CRITICAL LITERATURE REVIEW
OF ACID DRAINAGE FROM
WASTE ROCK

MEND Project 1.11.1

April 1991
CRITICAL LITERATURE REVIEW
OF ACID DRAINAGE FROM WASTE ROCK

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April 1991
PROJECT SUMMARY
CRITICAL LITERATURE REVIEW OF ACID DRAINAGE FROM WASTE ROCK

This review of existing information on acid-generating waste rock was based on searches of numerous computerized databases, several visual searches of libraries, and direct contacts with researchers, technical organizations, and mining companies. Relevant documents were examined for detailed information on theory, laboratory experiments, modelling, and field studies. Documents were also critically assessed to determine their validity, applicability, and weaknesses.

In order to organize and present the findings of the critical review, waste-rock piles were conceptually viewed as natural systems with transport of water, solids, and gases through the piles as well as reactions operating within the piles. The internal reactions included acid generation, bacterial activity, acid neutralization, and metal leaching. The effects of pile construction, phase transport and acid-control technologies on the system were also addressed. Finally, recommendations were offered for further studies and for decommissioning of waste-rock piles.

This review demonstrated that groundwater movement through and beneath waste-rock piles represents the primary pathway for contaminant migration. Consequently, detailed hydrogeologic studies of piles and their surrounding environments are primary requirements in understanding and predicting the migration of acid drainage. Furthermore, the process of acid generation was found to be highly complex and most published assessments of acid generation failed to consider this complexity.
SOMMAIRE DU PROJET
ÉTUDE DOCUMENTAIRE CRITIQUE DU DRAINAGE ACIDE DE ROCHES STÉRILES

La présente étude de l'information qui existe sur les stériles acidogènes se fonde sur la recherche de nombreuses bases de données informatisées, la recherche visuelle de plusieurs bibliothèques et la communication directe avec des chercheurs, des organismes techniques et des sociétés minières. Les documents pertinents ont été examinés afin d'en retirer des renseignements détaillés sur la théorie, les expériences de laboratoire, la modélisation et les études sur le terrain. Une évaluation critique des documents a été effectuée afin de déterminer leur validité, leur applicabilité et leurs lacunes.

Afin d'organiser et de présenter les résultats de l'étude critique, on a considéré les parcs de stériles comme des systèmes naturels dans lesquels il y a transport de l'eau, des solides et des gaz et production de réactions, notamment la production d'acide, l'activité bactérienne, la neutralisation des acides et la lixiviation des métaux. On a également étudié les effets, sur le système, de la construction des parcs de stériles, du transport des phases et des techniques de contrôle des acides. Enfin, on a formulé des recommandations visant l'étude plus poussée et le démantèlement des parcs de stériles.

L'étude documentaire montre que la circulation des eaux souterraines sous les parcs de stériles et à l'intérieur de ceux-ci constitue le mécanisme de cheminement principal des contaminants. Par conséquent, il importe d'entreprendre une étude hydrogéologique détaillée des parcs de roches stériles et des milieux environnants afin de comprendre et de prévoir le déplacement du drainage acide. En outre, la production d'acide est un processus très complexe, ce dont ne tient pas toujours compte la plupart des évaluations publiées.
## TABLE OF CONTENTS

1.0 INTRODUCTION .................................................. 1

2.0 CONSTRUCTION OF WASTE-ROCK PILES ......................... 4
   2.1 Introduction ................................................. 4
   2.2 Construction Methods ........................................ 4
   2.3 Case Studies ................................................ 5

3.0 WATER MOVEMENT .............................................. 9
   3.1 Theory ....................................................... 9
      3.1.1 Introduction ............................................. 9
      3.1.2 Surrounding Environment ................................. 15
      3.1.3 Waste-rock Pile .......................................... 16
         3.1.3.1 Climatic and Surficial Processes ............... 16
         3.1.3.2 Internal Processes ................................. 18
   3.2 Case Studies ................................................ 31

4.0 MIGRATION OF SOLIDS ......................................... 51
   4.1 Theory ....................................................... 51
   4.2 Case Studies ................................................ 55

5.0 GAS TRANSPORT ................................................. 58
   5.1 Theory ....................................................... 58
      5.1.1 Gaseous Diffusion ..................................... 58
      5.1.2 Gaseous Advection ...................................... 61
      5.1.3 Aqueous Diffusion ..................................... 63
      5.1.4 Aqueous Advection ..................................... 64
   5.2 Case Studies ................................................ 64

6.0 INTERNAL REACTIONS ........................................... 75
   6.1 Abiotic Acid Generation .................................... 75
   6.2 Bacterial Aspects of Acid Generation ....................... 82
      6.2.1 Physiology of Thiobacillus ......................... 82
      6.2.2 Bacterial Leaching Methods ......................... 87
      6.2.3 Factors Affecting Bacterial Mediation of the Acid Generation Process .......................................... 90
      6.2.4 Bacterial Associations ................................. 95
      6.2.5 Metal Dissolution Reactions ......................... 96
   6.3 Acid Neutralization ........................................ 97
### 6.3.1 Aqueous-based Neutralization Reactions

6.3.2 Neutralizing Minerals

6.4 Metal Leaching

6.5 Modelling of Acid Drainage

6.6 Case Studies

### 7.0 CONTROL TECHNOLOGIES

7.1 Biocidal Control of Bacteria

7.2 In Situ Neutralization

7.3 Alternate Dump Construction

7.4 Covers and Seals

7.5 Underwater Disposal

### 8.0 RECOMMENDATIONS

8.1 Recommendations for Further Studies

8.1.1 General Recommendations

8.1.2 Water Movement

8.1.3 Solids Migration

8.1.4 Gas Transport

8.1.5 Internal Reactions

8.1.6 Control Technologies

8.2 Recommendations for Waste Rock Decommissioning

8.2.1 Recommendations Prior to Mining

8.2.2 Recommendations During Mine Operation

8.2.3 Recommendations After Decommissioning

### 9.0 SUMMARY

10.0 REFERENCES

11.0 ACKNOWLEDGEMENTS

APPENDIX A. Computerized Databases and Keywords

APPENDIX B. List of Contacts
<table>
<thead>
<tr>
<th>Table 3-1</th>
<th>Reported Factors Affecting Water Movement in Waste-Rock Piles</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 3-2</td>
<td>Factors Determining Water Movement in and Around a Waste-Rock Pile</td>
<td>13</td>
</tr>
<tr>
<td>Table 3-3</td>
<td>Results on the Ground Water Tracer Test at the Coedely Spoil Heap</td>
<td>41</td>
</tr>
<tr>
<td>Table 4-1</td>
<td>Modes of Solid-Phase Migration In and Around Rock Piles</td>
<td>51</td>
</tr>
<tr>
<td>Table 5-1</td>
<td>Temperature Survey with Waste Rock Dumps</td>
<td>74</td>
</tr>
<tr>
<td>Table 6-1</td>
<td>Examples of Sulfide Minerals</td>
<td>80</td>
</tr>
<tr>
<td>Table 6-2</td>
<td>Factors Determining the Abiotic Rates of Oxidation and Acid Generation</td>
<td>81</td>
</tr>
<tr>
<td>Table 6-3</td>
<td>Common Minerals Oxidized by Bacteria</td>
<td>94</td>
</tr>
<tr>
<td>Table 6-4</td>
<td>Primary Mechanisms Contributing to Metal Leaching</td>
<td>105</td>
</tr>
<tr>
<td>Table 6-5</td>
<td>Summary of Models Addressing Rock Particles</td>
<td>110</td>
</tr>
<tr>
<td>Table 6-6</td>
<td>Acid-Base Accounting, Halifax Airport Waste Rock</td>
<td>116</td>
</tr>
<tr>
<td>Table 6-7</td>
<td>Acid Leach Analysis, Halifax Airport Waste Rock</td>
<td>117</td>
</tr>
<tr>
<td>Table 6-8</td>
<td>Water Quality Results, Halifax Airport Waste Rock</td>
<td>118</td>
</tr>
<tr>
<td>Table 6-9</td>
<td>Water Chemistry of Seepage, Dunka Site, Minnesota</td>
<td>123</td>
</tr>
<tr>
<td>Table 6-10</td>
<td>Columns Containing Duval-Sierrita Waste Rock</td>
<td>128</td>
</tr>
<tr>
<td>Table 6-11</td>
<td>Summary of ABA Trends in Boreholes in Dump #1, Westmin Myra Falls Mine</td>
<td>133</td>
</tr>
<tr>
<td>Table 6-12</td>
<td>Statistical Summary of ABA Data from Dump #1, Westmin Myra Falls Mine</td>
<td>133</td>
</tr>
<tr>
<td>Table 6-13</td>
<td>Metal-leaching Loads from Various Sources at the Rum Jungle Mines Site During the 1973-74 Wet Season</td>
<td>138</td>
</tr>
<tr>
<td>Table 7-1</td>
<td>Alternative Cover Materials</td>
<td>147</td>
</tr>
<tr>
<td>Figure 1-1</td>
<td>Schematic Diagram of a Mining Operation</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1-2</td>
<td>Conceptual Waste-Rock-Pile System</td>
<td>3</td>
</tr>
<tr>
<td>Figure 2-1</td>
<td>Graph Showing the Relative Amount of Material Occurring at Slope Intervals in End-Dump and Push-Dump Conditions</td>
<td>6</td>
</tr>
<tr>
<td>Figure 3-1</td>
<td>Schematic Diagram of a Waste Rock Pile Located in a Groundwater Recharge Area</td>
<td>10</td>
</tr>
<tr>
<td>Figure 3-2</td>
<td>Schematic Diagram of a Waste Rock Pile Located in a Groundwater Discharge Area</td>
<td>10</td>
</tr>
<tr>
<td>Figure 3-3</td>
<td>Schematic Diagram of a Waste Rock Pile Located Between a Recharge and Discharge Area on a Sloping Surface</td>
<td>11</td>
</tr>
<tr>
<td>Figure 3-4</td>
<td>Schematic Diagram of Porous-Media and Fracture Flows</td>
<td>16</td>
</tr>
<tr>
<td>Figure 3-5</td>
<td>Schematic Diagram of a Waste Rock Pile with Low-Permeability Strata and Perched Water Tables</td>
<td>20</td>
</tr>
<tr>
<td>Figure 3-6</td>
<td>Relationships of Degree of Saturation to (a) Tension Head and (b) Hydraulic Conductivity</td>
<td>26</td>
</tr>
<tr>
<td>Figure 3-7</td>
<td>Relationship of $H_m/L$ to $K_s$ and $W$. Calculated from Equation 4</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3-8</td>
<td>Relationship of Particle Diameter to Water Volume to Initiate Flow and Specific Water Retention</td>
<td>32</td>
</tr>
<tr>
<td>Figure 3-9</td>
<td>Relationship of Percentage of Coated Surfaces to (a) Depth Within the Piles (Data from ElBoushi, 1975) and (b) Depth Normalized by the Cube Root of Particle Diameter (Calculated as Part of this Study)</td>
<td>32</td>
</tr>
<tr>
<td>Figure 3-10</td>
<td>Geophysical Logs for a Borehole in the Chino Dump, New Mexico</td>
<td>34</td>
</tr>
<tr>
<td>Figure 3-11</td>
<td>Geological Section Through Coedly Spoil Heap</td>
<td>39</td>
</tr>
<tr>
<td>Figure 3-12</td>
<td>Plan Map of the Coedly Spoil Heap</td>
<td>40</td>
</tr>
<tr>
<td>Figure 3-13</td>
<td>Waste Dumps at Fording Coal Operation</td>
<td>43</td>
</tr>
<tr>
<td>Figure 3-14</td>
<td>Water Movement in Spoils at the Diplomat Mine</td>
<td>45</td>
</tr>
<tr>
<td>Figure 3-15</td>
<td>Water Movement in Spoils at the Vesta Mine</td>
<td>46</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3-16</td>
<td>Water Movement in a Waste Rock Pile at the Halifax Airport</td>
<td>47</td>
</tr>
<tr>
<td>3-17</td>
<td>Borehole Locations and Surface Elevations at the Westmin Myra Creek Waste Rock Dump</td>
<td>49</td>
</tr>
<tr>
<td>3-18</td>
<td>Water Table Elevation In and Beneath the Westmin Myra Falls Dump</td>
<td>50</td>
</tr>
<tr>
<td>4-1</td>
<td>Mine Waste Embankments Possible Failure Modes</td>
<td>54</td>
</tr>
<tr>
<td>4-2</td>
<td>Estimated Grain Size Distribution for a Proposed Waste Rock Dump in Northern British Columbia</td>
<td>56</td>
</tr>
<tr>
<td>5-1</td>
<td>Schematic Diagram of Three Primary Causes of Pressure Gradients In and Around Waste Rock Piles</td>
<td>62</td>
</tr>
<tr>
<td>5-2</td>
<td>Temperature Contours in a Simulated Cylindrical Heap at Years 2, 3 and 4</td>
<td>65</td>
</tr>
<tr>
<td>5-3</td>
<td>Temperature and Oxygen Distributions in Intermediate Dump Before and After Rehabilitation</td>
<td>67</td>
</tr>
<tr>
<td>5-4</td>
<td>Map of the Upshur County Site</td>
<td>69</td>
</tr>
<tr>
<td>5-5</td>
<td>Temperature Probes in Waste Rock Dumps at Equity Silver Mines</td>
<td>72</td>
</tr>
<tr>
<td>5-6</td>
<td>Temporal Trend in Temperature in the Series 1270 and 1280 Probes</td>
<td>73</td>
</tr>
<tr>
<td>6-1</td>
<td>Scheme for Pathway of Electron Transfer in <em>T. ferrooxidans</em> during Oxidation of Fe²⁺</td>
<td>84</td>
</tr>
<tr>
<td>6-2</td>
<td>Scheme for Oxidative Phosphorylation in <em>T. ferrooxidans</em></td>
<td>84</td>
</tr>
<tr>
<td>6-3</td>
<td>Steps in the Oxidation of Different Sulfur Compounds by <em>Thiobacilli</em></td>
<td>86</td>
</tr>
<tr>
<td>6-4</td>
<td>Relationship of pH to Concentrations of Carbonate Species</td>
<td>100</td>
</tr>
<tr>
<td>6-5</td>
<td>Common Relationship of Aqueous Metal Concentration to pH</td>
<td>104</td>
</tr>
<tr>
<td>6-6</td>
<td>Sulfate-Contributing Spoil Volume, Controlled by Diffusion According to Particle Size</td>
<td>108</td>
</tr>
<tr>
<td>6-7</td>
<td>Rock Fragment Showing Pore Network and Diffusion of Ions</td>
<td>109</td>
</tr>
<tr>
<td>6-8</td>
<td>Schematic Diagram of the Acid Mine Drainage Model</td>
<td>113</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Cont’d)

Figure 6-9  Sources of Acid Generation, NB Coal Ltd. Fire Road Operation .............. 120
Figure 6-10 Sulfide and Sulfate Concentrations in Spoils: Sites A, B, and C ................. 121
Figure 6-11 Copper and Nickel in Dunka Rock Pile .............................................. 124
Figure 6-12 Metal Concentrations vs pH from Waste Rock Pile #2 ............................ 125
Figure 6-13 Annual Median pH of Test Pile Drainage from 1978 to 1989 ...................... 127
Figure 6-14 pH Data Showing Neutralization of the Duval-Sierrita Waste Rock ........... 129
Figure 6-15 Results of Acid-Base Accounting for Borehole 25 ..................................... 131
Figure 6-16 Results of Acid-Base Accounting for Borehole 15 ..................................... 132
Figure 6-17 Spatial Trends in Groundwater pH in 1988 and 1989 .............................. 135
Figure 6-18 Zinc vs pH for Groundwater Samples ..................................................... 136
Figure 6-19 Map of the Abandoned Mine Site at Rum Jungle ..................................... 137
Figure 6-20 Geological Cross-Section through the East Dump and Pit at the Mt. Washington Minesite ................................................................. 142
1.0 INTRODUCTION

Mining is a fundamental industry of the Canadian economy which supplies metals and non-metals to the refining and manufacturing sector. As with all industrial activity, mining activities generate waste materials which require proper handling and management in order to minimize degradation of the surrounding environment.

Proper waste management for mining operations begins with the identification of the components at a minesite which can have significant impacts on the local environment, including waste-rock, tailings, and mine walls (Figure 1-1). The next step in waste management involves a detailed inventory of the potential impacts of each component, followed by a site-specific delineation of the physical, chemical, and biological characteristics of the critical components. Through these site-specific studies, environmental management strategies can be reliably defined.

Despite the vital importance of site studies of mine components, there are no standard procedures for conducting them. As a result, the amount of information collected during any particular study, the interpretation of the data, and the selection of control strategies are usually dependent on the local knowledge of theory and of studies at other minesites. In order to provide guidance on conducting such studies and improve the quality of all studies in Canada, the Mine Environment Neutral Drainage (MEND) Program was formed by the Government of Canada and interested mining companies. The MEND Program has sponsored projects leading to general guidelines for site studies of acid drainage, as well as projects leading to component-specific guidelines for studies of waste-rock, mine walls, and tailings impoundments. These studies are of benefit to proposed mines by providing guidance on collecting critical information prior to mining and on avoiding problems encountered at existing minesites. These studies are also of benefit to operating mines through their suggestions of methods for examining and correcting existing problems.

This report contains the MEND-sponsored examination of acid drainage from waste-rock. The primary objective of this study was to critically review and assess published literature and unpublished data, leading to the illustration of typical results and unexpected findings in studies of waste-rock. To fulfill this objective, searches were made of numerous computerized databases (Appendix A), and researchers and mining companies were contacted directly (Appendix B). These tasks yielded a list of a few thousand titles and some abstracts, many dealing with coalmine spoils which share some characteristics with waste-rock. Titles judged not to be directly relevant to this project were eliminated from consideration. Hundreds of potentially relevant publications and reports were then retrieved and reviewed. This report provides more than a standard literature review by critically assessing the validity, strengths, and weaknesses of theory, laboratory experiments, and field studies.
FIGURE 1-1. Schematic Diagram of a Mining Operation (after Morin, 1988). Interactions among components are indicated by arrows (solid = liquid exchange, dashed = solids exchange).
To provide an overall structure to this review, waste-rock piles were conceptually viewed as natural systems (Figure 1-2). Once the system is constructed (Section 2.0), it is open for movement of water (Section 3.0), solid particles (Section 4.0), and gases (Section 5.0) across its boundaries, which can affect the extent and severity of acid drainage. Processes which are capable of affecting the water, solids, and gases may be operative within the system, including acid generation, bacterial activity, acid neutralization, and metal leaching (Section 6.0). Once delineated or predicted, the site-specific environmental impacts of the system on the local environment can be minimized through relevant control technologies (Section 7.0). Finally, based on the findings of this review, recommendations for further studies and for waste-rock decommissioning are presented (Section 8.0).

**FIGURE 1-2. Conceptual Waste-Rock-Pile System.**
2.0 CONSTRUCTION OF WASTE-ROCK PILES

2.1 Introduction

Various methods have been used to place waste-rock from open pit or underground mining operations onto the land surface. Geographical constraints of the mining operation, the type and size of equipment being operated, and the physical and chemical characteristics of the waste determine the method(s) employed at a particular minesite. In turn, the selected method has a major influence on the environmental impacts of the pile because it creates the physical characteristics which modify air and water movement. The size and shape of the dump may also affect internal physical and chemical processes. Consequently, construction methods can affect the extent and severity of acid drainage from waste rock, as discussed in Sections 3.0 through 3-6.

2.2 Construction Methods

Four general methods of dump construction are commonly employed, each leading to varying degrees of compaction and particle-size segregation. In the first method, end-dumping, the waste-rock is dumped directly over the crest of the dump face from a truck. In the second method, push dumping, the waste-rock is dumped near the crest of the pile by truck or conveyor and then the material is pushed over the crest with a dozer. In the third method, free dumping, waste is dumped in discrete piles approximately 2 m in height across the level surface of a dump. This waste material is then graded before additional lifts are built. The fourth method of dump construction results from drag-line spoiling, typical of large-scale coal mining. Variations of these primary methods can result in wrap-around benches, which are successive lifts constructed below the crest of the dump, or benches developed by stepping back the active dump face.

The four primary construction methods typically produce piles with very different distributions of rock particle size. In end-dumped construction the fine particles are generally concentrated near the crest, and the coarsest particles collect beyond the slope toe. Some authors indicate end-dumping results in a distribution of particle sizes grading from fine to progressively coarser proceeding from the level of the dump platform toward the base of the dump (Golder, 1989). However, in a field simulation of dumping methods, an end-dumped slope was found to have three distinct particle size groupings, a fine upper zone, a very coarse toe zone and an evenly distributed, evenly graded zone along the remainder of the slope (Nichols, 1986). Slope height was not found to change the type of gradation, but it did reduce the amount of segregation. The amount of segregation was also reduced by end-dumping a finer textured waste material, but the segregation into the three zones was still evident.
In the field simulated push-dumped waste slopes (Nichols, 1986) the coarse particles collected at the toe of the slope but the fines were not segregated at the top. Furthermore, the extent of coarse-material segregation was much less for push-dumped than end-dumped material. In the push-dumping tests an average of 40% of the largest particle size rolled beyond the slope toe compared to 75% for the end-dumping tests (Figure 2-1). The profiles confirmed that in these tests most of the material collects along the lower part of the slope when end-dumped and along the upper part of the slope when push-dumped. One of the main reasons given for the difference is the momentum gained by the coarse particles as they slide out of the shovel (truck) when end-dumped. This momentum causes the rocks to roll rather than slide down the slopes. Theoretically, since the angular momentum from end dumping is much greater than the frictional resistance of the material, the particles will not come to rest unless the slope flattens out or they hit particles greater than half their size. On the other hand, when material is push-dumped many of the coarse fragments get trapped in the fine aggregate on the slope crest. A comparison of the test results with actual dump conditions at open pit coal mines in the Elk Valley area of southeastern B.C. suggested that these end-dumped waste deposits exhibit segregation which is very similar to the test results.

The third basic method of dump construction, free-dumping, involves the hauling of waste into disposal areas with concurrent dumping, spreading, and compacting in layers of approximately 2 m in height. In this method there is little segregation of particle sizes and there is considerably more compaction than in the previous two methods.

The fourth method of dump construction results from dragline spoiling, where waste is placed directly on land surface. This method provides little segregation of particles and differs from free-dumping because it is seldom built in lifts and is therefore not as compacted.

2.3 Case Studies

Heap Leach Construction: Ruzycki and Womack (1987)

In the development of an acid heap leach pile, the effect of compaction in end-dumped construction had a significant effect on leach success. An initial pile 3 to 7 m in height of acid generating material was constructed by end-dumping and simultaneously smoothing the surface with a dozer. When the pile was completed, the upper 3 m was ripped with a shank attached to a Caterpillar D-9L dozer. This ripping eliminated excess compaction in the upper level of the pile but the consolidation due to construction traffic remained in the lower 4 m. Leaching displayed unsatisfactory recoveries owing to reduced permeability and the formation of fines into lenses. Subsequent lifts on the pile were constructed by free-dumping ore in rows across the width. The
FIGURE 2-1. Graph showing the relative amount of material occurring at slope intervals in end-dump and push-dump conditions. Note that the push-dump curve shows above average amount of material at the top, and below average amount at the bottom of the slope. This illustrates the oversteepened, understable condition of push-dump slopes.
existing surface was ripped just prior to placement of each row. This method of construction significantly improved permeability and leaching. Leaching of 50 to 100 d was required for satisfactory recovery in the more compacted leach pile and only 15 to 40 d in the free-dumped pile.

**Stratification in Heap-Leach Piles: Kinard and Schweitzer (1987)**

Heap leach piles approximately 8 m in height were constructed of argillized basaltic andesite with at least 60% clay content. The rock was crushed, agglomerated with lime (5 kg/t) to stabilize the clay, and then placed with a radial stacker. Four months after construction test pits were dug to 6 m. During stacking, coarser rock was seen to collect near the base of each stack. The test pits showed that there was actually alternating zones of coarse rock (1.3 to 5.0 cm diameter, with some fines), finer rock (90 to 100% passing #200 sieve), and well graded material (2.5 cm diameter to 3% passing #200 sieve). This type of gradation is similar to the types formed in the end-dump and push-dump simulations.


The waste-rock dumps at Mt. Washington were probably constructed using an end-dumping or push-dumping technique. When test holes were drilled the dump was found to be composed primarily of coarse to very coarse material and to display a degree of sorting, with finer material at the dump surface. Generally the material was 0.5 to 1 m diameter at the base of the dump and cobble sized at the crest. An upper layer of 0.5 to 2.0 m in thickness is composed of compacted sand to cobble size material. This is believed to represent an old traffic surface where dump material has been broken down and compacted by repeated truck and dozer traffic. Weathering and exposure may also have influenced the character of this upper layer since the sides of the dump have a similar but poorly defined surface layer of relatively fine material.

**Equity Silver Mines, British Columbia: Patterson (1987)**

Equity Silver (Patterson, 1987) has incorporated a layer of till materials into dump construction to reduce air exchange. Lifts are built 10 m in height and each stepped in to conform to an overall slope of 20°. Completed berms and side slopes are top-dressed with a 1 m layer of glacial till and seeded to establish a protective vegetative cover.
Dump #1, Westmin Myra Falls Operation: Northwest Geochem (1990)

The drilling of 57 boreholes into this waste-rock pile revealed the existence of random coarse and fine layers. The fine layers may have been traffic surfaces and the sporadic appearance of peat-like material is consistent with this scenario. At the base of the dump, waste-rock could not be distinguished from bedrock, indicating the rock was relatively homogeneous in physical and geochemical characteristics, including particle size.
3.0 WATER MOVEMENT

3.1 Theory

3.1.1 Introduction

The movement of water into, through, and out of a waste-rock pile represents a primary pathway for contaminant migration at a minesite. This water is capable of carrying acidity and other byproducts of acid generation as well as leached metals into the surrounding environment. For these reasons, the manner in which groundwater migrates through waste-rock warrants particular attention in this review (in this review, "groundwater" is defined as any water located beneath the surface of a pile or natural land).

Waste-rock is removed from a pit or underground mine and is often placed on the land surface (Section 2). It then becomes part of the local hydrologic system, with precipitation falling onto exposed surfaces, infiltrating into the rock, and moving towards the base of the pile. After reaching the base, the groundwater seeps into the underlying groundwater system or into surrounding surface watercourses. Instead of infiltrating into a pile, a portion of the precipitation may also become runoff over the surfaces of a pile, which represents another pathway for contaminant migration. In some cases, runoff may eventually infiltrate into a pile as it flows.

The specific behavior of water in and around waste-rock depends on the location of the pile in the local hydrogeologic system. Before proceeding to the literature review, three conceptual models of waste-rock piles, based on location within the local hydrogeologic system, will be formulated to simplify the review. Firstly, the waste-rock can be placed in a local recharge area (Figure 3-1) so that most of the local surface water and groundwater originates on the pile and passes over or through the pile. This is the typical scenario in relatively flat terrain and at the top of hills and mountains. Secondly, the waste-rock may be located in the local discharge area (Figure 3-2) so that most surface and groundwater accumulating at the base of a watershed will pass through the rock. This scenario applies to waste-rock piles placed in the bottom of valleys. Thirdly, the waste-rock may be located at an intermediate point in the local hydrogeologic system between the recharge and discharge areas (Figure 3-3). This third scenario appears to be the most common because many mines lie in sloping terrain.

FIGURE 3-2. Schematic Diagram of a Waste Rock Pile Located in a Groundwater Discharge Area. Basal drainage is perpendicular to the plane of the page.
When a waste-rock pile is located in a recharge area (Figure 3-1), the primary source of water moving through the rock is infiltration of precipitation. The water balance for the pile is relatively simple and can be described by:

\[ D = P - R - E - T - dS \]  

(Equation 3-1)

where
- \( D \) = discharge of internal water at the base, as springs at the toe and/or as seepage to groundwater
- \( P \) = precipitation onto the pile
- \( R \) = runoff over the surface of the pile
- \( E \) = evaporation from the pile
- \( T \) = transpiration if vegetation is present
- \( dS \) = change in the amount of water retained or "stored" within the pile
As precipitation infiltrates into the pile and moves downward towards the underlying water table, the rock will retain some proportion of the water (dS). Although factors P, R, E, and T in Equation 3-1 can be characterized by surface monitoring, the delineation of the storage of water within the pile and the quantity and flow direction of D typically require drilling and monitoring installations within and below the pile. The less obvious complexities in this scenario are discussed later.

When a waste-rock pile is located in a discharge area (Figure 3-2), the water moving through or stored in the rock is derived from (1) precipitation, (2) the underlying groundwater system, and (3) the runoff from upslope areas. The water balance of the pile is thus more complex than in Figure 3-1 and a detailed study of the entire watershed and groundwater system may be necessary to understand water movement in this situation. Water movement within the pile will frequently be oriented downwards in the unsaturated zone, but significant lateral and upward movement can occur below the water table. Additional complexities in this scenario are discussed later.

Water movement in waste-rock piles on sloping land surfaces (Figure 3-3) is more difficult to define and predict, because the movement can reflect any combination of Figures 3-1 and 3-2. Precipitation provides water to the surficial unsaturated rock and the water then typically moves downward to the water table. For upslope runoff, the amount of water moving into and through the pile depends on the catchment area above the pile. For upslope groundwater flow, the amount of water movement into and through the pile depends on the distances to the recharge and discharge areas and on the depth of the water table. If the water table is below the base of the pile, the local groundwater system will not usually contribute to water movement in the pile. In this situation, however, unsaturated groundwater moving through the pile will eventually reach the underlying water table, permitting any water-quality impacts to appear later in discharge areas such as valley bottoms.

If Figures 3-1, 3-2, and 3-3 precisely represented water movement in and around waste-rock piles, the control of contaminant migration from waste-rock would be straightforward. In reality, water movement is dependent on a myriad of complex variables which result in each pile having unique aspects of water movement. Many of these variables have been reported and discussed by various researchers, primarily from the perspective of heap leaching (Table 3-1). However, many of the classifications in the literature have been found to be oriented towards engineering rather than environmental concerns and are sometimes confusing. For the purposes of this study, variables were assembled into environmentally oriented classes which can be used a checklist during the analysis of any waste-rock pile (Table 3-2). These variables will be discussed below.
### TABLE 3-1
Reported Factors Affecting Water Movement In Waste-rock Piles

*From Whitting (1981)*

<table>
<thead>
<tr>
<th>PHYSICAL</th>
<th>CHEMICAL</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratification</td>
<td>pH Control</td>
<td>Pollution Control Methods</td>
</tr>
<tr>
<td>Channelling</td>
<td>Precipitation</td>
<td>Precipitation Rates</td>
</tr>
<tr>
<td>Segregation</td>
<td>Aqueous Reactions</td>
<td>Evapotranspiration</td>
</tr>
<tr>
<td>Sorption</td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>Foundation</td>
<td>Alteration</td>
<td></td>
</tr>
<tr>
<td>Permeability</td>
<td>Oxidation</td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td>Solution Type</td>
<td></td>
</tr>
</tbody>
</table>

*From Gardiner and Woolhiser (1978)*

<table>
<thead>
<tr>
<th>Precipitation</th>
<th>Temperature</th>
<th>Evapotranspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infiltration</td>
<td>Surface runoff</td>
<td>Surface-water storage</td>
</tr>
<tr>
<td>Soil water</td>
<td>Groundwater</td>
<td>Streamflow</td>
</tr>
<tr>
<td>Erosion</td>
<td>Chemical transport</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3-2
Factors Determining Water Movement In And Around A Waste-rock Pile

**SURROUNDING ENVIRONMENT**

Climatic and Surficial Processes

- Physical
  - Precipitation
  - Rate
  - Distribution
  - Accumulation
  - Evaporation
  - Transpiration (biological)
  - Streamflow/runoff
  - Infiltration to groundwater

- Geochemical
  - Mineral precipitation-dissolution

...continued
### TABLE 3-2 continued
Factors Determining Water Movement In And Around A Waste-rock Pile

#### Subsurface Strata
- Physical
  - Porous-media vs fracture flow
  - Hydraulic conductivity
    - Range of values
    - Spatial distribution
    - Relationship to degree of saturation

- Geochemical
  - Hydraulic gradients
  - Mineral precipitation-dissolution

#### WASTE-ROCK PILE
- Climatic and Surficial Processes
  - Physical
    - Precipitation
      - Rate
      - Distribution
      - Accumulation
    - Evaporation
    - Transpiration (biological)
    - Runoff
    - Infiltration into pile
    - Springs/seeps
  - Geochemical
    - Mineral precipitation-dissolution

- Internal Processes
  - Physical
    - Solids migration (see Section 4)
    - Gas transport (see Section 5)
    - Hydraulic conductivity
      - Range of values
      - Spatial distribution
      - Relationship to density and viscosity
      - Relationship to degree of saturation
    - Laminar vs turbulent flow
  - Geochemical
    - Hydraulic gradients
    - Mineral precipitation-dissolution
3.1.2 Surrounding Environment

Because a waste-rock pile interacts with its surrounding environment, a study of a pile must include this environment. For water movement, the primary factors (Table 3-2) are site specific in nature, but can usually be delineated in a general sense using standard techniques. These factors for the surrounding environment are not a focus of this study and will thus only be briefly discussed. Detailed discussions can be found in textbooks and mining-specific publications such as Parizek (1985) and Gardiner and Woolhiser (1978).

Water movement in the local environment surrounding a waste-rock pile originates as (1) local precipitation, (2) surface streamflow from more distant locations into the area, (3) streamflow generated at the toe of a pile, (4) groundwater flow from more distant locations into the area, and (5) groundwater flow from the base of a pile. When and where local precipitation exceeds evaporation and transpiration, the excess water responds as either runoff to join existing streamflow or infiltration to join existing groundwater. Geochemical processes, particularly mineral precipitation-dissolution, are capable of affecting rates of evaporation, transpiration, streamflow, and infiltration, but the effects are usually significant only where acid-laden water is flowing from piles. Movement of groundwater beneath the surface may occur as porous-media or fracture flow (Figure 3-4). Fracture flow is frequently conceptualized as flow between parallel, impermeable plates whereas porous-media flow can be considered more random and distorted on a small scale. The direction, speed, and volume rate of groundwater flow under these conditions are affected by hydraulic conductivities and gradients. Hydraulic conductivities are subject to spatial variations due to depositional environments as well as to both temporal and spatial variations caused by unsaturated conditions and mineral precipitation-dissolution. As a result, patterns of groundwater flow are usually more complex than surface-water flow, requiring more intensive work to delineate groundwater movement in the subsurface near a waste-rock pile.
The quality of the environment surrounding a waste-rock pile will reflect the proportion of surface and groundwater passing through the pile and the chemical loadings in these waters. For example, Trudell and Moran (1984) report contaminant groundwater plumes up to 2 kilometres long extending from coal spoils. For these reasons, environmental impacts can only be accurately defined or predicted by assessing both the pile and its surrounding environment. The factors determining the quantity of water moving through and over a pile will be discussed in detail in the following section. The factors determining the chemical loadings are discussed in Section 6.

3.1.3 Waste-rock Pile

3.1.3.1 Climatic and Surficial Processes

Under Climatic and Surficial Processes (Table 3-2), precipitation is listed as a primary source of water to a pile, particularly in recharge areas (Figure 3-1). Accordingly, the delineation of precipitation rates, spatial distributions, and accumulations (ponding and snow) across the surface of a pile is a critical first step in defining and predicting water movement. In many cases, waste-rock piles do not occupy enormous tracts of land and are not significantly
elevated above surrounding land so that the precipitation data collected for the Surrounding Environment (Table 3-2) can also be applied to the pile. However, the loss of precipitation to evaporation and transpiration can differ significantly from the surrounding environment, resulting in different rates of runoff and infiltration. One cause of these differences can be geochemical processes, particularly mineral precipitation-dissolution, which creates such effects as infilling of shallow porespace and increased infrared absorption by surface coatings.

Although there have been no detailed studies published on the nature of precipitation onto the surfaces of waste-rock piles, there have been related studies of heap leaching due to the economic importance of enhancing flushing and water movement. Consequently, information from Whiting (1981) has been adapted to waste-rock piles to demonstrate the effect that precipitation events can have on surficial and internal water movement.

As part of the optimization of heap leaching, Whiting (1981) considered the effects of various types of leach-solution application to the top of a rock pile and identified five primary application techniques: (1) ponding, which can be compared to natural heavy rainfall or to snowmelt leaving ponded water on the pile, (2) trickle, corresponding to light and intermittent rainfall, (3) distributed low-pressure spray, corresponding to light to moderate rainfall, (4) high-pressure spray, which probably has no natural corresponding event, and (5) borehole injection of solution, which has no corresponding precipitation event, but probably resembles the effect of fluctuating water tables in some cases. Surface ponding of water was found to flush the exposed rock surfaces and a large proportion of the internal rock until the ponding disappeared. The analog to a light, intermittent rainfall was found to flush much of the surficial and internal surfaces of the rock, while not affecting the proportion of water held in the porespaces. The analog to a continuous light to moderate rainfall, like the intermittent rainfall, did not significantly affect the amount of water stored in the porespaces, but did result in a more homogeneous distribution of water across the dump surface. High-pressure spray has no directly corresponding natural event, but the associated migration of rock particles from the surface into the dump can also be initiated by natural rainfall (Section 4). These analogs support the emphasis placed on the rate, distribution, and accumulation of precipitation in Table 3-2. Borehole injection mentioned by Whiting was for the most part comparable to water-table fluctuations within the pile, resulting in the significant water movement deep in the pile and the flushing of deeper rock surfaces while shallower rock remains unflushed. The nature of this internal water movement will be discussed in greater detail in the following section (Section 3.1.3.2).
As a conclusion to this section on surficial processes, an example of water balances for waste-rock is useful to demonstrate the importance of Surficial Processes (Table 3-2) on determining the site-specific nature of water movement, the impacts on water quality, and the selection of a remediation method to control contaminant migration. This example is taken from the Rum Jungle Mine in northern Australia, where there are two primary waste-rock dumps, White's and Intermediate (Daniel et al., 1983; Harries and Ritchie, 1983). Evaporation accounted for 25-35% of total precipitation on the piles, runoff from the piles accounted for 10-22%, and seeps at the toes accounted for 5% of total precipitation at White's and none at Intermediate. The remaining water, 38-60% at White's and 43-65% at Intermediate, passed through the base into the underlying groundwater system, which was found to be heavily contaminated. Because the acid generation and metal leaching occurred within the dumps, this balance highlighted the importance of reducing internal water movement. As a result, capping with relatively impermeable material was selected as the control method. Gardiner and Woolhiser (1978) also pointed out the benefits of minimizing infiltration through the enhancement of runoff, evaporation, and transpiration in order to decrease both groundwater flow through piles and the mobilization of large amounts of "chemicals".

### 3.1.3.2 Internal Processes

Internal Processes (Table 3-2) address the migration of solids, gases, and water through a waste-rock pile and internal reactions. Water movement only will be addressed in this section, whereas the other issues are addressed in other sections of this report.

Groundwater flow is mathematically described by partial differential equations (e.g., Freeze and Cherry, 1979) which can be simplified under steady-state, saturated conditions to Darcy's Law:

\[
Q = K \times i \times A
\]

(Equation 3-2)

where \( Q \) = rate of flow \( (m^3/s) \)

\( K \) = hydraulic conductivity \( (m/s) \)

\( i \) = hydraulic gradient \( (m/m) \)

\( A \) = cross-sectional area of flow \( (m^2) \)

From this equation, the parameters of hydraulic conductivity and hydraulic gradient, with the gradient derived from differences in hydraulic head over a length of flow path, are the determining factors in the volume rate and velocity of groundwater movement. This section will address the theory behind hydraulic conductivity and hydraulic head as applied to waste-
rock piles. The importance of complexities such as channelling and unsaturated conditions will also be demonstrated.

Hydraulic Conductivity

Values for hydraulic conductivity ranging from $10^{-2}$ m/s with porosities of 35-40% for igneous/metamorphic waste-rock (Wadsworth, 1981) to as low as $10^{-9}$ m/s for clayey basaltic andesite (Kinard and Schweitzer, 1987) have been located during this review. As shown in Equation 3-2, the value of hydraulic conductivity for a pile will play a major role in determining the rate of internal water movement, but could also determine the amount of runoff. If the rate of precipitation exceeds the capacity of the pile to transmit it, then ponding and runoff at the surface of the pile could be expected. Through computer simulations of waste piles of "spent shale" from an oil shale operation, Bloomsburg and Bloomfield (1979) found that one type of shale would accept all precipitation from 100-y storms of 1-h and 6-h durations as infiltration, whereas another shale caused most of the precipitation to run off the pile. Consequently, the Internal Processes and the Climatic and Surficial Processes of Table 3-2 result in a balanced, interactive hydraulic system in and around waste-rock piles.

A single value of conductivity likely cannot be used to represent an entire waste-rock pile and a range of values should be expected in any particular pile due to variations in particle size, rock characteristics, and construction techniques (Section 2.0). For example, Whiting (1981) presented unpublished data from an unidentified waste-rock pile showing that bulk conductivity generally ranged from $10^{-4}$ to $10^{-5}$ m/s based on measurements in 9 boreholes over several meters length of borehole. Two additional low values of about $10^{-6}$ m/s were also reported. For ease of discussion, the variations in hydraulic conductivity are conceptually divided into (1) relatively low-permeability layers within high-permeability rock where groundwater is forced to flow around the layers and (2) relatively high-permeability layers within low-permeability rock where groundwater preferentially flows through the layers. In reality a continuum exists between these two endpoints. A review of the literature indicates that the former scenario is often referred to as "stratification", whereas the latter is termed "channelling".

Horizontal, low-permeability strata can retard and redirect water movement within the rock pile. Where the water is significantly retarded, saturated zones with perched water tables (Figure 3-5) may develop and water may be retained for relatively long periods of time, which would lessen the variability of water flow initiated by intensive precipitation events. Surface seeps (springs) may develop on the face of the rock pile (Figure 3-5) if the low-permeability stratum extends to the face. If the water accumulates quickly above a stratum near the face and hydraulic pressures are not relieved, Whiting (1981) reported the possibility of "blow-outs"
where the force of the hydraulic pressures caused water and rock to be ejected from the face and carried downslope (Section 4.0).

Stratification can also have geochemical implications in that the extended retention time within the pile can increase rock-surface contact and contaminant loadings. However, the impacts of stratification are not always significant because other factors such as rates of precipitation also determine the extent of impacts. During times of little precipitation, water movement to the low-permeability layer may be insufficient to establish a perched water table.

There are two primary causes of stratification: low-permeability layers formed during construction such as on travelled surfaces or low-permeability layers arising through time due to weathering and solids migration (Sections 2.0 and 4.0). The latter cause of stratification includes the development of a "Phase-Migration Barrier" at the top of the pile as reported for coal spoil piles and a low-permeability layer at the base of, or below, the pile. Stratification will enhance the temporal variations in water movement through and over a pile, and drilling with subsequent monitoring is required to understand or predict fluctuations in water movement and contaminant migration.
The "channelling" of water movement by vertical or horizontal high-permeability strata in a pile effectively isolates nearby rock surfaces from the flushing action of the water. This isolation of nearby surfaces can be expected to continue until the volume rate of flow into the channel exceeds the capacity of the channel. At that point, water would begin moving through adjacent channels. Based on the review of literature, high-permeability channelling is thought to be a primary control on water movement through waste-rock, although widespread confirmation through field observations is lacking. Due to the probable random nature of channelling and the practical difficulty in monitoring water movement through unsaturated coarse rock, the lack of field observations is expected to persist. For this reason, theoretical expectations form much of the current understanding on channelling with most of the information summarized by Whiting (1981).

Whiting (1981) reports in-field tests by other researchers in which water was poured into piezometers. The water levels initially dropped quickly then decreased more slowly and the initial rapid draining was interpreted as flow through a channel. However, such a trend is typically expected during a "falling head" test in a piezometer, so it appears that this field method may not be a realistic test for channelling.

Preferential channels for groundwater flow in waste-rock are usually considered to be series of large, interconnected porespaces. However, Whiting (1981) briefly mentions contradictory field observations which demonstrate that narrow channels are the preferential flowpaths, although no data or references are given to support the observations. Two potential explanations for this discrepancy might be (1) Whiting based his conclusion on observed rock weathering and/or metal-hydroxide staining, which would be greater in finer-grained pores due to finer grain size and greater water retention and would thus not be indicative of preferential water flow, or (2) natural processes such as capillary action or laminar vs. turbulent flow account for the channelling in narrow porespaces. The latter processes are discussed in greater detail below.

Because channels carry water as well as any suspended solids, the potential exists for channels to become plugged with solids (Section 4). Additionally, Whiting (1981) pointed out that several physical and geochemical processes such as weathering can cause channels to become partially or fully plugged, accounting for the reported bulk decrease in permeability in rock piles through time. This plugging changes the pattern of water movement by causing water to move through new, less permeable porespaces and can then result in temporal changes in water quality as the water moves over previously unflushed rock surfaces.

Although channelling is believed to develop locally throughout a waste-rock pile, channelling at the base of piles beneath a water table could have the greatest effect on the pattern of
water movement. For some types of construction techniques (Section 2.0), coarse rock preferentially collects at the base of a pile. In such cases, the channelling is abundant so that the entire base can be considered a high-conductivity layer rather than a discrete series of channels. Conceptual models (Cedergren, 1981) and simulations (McLaren, 1986) have demonstrated that a coarse-grained basal layer at the base of a pile or below a pile will act as the primary conduit for much of the water movement and will minimize the elevation of the water table. As with channels higher in the pile, Whiting (1981) reported that permeable foundations rapidly fill with rock particles and weathered clays that are flushed to the base of the pile and with mineral precipitants that form at the base. These processes can affect the geotechnical stability of a rock pile due to blockage of drainage, potentially leading to large-scale failure and collapse.

The Chemical Factors of Table 3-1 were not explicitly discussed by Whiting (1981), but it appears that these Factors were intended to represent the geochemical causes of mineral precipitation-dissolution and formation of clay minerals. Evangelou et al. (1982) examined these geochemical effects on water movement in more detail, reporting that solid-liquid as well as liquid-gas reactions significantly affected hydraulic conductivity. These researchers placed pyritic coal spoils, which were air dried, ground, and sieved, into 5-8 cm diameter columns and hydraulic conductivity (K) was measured at approximately 5 x 10^-6 m/s. Initial passes of water through the columns revealed depressed values of K which then increased to steady values with continued flushing. Numerically, the initially depressed values were usually less than a factor of 2 below the steady value, although an extreme difference of about 10 was measured in a large column. Evangelou et al. attributed the depressed values to mineral precipitation-dissolution, elevated viscosity (from dissolved solids), clay-mineral expansion and destabilization, and, where carbonate was present, to degassing of CO₂ gas to form an independent gas phase in pores. Many of these causes would be minimized by continued flushing, as observed. However, these results are prone to errors not mentioned by the authors, including (1) errors in calculated K due to the use of flux at the base of the columns and the gradients measured across short distances within the columns, (2) removal of air trapped in pores as flushing progressed, and (3) removal of fine-grained particles from the columns as flushing progressed. In light of these potential errors, a reasonable conclusion is that geochemical reactions do not have significant effects on water movement in spoils over relatively short time periods.

At this point, a more detailed evaluation is warranted on the concept of hydraulic conductivity and its application to waste-rock piles, independent of the nature of channelling and stratification. Whiting (1981) discussed various types of permeability, and, although his discussion is somewhat confusing, a re-interpretation leads to the delineation of two distinct types of permeability in waste-rock piles. The first is the bulk hydraulic conductivity of rock
to water flow, reflecting the quantity and interconnection of porespaces and channels. The second is matrix hydraulic conductivity, which is the conductivity of only the rock particles themselves to water. This latter type of conductivity is often negligible relative to the former and often has no effect on overall water movement. Nevertheless, even a negligible matrix conductivity can have a major impact on overall water chemistry if significant acid generation is occurring within the particles and the acidity is flushed out of the particles.

Although simple in concept, hydraulic conductivity is actually a parameter representing a composite function of characteristics of the rock, characteristics of the porespaces, and the density and viscosity of the water. The relevant characteristics of rock and porespaces have been discussed above under channelling and in other sections of this report, leaving density and viscosity to be discussed here. Whereas the characteristics of rock and its porespaces are highly variable and site-specific, the variability of density and viscosity in natural waters is relatively minor in near-surface environments. Where acid generation is occurring within a pile, there may be significant temperature variations and variations in total dissolved solids throughout the pile. However, these variations will in virtually all cases affect the value of hydraulic conductivity by less than a factor of 2. Consequently, variations in the characteristics of the water phase can usually be ignored in analyses of hydraulic conductivity for waste-rock piles.

Because the characteristics of the water phase in waste-rock piles do not affect the values of hydraulic conductivity, these characteristics can be removed through mathematical manipulation from "conductivity", leaving a parameter called "permeability" which is theoretically dependent only on the rock and porespace. Permeabilities of natural materials are often expressed in units of darcies and m². Because permeability is theoretically independent of the fluid, the permeability of waste-rock to water should be identical to that for air. However, Whiting (1981) presented unpublished data from an unidentified waste-rock pile which showed that measured permeabilities to air exceeded those to water by approximately a factor of 10. No explanations of the discrepancy were offered, but it could be an artifact of the test techniques or of the test intervals of boreholes. In any case, the calculation of permeability for gas transport (Section 5.0) based on measurements of hydraulic conductivity should be treated as tentative at this time.

Hydraulic Gradient

Another factor affecting water movement in waste-rock piles is hydraulic gradient (Equation 3-1), which represents variations in hydraulic potential (or head) from one point on a flow path in a pile to another. Water will move from a point of higher total head towards a point of lower total head in a three-dimensional pattern with components of lateral and
vertical flow. Total head is usually calculated from elevation head and pressure head (Freeze and Cherry, 1979), although other heads such as from velocity and osmotic pressure may be significant in some cases. At or below a water table, pressure head is typically monitored by installing a piezometer or well at the desired location and measuring the water level in the piezometer. Above a water table, pressure head is typically negative in value reflecting the presence of a suction or vacuum head. Nevertheless, water will move from locations of higher total head to lower head, with velocity and flow rate determined by a combination of hydraulic conductivity and the magnitude of the gradient (Equation 3-2).

The value of total head at any location in and around a waste-rock pile reflects a dynamic balance among such factors as rate of precipitation, surface topography, and distributions of hydraulic conductivity. For this reason, head distributions and hydraulic gradients are site-specific and not easily inferred. The general description of waste-rock piles (Figures 3-1 to 3-3) indicates that typically a downward movement of infiltration from the top of a pile can be expected, indicating the highest total head would usually be found near the top of the pile. As the water moves towards the base of the pile, head distributions and gradients become less predictable as suggested by Figures 3-1 to 3-4. A water table with significant lateral gradients may form at the base of the pile and may have its highest point in the center or towards one side of a pile.

Through computer simulations of spoil piles similar to Figure 3-1, Schwartz and Crowe (1987) found that the height and width of a pile has a major influence on the location of the water table and the hydraulic gradients. The simulations supported the reasonable conclusions that, at constant recharge (infiltration):

- as hydraulic conductivity (K) increases, the elevation of the water table will decrease (likely due to the enhanced drainage of water from the pile at higher K), and
- as the width of a pile increases, the gradients and water-table elevations increase (likely due to the increased volume of water to be transmitted through the pile).

Significant differences in gradients and water-table configurations were obtained upon varying conductivity by a factor of 10, indicating that conductivities measured within piles should be accurate to less than one order of magnitude. In the simulations of continuous basal drainage layers, the drains were only successful in maintaining a low water table in relatively small piles (small width) or in situations where conductivity contrasts between the pile and the drain were tremendous.

Maathuis and van der Kamp (1984) and van der Kamp and Maathuis (1985) showed that even the process of loading during construction can affect local hydraulic gradients. Based
on theory and field observations, hydraulic heads can be expected to increase in underlying strata during construction due to compression of the strata. The resulting enhanced gradients from the compression could lead to the migration of groundwater upwards into the base of a pile.

Groundwater Flow

The remaining factor affecting conductivity (Table 3-2) as well as hydraulic heads and gradients is the degree of water saturation or, in other words, the proportion of porespace containing water and gas. Rogowski and Weinrich (1977) described the dependency of groundwater flow on the degree of saturation in coarse mine spoils (presumably from a coal mine) with an average particle diameter of 1 cm and a range of about 0.1 mm to 10 cm. The effects of degree of saturation were evaluated by separating the finer fraction (< 2 mm) from the coarser fraction, testing each fraction independently, then mathematically combining the results. The observed relationship of degree of saturation (reported as water content by the authors) to hydraulic head, which is a negative value under unsaturated conditions, showed that a minor change in water content significantly affected the tension head (Figure 3-6). This behavior indicates that most of the water is tightly retained by the spoils. Similarly, a minor change in water content significantly decreased the hydraulic conductivity of the spoils (Figure 3-6). These relationships demonstrated that a small influx of water into the unsaturated spoils or slight drainage of saturated spoils can produce significant changes in the rate of water movement.

The issue of laminar vs turbulent flow in waste-rock piles is also important because it determines the physical behavior of water flow and the mathematical equations to accurately describe it. Groundwater flow is often laminar in nature, that is, without eddies or vortices, because of its typically slow rate of movement. The aforementioned concept of Darcy's Law (Equation 3-2) implicitly assumes that laminar flow is present in waste-rock piles. In the large porespaces that exist in coarse-grained rock, the potential exists for turbulent flow with local eddies, vortices, and other irregularities, which would render Darcy's Law and related equations inaccurate descriptions of flow. A parameter known as the (dimensionless) Reynold's Number indicates conditions under which turbulent flow could be expected. For a porous medium,
\[ \text{Re} = \frac{pqd}{u} \]
\[ = \frac{qd}{v} \]

(Equation 3-3a)
(Equation 3-3b)

where \( \text{Re} \) = Reynold's Number (dimensionless)
\( p \) = density (kg/m\(^3\))
\( q \) = K i (derived from Equation 1, m/s)
\( d \) = mean pore diameter, mean grain diameter,
or a function of the square root of permeability (m)
\( u \) = dynamic viscosity (Ns/m\(^2\))
\( v \) = kinematic viscosity (m\(^2\)/s)

FIGURE 3-6. Relationships of Degree of Saturation to (a) Tension Head and (b) Hydraulic Conductivity (adapted from Rogowski and Weinrich, 1977).

Values of Re greater than 1 to 10 for groundwater flow in a porous medium typically indicate the existence of turbulent flow (Freeze and Cherry, 1979).

For dilute groundwater at 20°C, kinematic viscosity (v) is \( 1.5 \times 10^{-5} \) m\(^2\)/s. If this groundwater were moving through a rock pile with a conductivity (K) of \( 10^{-3} \) m/s, which is typical of gravel, at a gradient (i) of 1.0, then \( \text{Re} = 66.7 \) d. Consequently, any value for \( d \) (grain diameter) greater than about 0.1 meters would be expected to produce turbulent flow. If \( K \) were \( 10^{-5} \) m/s, then only a \( d \) greater than approximately 10 m would lead to turbulent flow. Based on these calculations, turbulent flow should only be anticipated in very coarse rock piles with high values of hydraulic conductivity.

As explained in textbooks on fluid engineering, turbulent flow is conceptually and mathematically more complex than laminar flow. Characteristics of turbulent flow in pipes can
be described by complex functions of Re, but simplifications can be made based on experimental observations. The simplification reported for coarse rock is a power function of gradient or hydraulic conductivity (McLaren, 1986):

\[ q = K i^n \]  \hspace{1cm} \text{(Equation 3-4)}

where \( n = 0.5 \) for fully turbulent flow and 1.0 for fully laminar flow
\( q \) = normalized flux (flow through a 1 m² cross-section),
incorrectly reported as "groundwater flow velocity" by McLaren

Based on a literature review, Gill (1976) reported the equation for steady-state flow as:

\[ i = aq + bq^2 \]  \hspace{1cm} \text{(Equation 3-5)}

where \( a \) = coefficient of linear (laminar) resistivity
(reciprocal of Darcy hydraulic conductivity, s/m)
\( b \) = coefficient of quadratic (turbulent) resistivity
(s²/m², units are reported incorrectly Gill)
\( q \) = "seepage velocity" or, more correctly, normalized flux (m/s)

For laminar flow, \( b=0 \) and, for turbulent flow, \( a=0 \). For mathematical validity, either \( a \) or \( b \) must be zero, which results in an equation equivalent to Equation 3-4. This implied limitation, as well as non-standard terminology throughout the paper, redefinition of variables within the paper, and simplifications in deriving other equations suggest that Gill (1976) should not be consulted for detailed information on turbulent flow.

In order to simplistically predict water movement in rock piles by usually avoiding the complexity of turbulent flow, several authors have resorted to basic mass-balance equations. Wardwell et al. (1982) and Nelson and McWhorter (1981) provided such equations, some assuming laminar flow, but due to their generally simplistic nature these equations should be used with caution. The most valuable equations will be presented below and the simplifying assumptions will be highlighted.

Wardwell et al. (1982) and Nelson and McWhorter (1981) envisioned a symmetrical homogeneous rock pile in a recharge area (similar to Figure 3-1) exposed to a long, continuous rainfall. The pile is assumed to rest on a horizontal, impermeable stratum (unlike Figure 3-1). Prior to the rainfall, the water content of the rock (\( O_d \)) is homogeneous throughout the pile. The rainfall onto of the pile creates a "wetting front" of greater water
content moving downwards from the surface. This conceptualization assumes that channelling is negligible. The time for the wetting front to reach the base of the pile, or a perched low-permeability stratum, assuming full infiltration of rainfall is:

\[ t = (O_f - O_i) \frac{D}{W} \]  \hspace{1cm} (Equation 3-6)

where \( t \) = time to reach the base or perched stratum (s)
\( O_f \) = water content above wetting front (m\(^3\)/m\(^3\))
\( O_i \) = initial water content (m\(^3\)/m\(^3\))
\( D \) = depth to base or stratum (m)
\( W \) = rainfall rate (m/s)

As the rainfall continues and the wetting front reaches the base of the pile, a water table forms and begins to rise upwards into the pile with the greatest height found at the center of the pile (e.g., Figure 3-1). When steady-state flow is attained (as the rainfall continues), the maximum height of the water table (\( H_m \)) is:

\[ H_m = \left(\frac{W L^2}{4 K_s}\right)^{1/2} \]  \hspace{1cm} (Equation 3-7)

where \( H_m \) = maximum height of the water table above the base of perched stratum (m)
\( W \) = rainfall intensity (m/s)
\( L \) = lateral width of the pile's base from toe to toe (m)
\( K_s \) = saturated hydraulic conductivity (m/s)

Equation 3-7 assumes that all groundwater leaves the pile at saturated seepage faces at the toe because the underlying stratum is assumed to be impermeable.

Equation 3-7 can be translated into a design chart which simplifies its use (Figure 3-7). This chart graphically shows that \( H_m/L \) increases as \( K_s \) decreases or as \( W \) increases. If \( K_s = 10^{-4} \) m/s and \( W = 0.01 \) m/d (1.2 x 10\(^{-7} \) m/s), then \( H_m/L = 0.017 \) and, if the width of the pile is 200 m, then \( H_m = 3.4 \) m.

The time to reach the steady-state value of \( H_m \) can be calculated from the time for the wetting front to reach the base and the time for the water table (the top of the zone of full saturation) to rise to the maximum height. The authors calculated this time by assuming that no lateral flow occurs below the water table, which would often result in a significant underestimation of the actual time. The equation is:
\[ T = H_m(n-O_f)/W + (O_f-O_i)D/W \]  

(Equation 3-8)

where \( T \) = time for the water table to reach \( H_m \) from the start of rainfall (s)  
\( n \) = porosity

Using the previous example of \( H_m = 3.4 \text{ m} \) and \( W = 0.01 \text{ m/d} (1.2 \times 10^{-7} \text{ m/s}) \) as well as \( D=20 \text{ m}, n=0.20, O_f=0.05, O_i=0.10, \) then \( T=129 \text{ d} \). As mentioned above, this value is probably unrealistically low. If the steady rainfall were to cease before \( T \), then most of these simplistic equations would not be applicable. This requirement of a constant, long-term rainfall is a major weakness in this model.

East et al. (1987) also considered the same scenario, but with a sloping impermeable base for heap leaching. The highest point of the base was assumed to be beneath the center of the pile so that only one-half of a pile would have to be considered due to symmetry. The resulting equation is:

\[ h_t = \left\{ h_o^2 - W[(x^2-(L/2)^2)]/K - Lh_0\tan(a) + x^2\tan^2(a) \right\}^{1/2} - x\tan(a) \]  

(Equation 3-9)

where \( h_t \) = height of water table above the pile's toe (m)  
\( h_o \) = height of seepage face at the pile's toe (m)  
\( W \) = steady-state infiltration rate (m/s)  
\( x \) = distance from pile's centerline for \( h_t \) (m)  
\( L \) = total distance from centerline to toe (m)  
\( K \) = hydraulic conductivity (m/s)  
\( a \) = angle of sloping base from horizontal (deg.)

The applicability of this equation is limited by the same assumptions as the model with the preceding equations.

Despite the well recognized stature of the modelling of acid drainage by Jaynes et al. (1984 a and b), their work suffered from unrealistic simplification on the aspect of water movement. These researchers envisioned a spoils pile comprised of a series of horizontal layers with water movement in the vertical direction only. The water leaving the base of any one layer was proportioned among all underlying layers as a function of the distance between the layers (later in the papers, changed to a function of the depth). The water transferred to deeper layers was assumed to arrive in each layer instantaneously with no contact with intervening layers. This model apparently simulates some type of discontinuous channelling, but the researchers neither justify this approach nor indicate the physical evidence needed to establish the applicability of this model to a field site.
In conclusion, water movement in and around waste-rock piles represents the primary pathway for contaminants to migrate from a pile into the local environment. Three conceptual models were developed to describe a continuum of hydrogeologic conditions, ranging from a recharge area to a discharge area (Figures 3-1 to 3-3). The review of literature has demonstrated that these models are compatible with all conceptualizations of rock piles.

The nature and pattern of water movement reflect the interaction of several processes including climatic events, primarily precipitation, surficial events, such as runoff, and internal factors, such as hydraulic conductivity. Because the water that moves through rock piles frequently accumulates the greatest loadings of contaminants, emphasis has been placed on internal controls of water movement. These controls were identified as site-specific distributions of hydraulic conductivity, hydraulic gradients, and laminar/turbulent flow. Spatial and temporal distributions of hydraulic conductivity within rock piles was found to be particularly sensitive to factors such as stratification and degree of saturation.
This section on theory of water movement is critical to the understanding of contaminant migration in and from waste-rock piles, because no well-documented case studies of water movement have been located. Consequently, many conclusions derived from theory cannot be confirmed with field observations, but provide topics for further study in future studies of piles.

3.2 Case Studies

This section presents case studies drawn from the literature review. Most of the studies are in-field programs although a few valuable bench-scale and pilot-scale studies are included. None of the reviewed reports and publications contained an integrated hydrologic study of a dump as suggested in Section 3.1. Consequently, most of the following case studies are limited to one aspect of water movement such as hydraulic conductivity.

The findings of each study are site-specific so that detailed comparisons are not made among the studies. Each case study is presented independently to illustrate its relationship to various aspects of theory of water movement from Section 3.1.

Small-scale and Pilot-scale Study of Water Movement Through Waste-rock Piles: ElBoushi (1975)

ElBoushi (1975) examined small-scale water movement in small rock piles and rock-filled cylinders with volumes up to 1.7 m$^3$. Beginning with completely dry basaltic rock, water was sprayed evenly on top of the rock until flow from the bottom was visually observed. The amount of sprayed water (as percentage of total rock volume) to initiate flow and the bulk specific water retention of the rock were compared to particle size (Figure 3-8), leading to two major observations. Firstly, in contradiction to the soil literature, flow was initiated at levels below specific retention. However, extrapolation of the curves to a diameter of 0.15 mm (Figure 3-8) showed that the typical relationship would be found at diameters less than 0.15 mm, which is more typical of soils. Secondly, in coarse rock, less than 1% of water (as percentage of total rock volume) was needed to initiate water flow. The suspected explanation for these observations was the formation of distinct rivulets in the deeper rock (channelling) so that much of the deeper rock surface was not contacted by the water.

To confirm the suspected channelling, diluted white paint was sprayed onto rock after bottom flow had been observed and visual estimates of paint-coated surfaces were made as the rock piles were dismantled. The results (Figure 3-9) showed that only 15-20% of surfaces were coated at depths of 20-30 cm in the finer-grained rock and at depths greater than 90 cm in
FIGURE 3-8. Relationship of Particle Diameter to Water Volume to Initiate Flow and Specific Water Retention.

FIGURE 3-9. Relationship of Percentage of Coated Surfaces to (a) Depth Within the Piles (Data from ElBoushi, 1975) and (b) Depth Normalized by the Cube Root of Particle Diameter (Calculated as Part of This Study).
a coarser-grained field test. This indicated that all of the water infiltrating through the surface rock was channelled into 15-20% of the rock porespace at these depths. Analysis of ElBoushi's data for presentation in this report revealed a relationship of surface coverage to grain size and that consistent results were obtained for all three grain sizes when the depths in centimetres were divided by the cube root of the particle diameter in mm (Figure 3-9). This relationship may allow an extrapolation to other grain sizes and to other sites, although the validity of the extrapolation is unknown.

Small-scale Tests of Channelling: Nalsmith and Kirchner (1980)

Upon conceptualizing a rock pile as a packed bed, these researchers reviewed relevant literature and conducted laboratory studies of water movement and distribution. Previous studies had considered the nature of unsaturated flow through packed beds as either a diffusion-related process (essentially described by Fick's Laws, see Section 4) or a flow-rate dependent process.

A container in the shape of an inverted triangle (pointing downwards) and of unspecified dimensions (presumably on the order of about 1 meter on a side) was constructed with "collector outlets" placed at various lateral and vertical spacings. This container was filled with "crushed copper ore" of an average size of 5 cm diameter. Water was applied to a single location (presumably at the top center of the container) at rates of 0.2-6 L/min (said to be equivalent to 0.03-0.8 L/s/m²). Few details are presented on the application of the different flow rates, the grain size distributions, the nature of the various "packings" used by the researchers, and the design of the collector outlets so that interpretations cannot be confirmed.

These researchers found that channelling was the predominant flow pattern at flow rates below 3 L/min. Above this rate, "sheetlike flow" was predominant. Water movement was then simulated mathematically using a node system with a random number generator. Their model is not considered valuable because it is not based on physically defined parameters and apparently requires random manipulation of the random number generator for calibration to each flow condition.

Kennecott's Chino Dump, New Mexico: Wadsworth (1981)

Wadsworth (1981) presented the only borehole geophysical log located by this review. The borehole was drilled in Kennecott's Chino Dump in New Mexico (Figure 3-10) and the log revealed the presence of stratification. The zones of high bulk density on the gamma-gamma
FIGURE 3-10. Geophysical logs for a borehole in the Chino Dump, New Mexico (from Wadsworth, 1981).
log can be interpreted as regions of higher compaction and smaller grain size. These high density zones are correlated with high moisture on the neutron-neutron log, suggesting the reasonable relationship that finer-grained layers retained more moisture. Nevertheless, perched water tables do not seem to have accumulated above the finer-grained layers so that unsaturated water movement is predominant in the area around the borehole. Borehole geophysical logs may be a useful tool in defining water movement and stratification in waste-rock dumps because current drilling techniques which grind the waste rock preclude a reliable assessment of in-situ grain size.


The Rum Jungle Mine in northern Australia is an internationally recognized case study of acid generation and control technologies. There are two major waste-rock piles at the minesite, the White’s and Intermediate Dumps (Figure 6-18). Water balances for these two dumps were found to be:

<table>
<thead>
<tr>
<th>AS PERCENTAGE OF PRECIPITATION:</th>
<th>White’s</th>
<th>Intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation</td>
<td>25-35%</td>
<td>25-35%</td>
</tr>
<tr>
<td>Runoff over dump</td>
<td>10-22%</td>
<td>10-22%</td>
</tr>
<tr>
<td>Springs at toe</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>Seepage to underlying groundwater</td>
<td>38-60%</td>
<td>43-65%</td>
</tr>
</tbody>
</table>

Consequently, the largest portion of the water remained in the subsurface, internally moving through the dump into the underlying groundwater system. The pollution loadings in the runoff were only a few percent of those in the groundwater seepage due to the greater rock-surface contact in the subsurface. The loadings in the groundwater are expected to persist for another 10 to 20 years.

Several hydrologic observations were made on White’s Dump. Firstly, moisture content from neutron and gamma probes was found to be constant at depths greater than 2 m. This indicates that surficial processes such as evaporation (Table 3-2, Section 3.1) are negligible below that depth and that water movement from rainfall events is highly channelized and transient and thus not significantly affecting bulk moisture content at that depth, in agreement with ElBoushi’s work (Figure 3-9). Secondly, "quite large" cavities and pores were observed around the perimeter of the dump, although there was no evidence to indicate that the large
cavities continued into the interior of the dump. Even if the cavities were continuous, the water balance showed that their presence did not significantly affect water movement (5% of flow from toe springs). Thirdly, the top of the dump contained flat stones of 1-2 cm diameter, probably reflecting the removal of surficial finer-grained particles by runoff and migration into the dump (Section 4). The impact of this migration of solids on water movement was not explored by the authors. Fourthly, measurements of hydraulic conductivity were made on several rock types found in the dump.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>$K$ (m/s, geometric mean)</th>
<th>% Area of Dump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey-black shale and slate</td>
<td>$3.7 \times 10^{-6}$</td>
<td>71</td>
</tr>
<tr>
<td>Red-brown shale and slate</td>
<td>$3.6 \times 10^{-6}$</td>
<td>1</td>
</tr>
<tr>
<td>Quartz and dolomite</td>
<td>$2.7 \times 10^{-7}$</td>
<td>6</td>
</tr>
<tr>
<td>Fine alluvial material</td>
<td>$7.4 \times 10^{-7}$</td>
<td>2</td>
</tr>
<tr>
<td>Coarse alluvial material</td>
<td>$2.3 \times 10^{-5}$</td>
<td>1</td>
</tr>
<tr>
<td>Loose rock heaps</td>
<td>$5.7 \times 10^{-4}$</td>
<td>17</td>
</tr>
</tbody>
</table>

These values, except for the rock heaps, spanned a relatively narrow range of two orders of magnitude. The highest value for the rock heaps probably reflected the coarser nature of the rock. Fifthly, flow from springs on the northeast corner continued half-way through the dry season, suggesting the presence of a perched water table which slowly released water. The implications of hydraulic conductivity on water movement and contaminant migration were not discussed in detail in the publications.

**Stratification in a Heap-leach Pile: Kinard and Schweitzer (1987)**

These researchers examined a heap leach pile of dimensions 150 x 225 m with an average height of 9 m. The pile contained argillized basaltic andesite with at least 60% clay (kaolinite and montmorillonite), placed with a radial stacker after crushing and agglomeration with lime (5 kg/t). Four months after placement, tests pits up to 6 meters deep were dug into the pile. These pits showed that there were alternating zones of: coarse rock (1.3-5.0 cm diameter, with some fines), fine-grained rock (90-100% passing #200 sieve), and well-graded material (2.5 cm to 3% passing #200 sieve).

Measurements of hydraulic conductivity were performed on saturated and consolidated undisturbed samples and on recompacted samples. The values ranged from approximately $1 \times 10^{-6}$ to $5 \times 10^{-9}$ m/s, generally showing a trend of decreasing $K$ with increasing dry density.
Lignite Spoil Piles, North Texas: Kuhlmeier (1985)

Kuhlmeier (1985) examined three spoil piles of approximately 15 m height from lignite mining in north Texas. The grain-size distribution of the spoils were found to be predominately silt with no clear trend towards sand or clay with depth. Approximately 56 cm of the annual precipitation of 117 cm was calculated to be available for infiltration.

Two boreholes were drilled in each pile and short cores (split-spoon samples) were collected every 1 m. Composites were created for 0-33%, 34-67%, and 68-100% of total depth. Hydraulic conductivities for the three intervals were approximately $1 \times 10^{-9}$, $7 \times 10^{-8}$, and $3 \times 10^{-7}$ m/s, respectively. This trend in average values was not explained by the author, although it contradicted the lack of trends toward coarser material with depth. Porosity was found to be approximately 30%.

Movement of a wetting front downward through the spoils was predicted with the unsaturated Darcy Equation. The equation provided a good match to field results.

BHP-Utah’s Navajo Mine, New Mexico: Stone (1988)

Due to the difficulty in monitoring water movement through unsaturated spoils, Stone (1988) attempted to use stable isotopes and chloride to delineate recharge events and moisture accumulation in spoils contained in a coal-strip pit at BHP-Utah’s Navajo Mine in northwestern New Mexico. Annual precipitation at the site was 14.5 cm and evaporation was 142.0 cm so that significant recharge to the spoils was not anticipated. Seven undisturbed and 25 reclaimed sites were sampled and analyzed, but erratic results yielded little information. Nevertheless, Stone concluded that moisture and solute profiles in the area recovered in 6-10 y after mining was terminated.

Two Mine Spoil Piles, Pennsylvania: Ladwig and Campion (1985)

These researchers studied water movement in detail at two mines with spoil piles in Pennsylvania. Site 1 (111 ha) in south-central Pennsylvania contained coal-bearing spoils from clay mining with an unsaturated zone of 25 to 30 m in thickness, localized perched water tables, and a primary water table 1 to 5 m above the base of the spoils. The slope of the water table was found to be determined by the slope of the underlying impermeable mine floor. Despite high seasonal variations in precipitation and runoff, water-table fluctuations were mostly less than 0.5 meters. Figure 3-3 of Section 3.1 indicates best the generalized depiction of the flow system at the site.
The hydraulic conductivity of the spoils at Site 1 were measured by pump and slug tests at $10^{-3}$ to $10^{-5}$ m/s with unmined strata at $10^{-5}$ to $10^{-6}$ m/s. A tracer test indicated that the highest K values ($10^{-3}$ m/s) described best the transport of the tracer, demonstrating that channelling was probably the dominant control on water movement in the spoils.

A water balance for Site 1 indicated that 10-20% of the basal discharge from the spoils (23,000-46,000 m$^3$/y) was derived from lateral flow from laterally adjacent unmined strata and the remainder was derived from infiltration of precipitation. The volume rate of infiltration represented approximately 25% of total precipitation at the site.

Site 2 was a 43-hectare surface coal mine in southwestern Pennsylvania with two laterally adjacent flow zones in the spoils. The downgradient saturated zone formed against a clay barrier which retarded groundwater flow. The laterally upgradient zone was unsaturated and recharged the downgradient zone through channelling.


In a demonstration of the site-specific nature of hydraulic conductivity, these researchers reported that pumping tests at six AMAX coal mines across the midwest USA yielded conductivities of $4.6 \times 10^{-7}$ to greater than $4.7 \times 10^{-4}$ m/s. At one mine alone, 17 wells yielded conductivities of $8.1 \times 10^{-6}$ to greater than $4.7 \times 10^{-4}$ m/s with a median value of $3.5 \times 10^{-5}$ m/s. The variability was attributed to such factors as pre-mining overburden properties, methods of overburden handling and replacement, and time since initiation of mining. Herring and Shanks concluded that large variations in conductivity of mine wastes should be expected at any mine.

**Coedely Spoil Heap, Wales, Great Britain: Martin and Thomas (1974)**

This spoils heap was a large conical pile which had expanded laterally due to geotechnical failures (Figures 3-11 and 3-12). Groundwater was found to flow through the natural strata from an upgradient recharge area, discharge upwards from the strata into the spoils, and then move downslope parallel to the spoil-strata contact (similar in many ways to Figure 3-3 in Section 3.1).

Following the subsurface injection of bacteriophage (parasites of bacteria) as a conservative tracer upgradient of the spoils, water samples were periodically collected from piezometers,
FIGURE 3-11. Geological Section Through Coedely Spoil Heap (from Martin and Thomas, 1974).
monitor wells, springs, and streams over a period of 25 days. Although there were problems with sampling and analysis, the results were informative (Table 3-3).

### TABLE 3-3
Results Of The Ground Water Tracer Test At The Coedely Spoil Heap.

<table>
<thead>
<tr>
<th>SAMPLING POINT</th>
<th>TIME TO PEAK (hrs)</th>
<th>DISTANCE FROM WELL #16 (m)</th>
<th>INJECTION CALCULATED VELOCITY (m/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piez 13</td>
<td>&lt; 52</td>
<td>240</td>
<td>&gt;4.6²</td>
</tr>
<tr>
<td>Piez 1</td>
<td>76</td>
<td>530</td>
<td>7.0</td>
</tr>
<tr>
<td>Piez 2</td>
<td>76</td>
<td>510</td>
<td>6.7</td>
</tr>
<tr>
<td>Piez 15</td>
<td>&lt;192</td>
<td>30</td>
<td>&gt;2.8²</td>
</tr>
<tr>
<td>Well 14</td>
<td>76</td>
<td>570</td>
<td>7.5</td>
</tr>
<tr>
<td>Spring 9</td>
<td>76</td>
<td>500</td>
<td>6.6</td>
</tr>
<tr>
<td>Spring 12</td>
<td>&lt;192</td>
<td>540</td>
<td>&gt;2.8²</td>
</tr>
<tr>
<td>Stream (16)</td>
<td>&lt;192</td>
<td>620</td>
<td>&gt;3.2²</td>
</tr>
<tr>
<td>Spring 17</td>
<td>&lt;192</td>
<td>630</td>
<td>&gt;3.3²</td>
</tr>
<tr>
<td>Spring 18</td>
<td>&lt;192</td>
<td>680</td>
<td>&gt;3.5²</td>
</tr>
<tr>
<td>Stream (4)</td>
<td>192</td>
<td>290</td>
<td>1.5</td>
</tr>
</tbody>
</table>

1. see Figures 3-11 and 3-12 for locations
2. sampling problems prevented confirmation of peak arrival
These results indicated that lateral spreading over 100 m (to Stream (4)) occurred within 8 d, compared to 680 meters of downgradient flow.

**Fording River Mine, British Columbia: Nichols and Rutledge (1982)**

Nichols and Rutledge examined three waste dumps from coal mining at the Fording River Minesite in southeastern British Columbia. Waste materials were partitioned into three categories: waste-rock, overburden, and "rehandle". The latter two groups contained a high percentage of fine-grained particles, were relatively impermeable to water, and were not examined in the study. The waste-rock consisted on average of 55% siltstone, 28% sandstone, 15% carbonaceous mudstone, and 2% coal. Both the sandstone and siltstone were well indurated and thus only broke along orthogonal joints into rocks of 0.1 to 1.0 meter diameter. The mudstone was observed to weather into fine-grained particles.

The first dump, "K Spoil" (Figure 3-13), was 30 m high, built on till with a slope of 12°, and was apparently built by end dumping causing coarser rock to collect at the base (Section 2.0). This pile was composed of an estimated 85% unweathered siltstone and 15% weathered siltstone and till. When a diversion ditch became plugged, up to 56 L/s flowed through a small section of the base of the dump, along the former creek bed. This water carried 1800 mg/L of suspended solids, which represented an increase of 600 mg/L over the inflow concentration. This was thought to show that plugging was not likely.

The second dump, "Turnbull Spoil" (Figure 3-13), was 50 m high, built on till with a slope of 10°, and was composed of an estimated 90% sandstone. This pile was apparently formed by end dumping, but was re-sloped for reclamation. As with the K Spoil, surface-water diversion was not fully successful and up to 116 L/s flowed through the base of the dump. However, suspended solids were only 1 mg/L, which was said to indicate no erosion of the base.

The third dump, "A Spoil" (Figure 3-13), was 48 m high and built on till with a slope of 5°. This dump was composed of 80% carbonaceous mudstone, placed and compacted in 1.6 m lifts. A flow rate of 32 L/s was measured with suspended solids of 1 mg/L, which was interpreted as reflecting the stability and non-erodibility of the fine wastes. However, unlike the other dumps, the flow originated only through infiltration of precipitation and gravity drainage of the moist waste material. A piezometer placed in the dump indicated that no water table existed in the wastes and the underlying till was considered impermeable so that the pattern of water movement through the dump was apparently not well defined.
FIGURE 3.13. Waste Dumps at Fording Coal Operation (from Nichols and Rutledge, 1982).

These mines are located on opposite sides of the Battle River, approximately 200 km southeast of Edmonton. The local stratigraphy consists of Cretaceous sandstone, siltstone, shale, coal, and bentonite beds. These strata are overlain by glacial deposits, which are predominately till. The spoils from mining were placed in the pits and the pattern of water movement through the spoils represents the only detailed case study similar to Figure 3-2 found during the literature review.

At the Diplomat Mine on the north side of the river, 33 piezometers were installed in 10 nests over a 0.8 km² reclaimed area of the pit. Ponds had formed in depressions on the reclaimed surface and were found to play a major role in determining groundwater movement (Figure 3-14). As well, a portion of water movement was derived from lateral groundwater flow across the north pit wall into the spoils. Most of the groundwater moved to the center of the cross-section depicted in Figure 3-14 and then moved towards the southwest (out of the plane of the page) and the Battle River. This water reportedly moved preferentially at the base of the spoils where rubble zones and unmined fractured coal formed conduits. The potentiometric surface map for the base of the spoils (not shown) formed a more regular pattern than the shallow water table, indicating that the surface ponds did not significantly affect the deeper flow.

At the Vesta Mine on the south side of the Battle River, 26 piezometers were installed in 8 nests over a reclaimed area of 1.0 km². As with the Diplomat spoils, the surface ponds regulated shallow water movement (Figure 3-15). Depending on the location within the pit, the spoils were found to either recharge the adjacent unmined strata or accept water from them.


In 1982, approximately 200,000 m³ of highly mineralized slate was excavated and placed in a waste-rock dump for taxiway construction at the Halifax Airport. The dump was constructed on a sloping till layer (Figure 3-16) and monitoring wells were installed in and around the pile. Water levels indicated that the water table was beneath the waste-rock in the elevated portion of the pile and generally 1 meter above the waste-rock-bedrock contact in the lower portion. Hydraulic gradients were found to be 0.01 to 0.02 laterally and 0.3 to 0.8 vertically so that groundwater flow was predominately vertical. Values of hydraulic conductivity were similar
FIGURE 3-15. Water Movement in Spoils at the Vesta Mine (from Trudell and Moran, 1982).
FIGURE 3-16. Water Movement In a Waste Rock Pile at the Halifax Airport (from Lund, 1987).
for bedrock \((6.67 \times 10^{-6} \text{ m/s})\) and waste-rock \((2.55 \times 10^{-6} \text{ m/s})\), indicating the waste-rock and bedrock can essentially be treated as one stratum relative to groundwater flow. This scenario was also found at the Westmin Myra Falls Mines (below). Based on the hydrogeologic information, groundwater velocity was calculated to be on the order of 0.6 m/d.

**Waste-rock Dump #1, Westmin Myra Falls Mine, British Columbia:**

*Northwest Geochem (1990)*

The Myra Falls Minesite is located in a relatively narrow and steep valley in the central region of Vancouver Island, British Columbia. Beginning in 1967 and continuing sporadically to the present, the waste-rock was placed in lifts on the valley floor against the valley wall, as generally depicted in Figure 3-3 of Section 3.1. The pile has a maximum thickness of 42 m.

Fifty-seven boreholes were drilled into the pile (Figure 3-17) to obtain solid samples and to allow the installation of 51 monitor wells in 22 of the boreholes. During drilling, difficulties were encountered in distinguishing deep waste-rock from bedrock, suggesting that the physical and geochemical characteristics of the two rock types were similar as also noted at the Halifax Airport (above).

Based on water levels in the wells, the water table was either within the pile or in the bedrock depending on location. Nevertheless, the water table generally displayed a smooth lateral gradient from contact with the valley wall to the valley floor (Figure 3-18). Seasonal water-quality analyses suggested that the primary source of groundwater flowing through the pile was, during drier times of the year, pH-neutral background water from the adjacent valley wall and, during wetter times, acidic infiltration through the acid-generating waste-rock.

Hydraulic conductivities of the fractured bedrock ranged from \(3.2 \times 10^{-8}\) to \(1.6 \times 10^{-6} \text{ m/s}\) and conductivities of coarse waste-rock were found to be greater than \(10^{-4} \text{ m/s}\). For the purposes of calculations, the deeper waste-rock and the underlying shallow fractured bedrock of similar characteristics were assumed to have conductivities in the range of \(10^{-6}\) to \(10^{-5} \text{ m/s}\). With the measured gradient of 0.2 and an assumed porosity of 0.1, average linear groundwater velocities beneath the water table were calculated to be 0.17 to 1.7 m/d. At this rate, up to hundreds of days would be required for groundwater to flow from the valley wall to the toe of the pile. On the other hand, rainfall on the exposed surfaces of the dump probably reached the water table with a few hours to days, causing the water table to fluctuate up to a few meters throughout the year.
FIGURE 3-17. Borehole locations and surface elevations at the Westmin Myra Creek waste rock dump.
WATER TABLE ELEVATIONS
(9/26/88)

MINE NORTH

CONTOUR INTERVAL = 4 M

FIGURE 3-18. Water table elevation in and beneath the Westmin Myra Falls dump.
4.0 MIGRATION OF SOLIDS

4.1 Theory

In addition to water movement and gas transport, the third type of phase transport is the migration of solid (rock) particles through waste-rock piles. From the conceptual perspective of a system (Figure 1-2), there are two basic modes for migration of solids in and around waste-rock piles (Table 4-1). The first is Internal Migration of smaller rock particles downward around coarser rock particles and the second is Geotechnical Failure where entire portions of piles are mobilized downwards toward, and/or outwards from, the toe of the pile. These modes of migration can influence the severity and extent of acid drainage from a pile through such effects as increased or decreased permeability to water (Section 3.0) and air (Section 5.0) or transport of sulfide minerals (Section 6.0) to or from regions of enhanced oxidation.

| TABLE 4-1 |
| Modes of Solid-Phase Migration In and Around Rock Piles |

Internal Migration

- downward migration of finer rock particles around coarser particles, caused by physical and geochemical processes with the dump

Geotechnical Failure

- externally visible, downward movement of entire portions of a dump towards its toe, caused by:
  - (a) internally generated forces,
  - (b) external slope erosion, and
  - (c) foundation failure

There is a major discrepancy in the literature regarding the internal migration of particles. Some publications indicate this migration rarely occurs, whereas numerous publications state that such migration is common. On the basis of number of references, internal migration of solids should be expected in waste-rock piles unless demonstrated otherwise on a site-specific basis. This process will be discussed in greater detail below so that the conditions leading to the migration will be better understood.
Due to physical processes such as weathering and geochemical processes such as mineral precipitation, Whiting (1981) reported that internal migration of particles led to clogged channels within piles and a relatively low-permeability layer at the base of piles. This accounted for the typically observed decrease in permeability of piles through time. Similarly, Wadsworth (1981) reported that a pile with igneous and metamorphic rock had an initial porosity of 35-40%, which decreased to 25% after compaction and weathering. This was expected to lower hydraulic conductivity as well.

From the perspective of heap leaching, internal migration can cause economic problems by reducing permeability and isolating sulfide minerals from the leach solutions. Consequently, field studies have been conducted in heap-leach piles to determine methods to reduce the migration. The typical method is to blend a compound with the rock such as cement and lime during construction of the pile (e.g., Kurtz et al., 1987; Zarate and Guzman, 1987).

The pattern of weathering of waste rock to smaller particles within a pile has not been addressed in the literature and is probably not easily predicted or determined. This difficulty, combined with the general lack of drilling and monitoring in waste-rock piles, may account for the conflicting opinions in the literature on the extent of internal migration. There is some capability for prediction for the simple scenario where a fine-grained layer lies directly over a coarse-grained layer. To prevent migration of solids into the underlying coarse-grained layer ("piping") in this scenario, field observations have shown that the following relationship must be fulfilled (Cedergren, 1981):

\[
\frac{D_{15,\text{coarse}}}{D_{85,\text{fines}}} < 4
\]  

(Equation 4-1)

where \(D_{85,\text{fines}}\) = the grain diameter at which 85% of the fine layer has a smaller diameter

\(D_{15,\text{coarse}}\) = the grain diameter at which 15% of the coarse layer has a smaller diameter

Joy (1989) and Joy et al. (1990) carried this analysis further through laboratory experiments and predictive mathematical simulations. In the laboratory experiments, solids migration was examined in porous media similar to waste rock and valley fills, and through variations in sediment size, fluid velocity, Reynold's Number (180 to 940), slope of basal surface (9 to 60%), and ratio of immobile media to mobile sediment (13.9 to 91.7). The conclusion derived from these experiments was that internal sediment transport was site specific and should be evaluated and simulated independently. However, Joy (1989) found that one equation could
describe sediment transport in the experiments with an error of apparently one order-of-magnitude or less. This equation is:

\[ q_* = 26.2 R_m^{-1.23} S_r^{0.540} S_s^{-1.39} \]  

(Equation 4-2)

with

\[ q^* = q_a n/(p_s d_s V_b) \]  

(Equation 4-3)

\[ R_m = V_b d_m/(n k) \]  

(Equation 4-4)

\[ S_r = d_m/d_s \]  

ratio of immobile media to mobile sediment  

(Equation 4-5)

\[ S_s = \tan(a-t) \]  

slope parameter  

(Equation 4-6)

where

\[ q_* \]  

unit-width sediment transport rate (kg/m/s)

\[ n \]  

porosity of immobile media

\[ p_s \]  

density of mobile sediment (kg/m³)

\[ d_s \]  

diameter of mobile sediment (m)

\[ V_b \]  

apparent fluid velocity (m/s)

\[ d_m \]  

diameter of immobile media (m)

\[ k \]  

kinematic viscosity of fluid (m²/s)

\[ a \]  

angle of repose of sediment within media (degrees)

\[ t \]  
	slope of basal layer (degrees)

Two critical assumptions made by Joy (1989) and Joy et al. (1990) for predictive simulations were that only sediment particles less than 2.0 mm in diameter were mobile and that only sediment below the water table could be transported. The latter assumption established the importance of defining water movement through the rock (Section 3.0)

The second basic mode of migration of solids is geotechnical failure (Table 4-1). There is significantly more literature on this issue than on internal migration.

Geotechnical failures can occur in many ways (e.g., Figure 4-1) and many authors have presented various classifications schemes for the failures (e.g., Caldwell and Moss, 1981; Cavers, 1987). However, for simplicity, the scheme of Whiting (1981) will be reviewed here.

Whiting (1981) reported three primary types of geotechnical failures that can result in significant movement of waste rock. The first type can be labelled "internally generated" and include the extreme example of "blow-outs". Because stratification in a rock pile can retard groundwater movement (Section 3.0), intense periods of precipitation may cause elevated hydraulic pressures to accumulate in some layers, decreasing internal effective stress and stability. Under extreme conditions, this process can lead to "blow-outs" where the rock and overpressured water are ejected outwards from the face of a pile.
FIGURE 4-1. Mine Waste Embankments Possible Failure Modes (from Caldwell and Moss, 1981).
The second primary type of geotechnical failure according to Whiting is caused by slope erosion by runoff and groundwater discharge onto the slope (Figure 3-3), which can be labelled "externally generated". If surface slopes increase as a consequence of erosion, portions of a pile may collapse towards the toe.

The third type according to Whiting (1981) is failure of the sediments or rock beneath a rock pile, or "foundation failure". Both rock and sediments are capable of failure, although the modes of failure differ in that rock is susceptible to bedding-plane separation and fracture separation. Although foundation failure is often attributed to the increased stress of a rock pile on the subsurface materials, the weight of the rock also leads to elevated hydraulic pressures in the underlying groundwater system which lessens effective stress (van der Kamp and Maathuis, 1985; Maathuis and van der Kamp, 1984).

Overall, Whiting felt that "almost all failures are due to dump flow problems [and by] understanding dump flow technology ... water pollution potential will be greatly minimized." Relevant flow problems have been reviewed in Section 3.0.

4.2 Case Studies


Waste-rock management at a molybdenum mine called for a rock pile to be placed over a stream and simulations were used to predict the resulting impacts from suspended solids. A simplifying assumption was made that suspended solids would be flushed only from the saturated zone of the pile at a rate proportional to lateral groundwater velocity through the pile. The behavior of the suspended solids was based on the predicted grain-size distribution within the pile (Figure 4-2), which was derived from nearby waste rock and rock structures. In the simulation, no consideration was given to other complexities such as stratification and potential plugging of a proposed basal drain layer.

Rum Jungle Mine site, Australia: (Daniel et al., 1983; Harries and Ritchie, 1983)

A detailed examination of the surface of White's Dump showed that finer-grained particles had been preferentially removed, leaving flat stones of 1 to 2 cm diameter. The removal was attributed to runoff over the surface of the dump and migration with infiltration into the dump.
Migration of Solids, Coal Spills: Ricca (1979)

Based on field studies, Ricca found that precipitation initiated the migration of surficial fine-grained particles in runoff and infiltration into the spoils. This removal of fines created a surficial, relatively permeable "Outer Mantle" which enhanced infiltration and gas transport. The thickness of this Mantle was found to be in the range of 1 to 25 cm. The underlying second layer in the spoils, where the fine-grained particles collected and plugged porespaces, was called the "Oxygen Barrier". This Barrier likely limits the migration of all gases, water, and solids, rather than only the movement of oxygen. Beneath the Oxygen Barrier, the remainder of the pile was labelled the "Main Body", which was not subject to significant weathering and oxidation.

This work by Ricca is consistent with observations such as at Rum Jungle which also show surficial depletion of fine-grained particles. However, the natural formation of a continuous
Oxygen Barrier in a particularly coarse waste-rock pile may be unlikely or, at least, require many years of weathering and migration.

**Leach Columns of Coal Spoils: Libicki (1982)**

Coal spoils from a mine in Poland were placed in glass leach columns of 1 m height and 12 cm diameter containing a basal sand layer. Leaching with a few pore volumes of water caused migration of colloidal particles from the spoils into the sand. This internal migration led to a gradual then complete plugging of the sand through time. Another potential explanation, chemical precipitation, within the sand was ruled out, but it is not clear if dismissal was based on observation and analysis. The observed plugging in the columns was then used as one potential explanation for the field observations of decreasing contaminant loadings from spoil piles after 2-1/2 y.

**Dump #1, Westmin Myra Falls Minesite: Northwest Geochem (1990)**

Fifty-seven boreholes were drilled into this dump in 1988. Based on the information from the drillers and observations of samples, the deeper waste rock could not be easily distinguished from the underlying bedrock. This indicated that the deeper waste rock was similar in physical characteristics such as particle size and in chemical characteristics to the bedrock. Indirect evidence based on water-table elevations and groundwater flowpaths also suggested that the hydraulic conductivities of the deeper waste rock and bedrock were similar. These similarities may reflect rapid weathering of the deeper rock over 20 y or crushing of the deeper rock by the overlying rock, rather than internal migration.

**Fording River Coal Operations, British Columbia: Campbell (1989)**

Excavation of rock spoils at this minesite allowed the examination of the spoil profile and the contact between the spoils and underlying natural stratum after 12 y of spoil placement. This examination found that no finer-grained particles had migrated from the upper levels to the basal spoils.
5.0 GAS TRANSPORT

Because water tables within waste-rock piles are typically located near the base (Section 3.0), large portions of piles will be unsaturated with gases occupying a significant volume of porespace. The gas phase will consist of gases such as nitrogen, oxygen, and carbon dioxide, which initially are derived from the atmosphere but whose relative proportions are determined by geochemical and bacterial reactions within a pile (Section 6.0). For example, oxygen may be consumed in a pile where the rate of acid generation is high and carbon dioxide may be at high levels if carbonate mineral dissolution is significant. Other gases may also be found in waste-rock porespaces such as methane or hydrogen sulfide if organic materials were placed with the waste-rock and bacterial activity is significant.

The primary reason that gas transport has been examined in waste-rock piles is that oxygen is a key requirement for acid generation (Section 6.1) and carbon dioxide enhances bacterial activity (Section 6.2). However, other gases such as nitrogen and hydrogen sulfide can have significant geochemical effects. Consequently, the following discussion has been written so that it is applicable to any gas found in waste-rock dumps.

The four primary modes of transport within a waste-rock dump are gaseous diffusion, gaseous advection, aqueous diffusion, and aqueous advection. The first two modes are relevant for all gases whereas the latter two are relevant only for gases which dissolve in water to geochemically significant levels.

5.1 Theory

5.1.1 Gaseous diffusion

Gas molecules move in random patterns due to their kinetic energy and collisions with other molecules. If two gases coexist in a sealed container and one portion of the container contains a higher concentration of one gas, then random motion will eventually equalize concentrations throughout the container. This is an example of gas transport by gaseous diffusion. Diffusion results in a relatively slow movement so that, if there is any significant bulk movement of a gas such as by wind currents, then diffusion will be relatively unimportant.

The basic process of diffusion can be described by Fick’s First Law which indicates the flux of gas that can be expected under ideal conditions from one point of higher concentration to a point of lower concentration:
\[ F = -D \frac{dC}{dx} \]  
where \( F \) = flux of gas (moles/m² s)  
\( D \) = diffusion coefficient (m²/s)  
\( dC \) = difference in concentration between two points (moles/m³)  
\( dx \) = distance between the two points (m)

With the inclusion of the concept of mass balance and continuity, Fick's Second Law can be derived, relating the variables of time, space, and concentration:

\[ \frac{dC}{dt} = D \frac{d^2 C}{dx^2} \]  
where \( t \) = time (s)

There is a common misinterpretation in the literature regarding these equations in that the difference in concentration is said to "drive" the flux. In fact, because diffusion can be attributed to Brownian (random) motion, the flux of gas is an on-going process independent of a concentration gradient. However, the flux is only obvious and readily measured when a gradient exists.

When a waste-rock pile is initially constructed, the types and concentrations of gases in the porespaces can be expected to reflect those of the atmosphere. As a result of geochemical reactions within the pile, the relative concentrations of gases change through the consumption of some gases and production of others. This leads to concentration gradients between the porespace of the pile and the atmosphere in contact with the outer surfaces of the pile. In the case of consumption of a gas, the gradient is oriented into the pile.

With a concentration gradient defined over some distance within the pile, Equation 5-1 can be used to define gas flux into or out of a pile when a value of \( D \) is specified. Each gas has a unique diffusion coefficient in each gas mixture at a specified temperature and pressure. For example, the value of \( D \) for oxygen in open air at STP is \( 2.1 \times 10^{-5} \) m²/s and this value can probably be used as a general value for most gases of interest in waste-rock studies. However, diffusion in porespace is more restricted than in air so that the aforementioned value for \( D \) would be reduced in a porous medium. Based on work on mill tailings in Elliot Lake (Reardon and Moddle, 1985), an experimentally derived relationship between \( D \) for oxygen and gas-filled porosity was defined:
\[ D = 2 \times 10^{-5} \left( (n_a - 0.05)/0.95 \right)^{1.7} \]  

(Equation 5-3)

where \( D \) = effective diffusion coefficient in porespace (m²/s)

\( n_a \) = gas-filled porosity (m³ gas/m³ bulk material);

value must be greater than 0.05

For a value of \( n_a = 1.0 \) (open atmosphere), a reasonable value is obtained for \( D \) of \( 2 \times 10^{-5} \) m²/s. Because similar testing could not be located for waste-rock, Equation 5-3 is assumed to be applicable for waste-rock.

As an example, a waste-rock pile with \( n_a = 0.4 \) has an oxygen concentration gradient of approximately 1 mole/m³/m (from atmospheric to zero concentration) over a distance of 10 m within the pile. The diffusive flux through a 1 m² plane perpendicular to the gradient is then \( 3.6 \times 10^{-6} \) moles \( O_2 \)/m²/s or 0.3 m³ \( O_2 \)/m²/day. If the gas is consumed or produced along the gradient pathway (rather than at the endpoint), proper mass balance calculations require the incorporation of this process into Fick's Laws. The expanded equation can be highly complex depending on the nature of the reaction describing the consumption or creation. For example, for a first-order reaction depending on a reaction rate and the concentration of only the gas of interest, Fick's Second Law becomes:

\[ \frac{dC}{dt} = D \left( \frac{d^2C}{dx^2} \right) - kC/n_a \]  

(Equation 5-4)

where \( k = \) first-order reaction rate (s⁻¹)

Further discussion on this topic relative to acid generation can be found in Section 6.0.

Much of the current knowledge of gas transport in mine components is derived from tailings (e.g., Senes Consultants Ltd., 1986), which leads to problems with extrapolation of results to waste-rock piles. Tailings are typically finely ground and deposited as a slurry, which minimizes channelling, results in a relatively low permeability, creates small pores, and sometimes causes the water table to be near the tailings surface. Coal-mine spoils often share many of these characteristics. Under these conditions, gaseous transport can be expected to be a slow process which is a consequence of diffusion. On the other hand, waste-rock commonly has channelling, large pores, and typically a low water table and under these conditions, advection can be significant (Section 5.1.2) and diffusion would then be considered a negligible contributor to gaseous transport.
5.1.2 Gaseous advection

This type of advection represents the bulk movement of a gas phase through porespace under a pressure gradient. In this respect, it is similar to water movement described in Section 3.0.

As with water movement, gas advection is a response to permeability and a pneumatic gradient, and is capable of driving gas deep into a waste-rock pile. Parizek (1985) reported that advection was the major transport mode for oxygen in spoils and that advection could carry oxygen to depths greater than 20 m in unsaturated spoils. Similarly, oxidation to depths in excess of 10 m were reported in waste-rock piles at Equity Silver Mines in central British Columbia (Patterson, 1987) and at Westmin Myra Falls Minesite on Vancouver Island (Northwest Geochem, 1990). Wadsworth (1981) indicated even greater transport distances of 60 m from an exposed surface.

The first factor regulating advection, permeability, is an indicator of the capability of the rock mass to conduct a fluid and is usually expressed in units of darcies or m² (1 darcy = 9.87 x 10⁻¹³ m²). Whiting (1981) presented unpublished data from three boreholes in an unidentified dump in which bulk permeabilities were measured in the range of 9.9-197 x 10⁻¹³ m² with one high value of 2000 x 10⁻¹³ m². The high value corresponds to a hydraulic conductivity of 10⁻⁵ m/s if water were the fluid moving through the porespace. Two-dimensional modelling of advection by Bennett et al. (1989) suggested that such a high permeability is necessary before transport by advection surpasses diffusion.

The second factor regulating advection is gradient. There are three primary processes which cause pressure gradients to form in and around waste-rock piles (Figure 5-1). The first process, wind current, causes higher pressure to develop on the upwind side. In response, air moves into the pile and flushes internal gases from the porespace. No literature could be located addressing wind advection in waste-rock piles so it is not clear how significant this process might be. Wind advection may only be important for piles which are elevated above the surrounding land surface (Figure 3-1) and less important for other situations (Figures 3-2 and 3-3).

The second process leading to gradients is internal heat production from geochemical reactions such as acid generation (Figure 5-1 and Section 5.2 under Run Jungle Minesite.) The heat lowers the density of the surrounding gases which causes them to move upwards and out of the upper surfaces of a pile. This thermal advection accounts for the commonly reported observation of localized winter snowmelt on acid-generating waste-rock piles. As the heated gases move upwards, gases from more distant locations, and ultimately from the
FIGURE 5-1. Schematic diagram of three primary causes of pressure gradients in and around waste rock piles.
atmosphere, move in to the heated area. In the case of acid generation, the delivery of oxygen to the "hot spot" could accelerate the rate of heat production and advection. Consequently, the rate of advection could attain relatively high levels.

Based on the volume of published and unpublished literature on temperature distributions within waste-rock (Section 5.2), thermal advection is considered by many researchers to be the dominant form of gaseous advection. In agreement, Parizek (1985) indicated that other modes of oxygen transport into acid-generating spoils could not account for the observed volume of acid products.

The third primary process creating gradients, barometric pumping, reflects the delay in pressure adjustment within porespaces of waste-rock piles as external atmospheric pressure changes. As external pressure increases, the internal gases are compressed and some air moves into the pile (Figure 5-1). Conversely, the internal gases expand and migrate out of the dump as external pressure decreases. As an isolated process, the extent of advection expected from barometric pumping is considered minor for two reasons. Firstly, this pumping would only affect gas concentrations in the outer portions of the dump where the gases are entering and exiting (this could be important, however, for acid generation). Secondly, the volume of gases moving into and out of a pile would be a function of the compressibility of the gases. For an ideal gas, a change in volume is directly related to a change in pressure. As a result, the commonly observed variations in air pressure (excluding hurricanes, tornadoes, etc.) of up to a few percent would lead to a few percent compression and expansion of the gas phase within the porespaces.

5.1.3 Aqueous diffusion

For gases which dissolve in water to a significant level, migration with and through water can be an important mode of transport. Rather than being strictly gas transport, aqueous transport of dissolved gases represents complex combinations of gaseous transport to the water (Sections 5.1.1 and 5.1.2) and water movement (Section 3.0).

In some situations water can be essentially stagnant such as in low-permeability strata and in water films surrounding rock particles. In these cases, gases would dissolve into the water and diffuse through the water following the same principles for gaseous diffusion (Section 5.1.1). However, the diffusion coefficients of many gases in water are orders of magnitude lower than in air. For example, the coefficient for oxygen in water is $1.8 \times 10^{-9}$ m$^2$/s compared to $2.1 \times 10^{-5}$ m$^2$/s in air. Consequently, aqueous advection (Section 5.1.4) can overwhelm aqueous diffusion in more situations than gaseous advection can overwhelm gaseous
diffusion. For waste-rock, the most important application of aqueous diffusion of dissolved gases is probably in the transport of oxygen through a water film to acid-generating minerals on rock particles (Davis and Ritchie, 1986, and Section 6).

5.1.4 Aqueous advection

Once dissolved in water, gases will be transported with the water as described in Section 3. The flux of gas will be dependent on the rate of water movement, reflecting applicable hydraulic conductivities and gradients, and on the rate of dissolution into the water up to a solubility limit. For example, dissolved oxygen can reach a limit of $3.6 \times 10^4$ mol/L (12 mg/L) at 10°C and atmospheric pressure. If this oxygen level is carried in water through waste-rock with a hydraulic conductivity of $10^{-5}$ m/s and hydraulic gradient of 1.0, then the flux of oxygen would be $3.6 \times 10^{-6}$ moles O$_2$/m$^2$/s, which is equivalent to the example given for gaseous diffusion (Section 5.1.1). However, this flow is equivalent to an infiltration rate of 315 m/year and, thus, if direct precipitation is the only source of oxygenated water on the pile, the flow and associated oxygen flux would be significantly less. Consequently, aqueous advection of dissolved gases can be a major mode of transport in highly permeable (>10$^{-5}$ m/s) waste rock with a significant source of oxygenated water (e.g. Figure 3-2). This understandably contradicts the findings of tailings research which indicate that aqueous advection of dissolved oxygen is relatively minor and that subaqueous deposition of tailings is a viable control option (Section 7.0), due to the typically lower hydraulic conductivities of tailings relative to waste-rock.

5.2 Case Studies

Computer Simulations: Bennett et al. (1989)

Gaseous diffusion and advection as well as heat production from acid generation were simulated in a two-dimensional model applicable to a small range of geometries. Simulations showed that diffusion was an important mode of transport for the first two years in all piles, and the relative importance of diffusion to thermal advection was determined in later years by permeability. At permeabilities greater than $10^{-10}$ m$^2$, transport by advection dominated that by diffusion. Figure 5-2 depicts simulated temperature distributions and gas flowpaths in a vertical-plane simulation along the radius of a circular pile.
FIGURE 5-2. Temperature Contours in a Simulated Cylindrical Heap at Years 2, 3 and 4 (Permeability $K=10^{-10}$ m$^2$ and the particle size $a=0.005$ m). Arrowed Solid Lines Indicate Air Flowpaths (from Bennett et al., 1989).
Rum Jungle Minesite, Australia: Harries and Ritchie (1985 and 1987)

Probe holes into the waste-rock piles at Rum Jungle provided access for the measurement of temperature and collection of gas samples. Periodic monitoring indicated that oxygen was transported into the piles by a combination of diffusion, thermal advection, and barometric pumping and each mode of transport produced a recognizable trend in oxygen concentration. Diffusion caused oxygen concentrations to decrease linearly with depth. Thermal advection was driven by heat production from acid generation to depths of 14 m (see following paragraphs) and resulted in elevated oxygen concentrations near the base of the dumps. Barometric pumping was the result of atmospheric tides with two maxima and two minima a day and oxygen concentrations reflected this tidal effect. Because acid generation and heat production was found to be limited by oxygen transport, remediation focused on capping exposed surfaces to further limit oxygen transport. The decreases in temperature and oxygen concentrations at depth (Figure 5-3) indicated the success of remediation.

Advective movement of gases (Figure 5-1) within White’s dump was caused by thermal gradients from the warmer interior to the exposed surfaces, which were usually less 2°C/m, but reached a maximum of 4°C/m. The gradients were a consequence of heat evolution during oxidation of pyrite.

In order to interpret and simulate the thermal gradients, Harries and Ritchie (1987) calculated that pyrite (FeS₂) which oxidized to aqueous ferrous iron and sulfate at a rate of $7 \times 10^{-7}$ mol FeS₂/m³/(of rock)/s by consuming $2.4 \times 10^{-6}$ O₂/m³/s would release 1 W/m³. This heat was then transported or stored according to:

$$ X = \frac{K}{(pC)} $$

(Equation 5-5)

where

- $X$ = thermal diffusivity (m²/s)
- $K$ = thermal conductivity (W/(m K))
- $p$ = density (kg/m³)
- $C$ = thermal capacity (J/(kg K))

The bulk density of rock in White’s Dump ($p$ in Equation 5-5) was measured and calculated to be approximately 1670 kg/m³ dry and 1862 kg/m³ with an average and relatively constant moisture content of 11.5 weight-percent (wt-%). Thermal conductivity ($K$) was measured at 2.3 W/(mK), which was somewhat higher than values of 0.2 to 1.7 W/(mK) for various literature-reported soils with water contents between 0.02 to 0.20 wt-%. Thermal capacity ($C$) of dry White’s rock averaged 867 J/(kg K) and, with the average water content of 11.5 wt-%,
was 1350 J/(kg K). Based on these values, the calculated value of thermal diffusivity (α) was within a factor of 2 of the measured value of approximately $5 \times 10^{-7}$ m$^2$/s, which is similar to literature values for sand and loam. For consistency, the researchers then averaged the calculated and measured diffusivities to obtain a value of $7 \times 10^{-7}$ m$^2$/s, leading then to a conductivity of 1.8 W/(mK). This information then permitted the simulation of heat transport and temperature distributions (e.g., Figure 5-2).

**Coal Spoils, Upshur County, West Virginia: Erickson et al. (1985) and Erickson (1987)**

At this site, spoils were placed against the pit wall (Figure 5-4) with a relatively flat upper surface and a 12-meter slope to the toe. Gas sampler 8 (GS8 located near Well 8) is located near the pit wall, downgradient of an area containing black (organic), pyritic material. Gas analyses from various ports in GS8 from May, 1983 to February, 1984 indicated:

<table>
<thead>
<tr>
<th>DEPTH (m)</th>
<th>OXYGEN</th>
<th>CARBON DIOXIDE</th>
<th>METHANE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>15.3-20.3</td>
<td>0.9-5.0</td>
<td>ND-0.9</td>
</tr>
<tr>
<td>1.2</td>
<td>1.9-3.1</td>
<td>1.8-4.0</td>
<td>0.7-3.4</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6-3.8</td>
<td>3.1-10.9</td>
<td>20.7-33.0</td>
</tr>
</tbody>
</table>

The methane concentrations indicated significant anaerobic decomposition, presumably of the black material, at depth. The researchers pointed out that the sum of oxygen and carbon dioxide near the surface approximately equalled atmospheric oxygen, which was interpreted simply as replacement of oxygen by carbon dioxide. However, with depth, carbon dioxide increased at a slower rate than oxygen decreased, indicating a net consumption of oxygen which was consistent with the observed pyrite oxidation in the black material. The increase in carbon dioxide was attributed to dissolution of carbonate minerals (Section 6.3) and bacterial activity which may also account for the methane.

Gas sampler 5 near well 5 (Figure 5-4) was located near the outer slope of the spoils pile. Gas analyses from May, 1983 to February, 1984 indicated:
FIGURE 5-4. Map of the Upshur County Site (from Erickson, 1987).
CONCENTRATION
(volume percent, moisture free)

<table>
<thead>
<tr>
<th>DEPTH (m)</th>
<th>OXYGEN</th>
<th>CARBON DIOXIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>7.3-14.9</td>
<td>2.2-4.9</td>
</tr>
<tr>
<td>2.1</td>
<td>10.4-17.6</td>
<td>1.8-4.5</td>
</tr>
<tr>
<td>3.7</td>
<td>16.2-16.4</td>
<td>1.8-4.3</td>
</tr>
<tr>
<td>5.2</td>
<td>12.1-20.9</td>
<td>0.1-8.8</td>
</tr>
</tbody>
</table>

These results suggested that there was advection of air laterally through the exposed slope into the entire thickness of the spoils. The presence of significant levels of oxygen was also attributed to the lack of consumption by acid generation in the area.


This minesite includes three waste-rock piles known as the East, West, and South Dumps and the number of boreholes drilled into each were three (Boreholes 1-3), two (Boreholes 4-5), and one (Borehole 6), respectively. The holes were drilled through the entire thickness of the pile (5-11 m) and gas and temperature probes were installed. Pea-gravel packs and bentonite seals between probes in each borehole could not be placed due to the coarse nature of the rock so the potential exists for artificially enhanced gas connections among the ports.

Measurements for oxygen, carbon dioxide, and temperature were made in 1988 on August 9, August 18, August 19, October 24, November 5, and December 7. The results for Boreholes 4, 5, and 6 (west and south dumps) indicated that contents of oxygen and carbon dioxide were generally constant near 21% and 0.1 to 0.2%, respectively, throughout the entire lengths of these boreholes on all sampling dates. Temperature variations at the surface of these boreholes reached 20°C, reflecting seasonal climatic changes. These variations also occurred at the bases of the dumps, although the extent of the variation was dampened to less than 8°C. These data suggest that air advection occurs throughout the entire depths of the West and South Dumps, and that relative to gas advection, little oxygen is consumed and little carbon dioxide is generated. The potential for rapid advection along the borehole due to the lack of bentonite seals cannot be evaluated based on available information, but could also potentially account for these remarkably consistent results.

Between the August and October measurements, approximately one meter of till was placed on the East Dump and additional probes were placed in Boreholes 1 to 3 to monitor the till.
Prior to till placement, oxygen and carbon dioxide contents were generally consistent with the boreholes in the other dumps near 21% and 0.1 to 0.2%, respectively, throughout the depth of the boreholes on all sampling dates. Following placement, oxygen contents decreased somewhat to approximately 18% in the till and 19.5% in the underlying waste-rock in all three boreholes whereas carbon dioxide remained essentially constant around 0.1 to 0.2% (except for the November 5 measurements which were considered anomalous). The corresponding temperature measurements showed seasonal variations of up to 16°C at the surface, but variations were significantly dampened at depth to less than 4°C. Although the till cover has apparently affected oxygen transport and/or oxygen consumption, the relative effects appeared to be minor as of the end of 1988.

**Equity Silver Mines, Houston, British Columbia: Equity Silver Mines Ltd. (1989)**

With the intent of obtaining information on rates of acid generation based on heat production, temperature probes were placed in various locations throughout the waste-rock dumps (Figure 5-5). One set of five probes (Series 1270 and 1280) were placed horizontally on two berms in 1983 as dump construction proceeded. Results showed that soon after the waste-rock was placed the internal temperature began rising due to acid generation (Figure 5-6). By 1989, temperatures had reached a maximum of 58°C.

A second set of 31 probes were placed in the waste-rock dumps at the contact of waste-rock and the overlying one meter cap of till (Figure 5-5). For example, on August 20, 1987, the following temperatures measured in the probes are listed in Table 5-1.
These and other temperature measurements showed that external air temperatures were influencing temperatures within the till cap. However, "hot spots" could still be located by the spatial variations of up to 44°C. Implications of these temperature profiles on gaseous advection were not addressed in the reference.
6.0 INTERNAL REACTIONS

Acid drainage is the result of a complex and interactive suite of physical and geochemical processes operating within a waste-rock pile. The physical aspects of acid drainage include hydrogeologic processes (Section 3.0) which carry the acidic water through unsaturated and saturated zones within the rock dump to the local environment. The geochemical aspects of acid drainage include acid generation, bacterial acceleration of reaction rates, acid neutralization, and metal leaching, which lead to the release of acidity, sulfate, alkalinity, and metals from waste-rock into the water passing over the rock surfaces. This section focuses on geochemical and biological aspects of acid drainage within waste-rock piles.

The suite of processes that may or may not be operative at a particular site of acid drainage are so complex that some researchers have created sub-classes of acid drainage. For example, Bell and Reeves (1982) reported 5 classes of "acid ferruginous drainage" as:

#1: acid drainage with little Fe\(^{2+}\) and Fe\(^{3+}\)
#2: acid drainage with Fe\(^{3+}\)
#3: acid drainage with Fe\(^{2+}\)
#4: neutralized drainage with Fe\(^{2+}\) in solution
#5: neutralized drainage with Fe\(^{3+}\) in suspension (presumably as Fe-OH floc)

This system of classification is based simply on measurable parameters at external discharge locations and does not necessarily reflect reactions occurring in various internal locations within a pile. Furthermore, more than one type of drainage could be found at a site and, in fact, a sample of acid drainage could evolve from one type to another during storage. For these reasons, an empirical classification scheme for acid drainage is not a viable substitute for defining the physical and geochemical processes operating within a particular waste-rock pile.

6.1 Abiotic Acid Generation

In a large portion of the literature of acid drainage, acid generation is summarized by the equation:

\[ \text{FeS}_2 + 7/2 \text{H}_2\text{O} + 15/4 \text{O}_2 \leftrightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad \text{(Equation 6-1)} \]

In this equation, pyrite (FeS\(_2\)) is oxidized by molecular oxygen and water to form an iron mineral, sulfate and hydronium ions or acidity). The ratio of pyrite:sulfate:hydronium (acidity)
is 1:2:4. Acid generation, however, is phenomenally more complex than this equation suggests. The degree of complexity will be demonstrated in the following paragraphs.

Aqueous iron is affected by pH, redox conditions, and other chemical and biological factors, and may thus not precipitate from solution as Fe(OH)_3 as indicated in Equation 6-1. If pH was significantly acidic (pH<2.5), the iron may not precipitate at all and the appropriate equation would be:

\[ \text{FeS}_2 + 1/2\text{H}_2\text{O} + 15/4\text{O}_2 \leftrightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^+ \]  \hspace{1cm} (Equation 6-2)

The ratio of pyrite:sulfate:hydronium in this case is 1:2:1, or four times less hydronium than generated by Equation 6-1. However, in an acidity titration to pH 8.3, the aqueous Fe^{3+} may hydrolyze and precipitate as Fe(OH)_3, producing a net acidity equivalent to Equation 6-1. Alternatively, the iron could precipitate at strongly acidic pH as a mineral such as jarosite, resulting in a different aqueous acidity level at pH 8.3 than that of Equation 6-1. Under generally reducing (anaerobic) conditions, the ferrous iron in pyrite may not even oxidize to ferric iron upon dissolution, leading to:

\[ \text{FeS}_2 + \text{H}_2\text{O} + 7/2\text{O}_2 \leftrightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \]  \hspace{1cm} (Equation 6-3)

The ratio of pyrite:sulfate:hydronium in this case is 1:2:2, or one-half of the hydronium generated by Equation 6-1 and twice that of Equation 6-2. Depending on pH and other aqueous conditions, the Fe^{2+} may remain in solution or precipitate as Fe(OH)_2 or FeCO_3, thereby affecting the overall titratable acidity.

Another level of complexity lies in the oxidant used in the acid-generation equation. Molecular oxygen is only one oxidant that is found in natural environments. For example, another is manganese and, in the absence of molecular oxygen, a possible reaction without iron oxidation and precipitation is:

\[ \text{FeS}_2 + 8\text{H}_2\text{O} + 12\text{Mn}^{3+} \leftrightarrow 12\text{Mn}^{2+} + \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \]  \hspace{1cm} (Equation 6-4)

In this case, the ratio of pyrite:sulfate:hydronium is 1:2:16, which represents a more significant source of acidity than the previous reactions and would be enhanced further if the aqueous manganese and iron precipitated as hydroxide compounds. Similarly, oxidation by ferric iron in the absence of molecular oxygen is:

\[ \text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} \leftrightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \]  \hspace{1cm} (Equation 6-5)
With this equation, the source of ferric iron becomes an important factor. If the ferric iron is derived from nearby pyrite oxidation, then the reaction in Equation 6-5 occurs once for each fourteen executions of Equation 6-2 which provides the 14 ferric-iron ions. As a result, the overall ratios of pyrite:sulfate:hydronium for this scenario are 15:30:30 (1:2:2). On the other hand, if the ferric iron is pre-existing in solution, the applicable ratio is 1:2:16. If this ferric iron then precipitated as Fe(OH)$_2$, such as might happen during an acidity titration to pH 8.3, the ratio would be 1:2:46.

The previous discussion provides an indication of the complexity in the interpretation, prediction, and analysis of acid generation in any particular waste-rock pile. However, there are even greater degrees of complexity that are the result of sulfur oxidation, types of sulfide minerals, and bacterial participation in the reactions. The first two issues are discussed in the remainder of this section whereas bacterial effects are reviewed in Section 6.2.

The oxidation of sulfur in Equations 6-1 to 6-5 is assumed to begin at sulfide and end at sulfate. Alternatively, in low-temperature and near-surface mineral deposits such as coal, a portion of the sulfur may exist in organic forms which would follow different oxidation pathways (e.g., Attar and Corcoran, 1977; Dollhopf, 1984; and Spiro et al., 1984). However, this review focuses on waste-rock from base-metal and precious metal deposits where organic sulfur is likely to be low and sulfide-to-sulfate is expected to be the primary pathway of sulfur oxidation.

Sulfide-to-sulfate oxidation is actually a series of reactions, involving sulfide ($S^{2-}$), elemental sulfur ($S^0$), various intermediate sulfur forms such as polythionates and thiosulfate, and sulfate ($SO_4^{2-}$) as the final form of complete sulfur oxidation in natural waters. Under various environmental conditions, one or more of these reactions may be extremely slow or inoperative, affecting the overall extent of acid generation as predicted by Equations 6-1 to 6-5.

Sulfur exists in sulfide minerals as forms such as $S_2^{2-}$ in pyrite and $S^{2-}$ in sphalerite (ZnS). One potential oxidation sequence for $S_2^{2-}$ using molecular oxygen and water as oxidants is:

\[
\begin{align*}
S_2^{2-} & \leftrightarrow S^0 + S^{2-} \quad \text{(Equation 6-6a)} \\
S^0 + S^{2-} + H_2O + 1/2O_2 & \leftrightarrow 2S^0 + 2OH^- \quad \text{(Equation 6-6b)} \\
2S^0 + H_2O + O_2 & \leftrightarrow S_2O_3^{2-} + 2H^+ \quad \text{(Equation 6-6c)} \\
S_2O_3^{2-} + H_2O + O_2 & \leftrightarrow 2SO_3^{2-} + 2H^+ \quad \text{(Equation 6-6d)} \\
2SO_3^{2-} + O_2 & \leftrightarrow 2SO_4^{2-} \quad \text{(Equation 6-6e)}
\end{align*}
\]

for a net reaction of:
\[
\text{S}_2^{2-} + \text{H}_2\text{O} + 7/2\text{O}_2 \leftrightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ \quad \text{(Equation 6-6f)}
\]

This series indicates that alkalinity (hydroxyl ion) is generated in the initial stage of sulfur oxidation, but the alkalinity is overwhelmed by acidity generated in the later stages so that the net reaction is acid generating. The stoichiometry of the net reaction (1 mole of \text{S}_2^{2-}:2 moles of \text{SO}_4^{2-}) is reflected in the stoichiometry of Equations 6-1 to 6-3.

For \text{S}^{2-} (rather than \text{S}_2^{2-}), the corresponding series of reactions is:

\[
\begin{align*}
2\text{S}^{2-} + 2\text{H}_2\text{O} + \text{O}_2 & \leftrightarrow 2\text{S}^0 + 4\text{OH}^- \\
2\text{S}^0 + \text{H}_2\text{O} + \text{O}_2 & \leftrightarrow \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \\
\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} + \text{O}_2 & \leftrightarrow 2\text{SO}_3^{2-} + 2\text{H}^+ \\
\text{SO}_3^{2-} + \text{O}_2 & \leftrightarrow 2\text{SO}_4^{2-} 
\end{align*}
\]  
\text{(Equation 6-7a) to (Equation 6-7d)}

for a net reaction of:

\[
2\text{S}^{2-} + 4\text{O}_2 \leftrightarrow 2\text{SO}_4^{2-} 
\]  
\text{(Equation 6-7e)}

In this case, the alkalinity generated in the initial stage of oxidation equals the acidity produced during later stages so that the net reaction is neutral. Based on this series, full abiotic oxidation of sulfur in minerals such as sphalerite (ZnS) and galena (PbS) with molecular oxygen may not generate net acidity. However, precipitation of the associated metal from solution as a hydroxide or carbonate mineral could lead to the net creation of acidity.

Experimental observations of elemental sulfur on surfaces of sulfide minerals and detection of intermediate aqueous sulfur species indicate that the oxidation of sulfide minerals will not necessarily proceed completely to sulfate (Kwong and Ferguson, 1990). In these cases, the amount of acidity generated by oxidation of the mineral will be less than that indicated in Equations 6-1 to 6-5 and, in fact, the oxidation could result in net consumption of acidity. Furthermore, other intermediate sulfur species have been observed upon oxidation of sulfide minerals (Moses et al., 1987) and elemental sulfur, including \text{S}_4\text{O}_6^{2-} (e.g., Nor and Tabatabai, 1977), \text{S}_2\text{O}_2^{2-} (Thom et al., 1978; Meyer, 1979; Lotens and Wesker, 1987), and OCS and CS\textsubscript{2} gases if organic matter is present (Stedman, 1984). These species would change the stoichiometry of the oxidation and acid-generating reactions. Additionally, experimental observations by Goldhaber (1983) of pyrite oxidation at pH 6-9 indicated that \text{S}_4\text{O}_6^{2-} and \text{SO}_4^{2-} were the dominant aqueous species in the lower range of pH and \text{S}_2\text{O}_3^{2-} and \text{SO}_3^{2-} were dominant in the higher range. Other researchers apparently accept sulfide oxidation to sulfate in one step without intermediate species (Lowson, 1982). These discrepancies in
the literature highlight the alternative reactions available for oxidation of sulfide to sulfate and suggest that the stoichiometry of the net reaction is likely dependent on local environmental conditions in a waste-rock pile.

The half-cell reaction for Equations 6-6b and 6-7a, that is, the reaction with no oxidant specified, is:

\[ \text{S}^{2-} \leftrightarrow \text{S}^0 + 2e^- \]  \hspace{1cm} (Equation 6-8)

In contradiction of standard accepted concepts, there is some suggestion that bacterial oxidation may delay the transfer of the electrons to the oxidant (Section 6.2). This has significant implications on the levels of acidity generated by sulfur oxidation. Without the electrons from Reaction 6.8 to reduce oxygen, there would be no alkalinity (OH-) generated in Equations 6-6b and 6-7a. As a result, 2 moles of additional acidity would be generated over that indicated in net Equations 6-6f and 6-7e. This bacterial effect could be misinterpreted as an increase in the rate of acid generation rather than a stoichiometric increase in acidity.

Various metals exist in combination with sulfide as minerals (Table 6-1). For these and other sulfide minerals, oxidation reactions similar to Equations 6-1 to 6-5 can be written, although the stoichiometries and amounts of acid generation would often differ from Equations 6-1 to 6-5. For example, the full oxidation of chalcopyrite with molecular oxygen and water to produce cupric copper, ferric iron, and sulfate, followed by precipitation of the metal ions as hydroxide minerals, is:

\[ \text{CuFeS}_2 + 11/2\text{H}_2\text{O} + 17/2\text{O}_2 \leftrightarrow \text{Cu(OH)}_2 + \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \]  \hspace{1cm} (Equation 6-9)

As with Equation 6-1, the ratio of chalcopyrite:sulfate: acidity is 1:2:4. The oxidation of galena by molecular oxygen would yield no net acidity:

\[ \text{PbS} + 2\text{O}_2 \leftrightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} \]  \hspace{1cm} (Equation 6-10)

Some net acidity could arise if the aqueous lead hydrolized or precipitated from solution such as a hydroxide or carbonate mineral. Additionally, other oxidants could directly produce acidity through galena oxidation.

The preceding discussion on the stoichiometry of oxidation reactions demonstrates the complexity involved in delineating and predicting sulfide-mineral oxidation and acid generation. This complexity is compounded upon the consideration of rates of oxidation.
Oxidation rates can be environmentally important, for example, because little acidity would be generated by a slowly oxidizing mineral. Each mineral in Table 6-1 could be expected to have a unique rate of oxidation due to its unique physical and chemical properties.

**TABLE 6-1**

*Examples of Sulfide Minerals*

*(selected from Table 1 in Lowson, 1982)*

<table>
<thead>
<tr>
<th>MINERAL NAME</th>
<th>CHEMICAL COMPOSITION</th>
<th>MINERAL NAME</th>
<th>CHEMICAL COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alabandite</td>
<td>MnS</td>
<td>Linnaeite</td>
<td>Co$_2$S$_4$</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
<td>Marcasite</td>
<td>FeS$_2$</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu$_3$FeS$_4$</td>
<td>Millerite</td>
<td>NiS</td>
</tr>
<tr>
<td>Chalocite</td>
<td>Cu$_2$S</td>
<td>Molybdenite</td>
<td>MoS$_2$</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>Orpiment</td>
<td>As$_2$S$_3$</td>
</tr>
<tr>
<td>Cinnabar</td>
<td>HgS</td>
<td>Pyrite</td>
<td>FeS$_2$</td>
</tr>
<tr>
<td>Cobaltite</td>
<td>CoAsS</td>
<td>Pyrrhotite</td>
<td>Fe$_{0.8-1}$S</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>Realgar</td>
<td>AsS</td>
</tr>
<tr>
<td>Cubanite</td>
<td>CuFe$_2$S$_3$</td>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu$_3$As$_4$</td>
<td>Stibnite</td>
<td>Sb$_2$S$_3$</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>Tennantite</td>
<td>Cu$_2$As$<em>2$S$</em>{13}$</td>
</tr>
<tr>
<td>Greenockite</td>
<td>CdS</td>
<td>Troilite</td>
<td>FeS</td>
</tr>
<tr>
<td>Greigite</td>
<td>Fe$_3$S$_4$</td>
<td>Violarite</td>
<td>FeNi$_2$S$_4$</td>
</tr>
<tr>
<td>Hauerite</td>
<td>MnS$_2$</td>
<td>Wurtzite</td>
<td>ZnS</td>
</tr>
</tbody>
</table>

Published literature on rates of oxidation and acid generation indicates that several factors determine the abiotic rates (bacterial effects are addressed in Section 6.2). These factors (Table 6-2) include obvious dependencies such as concentration of oxidant and less obvious dependencies such as contact with other sulfide minerals. If acid generation rather than simple oxidation is of interest, other factors such as the stoichiometry and rate of metal precipitation are also important.

In the course of this literature review, no papers were found addressing or acknowledging all of the factors listed in Table 6-2 in theoretical, laboratory, or field situations. This is probably a major reason for significant discrepancies and misunderstandings in the literature (e.g., Lowson, 1982) and for the current difficulty in relating theory to laboratory and field data. Furthermore, the numerous factors determining rates of acid generation produce a highly complex situation in which an integrated study addressing all factors can probably not be performed in a timely and economic manner. Consequently, a fully integrated explanation of acid generation is probably not imminent and the ability to assess, predict, and control acid drainage must therefore depend on modelling of some factors (Section 6.5) and case
### TABLE 6-2
Factors Determining The Abiotic Rates of Oxidation and Acid Generation

**Rates of Oxidation**

<table>
<thead>
<tr>
<th>FACTOR</th>
<th>EXAMPLE REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Goldhaber (1983)</td>
</tr>
<tr>
<td>Eh</td>
<td>Lowson (1982)</td>
</tr>
<tr>
<td>Temperature</td>
<td>Steger (1982)</td>
</tr>
<tr>
<td>Ratio of sulfide mineral to solution</td>
<td>Wiersma and Rimstidt (1984)</td>
</tr>
<tr>
<td>Surface area (particle size)</td>
<td>Pugh et al. (1981)</td>
</tr>
<tr>
<td>Surface roughness</td>
<td>Yamada et al. (1979)</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>Hammack et al. (1988)</td>
</tr>
<tr>
<td>Saturated/unsaturated condition</td>
<td>Sections 3 &amp; 5, this report</td>
</tr>
<tr>
<td>Humidity in unsaturated zones</td>
<td>Steger, 1982</td>
</tr>
<tr>
<td>Types and concentrations of oxidants</td>
<td>Moses et al. (1987)</td>
</tr>
<tr>
<td>Catalysts such as Ag⁺</td>
<td>Price and Warren (1986)</td>
</tr>
<tr>
<td>Associated precipitation of minerals</td>
<td>Munoz et al. (1979) and</td>
</tr>
<tr>
<td></td>
<td>Mateos et al., (1987)</td>
</tr>
<tr>
<td></td>
<td>Chmielewski (1985)</td>
</tr>
</tbody>
</table>

**Rates of Acid Generation**

**FACTOR**

All preceding factors, plus

- stoichiometry and extent of sulfur oxidation
- stoichiometry and extent of metal oxidation
- stoichiometry and extent of metal precipitation

---

studies (Section 6.6). For waste-rock piles, the number of detailed modelling efforts and case studies is limited.
6.2 Bacterial Aspects of Acid Generation

Information on bacterially mediated dissolution reactions is generally obtained from three major areas of research, involving: 1) heap leach operations or bacterial optimization literature, 2) basic microbiological research; and, 3) acid mine drainage research. The volume of literature and the extent of research in the first two areas far exceeds that of the acid mine drainage research because of the ubiquitous nature of the *Thiobacillus* genus and the economic benefits of bacterial action in biohydrometallurgy. In general, the most applied microbiological literature was selected for review and information from the biohydrometallurgy literature was extrapolated to acid generation within waste-rock piles, whenever possible.

Sulfide minerals can oxidize abiotically (Section 6.1), however, the reaction is reportedly too slow at pH's less than 5 to generate the amount of acidity observed in nature (Lund, 1987). Because the bacterium *Thiobacillus ferrooxidans* is ubiquitous in acid mine drainages, accelerated rates of acid production have been attributed to biological mediation of the oxidation process. Although abiotic oxidation of pyrite by ferric ions at pH's less than 4 is quite fast, regeneration of ferrous to ferric iron occurs slowly in acidic conditions. *Thiobacillus* organisms can act as a catalyst for the oxidation of aqueous ferrous iron to ferric, enhancing the abiotic chemical oxidation of metal sulfides by ferric iron (LeRoux, 1970). *T. ferrooxidans* is also believed to be capable of a direct leaching method in which the organisms contact and adhere to the mineral surface and oxidize the mineral without the use of ferric iron as the oxidant (Lundgren and Silver, 1980; Berry and Murr, 1978; Brierley and Brierley, 1986; Rodriguez-Leiva and Tributsch, 1988). Under ideal conditions, bacterial mediation of the acid generation process may increase the rate of oxidation by $10^5$ to $10^6$ over the abiotic rate (Lacey and Lawson, 1970). However, bacterial enhancement of the oxidation process may be limited by varying environmental conditions in the field.

6.2.1. Physiology of *Thiobacillus*

Almost since its isolation in 1947, *Thiobacillus ferrooxidans* has been regarded as a possible agent in the problem of acid generation in mine waters. Although it was first thought that the bacteria merely accelerated the precipitation of Fe(OH)$_3$, later experiments suggested that the bacteria also increased the rate of pyrite oxidation. In 1970, Singer and Stumm showed that the direct oxidation of pyrite by air was too slow at acidic pH's (<5) to generate the amount of acidity observed in acid mine drainages and suggested that the bacteria acts as a catalyst for the relatively rapid oxidation of pyrite by aqueous ferric iron. The biologically mediated oxidation of pyrite by ferric iron was calculated to be $10^6$ times more rapid than abiotic oxidation by oxygen (Singer and Stumm, 1970).
Oxidation of Fe$^{2+}$, S$^0$, and sulfide minerals is mediated primarily by bacteria of the genera *Thiobacillus, Leptospirillum, Sulfotobus, Sulfobacillus* and *Acidianus* (UNEP, 1989). The mechanism of bacterial oxidation is a complex and multistage process and is not fully understood (UNEP, 1988; Ehrlich, 1981). The process includes: bacterial adhesion to the mineral surface, solubilization of sulfur, transport of S$^0$, Fe$^{2+}$, and other ions across the cell membrane and oxidation.

The most widely studied organism is *Thiobacillus ferroxidans*, a gram-negative, acidophilic, mesophilic chemoautotroph. *T. ferroxidans* derives energy for growth from the oxidation of reduced forms of sulfur (metal sulfides) and ferrous iron. The bacterium uses inorganic CO$_2$ as its sole carbon source. The organism is acidophilic and mesophilic with an optimum temperature range of 15 to 35$^\circ$C, although the bacteria can tolerate temperatures up to 45$^\circ$C. Iron oxidation by resting cells is optimal at pH in the range of 2.5 to 4.2. However, a lower pH limit for activity of acidophilic bacteria has not been established.

Ferrous iron is a stable energy source for *Thiobacillus* in acid solutions (eg., pH <5; above which autooxidation takes place under ambient environmental conditions to ferric iron). Ferrous iron is one of the most easily oxidized substrates for *Thiobacillus ferroxidans* and certain other bacteria (UNEP, 1988). The oxidation reaction takes place according to:

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$

The oxidation of iron from the ferrous to ferric state is an energy-yielding reaction for the bacteria. However only a relatively small amount of energy is available from this reaction as compared with energy yields from the oxidation of other inorganic energy sources, such as elemental sulfur (ie., 118 kcal for sulfur oxidation and 40 kcal for ferrous iron oxidation, on a molar basis). Consequently, the bacteria must oxidize large amounts of iron sulfides to obtain sufficient ferrous iron and energy to maintain cellular processes and growth.

Physiologically, the following events occur in the oxidation by iron for *Thiobacillus ferroxidans* (Lundgren and Silver, 1980). Ferrous iron is oxidized to ferric iron by an iron-oxidizing enzyme, Fe$^{2+}$-cytochrome c oxidoreductase, with the release of electrons:

$$2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{e}^-$$

The ferrous iron oxidation system of *T. ferroxidans* is believed to be associated with the cellular membrane/envelope. Figures 6-1 and 6-2 illustrate a proposed scheme of electron transfer and ATP synthesis during oxidation of Fe$^{2+}$ by *T. ferroxidans* (UNEP, 1988; Ehrlich, 1981; Hutchins et al., 1986).
FIGURE 6-1. Scheme for Pathway of Electron Transfer in *T. ferrooxidans* during Oxidation of Fe$^{2+}$ (from UNEP, 1988).

Molecular oxygen serves as the terminal electron acceptor where it is reduced to water:

$$\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$$

A copper containing protein, rusticyanin, has also been reported to serve as an intermediate electron acceptor upon oxidation of ferrous iron (Hutchins et al., 1986)

The pair of transferred electrons yields enough energy to insure the formation of ATP by oxidative phosphorylation (converting electron energy to ATP functions to store the energy by forming a high energy bond).

Combining the two equations above gives:

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$$

which is the rate determining step for the oxidation of pyrite by ferric iron. The oxidation rate of Fe$^{2+}$ to Fe$^{3+}$ is pH dependent above pH 2.2 and independent of pH under more acidic conditions (Pesic, 1989).

The CO$_2$ fixation reactions in *Thiobacillus ferrooxidans* are coupled to the production of energy from ferrous iron oxidation. The reduction of pyridine nucleotides (NADH, NADPH) provides the organism with reducing power to fix CO$_2$. However, because the oxidation of ferrous to ferric iron has a higher oxidation-reduction potential (+0.77) than that of the reduction of pyridine nucleotides (NADH $\rightarrow$ NAD; -0.32), the oxidation of iron cannot be directly coupled to the reduction of NAD to NADH. To circumvent this difficulty the organisms reduce NAD by a "reversed electron transport" process where the electrons derived from the oxidation of ferrous iron probably enter the respiratory chain at cytochrome c and compensate for the high oxidation potential of ferrous to ferric iron by going "uphill" or the reverse direction from normal electron flow. In other words, electrons flow to NAD rather than O$_2$, with the consumption of ATP and the formation of NADH. Therefore, ATP formed by oxidative phosphorylation is used to synthesize NADH which is needed for CO$_2$ fixation. These processes are incompletely understood (Lundgren and Silver, 1980).

Elemental sulfur may be biologically oxidized to sulfate and acidity ($H^+$) by the following reaction:

$$S^0 + \frac{3}{2}O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$$
Sato (1960) concluded that sulfur released from the crystal structure, in minerals such as pyrite or marcasite, was converted to unstable $S_2$ molecules, which would quickly be oxidized to sulfate (Section 6.1). On the other hand he reported that, solid stable sulfur was released by other metal sulfides and that this sulfur was only slowly oxidized by ferric iron in the absence of bacteria. Therefore, under oxygen limiting conditions sulfur oxidizing bacteria appear able to utilize ferric iron as an electron acceptor in the oxidation of metal sulfides other than iron sulfide.

The oxidation of sulfide and sulfur is an energy yielding process with the formation of ATP from the transfer of electrons to oxygen during oxidation of sulfite to sulfate and entry of the transferred electrons to the oxidative phosphorylation cycle as discussed for iron oxidation. Steps in the oxidation of sulfur by *Thiobacilli* are shown in Figure 6-3. *Thiobacillus ferrooxidans* can oxidize both iron and sulfur compounds while *T. thiooxidans* is restricted to the oxidation of sulfur only.

![Figure 6-3](image)

**FIGURE 6-3.** Steps in the Oxidation of Different Sulfur Compounds by *Thiobacilli*.

Beck and Brown (1967) studied suspensions of *T. ferrooxidans* over extended periods of time and found that the sulfur oxidation system aged more quickly than the iron oxidation system, and that with diminished ability to oxidize sulfur the cell suspensions were unable to oxidize pyrite or chalcopyrite. The researchers concluded that the iron and sulfur oxidation systems are different and that the sulfur system appears essential for the solubilization of sulfide ores.

These energy yielding bacterial reactions may delay the transfer of electrons to the abiotic medium during the mineral sulfide oxidation process. The reactions described for the abiotic acid generation process (Section 6.1) do not take into account this potential delay and
therefore, may underestimate the amount of acidity produced during bacterial mediation of the acid generation process. The importance of the association of these bacteria and other acid tolerant autotrophic species in waste-rock piles will be discussed in a later section.

6.2.2  Bacterial Leaching Methods

The role of bacteria and chemical processes in the dissolution of sulfide minerals has been summarized by UNEP (1988) for oxidation of pyrite.

\[
\begin{align*}
1. & \quad 2\text{FeS}_2 + 15/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \\
2. & \quad \text{FeS}_2 + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+} + 2\text{S}^0 \\
3. & \quad 2\text{Fe}^{2+} + 1/2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \\
4. & \quad \text{S}^0 + \text{H}_2\text{O} + 3/2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \\
5. & \quad \text{S}^0 + 6\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow 6\text{Fe}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+
\end{align*}
\]

The increased rate of solubilization of sulfide ores by *Thiobacillus ferrooxidans* has been attributed either to direct action of the bacteria on the sulfide mineral surface or to an indirect effect whereby ferric iron is presumed to chemically oxidize the ore and is returned to the active, oxidized state by the action of iron-oxidizing bacteria. Attempts by researchers to demonstrate that microbial action could be duplicated by the presence of ferric iron alone have not been definitive, and have led to the suggestion that both direct and indirect bacterial action may be operating simultaneously (Beck and Brown, 1968; Brierley, 1978; Silverman and Lundgren, 1980; Ehrlich, 1981).

In direct microbial oxidation on metal sulfides, the crystal lattice of susceptible sulfides is attacked through enzymatic oxidation. Therefore, it is important that the microbes are in intimate contact with the mineral they metabolize (Ehrlich, 1981). Evidence for direct microbial leaching is inferred from observations of microbial attachment to sulfide minerals (Berry and Murr, 1978). The literature cites the best evidence for direct bacterial leaching in studies using synthetically prepared metal sulfide minerals free of iron; however, extrapolating this evidence to complex mineral associations with abundant iron presents complications. Recent studies, using direct physical observation of minerals, provide a more accurate assessment of direct bacterial leaching of sulfide minerals. Several researchers have shown selective attachment of autotrophic bacteria on pyrite, chalcopyrite and molybdenite surfaces using scanning electron microscopy (Murr and Berry, 1978; Chakraborti and Murr, 1980;
Gormely and Duncan, 1974; Baldensperger et al., 1974; Rodriguez-Leiva and Tributsch, 1988).

Southwood and Southwood (1986) examined bacterially leached pyrite residue microscopically and by electron microprobe. Deeply penetrating pores were observed, occurring most commonly in structurally disturbed regions of the pyrite crystals. They concluded that structural imperfections in the pyrite crystal lattice provide preferred sites for bacterial attachment. It is also possible that in directly attacking sulfide minerals bacteria enhance the deformation of the crystal structure thereby facilitating the oxidation process (UNEP, 1988).

The direct microbial oxidation of pyrite likely follows the reaction:

\[ \text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{H}^+ + 2\text{SO}_4^{2-} \]

The ferrous iron generated in the reaction is further oxidized by the bacteria as discussed in previous sections.

Attachment of the bacteria to the surface of the minerals is obviously an important step for the direct leaching method. Duncan and Drummond (1973) suggested that bacteria may produce surface-active agents to enhance attachment to sulfide mineral grains. Wakao et al. (1984) reported that pyrite oxidation was markedly improved when bacterial cells were released into a mineral sulfide medium with organic surface active agents. The authors suggest that the organic additives do not have a physiologically stimulating effect on the growth of the bacteria but rather may have a physico-chemical effect on the interrelationship between the sulfide mineral surface and the bacterial cells. Wakao et al. (1983) in a study examining the effect of various organic substances on release of iron from pyrite by T. ferrooxidans noted that non-specific organic substances such as protein and nucleic acid extracted from cells of Thiobacillus were regarded as promoting factors in the oxidation of pyrite by these organisms. Rodriguez-Leiva and Tributsch (1988) using scanning electron microscopy have shown that bacterial attack of the sulfide interface starts by secretion of either an aqueous or organic substance around the contact area between the bacterial cell and the sulfide energy source. The composition of this contact film has not been determined; however, it appears to be important to the mechanism of direct bacterial dissolution of metal sulfides. This contact film likely functions as a molecular carrier for removing and transporting sulfur, the main energy source for the bacteria, from the sulfide surface into the bacterial cell.
Evidence for a direct mechanism of sulfide mineral oxidation by bacteria has also been demonstrated by leaching studies on pyrite and chalcopyrite using metabolic inhibitors to separately observe the oxidation of the sulfur and iron moieties (Silver, 1987). Kleinmann and Crerar (1979) demonstrated that T. ferrooxidans is capable of colonizing and acidifying a near-neutral pH environment of crushed coal or overburden, without prior establishment of a pH-dependent succession of bacteria. They suggested that T. ferrooxidans accomplished this through direct oxidation of pyrite. Indirect oxidation of pyrite by bacteria has been reported to be approximately 7 times faster than direct oxidation (Walsh, 1978), however, based on the results of Kleinmann and Crerar (1979) it appears that direct oxidation is a faster initiator mechanism for acid generation.

Metal dissolution using ferric iron or ferric sulfate (commonly used in commercial leaching operations) is usually referred to as indirect bacterial oxidation because the regeneration of ferric iron by abiotic oxidation is reportedly too slow at acidic pHs to be significant without bacterial mediation. Brock and Gustafson (1976) using three common acidophilic bacteria, T. ferrooxidans, T. thiooxidans and S. acidocaldarius, demonstrated bacterially mediated reduction of ferric iron using elemental sulfur as the electron donor. The study was conducted under anaerobic conditions, since the ferrous iron formed by the reduction would be oxidized by oxygen. As discussed earlier the researchers used evidence from a study conducted by Sato (1960) to show that ferric iron could be used as an electron acceptor by bacteria to oxidize metal sulfides which did not contain iron under oxygen limiting conditions.

Discussion in the literature as to which mechanism dominates has not been conclusive and it is likely that both bacterial leaching mechanisms occur. Brierley and Brierley (1986) suggest that the "direct" leaching mechanism has not been conclusively demonstrated for iron-containing minerals, because the presence of any iron in the medium will initiate an "indirect" leaching mechanism. Brierley (1978) discussed inhibition by ferric iron of T. ferrooxidans iron oxidation. Brierley cited studies by Wong et al (1973) and Kelly et al (1978) in which it was found that low ferric iron concentrations enhance oxygen uptake but as the ferric iron concentration increases, oxygen decreases, with ferric iron acting as a competitive inhibitor. The researchers postulated that the competitive inhibition by ferric iron decreases the organism's affinity for ferrous iron, although this trait was found to be dependent on the strain of bacteria. Taylor et al (1984a, 1984b) in a study comparing inorganic and bacterially mediated mechanisms of pyrite oxidation using stable isotopes concluded that the dominant oxidation mechanism is dependent on environmental conditions. Their research showed that in well-aerated, near surface environments a large amount of pyrite oxidation may occur by "direct" bacterial action, whereas in water-saturated, low oxygen environments ferric iron is believed to be the primary oxidant (indirect bacterial action).
6.2.3. Factors Affecting Bacterial Mediation of the Acid Generation Process

An important aspect of bacterial activity is the elucidation of environmental factors which influence metal dissolution by bacteria. The chemical factors which determine the rate of acid generation were discussed in Section 6.1. Environmental factors which enhance or inhibit bacterial activity include:

- pH;
- Temperature;
- Concentration and reactivity of redox species;
- Nutrient requirements;
- Presence and concentration of bacterial inhibitors;
- Oxygen availability;
- Carbon dioxide content;
- Water potential;
- Electrochemical effects (galvanic interactions);
- Particle size; and
- Formation of secondary sulfide phases.

*Thiobacillus ferrooxidans* and other acidophilic bacteria involved in the dissolution of mineral sulfides are physiologically most active in the pH range of 1.5 to 5 (Silver, 1987). An optimum pH range between 1 and 2.5 has been reported for the bacterially mediated oxidation of ferrous iron sulfide minerals including: pyrite, sphalerite, galena, chalcopyrite, covellite and chalcocite (Lundgren and Silver, 1980), although no lower limit for the acidophilic bacteria has been established. Effective mechanisms exist, under natural conditions, to ensure the maintenance of optimum pH conditions for bacterial growth in response to changes in pH resulting from oxidation reactions. The formation of insoluble sulfates at certain pH values is one such mechanism. For example, above pH 1.7 insoluble secondary minerals such as jarosite precipitate and may influence sulfide oxidation in two ways: the removal of ferric iron as an oxidizing agent may decrease the rate of acid production; and, it may insulate the mineral surfaces from further attack by coating with an insoluble precipitate (Brierley, 1978; Silver 1987).

Most physiological studies of iron oxidizing bacteria have indicated optimal temperatures of 25 to 35°C, with a maximum of 45°C for mesophilic bacteria. 55°C was previously considered to be the limit of biological oxidation, above which only chemical oxidation would take place. The isolation of thermophilic bacteria (Section 6.2.5) has increased the temperature at which biological oxidation is known to occur to 90°C (Brierley, 1978). Lower temperature limits for bacterial activity have not been established, however, bacterial oxidation in mines, soils and
natural waters has been reported at temperatures below 10°C. It is generally accepted that temperatures near the freezing point of water are limiting (Lundgren and Silver, 1980).

The oxidation-reduction potential will increase during the oxidation of ferrous iron by *T. ferrooxidans*. However, the amount of the increase will not closely approach that of the ferric/ferrous system which is +747 mV at 25°C, except at very low iron concentrations or at high acidity (i.e., below pH 1.7), because oxidized iron is precipitated from the medium and/or quickly reduced to ferrous iron (Silver, 1987). Oxidation-reduction potentials between +200 and +550 mV have been measured during oxidation of metal sulfides by acidophilic bacteria (Lundgren and Silver, 1980).

Nutrient requirements of sulfide mineral oxidizing bacteria have been reviewed by several authors (Tuovinen et al., 1971; Brierley, 1978; Lundgren and Silver, 1980; and Ehrlich, 1981). Ammonium-nitrogen, phosphorus, sulfate and magnesium have been reported to be essential for cellular processes of *Thiobacillus ferrooxidans* (Tuovinen et al., 1971). Magnesium is necessary for the fixation of carbon dioxide and phosphorus is required for energy metabolism and iron oxidation (Brierley, 1978). Nutrients such as nitrogen and phosphorus are generally not limiting because very small concentrations are sufficient for growth (Nordstrom, 1982a). Nitrogen has been reported to be fixed by *T. ferrooxidans* (Tuovinen and Kelly, 1973). Bacteria appear to require sulfate for iron oxidation. Researchers have postulated that 1) sulfate may control the entrance of ferrous iron into the cell or enhance the organisms affinity for ferrous iron and, 2) sulfate may be required in energy transfer for the iron oxidase system. Schnaitmann et al (1969) reported that adding sulfate in concentrations of 0.2 to 2.8 g/L doubled the iron oxidation rate.

Certain organic and inorganic chemicals are known to inhibit autotrophic, acidophilic bacterial activity. Matin (1978) showed that organic acid concentrations as low as 0.1 mol/L inhibit the growth of *T. ferrooxidans*. At low concentrations, surfactants may accelerate the oxidation of copper sulfide minerals (Bruynesteyn et al., 1971). However at higher concentrations these substances are bactericidal because they reduce the surface tension and decrease the mass transfer of oxygen (Lundgren and Silver, 1980). *Thiobacillus ferrooxidans* has a high tolerance to toxic metal ions compared with other microorganisms. However, tolerance to heavy metals varies with environmental conditions as well as the strain of bacteria and is largely dependent on acclimation (or adaptability) of the bacteria to the sulfide mineral matrix or association. *T. ferrooxidans* has shown an increased tolerance to heavy metals during iron oxidation as compared with thiosulfate oxidation, suggesting that enzymatic differences contribute to metal tolerance (Tuovinen et al., 1971). The molybdate ion is extremely toxic to *T. ferrooxidans*. Its toxicity may be due to competition with the sulfate anion which is postulated to be a nutritional requirement for the bacteria (Lees et al., 1969). Inhibitory effects by the following
cations and anions have been investigated: uranium, arsenic, selenium, molybdate, mercury, silver, gold, chromium, thallium, rubidium, chloride, fluoride, nitrate, cyanide, and azide.

The iron oxidizing bacteria are strict aerobes and limitations in oxygen availability affect the rate of ferrous iron oxidation and dissolution of metal sulfides. Erikson (1985) mentioned literature that showed a range of values between 2 and 20% for oxygen limitations on bacterial oxidation. However, oxygen availability has been found to be of less importance the further along the acid generating process has progressed. Once the ferrous/ferric iron couple has been established, oxidation of sulfides has been shown to occur under anaerobic conditions (section 6.2.3). It is not known how extensive the use of oxidants other than oxygen is for bacteria in a sulfidic waste-rock environment.

*Thiobacillus ferrooxidans* and other autotrophic bacteria obtain all of the carbon required for cell biosynthesis from CO₂. Carbon dioxide solubility is low in acidic environments and therefore may be a limiting parameter for growth, especially in environments where heterotrophic growth is inhibited. Carbonate gangue minerals will provide an ample supply of CO₂ (Harries and Ritchie, 1983b); however, the supply of these minerals will become increasingly limiting as acid generation progresses and the carbonate minerals are dissolved and transported away from the site of acid generation activities. Torma et al. (1972) noted that the optimum CO₂ content in the gaseous phase was 0.22%, over a range of 0.03 to 7.92%. Therefore, increasing the CO₂ concentration increases sulfide mineral dissolution, but will also increase the amount of CaCO₃ solubilized, which will neutralize or inhibit further mineral dissolution reactions. Little information is available on the lower limits of CO₂ availability for bacterial oxidation of sulfide minerals.

Water potential or availability is an important parameter in controlling the activity of *Thiobacillus ferrooxidans*. However, because the organisms also require oxygen, a balance must be maintained between moisture and aeration in a waste-rock dump to ensure favorable conditions for bacterial activity. Brock (1975), studied the activity of *T. ferrooxidans* in coal refuse materials at different water potentials and determined that the lowest water potential causing complete inhibition of bacterial ferrous iron oxidation was -32 bars. A water potential of -23 bars was found to be the minimum for bacterial growth; however, water potentials greater than -15 bars were considered a requirement for sustained bacterial activity. Moistened fine ore was found to contain the highest number of microorganisms (10⁶ to 10⁸ cells/cm³) in a case study on dump leaching of copper at Nikolayev mine in the USSR (UNEP, 1988).

The biohydrometallurgy literature has shown that the presence of different base metal sulfides may significantly modify the leaching kinetics of the desired metal due to electrochemical
effects. In addition to such galvanic effects, resulting from two minerals being in close contact, metal sulfide solubility may also be affected by the differences in their electrode potentials. The subject of galvanic interactions between sulfide minerals is very large and well developed, hence the subject is only briefly covered for the purpose of elucidating the role of bacteria in the process.

Several papers have addressed the subject of galvanic interactions and electrochemical nobility scales have been proposed (Sato, 1960; cited in UNEP p. 162). Galvanic and electrochemical processes are relevant to sulfide mineral oxidation in waste-rock dumps because of the polymineral associations of ores. Oxidation of each sulfide becomes a more complex process, because it is then directed and controlled by particular characteristics of the electrochemical reactions between contacting minerals. For example, a mineral having a higher electrode potential (EP) plays the role of cathode and accelerates the oxidation of the mineral having a lower EP, the anode. In other words, galvanic interaction favors the oxidation of the mineral with the lowest electropotential. The greater the difference between the EP of the two minerals the higher is the rate of the anode-mineral decomposition. In studies on the bacterial leaching of sulfide pairs having pyrite as one of the members, the extraction of copper from chalcopyrite, chalcocite, and bornite was more intensive than for leaching of the minerals individually (Table 6-3). The EP of pyrite is higher than the copper minerals therefore pyrite acts as the cathode and remains intact, while the copper sulfides are decomposed. Natarajan and Iwasaki (1985) also noted accelerated dissolution of chalcopyrite in the presence of pyrite, molybdenite and stibnite while galena retarded dissolution. _T. ferrooxidans_ may accelerate the galvanic reactions by continuously oxidizing the film of elemental sulfur that would form a physical barrier to diffusion of copper and iron salts away from the reacting phase (Hutchins _et al._, 1986). _T. ferrooxidans_ may also enhance the effects of natural galvanic interaction in polymineral associations by regenerating ferric iron and thereby maintaining a high redox potential in the medium.

The rate of pyrite oxidation is widely considered a function of surface area (Silver, 1987). Evidence for bacterial attachment and a subsequent direct method of pyrite oxidation was discussed in section 6.2.3. The "shrinking core" model of pyrite oxidation suggests that the surface of pyrite particles decreases as oxidation proceeds (Letowski, 1980). Southwood and Southwood (1986) have alternatively proposed a "propagating pore" theory which implies that the surface area increases as leaching of the pyrite particle progresses. Both models of pyrite oxidation assume that small grains with a proportionally higher surface area to mass ratio are depleted more quickly than larger particles. However, if the sulfide particle sizes are small the surface area of gangue minerals will be correspondingly large and available for neutralization of acidity produced. Extraction rates may also decrease because of the interference of solids (Lundgren and Silver, 1980).
### Table 6-3
Common Minerals Oxidized by Bacteria
(from Brierley, 1978 and UNEP 1988)

<table>
<thead>
<tr>
<th>Sulfide Minerals Known to be Oxidized by Bacteria</th>
<th>Minerals in Order of Increasing Resistance to Bacterial Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>Pyrrhotite</td>
</tr>
<tr>
<td>Marcasite</td>
<td>Chalcocite</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Covellite</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Tetrahedrite</td>
</tr>
<tr>
<td>Bornite</td>
<td>Bornite</td>
</tr>
<tr>
<td>Covellite</td>
<td>Galena</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Arsenopyrite</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>Enargite</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>Enargite</td>
</tr>
<tr>
<td>Realgar</td>
<td>Marcasite</td>
</tr>
<tr>
<td>Orpiment</td>
<td>Chalcocpyrite</td>
</tr>
<tr>
<td>Cobaltite</td>
<td>Molybdenite</td>
</tr>
<tr>
<td>Pentlandite</td>
<td></td>
</tr>
<tr>
<td>Violarite</td>
<td></td>
</tr>
</tbody>
</table>

Jarosite precipitated on the surface of a mineral particle has been shown to inhibit the bacterial leaching process (Brierley, 1978). Chemical formation of jarosite occurs at pHs greater than 1.7, and depletes the leach solution of nutrient cations such as potassium, sodium and ammonium required for cellular metabolism of chemoautotrophic bacteria (Ivarson, 1973). Pool et al (1989) studied the oxidation of chalcocrytite under dump leach conditions. Results indicated that the copper leaching rate is controlled by reactions at the surface of minerals and passivation of chalcocpyrite surfaces during oxidative leaching is the rate limiting factor in copper extraction. The data presented indicated that the decrease of leaching (passivation) noted by the authors and others appears to be the result of formation of an unidentified, passivating, intermediate copper sulfide phase, which affects both the chemical and biological oxidation of chalcocpyrite surfaces. Although evidence for the formation of secondary precipitates of iron, sulfur and other inorganic elements has been shown, the rate and environmental conditions of their formation are not completely understood.
6.2.4  Bacterial Associations

Although the bacterially mediated leaching and oxidation of sulfide minerals is a widely used process in the mining industry, it is poorly understood ecologically. The function of bacteria involved in the dissolution of sulfide minerals is fairly well understood, however not many studies have addressed the relationship of the organism with the leaching environment and with other indigenous microbes (Hutchins et al., 1986).

*Thiobacillus ferrooxidans* has been the most extensively studied organism associated with metal sulfide oxidation; however, other bacteria of the genera *Leptospirillum, Sulfolobus, Sulfobacillus* and *Metallogenium* (Ehrlich, 1981) have also been implicated in the mediation of acid generation from metal sulfides. These organisms are also capable of oxidizing ferrous iron enzymatically and a majority are chemolithotrophs.

Temperature and pH appear to be the determining factors for microbial succession in sulfide deposits. At pH in the range of 3.5 to 4.5, a filamentous iron-oxidizing bacterium, *Metallogenium spps.*, has been implicated in the establishment of acid conditions (Walsh and Mitchell, 1972). LeRoux et al (1979) examined the microbial role in pyrite oxidation at alkaline pH in coal spoils. The results indicated that indigenous bacterial species were successful in growing and acidifying the solution pH from a neutral pH to a pH less than 3 in a time period ranging from 3 to 10 d. Plating of the bacteria revealed a mixed culture of autotrophs and heterotrophs. Chemical oxidation at the initial stages of acid generation was ruled out on the basis of oxygen uptake experiments using antimicrobial agents. Although the presence of iron oxidizing organisms at near-neutral pH has been noted, acidophilic bacteria of the genera *Thiobacillus, Sulfolobus, Sulfobacillus, and Leptospirillum* predominate at pHs below 4.

The existence of thermophilic bacteria, capable of oxidizing sulfide minerals at temperatures exceeding those tolerated by *Thiobacillus* species has long been suspected. Significant amounts of heat are generated in the oxidation of sulfide ore bodies and leach dumps, which may raise the interior temperature to 80°C (Ehrlich, 1978). Brierley and Brierley (1973) isolated the first thermophilic, acidophilic bacteria capable of oxidizing iron and sulfur from an acid hot spring. The organism was characterized as an obligate thermophile requiring a temperature in the range of 45 to 70°C and was grouped with the *Sulfolobus* spp. Another acidophilic, thermophilic bacteria capable of pyrite oxidation at 55°C was isolated by LeRoux et al (1977). The bacteria was grouped under the genera *Sulfobacillus*. A species of extremely thermophilic organisms, *Sulfolobus spps.*, has recently been characterized (Marsh and Norris, 1983). The organisms grow autophytically at pH 1 to 3 with a temperature range from 50 to 90°C. Leaching with *Sulfolobus* has been confined to molybdenite and several
copper sulfide minerals (Brierley and Brierley, 1986), likely because of difficulties encountered in leaching these minerals using the moderately thermophilic organism, *T. ferrooxidans*. The ability of *Sulfolobus* to oxidize molybdenite is a unique property of this bacterium since *T. ferrooxidans* is inhibited by the oxidation product of the molybdate ion (Tuovinen et al., 1971). Murr and Brierley (1978) reported that an increase in temperature from ambient to 59°C resulted in a significant decline in *T. ferrooxidans* population after which moderately thermophilic microorganisms were found. The *T. ferrooxidans* population numbers returned to normal once the temperature decreased to less than 40°C. These results suggest a succession of species based on temperature requirements of the acidophilic sulfide oxidizing bacteria. *Sulfolobus* spps. bacteria were first identified in water samples originating from a coal pile drainage channel in England (Marsh and Norris, 1983) suggesting that the organisms may also be active in the interior of waste-rock piles.

*Leptospirillum ferrooxidans* can also attack mineral sulfides under acidic conditions. *L. ferrooxidans* is a gram-negative, mesophilic, acidophilic, obligate autotroph which is capable of oxidizing ferrous iron, but not sulfur. The energy and habitat requirements of this bacterial species suggest that it may co-exist with *Thiobacillus* spps. in waste rock. *Leptospirillum*-like bacteria have been isolated from mines and mine-waters at various locations (Norris, 1983).

Although characterization of other bacterial species capable of oxidizing metal sulfides is important in bacterial optimization processes, the significance to acid generation in waste-rock dumps has not been defined. The majority of these organisms have been isolated from extreme environments such as thermal hot springs but have not been shown to colonize sulfidic waste-rock dumps naturally.

6.2.5 Metal Dissolution Reactions

Bacterial oxidation of pyrite is the most frequently used example of bacterially mediated sulfide mineral dissolution reactions; however, microbes are capable of oxidizing a great many sulfide minerals (Brierley, 1978; Natarajan and Iwasaki, 1985; UNEP, 1988). Table 6-3 provides a list of minerals known to be oxidized by bacteria and the order of resistance of some common sulfide minerals.

On a commercial scale biological leaching of copper and uranium is the most successful and widely used application. Recent interest has focused on the use of microorganisms in the leaching of gold and silver, although the bacterially-mediated leaching functions only to solubilize the gangue minerals which encapsulate the precious metal rather than acting on the gold directly (Hutchins et al., 1986).
Natarajan and Iwasaki (1985) indicated that *Thiobacillus ferrooxidans* can oxidize sulfide minerals in the absence of iron. Dissolution studies with bacteria using prepared zinc sulfide and copper sulfide demonstrated that zinc oxidation was enhanced in the presence of CuS, while copper dissolution decreased with the addition of ZnS. Although zinc dissolution occurred largely through galvanic interaction, the presence of bacteria enhanced the oxidation reaction.

### 6.3 Acid Neutralization

The suite of geochemical reactions referred to as "acid neutralization" minimize the impacts of acid generation by decreasing levels of acidity, increasing pH towards neutral values, and causing aqueous metals to precipitate from the water. In this section, the discussion of acid neutralization focuses on natural and in-situ neutralization that could occur within a waste-rock pile rather than neutralization within an engineered treatment plant.

In a relatively simple context, neutralization can be conceptualized as acid-neutralizing minerals being in contact with acid-generating minerals. However, the process is more complex because it requires the presence of water. This aqueous connection leads to three primary scenarios for neutralization: (1) the water passes over neutralizing minerals, dissolving a portion of the minerals and accumulating aqueous alkalinity, and then flows over acid-generating minerals, (2) the water passes over acid-neutralizing and acid-generating minerals almost simultaneously, and (3) the water passes over acid-generating minerals, accumulating aqueous acidity, and then flows over acid-neutralizing minerals. In the first scenario, the extent of neutralization is determined by the amount of accumulated alkalinity prior to contact with acidity, whereas the latter two scenarios allow neutralization to proceed in response to aqueous acidity. As a result, the first scenario is usually considered the poorest for environmental protection because neutralization in response to acid generation is absent. In all cases, neutralizing minerals are progressively consumed through time and, if the neutralizing minerals are consumed completely before the rate of acid generation slows, the severity of the acid drainage may increase.

In any acid-generating waste-rock pile, the initial contents of acid-neutralizing and acid-generating minerals and their contrasting rates of consumption will determine the geochemical nature of the drainage from a pile. If the initial content of neutralizing minerals is greater than acid-generating minerals, large-scale acid drainage may not be expected. However, there are complications which could still lead to acid drainage in this case, such as: (1) the consumption rate of acid-neutralizing minerals is greater due to other factors such as flushing by rainfall, so that acid drainage could appear at some future point in time, (2) the
distribution of neutralizing minerals is not consistent with the distribution of acid-generating minerals, so that localized areas of acid drainage develop, and (3) the neutralizing minerals become coated by secondary mineral precipitates and are thus isolated from the acid drainage. On the other hand, if the initial content of acid-generating minerals is greater, large-scale acid drainage may be expected at some time. Again, there are complexities such as: (1) an initial content of neutralizing minerals would prevent the onset of acid drainage for some length of time and (2) there would be no acid drainage if the sulfide minerals are essentially non-reactive. These complexities as well as those discussed elsewhere in this report demonstrate the caution which must be used in defining the potential for acid drainage through the pre-mining, operational, and decommissioned stages of a mining operation. This section, in particular, will highlight the importance of understanding acid neutralization as a key element in water-quality prediction, environmental protection, and implementation of control measures (Section 7.0).

The overall process of acid neutralization is dependent on both aqueous reactions and the dissolution (consumption) of neutralizing minerals. This two factors are discussed independently in the following sections.

### 6.3.1 Aqueous-based Neutralization Reactions

According to the commonly-used ionic model of water chemistry, elements dissolved in water exist as hydrated ions with an electrical charge. Some ions combine with others to form ion pairs or aqueous complexes referred to as "speciation". For example, some common forms of sulfate (a combination of oxidized sulfur and oxygen) in acid drainage waters include: free sulfate ($\text{SO}_4^{2-}$), bisulfate ($\text{HSO}_4^-$), $\text{CaSO}_4^0$, $\text{FeSO}_4^0$, and other complexes depending on the concentrations of cations (positively charged ions such as many base metals) and on the concentrations of other anions (negatively charged ions such as carbonate and nitrate). Each of these complexes has unique implications on acid neutralization. For example, $\text{HSO}_4^-$ will release the $\text{H}^+$ (acidity) from the complex as neutralization is initiated, requiring additional neutralization to attain an environmentally acceptable pH. Also, $\text{FeSO}_4^0$ could release its iron for mineral precipitation as siderite ($\text{FeCO}_3$), which removes one mole of aqueous carbonate (alkalinity) for each precipitated mole of iron, or as $\text{Fe(OH)}_2$ or $\text{Fe(OH)}_3$, which creates two and three moles of aqueous acidity, respectively, for each mole of precipitated iron. These implications of speciation are usually reported in literature from an empirical perspective, such as in Shoemaker et al. (1961) where extractable aluminum was found to consume alkalinity during neutralization of acidic soils.
The geochemical implications as described in the previous paragraph are not obvious from standard water analyses which typically report only concentrations of elements. For example, an analysis for dissolved sulfate yields only total dissolved sulfate, which is the sum of the concentrations of sulfate complexes, ion pairs, and free sulfate. Consequently, full water-chemistry scans of all relevant elements and subsequent speciation analyses of the results are required to thoroughly understand (1) the conditions within a waste-rock pile which create a particular water chemistry and (2) the manner in which the chemistry might change through time and distance during flow. Some speciation analyses can be conducted using special laboratory techniques, but are usually performed theoretically using computer programs. Speciation programs such as WATEQ4F (Ball et al., 1987) and MINTEQ (Felmy et al., 1984) perform a speciation analysis using principles of equilibrium chemistry, published equilibrium constants of aqueous reactions, and iterative calculations to account for all the interactions among the aqueous species. Because of the time and cost involved in full chemical scans and speciation analysis, this type of detailed evaluation of water chemistry is rarely performed. This lack of detailed interpretation of water chemistry is found in much of the existing literature on acid drainage.

To continue this discussion of acid neutralization, the complexities of aqueous speciation will be significantly simplified in order to define some basic reactions. This simplification introduces unavoidable error into the discussion.

The two major neutralization reactions involve forms of carbonate (CO$_3^{2-}$) and hydroxide (OH$^-$) ions, which often represent total alkalinity in water, although other species such as ammonia and boron may contribute significantly to total alkalinity. From a simplistic viewpoint, the primary forms of aqueous carbonate are free carbonate (CO$_3^0$), bicarbonate (HCO$_3^-$), and carbonic acid (H$_2$CO$_3$) and dissolved CO$_2$ gas. The sum of free carbonate and bicarbonate is usually referred to as carbonate alkalinity.

The primary carbonate species are related by the following pH-dependent reactions.

$$
\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3^0 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad \text{(Equation 6-11)}
$$

$$
\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad \text{(Equation 6-12)}
$$

At any particular pH, one of these species will be dominant in terms of concentration (Figure 6-4) with H$_2$CO$_3^0$ dominant below a pH of approximately 6.3 to 6.4 (depending on temperature and pressure) and CO$_3^{2-}$ dominant above a pH of approximately 10.3. At pH values close to 6.3 and 10.3, two species will be similar in concentration and significant pH
buffering can occur which would allow pH to remain nearly constant despite the addition of acidity or alkalinity.

![Figure 6-4](image)

**Figure 6-4.** Relationship of pH to Concentrations of Carbonate Species (from Freeze and Cherry, 1979).

These reactions and the capacity for pH buffering have major implications for neutralization of acid drainage. For example, if \( \text{CO}_3^{2-} \) from the dissolution of a carbonate mineral is continuously added to acidic water (e.g., pH 2), pH will slowly increase towards 4 as effects of species such as \( \text{HSO}_4^- \) are overcome. The pH will then increase towards 6 through the reverse reactions of Equations 6-11 and 6-12 forming \( \text{H}_2\text{CO}_3 \) by consuming 2 moles of acidity (H\(^+\)) for each mole of \( \text{CO}_3^{2-} \). Around pH 6.3, \( \text{HCO}_3^- \) begins forming in preference to \( \text{H}_2\text{CO}_3 \). Because \( \text{HCO}_3^- \) represents a consumption of only 1 mole of acidity for each mole of carbonate, neutralization beyond this point becomes less efficient. As \( \text{CO}_3^{2-} \) continues to be added to this water, pH begins to rise above 6.4; however, this is resisted by \( \text{H}_2\text{CO}_3 \) which begins to break down to \( \text{HCO}_3^- \) and releasing acidity according to Equation 6-11. This release of acidity requires additional carbonate to raise the pH above 6.4.

An important conclusion from the discussion in the preceding paragraph is that neutralization with carbonate to pH 7 requires significantly more carbonate than for neutralization to pH 6. As a gross estimation, Equations 6-11 and 6-12 indicate that twice as much carbonate is required for neutralization to pH 7 than to pH 6, although the actual ratio is dependent on the other aqueous species in the water as well as the exchange of \( \text{CO}_2 \) gas with the water. Because a pH near 6 may not be sufficiently neutral to ensure the protection of freshwater life and the precipitation of metals to acceptable levels, carbonate consumption to reach a
pH of 7 to 8 may often be a more reliable target for neutralization, in general requiring significantly more carbonate. The increased consumption for full neutralization is rarely acknowledged in the literature on acid neutralization because the assumption is made that each mole of carbonate will neutralize two moles of acidity. Careful attention to speciation would help in this situation.

On a simplistic level, the behaviour of hydroxide ions (OH\(^-\)) appears simpler than that of carbonate because it engages in one primary neutralization reaction:

\[
\text{OH}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O} \text{ (water)} \quad \text{(Equation 6-13)}
\]

In this case, one mole of hydroxyl ions neutralizes one mole of acidity (H\(^+\)) by forming water. However, neutralization by hydroxide is complicated by factors such as: (1) water is the reaction medium and represents a large "reservoir" of both hydroxide and H\(^+\), (2) concentrations of free OH\(^-\) below pH 7 are very low (< 0.01 mg/L), and (3) concentrations of metal-OH complexes such as Al(OH)\(^2+\) and Fe(OH)\(^2+\) are relatively high at acidic pH. As a result, neutralization by OH\(^-\) will be strongly dependent on site-specific concentrations and speciation of metals. Full-scale speciation analyses would thus be critical in understanding and predicting the potential for neutralization of acid drainage as it migrates through and out of a waste-rock pile.

**6.3.2 Neutralizing Minerals**

Based on Section 6.3.1, neutralizing minerals can be gathered into two primary groups: (1) those providing carbonate to acidic water and (2) those providing hydroxide to acidic water. In fact, some minerals belong to both groups and some minerals may be considered neutralizing under some site-specific conditions and acid-generating under other conditions. The following discussion provides an overview of these minerals.

Carbonate minerals include calcite and argonite (CaCO\(_3\)), siderite (FeCO\(_3\)), rhodochoosite (MnCO\(_3\)), dolomite (CaMg(CO\(_3\))\(_2\)), ankerite (CaFe(CO\(_3\))\(_2\)), and many others which can be found in books on mineralogy. Upon dissolution, each of these minerals releases a cation and carbonate to the water with the carbonate participating in aqueous reactions described in Section 6.3.1. However, each mineral has a different extent to which it can neutralize acidity and pH before a solubility limit is reached and dissolution ceases. This neutralization capacity is dependent on such site-specific factors as concentrations of various cations and anions in the water (speciation) and the aqueous pH. In fact, one field study of natural neutralization by in-situ calcite has indicated that siderite formed as calcite dissolved, thereby
removing some of the carbonate from solution before it could participate in aqueous neutralizing reactions (Morin et al., 1988; Morin and Cherry, 1988).

Hydroxide minerals include various combinations of metals and hydroxide such as gibbsite (Al(OH)$_3$), boehmite (AlOOH), basaluminite (Al$_4$(OH)$_{10}$SO$_4$), amorphous ferric hydroxide (Fe(OH)$_3$), goethite (FeOOH), and potassium jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$). Like carbonate minerals, the neutralization capacity of each mineral is dependent on such site-specific factors as concentrations of various cations and anions and aqueous pH. Another common complication with some of these minerals is that solubility varies with the degree of crystallinity. The abundant numbers of minerals in this group and the geochemical and site-specific complications in their behaviour cause great difficulty in understanding acid neutralization by these minerals. For example, Nordstrom (1982b) demonstrated the complexity in delineating the occurrence of aluminum-hydroxide-bearing minerals based on the chemistry of water in contact with the minerals.

A mineral’s neutralization capacity can be expressed in a simplistic manner by using the concept of an "equilibrium pH". This value expresses the pH to which acidic water would be neutralized by a mineral and, because of site-specific factors, a mineral can be expected to have a different equilibrium pH at each site of acid drainage, although a definable range can be expected among most sites. Based on speciation and mineral-solubility calculations with data from six published field investigations and one laboratory study (Morin, 1988b), the ranges of equilibrium pH for several minerals suites are:

<table>
<thead>
<tr>
<th>Range of Mineral Suite</th>
<th>Equilibrium pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium-based carbonates</td>
<td>5.5-6.9</td>
</tr>
<tr>
<td>Iron-based carbonates</td>
<td>5.1-6.0</td>
</tr>
<tr>
<td>Aluminum-hydroxide-bearing minerals</td>
<td>4.3-5.0</td>
</tr>
<tr>
<td>Iron-hydroxide-bearing minerals</td>
<td>3.0-3.7</td>
</tr>
</tbody>
</table>

The preceding discussion carried the implied assumption that the minerals dissolved to equilibrium. In reality, some period of time is required to reach equilibrium and, if acidic water quickly moves out of contact with a neutralizing mineral, the concepts of chemical equilibrium, solubility limits, and equilibrium pH are no longer applicable. In waste-rock piles where water movement can be rapid (Section 3), time-dependent chemical kinetics (e.g., Lasaga and Kirkpatrick, 1981; Pearson and McDonnel, 1975) may be necessary to describe and predict mineral dissolution and aqueous chemistry. For example, Evangelou et al. (1985) examined
kinetics of dissolution of siderite, calcite, and dolomite in excess hydrochloric acid and found that dissolution essentially followed a first-order equation simplified to:

\[
\ln [XCO_3] = -kt + \ln[XCO_3^0]
\]

(Equation 6-14)

where \( t \) = elapsed time of dissolution

\([XCO_3^0] = \) initial amount of carbonate mineral

\([XCO_3] = \) amount of carbonate remaining at time \( t \)

Values for \( K \) were found to be 27.64, 6.75, and 0.23 hr\(^{-1}\) for siderite, calcite, and dolomite, respectively. These values indicated the following temporal trends in dissolution:

<table>
<thead>
<tr>
<th>Percentage of Complete Dissolution</th>
<th>Elapsed Time (hours)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Siderite</td>
<td>Calcite</td>
<td>Dolomite</td>
</tr>
<tr>
<td>10%</td>
<td>0.0038</td>
<td>0.016</td>
<td>0.46</td>
</tr>
<tr>
<td>50%</td>
<td>0.025</td>
<td>0.10</td>
<td>3.01</td>
</tr>
<tr>
<td>90%</td>
<td>0.083</td>
<td>0.34</td>
<td>10.0</td>
</tr>
</tbody>
</table>

These results show that significant dissolution will occur within several hours. However, the values of \( K \) are dependent on such factors as mineral impurities, the acid initiating the dissolution, and the speciation of the acidic water and thus values will be site-specific. For example, there are several geochemical and practical problems with siderite dissolution (Morin and Cherry, 1986).

6.4 Metal Leaching

The environmental toxicity associated with acid drainage is the result of not only acidic pH (Sections 6.1 to 6.3), but also the elevated concentrations of metals in the drainage. Aqueous concentrations of many metals can be correlated with pH and are typically highest at acidic pH, minimal near neutral pH, and minimal to somewhat elevated at alkaline pH (Figure 6-5). This trend is typical, but not without many exceptions. For example, metals such as molybdenum may have lower concentrations at acidic pH than at neutral pH and metals such as zinc may have equivalent concentrations at both acidic and neutral pH under some conditions. This section on theory of metal leaching addresses the reasons for the typical relationship and the exceptions.
There are several primary mechanisms that account for the correlation depicted in Figure 6-5 and these mechanisms collectively define "metal leaching" (Table 6-4). One mechanism is the release of metals during oxidation of sulfide metals which can be an integral part of acid generation (Section 6.1). For example, iron is released during oxidation of pyrite and mercury is released during oxidation of cinnabar.

Another mechanism of metal leaching is the enhancement of solubility of many non-sulfide minerals at acidic pH. As a result, aqueous metal concentrations increase as acid generation lowers pH.

A third mechanism for metal leaching involves ion exchange or, in its simpler form, sorption. Relative to pH-neutral conditions, acidic conditions result in less capacity for removal or exchange of toxic metals from water, leading to relatively high concentrations.

A fourth mechanism is speciation or aqueous complexing of metals with anions such as sulfate which are typically found in high concentrations in acidic drainage. This aqueous complexation, which was discussed in greater in Section 6.3, can allow total metal concentrations to rise above those predicted by simple solubility calculations.

The previous mechanisms can usually be evaluated through chemical equilibrium, which implicitly assumes that concentrations arise instantaneously and remain independent of time. Under some conditions, equilibrium is not applicable and kinetic aspects dominate. These time-dependent aspects represent the fifth primary mechanism. Through kinetic processes, aqueous concentrations of metals would depend on such factors as retention times of water within a waste-rock pile and the length of the flowpath of water through a pile.

Because of the complexities of, and interactions among, these mechanisms, metal leaching is site specific and dependent on time and distance. As with acid generation, bacterial
TABLE 6-4

Primary Mechanisms Contributing to Metal Leaching

<table>
<thead>
<tr>
<th>MECHANISM</th>
<th>EXAMPLE REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation of sulfide minerals</td>
<td>Sections 6.1 &amp; 6.2, this report</td>
</tr>
<tr>
<td>Enhanced solubility at acidic pH</td>
<td>McKnight and Bencala (1989)</td>
</tr>
<tr>
<td></td>
<td>Bosch et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>Karathanasis et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>Heiz et al. (1987)</td>
</tr>
<tr>
<td>Ion exchange/sorption</td>
<td>Dudley et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>Crosby et al. (1983)</td>
</tr>
<tr>
<td>Aqueous complexing</td>
<td>Saether et al. (1988)</td>
</tr>
<tr>
<td></td>
<td>Karathanasis et al. (1988)</td>
</tr>
<tr>
<td>Dependency on time and distance</td>
<td>Banaszak (1981)</td>
</tr>
<tr>
<td></td>
<td>Gruner and Hood (1981)</td>
</tr>
<tr>
<td></td>
<td>Miller and Murray (1988)</td>
</tr>
</tbody>
</table>

activity, and acid neutralization (Sections 6.1 to 6.3), the detailed results of metal leaching may be too complex to understand and predict accurately with current knowledge. Nevertheless, some currently available, but under-utilized, techniques such as speciation analysis (Section 6.3) could be used to advance existing knowledge and provide more reliable predictions.

6.5 Modelling of Acid Drainage

Acid drainage is a consequence of the many physical, geochemical, and biological processes discussed throughout this report. Due to the multitude of factors involved, computer models which simulate some processes provide insights into the development of acid drainage beyond those possible by theoretical analysis alone. This section discusses the major advancements in modelling of acid drainage in waste-rock piles and spoils.
Simplified models based on stoichiometry of reactions (Section 6.1) and Fick’s Laws of gas diffusion (Section 5.0) have been available for decades. However, the development of the first detailed computer model for the simulated formation and migration of acid drainage is attributed by Rogowski et al. (1977) to Ohio State University (OSU). Numerous research projects and theses were completed at OSU through the 1960’s and early 1970’s on various aspects of acid drainage, culminating in a comprehensive computer model (Morth et al., 1972). Although this model was developed for underground mine walls, many of its aspects can be extended to waste-rock piles.

Morth et al. (1972) developed equations to simulate and predict oxygen movement into a pore channel through gaseous diffusion and barometric pumping (Section 5.0). Oxidation rates were normalized to the experimental determination of one g of concentrated pyritic material at a size of 60 mesh consuming 25 ug O₂/h/g at 25°C.

Based on field observations, Morth et al. (1972) defined three modes of water movement:

- unsaturated flushing of rock surfaces by trickling water,
- saturated flushing of porespaces, halting acid generation until the porespaces are drained [note: this assumes no oxygen transport in water, see Section 5.0], and
- migration of acidic condensation originating from moist air in the porespaces and the hygroscopic nature of concentrated acidic solutions around pyrite.

The first two modes are discussed in Section 3.0. The third mode is not expected to result in flows comparable to the others; however, Morth et al. concluded that the loadings of acidity (concentration multiplied by water volume) were comparable to the first two modes. This may also be true of waste-rock piles.

The information gathered by Morth et al. (1972) on acid generation, gas diffusion, and water movement was coded into a computer program and comparisons of the simulations to field data indicated the model was successful in predicting the volumes and severity of acid drainage. The model also indicated that significant volumes of acidity remained “stored” on rock surfaces, available for later flushing. Many of the concepts presented in Morth et al. (1972) were extended to the simulation of acid drainage from open-pit walls (Morin, 1990) and can likely be extended to waste-rock piles.

This OSU model was later combined with the Stanford Watershed Model which simulates many of the surficial and climatic processes listed in Table 3-2. This hybrid model was used by Ricca and Chow (1974) and Ricca and Hemmerich (1978) to simulate discharges of acid drainage from underground mines and watersheds.
Waste rock consists of particles of various sizes with the potential for reactive minerals to be located within the particles. As particles size increases, the ratio of minerals within a particle to minerals exposed on the surface increases. If the interior minerals are beyond the reach of oxygen diffusion and water movement, they will be dormant and the total cumulative loading of acidity and metals will be less than predicted on the basis of total volumes. Based on experimental results and conceptualization of rock particles as cylinders, Pionke and Rogowski (1979) found that only 0.1% of the total volume of boulders of 0.5-meter diameter would be available for oxidation and acid generation/neutralization (Figure 6-6). At 0.22 millimetres, the entire volume of a particle would be available. Consequently, the models that are most relevant to waste-rock piles are those which address reactions on surfaces and interiors of particles as well as the other processes such as diffusion and water movement.

In reality, oxidation and leaching of a rock particle is complex and irregular (Figure 6-7). Because this cannot be easily described mathematically or simulated, oxidation of a particle is usually conceptualized as an oxidation zone or front migrating from the surface to the center of a particle. This conceptualization is frequently referred to as the "shrinking core" or "reaction zone" model, although such models will differ in the assumed thickness of the zone and the distribution of unoxidized minerals across the zone.

In a review of heap, dump, and vat leaching, Whittemore (1981) compiled a summary of models through the 1970's (Table 6-5) and concluded that the models of Madsen and Wadsworth and of Cathles and Apps were the most useful and widely applicable. In later work, Derry and Whittemore (1983) collected data on acid drainage from the Avoca Mine in Ireland to test the validity of three models: the diffusion-control model of Roach and Prosser (1978), the sharp-edge reaction zone model of Braun, Lewis, and Wadsworth (1974), and the diffuse reaction zone model of Bartlett (1972). For larger-sized, saturated rock, all three models described the progress of leaching reasonably well. For smaller particles, the Bartlett model provided the best overall fit.

In the 1980's, efforts to construct more detailed and comprehensive models continued. Cathles and Schlitt (1980) expanded the 1975 model to allow two-dimensional air advection, which has produced detectible changes in predictions. Madsen and Wadsworth (1981) extended their 1977 model to oxidation of rock containing chalcopyrite, chalcocite, covellite, and pyrite. Results of large-scale, long-term laboratory tests were used to derive the model and to allow comparisons with simulated results. Madsen and Wordsworth defined the consumption of ferric iron, which was considered the oxidant for all minerals, at a particular location within a particle as:
*Calculated for a cylindrical particle for which the top and bottom of the cylinder is considered impermeable and a diffusion coefficient of $6 \times 10^{-9}$ mm$^2$/sec.

FIGURE 6-6. Sulfate-Contributing Spoil Volume, Controlled by Diffusion According to Particle Size (from Pionke and Rogowski, 1979).
<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Type of Model</th>
<th>Application for Which Model Was Developed</th>
<th>Method of Application Used by Author</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harris et al. 1969</td>
<td>Based on oxygen diffusion and and surface reaction in heap.</td>
<td>Lab-scale tests and full-size heaps of copper sulphide ore from Rum Jungle.</td>
<td>Mainly descriptive.</td>
<td>Made useful distinction between dump leaching processes controlled by properties of the dump itself and those controlled by properties of individual particles.</td>
</tr>
<tr>
<td>Braun, Lewis and Wadsworth (BLW) 1974</td>
<td>Particulate leaching model based on a shrinking core model with a narrow reaction zone, and controlled by a combination of diffusion and chemical reaction.</td>
<td>Leaching of chloropyrite ores at high temperatures and pressures with oxygen as oxidant at scales from 200 g to 61 - simulation of deep in-situ leaching.</td>
<td>By curve-fitting, with some predictive application.</td>
<td>Type of model which has attracted wide interest. The assumption of a narrow reaction zone may be unsound but reasonable correlations have been obtained, although modifying parameters were necessary to account for some discrepancies.</td>
</tr>
<tr>
<td>Madsen, Wadsworth and Groves 1975</td>
<td>BLW model with slight modifications.</td>
<td>Add ferric leaching of monzonite and quartz monzonite copper sulphide ores at pilot scale.</td>
<td>Parameters from leaching data at one particle size used in model to predict leaching at another particle size.</td>
<td>Showed BLW model to be applicable to different systems. Predictions gave good agreement with experiment in one case, but not in the other because of solution flow problems.</td>
</tr>
<tr>
<td>Roman, Benner and Becker 1974</td>
<td>BLW model, with diffusion control only. Includes algorithm for obtaining leachant concentraion profile in heap.</td>
<td>Add leaching of mafic rocks from sandstone ore, on 75-120 kg samples.</td>
<td>Same parameters found to enable model to be fitted to two tests under different conditions.</td>
<td>Assumption of narrow reaction zone probably more valid in case of diffusion control only. Results interpreted as showing model could be used predictively.</td>
</tr>
<tr>
<td>Stefer, White and Caenenpeel 1979</td>
<td>BLW model as used by Roman et al. with slight modifications.</td>
<td>Add leaching of copper oxide ore on pilot-scale (40 kg t -1).</td>
<td>Parameters defined by data from small-scale tests used in model to predict leaching from large-scale test.</td>
<td>Reasonable correlations obtained.</td>
</tr>
<tr>
<td>Averill 1978</td>
<td>BLW model with diffusion and chemical control, and with diffusion control only, with more sophisticated algorithm for extracting concentration profile than used by Roman et al.</td>
<td>Leaching of chalcopyrite and copper sulphide ores, on lab-scale.</td>
<td>As Braun, Lewis and Wadsworth.</td>
<td>Reasonable correlation obtained.</td>
</tr>
<tr>
<td>Bartlett 1972</td>
<td>Continuity equation model based on Fick’s law diffusion equation and chemical reaction parameters.</td>
<td>As Braun, Lewis and Wadsworth, on 8 t scale.</td>
<td>Predictively, using measured physical parameters and known kinematic data.</td>
<td>Quite rigorous model, but requires very complex computations. Problems in measuring required parameters. Reasonable agreement obtained between predictions and experimental results.</td>
</tr>
<tr>
<td>Brathwaite 1978</td>
<td>Modification of the Bartlett model to give a quasi-steady-state form.</td>
<td>System similar to that studied by Braun, Lewis and Wadsworth, on 8 t scale.</td>
<td>As Bartlett.</td>
<td>Computation simpler than with original Bartlett model.</td>
</tr>
<tr>
<td>Madsen and Wadsworth 1977</td>
<td>Effectively Brathwaite’s version of the Bartlett model, includes algorithm for obtaining leachant concentration profile.</td>
<td>As Madsen, Wadsworth and Groves, with addition of granitic chalcopyrite ore at pilot scale.</td>
<td>As Bartlett.</td>
<td>A combination of curve-fitting and use of measured parameters to give some predictions.</td>
</tr>
<tr>
<td>Roach and Prosser 1975, 1978</td>
<td>Based mainly on diffusion control, with optional method of making allowances for chemical reaction.</td>
<td>As Braun, Lewis and Wadsworth; also synthetic minerals.</td>
<td>As Bartlett.</td>
<td>Resembles the diffusion-controlled version of the BLW model. Rather empirical method of allowing for chemical reaction control. Fairly simple to use. Fair correlations obtained for leaching rates, but poor correlations for maximum possible recovery.</td>
</tr>
<tr>
<td>Cashels and Appel 1975</td>
<td>Combines BLW-type particle reaction model with heat and reagent balances in heap.</td>
<td>93,000 t dump of copper sulphide ore at Bingham Canyon.</td>
<td>As Bartlett.</td>
<td>Useful attempt to include properties of dump in leaching model. Some difficulties in measuring required parameters. Reasonable agreement between predictions and experiential results.</td>
</tr>
</tbody>
</table>
\[ R = \left[ \left( \frac{O_k p G}{M} \right) (da/dt)_k \right] \]  
\text{where} \quad R = \text{consumption rate of ferric iron as oxidant} 
\quad (\text{moles/s/cm}^3 \text{ of particle volume}) 
\quad O_k = \text{ratio of ferric iron to copper extracted from mineral k} 
\quad p = \text{rock density (g/cm}^3\text{)} 
\quad G = \text{copper concentration in rock (g Cu/g rock)} 
\quad M = \text{molecular weight of copper} 
\quad (da/dt)_k = \text{dissolution rate of mineral k as fraction of total copper per unit time (s}^{-1})\text{)}

The factor \((da/dt)_k\) was then defined for each mineral at various stages of dissolution.

With \(R\) defined, spatial dependencies were defined using a finite-difference solution of:

\[ R = D_e \left[ \left( \frac{d^2 C}{dr^2} \right) + 2\left( \frac{dC}{dr} \right) \right] \]  
\text{where} \quad D_e = \text{effective diffusion coefficient} 
\quad C = \text{concentration} 
\quad r = \text{distance from center of particle} 

This equation assumes that all ferric iron is consumed upon reaching reaction sites. With this model, Madsen and Wadsworth found that simulated results matched measured data over time periods of several hundred days.

From 1977 to 1987, Davis and Ritchie developed a series of models simulating diffusion into rock piles. The initial model, now referred to as the simple homogeneous model, simulated oxygen diffusion from the top of a pile downwards to oxidation sites (Ritchie, 1977). Particle size was assumed to be very small with relatively low internal volume. Simulated results showed that a pile-wide oxidation zone moved downward through time. Davis and Ritchie (1986) extended this model to include reaction zones within particles, producing the single-sized particle model. The model was based on the assumption that oxidation was limited by the transport of oxygen to internal portions of particles. The model equations were solved by assuming pseudo-steady-state diffusion within the particles and the model was used to predict oxidation rates, sulfate production, and heat distribution in rock piles (Davis \textit{et al.}, 1986). Simulations of the Rum Jungle site showed that a dump could require 250 years to oxidize fully. Davis and Ritchie (1987) further extended the model to include a range of particle sizes, resulting in the distributed particle size model. This model did not significantly change the predicted magnitude and temporal duration of acid drainage from the earlier models, but did alter the heat and oxygen distribution.
As a major advancement over the earlier models, Bennett et al. (1989) developed a two-dimensional model which included thermal advection, although it is only applicable to a small range of geometries. Gas advection is assumed to be driven only by the heat produced by acid generation. Simulations showed that gaseous diffusion was a critical mechanism for oxygen transport for the first two years. At later times, the relative importance of gaseous diffusion and advection depended on the permeability of the rock pile.

Prosser and colleagues developed models which included emphasis on mineralogy and aqueous reactions (Prosser et al., 1981; Prosser and Box, 1983; Box and Prosser, 1986). Their modelling efforts centered on the development of a generalized procedure which could address non-sulfide minerals such as calcite and malachite (Section 6.3) and aqueous reactions involving ferric and copper complexes (Section 6.4). Rock particles were viewed as holding numerous small reactive minerals with a distinct boundary separating outer reacted and inner unreacted zones for each mineral. The aqueous and solid-phase geochemical systems were partitioned into independent subsystems and then further partitioned into reaction groups. Reaction rates were then applied to each group. This approach was tested against several column experiments and found to give reasonable results without using any adjustable parameters.

In the mid-1980’s, Jaynes and colleagues (1984a and 1984b) presented an acid-drainage model for coal spoils based on the model of Cathles and Apps (1977). Their extension of the earlier model was designed to overcome some earlier assumptions which were: (1) gaseous advection was the primary mechanism for gas transport, which Jaynes et al. felt was reasonable for coarse rock piles but not finer-grained spoils, (2) the primary oxidant was ferric iron, and (3) concentrations of ferric iron were maintained at a constant level by bacterial activity. As a result, the model of Jaynes et al. specified gaseous diffusion as the mechanism of oxygen transport, allowed both ferric iron and molecular oxygen as oxidants, and simulated bacterial activity based on details of their substrates and local environmental conditions (Figure 6-8).

In the model of Jaynes et al. (1984a and 1984b), pyrite was the only sulfide mineral considered and its oxidation was simulated with the reaction-zone concept within particles. The model accounted for conditions where the rate of diffusion into a particle limited oxidation and where sufficient diffusion occurred to allow unhindered oxidation.

Oxygen diffusion in the model was simulated by a refinement of Fick’s Second Law (Section 5.0). This refinement included an effective diffusion coefficient calculated from binary coefficients of one gas through another and the consumption of oxygen during diffusion.
FIGURE 6-8. Schematic Diagram of the Acid Mine Drainage Model (from Jaynes et al., 1984a).
For the calculation of bacterial activity, Jaynes et al. presented the most detailed set of equations of any integrated acid-drainage model reviewed here. The equations were based on both theory and experimental data, which necessarily ignored the potential for bacterial adaptation to site-specific conditions and the participation of bacteria other than Thiobacillus.

Although aqueous complexation of ferric iron was simulated, other significant complexes were not included in the Jaynes et al. model. Moreover, pH and buffering were calculated in an overly simplistic manner which prevented pH from decreasing below a value specified by the user. This simplistic treatment cannot accurately simulate the reactions which determine pH, neutralization, and metal leaching and thus this model can only supply generalized information on the geochemistry of acid drainage.

A primary weakness in the model of Jaynes et al. was the simulation of water movement. Water exiting the base of one horizontal layer was distributed among deeper layers using a function of depth and this water instantaneously appeared in the deeper layers. Although this approach may reflect some type of channelling (Section 3.0), it probably does not accurately reflect the nature of water movement in waste-rock and spoils.

A significant advancement in modelling of acid drainage was released in Canada in 1986 (Senes, 1986). In this model known as RATAP, the processes determining acid drainage were treated stochastically rather than deterministically so that gaseous diffusion, for example, produced a probability distribution of gas flux rather than one value. However, like previous models, several simplifying assumptions were included. Because the model was designed for fine-grained tailings piles, gaseous advection was not considered and oxygen transport was attributed to gaseous diffusion and aqueous advection (Section 5.0). Acid generation within particles was simulated with the reaction-zone concept. Aqueous complexation was more advanced than most models, including some species of ferric iron, aluminum, sulfate, and carbonate.

Based on the findings of this review, no model currently exists which can even generally simulate the most critical physical, geochemical, and biological processes in waste-rock piles. This deficiency is attributed to combined lack of funding and time rather than technical limitations, because theory is sufficiently well developed, conceptual models exist, and existing models simulate one or more of the critical processes. If appropriate models were developed, however, the number of case studies for comparison and calibration of the models are limited (Section 6.6). Nevertheless, modelling of acid drainage in waste-rock piles is an area for future research that may enhance the current capability to understand, predict, and control the environmental impacts of acid-generating waste-rock.
6.6 Case Studies

As found with modelling (Section 6.5), there is a general lack of detailed case studies of waste-rock piles. The literature search (Appendix A) and direct contacts (Appendix B) provided few published and unpublished studies. These studies are summarized below, and information on coal spoils are included to illustrate critical aspects.


In 1982, approximately 200,000 m$^3$ of slate was excavated for taxiways at the Halifax Airport, placed on a sloping seven-hectare area (Figure 3-16), and capped with 0.6 m of clayey glacial till. Within two months after construction was completed, drainage at pH 3 began discharging from the base of the waste-rock pile and the adjacent groundwater-stormwater collection system. Relevant details of water movement were summarized in Section 3.2. A lime treatment facility was constructed to handle this drainage for the estimated two years that acidic conditions were expected to persist. After two years, the levels of acidity and metals were still increasing, leading to a detailed study of the pile and the local groundwater and surface water. Levels continued to increase generally at the time the paper was written. However, Lund noted that peak levels were obtained during high-intensity rainfall due to flushing of stored acidity.

Acid-base accounting (Table 6-6) indicated that all rock samples were capable of generating net acidity and, because the slate was capable of weathering to a fine black powder, all of the sulfur was thought to be available for oxidation. Moreover, acid production was found to increase significantly below a particle diameter below 10 millimetres.

Acid-leach testwork (Table 6-7) showed that toxic levels of metals could be leached from the rock. Based on whole-rock analyses, the iron and aluminum concentrations represented 84-88% and 13-18% of total metal, respectively.

The acid-base accounting and metal-leaching tests confirmed the observed severity of acid drainage (Table 6-8). However, the general increase in pH and the decrease in acidity and other parameters from within the pile to the seepage site were interpreted as partial in-situ neutralization. Alternative explanations include the possibility that dilution with cleaner water is occurring or the wells within the dump are monitoring a different flowpath with a different chemistry than the one appearing at the seepage site.

The presence of dissolved oxygen and elevated levels of total organic carbon and ammonia suggested the presence of aerobic bacteria in the waste-rock and underlying bedrock. Also,
<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Sample</th>
<th>Depth (ft)</th>
<th>Percent Sulphur</th>
<th>Maximum Potential Acidity (l/1000l)</th>
<th>Neutralization Potential (l/1000l)</th>
<th>Net Neutralization Potential (l/1000l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vein in quartzite</td>
<td>TH#4</td>
<td>2.0 - 2.2</td>
<td>1.32</td>
<td>40.7</td>
<td>4.9</td>
<td>-35.8</td>
</tr>
<tr>
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<td>5.10</td>
<td>157.1</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
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<td>0.65</td>
<td>20.0</td>
<td>3.5</td>
<td>-16.5</td>
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<td>20</td>
<td>0.3</td>
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<td></td>
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<td>25</td>
<td>0.296</td>
<td>9.1</td>
<td>3.0</td>
<td>-6.1</td>
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<td>0.22</td>
<td>32.8</td>
<td>4.3</td>
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<td>1.21</td>
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<td></td>
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<td>0.88</td>
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<td>8.3</td>
<td>2.5</td>
<td>-5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 - 22</td>
<td>0.29</td>
<td>8.9</td>
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<td>-7.0</td>
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<td>0.72</td>
<td>22.2</td>
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<td>0.32</td>
<td>9.9</td>
<td>2.6</td>
<td>-7.3</td>
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<td>Depth (ft)</td>
<td>Cu</td>
<td>Pb</td>
<td>Zn</td>
<td>Ni</td>
</tr>
<tr>
<td>------------</td>
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<td>------------</td>
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<tr>
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<td>25</td>
<td>41</td>
<td>18</td>
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<td>25 - 27</td>
<td>19</td>
<td>20</td>
<td>65</td>
<td>21</td>
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<td>20</td>
<td>18</td>
<td>70</td>
<td>23</td>
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<tr>
<td>quartzite</td>
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<td>47</td>
<td>24</td>
<td>196</td>
<td>59</td>
</tr>
<tr>
<td>slate</td>
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<td>28</td>
<td>22</td>
<td>75</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Bedrock Undisturbed</td>
<td>Bedrock Disturbed</td>
<td>Taxiway Underdrain</td>
<td>Stormwater Interceptor</td>
<td>Waste Rock Pile</td>
<td>Waste Rock Seepage</td>
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<td>--</td>
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<td>0.6 - 33</td>
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<td>39 - 106</td>
<td>41 - 207</td>
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<td>99 - 543</td>
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<td>4.6</td>
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<td>--</td>
<td>--</td>
<td>130 - 2,800</td>
<td>150 - 1,000</td>
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<td>1,840 - 2,300</td>
<td>6,000 - 80,100</td>
<td>7,000 - 27,000</td>
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<td>3.30</td>
<td>2.8</td>
<td>19 - 61</td>
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<tr>
<td>Tot. Hd.</td>
<td>--</td>
<td>220 - 750</td>
<td>1,100</td>
<td>707</td>
<td>3,600 - 15,000</td>
<td>1,400 - 6,250</td>
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<td>&lt;0.05</td>
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<td>2.6 - 3.8</td>
<td>2.4 - 5.1</td>
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<td>310 - 2,700</td>
<td>53 - 2,970</td>
<td>10,000 - 98,000</td>
<td>1,450 - 22,000</td>
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<td>11 - 591</td>
<td>20 - 473</td>
<td>4,472 - 15,200</td>
<td>1,500 - 3,800</td>
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<td>38 - 244</td>
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<tr>
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<td>2.3</td>
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<td>15 - 53</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.05</td>
<td>&lt;0.05 - 0.01</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>0.94 - 9.0</td>
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<tr>
<td>TDS</td>
<td>199 - 404</td>
<td>342 - 5,572</td>
<td>614 - 4,600</td>
<td>220 - 3,645</td>
<td>12,870 - 94,852</td>
<td>3,757 - 21,400</td>
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<tr>
<td>TOC</td>
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<td>11.0</td>
<td>3.20</td>
<td>--</td>
<td>460</td>
<td>30 - 33</td>
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<tr>
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<td>0.5</td>
<td>3.5</td>
<td>5.0</td>
<td>1.2 - 3.3</td>
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<tr>
<td>D.O.</td>
<td>2.8</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>0.15 - 0.50</td>
<td>1.2 - 1.4</td>
</tr>
</tbody>
</table>
one of five samples of waste-rock tested positive for *Thiobacillus ferrooxidans*. Based on this information, acid generation in the waste-rock was attributed to bacterial activity.

**Waste-rock, NB Coal Ltd. Fire Road Mine, Minto, New Brunswick: Phinney (1987)**

Coal was extracted at the Fire Road site using cut-and-fill methods, producing approximately 50,000 tonnes/year. Within one year after initiation of mining in late 1983, discharge of minewater, which was a combination of surface water and groundwater, had reached 400-900 m$^3$/hr and pH had decreased from 4.8-7.4 to 3.0-4.0. Discharge was halted and by May 1986 the pit contained 64,000 m$^3$ of water with an acidity of 400 mg CaCO$_3$/L. The source of the acid drainage was attributed to the adjacent waste-rock pile which contained "iron sulfide" minerals (Figure 6-9). The source was confirmed by the seepage survey along the perimeter of the pile, which identified localized areas of acid drainage, and the lack of acidic discharge from the natural strata on the north side of the cut.

**Coal Spoils, Henry County, Missouri: VonDemfange and Warner (1975)**

In order to determine the extent of past acid generation and the depths of oxidation, acid-base accounting was performed on subsurface cores of coal spoils from two mines in Henry County, Missouri. Most samples were collected from shallow depths to delineate more accurately the shallow oxidation zone.

The first location was the Power Mine of the Peabody Coal Company, at which the sampled spoils had been exposed to eight years of weathering. The nearby pit was filled with dark red water at pH 2.8, indicating the spoils were generating acidity. Cores were obtained from two sites. "Site A" was at the top of the pile near the acidic pond, approximately 12 m above the pond surface. Samples were taken to a depth of 6 m and no water table was intercepted. "Site B" was located on a lower portion of the spoils and samples were taken to a depth of 2.4 m with a water table at 1.8 m. Vertical profiles of solid-phase sulfate and sulfide (Figure 6-10) showed that sulfate was highest in the shallow samples and sulfide was variable, but generally low in the shallow samples. These trends were interpreted as indicating a depth of oxidation of 0.6 m.

The second location was an abandoned strip mine where the spoils had been weathered for 16 years. An adjacent pond contained green water at pH 3.2, indicating acid generation in the spoils. At the coring site ("Site C"), a water table was not intercepted and an unidentified obstruction prevented sampling below 4.3 m. Nevertheless, trends in sulfate and sulfide were found to be consistent with those at Sites A and B, indicating a shallow oxidation zone.
NOTE:
ACIDITY - TO pH 8.5 AS CaCO₃
Al, Fe, SO₄ - mg/L
WR - SEEPAGE FROM WASTE ROCK
POOL - POOL OF WATER AT TOE OF WASTE ROCK
GW - GROUNDWATER FLOW ON HIGHWALL SIDE OF CUT

<table>
<thead>
<tr>
<th>STATION</th>
<th>pH</th>
<th>ACIDITY</th>
<th>Al</th>
<th>Fe</th>
<th>SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-WR</td>
<td>6.6</td>
<td>-</td>
<td>7.6</td>
<td>11.7</td>
<td>316</td>
</tr>
<tr>
<td>2-WR</td>
<td>3.1</td>
<td>-</td>
<td>15.2</td>
<td>40.6</td>
<td>484</td>
</tr>
<tr>
<td>3-WR</td>
<td>3.3</td>
<td>-</td>
<td>19.6</td>
<td>6.49</td>
<td>456</td>
</tr>
<tr>
<td>4-WR</td>
<td>6.0</td>
<td>-</td>
<td>2.6</td>
<td>6.70</td>
<td>87.0</td>
</tr>
<tr>
<td>5-WR</td>
<td>3.2</td>
<td>298</td>
<td>32.8</td>
<td>8.91</td>
<td>710</td>
</tr>
<tr>
<td>6-WR</td>
<td>2.8</td>
<td>607</td>
<td>108</td>
<td>109</td>
<td>2000</td>
</tr>
<tr>
<td>7-POOL</td>
<td>2.7</td>
<td>2890</td>
<td>260</td>
<td>306</td>
<td>4520</td>
</tr>
<tr>
<td>8-GW</td>
<td>7.7</td>
<td>-</td>
<td>0.10</td>
<td>0.40</td>
<td>20.8</td>
</tr>
</tbody>
</table>

FIGURE 6-9. Sources of Acid Generation, NB Coal Ltd. Fire Road Operation (from Phinney, 1987).
On a depth-integrated basis, the spoils reportedly had sufficient neutralization potential to consume the acidity that could be generated by the remaining sulfide content of the oxidation zone. However, this neutralization potential was judged to be unavailable for reaction because of the acid drainage found at both mines.

**Metal Leaching from Waste-rock and Lean Ore Piles, Minnesota: Lapakko and Eger (1980) and Minnesota Department of Natural Resources (1990)**

At the Dunka site of the LTV Steel Mining Company, field studies were conducted to assess the quantity and quality of leachate flowing over and from waste-rock piles and lean ore. These piles were placed in the mid-1960's, contained more than 45 million tonnes, and covered an area of 130 hectares.

Water flow from the piles was noted only in April through November at flow rates ranging from a "trickle" to 0.15 m³/s. Also, runoff from the piles, which was significant, was estimated to be on average 50% of the annual precipitation of 72.6 cm and predicted to be 65% of a 100-year wet year precipitation of 99.1 cm. Total average flow from the piles and remaining watershed was estimated to be around 2 million m³ a year.

Median water quality (Table 6-9) of seepage indicated that pH was near neutral, sulfate was elevated and probably near saturation with gypsum, and some metals were above guidelines. However, the reported statistical analysis of the data (Figure 6-11) revealed that significantly higher concentrations were occasionally obtained. The higher concentrations from the lean ore pile were attributed to the higher solid-phase concentrations of metals in this pile, thereby suggesting that kinetics rather than chemical equilibrium (Section 6.4) was regulating aqueous metal levels.

Some of the variability in metal concentrations could be explained by variations in pH (Figure 6-12), which reached values as low as 4.5, although another factor implicated in elevated metal levels was aqueous complexation with organic species. For waste-rock and ore rock, loadings of copper were calculated to be 0.04 to 0.4 and 3.3 to 20 mg Cu/tonne/yr, respectively. Nickel loadings were calculated at 3 to 100 and 100 to 500 mg Ni/tonne/yr, respectively. Based on whole-rock analyses, these leaching rates could continue for hundreds of years.

Because aqueous pH was as low as 4.5, acid generation was occurring in the piles. Lapakko and Eger reported limited observations that rock with more than 2.5% S has produced net acidity where rock with less than 1% S had not.
### TABLE 6-9
Water Chemistry of Seepage, Dunka Site, Minnesota
(Median Values\(^1\) 1976 - 1979)
(From Lapakko and Eger, 1980)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Waste Rock Pile #1</th>
<th>Waste Rock Pile #2</th>
<th>Lean Ore Pile</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.16 (59)(^a)</td>
<td>6.70 (51)</td>
<td>7.10 (48)</td>
<td>6.9</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1200 (50)</td>
<td>3400 (42)</td>
<td>1364 (42)</td>
<td>6.6</td>
</tr>
<tr>
<td>Copper(^3)</td>
<td>0.030 (67)</td>
<td>0.036 (48)</td>
<td>0.270 (50)</td>
<td>0.0013</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.14 (62)</td>
<td>6.13 (50)</td>
<td>13.3 (51)</td>
<td>0.001</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.195 (14)</td>
<td>0.64 (19)</td>
<td>0.790 (19)</td>
<td>0.004</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.10 (33)</td>
<td>1.45 (35)</td>
<td>0.18 (37)</td>
<td>0.002</td>
</tr>
</tbody>
</table>

\(^1\) Concentration in mg/L  
\(^2\) Numbers in parentheses indicate number of samples  
\(^3\) Metal concentrations as total metal
FIGURE 6-11. Copper and Nickel in Dunka Rock Pile (from Lapakko and Eger, 1980).
FIGURE 6-12. Metal Concentrations vs pH from Waste Rock Pile #2 (from Lapakko and Eger, 1980).
At a second mine, the Minnamax site, six in-field test piles with underdrains were constructed in 1977 (one was later dismantled), each containing roughly 1000 tonnes of rock. Metal leaching was found to be pH-dependent as at the Dunka site. By 1980, acidic drainage from the piles was noted for rock with 0.8% and 1.45% S, but not from rock with 0.6% S. (Figure 6-13). However, by 1989, the seepage from the 0.6% S piles had also become acidic (pH<6).

Pilot-scale Columns of Waste-rock: Murr et al. (1977)

Two large pilot-scale columns with heights of 10.5 m and diameters of 3.1 m were constructed to hold 170 tonnes of waste-rock. Each column was equipped with: overhead systems for acid-solution application, side ports for the collection of rock particles for bacterial analysis, thermocouples for temperature measurements, and bottom drains and porous-cup suction lysimeters at various depths to collect water samples. Smaller columns were constructed for comparison with one of the larger columns in order to test effects of scale (size).

One column was filled with Duval-Sierrera waste-rock with diameters generally less than 15 cm. This rock contained about 2% carbonate and approximately 1-2% sulfide minerals with a pyrite:chalcopyrite ratio of 4. Copper in the rock was found to be at 0.34% with 0.03% as non-sulfide copper and the remainder as chalcopyrite. Permeability varied with depth in the column, but was generally in the range of 4.9-24.7 x 10^{-13} m^2. Unlike the second column with Santa Rita rock, this one was equipped with probes to measure oxygen concentrations with depth.

In addition to the large column, Duval-Sierrrita waste-rock was also placed into two smaller columns (Table 6-10). Dimensions and flowrates were designed to be proportional to those of the larger column to determine scaling effects on leaching.

Water at pH 2 was applied to the rock in the large column at an initial flowrate of 2 L/min, but effluent pH remained around 6.5-7.0 due to the carbonate content (Figure 6-13). At Day 10, airflow was slowed to 8 L/min and influent water flow was increased to 2.75 L/min with a lower pH of 1.0. In response, effluent pH increased to more than 7.5 at Day 20, then gradually decreased to 5.0 by Day 80 which included a 15-day stagnant (rest) period. By Day 90 effluent pH had dropped sharply to 2.0, likely indicating the general depletion of soluble neutralizing minerals containing carbonate and/or hydroxide. Although acidity levels in the influent solution were not reported, calculations based on 2% CaCO₃ and an average flowrate
(from Minnesota Department of Natural Resources, 1990)
### TABLE 6-10
Columns Containing Duval-Sierrita Waste-rock
(from Murr et al., 1977)

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>LARGE</th>
<th>MEDIUM</th>
<th>SMALL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (meters)</td>
<td>3.05</td>
<td>0.38</td>
<td>0.10</td>
</tr>
<tr>
<td>Height of rock (meters)</td>
<td>9.75</td>
<td>2.64</td>
<td>0.69</td>
</tr>
<tr>
<td>Maximum rock size (cm)</td>
<td>15</td>
<td>1.9</td>
<td>0.51</td>
</tr>
<tr>
<td>Initial drain rate (L/min)</td>
<td>4</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>Initial air flow (L/min)</td>
<td>17.5</td>
<td>0.875</td>
<td>0.044</td>
</tr>
<tr>
<td>Initial solution flow (L/min)</td>
<td>2</td>
<td>0.100</td>
<td>0.005</td>
</tr>
<tr>
<td>Retained/saturated solution</td>
<td>0.77</td>
<td>0.72</td>
<td>0.68</td>
</tr>
<tr>
<td>Weight of rock (kg)</td>
<td>170,000</td>
<td>405</td>
<td>7</td>
</tr>
</tbody>
</table>

A flowrate of 2.6 L/min over 90 days indicates average acidity should have been on the order of 10,000 mg CaCO₃/L, which may be reasonable for influent solutions with pH as low as 1.0. However, when the water flowrate was then slowed and pH raised to 2.0, effluent pH increased to 5.0, suggesting that all neutralization capacity had not been removed. As flowrate was increased and pH lowered to 1.5, effluent pH fell to about 2.5-3.0.

Bacterial populations of *Thiobacillus ferrooxidans* were found to increase in the shallow rock to Day 30, then remain variable but generally in the range of 10⁴-10⁶ cells/gram, whereas the deeper rock consistently had populations less than 5 cells/gram. Because populations did not correlate with pH and the bacterial populations grew rapidly at neutral pH, bacterial oxidation may not have been significant. In agreement, Murr *et al.* indicated that temperature did not rise above 10°C and average copper concentrations were only around 50 mg/L.

The smaller columns generated similar trends in pH (Figure 6-14) as the larger column. This was taken to be successful scaling of the leaching process.
FIGURE 6-14  pH Data Showing Neutralization of the Duval-Sierra Waste Rock (from Murr et al., 1977).
Due to the unexpected results on bacterial activity in the large column, rock particles were used in laboratory tests in which high-temperature *Sulfobolus*-like bacteria were added and temperature was maintained at 55°C. Relative to the uninnoculated control samples, copper concentrations and the extent of iron oxidation to the ferric state were higher and could be correlated with population levels. This demonstrated that bacterial leaching could be significant in a full-scale pile when internal temperatures could rise above ambient values.

The second large column was filled with Santa Rita waste-rock with particle diameters less than 19 cm from Kennecott's Chino Mines Division. The rock was mineralogically described as a quartz monzonite with little neutralization potential and approximately 1 to 3% sulfide minerals with a pyrite:chalcopyrite ratio of 10.6. Copper in the rock was measured at 0.36% with 0.14% as non-sulfide leachable copper and the remainder as mostly chalcocite and some chalcopyrite. Permeability was in the range of 2.0-3.9 x 10^{-13} m².

The rock in this column was periodically leached with an acidic solution over a period of 300 days. The influent water contained *Thiobacillus ferrooxidans* and, from the beginning of the test, populations were in the range of 10^5 to 10^7 cells/gram. Because there was little neutralization potential in the rock, effluent pH was acidic in the range of 2 to 4. When internal temperatures rose above 30°C around Day 80, oxygen consumption increased sharply from less than 2 to 10 kg/d and free oxygen in the porespaces decreased significantly. As the temperature rose above 45°C, there was a decline in bacterial population, but the rate of oxygen consumption remained high and temperature continued to climb to 60°C. The researchers attributed these trends to a high-temperature bacterium because they felt that inorganic rates could not be high even at elevated temperatures.

**Waste-Rock Dump #1, Westmin Myra Falls Mine, British Columbia:**

*Northwest Geochem* (1990)

In 1988, 57 boreholes were drilled into the dump at an average depth of 29 meters (Figure 3-17: borehole locations). Samples of drill cuttings were collected over specific depth intervals and submitted for acid-base accounting (ABA). Results showed that trends in ABA parameters occurred with depth. For example, ABA from Borehole 26 (Figure 6-15) suggested that most of the acid generation occurred within the upper 10 meters of waste-rock and values of paste pH, Neutralization Potential, and Net Neutralization Potential (NNP) became more positive with depth. ABA results from other boreholes revealed acid-generating zones at depth (Figure 6-16), acidic conditions throughout the waste-rock, and mostly neutral conditions throughout the waste-rock (Table 6-11). Despite the measurements of neutral values of paste pH, most samples of waste-rock had negative values of NNP with a mean of -
FIGURE 6-15. Results of Acid-Base Accounting for Borehole 25 (Northwest Geochem, 1990). NNP (Net Neutralization Potential) and NP (Neutralization Potential) are in Units of Tonnes CaCo$_3$/1000 Tonnes.
FIGURE 6-16. Results of Acid-Base Accounting for Borehole 15 (Northwest Geochem, 1990). NNP (Net Neutralization Potential) and NP (Neutralization Potential) are in Units of Tonnes CaCO₃/1000 Tonnes.
TABLE 6-11
Summary of ABA Trends in Boreholes in Dump #1, Westmin Myra Falls Mine
(from Northwest Geochem, 1990)

- Boreholes Showing No Clear Trends (Mostly All Neutral)
  1, 2, 12, 13, 16, 18, 23, 25, 27, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 45, 46, 48, 49, 50, 52, 53, 54, 56, 57, 58, 59, 60

- Boreholes Showing A Shallow Acid Zone (Depth to Acid Front in Meters)
  3 (14m), 4 (8), 6 (8), 9 (8), 10 (15), 11 (20), 19 (14), 20 (8), 24 (8), 26 (8), 28 (8),
  40 (14), 41 (8)

- Boreholes Showing Distinct Acid Zones at Depth (Depth in Meters)
  5 (9-13), 9 (20-26), 14 (20-26), 15 (8-14), 17 (14-26), 21 (23-26),
  22 (9-13 & 27-31), 55 (9-20)

- Boreholes Showing No Neutral Zone in Waste-rock (All Acidic)
  7, 8, 47, 51

---

TABLE 6-12
Statistical Summary of ABA Data From Dump #1, Westmin Myra Falls Mine
(from Northwest Geochem, 1990)

<table>
<thead>
<tr>
<th>Waste-rock (No. of Samples = 169)</th>
<th>MEAN</th>
<th>MINIMUM</th>
<th>MAXIMUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA(^1)</td>
<td>111.7</td>
<td>0.6</td>
<td>437.5</td>
</tr>
<tr>
<td>NP(^2)</td>
<td>23.6</td>
<td>1.7</td>
<td>50.4</td>
</tr>
<tr>
<td>NNP(^3)</td>
<td>-86.1</td>
<td>-423.6</td>
<td>25.7</td>
</tr>
<tr>
<td>Paste pH</td>
<td>7.22</td>
<td>4.00</td>
<td>8.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organics (No. of Samples = 18)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA(^1)</td>
<td>23.1</td>
<td>0.9</td>
<td>176.3</td>
</tr>
<tr>
<td>NP(^2)</td>
<td>13.6</td>
<td>4.0</td>
<td>29.1</td>
</tr>
<tr>
<td>NNP(^3)</td>
<td>-9.4</td>
<td>-159.3</td>
<td>25.0</td>
</tr>
<tr>
<td>Paste pH</td>
<td>7.47</td>
<td>6.47</td>
<td>8.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bedrock (No. of Samples = 42)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA(^1)</td>
<td>7.3</td>
<td>0.3</td>
<td>122.5</td>
</tr>
<tr>
<td>NP(^2)</td>
<td>12.9</td>
<td>5.1</td>
<td>67.4</td>
</tr>
<tr>
<td>NNP(^3)</td>
<td>5.8</td>
<td>-69.7</td>
<td>66.5</td>
</tr>
<tr>
<td>Paste pH</td>
<td>7.68</td>
<td>6.19</td>
<td>8.45</td>
</tr>
</tbody>
</table>

\(^1\)MPA = Maximum Potential Acidity as tonnes CaCO\(_3\) equivalent/1000 tonnes of rock
\(^2\)NP = Neutralization Potential as tonnes CaCO\(_3\) equivalent/1000 tonnes of rock
\(^3\)NNP = Net Neutralization Potential as tonnes CaCO\(_3\) equivalent/1000 tonnes of rock
88.1 tonnes CaCO₃ equivalent/1000 tonnes of rock (Table 6-12), which indicated the potential for net acid generation in the rock and was consistent with the acidic water known to be moving through the pile at least since the early 1980’s. Acid-generating waste-rock was tested on a laboratory scale in leach columns and humidity cells for approximately two years. Results showed that rates of acid generation were approximately 2-4 mg CaCO₃ equivalent/day/kg of rock, which is equivalent to the rate measured in White’s Dump at Rum Jungle when converted to similar units. The impact of this rate on water quality within the dump is discussed below.

Based on water samples from monitor wells within the dump, aqueous pH in the saturated zone spanned a range from approximately 2 to less than 9 (Figure 6-17). The pH values showed a spatial dependency in that lower pH values typically appeared in the lower end of the flow system near the toe of the dump. (The pattern of water movement in this dump has been discussed in Section 3.2.) These trends in pH were attributed to the progressive addition of acidic water from the overlying unsaturated zone of the waste-rock during lateral flow of groundwater towards the toe.

The lowest pH values in the saturated zone were typically observed during wet winter months and were attributed to the enhanced flushing of acidity from the waste-rock during more intense rainfall. In this way, the aqueous alkalinity which is present in the groundwater moving laterally into the dump from the adjacent valley wall is eventually overwhelmed by the addition of acidity. Sulfate concentrations which are indicative of sulfide oxidation were found to be consistent with this scenario. However, based on the laboratory-defined rate of acid generation, less than 10% of the annual acid production was flushed from the dump in a year. Consequently, the dump is thought to contain a significant level of stored acidity which must be controlled or neutralized for safe decommissioning of the dump.

In agreement with the theory of metal leaching, elevated aqueous concentrations of metals were related to lower pH values. However, independence of some metals was noted around neutral pH (Figure 6-18), suggesting another geochemical control regulated concentration in this pH range.

**Rum Jungle Minesite, Australia: Harries and Ritchie (1982)**

Mining for uranium began at this site in 1954 with White’s orebody, which was exhausted in 1958, and followed by Dyson’s and Intermediate orebodies (Figure 6-19). Mining was completed at the site by 1965.

Pyrite and other sulfide minerals in the rock and tailings led to the development of widespread acid drainage and metal leaching. Based on loadings of metals (Table 6-13), the
FIGURE 6-19. Map of the Abandoned Mine Site at Rum Jungle (from Harries and Ritchie, 1982).
### TABLE 6-13

Metal-Leaching Loads from Various Sources at the Rum Jungle Mine Site During the 1973-74 Wet Season (From Harries and Ritchie, 1982).

<table>
<thead>
<tr>
<th>Source</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyson's opencut</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Dyson's waste rock</td>
<td>0.2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>White's opencut</td>
<td>8</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>White's waste rock</td>
<td>29-53</td>
<td>11-19</td>
<td>17-31</td>
</tr>
<tr>
<td>Intermediate waste rock</td>
<td>16-30</td>
<td>2.5-4.5</td>
<td>13-25</td>
</tr>
<tr>
<td>Heap leach pile</td>
<td>32-42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tailings area</td>
<td>5</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Old Acid Dam</td>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>95-142</td>
<td>70-80</td>
<td>30-56</td>
</tr>
</tbody>
</table>

Waste-rock and heap-leach piles were identified as the largest sources of contamination. In 1975, a program of detailed field studies of the piles began, addressing such issues as runoff, evaporation, and oxygen concentrations within a pile. These efforts focused on White's Dump with lesser emphasis on the Intermediate Dump.

White's Dump had a height of 13 to 18 m and a lateral extent of 0.264 km², 26% of which was side slope. The volume of rock placed in this dump was estimated at 4 x 10⁶ m³, mostly carbonaceous slates and graphitic schists. The smaller Intermediate Dump covered 0.069 km², 30% of which was side slope.

Water movement in and over White's Dump was discussed in Section 3.2. The chemistry of the springs at the base of the dump indicated an average pH of 3.6 during the high-rainfall season (1996 mm) and 2.8 during the low-rainfall season (959 mm). The average levels of sulfate, copper, zinc, and manganese were 17,000, 80, 45, and 35 mg/L, respectively, which were about 1 order of magnitude above runoff concentrations.

Based on temperature measurements, temperatures were generally around 33 to 37°C, which was near the maximum viable temperature for *Thiobacillus ferrooxidans*, and reached levels
above 50°C. Heat production indicated that the rate of sulfate production was approximately 0.5 kg SO₄/month/m² of dump surface. This production generally occurred within the upper 5 m of the dump, although oxidation depths to 15 m were found. This rate was reportedly independent of the seasonal wet/dry cycling. On a unit weight basis, this rate is approximately 2 mg SO₄/d/kg of rock, which is equivalent to the rate identified in the Westmin Dump (Northwest Geochem, 1990). The sulfate production rate in White's Dump was found to be consistent with the measured sulfate loadings at the basal springs, indicating that most of the acidity was flushed out of the dump within a year although additional work contradicted this conclusion (Harries and Ritchie, 1983).

Gas sampling in tubes at 0.3 to 2.0 m depth showed that oxygen concentrations decreased with depth, suggesting that gaseous diffusion limited the rate of oxidation. Additionally, carbon dioxide was found to be 1 to 2 orders of magnitude above atmospheric levels.

For bacterial characterization, solid samples were taken from the surfaces and from trenches as deep as 5 m into the tops and side slopes of White's and Intermediate Dumps. *Thiobacillus ferrooxidans* and several types of autotrophic sulfur-oxidizing bacteria were identified in both dumps and seasonal variations in population levels were detected. White's Dump was found to contain more abundant acidophilic heterotrophs, whose role in acid generation was reportedly ambiguous.

Although oxygen levels decreased significantly with depth in the upper few meters of the dumps, bacterial types and population levels were found to remain consistent throughout the upper 5 m. This was interpreted as bacterial activity under anaerobic or microaerophillic environments. However, some publications (Section 6.2) suggest that the reported low levels of 0.1% O₂ are sufficient to maintain *Thiobacillus* activity. During the bacterial studies, no anaerobic bacteria were detected in the upper 5 m of the dumps and no attempts were made to identify thermophilic bacteria which might populate the hotter regions of the dumps.

In order to experimentally determine the bacterial acceleration of acid generation, rock from White's Dump was placed in 10-litre stirred reactors and some of the reactors were inoculated with *Thiobacillus ferrooxidans*. At pH 2.5, little difference was noted in the inoculated and control (abiotic) reactors, which is reasonable in light of the low activity of *T. ferrooxidans* at this pH. At pH 3.5 typical of seepage from White's Dump, the abiotic reactors were showing no sulfide oxidation (based on sulfate analyses) at the time that the inoculated reactors were showing 50% oxidation of sulfide minerals. Levels of bacterial populations in these experiments were found to increase a few orders of magnitude in the first 15 days, then generally remained constant even when an "anaerobic" atmosphere (5% CO₂ in N₂) was placed in the reactors. This was taken by the researchers as further evidence that sulfur-
oxidizing bacteria were active in anaerobic environments, although it is likely that some low level of oxygen was present in the reactors.

Captain's Flat, Australia: Harries and Ritchie (1982)

Mining began at this lead-zinc mine in 1874 and continued sporadically until 1962. By this time, the waste rock dumps contained approximately $2.4 \times 10^6$ tonnes and covered an area of 15 hectares.

The dumps were found to have a high pyrite content of 17-21%S. This high level limited oxidation to the upper 2 m of the waste rock, presumably because of rapid oxygen consumption, and the highest acidity was found in the upper 0.3 m. Water draining from the dumps had a pH as low as 1.5 with zinc up to 6200 mg/L. Zinc loadings in a nearby river showed that 42% of the dissolved and suspended zinc originated in the dumps, 20% from outflow of underground minewater, 30 to 35% from mine waste deposited in the river, and the remainder from other minor sources.

Solids migration in the dumps was found to be significant. Erosion of the dump surfaces and at least two slope failures had carried more than 30,000 m$^2$ of material into a nearby river.

Hydraulic conductivity had been significantly lowered due to the chemical precipitation of "salts". These precipitants had filled in porespaces and cemented particles together.


A detailed bacteria study was conducted in a dump at this low-grade copper-zinc mine which was 15 to 25 m high, and actively leached for copper. Four bacteria were found in effluent at the base of the dump: *Thiobacillus ferrooxidans*, *T. thiooxidans*, *Leptospirillum ferrooxidans*, and *Sulfobacillus thermosulfidooxidans*.

Despite the relatively high numbers of bacteria, bacterial activity was found to be low as measured by $^{14}$CO$_2$ fixation. Although activity was found to increase over the temperature range of 15 to 26°C, it remained insufficient for acceptable oxidation rates of aqueous ferrous iron and sulfide minerals. An investigation revealed that the probable causes for the low activity included high zinc content of the rock, high aqueous iron (20 to 30 g/L), and total dissolved solids (70 to 120 g/L). As a result, the leaching solutions were adjusted by removing excess zinc, iron, and copper and adding phosphorus and nitrogen.

The East Dump at this minesite was targeted for capping with a till cover to reduce the acid drainage and copper leaching that were entering the local environment. Initial results of the capping produced minor changes in oxygen levels within the dump (Section 5.2). Furthermore, the severity of acid drainage did not lessen.

Additional investigations at this site showed that the dump, which was constructed downslope of an adjacent pit (Figure 6-20), was conducting groundwater that originated as precipitation at higher elevations in the pit (similar to Figure 3-3). The veneer of acid-generating rock on the pit floor was found to be a significant source ("if not the major source") of acid drainage in the area. One piezometer (BH 89-4, Figure 6-20) was found to have a copper concentration of 1.6 mg/L during the drier fall season and of 70.4 mg/L during the wetter early winter, which probably reflects the flushing of unsaturated rock which had accumulated acidity during drier times. Emphasis is now being placed on delineating the patterns of groundwater movement in the area and on designing control measures for the pit area.
7.0 CONTROL TECHNOLOGIES

Based on the technical review of the acid generation process and transport mechanisms this section will present a summary of practical considerations in preventing or controlling acid generation in waste rock piles. A detailed review of methods of acid generation control and their relative effectiveness can be found in SRK (1989).

The most important environmental parameters for acid generation control in waste rock are (Bell, 1988):

- To reduce permeability of the waste rock pile to air;
- Prevent oxidation and the associated exothermic reaction from significantly raising dump temperature;
- Minimize leachate production and transport; and
- Prevent the ingress of seepage to the more reactive portions of the dump (e.g., toe of the dump).

Preventative management methods for the problem of acid generation in waste rock do not presently provide a long term solution. Research to control the acid generation process has focused on:

- Biocidal control of the bacterial population;
- Use of surface covers and liners to restrict the infiltration of oxygen and water movement into the waste rock;
- Use of neutralizing compounds or alkaline recharging;
- Use of metal precipitating agents to coat waste surfaces;
- Waste segregation and selective dump placement; and
- Underwater disposal.

7.1 Biocidal Control of the Bacteria

Anionic surfactants have been used to control the bacterial population associated with acid generation with some degree of success, mainly in coal mine applications (Degan, 1975; Kleinmann and Erickson, 1982; Kleinmann and Erickson, 1983; Erickson et al., 1985; Shellhorn and Rastogi, 1985). Although anionic surfactants are proven biocidal agents, the duration of their effectiveness as a control method may be limited due to the high solubility and easily degradable nature of these compounds, particularly under acid conditions. There is a general consensus in the literature that direct addition of anionic surfactants to
revegetated sites or sites subject to high rates of water movement may be of limited value (Erickson and Ladwig, 1985). Patterson (1984) reported unsatisfactory results during field-testing of sodium lauryl sulfate at Equity Silver Mines. Failure of the product to maintain long-term control of acid drainage was attributed to the high solubility and the inability of the surfactant to penetrate to oxidation zones within the interior of the waste rock pile.

The effectiveness of chemical treatment methods to inhibit bacterial activity or coat particle surfaces and thereby reduce acid generation from waste rock has been studied by a number of researchers (Schnaitmann et al., 1969; Erickson and Ladwig, 1985; Erickson et al., 1985; Onysko et al., 1984; Siwik et al., 1989). Organic and inorganic chemicals have been tested including: food preservatives such as sodium and potassium benzoate, potassium sorbate salts, sodium chloride, and low molecular weight organic compounds such as propionic, butyric acid and formate; detergents such as sodium lauryl sulfate, AJAX and ALCONOX; and alkaline chemicals such as lime, sodium carbonate and potassium phosphate. Drawbacks to the use of these compounds, as with all surface amendments, is the inability to provide control of acid generation reactions occurring at depth in a waste rock pile. In addition, the expense associated with re-application of the chemicals due to their solubility can be considerable. Siwik et al., (1989) have suggested a cost effective way to utilize this technology by limiting use of bactericidal agents to prevention of the initiation of acid generation in waste rock until the rock can be disposed of in a permanent manner. For example, application of bactericide to waste-rock surfaces during dump construction.

Predatory organisms such as rotifers and protozoa have been to shown to have a marked specificity for Thiobacillus spps. Use of these organisms can cause significant reductions in bacterial numbers over a relatively short period of time, provided suitable conditions prevail. (Christison et al., 1984). However, the predator organisms require a high cell density to induce feeding activity and once sated revert to a non-feeding encysted stage allowing the Thiobacillus population to recover. In addition, the predators are relatively large and cannot penetrate interstices less than 25 μm wide (McCready, 1987). Consequently, the use of predators to control bacterial populations is not considered an effective acid generation control technology.

7.2 In Situ Neutralization

Addition of alkaline materials provides pH control for acid generating waste rock. Methods of in situ neutralization include: blending of acid consuming and acid producing wastes, placement of alkaline materials above or upgradient of acid-generating rock, and the addition of alkaline materials such as limestone in a collection trench downstream of the acid source
(Caruccio et al., 1985). The success of neutralizing compounds to control acid generation depends to a large extent on the movement of water through rather than around or over the system as well as characteristics of the waste-rock and the proportion of excess neutralizing material (SRK, 1989). Caruccio and Geidel (1987) recognized the limitations of the alkaline trench method by recommending its use only in situations where the hydrologic system is well understood and amenable to manipulation. As a preventative measure, this approach is feasible, provided acid consuming materials are economically available (Bell, 1988). However, as a treatment method this technique appears suited only to mildly acid generating waste rock because the amount of neutralizing material required to treat a highly acidic waste rock could be prohibitive.

7.3 Alternate Dump Construction

Selective placement of reactive and neutralizing waste material during dump construction or reconstruction has been carried out as a reactive waste management method. The aim of this type of dump construction is to encapsulate the reactive waste within non-reactive material to prevent or control acid generation. Because this control method depends on in-situ neutralization, problems associated with it are similar to those discussed in section 7.2. Of critical importance to the success of this method is the degree of thoroughness which can be achieved in mixing of alkaline and acid-generating material. Dump construction of this type is only feasible where there is a sufficient volume of impermeable, neutralizing material within a reasonable haulage distance.

Dump construction using the concept of selective placement was used at Equity Silver Mines, where an intermediate glacial till layer was placed within a waste rock pile during construction. A monitoring program, presently in place, will provide information on the long-term integrity of the restricting layer.

Bell (1987) has proposed a similar type of dump construction method termed 'cellular construction' which incorporates features such as: placement of waste in a compacted layer to reduce pore space, placement of continuous horizontal and vertical barriers of compacted till, final capping of the waste pile with an impermeable material and finally vegetation.
7.4 Covers and Seals

Covers and seals are used to restrict water and oxygen access into reactive waste-rock. To effectively seal an acidic waste rock pile, Bell (1986) lists the following requirements:

- Top cover to prevent infiltration of rainfall and air diffusion;
- Sideslope cover to prevent infiltration of water as well as the diffusion or advection of air;
- Stabilization of top and side covers to prevent erosion; and
- Resistance of the cover to cracking, root penetration, burrowing by animals and deterioration due to weathering and freeze/thaw effects.

Various materials have been investigated for use as covers for acid generating waste rock dumps. Table 7-1 lists the advantages and disadvantages of several cover materials.

Topsisting and revegetation of acid generating waste rock does not appear to provide long-term control of acid generation although short term improvements have been documented (Bell, 1987; McCready, 1987; Schubert and Miller, 1982; Thurman et al., 1985). Veldhuizen et al. (1987) in revegetation trials on acid-generating base metal tailings concluded that pyrite oxidation was not restricted and water infiltration was not significantly limited to reduce water flow from the impoundment by direct vegetation of reactive tailings.

Although simple soil covers afford a measure of control in infiltration of rainfall, a layered soil cover system as described by Magnusson and Rasmuson (1984) (cited in SRK, 1989) may provide a more effective infiltration barrier. This type of cover system consists of coarse and fine grained soils placed in layers and includes capillary barriers formed at the interfaces between the coarse and fine textured soils. An extension of the layered soil cover system is the concept of engineered or composite covers. These covers utilize a layered system of various materials, including: compacted glacial till, clay, limestone, top soil, mine tailings, sand and rock or gravel. The layers each perform specific functions to restrict water and oxygen access and improve long-term stability. The function of the first layer is erosion control, typically provided by vegetation or coarse gravel or rip-rap. The second layer is placed to provide a zone of moisture retention for vegetation support and to prevent dessication and reduce oxygen diffusion. Medium to fine textured soils are generally used in this layer. The third layer is designed to provide a suction break to drain water away from the bottom, impermeable layer, and to prevent moisture loss from the infiltration barrier. The
<table>
<thead>
<tr>
<th>Cover Material</th>
<th>Permeability to Water (m/sec)</th>
<th>Advantages/Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compacted clay</td>
<td>$10^{-9}$ to $10^{-11}$</td>
<td>Availability of large quantities problematic in many areas. Subject to erosion, cracking, root penetration. Good sealing if protected and maintained.</td>
</tr>
<tr>
<td>Compacted till</td>
<td>$10^{-7}$ to $10^{-9}$</td>
<td>As above, but generally more permeable.</td>
</tr>
<tr>
<td>Compacted topsoil</td>
<td>$10^{-5}$ to $10^{-8}$</td>
<td>As above, but less robust, more permeable. Questionable longevity.</td>
</tr>
<tr>
<td>Peatland bog</td>
<td>$10^{-5}$ to $10^{-6}$</td>
<td>Need to maintain in a saturated condition. Normally impractical for elevated waste dumps and side slopes.</td>
</tr>
<tr>
<td>Concrete</td>
<td>$10^{-10}$ to $10^{-12}$</td>
<td>Subject to cracking, frost and mechanical damage.</td>
</tr>
<tr>
<td>Asphalt</td>
<td>$10^{-20}$</td>
<td>As above.</td>
</tr>
<tr>
<td>HPDE synthetic cover</td>
<td>Impermeable</td>
<td>Requires proper bedding and protective cover. Highly impermeable; lifespan unlikely to exceed 100 years. Subject to root and mechanical penetration.</td>
</tr>
<tr>
<td>Wax blends</td>
<td>Impermeable</td>
<td>Relatively inexpensive, flexible, self sealing, easily applied. Proper blending required for site specific conditions. Cannot be directly applied to uneven surfaces, requires proper bedding.</td>
</tr>
</tbody>
</table>
fourth layer serves as an infiltration barrier and it therefore consists of relatively impermeable material such as clay, compacted till, or synthetic materials.

A very limited number of composite or engineered covers have been applied under actual field conditions. The Rum Jungle mine in Australia is currently the best documented case of a soil cover in use on a waste-rock pile. A three layer composite cover system consisting of a 225 mm compacted clay layer, overlain by a 250 mm sandy clay loam soil retention zone, and overlain by a 150 mm gravelly sand erosion layer. Measurements of oxygen concentrations and infiltration have been presented elsewhere in this document (Section 3.0, Section 6.0). Although significant reductions in air and water access to the dump were reported, groundwater quality has failed to improve in the four years since the cover was placed. It appears that accumulated acidity in the waste rock dump has will require 10-15 y to flush out.

Several composite covers have been tested on waste rock piles at the Bersbo Mine site in Sweden (Sodermark and Lundgren, 1988). The covers consisted of a sealing layer of about 0.5 m depth beneath about 2 m of moraine as protection against freezing, dessication and root penetration. Three different sealing layers were tested: Cefill, which is a product consisting of a cement stabilized fly ash (5 to 10% cement) with a water content of 30-40%. Cefill solidifies in 24 hours to form a dense, hard sealing layer; two types of clay, one dense and one semi-solid; and a bentonite-sand layer with approximately 10% bentonite. The tests showed that all three methods produced satisfactory seals, with oxygen transport expected to decrease by more than 99%.

Synthetic covers include: asphaltic and spray-on seals, concrete, and flexible membrane liners. As shown in Table 7-1, asphalts, concrete and cementitious mixtures may crack or heave, or be susceptible to chemical degradation, depending on site conditions. Advantages to the use of these materials as surface sealants include their low permeabilities, load bearing strength and weatherability and ease of repair (when uncovered). Discrepancies were noted in the literature with respect to the hydraulic conductivity of asphalt seals. Bell (1987) reported a hydraulic conductivity of $10^{-20}$ m/sec, while Repa et al. (1987) found that an asphalt cap applied to a toxic waste dump was not an effective barrier due to unsatisfactory permeability characteristics. Information on field testing of asphalt sealants on acid generating waste-rock dumps was not found in the literature. Similarly, applications of concrete as covers to control acid generation in waste rock dumps has not been well documented in the literature. However, field testing of cementitious mixtures for use as surface sealants has been proposed by Northwest Geochem (1990).
Flexible membranes or geomembranes are effective impermeable covers provided they are installed correctly on a well-prepared base. Limitations of geomembranes include: susceptibility to puncture during installation, limited longevity or liner integrity due to differential settling of the waste material, susceptibility of certain products to photochemical degradation and expense (Northwest Geochem, 1988). In addition, Caruccio and Geidel (1987) specified that to restrict subsurface recharge, the liner must extend to the base of the backfill. Installation in this manner may be problematic. However, with proper installation of a polyvinyl liner Caruccio and Geidel (1986) reported substantial reductions in flow and acidity from acid generating waste. Geomembranes used in combination with composite covers, could prove to be very effective in limiting oxygen and water transport in acid generating waste-rock (SRK, 1989).

Geopolymers and wax blends are two very recent additions to the list of potential sealant materials on acid generating waste-rock dumps. Geopolymers are compounds containing silica, phosphate and oxygen that bond to form a ceramic type product (SRK, 1989). CANMET is currently investigating the suitability of this product as an acid generation control measure. Wax blends are also a relatively new product and have not received extensive testing for their applicability as a surface sealant material.

7.5 Underwater Disposal

It is generally recognized that a fluctuating water table within reactive waste-rock is an ideal situation for acid generation and migration (Bell, 1988; Northwest Geochem, 1990). Disposal of reactive waste-rock beneath the water table restricts oxidation to virtually a zero level due to the very low diffusivity of oxygen in water. Therefore, underwater disposal of reactive waste rock offers a genuinely long-term solution to the problem of acid generation (Pederson et al., 1990) provided the water table does not fluctuate and the material is kept flooded at a sufficient depth, at all times. However, if suitable natural bodies of water are not located a short haulage distance away, the cost of constructing a facility to provide water cover may not be cost effective. Other disadvantages to underwater disposal of waste rock include: concern over physical and chronic chemical impacts of waste-rock disposal on the benthic population in natural water bodies. Diffusion of oxygen is limited under saturated conditions; however, a small amount of oxygen transfer continues to take place.
8.0 RECOMMENDATIONS

As part of this review of acid drainage in waste rock, the following recommendations are offered for further studies and for decommissioning of waste rock piles. These recommendations reflect the findings of this review and the experience of the authors, but do not necessarily reflect the views of federal and provincial regulatory agencies nor the mining industry.

8.1 Recommendations for Further Studies

8.1.1 General Recommendations

1. A minimum of three Canadian acid-generating waste-rock piles should be targeted for detailed, integrated studies of phase migration and internal processes. These studies would provide a detailed database for developing a predictive capability of acid drainage in waste rock. Potential candidates for detailed studies are Dump #1 at Westmin’s Myra Falls Operation (British Columbia), the East Dump at Mount Washington (British Columbia, and the Dump at the Halifax Airport (Nova Scotia), based on existing data and extent of instrumentation at each site. Other candidate piles also exist and MEND could initiate a survey of mining companies who would want to participate in this study.

2. Due to the presence of coarse rock within many waste-rock piles, techniques for drilling into and instrumenting piles are limited. A detailed review of potentially applicable technology is warranted and may accelerate the number of field studies of piles by increasing efficiency and decreasing overall cost.

8.1.2 Water Movement

1. Water movement through acid-generating waste rock leads to the discharge of acid drainage to the local environment, emphasizing the importance of understanding the nature of this movement within all acid-generating piles. Although the theory of water movement through waste rock is relatively well developed, important practical aspects such as channelling remain essentially undefined and unpredictable. Numerous field studies on pilot scale and full scale would provide a database from which prediction
could be made. These studies would involve drilling, water-monitoring equipment, and excavation of some waste rock to examine wetting patterns.

8.1.3 Solids Migration

1. The physical movement of rock particles can result in a low-permeability layer directly beneath exposed surfaces or a low-permeability basal layer. This effect may not operate on a small scale over short periods of time such as in laboratory experiments. Consequently, field studies of existing waste-rock piles should be conducted by drilling and permeability testing to determine the importance of solids migration through time. The potential impacts of this migration on patterns of water movement, gas transport, and acid generation over long periods of time could affect the success of decommissioning plans.

8.1.4 Gas Transport

1. The movement of gases through a waste-rock pile can significantly affect reaction rates of acid generation and acid neutralization. There are more field studies and modelling of this phase transport within waste rock than of water and solids. However, most field studies focus on shallow depths where most oxygen consumption often occurs and on concentrations rather than patterns of transport. As a result, the extent and nature of gas transport in piles remain relatively undefined, particularly at depths greater than a few meters. Commonly observed "hot spots" which melt snow on some piles in British Columbia highlight the capacity for deep gas advection. Field studies of gas transport should examine the full depth of waste rock and determine transport and flux patterns.

8.1.5 Internal Reactions

1. Within waste rock, the processes of acid generation, bacterial acceleration, acid neutralization, and metal leaching occur primarily on the surfaces of rock particles. Although these processes can be relatively easily monitored in laboratory-scale experiments such as humidity cells and in fine-grained tailings, monitoring of coarse-rock surfaces is more difficult. Studies of internal processes should begin with the development of monitoring techniques such as custom-designed electrodes in direct
contact with rock surfaces. These data would be more informative than water-quality monitoring at the toes of piles.

2. Rigorous studies have not been carried out on the relative amount of metal dissolution and acid generation from abiotic reactions at acid pH, in the absence of bacteria. It is conceivable that abiotic reactions may be more significant than previously thought.

3. A consistent discussion of the theory of acid generation, focusing on reaction stoichiometry and rates, has not been located during this review. Such a discussion would prove valuable by providing an initial indication of the potential severity of acid drainage from a specific suite of minerals.

4. Data which cite the lack of evidence for significant enhancement of acid generation processes by bacterial activity are derived from field bactericide studies and low-level laboratory studies. There is a need for more fundamental studies on the relative contribution of bacterial processes in existing waste-rock piles.

8.1.6 Control Technologies

1. The currently proposed control technologies for waste-rock piles are similar to those for tailing sand and mine walls. Although these technologies have been directly extrapolated to waste-rock piles, there is a need for comprehensive testing, particularly on a field scale, and with appropriate instrumentation. Development and testing of alternative cover technologies appears to show promise and should be continued. Of particular interest are technologies which utilize mine waste materials, such as tailings and wastewater sludge. Potential impacts of underwater disposal of reactive waste-rock should also be further evaluated.

8.2 Recommendations for Waste-Rock Decommissioning

Reliable decommissioning plans can only be designed with the detailed understanding of the targeted waste-rock pile. This review has shown that critical aspects in the development, severity, and migration of acid drainage within waste rock are various internal processes and the phase transport of water, gases, and solids through the rock. Because of the number of factors affecting acid drainage, each pile will have unique characteristics and will require detailed studies to delineate these characteristics.
Proper planning for decommissioning should begin prior to mining and continue throughout the lifetime of the mine. Recommendations are presented below for each phase of mining.

8.2.1 *Recommendations Prior to Mining*

1. Detailed studies of the natural strata underlying the proposed pile should be conducted, addressing the nature of water movement, including permeability and flow directions, and the geochemistry of the sediment, rock, and groundwater. These studies will involve drilling, coring, and piezometer installation and will provide baseline information and data for predictions of potential impacts. However, all boreholes and piezometers within the perimeter of a proposed pile must be thoroughly sealed prior to dumping to prevent deep flow of waste-rock seepage. Wells around the perimeter of a proposed pile should remain on a periodic schedule of monitoring for physical and chemical parameters.

2. Laboratory testwork such as acid-base accounting and humidity cells should be conducted on drill core and hand samples of the rock that will be delivered to the pile. Rates of acid generation, acid neutralization, and metal leaching within the proposed pile should then be predicted.

3. Detailed plans for pile construction, environmental management, and acid control should be developed and submitted for review to regulatory agencies.

4. Preliminary decommissioning plans should also be designed and submitted for review by regulatory agencies.

8.2.2 *Recommendations During Mine Operation*

1. Monitor wells on the perimeter of the pile should continue to be periodically monitored for physical parameters, such as water levels and hydraulic conductivity, and water-quality parameters.

2. Detailed plans of pile construction should be kept including the origin(s) of various rock types and the locations in the pile where each type was placed. This inventory should include some testwork such as acid-base accounting and leach tests so that layers with enhanced or depressed capacity for acid generation, acid neutralization, and metal leaching are delineated. This information would prove valuable if portions
of a pile do not require acid-drainage control or if initial decommissioning plans fail due to unforeseen problems within the dump.

3. Instrumentation and monitoring of a pile should begin quickly as construction begins in order to compile a thorough database on internal processes and phase migration. This information would indicate the manner in which the pile could evolve through time after decommissioning and would allow the design of appropriate decommissioning plans.

4. Two years prior to decommissioning of a pile, a detailed review of the pre-mining information, inventory and construction data, and the monitoring database should be completed. Any significant lack of data should be identified and quickly eliminated. Detailed decommissioning plans should then be developed and submitted for review to regulatory agencies. Detailed contingency plans covering potential failures of the decommissioning plans should also be developed and submitted.

8.2.3 Recommendations After Decommissioning

1. Intensive monitoring should begin after decommissioning and decrease in intensity through time. The monitoring should be designed to detect quickly any unacceptable impact on the local environment and should take place within the pile as well as around the perimeter. Upon the detection of any unacceptable impacts, the contingency plans developed during operation should be implemented. An assessment of the causes of any failure should be undertaken as it might reveal the potential for other failures.
9.0 SUMMARY

This report contains a critical review of existing information on acid-generating waste rock. Numerous databases were accessed (Appendix A) and several visual searches of libraries were conducted in order to identify relevant published literature. As well, researchers, technical organizations, and mining companies were contacted directly (Appendix B) to obtain published papers and unpublished data. From this extensive body of information, selected documents (Section 10.0) were reviewed for relevant information on theory, laboratory experiments, modelling, and field studies. These documents were also critically assessed to determine their validity, applicability, and weaknesses.

In order to organize and present the findings of the critical review, waste-rock piles were conceptually viewed as a natural system with transport of water (Section 3.0), solids (Section 4.0), and gases (Section 5.0) through the piles and reactions operating within the piles (Section 6.0). The effects of phase transport, pile construction (Section 2.0) and control technologies (Section 7.0) on the system were also addressed. Finally, recommendations were offered for further studies and for decommissioning of acid-generating waste-rock piles (Section 8.0). Each section will be summarized below in numerical order.

Most waste-rock piles are constructed with a few basic techniques: end dumping, push dumping, series of small piles, and large-scale dragline dumping. An assessment of these construction techniques revealed the impacts that various techniques could have on phase migration through a pile. The choice of technique for a particular pile is usually based on economics and convenience rather than environmental control. As a result, the selection of construction technique as a successful control technology remains essentially unexplored.

Following the construction, a pile usually remains open to the passage of water, solids, and gases. For the proper delineation of water movement, surface and subsurface studies must be conducted on both the pile and the surrounding environment because of their interactive nature.

Water passing through and beneath piles was found to be the primary contaminant pathway of acid drainage to the local environment. Consequently, the significant hydrogeologic characteristics of waste-rock piles were summarized in three conceptual models, representing recharge areas (hilltops), discharge areas (valley bottoms), and intermediate areas (sloping terrain). Water movement within rock piles was found to be dependent on hydraulic conductivity, hydraulic gradients, degree of saturation, and laminar versus turbulent flow. Practical complexities such as channelling were also found to affect water movement, but were not easily predictable.
The migration of solids was found to occur in two basic modes. Firstly, internal migration carries rock particles into and through the pile, sometimes accumulating just below the surface, in subsurface channels, or at the base. This migration can significantly alter the patterns and rates of water and air movement through time. Secondly, geotechnical failures carry large quantities of rock downwards towards the base of the dump and/or outwards from the toe. Although many classification schemes were found for these failures, a simple scheme includes: internally generated failures, external slope erosion, and foundation failures.

The transport of gases were found to occur through gaseous diffusion, gaseous advection, aqueous diffusion, and aqueous advection. Gaseous advection appeared to be the primary mode of transport in coarse-rock dumps and is driven by thermal gradients from acid generation, wind currents, and barometric pumping. Aqueous advection and gaseous diffusion may also result in significant transport of gases, depending on permeabilities and water movement within a particular pile.

Although water movement through waste-rock piles is the primary pathway for contaminant migration, no contaminants would appear if reactions were not taking place within piles. The primary reactions were identified as acid generation which may be driven by abiotic and biologic factors, acid neutralization, and metal leaching. Although acid generation is sometimes taken as synonymous with sulfide-mineral oxidation, this connection is not always warranted. The stoichiometries and rates of both sulfide oxidation and acid generation were found to be highly variable and this variability has not been considered in many acid-generation studies. Bacterial activity was often reported as significantly accelerating the rates of acid generation; however, detailed evidence for this is lacking and some studies have suggested that bacterial action may accelerate the rates by a low factor at most, that is, between a factor of 1 to 20.

Acid neutralization was also found to be a highly complex series of aqueous and mineral reactions. Speciation analyses were identified as a useful, but under-utilized, tool for understanding and predicting acid neutralization, particularly where relative consumptions of acid-neutralizing and acid-generating materials are important in the overall prediction of potential for acid generation.

In addition to acid generation and acid neutralization, metal leaching also has a significant impact on water quality. The rate and extent of metal leaching was found to be dependent on the oxidation of sulfide minerals which releases metals into solution, the enhanced solubility of minerals at acidic pH, ion exchange, aqueous complexation, time, and distance.
The review of modelling and the presentation of case studies of acid drainage highlighted the intensity of existing work, but also demonstrated the general lack of an integrated approach to assessing and predicting acid drainage. In light of the number of variables reviewed throughout this report, such an integrated study is probably not forthcoming in the near future. Consequently, existing and near-future assessments of acid drainage will likely remain fragmented, focusing only on selected variables.

Appropriate control technologies for acid-generating waste-rock piles were found to be essentially those for acid-generating tailings impoundments and mine walls. The effectiveness of these technologies for acid generation control in waste-rock has only been tested on a very limited scale.

Finally, recommendations were formulated for further studies and for decommissioning of waste-rock piles. Recommended further studies addressed the various modes of phase transport and internal reactions and included the suggestion for the selection of three Canadian waste-rock piles for detailed, integrated studies. Recommended criteria for decommissioning indicated the appropriate studies and procedures at pre-mining, operational, and post-decommissioning stages.

Based on this report, detailed site-specific environmental investigations of waste-rock piles can be designed and conducted. These investigations would provide the necessary information to understand the factors leading to and regulating acid drainage. From this information, the appropriate control technology can be selected, tested, and implemented.
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11.0 ACKNOWLEDGEMENTS

This literature review benefitted from the assistance of Keith Ferguson (Environment Canada), John Harries (Australian Nuclear Science and Technology Organisation), and Kirk Nordstrom (U.S. Geological Survey). The final report was improved through the reviews and comments of the aforementioned individuals as well as Patricia Erickson (U.S. Bureau of Mines), Ron Nicholson (University of Waterloo, Ontario), and Linda Broughton (SRK, British Columbia).
Keywords (used individually and in combinations)

Primary: Acid
        Mine(s)
        Drainage
        Mining
        Metal(s)
        Leach(ing)
        Ground(water)
        Hydrology
        Biohydrometallurgy

Limiting: Waste
          Rock
          Pile
          Spoil(s)
          Soil

Databases

Dialog Databases: Aquaculture
                    Aquatic Science Abstracts
                    Biosis Preview
                    CA Abstracts/Search
                    Chemical Engineering Abstracts
                    Compendex Plus
                    Current Technical Index
                    Engineering Materials Abstracts
                    Enviroline
                    Environmental Bibliography
                    Federal [U.S.] Research In Progress
                    Geoarchive
                    Geobase
                    Georef
                    Life Sciences Collection
                    Metadex
                    National Technical Information Service
                    Nonferrous Metals Abstracts
                    Oceanic Abstracts
                    Pascal
                    Pollution Abstracts
                    Scisearch
                    Supertech
                    Water Resources Abstracts
                    Waternet
                    World Aluminum Abstracts
                    World Translations Index
                    Zoological Record
QL Databases:  
Canadian Environmental Mining Technology

Others:  
Coal Research Projects
Environment Canada Library Network
APPENDIX B

LIST OF CONTACTS
List of Contacts

Mining Companies

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Tom Carnahan/Larry Schultze, U.S. Bureau of Mines, Reno, (702) 784-5386
Keith Ferguson, Environment Canada, Vancouver, 666-2399

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