton, Wisconsin area by the United States Geological Survey laboratory. These test results indicated crystalline intergrowths of cobaltite ($CoAsS$) and safflorite ($CoAs_2$), which are isomorphous with marcasite, in the marcasite crystal matrix. Heyl states that "Such intergrowths have been noted in cobaltious arsenopyrites in other districts." Percent abundances were found to be cobalt at 0.06 percent and arsenic at 0.20 percent. Heyl also states that the cobalt and arsenic are probably found associated with iron sulfides elsewhere in the district since the district pyrite-marcasite concentrates used for sulfuric acid production "... contain(ed) appreciable quantities of arsenic."

Graphite furnace atomic absorption analysis of the heavily weathered crusts of the arsenic-poor type of arsenopyrite, found in this study, shows arsenic present at 0.005 percent (50 ppm) as well as gold at 0.002 percent (20 ppm, note: aqua regia was required for this analysis). Arsenopyrite is often mined for its gold content under certain economic conditions.

The low arsenic percentage is to be expected from a heavily weathered specimen that has been partly converted to the mineral "limonite." Limonite is an iron oxide weathering product of iron sulfides, tends not to have a regular crystal lattice and will retain a small portion of the original arsenic and sulfur from the arsenopyrite. According to Schurmann's Series of Solubilities for sulfide minerals (Guilbert and Park, 1986; Krauskopf, 1979), arsenic and thallium bearing sulfides tend to have a relatively high solubility product and therefore would tend to readily decompose and go into solution when exposed to water. A large pool of published literature indicates that these compounds tend to readily leach into ground and surface waters. Some of these studies will be discussed in Appendix D.

Previous studies have found that arsenopyrite is not strictly a hypothermal (300°C to 500°C) depositional environment indicator mineral as many still believe. Arsenopyrite is now known to be associated with mesothermal (200°C to 300°C) deposits (Chesterman and Lowe, 1985, p 362; Krauskopf, 1979, p 405) which is in keeping with the upper temperature limit of 200°C (Gize and Hoering, 1980, p 384; Giordano and Barnes, 1981) calculated from sphalerite fluid inclusion studies for southwestern Wisconsin ores. If fluid inclusion studies could be performed on wurtzite crystals, an even higher upper temperature might be found. Also, recall that other mesothermal environment minerals have been identified in the previous mineral listing. It has been noted in the literature that there are loci of higher temperature mineral deposits within the district which would necessarily affect the type and abundance of mineral species distributed and found there.

Heyl also provides a generalized map of the Upper Mississippi Valley Zinc-Lead District (see Figure 2-Map of Regional Zoning of Zinc-Lead Mineralization) which shows regional zoning of the mineral deposits and known localities (as of 1959) of enrichments of lead, zinc, copper, barium, nickel, arsenic, cobalt, and gold bearing minerals. Information on other areas of enriched mineralization have yet to be made available to the general geologic community or the public because mining interests view this as confidential information. Other rare elements that have been found in southwestern Wisconsin ores include chromium, silver, germanium, molybdenum, zirconium and vanadium.

The importance of this section is to show the reader the types of locally abundant elements present in and around these mineral deposits, mines, and therefore in the mine waste piles themselves. The next section will briefly discuss the stability and solubility of these minerals both undisturbed in the mineral deposit and after mining, processing and concentrating on the land surface.

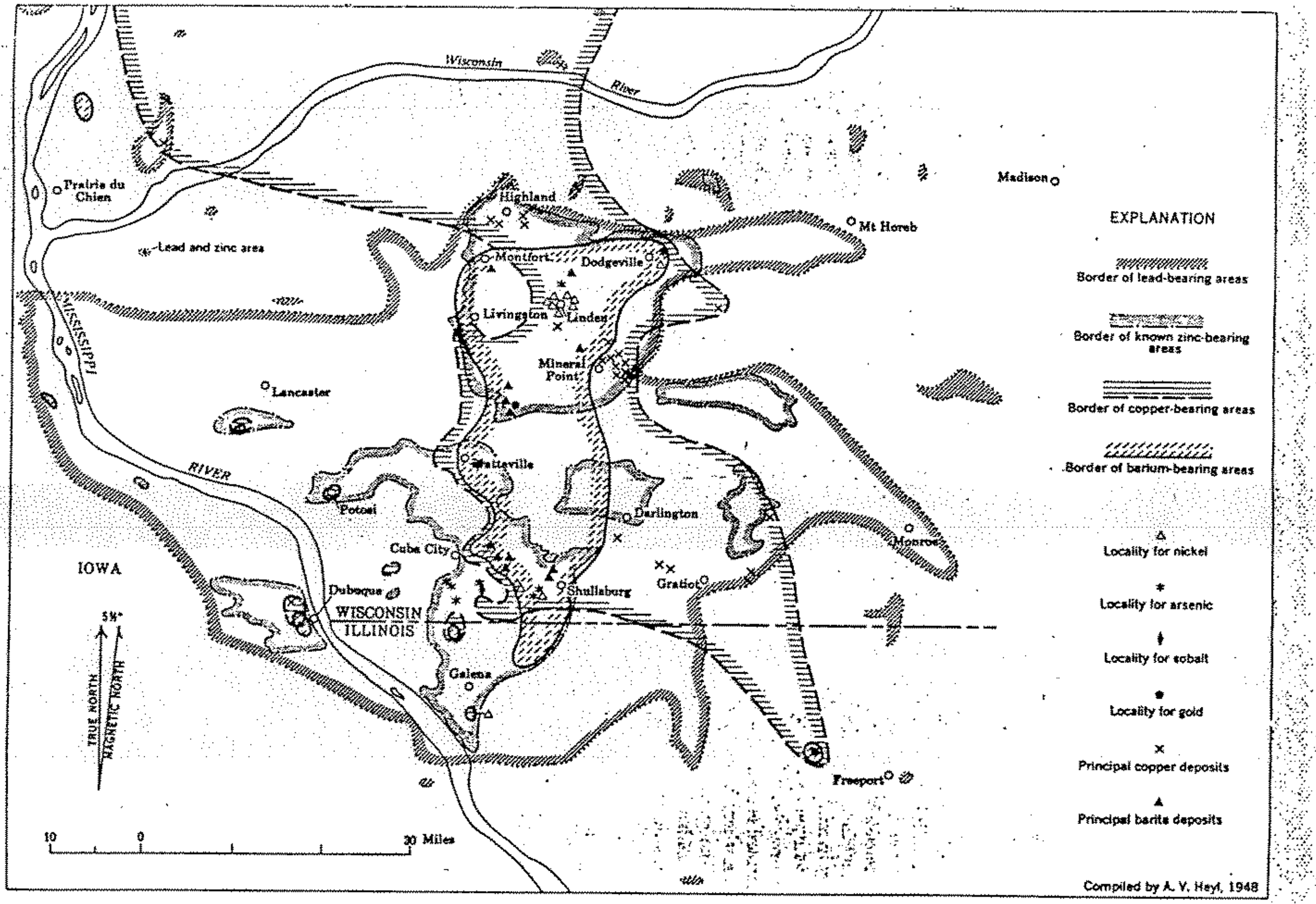

FIGURE 73.—Map of the Upper Mississippi Valley zinc-lead district showing regional zoning of mineralization.

FIGURE 2. Map of Upper Mississippi Valley Zinc-Lead District Regional Zoning of Mineralization, After Heyl, 1959.

# APPENDIX D: SOLUBILITY, MOBILITY AND FATE OF SELECTED SULFIDE MINERALS

Much literature currently exists concerning the stability and solubility of sulfide mineralizations above, at and below the water table because knowledge of these chemistry-based characteristics and reactions have been invaluable, in the past, to the mineral resource exploration geologist in locating new mineral deposits. More recently a heightened scrutiny has been made of these characteristics because of discovery of undesirable impacts of the heavy metal elements solubilized from sulfide mineral deposits on private and municipal water supplies and other surface and ground waters. Some of the literature deals with naturally occurring heavy metals (in ground and surface waters) from undisturbed sulfide mineral deposits that exceed safe levels in drinking water. Other papers deal with heavy metals in ground and surface waters due directly to past mining activities. Both conditions will be discussed here.

Geologists, specializing in exploration for ore deposits, have made an extensive study of the chemical means of formation of a large variety of ore deposit types in order to develop methods of predicting and identifying new deposits. An off-shoot of this study is the characterization of how sulfide mineral deposits chemically react and alter, through oxidation and reduction reactions in variable groundwater (and surface water) solutions. Many ore deposits (particularly copper deposits) of world-wide importance were formed because of sulfide interaction and leaching, with water as the solvent. For an in-depth explanation of the oxidation of sulfide ore deposits, please refer to Introduction to Geochemistry by Krauskopf. Also see The Geology of Ore Deposits by Guilbert and Park, Jr. and Contaminant Hydrogeology by Fetter. See also Hoffman (1984).

The solubilities for common metallic ions are shown in Table 5-Maximum Concentrations of Metals in Equilibrium with Common Ions (after Krauskopf, 1979). Table 6-Solubility Products for Selected Minerals and Compounds (after Fetter, 1993) also is important to review for the sulfide and sulfate compounds. Table 7-Schurmann's Series of Solubilities of Important Sulfides (after Guilbert and Park Jr., 1986) gives the reader a good qualitative feel for the relative solubilities of sulfide compounds. Schurmann's Series shows that manganese, thallium, arsenic, iron, cobalt, nickel and zinc have a low affinity for forming sulfide compounds in the presence of free reactive sulfur and are relatively soluble in water. Lead, tin, antimony, cadmium, bismuth, copper, silver and mercury have a higher affinity for forming sulfide compounds in the presence of free reactive sulfur. These sulfides are relatively less soluble than the previous list of compounds. The fact that they are less soluble does not mean that they are insoluble.

**TABLE 6.2** Solubility products for selected minerals and compounds.

| Compound | Solubility Product | Mineral Name |
|---|---|---|
| **Chlorides** | | |
| CuCl | $10^{-6.7}$ | |
| $PbCl_2$ | $10^{-4.8}$ | |
| $Hg_2Cl_2$ | $10^{-17.9}$ | |
| AgCl | $10^{-9.7}$ | |
| **Fluorides** | | |
| $BaF_2$ | $10^{-5.8}$ | |
| $CaF_2$ | $10^{-10.4}$ | Fluorite |
| $MgF_2$ | $10^{-8.2}$ | Sellaite |
| $PbF_2$ | $10^{-7.5}$ | |
| $SrF_2$ | $10^{-8.5}$ | |
| **Sulfates** | | |
| $BaSO_4$ | $10^{-10.0}$ | Barite |
| $CaSO_4$ | $10^{-4.5}$ | Anhydrite |
| $CaSO_4 \cdot 2\,H_2O$ | $10^{-4.6}$ | Gypsum |
| $PbSO_4$ | $10^{-7.8}$ | Anglesite |
| $Ag_2SO_4$ | $10^{-4.8}$ | |
| $SrSO_4$ | $10^{-6.5}$ | Celestite |
| **Sulfides** | | |
| $Cu_2S$ | $10^{-48.5}$ | |
| CuS | $10^{-36.1}$ | |
| FeS | $10^{-18.1}$ | |
| PbS | $10^{-27.5}$ | Galena |
| HgS | $10^{-53.3}$ | Cinnebar |
| ZnS | $10^{-22.5}$ | Wurtzite |
| ZnS | $10^{-24.7}$ | Sphalerite |
| **Carbonates** | | |
| $BaCO_3$ | $10^{-8.3}$ | Witherite |
| $CdCO_3$ | $10^{-13.7}$ | |
| $CaCO_3$ | $10^{-8.35}$ | Calcite |
| $CaCO_3$ | $10^{-8.22}$ | Aragonite |
| $CoCO_3$ | $10^{-10.0}$ | |
| $FeCO_3$ | $10^{-10.7}$ | Siderite |
| $PbCO_3$ | $10^{-13.1}$ | |
| $MgCO_3$ | $10^{-7.5}$ | Magnesite |
| $MnCO_3$ | $10^{-9.3}$ | Rhodochrosite |
| **Phosphates** | | |
| $AlPO_4 \cdot 2\,H_2O$ | $10^{-22.1}$ | Variscite |
| $CaHPO_4 \cdot 2\,H_2O$ | $10^{-6.6}$ | |
| $Ca_3(PO_4)_2$ | $10^{-28.7}$ | |
| $Cu_3(PO_4)_2$ | $10^{-36.9}$ | |
| $FePO_4$ | $10^{-21.6}$ | |
| $FePO_4 \cdot 2\,H_2O$ | $10^{-26.4}$ | |

Source: K. B. Krauskopf, *Introduction to Geochemistry*, 2d ed. (New York: McGraw-Hill, 1979).

TABLE 6 - After Fetter, 1993.

**Table 18-1 Maximum concentrations of metals in equilibrium with common anions at 25°C**

The numbers in each column show the maximum activity of each metal in equilibrium with the anion at the head of the column. Activities in moles per liter; for these metals an activity, or concentration, of $10^{-5}M$ is approximately equivalent to 1 ppm.

Assumed conditions:

Column 1: Activity of $OH^- = 10^{-8}M$ (pH 6) and Eh = 0.7 volt.

Column 2: Total dissolved carbonate = 0.001*M*, pH 6, Eh = 0.7 volt. Under these conditions $a_{CO_3^{2-}} = 10^{-7.7}M$.

Column 3: Activity of $SO_4^{2-} = 0.01M$, Eh = 0.7 volt, pH low enough to prevent hydrolysis.

Column 4: Activity of $Cl^- = 0.001M$, Eh = 0.7 volt, pH low enough to prevent hydrolysis.

Column 5: Eh = 0.3 volt, pH low enough to prevent hydrolysis. These figures show maximum concentrations of metal ions in equilibrium with native metals.

Column 6: Activity of $S^{2-} = 10^{-20}M$. This is roughly the concentration in equilibrium with sphalerite in a solution with pH = 3.

| | (1) $OH^-$ | (2) $CO_3^{2-}$ | (3) $SO_4^{2-}$ | (4) $Cl^-$ | (5) Eh | (6) $S^{2-}$ |
|---|---|---|---|---|---|---|
| Cu | $10^{-4.3}$ | $10^{-5.0}$ | > 1 | > 1 | $10^{-1.3}$ | $10^{-14.3}$ |
| Ag | > 1 | > 1 | > 1 | $10^{-6.7}$ | $10^{-8.5}$ | $10^{-15.0}$ |
| Hg | $10^{-6.8}$ | $10^{-6.8}$ | $10^{-3.9}$ | $10^{-9.5}$ | $10^{-16.3}$ | $10^{-33.3}$ |
| Pb | > 1 | $10^{-5.4}$ | $10^{-5.8}$ | > 1 | > 1 | $10^{-7.5}$ |
| Zn | 0.2 | $10^{-3.3}$ | > 1 | > 1 | > 1 | $10^{-4.7}$ |
| Cd | > 1 | $10^{-6.0}$ | > 1 | > 1 | > 1 | $10^{-7.0}$ |
| Sn | $10^{-7.8}$ | $10^{-7.8}$ | > 1 | > 1 | > 1 | $10^{-5.9}$ |
| Ni | 0.2 | 0.2 | > 1 | > 1 | > 1 | $10^{-6.6}$ |
| Co | > 1 | $10^{-3.3}$ | > 1 | > 1 | > 1 | $10^{-5.6}$ |
| Mn | $10^{-6.0}$ | $10^{-6.0}$ | > 1 | > 1 | > 1 | > 1 |
| Fe | $10^{-13}$ | $10^{-13}$ | > 1 | > 1 | > 1 | > 1 |

TABLE 5 - After Krauskopf, 1979.

**TABLE 17-3. Schürmann's Series of Solubilities of Important Sulfides**

| Affinity of Ion for Sulfur | Metal | Solubility of Sulfide in Water |
|---|---|---|
| High | Palladium | Low |
| | Mercury | |
| | Silver | |
| | Copper | |
| | Bismuth | |
| | Cadmium | |
| | Antimony | |
| | Tin | |
| | Lead | |
| | Zinc | |
| | Nickel | |
| | Cobalt | |
| | Iron | |
| | Arsenic | |
| | Thallium | |
| Low | Manganese | High |

Schürmann's series depicting relative solubilities and sulfur affinities of the heavy metals. It is also known as the electromotive series. A metal in solution that is higher on the list can galvanically appropriate sulfur from the sulfide of a lower one by replacement. Copper ions, for example, will replace the cations in galena, sphalerite, and especially pyrite, leaving Pb, Zn, and Fe ions in solution and chalcocite or covellite replacement rims on the sulfides (Figure 17-19). Silver enrichment is also clearly possible. The list is in effect a "pecking order" from top to bottom of the sulfides of the metals in supergene environments.

TABLE 7 - After Guilbert and Park Jr., 1986.

The following sections describing the solubility, mobility and fate of the selected elements common to this study are quoted from C.W. Fetter's 1993 text-Contaminant Hydrogeology:

> Sulfur is released to the environment by the weathering of minerals containing the element. Rock containing pyrite can be oxidized to release sulfur, with microorganisms acting as a catalyst and mediating the oxidation. This is the source of the acidic water that drains from many areas that have been mined. Sulfuric acid is widely used in industrial processes. Sulfur can be released to the environment by the processing of sulfide ores and by the burning of fossil fuels, all of which contain sulfur to some degree.
>
> Sulfur can exist in valance states ranging from $S^{-2}$ to $S^{+6}$. Figure 6.8 is an Eh-pH diagram showing the stability of the two oxidized forms of sulfur, $HSO_4$- and $SO_4^{2-}$, and the three reduced forms, $S^{2-}$, $HS^-$, and $H_2S$ (aqueous). The field of stability for elemental sulfur is also shown. The total sulfur activity used in computing the diagram is $10^{-3}$ mol/L or 96 mg/L as $SO_4^{2-}$. If a greater total sulfur activity were used, the stability field for elemental sulfur would be larger. Although this is a very useful diagram for understanding the equilibrium conditions for dissolved sulfur, the redox reactions can be slow if microbes are not mediating the reactions. Hence, it may take a long time for the system to reach equilibrium.

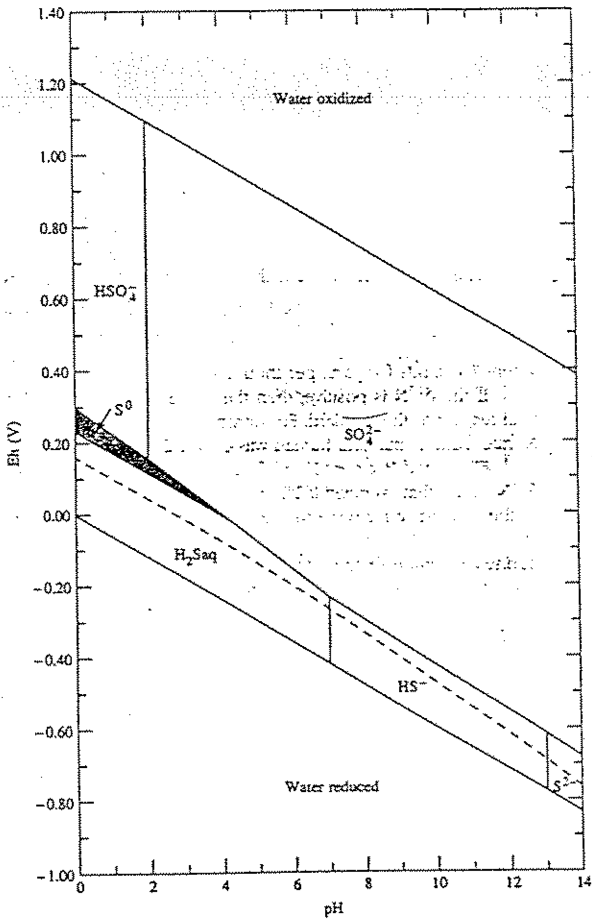

FIGURE 6.8 Eh-pH diagram for sulfur species at standard conditions with total dissolved sulfur activity of 96 mg/L. Source: J. D. Hem, *Study and interpretation of the chemical characteristics of natural waters*, U.S. Geological Survey Water Supply Paper 2254, 1985

Gypsum (calcium sulfate) is quite soluble in water (Keq=$10^{-4.6}$) and, except for waters with extremely high sulfate, would not be a sink for sulfate. Strontium sulfate is sparingly soluble (Keg= $10^{-6.5}$), whereas barium sulfate is nearly insoluble (Keq= $10^{-10.0}$). However, strontium and barium are not found in much abundance in natural waters. Sulfate could act as a sink for strontium and barium.

Arsenic can occur in valance states of +5, +3, +1, 0 and -3. However, the important states of dissolved arsenic in water are the arsenate $H_nAsO_4^{3-n}$, with a valance state of $^{+5}$, and the arsenite $H_nAsO_3^{2-n}$, with a valance state of $^{+3}$. An Eh-pH diagram for arsenic that shows the fields of stability for the arsenates and arsenites is given in Figure 6.9. Dissolved arsenic species can be absorbed by ferric hydroxides. Arsenic (+5) is more strongly sorbed than arsenic (+3). Ferric hydroxides are stable over a wide Eh-pH range, so this fact limits the mobility of arsenic. However, conditions that reduce $Fe^{3+}$ to $Fe^{2+}$ and $As^{5+}$ to $As^{3+}$ increase the mobility of arsenic in the environment, because the precipitated ferric hydroxides become soluble ferrous hydroxides (Matisoff, et al., 1982). In an oxidizing environment with a pH above 4.09, we will find colloidal ferric iron hydroxides, which will sorb arsenic and would thus expect to have little arsenic in solution. Under strongly reducing conditions, if both iron and hydrogen sulfide are present, arsenic sulfide coprecipitates with iron sulfide. Mildly reducing conditions that lack hydrogen sulfide present conditions under which one would expect to find the most mobile arsenic, as iron would be in the soluble ferrous state and arsenic would be in the arsenite form (Hounslow, 1980).

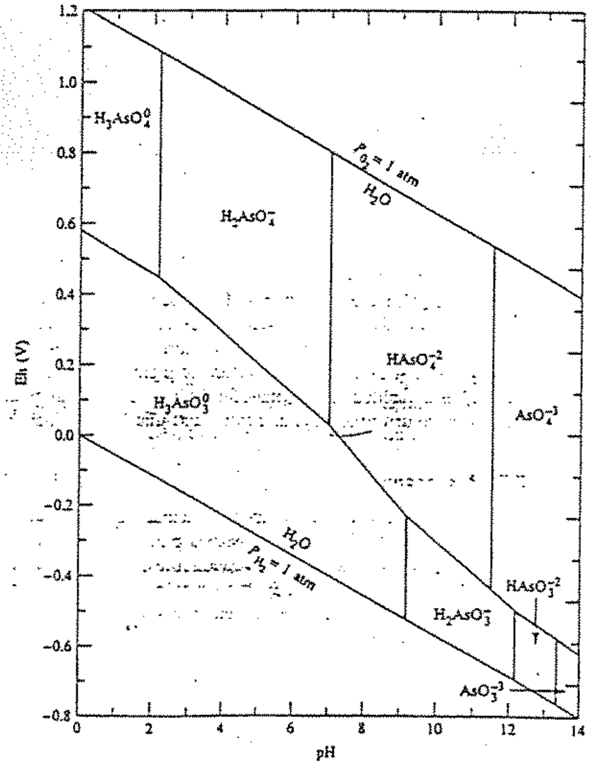

FIGURE 6.9 Eh-pH diagram for arsenic species under standard conditions. *Source:* A. H. Welch, M. S. Lico, and J. L. Hughes, *Ground Water* 26, no.3 (1988):333–47. Used with permission. Copyright © 1988 by Water Well Journal Publishing Co.

Arsenic has been released to the environment through the burning of coal and smelting of ores. In the past it was used in the formulation of insecticides and embalming corpses. Starting at the time of the Civil War in the United States (1860-1865), arsenic was an ingredient in a popular embalming fluid. As much as to 3 lb of arsenic could have [been] used per corpse. The use of arsenic in embalming fluids was banned by the federal government in 1910 because its use interfered with the investigation of suspected arsenic poisonings. However, graveyards from the Civil War and the late nineteenth century may be a source of arsenic contamination (Konefes, 1990). It has some modern industrial uses. Groundwater has been found to have high (up to 96 ug/L) concentrations from natural sources in northeastern Ohio (Matisoff et al., 1982). Elevated arsenic (up to 5 mg/L) in groundwater in Nova Scotia, Canada, was reportedly due to the weathering of piles of mining waste that contained arsenopyrite (Grantham and Jones, 1977). In the western United States high (>5 ug/L) concentrations of arsenic are common in groundwater. These are associated with areas of sedimentary rocks derived from volcanic areas, geothermal systems and gold and uranium mining districts. Irrigation in some areas has liberated arsenic to the extent that concentrations of up to 1 mg/L are found in shallow groundwater beneath irrigated fields (Welch, Lico and Hughs, 1988).

Cadmium has a very low maximum contaminant level (MCL) in drinking water - 10 ug/L - due to its toxicity. It exists in aqueous solution in the +2 valance state. Cadmium carbonate has a very low solubility product, $10^{-13.7}$. Although this could serve as a control on solubility under some conditions, cadmium can be mobile in the environment. On Long Island, New York, a metal-plating waste containing cadmium and chromium traveled about 3000 ft in a shallow aquifer (Perlmutter, Lieber and Frauenthal, 1963). Cadmium has been implicated in an outbreak of a disease in Japan resulting in a softening of the bones of the victims that resulted in extreme bone pain. The cadmium was traced to rice and soybeans grown in soil contaminated by airborne cadmium that came from a nearby lead-and zinc-smelting operation (Emmerson, 1970).

Chromium in natural waters occurs in a +3 and a +6 valance state. Stable ionic forms in aqueous systems include $Cr^{3+}$, $CrOH^{2+}$, $Cr(OH)^{2+}$, $Cr_2O7^{2+}$ and $CrO_4^{2-}$. Chromous hydroxide, $Cr(OH)_3$ is a possible precipitate under reducing conditions. Figure 6.10 is an Eh-pH diagram for the stability field for chromous hydroxide. Under some conditions chromate might react with ferrous iron to produce a chromous hydroxide precipitate (Robertson, 1975).

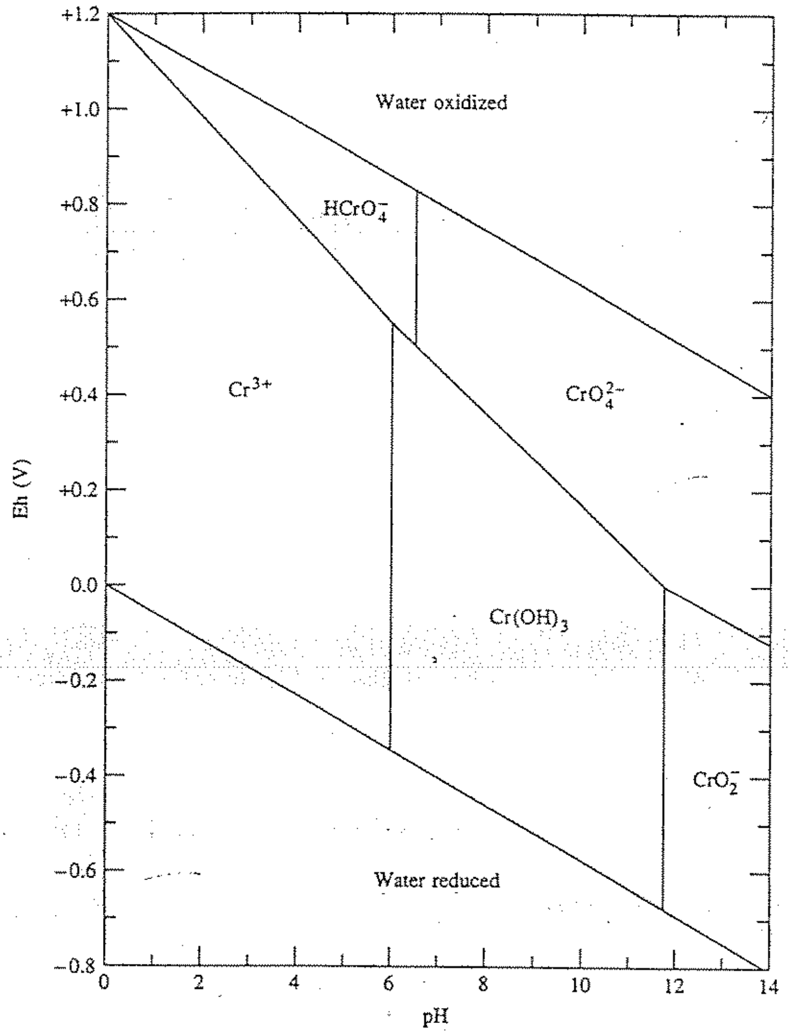

**FIGURE 6.10** Eh-pH diagram for chromium under standard conditions. *Source:* Modified from F. N. Robertson, *Ground Water* 13, no. 6:516–27. Used with permission. Copyright © 1975 by Water Well Journal Publishing Co.

$$Cr0_4^{2-} + 3Fe^{2+} + 8H_2O = 3Fe(OH)_3 + Cr(OH)_3 + 4H^+$$

In general the hexavalent chromium in groundwater is soluble and mobile and trivalent chromium will be insoluble and immobile. Industrial discharges of hexavalent chromium are common from metal-plating industries. This material may be quite mobile in groundwater. A hexavalent chromium spill on Long Island, New York, traveled more than 3000 ft from a waste discharge pond to a stream (Perlmutter, Lieber, Frauenthal, 1963). Hexavalent chromium from a natural source has been found in groundwater in Paradise Valley, Arizona (Robertson, 1975).

Cobalt occurs with valence states of +2 and +3. In the Eh and pH range of natural waters, only the +2 valence state is stable. It is thought that cobalt can coprecipitate or be absorbed by manganese and iron oxides. Cobalt carbonate has a solubility product of $10^{-10.0}$. At a pH of 8.0 with 100 mg/L of carbonate, the equilibrium solubility of cobalt is 6 ug/L (Hem, 1985). The solubility product of cobalt sulfide is very low, $10^{-21.3}$. Virtually no cobalt would be in solution in a reducing environment. Radioactive cobalt is a waste product of certain defense activities (Means, Crerar, and Duguid, 1978). Cobalt occurs in nature as smaltite ($CoAs_2$), and cobaltite (CoAsS).

Copper occurs in either a +1 or a +2 valence state. Dissolved copper species in water include $Cu^{2+}$, $HCu0^{2-}$, $Cu0_2^{2-}$, and $Cu^+$. Cupric copper and ferrous iron can undergo an oxidation-reduction:

$$Cu^{2+} + 2Fe^{2+} + 7H_2^0 = Cu_2^0 + 2Fe(OH)_2 + 8H^+$$

Both cupric and cuprous sulfides have very low solubility products. Copper concentrations can be very high in acid mine drainage from metal mines, up to several hundred milligrams per liter. Copper can be leached from copper water-supply pipes and fixtures, especially by waters that have a pH of less than 7 (Hem, 1985).

Lead occurs in aqueous solution as $Pb^{2+}$ and in various hydroxides. Various lead compounds have solubility products that indicate that under the right Eh-pH conditions, lead solubility would be limited in natural waters: $PbC1_2$, $Ksp=10^{-4.8}$; $PbF^2$, $Ksp=10^{-7.5}$; $PbSO_4$, $Ksp=10^{-7.8}$; $PbC0_3$, $Ksp=10^{-13.1}$ and PbS, $Ksp=10^{-27.5}$. Lead and the other metals are cations that can be expected to undergo cation exchange with clays. Hence, the mobility of lead in groundwater is limited.

This is born out by a study at a storage battery manufacturing facility at Medley, Florida. Soil near the facility was contaminated with lead in amounts of up to 98,600 mg/Kg. However, shallow groundwater immediately beneath the contaminated soil averaged less than 10 ug/L of lead, with the maximum being 31 ug/L. The soils at the site are high in carbonate, with some clay; however, the mechanism of lead removal by the soils is not known. Lead leached from lead pipes and solder used to join copper pipes is a potential threat for users of drinking water that is acidic or poorly buffered (Hem, 1985).

Mercury has the lowest MCL for any inorganic chemical, 2 ug/L. It is considered to be very toxic. It has been known to concentrate in the food chain, especially in fish. Several outbreaks of mercury poisoning have been confirmed in Japan. Local discharges of mercury from industrial processes into surface-water bodies resulted in high mercury levels in fish. Inhabitants of fishing villages ate fish up to three times a day. Mortality of those affected was about 40%, and the poisoning was passed to unborn babies by apparently healthy mothers (Waldbott, 1973). Mercury occurs as a metal and in the valance states of +1 and +2. Most of the inorganic mercury compounds have a low solubility. The solubility product of $Hg_2Cl_2$ is $10^{-17.9}$, and for HgS it is about $10^{-50}$. Under most natural conditions there is little soluble inorganic mercury. However, methane-generating bacteria can convert metallic mercury to organic forms such as methyl mercury, $HgCH^{3+}$. The monomethyl mercury ion is soluble in water. Bacteria can also produce dimethyl mercury, $Hg(CH_3)_2$ which is volatile. Other organic forms of mercury, such as ethylmercuric chloride ($C_2H_5HgCl$), are manufactured and used as fungicides.

Nickel - This metal occurs in aqueous solutions in the +2 valence state. Nickel ores include a variety of minerals, consisting of nickel, antimony, sulfur, and arsenic: NiSb, $NiAs_2$, NiAsS, and NiSbS. Nickel carbonate is more soluble than cobalt carbonate ($Ksp=10^{-6.9}$), whereas the sulfide has a similar solubility ($Ksp=10^{-19.4}$). Nickel is widely used in industry.

Zinc is a fairly common metal and is extensively used in metallurgy and as a pigment, zinc oxide, which is often worn on the noses of lifeguards and other people in the sun. It occurs in the +2 valence state. Zinc carbonate has a rather low equilibrium constant, $10^{-10}$, which would limit the solubility at pH ranges where the carbonate ion predominates. In a pH range of 8 to 11 and with 610 mg/L of $HC0_3^-$, there should be less than 100 ug/L of dissolved zinc (Hem, 1985).

This concludes the sections by Fetter (1993).

Recent technical papers covering both natural and anthropogenic (man-made; due to mining or industrial activities) sources of dissolved metals in ground and surface waters are very numerous.

An example of heavy metal impacts to groundwater and surface water is an article appearing in the June, 1993 edition of the Water Well Journal entitled "Abandoned Mine Holds Water Quality Problems" by Chris Ross. Ross interviews the engineering geologist involved in the investigation of heavy metal contamination of drinking water affecting the cities of San Francisco, Berkely and Oakland in California. The source of the contamination is mine wastes from the Penn Mine which operated between 1865 and 1953. This was a sulfide mine which produced copper, zinc, silver and gold. The engineering geologist related that a conservative estimate of how much the act of mining increased oxidation of the ore deposit was roughly three orders of magnitude. He indicated that the natural background level concentrations of zinc and copper were likely 1 part per billion (ppb). Yet, in the mined area, zinc and copper concentrations in groundwater currently run 100 to 1000 parts per million (ppm).

Similar circumstances were found as a result of an investigation into mining impacts to groundwater which were reported in Arsenic Speciation and Quality of Groundwater in a Lead-Zinc Mine, Idaho (1988) by Mok, Riley and Wai. The authors not only reported definite evidence of leaching of metals by groundwater but, they also linked the degree of metals leaching with pH and the degree of infiltration into the mine related groundwater system by oxygenated surface waters. They were able to correlate arsenic valence speciation with the redox potential (and dissolved oxygen) of the groundwater. In retrospect, this proved to be a very important study and is highly recommended as a reference.

Two additional studies have shown the chemical mobility and impacts of zinc-lead mine spoil on marine aquatic systems. Lead and Zinc Pollution for Marine Dumping of Waste Rock from Lead/Zinc Mining (1992) by Asmund and Heavy Metal Contamination of a Greenland Fjord System by Mine Wastes (1989) by Loring and Asmund both point out that the solubility and mobility of mineral elements are not constrained solely to underground leaching and solutioning environments. In these studies mine spoil (which was disposed both on the land surface and discharged through a sub-marine outfall pipe) through surface leaching and solubilization of the marine disposed tailings was found to contaminate both seaweeds and blue mussels on the west coast of Greenland.

Other recent and associated studies (Solubility of Heavy Metals in Lead Mine Spoil Extracts (1984) by Shaw, Rorison and Baker; Metalliferous Mine Spoil in Wales: A Toxic and Hazardous Waste (1983) by Davies, Jones and Peterson; Lead, Cadmium and Zinc Contamination in Southwest Missouri (1991) by Clevenger, Hinderberger, Roberts, Bush and Phillips; Characterization of Heavy Metal Contamination in the Lateral Lakes of the Lower Coeur d'Alene River Valley, Northern Idaho (1992) by Hoffman, Rabbi, Bender, Chamberlain and Sprenke; Distribution of Metal Contamination in the Floodplain Sediments of the Clark Fork River, Near Deer Lodge, Montana (1987) by Brooks and Moore;

Relationships Between Particle Size and Metal Concentrations in Contaminated Bed Sediment of the Clark Fork River, Western Montana (1987) by Brook and Moore; Heavy Metal Contamination in the Tanat Valley, North Wales (1989) by Fuge, Paveley and Holdham; Cadmium Contamination of Our Freshwater Resources (1986) by Nriagu; Evaluation of Hydraulic Interconnections of Two Aquifers Underlying the Smelterville Flats Area, Idaho (1989) by Adams; Impact of Industrial and Mine Drainage Wastes on the Heavy Metal Distribution in the Drainage Basin and Estuary of the Sado River (Portugal) (1989) by Quevauviller, Lavigne and Cortez; Environmental Impact of Base Metal Mining in the Himalaya: A Case Study with Special Reference to Rangpo Ore Field, Sikkim, India (1989) by Rai and Rao and Determining Heavy Metal Leaching and Transport from Abandoned Mine Waste and Subsequent Attenuation (1989) by Lambeth, Williams and Stewart) deal with either physical or chemical transport and migration of minerals and mine spoil chemical elements away from the original mine or mine dump through man's redistribution and use of the wastes as fill or paving materials, physical slumping, wind redistribution, surface water leaching and run-off or leachate plume migration in groundwaters.

Specific studies done on speciation, solubility and transport of heavy metals in sediments include Cadmium Bioavailability to Three Estuarine Animals in Relation to Geochemical Fractions to Sediments by (1990) Rule and Alden and Acid Volatile Sulfide Predicts the Acute Toxicity of Cadmium and Nickel in Sediments (1992) by Di Toro, Mahony, Hansen, Scott, Carlson and Ankley.

Finally, Fetter (1993) introduces an important concept of geochemical zonations which were originally observed under landfills and can readily be applied, with a few minor changes, to surface disposed mine wastes. Essentially, Fetter reports a three part chemical zonation under the landfill. The landfill, proper, is anaerobic. "This anaerobic zone extends along the plume of leachate mixing with groundwater. In this zone we find the production of methane and ammonia as microorganisms decompose organic matter and obtain oxygen from the reduction of sulfate and nitrate. Reduction will liberate soluble ferrous iron. Manganese may also become soluble due to dissolution of native minerals. Ferrous sulfide may precipitate in this zone."

Fetter continues . . . "As the leachate mixes with oxygenated groundwater, it becomes less reducing [mildly reducing] and forms a transition zone. Most of the soluble organic matter has already been decomposed in this zone. In the transition zone there is coprecipitation of trace metals with iron and manganese hydroxides. Ahead of the transition zone, there is an aerobic zone, where the leading edge of the leachate has changed the native groundwater quality, but not enough to deplete the oxygen. The aerobic zone contains nitrate and sulfate at the background levels of the aquifer."

Such a model might well be applied to a roaster pile and prove to be helpful in predicting the solubility and mobility of the metallic compounds coming off the surface of the pile, within the pile and below the pile as both leachate and base flowing groundwater interact under the pile. The additional complication of a rising and falling water table should also be taken into account with this model. Fetter's model indicates that laterally (basal) flowing oxygenated groundwater may remobilize the heavy metal sulfide precipitates under the roaster waste piles and that the current strictly anaerobic model may not appropriately depict what happens in the real world. This implies that the current practice of remediating roaster wastes by burial may not truly stop ground and surface water contamination by these wastes. Arsenic, cadmium, cobalt, chromium and thallium would be very mobile in this acidic and mildly reducing to mildly oxidizing environment.

Naturally occurring heavy metal contamination of surface waters is well discussed in Metals in Water: Determining Natural Background Concentrations in Mineralized Areas (1992) by Runnels, Shepherd and Angino. Mudrey and Bradbury (1993) demonstrate the true un-mined background levels of dissolved metals in groundwater for the entire upper half of the State of Wisconsin in their Wisconsin Geological and Natural History Survey publication entitled Evaluation of N.U.R.E. Hydrogeochemical Data for Use in Wisconsin Groundwater Studies. A couple of areas in Wisconsin (just recently discovered) are showing naturally high levels of dissolved arsenic in groundwater. The most recently discovered area is in Winnebago County near Algoma and Butte des Morts, Wisconsin. This area is part of a north-northeast trending band showing arsenic concentrations in well water from Marinette County through Oconto and Shawano Counties and down into Outagamie, Waupaca and Winnebago Counties. This band of counties also shows detectable concentrations of sulfate, barium, boron, calcium, cobalt, lithium, magnesium, molybdenum, nickel, silver, sodium, strontium, thorium, uranium, vanadium, yttrium, and zirconium.

The reader should understand from this section that metal bearing sulfide minerals are soluble under the right geochemical conditions (either man-made or natural), some being more soluble and therefore more environmentally mobile than others. One also should understand that acid mine drainage and heavy metal leaching are universal problems based on basic chemical reactions and concepts and observed whenever sulfide mining occurs. No nation of the world, that has had sulfide mining, has escaped from the predictable geochemical reactions leading to production of acid mine drainage and heavy metal leaching.

Progressive governments and state agencies are concluding that appropriate steps should be taken to identify and manage acid generating mining wastes (see Identification and Management of Acid Generating Mining Wastes in Australasia by Miller, Murray and Jeffery). Miller et al., (1990) propose a staged systematic approach to identifying and managing acid producing mine wastes by geochemical testing of the mineralization to be mined and integrating that information into development of appropriate mining and waste management strategies. They also propose continuing field monitoring techniques for rapid management of emerging problems. They conclude that "Identification of both inherently acid and potentially acid forming materials are essential for designing and operating an effective waste disposal and management strategy for the control of ADM [acid mine drainage]."

Author's Note: This Appendix may be especially useful to DNR staff engaged in reviewing environmental impact statements pertaining to proposed mining operations and in writing, reviewing and granting permits to those mining operations. Industrial Wastewater personnel also should be aware of the contents of this Appendix when reviewing a mining operation's wastewater treatment and site abandonment plans.

# APPENDIX E: TOXICOLOGY OF THE ELEMENTS FOUND IN THE MINED ORES OF SOUTHWESTERN WISCONSIN

It is appropriate to consider the general toxicological effects of the elements found in the mined ores of the Southwestern Wisconsin Zinc-Lead District. This Appendix, however, cannot and should not serve as a substitute for the involvement and independent expert assessment of risks and hazards of exposure to these elements by the State Toxicologist's Office.

Arsenic is a proven integral part of the iron sulfides of the mining district ores. It is also found bound up with cobalt in cobaltite and safflorite. Arsenic has been detected in mine waste piles, leachate from those waste piles, in surface waters and storm water run-off, in stream sediments, mine associated groundwater and public and private water supplies.

A new maximum contaminant level may be set by the U.S. Environmental Protection Agency in light of a recently reported eleven-year study on human health effects caused by drinking arsenic contaminated well water on the island of Taiwan (see Ecological Correlation between Arsenic Level in Well water and Age-adjusted Mortality from Malignant Neoplasms, 1990, by Chien-Jen Chen and Chih-Jen Wang). This report found a strong correlation between specific cancers - liver, nasal cavity, lung, skin, bladder, kidney and prostate - and ingestion of arsenic in drinking water.

Joseph P. Brown, a toxicologist with California's Environmental Protection Agency, indicates that a new risk assessment done by his agency and based upon lifetime consumption of drinking water with arsenic levels at the current federal limit of 50 ppb presents a one-in-100 risk of contracting cancer. This risk level is unacceptable when compared to the traditional acceptable risk level of one-in-one million. See Arsenic in Drinking Water - Bigger Cancer Threat by Raloff; Arsenic - Recommended Public Health level for Drinking Water by Brown and Fan; Arsenic in Drinking Water by Office of Envir. Health Hazard Assessment - California EPA; Toxicological Profile for Arsenic, Final Update - 1993 by Agency for Toxic Substances and Disease Registry, U.S. Dept. of Health and Human Services.

It is interesting to note that a treatise on mining techniques and methodology of the 16th century by Agricola indicates that miners and metal refiners knew well the toxic properties of arsenic and cobalt bearing ores. In more recent times, arsenic contamination in private water wells in Nova Scotia due to leaching of arsenic bearing mine waste piles has caused researchers to find that arsenic concentrations in well water which are equivalent to or exceed 0.01 ppm produce acute toxic effects in adult humans with chronic exposure. Also note that at this writing, the occupant (15 years occupancy) of the house 50 yards from the mine wastes over the Etna Mine (sample 001) has been diagnosed with skin cancer. Finally, there has been hearsay evidence of both a husband and wife, living near and downgradient from the Cuba City roaster pile, dying of cancer.

Chronic low level exposure to cadmium has been extensively studied by the Japanese (see "Ouch-Ouch" Disease: The Osteomalacia of Cadmium Nephropathy by Emmerson) since they also have famous zinc-lead sulfide deposits and smelting operations. The Japanese have noticed that local human populations around the mines and smelters exhibit a high incidence of a sort of severe osteoporosis called "Itai-Itai" disease (Morgan, 1989; Sax, 1986). Victims of this disease experience extreme bone pain and a literal deterioration of their skeletons due to pathologic fractures.

They found that the local populations were exposed to cadmium from the zinc-lead mineralized mine wastes and smelter stack particulate that were releasing this element into the environment by way of wind-borne dusts and waste pile leachates which impacted local soils, surface waters and groundwaters. The population's food supply came directly from the area and cadmium was found to be concentrating in the rice and soybeans being grown in the region.

Southwestern Wisconsin farmers, in the vicinity of mines, mine wastes and mineral deposits, could be faced with a similar problem. Cadmium is a common constituent of zinc ores and also occurs as greenockite (CdS) in the mining district. Cattle are grazed on roaster waste-cadmium contaminated soil. Livestock also drink at streams with detectable amounts of cadmium. It is not unreasonable to predict that the meat and milk products from these animals may carry detectable levels of cadmium. The livestock toxicity limit is 0.01 ppm (Sax, 1986).

Sax states that cadmium has a positive food chain contamination potential and that it is bioconcentrative by a factor of 3000. It can be accumulated by shellfish and other aquatic organisms with the hard water chronic aquatic toxicity limit being 0.0004 ppm. Cadmium has a "super toxicity rating" in man and has been linked with pulmonary emphysema, hypertension, prostate cancer and weight loss in babies born to occupationally exposed women.

Chromium, found in the mining district as a secondary component of pyrrhotite and other iron bearing minerals, is rated as highly toxic when inhaled or ingested; especially in its hexavalent form. This element is found to be corrosive to skin and potentially carcinogenic since a higher incidence of lung cancer is seen in chromate industry workers. The threshold for livestock toxicity has been found to be 1.0 ppm and the aquatic toxicity limit is 0.5 ppm (Sax, 1986).

Cobalt is found in the mining district as a major component of the minerals cobaltite and safflorite. It is also a minor constituent of several other minerals. Cobalt and arsenic bearing ores have long been known by miners, geologists and metallurgists as being toxic materials with harmful physical effects. Cobalt in quantities ranging from one teaspoonful to one ounce has been fatal to adult humans. Sax indicates the chronic livestock toxicity limit is 0.1 ppm and that cobalt is a known bioaccumulator. Cobalt has a naturally occurring radioactive isotope (Cobalt60) commonly used in medical applications. Medical grade radioactive cobalt wastes most usually require special low level radioactive waste repositories (Fetter, 1993). Cobalt compounds are suspected carcinogens of the connective tissues and lungs. There is no established maximum contaminant level for cobalt in drinking water.

Copper salts are classed as irritants to the skin, lungs and eyes in powder form. Copper in solution is corrosive to mucous membranes and the cornea (Morgan, 1989). The chronic livestock toxicity limit is 1.0 ppm and the chronic aquatic toxicity limit is 0.024 ppm. Livestock appear to be more sensitive to copper compounds (Sax, 1986). Copper is found in the mining district in chalcopyrite ($CuFeS_2$), chalcocite ($Cu_2S$), covellite (CuS) and bornite ($Cu_5FeS_4$). Copper is also found as a minor constituent in other minerals.

Lead also bioaccumulates and has been linked to nerve damage and measurable diminished mental capacity in humans, especially children (Moffat, 1989). Lead is found primarily bound with sulfur in galena (PbS). It is also found as a minor constituent of other minerals.

Mercury compounds damage the nervous system, sometimes causing a neurological disease resembling amyotrophic lateral sclerosis and readily accumulate in organisms, including man. Death due to ingestion of mercury laden fish has occurred in Japan where inhabitants of fishing villages eat fish up to three times per day. The maximum contaminant level for mercury is 2 ppb (Morgan, 1989; Fetter, 1993). Mercury may be found as a minor constituent of sphalerite (ZnS).

Nickel salts can be very toxic to aquatic life under certain chemical circumstances. The threshold acute hazard level for fish is 0.05 ppm. Chronic aquatic toxicity limit is 0.38 ppm. Chronic animal toxicity limit is 500 ppm. Airborne nickel is classed as a lung irritant. Humans can experience toxic effects but most usually are able to excrete ingested nickel compounds faster than they are absorbed into the system (Sax, 1986). Nickel is found in the mining district in millerite (NiS), pyrite ($FeS_2$), bravoite (Fe, Ni) $S_2$ and violarite ($NiS_2$ or $(Ni, Fe)_3S_4$).

Thallium is included here because of the strong potential of its presence in the ores of southwestern Wisconsin. Thallium is potentially found in sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and pyrite ($FeS_2$). Both sphalerite and pyrite are common minerals in the local ore deposits. Thallium is also very soluble, tends to remain in solution and can be transported in solution for a long distance.

Thallium, according to Sax, is a cumulative poison that affects the sympathetic nervous system, causes endocrine disturbances and hair loss. Progressive poisoning can occur by way of absorption through the skin as well as ingestion. Symptoms of acute poisoning occur at absorption or ingestion of 3 mg thallium per kilogram of body weight. The mean lethal dose for adults is about a gram. Thallium presents a chronic hazard because it is a slow acting cumulative poison and therefore has a threshold limit for skin contact of 1 mg per cubic meter of skin. Geologists, smelters, refiners and metallurgists have long known of the extreme toxicity of thallium (see Morgan, 1989).

Zinc has proven to be most toxic for aquatic life as it has been found to increase the susceptibility of salmon and other fishes to lethal ulceration. The acute hazard threshold for fish is 0.1 ppm. The chronic livestock toxicity limit is 5 ppm. Zinc is listed as an irritant to human beings and can be corrosive to the skin and gastrointestinal tract when concentration in solution reaches 675 to 2280 ppm. Zinc is found in the mining district in smithsonite ($ZnC0_3$) and sphalerite (ZnS) as well as being a minor constituent of other minerals.

Ecological assessments of hazardous waste sites normally include the components of hazard identification, exposure assessment, toxicity assessment and assignment of risk (Maughan, 1993). This also includes a baseline human health risk assessment through characterization of site conditions, identification of potential exposure pathways and quantification of exposure. Again, toxicity and risk assessment appropriately belong to the environmental toxicologist. This brief accounting of the general potential toxicological effects of these elements are no substitute for the disinterested and methodical evaluation of the State Toxicologist.

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