THE POTENTIAL USE OF COAL FLY ASH IN SUBSURFACE HAZARDOUS WASTE SITE REMEDIATION AND RECLAMATION

By

JEFFREY H. ELLARD

Bachelor of Science
University of Tulsa
Tulsa, Oklahoma
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Thesis Approved:

Douglas C. Kent

Thesis Advisor

Thomas C. Collins

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Purpose of Study

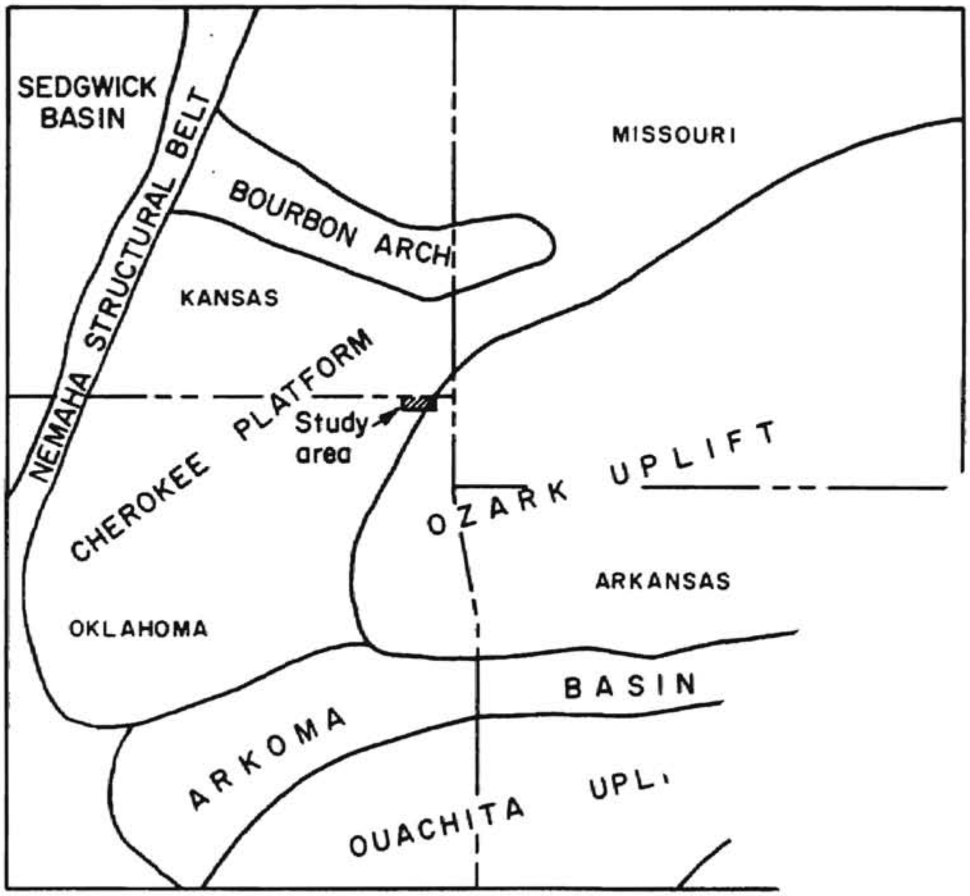
The purpose of this study is to determine the potential use of slurried and pumped coal fly ash, an inorganic, cementitious, environmentally benign waste product resulting from the burning of coal in electric power generation plants, as a method for remediating and restoring water quality and/or subsidence in mine fields through closed system underground slurried injection into abandoned subsurface mine works utilizing the contaminated waters contained within the mines. Furthermore, this study has been undertaken to evaluate the fixating, buffering, strength, stability, and leachability properties of the fly ash slurry mixed with the mine waters and the potential application of this process.

Field Study Location

The field site location selected and utilized in this study was the Picher Mining Field located in Townships 28 and 29 North, Ranges 22, 23, and 24 East, Ottawa County, Oklahoma. The Picher Mining Field, which is part of the greater Tri-States Mining District, adjoins the minerals mine fields located in southeastern Kansas and southwestern Missouri. The field study location and the surrounding areas are graphically depicted on Figure 1. A map depicting the horizontal extent of the underground mine workings of the Picher Mining Field is displayed on Figure 2.

FIGURE 1

AREA OF STUDY



The water samples utilized in this study were collected and taken from a site within the abandoned Picher Mining Field where an active water discharge from the underground mines occurs (Parkhurst 1987), (Parkhurst 1988). This location has been periodically monitored by governmental agencies and private parties for water quality studies since the early 1980's. All bulk water used in this study was collected from this site. The ore rock utilized in the lining of the simulated mine was collected from a boulder pile located next to an abandoned mine shaft located near the center of the mine field workings.

Laboratory Study Site

Laboratory work was undertaken at the Waste Water Research facility, the Civil/Environmental Engineering Research laboratory, the Scanning Electron Microscope laboratory, and the X-ray Diffraction laboratory all located on the Oklahoma State University campus in Stillwater, Oklahoma. Additional water analysis was performed by Stover Biometric Laboratories, also located in Stillwater, Bates Lab located in Sand Springs, Oklahoma, and core permeability analysis of the slurry batches was accomplished by Standard Testing Laboratories located in Oklahoma City, Oklahoma.

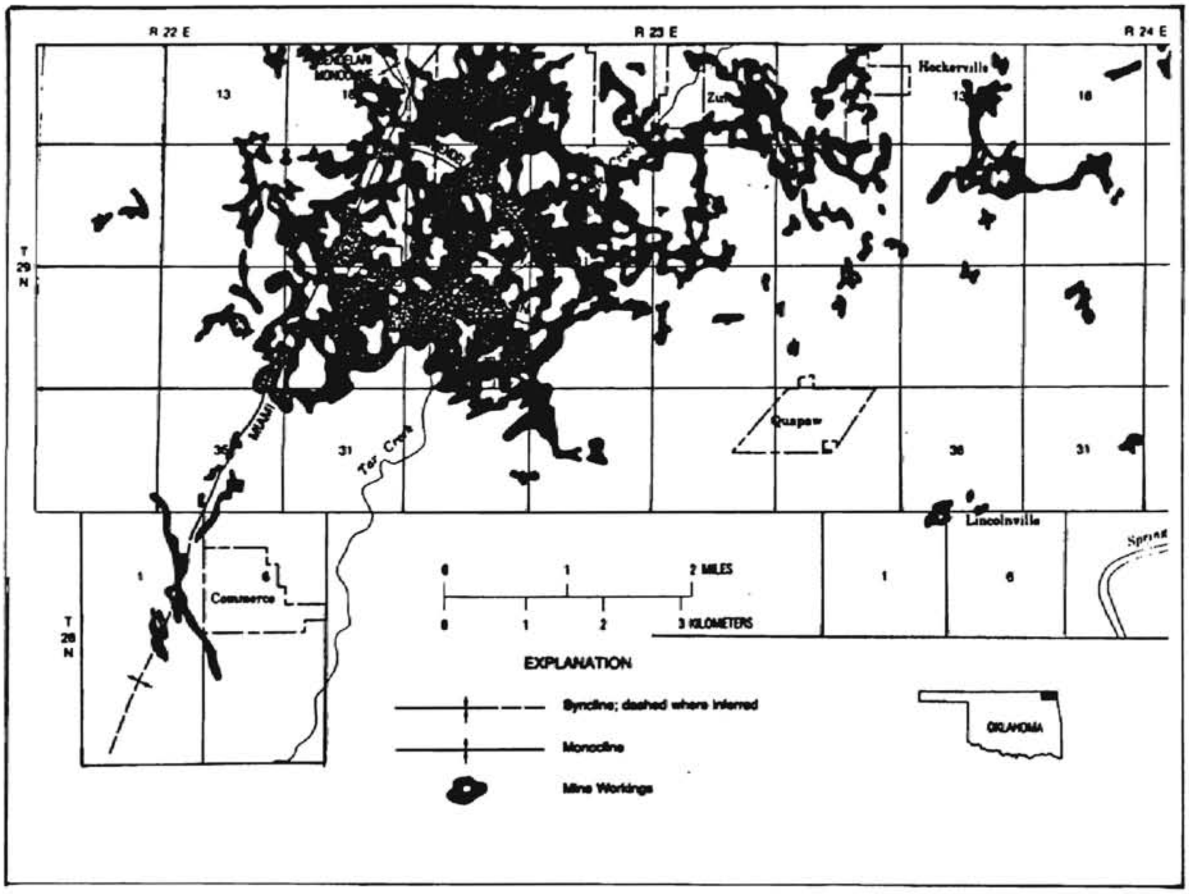
Scope of Study

The Picher Mining Field has been the subject of intense geological investigations since the discovery of shallow, commercial deposits of lead and zinc ore in the 1890's (McKnight 1970). Once the mining operations had removed the economically recoverable ore, the mines were abandoned in various states of disrepair and generally left open. Over time, the mine shafts and drifts filled with water resulting in substantial hydrogeological changes in the sub-surface leading to degradation of both sub-surface and surface waters (Luza 1986).

Due to the scope and size of the degradation to the water environment resulting

FIGURE 2

SUB-SURFACE MINES OF THE PICHER MINING FIELD,
OTTAWA COUNTY, OKLAHOMA



from the abandoned mining operations, the Picher Mining Field was placed on the United States Federal Government Environmental Protection Agency Superfund Sites List in 1980, specifically as the Tar Creek Superfund Site (Oklahoma Water Resources Board, 1983). Subsequently, multiple studies of the surface and sub-surface water quality associated with the abandoned Picher Mining Field have been conducted by most notably (Playton 1980), (Luza 1986), (Kent 1987), (Parkhurst 1987), (Parkhurst 1988), (Finney 1993), and on a continuing basis by the Oklahoma Water Resources Board. The primary focus of those studies was to identify the causes, sources, extent, intensity, and the physical and chemical properties of the water quality degradation of the surface and sub-surface waters as well as the hydrogeological characteristics of the Picher Mining Field.

Data obtained from these studies as well as water quality tests performed on water samples collected in this study have formed the basis for the hydrological fluids characteristics used in this study. The parameters of investigation included properties such as pH, Specific Conductance, dissolved metals concentrations, alkalinity, and other pertinent data.

Coal fly ash, in addition to being a well known component material of certain cements, has been utilized as an acidic balancing-neutralization agent for industrial waste products management for some time. Currently, several public and private sector projects are underway in the United States, Canada, and Europe involving coal fly ash in remediation of surface mining and industrial hazardous waste sites wherein the coal fly ash is used as a buffering agent for acidic materials, a physical barrier for surface/near surface water migration, and as a "cover" for waste piles to mitigate atmospheric weathering and leaching (Zimmerman 1985), (Smith 1985), (Burnham 1993), (Jones 1994), (Gabr 1994), (Bowders 1991), (Rose 1994), (Klimkos 1994).

Furthermore, high coal fly ash content cements are being used to arrest surface subsidence events associated with abandoned mining operations (Wood 1994) and (Brook 1994) and in municipal tunnel and sewer system backfills (Brendel 1987).

However, no current emphasis has been placed on utilizing this material, especially coal fly ash derived from high calcium-low sulfur western coals, in sub-surface mine waters remediation.

The coal fly ash used in this study was obtained from Oklahoma Gas and Electric Company at it's coal fired Sooner Power Generating Plant located south of Ponca City, Oklahoma. The power plant burns low sulfur coal mined in Wyoming and transported by railcar to the plant.

Thus this study will attempt to determine by chemical analysis, physical testing, trial application, and other relevant available means, the effects of slurried coal fly ash on heavily mineralized, acidic mine waters and the effects that these waters have on the fly ash slurry. Additionally, the effectiveness of the coal fly ash to set, seal, and stabilize in the simulated mine will be examined towards the purpose of determining the viability of utilizing coal fly ash in sub-surface hazardous waste site water reclamation and restoration.

CHAPTER II

LITERATURE REVIEW

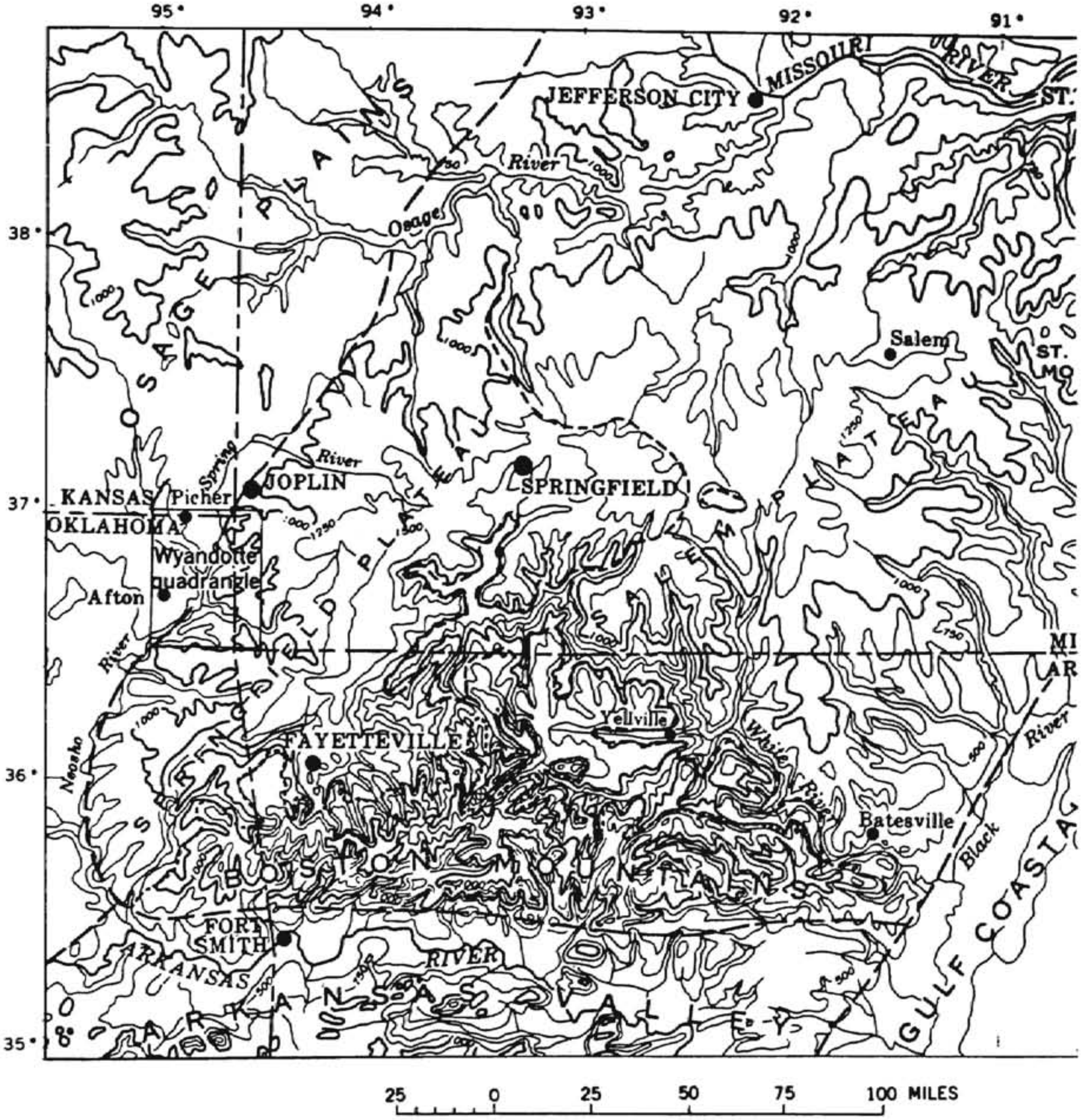
Field Site Geographical Setting

The Picher Mining Field lies in the northeastern most corner of Oklahoma, extends into southeastern Kansas, and is associated with the extensive mineral deposits of the Tri-States Mining District in nearby Missouri and Kansas as depicted on Figure 3. The topographic characteristics of the field site area proper consists of low relief prairie lands associated with the Osage Plains to the west and is bounded to the east by incised hill country which occupies the western edge of topographic influence associated with the Ozark Uplift. The mine field surface waters are drained by primarily shallow, slightly incised, intermittent to low flow volume streams which are generally north-south trending and discharge into the Neosho River. Due to the low relief and extensive modification of the historical topography resulting from the mining operations, many streams seasonally terminate to form shallow ponds or wetlands as shown on Figure 4 (McKnight 1970). Approximately 20 miles downstream, the Neosho River ultimately discharges into the Grand Lake of The Cherokees, the first substantial impoundment downstream from the Picher Mining Field.

Local topographic relief of the Oklahoma portion of the Picher Mining Field is to the south and total relief is approximately 120 feet over an area of roughly 72 square miles. The highest elevation is approximately 900 feet above mean sea level 2 miles east of Quapaw and the lowest elevation at 780 feet above mean sea level immediately south of

FIGURE 3

TRI-STATES MINING DISTRICT



the town of Commerce with an average elevation of 830 feet above mean sea level (Luza 1986), (McKnight 1970). Several man-made tailings piles resulting from mine operations surpass the original relief of the area and subsidence events associated with the collapse of abandoned mine shafts and drifts have formed topographic lows below that of the original landscape (Luza 1986).

Field Site Geological Setting

The macro-geological environment of the field study area has been affected by multiple major geological events. Geologically, the Picher Mining Field occupies a location which is on the eastern border of the Cherokee Platform and the western portion of the Ozark Uplift (Harrison 1979) within the interior of the North American Plate, Figure 5. The tectonic activities associated with both of these structural episodes influenced not only the stratigraphic composition of the field site investigation area but also the structural configuration of the country rock and, most economically important, the structural fabric of the insitu host rock for the mineral ore.

The Cherokee Platform has been a relatively geologically stable region since Pennsylvanian (Cherokee) time and is characterized as an area of low order structural deformation. However, the Ozark Uplift, a deep seated tectonic event, resulted in tremendous structural upwarping, folding, faulting, hydrothermal deposition, and subsequent erosion to such an extent that Pre-Cambrian Age Igneous rocks were exposed in the core area located in southern Missouri. To the west of the core, areas as far away as central Oklahoma were influenced creating a generally westward dip of the strata on a regional scale. The intensity of deformation of the geologic strata and associated erosion increased with the reduction in distance from the core.

In the Picher Mining Field a series of northeast-southwest trending parallel structural features are present expressed as folds, faults, and as sympathetic bedding outcrops all

FIGURE 4

TOPOGRAPHIC RELIEF AND DRAINAGE IN THE PICHER AREA

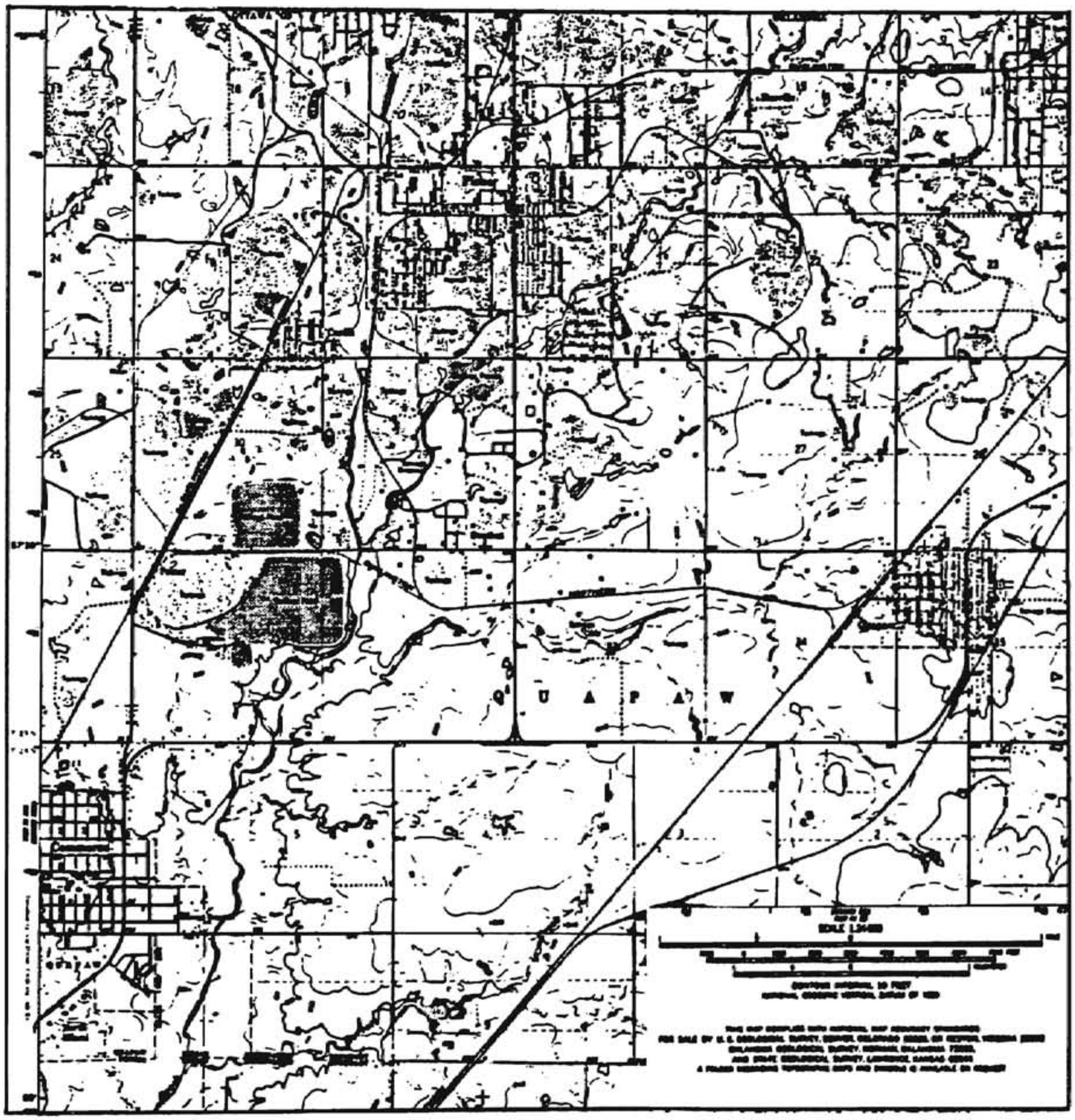
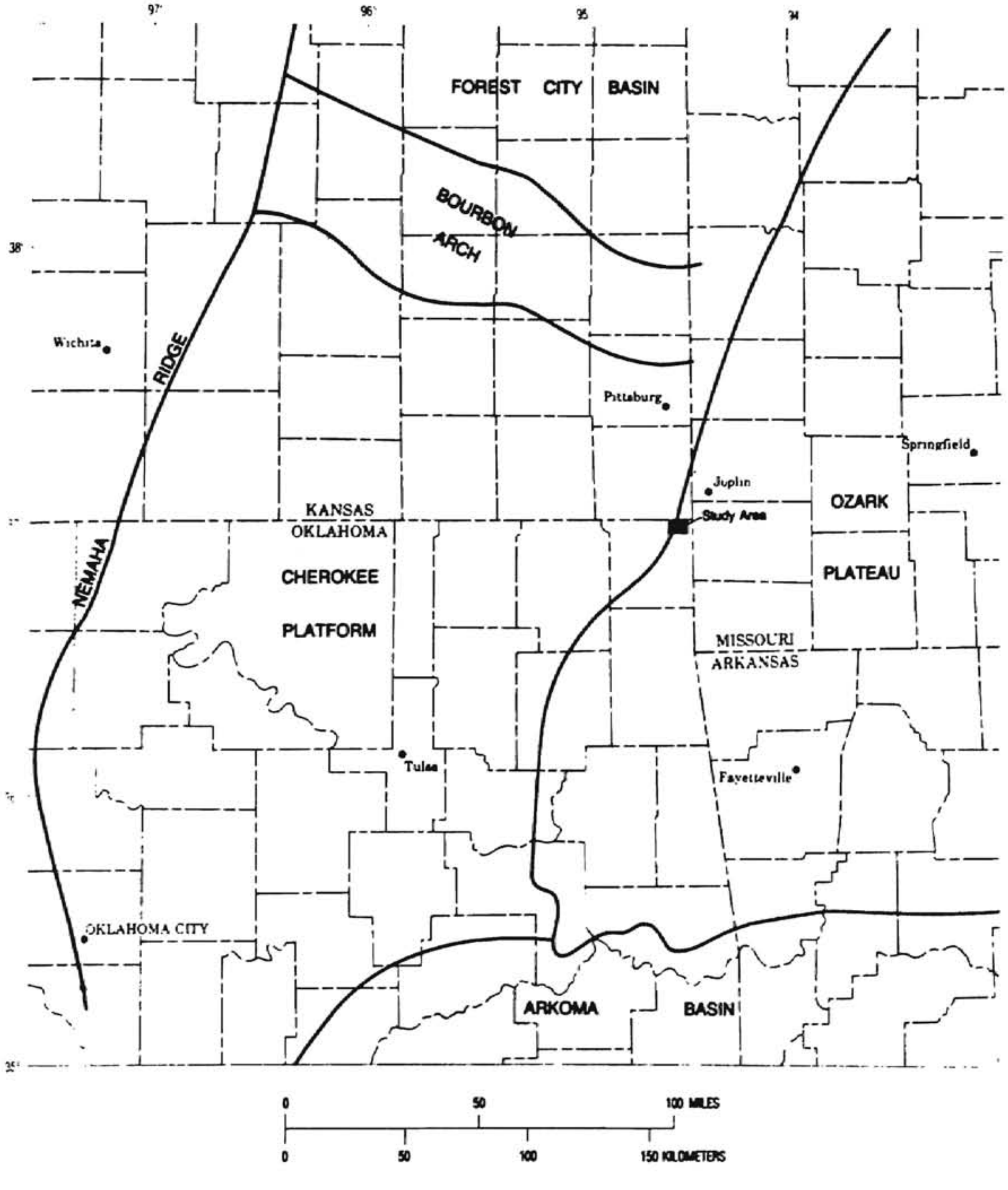


FIGURE 5

MACRO-GEOLOGIC MAP OF THE TRI-STATES AREA



directly related to the post-Boone, (Mississippian Age) Ozark Uplift. The principal structural features are the northeast-southwest trending Miami Trough or Syncline, and the transverse displacement related Bendelari Monocline and Rialto Basin (Luza 1986). The primary displacement associated with the Miami Trough is right lateral-transcurrent movement with associated conjugate shearing expressed as repetitive, minor displacement, northeast-southwest trending horizontal and transcurrent faulting, folding, and fracturing especially of the brittle, thinly-bedded ore host rocks (Weidman 1932). The transcurrent movement along the Miami Trough created a displacement of approximately 3/8ths of a mile on the Bendelari Monocline as shown on Figure 6.

The fracturing of the ore host rock modified or increased the original diagenetically related permeability and provided additional conduits for fluid migration of connate waters through the host rock which further opened permeability channels through solution modification, Figure 7. The area near and adjacent to the orogenic core in southern Missouri was subject to extensive hydrothermal activity which resulted in deposition of hydrothermal mineral deposits in receptive host rocks such as are located in the Tri-States Mining District.

The area now known as the Picher Mining District contained a section of Mississippian Age rock which was present throughout the Ozark Uplift event and thus experienced the effects of the orogenic effects and provided a host rock for the hydrothermal deposition of the mineral ore. This section of rock is known as the Boone Formation and is the principal ore bearing formation in the Picher Mining Field. The Boone Formation spans both the Osage and Merimec Series of the Lower Mississippian System and is composed of thinly bedded siliceous carbonate depositional sequences.

These depositional sequences contained in the Boone Formation have been subdivided into 7 members in the Picher Mining Field. These are in accending order, the St. Joe Limestone, Reed Springs, Grand Falls, Joplin, Short Creek Oolite, Baxter Springs, and the Moccasin Bend members (McKight 1970), Figure 8.

FIGURE 6

GEOLOGICAL MAP OF THE OKLAHOMA PORTION OF THE PICHER MINING FIELD

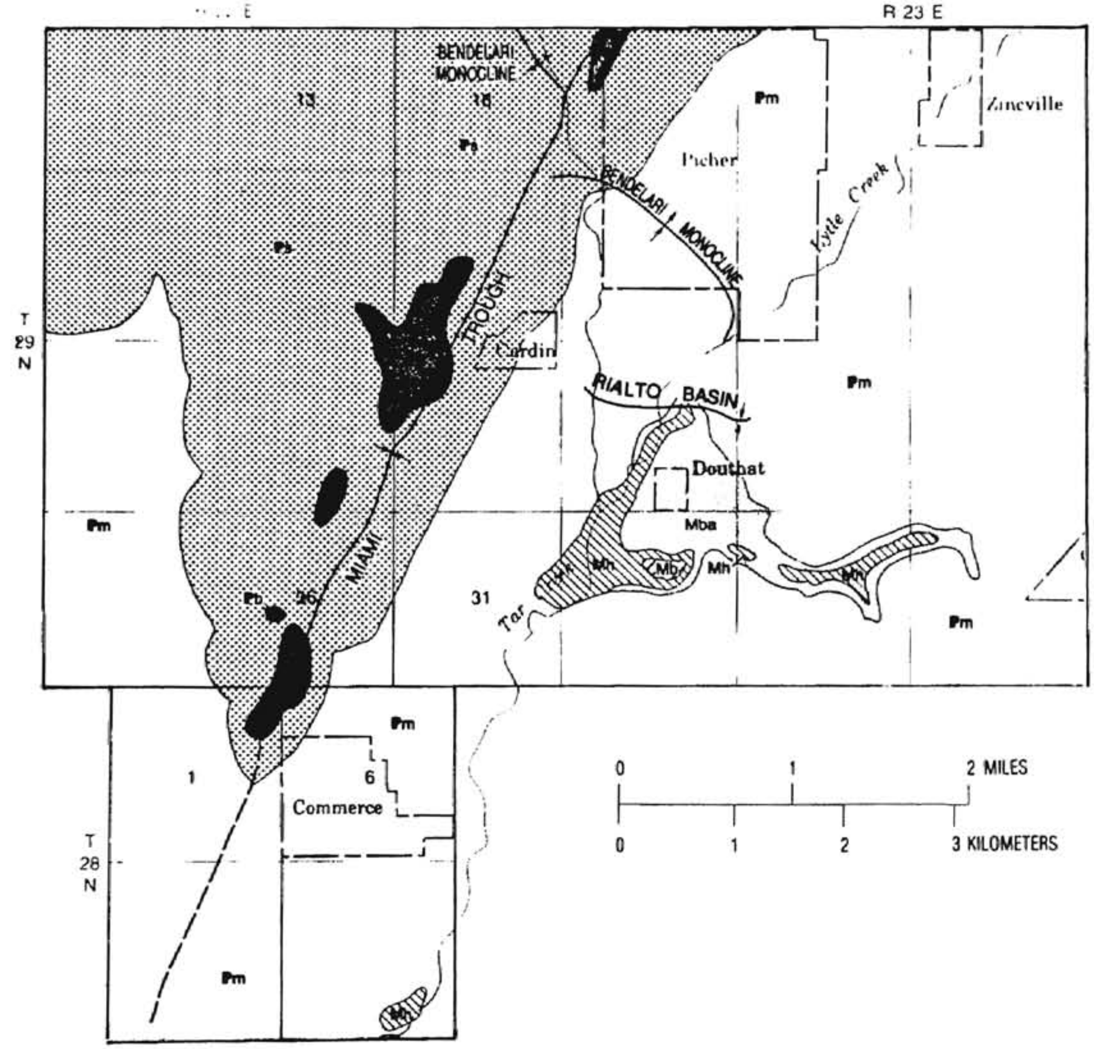
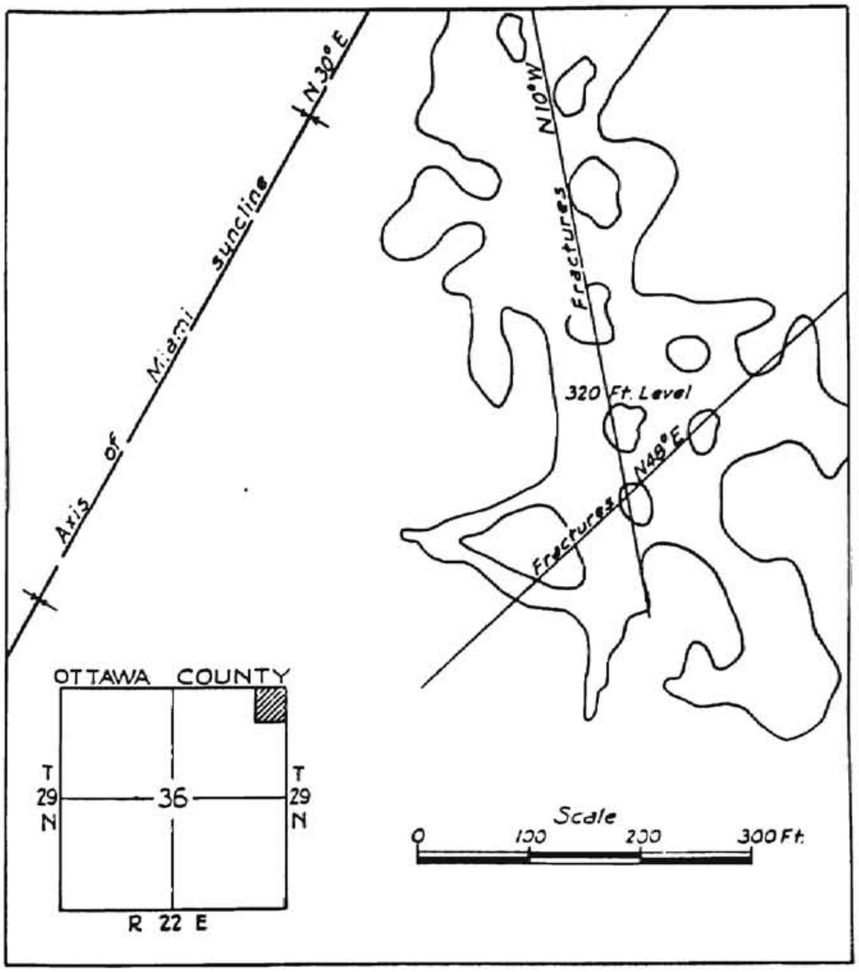


FIGURE 7

FRACTURE ORIENTATION ALONG THE MIAMI SYNCLINE



Map of S. S. and G. Mine showing relation of fractures to axis of Miami syncline.

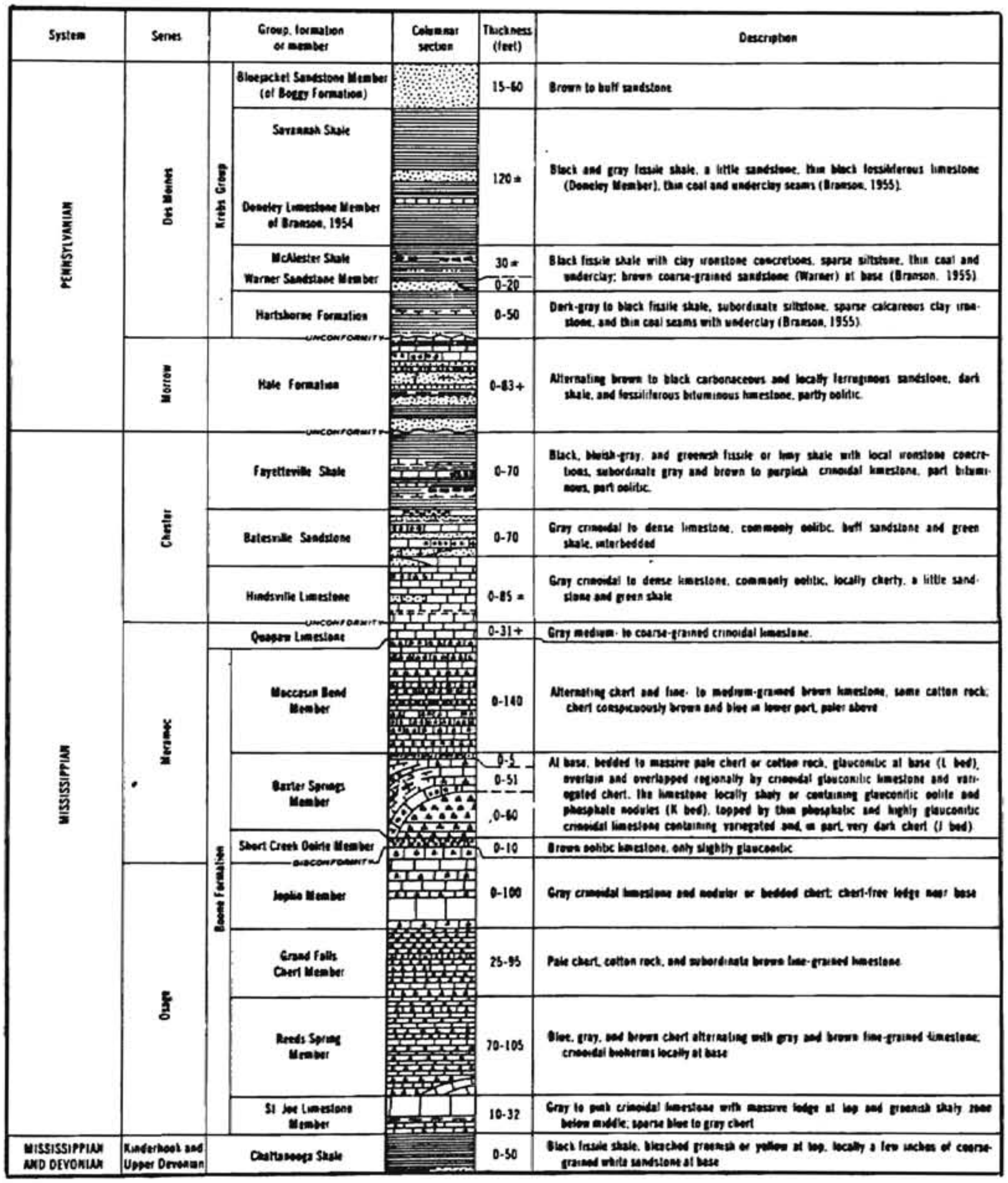
The individual members of the Boone Formation were all found to be productive of mineral ore in the Picher Mining Field especially where located near areas of intense fracturing where the mineral ore was concentrated in fractures, voids, cavities, or other related solution features (McKnight 1970), Figure 9. The members of the Boone Formation have been altered through the process of "chertification" resulting in replacement of original mineralization to hydrothermally deposited chert. This process further increased the brittleness of the host rock making it more susceptible to additional fracturing and subsequent fluid migration and eventual ore deposition (McKight 1970).

Several theories exist attempting to explain the origin of the ore deposits in the Mid-Continent Region of the United States (McKight 1970). The first theory is one of original syngentic deposition which is objected to based on the premise that syngentic deposition does not crosscut formations, faults, and ore beds contain fossils. The second theory attributes metamorphism as a vehicle for dispersed ore concentration however the Ozark Uplift if devoid of post-Pennsylvanian Age metamorphism. The third theory utilizes concentration of dispersed ore in sedimentary formations through circulating meteoric water moving downwards however this theory requires a Precambrian source which is lacking. The fourth theory reverses the third theory postulating minerals migration from lower sources upward through artesian water flow. The fifth and most widely accepted theory attributes the deposition of minerals from fluid migration from igneous rock sources hydrothermally. This holding is supported by the observed zoning of mineralized areas, high temperature requirements for mineral solution and transportation, and the similarity of mineral ores found in intrusive igneous ore deposits compared to those found in sedimentary settings (McKight 1970), (Tennissen 1974).

Following the hydrothermal deposition of the minerals the Picher Mining Field experience periodic structural flexure resulting in minor faulting, folding, and fracturing but on a significantly lesser order as evidenced in the preserved rock history. Due to the sealing nature of the overlying formations and the hydrothermally altered host rock, very

FIGURE 8

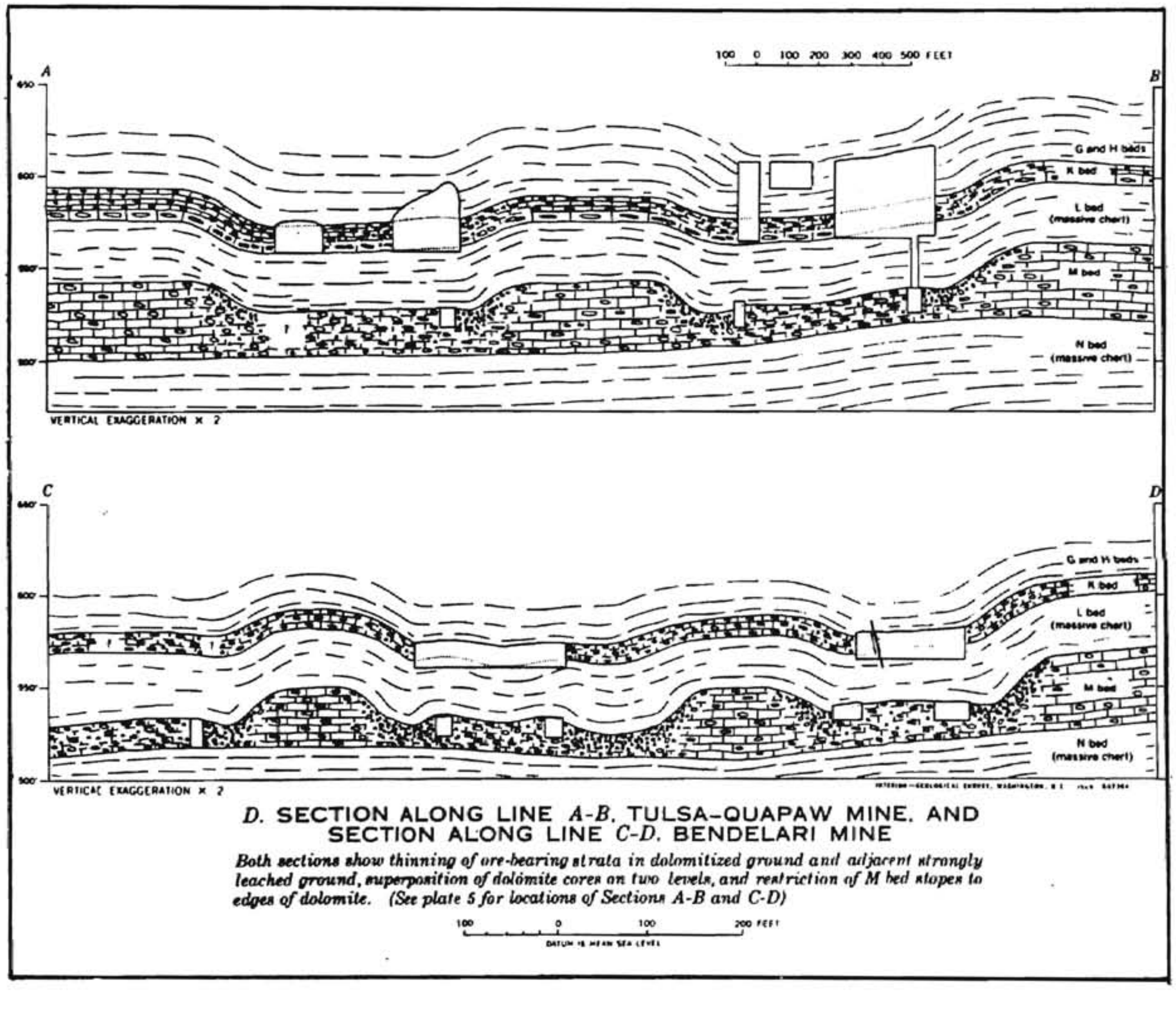
STRATIGRAPHY OF THE PICHER MINING FIELD



System	Series	Group, formation or member		Columnar section	Thickness (feet)	Description
PENNSYLVANIAN	Des Moines	Krebs Group	Bluejacket Sandstone Member (of Boggy Formation)		15-60	Brown to buff sandstone
			Savannah Shale Doneley Limestone Member of Branson, 1954		120 ±	Black and gray fissile shale, a little sandstone, thin black fossiliferous limestone (Doneley Member), thin coal and underclay seams (Branson, 1955).
			McAlester Shale Warner Sandstone Member		30 ± 0-20	Black fissile shale with clay ironstone concretions, sparse siltstone, thin coal and underclay; brown coarse-grained sandstone (Warner) at base (Branson, 1955)
			Hartshorne Formation		0-50	Dark-gray to black fissile shale, subordinate siltstone, sparse calcareous clay ironstone, and thin coal seams with underclay (Branson, 1955).
			UNCONFORMITY			
	Morrow		Hale Formation		0-83+	Alternating brown to black carbonaceous and locally ferruginous sandstone, dark shale, and fossiliferous bituminous limestone, partly oolitic.
			UNCONFORMITY			
MISSISSIPPIAN	Chester		Fayetteville Shale		0-70	Black, bluish-gray, and greenish fissile or limy shale with local ironstone concretions, subordinate gray and brown to purplish crinoidal limestone, part bituminous, part oolitic.
			Batesville Sandstone		0-70	Gray crinoidal to dense limestone, commonly oolitic, buff sandstone and green shale, interbedded
			Hindsville Limestone		0-85 ±	Gray crinoidal to dense limestone, commonly oolitic, locally cherty, a little sandstone and green shale
			UNCONFORMITY			
	Meramec		Quapaw Limestone		0-31+	Gray medium- to coarse-grained crinoidal limestone.
		Boone Formation	Moccasin Bend Member		0-140	Alternating chert and fine- to medium-grained brown limestone, some cotton rock; chert conspicuously brown and blue in lower part, paler above
			Baxter Springs Member		0-5 0-51 0-60	At base, bedded to massive pale chert or cotton rock, glauconitic at base (L bed), overlain and overlapped regionally by crinoidal glauconitic limestone and variegated chert. The limestone locally shaly or containing glauconitic oolite and phosphate nodules (K bed), topped by thin phosphatic and highly glauconitic crinoidal limestone containing variegated and, in part, very dark chert (J bed)
			Short Creek Oolite Member		0-10	Brown oolitic limestone, only slightly glauconitic
			DISCONFORMITY			
	Osage		Joplin Member		0-100	Gray crinoidal limestone and nodular or bedded chert; chert-free ledge near base
			Grand Falls Chert Member		25-95	Pale chert, cotton rock, and subordinate brown fine-grained limestone
			Reeds Spring Member		70-105	Blue, gray, and brown chert alternating with gray and brown fine-grained limestone; crinoidal bioherms locally at base
			St Joe Limestone Member		10-32	Gray to pink crinoidal limestone with massive ledge at top and greenish shaly zone below middle; sparse blue to gray chert
MISSISSIPPIAN AND DEVONIAN	Kinderhook and Upper Devonian		Chattanooga Shale		0-50	Black fissile shale, bleached greenish or yellow at top, locally a few inches of coarse-grained white sandstone at base

FIGURE 9

CROSS-SECTION OF THE BOONE FORMATION



D. SECTION ALONG LINE *A-B*, TULSA–QUAPAW MINE, AND SECTION ALONG LINE *C-D*, BENDELARI MINE

Both sections show thinning of ore-bearing strata in dolomitized ground and adjacent strongly leached ground, superposition of dolomite cores on two levels, and restriction of M bed stopes to edges of dolomite. (See plate 5 for locations of Sections A-B and C-D) little fluid migration took place in the ore bearing rock prior to mining operations. Subsequent erosion of post-Mississippian Age Formation has occurred to the present state.

The ore present in the Picher Mining District is composed primarily of zinc sulfide (dominant) and lead sulfide (subordinate) and are typically found in association with one another (McKnight 1970). The principal zinc mineral present is sphalerite (ZnS) which contains 67% zinc and 33% sulphur when in a pure state. Other zinc bearing minerals are smithsonite ($ZnCO3$) which contains 52.03% zinc when pure and calamine ($[ZnOH]2 SiO3$) which contains 54.2% zinc when pure (Weidman 1932). The principal lead mineral present is galena (PbS) which in a pure state contains 86.6% lead and 13.4% sulphur. Lead is also found in anglesite ($Pb SO4$) at a pure state level of 68.3% (Weidman 1932).

Other minerals of importance found in the Picher Mining Field are greenockite (CdS), pyrite ($FeS2$), marcasite ($FeS2$), melanterite ($FeSO4+7H2O$), calcopyrite ($CuFeS2$), and small traces of gauge minerals such as silver (Weidman 1932).

Field Site Historical Prospective

The discovery of ore near Joplin, Missouri in 1848 marked the discovery of the Tri-States Mining District which, once fully developed, covered an area approximately 125 miles east to west and 50 miles north to south (McKnight 1970). The richness of the ore bodies and need for raw materials led to the exploration for and development of ore deposits in the nearby surrounding areas of Missouri.

Subsequent exploration led to development mining operations extending westward into Kansas and in 1891 lead and zinc ore was discovered and mined at Peoria, Oklahoma, leading to the discovery of the Picher Mining Field at Lincolnville, Oklahoma in 1904 (Luza 1986). Further discoveries were made in 1905 near Commerce, Oklahoma which, with development mining, were soon recognized to be part of a large, fairly continuous mineral ore body covering over 2500 semi-contiguous acres in Oklahoma alone (Luza 1986).

The initial mining operations were carried out on the eastern side of the mineral ore body where the depth to the upper portions of the ore rock was from 90 to 130 feet below ground level (Wiedman 1932). Continuing development westward required deeper mining to reach the ore bearing beds.

With further exploration and development of the field, it was discovered that stratigraphically lower mineral bearing ore rock was present in the lower members of the Boone leading to some areas of the Picher Mining Field to have multiple working levels. Mature development of some mine resulted in drifts with over 100 feet of open work space from floor to roof attaining a total depth of over 450 feet below ground level (Luza 1986).

The mine field was developed in the following manner. Typically, cable tool drilling rigs were used to drill and core exploration holes to locate ore bearing strata. Often as many as 100 drill holes were drilled on a 40 acre tract to determine the parameters of the ore body (Weidman 1932). Once favorable indications were obtained, a mine shaft with roughly a 6 feet x 6 feet cross section was dug and timber cribbed to a depth 5 feet to 12 feet below the ore depth of the mine. This procedure created a support for the walls of the mine shaft as well as a sump for water collection and removal via pump (Wiedman 1932). A second auxiliary shaft was then dug usually about 300 feet from the mine shaft to aid with ventilation and other operations. Additionally, air shafts were drilled into mine drifts or stopes in larger mine operations.

Once the mine shafts were dug, the mining operation became horizontal usually in a radial pattern away from the shaft. This method is called stoping and involves mining by the room and pillar process in which a section of ore is removed by blasting and excavation while others are kept in place to support the roof of the mine in a checkerboard fashion (Wiedman 1932), Figure10.

During the early development of the Picher Mining Field small gauge rails systems were installed to move the mined ore rock from the drifts to the shaft in large buckets, typically by hand or mule teams Figure11, Figure 12. By the 1940's the underground rail system was replaced by low profile, diesel or electric powered prime movers in the larger mines, Figure 13. Once placed in the shaft, the buckets were mechanically hoisted to the surface by electric or steam powered drawworks where the ore was loaded into wagons, trucks, or later, railcars, and shipped to the processing mills located in the field, Figure 14.

From 1918 to 1945 the state of Oklahoma lead the nation in the production of zinc almost every year with the Picher Mining Field accounting for practically all of the mineral ore production in the state (Luza 1986), Table1. Since the discovery of mineral ore in Ottawa in 1891 through 1964, the last year of significant mineral ore production, the Picher Mining Field produced 1.766 million tons of lead and 7.283million tons of zinc (McKight 1970). The mines were for all intensive purposes abandoned in 1970 due to the low yield of the remaining ore, low prices, and foreign competition, Figure 15.

During the operation of the mines substantial quantities of water were encountered where mine drifts penetrated out of the low permeability mineralized borders of the ore rock formations, through mechanically incompetent well bores drilled to the lower Roubedoux aquifer, and by surface water migration through open shafts and boreholes. This required the installation of large capacity, acid resistant pumps be installed in the lower elevations of the mines to remove the water from the mines. During World War II, pumping operations from multiple lift stations in the Picher Mining Field were in excess of 13 million gallons per day. Upon abandonment of the mines all pumping operations were stopped which allowed the hydrostatic high-head contained in the surrounding Boone Formation, as well as surface inflow to begin filling the low hydrostatic head open mines. By 1979, the abandoned mines had filled with an estimated 76,000 acre-feet of water, over 54,000 acre-feet in the Oklahoma portion of the Picher Mining Field alone, and began discharging from several surface locations (Luza 1986). Because the mine shafts, drifts,

FIGURE 10

ROOM AND PILLAR MINING METHOD

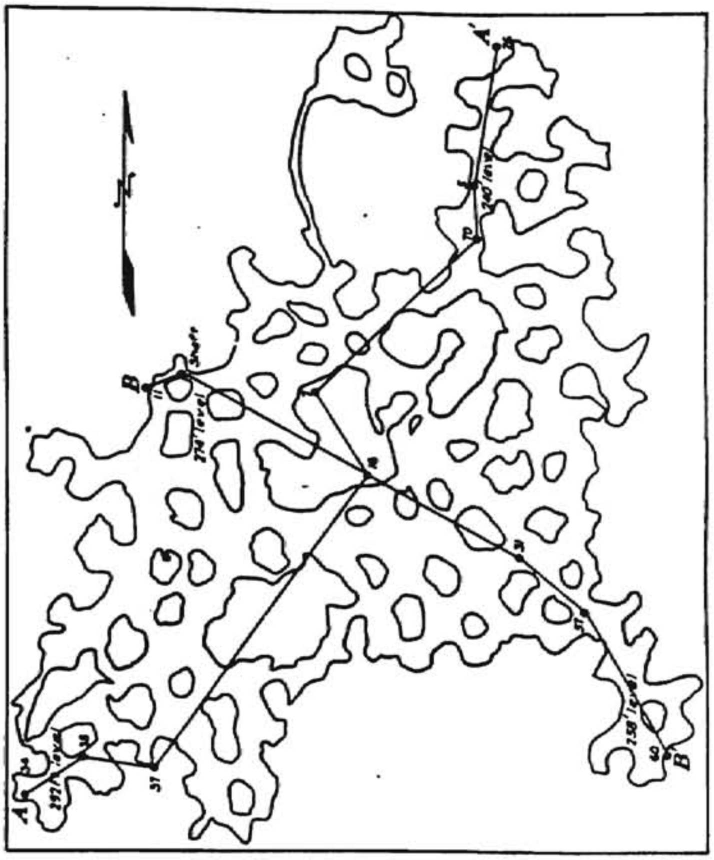


FIGURE 11

HAND LOADING ORE IN THE MINES

FIGURE 12

HAULING ORE BY MULE TEAMS

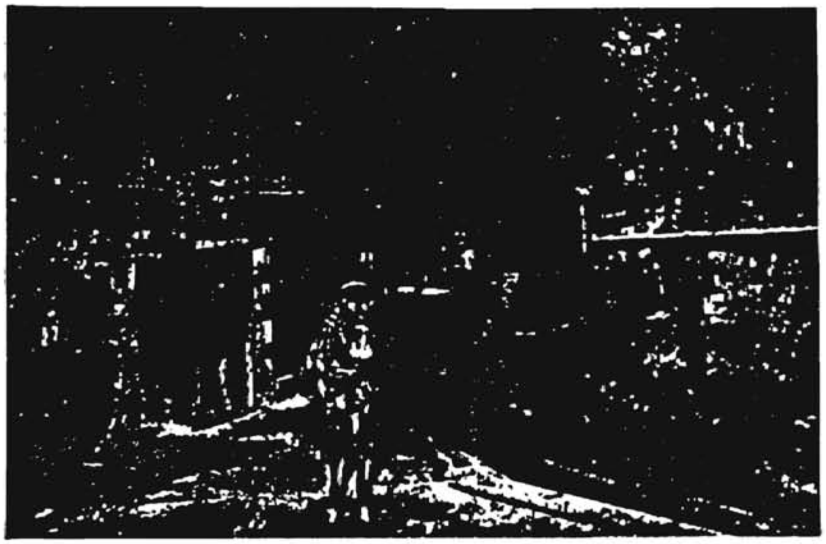


FIGURE 13

HAULING ORE BY ELECTRIC TRAIN

and boreholes provide excellent permeability avenues, any upgradient inflows of water are readily transported through the mines. The recharge and throughflow of water in the mines is continuous and migrates not only through the surface discharges but also through the groundwater aquifers, Figure 16. Currently, no effective means of stopping or containing the contamination has been implemented by the regulatory agencies of the State of Oklahoma or by the Environmental Protection Agency.

Further, the waters filling the mines interacted with and were contaminated by the now oxidized-reducing minerals and equipment left in the abandoned mines. High levels of lead, zinc, aluminum, sulfides, and lesser amounts of other heavy metals were found in the discharging mine waters which began threatening the surface and sub-surface waters supplies of the Picher Mining Field as well as down gradient receptive areas (Luza 1986), (Parkhurst 1988).

Another problem associated with the Picher Mining Field is collapse of abandoned shafts and drifts. The collapse of mine shafts is due to the incompetentcy of the post-Boone overlying strata which consists primarily of shales. In many instances the old cribbing timbers of the mine shafts were been remove or deteriorated to the extent that they are unable to support the walls of the shafts.

During the development of the Oklahoma portion of the Picher Mining Field over 1000 known mine shafts were dug. Field investigations conducted in 1986 found that at least 481 mine shafts remain open or are in a state of partial collapse (Luza 1986), Figure17. In the same study, 55 non-shaft related collapses were found and attributed to drift collapse. The possible cause of the drift collapse features was the practice of removal of roof supporting pillars known as stripping upon abandonment of a mine. Many sites in the old mining area have the potential to experience new or continued surface collapse events (Luza 1986).

FIGURE 14

MINE OPERATION NEAR PICHER, OKLAHOMA

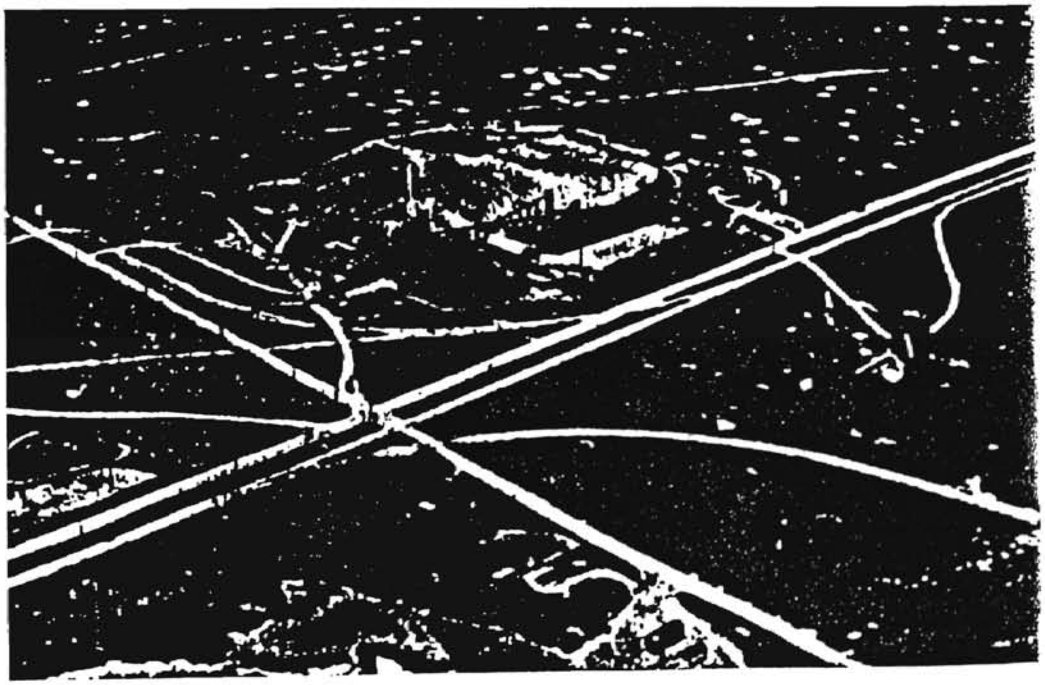


FIGURE 15

GRAPH OF ORE PRODUCTION, YIELD, AND PRICE

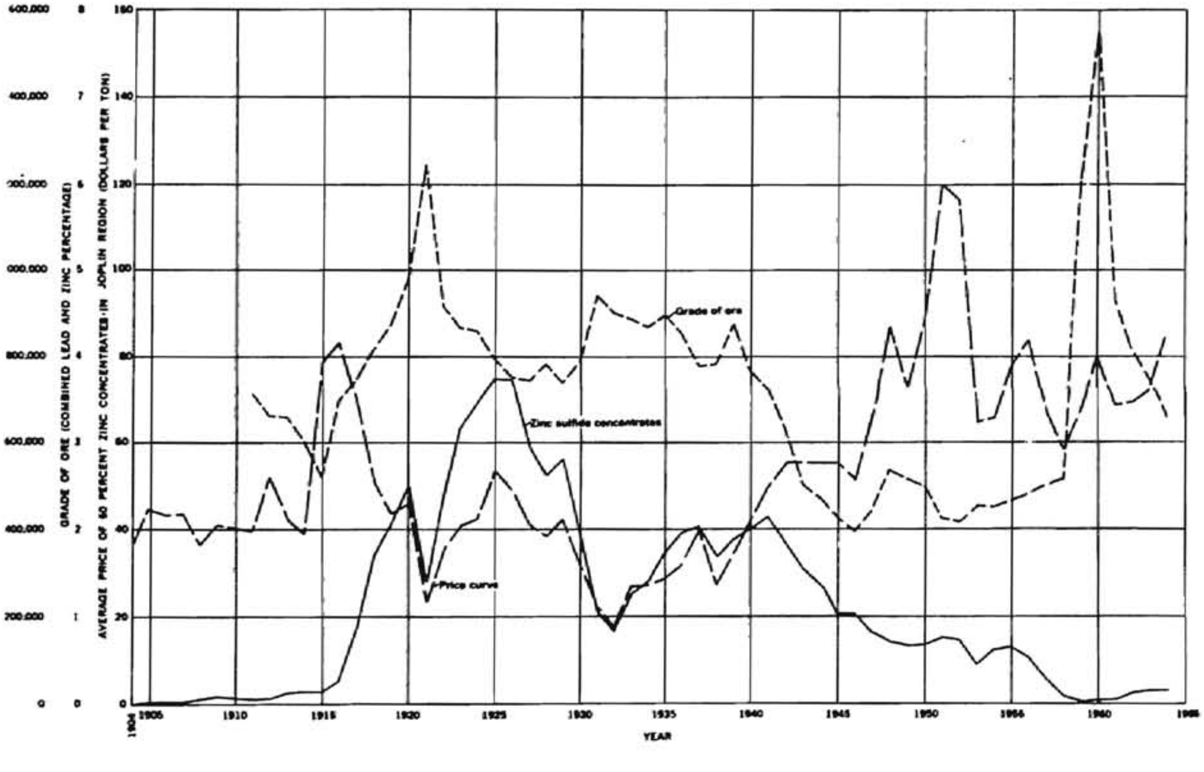
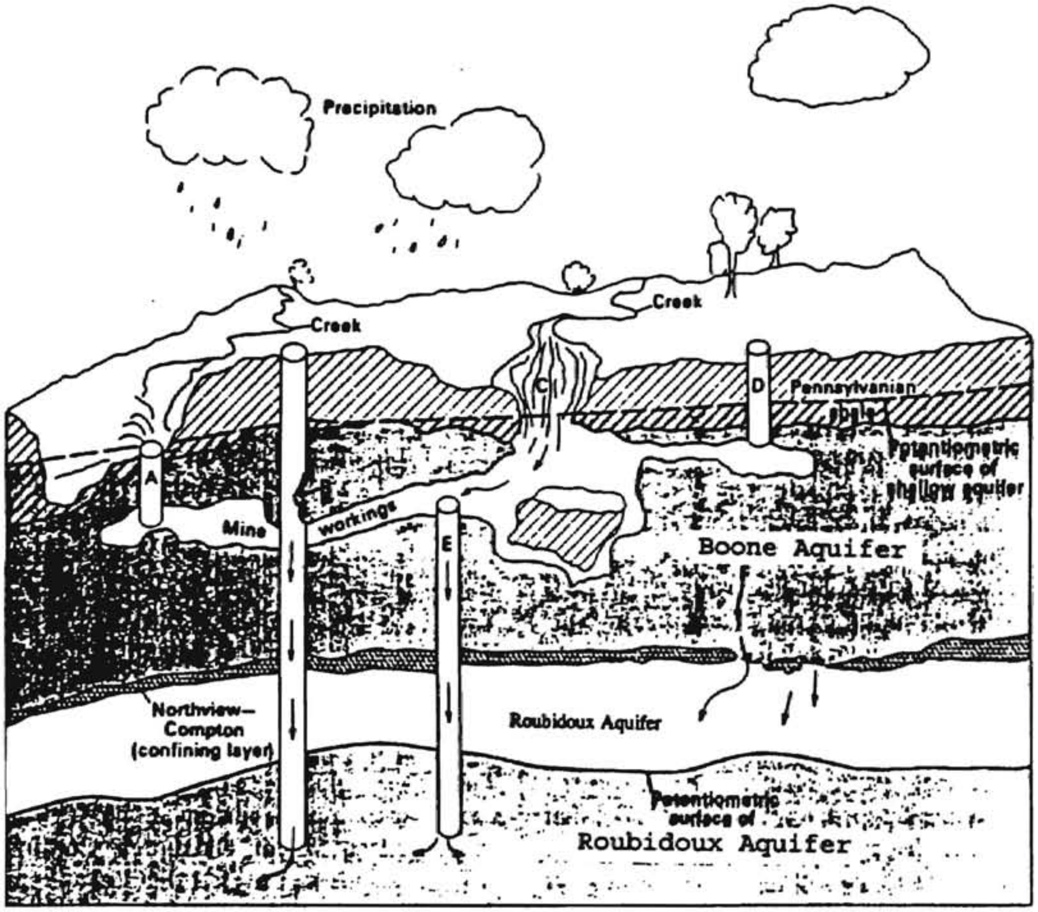


FIGURE 16

WATER DISCHARGE AND RECHARGE IN UNDERGROUND MINES



NOT TO SCALE

EXPLANATION

- A DRILL HOLE DISCHARGING TO CREEK—Bed below potentiometric surface
- B CORRODED CASING
- C WATER RECHARGING SHALLOW AQUIFER THROUGH COLLAPSE ON STREAMBED—Bed above potentiometric surface
- D DRILL HOLE ALLOWING RECHARGE TO SHALLOW AQUIFER
- E OPEN ABANDONED WELL
- F LEAKAGE FROM SHALLOW AQUIFER THROUGH BREAK IN CONFINING LAYER

TABLE I

ZINC AND LEAD PRODUCTION FROM THE PICHER MINING FIELD

Year	Concentrates		Recoverable Metal	
	Lead (tons)	Zinc (tons)	Lead (tons)	Zinc (tons)
1904	150	633	112	317
1905	566	2,670	422	1,334
1906	669	3242	498	1,624
1907	647	3,159	500	1,495
1908	2,234	10,033	1,726	4,404
1909	4,300	16,622	3,319	7,665
1910	3,634	13,976	2,798	6,305
1911	3,177	10,642	2,416	4,963
1912	4,257	11,881	3,286	5,627
1913	7,807	24,097	6,039	11,649
1914	9,402	28,367	7,329	13,990
1915	9,058	28,280	6,934	14,191
1916	15,206	54,932	11,777	28,498
1917	33,770	171,726	26,624	92,339
1918	77,487	341,175	60,924	183,434
1919	81,290	413,418	63,427	219,792
1920	101,285	502,134	79,755	270,610
1921	74,580	278,331	59,977	149,623
1922	108,510	482,970	85,628	260,119
1923	107,496	633,035	84,045	332,224
1924	113,363	690,809	88,074	361,073
1925	130,410	749,254	99,998	387,890
1926	124,361	744,028	95,832	382,683
1927	99,524	591,447	76,404	303,298
1928	87,238	527,495	67,406	271,116
1929	91,087	562,371	69,699	290,375
1930	45,492	394,459	34,291	204,363
1931	24,565	218,689	18,990	115,569
1932	21,130	167,725	16,461	89,686
1933	30,820	248,933	23,643	131,761
1934	30,222	276,887	23,250	145,900
1935	44,715	344,927	34,035	182,300
1936	48,545	391,383	36,778	206,974
1937	59,906	403,783	45,799	214,080
1938	47,461	335,927	36,200	182,463
1939	53,654	379,435	41,396	206,598

1940	43,290	400,647	33,131	217,028
1941	51,301	429,660	39,391	233,173
1942	41,942	369,043	32,146	198,931
1943	38,536	310,980	28,851	166,850
1944	29,952	275,220	22,817	148,125
1945	25,813	206,580	19,043	111,486
1946	25,880	206,764	19,800	111,558
1947	27,805	164,574	21,104	88,634
1949	38,785	134,513	28,787	71,895
1950	39,073	137,275	29,910	73,701
1951	34,468	152,853	25,474	82,333
1952	28,010	148,488	20,887	80,229
1953	16,608	90,541	12,649	48,917
1954	24,394	123,340	18,237	62,281
1955	26,917	129,978	19,624	69,154
1956	28,101	106,135	19,985	56,180
1957	15,901	56,891	11,440	30,810
1958	7,041	18,001	4 ,991	9,688
1959	1,607	4,061	1,082	2,068
1960	3,098	8,877	1,717	4,449
1961	3,243	10,666	2,429	5,594
1962	4,890	25,564	3,680	13,956
1963	5,719	30,762	4,219	16,753
1964	5,333	31,228	3,966	16,824
Total	2,298,117	13,774,945	1,766,266	7,282,668

Minerals and coal mining operations have long been known to have the potential to produce acidic conditions in operational area waters and soils where the presence of soluble sulfides interact with oxygen and water (Finney 1993), Figure 18. The hydrothermal deposits found in the Picher Mining Field contain, among other minerals, pyrite and marcasite in great abundance. These sulfide minerals are commonly found in association other hydrothermally generated minerals such as those found in the mineral ore beds of the Picher Mining Field, especially galena, sphalerite, and chalcopyrite as shown on Table 2.

Pyrite and marcasite are polymorphs composed of iron sulfides which, by their nature contain more sulfur than is required to produce iron salts such as $FeSO_4$ (Tennissen 1974), (Finney 1993). The iron sulfides in the mines initially become oxidized as a result of their exposure to atmospheric oxygen during the mining process and are further oxidized through by the presence of water. This reaction creates acid in the water filled mines by producing two moles of sulfur or sulfur dioxide for every one mole of ferrous iron produced. Thus an unattached mole of free sulfur is released to hydrolyze with the oxygen and eventually form sulfuric acid by the following equation (Tennissen 1974), (Bhumbla 1987).

$$FeS_2 + 3.5\,O_2 + H_2O = Fe^{2+} + 2\,SO_4^{2-} + 2H^{+} \tag{1}$$

$$Fe^{2+} + 0.25\,O_2 + H^{+} = Fe^{3+} + 0.5\,H_2O \tag{2}$$

$$Fe^{3+} + 3\,H_2O = Fe(OH)_3 + 3\,H^{+} \tag{3}$$

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O = 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^{+} \tag{4}$$

Or more simply, the sulfuric acid producing reaction resulting from the oxidation of pyrite-marcasite minerals may be expressed as (Bowders 1991).

$$FeS_2\,(s) + 3.75\,O_2 + 3.5\,H_2O \rightarrow 2H_2SO_4 + Fe(OH)_3\,(s)$$

FIGURE 17

MINE SHAFTS, PITS, AND COLLAPSE FEATURES IN THE PICHER AREA

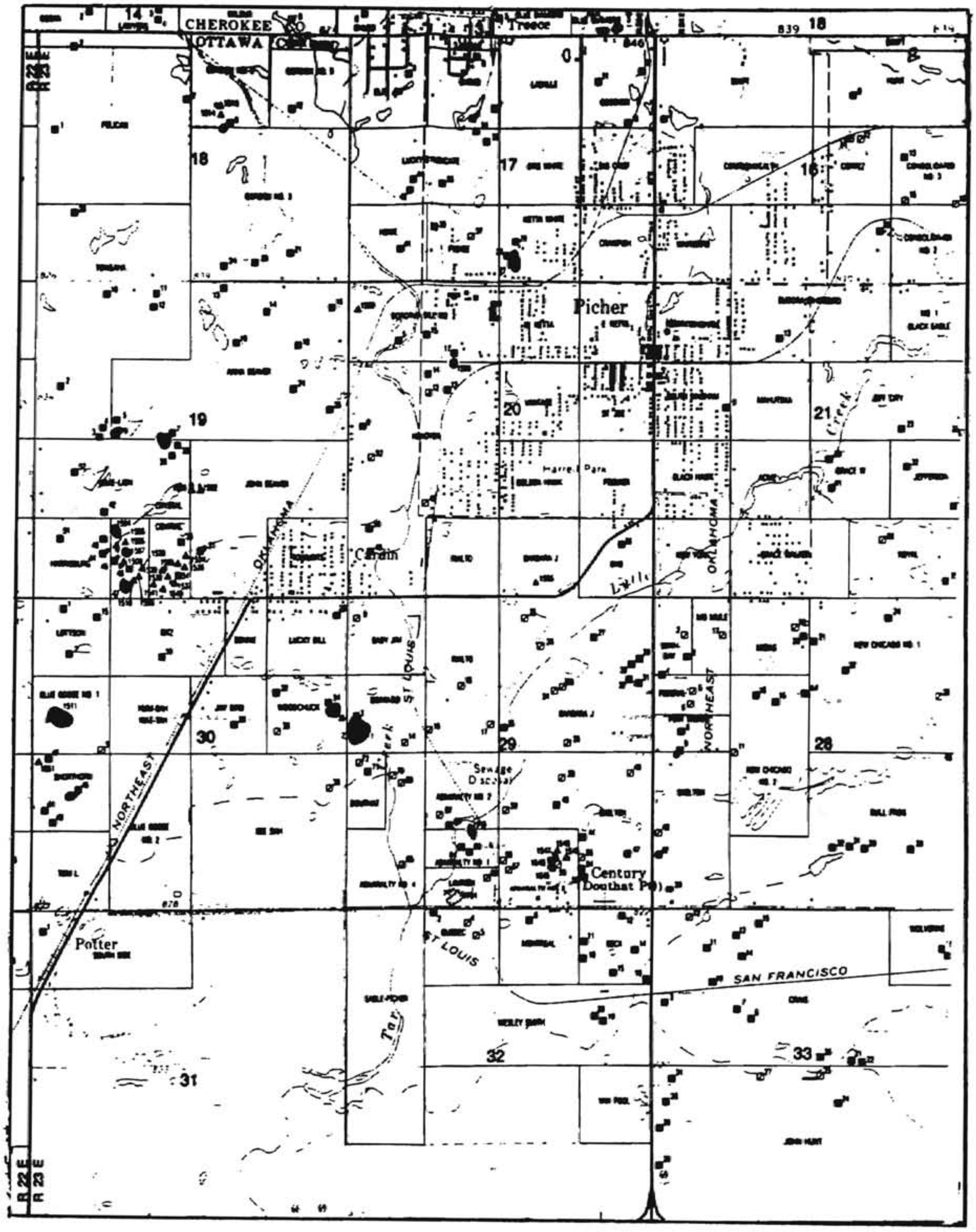
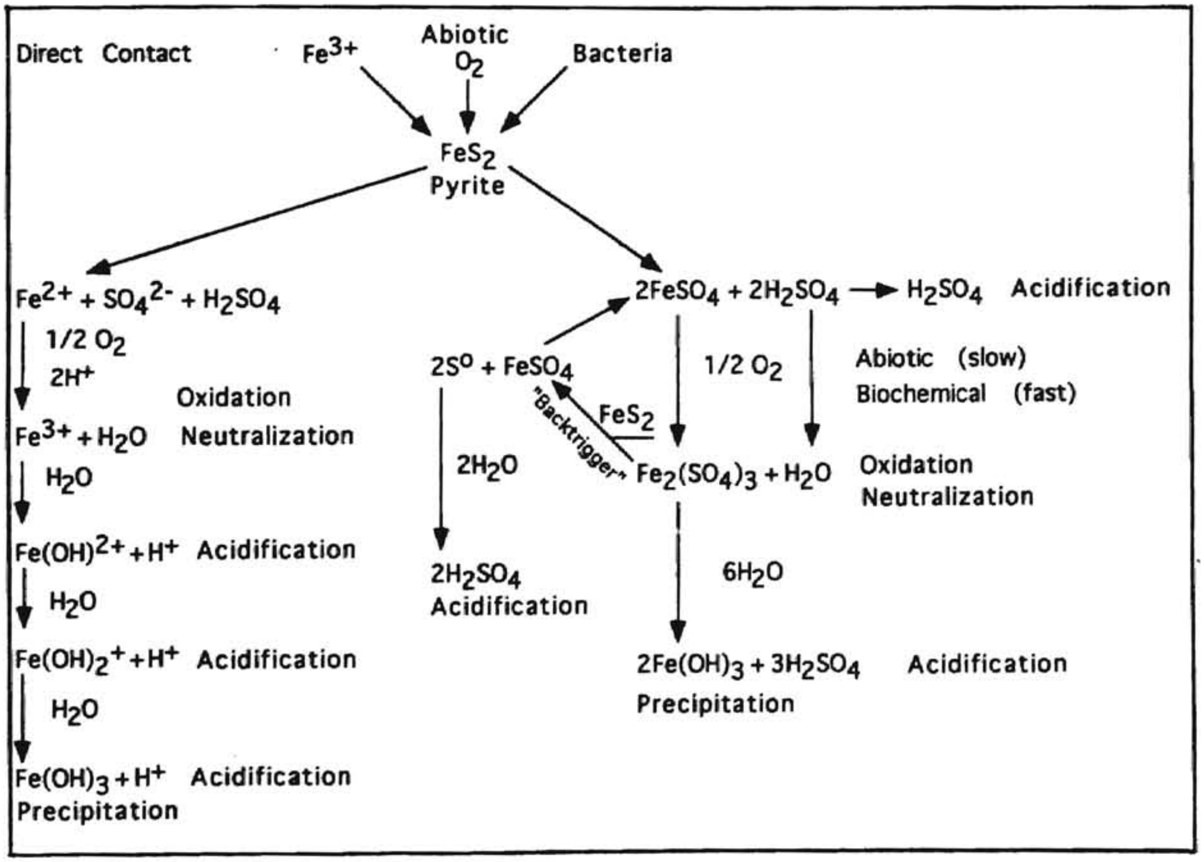


FIGURE 18

ACID PRODUCTION



Sympathetically, once the initial stage of acidification of the iron sulfides begins, the process self-accelerates as iron sulfides more readily oxidize in acidic environments leading to greater acidic conditions. Additionally, ferric salts combined with oxygen hydrolyze to form an insoluble ferric hydroxide further increasing acid production on the ratio of three moles of sulfuric acid to two moles of ferric hydroxide (Finney 1993).

The discharge waters of the mines which reaches the surface undergoes a second stage of acidifiction. Once these discharging waters come in contact with the atmosphere, the ferrous iron remaining in solution is oxidized to form ferric iron which, with the ferric sulfate in the solution, is hydrolyzed to form ferric hydroxide (Finney 1993), (Kent 1987). For each mole of ferric sulfate three moles of sulfuric acid are produced as expressed in the following equation (Kent 1987).

$$\mathrm{Fe(2+)} + 1/4\ \mathrm{O2} + \mathrm{H(+)} = \mathrm{Fe(3+)} + 1/2\ \mathrm{H2O} \qquad 1.$$

$$\mathrm{Fe(3+)} + \mathrm{H2O} = \mathrm{Fe(OH)(2+)} + \mathrm{H(+)} \qquad 2.$$

$$\mathrm{Fe(OH)(2+)} + \mathrm{H2O} = \mathrm{Fe(OH)(2+)} + \mathrm{H(+)} \qquad 3.$$

$$\mathrm{Fe(OH)(2+)} + \mathrm{H2O} = \mathrm{Fe(OH)3} + \mathrm{H(+)} \qquad 4.$$

Trace Metals Production

The production of sulfuric acid in the abandoned mines resulting from the iron sulfides-oxygen-water inter-reaction creates an environment in which the stable sulfide ore minerals are degraded through oxidation and become soluble. This reaction results in the release of zinc, lead, copper, and iron through ferric iron oxidation of sulfide minerals and the release of multiple trace metals through chemical oxidation processes (Finney 1993), Figure 19.

The primary minerals found in the Picher Mining Field are galena (lead sulfide), sphalerite (zinc sulfide), pyrite (isometric iron sulfide), marcasite (orthorhombic iron sulfide), chalcopyrite (copper-iron sulfide), calcite (calcium carbonate), and dolomite (calcium-magnesium carbonate), as well as chert (silica dioxide). Lesser minerals also present are enargite (copper-arsenic sulfide), barite (barium sulfate), anglesite (lead sulfate), smithsonite (zinc carbonate), luzonite (copper-arsenic sulfate), greenockite (cadmuim sulfide), and wuzite (zinc-iron sulfide) (Finney 1993), (Wiedman 1932).

The mineral ores composed of galena and sphalerite also contain the trace elements of iron, silver, germanium, gallium, indium, cobalt, mercury, copper, cadmium, lead, and antimony (Finney 1993). Mineral ores with marcasite, pyrite, and chalcopyrite have the trace elements of nickel, silver, copper, and cobalt present (Finney 1993). These mineral ores and their composite members are considered to be stable within undisturbed, below groundwater environments where oxidation is lacking. However, in disturbed ore bodies where oxidation through atmospheric and water sources is present, not only do the principal minerals become soluble but the trace elements may be leached from the ore rock, contaminating insitu waters with heavy metals, and may create secondary minerals such as gypsum, smithsonite, anglesite, greenockite which form as surface coatings (Finney 1993). Goslarite, melanterite, and copiapite are secondary minerals which form as efflorescence during dehydration of the mine waters (Finney 1993).

Due to the dissolution and leaching of the minerals and trace elements by the sulfuric acid-oxidation process in the mines, high levels of these minerals and elements have been found in subsequent water sampling. Periodic water sampling from the mines, discharge points, and on receiving surface waterbodies for parameters such as pH, specific conductance, hardness, calcium, magnesium, sulfate, trace metals, and total dissolved solids have been undertaken and reveal the presence of these contaminates in varying concentrations in differing localities. The greatest contamination levels are found in the lower levels of the mines where the acid generation and subsequent dissolution processes are the greatest (Finney 1993). Because the upgradient hydraulics of the surface and groundwater is positive into the mines, this highly polluted water will continue to be

FIGURE 19

OXIDATION OF SULFIDE MINERALS AND THE RELEASE OF ASSOCIATED TRACE METAL

Ferric Iron Oxidation

Sulfide minerals:

$$Fe^{3+} + MS + 4H_2O = FeSO_4 + 8H^{+} + M^{2+}$$

where M is Zn, Pb, Cu, or Fe

Chemical Oxidation

Sphalerite: $ZnS + 2O_2 = ZnSO_4$

releasing -> (Fe, Ag, Ge, Ga, In, Co, Hg, Cu, Cd, Pb)

Galena: $PbS + 2O_2 = PbSO_4$

releasing -> (Ag, Sb, Cu, Fe)

Chalcopyrite: $CuFeS_2 + 4O_2 = FeSO_4 + CuSO_4$

releasing -> (Ni, Ag, Cu)

Marcasite: $2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$

releasing-> (Ni, Co)

TABLE II

PRINCIPLE MINERALS OF THE PICHER MINING FIELD

Major Minerals:

Sulfates
- sphalerite
- galena
- chalcopyrite
- marcasite
- pyrite

Carbonates
- calcite
- dolomite

Silicates
- chert

Minor Minerals:

Native Elements
- Sulfur

Sulfides
- bornite
- wurtzite
- greenockite
- millerite
- covellite

Sulfosalts
- enargite
- luzonite

cerussite
aurichalcite
geothite
hemaitite

Sufates
- barite
- anglesite
- gypsum
- starkeyite
- chalcanthite
- melanterite
- epsomite
- goslarite
- linarite
- jarosite
- plumpojarosite
- aluminite
- coppiapite
- caledonite
- szomolnokite
- carphosiderite

Carbonates
- smithsonite
- arogonite
- hydrozincite
- malachite
- azurite
- leadhillite

Oxides
- cuprite
- pyrolusite

Silicates
- hemimorphite
- allophane
- chrysocolla
- kaolinite
- glauconite

Arsenates
- picropharmacolite
- mimetite

Phosphates
- vivianite
- apatite
- pyromorphite
- wavellite
- diadochite

(Wolf 1993)

pushed out of the downgradient orifices of the mines perpetuating the contamination. The estimate has been made that the water contained in the mine drifts has a 22 year residence time and that discharge from the mines is approximately 3400 acre-feet per year.

Natural Acid Neutralization

The mineral ore bodies of the Picher Mining Field are contained principally within brecciated cherts and chertified brecciated dolomites of the members of the Boone Formation (Wiedman 1932). Therefore the composition of the Boone Formation in the highly mineralized ore body zones consists primarily of silica based minerals which have little or no acid neutralization capacity. The surrounding country rock and overlying formations can and do contain beds of limestone, dolomite, and alterations thereof which have the capacity to react with the sulfuric acid generated in the mines when the low pH waters migrate from the mines and come in contact with these carbonate beds or with waters which have high dissolved calcium contents (Finney 1993), (McKnight 1970). However, the magnitude of the acid generation and lack of substantial carbonate beds along the path of fluid migration downgradient from the mines has resulted in low neutralizations.

The sulfuric acid generated by the mines may be controlled by direct contact with calcite in the following manner.

$$H_2SO_4 + CaCO_3 = Ca^{2+} + SO_4^{2-} + H_2CO_3$$

This buffering action results in the increase of Ca^{2+} and SO_4^{2-} to the extent that the solution becomes supersaturated with respect to gypsum and begins to precipitate gypsum which in turn regulates the concentrations of Ca^{2+} and SO_4^{2-} in the solution (Finney 1993). This creates a solution in which the H_2CO_3 becomes the primary carbonate present. Once the concentration of H_2CO_3 reaches the saturation point of the solution, carbonic acid dissociates and H_2O and CO_2 gas are released in the following manner (Finney 1993).

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2$$

Thus, although the acidic solutions generated and discharged by the mines are eventually neutralized by carbonates, this occurs far down gradient from the abandoned mine works area in the Neosho River (Finney 1993), Figure 20. As a result, all the downgradient water resources between and including the Picher Mining Field and the point of neutralization in the Neosho River are being adversely impacted by low pH and heavy metals in solution in the discharge waters from the mines due to a lack of buffering capacity in the near source environment.

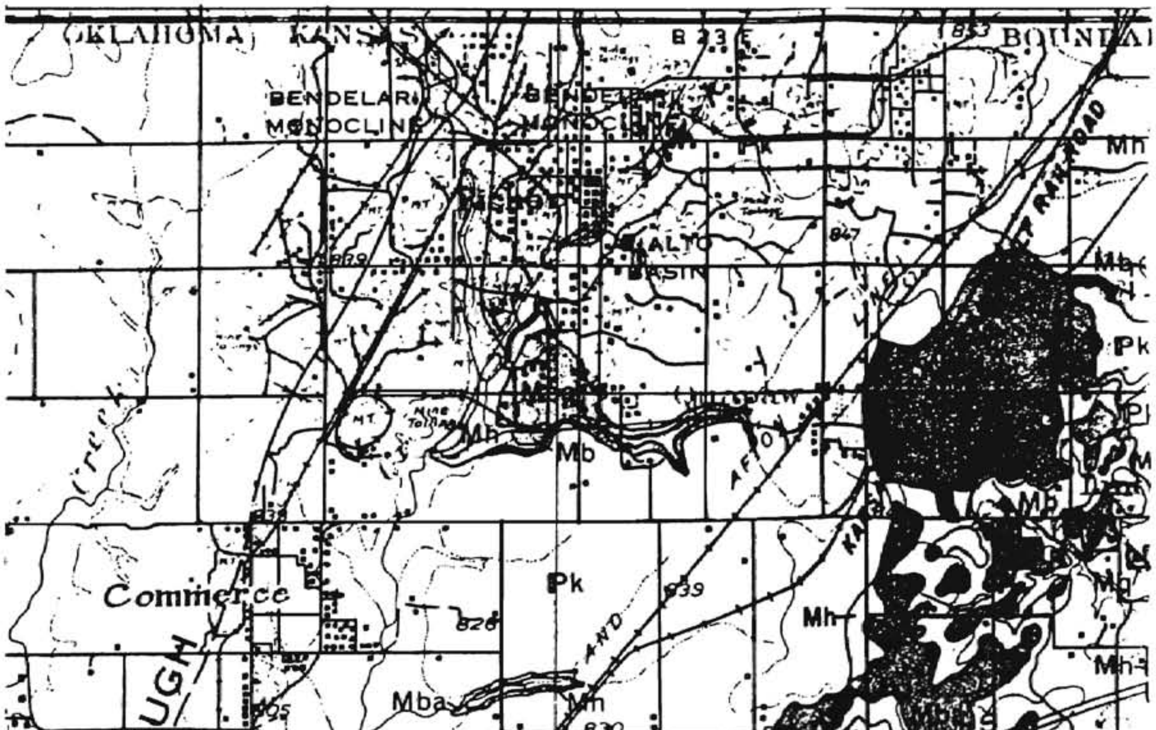
Fly Ash Properties

Coal fly ash is the inorganic, microscopic particulate residual material remaining after the combustion burning of coal. This material is collected and removed from the exhaust gases in the emission control stacks of modern coal-fired industrial plants such as coal-fired electric generation facilities. Currently, the American Society of Testing Materials (ASTM) identifies two broad classes of coal fly ash; "C" class coal fly ash and "F" class coal fly ash (Kosmatka 1988).

Volumetrically and by proportional bulk mass, silica is the dominant mineral component of all classes of coal fly ash. The ASTM requires class "C" coal fly ash to have pozzolans, compounds consisting of silicon, aluminum, and iron oxides, occupy 50% to 69% by weight of the total weight of the coal fly ash. Class "C" or "cementitious" coal fly ash is composed of from 10% to 40% (typically 20%) by weight of total weight, calcium.

FIGURE 20

GEOLOGIC FORMATIONS ON THE SURFACE
OF THE PICHER AREA



The calcium is present in the form of calcium carbonate (CaCO3) which conveys to the coal fly ash the capacity to develop a self induced pozzolanic set in the presence of water. The high calcium content of class "C" coal fly ash also acts to provide compressive strength and stabilization to the material set in addition to a high buffering or acid neutralization capacity (Baldwin 1993), (Bhumbla 1987). Sources of low sulfur, low trace metals content parent coals from which class "C' coal fly ash is derived are found in great abundance in the United States especially in the Powder River Basin and Uinta Basin in the northern Rocky Mountains region.

Class "C" coal fly ash is being utilized for industrial applications in increasing amounts (Baldwin 1993). In 1990, 25.4% of all domestically produced coal fly ash in the United States was constructively utilized (Novavinakere 1993). An example of a typical class "C" coal fly ash obtained from samples collected and analyzed from the Ottumwa Generating Station located in Ottumwa, Iowa for the years 1983 and 1984 is shown on Table 3. The parent coal was a sub-bituminous, low sulfur coal mined from the Codero Mine in the Powder River Basin of Wyoming (Zimmerman 1985).

Class "F" or non-cementitious coal fly ash contains significantly lower amounts of calcium and higher amounts of the associated pozzolans of silica, aluminum, and iron oxide than class "C" coal fly ash. ASTM specifications for class "F" coal fly ash maintain that at least 70% by weight of the total weight of the coal fly ash must be comprised of the associated pozzolans. Abundant reserves of class "F" coal fly ash are found in the United States east of the Mississippi River (Baldwin 1993). Examples of "typical" class "F" coal fly ash ASTM specifications are on Table 4.

The properties of both classes of coal fly ash are directly related to the parent coals composition, location, depositional environment, lithification, diagenisis, and subsequent weathering. Further, the composition of the coal fly ashes can be modified by the extraction methods used, country rock inclusions associated with the mined coal, combustion technology employing the parent coal, operating temperatures in the combustion chambers, additives, scrubbing or collection mechanisms, transportation, and storage of the coal fly ash all influence the characteristics of the material and should be considered where applicable.

Many compounds, minerals, and elements compose the lesser constituent fractions of coal fly ash. In certain instances, coal fly ash may contain up to 5% by weight, non-combusted carbon particles. Aluminosilicates consisting of muscovite, illite, and kaolinite which are often found in association with the parent coal provide a source of potassium content for the coal fly ash. Muscovite by weight contains 11% and illite by weight contains 5% to 6% potassium as potassium oxide (K_2O) and are expressed as follows.

$[K_2O * 2Al_2O_3 * 6SiO_2 * H_2O]$ Muscovite
$[2K_2O * 3(Ca,Mg,Fe)O * 8Al_2O_3 * 24SiO_2 * 12H_2O]$ Illite

Potassium minerals are vitrified in the combustion process with a small fraction of potassium vaporized and converted to sulfates. In the presence of chlorides, the potassium-sodium ionic exchange reacts to form potassium chloride. In the presence of sodium, sodium chloride may be formed. The sulfates occurring in the greatest abundance are potassium sulfate (K_2SO_4) and sodium sulfate (Na_2SO_4). These compounds are found as sub-micronic size particles located on the surface of the coal fly ash particles. The formation process attributed to these compounds is the vaporization of alkali metals in the combustion process which are then captured at the surface of the silicate particles which are low in alkalinity. Hence, the alkali material present as oxides are sulfated by sodium dioxide (SO_2), and sodium trioxide (SO_3) as expressed in the following equations.

$$[SiO_2 + 2NaCl + H_2O \text{-->} SiO_2 * Na_2O + 2HCl]$$
$$[SiO_2 * Na_2O + SO_3 \text{-->} SiO_2 + Na_2SO_4]$$

TABLE III

OTTUMWA GENERATING STATION FLY ASH ELEMENTAL ANALYSIS

Average of 1983 and 1984 Sampling

OXIDE	AVERAGE	STD. DEV.	(MIN.	RANGE	MAX.)
SiO2	34.9%	1.4%	32.2%		38.2%
Al2O3	18.9%	0.9%	17.9%		20.5%
Fe2O3	5.18%	0.15%	4.82%		5.34%
CaO	24.0%	0.9%	22.3%		25.4%
MgO	4.72%	0.24%	4.39%		5.26%
SO3	1.99%	0.41%	1.37%		2.88%
P2O5	1.66%	0.32%	0.94%		2.23%
K2O	0.40%	0.04%	0.36%		0.48%
Na2O	2.36%	0.34%	1.56%		2.78%
TiO2	1.40%	0.07%	1.28%		1.54%

Analysis does not include elements with concentrations of less than 100ppm.

TABLE IV

EXAMPLES OF "TYPICAL" CLASS "F" COAL FLY ASH ASTM SPECIFICATIONS

COAL FLY ASH	#1	#2	#3	#4
CaO	6.69%	2.2%	1.53%	7.48%
SiO2	55.1%	48.3%	44.1%	48.9%
Al2O	12.1%	19.4%	19.6%	22.8%
MgO	1.61%	0.73%	0.70%	1.54%
Na2O	1.73%	2.12%	0.33%	2.86%
K2O	1.24%	------	2.39%	0.67%
Fe2O3	5.16%	11.8%	21.5%	6.09%
SO	0.52%	0.56%	0.77%	0.30%
LOI	0.62%	2.33%	4.93%	0.54%

Iron and iron oxides (Fe2O3) are found in most coals, hence, most coal fly ashes to one degree or another. These are generally the result of iron sulfides inclusions such as pyrite and marcasite or may be the result of the inclusion of siderite. Comparatively, the fly ashes derived from coals from the northern Rocky Mountains have a total sulfur content of approximately 2% whereas coal fly ashes from interior coals contain 7% sulfur.

Magnesium or magnesium oxide (MgO) is typically found in concentrations of between 2% and 5% in coal fly ashes, especially where the parent coal is associated with dolomitic country rocks which act as inclusions in the coal.

Various trace metals are also present in most fly ashes. However, the coal fly ash derived from the burning of coals found in the northern Rocky Mountains contain the contaminants listed as toxic under the Resource Conservation and Recovery Act (RCRA) such as arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver in such small quantities that they generally pose no discernible threat to the environment even though they may eventually be leached from the coal fly ash (Pflughoeft-Hassett 1987). Other trace elements which may be found in coal fly ash are boron, cobalt, copper, manganese, molybdenum, nickel, vanadium, yttrium, zinc, zirconium, and titanium dioxide (Pflughoeft-Hassett 1987).

There are four general chemical affiliations in coal fly ash. The first chemical affiliation is between the leachable fractions in which metals may be solublized in water or occur in ionic exchange phases, and include the carbonate mineral species and the amorphous oxides. The second chemical affiliation is between the H2O2 extractable fraction of metals which are related to the sulfide minerals and organic material present in coal fly ash. Third, the reducible fraction consisting of metals associated with various oxides and amorphous oxides. The fourth chemical affiliation is between the residual fraction composed of metals that remain in the lattice structure (Wu 1980).

Because the residual fraction is stable under most conditions in nature precluding it from dissolution, the elements of that fraction tend to pose a low risk to the environment.

In contrast, the H2O2 extractable fraction which is non-residual and leachable together with the reducible fraction both may be subject to conditions in nature which result in their deterioration. As a consequence, these fractions have the potential to adversely effect the environment relative to the function of the toxicity levels, concentrations, and environmental settings to which exposure occurs (Wu 1980). However, these fractions are generally present in such minute amounts in the coal fly ash derived from the Powder River Basin and Uinta Basin coals that the trace elements have no impact on the environment.

The elements present in coal fly ash may be divided into four geochemical classifications. Class I, is composed of lithophiles or elements which have the potential of having greater free energy of oxidation per unit mass of oxygen per mass of oxygen than the same unit mass of iron which occurs as an oxide or an oxysalt. The elements of aluminum, barium, beryllium, calcium, cobalt, iron, potassium, magnesium, manganese, silicon, strontium, and titanium, all associated with aluminosilicate minerals commonly found in coal fly ash (Wu 1980). The class I elements are characteristic of having stability in the combustion process and have high boiling points.

The Class II elements are known as calcophiles and are represented in the coal fly ash as sulfides. The elements of arsenic, cadmium, copper, gallium, lead, antimony, zinc, and selenium comprise this group. As sulfides, these elements are readily decomposed (Wu 1980).

Mercury, chlorine, bromine, and fluorine are the elements which make up the Class III geochemical group. These elements rarely occur in more than trace concentrations, are unstable in the combustion process, and are easily volatilized and decomposed (Wu 1980).

The Class IV elements occurrence is extremely rare in coal fly ash. Typically, the elements composing the group, chromium, cesium, nickel, uranium, and vanadium exhibit the same properties as the Class I or Class II elemental groups. Because the elements found in the Class II and Class III geochemical groups have a low boiling point compared to the Class I elements, the Class II and Class III elements are more easily volatilized and vaporized during the combustion process. Therefore, the Class II and Class III elements have the capacity for enrichment on the surface of the Class I elemental particle surfaces during the cooling-solidification stage of the combustion process.

The elements contained within the Class II and Class III geochemical groups are less stable than the Class I or Class IV elements. As a result of the enrichment process, the Class II and Class III elements tend to be more susceptible to leaching from the coal fly ash particle surfaces by extraction and fractionation than the more stable, non-enriched Class I and Class IV elements although the leaching process occurs slowly in the residual stage (Wu 1980). Sympathetically, sulfide associated minerals such as zinc, copper, arsenic, lithium, lead, and manganese have a higher leaching potential than those elements associated with the coal fly ash aluminosilicates minerals such as iron, cobalt, beryllium, and aluminum again, due to the higher boiling points of the aluminosilicate associated minerals (Wu 1980).

The particulate size of the Class I and Class IV coal fly ash particles directly influences the Class II and Class III elemental enrichment concentration on the surface of the Class I and Class IV particles. The smaller the size of the Class I and Class IV particles, the greater the concentration of surface enrichment by the Class II and Class III elemental particles. The position forwarded to explain this characteristic proposes that first, this condition is due to the vaporization and re-condensation of the Class II and Class III elements onto the Class I and Class IV particles. Second, that the smaller the size of the Class I and Class IV particles per unit mass, the greater the surface area available for the enriched elements to assimilate with. These positions have been supported by chemical analysis which confirms that Class II and Class III elements such as lead, zinc, beryllium, potassium, and sodium are found in greater concentrations on the enrichment surfaces of the smaller Class I and Class IV particles than elsewhere in the matrix of the coal fly ash (Mims 1980).

The pozzolanic compounds composed of siliceous or aluminosiliceous materials found in coal fly ash, are present in a finely divided particulate form. When these compounds are exposed to high temperature, and physically contact water, they can chemically react with calcium hydroxide to form calcium silicate hydrate as follows (Mindess 1981).

$$[CH + S + H > C\text{-}S\text{-}H]$$

The approximate chemical formula for C-S-H is C3S2H3 but may vary with alterations in the stochiometry. The ratio of C to S ranges from between 1.5 and 2.0 and is dependent upon such factors as age of the paste, hydration temperature, water to cement ratio, and associated oxide impurities contained in the material. C-S-H is a semi-amorphous material composed of very finely divided, irregularly shaped particulates which exhibit multiple morphological features and lacks good crystallization development (Mindess 1981).

C-S-H is thought to have a layered structural configuration in which sheets of calcium silicate are preferentially built upon successive sheets. The space between the sheets is occupied by calcium ions and water. The microstructure of the C-S-H is irregular with the resulting sheets exhibiting a random alignment and the space between the sheets having considerable variation. Furthermore, the structure of the C-S-H exhibits a spiked outer surface as opposed to the layered configuration matrix on the inner surface. As a result, the structural fabric of the C-S-H develops two distinct pore systems, micropores and capillary pores (Mindess 1981), Figure 21.

The development of capillary pores which become discontinuous with age of the C-S-H acts to decrease the permeability of a fly ash concrete. Further, the capillary pore walls provide more surface area for the coal fly ash cement to react with acidic solutions. Micropores in the C-S-H act to provide reservoirs for water contained in the mix and provides spacing between the sheets of calcium silicates (Mindess 1981). If aluminum is reactively present then the following reaction may occur to produce calcium aluminate hydrate, another cement compound (Mindness 1981).

$$[\mathrm{CH + A + H > C\text{-}A\text{-}H}]$$

CH or calcium hydroxide occurs as a discontinuous phase of the cement forming reaction. The formation of CH results in well developed, non-porous, striated, crystalline structures within the matrix of the C-S-H much like phenocrystic material found in igneous rocks. Fully developed CH crystals are generally not found in abundance in fly ash cements as evidenced by the dominance of sphereoidally shaped morphological features of fly ash particles.

Ettringite and monosulfoaluminate formation in coal fly ash cements are of considerable importance. Ettringite is a mineral that is formed by the interaction of sulfate ions with tricalcium aluminate in the presence of water as expressed by the following equation (Mindess 1981).

$$\mathrm{C3A + 3CSH2 + 26H \dashrightarrow C6AS3H32} \quad \text{or} \quad \mathrm{C3A * 3CS * H32}$$

The calcium sulfoaluminate hydrate or ettringite is a stable hydrate in the presence of sufficient sulfate ions and contributes to the strength of the fly ash cement if unaltered. Ettringite develops the morphological shape of elongate, prismatic needles. The C3A reaction is very rapid in the absence of sufficient amounts of sulfate ions.

The formation of ettringite acts to slow the hydration of C3A by creating a diffusion barrier around the C3A. If sufficient sulfate ions are available to continue the reaction until all the C3A is hydrated, then ettringite formation is the non-reversible end product adding strength and stability to the coal fly ash (Mindess 1981). Additionally ettringite exhibits the capacity to bind hazardous trace elements such as boron and selenium

FIGURE 21

C-S-H AND PORE STRUCTURE DEVELOPMENT

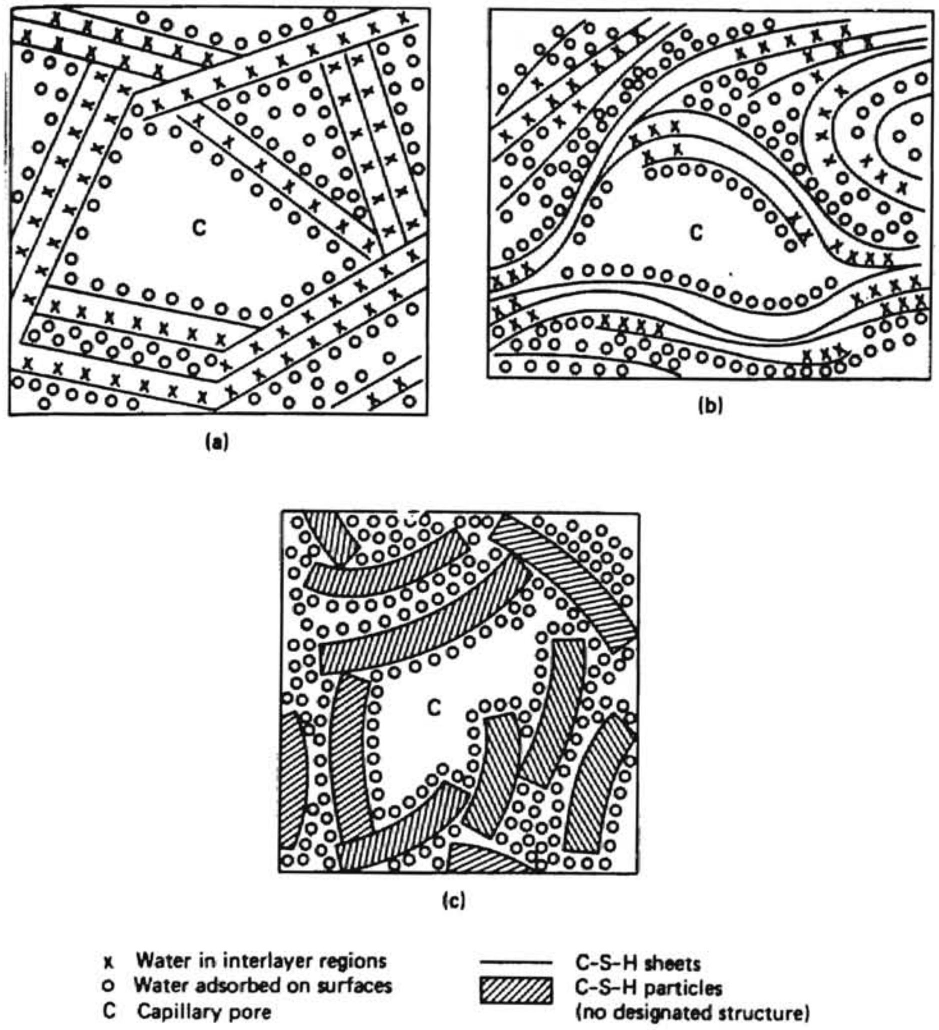


Figure 4.6 Schematic representation of various models of C–S–H. (a) Powers-Brunauer, adapted from T. C. Powers, *The Physical Structure and Engineering Properties of Concrete,* Bulletin No. 90, Portland Cement Association, Skokie, Ill., 1958, and S. Brunauer, *American Scientist*, Vol. 50, No. 1, 1962, pp. 210–229; (b) Feldman-Sereda, from R. F. Feldman and P. J. Sereda, *Engineering Journal (Canada)*, Vol. 53, No. 8/9, 1970, pp. 53–59; (c) Munich, adapted from F. H. Wittman, *Cement Production and Use,* Publication No. 79-08, Engineering Foundation, New York, 1979, pp. 143–161.

(Hassett 1991). If the sulfate ions concentration is depleted prior to the complete hydration of the C3A, then ettringite is altered into monosulfoaliminate.

Monosulfoaluminate is the morphologically platey transformation product of ettringite that requires less sulfate ion concentration to produce calcium sulfoaluminate hydrate called tetracalcium aluminate monsuflate-12-hydrate, and continues to be formed from the available aluminate ions. The conversion of ettringite into monosulfoaluminate results in high heat evolution due to the return of accelerated C3A hydration, significant total volume change of -24%, and is reversible back to ettringite if sulfate ions are again made available to the cement. This reversible process is only possible if during the initial formation of ettringite insufficient sulfate ions are available to react with all the aluminate ions present. Because the conversion from monosulfoaluminate and ettringite involves an additional volume change, the cement is potentially exposed to sulfate attack if another source of sulfate ions is made available (Mindess 1981). The equation expressing the conversion of ettringite to monosulfoaluminate is as follows.

$$2C3A + C6AS3H32 + 4H \dashrightarrow 3C4ASH12 \text{ or } C3A * CS * H12$$

The reversible reaction of monosulfoaluminate back to ettringite is expressed as follows.

$$C4ASH12 + 2CSH2 + 16H \dashrightarrow C6AS3H32$$

The presence of iron or iron oxides in the coal fly ash or in the associated mix solution, allow the formation of ferric phase cement, C4AF, in the coal fly ash provided sufficient aluminate and calcium are available. This type of cement does not attain the same strength as C2S or C3S cements but has a high resistance to sulfate attack. Further, the presence of the ferric coal fly ash in the cement may allow the formation of iron substituted ettringite expressed by the following equation (Mindess 1981).

$$C4AF + 3CSH2 + 21H \longrightarrow C6(A,F)S3H32 + (A,F)H3$$

Additionally, the ferric coal fly ash formed ettringite may be converted to iron substituted monosulfoaluminate which, unlike C3A generated monosulfoaluminate, is not a reversible reaction. Consequently, the iron substituted ettringite and monosulfoaluminate have a high degree of stability and impart to the coal fly ash cement greater resistance to volume change and sulfate attack. The equation for iron substituted monosulfoaluminate formation is as follows (Mindess 1981).

$$C3(A,F)\ 3CS\ 32H + C4AF + H \longrightarrow 3C4(A,F)S\ H12 + (A,F)\ H3$$

Typically, the pozzolanic reaction which occurs in class "C' coal fly ash requires all three of the pozzolanic compounds of silica oxides (SiO), aluminum oxides (AlO), and iron oxides (FeO) with an alkaline co-reactant which is generally calcium oxide [Ca(OH)2) to develop and optimize both the chemical binding of contaminants as well as the physical properties of the solidified coal fly ash such as compressive strength and durability (Baldwin 1993), (Smith 1985). This reaction is beneficial in that it imparts the capacity to the coal fly ash material to impede and or arrest the influx of contaminates into the environment through physical binding, physical blocking, chemical binding, and or chemical alteration of the environment (Baldwin 1993).

Surface precipitation is considered to be the primary mechanism involved in the removal of metals by coal fly ash. The adsorption and surface precipitation of metals in solution in the presence of coal fly ash is attributed to the high oxide content of the coal fly ash. Metal ions are thought to precipitate onto the surface of the alumina, silica, ferric, and or other oxides contained in the coal fly ash (Novaninakere 1993). Additionally, coal fly ash has been demonstrated to exhibit the capacity to solidify contaminated solutions as well as fixate contaminates through assimilation into the matrix of the coal fly ash concrete (Smith 1985).

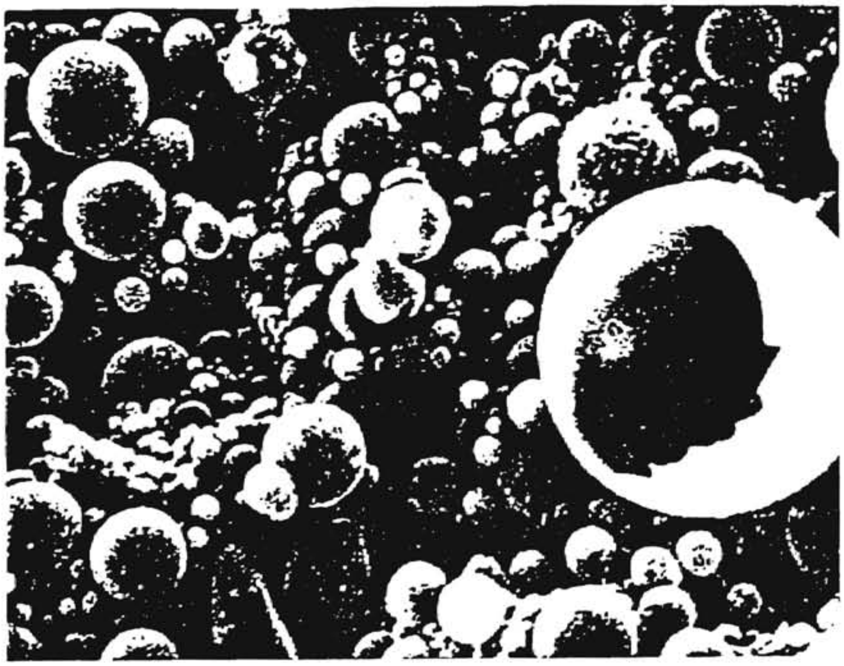
The compounds present in the pulverized coal which is burned in coal fired industrial plants become pozzolanic as a result of the combustion process exerted on the coal. During the ignition of the coal in the combustion chamber, carbon and volatile materials contained in the coal are consumed. The impurities contained in or associated with the parent coal feedstock composed of clays, feldspar, quartz, shale, calcareous material, and other contaminants are fused in suspension in the presence of combustion chamber temperatures which are between 1200oF and 1800oF. These impurities are carried away from the combustion chamber in the exhaust gases where cooling takes place. As the cooling process occurs, the material solidifies into primarily spherical or sub-spherically shaped particles of coal fly ash and is collected and removed from the cooling towers of the electric generating plants by electrostatic filters or screening devices and disposed of. These microscopic particles range in size of from less than 1 micron to 100 microns but are generally less than 20 microns in diameter (Kosmatka 1988), Figure 22. Although this material is utilized in multiple industrial, construction, and agricultural applications, it is considered a waste produce of coal fired electric generation (Kosmatka 1988).

The forms of the metal compounds found in coal fly ash are considered to be the result of the utilization variables comprising the combustion processes. These variables include temperature, combustion process, furnace design, electrostatic precipitators, mode of combustion, additives, operating pressures, water content, and the fuel to oxygen ratios present. In the normal range operating temperatures of the combustion chambers where the ashing of the coal occurs, a series of reactions take place within and between the minerals present in the coal which are assimilated into the resulting coal fly ash.

Only quartz, of the major mineral groups present in the coal to coal fly ash transformation, remains unaltered during the combustion process due to the high boiling point required for quartz (Ponder 1980). Associated clay minerals release bound water,

FIGURE 22

MORPHOLOGY OF COAL FLY ASH PARTICLES



sulfide based minerals are oxidized to sulfur dioxide (SO2) sulfur trioxide (SO3), or associated oxides. Sulfur dioxide may be lost through the volatilization process or, in the presence of calcium, combine with the calcium contained in the coal fly ash. If the sulfur dioxide is volitilized to a gaseous state, it is removed from the exhaust gases through a scrubbing process which utilizes a sodium sulfite-sodium bisulfite solution as an absorbent agent. This process is expressed by the following equation (Ponder 1980).

$$Na2SO3 + SO2 + H2O > 2NaHSO$$

The carbonate minerals contained in coal fly ash are primarily expressed as calcite (CaCO3). These minerals are converted to oxides expressed as calcium oxide (CaO) with the associated carbon dioxide released and lost through the volatilization process to a gaseous state as follows (Wu 1980).

$$CaCO3 > CaO + CO2$$

Thus, in the thermodynamic process, the components of the mineral groups contained in the parent coal become constituents of the coal fly ash through volatilization (Wu 1980).

The pH level of a coal fly ash is typically related to the calcium content of the coal fly ash. This calcium, or the calcium related minerals content level, conveys to the coal fly ash it's alkalinity or buffering capacity in solutions. Studies conducted as the Department of Civil Engineering located in Haifa, Israel found that the coal fly ash in the departments tests had a specific neutralization capacity (acidic to basic) that was 23% that of pure cement (Schwartz 1993).

The acid neutralization potential of the calcite minerals group contained in class "C" coal fly ash may be resolved by the determination of what mass of calcium, expressed as CaCO3, is required to neutralize a given volume of acidic solution. This may be accomplished by titration of an acidic solution to a selected pH value and then adding known volumes of class "C' coal fly ash to the solution until a desired pH value is obtained (Lapakko, 1994). In addition, class "C" coal fly generally contains another potential acid neutralizing agent, a small percentage of magnesium or magnesium associated minerals expressed as MgO or MgCO3. Magnesium minerals also has the capacity to neutralize acidic solutions albeit at a lesser rate than CaCO3 minerals. The dominant neutralization reactions involving CaCO3 and MgCO3 for solutions with pH values of above 6.3 are as follows (Lapakko 1994).

CaCO3 (s) + H(+) (aq) = HCO3(-) (aq) + Ca(2+) (aq) 1.

MgCO3 (s) + H(+) (aq) = HCO3(-) (aq) + Mg(2+) (aq) 2.

The dominant neutralization reactions involving CaCO3 and MgCO3 for solutions with pH values of less than 6.3 are as follows (Lapakko 1994).

CaCO3 (s) + 2H(+) (aq) = H2CO3 (aq) + Ca(2+) (aq) 3.

MgCO3 (s) + 2H(+) (aq) = H2CO3 (aq) + Mg(2+) (aq) 4.

Taken further, the calcite requirements for the neutralization of the acidic solutions resulting from pyrite oxidation and acid production are as follows (Morin 1994).

for pH<6.3

FeS2 + 7/2 H2O + 15/4 O2 + 2CaCO3

-> Fe(OH)3 + 2SO4(2-) + 2H2CO3 + 2Ca(2+)

for 6.3<pH<10.3

FeS2 + 7/2 H2O + 15/4 O2 + 4CaCO3

$$\rightarrow Fe(OH)_3 + 2SO_4(-2) + 4HCO_3(-) + 4Ca(2+)$$

As these equations demonstrate, the calcium requirement for an acidic solution to reach neutralization is twice the amount required for the solution to reach slightly acidic pH. Further, the aqueous ratio of calcium to sulfate is 1 to 1 at acidic pH levels and 2 to 1 at neutral pH levels (Morin 1994).

Most coal fly ash possesses morphological characteristics consisting of finely divided particles which appear as solid spheres or hollow cenospheres. Competent minerals primarily consisting of silicates, aluminosilicates, carbonates, or iron compose the solid spheres whereas the cenospheres are thought to be the result of gaseous bubbles which are created in the combustion process. These gaseous bubbles are entrapped in spherioids by the presence of iron and or other metals reacting with silica to form carbon monoxide in the combustion chamber under the influence of the high operating temperatures. The reaction and subsequent creation of the cenospheres is as follows (Raask 1985).

$$[2Fe_3C + SiO_2 \Longleftrightarrow Fe_3Si + 3Fe + 2CO]$$

In addition, large spheres containing smaller spheres which are known as plerospheres, are commonly found in association with cenospheres. The formation of these structures is thought to be the result of the parent coal and related mineral impurities being in close areal proximity during the combustion process and develop a minimum initial density of 2000kg/m3. During combustion, lattice structural features may develop in the coal fly ash if the parent coal contains sufficient amounts of pyrite (Raask 1985).

During the combustion process and subsequent exposure to high temperatures, clay minerals associated with the parent coal, assume sphereoidal shapes consisting of solid spheres, cenospheres, plerospheres, and or spheres with crystalline inclusions. These spheres of coal fly ash comprised of clay materials become non-opaque whereas iron or carbonaceous materials are opaque.

The opaque, amorphous, vesicular particles as well as cenospheres become more common with increases in particle size. Conversely, the non-opaque, solid spheres become more abundant with decreasing particle size. Decreases in particle size is inversely proportional to the increase in particle density possibly due to the direct size dependence of cenosphere and vesicular particles and the inverse size dependency of the solid, non-opaque spheres of coal fly ash (Fisher 1980).

The preponderance of coal fly ash occurs in spherical particles which have a diameter of less than 45 microns which accounts for between 70% to 90% of the total weight of a coal fly ash. The average surface area of coal fly ash is between 300 m2/kg to 500 m2/kg although the range of surface area extends to from 200 m2/kg to 700 m2/kg. Since coal fly ash is predominantly silica glass composed primarily of silica, alumina, iron, calcium, and subordinantly of magnesium, sulfur, sodium, potassium, carbon and trace compounds, the specific gravity of coal fly ash ranges from 2.2 to 2.8 and averages 2.65, the same as silica material (Fisher 1980).

Upon setting in non-mineralized water, class "C" coal fly ash cement develops a permeability which ranges from (6x10)-7 to (2x10)-6 cm/sec. with no additives. With the addition of 10% bentonite to the coal fly ash mix, the resulting cement develops a permeability of (1x10)-7 cm/sec. and with a 15% bentonite addition to the coal fly ash mix the permeability drops to (1x10)-9 cm/sec., which is in excess of current landfill requirements.

Typical class "C" coal fly ash cement, when subjected to a constant hydrostatic pressure of 20 psi, will develop a permeability of (1.6x10)-6 within 150 hours. The results of this test indicate that the permeability of the coal fly ash cement is relatively independent of the molding, moisture content, molded dry density, curing method, and test time (Farah, 1993).

The effects of certain metals, elements, and other physical factors on coal fly ash cements may have a positive or negative impact on the desired properties of the coal fly ash in a specific application. The presence of lead in solution in association with coal fly ash has no effect and cadmium has only a slightly deleterious effect on the compressive strength of the cement. Conversely, zinc has a significant negative effect on the compressive strength of coal fly ash cement reducing it by approximately 2/3rds (Schwartz, 1993), Figure 23. The water-cementitious materials ratio of the mix affect compressive strength in the following manner. The higher the water to cementitious materials ratio the less strength and less permeability contained in the coal fly ash cement. Tests indicate that any water-cementitious materials ratio above 0.55 results in an unprocessable paste and that useable pastes have a ratio of less than 0.45. Further, leachate concentrations are found to be lower in low water- cementitious ratio cements. The time of set for the coal fly ash cement also exhibits a direct correlation between length of time and strength gain (Schwartz, 1993), Figure 24.

During the combustion process the particles of coal fly ash are subjected to high temperatures which results in the particles acquiring an electrical charge. This is due to the high resistivity and lack of homogeneous composition of the partially devitrified layer of elements on the surface of the particles. The dipolar moment of the charge is then acquired and maintained by the particle.

Fly Ash Utilization

Many of the multiple beneficial properties contained within coal fly ash have through time been realized and exploited. While the majority of the 50 million tons of coal fly ash produced in the United States is simply disposed of, the remainder is used in a variety of applications in industry, agriculture, construction, and manufacturing (Bowders 1991).

Industrial applications for coal fly ash include stabilization of industrial waste. This involves the introduction of the material into industrial waste sludge to act as an alkaline admixture to neutralize the sludge with respect to sludge acidity and as a fixating agent in open sludge pits. Furthermore, coal fly ash directly applied to lead contaminated soils has been demonstrated to have the capacity to fixate the lead in the soil through the pozzolanic reaction. This application also serves to retard the leachability of metals of soils by reducing the acidity of the soil through the neutralizing effects of the calcium related minerals in the coal fly ash (Baldwin 1993).

Industrial discharges containing trace metals into streams may also be reduced by "filtering" the discharges through pits containing fly ash prior to final release wherein the metals are fixated to the fly ash and or are precipitated out of solution by the alteration of the streamflow pH (Nonavinakere 1993). Other waste products are blended into coal fly ash such as incinerator waste and utilized in concrete containing the material.

Industry also uses coal fly ash in surface mine reclaimation as a means to prevent acid mine drainage from mine tailings, and refuse piles. This application deals primarily with filling inactive strip mines and processing ponds as well as encapsulation or walling of mine tailings or refuse piles. As with other industrial applications, the acid neutralization capacity and fixating ability of the coal fly ash on acidic pH discharges and fixating potential of metals are beneficially utilized.

Agricultural applications of coal fly ash are primarily undertaken where acidic soils preclude the development of desirable vegetation. Again, the introduction of coal fly ash has the capacity to raise the pH of the soil thereby allowing vegetation to grow and prosper. Further,, the blending of the material with compost has been demonstrated to provide a desirable admixture to soils which is not easily eroded and provides nutrients to the soil.

Coal fly ash has historically been used as a construction material primarily as a cement additive. Cement mixes incorporate variable amounts of coal fly ash for multiple functions depending upon the properties desired by the cement. The addition of coal fly ash into the hydrated paste of a cement, when properly proportioned, increases the compressive strength gain of cements. This occurs due to the rate of reaction of the coal fly ash being approximately the same as C2S which therefore allows more C2S to be formed during the hydration process (Mindess 1981). Further, because of the pozzolanic reactivity of coal fly ash within cement paste, a greater proportion of C-S-H is formed and sympathetically, a lesser portion of CH remains (Mindess 1981). Since the proper proportioning of coal fly ash concretes tends to react at a reduced rate, less heat generation and liberation is experienced lessening thermal fracturing or cracking of a concrete.

The finely divided spherical morphology of the coal fly ash tends to increase the workability of a concrete with only reasonable increases in water demands for adequate hydration of the paste. The increase in workability of the mix acts to decrease the permeability in addition to improving the durability of the concrete and resistance to sulfate attack by the demonstrated retardation of the expansive alkali-aggregate reaction (Mindess 1981). Finally, coal fly ash is a very economical admixture to cements due to low acquisition costs of the material and abundance provided a source is logistically located near enough to the construction site to mitigate transportation costs.

Coal fly ash is also used in offshore breakwaters, jetties, artificial reefs, and other aquatic fills. Due to the low leachability, low metals content, absorptive capacity, and the fact that coal fly ash is a hydraulic cement it is ideal for such projects and provides a useful application for the material generated by near shore sources (Schwartz 1993). In addition to the other previously mentioned uses, coal fly ash is being used as structural fill for construction projects and as base stabilization material, especially in highway construction (Brendel 1987).

Manufacturing processes are using coal fly ash as a modifier in low cost polymeric materials due to the insulating capacity, light weight, and chemically inert properties of coal fly ash. Additionally, coal fly ash has been demonstrated to perform as a composite alloy in aluminum. The inclusion of coal fly ash has been found to increase the modulus, decrease the density, and increase the abrasion resistance of aluminum alloys.

FIGURE 23

METAL CONTAMINATION EFFECT ON STRENGTH

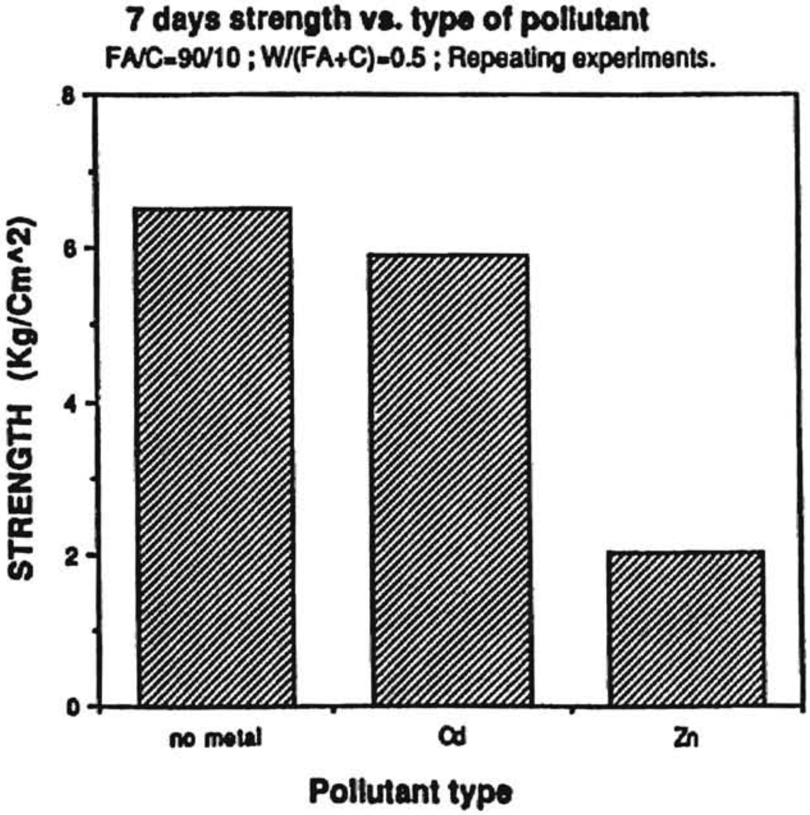
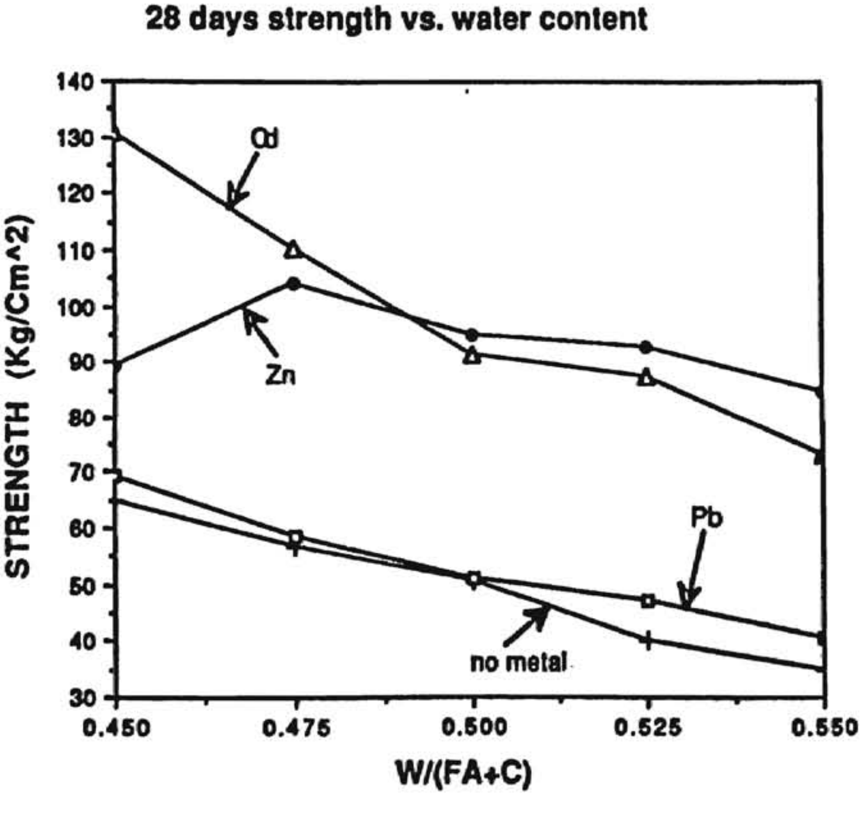


FIGURE 24

EFFECT OF WATER CONTENT ON STRENGTH



CHAPTER III

METHODOLOGY

Construction of Simulated Mine

To attempt to replicate the conditions found in the abandoned subsurface mines of the Picher Mining Field area, a simulated mine was constructed for the study. The simulated mine was built in an enclosed laboratory located at the Oklahoma State University Waste Water Research Facility located in Stillwater, Oklahoma.

The indoor laboratory site was selected in order to control the physical environment for the study and to ensure quality control of the materials used in the test and accuracy of the results obtained from the tests conducted. Additionally, the close proximity of the laboratory to other research and laboratory facilities utilized in the test aided in the logistics of the study.

The simulated mine dimensions were designed to create an enclosed mine shaft and drift with an area of 43.56 feet3 which is the equivalent of 1/1000th of one acre foot, Figure 25, Figure 26. Additional space was built into the mine shaft for freebore. This area was arrived at by the following equation.

1 Acre/Foot3 = 43,560 Cubic Feet 1.

1/1000 Acre/Foot3 = 43,560 Cubic Feet / 1000 = 43.56 Cubic Feet 2.

The volume required to fill the area of the simulated mine with 1/1000th of an acre/foot of mine water was determined by the following equation based on reservoir engineering.

FIGURE 25

END VIEW OF SIMULATED MINE

FIGURE 26

SIMULATED MINE CROSS-SECTION

1 Acre/Foot3 of Fluid = 7758 U.S. Barrels 1.

1 U.S. Barrel = 42 Gallons 2.

7758 U.S. Barrels x 42 Gallons = 325,836 Gallons 3.

1/1000th Acre/Foot3 of Fluid = 325,836 Gallons / 1000 = 325.84 Gallons 4.

To create the areal and volumetric dimensions required for the study, the simulated mine was constructed according to the following specifications listed on Table 5.

The simulated mine drift and roof plate wooden concrete forms were prefabricated in segments in Tulsa, Oklahoma from plywood and commercial grade lumber. The completed forms were then transported to the Waste Water Research Facility in Stillwater for final assembly and were coated with non-adhesive organic margarine spray prior to insitu casting of the cement used to construct the simulated mine.

The final assembly of the forms was followed by the placement of 2.5 cubic yards of Portland Type I cement into the wooden drift and roof forms. The cement utilized was purchased from Dolese Cement Company located in Stillwater, Oklahoma and was delivered by blender truck. The cement mix was a standard commercial design with no special additives and had a maximum aggregate size of 3/4 inches composed of crushed limestone aggregate to aid in the placement and workability of the mix. The cement was designed to yield 3500 psi compressive strength within 28 days with an initial slump of 2 inches to 4 inches. During the placement, 10 gallons of water was added to the mixer to increase the slump to 5 inches to 6 inches to further increase placement and workability.

Placement was performed in four phases. The first phase involved the casting of the cement on the floor of the simulated mine drift and shaft outside form to a uniform thickness of 5 inches. Following the working and finishing of the first pour, the inside drift form was lifted into place and secured. The second pour was then made down the free space between the inside and outside forms to create the vertical walls of the simulated mine. The walls were cast to a thickness of 5 inches along the longitudinal sides

TABLE V

SIMULATED MINE DIMENSIONS

Vertical Shaft Dimensions

Overall Height	3 Feet 7 Inches
Height over the Horizontal Drift	2 Feet 7 Inches
Inside Height	3 Feet 2 Inches
Floor Thickness	5 Inches
Overall Width	3 Feet 2 Inches
Inside Width	2 Feet 4 Inches
Side Wall Thickness	5 Inches
Overall Length	1 Foot 10 Inches
Inside Length	1 Foot 0 Inches
End Wall Thickness	4 Inches

Horizontal Drift Dimensions

Overall Height	1 Foot 5 Inches
Inside Height	1 Foot 0 Inches
Floor Thickness	5 Inches
Overall Width	3 Feet 2 Inches
Inside Width	2 Feet 4 Inches
Side Wall Thickness	5 Inches
Overall Length	18 Feet 8 Inches
Inside Length	18 Feet 0 Inches
End Wall Thickness	4 Inches

Roof Plate Dimensions

Width	3 Feet 2 Inches
Total Length	16 Feet 10 Inches
Thickness	4 Inches

and 4 inches on the lateral ends of the drift and shaft forms. These pours was worked and finished by hand and selectively spud vibrated to ensure consistency, compaction, and uniformity of the cast.

The roof plates were poured on segmented plywood-lumber forms to a thickness of slightly less than 4 inches. These segmented pours were also worked and finished by hand. All three of these cement pours were periodically sprayed with water for 3 days after initial set to enhance the crack resistance, proper hydration, and curing of the cement.

The wooden drift forms were removed from the simulated mine shaft and drift cement cast 4 days following the pours. The segmented roof plates were removed from the forms at this time. The prefabricated shaft uptake forms were then placed on the shaft foundation and 13-80 lb bags of Hurst Ready-Mix concrete were mixed and poured into the cast form. This mix was made with a low water-cement ratio allowing the form to be removed the following day and was periodically sprayed with water for 2 days following casting. As with the other pours, all placement, working, and finishing of the cement was performed by hand.

The interior surfaces of the simulated mine were then laminated with blended bentonite mud to an average thickness of 1/2 inch. This action was taken to effect a water-tight seal for the mine and provide an adhesive material for the ore rock to become affixed to the vertical and horizontal surfaces of the mine shaft and drift. Additionally, the bentonite lamination created a chemically inert, physical barrier between the mine water and the cement surfaces of the simulated mine precluding chemical reaction between the mine waters and the cementitious materials contained in the cement cast.

Ore rock from the Picher Mining Field, which had been transported to the Waste Water Research Facility, was selectively crushed by sledge hammer to a maximum aggregate size of 1 inch. This ore rock material was then broadcast on the interior floor and wall surfaces of the shafts and drifts in an attempt to recreate the physical environment of the subsurface mine walls of the Picher Mining Field. Only the bentonite lamination was applied to the lower surfaces of the roof plates to facilitate ease of handling and placement.

Seven days after the first pour phase the roof sections were placed by hand onto the drift walls of the simulated mine. All exposed seams were liberally coated with bentonite on the interior surfaces. Hurst Mortar Mix was then placed into the outside surfaces of the seams to bind the plates to one another and to the drift walls. Finally, a second coat of bentonite was applied to outer surface of the seams to stop or retard any leakage from the simulated mine.

Three 6 inch diameter holes were drilled through the placed roof plates of the simulated mine drift with a pavement coring machine and cased with 5 inch diameter PVC pipe. These holes were drilled to replicate air shafts or boreholes which would be utilized in the pumping and placement of coal fly ash slurries into underground mine works in addition to direct injection through the mine shaft.

Location Descriptions

Any sample site location used in this study is described according to the Public Land Survey system utilized by the United States Geological Survey. This method forms the basis for all land descriptions in the State of Oklahoma and consists of first, listing the township, followed by the range, followed by the section, followed by the quarter, followed by the quarter's quarter, followed by the quarter's quarter's quarter. This in effect lists the location of a sample site to within 10 acres of the site's location within a 640 acre section.

Ore Rock Characteristics, Location, and Selection

The ore rocks used to line the interior surfaces of the simulated mine were collected from an unprocessed boulder pile located in the Picher Mining Field. The boulder pile was positioned on the edge of the collapsed shaft entrance of the Skelton Number 4 Mine located in the Southwest corner of section 28, Township 29 North-Range 24 East, Ottawa County, Oklahoma, approximately 1 mile south of the townsite of Picher, Figure 27. The boulder pile was approximately 50 feet in height and covered approximately 3 acres in area. The boulders were from gravel chip size to over 2 feet in diameter and had been severely oxidized . However, the interior surfaces of the boulders had fresh, unweathered crystal faces consisting primarily of chert and ore.

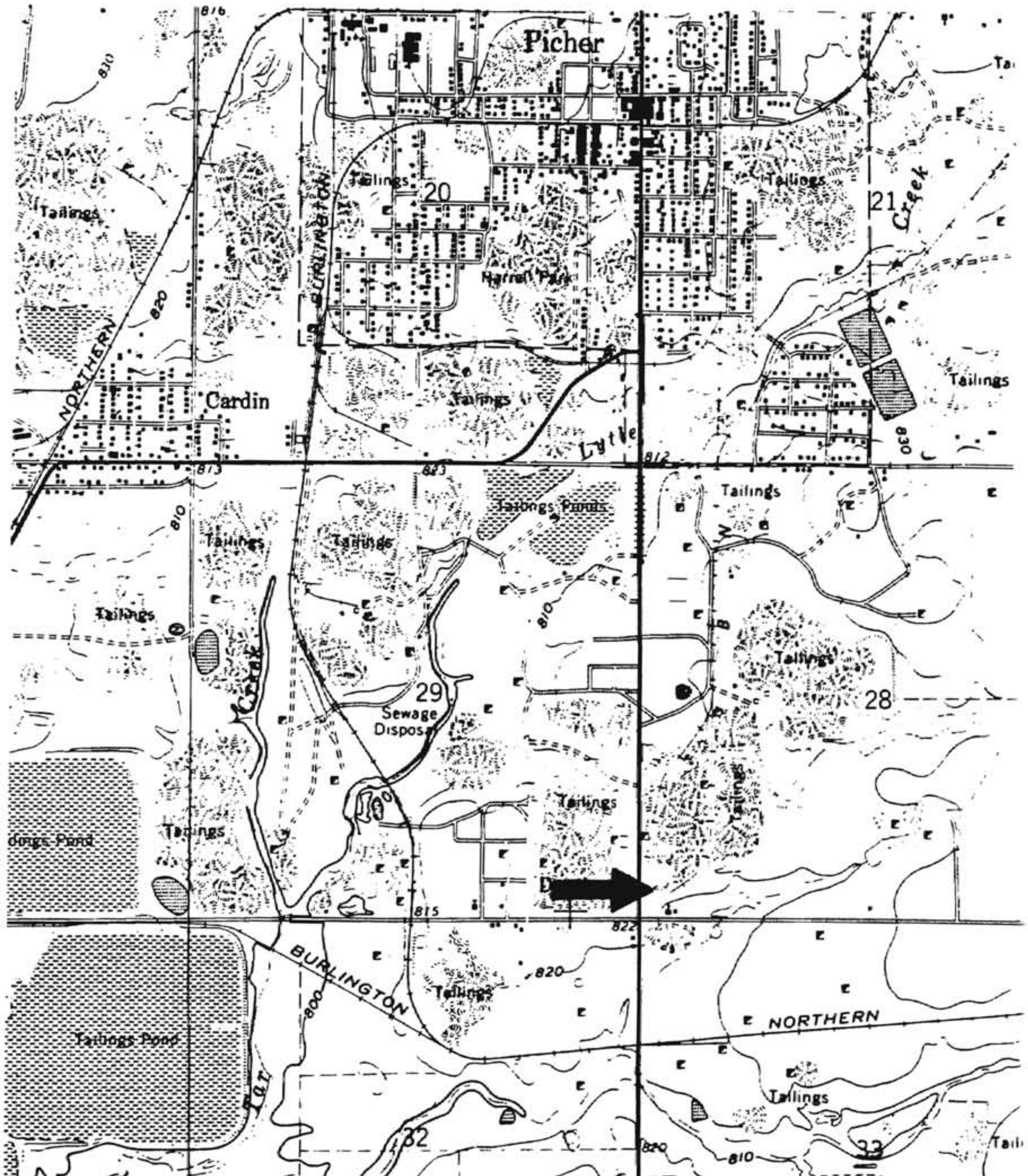
Well developed sphalerite crystals were found in abundance commonly filling solution channels or fractures in the rocks and occasionally were also observed within the matrix of the chert itself. The color of the sphalerite crystals varied from orange-yellow to black and the crystals were observed in both coarse to fine morphological masses. The sphalerite was almost always in found association with galena and or chalcopyrite although the chalcopyrite occurred in less abundance.

Galena was also readily found in the boulders and was easily identified by it's metallic luster, gun-metal gray color, cubic mineral cleavage. It was observed that boulders containing galena in abundance were considerably heavier than those with only sphalerite crystals. In contrast to the sphalerite, galena was only observed in solution channels or fractures and not insitu within the chert matrix indicating that the galena precipitated out of solution more readily than the sphalerite. Well developed galena crystals contained in the boulders were observable without the need for a hand lens.

Chalcopyrite was also easily found in the boulder pile but not in the abundance of either sphalerite or galena. Chalcopyrite was identified by a brassy-yellow to greenish color and metallic luster and was often found in boulders containing pyrite or marcasite in addition to sphalerite or galena. Pyrite and marcasite were present throughout the boulder pile and were easily observed by their brassy to yellowish color. Additionally,

FIGURE 27

SKELTON NUMBER 4 MINE, ORE ROCK SOURCE



almost all of the exposed surfaces of the boulders had yellow to red iron oxide staining indicating a high content of pyrite and or marcasite within the ore rocks. All the ore rocks from the boulder pile were examined by hand and those exhibiting the greatest amounts of mineralization were loaded onto a truck and hauled to the Waste Water Research Facility in Stillwater.

Mine Water Sample Selection and Location

Several sites in the Picher Mine Field were evaluated as a source for water for the study. Many of the locations where open mine shafts were located and had been previously evaluated in the Superfund project as being highly mineralized, acidic waters had restricted access and could not be used. However, one location with easy, non-restricted access was the Oklahoma Water Resources Board (OWRB) Site number 4, sample sites 22 and 24, located in the Southeast corner of the Southeast Quarter of the Southwest Quarter, Section 29,Township 29 North-Range 23 East, Ottawa County, Oklahoma, Figure 28.

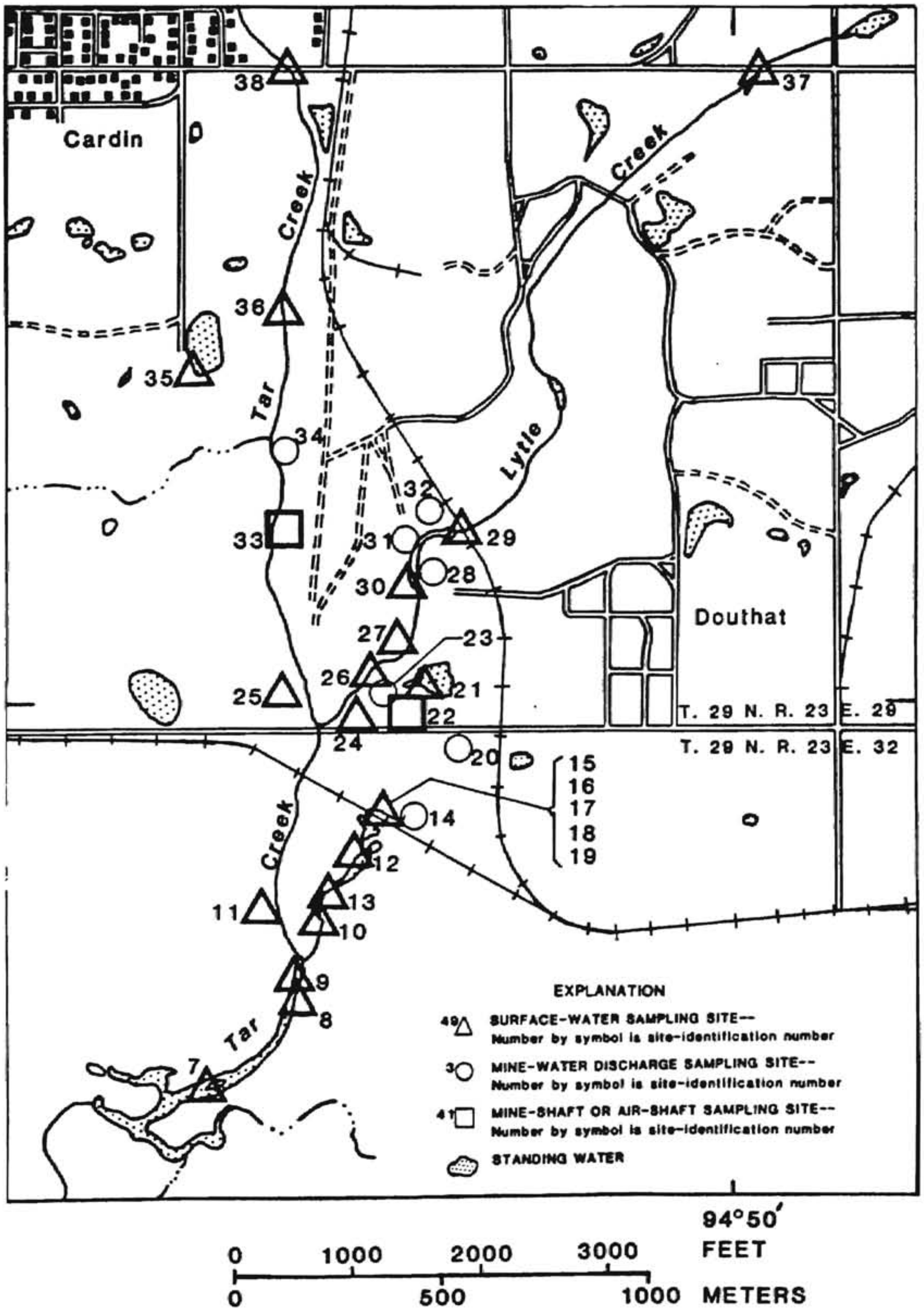
This location had been continuously monitored by the OWRB since the late 1970's and was located approximately 1/2 mile west of the town of Douthat. The water source location is an artesian type, year round active flow to the surface through an old borehole.

The borehole is directly connected to the "200" foot underground mine works level and contains highly mineralized, acidic waters (Parkhurst 1987). The discharge from the borehole creates a substantial and continuous flow into a county road bar ditch. The discharging water flows west from the borehole in the bar ditch approximately 150 feet where it enters Tar Creek.

The water sampled and collected for this study was observed to have a slightly sulfurous oder and orange-red foam collected on the surface of the water in low energy pools along the edge of the ditch. Both the vegetation along the ditch and the banks of

FIGURE 28

OWRB SAMPLE SITES



the ditch were stained red possibly from iron oxidation. Samples of the water were observed to contain a visibly high amount of suspended solids which were orange-red in color. Ph readings from the edge of the borehole varied from 3.8 to 4.8 whereas readings upstream 10 feet from the borehole were from 5.5 to 5.9. Downstream 20 feet from the borehole the pH value of the water was recorded from 4.2 to 4.6.

On January 31, 1995, bulk water was collected from the OWRB Site number 4. This was performed by placing a suction hose at the mouth of the borehole and pumping the water into 55 gallon drums with a 1 inch diameter centrifuge pump powered by a 1 horsepower gasoline engine. A total of 385 gallons of water was collected from the borehole for bulk blending in the study. The pH of the water was taken at the time of pumping and had a value of 4.2. Multiple water samples were taken at the time of pumping for physical and chemical analysis. Once pumping was completed, the drums were sealed and transported by truck to the Waste Water Research Facility in Stillwater.

Mine Water Quality Testing and Data

The water at the OWRB Site number 4, the source for the mine water used in this study, has been intensively analyzed for over 15 years, Appendix I. The water collected for this study was analyzed by Stover Biometric Laboratories located in Stillwater, Oklahoma, to ensure similarity with waters from the previous studies.

An abbreviated analysis of this water was undertaken to identify the physical and chemical properties of the water within certain parameters which included Ph values, Redox, Specific Conductance, Total Dissolved Solids concentration, Sulfides concentration, Trace Metals of lead, zinc, arsenic, cadmium, nickel, aluminum, iron, copper, Alkaline Minerals, and Total Field Alkalinity. This also would serve to verify the effects of the coal fly ash on highly mineralized, acidic waters of known composition and conversely, the effects of these waters on the coal fly ash.

Coal Fly Ash Selection, Characteristics, and Location

The coal fly ash used in this study was obtained from Oklahoma Gas and Electric Company's Sooner Generating Station located approximately 10 miles south of Ponca City, Oklahoma. The generating station produces several hundred tons of coal fly ash daily which is pneumatically loaded into heavy transport trucks and removed from the plant facilities for utilization or disposal. The coal burned in the plant is low in sulfur and contaminants but high in calcium content resulting in the production of Class "C' coal fly ash during the combustion process.

Arrangements were made with company officials to aquire 4000 lbs of same day burn, coal fly ash from the plant. This action was taken to lessen the opportunity of contamination of the coal fly ash from moisture or other factors. A pneumatic loading bin was closed off and partially filled with coal fly ash until the desired amount was collected. The ash was then hand shoveled into open top 55 gallon drums and placed on a 2 ton, power lift tailgate truck. The drums of the coal fly ash were then sealed and transported to the Waste Water Research Facility in Stillwater.

Chemical analysis indicates that the generating station produces a higher than average calcium content and lower than average sulfur content Class "C" coal fly ash. Because previous analysis of the coal fly ash produced by the generating plant indicated that such low concentrations of environmentally hazardous metals were present, chemical testing is now confined to oxides and sulfur concentrations. Physical tests are regularly taken on the coal fly ash to determine specific gravity, sieve-particle size analysis, water requirements, pozzolanic index, autoclave soundness, moisture content, and loss on ignition. Tests are based on ASTM C-618 specifications and utilize ASTM C-311 test procedures Table 6.

The coal fly ash was also studied by Scanning Electron Microscope and X-ray analysis at the Electron Microscopy Laboratory located on the Oklahoma State University

Campus. Mixed and set samples of the coal fly ash used to fill the simulated mine were selectively air dried, moist dried, and taken from the mine itself after 28 days of curing for examination.

The scanning electron microscope revealed the development of solid spheres, cenospheres, plerospheres, ettringite needles, non-crystalline masses, and micropores within the matrix of the cement. The solid spheres were most dominant and were generally well rounded. X-ray analysis indicated that these particles were composed primarily of calcium, with lesser amounts of silica, and aluminum. These particles often exhibited extremely finely divided surface coatings of indeterminable content.

The cenospheres were usually well rounded although some were observed to be poorly rounded to angular and were often associated with plerospheres. Again, X-ray analysis indicated that these particles were composed of calcium with lesser amounts of silica and aluminum.

Ettringite was found in abundance in the samples and was expressed by elongate, slender, rod shaped structures. Ettringite appeared in association with solid spheres, cenospheres, plerospheres, and the other morphological features observed in the sample. These crystals appeared to have no preferential orientation with respect to the longitudinal development axis of the crystal.

Other morphological structures seen in the samples were bent rod shaped ettringite crystals, thin platey crystals, non-symmetrical shaped plates, and voids, possibly due to air pockets in the mix slurry Figure 29, Figure 30.

Numerically, the preponderance of spheres were small in size with respect to the optics field covering an estimated 60% to 70% of the area. The larger size spheres occupied an estimated 5% to 10% of the total volume of the samples. Ettringite crystals were estimated to comprise another 20% to 25% of the sample volume, and the non-spherical particles less than 5%. No discernible variation of morphological composition was observed between the moist, dry, or mine cured samples Figure 31.

TABLE VI

CHEMICAL AND PHYSICAL PROPERTIES TEST OF COAL FLY ASH USED IN STUDY

Physical Test	Value	
Specifications		
Specific Gravity	2.68	....
Retained on Sieve No. 325	16.3%	34.0% Max.
Water Requirement	94.2%	105.0% Max.
Pozzolanic Index, % Control	101.9%	75.0% Min.
Moisture Content	+.025%	+0.8% Max.
Loss on Ignition	0.14	6.0 Max.
Chemical Test		
Total: SiO2, Al2O3, Fe203	61.46%	50.0% Min.
Sulfur Trioxide, SO3	2.04%	5.0% Max.
Magnesium Oxide, MgO	4.69%	....
Calcium Oxide, CaO	26.46%	....

FIGURE 29

FLY ASH CEMENT MORPHOLOGY

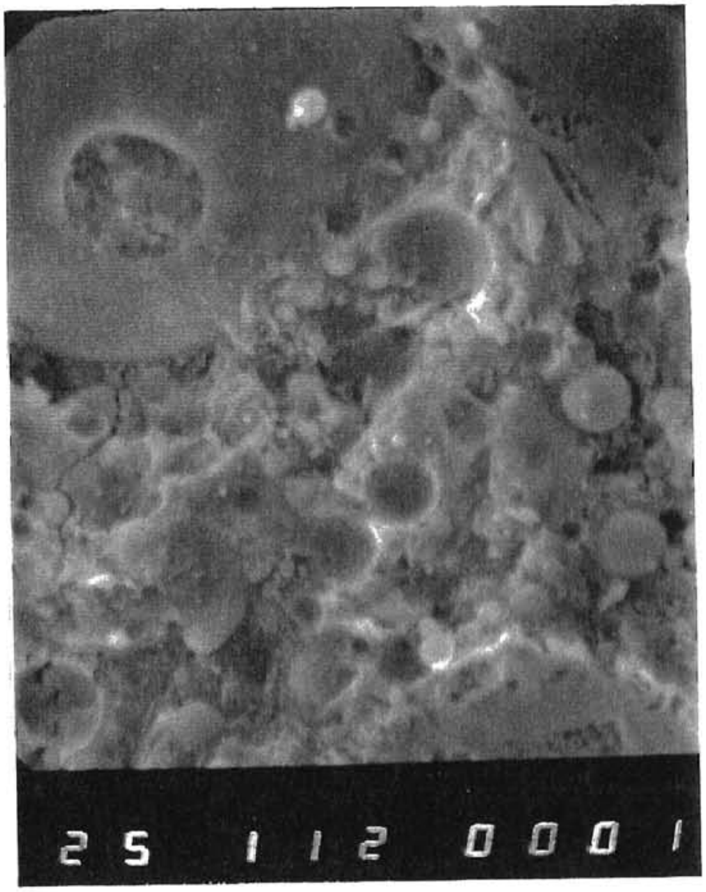
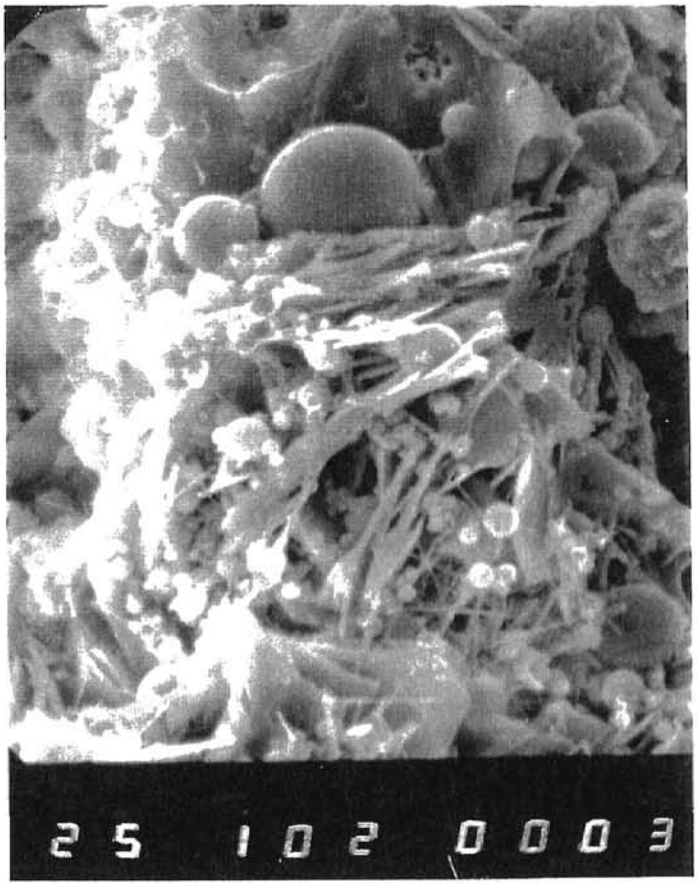


FIGURE 30

ETTRINGITE IN FLY ASH CEMENT



The samples were examined by X-ray analysis while in the Scanning Electron Microscope. This procedure exposed qualitatively the relative amounts of elements present in the samples. The vast majority of the elements in the sample were determined to be calcium followed by silica on an order of 3 to 1. Silica was detected at approximately twice the concentration of aluminum and 3 to 1 compared to iron. Iron and copper were found in trace amounts at approximately a 2 to 1 ratio with trace amounts of titanium, zinc, and gold also being detected Figure 32, Figure 33.

Multiple cores of 3 inch diameter x 6 inch length and 4 inch diameter x 8 inch length were cast from the mix batches and were moist or dry cured and monitored for compressive strength by destructive testing in a hydraulic press at 7, 14, and 28 days from casting time. Additionally, distructed cores were placed in distilled water baths and were examine at 7, 14, and 28 days from distruction for pH value of the water bath.

Further, the batch mix cores were tested for permeability, porosity, leachability, fixating capacity, bound heavy metals, bound trace metals, and absorptive capacity by Standard Testing located in Oklahoma City, Oklahoma and Stover Biometric Laboratories located in Stillwater, Oklahoma.

Preparation of the Simulated Mine for Testing

The simulated mine was filled with 325 U.S. gallons of the mine discharge water collected and hauled from the OWRB Site number 4. Pumping into the mine from the barrels was performed by an electric powered, 3/4inch centrifugal pump. The water was then periodically circulated with the centrifugal pump for 4 days between the mine shaft and the furthest drift borehole to ensure oxidation and uniform distribution of the suspended particles of the water. No leaks were detected from the simulated mine during the circulation of the water and no volumetric loss of water was observed from the mine indicating that the bentonite lamination had effectively sealed the simulated mine surfaces

FIGURE 31

SURFACE STRUCTURE OF FLY ASH CEMENT

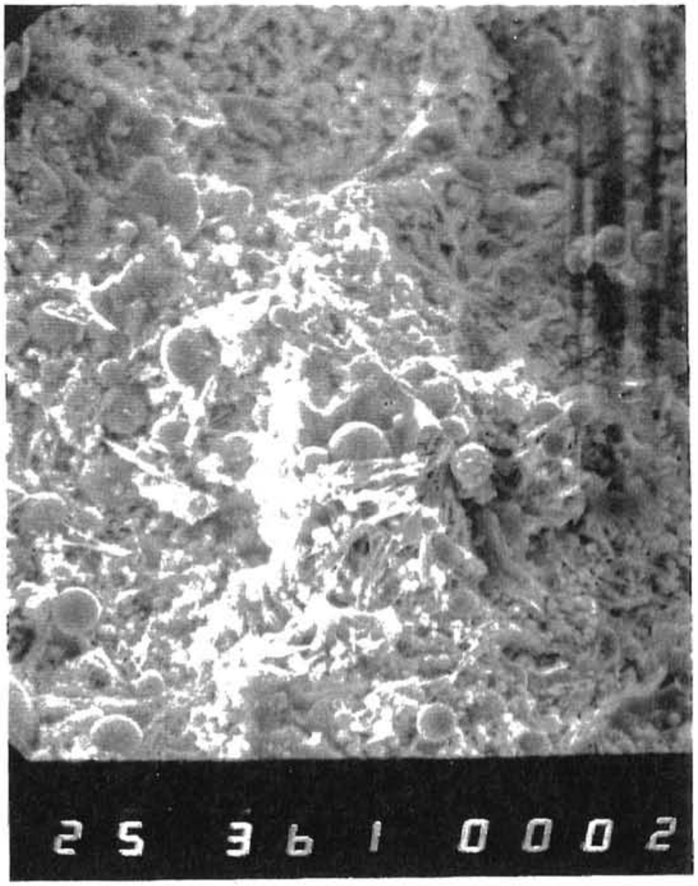


FIGURE 32

X-RAY ANALYSIS OF FLY ASH CEMENT,

FOCUSED ASPECT

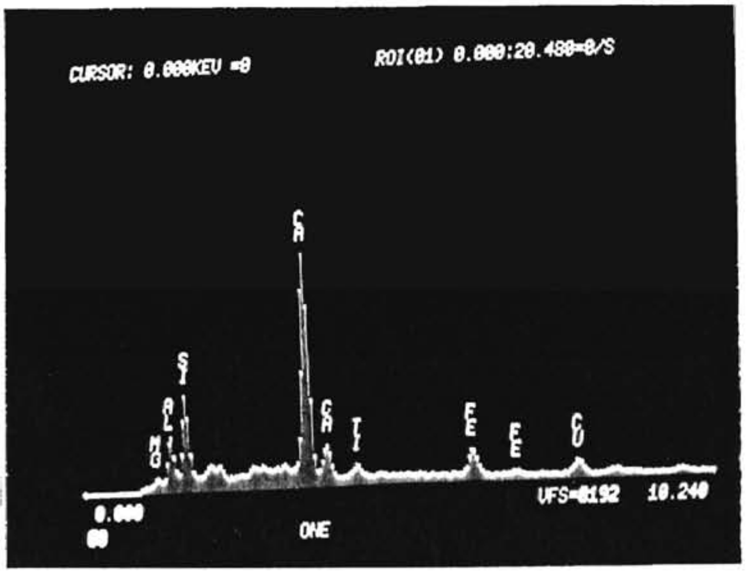
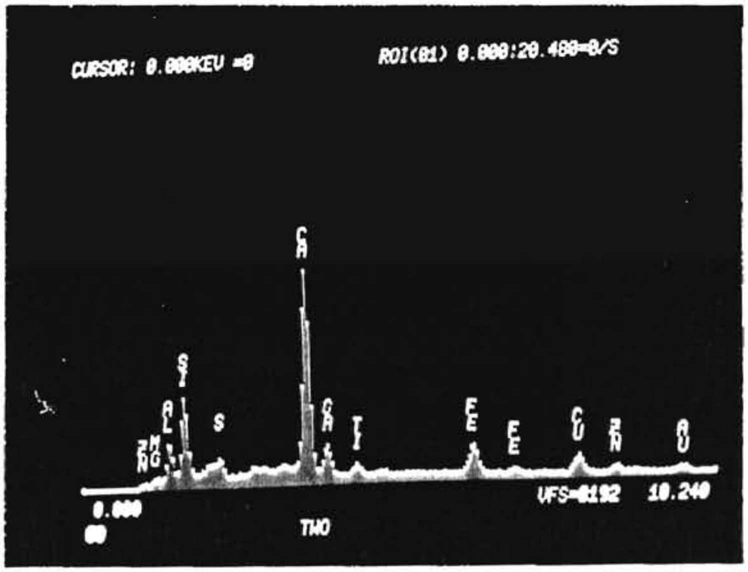


FIGURE 33

X-RAY ANALYSIS OF FLY ASH CEMENT,

BROAD ASPECT



and joints The water in the shaft was observed to be orange-red in color and had a pH value of 4.2.

Execution of Coal Fly Ash Slurry Filling of the Simulated Mine

The water in the simulated mine was pumped out of the simulated mine shaft in 16.75 gallon batches and placed into 5 gallon buckets to ensure the correct batch volume and for ease of handling. The water was then poured from the buckets into a electric powered mortar mixer into which a specifically measured weight of coal fly ash was added. The mix was blended to a uniform consistency and then dumped from the mixer into a 55 gallon open top drum from which it was pumped back into the mine in the borehole furthest from the shaft. Pumping was performed by the use of a 3 inch diameter diaphram pump, powered by a 12 horsepower gasoline engine. This process was repeated 4 times at each of the two furthest boreholes and 3 times at the nearest borehole to the shaft. Upon pumping the third batch into the borehole nearest the shaft, the shaft began filling up above the drift roof level leaving only enough free water for one final batch. The final batch was pumped into the mine through the shaft opening volumetrically filling the mine and leaving no free water.

The batches pumped into the mine were mixed with 3 different densities to compare the physical-chemical properties, and effectiveness of each density mix group. The batch densities, water-cement ratios, and other parameters are listed on table 7.

TABLE VII

SLURRY PARAMETERS

SLURRY	DENSITY	FA WT/GAL	FA WT/BATCH	WTR/BATCH	MIX TIME	CUM. VOL.
#1	16LBS/GAL	8LBS/GAL	60836GRAMS	16.75 GALS	10MIN	16.75 GALS
#2	16LBS/GAL	8LBS/GAL	60836GRAMS	16.75 GALS	12MIN	33.50 GALS
#3	16LBS/GAL	8LBS/GAL	60836GRAMS	16.75 GALS	10MIN	50.25 GALS
#4	16LBS/GAL	8LBS/GAL	60836GRAMS	16.75 GALS	10MIN	67.00 GALS
#5	18LBS/GAL	10LBS/GAL	76045GRAMS	16.75 GALS	14MIN	83.75 GALS
#6	18LBS/GAL	10LBS/GAL	76045GRAMS	16.75 GALS	15MIN	100.50 GALS
#7	18LBS/GAL	10LBS/GAL	76045GRAMS	16.75 GALS	15MIN	117.25 GALS
#8	18LBS/GAL	10LBS/GAL	76045GRAMS	16.75 GALS	15MIN	134.00 GALS
#9	20LBS/GAL	12LBS/GAL	91254GRAMS	16.75 GALS	18MIN	150.75 GALS
#10	20LBS/GAL	12LBS/GAL	91254GRAMS	16.75 GALS	19MIN	167.50 GALS
#11	20LBS/GAL	12LBS/GAL	91254GRAMS	16.75 GALS	20MIN	184.25 GALS
#12	20LBS/GAL	12LBS/GAL	91254GRAMS	16.75 GALS	20MIN	201.00 GALS

MAXIMUM FLY ASH WT PER GALLON 5448 GRAMS (12LBS)

MINIMUM FLY ASH WT PER GALLON 3632 GRAMS (8LBS)

AVERAGE FLY ASH WT PER GALLON 4540 GRAMS (10LBS)

MAXIMUM FLY ASH WT PER BATCH 91254 GRAMS (201 LBS)

MINIMUM FLY ASH WT PER BATCH 60836 GRAMS (134LBS)

AVERAGE FLY ASH WT PER BATCH 76045 GRAMS (167.5 LBS)

TOTAL WT OF FLY ASH PUMPED IN BATCHES 91254 GRAMS (2010BLS)

AVERAGE WATER VOLUME PER BATCH 16.75 GALLONS

TOTAL VOLUME OF WATER PUMPED IN SLURRY 201 GALLONS

MAXIMUM SLURRY DENSITY 20 LBS/GAL

MINIMUM SLURRY DENSITY 16 LBS/GAL

AVERAGE SLURRY DENSITY 18 LBS/GAL

CHAPTER IV

RESULTS

Water Quality after Filling Operation

Minor amounts of free water were observed in the cased boreholes of the simulated mine into which the 16 lbs./gallon and the 18 lbs./gallon slurries were injected. No free water was found in the cased borehole used for the 20 lbs./gallon slurry injection or the simulated mine shaft opening. The amount of free water in the subject boreholes decreased daily and could not be detected in the 18 lbs./gallon injection borehole 7 days after slurry injection. Free water was found in the 16 lbs./gallon injection borehole for a total of 21 days after slurry injection. The free water found in these boreholes were periodically sampled and examined for their pH value. The properties of the field collected water are listed on Table 8.

pH Variations

The water samples collected from the boreholes after the placement of the slurry all had pH values in excess of 10. In the 18 lbs./gallon slurry injection borehole, the pH of the water was recorded at 11.3 the first day, increased to 11.8 by the fifth day, and remained at that value until the seventh day when no more free water could be detected, Figure 34. The water in the 16 lbs./gallon slurry injection borehole recorded a pH of 10.8 on the first day, increasing to 11.2 by the fifth day, and slowly increased to 11.8 by the fourteenth day, Figure 35. No increase or decrease in the pH of the water from the 16 lbs./gallon slurry injection borehole was observed after the 14th day and could not be determined after the 21st day.

Although no free water could be detected in the 20 lbs./gallon slurry injection borehole or the simulated mine shaft opening an attempt was made to determine the qualitative effects of the solidified slurry on pH. One pound core samples from the 20 lbs./gallon slurry batches of coal fly ash which had been hydrated with the mine waters were placed in 2 gallon distilled water baths. Seven days after destructive testing of the cores the pH value of the bath was recorded. In all tests, the pH value of the distilled water bath was increased from a neutral value of 7 to a minimum alkaline value of 12 with the 28 day cured core samples raising the pH to 12.2, Figure 36.

Coal fly ash core samples which had been destructively tested were also placed in water baths containing the mine waters. The one pound core samples were placed in 2 gallons of acidic mine water and were measured for pH 7 days after destruction.

Again, the bath waters experienced a dramatic increase in the pH value from a neutral value of 7 to a minimum alkaline value of 11.8 and maximum of 12, Figure 37. This dramatic increase in the pH value of the bath water is thought to be partially due to the greater surface area of the core samples. This greater surface area of the destructed core sections would increase the amount of acid neutralizing elements capable of reacting with the bath waters.

The volume of the coal fly ash in the slurry developed an acid neutralization capacity far in excess of the acidity of the mine water contained in the simulated mine even though the slurry was hydrated with the acidic mine water. The acid neutralizing elements contained in the coal fly ash consisting primarily of calcium and magnesium oxides continued to raise the pH of the water after acid neutralization during the curing of the slurry as evidenced by the increasing pH values of the free water in the slurry injection boreholes. Further, after various periods of curing, re-hydration of the slurry cores led to

FIGURE 34

pH VALUES OF THE 18 LBS./GALLON

SLURRY FREE WATER

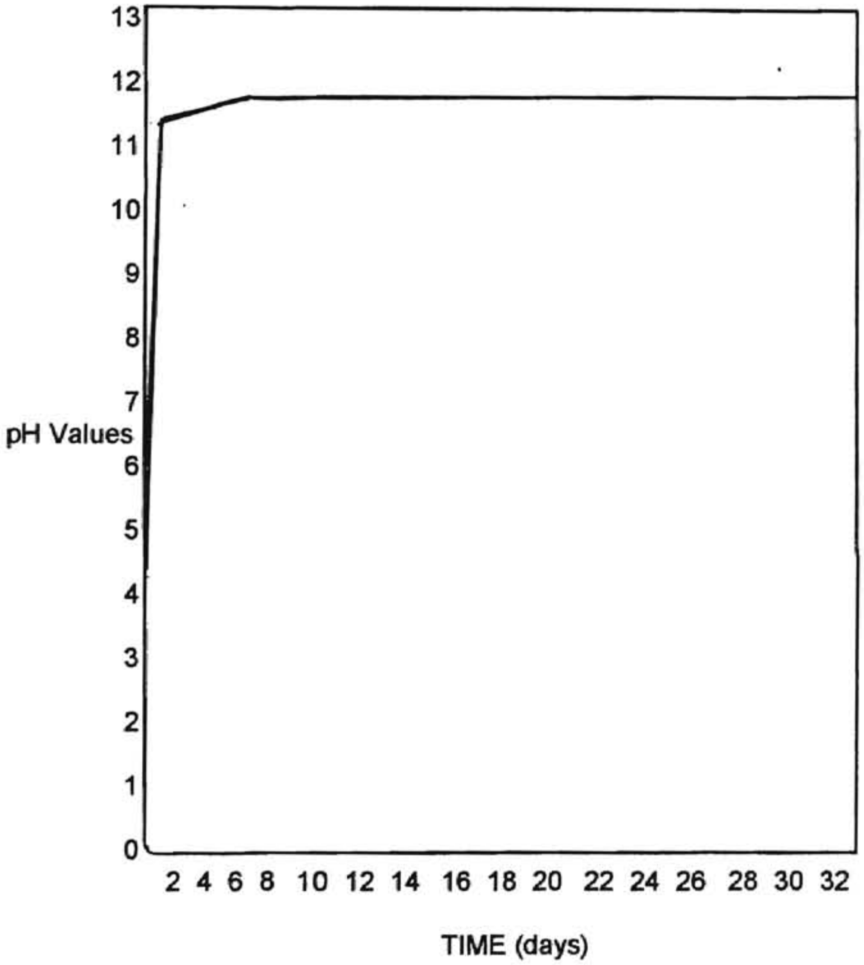


FIGURE 35

pH VALUES OF THE 16 LBS./GALLON SLURRY FREE WATER

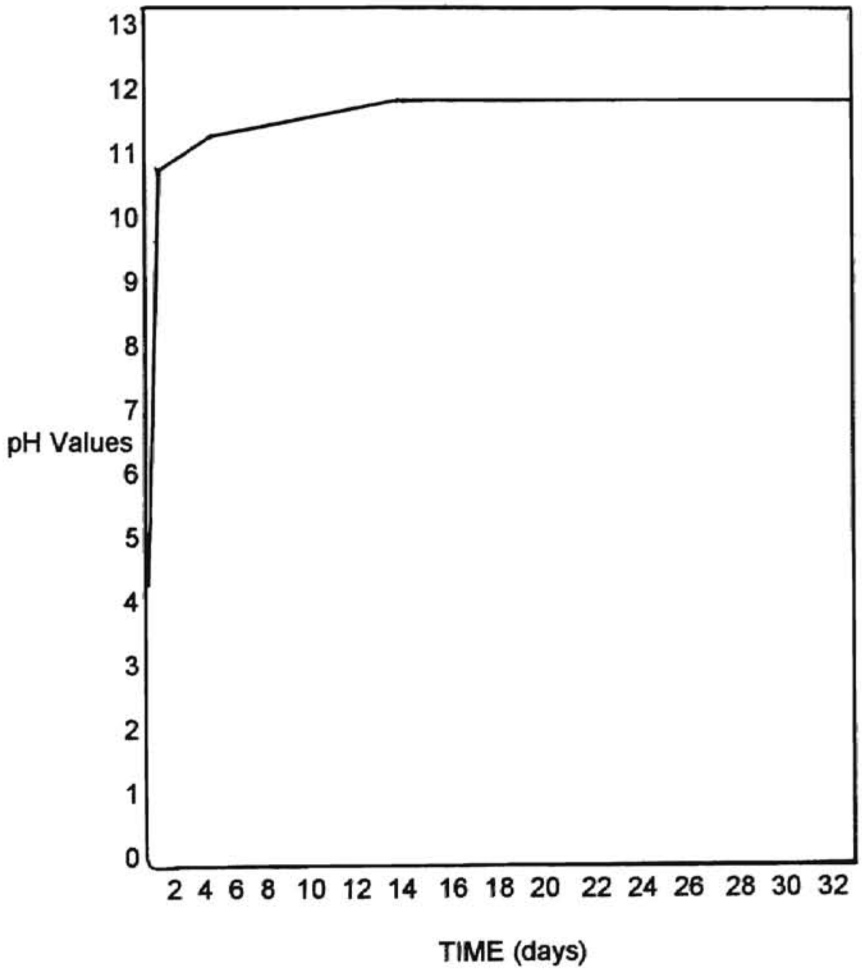


FIGURE 36

EFFECTS OF 20 LBS./GALLON SLURRY CORES ON DISTILLED WATER BATH

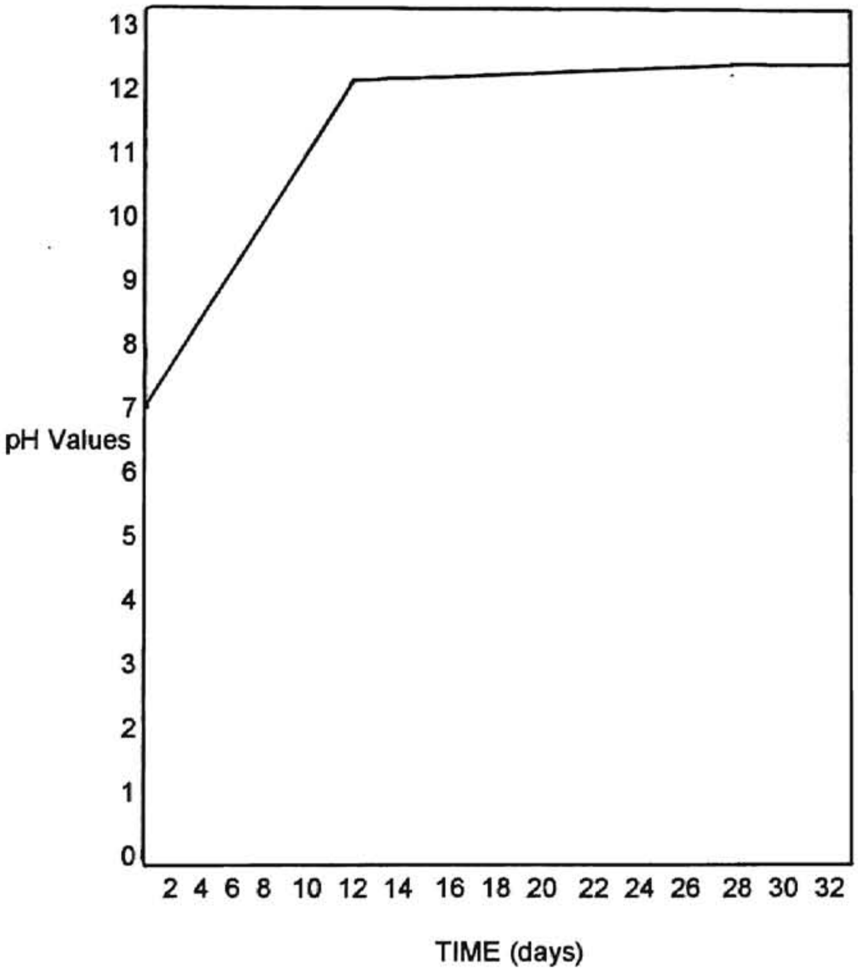
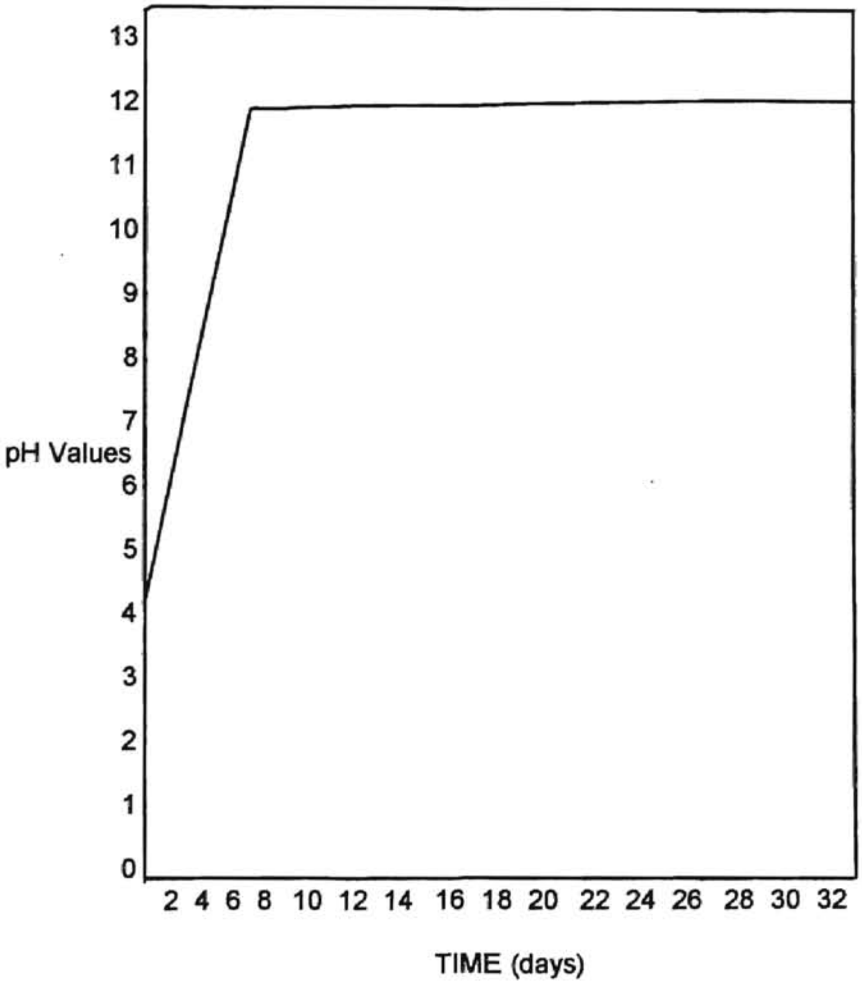


FIGURE 37

EFFECTS OF 20 LBS./GALLON SLURRY CORE ON MINE WATER BATH



substantial increases in the pH of the water baths indicating unspent calcium remained in the slurry cores. This abundance of non-reacted calcium would provide the additional acid neutralizing capacity exhibited in the test.

Redox

The reduction-oxidation reaction or Redox of the mine waters used in the study achieved a value of 311 mv prior to introduction of the slurry which compared favorably with the Redox value of 330 mv recorded at the OWRB site number 4 (Parkhurst 1987). The value of the Redox would indicate that the metals present in the mine water are actively participating in oxidation and reduction reactions.

In the Redox reaction both the processes of oxidation and reduction must occur simultaneously wherein the negatively charged reactant is oxidized at the same time that the positively charged reactant is reduced. Oxidation occurs when a reactant losses electrons while reduction involves the gaining of electrons by a reactant.

Electrochemical reactions involving metallic minerals results in the release of free energy expressed by the following equation.

$$\underline{\wedge}G = -nFE$$

(REDOX REACTION)

where $\underline{\wedge}G$ is the free energy, n is the number of electrons involved in the reaction, F is the Faraday constant, and E is the cell potential. Typically, the free energy is expressed in millivolts and the higher the number of millivolts, the greater the activity.

The minerals found in the mine waters which would react with hydrogen and oxidize most readily are calcium (Ca), magnesium (Mg), aluminum (Al), and zinc (Zn) in that order. Other minerals present in the mine water which would oxidize at a slower rate would be iron (Fe), nickel (Ni), lead (Pb), and copper (Cu). Conversely, the metals of copper (Cu+2) and lead (Pb+2) are most readily reduced followed by nickel (Ni+2), iron (Fe+2), zinc (Zn+2), aluminum (Al+3), magnesium (Mg+2), and calcium (Ca+2) in descending order (Brown 1977), Figure 38. The reactive minerals for the Redox reaction would be supplied by the discharge water form the mines. The hydrogen in the reaction would be supplied by the generation of acid within the mines.

In addition to reacting with hydrogen, many of the metallic minerals may react with one another. Zinc and copper may participate in the Redox reaction as follows.

$$Zn(s) + Cu2+(aq) \text{ ---------> } Zn2+(aq) + Cu(s)$$

In this reaction, zinc is more easily oxidized than copper and is more active because it has a weaker attraction for electrons. The Redox reaction between zinc and iron is as follows.

$$Zn(s) + Fe2+(aq) \text{ ----------> } Zn2+(aq) + Fe(s)$$

In this reaction zinc is again more easily oxidized than iron because of weaker bonding to it's electrons. The relatively high concentration of zinc compared to these other metals in the mine water solutions bear truth to these equations.

The Redox value for the mine water following the introduction of the coal fly ash slurry was found to be -55 mv. This negative value would indicate that a slightly greater amount of reducing agents are present in the amended mine water as opposed to the higher amount of oxidizing agents contained in the unamended mine water.

Specific Conductance

The mine waters used in the study had a value of specific conductance of 2390 yohms/cm which was approximately 58% of the average specific conductance value of

FIGURE 38

REDOX REACTION OF COMMON METALS WITH HYDROGEN

	Metal	Ion	
↑	K	K+	
	Ca	Ca2+	
	Na	Na+	
	Mg	Mg2+	
	Al	Al3+	
	Zn	Zn2+	
Most easily	Fe	Fe2+	Most easily
oxidized	Ni	Ni2+	reduced
	Sn	Sn2+	
	Pb	Pb2+	
	H2	H+	
	Cu	Cu2+	
	Ag	Ag+	
	Au	Au3+	↓

TABLE VIII

ANALYSIS OF SELECTIVE PROPERTIES OF THE MINE WATER PRIOR TO SLURRY INJECTION

pH	4.2
Specific Conductance	2390 milliohms/centimeter
Redox	311 millivolts
Total Dissolved Solids	2,436 milligrams/liter
Total Alkalinity	4 milligrams/liter
Soluble Calcium	572,000 micrograms/liter
Soluble Sulfate	1,722 milligrams/liter
Soluble Zinc	13,400 micrograms/liter
Soluble Aluminum	500 micrograms/liter
Soluble Nickel	340 micrograms/liter
Soluble Iron	100 micrograms/liter
Soluble Cadmium	4.6 micrograms/liter
Soluble Arsenic	3.3 micrograms/liter
Soluble Lead	2 micrograms/liter

Stover Biometrics Laboratory

4154 yohms/cm found in the OWRB studies for the study water source site. This reduced value would indicate that a lower concentration of dissolved minerals capable of ionic exchange are present in the water collected and used in the study compared to the previous OWRB studies. A possible explanation for this reduction in specific conductance is the higher water recharge into the mines and surface water runoff in the water source stream associated with the time of year the sample was collected. This would result in dilution of the discharge water from the borehole thereby lowering the concentrations of minerals in the study samples.

The specific conductance value of the mine water used in the study does indicate the presence of considerable concentrations of minerals which are exchanging ions. Because of the hazardous nature of the minerals present in the Picher Mining Field is known, and the fact that these hazardous minerals are known to exist in solution in the discharging water from the mines, the assumption may be reached that these minerals are present in the study sample waters which has been verified by chemical analysis of the water used in the study. Furthermore, the hazardous minerals in solution are actively participating in ionic exchange reactions.

The specific conductance of the mine water after slurry placement was found to have a value of 1900 milliohms/cm. This value represents a reduction in the specific conductance of approximately 20% indicating that greater ionic stabilization has been imparted to the mine water as a result of the slurry placement.

Total Dissolved Solids

The volume of total dissolved solids concentration for the water used in the study of 2,436 mg/L compared to an average of 4055 mg/L total dissolved solids found in previous OWRB studies. The reduction in total dissolved solids is sympathetically reflected in the lower Redox value of the study water relative to the Redox values found in the OWRB studies. The forwarded reason for the lower values of these two parameters is the same, dilution of the study sample water. The total dissolved solids concentration of the slurry amended mine water is 968 mg/L indicating that the fixating capacity of the slurry upon the mine water acts to bind the dissolved solids in solution into the slurry matrix both physically and chemically.

Trace Metals

Analysis was performed on the water samples collected from the study site to determine the chemical and physical properties as well as the composition of the water used in the study. The analysis for trace metals concentration was performed at Stover Biometrics Laboratory utilizing the company's "AA" furnace. Selected metals which had been previously detected in tests conducted as part of the OWRB studies of the site were analyzed to determine the concentration of those metals in the water used in the study as well as to establish the similarity of the study water to that of previous studies. This action would also verify that the degradation to the Picher Mining Field area waters was still ongoing and that the environmentally hazardous processes which had been determined in earlier studies was still occurring.

The water used in the study were examined for the trace metal concentrations of sulfates, calcium, zinc, arsenic, cadmium, lead, nickel, iron, and aluminum. These substances were all detected in the study water albeit at lower concentrations than found in the OWRB studies possible due to seasonal dilution as previously mentioned.

Soluble sulfates, expressed as SO4, comprised by far the largest percentage of detectable solids in the mine waters. The concentration of the soluble sulfates was determined to be 1,722 mg/L or 70.7% of the total dissolved solids in solution of the study water. This compares to a soluble sulfates concentration of 3,000 mg/L from the OWRB Site Number 4, sample site 24, or the same location. The OWRB value was obtained during the month of June, 1984 which may account for the higher concentration. The Environmental Protection Agency has established that a maximum concentration of 250 mg/L of sulfate may be present in it's Secondary Drinking Water Standards.

The soluble sulfates concentration found in the amended mine water was 49 mg/l. This considerable reduction is possibly attributable to the utilization of the SO4 in the hydration process involving the C3A, C4AF, and ettringite formation which all utilize sulfates within the reaction process.

The soluble calcium concentrations, expressed as Ca in the study water, was determined to be at 572 mg/L. The concentration found in the study water is somewhat higher than the soluble calcium value of 470 mg/L obtained during the OWRB study. The theory for the origin of the calcium in the discharge water from the mine is from recharge water sources, overlying calcareous bed dissolution, and or seasonally augmented surface water as has already been discussed. For most purposes, the calcium content of the water would lead to the water being considered hard. Analysis of the amended mine water indicated that the dissolved calcium concentration was 24.2 mg/L. This lower value would indicate that the calcium is bound in the slurry, had been partially spent by the acid in the solution, and was not readily leachable which is supported by the permeability tests performed on the cores.

The soluble zinc, expressed as Zn, was detected in the mine water used in the study at a concentration of 13.4 mg/L, considerably less than the 210 mg/L concentration found in the OWRB study. This dramatic drop in zinc occurrence possibly indicates that the dissolution of zinc in the mines is considerably less than in the past although other recently examined discharge sites in the Picher Mining Field continue to have very high soluble zinc concentrations. Another theory would be that the seasonal alteration of the mine hydraulics may act to restrict the discharge of the water contained in the lower portions of the mines in favor of discharge from the higher levels of the mine. Since the greatest degradation of water occurs in the lower abandoned mine working levels, a repression of influx of this water into the discharge stream would decrease the solublized minerals content of downgradient discharges from the mines (Finney 1993). The level of soluble zinc in the study water is over 2 1/2 times the maximum allowed concentrations per the Environmental Protection Agency Secondary Drinking Water Standards. After the slurry placement into the mine, the amended mine water was found to have a concentration of soluble zinc of 0.209 mg/L. This amount of zinc in solution is approximately 65 times less than that of the unamended mine water and would indicate that the slurry has a tremendous capacity to physically and chemically bind the zinc.

The concentration level of arsenic, expressed as As, in the mine water used in the study was determined to be 3.3 yg/L or 0.003 mg/L. Primary Drinking Water Standards established by the Environmental Protection Agency set the maximum level of arsenic at 0.05 mg/l. No tests for arsenic were conducted at the OWRB Site Number 4 in the previous studies however at other locations in the Picher Mining Field the arsenic concentrations were recorded. The range of concentrations for these sites was from 1 to 25 yg/L with an average of 2 yg/l.

Soluble cadmium, expressed as Cd, was measured at a level of concentration of 4.6 yg/L in the mine water for this study. This compares with an average winter months level of concentration of cadmium of in the OWRB studies of 20 yg/L and a summer months average concentration of 41 yg/L. The maximum allowable level of cadmium in the Environmental Protection Agency Primary Drinking Water Standard is 0.01 mg/L. The cadmuim concentration in the slurry amended mine water was found to be <0.05 yg/L.

Soluble lead, expressed as Pb, was detected at 0.002 mg/L in the study water. This concentration is considerably less than the 38 yg/L concentration found in the OWRB study for the site possibly due to the seasonally modified mine hydraulics as previously mentioned in this study. The level of lead in the study water is approximately 1/5th the maximum allowable Primary Drinking Water Standard established by the Environmental Protection Agency.

Soluble nickel, expressed as Ni, is a Environmental Protection Agency Priority Pollutant and was detected in the study water at a concentration level of 0.34 mg/L. This was approximately 1/8th the level of concentration of nickel in the OWRB study collected during the summer study sampling. The amended mine water was found to contain a soluble nickel concentration of 0.097 mg/L or approximately 1/3rd less than the original amount indicating that the slurry exerts a fixating influence of the nickel.

Soluble iron, expressed as Fe, was detected at a concentration of 100 mg/L. This amount of iron in solution in the study water in far in excess of the Secondary Drinking Water Standards of 0.3 mg/l set forth by the Environmental Protection Agency. Although the iron level found in the study water is considerably less than that of the OWRB studies, it indicates that the solublization of iron is still ongoing in the abandoned mines and poses a threat to the environment. In the slurry amended mine water, the concentration was found to be 0.08 mg/L indicating that the soluble iron is being fixated or utilized in the slurry cementation process. This high utilization level may manifest itself in the formation of iron substituted ettringite or other iron augmentable cement compounds.

Soluble aluminum, expressed as Al, was detected at a concentration of 0.5 mg/L in the study water. This compares to a concentration of 5.9 mg/L found in the summer study of the OWRB Site Number 4, sample site 24.

The concentrations of these trace metals found in the slurry amended mine water are listed on Table 9.

Alkalinity Minerals

Chemical analysis conducted on the mine water disclosed that the calcium, expressed as Ca, related alkaline minerals were present in a concentration of 572 mg/L. This concentration of calcium minerals in the mine water is thought to be the result of the recharge water entering the mines having a source origin high in calcium content and due

TABLE IX

WATER QUALITY IN SLURRY AMENDED MINE WATER

pH	11.5
Specific Conductance	1700 milliohms/centimeter
Redox	-55 millivolts
Total Dissolved Solids	968 milligrams/liter
Total Alkalinity	----
Soluble Calcium	24.2 milligrams/liter
Soluble Sulfate	49 milligrams/liter
Soluble Zinc	0.209 milligrams/liter
Soluble Aluminum	-----
Soluble Nickel	0.097 milligrams/liter
Soluble Iron	0.08 milligrams/liter
Soluble Cadmium	<0.05 milligrams/liter
Soluble Arsenic	-----
Soluble Lead	<0.02 milligrams/liter

to interaction of the discharging water with calcareous beds above the mine works. This concentration of potentially acid neutralizing minerals is thought to have exerted a buffering effect on the discharging water collected from the study sample site It has been demonstrated that this buffering action would not only raise the pH of the discharging water but also lead to the reduction of trace metals concentrations therein. The concentration of the alkalinity minerals detected in the slurry amended mine water is 136 mg/L.

Total Field Alkalinity

The total field alkalinity of the water, expressed as CaCO3, used in the study was found to have a concentration of 4 mg/l indicating that buffering of the mine water was taking place to some degree. However, the pH value of the mine water was still observed to have an average value of 4.2 which indicates that the acid production occurring in the mines is greater than the neutralizing capacity of the recharging water entering the mines.

Furthermore, the calcareous formations which the discharging water from the mines nor the surface runoff water in the bar ditch at the study site water source point do not have a sufficient calcium content to fully neutralize the acidity of the discharge water or preclude the transportation in solution of hazardous trace metals.

Fly Ash Slurry Characteristics

The coal fly ash slurries used in this study were tested for several physical and chemical parameters germane to the solidified mixes capacity to effectively neutralize, bind, or absorb the environmentally hazardous constituents contained in the mine waters. Further, tests were undertaken to determine the physical competence of the mixes with regards to solidification performance after placement.

Compressive Strength

Eighteen 3 inch diameter x 6 inch length and nine 4 inch diameter x 8 inch length cores were cast from each of the 16, 18, and 20 lbs./gallon batch slurries mixed and pumped into the simulated mine. Additionally, nine 3 inch diameter x 6 inch length cores and one 4 inch diameter x 8 inch length core were cast from a fourth slurry batch mix consisting of a 20 lbs./gallon density with volumetrically, a 5% bentonite inclusion. The 3 inch diameter cores were used exclusively for compressive strength whereas the 4 inch diameter cores were selectively utilized for determination of permeability, fixating capacity, binding capacity, leachability testing, and observation.

Three cores from each batch slurry were cured in a moisture room, and three were cured in a mine water bath. The cores were then destructively tested in a hydraulic press for compressive strength in groups of three. Tests were conducted at 7, 14, and 28 days from casting of the cores and the results recorded on Table 10.

The 16 lbs./gallon batch slurry cores which were moisture room cured developed an average compressive of 70.0 lbs./sq. inch in 7 days, 87.7 lbs./sq. inch in 14 days, and 91.9 lbs./sq./ inch in 28 days of curing. While the slurry mixes in the cores were observed to take an initial set in approximately 15 minutes, the water/cement (fly ash) ratio of 0.5 apparently retarded not only the early strength gain but the ultimate compressive strength of the core mix. When the cores were placed in the hydraulic press, all three failed due to plastic flow and not brittley.

The mine water bath cured 16 lbs./gallon batch slurry cores did not attain a true set, could not be successfully removed from the core forms, and throughout the 28 day test period did not develop sufficient form to be tested in the hydraulic press. Penetration of these cores by metal rod indicated that the 7 day and 14 day test cores were unconsolidated and the 28 day cores had a "waffered" consistency of alternately slightly

TABLE X

COMPRESSIVE STRENGTH TESTS

Slurry Density	Moist Cure			Hydraulic Cure		
	7day	14day	28day	7day	14day	28day
16 lbs./gal.	70.0	87.7	91.9	----	----	----
18 lbs./gal.	101.0	149.9	161.1	----	49.3	78.8
20 lbs./gal.	1025.7	1287.7	1351.0	164.4	198.4	217.0
20 lbs./gal. with 5% Bentonite	987.3	1238.8	1347.2	166.0	191.6	205.5

*** Values are the average for the three cores destroyed for a designated slurry batch on a test day.

*** Compressive strength values are in pounds per square inch.

solidified and liquid layers. The slurry mixes within the cores were flowable upon removal form the core forms.

The 18 lbs./gallon batch slurry cores which were moisture room cured developed a 7 day compressive strength of 101 lbs./sq. inch. The 14 day cure test attained a compressive strength of 149.9 lbs./sq. inch and the 28 day cure test value for compressive strength was 161.1 lbs./sq. inch. The 28 day compressive strength value for the slurry cores from this batch is approximately 1 3/4 times greater than that of the 16 lbs./gallon cores 28 day compressive strength.

The cores from the 18 lbs./gallon slurry batch which were immersion cured in the mine water did not develop any compressive strength in the 7 day test. However, the 14 day cured cores began to exhibit a competent set and developed 49.3 lbs./sq. inch compressive strength before plastic failure. The cores from this slurry batch which were tested at 28 days of curing attained 78.8 lbs./sq. inch compressive strength and also failed plastically. The water to cement (fly ash) ratio of the 18 lbs./gallon slurry was 0.45 which apparently allows sufficient hydration without oversaturation of the paste to the degree of precluding immersion (hydraulic) setting. However, failure is still plastic indicating that this water/cement (fly ash) ratio retards or arrests the C-S-H reaction prior to completion.

The 20 lbs./gallon slurry batch cores, having a water/cement (fly ash) ratio of 0.40, developed considerably higher compressive strength and competence over the cores of greater water/cement (fly ash) ratios. The moisture room cured 7 day compressive strength test value was 1025.7 lbs./sq. inch, the 14 day compressive test attained 1287.7 lbs./sq. inch, and the 28 day test developed 1351 lbs./sq. inch of compressive strength. Comparatively, the 28 day test value of compressive strength for this batch is over 8 times that of the 18 lbs./gallon slurry batch cores. These cores when destructively tested failed brittley. Visual examination of the cores from this batch indicated that no visible pore space could be seen and the exterior grains were effectively bonded to the cores. The hydraulically cured cores from the 20 lbs./gallon slurry batches developed compressive strength in all three tests. The 7 day, 14 day, and 28 day cured cores attained compressive strengths of 164.4 lbs./sq. inch, 198.4 lbs./sq. inch, and 217.0 lbs./sq. inch respectively. Primarily, failure of these cores was brittle although some plastic deformation was observed during the destructive testing of the cores. The degree of plastic failure decreased with the increase in length of curing time.

The 20 lbs./gallon slurry which included 5% bentonite developed moisture room cured compressive strengths of 987.3 lbs./sq. inch for the 7 day test, 1238.8 lbs./sq. inch for the 14 day test, and 1347.2 lbs./sq. inch for the 28 day test. The compressive strength values of these cores vary less than 50 lbs./sq. inch from the 20 lbs./gallon cores compressive strengths indicating that the volume of bentonite in the mix did not appreciably affect the core compressive strengths. Failure of the cores during destructive testing was brittle and visual observation revealed a smooth outer surfaces of the cores thought to be the result of the "waxy" texture of the bentonite.

The hydraulically cured cores from this slurry batch developed compressive strengths in all the tests. The 7 day, 14 day, and 28 day tests attained compressive strengths of 166.0 lbs./sq. inch, 191.6 lbs./sq. inch, and 205.5 lbs./sq. inch, respectively. Failure was observed to be primarily plastic with some minor brittle failure observed in the 7 day and 14 day tests.

Permeability

Three 4 inch diameter x 8 inch length cores, one each from the18 lbs./gallon, 20 lbs./gallon, and 20 lbs./gallon slurry batches, were examined for permeability. All cores were hydraulically cured in a mine water bath for 21 days and were then placed in the moisture room until they were placed in the permeability testing chamber on the 28th day following casting. The length of the permeability tests was 168 hours at which time the permeability of each core was calculated. The 18 lbs./gallon slurry batch cores developed a permeability of 1 x 10 5 cm/sec. and had a density of 60.4 lbs./foot3 with a moisture content of 55.4%. The unamended 20 lbs./gallon slurry batch cores had a permeability of 1.9 x 10 7 cm/sec. and a moisture content of 15.8%. The 20 lbs./gallon slurry batch core with the 5% bentonite admixture attained a permeability value of 7.3 x 10 9 cm/sec. with a moisture content of 10.8%.

Leachability

The cores examined for permeability were also examined for leachability. The leachability test was conducted over a 168 hour period. The fluid samples from the cores were collected and analyzed for physical characteristics and chemical composition. The 18 lbs./gallon slurry had the highest permeability and as expected leached more rapidly than the less permeable, higher density slurry cores.

Stability

The physical stability of the slurry batches injected into the simulated mine was examined to determine the set, curing, and competency of the different density slurries. At 28 days after placement of the slurries into the simulated mine the roof plates of the mine were removed to gain access to the fly ash cement in the drifts. The injection of different density coal fly ash slurries into different boreholes and the shaft opening of the mine allowed the for the examination of how the different slurry densities performed under the same conditions within the simulated mine.

The 16 lbs./gallon slurry batches were placed in the injection borehole furthest from the shaft of the simulated mine. No free water was observed at the surface of the however, the slurry had the consistency of a thick liquid and was easily deformable. Additionally, the slurry fill was flowable without observable surface cracking of breaks. Metal rod penetration tests were performed and found that a "waffered" structural development of thin (1/4 to 1/2 inch thick) consolidated, incompetent layers separated by liquid layers (1 to 2 inches thick) was present. After penetration of the slurry with the rod, minor amounts of free water were observed bleeding from the liquid layers, Figure 39.

The 18 lbs./gallon slurry batches were injected into the middle borehole. Upon removal of the roof plates for this section, some deformation could be induced on the surface of the slurry filler with some minor fracturing and as with the 16 lbs./gallon slurry filler, no free water could be found at the surface. The consistency of the surface of the slurry filler was that of an extremely thick liquid to a plastic and the overall description of the deformation would be considered to be plastic and somewhat flowable. Metal rod penetration testing revealed that the filler still had a "waffered" structure although the liquid layers were thinner (1/2 to 1 inch thick) and the consolidated layers were thicker (1 to 2 inches thick) and were considerably more resistant to penetration. Very minor amounts of free water were observed coming from the liquid layers and entering the excavation hole dug in the slurry filler.

The 20 lbs./gallon slurry was injected into the borehole closest to the simulated mine shaft opening. The removal of the roof plates over this section of the drift revealed a relatively hardened surface which had no free water. The slurry filler did not deform readily and tended to fracture although some plastic movement was observed. The surface of the slurry filler was devoid of visible individual grain structure and had a smooth appearance. Penetration tests of were undertaken and revealed almost complete solidification of the slurry filler with sporadically distributed, very thinly bedded liquid to plastic laminations within the slurry filler. The metal penetrator rod had to be driven through the slurry filler with a hammer and upon the digging of an excavation hole only traces of free water could be detected coming from the plastic-liquid laminations.

The final slurry batch was placed in the simulated mine shaft opening. This single batch was a mixture of coal fly ash and 5% bentonite. The mix was blended to a density of 20 lbs./gallon and was covered in the shaft with surplus mine water. The shaft was periodically refilled with the mine water to ensure hydraulic curing of this batch but was allowed to become dry on the 28th day from placement. The surface of this slurry filler was very hard, pasty dry, and had a smooth texture at the time of testing. The metal rod test was attempted but penetration could not be achieved. In all cases, the slurry was observed to be cohesive and did not disseminate in the presence of the mine water.

Formation of Cementitious Materials

The coal fly ash used in the slurry to fill the simulated mine has been determined by chemical analysis to contain sufficient quantities of calcium, magnesium, and aluminum oxides to form C-S-H, CH, ettrigite, and or monosulfoaluminate. The rapid rate of reaction typically experienced with high Class "C" coal fly ash content cements is somewhat slowed by the concentration of sulfates in the mine water used to hydrate the fly ash paste in the slurry.

This slowing of the reaction allows the tricalcium aluminate (C3A) to generate and liberate less heat than would otherwise occur. Additionally, the slowing of the reaction of C3A allows the formation of additional C2S. Both C3A and C3A (+ CSH2-calcium sulfate dihydrate in solution in the mine water) achieve over 90% hydration at 28 days following placement and attain almost all of their compressive strength within that time, Figure 40. Calcium oxide and aluminum oxide are both supplied to the C3A reaction by the Class "C" coal fly ash and the CSH2 is supplied to the reaction from the mine water used in the hydration process.

The C3A in the presence of the sulfates in the mine water leads to the development of ettringite during hydration. The formation of ettringite has been observed in the cured slurry core samples by Scanning Electron Microscopy. Since the supply of sulfates to the C3A reaction is quiet high the formation of ettringite is thought to proceed to completion

FIGURE 39

16 LBS./GALLON 28 DAY SET IN SIMULATED MINE

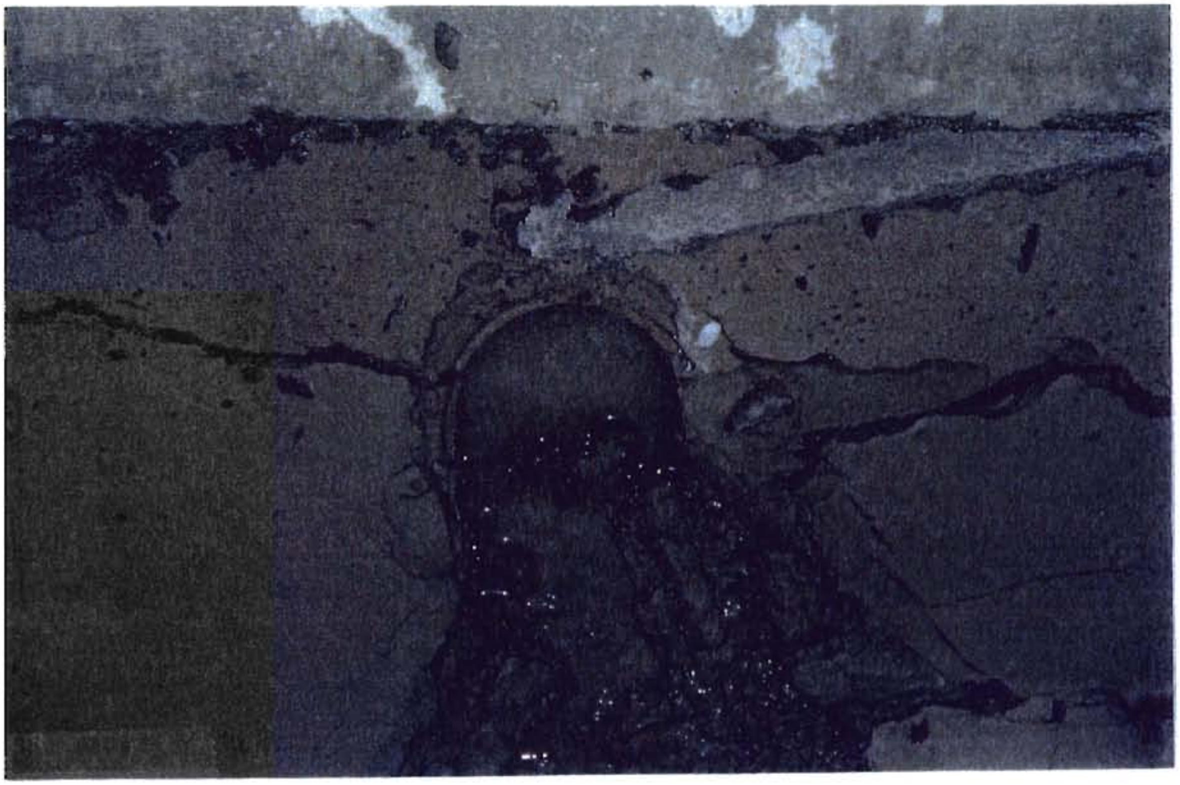
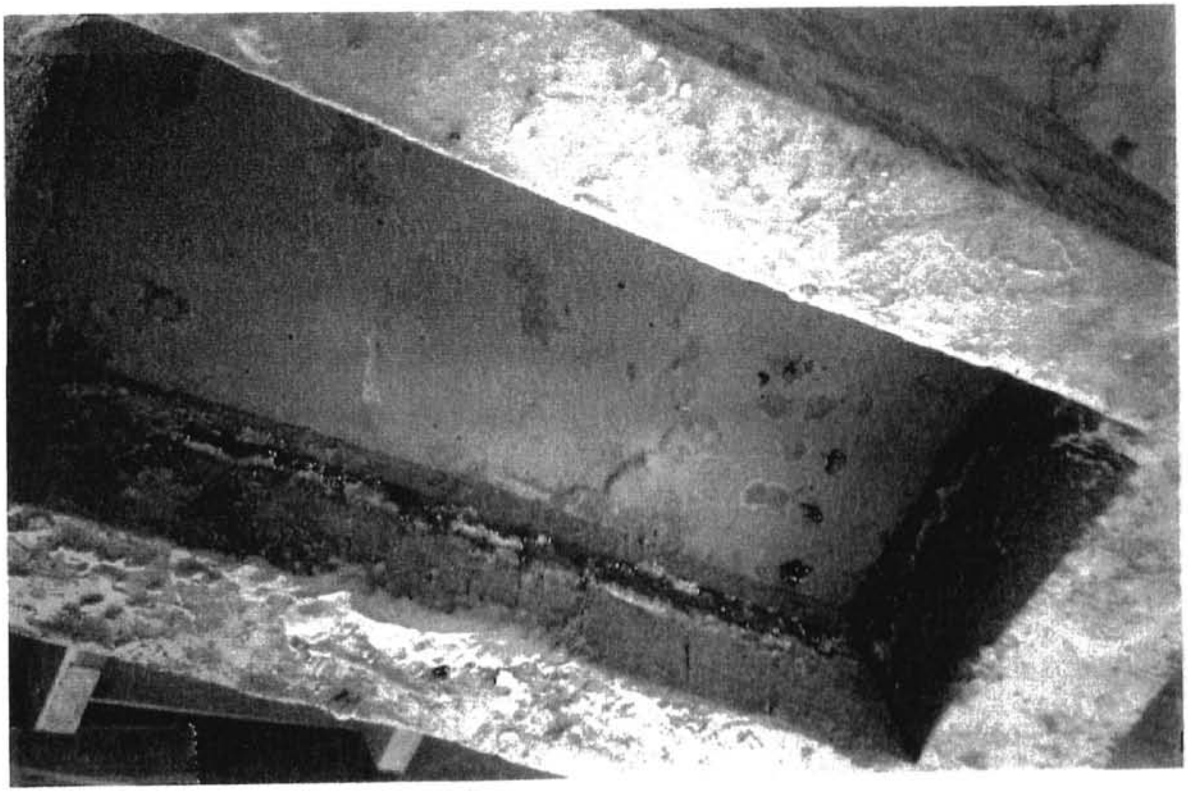


FIGURE 40

20 LBS./GALLON 28 DAY SET IN SIMULATED MINE



utilizing all the C3A in the slurry. Therefore, monosulfoaluminate would not be formed by the potential re-introduction of sulfates to the slurry since the ettringite would exist in a stable state. This would suppress the volumetric expansion and contraction cycle associated with the ettringite-monosulfoaluminate reversible reaction which would increase the soundness of the slurry filler after placement, setting, and curing.

The high concentration of silica oxide in the coal fly ash provides a source of extremely finely divided silica for the formation of the C2S and C3S in the slurry. The formation reaction for C2S, dicalcium silicate, is relatively slow and it initially develops low compressive strength which increases over time to approximately 75% that found in C3A.

At 28 days after placement, the C2S in the slurry would only be 30% hydrated and at 90 days only 50% hydrated. Thus, the slurry filler placed in the mine under hydraulic conditions would continue to gain strength for some time after placement, Figure 41, Figure 42.

The C3S, tricalcium silicate is responsible for the majority of the compressive strength found in the slurry. C3S has a moderate reaction rate and a high degree of heat liberation under normal placement and curing conditions and generally requires additional water application to the pour to aid in the hydration and to reduce heat generation and liberation which could lead to thermal cracking.

At 28 days following placement, C3S becomes approximately 75% hydrated and is approximately 90% hydrated at 90 days after placement under normal conditions. With hydraulic placement of the slurry, the hydration of the C3S may be accelerated due to the availability of water which may aid in the hydration process as well as cool the thermal generation of the C3S formation.

Additionally, tetracalcium aluminoferrite, C4AF, is potentially generated in the hydration process due to the availability of calcium oxide, aluminum oxide, ferric oxide from the Class "C" coal fly ash and the calcium sulfate dihydrate (gypsum) present in the mine water used in the slurry. The reaction rate of C4AF + CSH2 is moderate as is the heat liberation. C4AF develops a low compressive strength but imparts a degree of sulfate resistance to the slurry.

Fixating Capacity

The Class "C" coal fly ash used in the slurry upon achieving a set, acted to incorporate the contaminants contained in the mine water through chemically and physically binding them within the slurry batches. Leachability tests conducted on the cores revealed that the leachate water contained reduced amounts of the contaminants than were detected in the unamended mine water. The hydration of the cementitious materials contained in the coal fly ash is considered to have physically bound the mine water and constituents in the cement paste.

The soluble sulfides would be incorporated into the C3A and C4AF reactions as would any available aluminum in the solution. Further, ferric compounds in the solution would chemically bind in the C4AF reaction and any available silicates would be used in the C2S and C3S reactions. Sulfides in the mine water solution would also be available for the reaction which produces ettrigite.

Acid Neutralization Capacity

The bulk blending of the Class "C" coal fly ash into the simulated mine was performed to determine the applicability of using fly ash as a bulk filler and fixating agent in addition to determining the materials acid neutralization capacity of subsurface mine waters. The volume of coal fly ash introduced into the simulated mine overwhelmed the acidity of the water contained in the simulated mine and resulted in raising the pH of the free water remaining in the mine to a pH level approaching that of pure calcite. Therefore, since complete filling of abandoned acid mines with coal fly ash is uneconomical, impractical,

FIGURE 41

RATE OF HYDRATION OF CEMENT COMPOUNDS

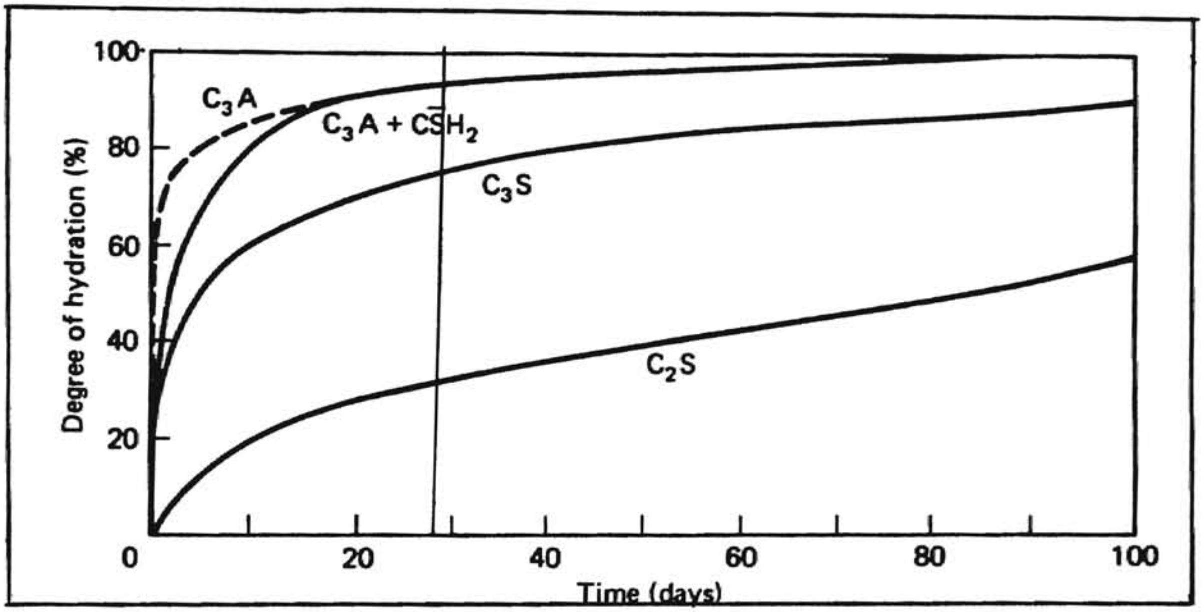


FIGURE 42

COMPRESSIVE STRENGTH DEVELOPMENT OF CEMENT COMPOUNDS

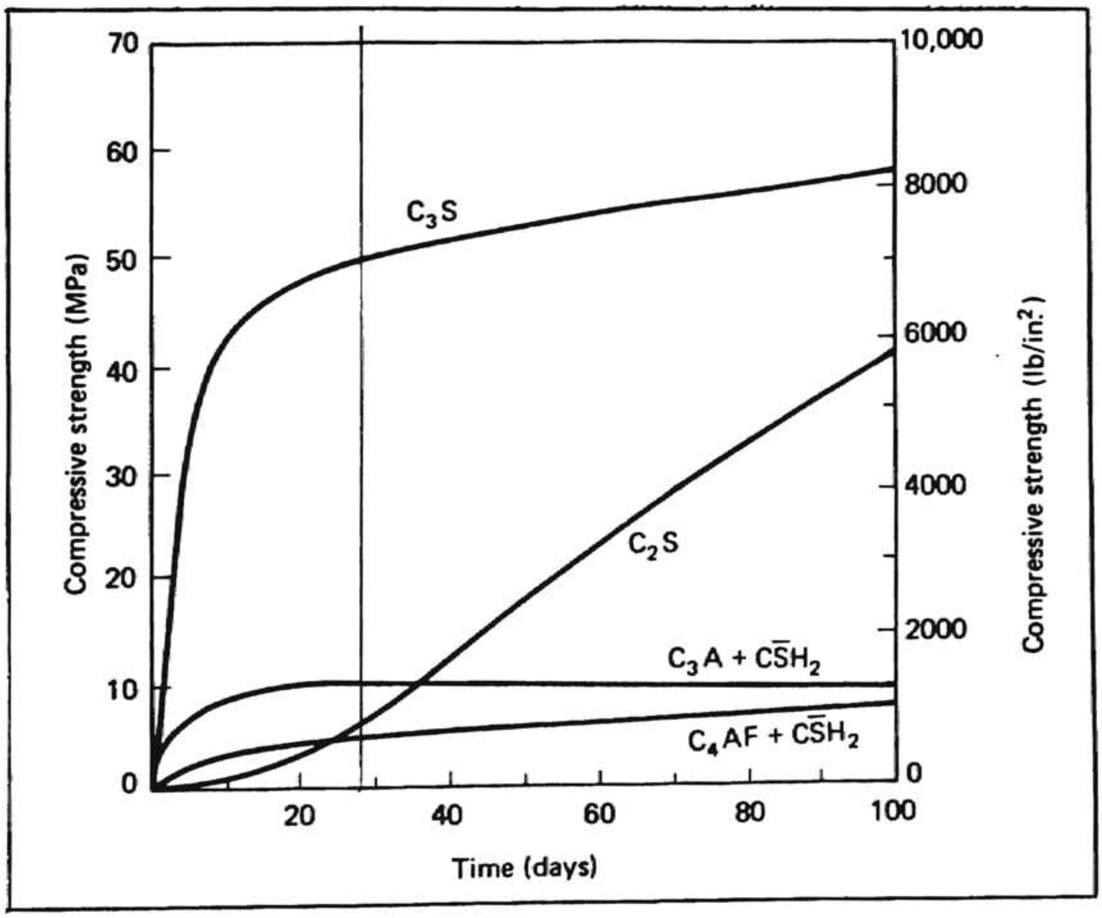


TABLE XI

ACID NEUTRALIZATION CAPACITY TESTS

pH	Grams of Class "C" Coal Fly Ash
2	15.50
3	1.55
4	1.10
5	0.75
6	0.35

*** The amount of Class "C" coal fly ash required to raise and maintain the pH of a 500ml solution to 7.0.

*** The acidity was the result of the addition of sulfuric acid mixed into a 500ml solution of distilled water.

and not a position advocated in this study, acid neutralization potential tests were conducted.

The tests were performed on acidic solutions prepared in the laboratory to determine the amount of the coal fly ash of the type used in this study would be required to effectively raise and maintain the pH of the acidic solutions to a value of 7 or neutral. Solutions of sulfuric acid were mixed in the laboratory to a volume of 500 ml for use in the test. Laboratory samples were prepared at pH values of 2, 3, 4, 5, and 6 to examine the effects of the coal fly ash on a range of acidic solutions. The measured pH of the mine water used in this study was 4.2.

The laboratory solution with a pH value of 2 was found to require 15.5 grams of the study fly ash to neutralize and maintain the pH of the solution at 7. The volume of study fly ash needed to amend the solution with a pH value of 3 was 1.55 grams. The amount of study fly ash necessary to neutralize the pH 4 and pH 5 solutions was 1.10 grams and 0.75 grams, respectively while 0.35 grams of study fly ash was required to neutralize and stabilize the pH of the solution with a pH value of 6.

The ratio of the study coal fly ash required to neutralize the solution with a pH value of 2 compared to the solution with a pH of 3 is 10 to 1. The ratio for the neutralization and stabilization of pH in the solution with a pH of 3 compared to the solution with a pH of 4 and from pH 4 to pH 5 is approximately 3 to 2. The pH 5 to pH 6 acid neutralization ratio requirements for the study coal fly ash is slightly greater than 2 to 1. Thus, the requirements for acid neutralization are dependent not only on the volume of the acidic solution but also on the degree of acidity.

CHAPTER V

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

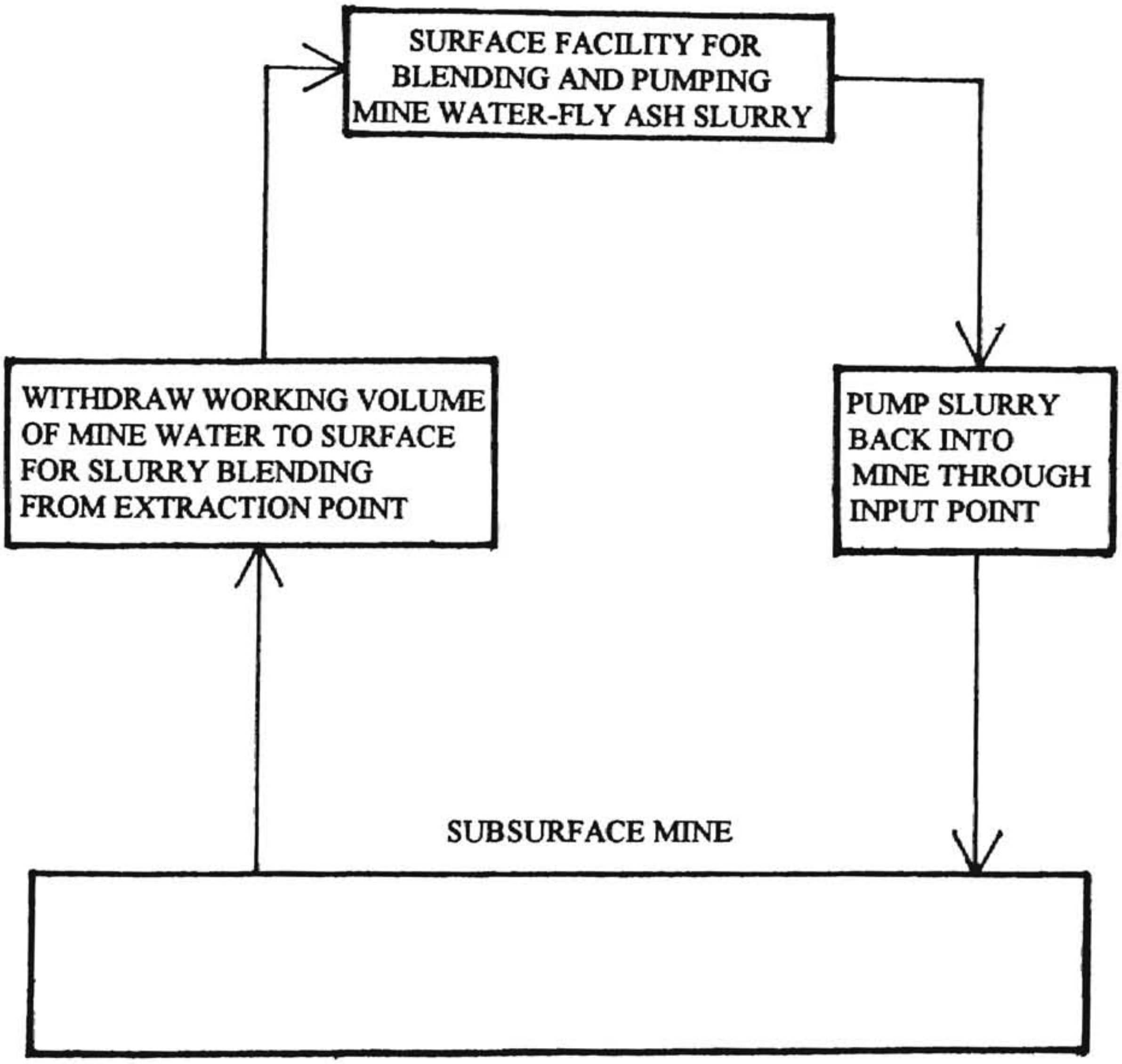
Summary

This study was undertaken to determine the viability of utilizing Class "C" coal fly ash for the remediation of hazardous waste discharges from subsurface sources through the placement of slurried fly ash into the subsurface hazardous waste sites. This would conceptually be performed in a closed-loop, insitu, extraction-treatment-injection system, wherein the acid neutralization and trace metals fixating capacities of the fly ash slurry could be exerted on hazardous waste at it's generation point in the subsurface, Figure 43. To accomplish this action, the Picher Mining Field, a subsurface, abandoned lead and zinc mine field currently on the Environmental Protection Agency Superfund list, was selected as a generic model for an underground hazardous waste site. The Class "C" coal fly ash used in this study was obtained from a local coal fired generating plant which uses low sulfur-high calcium content feedstock coal mined from the Powder River Basin in Wyoming.

The water used in this study was collected from a discharging mine air shaft directly connected to the underground mine working areas in the Picher Mining Field and was determined by chemical analysis to contain high to dangerously high concentrations of trace metals and acidity. The concentration of these trace metals, specifically lead, zinc,

FIGURE 43

CLOSED LOOP SYSTEM FOR REMEDIATION OF SUBSURFACE ACID MINE WATER



nickel, cadmium, copper, iron, sulfides, and the solution acidity are such that they pose a risk or potential risk to the human health, safety, and environment of the area and to receiving water bodies and aquifers downgradient from the abandoned mines.

To evaluate the premise of the study, a simulated mine was constructed and filled with the collected discharging water from the Picher Mining Field. Subsequently, the mine water was withdrawn in batches, blended with the fly ash to create variable density slurries, and pumped back into the simulated mine through different injection points to facilitate the evaluation of the different batches within the same environment. Additionally, core samples were taken from the different batches and tested for leachability, compressive strength, permeability, and structural development.

At specific time intervals following the placement of the slurry into the simulated mine, tests were conducted to determine the physical and chemical reactions, properties, and characteristics of the remaining water in the simulated mine as well as the slurry itself, Figure 44. This was followed by a dissection of the simulated mine at the completion of the study to observe the condition and stability of the slurry and the environment within the simulated mine. The conclusions reached in this study are based on the results of these tests and other supporting research.

Conclusions

Acid Production and Control

The water used in the simulated mine contained an acidic pH value of 4.2. The acidic content of the discharging mine water is due to the environment present in the underground mine working spaces in which sulfide minerals have been exposed to atmospheric oxygen and or oxygenated water. Through this exposure, oxidation and hydrolization has occurred with the sulfide minerals which leads to the production sulfuric

FIGURE 44

APPARENT INFLUENCE OF FLY ASH ON MINE WATER

MINE WATER

pH = 4.2
S.C. = 2390 milliohms/l
REDOX = 311
TDS = 2436 mg/l
SULFATES = 1722 mg/l

METALS
ZINC = 13,400 ug/l
NICKEL = 340 ug/l
IRON = 100 ug/l
CADMUIM = 4.6 ug/l
LEAD = 2 ug/l

+

FLY ASH SLURRY

POZZOLANS SiO2, Al2O3, and Fe2O3 = 61.46%
SO3 = 2.04%
MgO = 4.69%
CaO = 26.46%

↓

AMENDS MINE WATER

FROM	TO
pH 4.2	11.5
S.C. 2390 milliohms/l	1700 milliohms/l
REDOX 311	-55
TDS 2436 mg/l	968 mg/l
SULFATES 1722 mg/l	49 mg/l
ZINC 13,400 ug/l	209 ug/l
NICKEL 340 ug/l	97 ug/l
IRON 100 ug/l	80 ug/l
CADMIUM 4.6 ug/l	<50 ug/l
LEAD 2 ug/l	<2 ug/l

THROUGH CHEMICAL AND/OR PHYSICAL INCORPORATION IN THE SLURRY, AND CHEMICAL PRECIPITATION.

acid in the mine. Once the conditions within the mine becomes acidic, the further generation of acid is accelerated compounding the acidic content of the mines, especially in areas with little fluid migration. This sulfuric acid is then available to go into the water contained in the mines and be transported with that water to downgradient receiving areas, both through the surface and groundwater, adversely impacting them.

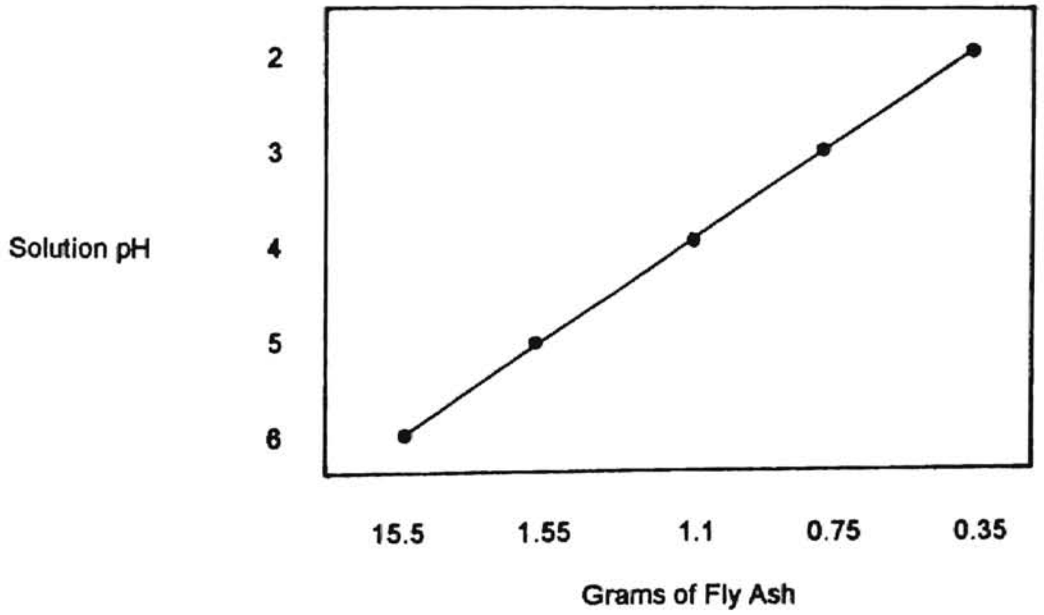
The introduction and assimilation of the Class "C" coal fly ash into the mine water in slurry form had the effect of altering the pH of the solution water from an acidic value of 4.2 to a stabilized basic value of over 11.5 at the conclusion of the 28 day test. This was accomplished even though the Class "C" fly ash slurry was blended with the acidic mine water and hydraulically cured in the presence of the acidic water in the simulated mine. The relatively high concentration of calcium and associated magnesium contained in the study fly ash imparts to the Class "C" fly ash a high acid neutralization capacity which exerts a buffering effect on the sulfuric acid solution.

The pH value of 11.5 is far in excess of what would generally be considered warranted for a solution but was a necessary by-product of the study because compressive strength tests of the variable density slurries needed to be determined. To develop a meaningful determination of the acid neutralization capacity for the specific Class "C" fly ash used in this study on the specific waters contained in the Picher Mining Field, sulfur acid titrations were conducted for solutions with a pH value of from 2 to 6. The methodology involved determining the volume of study fly ash required to neutralize and stabilize the acidic solution to a pH value of 7, Figure 45.

While the study fly ash produces specific acid neutralization capacity values for the environment present in the Picher Mining Field, these values have the potential to change in other settings due to variables such as different pH values, site specific requirements or goals, trace metals content and concentrations, mine hydraulics, geology, hydrology, types of acid being generated, pK points, and variations in the calcium/magnesium content of the Class "C" coal fly ash.

FIGURE 45

ACID NEUTRALIZATION CAPACITY OF STUDY FLY ASH



Sympathetically, the determination of the desired level of pH required to retard the mobilization of specific trace metals contained in the discharge solutions is required to properly size the volume of Class "C" fly ash to be placed in the subsurface site. While most trace metal mobilization is arrested when the solution is brought from acidic to neutral pH values, site specific conditions may require a stabilized solution pH of greater than 7 to achieve that goal. Additionally, long term acidic solution neutralization and or stabilization may require that the pH of the slurry amended solution be designed to initially exceed neutral if the potential for additional acid production exists. Supportively, if long term stabilization of the pH presents a continuing problem due to continued acid generation or influx into the treated area, periodic re-treatment of the site through the existing injection points may be performed.

Trace Metals Production and Control

The oxidation-reducing environment contained in the underground mine working spaces of the Picher Mining Field has lead to the solublization of the ore rocks which contain a variety of trace metals consisting primarily of zinc, lead, copper, cadmium, nickel, iron, and sulfides. With the generation of acid in the mines, many of these trace metals have been liberated from the ore rock and subsequently gone into solution in the waters contained in the mines. Once in solution, these trace metals may be transported out of the mines hydraulically through ground and surface water migration to downgradient receiving areas. In these receiving areas they may remain in solution and available for uptake through biota or precipitate out to form deposits, both potentially posing a threat to the human health and environment.

The water used to hydrate the fly ash slurry was collected from the Picher Mining Field and contained concentrations of trace metals in solution. Consequently, these trace metals were exposed to the fly ash both in the slurry and as free water in the simulated mine. The trace metals which were detected in the mine water used in the study were found to be physically and or chemically incorporated into the fly ash slurry through the hydration process. X-ray analysis of the hydraulically set and cured slurry indicated the presence of zinc, iron, copper, aluminum, silica, calcium, titanium, magnesium, and sulfides bound in the slurry.

The cement forming reactions which occur during the hydration process consists primarily of oxide reactions. This allows the Class "C" or cementitious coal fly ash to achieve a pozzolanic set by itself. The common oxides present in Class "C" coal fly ash are calcium oxide (CaO), silica oxide ($Si2O$), aluminum oxide ($Al2O3$), iron oxide ($Fe2O3$), magnesium oxide (MgO), and trace amounts of other oxides.

The study mine water from the Picher Mining Field has been analyzed and determined to contain metals of calcium, magnesium, aluminum, zinc, iron, nickel, and copper. These metals become oxidized and may therefore chemically participate and become incorporated in the cement forming reaction to become part of the cement paste by the following general reaction.

$$MO + H \dashrightarrow MH$$

This reaction taking place in the presence of calcium oxide silicates or aluminates, both occurring in abundance in the Class "C" coal fly ash used in this study, leads to the cement forming reaction upon hydration. Because the trace metals contained in the mine water used in the slurry hydration are chemically bound within the slurry and are in the alkaline environment of the slurry, they are relatively stable, have low mobility, and are not readily susceptible to leaching.

Trace metals found in the mine water solution such as lead may be physically bound within the slurry by incorporation of the trace metal into the cement matrix through the hydration process. This process acts to encapsulate the trace metals into the paste matrix wherein the alkaline environment tends to stabilize the trace metals and reduce or retard their mobility.

Additionally, depending on the density of the slurry placed in the mine environment, the set slurry develops resistance to permeability or fluid flow which is directly related to the density of the placed slurry. Permeability ranges from (10^{-5}) for 18 lbs./gallon slurries to (10^{-7}) for 20 lbs./gallon slurries.

The 20 lbs./gallon slurries amended with 5% bentonite achieve permeabilities of (10^{-9}) mixed with the mine water from the Picher Mining Field and cured in the simulated mine environment. The low permeability values associated with the Class "C" coal fly ash slurries would tend to reduce the potential leaching of trace metals from the slurry as well as retard fluid flow through the placed and set slurry.

Furthermore, the trace metals found in the Picher Mining Field are generally solublized in the subsurface, acidic mine environment and go into solution in the mine water. The buffering effect of the Class "C" coal fly ash slurry acts to neutralize or make basic the associated mine water not incorporated in the hydration process.

This buffering effect exerted on the associated mine water leads to the precipitation of the trace metals out of solution in the mine water within the mines mitigating the transportation of these trace metals out of the mines through downgradient discharges. The buffering effect of the slurry on the associated water also reduces or curtails the solublization of the trace metals from the ore rocks within the mines by reducing the acidity of the mine environment.

Mine Water Quality After Slurry Amendment

The overall effect of the Class "C" coal fly ash slurry on the mine water from the Picher Mining Field used in this study is seen as positive with regards to the concentration of trace metals and other properties found in the amended mine waters. Water samples were taken from bleed water occurring in the less dense slurry batch placements in the simulated mine and from leachate water collected from the permeability testing of the slurry cores.

As previously mentioned, the pH of the mine water was raised from 4.2 to 11.5+ due to the alkaline influence of the slurry. The Redox value of the mine water indicated that free energy was being released into the solution as a result of the oxidation-reduction process and that oxidation was the primary reaction due to the positive value of (+311). With slurry amendment of the mine water, the Redox value became a negative(-55), indicating that reduction was prevalent within the amended solution.

The specific conductance value of the mine water indicates the presence of considerable concentrations of ionically active minerals capable of exchanging electrical charges. The level of specific conductance would indicate that these discharging waters may be corrosive to metals and otherwise verify that the known environmentally hazardous trace metals are reacting within the solution. The slurry amendment reduced the specific conductance from 2390 milliohms/liter to 1700 milliohms/liter or approximately 29%, indicating that the presence of the slurry has retarded the reactivity of the solution through fixating the trace metals into the slurry, altering the chemical environment of the solution to a less reactive state, and precipitating reactive agents out of solution in the mine water. It is generally held that the less reactivity present in the solution, the less concentration of contaminants in the solution. Therefore, the slurry has exhibited a contaminant reducing effect on the mine water which would improve the quality of the discharges from the mines thereby reducing the impact of these waters on downgradient receiving waters. This is supported by the reduction in the concentrations of total dissolved solids and trace metals found in the slurry amended mine waters.

The total dissolved solids concentration found in the mine water was determined to be 2436 milligrams/liter and was composed primarily of soluble sulfates in addition to detectable amounts of trace metals considered to be hazardous to human health and the environment. The mine water following amendment by the fly ash slurry was determined to have a total dissolved solids concentration of 968 milligrams/liter. The effect of the Class "C" fly ash slurry on the total dissolved solids was to reduce the concentration by slightly over 60% with volumetrically, the preponderance of the reduction occurring in the soluble sulfates concentration.

The soluble sulfates concentration in the mine water from the Picher Mining Field was determined to be 1722 milligrams/liter. After amendment with the slurry, the soluble sulfates concentration was found to be 49 milligrams/liter or approximately 3% of the unamended concentration and well below the Environmental Protection Agency standards of 250 milligrams/liter for Primary Drinking Water Standards.

The concentration of soluble zinc in the discharging mine water was recorded at 13,400 micrograms/liter. The concentration of zinc following amendment of the mine water with the slurry was determined to be 209 micrograms/liter or a 98% reduction from the unamended concentration levels.

Soluble nickel, an Environmental Protection Agency priority pollutant, was reduced in concentration from 340 micrograms/liter to 97 micrograms/liter, representing a 73% reduction in concentration, as a result of the slurry amendment. Likewise, soluble iron was reduced by 20% from 100 micrograms/liter to 80 micrograms/liter through slurry amendment.

These trace metals were all capable of existing as oxides in solution and were therefore able to be incorporated chemically into the slurry hydration process as well as physically bound in the slurry matrix, or precipitated out of solution due to the alkalinity of the slurry amended solution.

Metals such as lead were reduced in concentration from 2 micrograms/liter to less than 2 micrograms/liter after amendment but are considered to have been physically bound in the slurry matrix and or precipitated out of solution since they will not readily chemically participate in the cement forming process.

Fly Ash Hydration and Products

Although the simulated mine was filled with 325 gallons of mine water, only 201 gallons could be extracted from the mine for slurry blending due to assimilation of the free water remaining in the mine into the injected slurry. The slurry acted to utilize or absorb the remaining free water over a period of 21 days following placement of the slurry. Even though the free water in the simulated mine was incorporated into the slurry over this time, not all of it was bound in the slurry as evidenced by the presence of bleed water from unconsolidated layers of the less dense slurry batches. The volume of bleed water occurrence was directly related to the increase in the density of the fly ash slurry batches indicating that the free water in the simulated mine was utilized in the ongoing hydration reaction of the slurry batches and bound into the higher density slurry batches.

The compressive strength of the slurry cores varied greatly whether moisture room or hydraulically cured in the mine water bath. This range of compressive strength was due to alterations in the density of the slurries (water to fly ash ratios), and the curing environment.

The higher water/cement (fly ash) ratio slurry cores cured in the moisture room attained the least compressive strength. This lack of meaningful compressive strength at water/cement ratios above 0.45 is due to the increase of porosity in the cementitious materials paste. As a result, substantial void space exists in the paste which precludes the development of competent C-S-H, CH, and other cementitious materials growth.

While a set was achieved in the 0.45 and above water/cement (fly ash) ratio slurries, these cores failed plastically on destructive testing. Conversely, the 20 lbs./gallon slurry batches, which were hydrated with a water/cement (fly ash) ratio of 0.4, exhibited several orders of magnitude higher compressive strength upon curing in the moisture room and failed brittley on destructive testing. The method of curing of the slurry batch cores produced a demonstrable change in the overall strength characteristics of the slurry cores.

The slurry batch cores which were hydraulically cured in the mine water bath were severely retarded with respect to development of compressive strength. The 16 lbs./gallon slurry cores failed to develop sufficient structure to be destructively tested and the 18 lbs./gallon slurry cores attained less than 100 lbs./sq. inch loading capacity before failing plastically. This is thought to be due to the excessive porosity present in the high water/cement (fly ash) ratio slurries, the supersaturation of the fly ash particles in the hydraulic environment which prevented proper hydration of the cementitious materials, and the strength inhibiting effects of certain trace metals, such as zinc, in the mine water.

This position is supported by the development of compressive strength in the 20 lbs./gallon slurry cores which were hydraulically cured. Apparently, adequate amounts of cementitious materials are present in the higher density slurry batches to proceed in the hydration reaction in the presence of the hydraulic environment and trace metals allowing the creation of cement hydration products. However, the compressive strength values for the hydraulically cured 20 lbs./gallon slurry cores are considerably less than those for cores cured in the moisture room indicating that the reactions and reaction rates among the cementitious compounds contained in the slurry are suppressed although failure of the cores was still somewhat brittle.

The porosity and permeability of the cores also varied in accordance with the density of the slurry mixes. The higher density slurry cores which correspondingly possess the lower water/cement (fly ash) ratios, were determined to have lower porosity and permeability values that the lower density, higher water/cement (fly ash) ratio slurry cores. This characteristic is due to the increase in particle packing and associated gel-spacing ratio found in lower water/cement ratio pastes. Additionally, fly ash particles, due to their small size, may attain relatively high densities per unit volume which is thought to aid in the segmented hydration of the hydraulically cured cores by developing an "outer skin" effect within the paste. This "outer skin" may act to retard the supersaturation effect of hydraulic curing by restricting fluid flow through the placed slurry.

The lower density slurry batches examined in the simulated mine exhibited a waffered structural development and a capacity to flow in addition to deforming plastically. While the 16 lbs./gallon slurry batches could be made to flow under physical pressure, the slurry did not disseminate or separate but rather acted as an extremely thick, viscous, semi-plastic fluid. The less viscose layers of the slurry batches were observed to bleed water upon penetration but would not release free water if left undisturbed. The higher density slurry batches appeared to hydrate completely and developed a competent set. Only very thinly bedded layers of less viscose slurry were observed to bleed water 28 days after placement and then only in trace amounts.

The chemical analysis of the Class "C" coal fly ash used in this study revealed the presence of high concentrations of pozzolans in addition to calcium oxide (CaO), magnesium oxide (MgO), and aluminum oxide (Al2O3) in amounts sufficient to lead to the formation of the principle cement compounds of C3A, C2S, C3S, and C4AF. The reactions of these compounds upon hydration in the mine water used in this study allowed the development of the cement products of C-S-H, CH, and ettringite. The cement compound products were developed primarily in the higher density slurry batches as evidenced by the higher compressive strengths and low permeability values compared to the lower density slurries. The slurry batches, as a result of the presence of these compounds, exert a fixating effect on the solubilized trace metals contained in the mine water used to hydrate the slurry batches by physically binding or encapsulating them into the slurry cement matrix and or by incorporating metal oxides in solution into the chemical reaction taking place in the hydration process. In this process, the trace metals incorporated into the slurry paste matrix impart their distinct influences upon the placed slurry cement.

The presence of sulfides in the mine water act to retard the otherwise rapid reaction rate of the C3A and C4AF in the Class "C" coal fly ash as well as provide a sufficient sulfide source for the formation and retention of ettringite in the placed slurry cement.

Since sulfides are bound chemically in the slurry paste, they are available to react with all the C3A present which allows not only the full development of the C3A but also non-reversible ettringite, and C2S, and C3S, producing a more stable cement. The presence of soluble iron in the solution also participates in the ettringite reaction to form the extremely stable iron-substituted ettringite. Soluble aluminum and other oxides in the solution are also available to react in the hydration process and may combine with the C3A, C4AF, C2S, C3S, or other, lesser compounds cement compounds depending on their particular chemical affinity.

The incorporation of these trace metals into the placed slurry acts to reduce the concentration of these pollutants into the discharging waters from a hazardous waste site. Further, by altering the chemical environment of the subsurface hazardous waste site from acidic to alkaline, and removing reactants from solution by the influence of the slurry on adjoining waters, the hazardous waste generating environment becomes less active. This reduction in the generation and concentration of hazardous wastes, specifically trace metals and acidity, through the influence of the fly ash slurry, results in the decrease in discharges of this type of hazardous waste into downgradient receiving waters. The overall effect of the placement of the slurried fly ash into subsurface hazardous waste sites is therefore an improvement in the water and soil quality of the site and downgradient receiving areas. This in effect serves to increase the quality of the environment and human health as well as the uses of the affected areas.

Evaluation

The purpose of this study was to determine the potential of utilizing Class "C" coal fly ash as a remediating agent in the treatment of hazardous waste sites in the subsurface. Briefly, the laboratory tests conducted in this study towards this purpose have indicated that the Class "C" coal fly ash used in this study has the capacity to successfully remediate the hazardous waste discharges associated with the Picher Mining Field. The considerable calcium content of this type of fly ash imparts a high acid neutralization capacity potential to the receiving solution which was desirable with regards to the acidity of the mine discharges. Further, the fly ash was demonstrated to be capable of being blended with the acidic, trace metals laden mine water and pump-placed without difficulty into the simulated mine.

The high sulfur minerals content of the mine water actually aided in the blending and placement of the slurry by retarding the rapid setting tendency of the C3A compounds present in the fly ash. Once placed, the slurry hydrated with the mine water and chemically incorporated the solublized metal oxides and sulfides into the slurry paste. Those metals not participating in the cement forming process were encapsulated or precipitated out of solution. The reduction in the concentrations of these metals in the slurry amended mine water was found to range from 20% for iron to over 97% for zinc, and sulfides and the total dissolved solids concentration was reduced by 60%. The high levels of trace metals removal and solution acidity modification were unexpected yet demonstrated the viability of the process.

The effects of the mine water on the hydration and subsequent strength of the placed slurry revealed that to develop a competent compressive strength set in the Picher Mining Field water, the slurry density needed to be at least 20 lbs./gallon. This slurry density also attains a permeability of (10 7) which would tend to retard leaching of the bound trace metals from the placed slurry. If long distance coverage of the exposed subsurface site is more desirable, 16 to 18 lbs./gallon slurries may be desired since the 16 lbs./gallon slurry exhibited the capacity to flow and deform plastically without disseminating in the solution. If subsidence of overlying strata is a concern, then slurries with a density of over 20 lbs./gallon would be needed to develop the desired compressive strength for support.

The Class "C" coal fly ash used in this study was found to achieve or exceed all the desired goals for acid neutralization and trace metals reduction set forth in this study pertaining to remediation of the waters associated with the Picher Mining Field. Only in the low development of hydraulically cured compressive strengths were the results less than expected. This was attributed to concentration of soluble zinc in the hydration solution which exerts a deleterious effect on compressive strengths in cements. Blending and placement of the slurry by mechanical and hydraulic means was easily accomplished with light duty rental equipment and it is held that full scale field placement could be readily achieved utilizing existing high capacity industrial equipment.

Economic Considerations

In considering the viability of the subsurface placement of Class "C" coal fly ash for the control of hazardous wastes as discussed in this report, a comparative analysis of the economic outlays of this process verses other alternatives must be made. This economic analysis should consider the cost of the implementing the application, cost of operating the application, length of time involved in administering the application, effectiveness of the application, and the cost of the loss of use of the impacted areas prior to restoration.

Because the study area uses the Picher Mining Field area as a model, non-specific economic comparisons for different treatment measures will be addressed for this area. First, Class "C" coal fly ash injection verses no action. This is not an acceptable option since several hundreds of acres have already had to be abandoned due to contamination and some nearby towns have had to abandon their water supplies.

Additionally, the city of Miami, Oklahoma with 10's of thousands of people is located in a downgradient, receiving area from the Picher Mining Field. Surface water contamination from the mines has already reached the city and wells on the upgradient side of the city have be found to contain increasing levels of contaminants from the mines. Replacement of the city water supplies would not be considered a warranted option nor would abandonment of the city.

Second, take action that alters the surface drainage of the mining area to divert surface water around the mine area and plugging wells, boreholes, and mine shafts lacking mechanical integrity to stop the flow of the mine water into the water supply aquifers. This is not effective in that groundwater migration into the mines will continue from adjacent formations and the topography of the area is of such low relief that during times of high precipitation the mine area will continue to receive upstream surface waters. Further, not all the old wells, boreholes, and mine shafts in the mine area are known and the plugging of those which can be located will serve only to stop contamination at that point. Finally, this action does nothing to arrest the downgradient migration of the discharging mine waters or stop the production of acid and trace metals in the mines.

Third, installing pump and treat equipment for the downgradient affected areas. This action would only be marginally effective in that only the withdrawn water could be remediated. The pump and treat system would have to of considerable size to supply the population, livestock, and other end users with treated water and would have to be operated continuously until the mines stopped their discharges and quit producing contaminants, in other words, for the foreseeable future.

Fourth, implement the closed-loop, slurry injection of Class "C" coal fly ash into the abandoned mine works. This could be accomplished by moving supplies of surplus fly ash form one or more of several nearby coal-fired generating stations to Picher Mining Field by rail car. Several wells could be drilled the 90 to 450 feet required to reach the mine working levels and completed for water withdrawal or slurry injection as needed. Mobile blending and pumping equipment could be set up on individual injection locations to place the slurry in the mines to site specific specifications, then relocated to other injection sites to repeat the process. In this manner, the water quality of the discharging mine water is improved to meet or exceed the Primary Drinking Water Standards established by the Environmental Protection Agency and the acidic-trace metals generation is reduced or eliminated at the source. Thus, once the currently inplace contamination plume passes the downgradient receiving areas, high quality water will return to these areas. Expenditures for fly ash transportation, well drilling, services, equipment and overhead are currently estimated to be approximately ten million dollars for the remediation of the Picher Mining Field and projections indicate that the project could be completed in approximately 3 years. This cost estimate is considerably less than the alternative of pump and treat which would have the greatest potential for effectiveness of the other remediation treatment actions.

Alternative Applications

The potential use of the closed-loop, subsurface Class "C" fly ash slurry injection method discussed in this study is not limited to the Picher Mining Field. The application of this remediation system has the potential to be used in not only lead and zinc mines but other subsurface ore mines where acid mine drainage and or trace metal contamination of soils and water supplies is an issue. In the United States, this would include the lead and zinc mineral mines of the Mississippi Valley as well as the minerals and precious minerals mines in the Rocky Mountains and the West Coast Ranges. Additionally, acid mine drainage from subsurface coal mines in the Appalachian Mountains and elsewhere would potentially be receptive to such treatment as prescribed herein. Site specific environments and individual Class "C" coal fly ash compositions will undoubtedly modify the application of this process on a case by case basis.

Recommendations

The laboratory tests conducted on the potential for the utilization of coal fly ash in subsurface acidic mine water remediation were undertaken in a manner in which the simulation of field conditions were replicated as nearly as possible. Due to the favorable results obtained and implied from the study it is recommended that a small scale field test be conducted.

The field site should be in an extensively studied, isolated location which has acidic water discharges containing high levels of environmentally hazardous trace metals resulting from the underground mining of ore rocks. Site specific conditions should dictate the spacing of injection wells, monitor wells, volume of Class "C" coal fly ash to be used, and mechanical requirements for transportation, mixing, and placement of the slurry. A small, shallow underground mine with approximately 10 to 20 acre feet of open mine workings could be evaluated for relatively small capital outlays especially considering the potential environmentally generated liability of subsurface hazardous waste discharges leading to water degradation.

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APPENDIX

SAMPLE PARAMETERS AND UNITS

SAMPLING DEPTH (FEET)
TEMPERATURE, WATER (DEG. C)
TURBIDITY (NTU)
OXIDATION REDUCTION POTENTIAL (MILLIVOLTS)
SPECIFIC CONDUCTANCE, MICROSIEMENS PER CENTIMETERAT 25 DEGREES CENTIGRADE
OXYGEN, DISSOLVED (MG/L)
PH (STANDARD UNITS)
CARBON DIOXIDE, DISSOLVED (MG/L AS CO2)
ALKALINITY, WATER, WHOLE, FIELD, FET, (MG/L AS CACO3)
ACIDITY, TOTAL (MG/L AS CACO3)
BICARBONATE, WATER, WHOLE, FIELD, FET, (MG/L AS HCO3)
CARBONATE, WATER, WHOLE, FIELD, FET, (MG/L AS CO3)
NITROGEN, AMMONIA, WATER, DISSOLVED, (MG/L AS N)
NITROGEN, NITRITE, DISSOLVED (MG/L AS N)
NITROGEN, NITRATE, DISSOLVED (MG/L AS N)
NITROGEN, NITRITE PLUS NITRATE, WATER, DISSOLVED, (MG/L AS N)
CARBON, ORGANIC, TOTAL (MG/L AS C)
HARDNESS, TOTAL (MG/L AS CACO3)
HARDNESS, NONCARBONATE, WATER, WHOLE, FIELD, FET,(MG/L AS CACO3)
CALCIUM, WATER, DISSOLVED, (MG/L AS CA)
MAGNESIUM, WATER, DISSOLVED, (MG/L AS MG)
SODIUM, WATER, DISSOLVED, (MG/L AS NA)
SODIUM ADSORPTION RATIO
SODIUM, PERCENT
POTASSIUM, WATER, DISSOLVED, (MG/L AS K)
CHLORIDE, WATER, DISSOLVED, (MG/L AS CL)
SULFATE, WATER, DISSOLVED, (MG/L AS SO4)
FLUORIDE, WATER, DISSOLVED, (MG/L AS F)
SILICA, DISSOLVED (MG/L AS SIO2)
ARSENIC, WATER, DISSOLVED, (UG/L)
ARSENIC, TOTAL (UG/L AS AS)
BARIUM, WATER, DISSOLVED, (UG/L)
BARIUM, TOTAL (UG/L AS BA)
BERYLLIUM, WATER, DISSOLVED, (UG/L)
BORON, WATER, DISSOLVED, (UG/L)
BORON, TOTAL (UG/L AS B)
CADMIUM, WATER, DISSOLVED, (UG/L)
CADMIUM, TOTAL (UG/L AS CD)
CHROMIUM, WATER, DISSOLVED, (UG/L)
CHROMIUM, TOTAL (UG/L AS CR)
COBALT, DISSOLVED (UG/L AS CO)
COBALT, TOTAL (UG/L AS CO)
COPPER, WATER, DISSOLVED, (UG/L)
COPPER, TOTAL RECOVERABLE (UG/L AS CU)
IRON, TOTAL (UG/L AS FE)
IRON, WATER, DISSOLVED, (UG/L)
LEAD, WATER, DISSOLVED, (UG/L)
LEAD, TOTAL (UG/L AS PB)
MANGANESE, TOTAL (UG/L AS MN)
MANGANESE, WATER, DISSOLVED, (UG/L)
MOLYBDENUM, WATER, DISSOLVED, (UG/L)
MOLYBDENUM, TOTAL (UG/L AS MO)
NICKEL, WATER, DISSOLVED, (UG/L)
NICKEL, TOTAL (UG/L AS NI)
STROTIUM, WATER, DISSLOVED (UG/L)
VANADIUM, WATER, DISSOLVED, (UG/L)
ZINC, WATER, DISSOLVED, (UG/L)
ZINC, TOTAL (UG/L AS ZN)

SAMPLE PARAMETERS AND UNITS, cont'

METHYLENE BLUE ACTIVE SUBSTANCE (MG/L)
SOLIDS, RESIDUE AT 110 DEG. C, SUSPENDED TOTAL, (MG/L)
SOLIDS, RESIDUE ON EVAPORATION AT 180 DEG C, DISSOLVED (MG/L)
SOLIDS, SUM OF CONSTITUENTS, DISSOLVED (MG/L)
SOLIDS, DISSOLVED (TONS PER ACRE-FOOT)
ACIDITY, WATER, WHOLE, TOTAL, (MG/L AS H)
NITROGEN, AMMONIA, DISSOLVED (MG/L AS NH4)
NITROGEN, NITRATE, DISSOLVED (MG/L AS NO3)
NITROGEN, NITRITE, DISSOLVED (MG/L AS NO2)
MERCURY, WATER, DISSOLVED, (UG/L)
MERCURY, TOTAL RECOVERABLE (UG/L AS HG)
C13/C12 RATIO BOT.MAT
ALUMINUM, TOTAL (UG/L AS AL)
ALUMINUM, WATER, DISSOLVED, (UG/L)
LITHIUM, DISSOLVED (UG/L AS LI)
SELENIUM, WATER, DISSOLVED, (UG/L)
SELENIUM, TOTAL (UG/L AS SE)

OWRB LISTING OF SAMPLING SITES

MAP NUMBER	STATION NUMBER	LOCAL IDENTIFIER	STATION DESCRIPTOR	STATE	SITE TYPE
1	365255094514301	28N-23E-30 AAC 1	TAR C AT ROCKDALE BLVD	OK	SW
2	365359094520401	28N-23E-19 ABB 1	OWRB 16, TAR C AT 22ND AVE	OK	SW
3	365522094521501	28N-23E-07 BDD 1	OWRB 14, COMMERCE SPRINGS	OK	SP
4	365523094503201	28N-23E-09 BCC 1	OWRB 15, GARRETT C	OK	SW
5	365544094513201	28N-23E-05 CCC 1	OWRB 5, TAR C NR COMMERCE	OK	SW
6	365637094511201	29N-23E-31 DCD 1	OWRB 10, TAR C AT HWY 66	OK	SW
7	365710094504401	29N-23E-32 BCA 3	TAR C BELOW MINE TRIB	OK	SW
8	365714094504401	29N-23E-32 BCA 1	MINE TRIB AT TAR C, SOUTH	OK	SW
9	365714094504402	29N-23E-32 BCA 2	MINE TRIB AT TAR C, NORTH	OK	SW
10	365715094504301	29N-23E-32 BBD 2	MINE TRIB POND	OK	SW
11	365716094504601	29N-23E-32 BBD 1	TAILINGS DISCHARGE, S OF 4	OK	SW
12	365720094503801	29N-23E-32 BAC 1	MINE TRIB S OF RR CULVERT	OK	SW
13	365720094504001	29N-23E-32 BBD 1	INFLOW TO MINE TRIB POND	OK	SW
14	365723094503501	29N-23E-32 BAB 1	RR BOREHOLE	OK	SP
15	365723094503511	29N-23E-32 BAB11	32 M FROM RR BOREHOLE	OK	SW
16	365723094503512	29N-23E-32 BAB12	16 M FROM RR BOREHOLE	OK	SW
17	365723094503513	29N-23E-32 BAB13	8 M FROM RR BOREHOLE	OK	SW
18	365723094503514	29N-23E-32 BAB14	4 M FROM RR BOREHOLE	OK	SW
19	365723094503520	29N-23E-32 BAB20	MINE TRIB, N OF RR CULVERT	OK	SW
20	365728094502901	29N-23E-32 BAA 1	QUEBEC BOREHOLE	OK	SP
21	365730094503301	29N-23E-29 CDC 3	LAVRION TAILINGS POND/COLLAPSE	OK	SW
22	365730094503801	29N-23E-29 CDC 1	AIR SHAFT PIPE AT SITE 4	OK	GW
23	365730094504001	29N-23E-29 CDC 5	OWRB 4S, BOREHOLE DISCHARGE	OK	SP
24	365730094504011	29N-23E-29 CDC 6	WEIR, OWRB SITE 4	OK	SW
25	365730094504601	29N-23E-29 CCD 1	OWRB 4T, TAILINGS RUNOFF	OK	SW
26	365734094503601	29N-23E-29 CDC 4	LYTLE C ABOVE OWRB WEIR	OK	SW
27	365735094503501	29N-23E-29 CDC 2	COLLAPSE DISCHARGE AT LYTLE C	OK	SW
28	365740094502901	29N-23E-29 CDA 1	COLLAPSE E OF LYTLE C	OK	SP
29	365744094502801	29N-23E-29 CAD 2	LYTLE C AT RR CROSSING	OK	SW
30	365744094503200	29N-23E-29 CAC 2	LYTLE C 400 M ABOVE SITE 4	OK	SW
31	365744094503201	29N-23E-29 CAC 1	COLLAPSE W OF LYTLE C	OK	SP
32	365746094503001	29N-23E-29 CAD 1	BOREHOLE NR LYTLE C RR CROSSING	OK	SP
33	365757094505501	29N-23E-29 CBA 1	ADMIRALTY SHAFT	OK	GW
34	365800094504501	29N-23E-29 BCD 1	BOREHOLE IN TAR C	OK	SP
35	365800094505001	29N-23E-29 HCC 1	DOMADO COLLAPSE	OK	SW
36	365807094504301	29N-23E-29 BCA 1	TAR C ABOVE MINE DISCHARGE	OK	SW
37	365811094501301	29N-23E-29 ABD 1	LYTLE C ABOVE MINE DISCHARGE	OK	SW
38	365821094504401	29N-23E-29 BBA 1	TAR C NR CARDIN	OK	SW
39	365845094505201	29N-23E-20 CBB 1	KENOYER SHAFT	OK	GW
40	365926094485501	29N-23E-16 DCA 1	CONSOLIDATED NO. 2 SHAFT	OK	GW
41	365937094511501	29N-23E-18 DBA 1	GORDON AIR SHAFT	OK	GW
42	365942094504201	29N-23E-17 BCD 1	LUCKY SYNDICATE AIR SHAFT	OK	GW
43	365951094464901	29N-23E-14 AAB 1	FARMINGTON SHAFT	OK	GW
44	365956094510701	29N-23E-18 AAC 1	OWRB 7, TAR C AT STATE LINE	OK	SW
45	370015094460601	35S-24E-10 CDA 1	SUNFLOWER COLLAPSE	KS	SW
46	370103094511301	35S-23E-02 DCD 1	MUNCIE SHAFT NR COLLAPSE	KS	GW
47	370103094511701	35S-23E-02 DCD 2	MUNCIE COLLAPSE	KS	SW
48	370108094510701	35S-23E-02 DDB 1	SOUTHERN SHAFT	KS	GW
49	370153094511101	34S-23E-35 DDC 1	TAR C AT RT 166	KS	SW

Parameter Code [1]	Parameter name Method	Method Code [2]	Laboratory Code [3]	Detection Limit [4]	Sampling period											
					1	2	3	4	5	6	7	8	9	10	11	12
01106	Aluminum (µg/L as Al)															
	AA, Chelation	1052-78	LC0004	10	x	x	x	x	x	x	x	x	x			
	DCP		LC1284	100										x	x	x
01105	Aluminum, Total (µg/L as Al)															
	AA, Chelation	3052-78	LC0003	10	x	x	x	x	x	x	x	x	x			
	AA, Direct	3051-78	LC0109	100										x	x	x
00410	Alkalinity (mg/L as CaCO3)															
	Field end-point titration			5	x	x	x	x	x	x	x	x	x	x	x	x
01000	Arsenic (µg/L as As)															
	AA, hydride	2062-78	LC0112	1								x[6]	x			
01005	Barium (µg/L as Ba)															
	ICP	1472-81	LC0641	2							x	x	x	x	x	x
	ICP	1472-81	LC0655	0.5							x	x	x	x	x	x
01025	Cadmium (µg/L as Cd)															
	AA, Chelation	1136-78	LC0073	1	x	x	x	x	x	x						
	AA, Direct	1135-78	LC0126	10												
	AA, GF	1137-84	LC1250	0.1												x
	ICP	1472-81	LC0673	1	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x	x	
01027	Cadmium, Total (µg/L as Cd)															
	AA, Chelation	3136-78	LC0242	1			x	x		x	x	x	x			
	AA, Direct	3135-78	LC0131	10										x	x	
	AA, GF		LC0713	0.1												x
00915	Calcium (mg/L as Ca)															
	AA, Direct	1152-78	LC0012	0.1	x[5]	x	x[5]	x[5]	x[5]	x[5]						
	ICP	1472-81	LC0659	0.02	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x[9]	x[9]	x
00940	Chloride (mg/L as Cl)															
	Colorimetric	2187-78	LC0015	0.1	x	x										
	Colorimetric	2188-83	LC1213	0.1			x	x	x	x	x	x	x	x	x	x
01035	Cobalt (µg/L as Co)															
	ICP	1472-81	LC0644	3							x	x	x	x	x	x
01037	Cobalt, Total (µg/L as Co)															
	AA, Direct	3239-78	LC0149	50							x	x		x	x	x
01040	Copper (µg/L as Cu)															
	AA, Chelation	1271-78	LC0022	1	x	x	x	x	x	x						
	AA, Direct	1270-78	LC0151	10												
	AA, GF	1272-84	LC1253	0.5												x
01042	Copper, Total (µg/L as Cu)															
	AA, Chelation	3271-78	LC0250	1			x	x		x	x	x	x			
	AA, Direct	3270-78	LC0156	10										x	x	x
00950	Fluoride (µg/L as F)															
	Ion-selective	2327-78	LC0031	0.1	x	x	x	x	x	x	x	x	x	x	x	x
01046	Iron (µg/L as Fe)															
	AA, Direct	1381-78	LC0172	10	x[5]	x	x[5]	x[5]	x[5]	x[5]						
	ICP	1472-81	LC0645	3	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x	x	x
01045	Iron, Total (µg/L as Fe)															
	AA, Direct	3381-78	LC0189	10			x	x		x	x	x	x	x	x	x
01049	Lead (µg/L as Pb)															
	AA, Chelation	1400-78	LC0038	1	x	x	x	x	x	x						
	AA, Direct	1399-78	LC0191	100												
	AA, GF	1401-84	LC1254	0.3											x	x
	ICP	1472-81	LC0646	10							x	x	x	x		

Parameter Code[1]	Parameter name Method	Method Code[2]	Laboratory Code[3]	Detection Limit[4]	Sampling period											
					1	2	3	4	5	6	7	8	9	10	11	12
01051	Lead, Total (µg/L as Pb)															
	AA, Chelation	3400-78	LC0257	1			x	x		x	x	x				
	AA, Direct	3399-78	LC0192	100									x	x		
	AA, GF	3401-78	LC0710	0.3										x[8]	x	x
01130	Lithium (µg/L as Li)															
	ICP	1472-81	LC0664	4							x	x	x	x	x	x
00925	Magnesium (mg/L as Mg)															
	AA, Direct	1447-78	LC0040	0.1	x	x	x	x	x	x						
	ICP	1472-81	LC0663	0.004	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x	x	x
01056	Manganese (µg/L as Mn)															
	AA, Direct	1454-78	LC0042	10	x	x	x	x	x	x						
	ICP	1472-81	LC0648	1	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x[9]	x[9]	x
01055	Manganese, Total (µg/L as Mn)															
	AA, Direct	3454-78	LC0041	10			x	x		x	x	x	x	x	x	x
01060	Molybdenum (µg/L as Mo)															
	ICP	1472-81	LC0649	10							x	x	x	x	x	x
01065	Nickel (µg/L as Ni)															
	AA, Chelation	1500-78	LC0044	1	x[5]											
	AA, Direct	1499-78	LC0197	100	x	x	x	x	x	x	x	x		x	x	x
	ICP			100									x[7]			
01067	Nickel, Total (µg/L as Ni)															
	AA, Chelation	3500-78	LC0267	1												
	AA, Direct	3499-78	LC0198	100			x	x		x	x	x	x	x	x	x
00608	Nitrogen, dissolved ammonia (mg/L as N)															
	Colorimetric	2523-78	LC0301	0.01	x						x	x	x	x	x	x
00613	Nitrogen, dissolved nitrite (mg/L as N)															
	Colorimetric	2540-78	LC0160	0.01	x											
00631	Nitrogen, dissolved nitrite + nitrate (mg/L as N)															
	Colorimetric	2545-78	LC0228	0.1	x											
00666	Phosphorus (mg/L as P)															
	Colorimetric	2600-78	LC0128	0.01	x											
	Colorimetric		LC0829	0.001			x	x	x		x	x	x	x	x	x
00935	Potassium (mg/L as K)															
	AA, Direct	1630-78	LC0054	0.1	x	x	x	x	x	x	x	x	x	x	x	x
01145	Selenium (µg/L as Se)															
	AA, Hydiride	2667-83	LC0087	1									x			
00955	Silica (mg/L as SiO_2)															
	Colorimetric	2700-78	LC0056	0.1	x	x	x	x	x	x						
	ICP	1472-81	LC0667	0.009	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x	x	x
00930	Sodium (mg/L as Na)															
	AA, Direct	1735-78	LC0059	0.1	x	x	x	x	x	x						
	ICP	1472-81	LC0675	0.2	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x	x	x
01080	Strontium (µg/L as Sr)															
	ICP	1472-81	LC0652	0.5							x	x	x	x	x	x
00945	Sulfate (mg/L as SO_4)															
	Turbidimetry	2823-83	LC1200	0.2	x	x	x	x	x	x	x	x	x	x	x	x
01085	Vanadium (µg/L as V)															
	ICP	1472-81	LC0653	6							x	x	x	x	x	x
01090	Zinc (µg/L as Zn)															
	AA, Direct	1900-78	LC0067	10	x	x	x	x	x	x						
	ICP	1472-81	LC0671	3	x[5]		x[5]	x[5]	x[5]	x[5]	x	x	x	x[9]	x[9]	x
01092	Zinc, Total (µg/L as															
	AA, Direct	3900-78	LC0296	10			x	x		x	x	x	x	x	x	x

OWRB CHEMICAL ANALYSIS OF PICHER AREA MINE WATER

MAP NUMBER	STATION NUMBER	DATE	TIME	SITE	SAMPLING DEPTH (feet) (00003)	STREAMFLOW, INSTANTANEOUS (ft^3/s) (00061)	SPECIFIC CONDUCTANCE (µS/cm) (00095)	SPECIFIC CONDUCTANCE LAB (µS/cm) (00995)	PH (standard units) (00400)	OXIDATION REDUCTION POTENTIAL (mv) (00090)	TEMPERATURE (°C) (00010)
1	365255094514301	06-12-84	2000	SW	--	7.3	--	1,920	4.10	590	26.0
		01-10-85	0900	SW	--	100	1,570	1,400	5.90	--	3.5
		03-28-85	0730	SW	--	45	--	1,950	5.80	295	17.5
		06-04-85	1130	SW	--	13	--	1,620	5.80	260	24.5
		04-18-85	0800	SW	--	19	--	1,890	5.60	380	18.0
2	365359094520401	06-11-84	1130	SW	--	9.2	2,280	2,330	3.60	600	23.0
		10-18-84	1100	SW	--	2.4	1,090	1,100	6.20	--	16.0
		01-09-85	0815	SW	--	27	1,910	1,570	5.70	350	5.0
		03-27-85	0730	SW	--	31	860	2,150	5.80	270	15.0
		03-29-95	1010	SW	--	E380	--	456	5.70	--	17.0
		04-24-85	1245	SW	--	11	2,130	--	5.30	--	18.5
		05-15-85	1200	SW	--	70	1,280	--	6.40	--	17.5
		08-14-85	1455	SW	--	31	--	--	--	--	25.0
		10-16-85	1400	SW	--	48	1,090	--	6.70	--	16.0
		10-18-85	1450	SW	--	1220	715	--	6.30	--	18.5
		02-13-86	1200	SW	--	17	1,730	--	6.52	--	1.5
		09-12-85	1440	SW	--	3.3	--	--	--	--	23.5
		04-17-85	0800	SW	--	20	1,840	1,880	5.80	260	18.0
		02-16-84	1010	SW	--	9.5	1,890	1,990	6.20	--	9.5
		03-19-84	0900	SW	--	1770	1,260	1,150	6.20	--	8.5
		03-20-84	1600	SW	--	115	1,170	1,160	6.30	270	9.0
		08-21-84	1016	SW	--	0.21	3,650	3,580	2.80	790	25.5
		05-14-85	0730	SW	--	500	--	1,180	6.20	170	17.0
		05-30-85	0900	SW	--	20	--	1,080	6.20	370	19.0
		06-01-85	0830	SW	--	6.5	--	--	5.20	--	21.5
		06-02-85	0915	SW	--	39	--	1,400	5.90	390	20.5
		06-03-85	1815	SW	--	9.2	--	1,710	5.50	210	26.5
		06-05-85	0840	SW	--	30	--	1,810	6.10	270	22.5
		06-07-85	0845	SW	--	630	--	1,290	6.20	320	20.5
		06-08-85	0815	SW	--	82	--	1,240	6.30	270	22.5
		06-09-85	0945	SW	--	35	--	1,490	6.10	440	25.0
		06-12-85	0800	SW	--	72	--	1,320	6.40	340	20.0
		08-23-85	0730	SW	--	665	--	--	--	--	--
3	365522094521501	06-14-84	1130	SP	--	0.32	--	3,840	6.10	190	21.0
		06-10-85	1015	SP	--	--	--	3,970	5.90	260	18.0
		03-29-85	0830	SP	--	E0.4	--	3,960	5.70	250	17.5
4	365523094503201	06-05-85	0915	SW	--	--	--	229	7.20	210	22.0
5	365544094513201	06-12-84	1500	SW	--	5.1	--	2,510	6.00	230	25.0
		03-28-85	0930	SW	--	37	--	1,820	5.90	255	18.0
		06-04-85	1000	SW	--	10	--	2,130	6.30	230	23.0
6	365637094511201	06-13-84	1200	SW	--	4.7	--	2,770	5.90	300	--
		05-31-85	0900	SW	--	--	--	1,920	6.30	395	20.5
		05-14-85	1600	SW	--	220	--	1,200	6.10	190	17.0
		06-02-85	1200	SW	--	--	--	1,890	6.20	180	22.0
		06-09-85	1215	SW	--	--	--	1,600	6.20	250	25.0
7	365710094504401	06-11-84	1800	SW	--	5.6	--	2,620	5.80	230	--
		01-09-85	1415	SW	--	24	--	692	5.70	--	6.0
		03-27-85	1100	SW	--	23	1,640	2,240	5.70	170	15.0
		06-03-85	1010	SW	--	10	--	2,250	6.00	220	24.0
		04-17-85	1000	SW	--	17	--	2,200	5.60	270	18.5
8	365714094504401	03-21-84	1100	SW	--	--	3,200	3,500	3.80	450	15.0
		06-10-84	1730	SW	--	--	--	3,250	3.00	655	30.0
		01-09-85	1600	SW	--	1.8	--	3,120	5.30	--	--
		03-27-85	1130	SW	--	1.5	3,150	3,330	3.50	450	16.5
		05-15-85	1300	SW	--	--	--	3,270	4.30	240	22.5
		04-17-85	1030	SW	--	1.1	--	3,620	4.50	390	19.0
9	365714094504402	06-06-85	1230	SW	--	--	--	3,500	3.70	440	21.0
		06-03-85	1030	SW	--	0.86	--	3,630	3.50	340	24.5
		05-15-85	1315	SW	--	--	--	3,310	4.10	250	23.0
10	365715094504301	06-10-84	1530	SW	--	--	--	3,310	2.90	485	34.0
		05-31-85	1600	SW	--	--	--	3,740	3.40	370	31.0
		06-06-85	0830	SW	--	--	--	3,550	4.50	410	20.0
		05-15-85	1320	SW	--	--	--	3,310	4.00	250	24.0
		04-18-55	1530	SW	--	--	3,490	3,720	3.20	520	27.0
11	365716094504601	06-03-85	1045	SW	--	--	--	2,290	7.70	235	26.0

MAP NUMBER	STATION NUMBER	DATE	TIME	SITE	SAMPLING DEPTH (feet) (00003)	STREAMFLOW, INSTANTANEOUS (ft³/s) (00061)	SPECIFIC CONDUCTANCE (µS/cm) (00095)	SPECIFIC CONDUCTANCE LAB (µS/cm) (90095)	PH (standard units) (00400)	OXIDATION REDUCTION POTENTIAL (mv) (00090)	TEMPERATURE (°C) (00010)
12	365720094503801	03-21-84	1530	SW	--	--	3,400	3,630	4.80	395	15.0
		06-06-85	1130	SW	--	--	--	3,570	5.40	350	19.0
		05-15-85	1350	SW	--	--	--	3,410	5.10	220	21.0
13	365720094504001	03-28-85	1700	SW	--	E1.4	--	3,470	3.50	610	23.0
		06-06-85	0745	SW	--	--	--	3,580	5.10	400	19.5
		05-15-85	1330	SW	--	--	--	3,360	4.20	260	24.5
		04-18-85	1600	SW	--	--	3,480	3,700	3.50	510	26.5
14	365723094503501	03-21-84	1430	SP	--	--	3,610	3,800	5.30	335	15.0
		06-06-84	1900	SP	--	--	3,440	3,690	5.40	295	15.5
		03-28-85	1500	SP	--	E1.2	--	3,540	5.50	300	15.0
		06-06-85	1000	SP	--	--	--	3,690	5.60	360	15.5
		05-15-85	1400	SP	--	--	--	3,350	5.00	140	15.0
		04-18-85	1330	SP	--	--	3,450	3,610	5.00	330	15.5
15	365723094503511	06-06-84	1030	SW	--	--	3,430	3,730	5.20	290	17.0
		05-15-85	1430	SW	--	--	--	3,480	5.40	190	17.0
15	365723094503511	04-18-85	1030	SW	--	--	3,450	3,610	5.30	330	16.0
16	365723094503512	06-06-84	1250	SW	--	--	3,450	3,700	5.30	285	16.5
17	365723094503513	06-06-84	1800	SW	--	--	3,370	3,710	5.40	290	16.0
		04-18-85	1400	SW	--	--	3,430	3,620	5.20	340	15.5
18	365723094503514	06-06-84	1830	SW	--	--	3,430	3,690	5.40	--	15.5
19	365723094503520	06-10-84	1400	SW	--	--	E3,000	3,700	5.20	320	19.5
		06-06-85	1100	SW	--	--	--	3,680	5.60	350	17.0
		04-18-85	1000	SW	--	--	3,410	3,670	5.30	330	18.0
20	365728094502901	03-21-84	1800	SP	--	--	3,200	3,290	5.20	340	--
21	365730094503301	06-08-84	1730	SW	--	--	1,550	1,540	4.20	620	26.5
22	365730094503801	11-28-83	1535	GW	180	--	4,500	4,410	4.80	--	--
		11-28-83	1615	GW	145	--	3,500	3,610	4.70	--	--
		11-28-83	1700	GW	160	--	4,300	4,060	5.80	--	--
		03-19-84	1545	GW	--	--	4,470	3,760	4.50	370	15.0
		08-21-85	1230	GW	184	--	4,420	4,820	5.50	--	15.5
		08-21-85	1235	GW	184	--	4,420	--	5.50	--	15.5
		08-21-85	1100	GW	135	--	3,100	3,510	5.20	--	15.5
		08-21-85	1200	GW	160	--	3,900	4,240	5.70	--	15.5
23	365730094504001	12-01-83	1615	SP	--	--	4,350	3,960	5.50	--	20.0
		12-19-83	0900	SP	--	--	E4,800	3,550	5.40	--	16.0
		12-19-83	0930	SP				3,400	4.70		16.0
		02-16-84	1315	SP	--	1.0	4,240	4,210	5.40	--	15.0
		06-13-84	1900	SP	--	--	--	4,250	5.60	285	16.0
		03-29-85	1130	SP	--	1.6	3,820	3,880	5.40	275	15.0
		01-09-85	1515	SP	--	1.7	--	3,930	5.30	--	15.5
		06-04-85	1700	SP	--	--	--	3,850	5.40	250	15.5
24	365730094504011	06-13-84	1800	SW	--	~~1.1~~	--	4,250	5.70	130	~~16.0~~
25	365730094504601	05-15-85	0930	SW	--	--	--	2,460	6.90	180	--
26	365734094503601	01-09-85	1450	SW	--	13	--	2,060	5.70	--	6.0
27	365735094503501	03-27-85	1600	SW	--	4.6	--	3,990	5.70	120	18.0
28	365740094502901	06-08-84	1100	SW	--	--	4,380	4,410	3.00	640	25.0
29	365744094502801	06-03-85	1430	SW	--	3.2	--	1,630	6.00	180	26.5
		04-17-85	1700	SW	--	6.0	--	1,680	5.60	330	22.5
30	365744094503200	03-27-85	1500	SW	--	9.9	--	2,210	5.60	150	18.0
31	365744094503201	06-08-84	1020	SW	--	--	4,110	4,200	5.50	270	18.0
		06-07-85	1220	SW	--	41	--	4,460	5.80	220	15.5
32	365746094503001	06-03-85	1445	SP	--	E1.0	--	4,320	4.80	150	15.5
		04-17-85	1730	SP	--	--	--	4,160	5.50	260	15.5
33	365757094505501	11-29-83	1415	GW	150	--	4,450	4,010	5.70	--	19.0
		11-29-83	1530	GW	150	--	4,450	3,930	5.80	--	19.0
33	365757094505501	03-23-84	0930	GW	180	--	4,100	4,090	5.70	200	15.0
		03-23-84	1030	GW	55.0	--	3,280	3,220	5.90	170	13.5
		06-11-85	1600	GW	190	--	--	4,020	5.90	320	18.0
34	365800094504501	02-16-84	1600	SP	--	--	4,240	4,050	5.70	--	15.5
		03-27-85	1700	SP	--	0.53	--	3,660	5.60	260	15.5
		06-03-85	1615	SP	--	0.4	--	3,940	5.10	130	16.5
		01-09-85	1115	SP	--	0.62	5,300	3,700	5.50	--	15.5
		04-17-85	1400	SP	--	0.49	3,700	3,840	5.20	220	15.5
35	365800094505001	06-08-84	1630	SW	--	--	2,440	2,410	7.70	410	25.5
36	365807094504301	06-11-84	1500	SW	--	1.4	1,020	990	7.30	390	26.5
		01-09-85	1100	SW	--	6.7	740	2,030	6.20	370	3.0
		03-27-85	1730	SW	--	8.6	--	739	7.30	350	19.0
		06-03-85	1600	SW	--	3.2	--	911	7.10	210	27.5
		04-17-85	1430	SW	--	5.4	711	723	6.60	330	22.0
37	365811094501301	06-11-84	2000	SW	--	0.78	--	978	7.40	400	--
		06-03-85	1730	SW	--	--	--	917	8.90	180	29.0
		05-14-85	1300	SW	--	53	--	356	7.00	390	17.5
38	365821094504401	05-14-85	1430	SW	--	85	--	254	7.00	380	17.5
39	365845094505201	11-29-83	1030	GW	184	--	4,000	3,580	5.60	--	19.0
		11-29-83	1120	GW	184	--	3,950	3,460	5.60	--	--
		03-22-84	0930	GW	185	--	3,600	3,520	5.70	240	16.0
		06-11-85	0840	GW	182	--	--	--	5.90	300	18.0
		06-11-85	0830	GW	182	--	--	3,330	5.90	300	18.0
40	365926094485501	11-30-83	0900	GW	226	--	4,050	3,570	5.70	--	17.0
		03-22-84	1345	GW	225	--	4,080	3,880	5.70	240	15.5

		06-11-85	1115	GW	228	--	--	4,020	5.80	350	17.5
41	365937094511501	11-30-83	1445	GW	170	--	4,700	4,270	5.70	--	19.0
42	365942094504201	11-30-83	1130	GW	70.0	--	2,750	2,550	6.70	--	19.0
		11-30-83	1200	GW	110	--	5,400	4,950	6.20	--	19.0
		03-23-84	1300	GW	110	--	4,830	5,060	6.00	230	17.5
		06-12-85	1615	GW	110	--	--	--	6.15	300	18.5
43	365951094464901	12-01-83	1200	GW	138	--	2,800	2,310	6.40	--	16.0
		12-01-83	1315	GW	176	--	3,950	3,350	6.00	--	17.5
		12-01-83	1345	GW	192	--	4,650	4,230	5.60	--	18.0
		03-22-84	1600	GW	140	--	2,730	2,690	6.40	190	15.5
		03-22-84	1700	GW	176	--	3,810	3,470	6.00	205	15.5
		03-22-84	1715	GW	192	--	4,730	4,490	5.60	240	15.5
		06-12-85	1330	GW	140	--	--	2,560	6.50	360	17.0
		06-12-85	1400	GW	176	--	--	3,490	6.10	140	17.0
		06-12-85	1430	GW	194	--	--	4,200	5.68	330	17.5
44	365956094510701	06-12-84	1700	SW	--	--	—	1,150	7.80	525	32.0
		06-05-85	1450	SW	--	E50	--	462	7.00	350	24.0
		06-09-85	1115	SW	--	E3.5	--	329	7.00	290	26.0
45	370015094460601	06-08-84	1400	SW	--	--	2,990	2,920	3.10	760	25.0
46	370103094511301	12-02-83	0930	GW	100	--	485	433	6.60	--	20.0
47	370103094511701	06-08-84	1500	SW	--	--	613	605	8.10	350	25.5
48	370108094510701	12-02-83	1145	GW	200	--	580	536	6.80	--	19.5
49	370153094511101	06-12-84	1630	SW	--	--	--	136	6.80	500	--
		06-05-85	1600	SW	--	--	--	149	6.60	370	24.0

MAP NUM-BER	STATION NUMBER	DATE	CALCIUM DIS-SOLVED (mg/L as Ca) (00915)	MAGNE-SIUM, DIS-SOLVED (mg/L as Mg) (00925)	SODIUM, DIS-SOLVED (mg/L as Na) (00930)	POTAS-SIUM, DIS-SOLVED (mg/L as K) (00935)	ALKA-LINITY WH WAT TOTAL FIELD mg/L as $CaCO_3$ (00410)	SULFATE DIS-SOLVED (mg/L as SO_4) (00945)	CHLO-RIDE, DIS-SOLVED (mg/L as Cl) (00940)	FLUO-RIDE, DIS-SOLVED (mg/L as F) (00950)	SILICA, DIS-SOLVED (mg/L as SiO_2) (00955)
1	365255094514301	06-12-84	270	69	40	5.0	0	1,100	13	1.2	13
		01-10-85	190	51	24	3.5	56	800	9.5	1.0	9.8
		03-28-85	280	86	40	4.0	28	1,200	12	1.2	11
		06-04-85	230	60	34	4.7	13	910	16	1.2	11
		04-18-85	270	76	36	4.2	15	1,200	12	1.1	11
2	365359094520401	06-11-84	310	88	38	3.8	0	1,400	9.7	2.0	14
		10-18-84	160	35	43	6.1	67	520	29	1.3	7.9
		01-09-85	240	65	27	3.6	68	1,000	8.3	1.1	11
		03-27-85	290	87	41	4.5	33	1,300	12	1.2	12
		03-29-85	56	15	8.6	2.9	--	200	1.9	0.4	4.8
		04-24-85	--	--	--	--	--	--	--	--	--
		05-15-85	--	--	--	--	--	--	--	--	--
		08-14-85	--	--	--	--	--	--	--	--	--
		10-16-85	--	--	--	--	--	--	--	--	--
		10-18-85	--	--	--	--	--	--	--	--	--
		02-13-86	--	--	--	--	--	--	--	--	--
		09-12-85	--	--	--	--	--	--	--	--	--
		04-17-85	270	74	33	3.9	29	1,100	10	1.0	11
		02-16-84	280	72	38	4.9	33	1,200	12	1.5	10
		03-19-84	120	49	18	2.9	53	670	4.6	1.2	7.9
		03-20-84	130	47	21	3.1	60	670	5.6	1.1	9.0
		08-21-84	490	120	110	12	0	2,200	36	1.7	14
		05-14-85	140	50	19	3.3	53	650	4.6	1.0	8.6
		05-30-85	150	35	20	4.0	28	560	13	0.8	8.4
		06-01-85	--	--	--	--	--	--	--	--	--
		06-02-85	180	48	24	4.2	15	750	11	0.8	8.4
		06-03-85	240	63	31	4.0	13	950	13	1.1	11
		06-05-85	230	65	31	4.2	20	1,100	9.7	1.0	11
		06-07-85	140	49	20	3.9	60	680	7.8	0.9	8.8
		06-08-85	160	51	22	4.0	53	680	9.5	1.0	10
		06-09-85	200	60	26	3.9	30	840	9.9	1.2	11
		06-12-85	180	52	24	3.6	60	720	8.9	1.1	11
		08-23-85	--	--	--	3.6	--	600	3.3	0.8	--
3	365522094521501	06-14-84	620	150	130	15	550	2,700	41	2.8	9.2
		06-10-85	610	140	120	15	560	2,800	46	1.4	12
		03-29-85	810	150	120	15	546	2,900	57	2.5	13
4	365523094503201	06-05-85	29	2.3	9.1	3.5	70	39	5.3	0.2	8.7
5	365544094513201	06-12-84	350	110	42	3.4	27	1,600	9.8	2.9	15
		03-28-85	260	80	34	3.5	71	1,100	10	1.2	11
		06-04-85	290	83	35	3.7	55	1,400	11	1.1	12
6	365637094511201	06-13-84	370	120	45	3.9	38	1,900	11	2.7	17
		05-31-85	280	72	30	3.5	80	1,200	8.1	1.1	11
		05-14-85	150	52	20	3.3	68	680	5.0	1.1	9.3
		06-02-85	280	72	29	3.2	78	1,200	8.1	1.2	11
		06-09-85	220	64	25	3.6	73	920	8.2	1.1	11
7	365710094504401	06-11-84	340	110	44	3.7	53	1,600	11	3.0	15
		01-09-85	280	80	28	3.6	84	1,200	7.3	0.2	12
		03-27-85	300	97	38	3.7	91	1,500	10	1.4	12
		06-03-85	320	88	36	3.4	90	1,500	8.7	1.3	13
		04-17-85	280	89	34	3.8	83	1,300	9.5	1.3	11
8	365714094504401	03-21-84	450	130	47	4.3	0	2,400	9.4	6.6	26
		06-10-84	420	110	46	3.6	0	2,100	8.0	4.7	27
		01-09-85	510	100	37	3.6	14	2,200	7.5	9.2	25
		03-27-85	490	120	48	3.8	0	2,400	9.4	4.0	23
		05-15-85	E480	110	42	3.4	0	1,900	9.3	4.1	25
		04-17-85	510	130	49	4.1	0	2,300	10	3.8	23

9	365714094504402	06-06-85	480	110	43	3.6	0	2,200	4.6	3.0	23
		06-03-85	490	110	49	4.1	0	2,400	11	3.0	22
		05-15-85	480	110	44	3.6	0	2,000	10	4.2	25
10	365715094504301	06-10-84	430	120	42	3.7	0	2,200	8.0	6.0	26
		05-31-85	520	120	46	4.1	0	2,500	5.2	3.9	23
		06-06-85	490	110	42	3.8	3	2,400	5.2	3.5	22
		05-15-85	480	100	42	3.6	0	2,100	8.7	4.4	24
		04-18-85	560	140	51	4.2	0	2,800	11	4.4	24
11	365716094504601	06-03-85	580	20	11	1.4	148	1,600	0.8	0.9	11
12	365720094503801	03-21-84	450	140	51	4.4	14	2,600	10	7.6	28
		06-06-85	500	110	43	3.8	45	2,400	6.4	4.0	24
		05-15-85	500	120	46	3.8	35	2,200	9.7	5.2	27
13	365720094504001	03-28-85	540	130	50	4.1	0	2,500	9.2	4.4	24
		06-06-85	490	110	42	3.8	15	2,400	7.5	3.8	22
		05-15-85	490	110	43	3.7	0	2,000	9.4	4.7	25
		04-18-85	560	150	55	4.1	0	2,700	11	4.4	25
14	365723094503501	03-21-94	490	170	55	4.6	91	2,900	11	7.7	28
		06-06-84	520	130	54	3.3	90	2,400	9.3	7.8	29
		03-28-85	560	150	53	4.1	105	2,600	10	4.4	25
		06-06-85	510	120	43	3.9	103	2,500	5.2	5.4	26
		05-15-85	510	110	44	3.8	100	2,200	11	5.6	25
		04-18-85	540	150	54	4.2	110	2,400	11	4.4	25
15	365723094503511	06-06-84	500	120	52	3.7	78	2,400	9.1	7.3	24
		05-15-85	510	120	49	3.9	83	2,300	10	5.5	27
15	365723094503511	04-18-85	520	140	53	4.2	102	2,300	11	4.2	24
16	365723094503512	06-06-84	500	120	53	3.5	83	2,400	9.1	7.1	24
17	365723094503513	06-06-84	510	120	53	3.4	93	2,400	9.0	8.0	25
		04-18-85	550	140	51	4.1	102	2,400	11	4.2	25
18	365723094503514	06-06-84	520	130	53	3.3	E90	2,400	9.1	7.3	24
19	365723094503520	06-10-84	510	130	49	3.5	53	2,300	9.1	7.0	24
		06-06-85	500	110	45	3.9	85	2,500	6.0	3.9	24
		04-18-85	540	140	51	4.2	77	2,400	11	4.2	24
20	365728094502901	03-21-84	510	92	37	3.6	71	2,400	6.9	9.1	37
21	365730094503301	06-08-84	240	40	14	2.9	0	910	1.7	2.2	10
22	365730094503801	11-28-83	500	260	91	10	E10	3,600	21	13	21
		11-28-83	470	130	56	6.9	E10	2,700	9.6	16	28
		11-28-83	570	270	78	6.4	150	3,000	19	7.0	16
		03-19-84	480	120	54	6.8	13	2,800	8.1	15	39
		08-21-85	--	--	--	9.6	155	2,500	14	9.6	--
		08-21-85	480	230	96	10	155	3,500	19		--
		08-21-85	510	86	43	7.2	40	2,200	13	8.4	28
		08-21-85	470	200	73	6.6	170	2,800	21	6.2	17
23	365730094504001	12-01-83	340	180	76	6.0	140	3,200	21	7.2	17
		12-19-83	490	150	51	3.7	145	2,600	17	7.1	5.2
		12-19-83	500	100	73	7.6	5	2,300	14	17	5.4
		02-16-84	480	250	80	6.5	145	3,400	19	7.2	16
		06-13-84	470	240	80	5.2	158	3,000	16	6.1	20
		03-28-85	500	220	75	5.6	164	3,100	16	5.7	18
		01-09-85	480	220	70	5.8	152	3,100	16	5.8	18
		06-04-85	480	210	71	5.7	160	3,000	28	5.3	17
24	365730094504011	06-13-84	470	230	78	5.2	153	3,000	16	5.9	21
25	365730094504601	05-15-85	410	170	12	1.3	75	1,600	1.7	0.6	7.4
26	365734094503601	01-09-85	270	94	33	4.0	--	1,300	8.4	1.4	11
27	365735094503501	03-27-85	510	240	91	5.7	214	3,100	24	2.9	15
28	365740094502901	06-08-84	480	230	79	5.5	0	3,000	16	7.6	18
29	365744094502801	06-03-85	240	65	26	3.1	115	910	9.6	1.2	11
		04-17-85	250	73	28	3.7	93	990	8.3	1.0	10
30	365744094503200	03-27-85	290	99	38	3.9	101	1,400	11	1.3	11
31	365744094503201	06-08-84	510	260	90	5.2	60	3,000	22	6.0	12
		06-07-85	490	240	89	7.1	240	3,000	25	3.7	15
32	365746094503001	06-03-85	470	220	82	5.8	238	3,000	24	2.6	13
		04-17-85	520	240	91	6.0	230	3,100	24	2.9	15
33	365757094505501	11-29-83	570	280	92	6.4	260	2,900	31	4.1	15
		11-29-83	570	280	93	6.2	260	3,200	33	4.5	16
33	365757094505501	03-23-84	490	250	89	6.5	260	3,200	28	6.1	19
		03-23-84	510	130	51	6.6	235	2,200	17	4.0	27
		06-11-85	510	190	88	5.7	232	2,900	30	2.5	15
34	365800094504501	02-16-84	510	260	96	6.4	240	3,200	31	3.7	15
		03-27-85	550	210	96	5.5	233	2,800	29	2.7	16
		06-03-85	500	180	86	5.4	233	2,700	32	2.4	14
		01-09-85	540	220	92	5.7	288	2,800	30	2.7	15
		04-17-85	560	210	92	5.4	224	2,900	29	2.6	16
35	365800094505001	06-08-84	400	120	36	6.0	88	1,500	5.1	1.5	7.4
36	365807094504301	06-11-84	180	22	9.7	2.0	105	490	2.7	0.3	9.7
		01-09-85	130	13	5.8	2.3	54	320	2.6	1.5	7.4
		03-27-85	140	14	8.2	2.7	68	360	3.4	0.2	7.5
		06-03-85	160	15	7.2	1.9	105	380	3.2	0.3	8.6
		04-17-85	140	13	6.8	2.6	75	300	2.8	0.3	6.6
37	365811094501301	06-11-84	160	19	17	3.4	140	410	9.1	0.3	10
		06-03-85	160	18	14	2.6	110	370	2.2	0.4	10
		05-14-85	63	5.5	4.0	2.4	53	120	10	0.2	8.0
38	365821094504401	05-14-85	39	3.9	2.8	2.5	40	76	0.4	<0.1	7.0
39	365845094505201	11-29-83	500	190	91	5.5	260	2,500	37	3.1	13
		11-29-83	500	190	88	5.7	240	2,500	35	3.1	13
		03-22-84	490	180	82	5.5	202	2,300	33	4.2	18
		06-11-85	490	130	75	5.0	180	2,300	29	--	--
		06-11-85	510	130	75	5.2	180	2,300	27	2.1	13
40	365926094485501	11-30-83	460	230	67	3.8	280	2,800	10	1.2	8.6
		03-22-84	470	250	73	4.2	288	2,900	9.6	1.7	12

		06-11-85	500	200	69	3.8	276	2,700	9.4	0.7	10
41	365937094511501	11-30-83	690	330	120	10	280	3,000	35	5.4	18
42	365942094504201	11-30-93	160	87	340	5.1	260	1,300	18	0.3	15
		11-30-83	540	440	310	43	1000	2,700	96	0.9	13
		03-23-84	510	360	340	44	870	2,900	85	0.6	14
		06-12-85	540	410	310	45	960	3,000	100	0.7	14
43	365951094464901	12-01-83	560	49	52	5.6	280	1,600	7.0	1.7	11
		12-01-83	640	210	81	9.2	680	2,100	12	2.0	9.6
		12-01-83	500	260	74	12	360	3,500	14	1.6	9.3
		03-22-84	560	45	51	5.7	350	1,600	4.8	1.3	13
		03-22-84	600	190	78	9.4	720	2,200	10	1.9	15
		03-22-84	450	250	72	11	375	3,700	11	1.0	11
		06-12-85	560	36	49	5.5	277	1,600	6.1	1.3	13
		06-12-85	590	180	84	9.9	732	2,300	6.6	1.0	13
		06-12-85	500	210	71	14	367	3,200	13	0.7	10
44	365956094510701	06-12-84	240	12	5.8	1.4	110	580	0.9	0.3	7.7
		06-05-85	76	7.0	3.5	3.2	83	150	3.7	0.2	7.0
		06-09-85	51	3.9	2.4	2.6	55	100	2.5	0.1	7.5
45	370015094460601	06-08-84	460	62	34	7.3	0	1,800	12	1.7	33
46	370103094511301	12-02-83	61	9.5	14	4.7	60	160	3.9	0.4	7.2
47	370103094511701	06-08-84	100	7.4	8.3	2.7	90	220	1.8	0.3	9.2
48	370108094510701	12-02-83	86	7.4	14	3.8	80	200	3.8	0.6	15
49	370153094511101	06-12-84	11	3.5	5.5	3.8	35	16	3.0	0.4	5.8
		06-05-85	14	3.3	4.4	4.3	30	25	7.8	0.2	9.2

MAP NUM-BER	STATION NUMBER	DATE	NITRO-GEN, NITRITE DIS-SOLVED (mg/L as N) (00613)	NITRO-GEN, NO2+NO3 DIS-SOLVED (mg/L as N) (00631)	NITRO-GEN, AMMONIA DIS-SOLVED (mg/L as N) (00608)	PHOS-PHORUS, DIS-SOLVED (mg/L as P) (00666)	ALUM-INUM, TOTAL RECOV-ERABLE (µg/L as Al) (01105)	ALUM-INUM, DIS-SOLVED (µg/L as Al) (01106)	ARSENIC DIS-SOLVED (µg/L as As) (01000)	BARIUM, DIS-SOLVED (µg/L as Ba) (01005)	BERYL-LIUM, DIS-SOLVED (µg/L as Be) (01010)
1	365255094514301	06-12-84	--	--	--	0.007	--	220	--	--	--
		01-10-85	--	--	0.46	<0.005	1,600	170	--	36	<0.5
		03-28-85	--	--	0.34	<0.01	260	140	--	35	<1
		06-04-85	--	--	0.46	<0.001	--	20	--	38	<0.5
		04-18-85	--	--	0.33	0.015	140	90	<1	31	<1
2	365359094520401	06-11-84	--	--	--	<0.001	--	510	--	--	--
		10-18-84	--	--	--	--	--	10	--	--	--
		01-09-85	--	--	0.44	<0.005	550	330	--	34	<1
		03-27-85	--	--	0.43	<0.01	310	200	3	37	<1
		03-29-85	--	--	0.16	<0.01	6,200	10	--	46	<0.5
		04-24-85	--	--	--	--	420	--	--	--	--
		05-15-85	--	--	--	--	640	--	--	--	--
		08-14-85	--	--	--	--	2,300	--	--	--	--
		10-16-85	--	--	--	--	200	--	--	--	--
		10-18-85	--	--	--	--	5,000	--	--	--	--
		02-13-86	--	--	--	--	200	--	--	--	--
		09-12-85	--	--	--	--	240	--	--	--	--
		04-17-85	--	--	0.34	0.015	130	80	<1	32	<1
		02-16-84	--	--	--	<0.01	--	340	--	--	--
		03-19-84	--	--	--	0.012	--	440	--	--	--
		03-20-84	--	--	--	<0.005	--	260	--	--	--
		08-21-84	--	--	--	--	--	2,200	--	--	--
		05-14-85	--	--	0.22	0.01	1,300	200	--	33	<1
		05-30-85	--	--	0.43	0.001	--	<10	--	60	<0.5
		06-01-85	--	--	--	--	180	--	--	--	--
		06-02-85	--	--	0.78	0.005	2,200	40	--	91	<0.5
		06-03-85	--	--	0.53	0.001	--	30	--	41	<0.5
		06-05-85	--	--	0.49	0.003	630	50	--	33	<0.5
		06-07-85	--	--	0.28	0.003	3,200	170	--	36	<0.5
		06-08-85	--	--	0.29	0.001	760	40	--	36	<0.5
		06-09-85	--	--	0.31	0.001	310	10	--	35	<0.5
		06-12-85	--	--	0.37	0.003	530	10	--	36	<0.5
		08-23-85	--	--	<0.01	0.06	2,000	350	--	--	--
3	365522094521501	06-14-84	--	--	--	0.075	--	930	--	--	--
		06-10-85	--	--	1.30	0.065	--	620	--	21	<1
		03-29-85	--	--	1.50	0.06	--	710	--	22	<2
4	365523094503201	06-05-85	--	--	0.41	0.048	--	270	--	68	0.5
5	365544094513201	06-12-84	--	--	--	<0.001	--	420	--	--	--
		03-28-85	--	--	0.33	0.02	610	190	--	39	<1
		06-04-85	--	--	0.57	0.001	--	40	--	30	<0.5
6	365637094511201	06-13-84	--	--	--	0.183	--	780	--	--	--
		05-31-85	--	--	0.40	0.003	--	80	--	33	<0.5
		05-14-85	--	--	0.21	0.02	2,200	300	--	34	<1
		06-02-85	--	--	0.28	0.001	710	60	--	31	<0.5
		06-09-85	--	--	0.28	0.003	770	70	--	34	<0.5
7	365710094504401	06-11-84	--	--	--	<0.001	--	780	--	--	--
		01-09-85	--	--	0.41	0.005	1,400	1,200	--	30	<0.5
		03-27-85	--	--	0.31	<0.01	1,400	570	3	29	<1
		06-03-85	--	--	0.40	0.005	--	320	--	33	<1
		04-17-85	--	--	0.30	0.014	940	450	3	27	<1
8	365714094504401	03-21-84	--	--	--	0.005	--	4,700	--	--	--
		06-10-84	--	--	--	<0.001	--	3,700	--	--	--
		01-09-85	--	--	0.61	<0.005	4,200	3,900	--	15	<1
		03-27-85	--	--	0.28	<0.01	3,500	3,300	6	6	<1
		05-15-85	--	--	0.47	0.01	--	2,600	--	22	<1
		04-17-85	--	--	0.26	0.016	2,800	3,000	3	5	<1
9	365714094504402	06-06-85	--	--	0.61	0.008	--	2,000	--	10	<1
		06-03-85	--	--	0.89	0.005	--	2,000	--	17	<1

10	365715094504301	06-10-84	--	--	--	0.003	--	4,000	--	--	--
		05-31-85	--	--	0.76	0.006	--	2,100	--	10	<1
		06-06-85	--	--	0.59	0.006	--	2,100	--	10	<1
		05-15-85	--	--	0.48	0.01	--	2,600	--	9	<1
		04-18-85	--	--	0.30	0.022	--	2,900	1	10	<1
11	365716094504601	06-03-85	--	--	0.32	<0.001	--	10	--	21	<1
12	365720094503801	03-21-84	--	--	--	0.009	--	5,300	--	--	--
		06-06-85	--	--	0.61	0.008	--	2,600	--	15	<1
		05-15-85	--	--	0.63	0.01	--	3,000	--	5	<1
13	365720094504001	03-28-85	--	--	0.22	<0.01	--	3,300	9	5	<1
		06-06-85	--	--	0.65	0.006	--	2,200	--	18	<1
		05-15-85	--	--	0.52	0.01	--	2,800	--	9	<1
		04-18-85	--	--	0.31	0.019	--	2,700	2	9	<1
14	365723094503501	03-21-84	--	--	--	0.193	--	5,200	--	--	--
		06-06-84	--	--	--	0.137	--	4,800	--	--	--
		03-28-85	--	--	0.68	0.05	--	3,400	16	2	<1
		06-06-85	--	--	0.76	0.191	--	2,900	--	4	<1
		05-15-85	--	--	0.71	0.02	--	2,900	--	<3	<1
		04-18-85	--	--	0.69	0.13	--	2,700	16	7	<1
15	365723094503511	06-06-84	--	--	--	<0.001	--	5,000	--	--	--
		05-15-85	--	--	0.74	0.01	--	2,900	--	<4	<1
15	365723094503511	04-18-85	--	--	0.75	0.022	--	2,700	--	7	<1
16	365723094503512	06-06-84	--	--	--	<0.001	--	5,000	--	--	--
17	365723094503513	06-06-84	--	--	--	0.014	--	5,000	--	--	--
		04-18-85	--	--	0.63	0.047	--	3,000	--	8	<1
18	365723094503514	06-06-84	--	--	--	0.014	--	4,900	--	--	--
19	365723094503520	06-10-84	--	--	--	<0.001	--	--	--	--	--
		06-06-85	--	--	0.72	0.022	--	2,800	--	5	<1
		04-18-85	--	--	0.67	0.02	--	2,800	--	8	<1
20	365728094502901	03-21-84	--	--	--	0.067	--	7,900	--	--	--
21	365730094503301	06-08-84	--	--	--	0.003	--	2,600	--	--	--
22	365730094503801	11-28-83	<0.01	<0.10	0.78	<0.01	--	7,700	--	--	--
		11-28-83	<0.01	<0.10	0.60	0.18	--	19,000	--	--	--
		11-28-83	<0.01	<0.10	0.66	<0.01	--	6,300	--	--	--
		03-19-84	--	--	--	>1.00	--	16,000	--	--	--
		08-21-85	--	--	<0.01	<0.01	--	7,200	--	--	--
		08-21-85	--	--	--	--	--	4,500	--	8	<10
		08-21-85	--	--	<0.01	0.50	--	5,800	--	11	2
		08-21-85	--	--	<0.01	<0.01	--	3,400	--	9	2
23	365730094504001	12-01-83	0.01	<0.10	0.35	<0.01	--	5,600	--	--	--
		12-19-83	--	--	--	--	--	3,800	--	--	--
		12-19-83	--	--	--	--	--	15,000	--	--	--
		02-16-84	--	--	--	0.067	--	6,500	--	--	--
		06-13-84	--	--	--	0.199	--	6,000	--	--	--
		03-28-85	--	--	0.98	0.06	--	4,800	14	5	<1
		01-09-85	--	--	0.88	0.061	5,500	5,400	--	12	3
		06-04-85	--	--	0.88	0.076	--	4,200	--	7	<1
24	365730094504011	06-13-84	--	--	--	~~0.010~~	--	3,200	--	--	--
25	365730094504601	05-15-85	--	--	0.19	<0.01	--	<100	--	18	<1
26	365734094503601	01-09-85	--	--	0.46	<0.005	1,200	970	--	28	<1
27	365735094503501	03-27-85	--	--	0.85	<0.01	2,400	1,900	--	8	<1
28	365740094502901	06-08-84	--	--	--	0.002	--	5,800	--	--	--
29	365744094502801	06-03-85	--	--	0.26	0.004	--	60	--	33	<0.5
		04-17-85	--	--	0.21	0.013	730	100	2	35	<1
30	365744094503200	03-27-85	--	--	0.27	<0.01	880	470	--	29	<1
31	365744094503201	06-08-84	--	--	--	<0.001	--	870	--	--	--
		06-07-85	--	--	0.94	0.028	--	2,500	--	13	<1
32	365746094503001	06-03-85	--	--	0.94	0.012	--	1,900	--	10	<1
		04-17-85	--	--	0.77	0.023	--	2,000	20	6	<1
33	365757094505501	11-29-83	<0.01	<0.10	0.59	<0.01	--	2,900	--	--	--
		11-29-83	<0.01	<0.10	0.53	<0.01	--	2,900	--	--	--
33	365757094505501	03-23-84	--	--	--	0.125	--	1,400	--	--	--
		03-23-84	--	--	--	0.79	--	,260	--	--	--
		06-11-85	--	--	0.89	0.08	--	1 600	--	9	<1
34	365800094504501	02-16-84	--	--	--	0.165	--	2,000	--	--	--
		03-27-85	--	--	0.69	--	--	1,700	--	7	<1
		06-03-85	--	--	0.92	0.01	--	1,500	--	10	<1
		01-09-85	--	--	0.88	0.171	1,700	1,900	--	13	<1
		04-17-85	--	--	0.73	0.148	1,700	1,800	25	7	<1
35	365800094505001	06-08-84	--	--	--	0.003	--	<10	--	--	--
36	365807094504301	06-11-84	--	--	--	0.016	--	<10	--	--	--
		01-09-85	--	--	0.11	0.02	310	<10	--	41	<1
		03-27-85	--	--	0.15	<0.01	--	20	--	49	<0.5
		06-03-85	--	--	0.20	0.005	--	<10	--	57	<0.5
		04-17-85	--	--	0.07	0.03	--	10	--	48	<0.5
37	365811094501301	06-11-84	--	--	--	0.216	--	10	--	--	--
		06-03-85	--	--	0.19	0.036	--	30	--	40	<0.5
		05-14-85	--	--	0.13	0.04	1,500	<100	--	37	<0.5
38	365821094504401	05-14-85	--	--	0.08	0.03	1,700	100	--	38	<0.5
39	365845094505201	11-29-83	<0.01	<0.10	0.59	<0.01	--	1,800	--	--	--
		11-29-83	<0.01	<0.10	0.53	<0.01	--	1,700	--	--	--
		06-11-85	--	--	--	--	--	--	--	7	<0.5
		06-11-85	--	--	0.73	0.00	--	750	--	10	<1
40	365926094485501	11-30-83	<0.01	<0.10	0.41	<0.01	--	690	--	--	--
		03-22-84	--	--	--	0.022	--	500	--	--	--
		06-11-85	--	--	0.68	0.029	--	450	--	12	<1
41	365937094511501	11-30-83	<0.01	<0.10	0.90	<0.01	--	3,400	--	--	--
42	365942094504201	11-30-83	<0.01	<0.10	0.14	<0.01	--	20	--	--	--
		11-30-83	<0.01	<0.10	0.85	<0.01	--	10	--	--	--
		03-23-84	--	--	--	<0.005	--	30	--	--	--

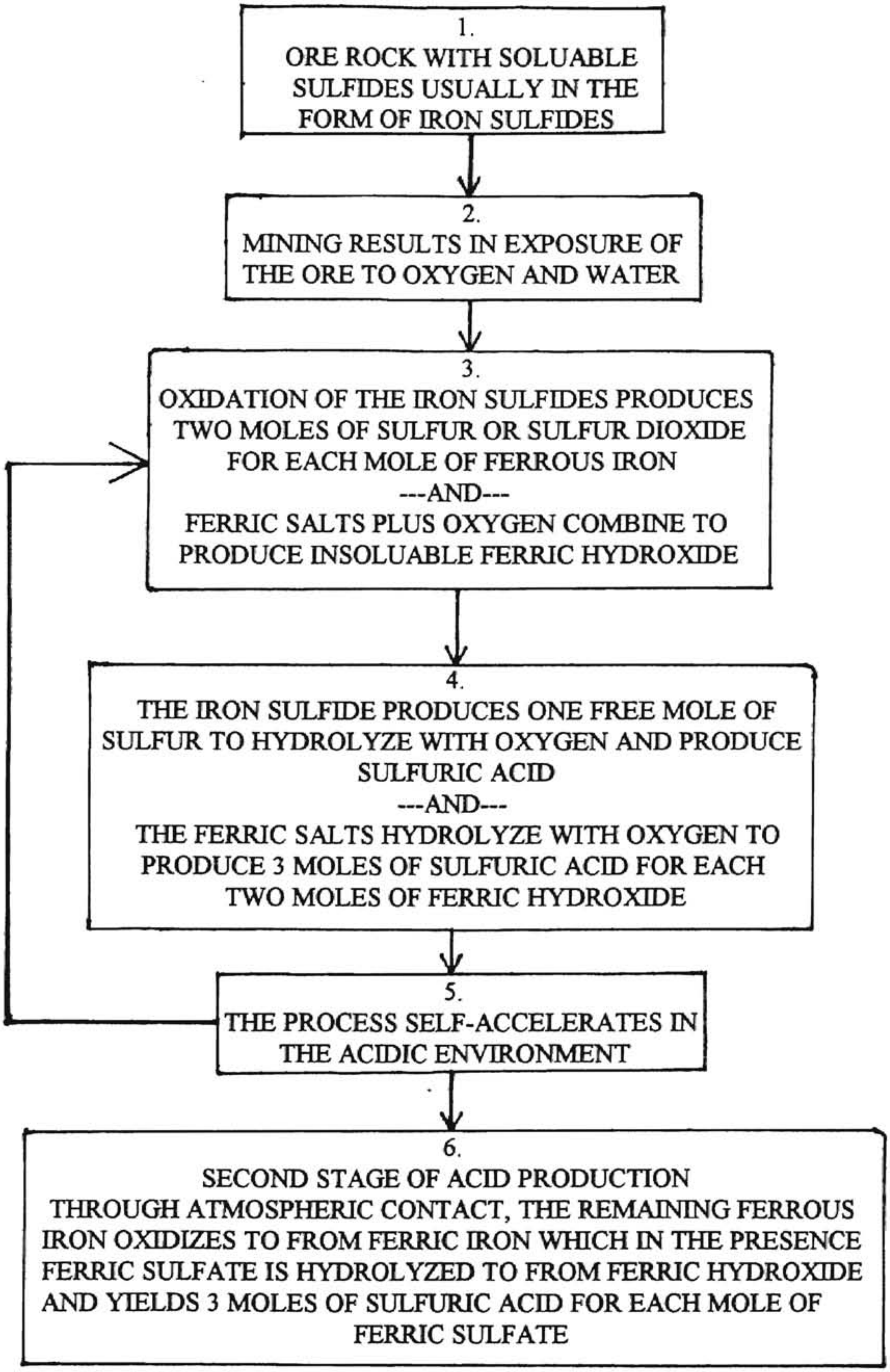
MAP NUMBER	STATION NUMBER	DATE	CADMIUM TOTAL RECOV-ERABLE (μg/L as Cd) (01027)	CADMIUM DIS-SOLVED (μg/L as Cd) (01025)	COBALT, TOTAL RECOV-ERABLE (μg/L as Co) (01037)	COBALT, DIS-SOLVED (μg/L as Co) (01035)	COPPER, TOTAL RECOV-ERABLE (μg/L as Cu) (01042)	COPPER, DIS-SOLVED (μg/L as Cu) (01040)	IRON, TOTAL RECOV-ERABLE (μg/L as Fe) (01045)	IRON, DIS-SOLVED (μg/L as Fe) (01046)	LEAD, TOTAL RECOV-ERABLE (μg/L as Pb) (01051)	LEAD, DIS-SOLVED (μg/L as Pb) (01049)
1	365255094514301	06-12-84	--	35	--	--	--	1	--	--	--	<1
		01-10-85	13	37	100	--	6	--	51,000	41,000	24	11
		03-28-85	11	30	150	130	2	<20	43,000	41,000	<1	<20
		06-04-85	--	13	--	90	--	<10	--	5,300	--	<1
		04-18-85	3	25	--	120	2	1	26,000	25,000	2	<20
2	365359094520401	06-11-84	--	2	--	--	--	2	--	27,000	--	<1
		10-18-84	20	15	--	--	4	<1	1,700	--	<1	<1
		01-09-85	9	43	150	--	1	--	58,000	55,000	3	<20
		03-27-85	23	30	150	140	<1	<20	59,000	53,000	<1	<20
		03-29-85	2	7	<50	20	10	<10	24,000	7,600	58	<10
		04-24-85	30	--	150	--	20	--	42,000	--	<0	--
		05-15-85	20	--	100	--	20	--	41,000	--	11	--
		08-14-85	40	--	100	--	20	--	5,000	--	--	--
		10-16-85	2	--	50	--	1	--	14,000	--	5	--
		10-18-85	16	--	100	--	18	--	43,000	--	110	--
		02-13-86	21	--	100	--	8	--	48,000	--	2	--
		09-12-85	4	--	150	--	1	--	14,000	--	3	--
		04-17-85	13	27	--	100	2	<20	33,000	33,000	3	<20
		02-16-84	3	36	--	--	2	6	55,000	53,000	<1	<1
		03-19-84	5	24	--	--	11	2	65,000	59,000	110	<1
		03-20-84	4	28	--	--	3	<1	48,000	50,000	21	<1
		08-21-84	8	9	--	--	22	11	23,000	23,000	140	160
		05-14-85	10	12	100	80	20	<20	43,000	50,000	100	<20
		05-30-85	--	16	--	50	--	<10	--	12,000	--	<1
		06-01-85	30	--	100	--	20	--	14,000	--	<0	--
		06-02-85	30	15	100	80	30	<10	19,000	17,000	3	<1
		06-03-85	--	16	--	90	--	<10	--	12,000	--	<1
		06-05-85	30	18	100	100	20	<10	29,000	27,000	1	<1
		06-07-85	30	14	100	80	20	<10	64,000	49,000	74	<1
		06-08-85	30	14	100	80	20	<10	40,000	34,000	15	<1
		06-09-85	20	15	100	90	20	<10	26,000	24,000	1	<1
		06-12-85	30	12	100	70	20	<10	29,000	26,000	5	<1
		08-23-85	30	--	100	--	<10	--	6,000	--	--	35
3	365522094521501	06-14-84	--	1	--	--	--	<1	--	410,000	--	<1
		06-10-85	--	4	--	240	--	20	--	390,000	--	<1
		03-29-85	--	12	--	380	--	<30	--	410,000	--	51
4	365523094503201	06-05-85	--	<1	--	<50	--	<10	--	180	--	1
5	365544094513201	06-12-84	--	2	--	--	--	1	--	52,000	--	<1
		03-28-85	19	30	150	110	3	<20	66,000	64,000	23	<20
		06-04-85	--	15	--	140	--	<10	--	51,000	--	<1
		05-31-85	--	17	--	110	--	<10	--	53,000	--	<1
		05-14-85	10	13	100	70	20	<20	48,000	52,000	100	<20
		06-02-85	40	18	150	110	90	<10	74,000	51,000	35	<1
		06-09-85	20	14	100	100	20	<10	47,000	49,000	38	<1
7	365710094504401	06-11-84	--	2	--	--	--	2	--	64,000	--	<1
		01-09-85	18	49	150	--	4	--	90,000	83,000	28	51
		03-27-85	24	32	150	170	9	<20	110,000	90,000	77	<20
		06-03-85	--	19	--	140	--	<20	--	78,000	--	<1
		04-17-85	7	28	--	120	--	10	82,000	84,000	41	<20
8	365714094504401	03-21-84	--	12	--	--	--	6	--	150,000	--	100
		06-10-84	--	2	--	--	--	8	--	54,000	--	140
		01-09-85	17	92	--	350	3	--	170,000	160,000	62	50
		03-27-85	110	74	350	330	10	<20	140,000	120,000	110	90
		05-15-85	--	41	--	280	--	<20	--	120,000	--	55
		04-17-85	13	45	--	290	--	14	--	160,000	53	46
9	365714094504402	06-06-85	--	40	--	300	--	<20	--	140,000	--	42
		06-03-85	--	26	--	290	--	190	--	130,000	--	45
		05-15-85	--	41	--	280	--	<20	--	130,000	--	64
10	365715094504301	06-10-84	--	1	--	--	--	9	--	49,000	--	83
		05-31-85	--	24	--	310	--	51	--	150,000	--	31
		06-06-85	--	42	--	280	--	<20	--	160,000	--	11
		05-15-85	--	38	--	280	--	<20	--	130,000	--	57
		04-18-85	--	38	--	450	--	15	--	--	--	49
11	365716094504601	06-03-85	--	8	--	<50	--	<20	--	260	--	2
12	365720094503801	03-21-84	--	54	--	--	--	2	--	200,000	--	35
		06-06-85	--	47	--	280	--	64	--	170,000	--	10
		05-15-85	--	44	--	340	--	<20	--	180,000	--	<20
13	365720094504001	03-28-85	--	67	--	360	--	<20	--	140,000	--	86
		06-06-85	--	42	--	280	--	220	--	170,000	--	4
		05-15-85	--	41	--	300	--	<20	--	140,000	--	54
		04-18-85	--	38	--	450	--	20	--	--	--	38
14	365723094503501	03-21-84	--	20	--	--	--	<1	--	290,000	--	32
		06-06-84	--	23	--	--	--	<1	--	240,000	--	36
		03-29-85	--	35	--	440	--	<20	--	260,000	--	23
		06-06-85	--	25	--	370	--	<20	--	230,000	--	19
		05-15-85	--	29	--	340	--	<20	--	220,000	--	24
		04-18-85	--	32	--	500	--	16	--	--	--	<20
15	365723094503511	06-06-84	--	10	--	--	--	<1	--	200,000	--	7
		05-15-85	--	28	--	370	--	<20	--	220,000	--	20
15	365723094503511	04-18-85	--	32	--	370	--	16	--	--	--	27
16	365723094503512	06-06-84	--	29	--	--	--	<1	--	210,000	--	13
17	365723094503513	06-06-84	--	35	--	--	--	<1	--	200,000	--	26
		04-18-85	--	32	--	520	--	15	--	--	--	<20

19	365723094503520	06-10-84	--	9	--	--	--	7	--	170,000	--	<1
		06-06-85	--	23	--	310	--	<20	--	210,000	--	5
		04-18-85	--	32	--	380	--	19	--	--	--	35
20	365728094502901	03-21-84	--	51	--	--	--	<1	--	240,000	--	49
21	365730094503301	06-08-84	--	39	--	--	--	2	--	--	--	36
22	365730094503801	11-28-83	--	20	--	--	--	4	--	390,000	--	45
		11-28-83	--	25	--	--	--	10	--	260,000	--	65
		11-28-83	--	15	--	--	--	2	--	300,000	--	53
		03-19-84	--	78	--	--	--	<1	--	300,000	--	79
		08-21-85	--	--	--	--	--	--	--	--	--	11
		08-21-85	--	54	--	2400	--	4	--	400,000	--	9
		08-21-85	--	16	--	530	--	24	--	220,000	--	12
		08-21-85	--	24	--	660	--	27	--	270,000	--	5
23	365730094504001	12-01-83	--	15	--	--	--	<1	--	310,000	--	60
		12-19-83	--	13	--	--	--	<1	--	240,000	--	35
		12-19-83	--	80	--	--	--	<1	--	320,000	--	68
		02-16-84	--	34	--	--	--	3	--	330,000	--	81
		06-13-84	--	24	--	--	--	<1	--	270,000	--	76
		03-28-85	--	58	--	500	--	<20	--	290,000	--	64
		01-09-85	60	93	550	500	<1	--	320,000	300,000	80	130
		06-04-85	--	42	--	410	--	<20	--	280,000	--	45
24	365730094504011	06-13-84	--	41	--	--	--	<1	--	290,000	--	36
25	365730094504601	05-15-85	--	270	--	<50	--	<20	--	86	--	13
26	365734094503601	01-09-85	8	38	200	<50	1	--	95,000	95,000	17	25
27	365735094503501	03-27-85	12	28	400	470	3	<20	300,000	260,000	74	36
28	365740094502901	06-08-84	--	3	--	--	--	2	--	140,000	--	62
29	365744094502801	06-03-85	--	6	--	90	--	<10	--	47,000	--	<1
		04-17-85	4	9	--	110	6	<20	57,000	31,000	95	<20
30	365744094503200	03-27-85	14	14	200	160	6	<20	97,000	90,000	63	<20
31	365744094503201	06-08-84	--	6	--	--	--	<1	--	190,000	--	<1
		06-07-85	--	21	--	440	--	96	--	290,000	--	18
32	365746094503001	06-03-85	--	18	--	360	--	30	--	250,000	--	6
		04-17-85	--	23	--	430	--	<20	--	270,000	--	24
33	365757094505501	11-29-83	--	25	--	--	--	<1	--	300,000	--	9
		11-29-83	--	22	--	--	--	<1	--	300,000	--	40
33	365757094505501	03-23-84	--	14	--	--	--	<1	--	280,000	--	28
		03-23-84	--	2	--	--	--	<1	--	190,000	--	<1
		06-11-85	--	8	--	320	--	<20	--	220,000	--	7
34	365800094504501	02-16-84	--	38	--	--	--	3	--	280,000	--	58
		03-27-85	--	12	--	350	--	<20	--	230,000	--	25
		06-03-85	--	8	--	260	--	33	--	210,000	--	2
		01-09-85	1	31	450	350	<1	--	270,000	240,000	42	100
		04-17-85	6	12	--	270	<1	<20	--	230,000	18	<20
35	365800094505001	06-08-84	--	17	--	--	--	1	--	60	--	7
36	365807094504301	06-11-84	--	9	--	--	--	3	--	25	--	<1
		01-09-85	12	42	50	<50	3	<20	320	29	11	<20
		03-27-85	--	30	--	<50	--	<10	--	120	--	<10
		06-03-85	--	14	--	<50	--	<10	--	37	--	<1
		04-17-85	--	29	--	<50	--	<10	--	100	--	<10
37	365811094501301	06-11-84	--	<1	--	--	--	2	--	11	--	<1
		06-03-85	--	<1	--	<50	--	<10	--	380	--	2
		05-14-85	<10	<1	<50	<50	10	<10	3,100	140	100	<10
38	365821094504401	05-14-85	<10	12	<50	<50	40	<10	1,800	160	100	<10
39	365845094505201	11-29-83	--	12	--	--	--	2	--	210,000	--	<1
		11-29-83	--	10	--	--	--	<1	--	200,000	--	24
		03-22-84	--	6	--	--	--	2	--	200,000	--	21
		06-11-85	--	3	--	<50	--	<1	--	140,000	--	8
		06-11-85	--	3	--	170	--	20	--	150,000	--	10
40	365926094485501	11-30-83	--	10	--	--	--	2	--	270,000	--	22
		03-22-84	--	14	--	--	--	<1	--	290,000	--	49
		06-11-85	--	27	--	320	--	33	--	--	--	39
41	365937094511501	11-30-83	--	4	--	--	--	1	--	390,000	--	<1
42	365942094504201	11-30-83	--	2	--	--	--	2	--	650	--	<1
		11-30-83	--	1	--	--	--	2	--	18,000	--	<1
		03-23-84	--	<1	--	--	--	<1	--	12,000	--	1
		06-12-85	--	<2	--	200	--	56	--	20,000	--	1
43	365951094464901	12-01-83	--	9	--	--	--	1	--	42,000	--	<1
		12-01-83	--	3	--	--	--	<1	--	180,000	--	<1
		12-01-83	--	29	--	--	--	1	--	600,000	--	22
		03-22-84	--	5	--	--	--	<1	--	43,000	--	<1
		03-22-84	--	2	--	--	--	<1	--	150,000	--	<1
		03-22-84	--	18	--	--	--	2	--	590,000	--	34
		06-12-85	--	8	--	70	--	20	--	23,000	--	1
		06-12-85	--	3	--	250	--	38	--	200,000	--	2
		06-12-85	--	28	--	560	--	62	--	590,000	--	24
		06-05-85	--	4	--	<50	--	<10	--	460	--	15
		06-09-85	--	8	--	<50	--	<10	--	250	--	15
45	370015094460601	06-08-84	--	3	--	--	--	24	--	17,000	--	190
46	370103094511301	12-02-83	--	3	--	--	--	3	--	3,000	--	<1
47	370103094511701	06-08-84	--	1	--	--	--	1	--	11	--	<1
48	370108094510701	12-02-83	--	<1	--	--	--	5	--	12	--	5
49	370153094511101	06-12-84	--	<1	--	--	--	2	--	280	--	<1
		06-05-85	--	<1	--	<50	--	<10	--	670	--	1

MAP NUMBER	STATION NUMBER	DATE	LITHIUM DIS-SOLVED (µg/L as Li) (01130)	MANGANESE, TOTAL RECOV-ERABLE (µg/L as Mn) (01055)	MANGANESE, DIS-SOLVED (µg/L as Mn) (01056)	MOLYBDENUM, DIS-SOLVED (µg/L as Mo) (01060)	NICKEL, TOTAL RECOV-ERABLE (µg/L as Ni) (01067)	NICKEL, DIS-SOLVED (µg/L as Ni) (01065)	SELENIUM, DIS-SOLVED (µg/L as Se) (01145)	STRONTIUM, DIS-SOLVED (µg/L as Sr) (01080)	VANADIUM, DIS-SOLVED (µg/L as V) (01085)	ZINC, TOTAL RECOV-ERABLE (µg/L as Zn) (01092)	ZINC, DIS-SOLVED (µg/L as Zn) (01090)
1	365255094514301	06-12-84	--	--	2,300	--	--	620	--	--	--	--	45,000
		01-10-85	46	1,200	1,200	<10	620	580	--	230	<6	39,000	37,000
		03-28-85	78	2,000	1,800	<10	850	970	--	420	<12	54,000	52,000
		06-04-85	60	--	1,600	<10	--	600	--	370	<6	--	29,000
		04-18-85	75	1,800	1,900	<20	1,400	800	<1	390	<12	40,000	46,000
2	365359094520401	06-11-84	--	--	2,800	--	--	740	--	--	--	--	62,000
		10-18-84	--	690	710	--	75	78	--	--	--	6,100	--
		01-09-85	62	1,500	1,500	<20	630	710	--	330	<12	48,000	49,000
		03-27-85	87	2,300	8,700	<20	1,300	950	--	440	<12	56,000	53,000
		03-29-85	12	420	350	<10	87	120	--	95	<6	8,700	7,900
		04-24-85	--	2,600	--	--	500	--	--	--	--	51,000	--
		05-15-85	--	1,200	--	--	300	--	--	--	--	25,000	--
		08-14-85	--	1,200	--	--	500	--	--	--	--	18,000	--
		10-16-85	--	790	--	--	400	--	--	--	--	1,800	--
		10-18-85	--	670	--	--	300	--	--	--	--	17,000	--
		02-13-86	--	1,600	--	--	700	--	--	--	--	32,000	--
		09-12-85	--	3,000	--	--	1,400	--	--	--	--	62,000	--
		04-17-85	75	1,900	1,900	<20	1,300	--	<1	380	<12	45,000	46,000
		02-16-84	--	2,100	1,900	--	260	370	--	--	--	56,000	59,000
		03-19-84	--	1,100	930	--	1,700	--	--	--	--	38,000	41,000
		03-20-84	--	990	890	--	800	--	--	--	--	33,000	38,000
		08-21-84	--	3,500	3,600	--	850	1,000	--	--	--	50,000	42,000
		05-14-85	42	900	760	<20	300	--	--	200	<12	27,000	31,000
		05-30-85	34	--	1,000	<10	--	300	--	230	<6	--	18,000
		06-01-85	--	1,900	--	--	300	--	--	--	--	31,000	--
		06-02-85	46	1,600	1,400	<10	500	500	--	270	<6	26,000	26,000
		06-03-85	61	--	1,600	<10	--	700	--	370	<6	--	31,000
		06-05-85	62	2,000	1,600	<10	800	800	--	330	<6	35,000	36,000
		06-07-85	43	1,200	850	<10	600	700	--	200	<6	31,000	30,000
		06-08-85	43	1,200	950	<10	600	600	--	240	<6	29,000	28,000
		06-09-85	54	1,500	1,400	<10	700	700	--	300	<6	28,000	32,000
		06-12-85	44	1,300	1,200	<10	500	600	--	280	<6	23,000	26,000
		08-23-85	--	970	--	--	600	500	--	--	--	21,000	--
3	365522094521501	06-14-84	--	--	3,300	--	--	1,000	--	--	--	--	58,000
		06-10-85	280	--	4,100	<20	--	1,300	--	1,700	<12	--	39,000
		03-29-85	310	--	1,900	<30	--	1,300	--	1,800	<18	--	43,000
4	365523094503201	06-05-85	<4	--	140	<10	--	<100	--	71	<6	--	50
5	365544094513201	06-12-84	--	--	3,300	--	--	970	--	--	--	--	80,000
		03-29-85	70	1,700	1,500	<20	1,000	900	--	370	<12	50,000	50,000
		06-04-85	73	--	2,200	<10	--	1,000	--	380	<6	--	47,000
6	365637094511201	06-13-84	--	--	3,200	--	--	1,100	--	--	--	--	97,000
		05-31-85	62	--	1,600	<10	--	800	--	370	<6	--	40,000
		05-14-85	43	1,000	800	<20	300	--	--	220	<12	30,000	32,000
		06-02-85	63	1,800	1,600	<10	800	900	--	370	<6	39,000	39,000
		06-09-85	54	1,600	1,600	<10	700	800	--	300	<6	32,000	36,000
7	365710094504401	06-11-84	--	--	3,200	--	--	1,000	--	--	--	--	84,000
		01-09-85	67	1,700	1,700	<10	990	970	--	330	11	65,000	62,000
		03-27-85	85	2,200	1,700	<20	1,400	1,100	--	410	<12	67,000	61,000
		06-03-85	78	--	1,800	<20	--	1,000	--	390	<12	--	53,000
		04-17-85	84	2,100	2,200	<20	2,700	1,100	<1	370	<12	56,000	59,000
8	365714094504401	03-21-84	--	--	4,600	--	--	--	--	--	--	--	140,000
		06-10-84	--	--	5,200	--	--	1,200	--	--	--	--	100,000
		01-09-85	130	3,300	3,500	<20	2,300	2,000	--	230	22	100,000	110,000
		03-27-85	150	4,100	3,400	<20	2,200	2,200	--	310	<12	120,000	100,000
		05-15-85	130	--	E3,600	<20	--	1,700	--	270	<12	--	E110,000
		04-17-85	150	4,100	4,100	<20	2,300	2,200	<1	320	<12	110,000	110,000
9	365714094504402	06-06-85	130	--	3,900	<20	--	1,900	--	290	<12	--	100,000
		06-03-85	130	--	3,100	<20	--	1,600	--	290	<12	--	81,000
		05-15-85	140	--	3,600	<20	--	1,700	--	270	<12	--	110,000
10	365715094504301	06-10-84	--	--	3,700	--	--	1,600	--	--	--	--	100,000
		05-31-85	140	--	2,600	<20	--	2,000	--	280	<12	--	87,000
		06-06-85	130	--	3,400	<20	--	1,900	--	270	<12	--	100,000
		05-15-85	130	--	3,100	<20	--	1,700	--	250	<12	--	100,000
		04-18-85	160	--	3,900	<20	--	2,300	<1	320	<12	--	120,000
11	365716094504601	06-03-85	36	--	650	<20	--	100	--	680	<12	--	5,700
12	365720094503801	03-21-84	--	--	4,600	--	--	--	--	--	--	--	140,000
		06-06-85	130	--	3,400	<20	--	2,000	--	250	<12	--	110,000
		05-15-85	150	--	3,300	<20	--	1,800	--	250	<12	--	110,000
13	365720094504001	03-28-85	160	--	4,000	<20	--	2,300	--	300	<12	--	120,000
		06-06-85	130	--	3,400	<20	--	1,900	--	260	<12	--	100,000
		05-15-85	140	--	3,200	<20	--	1,700	--	240	<12	--	110,000
		04-18-85	170	--	4,000	<20	--	2,400	<1	330	<12	--	120,000
14	365723094503501	03-21-84	--	--	4,500	--	--	--	--	--	--	--	160,000
		06-06-84	--	--	3,500	--	--	1,900	--	--	--	--	130,000
		03-28-85	160	--	4,100	<20	--	2,500	--	300	<12	--	120,000
		06-06-85	140	--	3,200	<20	--	2,200	--	250	<12	--	110,000
		05-15-85	150	--	3,300	<20	--	2,000	--	--	<12	--	120,000
		04-18-85	170	--	3,900	<20	--	2,500	<1	310	<12	--	120,000
15	365723094503511	06-06-84	--	--	3,800	--	--	2,300	--	--	--	--	130,000
		05-15-85	150	--	3,300	<20	--	1,900	--	260	<12	--	110,000
15	365723094503511	04-18-85	160	--	3,800	<20	--	2,500	--	300	<12	--	120,000

17	365723094503513	06-06-84	--	--	3,700	--	--	1,800	--	--	--	--	130,000
		04-18-85	160	--	3,900	<20	--	2,400	--	300	<12	--	120,000
18	365723094503514	06-06-84	--	--	3,600	--	--	1,800	--	--	--	--	130,000
19	365723094503520	06-10-84	--	--	3,600	--	--	2,000	--	--	--	--	120,000
		06-06-85	140	--	3,200	<20	--	2,100	--	250	<12	--	110,000
		04-18-85	160	--	3,800	<20	--	2,500	--	300	<12	--	120,000
20	365728094502901	03-21-84	--	--	3,100	--	--	--	--	--	--	--	110,000
21	365730094503301	06-08-84.	--	--	3	--	--	470	--	--	--	--	52,000
22	365730094503801	11-28-83	--	--	6,900	--	--	--	--	--	--	--	240,000
		11-28-83	--	--	4,700	--	--	--	--	--	--	--	190,000
		11-28-83	--	--	5,400	--	--	3,500	--	--	--	--	210,000
		03-19-84	--	--	5,000	--	--	--	--	--	--	--	180,000
		08-21-85	--	--	--	--	--	4,300	--	--	--	--	--
		08-21-85	230	--	6,600	<30	--	4,200	--	640	54	--	230,000
		08-21-85	200	--	1,900	<20	--	2,000	--	300	<12	--	90,000
		08-21-85	200	--	2,800	<20	--	3,000	--	610	<12	--	140,000
23	365730094504001	12-01-83	--	--	5,200	--	--	3,400	--	--	--	--	210,000
		12-19-83	--	--	3,300	--	--	2,400	--	--	--	--	170,000
		12-19-83	--	--	4,000	--	--	2,800	--	--	--	--	150,000
		02-16-84	--	--	5,200	--	--	210	--	--	--	--	220,000
		06-13-84	--	--	4,600	--	--	2,600	--	--	--	--	210,000
		03-28-85	200	--	4,900	<20	--	2,800	--	550	<12	--	170,000
		01-09-85	190	4500	4,300	<20	4300	3,100	--	500	45	200000	190,000
		06-04-85	180	--	4,500	<20	--	3,100	--	500	<12	--	190,000
24	365730094504011	06-13-84	--	--	4,000	--	--	2,600	--	--	--	--	210,000
25	365730094504601	05-15-85	29	--	19	<10	--	--	--	180	<12	--	48,000
26	365734094503601	01-09-85	78	1,900	1,900	<20	650	980	--	360	<12	67,000	68,000
27	365735094503501	03-27-85	200	4,400	3,100	<20	3,200	3,000	--	800	<12	150,000	130,000
28	365740094502901	06-08-84	--	--	5,300	--	--	2,800	--	--	--	--	200,000
29	365744094502801	06-03-85	52	--	1,200	<10	--	600	--	360	<6	--	30,000
		04-17-85	70	1,600	1,700	<20	1,200	--	--	<360	<12	37,000	44,000
30	365744094503200	03-27-95	84	2,200	1,700	<20	1,400	1,300	--	420	<12	63,000	58,000
31	365744094503201	06-08-94	--	--	5,000	--	--	2,800	--	--	--	--	180,000
		06-07-85	190	--	2,900	<20	--	3,300	--	780	<12	--	140,000
32	365746094503001	06-03-85	170	--	2,700	<20	--	2,800	--	710	<12	--	110,000
		04-17-85	190	--	4,600	<20	--	--	<1	800	32	--	140,000
33	365757094505501	11-29-83	--	--	4,900	--	--	3,600	--	--	--	--	170,000
		11-29-83	--	--	5,300	--	--	3,500	--	--	--	--	170,000
33	365757094505501	03-23-84	--	--	5,300	--	--	--	--	--	--	--	150,000
		03-23-84	--	--	4,800	--	--	--	--	--	--	--	54,000
		06-11-85	150	--	2,600	<20	--	2,900	--	880	<12	--	97,000
34	365800094504501	02-16-84	--	--	5,000	--	--	1,300	--	--	--	--	150,000
		03-27-85	170	--	4,100	<20	--	2,900	--	950	<12	--	110,000
		06-03-55	150	--	2,400	<20	--	2,500	--	860	<12	--	90,000
		01-09-85	170	3,800	3,900	<20	4,400	3,100	--	950	33	130,000	120,000
		04-17-95	160	3,700	4,100	<20	2,900	--	<1	960	<12	110,000	110,000
35	365800094505001	06-08-84	--	--	910	--	--	290	--	--	--	--	11,000
36	365807094504301	06-11-94	--	--	980	--	--	17	--	--	--	--	7,000
		01-09-85	11	140	130	<20	31	21	--	160	<12	14,000	12,000
		03-27-45	12	--	320	<10	--	23	--	190	<6	--	8,800
		06-03-85	15	--	670	<10	--	<100	--	230	<6	--	5,900
		04-17-85	11	--	430	<10	--	--	--	180	<6	--	8,100
37	365811094501301	06-11-84	--	--	560	--	--	14	--	--	--	--	310
		06-03-85	19	--	130	<10	--	<100	--	290	<6	--	270
		05-14-85	<4	120	85	<10	<100	--	--	96	<6	1,700	1,100
38	365821094504401	05-14-85	5	110	91	<10	<100	--	--	67	<6	2,500	2,100
39	365845094505201	11-29-83	--	--	3,800	--	--	2,500	--	--	--	--	120,000
		11-29-83	--	--	3,600	--	--	2,400	--	--	--	--	110,000

ORE ROCK ACID PRODUCTION



1\.
ORE ROCK WITH SOLUABLE SULFIDES USUALLY IN THE FORM OF IRON SULFIDES

2\.
MINING RESULTS IN EXPOSURE OF THE ORE TO OXYGEN AND WATER

3\.
OXIDATION OF THE IRON SULFIDES PRODUCES TWO MOLES OF SULFUR OR SULFUR DIOXIDE FOR EACH MOLE OF FERROUS IRON
---AND---
FERRIC SALTS PLUS OXYGEN COMBINE TO PRODUCE INSOLUABLE FERRIC HYDROXIDE

4\.
THE IRON SULFIDE PRODUCES ONE FREE MOLE OF SULFUR TO HYDROLYZE WITH OXYGEN AND PRODUCE SULFURIC ACID
---AND---
THE FERRIC SALTS HYDROLYZE WITH OXYGEN TO PRODUCE 3 MOLES OF SULFURIC ACID FOR EACH TWO MOLES OF FERRIC HYDROXIDE

5\.
THE PROCESS SELF-ACCELERATES IN THE ACIDIC ENVIRONMENT

6\.
SECOND STAGE OF ACID PRODUCTION
THROUGH ATMOSPHERIC CONTACT, THE REMAINING FERROUS IRON OXIDIZES TO FROM FERRIC IRON WHICH IN THE PRESENCE FERRIC SULFATE IS HYDROLYZED TO FROM FERRIC HYDROXIDE AND YIELDS 3 MOLES OF SULFURIC ACID FOR EACH MOLE OF FERRIC SULFATE

VITA

Jeffrey H. Ellard

Candidate for the Degree of

Master of Science

Thesis: THE POTENTIAL USE OF COAL FLY ASH IN SUBSURFACE HAZARDOUS WASTE SITE REMEDIATION AND RECLAMATION

Major Field: Environmental Science

Biographical:

Personal Data: Born in Tulsa, Oklahoma, on August 27, 1958, the son of Mr. and Mrs. I.W. Ellard.

Education: Graduated from Bixby High School, Bixby, Oklahoma in May 1976; received Bachelor of Scince degree in Geology from Tulsa University, Tulsa, Oklahoma in may of 1981. Completed the requirements for the Master of Science degree with a major in Environmental Science in May 1995.

Experience: Fourteen years experience in the petroleum industry, first as a staff geologist for Indian Wells Oil Company and Kiska Oil Company. From 1991 to 1994, Manager of Exploration Division for Calumet Oil Company.

Professional Memberships: American Association of Petroleum Geologists, Tulsa Geological Society.