Chapter 7

KINETIC (LEACHING) TESTS FOR THE PREDICTION OF MINE DRAINAGE QUALITY

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Introduction

The tests described in this chapter consist of the simulation of mine drainage production from samples of strata to be affected by mining, followed by chemical analyses of effluent quality produced from these simulated conditions. These tests are referred to as kinetic tests because they incorporate dynamic elements of the physical, chemical, and biological systems and processes which control the production of acidic or alkaline mine drainage. Specifically, these tests are designed and conducted to deal with the reaction kinetics, the rates and mechanisms of the chemical reactions which lead to the production of acidic or alkaline mine drainage. A thorough discussion of reaction kinetics may be found in Barrow (1973, chapter 16 & 17), Lehninger (1975, chapter 8) and Stumm and Morgan (1970, chapters 2, 4 and 10).

While some kinetic tests may be done in the field to promote a better approximation of the physical, chemical and biological systems; these tests are usually done in a laboratory environment with a variety of apparatus including leaching columns, humidity cells and soxhlet reactors.

The group of test procedures generically referred to as kinetic tests for the prediction of mine drainage quality may be contrasted to the group of tests labeled as "static" tests for the prediction of mine drainage quality. The term static may not be as fitting a descriptor, because static tests are not completely motionless, stable, or undynamic; but they do not typically incorporate reaction kinetics except in a theoretical manner. For example, in the acid-base accounting technique of Smith et al. (1974) and Sobek et al. (1978), the neutralization potential (NP) test is a measure of the amount of calcium carbonate in the sample (adapted from the work of Jackson, 1958) rather than an actual alkalinity concentration. This NP number is compared to the maximum potential acidity (MPA) which is calculated from the percent total sulfur in the sample, using stochiometric relationships. Therefore, of the three types of scientific evidence: theoretical, empirical, and experimental; the MPA component of acid-base accounting is theoretical, while the actual acidity and alkalinity concentrations in the effluent from a leaching column are experimental evidence.

A major advantage of kinetic tests for the prediction of mine drainage quality is that, since these types of tests produce an effluent of simulated mine drainage quality, the effluent may be tested for the same water quality parameters as the actual mine drainage to be produced from the proposed mining operation. The water quality parameters typically included in the leachate analyses are pH, acidity, alkalinity, sulfates, iron, manganese and aluminum. These are the same water quality parameters typically monitored as required by NPDES permit conditions for an active mining operation. If the physical, chemical, and biological conditions of the kinetic tests are representative of those found in the mine environment, the concentrations of the water quality parameters in the leachate may be used to predict or estimate the concentrations of these parameters in the actual mine drainage from the proposed mining operation.

Unfortunately, there are several potential disadvantages of some kinetic tests for the prediction of mine drainage quality. A major problem with these types of tests is the interpretation of the results of the experimental process and the extrapolation to the actual environment of the proposed mine site. It is easy to be fooled by the laboratory results, where test procedures are simplified or some component of the physical, chemical, or biological systems is either underestimated or overestimated. Then, the apparently precise laboratory analyses may not be accurate, and in fact, may be meaningless. Further, it is difficult enough to test a single representative sample of a lithologic unit. Some kinetic tests attempt to combine numerous strata in the same test apparatus to simulate

the configuration of the active mine or backfilled mine spoil. That is a very difficult, if not an impossible task, within the average laboratory kinetic test apparatus.

What follows in the remainder of this chapter is:

(1) a chronology and synopsis of scientific literature on these kinetic tests as they have developed throughout the past 45 years,

(2) an evaluation of the factors to be considered involving physical, chemical, and biological processes, and

(3) general guidelines for test procedures, data interpretations, and recommendations for further research to develop standard methods.

The two major sections of this chapter are the chronology of the development of kinetic tests for mine drainage, and the evaluation of physical, chemical, and biological factors in kinetic tests. These two sections may be treated in an integrated manner or taken separately. The reader who is merely searching for a summary of kinetic test design and performance may want to review the nine general principles in the summary and recommendations section of the chapter.

In compiling the information contained in this chapter, more than 275 pieces of scientific literature have been cited. These references and related information have been compiled in a computer data base which may be sorted chronologically or by key words. A copy of this bibliographic data base may be obtained from the authors.

Chronology of the Development of Kinetic Tests for Mine Drainage

This section of the chapter is an attempt to summarize the development and use of kinetic tests in mine drainage research, and applications to mine sites by university researchers, state and federal agencies, and the mining industry and their consultants. Most of the literature cited pertains to surface coal mining in the Appalachian coal fields of the eastern United States, but a significant amount of the references are associated with metal mining activities in the western United States, Canada, and elsewhere. Many of these works have been primarily oriented toward the development of techniques for the pre-mining prediction of mine drainage quality with a reasonable degree of accuracy and precision. However, very significant developments in kinetic tests have also occurred in acid mine drainage abatement studies, and in contrasting efforts by the metal mining industry to optimize acid production in heap leaching operations.

An effort has been made by the writers to locate and include a representative sample of the scientific literature on this subject, but this chapter does not purport to be a comprehensive bibliography on kinetic tests. The format of this section is an approximate chronological order of studies on various types of kinetic tests (i.e., leaching columns, humidity cells, Soxhlet reactors, etc.) intertwined together, in order to demonstrate, that like most scientific developments, there has been an effort to converge on the truth by refining successes and eliminating failures through time. Unfortunately, this chronology also demonstrates that after more than forty years of research, some of the early failures are still being repeated and promoted today; and some of the early successes have been repeated and refined through time, but have not achieved sufficient widespread acceptance to be uniformly applied by the majority of the workers in the field. Perhaps M. K. Hubbert's classic paper, "Are We Retrogressing in Science?" (1963) is relevant to some of this research.

A summary of the chronology follows on the next few pages. The entire chronology is presented in Appendix A at the end of this chapter due to its length and the large number of references and figures used in its construction. Examples of leaching columns, humidity cells, and Soxhlet reactors are shown in Figures 7.1, 7.2, and 7.3. For other graphic and written descriptions of kinetic test apparatuses, refer to Appendix A. The 45-year chronology on the development of kinetic tests for the prediction of mine drainage quality commences in 1949 and concludes in 1994 for reasons described below. A few earlier references may be found, but probably the most significant early work on this subject started in this country with the leaching columns of S. A. Braley at the Mellon Institute in Pittsburgh in 1949. The chronology outlines the post-World War II awakening to the impacts that acid mine drainage from coal surface mining in the Appalachian Basin was having on the surface waters and ground waters of the northern Appalachian Region. This period of awareness and assessment of the problem lasted through the 1950s and 1960s. During this time, state and federal regulatory and research agencies and university researchers, particularly in Pennsylvania, Ohio and West Virginia, began to develop a variety of laboratory and field kinetic tests for AMD prediction including leaching columns, humidity cells, Soxhlet

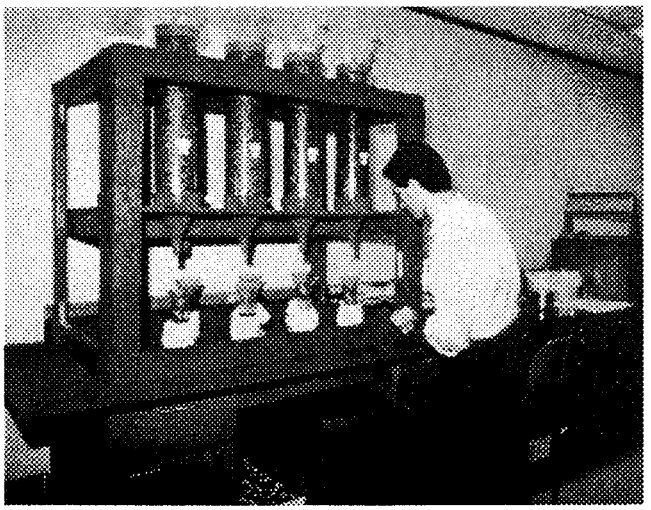

Figure 7.1 Leaching columns (from Bradham & Caruccio, 1995).

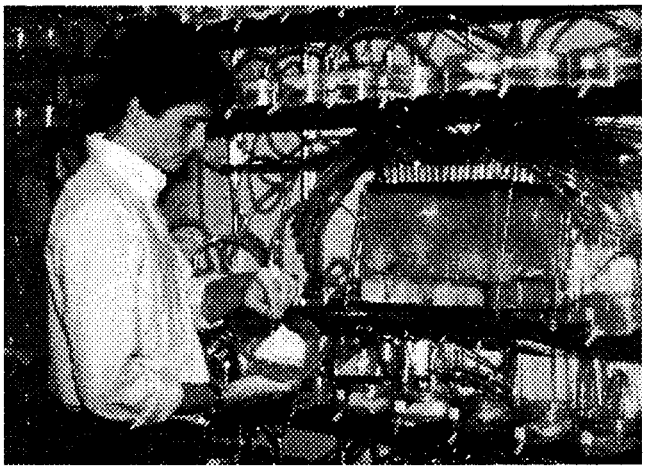

Figure 7.2 Humidity cells (from Bradham & Caruccio, 1995).

reactor techniques, and field scale tests. These kinetic tests were refined and applied throughout the Appalachian Coal Basin during the 1970s and into the 1980s, principally by researchers at the Pennsylvania State University, West Virginia University, and the University of South Carolina.

The Arab oil embargo of 1973, and perhaps other economic factors, led to a boom in coal mining in the United States that lasted throughout the remainder of the 1970s and into the 1980s. Proposed surface mining operations were spreading out from previously mined watersheds into unmined watersheds, where AMD impacts were threatening high quality streams and public water supplies. In a landmark 1977 Environmental Hearing Board decision of Pennsylvania case law, (Harman Coal Company), which was affirmed by Commonwealth Court in 1978, the courts determined that pursuant to 25 Pa. Code Section

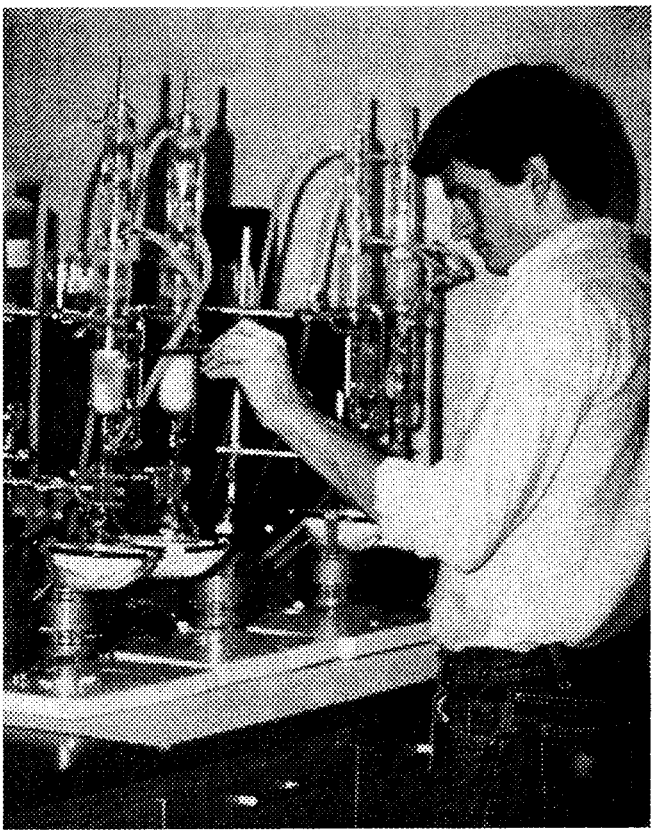

Figure 7.3 Soxhlet reactor (from Bradham & Caruccio, 1995).

99.35(a) it is a permit applicant's responsibility to affirmatively demonstrate that there is no presumptive evidence of potential pollution from the proposed mining activities.

A significant milestone during this period was the enactment of the Federal Surface Mining Conservation and Reclamation Act of 1977 (SMCRA). Prior to that law, some state regulatory agencies required predictions or assessments of AMD potential in mining permit applications, but overburden analysis tests were not routinely required. SMCRA and associated federal regulations required that permit applicants determine the Probable Hydrologic Consequences of proposed mining activities, including the chemical analyses of the coal and overburden strata for AMD potential. Pennsylvania obtained primacy under SMCRA in 1980 and the Pennsylvania mining regulations, 25 Pa Code Chapters 86 through 90, were promulgated to meet requirements in the federal and state laws. While some overburden analyses were required prior to primacy, the OSM approved program and corresponding DER policy and procedures established relatively routine overburden analysis requirements under certain criteria. Section 86.37(a)(3) of the regulations requires

that, "The applicant has demonstrated that there is no presumptive evidence of potential pollution of the waters of the Commonwealth." The federal and state regulations requiring the chemical testing of coal, overburden, and underclay samples as part of the surface mining permit application created a major demand for the development, routine use, and interpretation of kinetic and static tests to predict mine drainage quality by the regulatory agencies, mining industry consultants, and commercial laboratories. This demand forced a search of available laboratory methods used in AMD research and other sciences, that might be used to obtain accurate and precise results. It also initiated the adaptation of some test methods from a university research study environment to the routine sample production environment of commercial laboratories. Unfortunately, the rapid growth in the development and application of these tests was accompanied by significant confusion in the interpretation of test results and apparent contradictions among some test predictions. The scientific and legal controversies surrounding the various static and kinetic overburden analysis methods in use at that time prompted state and federal regulatory and research agencies and other researchers to conduct comparisons of test results in an attempt to determine whether any of the available overburden analysis methods produced accurate and precise premining predictions of postmining water quality. Several of these comparative studies were published between 1986 and 1992, and additional work in this area continues today to determine the best predictive test methods.

In other areas of the United States, outside of the Appalachian Coal Basin, including Illinois, Montana, Minnesota, Utah, and Washington, kinetic test methods were being developed and applied in mine drainage work for coal mines, metal mines, and associated tailings deposits throughout the 1980s. In fact, some of the very best kinetic test studies were done by the metal mining industry to optimize acid leaching and metal recovery from mine waste dumps, commencing in approximately 1975. In Canada, particularly British Columbia, research on static and kinetic tests to evaluate AMD potential was ongoing during the late 1970s and 1980s, primarily for metal mines and associated tailings deposits.

Significant collaboration among state and federal regulatory and research agencies, the mining industry, and university researchers on solving mine drainage problems occurred in the mid-1980s in West Virginia with the Acid Mine Drainage Technical Advisory Committee (AMDTAC) and from the late 1980s to the present in Canada with the Mine Environment Neutral Drainage (MEND) program. Both of these groups and their participating scientists and engineers have made significant advances in the field of mine drainage prediction (including the use of kinetic tests) and mine drainage abatement.

During the 1990s, very extensive work on the evaluation of critical parameters and performance of kinetic tests, particularly humidity cells and leaching columns, has been done by researchers at the USBM Pittsburgh, Salt Lake City, and Spokane Research Centers, and other researchers in university research programs. The 45-year chronology concludes with the publication of the proceedings of the Third International Conference on the Abatement of Acidic Drainage in Pittsburgh in 1994, because this conference was the focal point on the status of mine drainage prediction throughout the world, among other things. At least 45 of the 186 papers presented included kinetic test developments, evaluations, and applications. These 1648 pages of conference proceedings are an accurate indicator of the current state of the art, science, or confusion surrounding kinetic tests for the prediction of mine drainage quality.

The 45-year chronology was written for the following four reasons:

(1) it documents the historical development of kinetic tests for mine drainage prediction and practical applications of the test results on mine sites in the Appalachian coal fields and elsewhere,

(2) it provides the reader with a fairly complete list of references on the origin and development of the various kinetic tests for mine drainage prediction in the event that additional research is contemplated, or additional, more detailed information on the test developments and field applications is needed,

(3) it demonstrates that most of the kinetic test methods in use today were substantially developed and applied more than 30 or 40 years ago, including leaching columns (Braley, 1949), humidity cells (Hanna and Brant, 1962), Soxhlet reactors (Pedro, 1961), and field scale tests with actual precipitation (Glover and Kenyon, 1962),and

(4) it depicts the present state of confusion concerning the use and interpretation of specific kinetic test procedures for mine drainage prediction, and

promotes a concerted effort to converge on a practical solution to the problems in the near future.

After at least 45 years of kinetic test developments, at least 45 technical papers on kinetic test developments and applications were presented at the 1994 AMD conference in Pittsburgh. To witness many of these presentations and later review the more than 1600 pages of proceedings for the preparation of this chapter was mind-boggling and frustrating. A tremendous amount of kinetic test information now exists, but the variety of test apparatus and procedures in use is so great that it is very difficult to interpret the results and make meaningful comparisons of data from different studies in similar or different lithologic settings. If, after 20 years of personal experience with kinetic tests and other aspects of AMD research, the authors of this chapter struggle to make sense out of much of this data; it should be no wonder that mine operators and consultants new to the subject of AMD prediction would shy away from kinetic tests because they don't know which apparatus or procedure to use, nor how to interpret the results.

Notwithstanding the millions of dollars of research expended, is the state of affairs in kinetic test development and application really much better off now than it was 20 years ago? Hopefully, researchers and research users will unite and develop a consensus on kinetic test procedures and interpretation for mine drainage prediction, in order to facilitate the meaningful comparison of test results from rock sample to rock sample, mine to mine, state to state, and nation to nation, in order to make sound decisions. We will remain optimistic that researchers and research users will ultimately develop a consensus on kinetic test procedures and interpretation for mine drainage prediction within the next few years. In the interest of advancing that process, the following discussion of essential physical, chemical and biological factors is offered.

Evaluation of Physical, Chemical, and Biological Factors in Kinetic Tests

The kinetic tests described in the 45-year chronology above, incorporate physical, chemical, and biological processes and constraints. The scientific literature on physical, chemical, and biological controls on AMD production and other natural or man-induced acidity- and alkalinity-generating processes is much more voluminous and long-term than the 45-year chronology. Consequently, the role of these physical, chemical, and biological factors in natural systems is largely understood, and these factors must be considered and incorporated in the design, operation, and interpretation of kinetic tests for AMD prediction, or the laboratory data will have little or no relevance to the real world.

Physical factors include: the size, shape, and structure of the apparatus used to conduct the tests; the volume, texture, and particle size distribution of the sample to be tested; and the volume, pathway, and resultant saturation conditions (e.g. saturated zone, capillary fringe or relative humidity of pore spaces) of the fluids introduced into or removed from the apparatus for analysis.

Chemical factors include: the mineralogical composition of the rock sample, the composition (i.e. concentration of cations and anions) of the influent and effluent fluids; the solubility controls on the acidity- and alkalinity-generating processes, the interrelationships between these processes and other constraints affecting the reaction kinetics, and the composition of gaseous phases (e.g. partial pressures of oxygen and carbon dioxide) in the fluids and void spaces within the kinetic test apparatus.

Biological factors include: the presence and relative abundance of bacteria (e.g. *Thiobacillus*,) that catalyze the AMD producing reactions; the availability of nutrients and other life-supporting ingredients; and the interrelationships among controls on the biological system, such as temperature and pH, which determine whether various organisms flourish, barely survive, or die.

A complete discussion of all of the chemical reactions associated with acidity and alkalinity production is not included in this chapter because those reactions are explained elsewhere in this volume and in many other references. However, it is useful to briefly review the controls and range of acidity, alkalinity, sulfate, and metals concentrations which may be found in nature, particularly mine environments, in order to demonstrate the variations in mine drainage composition associated with the range of geologic settings in Pennsylvania and elsewhere, and to place some expectations on the variations in leachate composition from kinetic tests.

Excellent explanations of the series of chemical reactions by which AMD is produced from pyrite and other iron sulfide minerals, are found in Lovell (1983), Barnes and Romberger (1968), Singer and Stumm

(1968, 1970), Kleinmann et al. (1981), Evangelou (1995) and Chapter 1 (this volume). Singer and Stumm (1970) simplify the explanation by describing an indicator reaction and a propagator reaction, in a process where the rate determining step is the oxidation of ferrous iron, and where the presence of iron-oxidizing bacteria catalyzes the oxidation by a factor greater than 10^6. As pyrite is formed in a reduced depositional environment, it is unstable in the oxidizing conditions of most surface and underground mines. However, secondary mineral phases formed from pyrite weathering, such as jarosite, alunite, and melanterite, are capable of dissolving or precipitating in mine environments. Additional information on these and other secondary mineral phases is found in Nordstrom (1982) and Cravotta (1994). According to Lovell (1983), of the various iron sulfates which are several orders of magnitude more water-soluble than pyrite, melanterite has a solubility of 156,500 mg/L, while coquimbite has a solubility of 4,400,000 mg/L. Lovell (1983) also lists ranges of component concentrations in Appalachian acid mine drainage where pH may be as low as 1.4, and maximum concentrations for the following parameters are: acidity of 45,000 mg/L, total iron or ferrous iron of 10,000 mg/L, aluminum of 2,000 mg/L, and sulfate of 20,000 mg/L.

According to Krauskopf (1967, p. 35): "The lowest recorded pH's in nature are found in solutions in contact with oxidizing pyrite; values even less than zero have been recorded from such environments". An outstanding example of this phenomena is the study by Alpers and Nordstrom (1991) at the Iron Mountain mine in Shasta County, California that is producing some of the most acidic and metal-rich mine drainage in the world. Alpers and Nordstrom (1991, p. 323) state:

> "Oxidation of pyrite is well known to cause acidification of surface and ground waters. Minimum pH values tend to be in the range of 1.5 to 2.5 for natural waters infiltrating disseminated sulfide deposits, base metal tailings, and sulfidic waste rocks, where some degree of neutralization by gangue minerals accompanies pyrite oxidation. However, within massive sulfide deposits and in sulfide-rich tailings and waste rock, extremely high aqueous concentrations of sulfate, iron, and other metals can develop, accompanied by pH values less than 1.0. In at least one extreme case, at Iron Mountain, California, pH values less than 0.0 have now been documented."

The most extreme values reported by Alpers and Nordstrom (1991) for a ground-water seep from a stalactite of melanterite or rhomboclase collected within the underground mine were a field pH of -1.0, sulfate of 760,000 mg/L, and total iron of 111,000 mg/L.

In Pennsylvania coal mine drainage, some of the most extreme concentrations of acidity, iron and sulfate have been found at the Leechburg Mine refuse site in Armstrong County, and at surface mine sites in Centre, Clinton, Clarion and Fayette Counties as shown in Table 7.1. The acidity concentrations of seeps from Lower Kittanning Coal refuse at the Leechburg site exceed 16,000 mg/L (Table 7.1), while the sulfate concentration of one sample exceeds 18,000 mg/L. At the Stott surface mine site on the Clarion Coal in Centre Co., a 35 gpm (132.5 lpm) post-mining discharge had an acidity concentration over 9,700 mg/L with an iron concentration of almost 2,000 mg/L (Table 7.1). A pit water sample at the Lawrence site in Fayette County was found to have an acidity concentration greater than 5,900 mg/L and an iron concentration greater than 2,000 mg/L (Table 7.1). Schueck et al. (1996) report on detailed AMD abatement studies conducted at a backfilled surface mine site in Clinton County, where a monitoring well that penetrated a pod of buried coal refuse produced a maximum acidity concentration of 23,900 mg/L and a mean acidity concentration of 21,315 mg/L based on 13 samples. The maximum concentration of iron was 5,690 mg/L and the maximum sulfate concentration was 25,110 mg/L in the same monitoring well, as reported in Schueck et al. (1996). Toe of spoil seeps at the Clinton County site have acidity and sulfate concentrations greater than 3,500 mg/L and 3,700 mg/L, respectively.

The alkalinity production process has a dramatically different set of controls, and the resultant maximum alkalinity concentrations are typically one or two orders of magnitude less than the maximum acidity concentrations found in mine environments. The carbonate rocks which produce significant alkalinity or bicarbonate concentrations in groundwater, surface-water, and mine drainage samples (i.e., coal surface mines, stone quarries, and coal and noncoal underground mines) are limestones and dolomites and the principal carbonate minerals are typically calcite (calcium carbonate) and dolomite (calcium-magnesium carbonate).

Table 7.1 High Concentrations of Acidity and Related Water Quality Parameters in AMD at Bituminous Coal Mine Sites in Pennsylvania.

Site Name	SMP #	County	Township	MP ID	Date	pH	Conduct.	Alkalinity	Acidity	Iron	Mn	Al	SO_4	TSS	Flow	Type of Sample
					Sampled		umhos/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	(gpm)	
Leechburg	03-92-01	Armstrong	Kiskiminetes	8	6/29/94	2.4	N.D.	0.0	**16594.0**	> 300.0	16.5	> 500.0	11454.0	10.0	1.0	Seep
Leechburg	03-92-01	Armstrong	Kiskiminetes	8	10/26/94	2.4	N.D.	0.0	**16718.0**	> 300.0	19.3	> 500.0	18328.0	74.0	2.0	Seep
Leechburg	03-92-01	Armstrong	Kiskiminetes	1	6/29/94	3.1	N.D.	0.0	**1368.0**	> 300.0	13.9	82.3	1896.0	34.0	200.0	Deep Mine Discharge
Leechburg	03-92-01	Armstrong	Kiskiminetes	3	5/3/96	2.0	9800	0.0	**10383.5**	2200.0	3.3	N.D.	14565.2	14.0	3.5	Diversion Ditch Discharge
Trees Mills	65880112	Westmoreland	Salem	MP-1	11/29/90	2.5	2700	0.0	**3616.0**	190.4	13.5	73.1	1497.8	10.0	13.0	Deep Mine Discharge
Lawrence	3376SM15	Fayette	Springfield	1063-5	1/18/82	2.2	11000	0.0	**5938.0**	2060.0	73.0	146.0	3600.0	N.D.	0.0	Pit Water
Lawrence	3376SM15	Fayette	Springfield	Breakout	12/14/81	2.6	5500	0.0	**1840.0**	166.0	89.0	85.0	2700.0	N.D.	25.0	Surface Mine Discharge
Blue Lick	56880109	Somerset	Brothersvalley	N.D.	3/28/96	2.9	N.D.	0.0	**2594.0**	> 300.0	35.7	180.0	2701.0	5.0	N.D.	Seep
Stott	14673012	Centre	Rush	B1P	6/27/84	2.7	25000	0.0	**9732.0**	1959.8	205.3	N.D.	4698.0	N.D.	35.0	Surface Mine Discharge
Stott	14673012	Centre	Rush	B1P	5/15/89	2.8	9400	0.0	**4520.0**	4880.0	149.5	N.D.	5139.4	N.D.	40.0	Surface Mine Discharge
Stott	14673012	Centre	Rush	A5P	5/8/93	2.8	5400	0.0	**1450.0**	215.8	44.3	N.D.	2886.1	N.D.	1300.0	Surface Mine Discharge
Orcutt	33803040	Jefferson	Union	S-2	10/2/86	3.2	9536	0.0	**4784.4**	6118.4	510.0	N.D.	7500.0	22.0	0.0	Spoil Piezometer
Orcutt	33803040	Jefferson	Union	S-2	10/16/86	3.9	8040	0.0	**5179.6**	2848.0	349.0	N.D.	11120.0	43.0	0.0	Spoil Piezometer
†Fran	4674SM21	Clinton	Keating	K-23	7/28/92	2.2	N.D.	0.0	**23900.0**	5690.0	79.0	2240.0	25110.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 1	11/12/85	2.2	15000	0.0	**10000.0**	3200.0	260.0	550.0	14000.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 1	4/7/87	1.9	17000	0.0	**9200.0**	2200.0	120.0	370.0	6800.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 1	9/15/87	1.8	14000	0.0	**8600.0**	2400.0	< 1.0	440.0	8200.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 5	3/4/86	2.0	12800	0.0	**9400.0**	2400.0	62.0	480.0	10000.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe	C 5	12/10/86	2.0	13100	0.0	**10000.0**	44.0	92.0	380.0	10000.0	N.D.	0.0	Monitoring Well
††Old 40	3671BSM19	Clarion	Monroe		6/7/83	2.4	6000	0.0	**5000.0**	700.0	90.0	180.0	3300.0	N.D.	22.5	Spoil Drain
††Old 40	3671BSM19	Clarion	Monroe		3/13/89	2.2	5000	0.0	**4400.0**	1200.0	75.0	250.0	4000.0	N.D.	4.5	Spoil Drain
††Old 40	3671BSM19	Clarion	Monroe		10/12/83	3.1	3200	0.0	**1100.0**	260.0	55.0	26.0	2100.0	N.D.	4.5	Seep
††Old 40	3671BSM19	Clarion	Monroe		6/4/86	2.6	3140	0.0	**1200.0**	1900.0	140.0	58.0	1900.0	N.D.	0.0	Seep
Zacherl	2769BSM28	Clarion	Clarion		9/17/81	2.3	N.D.	0.0	**9870.0**	2860.0	136.6	583.0	7600.0	N.D.	N.D.	Toe-of-spoil Discharge

* N.D. = No Data

† data from Schueck et al (1996)

†† data from Dugas et al (1993)

Very thorough discussions of the chemical reactions of carbonate mineral dissolution and precipitation and associated solubility and chemical equilibria controls are found in Stumm and Morgan (1970), Krauskopf (1967), Garrels and Christ (1965), Freeze and Cherry (1979), Plummer et al. (1978) and White (1988). According to Krauskopf (1967, p. 52-55), the solubility of calcium carbonate is controlled by the pH of the environment, changes in temperature and pressure, and organic matter activity and decay. Freeze and Cherry (1979, p. 106) state that the solubility of carbonate minerals is dependent on the partial pressure of carbon dioxide (PCO_2), and list the solubilities of calcite and dolomite at partial pressures of 10^{-3} bar and 10^{-1} bar as an indication of the range of values that are relevant for natural groundwater. The solubility for calcite in water at 25° C, pH 7, 1 bar total pressure, and a PCO_2 of 10^{-3} bar is 100 mg/L, while the solubility at a PCO_2 of 10^{-1} bar is 500 mg/L according to Freeze and Cherry (1979, p. 106), using data from Seidell (1958).

However, these relationships may be more complex than they initially appear if the carbonate minerals do not dissolve congruently and the solution contains constituents other than "pure water" (e.g. if the starting solution is saturated with gypsum) according to Rose (1997), who calculated the range of bicarbonate concentrations for calcite dissolution in pure water from 83 mg/L at PCO_2 of 10^{-3} to 370 mg/L at PCO_2 of 10^{-1} using the methods (i.e. Case 4) described in Garrels and Christ (1965). Figure 7.4 from White (1988) shows solubility curves for calcite as a function of carbon dioxide partial pressure, and Rose and Cravotta (Chapter 1, this volume) depict bicarbonate and alkalinity concentration for a similar range of PCO_2, based upon Case 2 of Garrels and Christ (1965, p. 81). Additional diagrams of calcite and dolomite solubility at various carbon dioxide partial pressures are found in Faust (1949), Runnells (1969) and other sources.

Barrow (1973, p. 10) states that the term partial pressure denotes the pressure exerted by one component of a gaseous mixture, in accordance with Dalton's law of partial pressures. According to Stumm and Morgan (1970, p. 180-181) a partial pressure of carbon dioxide of $10^{-3.5}$ bars corresponds to atmospheric conditions, and "The distribution of the dissolved carbonate species at a given temperature is defined entirely by PCO_2." Concerning the partial pressures of carbon dioxide in the subsurface conditions of soil air, soil water, and groundwater; Brady (1974, p. 16, 257) and Hem (1970, p. 45) describe that carbon dioxide in soil air is often several hundred times more concentrated than the 0.03% commonly found in the atmosphere, as much as 10% for example. Also, water moving through soil dissolves some of this carbon dioxide, affecting pH, solubility, and weathering of minerals in the soil and underlying rock. Additional information on limestone dissolution, carbon dioxide partial pressures and the kinetics of chemical reactions involved in the neutralization of acidic water by limestone is found in Cravotta et al. (1994a), Pearson and McDonnell (1974, 1975a, 1975b, 1977, 1978) and Ziemkiewicz et al. (1995).

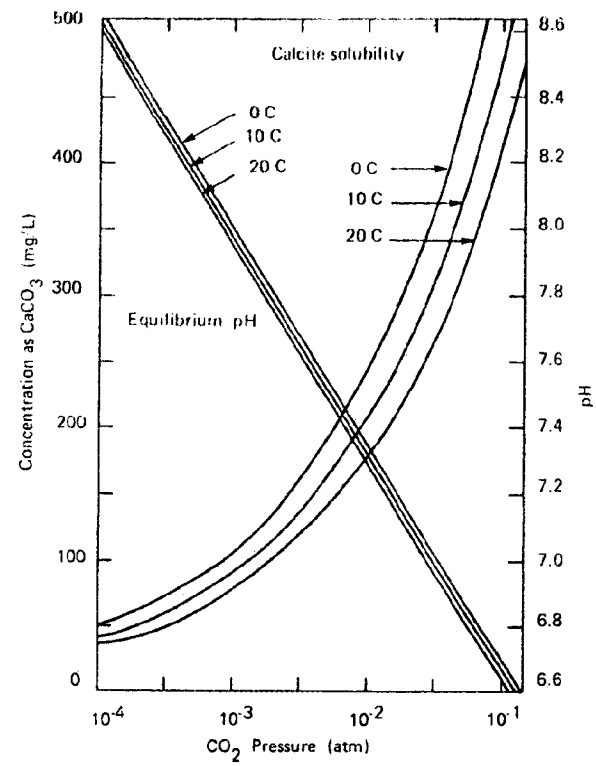

Figure 7.4 Solubility curves for calcite as a function of carbon dioxide partial pressure (from GEOMORPHOLOGY AND HYDROLOGY OF KARST TERRAINS by William B. White. Copyright © 1988 by Oxford Univ. Press, Inc. Used by permission of Oxford Univ. Press, Inc. See pp. 128-131 for equilibrium conditions related to figure).

Davis and DeWiest (1966) indicate that most groundwaters have pH values between 5.0 and 8.0 but that pH values as high as 11.0 have been reported for alkali-spring water in desert regions. Hem (1970) refers to two reported analyses of high pH spring waters in areas of ultramafic rocks, with values of 11.6 and 11.7. According to the National Academy of Sciences-National Academy of Engineering Committee on Water Quality Criteria (1972, p. 54) alkalinities of natural waters rarely exceed 400 to 500 mg/L (as $CaCO_3$).

However, in discussing the chemistry of seawater, Harvey (1957) indicates alkalinity may reach 2,600 mg/L, but rarely exceeds that value. Considering the portion of the alkalinity represented in bicarbonate concentrations, Hem (1970, p. 158) states: "The bicarbonate concentration of natural water generally is held within a moderate range by the effects of carbonate equilibria. ... Most surface streams contain less than 200 mg/L, but in groundwater somewhat higher concentrations are not uncommon". Very high bicarbonate concentrations in groundwaters of the Alto Guadalentin aquifer in the Murcia province of Spain are reported by Ceron and Pulido-Bosch (1996), who consider the high levels of carbon dioxide gas in the groundwater to be a pollutant because increases in the PCO_2 over time have been related to over-exploitation of the aquifer. They report a range of bicarbonate concentrations from 495 to 1890 mg/L with a median of 1010 mg/L for 23 samples from wells in the El Saladar area. The groundwater sample with the maximum bicarbonate concentration had an alkalinity concentration of approximately 1,550 mg/L and also had a sulfate concentration of 1,283 mg/L, chloride of 426 mg/L, calcium of 667 mg/L, magnesium of 244 mg/L, sodium of 181 mg/L, and a PCO_2 of 1.497 bars. Davis and DeWiest (1966, p. 107) indicate a general range of 10 to 800 mg/L for bicarbonate concentrations of groundwaters and state that "concentrations between 50 and 400 ppm are most common". Additional groundwater alkalinity data are in Brady et al. (1996).

Typical bicarbonate and alkalinity concentrations associated with limestones and dolomites in Pennsylvania are found in Langmuir (1971), Shuster (1970) and Shuster and White (1971). Langmuir (1971) reported bicarbonate concentrations ranging from 81 to 438 mg/L for wells and springs in limestone of central Pennsylvania. Shuster (1970) reported a maximum bicarbonate concentration of 292 mg/L from springs in carbonate rocks in central Pennsylvania. Examples of maximum and other relatively high alkalinity concentrations in mine drainage, groundwater and surface waters associated with surface and underground mines in Pennsylvania limestones and dolomites, bituminous and anthracite coals are shown in Table 7.2. The highest natural alkalinity concentration found in PA DEP mining permit file data and reported in Table 7.2 is 626 mg/L in a spring located near the cropline of the Redstone Coal in Fayette County. Thick sequences of carbonate strata, including the Redstone Limestone and the Fishpot Limestone underlie and overlie the Redstone Coal.

The alkalinity of quarry pit waters and underground mine waters in the Ledger Dolomite/Elbrook Limestone sequence in Chester County, the Kinzers Formation in York County, the Valentine Limestone in Centre County, and the Vanport Limestone in Armstrong County, typically range from 150 to 250 mg/L as shown in Table 7.2. It might be expected that underground mine sumps, groundwater inflow, and active deep mine discharges would have higher alkalinity concentrations and higher PCO_2 than surface mine waters open to the atmosphere, but that is not evident in the water samples shown in Table 7.2, apparently due to the properly functioning ventilation systems within the underground mines.

Some stream samples in the bituminous coal region exhibit alkalinities greater than 250 mg/L, and some springs, wells, and abandoned mine discharges have alkalinity concentrations greater than 300 mg/L as shown in Table 7.2. Curiously, the Wadesville shaft pumped discharge in the Southern Anthracite Field typically has alkalinity concentrations greater than 350 mg/L (including a sample from 1986 with 414 mg/L alkalinity), but there are no known major carbonate lithologic units in this stratigraphic section. Another curiosity is that some of the highest alkalinity concentrations shown in Table 7.2 are accompanied by equivalent or greater sulfate concentrations, so that bicarbonate may not be the dominant anion in some of these highly alkaline groundwaters and mine waters. An excellent example of this is found in research on the chemistry of pore gas and groundwater at a reclaimed bituminous coal mine in Clarion County by Cravotta et al. (1994a p. 371), who report a maximum alkalinity of 750 mg/L in an unsaturated zone lysimeter 15 ft (4.57 m) below the land surface, and a sulfate concentration of 3,600 mg/L in the same groundwater sample.

Given the ranges and extreme values of pH, acidity, alkalinity, iron, aluminum, and sulfate reported above, it is reasonable to expect that kinetic tests for AMD prediction should be capable of producing leachate with acidity and sulfate concentrations of several thousand to tens of thousands mg/L, and metals concentrations of several hundred mg/L from worst-case AMD-producing rock samples, and leachate with alkalinity concentration of several hundred mg/L from best-case carbonate rock samples. All of these expectations are possible, as shown in Figure 7.5, even with the use of a relatively crude kinetic test apparatus like that shown in Figure 7.11 in Appendix A.

Table 7.2 High Concentrations of Alkalinity in Mine Drainage, Groundwater and Surface Waters at Limestone and Dolomite Mines and Bituminous and Anthracite Coal Mines in Pennsylvania

Formation	SMP #	County	MP ID	pH	Alkalinity mg/L	Acidity mg/L	Iron mg/L	Mn mg/L	Al mg/L	SO_4 mg/L	TSS mg/L	Type of Sample
Waynesburg 1	30813009	Greene	DM-2	7.8	379.0	0.0	0.12	0.04	N.D.	165.0	17.0	Deep Mine Discharge
Waynesburg 2	30813009	Greene	SP-1A	7.9	296.0	0.0	0.49	0.09	< 0.1	124.0	N.D.	Stream
Redstone	26910115	Fayette	8	7.4	626.0	0.0	1.65	1.05	< 0.5	1440.0	12.0	Spring
Redstone	65930104	Westmoreland	8	8.1	338.0	0.0	0.66	0.33	0.5	181.0	< 3.0	Spring
Lower Freeport	17910103	Clearfield	I-511	7.8	238.0	0.0	0.01	0.01	N.D.	458.0	0.3	Deep Mine Discharge
Blue Lick	56880109	Somerset	Pit Sump	6.8	166.0	0.0	2.86	0.52	< 0.5	220.0	24.0	Pit Sump
Blue Lick	56880109	Somerset	SP15	7.9	276.0	0.0	< 0.3	< 0.05	< 0.5	436.0	< 3.0	Spring
Blue Lick	56880110	Somerset		7.7	138.0	0.0	1.12	0.86	< 0.5	494.0	10.0	Stream
Blue Lick	56880111	Somerset		6.9	226.0	0.0	0.81	0.83	< 0.5	1102.0	10.0	Stream
Lower Bakerstown	56920105	Somerset	L. Pit Water	7.3	118.0	0.0	2.63	5.87	1.2	566.0	8.0	Pit Pool
Vanport	3840105R	Armstrong	15	7.8	274.0	N.D.	0.01	1.13	N.D.	1645.0	1.0	Seep
Vanport		Lawrence	W-29	7.5	324.0	< 2	2.10	0.07	N.D.	40.0	4.0	Well
Wadesville	54713002	Schuylkill	N.D.	6.7	414.0	0.0	3.61	3.37	< 0.5	1038.0	26.0	Deep Mine Pumped Discharge
Wadesville	54713002	Schuylkill	1	6.9	370.0	0.0	1.95	3.42	< 0.5	884.4	< 3.0	Deep Mine Pumped Discharge
Valentine 1	4775SM10	Centre	172	7.5	226.0	0.0	< 0.01	< 0.01	< 0.135	145.0	< 2.0	Pit Water Outfall
Valentine 2	1479401	Centre	174	7.5	146.0	0.0	0.29	< 0.01	0.4	105.0	2.0	Pumped Pit Water
Valentine 3	14900301	Centre	175	7.6	102.0	0.0	2.07	0.05	3.9	44.0	100.0	Raw Pit Water
Valentine 4		Centre		8.0	164.0	0.0	0.22	< 0.01	0.59	68.00	94.00	Deep Mine Discharge
Ledger		Chester	167	8.0	284.0	0.0	0.04	0.01	< 0.135	41.0	4.0	Pit Sump
Loyalhanna	3472SM7	Westmoreland	502	7.7	152.0	0.0	< 0.3	< 0.05	< 0.5	143.2	< 3.0	Pit Water
Kinzers		York	299	7.7	190.0	0.0	0.09	< 0.01	< 0.135	N.D.	< 3.0	Underground Sump
Kinzers		York	300	7.6	178.0	0.0	0.20	0.02	< 0.135	N.D.	< 3.0	Fault
Kinzers		York	301	7.2	170.0	0.0	41.70	2.74	29.0	N.D.	576.0	Inflow
Kinzers		York	302	8.0	172.0	0.0	0.26	< 0.01	0.3	N.D.	< 3.0	Pumped Surface Discharge

* N.D. = No Data

The acidity concentration of 37,042 mg/L shown in Figure 7.5 was produced from a leaching column test on a sample of lower Freeport coal from Somerset County, Pennsylvania which had a total sulfur content of 6.44% and a pyritic sulfur content of greater than 5.5%. The leaching column tests on this coal sample from the Pennsylvania State University Coal Research Section sample repository (PSOC-317) also produced a pH of 1.71, a sulfate concentration of 44,000 mg/L, and a total iron concentration of 1605 mg/L in leachate samples collected during the 35-day leaching study. The leaching column apparatus and tests procedures were developed by Hornberger, Parizek and Williams (1981) as shown on Figure 7.11, and the resulting data, graphical and statistical analyses of variations in sulfur content, abundance of framboidal pyrite, and leachate chemistry are reported in Hornberger (1985). In these leaching column tests, precautions were taken to encourage and confirm the presence of *Thiobacillus* bacteria populations, and the leaching columns were maintained at a constant temperature of 25° C. in an incubator for the duration of the leaching study.

In order to produce the alkalinity concentration of 1,012 mg/L shown in Figure 7.5, a sample of Valentine Limestone from a quarry near Pleasant Gap in Center County, Pennsylvania was placed in a separate leaching column identical to that shown in Figure 7.11. Carbon dioxide gas was bubbled through the contact water during this test conducted in the Land and Water Research lab at Penn State University. The Valentine Limestone sample had a neutralization potential (NP) test result of 987.95 ppt $CaCO_3$ equivalents. Hence the limestone sample should be composed approximately of 98.8% calcium carbonate or calcite. This value is consistent with limestone purity data reported in O'Neill (1964, 1976) and Rones (1969) who show several analyses of the chemical composition of the Valentine Limestone in the same locale ranging from 96.8% to 98.6% calcium carbonate. Additional chemical composition data on the Valentine Limestone, Vanport Limestone, and other Pennsylvania limestones is shown in Chapter 8 (this volume). It can be interpreted using Figure 7.4, that the partial pressure of carbon dioxide in the leaching column was much greater than 10^{-1} bar in order to produce the alkalinity of 1,012 mg/L, (see White, 1988; Chapter 1, this volume).

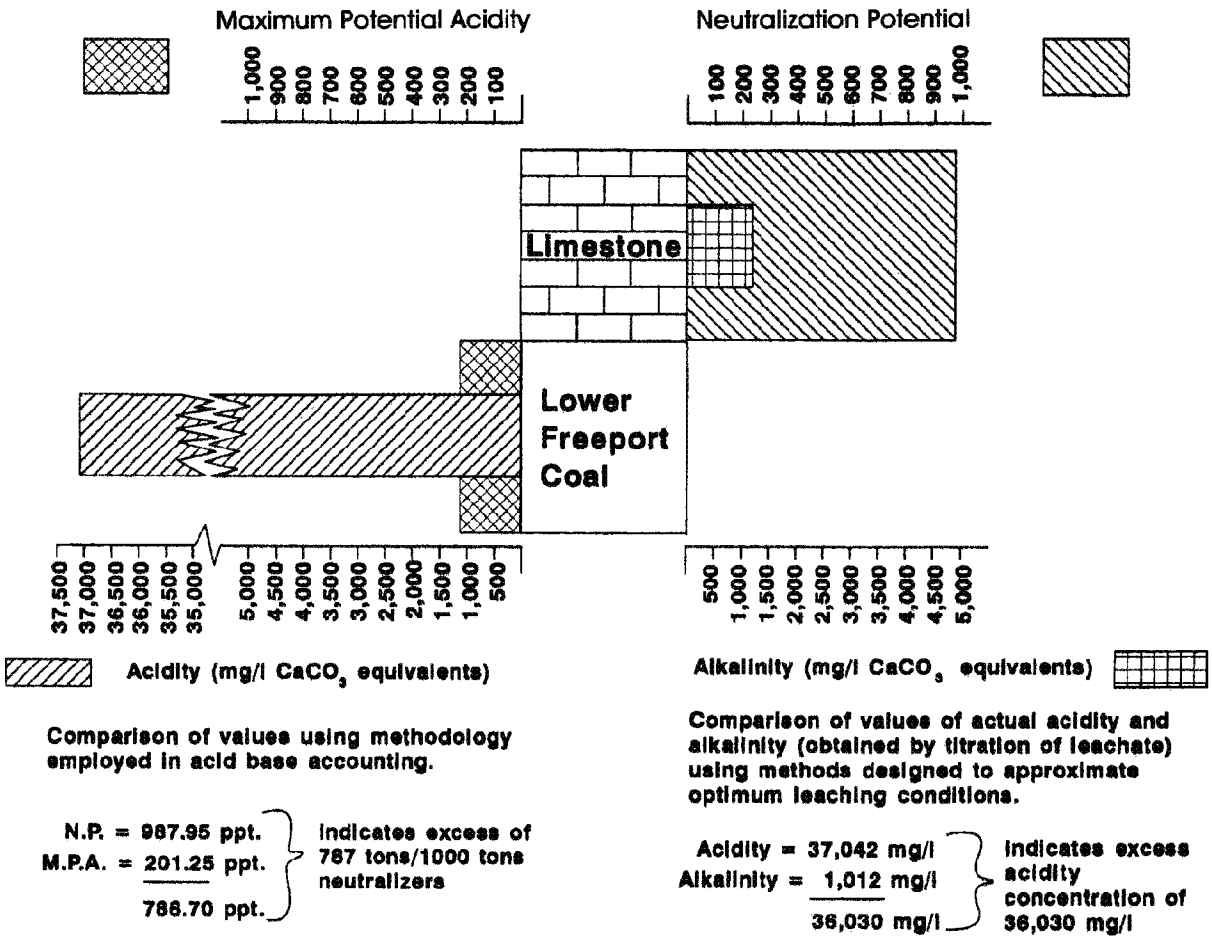

Figure 7.5 Comparison of acidity and alkalinity concentrations from leaching tests with acid-base accounting data from rock samples containing high sulfur and high neutralization potential.

Leaching tests on the same Valentine Limestone sample, without the introduction of additional carbon dioxide, produced alkalinity concentrations of less than 100 mg/L. Adjusting the partial pressure of carbon dioxide as a gas mixture within the leaching column to approximately 10^{-1} bar should be expected to produce alkalinity concentrations of approximately 350 mg/L for the Valentine Limestone sample and similar, relatively pure carbonate minerals.

Figure 7.5 was originally developed by the authors to depict the dramatic differences in the reaction kinetics of the acidity-producing and alkalinity-producing systems, and demonstrate why users of static tests for AMD prediction, like acid-base accounting, must be cautious. Interpretations of data on documented or implied excesses in neutralizers do not automatically translate to definite excesses in alkalinity over acidity concentrations in the mine environment. In this example, a potentially acidic stratum with 6.4% total sulfur content produced acidity concentrations many times greater than the alkalinity concentrations produced by an equivalent weight of rock that is 98.8% pure carbonate. However, the relative stratigraphic positions of these potentially acidic and potentially alkaline strata in the consolidated overburden and in the surface mine backfill, and the sequence and interactions of acidic and alkaline rocks encountered in the groundwater flow system may greatly influence the alkalinity and acidity concentrations of the resultant mine drainage. In the context of this chapter on kinetic tests, Figure 7.5 illustrates why properly designed kinetic tests may be helpful in predicting mine drainage chemistry, especially where static test results are inconclusive or subject to misinterpretation. The remaining discussion in this section of the chapter outlines specific physical, chemical and biological factors to be considered in kinetic test design, performance, and data interpretation.

Size, Shape, and Structure of the Kinetic Test Apparatus

The chronology section of this chapter (see Appendix A) reviews a wide range of kinetic test apparatus used during the past 45-years. Relatively simple leaching columns with a wide variety of diameters and heights and some more complex leaching columns of various dimensions are described. For example, the leaching columns described in Appendix A range in diameter from 1.3 in (3.30 cm) (Hood and Oertel, 1984) to 10 ft (3.08 m) (Murr et al., 1977). The range of size and shapes of humidity cells described in the chronology is apparently not as great as that of the leaching columns, but the complexity of the humidity cell apparatus and peripheral equipment varied substantially from the early work of Hanna and Brant (1962) to the CARWA of Harvey and Dolhopf (1986) and some other recent work with large arrays of humidity cells. Other types of kinetic test apparatuses with substantial complexity of external form and internal structure have been utilized, such as the Warburg respirometer used by Lorenz and Tarpley (1963) and the Soxhlet reactors used by Renton et al. (1973), Sobek et al. (1982), and other researchers.

The Principle of Simplicity (Occam's Razor; see Bross 1981, p. 58 for additional information) may be applicable here, in that the kinetic test apparatus should not be more complicated than it absolutely needs to be, especially considering that multiple arrays of these apparatuses are frequently used concurrently to test multiple rock samples from a proposed mine site. However, the kinetic test apparatus may need some complexity in external form or internal structure to allow fluids and gases (i.e. oxygen and carbon dioxide) to enter, circulate through, and exit the apparatus, in a manner that is representative of weathering conditions of the mine environment.

The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested must be considered in order to prevent adverse interactions between the sample and the container. For example, in some leaching column studies, including Hood and Ortel (1984), and some studies to compare numerous overburden analysis procedures including Bradham and Caruccio (1990, 1995), problems with airlocks within the leaching columns are discussed. These types of problems or artifacts of kinetic test apparatus and procedures must be prevented or minimized because they may skew the test results. In the mine environment, the rock samples within spoil piles and surface mine backfills are not typically in containers when they weather in contact with rainwater and groundwater. Hence, the interaction between the container and the sample should not be a major factor in the test results. According to Potter (1981) and Cathles and Breen (1983, p. E-1) "Solution flow within the column is a critical operating parameter and to avoid undue wall effects the column diameter (I.D) should be four times the largest particle diameter in the aggregate of particles being leached." Murr et al. (1977) developed scaling factors considering the ratio of column diameter and column height and maximum rock size within the column in order to scale solution and air flow rates within the columns. The range of leaching column diameters studied by Murr et al. (1977) were 0.10 m, 0.39 m, and 3.08 m. The large columns were actually stainless steel tanks 40 ft (12.19 m) high and 10 ft (3.08 m) in diameter as further described in Cathles et al. (1977). Additional information on stainless steel leaching columns and elements of leaching theory and practice is contained in Murr (1980).

Another group of studies has evaluated humidity cell performance and parameters including Bradham and Caruccio (1995), Pool and Balderama (1994), and White and Jeffers (1994). In addition, within the last ten years, there have been a number of studies comparing various test methods to determine which is the best AMD predictor, including Caruccio and Geidel (1986a), Erickson and Hedin (1988), Ferguson and Erickson (1986, 1987, 1988), and Bradham and Caruccio (1990, 1995). While most of this discussion and scientific debate has been useful, it may be more productive now to focus on similarities among the various kinetic test methods rather than the differences between them. For example, there are some kinetic tests which have combined features of leaching columns and humidity cells; so that the name or type of kinetic test apparatus may not be as important as the factors affecting the design, performance, and data interpretation of kinetic tests. In the remainder of this chapter, references to specific kinetic test apparatus will be avoided whenever practical, because the following physical, chemical, and biological considerations should be incorporated in any kinetic test.

Particle Size Distribution and Composition of Rock Sample

The mineralogic composition and size distribution of rock materials within a backfilled surface mine are important factors in determining whether the mine spoil

produces concentrations of acidity or alkalinity. Several factors interact to determine the sizes of blocks or particles or rock materials within the backfill, and the corresponding size and distribution of the voids which serve as pathways and storage spaces for the various fluids and gasses contained in and moving through the backfill. These factors are:

(1) the blasting practices used to fragment and cast consolidated overburden strata,

(2) the effects of heavy equipment used to remove overburden strata and conduct backfilling and grading operations,

(3) the fundamental properties of the various lithologic units (i.e. mineralogic composition, grain size, hardness, degree of cementation, porosity, linear sedimentary features (e.g. bedding planes), and

(4) linear structural features (e.g. joints and fractures), within the overburden strata.

The same types of factors are operational within a kinetic test apparatus, but on a different scale. Occasionally, the kinetic test apparatus and type of material being tested may be large enough to use mine spoil or mine refuse samples with rock sizes (particle sizes) as large as those found in the mine environment. Examples include the studies by Renton et al. (1984, 1985) using field barrels of coal refuse samples, and the large tank studies of Cathles et al. (1977) and Murr et al. (1977) using the 10 ft (3.08 m) diameter by 40 ft (12.19 m) high stainless steel tanks for copper ore tailings and leach dump samples. In addition, Caruccio and Geidel (1983) and Geidel et al. (1983) conducted field particle size studies of sandstone and shale samples in 4 ft (1.22 m) by 8 ft (2.44 m) field tubs, to evaluate variations in acid production from 5 different classes of particle sizes ranging from less than 1 in (2.54 cm) to greater than 8 in (20.32 cm) in diameter.

Usually, for the purposes of pre-mine prediction of AMD potential, the rock samples will be obtained from exploration drill holes, and the particle size distribution of the rock sample used in the kinetic test will be determined by the type and method of drilling equipment and by any subsequent crushing or other sample preparation equipment and procedures. As most exploration drilling for coal surface mines is done by air-rotary methods, a maximum particle size of approximately ½ in (1.27 cm) and a nominal or mean particle size of approximately ¼ in (0.635 cm) should be expected for most overburden lithologic units, except where drilling equipment tends to pulverize some lithologies (e.g. coal) into finer grained particles. Therefore, the kinetic test apparatus and procedures should be designed to perform optimally on the particle size distribution produced by air-rotary drilling methods; unless further sample preparation is warranted for other purposes. Some consideration should be given to whether core drilling of overburden analysis test holes is warranted in some circumstances because air rotary drilling methods may mix particles from different lithologic units encountered during drilling and cause interferences in overburden analyses such as the NP test. In addition to preventing sample mixing and resultant chemical analysis problems, core drilling provides for (1) better definition of lithologic descriptions and stratigraphic intervals, and (2) greater control of sample preparation procedures and the resultant particle size distribution of the sample used for kinetic tests.

The particle size distribution of an overburden sample may be determined through a sieve analysis of the sample. In soil classification and analysis, a mechanical analysis is conducted using a series of sieves and other physical methods (e.g. settling, suspension) to separate soils into sand, silt, and clay-sized particles as described by Brady (1974), Terzaghi and Peck (1967), Folk (1968), and others. There are a number of different grain-size classification systems in use, but most of them typically consider particles greater than 2.0 mm to be gravel and particles less than 0.002 mm to be clay sized. The USDA system classifies particles less than 0.002 mm as clay, silt from 0.002 through 0.05 mm, sand from 0.05 through 2.0 mm, and gravel greater than 2.0 mm. The particle size distribution of soils or unconsolidated overburden units, such as glacial till, may then be plotted on a triangular diagram depicting the percentages of sand, silt, and clay-sized particles. Examples of these diagrams are found in Flint (1971, p. 157) for glacial tills, and Terzaghi and Peck (1967) and Brady (1974) for some soils.

As most consolidated rock overburden strata should yield a relatively large percentage of gravel-sized particles in samples obtained from air-rotary drilling (or crushing to a nominal ¼ in (6.35 mm), it is probably not necessary to conduct a complete mechanical analysis to obtain an estimate of the particle size distribution for most kinetic test samples. However, a relatively crude mechanical analysis may be useful to determine the percentages of coarse and fine particles in a few size classes for some specific kinetic test purposes, or in general for different overburden lithologic units. For

example, where samples have been crushed to a nominal ¼ in (6.35 mm) by a jaw crusher, a U.S. series #10 sieve would separate the size fraction less than 2 mm, to retain the gravel-sized particles of nominal ¼ in (6.35 mm); and a #200 sieve with a 74 micron opening would retain the sand-sized grains, and pass the finer silt and clay-sized grains. Alternatively, a #270 sieve equals 53 micron openings which approximates the sand/silt size interface. Additional information on these sieve sizes and procedures is found in soils texts such as Scott and Schoustra (1968, p. 7) and Bowles (1970, p. 35). It could be expected that sandstone overburden samples would possess a relatively large percentage of coarse particles and relatively few fines, especially where the sample is indurated, well-cemented sandstone; and that overburden samples from more fine-grained rocks, like shales and underclays, would possess larger percentages of silt and clay-sized particles.

The presence of a relatively large percentage of fine-grained particles in an overburden sample may have positive and negative effects upon the kinetic test results. According to Bradham and Caruccio (1990), the fine-grained nature of the Canadian metal mines tailings that they tested in leaching columns, caused high specific retention of fluid and created air locks within the columns which skewed the results. In addition, the particle size distribution at the conclusion of the kinetic test may be different (i.e. more fine) than the original particle size distribution of the sample, due to particle decomposition during the test.

Another potential problem is that sorting by grain size can bias a sample. Several studies have shown a disproportionate percentage of total sulfur in the finer-grained portion of a sorted sample. Geidel et al. (1983) evaluated pyritic sulfur contents of 5 particle size fractions (i.e. ranging from greater than 6 in (15.2 cm) to less than 1 in (2.54 cm) of a sandstone sample and a binder sample from a West Virginia surface mine. They found the pyritic sulfur content of the binder increased from 0.28% to 0.74% with decreasing particle size, while the sandstone sample exhibited a general decrease in pyrite sulfur from 0.26% to 0.14% with decreasing particle size. However in field leaching tests (i.e. using plastic lined tubs 8 ft (2.44 m) x 4 ft (1.22 m) x 2 ft (0.61 m) connected to 30 gal (113.56 l) plastic barrels) using natural precipitation, the smallest size fraction of sandstone produced the highest acid loads for the sandstone samples, and the smallest size fraction of the binder produced nearly 10 times the total acid load of the larger particle sizes of binder. The cumulative acid load of the less than 1 in (2.54 cm) binder sample was approximately four times larger than the cumulative acid load of the same size fraction of sandstone sample as shown on plots of the acidity data in Geidel et al. (1983). In a study of more fine grained coal refuse from a West Virgina preparation plant, Renton et al. (1984) initially screened the refuse sample to exclude particles greater than 5/8 in (1.59 cm) diameter, and subdivided the sample into 6 size classes. The largest particle size class ranged from 0.375 in (0.953 cm) to 0.625 in (1.59 cm), while the smallest size class was less than 0.0016 in (0.004 cm). There was a general increase in total sulfur content from 2.58% to 3.90% with decreasing particle size in the coal refuse sample.

Notwithstanding the potential operational problems with some fine-grained samples and some types of kinetic test apparatus, variations in the surface area available for reaction may have dramatic effects upon the chemical reactions of acidity and alkalinity production. According to Brady (1974, p. 43) concerning silt and clay-sized particles in soil:

> "Surface area is the characteristic most affected by the small size and fine subdivision of silt and especially clay. A grain of fine colloidal clay has about 10,000 times as much surface area as the same weight of medium-sized sand. The specific surface (area per unit weight) of colloidal clay ranges from about 10 to 1,000 square meters per gram. The same figures for the smallest silt particles and for fine sand are 1 and 0.1 square meters per gram. Since the adsorption of water, nutrients, gas, and the attraction of particles for each other are all surface phenomena, the significance of the very high specific surface for clay is obvious."

Morin and Hutt (1994a) found that the fine (i.e. less than ¼ in (6.35 mm)) size fraction dominates the surface area of typical waste rock, and recommended expressing rates as mass of acid per gram per week, or mass per unit surface area per week. The fine particles have more surface area per unit mass, and reactivity is proportional to surface area, according to Rose (1997). Additional information on particle size and surface area effects of iron sulfide and carbonate minerals in kinetic tests is found in Lapakko et al. (1995).

Numerous studies have examined the potential effects of pyrite surface area and crystallinity upon AMD production and related topics of pyrite morphol-

ogy (particularly the framboidal form) and depositional environments including Caruccio et al. (1977), Reyes-Navarro and Davis (1976), Rickard (1970), Love and Amstutz (1966), Pugh et al. (1981, 1984), Hornberger (1985), McKibben and Barnes (1986), and Chapter 1 (this volume). According to Rose and Cravotta in Chapter 1 "Kinetic studies indicate that the rate of acidic generation depends on the surface area of pyrite exposed to solution, and on the crystallinity and chemical properties of the pyrite surface."

The consideration of surface area available for reaction in kinetic tests leads to the evaluation of the ratio of the surface area to the volume of leachate, which may be the most important factor in kinetic test design, performance, and data interpretation. This factor will be discussed in the succeeding section on water handling procedures.

Volume and Placement of Overburden Samples in Kinetic Test Apparatus

The volume of sample needed to conduct kinetic tests is related to the size of the kinetic test apparatus and a function of representative sampling considerations. The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested was discussed in a previous section of this chapter in the context of preventing adverse interactions between the sample and the container, particularly where the container was too small or confining. A corollary to that principle is that the amount of sample typically available for the kinetic test should be a determining factor in the dimensions of the apparatus. For example, while the 30-gal (113.56 l) field barrels used by Renton et al. (1984, 1985) were ideally suited to testing representative samples of large volumes of coal refuse; it is unlikely that this apparatus would be suitable for testing the volume of sample available from an air-rotary drill hole intercepting a 2 ft (0.61 m) thick black shale unit. The mass of rock chips and fines from a 5 5/8 in (14.29 cm) diameter air-rotary drill hole, typically used for blast hole drilling and overburden analysis sampling, is approximately 12 kg of sample per foot of rock drilled. According to overburden sample collection procedures outlined by Sobek et al. (1978), Noll et al. (1988), and Chapter 5 (this volume, rock samples from air-rotary drilling methods should be collected at 1 ft (0.305 m) intervals; but several feet of successive samples of the same lithologic unit may be combined or composited for testing purposes. As some significant lithologic units may only have 1 ft (0.305 m) thickness, and representative splits of the sample are typically needed for other overburden tests, including NP and total sulfur content, a sufficient amount of the sample should be allocated for kinetic tests. Generally, the volume of sample available for kinetic tests should be at least 1,000 g for each lithologic unit to be tested.

Where the available volume of rock sample is greater than that needed for the kinetic test, a riffle splitter should be used to obtain a representative split of the sample in the desired volume. That split should be physically representative of the particle size distribution of the available sample, and chemically representative of the mineralogical and bulk chemical composition of the lithologic unit being tested. If the sample has been subjected to a mechanical analysis to determine the particle size distribution (as described in the preceding section of this chapter), the coarse and fine fractions should be recombined by passing them through a riffle splitter or similar device to restore the original particle size distribution of the sample prior to kinetic testing because of the potential to have an unequal distribution of pyrite content in different size fractions.

In kinetic tests where a representative sample from a single lithologic unit is being tested, the method of placement of the sample within the kinetic test apparatus may not be critical, except for the particle size distribution concerns and related potential operational problems (e.g. air locks) described above. Where representative samples from more than one lithologic unit have been combined in the same kinetic test apparatus, particularly when there has been an attempt to construct layers of samples to simulate the configuration of the backfilled spoil, the placement of the sample becomes much more problematic. Chapter 1 and Evans and Rose (1995) describe the significance of microenvironments within coal mine spoil in the production of AMD. Rose and Cravotta state in Chapter 1: "Within a mass of broken pyritic rock in the unsaturated zone, water fills fine pores and occurs as films on grain surfaces. Flow rates of water vary widely as a result of channeling along open pathways vs. near stagnation in water films or fine pores. Also, the abundance of pyrite varies widely from one fragment to another. Because of these factors, the chemical environment within spoil can be very heterogeneous. Small volumes with high pyrite, access to the gas phase, and slow flow of water are expected to develop high acidities compared to volumes lacking pyrite, or with complete water saturation. In addition, *T. ferrooxidans* may attach itself to

pyrite surfaces and create its own microenvironment favorable to oxidation. For all these reasons, it seems likely that no simple characterization of chemical conditions (pH, O_2, Fe^{3+}, etc.) is possible for unsaturated spoil. The solution leaving a mine spoil is a mixture of AMD generated in a variety of microenvironments within the spoil."

The differences in scale between the backfilled surface mine site and the typical kinetic test apparatus are many orders of magnitude apart. However, the potential to have similar microenvironments within the kinetic test apparatus is significant, based upon potential variations in particle size, mineralogy, void spaces, and flow paths. The potential problems are further complicated if different minerals with significant potential acidity and potential alkalinity are combined in the same kinetic test apparatus. Another potential problem with the volume and placement of multiple overburden samples in a kinetic test is that approximately 95% of the total volume of overburden may be relatively inert, with respect to significant acidity or alkalinity production. Then the approximately 5% of sample volume containing minerals with significant acidity or alkalinity potential may become dilluted or misplaced within the test apparatus. In some large kinetic test apparatuses like the 40 ft tall tanks of Cathles et al. (1977) and Murr et al. (1977), it may be possible to create layers of different lithologic units and simulate waste dump, spoil pile, or surface mine backfill behavior of different lithologic units. Actually, while it is possible to construct a replica of a ship in a bottle, it is improbable that the conditions of a stratified surface mine backfill can be replicated in a test tube or even the average sized leaching column.

Water Handling Procedures

The importance of the ratio of the surface area of sample to the volume of leachate from a kinetic test was mentioned in an earlier section of this chapter. Obviously, the volume of leachate or effluent from a kinetic test is related to the volume of influent fluid and other factors including water handling procedures during the test and interactions among the solid sample, fluids, and gaseous phases within the kinetic test apparatus. The importance of water handling in kinetic tests cannot be overstated because the final analytical result of the test will be a set of numbers, usually concentrations of acidity, alakalinity, sulfate, and metals (e.g. iron, manganese, aluminum), of the effluent water samples, which will be used to predict the quality of mine drainage waters located within or emanating from mine sites. The bulk chemistry and mineralogy of the rock samples being tested are no doubt important in the laboratory and in the field setting, but the kinetic test results are expressed in and based upon effluent water quality parameters.

Distilled, deionized water will be the influent in most laboratory kinetic tests for mine drainage prediction, while natural rainfall will be the influent in most field-scale kinetic tests, like those described in Emrich (1966), Glover and Kenyon (1962), Renton et al. (1984, 1985), Pionke et al. (1980), and Pionke and Rogowski (1982). There is probably no good reason to use synthetic precipitation or simulated AMD instead of distilled, deionized water in these laboratory kinetic tests, providing that the physical, chemical, and biological conditions of the test facilitate the oxidation and weathering of pyrite or other iron disulfide or iron sulfate minerals, and the dissolution of carbonate minerals, if present in the rock sample. It is not difficult to achieve these conditions in the average laboratory setting. Distilled deionized water is abundantly available in most laboratories, and will very quickly change from pH 7 to pH 5.7 when exposed to air in atmospheric carbon dioxide concentrations, according to Krauskopf (1967, p. 40) and Hem (1970, p. 91). If an abundance of calcareous minerals is present in the sample and the partial pressure of carbon dioxide within the kinetic test apparatus is greater than atmospheric conditions, influent distilled deionized water (actually a weak carbonic acid of pH 5.7), will generate an effluent of significantly higher pH and alkalinity as carbonate minerals dissolve, to produce more bicarbonate anions in the contact water. Conversely, if an abundance of pyrite or other potentially acidic minerals is present in the sample, and oxygen and iron oxidizing bacteria are readily available, the influent distilled deionized, pH 5.7 water, will readily generate an effluent of significantly lower pH and higher acidity, metals, and sulfate concentrations, indicative of acid mine drainage production.

The volume of influent water must be sufficient to obtain enough effluent water for all desired laboratory analyses, and must be in proportion to the volume of rock sample used in the kinetic tests. Further, the volume of water should simulate or approximate the hydrologic conditions of rainfall, surface water, or groundwater that will be operative in the mine environment. A principal objective of many kinetic test procedures is to perform a short term laboratory simulation of many years of weathering in the mine

environment. However, frequent leaching episodes with relatively large volumes of water may simulate the conditions of a tropical rain forest (i.e. abnormally high infiltration rates) rather than the mine environment within the humid Appalachian Coal Basin or the more arid conditions of the western United States. If the ratio of the volume of influent water to volume of rock sample is much greater than will occur in the mine environment, the concentrations of cations and anions in the leachate will probably be much less (i.e. more diluted) than in the actual mine drainage. For example, the fluid volume to sample volume ratio of 4:1 used in the ASTM Water-Shake Extraction Procedure (1983) floods the sample in a manner that is not representative of most surface mine backfills, which is one of several significant reasons why this technique did not work well for AMD prediction. Therefore, the volume of influent water in kinetic tests is critical for determining dilution of the mass of leached constituents.

This portionality consideration is analogous to the concept of pollution load and other relationships between flow and concentration (Gunnerson, 1967; Smith, 1988, and Hornberger et al., 1990) where high-flow hydrologic conditions produce low concentrations of water quality parameters, and low-flow conditions produce high concentrations. The extremely acidic Iron Mountain mine drainage samples reported in Alpers and Nordstrom (1991) are seepage drip waters within the underground mine and a floor drainage sample, which was representative of the effluent from the portal during low-flow conditions. The worst case samples were "drippings of groundwater seeps from stalactites of either melanterite or rhomboclase under humid, warm conditions" (p. 326), which produced a pH of -1.0, total iron concentration of 111,000 mg/L, and sulfate concentration of 760,000 mg/L; while the floor drainage/portal effluent sample had a pH of 0.48, total iron concentration of 20,300 mg/L and sulfate concentration of 118,000 mg/L. No doubt, if the mine drainage from the Iron Mountain mine was sampled after commingling with the waters of a receiving stream, the total iron and sulfate concentrations would be much lower, following dilution and/or precipitation of the iron, further emphasizing the relationship between flow or water volume and the resulting concentrations of water quality parameters.

The USBM has evaluated the major parameters associated with humidity cell tests to determine their effect on the test precision or repeatability according to Pool and Balderama (1994, pp. 330-331), who reported on two of these parameters, effluent volume and airflow rate and stated:

> "These data indicate that the degree of drying, and the amount of effluent recovered from these tailings affected the amount of acid generated.... The optimum amount of leachant, to generate the most acid, is dependent on the amount required to replace evaporation and control the chemical and biological environment. For these tailings, to produce the most acid approximately half the weight of the sample was added as leachant with a subsequent recovery of only a third of the sample weight as effluent."

It appears that for optimum kinetic test performance, the volume/weight of influent water in any single leaching episode should not be greater than 1 times the rock sample weight; (and normally not greater than 0.5 times the rock sample weight) regardless of whether the apparatus is a humidity cell, leaching column or other device (Bradham and Caruccio, 1995). In fact, in field leaching column tests using actual precipitation as the influent water (Emrich, 1966; Glover and Kenyon, 1962; Renton et al., 1984, 1985; and Pionke and Rogowski, 1982), approximately 45 in (1.14 m) of influent would be used in an entire year, based upon average precipitation rates for Pennsylvania. Renton et al. (1984, 1985) used 35-gal (132.49 l) plastic barrels, filled with 300 lbs (136.08 kg) of rock samples; so the ratio of the rainfall volume to rock sample volume was much less than 1:1 for these rainfall-induced leaching episodes (i.e. approximately 5 gal (18.93 l) of water to 35 gal (132.49 l) of rock, equals 1:5).

The importance of the relationships among the volume of rock sample, surface area of the rock sample, volume of the influent water, amount of water consumed/lost during testing, and volume of effluent from kinetic tests have been discussed above. Now, the effects of water in saturating, humidifying, weathering, and flowing through the rock sample in kinetic tests should be given additional consideration. These factors and associated physical, chemical, and biological interrelationships will affect kinetic test performance and extrapolation to hydrologic conditions in the mine environment.

Overburden rock materials in spoil piles in active surface mine sites will weather when infiltrating rainwater and groundwater pass through the spoil pile, but most of the spoil would not be completely saturated all of the time. In typical backfilled surface mine sites, some of the spoil positioned high in the backfill will be

unsaturated most of the time; some of the spoil located close to the pit floor/underclay may be saturated most of the time; and some spoil in an intermediate position may be alternately saturated and unsaturated as groundwater levels rise and fall within the backfill. The hydrogeologic setting of the mine site (i.e. groundwater recharge area, transition area, or groundwater discharge area) should be considered in determining the appropriate kinetic test procedures. For the above reasons and others that will follow, rock samples in kinetic tests should usually not be completely submerged for the duration of the test. Watzlaf (1992) evaluated pyrite oxidation in saturated and unsaturated coal waste samples in leaching columns using influents of distilled, deionized water and recycled AMD (i.e. previously collected leachate laden with ferric iron). The cumulative loads of sulfate, acidity, iron, manganese and aluminum produced from 189 days of leaching were much greater (i.e. 1 to 3 orders of magnitude) for unsaturated conditions, regardless of whether the influent was distilled water or recycled AMD. Watzlaf (1992, p. 203) concluded that:

> "Saturation of the pyritic coal refuse significantly reduced the rate of pyrite oxidation. The sulfate load produced by the unsaturated columns after 189 days would take 118 years to be generated under saturated conditions in the columns receiving the deionized water leachant...
>
> Theoretical calculations, column leaching, and experience from the metal mining industry show the disposal under saturated conditions can significantly reduce contaminant concentration from pyritic material. A field scale study is needed to demonstrate the utility of this approach."

The effectiveness of submergence of the rock samples in kinetic tests is also discussed in Leach (1991) and Caruccio et al. (1993) who describe:

> "... a series of weathering tests using columns whereby samples of acid producing sandstone and shale would be weathered under vadose conditions, the zone of fluctuating water table and the zone below the water table... The results clearly show that submerging acid producing material below the water table have a dramatic effect on inhibiting acid production." (p. 11)

Within the unsaturated zone of a kinetic test apparatus or a surface mine backfill, the humidity in the void spaces and episodes or cycles of infiltrating water facilitate weathering of the rock sample and the production of acidity or alkalinity in the leachate. The effects of humidity on pyrite oxidation have been evaluated by Borek (1994, p 31) who states:

> "Humidity is an important factor in pyrite oxidation as it has been shown that pyrites weather differently depending on the humidity. The formation of oxidation products is also determined by humidity. These observations suggest that if pyritic waste materials are not in direct contact with water (i.e. high and dry), the exclusion of water is not guaranteed. High humidity conditions can contribute the water needed for pyrite oxidation."

Borek (1994) quantified "the amounts of weathering products formed during abiotic chemical pyrite oxidation of six pyrite samples (i.e. three sedimentary pyrites, and three hydrothermal pyrites) under four relative humidity conditions (i.e. 34%, 50%, 70% and 79%); using Mossbauer spectroscopy to determine the types and amounts of weathering products formed." The principal weathering products identified included two ferrous sulfates, melanterite and rozenite.

Generally, Borek (1994, p. 44) found that:

> "While the amount of product was found to be dependent on the humidity and time, the type of product produced seems dependent on the mode of pyrite formation. The physical properties of pyrite, such as crystal structure, may need to be introduced as contributing factors in oxidation and should be examined like other factors (e.g. oxygen partial pressures, temperature, etc.)."

However, Borek (1994, p. 39) also stated: "Two hydrothermal pyrites (Iron Mountain and Noranda) produced no detectable weathering products at any humidity tested. However, both pyrites are believed to be responsible for contaminating water at their field sites." Unfortunately, there was an absence of iron-oxidizing bacteria in these laboratory experiments.

Incredibly, the Mossbauer spectra of hydrothermal pyrite samples from Iron Mountain, California showed no significant difference (i.e. no weathered/oxidized products) from before weathering and after 250 days in 79% relative humidity conditions; while the actual mine drainage from the Iron Mountain mine reported by Alpers and Nordstrom (1991) had a pH less than 0, sulfate greater than 100,000 g/L, and iron greater than 20,000 mg/L.

The water-handling procedures in kinetic tests, especially within unsaturated zones, and the interactions among the kinetic test apparatus, the rock sample, and the water conditions during the test, are most important for a variety of reasons. According to Caruccio et al. (1993 p. 6): "The physical configuration of the testing method may impact the leachate quality more so than the chemistry of the sample. These artifacts in leachate production may be more directly related to the mechanics of the test rather than reflect the chemistry of the rock." They evaluated artifacts of humidity cells (weathering cells), large and small leaching columns, and Soxhlet reactors, and considered a variety of factors including humidity, ambient temperature, leachant temperature, particle size, infiltrating wetting fronts, capillary zones, porosity, permeability, effects of air locks, effects of submergence, presence of iron-oxidizing bacteria, and leaching interval. Humidity cells and the large leaching columns each had certain factors or features which approximated the hydrologic conditions in the mine environment. The ideal kinetic test probably contains some features from both of these methods.

Leaching Cycles

The procedures and elapsed times that occur when water is introduced into kinetic tests, circulated through and/or stored in a test, and withdrawn from the apparatus as leachate will be referred to as a leaching cycle. Within that cycle, the amount of time allocated to circulation and/or storage may be referred to as the residence time, analogous to the elapsed time between groundwater recharge and discharge in a groundwater flow system. Some kinetic test procedures flush accumulated weathering products from the unsaturated zone with relatively small storage times; other kinetic test procedures may leave some components of the water in storage (i.e., in saturated or unsaturated zones) for longer amounts of time within the leaching cycle. Numerous kinetic test procedures described in the 45-year chronology section of this chapter including Caruccio and Parizek (1967), Geidel (1979), and Rose and Daub (1994), used 1-week leaching cycles, with a variety of differences in procedures within the 1-week cycles. Hornberger et al. (1981, 1985) found significantly higher acidity, sulfates, and metals in 1-week contact samples than 1-hour contact samples from the same leaching columns; presumably due to longer residence time of the water within the test apparatus.

Bradham and Caruccio (1995) evaluated variability in leachate quality from humidity cells, Soxhlet extractors and leaching columns due to the factors of leaching interval, leachate temperature, storage conditions (i.e. the conditions of temperature and humidity under which the rock samples are stored between leachings), particle size, and particle sorting efficiency. They found that storage condition and leaching interval were the factors that had the most significant influence on contaminant production from Soxhlet reactors and humidity cells, while particle size effects played a subordinate, although important role in controlling leachate quality. However, in comparing leachate quality from leaching columns and humidity cells, Bradham and Caruccio (1995) concluded that particle size effects were the dominant factor. The leaching interval and associated time factors may also be critical, depending on whether the kinetic test is an acidity generating system or an alkalinity generating system, according to Geidel (1979) who found that the results of more frequent intervals may produce opposite results in terms of rates of alkalinity and acidity production.

The total number of leaching cycles, therefore the total duration or elapsed time of a kinetic test, varied greatly within the procedures outlined in the 45-year chronology. From the scientific and technical standpoint of accuracy, precision and predictability, the number of leaching cycles, and the total duration of the kinetic test must be sufficient to simulate weathering and natural hydrologic conditions of the mine environment, and to guarantee acceptable reproducibility and repeatability of test results with the same rock samples and same kinetic test conditions. From the standpoint of economics and practicality, the number of leaching cycles and duration of the kinetic test should be short enough to be compatible with time and cost constraints of typical mine permitting. Hopefully, both goals can be satisfied within the same kinetic test.

Gas Handling Provisions (oxygen and carbon dioxide)

The significance of oxygen and carbon dioxide in acidity and alkalinity production in the mine environment and in kinetic tests to predict mine drainage quality has been noted throughout this chapter and elsewhere. Without sufficient oxygen and aeration of the rock samples, pyrite oxidation and weathering will be impeded and AMD production will not reach its full potential. Without sufficient carbon dioxide, the dissolution and maximum solubility concentration of car-

bonate rocks will be reduced dramatically, and alkalinity production will not reach the full potential of the carbonate rocks. This section of the chapter will briefly summarize studies on pore gas composition in mine environments and the effects of oxygen and carbon dioxide upon effluent quality in the field and laboratory settings.

The composition of gases within void spaces and backfilled surface mine spoil located in Pennsylvania and elsewhere has been studied by Jaynes et al. (1983), Lusardi and Erickson (1985), Cravotta et al. (1994a), Guo et al. (1994), Guo and Parizek (1994) and others. Jaynes et al. (1983) found that decreases in oxygen concentration with depth were strongly correlated with increases in carbon dioxide concentrations with increasing depth, but that most of the mine site remained well oxygenated (i.e., oxygen greater than 10%) down to 12 m depth throughout the 2-year study. The highest carbon dioxide concentrations reported were 16.61% at 7 m depth. Cravotta et al. (1994a, p. 368) reported that:

> "Partial pressures of O_2 and CO_2 in spoil are expected to vary depending on the predominant reactions involving the gases, relative rates of the reactions, and rates of gas exchange with surrounding zones (Jaynes et al. 1984a,b; Lusardi and Erickson 1985). In general, where pyrite-oxidation and carbonate-dissolution reactions are active, Po_2 will decrease and Pco_2 will increase. Data on pore-gas compositions at the mine indicate that Po_2 decreases from about 21 volume percent (vol %) at the land surface to less than 2 vol % at 10.7 m below the surface, with corresponding increases in Pco_2 with increasing depth in all three areas."

Guo et al. (1994, p47) found oxygen concentrations deep within mine spoil to be greater than 18% at a Clearfield County, Pennsylvania surface mine site, and they state:

> "The field data and a simple model show that thermally induced air convection can be a dominant process maintaining high O_2 concentration in deep mine spoil...
>
> The major hypothesis of this paper is that the thermal anomalies generated by acid-forming, exothermic, pyrite oxidation reactions induce thermal convection that causes significant transport of O_2 into mine spoil."

In a related area of research concerning oxidation concentrations and transport processes within metal mine leach dumps and reclaimed coal surface mine sites, mathematical models have been developed and tested to simulate pyrite oxidation rates and AMD production. Cathles and Apps (1975) and Cathles (1979) describe models of waste dump leaching processes that incorporate air convection, heat balance, temperature dependent oxygen kinetics, and bacterial catalysis. Modeling of pyrite oxidation in reclaimed coal strip mines by gas diffusion processes is described by Rogowski et al. (1983), Jaynes et al. (1984a, 1984b) and Jaynes (1991). According to Jaynes (1984a) the air convection mechanism of oxygen movement used by Cathles and Apps (1975) represents reasonable assumptions for coarse waste dumps, but they believe that diffusion processes would dominate within backfilled coal mine spoil. However, Guo et al. (1994, p. 54) concluded that the: "Results of both field investigation and analytical calculation suggest that the high O_2 concentration (18% or higher) observed in mine spoil cannot be the result of diffusion but, instead, is caused by advection, probably due to thermal convection."

Additional information on oxygen transport is found in Guo and Cravotta (1996). Pyrite oxidation in laboratory kinetic tests has been studied by USBM researchers for more than 60 years including Leitch et al. (1930), Lorenz and Tarpley (1963), Watzlaf and Hammack (1989), Hammack and Watzlaf (1990) and Watzlaf (1992). Oxidation rates of pyrite (with and without bacterial catalysis) were measured by Lorenz and Tarpley (1963) using a Warburg Respirometer, which facilitated the measurement of oxygen consumption during the kinetic test. Hanna and Brant (1962) used the Warburg Respirometer to evaluate oxygen uptake during laboratory weathering of pyrite materials in differing lithological units and particle sizes, in order to compare the oxidation potential of these samples to the results of laboratory leaching methods from the humidity cell type of apparatus they developed. Hammack and Watzlaf (1990) measured abiotic and biotic oxidation rates of pyrite in leaching columns, wherein certified gas mixtures ranging from 0.005% to 14.5% oxygen (plus 5% carbon dioxide and the remainder nitrogen gas) were introduced into the leaching columns via compressed gas cylinders and a gas humidifier. Watzlaf (1992) studied pyrite oxidation in saturated and unsaturated coal waste in leaching columns to determine the effects of dissolved oxygen in

water and the presence of ferric iron upon the pyrite oxidation. According to Watzlaf (1992):

> "To limit pyrite oxidation, oxygen levels must be reduced from an atmospheric level of 21% (0.21 atm) to extremely low levels. It has been shown that the biotic rate of pyrite oxidation is not limited unless pore gas oxygen is reduced to less than 1% (0.01 atm) (Carpenter, 1977; Hammack and Watzlaf, 1990). With current reclamation practices, limiting oxygen to less than 1% is not feasible. At the current time, the only practical method to reduce oxygen to levels low enough to limit pyrite oxidation is by saturating the pyritic material with water (p. 192).... In an unsaturated system, pyrite oxidation has been found to be independent of oxygen levels down to about 1% (Myerson 1981 and Hammack and Watzlaf 1990). Pore gas oxygen levels in surface mine spoil or in coal refuse piles are almost always above 1% .... In a saturated system, pyrite would oxidize at a very low rate that is dependent on the amount of dissolved oxygen and ferric iron in the contacting water. Once dissolved oxygen is consumed, the rate of diffusion of pore gas oxygen through water becomes limiting. (p. 203)"

Watzlaf (1992) also compiled data on pyrite oxidation rates from other studies (expressed in mg of sulfate per gram of pyrite per hour) ranging from 0.06 to 0.16, including data from Braley (1960), Clark (1965), Nicholson et al. (1988), and Hammack and Watzlaf (1990). Cravotta (1996, p. 90) provides a more recent compilation and comparison of pyrite oxidation rates from laboratory experiments ranging from 0.02 to 0.96 (expressed in the same units as above) including data from Rimstidt and Newcomb (1993), Moses and Herman (1991), McKibben and Barnes (1986), and others. These significant studies, including the work of Moses et al. (1987) and Cravotta (1996), evaluated differences in pyrite oxidation rates on the basis of particle size (surface area), pH of initial solution, and availability of oxygen and ferric iron.

In a practical guide to acid mine drainage prediction, Hyman et al. (1995) further summarized laboratory and field studies on the placement of potentially acidic materials below the water table and state that "The dissolved oxygen in the water is too low to create appreciable amounts of CMD (contaminated mine drainage)" p. 25. According to Cathles (1980, personal communication), the dissolved oxygen in groundwater in contact with pyritic materials would not typically be capable of producing an effluent pH less than 3.8; therefore mine drainage with a lower pH emanating from a sealed deep mine, for example, is indicative of an air leak in the system that is augmenting the dissolved oxygen in the groundwater.

Concerning the role of gases in laboratory kinetic tests, Hyman et al. (1995, p. 11) state, "Gas phases, such as oxygen and carbon dioxide, that occur in field conditions may not be represented appropriately in the laboratory test conditions." Gas handling provisions in kinetic test design and operation should account for: (1) percentages of oxygen and carbon dioxide within the test apparatus that are representative of field conditions of the mine environment (e.g., pore gas composition of a backfilled surface mine) and (2) mechanisms to circulate the gas mixture through the apparatus to ensure that chemical reactions (oxidation and dissolution) may take place and promote weathering of the rock samples. From the discussion on pyrite oxidation above, it appears that there should be more than enough oxygen available for pyrite oxidation in the normal laboratory setting if the kinetic test apparatus is open to the air and the rock samples are not entirely saturated within the apparatus. However, the amount of carbon dioxide needed to facilitate significant dissolution of carbonate minerals is more than can be achieved under normal atmospheric conditions, as described in a previous section of this chapter. Therefore, carbon dioxide generally needs to be added to or concentrated within the kinetic test apparatus to enrich the carbon dioxide concentration within the gas mixture unless interactions of minerals (e.g. pyrite) and fluids will increase the PCO_2. If the partial pressure of carbon dioxide in the gas mixture is $10^{-3.5}$ bars (i.e. atmospheric conditions) within the kinetic test apparatus, the maximum alkalinity/bicarbonate concentrations in the leachate will be less than 100 mg/L, even with pure limestones and dolomites. If there is too much carbon dioxide in the gas mixture (e.g. greater than 10^{-1} bars, PCO_2 typically found in groundwater systems and pore gas of surface mine backfills) the bicarbonate and alkalinity concentrations may be greater than 500 mg/L, for example, as shown on figure 7.4 (see also Chapter 1, this volume). To ensure a representative and realistic gas mixture in kinetic tests for mine drainage prediction, it may be necessary to have the kinetic test apparatus fitted with gas ports to enable the constant or intermittent introduction of a controlled gas mixture (for carbon dioxide enrichment) into the apparatus. For example, a gas mixture of 10% oxygen,

10% carbon dioxide and 80% nitrogen in a compressed gas cylinder would probably supply adequate and representative amounts of oxygen for pyrite oxidation and carbon dioxide for carbonate mineral dissolution.

Most of this section of the chapter on gas handling provisions in kinetic tests has emphasized the composition of gases, but the circulation of gases during the test, or air flow is also important. Pool and Balderrrama (1994) evaluated the effects of air flow rate upon humidity cell tests and found that:

> "Changes in air flow rate and effluent volume affected the amounts of sulfate and acid reporting to effluent. Increased air flow rate resulted in more moisture removal and increased acid generation. (p. 1)... In the absence of air flow, evaporation was nearly zero.(p. 9).... The important parameters which affect the acid production in the constant temperature humidity cell apparatus were the pct water removed and the amount of effluent recovered. The pct water removed was controlled by airflow through the cell and across the sample surface, and the amount of effluent recovered was dependent on the amount of leachant used and the airflow." (p. 13)

Biological Considerations in Kinetic Tests

The importance of the role of bacteria in AMD production has been known for more than forty years, and significant early work on this subject in field and laboratory settings is described in Leathen and Braley (1954), Leathen et al. (1953a,b, 1956), Temple and Delchamps (1953), Braley (1954), Silverman and Lundgren (1959), Silverman et al. (1961), Unz and Lundgren (1961), Lorenz and Tarpley (1963), and Razell and Trussell (1963). Braley (1954) discusses the studies at the Mellon Institute that were funded by the Pennsylvania Department of Health to investigate the role of bacteria in acid mine drainage formation. Hanna and Brant (1962) describe the design and performance of a humidity-cell type of laboratory "acid generator apparatus," which they developed in Ohio to study, among other factors, "the effects of bacteria on the acid production process." Lorenz and Tarpley (1963), at the USBM Coal Mining Research Center in Pittsburgh, studied pyrite oxidation in laboratory kinetic tests. They compared oxidation rates with and without the introduction of the iron-oxidizing bacterium, *Ferrobacillus ferrooxidans*, utilizing the bacterial culture medium, growth and harvesting procedures developed by Silverman and Lundgren (1959).

The dramatic effect of iron-oxidizing bacteria populations on AMD production has been described in Singer and Stumm (1970), Brierley (1982), Kleinmann et al. (1981), and elsewhere. Singer and Stumm (1970) found that the rate-determining step in AMD production is the oxidation of ferrous iron wherein the bacteria catalyze the reaction by a factor greater than 10^6. Kleinmann et al. (1981) describe three stages to the AMD production process involving four chemical reactions wherein Stage 1 occurs at a pH above approximately 4.5 with high sulfate but little or no acidity; Stage 2 occurs between pH 2.5 and 4.5 with increasing acidity and low ferric to ferrous iron ratio; and Stage 3 occurs at a pH below approximately 2.5 with high acidity, sulfate, total iron and ferric to ferrous iron ratios. The most significant differences between these stages is the increasing influence of *Thiobacillus ferrooxidans*, to the point that reaction 3 proceeds at a rate totally determined by the activity of *T. ferrooxidans*. Concerning Stage 3, Kleinmann et al. (1981) state that a "vicious cycle of pyrite oxidation and bacterial oxidation of ferrous iron results from the combined effects of reactions 3 and 4."

Concerning the metal mining and dump leaching industry, Brierley (1982, p 44), stated that, while the relatively large-scale leaching of copper was well established by the eighteenth century, the miners did not realize until about 25 years ago "that bacteria take an active part in the leaching process." Brierley also states "Today bacteria are being deliberately exploited to recover millions of pounds of copper from billions of tons of low-grade ore."

There are a number of genera and species of bacteria relevant to acidic drainage production and leaching processes. A large portion of the scientific literature on this subject is devoted to the bacterium, *Thiobacillus ferrooxidans*. According to Brierley (1982), bacteria of the *Thiobacillus* genus are essential to the leaching of metals from sulfide minerals, but other microorganisms may have important roles including *Thermothrix, Leptospirillium* and *Sulfolobus* genera. *Ferrobacillus ferrooxidans*, which has been referred to earlier in this chapter, was subsequently reclassified as a strain of *Thiobacillus ferrooxidans*. Another bacterium, *Metallogenium*, is discussed in Kleinmann and Crerar (1979). All of these bacteria vary in their acidophilic (acid loving) and thermophilic (heat loving) preferences or tolerances, therefore ranges in temperature and pH in natural or constructed/controlled environments may determine which bacteria are present or

absent. According to Brierley (1982, p. 44): "The bacteria involved in the leaching of metals from ores are among the most remarkable life forms known. The microorganisms are said to be chemolithotrophic ("rock-eating"); they obtain energy from the oxidation of inorganic substances. Many of them are also autotrophic, that is, they capture carbon for the synthesis of cellular components not from organic nutrients but from carbon dioxide in the atmosphere."

As stated in Chapter 1, these bacteria, "produce enzymes which catalyze the oxidation reaction, and use the energy released to transform inorganic carbon into cellular matter." While these bacteria require oxygen and carbon dioxide for their metabolism, it appears that relatively low percentages of these gases are sufficient for their survival because, *T. ferrooxidans* obtains carbon autotrophically from atmospheric carbon dioxide (i.e. 0.035%). Brierley (1982) and Cathles and Apps (1975, p. 619) report that "the bacterial oxidation rate of ferrous iron is essentially independent of oxygen concentration in the air until the concentration falls below 1%."

T. ferrooxidans thrives in the temperature range between 20 and 35 ° C, according to Brierley (1982), who classifies the bacterium as moderately thermophilic. Murr et al. (1977, p. 222) report that "The optimum temperature for sulfide leaching catalyzed by *T. ferrooxidans* is 35° C, and that biological oxidation appears to cease at around 55°C (see also Bryner et al., 1967). In large scale leaching column experiments with low-grade copper waste rock, Murr et al. (1977, p. 222) found that... "the population of *T. ferrooxidans* began to decline at approximately 45° C." In related leaching column studies, field measurements of actual industrial sulfide waste dumps, and mathematical models developed to simulate waste dump performance, it has been assumed that, "the bacteria become sick at about 50° Centigrade and finally die or become inactive at about 55° Centigrade" (Cathles (1979); Cathles et al. (1977); and Murr et al. (1977)). According to Cathles (1979, p. 185)... "low grade sulfide waste dumps are only very rarely (if ever) observed to have internal temperatures greater than 65°C." In addition Cathles et al. (1977) state: "The fact dumps always appear to operate at temperatures below 55°C is thus direct evidence of the importance of bacteria in at least one step of the leaching process." From some evidence collected by Murr et al. (1977) it appears that a high-temperature microbe, like *Sulfolobus*, was present to account for bacterial oxidation and catalysis of reactions at temperatures somewhat greater than 50° C.

Brierley (1982, p. 47) states that:

> "The most robust of the leaching microorganisms are the extremely thermophilic and acidophilic species of the genus *Sulfolobus*. These bacteria flourish in acidic hot springs and volcanic fissures at temperatures that can exceed 60 degrees C. Some strains of *Sulfolobus* have been observed in springs at temperatures near the boiling point of water."

Some kinetic tests for AMD prediction have incorporated special equipment or procedures in the test to control and/or monitor temperature during the tests; others simply rely upon room temperature in the laboratory or ambient temperature in the field to provide acceptable temperatures for the AMD reactions to take place. Hornberger et al. (1981) placed leaching columns in an incubator within the laboratory and maintained temperatures within the incubator at a constant 25°C. That temperature was selected because 25°C and 1 atmosphere pressure are standard conditions frequently used in studies of chemical reactions as described by Hem (1970, p. 22), Garrels and Christ (1965, Chapter 9) and others. The temperature of 25°C is also within the range between 20°C and 35°C where *Thiobacillus* bacteria flourish (see Brierley, 1982). Cathles and Breen (1983) coiled ¼ in (6.35 mm) copper tubing around their leaching columns and circulated distilled, deionized water from a constant temperature bath through the coils. Fiberglass pipe insulation was used to jacket the column to prevent heat loss and the column was fitted with three thermocouple ports to constantly measure temperature within the column. Temperatures of 35°C and 50°C were selected by Cathles and Breen (1983) because of optimum and upper limits of "non-thermophilic, iron-oxidizing" bacteria performance reported in previous studies (Murr, 1980 and Murr et al., 1977). The effluent solutions from the 50°C column experiments were more concentrated in iron than the 35°C column experiment. Room (laboratory) temperature at 73°F. equals 22.8°C, and is within the range of *Thiobacillus*.

In addition to the fact that optimum temperature for *Thiobacillus* bacterial catalysis of reactions is 35°C, there are other reasons why it may be advantageous to maintain temperatures at 35°C rather than 25°C. Concerning the effect of temperature on chemical reaction rates, Hem (1970, p. 32) states: "The generalization is

commonly made that a 10°C change in temperature changes the rate of reaction by a factor of about 2. The term "reaction" here includes biochemical processes as well as inorganic reactions.

While this increased temperature may be advantageous in optimizing pyrite oxidation, it may be disadvantageous if carbonate minerals are present in the kinetic test, as the solubility of calcite decreases with increasing temperature. Some kinetic test procedures operate at significantly higher temperatures, specifically Soxhlet reactors heat to boiling, then cool to condense water. These test procedures and others including oven drying at 105° C, probably kill bacteria populations between leaching episodes. The fact that there are relatively few sterile natural environments without bacteria has been documented by Bass-Becking et al. (1960), who define the limits of the natural environment in terms of pH and oxidation-reduction potentials (Eh).

The iron-oxidizing bacteria are typically abundant in mine environments, and they can be readily adapted to survive and flourish in a kinetic test apparatus in a laboratory setting without great difficulty. According to Brierley (1982, p. 48):

> "The dumps are not inoculated with the leaching bacteria. The organisms are ubiquitous, and when conditions in the rock pile become suitable for their growth, they proliferate. Rock samples collected near the top of a leach pile typically harbor more than a million bacteria of the species *T. ferrooxidans* per gram."

It appears that there is almost no lower limit to the pH where iron-oxidizing bacteria will survive, but there is some debate and uncertainty on the effects of a pH regime below approximately 2.0 upon *T. ferrooxidans*. Nordstrom and Potter (1977) and Kleinmann et al. (1981) report a 0.8 pH tolerance level of *T. ferrooxidans*. However, laboratory tests indicate that the bacterial oxidation of ferrous iron slows below pH 1.5 (see Silverman and Lundgren (1959), Schnaitman et al. (1969) and), Chapter 1, this volume). Alpers and Nordstrom (1991, p. 327) describe the most extreme conditions of natural acidity developed from pyrite oxidation yet reported (including published documentation of mine water with a pH less than 0), but state that the Iron Mountain, California site contains optimal conditions for all five hydrogeochemical factors required for production of acid mine waters, including iron-oxidizing bacteria (p. 332).

It also appears that there is an upper pH limit where the acidophilus, iron-oxidizing bacteria will not survive, but there is similar debate and uncertainty on the effects of the higher pH regime upon *T. ferrooxidans*. According to Wadell, Parizek, and Buss (1980), the bacteria tend to die off at pH of 5.5 as shown on Figure 7.6. Lovell (1983), Wadell et al., (1980), and others (Chapter 13, this volume) have advocated the development and maintenance of an alkaline environment in mine spoil in order to inhibit pyrite oxidation, including bacterial catalysis. However there is some doubt that the *T. ferrooxidans* actually die off above pH 5.5, according to Rose (1997), who states: "At near-neutral pH, the *T. ferrooxidans* attach directly to the pyrite surface and create a microenvironment at the attachment point where they carry on their chemistry. However, the reaction is much slower than that in solution at a more acidic pH." Additional information on *T. ferrooxidans* survival in this higher pH regime is found in Ehrlich (1962; 1990), who demonstrated tolerance up to pH 6.98 in synthetic buffered media. Kleinmann and Crerar (1979) found the bacteria in a mine drainage-contaminated stream in southwestern Pennsylvania at pH 6.4. "Such presence does not imply acid-producing activity, but it does indicate that the bacteria are available should a suitable environment appear," according to Kleinmann and Crerar (1979, p. 383).

Most of the discussion in this section of the chapter has involved the importance of the presence of iron-oxidizing bacteria upon AMD production in field and laboratory settings, within certain ranges of temperature and pH. In contrast, a brief discussion on promoting the absence of bacteria in mine environments or laboratory settings will follow. As described earlier in the water handling section of this chapter, it is almost beyond belief that the Iron Mountain pyrite samples, "displayed no significant weathering over time in any relative humidity" (Borek, 1994, p. 31) in the absence of iron-oxidizing bacteria in the laboratory; while the Iron Mountain pyrite weathering in the presence of bacteria in the mine environment (i.e. field conditions) produces the most extreme conditions of natural acidity developed from pyrite oxidation including pH less than 0.0.

The use of alkaline addition materials (e.g. limestone crusher fines and lime plant fluedust) to promote an alkaline mine environment and thereby inhibit the bacterial oxidation of pyrite, has been evaluated in laboratory kinetic tests by Rose and Daub (1994), and

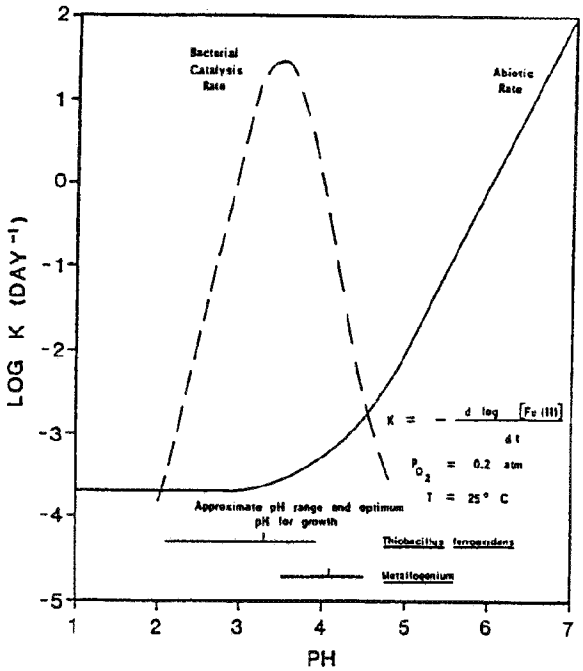

Figure 7.6 Reaction rate as a function of pH for the oxidation of ferrous iron (from Waddell et al., 1980).

in surface mine environments by Waddell et al. (1980), Dugas et al. (1993), Evans and Rose (1995), Rose et al. (1995), Perry and Brady (1995), and Williams et al. (in press).

There also have been significant efforts to use bactericides (e.g. Sodium lauryl sulfate and other anionic detergents) to inhibit, control or minimize AMD production at mine sites, including the work of Walters (1965), Dugan (1975), Walsh and Mitchell (1975), Kleinmann and Crerar (1979), Kleinmann et al. (1981) and Parisi et al. (1994). Additional information on these bactericidal controls is found in Chapter 15.

From all the above discussions on biological considerations in kinetic tests, it should be obvious that iron-oxidizing bacteria must be allowed to be active in the kinetic test apparatus if the test conditions and results are expected to be representative of pyrite oxidation potential in the mine environment. In some laboratory kinetic test procedures, the presence of iron-oxidizing bacteria is guaranteed by the use of relatively formal inoculation procedures including the work of Lorenz and Tarpley (1963), Cathles and Breen (1983), and others. In field scale kinetic tests, it is not necessary to inoculate the rock samples with iron-oxidizing bacteria because they are ubiquitous in the mine environment (Brierley, 1982).

Some kinetic test procedures have ensured the presence of iron-oxidizing bacteria in the laboratory by wetting the rock sample with mine drainage collected in the field. Hornberger et al. (1981, 1985) demonstrated that *Thiobacillus* bacteria can survive from the field to laboratory leaching columns, including rock crushing and other sample preparation procedures, by simply wetting the rock samples with pit water at the surface mine site, and keeping the samples moist through storage in plastic bags until placement in the leaching columns. Numerous studies have informally inoculated the rock samples in laboratory kinetic tests by adding AMD from a deep mine or surface mine to the kinetic test apparatus during the initial wetting of the rock sample or at some other point in the test, including the work of Smith et al. (1974), Poissant (1986), and Poissant and Caruccio (1986).

Regardless of how the iron-oxidizing bacteria have arrived in the laboratory kinetic test apparatus, their presence and relative abundance in the sample may be determined and quantified using a culture medium and a Most Probable Number method (see Standard Methods, Greenberg, et al. Eds. (1980, p. 802)). Bacteria populations determined by this MPN method in AMD studies are reported in Murr et al. (1977),Cobley and Haddock (1975), Olem and Unz (1976, 1977), Cravotta (1996), and other references. These techniques may be used to document that adequate biological considerations have been included in the kinetic test, and that the test conditions and results are representative of the mine environment.

Summary and Recommendations

The role of physical, chemical and biological factors in mine environments and in kinetic tests has been described in the preceding sections of this chapter and numerous examples are given in the chronology in Appendix A. Most of these factors must be incorporated into the design, operation and interpretation of kinetic tests for AMD prediction, or the laboratory data will have little or no relevance to the real world. Given the ranges and extreme values of pH, acidity, alkalinity, iron, aluminum, and sulfates found in mine environments as shown in Tables 7.1 and 7.2, it is reasonable to expect that kinetic tests for AMD prediction should be capable of producing leachate with acidity and sulfate concentrations of several thousand to tens of thousands mg/L, and metals concentrations of several hundred mg/L from worst- case AMD producing rock samples, and leachate with alkalinity concentrations of several hundred mg/L from best-case carbonate rock

samples. If the concentrations of acidity, alkalinity, sulfates, and metals in the leachate from a kinetic test are equivalent to the concentrations of these parameters in the mine environment, the interpretation of the test results will be more straightforward than applying a dillution factor or some other transformation of the leachate data. Also, if the leachate data will be subjected to some further graphical or mathematical analysis (e.g. converting the concentration data to mg acidity/g sample/day and plotting the cumlative acidity), it may be helpful to refer back to the original concentration data and find a range of concentrations that can be directly related to post-mining discharge concentrations in the field.

Therefore, a major objective of kinetic tests for mine drainage prediction should be to simulate the quality of effluent from the rocks to be mined with a reasonable degree of accuracy and precision. The following nine general principles of kinetic test design and performance constitute a summary and guidelines of the major factors to be considered in that simulation:

1. The size, shape and structure of the kinetic test apparatus should be as simple as is practicable, given that multiple arrays of these devices may be needed to concurrently test multiple rock samples from a proposed mine site. Yet, the apparatus may need some complexity in external form or internal structure to allow fluids and gases (i.e. oxygen and carbon dioxide) to enter, circulate through and exit the apparatus in a manner that is representative of the weathering conditions of the mine environment.

2. The dimensions of the kinetic test apparatus should be in proportion to the particle size distribution and volume of the rock sample to be tested, so that there are no adverse interactions (e.g. airlocks or other testing artifacts) between the sample and its container. For example, with a columnar shaped apparatus, the inside diameter of the column should be at least several times greater than the largest particle diameter within the volume of rock samples.

3. The goals of sampling for kinetic testing should be to obtain rock samples that are representative of the physical (i.e. particle size distribution) and chemical (i.e. mineralogic composition) characteristics of the consolidated overburden strata, or backfilled mine spoil, or waste dump to be simulated in the test. If the rock samples are obtained from air rotary drilling procedures typically used in overburden analysis testing, the particle size distribution within the kinetic test apparatus will probably not be truly representative of the particle size distribution within the mine spoil. Consideration should be given to the percentage of relatively coarse (i.e. gravel sized) particles and relatively fine grained particles in the sample. A greater percentage of fine particles increases the surface area available for reaction, which is a critical parameter in the production of acidity or alkalinity.

4. Multiple lithologic units should not be combined in the same kinetic test apparatus, in composite samples, or especially not in layers, unless the potential acidity or alkalinity of the individual lithologies is already known from similar kinetic tests, static tests or equivalent geochemical information. If more than one lithologic unit is contained in the same kinetic test apparatus, the method of placement of the sample within the apparatus becomes more problematic, and the effect of microenvironments with the apparatus should be evaluated.

5. The volume of influent water minus the volume of water consumed during the kinetic test determines the volume of effluent water or leachate. These volumes of water should be properly proportioned to the volume of rock sample being tested and should simulate or approximate the hydrologic loading conditions (i.e. amounts of rainfall, surface water or groundwater) that will be encountered in the mine environment. The ratio of the surface area of rock sample to the volume of leachate may be the most important parameter in kinetic test design, performance and data interpretation.

6. Rock samples in kinetic tests usually should not be in a completely saturated condition for the duration of the test, because pyrite oxidation rates will be greatly diminished when the samples are submerged, and the kinetic test effluent water samples may not be indicative of the concentrations of acidity, sulfate, and metals that will be produced in the actual mine environment. To simulate the weathering conditions of a surface mine or mine waste dump, the rock samples should be in a partially saturated, or intermittently saturated and unsaturated condition during the test, which approximates the effects of episodes of infiltrating rainfall and the groundwater flow system within the mine environment. In these unsaturated zones within the kinetic test apparatus, weathering of the rock samples will be enhanced by alternating wetting and drying cycles, and the effects of humidity, water flow and air flow through the voids or pore spaces.

7. The pore gas composition within the kinetic test apparatus should be similar to that within reclaimed surface mine spoil, particularly to have a partial pressure of carbon dioxide sufficient to facilitate the dissolution of carbonate minerals. To ensure a representative and realistic gas mixture in kinetic tests for mine drainage prediction, it may be necessary to have the kinetic test apparatus fitted with gas ports to enable the constant or intermittent introduction of a controlled gas mixture into the apparatus (i.e. for carbon dioxide enrichment). For example, a mixture of 10% oxygen, 10% carbon dioxide and 80% nitrogen in a compressed gas cylinder would supply adequate and representative amounts of oxygen for pyrite oxidation and carbon dioxide for carbonate mineral dissolution.

8. Iron-oxidizing bacteria must be present and relatively abundant within the kinetic test apparatus, if the test conditions and results are expected to be representative of pyrite oxidation potential in the mine environment, because abiotic pyrite oxidation rates are 6 orders of magnitude less than bacterially catalyzed pyrite oxidation rates, and because the iron-oxidizing bacteria will be ubiquitous in the mine environment, unless conditions of high pH or very high temperature adversely affect their survival. It may be necessary to inoculate the rock sample with *Thiobacillus* bacteria at the commencement of the kinetic test, and maintain temperature conditions between 20°C and 40°C during the test to provide optimum conditions for a healthy bacteria population.

9. The ideal kinetic test for the prediction of mine drainage quality will be: (a) practical to construct and operate, (b) of reasonable time and cost requirements to encourage widespread acceptance and use, (c) representative of the physical, chemical and biological conditions of the mine environment (i.e., in conformance with the preceding 8 principles), and (d) readily interpretable due to the capability of producing the range of acidity, alkalinity, sulfate, and metals concentrations found in acidic and alkaline mine drainage. From the scientific and technical standpoint of accuracy, precision, and predictability, the number of leaching cycles and the total duration of the kinetic test must be of sufficient length to simulate mineral weathering and natural hydrologic conditions of the mine environment, and to guarantee acceptable reproducibility and repeatability of test results with the same rock samples and same kinetic test conditions. From the standpoint of economics and practicality, the number of leaching cycles and duration of the kinetic test should be short enough to be compatible with time and cost constraints of typical mine permitting. It may be necessary to employ interpretative tools (e.g. mathematical models) and interfaces between long-term laboratory research studies and short-term leachate production tests to satisfy all of these goals and correctly predict mine drainage quality in some relatively complex geochemical or hydrogeologic settings.

Development of Standard Kinetic Test Procedures for the Prediction of Mine Drainage Quality

The goal of developing standard kinetic test procedures for predicting mine drainage quality has been emphasized throughout this chapter. In the four years since the Third International Conference on Acidic Drainage in Pittsburgh in 1994, several significant steps have been taken toward consensus building on acid mine drainage research and development issues among Federal government regulatory and research agencies, state regulatory agencies, mining industry representatives, and university researchers. Recently the Acid Drainage Technology Initiative (ADTI) has been formed by a group of Federal agencies under the leadership of the U.S. Office of Surface Mining (OSM), the National Mining Association, the Interstate Mining Compact Commission, and the National Mine Land Reclamation Center. One of the two major working groups of this initiative is on prediction. It is hoped that this group may be able to develop a consensus on kinetic test procedures for the prediction of mine drainage quality as one of its primary goals. Two major advantages of developing standard kinetic procedures through this consensus building effort are that almost everyone, especially for mine permitting purposes, would be using the same test procedures (which facilitates data comparison and data base building) and that scientific and legal controversies between government and industry users of prediction techniques over interpretations of the test results and accuracy of the predictions would be substantially reduced.

Much can be learned from work completed in other industries on the development in application of standard kinetic test procedures. In the residual and hazardous waste industry, the Environmental Protection Agency, the state regulatory agencies, the industry and their consultants are consistently using the Toxicity Characteristic Leaching Procedure (TCLP) and the

Synthetic Precipitation Leaching Procedure (SPLP) and are building an acceptable data base from which scientific inferences, permitting decisions, and case-to-case comparisons can be made. In the nuclear waste industry, a significant amount of research was done on leaching processes leading to the development of ANS 16.1 (American Nuclear Society, 1984) and the MCC1 leach test (Pacific Northwest Laboratory, 1980). An example of the use of the MCC1 leach test on nuclear waste is described in Ebert and Bates (1992), while Zhao (1995) provides extensive data on leach testing of flyash and fluidized bed combustor (FBC)ash cements using the MCC1 test. The work of John K. Bates and associates at Argonne National Laboratory on nuclear waste glass also provides relevant information on surface area/leachate volume ratios (Aines et al., 1986; Ebert and Bates, 1992; Feng and Bates, 1993; Feng et al., 1994), which were discussed in the water handling section of this chapter. A summary description of the MCC1 test, ANS 16.1 and numerous other leaching methods is presented in Sorini (1997).

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill, and is found as Method 1311 in the EPA manual entitled Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846. The Synthetic Precipitation Leaching Procedure (SPLP) is Method 1312 and it is designed to determine the mobility of both organic and inorganic analytes present in samples of soils, wastes, and waste waters. While both of these standard test methods are now well founded in the waste industry, it appears that neither of these methods is appropriate for the prediction of mine drainage quality, based in part, on studies by Franklin and Zahl (1988) and Boyle and Smith (1994). It would be desirable to develop a standard Mine Drainage Leaching Procedure (MDLP) for use by the mining industry and its consultants, state regulatory agencies, and Federal regulatory and research agencies, with the support and approval of the EPA, OSM, IMCC, and the NMA.

It would be unrealistic to expect that the development of a MDLP test would instantly be accepted and used by all mine drainage researchers and research users in the United States and elsewhere, and that long-standing kinetic test research programs at universities and Federal research centers would all abandon their efforts in favor of the new MDLP. That is not our expectation. After the development of a MDLP test, there would probably always be some specific research purpose that would require a kinetic test apparatus of greater sophistication, or a greater test duration than the MDLP. Those specific research purposes may be largely unaffected by the development of a MDLP test or suite of test methods. The real beauty of a standard MDLP for the prediction of mine drainage quality would be that it would be required or recommended as the preferred method where needed, as part of mining permit applications by the state and Federal regulatory agencies. Finally, it would facilitate a meaningful comparison of kinetic test results from rock type to rock type, mine site to mine site, state to state, and nation to nation in order to make sound permitting decisions, prevent mine drainage pollution problems which financially cripple mining companies, and build effective data bases for future use by all stakeholders.

Relationships Among Kinetic Tests, Static Tests, and Other Methods of Predicting Mine Drainage Quality

Kinetic tests alone are not the answer to the prediction of mine drainage quality. They should be used in combination with static tests and other predictive techniques including evaluation of background water quality, mine drainage quality produced at nearby mine sites or mines in similar lithologic settings, and detailed stratigraphic analyses. Kinetic tests will usually be more expensive and more time consuming than static tests; therefore the kinetic tests should be used selectively when needed because the static tests are inconclusive or require augmentation.

It may be appropriate to use a phased approach to the prediction of mine drainage quality for a proposed mine site, wherein all rock samples to be evaluated are initially subjected to relatively simple static tests, such as neutralization potential (NP) and total sulfur content; whereupon these indicators or surrogate measures of potential alkalinity and potential acidity of all strata to be affected are used to determine which of these rock samples should be subjected to kinetic tests for a more realistic simulation of mine drainage quality. The B.C. Research Initial Test and B.C. Research Confirmation Test described in Bruynesten and Hackl (1984) are an example of this type of approach, where the initial static test is followed by the kinetic test if the sample is initially found to be a potential acid producer. Another example is the Knoxville, Tennessee OSMRE Field Office guidelines on kinetic testing described in Maddox (1988), wherein experience proved that the net acid base account by itself on some samples, was not a reliable predictor of acid mine drainage generation, and

further kinetic testing of these samples was recommended.

A conceptual method of implementing a phased static and kinetic testing protocol for mine drainage quality prediction would be to construct a 3 x 3 matrix (9 cells) where on one axis three classes of percent sulfur values represent low, medium and high potential acidity, and on the other axis, three classes of neutralization potential values represent low, medium and high potential alkalinity. Based upon these static test results, each rock sample from an overburden analysis would be classified in one of these nine cells. By operational rules it could be determined which of these nine classes demonstrate that the static test results are sufficient for mine drainage quality prediction purposes, which of the nine classes demonstrate that kinetic tests are needed for a further simulation of mine drainage quality, and which of these nine classes would require some other type of predictive analysis.

Regardless of whether kinetic tests are used alone or in combination with other methods of predicting mine drainage quality, hopefully this chapter has presented a foundation and sufficient reasons why practical, efficient, reliable and interpretable standard kinetic test methods should be developed for use by the mining industry and regulatory agencies in the prediction of mine drainage quality.

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APPENDIX A

Chronology of the Development of Kinetic Tests for Mine Drainage: 1949 - 1994

Early History

One of the earliest workers in the field of coal mine drainage was S. A. Braley (1949, 1960) from the Mellon Institute of Industrial Research in Pittsburgh, Pennsylvania. Braley (1949) described experiments in which glass columns were filled with crushed coal samples, distilled water was added and aeration of the sample and influence of bacteria on AMD production were evaluated. Braley (1960) developed a test to estimate the oxidation of pyrite wherein 100 g of weathered crushed sample were placed in a 400 ml. beaker and submerged with 250 ml. of distilled water for 24 hours; then drained, filtered, diluted and analyzed for pH, acidity, calcium and sulfate. The residue was then returned to the beaker, flooded with 250 ml. of distilled water, and covered with a watch glass for repeated iterations of the test.

As coal surface mining in Appalachia flourished from World War II into the 1950's and 1960's, state and federal agencies and universities in the Appalachian states became increasingly more involved in acid mine drainage research when AMD impacts on surface waters and groundwaters increased in these areas. The Pennsylvania Sanitary Water Board (1952, 1958), Temple and Koehler (1954) in West Virginia, and Moulton (1957) and Brant and Moulton (1960) in Ohio, produced reports and manuals on the control, treatment, and prevention of AMD from bituminous coal mines in these states.

The U. S. Bureau of Mines (e.g. Lorenz and Tarpley, 1963), the U. S. Geological Survey (Biesecker and George, 1966), and the Appalachian Regional Commission (1969, a federal and state agency consortium) were working on the documentation of the magnitude of the AMD problem in Appalachia at that time, and were conducting research on the production, prevention, and abatement of AMD. Some of the publications referenced above, and related studies by some of the researchers, such as Hanna and Brant (1962), Lorenz and Tarpley (1963), and Emrich (1966) contain significant information on kinetic test developments and applications.

Hanna and Brant (1962, p. 483) describe leaching studies, in which "several basic laboratory apparatuses were designed and tested for the purpose of acid gen-

eration in order to simulate acid production in nature, but under controlled laboratory conditions." They describe the acid generator apparatus that was developed and used in their research, (shown on Figure 7.7), as follows:

> "The generator consists of a sample cell, a diffusion unit to supply saturated water vapor, a separatory funnel used for flushing, and a receiver. It is anticipated that this basic cell with modifications will make it possible to continue studies on various phases of the work, such as relationships between acid produced and particle size or reactive area exposed; the effects of bacteria on the acid production process; the effects of applications of various inhibitors to the sample; and many other factors which must be investigated in order to more thoroughly understand the acid formation phenomena."(p. 484)

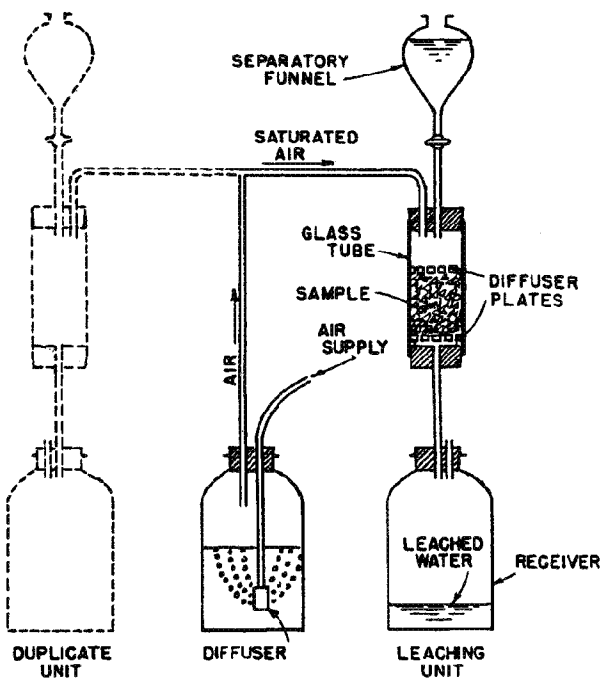

Figure 7.7 Acid generator apparatus (humidity cell) (from Hanna & Brant, 1962).

Hanna and Brant (1962) conducted comparative leaching studies on various particle sizes of coal, shales and sandstones from high walls and spoil piles. Because the samples were continuously exposed to water vapor between daily flushing episodes that removed accumulated weathering products, this type of kinetic test apparatus became generically called a humidity cell.

In studies at the U. S. Bureau of Mines in Pittsburgh, Lorenz and Tarpley (1963) used a laboratory apparatus called the Warburg constant-volume respirometer to evaluate pyrite oxidation. This apparatus, shown on Figure 7.8, was attached to a shaker arranged so that the sample in the reaction flask was immersed in a constant-temperature water bath, and that the liquid in the reaction flask was saturated with air. Lorenz and Tarpley (1963) evaluated the effect of iron oxidizing bacteria, the presence of calcite, and ferrous/ferric sulfate solutions on the pyrite oxidation in these laboratory studies. They also conducted X-ray diffraction, emission spectrography, and microscopic analyses of the pyrite samples. Hanna and Brant (1962) also used the Warburg Respirometer method on selected samples to measure the oxidation of pyritic materials, and to provide comparison to their leaching studies described above.

Emrich (1966) presents a survey of scientific literature and associated test methods for estimating the oxidation or acid potential of acid-forming material in coal seams and associated rocks (p. V-7). That technical bulletin is contained in the publication entitled "Mine Drainage Manual" by the Pennsylvania Department of Environmental Resources (1973), which is a precursor to this book. In fact, Emrich (1966) states, "The Pennsylvania Sanitary Water Board now requires that the quality and quantity of drainage from a proposed operation be estimated" (p. V-6). Emrich (1966) recognized that the beaker test described above from Braley (1960) has serious limitations for evaluating acid mine drainage potential including that: "During the test, the sample is continually submerged in distilled water and there is, at best, only an extremely limited opportunity for future oxidation of the acid-forming material." (p. V-8). Emrich (1966) also gave credit to the glass leaching column method of Braley (1949) in that: "This method very closely simulates conditions that occur in nature when coal is mined except for the periodic wetting, drying and oxidizing of the sample." (p. V-8). Emrich (1966) also describes a "European method" of Glover and Kenyon (1962) of evaluating the chemical character of drainage from coal stockpiles, using drain-tile leaching columns (12 in (0.305 m) diameter x 3 ft' (0.914 m) length) shown on Figure 7.9, constructed outdoors to utilize actual precipitation. Additional information on this kinetic test and European mine drainage control procedures is reported in Lyon and Maneval (1966). Finally, a kinetic test method is presented that was developed by

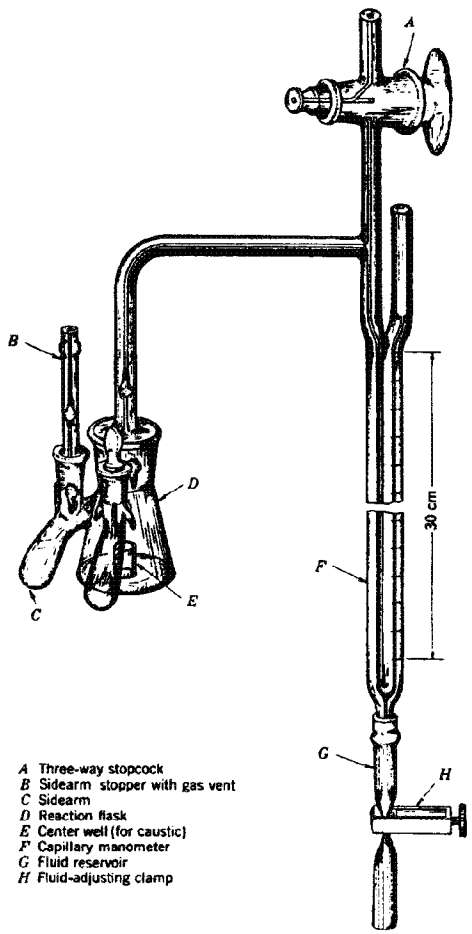

Figure 7.8 Warburg Respirometer (from Lorenz & Tarplev, 1963).

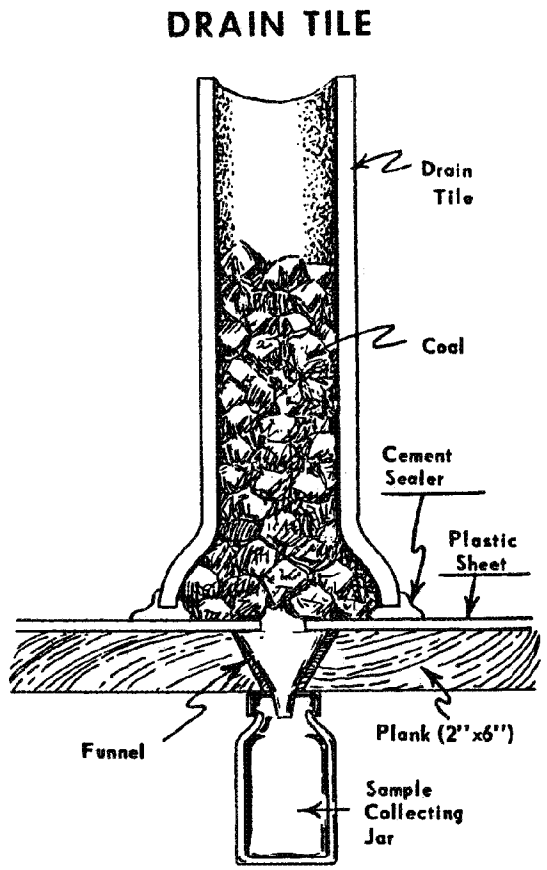

Figure 7.9 Field (drain-tile) leaching column (from Emrich, 1966).

Emrich (1966) and others at the Pennsylvania Department of Health, in which a Soxhlet Extractor (Figure 7.10), is used in a laboratory setting to accelerate the weathering process through repeated iterations or "passes" where the rock samples are aerated, heated, humidified, and flushed with distilled water.

The Pennsylvania State University has made significant contributions to the field of coal mine drainage research for many years. Some of the early work is summarized in Dutcher et al. (1966, 1967) and Parizek and Tarr (1972); while more recent summaries are found in Lovell (1983) and Hornberger et al. (1990). A long line of research reports involving kinetic test developments, refinements and applications in coal mine drainage research from the Department of Geosciences at Penn State commenced with the publications by Caruccio and Parizek (1967, 1968) and Caruccio (1967).

Caruccio and Parizek (1967, 1968) developed a humidity cell apparatus, similar in principle to that of Hanna and Brant (1962). The "simulated weathering" test method of Caruccio and Parizek (1967) emphasizes the continuous exposure of the rock sample to humid air piped into the sample container, and the regular flushing of accumulated weathering products with distilled water at intervals of 7 days. The paper by Caruccio and Parizek (1968) appeared in the Second Symposium on Coal Mine Drainage Research in Pittsburgh. Numerous other papers on kinetic test developments, including Singer and Stumm (1968), appeared in the symposium series, which originated in Pittsburgh under sponsorship by Bituminous Coal Research and the Mellon Institute.

Later, at the University of South Carolina, Dr. Frank T. Caruccio continued to conduct simulated weathering tests with the humidity cell apparatus(shown on Figure 7.2) on coal and overburden samples from the Appalachian Region, as reported in

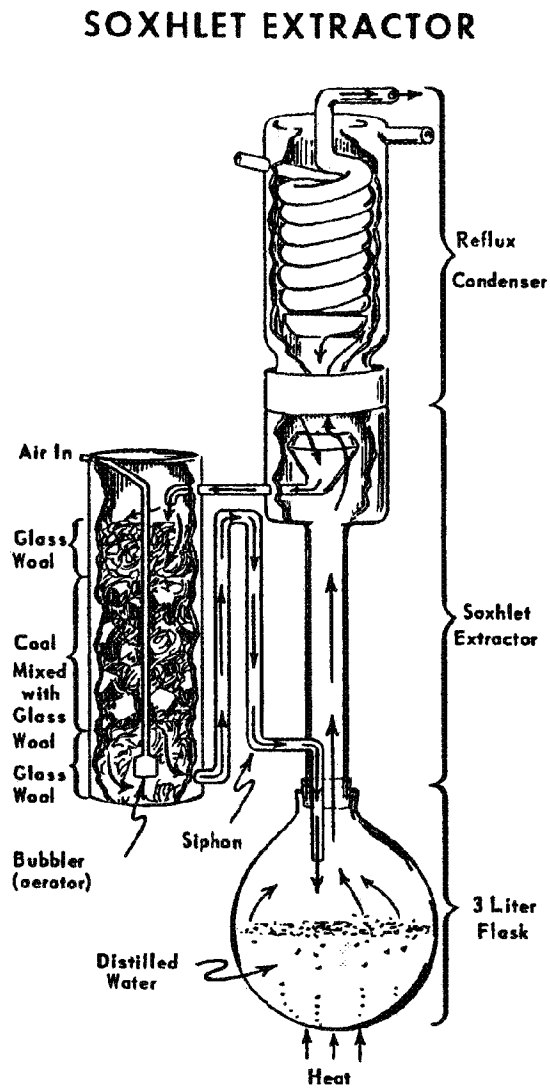

Figure 7.10 Soxhlet extractor (from Emrich, 1966).

Caruccio and Ferm (1974), Caruccio and Geidel (1978, 1980, 1981a, 1981b), and Caruccio et al. (1976, 1977, 1981). Dr. Frank Caruccio, Dr. Gwen Geidel and associates have been leaders in kinetic test developments and applications, some of which will be referred to later in this section (Caruccio and Geidel, 1986a; Bradham and Caruccio, 1990).

At West Virginia University, Dr. Richard M. Smith and associates, principally soil scientists, were conducting AMD research funded by the U. S. Environmental Protection Agency, including the development and use of static and kinetic tests for predicting mine drainage quality, as described in Grube et al. (1971), Smith et al. (1974), Smith et al. (1976), and Sobek et al. (1978). Laboratory weathering studies are described by Smith et al. (1974) in a section entitled, "Simulated Chemical Weathering With Intense Aeration." In this study, humidity cell type containers, 4 in (10.16 cm) x 12 in (30.48 cm) x 6 in (15.24 cm) plastic boxes, were utilized, and rock chip samples placed in the boxes were "inoculated with acid mine water from a deep mine to provide the essential microorganisms for reduced sulfur and iron oxidation" (p. 200). Moist air was passed through the plastic boxes for 3 1/2 days, followed by dry air for 3 days, and 1/2 day to leach the boxes and analyze the leachate; hence completing a 7-day cycle.

Regulatory Induced Developments

The Federal Surface Mining Conservation and Reclamation Act was enacted in 1977 and required that permit applicants determine the Probable Hydrologic Consequences of proposed mining activities, including the chemical analyses of the coal and overburden strata for AMD potential. Pennsylvania obtained primacy under SMCRA in 1982 and the Pennsylvania mining regulations, 25 PA Code Chapters 86 through 90, were promulgated to meet requirements in the federal and state laws. The federal and state regulations requiring the chemical testing of coal, overburden, and underclay samples as part of the surface mining permit application created a major demand for the development, use, and interpretation of kinetic and static tests to predict mine drainage quality by the regulatory agencies, mining industry consultants, and commercial laboratories. This demand forced a search of available laboratory methods used in AMD research and other sciences that might be used to obtain accurate and precise results, and also initiated the adaptation of some test methods from a university research study environment to the routine sample production environment of commercial laboratories.

The ASTM water shake extraction procedure (ASTM, D3987, 1978, 1983) initially appeared to be attractive to some regulatory agency personnel and some commercial laboratories because the test procedure was published and disseminated by the ASTM, the laboratory apparatus was in use in commercial labs, and the procedure and analytical results on residual waste and hazardous waste samples had received some degree of acceptance by regulatory agencies and the waste industry consultants. However, the procedure flooded the sample with a fluid to sample ratio of 4:1, and the 48-hour shaking cycle in sealed containers did little to promote oxidation of the sample. Conse-

quently, the diluted leachate usually had relatively low concentrations of acidity, sulfate, iron, manganese, and aluminum, even for rock samples with significant AMD potential. Most researchers ultimately concluded that the ASTM water shake extraction procedure was not principally designed nor intended for use in the analysis of overburden, coal, or coal refuse for AMD potential; and the procedure soon faded from use by most mining regulatory agencies, mining consultants, and commercial laboratories conducting mine drainage analyses.

Some commercial laboratories, such as Sturm Environmental Services in West Virginia, and West Penn Analytical Labs in Brookville, Pennsylvania, developed their own procedures or modified existing procedures for kinetic testing of overburden samples. The Sturm Environmental Services procedure is described in Sturey et al. (1982).

In an attempt to provide guidance to regulatory agencies, the mining industry, their consultants, and commercial laboratories, the EPA published "Field and Laboratory Methods for the Analysis of Overburden and Minesoils", by Sobek et al. (1978), which was rapidly and widely disseminated throughout the research user community. This manual had a primary focus on static test procedures, principally acid-base accounting, but also featured kinetic test procedures including simulated weathering tests.

In 1979, the PA DER distributed informal guidance to the mining industry on available overburden analysis methods, (static and kinetic), and was accepting analyses performed by acid-base accounting (Sobek et al. 1978), humidity cell methods (Caruccio et al. 1976, 1977) and the ASTM water shake extraction procedure (ASTM, D3987, 1978, 1983). As the data base of completed overburden analysis studies in DER permit files began to grow, results of various static and kinetic test methods on surface mine sites in the same vicinity and lithologic setting could be compared. Problems with test methods and data interpretation became evident. For example, in Big Sandy Creek watershed in Fayette County, Pennsylvania, Dr. Frank Caruccio and his associates conducted humidity cell tests as part of overburden analysis studies on 13 proposed surface mine sites, under contract to DER and in cooperation with mining industry permit applicants. On several of these sites where humidity cell tests found significant AMD potential, surface mining permit applications were denied. On three of these sites, the original permit applicant or a new applicant filed new permit applications including acid-base accounting data, which under literal interpretation, indicated a "net excess of neutralizers." In one case, where the new permit was issued based upon the acid-base accounting data, serious AMD discharges developed, and three miles of the Stony Fork tributary of the Big Sandy Creek watershed were degraded from the AMD pollution. On one of the other sites where the new permit application was denied (i.e. Boyle Land and Fuel Company), extensive litigation resulted over the accuracy of the various static and kinetic test methods used in the overburden analysis studies. Some of the geologic and mine drainage quality data for this watershed are explained by Brady et al. (1988).

The scientific and legal controversies surrounding the various static and kinetic overburden analysis methods in use at that time prompted state and federal regulatory and research agencies and other researchers to conduct comparisons of test results and to attempt to determine whether any of the available overburden analysis methods produced accurate and precise premining predictions of post-mining water quality. In 1982, U.S. Bureau of Mines, under the direction of Dr. Robert L. P. Kleinmann at the Pittsburgh Research Center, commenced a large research project to evaluate the effectiveness of various overburden analysis methods at a range of surface mine sites throughout the bituminous coal fields of the eastern United States. The USBM funded the consulting firm, Engineers International, as the contractor of the project and its subcontractor Sturm Environmental Services conducted the laboratory analyses. A team of researchers from Engineers International, including A. A. Sobek, evaluated overburden samples from mine sites in Pennsylvania, West Virginia, Maryland, Kentucky, and Illinois, using static and kinetic test methods. USBM researchers conducted additional data analyses following completion of the contract. Results of the research were ultimately published in USBM Information Circular 9183 in 1988 in papers by Erickson and Hedin (1988) and Hedin and Erickson (1988). These works and additional studies on the comparison of various kinetic and static overburden analysis methods, will be discussed further at a later point in this chronology. Meanwhile, additional kinetic test developments were occurring throughout the United States and Canada.

The Middle Years - Penn State University

From the 1970s through the 1980s, researchers at the Pennsylvania State University were continuing to use kinetic test methods in a series of research projects

oriented toward evaluating the AMD potential of stratigraphic units in the bituminous coal fields of western Pennsylvania. These studies are related to the overburden characterization and kinetic test work commenced by Caruccio and Parizek (1967), and include reports by Hornberger, Parizek and Williams (1981), Waters (1981), Williams, Rose, Parizek and Waters (1982), Rose, Williams and Parizek (1983), Cathles (1982), Cathles and Breen (1983), Williams, Rose, Waters, and Morrison (1985), Hornberger (1985), and Morrison (1988).

Hornberger, Parizek and Williams (1981) conducted leaching tests on coal and overburden analyses in 1977, which are described briefly in Hornberger et al. (1981) and in greater detail in Hornberger (1985). They constructed simple leaching columns from 1/2 gal (1.89 l) plastic containers, as shown in Figure 7.11, which combined some features of humidity cells and leaching columns. The lower half of the leaching column was kept saturated, which provided a constant source of water and humidity within the container to facilitate the chemical reactions and promoted survival of the bacteria. Weekly leaching episodes produced two types of effluent from the columns: (a) "1-week" contact leachate drained from the bottom of the column, and (b) "1-hour" contact leachate which flushed accumulated weathering products from the upper half of the column.

Williams et al. (1982) used the same leaching columns, and essentially the same leaching procedure as Hornberger et al. (1981) but filled the lower portion of the column with glass beads, in order to place most of the rock sample in humid, but unsaturated conditions. Morrison (1988) and Williams et al. (1985) also used the same laboratory leaching vessels shown in Figure 7.11, but "slightly modified" the methodology of these kinetic tests.

Dr. Larry Cathles came to Pennsylvania State University in 1978, bringing with him a wealth of leaching experiences from the metal mining industry, especially Kennecott Copper Corporation, including studies by Cathles and Apps (1975), Cathles et al. (1977), Murr et al. (1977), Cathles (1979), Cathles and Murr (1980) and Cathles and Schlitt (1980). These studies involve a variety of leaching experiments including small-scale laboratory leaching columns, large-scale (i.e., 40 ft (12.19 m) high x 10 ft (3.05 m) diameter) column leaching experiments and the development of mathematical models to simulate the leaching process. At

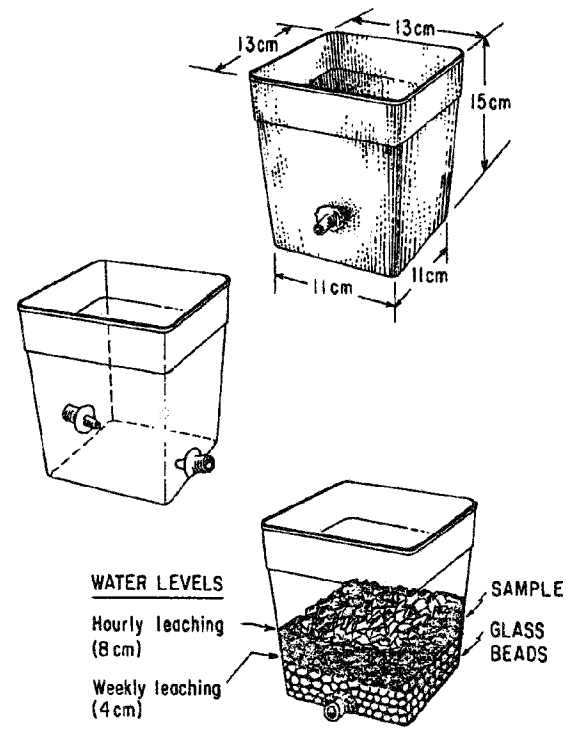

Figure 7.11 Simple leaching column (from Williams et al., 1982).

Penn State, Cathles and Breen (1983) studied the removal of pyrite from coal by heap leaching processes and utilized a constant temperature leaching column, shown in Figure 7.12, to conduct laboratory leaching experiments.

The Middle Years - West Virginia University and Related Work

While much of the effort to predict mine drainage quality in West Virginia during 1970s and 1980s was focused on the acid-base accounting method (i.e. static test), a significant interest in kinetic test developments was shown by the work of Renton and Stiller at West Virginia University and others associated with the West Virginia Department of Natural Resources, the West Virginia Surface Mine Drainage Task Force, and the West Virginia Acid Mine Drainage Technical Advisory Committee (AMDTAC). Accelerated weathering methods employing Soxhlet reactors in a laboratory setting were utilized by Renton, Hidalgo and Streib (1973), and Renton et al. (1984, 1985). Field-scale leaching column procedures were also developed as described by Stiller (1983) and Renton et al. (1984, 1985). In these field leaching tests, 35-gal (132.5 l) plastic barrels, fitted with plastic distribution plates,

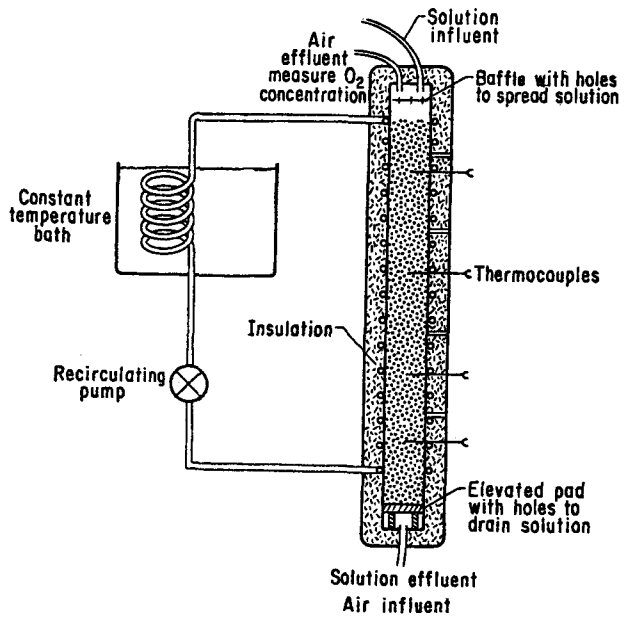

Figure 7.12 Constant temperature leaching column (from Cathles & Breen, 1983).

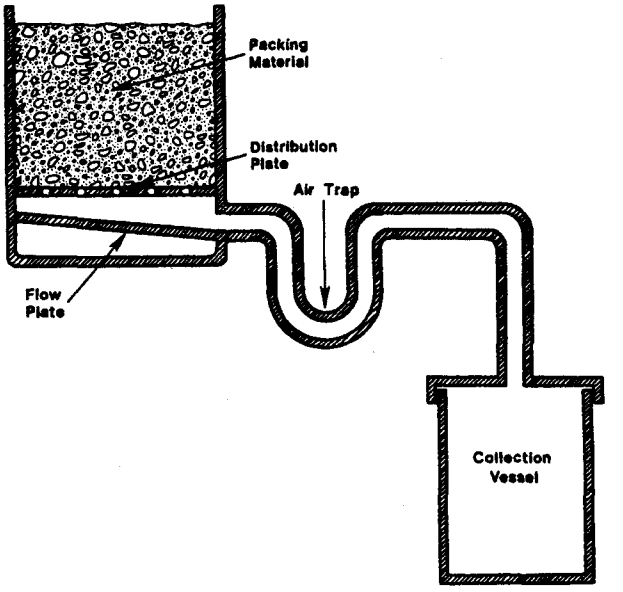

Figure 7.13 Field leaching barrel fitted with distribution and flow plates, and leachate collection vessel. (from Renton et al., 1984).

flow plates and leachate collection vessels, as shown in Figure 7.13 from Renton et al. (1984), were entirely filled with 300 lbs (136.1 kg) of coal preparation plant wastes, and leached by actual precipitation events to simulate normal weathering conditions. The primary objective of the study described by Stiller (1983) was to test the effectiveness of various ameliorants (i.e. agricultural lime, sodium lauryl sulfate, and apatite rock), in abating or preventing AMD production.

Dr. Frank T. Caruccio and Dr. Gwendelyn Geidel of the University of South Carolina and Dr. Robert L. P. Kleinmann from the U.S. Bureau of Mines in Pittsburgh were official members of the West Virginia Acid Mine Drainage Technical Advisory Committee (AMDTAC), a consortium of West Virginia DNR staff, West Virginia coal industry technical representatives, and AMD researchers from universities and government agencies, including Dr. Jack Renton and Dr. Al Stiller from West Virginia University. AMDTAC provided an excellent format and opportunity for the DNR, mining industry and researchers to interact and cooperate in projects on AMD prediction and abatement, including the development and practical application of kinetic tests at surface mine sites. Examples of these cooperative research projects on West Virginia surface mines are reported in Caruccio et al. (1984), Caruccio and Geidel (1983, DNR grant R-83-063), Renton et al. (1988), and Caruccio and Geidel (1986b, 1989). Kinetic test methods employed in these AMDTAC studies included humidity cells, Soxhlet reactors, and field-scale leaching columns or barrels.

During the same time period, related work on the use of Soxhlet reactors in the weathering of overburden and coal refuse samples was being conducted by researchers at Argonne National Labs and elsewhere, including Sobek et al. (1982) and Sullivan and Sobek (1982). Sobek et al. (1982) describe modifications to the Soxhlet reactor developed by them and Singleton and Lavkulich (1978), which were designed to improve simulated weathering studies and duplicate field conditions. Davies (1979, 1980) also discusses improving the efficiency and optimizing the performance of Soxhlet reactors. Sobek et al. (1982) credit Pedro (1961) as the first researcher to use the Soxhlet reactor in rock weathering studies, with further work reported in Henin and Pedro (1965). The study by Sullivan and Sobek (1982) contains a comparison of the leachate characteristics of Soxhlet reactors and humidity cells. Additional kinetic test research utilizing Soxhlet reactors to test pyritic coal waste is found in Sullivan et al. (1986).

Kinetic Test Developments in Central and Western U. S. and Canada

In other areas of the United States, outside of the Appalachian Coal Mining Region, kinetic test methods were being developed and evaluated including the studies by Infanger and Hood (1980), Hood and Oertel (1984) and Hood (1984) in Illinois, and Dolhopf

(1984) and Harvey and Dolhopf (1986) in Montana. In the Illinois studies, leaching columns were used. Infanger and Hood (1980) constructed leaching columns from 2 in (5.08 cm) PVC pipe in 7-ft (2.13 m) lengths, and filled the columns with three, 2-ft (0.61 m) thick layers of different overburden lithologies, which were subjected to fifteen leaching cycles of 1-, 2- or 3-week duration, between the introduction of one liter of influent water and collection of the effluent sample. Hood and Oertel (1984) and Hood (1984) constructed leaching columns using glass tubes 122 cm long by 3.5 cm inside diameter, shown in Figure 7.14, wherein distilled water was introduced into the columns from the bottom upward in order to avoid air locks, and a 1-week total cycle time was selected, using a 2-day rock-water contact time. Hood (1984) describes one set of leaching experiments in which "air was not permitted to enter the column" in order to simulate conditions below the water table; and a second set of experiments where the columns were open at the top to simulate conditions above the groundwater table.

Harvey and Dolhopf (1986) developed a "computerized automated rapid weathering apparatus" (CARWA), shown in Figure 7.15, which consists of three humidity-cell type "weathering chambers or compartments" with extensive mechanical and electrical supporting equipment. In describing the operation of the CARWA, Harvey and Dolhopf (1986, p. 14) state:

> "A bacteria inoculated... 200 gram minesoil sample (<2mm fraction) was placed into each of three acrylic weathering compartments. An automated weathering cycle began by spraying 200 ml of distilled/deionized water into each compartment. The minesoil solution was mechanically agitated for one hour, and then the water was extracted, under a vacuum suction, into a holding column. The minesoil was aerated for 30 minutes by an overhead fan to encourage oxygenation and partial drying. The extracted water was discharged into a beaker positioned on an automatic turntable, and the next cycle began... The computer control automatically conducted six weathering cycles of approximately 2.5 hours each on the samples. The extracts were monitored for volume, pH and titratable acidity."

In Canada, particularly British Columbia, research on static and kinetic test developments to evaluate AMD potential was ongoing during the 1970s and

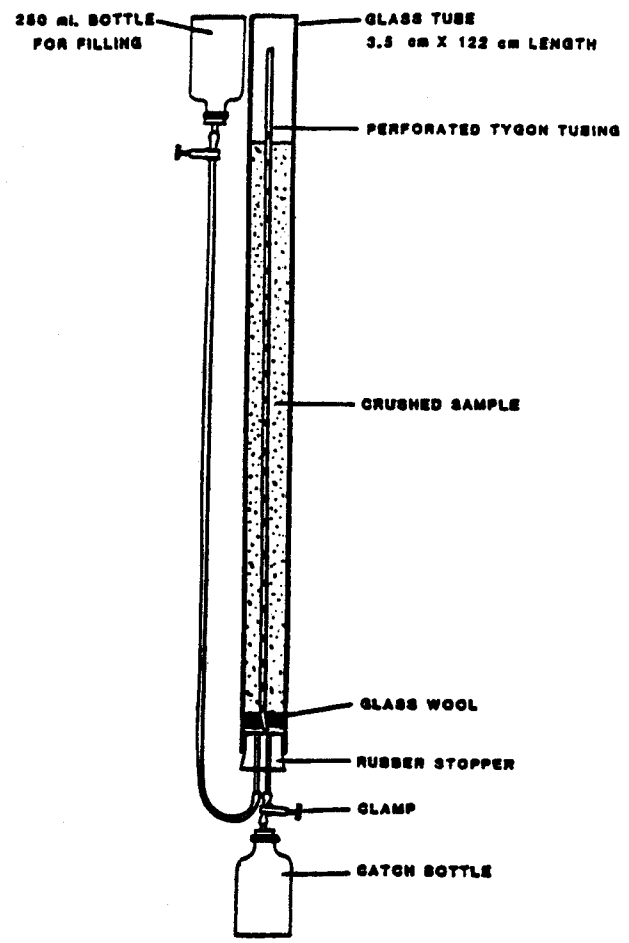

Figure 7.14 Leaching column with influent water entry at bottom.

1980s, including Bruynesten and Duncan (1979), Bruynesten and Hackl (1984), Ferguson (1985) and Ferguson and Mehling (1986), which paralleled similar efforts in the United States described previously in this section. The British Columbia research is primarily oriented toward metal mines and associated mine tailings. A static test, named the B. C. Research Initial Test and described in Bruynesten and Hackl (1984), is similar in procedure and interpretation to the acid-base accounting procedure described in Smith et al. (1974) and Sobek et al. (1978). If the B. C. Research Initial Test indicates the sample to be a potential acid producer, the static test is typically followed by a kinetic test named the B. C. Research Confirmation Test as described in Bruynesten and Hackl (1984), wherein the rock sample is placed in a 250-ml Erlenmeyer Flask with 70 ml of nutrient media and Thiobacillus bacteria culture. The flask is maintained in a carbon dioxide enriched atmosphere at a temperature of 35°C and placed on a gyratory shaker to monitor pH changes

(see also Ferguson 1985, Ferguson and Mehling 1986, and Ferguson and Erickson 1986). Additional Canadian kinetic test developments and field applications, including the use of shake flasks and lysimeters, are discussed in Duncan (1975), Ritcey and Silver (1981), Davidige (1984), Halbert et al. (1983), Wilkes (1985) and Ferguson and Erickson (1988).

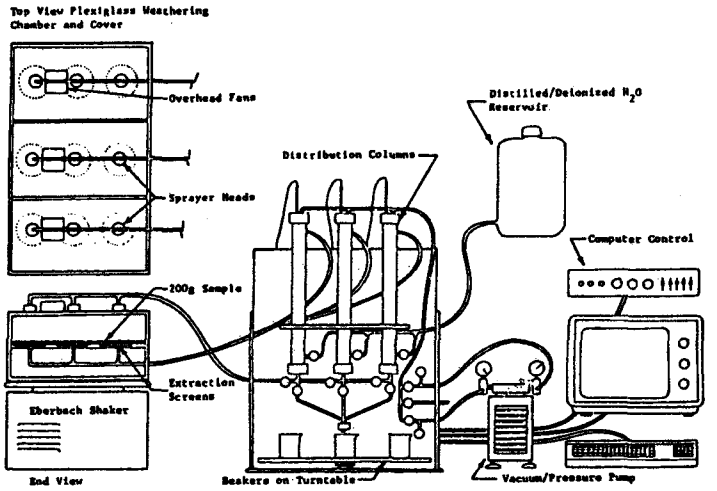

Figure 7.15 Diagram of the computerized automated rapid weathering apparatus (CARWA) prototype (from Harvey & Dolhopf, 1986).

Comparison of Test Methods 1985 to 1994

This chronology demonstrates that by the mid-1980's a wide variety of kinetic and static tests to predict AMD had been developed and used throughout the United States and Canada. Attention then focused on studies to evaluate and compare the various test methods to determine which provided the best prediction of AMD potential, and whether any method produced accurate and precise pre-mining predictions of post-mining water quality. Some of the literature cited earlier, including Hanna and Brant (1962) and Sullivan and Sobek (1982), contain comparisons of two kinetic test methods. The scientific and legal controversy surrounding various static and kinetic overburden analysis methods of concern to government research and regulatory agencies, and the genuine scientific curiosity to advance the process of AMD prediction led to a number of rigorous studies to either compare a wide variety of test methods or to evaluate overburden analysis test results over a wide geographic area or differing lithological units. Caruccio and Geidel (1986 a) conducted an excellent study to compare the results of humidity cells (with 200 g. of <4 mm. sample), Soxhlet reactors (with <125 micron particle size), leaching columns (9 cm. diameter, 30 cm. height, with sample of unspecified particle size), the B. C. Research Initial Test, the B. C. Research Confirmation Test, and acid-base accounting, in order "to determine which one most closely approximates the observed field conditions" (p. 147). Plastic tubs (approximately 0.5 m x 0.5 m x 0.3 m deep) and plastic barrels were installed in the field in order to weather samples with actual precipitation under natural climatic conditions for two years, for control purposes to compare to the laboratory results (similar to the field methods described by Renton et al. 1984, 1985). The advantages and disadvantages of all of these overburden analytical methods, plus the beaker leachate test (as described by Sobek et al. 1978) were listed by Caruccio and Geidel (1986 a, Table I, p. 149), who concluded that "All things considered, the column tests more clearly approximate the observed field results than the other analytical tests" (p. 153). They also concluded that the effluent acidity was markedly higher for finer particle size.

Erickson and Hedin (1988) evaluated overburden analysis data from 32 surface mine sites in Pennsylvania, West Virginia, Maryland, Illinois, and Kentucky where overburden samples and post-mining water quality samples were collected by Engineers International under USBM Contract No. J0328037. Acid-base accounting analyses and simulated weathering tests using humidity cells (with 300 g of <2 mm particles, leached weekly with 300 ml of water) were correlated with the actual mine drainage analyses from these mine sites. Concerning the kinetic test data, the only significant correlation found was between the sulfates in the simulated weathering test and sulfates in the actual mine drainage. However, the correlation coefficient of $r = 0.4059$ when squared, yields a coefficient of determination, $r^2 = 0.1648$, which indicates that sulfate in the test leachate explains only 16.5% of the variation in the sulfate data for the mine drainage. Erickson and Hedin (1988) concluded that :

> "The results of this study confirmed that the overburden analysis methods tested do not adequately predict post-mining drainage quality when used alone. This result is not surprising, as overburden analytical data is only one component of the pre-mining site assessment. Mine operators and regulatory authorities utilize other data and past experience in judging the environmental suitability of a proposed mine... The weathering procedure used in this study failed to yield an accurate prediction of water quality and failed to delineate boundaries for drainage of differing acid/alkaline character. The correla-

tion between sulfate produced during simulated weathering and sulfate concentrations observed in the field suggested that pyrite oxidation can be mimicked in the laboratory. Alkalinity-generating processes were not mimicked by this method. Limited data from laboratory weathering showed at least a potential for better simulation of neutralization processes when the overburden strata were composited into a single sample prior to weathering."

The authors also point out that no leachate sample from the kinetic tests exceeded 100 mg/L net alkalinity, while field samples of post-mining drainage had net alkalinity in the range of 100 to 620 mg/L. The low PCO_2 of the laboratory tests is suggested as a cause by Erickson and Hedin (1988). In a companion study, Hedin and Erickson (1988) evaluated the relationships between the initial geochemistry and leachate chemistry of overburden samples from the same 32 mine sites, using the humidity cell apparatus in simulated weathering tests to provide the leachate chemistry. Concerning, "the problem of predicting drainage chemistry on a mine level", Hedin and Erickson (1988, p. 28) state:

"Are the errors calculated and discussed in this paper responsible for predictive failures? We think not. The error of our relationships is about 25%, which is not great enough to account for the large differences between expected and actual drainage chemistry observed in our study... More likely, the failure of the methods lies in conservative assumptions and design features that are inappropriate... In our weathering tests, we produced conditions that maximized pyritic oxidation and minimized alkalinity. Both of these problems can be justified when one wishes to make conservative judgments. However, if accurate predictions are the goal, the assumptions and methodologies must be thoroughly reevaluated."

Comparisons of static and kinetic AMD prediction techniques in use in Canada and the United States were also presented in tabular and graphic format and discussed in Ferguson (1985), Ferguson and Mehling (1986), Ferguson and Erickson (1986, 1987, 1988), and Lapakko (1993). Additional comparative overburden analyses reports are found in Bradham and Caruccio (1990) and Caruccio et al. (1993).

A Plethora of Variations on a Theme

In addition to the papers by Erickson and Hedin (1988) and Hedin and Erickson (1988), the Mine Drainage and Surface Mine Reclamation Conference held in Pittsburgh in 1988 (and published as USBM Information Circular 9183), featured other papers on kinetic test developments and applications including Doepker (1988), Renton et al. (1988), Backes et al. (1988), Bennett et al. (1988), Watzlaf (1988), Hammack et al. (1988), Stahl and Parizek (1988), Lapakko (1988), Sullivan and Yelton (1988), Franklin and Zahl (1988), and Ammons and Shelton (1988). In these studies a variety of kinetic test procedures were employed involving leaching columns, humidity cells and other weathering chambers, Soxhlet reactors, field-scale barrels, and lysimeters, most of which have already been described herein. One new development was the evaluation by Franklin and Zahl (1988) of EPA's Toxicity Characteristics Leach Procedure (TCLP), "to determine what, if any, applicability the test has in evaluating mine wastes" (p. 205). After using the standard TCLP method and developing modified TCLP tests, Franklin and Zahl (1988, p. 205) concluded that: "Based on these results and other similar research at SRC, it appears that better laboratory assessment methods could be developed that more appropriately aid in the simulation or prediction of contamination from mine wastes."

Doepker (1988) constructed leaching columns from 2 ft (0.61 m) and 4 ft (1.22 m) lengths of 3 in (7.62 cm) inside diameter PVC pipe "equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed" (p. 211) ..."A series of ten similarly constructed 1½" (3.81 cm) ID PVC columns were used to examine the effects of sample depth and column surface-to-volume ratios" (p. 211). Additional kinetic test research at the USBM Spokane Research Center, including a series of at least four leaching column studies, is reported in Doepker and O'Conner (1991a, 1991b) and Doepker (1991a, 1991b, 1994). Experimental methods utilized in Doepker (1994) "included leaching columns, perforated baskets, and Buchner funnels, coupled with humidity and controlled atmosphere chambers" (p. 55). A kinetic technique for carbonate species is in Roberts et al. (1984).

In 1988, the Knoxville, Tennessee Field Office of OSMRE released an outline of an acceptable procedure for conducting leaching tests as described in Maddox (1988). This leaching procedure or simulated

weathering test is designed to augment acid-base accounting results because:

> "It is likely that some permit applicants will not recognize the overburden conditions that may result in a deficiency requiring a leach test on overburden samples that have been defined as nonacidic by the net acid-base account (NAB)... based on OSMRE, Division of Tennessee Permitting's experience, it has become obvious that, in Tennessee at least, the NAB by itself is not a reliable predictor of acid mine drainage (AMD) generation... Therefore, whenever there is no "fizz" but the analysis shows a potential acidity of 5 or more, an NAB indicating nonacidic strata is suspect and may require a leach test... So, even though the NAB indicates an excess of neutralization capacity, the reaction kinetics actually occurring under natural weathering conditions may still result in acid production. The acid-forming process is quite efficient because the acidic products of pyrite oxidation are highly soluble in water and are readily mobilized."

In this Tennessee OSMRE procedure, an advantage of using a leaching column is noted, but other appropriate apparatus may be used, and the test method includes some features of humidity cell methods.

At the 1990 Mining and Reclamation Conference in Charleston, West Virginia, Bradham and Caruccio (1990) presented the results of a comparative analytical study of Canadian metal mines tailings using acid-base accounting, humidity cells, leaching columns (Hood-Oertel type), and Soxhlet reactors. In contrast to the comparative study by Caruccio and Geidel (1986a), wherein leaching columns were found to be the most accurate predictive test, Bradham and Caruccio (1990) found that the humidity cells were the most accurate predictor, and the leaching columns were the least accurate. According to Bradham and Caruccio (1990, p. 19):

> "The fine-grained nature of the tailings afforded high specific retention of fluid, creating airlocks within the columns that skewed the results. When the leachate quality predicted and obtained by the various tests was compared to the actual drainage quality emanating from the sites from which the samples were collected, the least accurate were the column tests, next were the acid/base accounting projections, then the soxhlets, with the weathering cell tests being most accurate."

The 1990 Charleston conference proceedings contain other papers using kinetic tests including Halverson and Gentry (1990), Hart et al. (1990), Morrison et al. (1990a, 1990b), and Hammack and Watzlaf (1990). In the study by Halverson and Gentry (1990), the leaching column method of Doepker (1988) was used to conduct weekly leaching episodes with simulated precipitation for fifty weeks. Morrison et al. (1990b) used the leaching column method described in Hornberger et al. (1981), Waters (1981), Williams et al. (1982, 1985), Hornberger (1985), and Morrison (1988). In Hammack and Watzlaf (1990), small leaching columns (i.e. 40 cm length x 2.54 cm ID) and large leaching columns (i.e. 1.92 m length x 0.25 m diameter) were used to evaluate pyrite oxidation rates. Hart et al. (1990) used the Soxhlet extraction procedures previously described in Renton et al. (1973, 1984, 1985, 1988).

Watzlaf (1992) used "small leaching columns" to evaluate pyrite oxidation of coal waste samples under saturated and unsaturated conditions. These 5.1 cm diameter x 46 cm length columns were larger than the small leaching columns, but smaller than the large leaching columns used by Hammack and Watzlaf (1992). Four different leaching scenarios (i.e. combinations of saturated and unsaturated conditions with distilled water or recycled AMD influents) were evaluated by Watzlaf (1992), who concluded that saturated conditions can significantly reduce the rate of pyrite oxidation.

Filipek et al. (1991) developed and evaluated a kinetic test method named the "shake flask/humidity cell test" in order to predict the chemistry of drainage from exploration tunnels in a massive sulfide deposit in Maine. The method modified and combined some kinetic test features of shake flask tests and humidity cell tests because, "water discharging from the tunnel is expected to react with the associated rocks in a manner somewhere between the two extremes tested by the shake flask and humidity cell tests." Filipek et al. (1991) also evaluated the effect of test-water chemistry on the results of the kinetic tests using a "simulated acid-rain" influent water, and the effect of the rock:water ratio on leachability.

Lapakko and Antonson (1994) conducted a laboratory study of the oxidation of sulfide minerals associated with copper and nickel deposits in the Duluth Complex in northwestern Minnesota , "to examine the

quality of drainage generated by potential Duluth Complex mining wastes" (p. 593). To conduct these kinetic tests, they used a reactor apparatus shown in Figure 7.16 (from Lapakko 1994a, p. 272), which was also used in studies by Lapakko (1988) and Lapakko (1990). This apparatus and kinetic test procedure is essentially a humidity cell method, because humidity and temperature conditions are controlled and monitored between weekly flushing episodes. Lapakko and Antonson (1994) reported on leachate data from 150 weeks of leaching experiment duration, as Lapakko (1988) considered kinetic test performance for 70 weeks duration, and Lapakko (1990) demonstrated that some samples require at least 50 to 80 weeks of laboratory accelerated weathering before NP is deleted and actual acid production occurs.

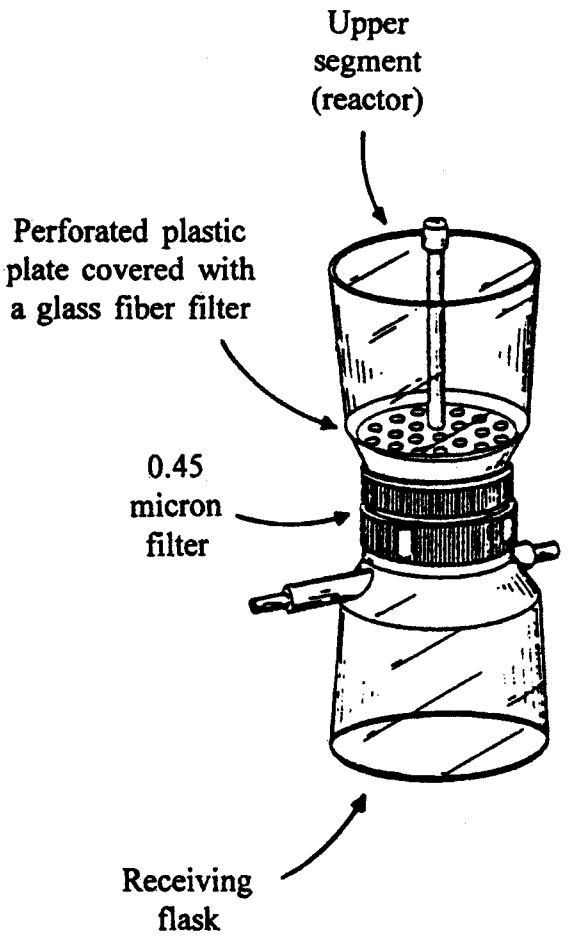

Figure 7.16 Reactor apparatus (from Lapakko, 1994a).

White and Jeffers (1994), from the Salt Lake City Research Center of USBM, conducted humidity cell tests as part of an effort to develop a "geochemical predictive model for acid mine drainage (AMD) from waste rock associated with metal mining" (p. 608). They used a humidity cell array described as follows:

> "...comprised of sixteen individual cylindrical cells, each 20.32 cm long, with an inside diameter (I.D.) of 10.16 cm. Waste-rock charges for each cell are comprised of 1,000 g of sample crushed to 100 % passing 1/4 inch. The test protocol is comprised of weekly leach cycles that include 3 days of dry air and 3 days of wet air pumped up through the sample, followed by a drip-trickle leach with 500 ml of de-ionized water on day 7. Duration of the leach is approximately 2 hours. Bureau tests are continued beyond the 20-week duration currently used in commercial practice; the rationale is to evaluate calculated rates of NP depletion and subsequent acid production from samples whose effluents may appear benign at the end of 20 weeks of testing". (p. 612)

In the study by White and Jeffers (1994), the humidity cell test results for 51 weeks of leaching cycles were reported and sulfate release rates after 21 weeks and 51 weeks were compared. From combined static and kinetic test results it was predicted that some samples may initially have neutral to alkaline leachates, but because their acid-producing potentials were greater than their neutralization potentials in acid-base accounting tests, AMD should develop after 110 through 130 weeks of laboratory accelerated weathering. According to White and Jeffers (1994, p. 628):

> "The ultimate goal of this modelling approach is to enable the mine operator to use short-term laboratory static- and kinetic-test data along with field measurements to make long-term predictions about rates of AP and NP depletion and consequent acid-generation behavior."

This chronology concludes with the publication of the proceedings of the International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage held in Pittsburgh, PA in 1994. The proceedings were published in four volumes (USBM Special Publication No. SP-06A-94 through SP-06D-94) and total 1648 pages. A wide array of mine drainage and mine reclamation subjects were presented in a total of 186 papers, of which at least 45 include kinetic test developments, evaluations, and applications. Of these papers, at least 21 involve the use of leaching columns including the work of Moran and Hutt (1994b), St-Arnaud (1994), Davé and Vivyurka (1994), Rich and Hutchinson (1994), Day (1994), Evangelou (1994), Aachib et al. (1994), Kuyucak and St-Germain (1994a, 1994b),

Rose and Daub (1994), and Stromberg et al. (1994). Of the five kinetic test papers involving the use of humidity cells, Pool and Balderrama (1994) from the USBM Reno Research Center, provided an excellent evaluation of humidity cell parameters; while additional humidity cell testing is described in Moran and Hutt (1994a), White et al. (1994), and Domvile et al. (1994). Two papers incorporate the use of Soxhlet reactors (Adams et al. 1994 and Rich and Hutchinson 1994), in combination with other test procedures. At least six test kinetic test papers involve the use of a field scale apparatus such as a barrel, test pile, or leach pad, including studies by Ferguson and Robertson (1994), Donovan and Ziemkiewicz (1994), Moran and Hutt (1994b), Lapakko (1994b), and Ziemkiewicz and Meek (1994). Thirteen additional papers contain some type of kinetic testing involving a wide variety of apparatus and procedures including beakers (Miller et al. 1994) reactor vessels (Lapakko 1994a, Kuyucak and St-Germain 1994a and 1994b, and Wildeman et al. 1994), shake flasks or batch flasks (St-Arnaud 1994, Kuyucak and St-Germain 1994a), bubbler tanks (Adams et al. (1994), Buchner funnels and leaching racks (Gentry et al. (1994), the Ontario Regulatory Extraction Procedure (Rao et al. 1994), the Sequential Extraction Analysis Procedure (Prairie and McKee 1994, Hakansson et al. 1994), and the TCLP (Boyle and Smith 1994).

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