
Swedish Nuclear Fuel and Waste Management Co, Stockholm

June 1987

DOCUMENT HAS BEEN REVIEWED AND APPROVED
BY DOE AND SNL

TECHNICAL REPORT

An OECD/NEA International project managed by:
SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO
Division of Research and Development
State-of-the-Art Report On
Potentially Useful Materials For Sealing
Nuclear Waste Repositories

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June 1987

This report concerns a study which was conducted for the Stripa Project. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

A list of other reports published in this series is attached at the end of the report. Information on previous reports is included in the report.
FOREWORD

On May 20-21, 1986 the Joint Technical Committee of the OECD/NEA Stripa Project established a Task Force on Sealing Materials and Techniques, with a membership composed of representatives from Canada, Finland, Japan, Sweden, Switzerland, and the United Kingdom, and the United States of America. The Task Force was chartered to serve in an advisory capacity to the Task on Sealing of Fractured Crystalline rock in Phase III of the Stripa Project and, as such, to perform two specific functions: (1) prepare a state-of-the-art report on repository sealing materials and techniques for application to crystalline rock and (2) provide guidance to the Principal Investigator on (a) the selection of candidate sealing materials for evaluation by laboratory and in situ tests, (b) the selection and implementation of the laboratory tests, and (c) the design and implementation of a pilot-scale in situ test in the Stripa Mine. The Principal Investigator for the task on sealing of fractured rock is Professor Roland Pusch.

On September 10-11, 1986, the Task Force met in Lund, Sweden, and prepared an outline of the contents of the state-of-the-art report and appointed Dr. William Coons to write the report on the basis of contributions provided by the representatives of the member countries. In late January 1987, a draft copy of the report was completed by Dr. Coons, who was aided substantially by his colleague, Mr. Dann Myer. Dr. Coons and Mr. Meyer sent copies of the draft to the representatives for review. On March 20, 1987, the Task Force met in Grythyttan, Sweden, and completed the review of the report with the inclusion of some additional information on cements and recommendations for incorporating a more detailed treatment of cementitious materials.
The Task Force, which consisted of the members listed below, worked individually in their own countries to collect the information contained in the report. Dr. William Coons was responsible for compiling the information into a readable and meaningful document.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ABSTRACT</strong></td>
<td>viii</td>
</tr>
<tr>
<td><strong>EXECUTIVE SUMMARY</strong></td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 HISTORY OF THE STRIPA PROJECT</td>
<td>1</td>
</tr>
<tr>
<td>1.2 SCOPE OF THE REPORT</td>
<td>5</td>
</tr>
<tr>
<td>1.3 FORMAT OF THE REPORT</td>
<td>6</td>
</tr>
<tr>
<td>2. PERFORMANCE OBJECTIVES OF SEALING MATERIALS AND SELECTION OF PRIORITY MATERIALS</td>
<td>8</td>
</tr>
<tr>
<td>2.1 RECOMMENDED PERFORMANCE PROPERTIES</td>
<td>8</td>
</tr>
<tr>
<td>2.2 LONGEVITY EXPERIENCE WITH LOW PERMEABILITY SEAL MATERIALS</td>
<td>10</td>
</tr>
<tr>
<td>2.3 OTHER CONSIDERATIONS AFFECTING SELECTION OF LOW PERMEABILITY SEAL MATERIALS</td>
<td>13</td>
</tr>
<tr>
<td>2.4 SUMMARY OF CRITERIA FOR COMPARATIVE EVALUATION OF SEAL MATERIALS</td>
<td>16</td>
</tr>
<tr>
<td>2.5 DESCRIPTION AND SCREEN OF PRELIMINARY CANDIDATE SEAL MATERIALS</td>
<td>19</td>
</tr>
<tr>
<td>2.5.1 Cementitious Materials</td>
<td>21</td>
</tr>
<tr>
<td>2.5.2 Earthen Materials</td>
<td>29</td>
</tr>
<tr>
<td>2.5.3 Mixtures of Clay and Cement</td>
<td>37</td>
</tr>
<tr>
<td>2.5.4 Chemical Grouts</td>
<td>39</td>
</tr>
<tr>
<td>2.5.5 Synthetic Minerals</td>
<td>46</td>
</tr>
<tr>
<td>2.5.6 Ceramics</td>
<td>48</td>
</tr>
<tr>
<td>2.5.7 Metals</td>
<td>49</td>
</tr>
<tr>
<td>2.5.8 Bitumen</td>
<td>50</td>
</tr>
<tr>
<td>3. DISCUSSION OF CANDIDATE SEALING MATERIALS</td>
<td>52</td>
</tr>
<tr>
<td>3.1 HYDRAULIC CONDUCTIVITY OF CANDIDATE SEAL MATERIALS</td>
<td>53</td>
</tr>
<tr>
<td>3.1.1 Cementitious Materials</td>
<td>53</td>
</tr>
<tr>
<td>3.1.2 Earthen Materials</td>
<td>60</td>
</tr>
<tr>
<td>3.2 STRUCTURAL/MECHANICAL PROPERTIES</td>
<td>62</td>
</tr>
<tr>
<td>3.2.1 Cementitious Materials</td>
<td>62</td>
</tr>
<tr>
<td>3.2.2 Earthen Materials</td>
<td>64</td>
</tr>
<tr>
<td>3.3 LONGEVITY CONSIDERATIONS</td>
<td>65</td>
</tr>
<tr>
<td>3.3.1 Cementitious Materials</td>
<td>71</td>
</tr>
<tr>
<td>3.3.2 Earthen Materials</td>
<td>76</td>
</tr>
<tr>
<td>3.4 SUMMARY OF PROGRAM OF RESEARCH FOR PRIORITY SEAL MATERIALS</td>
<td>101</td>
</tr>
<tr>
<td>3.5 EMPLACEMENT CONSIDERATIONS</td>
<td>106</td>
</tr>
<tr>
<td>3.5.1 Cementitious Materials</td>
<td>106</td>
</tr>
<tr>
<td>3.5.2 Earthen Materials</td>
<td>109</td>
</tr>
<tr>
<td>3.6 FORMULATIONS OF PRIORITY MATERIALS</td>
<td>110</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6.1</td>
<td>Cementitious Materials</td>
<td>111</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Earthen Materials</td>
<td>113</td>
</tr>
<tr>
<td>3.6.3</td>
<td>Description of Likely Compositional Ranges</td>
<td>115</td>
</tr>
<tr>
<td>4</td>
<td>EMPLACEMENT TECHNIQUES</td>
<td>120</td>
</tr>
<tr>
<td>4.1</td>
<td>FRACTURE SEALING METHODS</td>
<td>120</td>
</tr>
<tr>
<td>4.2</td>
<td>LIMITATIONS IMPOSED BY REPOSITORY DESIGN</td>
<td>125</td>
</tr>
<tr>
<td>4.3</td>
<td>EMPLACEMENT TEST CONSIDERATIONS</td>
<td>126</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Selection of Injection Techniques</td>
<td>127</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Selection of Fractured Rock Type</td>
<td>128</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Selection of Candidate Material</td>
<td>130</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Space Requirements</td>
<td>131</td>
</tr>
<tr>
<td>4.4.5</td>
<td>Thermal Considerations</td>
<td>131</td>
</tr>
<tr>
<td>4.3.6</td>
<td>Monitoring of Injection Test</td>
<td>133</td>
</tr>
<tr>
<td>4.3.7</td>
<td>Post-test Sampling Concepts</td>
<td>134</td>
</tr>
<tr>
<td>5</td>
<td>CONCLUSIONS AND RECOMMENDATIONS</td>
<td>135</td>
</tr>
<tr>
<td>5.1</td>
<td>CONCLUSIONS</td>
<td>135</td>
</tr>
<tr>
<td>5.2</td>
<td>RECOMMENDATIONS</td>
<td>135</td>
</tr>
<tr>
<td>6</td>
<td>REFERENCES</td>
<td>137</td>
</tr>
<tr>
<td>7</td>
<td>GLOSSARY OF TERMS RELATING TO GROUTING</td>
<td>148</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Criteria for comparative evaluation of seal materials</td>
</tr>
<tr>
<td>2-2</td>
<td>Summary of additives for cementitious materials mixes</td>
</tr>
<tr>
<td>2-3</td>
<td>Summary of chemical grouts</td>
</tr>
<tr>
<td>3-1</td>
<td>Physical properties of grout (approximately 130 days water curing at 7°C)</td>
</tr>
<tr>
<td>3-2</td>
<td>Summary of permeability and erodability studies on bentonite-bearing grouts (Chan, 1986)</td>
</tr>
<tr>
<td>3-3</td>
<td>Summary of general issues for priority seal materials for fracture sealing</td>
</tr>
<tr>
<td>3-4</td>
<td>Shear strength and plastic viscosity of neat cement grouts</td>
</tr>
<tr>
<td>3-5</td>
<td>Compositional ranges of priority sealing materials</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Screen of preliminary candidate seal materials</td>
</tr>
<tr>
<td>2-2</td>
<td>Crystal structure of smectite</td>
</tr>
<tr>
<td>2-3</td>
<td>Calculated and measured effects of density on the maximum swelling pressure of a compacted Wyoming (Na-rich) bentonite</td>
</tr>
<tr>
<td>2-4</td>
<td>Hydraulic conductivity of compacted bentonite/sand mixtures as a function of bentonite content</td>
</tr>
<tr>
<td>3-1</td>
<td>The solubility of silica and alumina as a function of pH (after Correns, 1949)</td>
</tr>
<tr>
<td>3-2</td>
<td>Differential thermal analysis (DTA) curve for a smectite (nontronite) with quartz added as an internal standard. The magnitude and locations of peaks are characteristics of exothermic or endothermic reactions occurring at elevated temperatures</td>
</tr>
<tr>
<td>3-3</td>
<td>Illite/smectite expandabilities in natural mix-layer clays versus the temperature of the formation in which they occur.</td>
</tr>
<tr>
<td>3-4</td>
<td>Illite/smectite expandabilities for selected Gulf Coast shales as related to age.</td>
</tr>
<tr>
<td>3-5</td>
<td>Extent of reaction for a beidellite composition glass reacting to illite as a function of time (slope of each isotherm provides a rate constant for the illitization reaction), at 200 MPa (29,000 psi).</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>TITLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-6</td>
<td>Relationship between temperature and the time for the illitization reaction of a beidellite composition glass calculated from experimentally determined rate constants (Figure 3-5), at 200 MPa (29,000 psi)</td>
</tr>
<tr>
<td>3-7</td>
<td>Stability relationship diagrams for several common low-temperature clay minerals calculated for the activity of several cations ($K^+$, $Na^+$, $Mg^{2+}$, $H^+$) against silica activity, at 25°C, 1 atmosphere</td>
</tr>
<tr>
<td>4-2</td>
<td>Major fractures in heater hole no. 1 of the Buffer Mass Test at Stripa</td>
</tr>
<tr>
<td>4-3</td>
<td>Prototype for sealing of BMT heater holes. The grout is injected through the 1&quot; tube, fills the space between the rubber sealings (R) and enters fractures which are exposed in the rock (F)</td>
</tr>
<tr>
<td>4-1</td>
<td>Principle for injecting rock with &quot;dynamic injection technique&quot;.</td>
</tr>
</tbody>
</table>

A) percussion drilling machine, B) steel cylinder, C) slurry container, E) transducer F) valves, G) air pressure, I) borehole, 2) packer, 3) high-pressure hose, 4) valve
EXECUTIVE SUMMARY

This state-of-the-art report has been prepared by the members of the technical OECD/NEA-sponsored Stripa Task Force on Sealing in furtherance of Phase III of the Stripa Project. The objectives of the report are: 1) to review progress in the development of seal materials and emplacement techniques; 2) to identify priority issues and materials for sealing narrow aperture fractures; and by so doing, 3) to provide a basis for developing seal test programs such as that intended for implementation at the Stripa Facility.

A system of seals may be a desirable or necessary element to assure that repositories prevent release of unacceptable amounts of radioactive waste. Although such seals may be included in repository systems, quantitative performance objectives cannot be specified generically; rather, performance specifications await definition on a case-by-case basis. Generalized performance objectives can be defined, however. These objectives include restricting water flow through the repository, working compatibility with the in situ environment and other repository barrier components, and maintaining performance over an unspecified but long duration of time (many thousands to perhaps millions of years). During analysis and recommendation of materials, practical constraints such as the ability to emplace seals, a history of successful use of the material, the availability and cost of materials, and the desire to use comparatively safe (i.e., non-toxic) materials were also considered.
The initial list of material classes analyzed included cementitious materials, ceramics, chemical grouts, clay materials, cement/clay materials, metals, and organic substances (bitumen, tars, etc.). Of these, cementitious materials and clay materials are recommended as priority materials because they can be designed to meet all of the desired performance characteristics, there is a considerable history of successful use in similar engineering applications, and there is indirect evidence that they will continue to perform for long periods of time. Chemical grouts are identified as a promising class of materials that could be very useful for specialty applications. Chemical grouts were not selected as a priority material because of their cost and because evidence for long-term performance is lacking. Cement/clay and bituminous materials may possess important performance characteristics but have uncertain long-term performance. Both chemical grouts and bitumen have uncertain effects on radionuclide mobility because of the introduction of organic substances into the repository system. Synthetic materials, ceramics, and metals, are deferred in this report either for practical reasons (e.g., emplaceability) or because the ability to provide seal functions appears unlikely. Figure ES-1 illustrates an example of the material screening process and results. The significance of the figure is the process of materials screening, a technique applicable to all programs. The ranking of criteria and materials shown in the figure may vary from site to site and do not necessarily represent a consensus of all contributors to this report.
### Figure ES-1. Screen of preliminary candidate seal materials*

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Ability to Perform as Hydrologic Barrier</th>
<th>Emplaceability</th>
<th>Long-Term Stability</th>
<th>Effect on Mobility of Radionuclide</th>
<th>Materials Availability</th>
<th>History of Usage in Engineering Practice</th>
<th>Extensive Systematic Data Base on Chemistry and Performance</th>
<th>Low Cost</th>
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<tbody>
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<td>Significance of Criteria</td>
<td>Very Important</td>
<td>Important</td>
<td>Desirable</td>
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<td>Cementitious Materials</td>
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<td>Clays (Bentonite)</td>
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<td>Cement-Clay Mixtures</td>
<td>•</td>
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<tr>
<td>Chemical Grouts</td>
<td>•</td>
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<td>Bitumen</td>
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<td>Ceramics</td>
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<td>Metals</td>
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<tr>
<td>Synthetic Fracture-Filling Minerals</td>
<td>•</td>
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</tbody>
</table>

- • acceptable performance
- ■ acceptable performance probably achievable
- ▲ performance uncertain
- ○ probably unacceptable performance

*Mixtures and combinations may be used.

†Unacceptable performance will disqualify materials from priority consideration for grouting.
With clay materials and cementitious materials identified as priority candidate materials, each material class is discussed in terms of behavior. Cementitious materials achieve low permeability by being formulated to have minimum porosity and by avoiding shrinkage and fracturing. Hydraulic conductivities in the range of $10^{-8}$ to $10^{-10}$ cm/sec are achievable if water:cement ratios are in the range of 0.3 to 0.5. The materials will probably require the use of pozzolanic additives and plasticizers. Conductivities in this range can probably be maintained if cementitious materials are not exposed to temperatures above 100°C. Clay materials achieve low permeability by a combination of physical and chemical processes. Clays absorb water into their structures and develop internal swelling pressures that resist water flow (both internally and at interfaces). Conductivities less than $10^{-10}$ cm/sec can be achieved with Na-bentonite so long as a reasonable dry density is engineered on emplacement. Emplacement considerations (i.e., mix design requirements to achieve a pumpable, high penetration grout) may affect the properties of the material.

Clay materials deform plastically and reversibly at temperatures below about 300°C; hence, they may be preferred for high temperature applications. Note, however, that depending on water chemistry, elevated temperatures may enhance the kinetic rates of alteration to less favorable clays (e.g., illite). Clay grouts also tend to be eroded under high hydraulic gradients and groundwater flow rates. Detailed discussion along these lines results in identification of a preliminary set of
issues that can be resolved through field or laboratory tests so that confidence in acceptable performance of designs is ultimately increased. These issues are shown on Table ES-1. It should be emphasized, however, that this list is preliminary and may be augmented or diminished as Stages III and IV of Stripa Phase III progress or as member countries advance seal system designs.

Familiar technologies for emplacing seals in fractures include pressure injection, dynamic (or vibratory) injection, and electrophoresis. Electrophoresis, the process of inducing clay migration into fractures by imposing an electrostatic potential along the fracture, is least promising because of the need to drill additional holes for electrodes and uneven results in field trials. Normal pressure injection will probably prove satisfactory for many fracture sealing needs. Attempts to seal narrower fractures using this standard technique are likely to result in damage to the host rock. There are, however, two dynamic injection techniques. One utilizes mechanical vibration (Pusch, et al., 1985) and the other employs ultrasonic wave energy (Kameda, 1983). These vibratory techniques are superimposed on standard pressure injection techniques and enhance penetration by decreasing the internal friction between particles in the grout slurry. Both techniques can be applied to either cementitious or clay grouts, with penetrations on the order of decimeters reported in fractures with apertures on the order of 0.1 mm.
Table ES-1. Summary of general issues for priority grouting materials for fracture sealing

<table>
<thead>
<tr>
<th>Issue</th>
<th>Proposed Approach</th>
</tr>
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<tbody>
<tr>
<td>(1) Define materials performance requirements.</td>
<td>Perform modeling of seal performance under several release scenarios including site geology, site hydrology, site geochemistry, repository design and (in situ conditions) site performance regulatory criteria (if any) to determine seal performance requirements for hydraulic conductivity, retardation potential, performance longevity, mechanical properties. Performance requirements are site specific based on (1), select cementitious materials and additives likely to produce desirable characteristics using test data and industry literature; priority should be given to inexpensive, available materials.</td>
</tr>
<tr>
<td>(2) Select starting materials and prepare mix design(s); characterize selected materials.</td>
<td>Determine limited range in which design parameters may be varied from literature. Perform trial mixes and preliminary laboratory tests (e.g., viscosity, penetrability, bleed, strength, hydraulic conductivity); select mix(es) based on (1) for further study.</td>
</tr>
<tr>
<td>(3) Select key materials properties and determine materials performance with respect to performance with respect to performance requirements; optimize materials properties.</td>
<td>Select key properties of grout based on (1) and devise test program. Perform standard laboratory tests to evaluate properties of selected materials. Materials properties may include:</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
</tr>
<tr>
<td></td>
<td>Bleed</td>
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<td></td>
<td>Penetrability/set time</td>
</tr>
<tr>
<td></td>
<td>Hydraulic conductivity</td>
</tr>
</tbody>
</table>
Table ES-1. Summary of general issues for priority grouting materials for fracture sealing (continued)

<table>
<thead>
<tr>
<th>Issue</th>
<th>Proposed Approach</th>
</tr>
</thead>
</table>
| (3) (Continued) | Interface hydraulic conductivity  
Unconfined/confined compressive strength  
Thermal expansion  
Tensional strength  
(flexural)  
Shear strength/erodability |
| (4) Establish longevity requirements for grout and determine materials performance longevity (stability). | Based on (1), establish the longevity requirements for grout performance; longevity requirements will be site-specific and probably specific to individual seals, materials, seal functions, or locations within the facility; estimate long-term compatibility to performance of grout in host environment through real-time and accelerated laboratory testing of grout materials; perform geochemical modeling, thermodynamic and kinetic calculations to estimate types and rates of materials alteration and consequences on performance; host environment includes host rock, ground water, waste, adjacent seals, backfills, waste package, temperature and pressure conditions. |
| (5) Determine effects of grout material, emplacement, or alteration products on radionuclide mobility. | Perform laboratory solubility and sorption testing using selected grout materials, alteration products (4), and altered ground water compositions and key radionuclides or analogs. |
Table ES-1. Summary of general issues for priority grouting materials for fracture sealing (continued)

<table>
<thead>
<tr>
<th>Issue</th>
<th>Proposed Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6) Confirm material's emplaceability and emplacement equipment;</td>
<td>Perform field tests in test facilities comparable to repository conditions; determine:</td>
</tr>
<tr>
<td>optimize grout emplacement.</td>
<td>• Grout delivery rates</td>
</tr>
<tr>
<td></td>
<td>• Penetration of grout</td>
</tr>
<tr>
<td></td>
<td>as a function of grout type, equipment, nature of fracture (e.g., aperture, tortuosity, etc.); perform post-test analysis (including destructive tests) to determine:</td>
</tr>
<tr>
<td></td>
<td>• Uniformity of grout penetration</td>
</tr>
<tr>
<td></td>
<td>• Permeability of treated fractures.</td>
</tr>
</tbody>
</table>
INTRODUCTION

This State-of-the-Art Report on sealing small aperture fractures in mined nuclear waste repositories is a compilation and summary of information provided by international participants in the Stripa Project. Contributors to this document are:

- Atomic Energy of Canada, Ltd.
- Building Research Establishment (UK)
- Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle (NAGRA) (Switzerland)
- Office of Crystalline Rock Development, Battelle Memorial Institute (USA)
- Swedish Geological Co.
- Swedish Nuclear Fuel and Waste Management Co. (SKB)
- Technical Research Centre of Finland
- University of Tokyo (Japan).

The information presented and the conclusions drawn in this report are the result of discussions and acceptance among the participants representing these institutions. The conclusions, however, do not represent consensus among the contributors for the materials, issues, or research requirements applicable to their individual programs.

1.1 HISTORY OF THE STRIPA PROJECT

The Stripa Project is an international cooperative effort in the study of nuclear waste management. The Stripa Mine in central Sweden is an iron ore
mine in granitic host rock that has been actively exploited since the Middle Ages. In 1977-1980, after it was abandoned for iron mining, the Stripa Mine was the site of a series of investigations related to nuclear waste storage. Tests were performed in facilities excavated in the mine as part of a cooperative agreement between the Swedish Nuclear Fuel and Waste Management Co. (SKB) and the United States Department of Energy (DOE).

The investigations included in situ tests to examine the thermomechanical and hydrological properties of fractured, saturated granite as part of an effort to improve understanding of conditions expected in the disposal of nuclear wastes in crystalline rock bodies. The particular tests included a time-scaled heater test to investigate the long-term thermomechanical response of granite to thermal loading; a full-scale heater test that simulated the short-term, near-field effects of the thermal pulse from emplaced nuclear wastes; and hydrological tests that included large-scale measurements of the hydraulic conductivity of the fractured rock mass. This series of tests provided the foundation of knowledge upon which the Organization for Economic Cooperation and Development/Nuclear Energy Agency (OECD/NEA) Stripa Project was based.

In 1980, a cooperative effort for research at the Stripa Mine was organized in the form of the autonomous OECD/NEA Stripa Project. Under the management structure for the Stripa Project, the responsibility for supervision for the research program and for its finance resides with the Joint Technical Committee (JTC) which is composed of
representatives from each of the participating countries. The JTC also provides information on the general progress of work to the OECD Steering Committee for Nuclear Energy, through the NEA committee on Radioactive Waste Management and its Coordinating Group on Geological Disposal. Each research investigation is assigned to a principal investigator. The conception of the experiments and their realization are periodically reviewed by two Technical Subgroups that deal with (a) hydrogeology, chemical transport, and geophysics and (b) engineered barriers and rock mechanics. These Technical Subgroups are composed of scientists and engineers from the participating countries. The SKB acts as the host organization and provides the day-to-day management for the project.

The Stripa Project has been organized into Phases. Phase I and Phase II are complete, and Phase III is currently being performed. During Phase I, which lasted from 1980 until 1984, the participating countries were Canada, Finland, France, Japan, Sweden, Switzerland, and the United States. The first phase of the Stripa Project consisted essentially of three principal investigations:

- Hydrogeological and geochemical investigations of the granite rock mass to a depth of 1,230 meters below the ground surface
- Tracer migration tests to study mechanisms of radionuclide transport in the rock fractures
- Large-scale tests of the behavior of bentonite backfill material in waste emplacement boreholes and tunnels under conditions of elevated temperature.
Phase II of the Stripa Project began in 1983 and was completed in early 1987. The original seven countries continued to participate in the Project and were joined by Spain and the United Kingdom. The investigations that were performed in the Stripa Mine in this second phase were:

- The development of crosshole geophysical and hydraulic methods for the detection and characterization of fracture zones
- Extended tracer migration experiments to study further the mechanisms of radionuclide transport in fractured granite
- The sealing of boreholes, tunnels, and shafts by use of highly compacted bentonite.

In 1985, the elements of a third phase of investigations for the Stripa Project were first conceptualized and then incorporated into a Program Plan for review by technical experts of the participating countries. After completion of the review of the Program Plan and accompanying modifications during the early part of 1986, Phase III of the Stripa Project was initiated in late 1986. The participating countries include Canada, Finland, Japan, Sweden, Switzerland, the United Kingdom, and the United States. Under Phase III, which is scheduled for completion in 1991, there are three principal investigations:

- Characterization and validation of geologic structure, groundwater flow, and nuclide transport in a large, previously unexplored mass of Stripa granite
- Continued development of site characterization methods and concepts, including those related to borehole radar, borehole seismics, fracture-flow network modeling, in situ fracture characteristics, and tracer migration in fractured rock
• Identification, selection, and evaluation of materials (e.g., bentonite, cementitious or other grout) for the long-term sealing of fractured rock, including an in situ demonstration of the effectiveness of such materials for the long-term sealing of fractures that may act as groundwater flow paths.

Because of the integrated nature of these investigations, the two Technical Subgroups (hydrology/transport/geophysics and engineered barriers/rock mechanics) have been combined into a single group for Phase III.

Rock sealing activities, as part of Phase III, are subdivided into five stages:

• Stage I - State-of-the-art survey of fracture sealing materials
• Stage II - Determination of the physical properties of the grouts in the injection phase and in the injected state
• Stage III - Determination of the long-term stability
• Stage IV - Field pilot tests
• Stage V - Planning of large scale sealing test in deposition holes.

This report represents a first stage in the investigation of the sealing of fractured rock.

1.2 SCOPE OF THE REPORT

This state-of-the-art report on sealing small aperture fractures in nuclear waste repositories is intended to aid selection and characterization of materials that are most promising for long-term sealing of groundwater flow paths in fractured rock.
crystalline rock. The results of this survey will contribute materials and materials handling input to Stage I of the Phase III investigations at Stripa that address sealing of fractures, particularly fractures such as those that intersect waste emplacement boreholes.

Topics to be covered in this report are the identification and discussion of:

1. Priority candidate materials for sealing fractures in crystalline rock (based on performance properties, chemical or physical stability);
2. Lower priority seal materials;
3. Handling and emplacement techniques that produce significant reduction in the mass permeability of the fractured rock; and
4. Recommendations for continued sealing materials and emplacement research.

This document is derived from the review and interpretation of current literature and does not represent a report of original research or testing results. It covers literature related to repository sealing, with emphasis on discussions that pertain to sealing small aperture fractures. This report is not intended to summarize the entire repository sealing literature or to incorporate generic engineering literature that may be only peripherally relevant.

1.3 FORMAT OF THE REPORT

Following this Introduction (Section 1), Section 2 describes the performance objectives of seals, emphasizing seals placed in fractures, shows an example of a screen of the materials that have been
considered candidate fracture sealing materials, and identifies the priority materials for sealing fractures in granitic rock. Section 3 presents an overview of the sealing properties of the priority candidate sealing materials. Formulations of these materials that appear to meet sealing objectives are also presented in Section 3. Section 4 summarizes the techniques that have been investigated to emplace seals in fractures. Section 5 states the conclusions of this report and recommendations for materials development, emplacement techniques, and further research. References and a glossary of terms are included in the final two sections (Sections 6 and 7).
2 PERFORMANCE OBJECTIVES OF SEALING MATERIALS AND SELECTION OF PRIORITY MATERIALS

2.1 RECOMMENDED PERFORMANCE PROPERTIES

Repository seals may be used in nuclear waste repositories to limit groundwater flow into and away from the facility. Radionuclide transport is expected to occur chiefly by means of dissolved, colloidal, or suspended material in groundwater. Therefore, limiting the movement of groundwater through the repository by the use of seals may contribute to meeting performance objectives of the facility.

If seals are either necessary or desirable to meet repository performance, at least two sealing strategies may be employed; moreover, the strategies may be employed either separately or in combination. The first strategy is to limit flow through the mined accesses (drifts, shafts, etc.) to the waste emplacement rooms. This strategy emphasizes intercepting main flow channels and diverting flow into the county-rock (i.e., restoring the host rock to a semblance of its preconstruction condition). Seal system designs for plugging man-made openings may include seals for fractures that would otherwise short-circuit seals placed in shafts and drifts. Such fractures include natural joints and faults, random fractures, and fractures related to construction activities, such as the damaged rock zone surrounding the openings.
The second sealing strategy is to limit the access of water to the waste by focusing on the pathways that groundwater must traverse to reach the waste. Although groundwater flowpaths in fractured rock are difficult to predict, it can be stated with certainty that if groundwater is to transport radionuclides away from the repository, it must pass through the fractures that emanate from the waste disposal holes drilled into the floor or ribs of the mined facility. If those fractures are sealed effectively no waste can be accessed by water; hence, no waste can be dissolved or transported from the repository. Moreover, Pusch et al. (1985) have suggested that if fractures intersecting waste emplacement holes were sealed such that groundwater flow were virtually nil within several meters of the emplaced waste, then the stability of the waste canister and overpack would be improved, and the diffusional migration of radionuclides through the canister overpack following canister breach would be ensured.

As implied above, it is not clearly established that a system of repository seals is necessary to achieve acceptable performance by repositories. However, in those cases where seals are desirable or necessary, the general performance characteristics for seals, including fracture seals, in a nuclear waste repository include:

- Low hydraulic conductivity, including the seal itself and the interfaces between the seal and the host rock to minimize groundwater flow in sealed zones
- Physical properties that will permit the seal to maintain low hydraulic conductivity under in situ thermal and mechanical stresses
• Chemical compatibility with the host rock, groundwater, and the physico-chemical environment in the seal zone to limit any alteration of the seal that would increase its hydraulic conductivity

• With respect specifically to fracture sealing, desirable physical and chemical properties of the sealing material will include those that significantly reduce the erodability of the material from fractures under significant hydraulic heads (up to several MPa).

Longevity of performance is an issue that must be addressed during candidate material selection. Longevity is discussed further in Section 2.2. All contributors generally agree that seals, if used, should perform for a long period of time; however, the exact length of time that seals should operate is not well-defined. For the purposes of this document, "a long time" is qualitatively considered to be on the order of thousands to millions of years following the operational period of the repository. Physical and chemical compatibility between the seal materials and the host environment are required to assure long-term performance of the seals.

2.2 LONGEVITY EXPERIENCE WITH LOW PERMEABILITY SEAL MATERIALS

As noted above, neither the need for seals nor the longevity requirements for seal functions have been uniformly agreed upon by participating countries. Nevertheless, seal longevity is an issue that members have agreed should be addressed. The most commonly accepted approach to determining long-term seal performance is to establish the long-term
physical and chemical stability of the seal material itself. By inference, the seal functions will be achieved so long as the material remains intact or any alteration can be shown to have no effect on critical seal performance properties, such as low hydraulic conductivity. In this regard, several quantitative research programs have been established in member countries to evaluate the longevity of selected candidate seal materials. These include laboratory studies and natural analog studies. The results of these quantitative studies are summarized in Section 3.3. In this section, however, a general overview of experience with the longevity of common sealing and grouting materials is presented.

Inference regarding materials longevity may be derived from several disciplines. These include:

- History of engineering applications
- Archeology
- Geology.

Inferences derived from these disciplines are, for the most part, qualitative and can only be coarse indicators of longevity of candidate seal materials. Materials that have considerable history of engineering applications and may have importance in repository sealing are cements, clays, ceramics, metals, bitumen and tars, chemical grouts, quartz sand, and almost all common rock types and minerals (crushed and intact).

Inferences drawn from engineering applications - Engineered structures to retain or seal out moisture, have been fabricated for several millennia primarily from cementitious, rock, and bituminous
materials. However, applications such as aqueducts, cisterns, etc. are generally poor analogs for saturated, subterranean environments. More modern structures such as cementitious and earthen material dams, shaft liners, borehole plugs, and rock seals, have shown that sealing materials can be engineered to remain intact and perform satisfactorily under in situ conditions for periods on the order of decades or, more rarely, a century or more. Thus, indirect evidence for longevity of performance is promising but inconclusive. If repository seals must perform for many thousands or millions of years, then the practical experience with sealing and grouting materials is too incomplete to provide a reliable measure of seal material longevity for repository sealing purposes.

Inferences from archeology - Several types of man-made materials that may act in low permeability seals are found in ancient artifacts and structures which suggest the materials are stable under some conditions for thousands of years. These materials include ceramics (among the oldest man-made materials), cementitious materials (a type of ceramic), and metals. Much like engineered structures, inferences based on archeological evidence are limited because the conditions to which the materials have been exposed are probably unlike repository conditions. In addition, raw materials and ancient production practices are largely unknown, and several millennia represents less time than the expected longevity requirements of repository seals.

Inferences from geology - Inferences concerning potential seal longevity for periods that exceed
human experience requires reference to geologic
time and geologic materials. Although frequently
uncertain, the age of most geologic materials is as
great or exceeds the many thousands to millions of
years that seal materials may be required to
function. In addition, geologic environments are
occasionally not unlike repository conditions.
Examples of such environments may be found in dia-
genetic and metamorphic terrains, and geothermal
environments. Key geologic materials that may be
significant for sealing applications are clays,
naturally-occurring fracture-filling minerals,
bitumen, as well as rock, sand, and gravel. The
very persistence of repository host rocks infers
that, if crushed to a sufficiently fine size or if
used in combination with other low permeability
materials, utilization of crushed host rock in seal
components may be a simple approach to obtaining
long-lived seals.

2.3 OTHER CONSIDERATIONS AFFECTING SELECTION OF LOW
PERMEABILITY SEAL MATERIALS

Several additional factors, not directly related to
materials performance as a long-lived hydrologic
barrier, will strongly affect the performance of
seals and seal materials and the selection of seal
materials for a nuclear waste repository. For
example, key to the selection of any seal material
must be evidence that the material can be emplaced
effectively using existing technologies or practi-
cal new emplacement methods. With specific
reference to fracture sealing, the seal material
should be injectable into rock fractures with
little or no additional damage to the rock and with
penetration on the order of several decimeters.
Note that materials and emplacement technologies will be required to seal fractures on the order of 0.1 mm aperture and smaller (Pusch et al., 1985; Pusch, 1986). This requirement places additional constraints on seal material and emplacement technology selection as discussed further in Sections 3 and 4.

An additional consideration for selecting seal materials is to evaluate whether the waste isolation capacity of the repository and other engineered barriers will be enhanced or compromised by the seals or by their alteration products and by-products. For example, the degradation of seal materials should not significantly enhance the chemical mobility of radionuclides. Accordingly, the potential effects of by-products of seal material alteration, interactions between seals and the host environment, or irradiation of seal materials on radionuclide mobility must be considered in materials selection.

Some candidate seal materials (e.g., clays) may enhance the isolation ability of a repository by retarding the migration of cationic species by sorption or reaction (i.e., adsorption, cation exchange, precipitation). Other materials, however, may enhance radionuclide mobility by introducing chemical complexing agents (e.g., carbonate, sulfate) or organic materials capable of chelating radionuclides. These materials must be excluded from priority consideration for sealing. This consideration is further described in Section 2.3.
Priority materials recommended in this report for sealing of fractures are familiar in engineering applications, with strong evidence that the materials have been successfully emplaced and performed adequately for the functional lifetime of the engineered structure. Familiar materials with well-known engineering properties will help reduce research and development costs for both materials and emplacement technology. The preferred materials should be reasonably safe to handle and should not contain excessive amounts of hazardous substances that may present additional environmental, logistical, or licensing issues. This rationale also extends to early demonstrations of materials for sealing (such as Stages III and IV of Phase III tests); hence, the use of established materials for sealing purposes is a constraint adopted in this document. Logistics and limitations on the emplacement of seal materials must be considered in selection of seal materials and a sealing strategy. Limitations may arise due to the space requirements for machinery, energy input requirements to obtain adequate sealing, and safety/precautionary measures required during seal emplacement.

Priority sealing materials must be available in large quantities. Variability in materials composition and performance between batches of starting materials (e.g., cement, bentonite, additives, aggregate, water, etc.) should be minimal. Cost will be a secondary consideration relative to performance. Thus, additional considerations for selecting priority candidate seal materials include:
• Emplaceability, with adequate seal performance and assurance that a high quality seal will be produced

• Chemical effects on radionuclide mobility

• Experience in using and handling the material during engineering projects, particularly mining, tunneling, or other groundwater control projects

• Emplacement logistics and limitations related to emplacement of the materials in a confined underground space (space limitations, power consumption, toxicity, safety, etc.)

• Material availability and uniformity

• Materials cost.

2.4 SUMMARY OF CRITERIA FOR COMPARATIVE EVALUATION OF SEAL MATERIALS

Criteria for materials selection for repository seals based on seal performance properties and additional considerations for sealing are summarized in Table 2-1. The criteria fall into two categories: those necessary for acceptable seal performance and those that are desirable but not necessary to achieve adequate performance. Materials that possess the necessary characteristics but do not possess the other, desirable characteristics, may nevertheless be successfully applied in repository sealing. These latter characteristics may discriminate between materials possessing otherwise equivalent properties. In general, development of a seal material meeting these desirable criteria would consume fewer resources (research, laboratory and field testing, etc.) than materials that do not meet these criteria.
Table 2-1. Criteria for comparative evaluation of seal materials

NECESSARY CHARACTERISTICS

1. Ability to perform as hydrologic barrier

   Low intrinsic permeability

   Low interface permeability (interface between seal and host materials)

2. Emplaceable in repository environment

   Emplaceable using existing or practical new technology

   Penetrate fractures uniformly, with good void filling to several decimeters depth or more with little or no damage to host rock

   At least some material will meet the above criteria for fracture apertures as small as 0.1 mm

   Minimum environmental hazard inherent in utilization

3. Ability to perform #1 over the long-term

   Chemical stability under in situ physico-chemical conditions, or alteration does not impact ability to achieve criteria in #1 (above).

   Physical stability under in situ stresses (mechanical, thermal, hydrologic)

4. Cause no enhancement of radionuclide mobility

   Seal material, alteration products, and by-products do not increase radionuclide solubility, do not reduce radionuclide sorption by host rock or other seal components, etc.

5. Available in large volumes with uniformity between batches
Table 2-1. Criteria for comparative evaluation of seal materials
(Continued)

DESI RABLE CHARACTERISTICS

1. Long history of use and well-documented performance in engineering projects similar to nuclear waste repositories (dams, tunnels, mines, foundations)

2. Extensive and systematic data bases on:
   - Material chemistry
   - Performance as function of chemistry, preparation procedures, environmental conditions
   - Emplacement technology

3. Low cost
   - Low materials cost
   - Minimal research and development cost
   - Low emplacement equipment cost (including research and development)
The criteria presented in Table 2-1 are qualitative. This situation necessarily arises because no quantitative criteria will universally apply to all repository programs. The specific requirements for seals, if any, will undoubtedly be site specific and may vary widely from site to site. For purposes of this report, however, these general and widely applicable criteria are presented.

2.5 DESCRIPTION AND SCREEN OF PRELIMINARY CANDIDATE SEAL MATERIALS

Several studies have included comparisons among materials groups with respect to the potential for use in seals for nuclear waste repositories (e.g., Taylor et al., 1980; ONWI, 1980; Pusch et al., 1985; Gray, 1986). These reports have identified several groups of materials and several specific materials that may be considered for sealing. Among the candidate materials types that may be used in fracture sealing (specifically) are:

- Cementitious materials
- Earthen materials, particularly clays
- Cement/clay materials
- Chemical grouts
- Bitumen
- Fracture filling minerals
- Ceramics
- Metals.

The following sections define these materials and describe a preliminary screen of the materials with respect to the criteria on Table 2-1. The screen is illustrated in Figure 2-1. The screening mechanism is widely applicable to the members' repository programs and represents an agreement among the participants on the overall screening.
Figure 2-1. Screen of preliminary candidate seal materials

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Ability to Perform as Hydrologic Barrier</th>
<th>Emplaceability</th>
<th>Long-Term Stability</th>
<th>Effect on Mobility of Radionuclide</th>
<th>Materials Availability</th>
<th>History of Usage in Engineering Practice</th>
<th>Extensive Systematic Data Base on Chemistry and Performance</th>
<th>Low Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Significance of Criteria</td>
<td>Very Important</td>
<td>Important</td>
<td>Desirable</td>
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<tr>
<td>Cementitious Materials</td>
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<tr>
<td>Clays (Hentonite)</td>
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<tr>
<td>Cement-Clay Mixtures</td>
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<tr>
<td>Chemical Grouts</td>
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<tr>
<td>Bitumen</td>
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<td></td>
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<tr>
<td>Ceramics</td>
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<tr>
<td>Metals</td>
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<td></td>
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<tr>
<td>Synthetic Fracture-Priming Minerals</td>
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</tbody>
</table>

- ✔ acceptable performance
- □ acceptable performance probably achievable
- ▲ performance uncertain
- ○ probably unacceptable performance

Mixtures and combinations may be used.

Unacceptable performance will disqualify materials from priority consideration for grouting.
approach. The ranking of selection criteria and the outcome of the screening may vary from program to program, however, and should not be interpreted as a consensus of the participants.

2.5.1 Cementitious Materials

2.5.1.1 Definition and Overview of Cementitious Materials

For purposes of this report, cementitious materials include portland cement-based grouts, mortars, and concretes. Portland cement is a complex material composed of six major compounds (Aitcin, 1986):

- Tricalcium silicate
- Dicalcium silicate
- Tricalcium aluminate
- Tetracalcium ferroaluminate
- Gypsum
- Alkali sulfate.

The cement is manufactured by heating siliceous limestone and combining the resulting clinker with gypsum during grinding. The cementitious property of these materials is obtained by the formation of a hydrous calcium-silicate gel resulting from the mixing of and exothermic reaction between water and cement. Neat cement paste (the plastic material obtained by mixing water with powdered cement) contains no aggregate. Mortar contains fine aggregate (sand), and concrete contains both fine and coarse aggregate. Cementitious grout is any cementitious mixture that can be injected into a formation without regard for the amount or size of aggregate that may be included.

The properties of both the cementitious slurry and the cured grout can be varied, and certain
desirable properties can be enhanced, through mix
design. Common mix design variables include cement
type, water:cement ratio (w/c), the type of aggre­
gate, if any, and the types of additives included:
pozzolans, accelerators, expansive agents,
plasticizers, etc.

Portland cements commonly used in engineering
applications and applicable to repository sealing
include Ordinary Portland Cement (ASTM Type I, API
Class A, CSA Type 10), Sulfate Resistant Cement
(ASTM Type V, CSA Type 50, as well as most API
cement classes in sulfate resistant form) and High
Early Strength Cement (ASTM Type III, API Class C,
CSA Type 30) (e.g., Roy et al., 1985; Gray, 1986).
Some repository sealing studies have emphasized API
Class H cement, a basic well cement available as
moderate and high sulfate resistant types (e.g.,
Roy et al., 1983, 1985). Expansive ("shrinkage-
compensating") cements (e.g. Class K, ChemComp)
have also received some attention in sealing
studies (Gulick, 1978; Ballivy, 1986), and ordinary
cements can be formulated to be expansive with
appropriate additives in the mix.

Several types of additives are regularly used in
the preparation of cementitious materials. Addi­
tives are materials added to the mix after manufac­
turing the cement, except water. The significance
of these materials is summarized in Table 2-2. A
key additive to improve stability and long-term
performance of portland cement-based materials is
pozzolan. Pozzolan is a group of reactive
siliceous materials (e.g., fly ash, silica fume,
etc.) that combine with free Ca(OH)₂ in the
hydrated cement paste during the curing of the
### Table 2-2. Summary of additives for cementitious materials mixes

<table>
<thead>
<tr>
<th>Type of Additive</th>
<th>Examples of Typically Used Additives</th>
<th>Comments on Usage of Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pozzolans</td>
<td>Silica fume, Silica flour, Fly ash (several sources), Blast furnace slag</td>
<td>Promote &quot;pozzolanic&quot; reaction between products of cement hydration (e.g., CaOH) and reactive silica (pozzolan) to produce cementitious C-S-H, reduce porosity, and improve strength.</td>
</tr>
<tr>
<td>2. Plasticizers</td>
<td>Melamine formaldehyde, Sulfonated naphthaene formaldehyde, Lignosulfonic acid and their salts, Hydroxylated carboxylic acid and their salts</td>
<td>Lower water requirement for a given slump or degree of workability; improves workability and lowers viscosity of low water:cement ratio mixes; may tend to retard set of material.</td>
</tr>
<tr>
<td>3. Mineral additives</td>
<td>Clay, quartz powder, ground limestone, bentonite</td>
<td>Improve workability and reduce bleed, improve suspension of aggregate and particulates; increase stiffness and density of paste.</td>
</tr>
<tr>
<td>4. Accelerators</td>
<td>CaCl₂, Other chlorides, carbonates, silicates, and organic compounds (e.g., triethanolamine)</td>
<td>Achieve early setting time. CaCl₂ is used up to 2 wt% of cement. May be detrimental to cementitious materials at high temperature, reduce sulphate resistance, and increase shrinkage.</td>
</tr>
<tr>
<td>5. Retarders</td>
<td>Lignosulfonic acid salts, hydroxylated carbonic acid salts</td>
<td>Generally the same materials as water reducers; set time can be extended 30-50%; often used to offset accelerating effects of high temperature emplacement environment.</td>
</tr>
</tbody>
</table>
Table 2-2. Summary of additives for cementitious materials mixes
(Continued)

<table>
<thead>
<tr>
<th>Type of Additive</th>
<th>Examples of Typically-Used Additives</th>
<th>Comments on Usage of Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. Expansion-producing additives</td>
<td>a) Aluminum, magnesium powders</td>
<td>a) Gas (H₂, O₂, N₂) producing, cause expansion in plastic state</td>
</tr>
<tr>
<td></td>
<td>b) Calcium sulfo-aluminate</td>
<td>b) Produce expansive phase ettringite in hardened state</td>
</tr>
<tr>
<td></td>
<td>c) Iron/iron-based compounds, magnesium</td>
<td>c) Produce high volume oxidation products in hardened state</td>
</tr>
<tr>
<td>7. Air-entraining additives</td>
<td>Salts of wood resins, synthetic detergents, salts of sulfonated lignin,</td>
<td>Make foam; derived from resins, fats, or oils; cause air bubbles in</td>
</tr>
<tr>
<td></td>
<td>salts of petroleum acids, salts of proteinaceous materials, fatty and</td>
<td>cement paste, designed to prevent freeze-thaw damage in water</td>
</tr>
<tr>
<td></td>
<td>resinous acids and their salts</td>
<td>saturated grout, concrete, etc.; may decrease slurry viscosity;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>utilized at about 0.5 wt% cement</td>
</tr>
<tr>
<td>8. Defoamers</td>
<td>Tributyl phosphate</td>
<td>Dissipate air or other gas bubbles that may be caused by natural</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aggregate, retarders, or water reducers</td>
</tr>
<tr>
<td>9. Permeability reducers</td>
<td>Soaps, oils, resins</td>
<td>&quot;Water-proofing&quot; agents to prevent wetting of cementitious material;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>generally used as surface treatment on hardened material</td>
</tr>
<tr>
<td>10. Corrosion inhibitors</td>
<td>Sodium benzonate, calcium lignosulfonate, stannous chloride, sodium</td>
<td>Prevent rusting of embedded iron and steel components</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nitrate</td>
</tr>
</tbody>
</table>

References: Gray, 1986
Klieger, 1978
Littlejohn, 1982
B. Mather, 1967b, 1978
material. This pozzolanic reaction ties up soluble Ca in the concrete or grout and produces CaO-SiO₂-H₂O (C-S-H) cementitious phases. By limiting the presence of the highly soluble Ca(OH)₂ and by production of additional C-S-H cementitious phases, the pozzolanic reaction reduces the development of porosity and enhances the strength of the material.

Strong, dense, and low permeability cementitious materials generally require carefully controlled mixing and low water:cement ratios. The use of additives, such as plasticizers (water-reducing agents), improves the handling, pumpability, and homogeneity of cementitious materials and lower the viscosity of the fresh cementitious paste without requiring substantial increases in the amount of mix water. Plasticizers are used in very small quantities in the mix (as little as grams per cubic meter of concrete). Commonly used plasticizers are melamine formaldehyde and sulphonated napthalene formaldehyde, although a number of other compounds are occasionally used. These compounds have no apparent adverse effect on the stability or longevity of the final material; however, there appears to have been very little research into this matter.

Common aggregate, or inert additives and extenders in cementitious materials are sand, gravel, silt, and clay. These materials are often included to improve the strength, handling, and other properties of cementitious materials. For grouting of small aperture fractures, clay and silt are most useful because coarse grained aggregate is not easily injectable.
Clay, particularly Na- or Ca-bentonites, may be added to high w/c, low viscosity cementitious grouts to reduce bleed ("stabilize") the grout and act as a suspending agent that will reduce sedimentation of particles during injection (Littlejohn, 1982). The Na form is more effective in improving grout properties. Other clays, such as illite or kaolinite, have very little beneficial effects, other than use as inert, inexpensive filters. Schaffer and Daemen (1987) cite evidence that up to three percent bentonite (by weight of dry cement) in a mix produces a stable grout and insignificant changes in materials properties. They also showed that the addition of small amounts of clay (up to 2.5 percent) to an unstable (high bleed capacity) cementitious grout to stabilize the material may increase the material's unconfined compressive strength. This probably reflects improved homogeneity of the cured stable grout. The addition of clay in large quantities may affect strength and setting properties of cementitious materials. (Cementitious materials that have clay contents in excess of a few weight percent of the cement may be considered clay-cement mixtures and are discussed in Section 2.5.3).

Several other cementitious materials (that are not based on portland cement) may be applied in repository sealing. These materials have been studied far less frequently in recent sealing technology studies and include high alumina cements, oxychloride and oxysulphate cements. High alumina cements have high sulfate resistance and are generally used in environments that will exceed several hundred degrees C; however, at 100 to 200°C, high aluminum cements generally undergo greater degradation than
Portland cement-based materials (Nelson, 1986). The oxychloride and oxysulphate cements are not widely used in engineering applications although some desirable properties may be achievable with them. Because of their limited advantages and the uncertainties surrounding their performance, these cements probably do not merit high priority consideration for near-term repository sealing research and testing.

2.5.1.2 Screen of Properties of Cementitious Materials for Sealing

Figure 2-1 represents a materials screen of seven preliminary candidate materials, including cementitious materials. The screening criteria are those shown in Table 2-1. Cementitious materials appear to be satisfactory with respect to most criteria. The properties of cementitious materials that can be applied in repository sealing include:

- Low hydraulic conductivity
- Familiar utilization in engineering projects
- Familiar emplacement technology
- Extensive research for sealing programs
- Availability
- Low cost.

As a result, cementitious materials have been selected for priority consideration in continued research in repository sealing and for inclusion in planning and testing leading up to pilot and full-scale sealing tests at Stripa. The properties and basis for the properties of priority seal materials are described further in Section 3.

Although selected as a priority material, the performance of cementitious materials in seals is
uncertain in several regards. These issues are further described in Section 3. The first issue of concern is that the hydrologic barrier provided by cementitious materials may be compromised if interface permeability cannot be controlled. Experience suggests the cement-host interface is more permeable than the material itself (Section 3.1.1). Studies have shown that the cementitious mix can be designed to improve interface permeability (Roy et al., 1983). Expansive materials that limit shrinkage during material cure or provide a small compressive stress on the interface appear effective in reducing interface permeability. The shrinkage of the material, and consequent increase in the potential for flow at the interface, may be reduced by the use of inert fillers and aggregate. This issue, particularly with respect to fracture sealing, requires further study but appears resolvable through appropriate mix design.

The longevity of cementitious materials under repository conditions is also uncertain although there is no definitive evidence that the long-term performance of cementitious materials, at least in some applications, is unacceptable. These materials perform most satisfactorily at temperatures below about 100°C and may degrade under acidic, sulfate-rich, or carbon dioxide-rich conditions, and under conditions that include thermal cycling. The stability of cementitious materials may be improved under adverse conditions by use of sulfate-resistant cement, pozzolanic additives, and by producing high strength, low porosity, and low permeability materials through high-quality workmanship. The evidence for cement longevity from
current research results is summarized in Section 3.3.1.

2.5.2 Earthen Materials

Earthen materials that may be used in repository sealing include clays, gravel, crushed rock, sand, or combinations of these materials. Any earthen material used to seal narrow fractures will be a fine-grained material; thus, clays are of greatest intrinsic interest. "Clay," as used in this report, refers to earthen, granular materials that contain a substantial amount of clay minerals (>30 percent). At this proportion, the clay mineral component is generally great enough to fill void spaces and surround all non-clay grains; hence the clay component controls the material properties of the mixture (Mitchell, 1976). Clays include any material containing unfired clay minerals, such as soils, pulverized shales, argillites and bentonites, etc., regardless of the type or quantity of the other granular materials present so long as the clay mineral component controls the material behavior. One of these clays, bentonite, refers to a natural material containing a large portion of smectite resulting from the devitrification of volcanic ash. Bentonite is the clay that has received the most attention in terms of repository sealing and sealing properties and has a history of usage for fracture sealing. Accordingly, this discussion will emphasize bentonite and its major component, smectite. Minor components in bentonite include quartz, feldspars, gypsum, calcite, other minerals, and glass.
2.5.2.1 Definition and Overview of Smectite and Bentonite

Smectite is a group of clay minerals that share a number of crystal structure, crystal chemical, and behavioral characteristics. Smectites tend to be very fine grained (<1-2μm diameter, 10^1 to 10^6 Å thick), and have the characteristic platey habit of most clay minerals. The smectite crystal structure contains clay (silicate) layers separated by interlayer positively-charged ions (cations) (Figure 2-2). The interlayer cations are loosely held, such that they can exchange for cations that are dissolved in solutions with which they come into contact. This ability to exchange cations is known as the cation exchange capacity. Na^+ is a common interlayer cation in smectites and is readily exchanged for many other cations in solutions. Upon contact, the smectite absorbs water between clay sheets, increasing the unit cell dimension in the direction perpendicular to the clay layers. The "swelling" capacity permits a smectite-bearing clay to fill void spaces, heal fractures that occur through desiccation or stress, and, if the swelling is restrained, to develop a swelling pressure against the confinement. The ultimate swelling pressure that is reached upon hydration is determined by the nature of the interlayer cation(s), composition of the hydrating fluid, the amount of swelling allowed prior to confinement, and the compacted density of the bentonite prior to hydration. Swelling pressure under fully restrained conditions, as a function of the compacted density of bentonite, is shown in Figure 2-3. The swelling capacity (volume change) and swelling pressure tend to be lower if a high ionic strength fluid is in contact with the bentonite.
Figure 2-2. Crystal structure of smectite.

REFERENCE: GRIM, 1968
Figure 2-3. Calculated and measured effects of density on the maximum swelling pressure of a compacted Wyoming (Na-rich) bentonite.
Saturated bentonite forms a very low permeability gel [as low as $10^{-11}$ cm/sec (Pusch, 1978b)] depending on many of the factors that control swelling pressure (interlayer cation, composition of permeant fluid, compacted density of the material). Bentonite imparts very low permeability to mixes in which it is included above about ten weight percent. Figure 2-4 shows the effect of bentonite contents, density, and cation type on the hydraulic conductivity of bentonite-sand mixes.

The mechanical properties of smectites (and bentonites) are strongly dependent on the water content of the materials. Smectites generally require a higher water content before losing their strength and behaving plastically ("plastic limit"). Sodium smectites retain plastic properties up to several hundred weight percent water before behaving as a liquid ("liquid limit"). The plastic behavior of bentonite is one of its key characteristics, and the property of plasticity is imparted to non-clay granular materials (e.g., sand) to which smectite is added in small quantities. Under a wide range of water contents, therefore, bentonite and bentonite-bearing mixes will deform plastically, rather than by brittle fracture. Among common clay minerals, smectites impart low shear strength to materials in which they are incorporated, and the shear strength of such materials drops rapidly as smectite content increases. Increased water content generally reduces shear strength of clays, such as bentonite, although this relationship is not regular. As a clay, such as bentonite, is left undisturbed it tends to increase in shear strength. This "thixotropic" behavior is pronounced in bentonites and is probably the result of rearrangement and
Figure 2-4. Hydraulic conductivity of compacted bentonite/sand mixtures as a function of bentonite content.
organization of particles in the gel in response to the electrostatic charges of the clay particles.

2.5.2.2 Screen of Properties of Bentonite for Sealing

Figure 2-1 shows the screen of bentonite properties with respect to eight criteria listed in Table 2-1. Bentonite is considered a priority material for further sealing research including Stripa Phase III testing, because it appears to possess many favorable properties. Uncertainties with bentonite merit further study, but appear manageable.

Among the desirable properties of bentonite are:

- Low hydraulic conductivity
- Ability to achieve low hydraulic conductivity at the interface with the host, due to swelling capacity and ability to conform to irregularities in host and fill small voids, crevasses, and fractures
- Sorption of radionuclides by smectite (summarized in Meyer and Howard, 1983)
- Familiar utilization in engineering practice for sealing water-bearing formations
- Familiar and successful emplacement technology and experience, availability of material, and low cost
- Extensive data base in sealing properties and performance
- Fracture resistance through plastic deformation, and fracture healing capacity.

Major uncertainties in the use of bentonite for sealing may be resolved through further research and testing. These uncertainties are:

- Longevity under repository conditions
Very low shear strength (high erodability) that may limit the applicability of the material where high hydraulic gradients and groundwater flow rates may occur.

The longevity issue, particularly the alteration of smectite, has been extensively studied. Section 3.3.2 includes a summary of recent research. There are conflicting data on smectite alteration rates, particularly with respect to the growth of nonswelling illite in smectite ("mixed-layer clays") under hydrothermal conditions. Smectite stability does not appear to be a serious issue under dry heating conditions up to a maximum temperature for most seals (e.g., -95°C in fracture seals intersecting waste disposal boreholes in crystalline rock). Such conditions appear to have no effect on the crystalline structure of smectite, its swelling capacity, or its hydrologic properties.

Erodability of bentonite gel under high hydrologic gradients appears to limit its utility significantly. If the material has the potential to be washed from a seal zone or fracture, it probably will not provide a reliable hydrologic barrier. Increasing the shear strength of the material by admixing sand, silt, or higher-strength clays (illite, kaolinite) may be effective. Cementitious solids may also be admixed (see Section 2.5.3). Sandwiching clays between strong seal components (e.g., cementitious materials) is a design alternative. By grouting a fracture with alternating cementitious and clay materials, the clay may retain its low hydraulic conductivity and plasticity while the cementitious grout provides a strong, rigid barrier to limit erosive groundwater flow through fractures and to confine the clay within the fracture. The clay grout interlayer
provides a degree of flexibility that may limit through-going fractures under in situ stresses. This design is being pursued in Japan (Tokonami, personal communication, 1987). The erodability issue requires further study.

2.5.3 Mixtures of Clay and Cement

As already mentioned in the previous sections, the addition of clay to cementitious grout mixes, as the addition of cement to clay grouts, in small proportion, may be used in grouting to offset some of the potential problems encountered in application of these grouting materials without additives. These problems include, for example:

- Cementitious grouts have high bleed and sedimentation when high water contents are used to achieve low viscosity slurries
- Clay grouts have generally poor resistance to erosion.

Larger proportions of additive clay or cement have also been utilized. These are included in this report as clay/cement mixtures. Cementitious grouts with up to ten percent bentonite additive, by weight of dry cement, have been used in Europe for rock grouting (Cambefort, 1967). Cambefort (1967) also notes that clay grouts with up to 20 percent (and occasionally more) cement additive, by weight of dry clay, are also used. The addition of cement imparts strength to the clay grout that reduces its erodability under hydraulic gradient.

The addition of clay to cementitious grout appears to affect grout properties significantly as the clay content of the mix increases above a few percent. For example, the addition of larger
proportions of clay (over about three percent) tends to alter the setting properties and slow the development of strength of the grout (Schaffer and Daemen, 1987). Such grouts might be useful where strength (including resistance to erosion or prevention of fracturing under thermal or mechanical stress) is not a significant performance requirement.

There appears to be relatively little systematic research on the properties and the performance of clay-cement mixtures; i.e., clay-bearing (greater than five percent) cementitious grouts and cement bearing clay grouts. Chan (1986) measured the hydraulic conductivity in artificial "fractures" grouted by clay (Na- and Ca-bentonite) and by clay-cement mixtures subjected to incrementally increased hydraulic gradients. In general, Chan found that the clay-cement grouts emplaced under low gradients had initially higher hydraulic conductivities than clay grouts alone. Also, the addition of cement improved the resistance of the clay grouts to erosion or channeling under high hydraulic gradients; i.e., several times greater than the injection pressure used to emplace the grout. Chan noted, however, that the neat clay grouts performed adequately if hydraulic gradients did not exceed the initial injection pressure of the grout. He also notes that if a clay grout were confined between erosion-resistant components, such as cementitious grouts, clay grouts would not be subject to erosion.

Although mixtures have been used for grouting and other engineering purposes for several decades, no systematic study of the materials longevity or the influence of one material on the properties and
stability of the other are only beginning to be performed. Heimann and Hooton (1986) showed leach rates of some constituents in sulfate resistant portland cement may be enhanced in the presence of Ca- and Na-bentonite in experimental systems containing saline Canadian Shield groundwater at 150°C. They attributed the increased leach rates to the ability of impurities in the clay to produce lower pH in the associated fluid, possibly through hydrolysis of adsorbed Al³⁺ ions. They also recognized enhancement of phase transformations of primary cementitious phases to stronger but lower volume 11 Å tobermorite in the presence of clays, particularly Na-bentonite. This phase transformation may increase the porosity of the cementitious solids, and, consequently, the permeability of the grout seal.

Current data suggest that mixtures of clay and cement may have properties that can be well-applied in fracture sealing. Limited test results indicate that significant questions remain with regard to materials longevity and long-term performance. The desirable characteristics of cement-clay mixtures, in light of uncertainties and the additional complexity of the materials, suggest that these mixtures should not be dismissed but merit lower priority consideration relative to simpler cementitious or clay grouts containing no more than a few weight percent of the other as an additive.

2.5.4 Chemical Grouts

2.5.4.1 Description of Chemical Grouts

Chemical grouts are true solutions that include inorganic (silicate/aluminate type) and organic
materials. Chemical grouts act in one of two ways: 1) aqueous solutions of two or more chemicals which, when mixed and injected, react to form gels or solids which fill any voids; and 2) resin based materials which when mixed with a catalyst, or on contact with groundwater, set to a pseudo-solid with low hydraulic conductivity. The most frequently used chemical grouts are silicates and acrylamides, based on aqueous solutions. Other chemical grouts include lignosulfites, phenoplasts, aminoplasts, polyacrylamide, acrylate, epoxy resins, polyester resins, and polyurethane (Karol, 1982a). A summary of the nature of these materials is shown in Table 2-3.

Experience has shown that most chemical grouts appear to be permanent and inert, with respect to the requirements of engineering applications. They effectively provide additional strength to soils or rock into which they are injected and provide the required seepage control. Chemical grouts generally can be emplaced with good penetration, and their properties can be controlled as required for specific applications.

The penetrability of chemical grouts generally is due to the low viscosity of the grout fluids relative to most other grouting materials (e.g., the viscosity of chemical grouts may approach that of water). Unlike cementitious and clay grouts, chemical grouts contain no suspended particulates (unless these are added as fillers); therefore, they can be successfully emplaced in fractures as small as 0.1 mm and less. Because the grouts are emplaced as fluids, they should fill any voids in fractures and substantially reduce the permeability of the fracture. As shown in Table 2-3, several
<table>
<thead>
<tr>
<th>Grout Type</th>
<th>Composition</th>
<th>Viscosity</th>
<th>Strength</th>
<th>Permeability</th>
<th>Corrosivity/Toxicity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicates</td>
<td>Dilute sodium silicate ((n\text{SiO}_2\cdot\text{Na}_2\text{O} \cdot m^3 \text{H}_2 \text{O})) + acid or acid salt ((e.g., \text{NaHCO}_3)) or dilute sodium silicate and organic compound ((\text{ethyl acetate or formaldehyde}) &amp; \text{accelerator (salt)})</td>
<td>Very low (3-10 cp); increases during induction period</td>
<td>Very low; see note 3</td>
<td>Generally low; organic reactants and soluble Na may represent hazards</td>
<td>1. Higher silicate content increases strength but increases viscosity and lengthens gel time. 2. Poor gel control. 3. If permitted to dry out after emplacement, is subject to syneresis, or shrinkage due to loss of water; results in a residual permeability; increased silicate content reduces syneresis effect. 4. Subject to dissolution of unreacted soda. 5. Gel time may be affected by impurities or dissolved salts in groundwater.</td>
<td></td>
</tr>
<tr>
<td>Acrylamide</td>
<td>Acrylamide monomer + binder ((-3% \text{ solids})) in water solution and catalyst ((\text{peroxides or peraminit})) + accelerator ((\text{organic} &amp; \text{inhibitor \text{instantaneously}})) gel + accelerator ((\text{salt}))</td>
<td>Low; constant</td>
<td>Low; constant</td>
<td>Very low</td>
<td>Acrylamide in solution is neurotoxic; accelerators may be health hazards</td>
<td>1. Subject to shrinkage due to dehydration, particularly if accompanied by heating; will re-expand upon application of hydraulic pressure; can re-seal but not heal shrinkage fractures; may increase permeability; shrinkage can be minimized by use of fillers. 2. Ions may migrate through water incorporated in gel.</td>
</tr>
</tbody>
</table>
### Table 2.3. Summary of chemical grouts (Continued)

<table>
<thead>
<tr>
<th>Class</th>
<th>Composition</th>
<th>Viscosity</th>
<th>Grout Strength</th>
<th>Permeability</th>
<th>Corrosivity/Toxicity</th>
<th>NOTES</th>
</tr>
</thead>
</table>
| Lignosulfonate + Cr\textsuperscript{6} compound \((\text{Na}_2\text{Cr}_2\text{O}_7\cdot2\text{H}_2\text{O})\) \((200-600 \text{ g solids/ P solution})\) | low \((3-8 \text{ cp})\) increasing after catalysis                                                                                                 | low; increases with increasing solids content and \text{Cr}_2\text{O}_7\cdot2\text{H}_2\text{O} content | low                        | high toxicity of \text{Cr}\textsuperscript{6} compound                                                                | 3. Gel time controlled by temperature, concentration of catalyst, activator, inhibitor.  
4. \text{NaCl} or \text{CaCl}_2 dissolved in groundwater tend to shorten gel time. |
| Phenoplast \( \text{phenol (e.g., resorcinal)} + \text{aldehyde (formaldehyde)} + \text{catalyst (NaOH)} \) | very low \((1.5-3.0); \text{constant until gelation starts})                                                                                           | low \((\text{proportional to resin content})\)                                               | low                        | all components are potential health hazards or pollutants                                                       | 1. Lignosulfonate tends to be variable in composition.  
2. Set time decreases with increased solids content and decreases with increased \text{Na}_2\text{Cr}_2\text{O}_7\cdot2\text{H}_2\text{O} content.  
3. Higher strength obtained in shorter gel time mixes.  
4. Subject to degradation by wet-dry cycles. |
| Acrylamide (continued) |                                                                                                                                                                                                              |           |                |              |                       | 1. Set control by dilution of components or \text{pH} control \((\text{minimum gel time at } \text{pH} = 9)\).  
2. Optimum percent at short gel time.  
3. Very low resistance to wet-dry cycles; cannot be emplaced in dehydrating environment. |
<table>
<thead>
<tr>
<th>Ass</th>
<th>Composition</th>
<th>Viscosity</th>
<th>Strength</th>
<th>Permeability</th>
<th>Corrosivity/Toxicity</th>
<th>NOTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inoplast</td>
<td>urea + formaldehyde + acid catalyst + heat or prepolymer or precondensates (polymers in which polymerization is suspended)</td>
<td>very low</td>
<td>low</td>
<td>low</td>
<td>grout solutions are toxic</td>
<td>1. Gel time is difficult to control and rapid.</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>polyisocyanate + polyol or polyethers, polyesters and glycols + catalyst (tertiary amines and tin salts)</td>
<td>moderate</td>
<td>10-20 cp</td>
<td></td>
<td>all components are health hazards</td>
<td>2. Prepolymers are easier to handle and provide better gel control.</td>
</tr>
<tr>
<td>Acrylate</td>
<td>similar to acrylamide grouts</td>
<td></td>
<td></td>
<td></td>
<td>not a neurotoxin</td>
<td>3. Break down under wet-dry cycles.</td>
</tr>
<tr>
<td>Epoxy</td>
<td>resin base (polysulide) + catalyst (hardener)</td>
<td>relatively high</td>
<td>high (maintained through gel time)</td>
<td>low</td>
<td>possible irritant</td>
<td>1. Performance and properties generally similar to acrylamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1. Generally inert, heat resistant, with minimum shrinkage due to curing or heating.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2. Gel time controlled by temperature, hardener concentration, and use of fuller materials.</td>
<td></td>
</tr>
</tbody>
</table>

References: McMillan, 1982a, b, Department of the Army, 1973
types of chemical grouts have the characteristic of maintaining their initial viscosity after catalyzation, gelling almost instantaneously at the end of the injection period. Others do not maintain low viscosity through the injection period but become increasingly viscous after catalyzation.

2.5.4.2 Screen of Properties of Chemical Grouts

Chemical grouts have several desirable properties that may be usefully applied in repository sealing. As shown in Figure 2-1, however, chemical grouts have been assigned a low priority for continued research and may not merit further consideration for near-term research, including testing at Stripa, unless the priority materials prove unsatisfactory. The principal favorable characteristics of chemical grouts are:

- Low hydraulic conductivity
- Familiar usage in engineering projects, particularly in sealing water-bearing zones to eliminate seepage
- Material emplaceability in fine fractures
- Well-developed emplacement technology.

Chemical grouts present several problem areas for repository sealing. Most, if not all, can be resolved by further research; however, extensive research is likely to be costly and time-consuming and, as a basic guideline for materials selection, should be avoided (Section 2). Characteristics of chemical grouts that require additional study and may restrict the use of chemical grouts over the near-term include:

- Tendency to shrink (syneresis) due to dehydration that may irreversibly increase
the permeability of grouted seal zones or fractures

- Limited length of engineering experience with these materials (30-40 years) to provide a substantial indication of long-term performance under repository conditions
- Uncertain stability in irradiated environments
- Uncertain effects of radionuclide migration; in general, complex organic substances that have unknown effects on the mobility of radionuclides should not be introduced to the repository environment, if avoidable
- Potential toxicity and additional environmental hazards of many grouts or constituents; the toxicity of alteration products, if any, are unknown
- High cost.

Chemical grouts are available under a variety of commercial names. Many are proprietary and the formulas of the constituents are not readily available for study and analysis by repository sealing programs. Some chemical grouts tend to be difficult to work with and several are toxic, as shown in Table 2-3. In addition, sensitivity (alteration of fluid and gel properties due to contact with foreign substances such as metals, dissolved constituents, etc.) is a potential problem presented by chemical grouts. The chemical stability of these materials must be demonstrated for individual applications because interactions with constituents in groundwater or associated with the host formation may result in unstable or soluble compounds in the grouts.

Many of these materials tend to shrink in volume due to dehydration (syneresis) causing an increase
in the permeability of grouted fractures over time. This may present some problems for grouting in waste disposal boreholes or other repository areas that may be subject to drying or cyclic drying and wetting due to the proximity of heat-producing waste. Although limited experience suggests no other apparent problems with the stability of the materials themselves or degradation of their hydraulic or mechanical properties, chemical grouts may suffer microbial attack or degradation due to time, temperature, or irradiation. Because of these uncertainties, and the lack of clear advantages in their use relative to the priority materials, chemical grouts are not considered to be priority materials for repository sealing. Chemical grouts are worthy of further consideration if the performance of priority materials is unsatisfactory or can be enhanced by combination with chemical grouts.

2.5.5 Synthetic Minerals

2.5.5.1 Definition of Synthetic Minerals

As proposed by Smith et al. (1980), it may be possible to fill fractures by inducing the precipitation of common fracture filling minerals. Pusch et al. (1985) have provided an extensive review of the feasibility of fracture sealing by the precipitation of minerals and the synthetic production of fracture fillings that duplicate mineral fracture fillings. The options discussed included 1) injection of vapor or solutions that react with the host rock producing fracture-filling phases; 2) injection of supersaturated solutions that precipitate fracture filling phases as temperature decreases; and 3) injection of clay gels (discussed
separately, elsewhere). Pusch et al., concluded that low temperature artificial crystallization was the only promising approach to fracture sealing by synthesizing or emplacing fracture filling materials in situ.

For use in crystalline (granitic) host rock, a candidate reactive solution may include hydrofluoric acid, which may precipitate amorphous silica phases and fluorite. Hot CO$_2$ solutions may also cause artificial "weathering" of siliceous minerals in the host rock, filling voids with amorphous silica phases or clays. Supersaturated solutions may be used to precipitate phases such as:

- Calcite
- Zeolites
- Gypsum
- Iron oxides and hydroxides
- Magnesium hydroxide.

2.5.5.2 Screen of Properties of Synthetic Materials

Pusch et al.'s (1985) review of synthetic minerals for sealing fractures concluded that a low permeability seal was unlikely to be obtainable, and probably would not persist for a significant length of time. First, as Pusch et al. (1985) pointed out, completely filling a fracture by reaction products or precipitates is very difficult because the reactive or saturated solutions will necessarily have to enter and move through the fracture and occupy some of the void space. Thus, some portion of the void space cannot be completely filled by reaction products or precipitate. Second, the resulting fracture filling is likely to be brittle and subject to reopening under mechanical or thermal stresses imposed by construction,
waste emplacement, or tectonics. Third, the precipitates from solution may be redissolved by intrusion of unsaturated groundwater in fractures, particularly in the rock volume adjacent to the emplaced, heat-producing waste. Because of these uncertainties and the total lack of field and engineering experience with the methods of synthetic production of fracture-filling minerals, the method is deferred from consideration for near-term sealing studies (see Figure 2-1).

2.5.6 Ceramics

Ceramics encompass a wide variety of inorganic nonmetallic materials, dominated by silicates and aluminosilicates, that are brittle and fracture without significant plastic deformation. Ceramics may be crystalline to acrystalline (glasses). The starting materials in ceramic manufacturing are almost always granular or powders. Heat is essential to the manufacture of ceramics either by heat treatment (e.g., firing) or fusing of raw materials. In situ vitrification of host rocks to provide sealing or to heal fractures and damaged zones may be considered, essentially, a process not unlike the production of ceramics. Cements are ceramics that are considered separately here.

Although, ceramics provide a wide range of desirable physical properties, including high strength, low permeability, and long-term stability, Lankard's (1980) evaluation of ceramics for use in repository sealing concluded that emplacement of ceramics is unfeasible and that these materials are inappropriate for repository sealing. High energy input requirements, technology development for materials emplacement and
application of heat, and possible thermal stresses on host rocks have been cited (ONWI, 1980) as additional reasons to defer ceramics for use in repository sealing, including fracture sealing. As shown in Figure 2-1 of this report, ceramics have been deferred from near-term consideration in repository sealing because of these important emplacement considerations.

2.5.7 Metals

Metal components have been considered in some repository sealing applications, such as shaft seals (Clayton et al., 1984). Metals that may be utilized include copper and low carbon steel. These materials may be used in structural members in a seal system, for reinforcement, or as low permeability barriers. Metals appear to be most usefully applied to repository sealing in combination with other seal materials and components, such as concrete or clay bulkheads. The long-term stability of metals in the repository environment depends on the physico-chemical conditions present in situ. The reducing conditions expected in a basalt repository, for example, should favor the use of some metals, e.g., copper. In contrast, oxidizing conditions and high ionic strength brines, such as may prevail in salt repositories, may be corrosive to most metals. In the current context, however, metals appear to have little application for sealing fractures in the host rock because emplacement appears impossible without thermal or mechanical damage to host rock, high energy requirements, and technology development. As shown in Figure 2-1, for the purpose of this report (and for use in Stages III and IV of Phase III investigations at Stripa) metals have been
deferred from consideration for sealing fractures. Note, however, metals may be effectively applied in sealing man-made access-ways and in other engineered barriers in a nuclear waste repository.

2.5.8 Bitumen

Bitumen is a group of materials made up of complex colloidal mixes of heavy aliphatic and aromatic hydrocarbons. Natural bitumens, such as tars, gilsonite, and other materials, clearly demonstrate the longevity of these materials under some conditions. Bitumen is also produced as the "heavy" residual in petroleum refining and may be treated after refining to produce a range of different materials (industrial bitumens).

Bitumen has characteristically very low hydraulic conductivity. Bituminous materials are frequently used for sealing structures from moisture and have a long history of use in construction. Many bitumens have a degree of plasticity that would prevent the occurrence of propagation of through-going fractures in the materials. Because many bituminous substances have thermosetting properties, their viscosity can be reduced sharply by application of moderate amounts of heat, allowing flow, pumping, and injection of the materials. These properties, in concert with the expected longevity of bitumens, suggests the materials may be valuable in fracture sealing for a nuclear waste repository.

Naturally occurring bitumens may have highly variable compositions, including mineral content (e.g., clay minerals), trace element, and organic constituents. For this reason, as well as the
relatively low cost of industrial bitumen derived from ordinary petroleum refining, the Commission of the European Communities (1984) dismissed natural bitumens from consideration for repository sealing.

Although bitumens appear to possess favorable properties, there are several significant uncertainties regarding their applicability to sealing a nuclear waste repository. For example, bitumens are long-lived, but may be subject to oxidation, biodegradation, and radiolysis effects that may alter the hydraulic and mechanical properties of the materials in the long term. Bituminous materials are also subject to physical aging, due to ordering of colloids. Stiffening, embrittlement, and growth of porosity with the generation of radiolytic hydrogen or methane gas may be among the most significant effects of alteration and aging (Valkianinen and Vuorinen, 1985). Complexing of radionuclides by organic substances may increase the mobility of radionuclides released from waste packages. Thus, bituminous materials and their alteration products containing organic substances may enhance radionuclide mobility. Because of the potential for enhanced radionuclide mobility, somewhat uncertain long-term performance characteristics, and likelihood that other materials will perform adequately, bitumens should be considered low priority materials for fracture sealing.
DISCUSSION OF CANDIDATE SEALING MATERIALS

The previous section defined and described the general nature of several types of candidate seal materials. Based on these discussions, cementitious and earthen materials, particularly bentonite, appear to hold the greatest promise for fracture sealing and are recommended as priority materials for near-term sealing studies including Stripa Project Phase II, III, and IV research and testing. As noted earlier (Section 2.1), the key performance objectives and other characteristics of materials used for sealing a nuclear waste repository, including fracture sealing, are, at least:

- Low hydraulic conductivity, including forming a low hydraulic conductivity interface with the host formation
- Emplaceability, within practical constraints and using existing or new technology, without damage to the host rock.
- Structural and mechanical properties (strength, bond strength, flexibility, etc.) to maintain low hydraulic conductivity and materials durability under in situ mechanical and thermal stresses
- Long-term stability under in situ physico-chemical conditions

Summary discussions of priority materials with respect to how they achieve their desired performance properties are contained in this section. Specific discussions relate to the hydrologic and mechanical properties of priority candidate seal materials as they pertain to fracture sealing or grouting, as well as evidence regarding material
stability, and emplaceability. These discussions are provided as an aid for identifying issues that should be pursued prior to or coincident with development of detailed test plans or seal system designs (Section 3.4).

3.1 HYDRAULIC CONDUCTIVITY OF CANDIDATE SEAL MATERIALS

3.1.1 Cementitious Materials

A very large number (hundreds) of cementitious materials have been studied (or recommended) for the sealing of fractures in component rock. Within the scope of this document, it is possible only to present details of the performance for a few representative mixtures and to discuss the performance properties and mechanisms of cements in general (but quantitative) terms. These summaries are intended to provide the reader with a perception of the type of performance that can be expected or achieved with cementitious materials that might be developed or used in a repository seal system. Several relatively comprehensive comparative studies of grout performance form the basis for this review. Studies completed by Hooton (1983, 1986a, 1986b), Hooton and Mukherjee (1982), Pusch et al. (1985) and Lau and Crawford (1986) are of note. The results from physical tests on several materials conducted by Hooton on five candidate grout materials are given in Table 3-1. The data lead to the conclusion that it is possible to achieve a hydraulic conductivity in normal portland cement grout on the order of \(10^{-8}\) to \(10^{-9}\) cm/sec (\(10^{-10}\) to \(10^{-11}\) m/sec).
Table 3-1. Physical properties of grout (approximately 130 days water curing at 7° C)

<table>
<thead>
<tr>
<th>Grout</th>
<th>Water:Cement Ratio (Constant Flow)</th>
<th>Average Apparent Porosity (%)</th>
<th>Average Compressive Strength (MPa)</th>
<th>Hydraulic Conductivity (cm/s g•c x 10^-9)</th>
<th>Average Bulk Density kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. API Class G</td>
<td>0.393</td>
<td>25.7</td>
<td>72.8</td>
<td>0.5</td>
<td>2035</td>
</tr>
<tr>
<td>2. API Class G + Fly Ash</td>
<td>0.471</td>
<td>36.1</td>
<td>39.2</td>
<td>22</td>
<td>1852</td>
</tr>
<tr>
<td>3. API Class G + Bituminous Fly Ash</td>
<td>0.450</td>
<td>30.7</td>
<td>50.7</td>
<td>1.1</td>
<td>1925</td>
</tr>
<tr>
<td>4. Ordinary Portland Cement (CSA Type 10)</td>
<td>0.471</td>
<td>31.3</td>
<td>52.0</td>
<td>&lt;0.13</td>
<td>1884</td>
</tr>
<tr>
<td>5. Ordinary Portland Cement + Fly Ash</td>
<td>0.550</td>
<td>39.6</td>
<td>28.7</td>
<td>73</td>
<td>1785</td>
</tr>
<tr>
<td>6. Ordinary Portland Cement + Bituminous Fly Ash</td>
<td>0.493</td>
<td>31.8</td>
<td>48.5</td>
<td>0.4</td>
<td>1857</td>
</tr>
<tr>
<td>7. High Alumina Cement</td>
<td>0.436</td>
<td>36.4</td>
<td>50.3</td>
<td>1.5</td>
<td>2071</td>
</tr>
<tr>
<td>8. High Alumina Cement + Fly Ash</td>
<td>0.486</td>
<td>42.4</td>
<td>38.1</td>
<td>140</td>
<td>1895</td>
</tr>
<tr>
<td>9. High Alumina Cement + Bituminous Fly Ash</td>
<td>0.379</td>
<td>33.5</td>
<td>66.7</td>
<td>1.2</td>
<td>2087</td>
</tr>
</tbody>
</table>

Reference: Gray, 1986
Hydraulic conductivity ($K_i$) may be the most important performance parameter when developing cementitious seal materials. $K_i$ is primarily a function of several factors:

- Porosity of the paste
- Cured porosity
- Fracture porosity and other secondary porosity.

In general, reduction in porosity (or increases in density) and decreasing continuity (interconnection) of pore spaces will decrease $K_i$ in cementitious materials. Several types of porosity and means commonly used to reduce porosity in cementitious materials are described below.

3.1.1.1 Cement Paste Porosity

Cement paste porosity ("capillary space") is commonly controlled in cementitious materials by maintaining low water/cement ratios (w/c) in mixes. Low w/c ratios result in low porosity pastes because free water, i.e., water capable of occupying and maintaining pore space in the paste, is minimized. Specific guidelines for mix design have been identified. Verbeck (1978) shows that a decrease in w/c from 0.8 to 0.4 in well-cured cementitious paste can result in decreasing the permeability of the material by a factor of $10^3$. Moreover, Pusch (1986), found that a w/c ratio of about 0.5 produced hydrologic conductivities in the range of $10^{-6}$ to $10^{-8}$ cm/sec, which he considered adequate for fracture sealing application. Lowering w/c ratios also limits bleeding. The volume of bleed water is important because it may occupy
space in or surrounding a cementitious material emplacement, such as an injected grout. This may increase interconnected pore volume in the paste or at the interface between the seal and the host (see below). Such conditions lead directly to substantial increase in the apparent $K_i$ of the seal.

3.1.1.2 Cured Grout Porosity

While original porosity in the fresh paste should be minimized, one of the phenomena that attends the curing of cement is a reduction of porosity. This occurs because of the slow growth of cementitious hydration products ("gel") into the original pore space in the paste. With growth of hydration products, porosity becomes decreasingly interconnected and permeability decreases markedly. While this is a general phenomenon, the time required before $K_i$ begins to decrease is a function of w/c. The cure time required to reach this condition is shorter if the w/c ratio is low (Verbeck, 1978). The reduction of porosity during cure can be enhanced through:

- Long cure times to enhance hydration of cement
- Use of additives, such as pozzolans, that increase the growth of cementitious phases while consuming soluble byproducts of the cement-water reaction.

Long cure will enhance the growth of hydration phases, promoting full hydration of the cement by controlling and limiting the loss of moisture from the emplaced grout. Pozzolans enhance the growth of C-S-H phases in the presence of $\text{Ca(OH)}_2$ during the cure. In the absence of pozzolans, the free calcium byproduct of the cement hydration reaction
remains soluble and may contribute to secondary porosity.

A possible source of porosity in cured cementitious materials may reside within the gel phase itself. The C-S-H gel may nucleate and grow in a crumpled sheet-like or tubular habit that appears to be most pronounced if pore volumes are large, such as in high w/c mixes. These phases may recrystallize with further growth, but may contribute to the total porosity of a material if recrystallization is incomplete (Grudemo, 1964).

3.1.1.3 Fracture and Other Secondary Porosity

Porosity developed following cure may be considered "secondary." As mentioned above, the secondary porosity of cementitious materials can be reduced by limiting dissolution of soluble Ca(OH)$_2$ through the use of pozzolanic additives in the mix. During cure, the free calcium is combined with the siliceous pozzolan to produce hydrated calcium silicate phases and further reduce the pore volume of the paste. Because of this, pozzolanic mixes tend to result in lower permeability materials than equivalent non-pozzolanic materials.

The permeability of cementitious materials can be compromised by fractures. Secondary porosity resulting from fractures can occur from:

- Failure under stress
- Shrinkage
- Unrestrained expansion
- Degrading reactions.

Failure under stress can be eliminated by improving materials strength. Strength is discussed further
below (Section 3.2.1). Of note, however, is that the mechanical properties of cementitious materials are largely dependent on porosity (Verbeck, 1978) and, as with $K_i$, are improved by low w/c ratios, extended cure time, and pozzolanic admixtures.

Shrinkage is a complex phenomenon and may be due to several factors. The most common cause of shrinkage is loss of moisture. Shrinkage can be minimized by low w/c ratios (i.e., minimizing free water), preventing water loss during cure, judicious control of temperature, the use of additives, and the use of large amounts of volume-stable aggregate (e.g., sand, hard rock gravel, etc.); clayey aggregate may enhance shrinkage. Expansive (shrinkage-compensating) cements are also available and can be prepared. High volume products of cement hydration (calcium sulfoaluminates-hydrates) or gas production in the paste provide compensation for cement shrinkage during or after cure. Expansive phases grow in both the plastic and hardened grouts. If unrestrained, therefore, expansion can fracture the cementitious material; hence, in ordinary engineering application, expansivity is often not desirable. In sealing practice, however, unrestrained expansion is unlikely because the rock will confine the expanding cement. Restraint causes internal stress to develop due to volume increasing reactions ("self-stress") and a compressive stress can be generated at the cement-host container interface. This is an important consideration because of the nature of the seal-rock interface.

Sulfate attack or alkali-aggregate reaction may degrade and promote fracturing in cementitious
materials. Sulphate-resistant cements may be used to minimize the effects of sulphate. Opaline aggregate is most likely to react with alkalis in the cement matrix and should be avoided. High quality mix design is essential to minimizing materials degradation.

3.1.1.4 Interface Permeability

The interface between a cementitious seal and host rock may be more permeable than the cement material itself (e.g., Wakeley and Roy, 1982; Roy et al., 1983). The interface permeability may reflect:

- Poor conformance between the host and the seal, due to emplacement, leaving large void spaces, bleed water, etc.

- Chemical incompatibility between the seal and host resulting in a weak, permeable bond, or a permeable reaction rim

- Mechanical incompatibility between the seal and host due to differential thermal and mechanical properties causing a porous or fractured bond

- Shrinkage of the cementitious material away from the rock after emplacement.

Very limited results (Roy et al., 1983) suggest that under optimum conditions the interface permeability may be equivalent to the material permeability, but more commonly, it may range to one or two orders of magnitude more permeable than the seal materials itself. The hydrologic nature of the interface bond is only beginning to be studied intensely. Shrinkage compensating cement may be effective to assure a mechanically tight interface is maintained that will help to keep permeability as low as possible at the interface. The strength
of the bond between grout and rock which appears to correlate with the hydrologic behavior of the interface, is described in Section 3.2.1.

3.1.2 Earthen Materials

Clay-based grouts, including both bentonite- and non-bentonite-based materials, incorporate a wide range of performance characteristics (Cambefort, 1967). Extensive research, particularly by Pusch (1978a, b, c; 1980, 1981, 1986) has been directed toward the bentonite-rich materials on which this summary will concentrate.

The very low permeability of saturated bentonite gel (Figure 2-4) depends on the void ratio of the material (a function of original density and the amount of swelling that occurs before confinement, measured as the ratio of void volume to solid volume), the proportion of bentonite (or more precisely, the proportion of smectite) in the material, the interlayer cation species in the smectite, the fabric of the clay (arrangement of clay particles), and the ionic strength of the permeant (Pusch, 1978a; Meyer and Howard, 1983; Chan, 1986). The bentonite gel is composed of the many fine smectite particles each surrounded by thick adsorbed water layers. The low permeability of the gels is, therefore, the result of the small pore spaces that occur between very fine-grained particles, and the "clogging" of pore spaces by the adsorbed water layers. Because hydraulic conductivity in bentonite gels tends to be very low, diffusion of dissolved species may be the most significant means for radionuclide transport. Diffusion coefficients for radionuclides are generally less than $10^{-7}$ cm$^2$/sec, which may represent, as an
approximation, movement of about six centimeters per year.*

The data show that above a critical clay density of about 1.3 g/cm³ hydraulic conductivity, diffusivity, and swelling pressure tend to be largely independent of temperature and, with the exception of swelling pressure, tend to be independent of groundwater composition. In addition, for mixtures of bentonite and inert, fine aggregates, such as silica sand, the hydraulic, diffusion and swelling properties depend principally on the effective clay dry density (i.e., the ratio of the mass of dry bentonite to the sum of the volumes of the clay plus voids) and are independent of the sand content. It is probable that this also holds true for mixtures of bentonite and inert silt and clay sized materials and may apply in the design of fine clay-based grouts containing fine particulates such as silica fume (Dixon and Gray, 1985; Cheung et al., 1985; Gray et al., 1984; Pusch, 1978a, b, 1980).

To determine some pertinent properties of clays after injection into fractures, Chan (1982) injected a number of clay-based materials at different water contents into a model fracture with a 0.25 mm aperture similar to that described by Lau and Crawford (1986). A maximum hydraulic gradient of approximately 3 was used. The lowest hydraulic conductivity (-2.5 x 10⁻⁸ cm/sec) was observed during tests on Avonseal (commercial) bentonite after injection at the lowest possible water:clay ratio (by mass) of 4. The liquid limit of the

*Based on the linear mean of the square (Δx) of the displacement due to diffusion, disregarding tortuosity, expressed as Δx = [2 x diffusion coefficient (D) x time between observations (Δt)]⁰ (Daniels and Alberty, 1966).
material is approximately 325 percent. It is noted that the predominant exchangeable cations on the montmorillonite clay mineral in Avonseal are Na\(^+\) and Ca\(^{2+}\), with Na\(^+\) in larger proportion [Quigley (1984)]. The effects of exchange of the cations on the clay at injection for those present in the groundwater on the mechanical and hydraulic properties of the clay grout require investigation.

3.2 **STRUCTURAL/MECHANICAL PROPERTIES**

3.2.1 **Cementitious Materials**

The strength of cementitious grouts may be a key advantage in their use as seals if the seals are to resist structural loads, thermal stress, or hydraulic stresses. Grouts should resist fracturing (and maintain low permeability) under in situ stresses. The strength of these materials may vary widely depending on temperature, water:cement ratio, aggregate type and content, additives, curing conditions, and age. Data from Hooton shown in Table 3-1 indicate a range of compressive strengths for portland cement-based grouts of 29-73 MPa. This range lies in the middle of the values for the unconfined compressive strengths of portland cement based concretes [between 7-124 MPa, (e.g., B. Mather 1966; 1967a; K. Mather, 1965). Grouts should possess an equally wide range.

Based on portland cement-based concrete, the tensile strength of cementitious materials should be 10-12 percent of the unconfined compressive strength, and flexural strength should be about 15-20 percent of the unconfined strength (Derucher, 1978). Shear strength of concretes is usually 40-80 percent of the compressive strength. Thus, the
failure of cementitious materials used in fracture seals occurs under lower tensile or flexural stresses than compressive stresses. Tensile stresses may result from heating-cooling cycles proximal to the waste disposal borehole, material shrinkage, construction activities, or tectonics.

The strength of cementitious materials, like permeability, is largely a function of material porosity. Strength generally increases as porosity decreases; thus, strength is enhanced in low w/c mixes, pozzolanic, and well-cured materials. The emplacement requirements of a cementitious grout, such as fluidity and low viscosity (Section 3.6) may work against achieving optimal strength in grouts designed for sealing fine fractures.

Resistance to fracture may be achieved through high strength materials; however, these materials also tend to be brittle. Alternatively, more plastic, low strength materials may be designed that respond to stress by deformation without fracturing. Although achieving truly plastic cementitious materials is severely limited, lower elastic moduli can be obtained using low strength aggregate or fillers, such as clays, in substantial quantities in the mix design. This option remains open as a low priority for near-term studies.

Bond Strength

Preliminary studies of bond strength of cementitious grouts for repository sealing (Roy et al., 1983) showed an expected correlation between interface permeability and bond strength measured in shear. These studies suggest the bond strength has physical and chemical components. The physical
component is evident in the higher bond strengths measured on expansive mixes relative to non-expansive mixes. The expansive cements, particularly, tend to be "locked" to the host and irregularities in the grouted surfaces of the host. The chemical component of bond strength is enhanced in siliceous host rock, which participates in a pozzolanic reaction with free Ca(OH)$_2$ that tends to accumulate at the interface (probably as a component in bleed water). Bond strength is also enhanced at low w/c, much like other physical properties. The range of bond strengths measured by Roy et al. (1983) for expansive grout emplaced in quartzite cores is 4-10 MPa (60°-90°C, 14 and 28 days).

3.2.2 Earthen Materials

Bentonite grout will maintain low permeability under in situ stresses in its soft, plastic state by deforming without fracture. Bentonite remains plastic under a wide range of water contents. If dehydrated and fractured, the bentonite is expected to rehydrate and heal any fractures by reswelling upon contact with water. This reversible behavior is a decided advantage of bentonite for use in seals or seal components that have no structural bearing requirements.

The major concern with respect to the mechanical durability properties of bentonite is its low shear strength when saturated, and the well-known tendency for bentonite gel to be eroded from fractures subject to high hydraulic gradients. Pusch et al. (1985) indicate that flow rates of $10^{-2}$ to $10^{-3}$ cm/sec are sufficient to erode bentonite grouts consisting of soft Na-smectite gel. They suggest
that addition of sand or cement to the grout markedly improves the erosion resistance of the grout.

Chan (1986) investigated the potential for bentonite-based grouts to erode under increasing hydraulic gradient. The apparatus for preliminary studies on hydraulic conductivity of bentonite grouts was used. Bentonite with admixtures of ordinary portland cement and silica fume in various proportions were investigated. The data show that the cement admixtures (CSA Type 10 cement), which never exceeded 25 percent by dry mass of the solids of the grout, tend to increase the erosion resistance of the grout (Table 3-2). The silica fume appears to have a similar effect, at least in combination with the cement. Critical hydraulic gradients are defined for each mixture, above which erosion is significant. These tests provide data which, once the maximum hydraulic gradient to which a grout will be subjected is known, will contribute to material selection or form the basis for the decision to include clay-based grouts in the seal designs.

3.3 LONGEVITY CONSIDERATIONS

Investigations on the priority sealing materials have included long-term stability studies on the materials or components of the materials. The study of clay minerals alteration has proceeded as a scientific research area independent of repository sealing studies; thus, clay alteration research incorporates a large body of data produced over many years. The summary on clay minerals alteration (Section 3.3.2) based on Meyer and Howard (1983) is, therefore, far more extensive
Table 3-2. Summary of permeability and erodability studies

<table>
<thead>
<tr>
<th>GROUT MIX</th>
<th>GAP THICKNESS (mm)</th>
<th>AVERAGE LENGTH OF GROUT THICKNESS SPECIMEN, t (mm)</th>
<th>MAXIMUM INJECTION PRESSURE (kpa)</th>
<th>APRESSURE (kpa)</th>
<th>HYDRAULIC GRADIENT</th>
<th>DURATION (DAYS)</th>
<th>EQUIVALENT &quot;k&quot; (m/s)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>255</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>50</td>
<td>150</td>
<td>750</td>
<td>1530</td>
<td>80</td>
<td>0.6x10^-11</td>
<td>--</td>
<td>Grout taking on water.</td>
</tr>
<tr>
<td>0.25</td>
<td>50</td>
<td>150</td>
<td>750</td>
<td>1530</td>
<td>80</td>
<td>0.6x10^-11</td>
<td>--</td>
<td>Grout was effective at AP 9 times of max injecting pressure.</td>
</tr>
<tr>
<td>0.25</td>
<td>50</td>
<td>150</td>
<td>750</td>
<td>1530</td>
<td>80</td>
<td>0.6x10^-11</td>
<td>--</td>
<td>Channelling in grout, &quot;k&quot; value greatly increased.</td>
</tr>
</tbody>
</table>

- Some unconnected fine cracks perpendicular to the direction of water flow appeared 14 days after test, but they were closed up 42 days after their appearance.
Table 3-2. Summary of permeability and erodability studies
(Continued)

<table>
<thead>
<tr>
<th>GROUT MIX</th>
<th>AVERAGE GAP THICKNESS SPECIMEN, t</th>
<th>MAXIMUM METER PRESSURE ΔP (kpa)</th>
<th>HYDRAULIC GRADIENT 1</th>
<th>DURATION 2</th>
<th>EQUIVALENT &quot;k&quot; 3</th>
<th>COMMENTS</th>
</tr>
</thead>
</table>
| 1 part of water, 2 parts of Avonlea bentonite, 1 part Type 10 cement | 0.25 280 | 5 | 50 | 18 | 3 | 2.3 x 10^-7 | - Grout specimen cured for 7 days before the flow test.  
- Injection easier for this grout than for bentonite grout (10^-7 vs 10^-10). It appeared that the addition of cement to bentonite caused the grouting material to form larger "aggregates."  
- No channeling in grout when the applied water pressure was 10 times of the injection pressure. |
| 1 part of water, 2 parts of Avonlea bentonite, 1 part Type 10 cement | 0.25 220 | 2 | 50 | 23 | 20 | 5.9 x 10^-8 | - Grout specimen cured for 7 days before the flow test.  
- Some fine channels developed in the grout, "k" value increased. |
Table 3-2. Summary of permeability and erodability studies (Continued)

<table>
<thead>
<tr>
<th>GROUT MIX</th>
<th>AVERAGE LENGTH OF GROUT SPECIMEN, t</th>
<th>MAXIMUM INJECTION PRESSURE</th>
<th>APPLIED METER PRESSURE</th>
<th>HYDRAULIC GRADIENT</th>
<th>DURATION (DAYS)</th>
<th>EQUIVALENT &quot;k&quot; (m/s)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 parts of water, parts of Avonlea bentonite, 1 part Type 10 cement</td>
<td>0.25 220</td>
<td>3</td>
<td>50</td>
<td>23</td>
<td>14</td>
<td>1.0×10⁻⁶</td>
<td>• Grout specimen cured for 7 days before the flow test. • Grout mix same as the above specimen. Initial &quot;k&quot; value much larger because the grout was not filling the gap as well as the above specimen.</td>
</tr>
<tr>
<td>6 parts of water, 1 parts of Pembina Bentonite, 1 part of cement</td>
<td>0.50 155</td>
<td>10</td>
<td>100</td>
<td>66</td>
<td>15</td>
<td>2.8×10⁻⁸</td>
<td>• Grout specimen cured for 7 days before the flow test. • Channels in grout visible, &quot;k&quot; value greatly increased.</td>
</tr>
<tr>
<td>6 parts of water, 1 parts of Pembina Bentonite, 1 part of cement</td>
<td>0.50 220</td>
<td>10</td>
<td>100</td>
<td>46</td>
<td>1</td>
<td>3.3×10⁻⁸</td>
<td>• Grout specimen cured for 7 days before the flow test. • Some channels appeared in the grout but they were not interconnected.</td>
</tr>
</tbody>
</table>

200 93 4 7.5×10⁻⁶ 2.1×10⁻⁷
Table 3-2. Summary of permeability and erodability studies

(Continued)

<table>
<thead>
<tr>
<th>GROUT MIX</th>
<th>GAP THICKNESS (mm)</th>
<th>AVERAGE LENGTH OF GROUT SPECIMEN, t (mm)</th>
<th>MAXIMUM INJECTION PRESSURE (kpa)</th>
<th>AP (kpa)</th>
<th>HYDRAULIC GRADIENT</th>
<th>DURATION (DAYS)</th>
<th>EQUIVALENT &quot;k&quot; (m/s)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>parts of water, parts of Pembina</td>
<td>0.25</td>
<td>115</td>
<td>10</td>
<td>50</td>
<td>44</td>
<td>7</td>
<td>4.2x10^-9</td>
<td>*Grout specimen cured for 7 days before the flow test.</td>
</tr>
<tr>
<td>1) Bentonite,</td>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>133</td>
<td>14</td>
<td>2.6x10^-8</td>
<td></td>
</tr>
<tr>
<td>part of cement</td>
<td></td>
<td></td>
<td></td>
<td>200</td>
<td>177</td>
<td>6</td>
<td>5.3x10^-8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>250</td>
<td>222</td>
<td>4</td>
<td>8.0x10^-8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>266</td>
<td>31</td>
<td>3.8x10^-7</td>
<td>*Some small channels developed by erosion or movement of particles but they were not interconnected. &quot;k&quot; value increased.</td>
</tr>
<tr>
<td>parts of water</td>
<td>0.50</td>
<td>175</td>
<td>50</td>
<td>100</td>
<td>58</td>
<td>5</td>
<td>3.9x10^-9</td>
<td></td>
</tr>
<tr>
<td>parts of Pembina</td>
<td></td>
<td></td>
<td></td>
<td>200</td>
<td>116</td>
<td>3</td>
<td>3.1x10^-9</td>
<td></td>
</tr>
<tr>
<td>1) Bentonite,</td>
<td></td>
<td></td>
<td></td>
<td>250</td>
<td>145</td>
<td>5</td>
<td>2.8x10^-9</td>
<td></td>
</tr>
<tr>
<td>parts of cement, parts of silica fume</td>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>174</td>
<td>11</td>
<td>2.6x10^-9</td>
<td></td>
</tr>
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<td></td>
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<td>203</td>
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<td></td>
<td></td>
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<td></td>
<td>400</td>
<td>233</td>
<td>7</td>
<td>2.5x10^-9</td>
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<td></td>
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<td></td>
<td></td>
<td>450</td>
<td>262</td>
<td>1</td>
<td>2.5x10^-9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>291</td>
<td>2</td>
<td>2.5x10^-9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>700</td>
<td>407</td>
<td>4</td>
<td>2.3x10^-8</td>
<td>*No visible channels.</td>
</tr>
</tbody>
</table>
Table 3-2. Summary of permeability and erodability studies
(Continued)

<table>
<thead>
<tr>
<th>GROUT MIX</th>
<th>GAP THICKNESS (mm)</th>
<th>AVERAGE LENGTH OF GROUT SPECIMEN, t (mm)</th>
<th>MAXIMUM INJECTION PRESSURE (kpa)</th>
<th>AP (kpa)</th>
<th>HYDRAULIC GRADIENT</th>
<th>DURATION (DAYS)</th>
<th>EQUIVALENT &quot;k&quot; (m/s)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 parts of water</td>
<td>0.50</td>
<td>175</td>
<td>50</td>
<td>50</td>
<td>13</td>
<td>1</td>
<td>2.3x10^-8</td>
<td>• Plug &quot;A&quot; was injected by Plug &quot;B&quot; and there was some mixing or blending at the boundary of the plugs. Plug &quot;A&quot; provided confinement to Plug &quot;B&quot; (clay and water grout).</td>
</tr>
<tr>
<td>0 parts of Pembina</td>
<td>100</td>
<td>27</td>
<td>1</td>
<td>2.4x10^-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) Bentonite</td>
<td>150</td>
<td>41</td>
<td>0.1</td>
<td>2.3x10^-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>parts of cement</td>
<td>100</td>
<td>27</td>
<td>6</td>
<td>8.5x10^-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>part of silica fume</td>
<td>200</td>
<td>55</td>
<td>9</td>
<td>5.2x10^-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plug &quot;A&quot;)</td>
<td>250</td>
<td>69</td>
<td>4</td>
<td>5.3x10^-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>parts of water</td>
<td>300</td>
<td>82</td>
<td>5</td>
<td>5.3x10^-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>part of Avonitea</td>
<td>350</td>
<td>96</td>
<td>4</td>
<td>5.5x10^-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) Bentonite</td>
<td>400</td>
<td>110</td>
<td>2</td>
<td>4.3x10^-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plug &quot;B&quot;)</td>
<td>500</td>
<td>137</td>
<td>3</td>
<td>3.3x10^-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>parts of water</td>
<td>600</td>
<td>165</td>
<td>1</td>
<td>3.1x10^-9</td>
<td>• At AP-600 kpa, Plug &quot;A&quot; could still confine Plug &quot;B&quot;. The &quot;k&quot; value of the composite grout was small.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>part of Avonitea</td>
<td>7 mins</td>
<td>8.1x10^-7</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>a) Bentonite</td>
<td>5 mins</td>
<td>1.0x10^-6</td>
<td>• Channeling through sample.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Thickness of gap between 2 smooth plates.
- Length of grout specimen injected in the gap by a certain injecting pressure.
- Maximum pressure used for injection.
- Water pressure used to force water through the grout specimen. Pressure was increased in steps.
- Hydraulic gradient \( I = \frac{A}{A} \) = Applied water pressure/Average length of grout specimen.
- Number of days the water pressure was applied to the grout specimen.
- Equivalent hydraulic conductivity \( k \) is equal to: \( \frac{Q}{I} \), \( Q \) = flow rate through the specimen; \( I \) = hydraulic gradient; and \( A \) = cross-sectional area of grout specimen perpendicular to the flow direction.
than the summary of cementitious materials longevity in the following section.

3.3.1 Cementitious Materials

The longevity and stability of cementitious materials remains a significant issue related to their use in repository sealing. To perform effectively as components of seals, concretes and cements are required to maintain low hydraulic conductivity both intrinsically and at interfaces with the rock. Atkinson and Hearne (1984) identified a number of factors that can affect possible changes in cement material properties. These are:

- Continued internal microstructural changes and phase transformations. The cement will tend toward its most stable state, amorphous material may crystallize, reactions with aggregates may occur, and hydration reactions will tend towards completion

- Reactions with the groundwater; these include dissolution (leaching) or reactions with ionic species such as \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) and \( \text{HCO}_3^- \) that enhance dissolution or promote growth of expansive (high volume) phases that, if unrestrained, will cause fracturing of the cement matrix

- Corrosion of metal reinforcements, if present

- Action of microorganisms

- Radiation effects.

In addition to these, differential thermal expansion between the rock and the seal could cause excessive loads and may be physically disruptive. In large concrete masses, such as those that may be used to plug shafts, the exothermic hydration reactions could cause considerable temperature rise.
On cooling rock-seal interface permeability could be increased. Moreover, cements used for grouts may react chemically with fracture infills, such as clays and calcite, or may separate from the rock due to temperature induced stress changes across the sealed fracture. These physical processes will increase the rate of ingress and egress of leaching groundwaters.

Langton and Roy (1983), Taylor-Woodrow (1986), Aitcin (1986), and Hooton (1986a) have examined the properties of ancient cements and concretes. These studies provide an analog against which the performance of cementitious materials emplaced in a repository can be qualitatively assessed. They indicate that the chemistry and mineralogy of the cementitious phases in ancient materials are similar to those in a modern product containing portland cement. Characterization of the calcium silicate hydrate (C-S-H), which is responsible for the hydraulic properties of ancient and modern cements, has indicated that C-S-H may still be X-ray amorphous after aging for as long as 3,000 years (Hooton, 1986b). This suggests that crystallization and/or other changes in C-S-H structure can be expected to be very slow in cement-based repository seals. The slow rate of alteration has been substantiated in experimental programs described below.

Based on archaeological evidence, engineering experience and thermodynamic studies, Atkinson and Hearne (1984) concluded that for Ordinary Portland Cement, the most likely mechanisms of degradation are sulphate attack and Ca(OH)$_2$ leaching. Other factors are likely to have negligible effects. From imperfect calculations using diffusion
equations it is concluded that the time required to totally leach Ca(OH)$_2$ from a one meter-thick cured Ordinary Portland Cement paste could range from 350 to $5 \times 10^5$ years. The authors recognize that the 350 year estimate is extremely pessimistic (a worst case scenario) especially for a "deep" repository.

If sulphate-resistant portland cement is used, leaching of free Ca(OH)$_2$ is the most significant factor leading to concrete degradation. Pozzolanic additives may be used to limit free lime in the cured material. A number of studies have been directed to develop pozzolanic cements. Burnett et al. (1985) has confirmed that admixing silica fume not only significantly decreases the free Ca(OH)$_2$ in the cement paste, it also decreases the hydraulic conductivity of sulphate-resistant portland cement. Moreover, partial replacement of sulphate-resistant portland cement with silica fume produces a material that, when injected into a laboratory model of a rock fracture, produced a material with a hydraulic conductivity which was less than $10^{-13}$ cm/s (Hooton, 1986). In addition, the expansion of sulphate-resistant portland cement pastes in strong chloride and sulphate solutions were markedly reduced by the addition of pozzolan.

Microscopic examination of cements invariably reveals cement particles that are incompletely hydrated. Hydrated boundaries surround unhydrated particle centers. It was noted earlier that it is now possible, through the use of superplasticizers, to produce concretes which, on emplacement, possess water contents that are insufficient to stoichiometrically satisfy the hydration reaction. Water flowing through microcracks in such concretes would be incorporated in the cement by further hydration.
This should enhance longevity. It is pertinent that increased cement grain size should decrease the degree of cement hydration; increased fineness is generally favored for high strength/low permeability concretes. Research is necessary to optimize material properties. Although the behavior, fate, and long-term stability effects of superplasticizers added to cementitious mixes are receiving increasing attention, research is necessary to show that the small quantities of organic polymers added to the cement do not adversely affect chemical interactions between the groundwater and the cement.

Several laboratory studies have concentrated on the alteration of cements under controlled conditions. Recent studies by Scheetz and Roy (1986) on concretes designed to be compatible with a siliceous tuff environment show that low temperature cementitious C-S-H phases are altered to crystalline tobermorite (also a cementitious phase) due to hydrothermal treatment at temperatures between 90° and 300°C. The reaction leads to a decrease in molar volume which may increase porosity and permeability of the materials.* The associated fluids increase in silica, sulfate, calcium, sodium, and potassium concentrations due to interaction with the concrete materials.

In the range of temperatures up to 95°C, reactions in cementitious systems are expected to be very slow, and alteration effects, if any, may be imperceptible except in very long-term experiments.

*This increase in permeability has not yet been estimated; however, it seems likely that relatively simple bounding calculations could be performed to see if \( K_i \) increases due to increased porosity would be significant.
Grouts stored at temperatures up to 54°C showed little difference from those stored at room temperature, in a study at Waterways Experiment Station (WES) (Buck et al., 1981). Over a three year study, Ca(OH)$_2$ decreased and the C-S-H cementitious phase grew with time.

Roy et al. (1983) show that ettringite, an expansive phase in some candidate cementitious materials, is unstable only above about 130° to 150°C in deionized water. Buck et al. (1985), however, showed that ettringite appears to become unstable between about 75° and 100°C when grout samples are stored in closed vials.

In separate studies by the Canadian Nuclear Fuel Waste Management Program (Heimann and Hooton, 1986), the interactions of cements, clays, and saline groundwater at 150°C have been examined. The presence of clay, which may be introduced to a repository system in waste package buffer materials, backfills, seal components, and fracture seals, appears to enhance the release of cations from the cementitious materials. This phenomenon may be related to the ability of the clay to suppress the pH buffering capacity of cementitious materials and prevent the rise of groundwater pH. Pozzolanic additives appear to counteract the effects of the clay, perhaps by tying up free Ca(OH)$_2$ and by reducing the porosity and permeability of the cementitious materials. An interesting result of these experiments pertains to the mechanical properties of the cementitious materials. In the presence of Na-bentonite, the phase transformation of the amorphous and poorly crystalline C-S-H cementitious phase to Al-substituted-11Å tobermorite was enhanced, probably due to excess silica.
released by the clay. At lower temperatures (<100°C), this phase transformation will produce another high-strength C-S-H phase. This result suggests the presence of clay may enhance the longevity (stability) and strength of the material. Agreeably, however, this phase transformation may result in higher porosity of the cementitious matrix because of the decrease in molar volume of reaction products; which may increase the permeability of the material and enhance dissolution or alternative of the cementitious matrix.

An additional design approach to enhance longevity of cementitious materials for borehole and shaft seals has been proposed by Roy (1980) and Grutzeck et al. (1980). This involves proportioning the concrete/mortar mix to match that of the rock mass with which it is in contact to the degree possible. Using this approach for candidate host rock such as granite, silica fume or other pozzanic additive may be replaced with rock flour as the principal pozzolanic agent. Such suggestions are now being studied in the International Stripa project and at the Underground Research Laboratory in Canada.

3.3.2 Earthen Materials

The sealing functions of earthen seal materials, such as low hydraulic conductivity, expansivity, and self-healing of fractures generally are attributable to the clay mineral fraction in the material. The longevity of these materials as seals, therefore, largely depends on the nature of the clay minerals. This section emphasizes research results on the stability of clay minerals. The literature on clay mineral stability and alteration
is extensive. This summary is largely derived from the review by Meyer and Howard (1983).

3.3.2.1 Clay Solubility

Results of hydrothermal alteration experiments on Na-montmorillonite at 250°C and less have recently been reported (Howard and Roy, 1985). Using a low ionic strength synthetic basaltic groundwater, a small percentage of smectite layers collapsed, apparently as an initial step toward illitization. Enrichment of the reacted fluid in silica, aluminum, sodium, calcium, and potassium indicated clay dissolution under hydrothermal conditions. Similar results were obtained by Taylor et al. (1980) on Na-bentonite tested in synthetic basaltic groundwater at 250°C. The effects of dissolution, however, are undoubtedly site specific and depend on the groundwater chemistry and in situ temperatures. Below about 100°C and at near neutral pH, dissolution should be negligible. If the clay materials (along with other seals) effectively limit the groundwater flow rates, the effects of dissolution will be further reduced.

Clay solubility may be affected by changes in pH accompanying the alteration of host rock or cementitious materials. For example, if alteration of cements increased the pH of ground water to about 9 or higher, the solubility of silica in the clay may be increased substantially (Figure 3-1). The release of silica from clay tetrahedral sheets would be expected to alter the properties of clays significantly. This would be particularly true in fracture seals where any buffering capacity of the relatively small amount of clay minerals present in the seal clays would be overcome. In an open
system, species dissolved from a clay grout may be transported from the fracture over time, and the fracture permeability will increase. The compatibility between clay and cementitious materials, particularly in open systems dominated by the cementitious material, requires further investigation.

3.3.2.2 Clay Dehydration

Temperature is a key factor in the stability of clays (or clay minerals). Grim (1968) cites several studies in which individual clay minerals were heated and the effects determined. A general conclusion from Grim's summary is that many clay minerals undergo some degree of dehydration of interlayer water at temperatures up to 300°C. The amount and rate of water loss vary among clay minerals and are dependent upon the environment in which the clays are heated. Under hydrothermal conditions, in which the partial pressure of water is significant, dehydration of interlayer water in clays occurs at higher temperatures than under dry conditions. The difference between the dehydration temperature under dry and hydrothermal conditions depends on the clay mineral.
Figure 3-1. The solubility of silica and alumina as a function of pH (after Correns, 1949).
Under dry conditions, the water loss in most clays due to heating up to 300°C is generally interlayer (or absorbed) water only, and is not due to dehydroxylation (removal of OH\(^-\)) from the crystal structure. As such, the dehydration occurring with heating up to 300°C does not disrupt the clay structure, although shrinkage along the C-axis may be evident. Except for Li-montmorillonite, which will permanently dehydrate at 105-120°C, hydrated halloysite which will not rehydrate lost interlayer water, and kaolinite and chlorite which display little or no dehydration up to 400-500°C, clays will rehydrate rapidly upon cooling from 300°C, particularly if interlayer water is not completely removed in the heating cycle. In general, loss of structural water or hydroxyl ions (OH\(^-\)) will occur at a lower temperature when the clay minerals are treated hydrothermally than when heated dry because of faster reaction kinetics under hydrothermal conditions.

Differential thermal analysis (DTA) curves under dry conditions (Figure 3-2) show that smectites tend to lose considerable interlayer water at 200°C or lower, and some expulsion of structural hydroxyl ions (OH\(^-\)) may occur as low as 300°C. The rate and amount of loss of both interlayer and structural water depends on the interlayer cation to some extent, as does the ability of the clay to rehydrate (Eberl, 1978; Eberl et al., 1978). Nonetheless, the structure of the silicate framework, and the rehydration ability of most smectites (Li and possibly NH\(_4^+\) smectites, excepted) are largely unaffected at temperatures up to 300°C. Illite may lose interlayer water at or below 100°C.
Figure 3-2. Differential thermal analysis (DTA) curve for a smectite (nontronite) with quartz added as an internal standard. The magnitude and locations of peaks are characteristics of exothermic or endothermic reactions occurring at elevated temperatures.
Dehydration does not, in itself, carry an especially serious consequence for the overall application of clays to sealing. Many seals will not be subjected to temperatures significantly higher than ambient (Kelsall et al., 1982). The effect on fracture seals near waste emplacement holes, however, may require further study. Should volume reduction and cracking occur, with a concomittant increase in the permeability of the seal, aqueous fluids in contact with most dehydrated clays would rehydrate and heal the clay seal to some degree. The low permeability of the seal or backfill may be largely restored, assuming temperatures did not exceed the restorative ability of the clay. Other consequences may be worthy of further research. A dehydrated clay mass will not respond to mechanical stresses as do soft clay gels, such as those examined in past research. Similarly, the thermal properties of clay seals may be substantially changed by dehydration. The use of admixtures such as silica fume or quartz sand, which remain relatively unaffected up to 300°C, may be used to minimize any mechanical or thermal effects due to dehydration.

3.3.2.3 Phase Transformations and Reaction Rates

Although Grim's (1968) summary shows that heating of pure clay phases to 300°C during DTA causes no phase transformations and little or no breakdown of the crystal structure of clays, evidence exists that equilibrium phase transformations in clays may occur at temperatures well below 300°C when time and reactive fluids are available to overcome sluggish reaction kinetics (Weaver, 1976; 1979).
The literature on clay mineral stability is divided between laboratory synthesis experiments, where particular phases are created and destroyed under varying run conditions, and observations of natural clays undergoing diagenetic and low-grade metamorphic alteration. Hydrothermal experiments emphasize the definition of boundary conditions under which each clay mineral species is presumably most stable. The rate at which many of these reactions proceed and the mechanisms involved have received little attention, until recently.

The fact that many clay minerals undergoing diagenetic alteration do not attain an equilibrium state is apparent in many observations of metamorphosed clays. The persistence of metastable species under anticipated repository conditions requires an understanding of the kinetics of these various transformations along with simple thermodynamic, equilibrium state calculations.

Stability relationships for smectites in anticipated repository environments are viewed to be more important than those for other clay minerals because of the proposed usage of large amounts of this highly sorptive and relatively low permeability clay mineral in backfills and seals, including clay grouts for fracture sealing. Increasingly, attention is being given to the stability of smectite, and the retention of its favorable properties at elevated temperatures. At the heart of the matter is the possible transformation of smectite to a nonexpandable illite at temperatures proposed in many repository designs. The solution of this problem lies in the ability to
determine the rate of this diagenetic transformation accurately and to identify those factors that can retard the reaction rate.

Smectites are stable and pervasive phases at the earth's surface and at slightly elevated temperatures. Smectites have also been formed experimentally at higher temperatures, though equilibrium states in most cases have not been established; i.e., reaction reversibility is not documented. In these very short duration hydrothermal experiments (runs usually are less than 14 days), smectites are identified as remaining present at temperatures of 300°-400°C (Velde, 1977). With longer duration experiments, the maximum temperature at which smectites are still stable decreases significantly (Eberl and Hower, 1976). This result agrees with observations made in many low-grade diagenetic sequences that smectites which may be millions of years old begin to disappear at temperatures below 100°C.

The most frequently observed alteration of smectite clays is the incorporation of illite layers as the smectite is progressively transformed to illite through a series of intermediate steps represented by a mixed-layer illite/ smectite (I/S) clay. The progressive increase of nonexpandable illite layers in the I/S clays with increased burial depth and temperature is observed in sedimentary basins of all ages throughout the world (Perry and Hower, 1970; Weaver and Beck, 1971; van Moort, 1971; Heling, 1974; Hower et al., 1976; Srodon, 1979; Boles and Franks, 1979; Weaver, 1979). Therefore, it is of prime importance to identify the causes of the transformation of smectite to illite and to
determine whether the illitization reaction is controlled by equilibrium or kinetic considerations.

The transformation of a smectite layer to an illite layer requires an increase in the negative charge in the structure and the incorporation of potassium in the interlayer which collapses to a 10Å spacing and reversibly expels interlayer water. The increased negative charge is usually created by Al$^{3+}$ for Si$^{4+}$ substitution in the smectite tetrahedral sheet, through substitution within the octahedral sheet of Mg$^{2+}$ for Al$^{3+}$ or the reduction of Fe$^{3+}$ to Fe$^{2+}$ can also enlarge the structure's positive charge deficiency. A generalized equation for the illitization of smectite is:

\[
\text{Smectite} + \text{Al}^{3+} + \text{K}^+ \rightarrow \text{Illite} + \text{Si}^{4+} \quad (\text{Hower et al., 1976})
\]

The actual reaction is not as simple as this, for water is also released (Burst, 1969; Perry and Hower, 1970). Magnesium released to solution is also a common byproduct associated with illitization and is often correlated with the appearance at depths of authigenic chlorite (Weaver and Beck, 1971; Hower et al., 1976; Boles and Franks, 1979). The dissolution of K-feldspar and discrete illite or mica flakes which is also observed with increasing burial depths is the most probable source of the Al$^{3+}$ and K$^+$ required for illitization (Hower et al., 1976).

The observation that the percentage of illite layers in the mixed-layer I/S clay increases at greater burial depths led early investigators to
consider that temperature is the primary driving force behind the illitization process (Burst, 1969; Perry and Hower, 1970; Weaver and Beck, 1971). Contrary to early work by some Europeans, the illitization mechanism is not significantly affected by increases in pressure (Dunoyer, 1970). Pressure plays a minimal role because illitization is not simply a dehydration reaction, but rather one that includes major chemical changes in the clay structure.

A major uncertainty concerning the observed illitization of smectite is whether the reaction is controlled by equilibrium or by reaction kinetics. If the illitization reaction is controlled by equilibrium considerations, then the percentage of illite layers in the I/S mixed-layer clay is determined by prevailing temperature, pressure, and chemical conditions. The attraction of the equilibrium model is its potential for using I/S clays as a geothermometer in thermally altered shales. The kinetic argument implies that illite is an inevitable reaction product of smectite subjected to increased temperatures, and that the rate at which the end product is achieved is dependent upon those factors which affect the rate constants. These rate determining factors include temperature, thermal history of the sediment, and the presence of inhibiting ions in the interstitial fluid.

The resolution of this controversy is not readily apparent from observations of I/S clays in natural diagenetic sequences. A plot of I/S expandability against temperature reveals that from basin to basin, and sometimes within the same basin, there is a wide range in I/S clay mineral expandabilities...
at any temperature (Figure 3-3). The first occurrence of illite layers in the smectite clays occurs around 50-80°C, while expandable layers seem to persist at temperatures as high as 250°C (Weaver, 1979). The major change in I/S expandability between 90 percent to 20 percent expandable layers occurs over a fairly short temperature range, the magnitude of which is dependent upon geothermal gradient (Weaver, 1979). At a low geothermal gradient this change in I/S expandability occurs over a 70°C temperature range, while the same change in I/S clays found in high geothermal gradient areas occurs within a 40°C range. Eberl and Hower (1976) also found that the rate at which a minimum reaction temperature is attained influences illitization rates. This minimum reaction temperature is associated with the activation energy required to break bonds in the lattice, the first step in the creation of excess layer charge and subsequent collapse of the expandable layer.

The kinetic interpretation of the illitization reaction is hampered by the lack of simple, observable time dependency on I/S expandability. A plot of I/S expandabilities versus age of sediments, shows that a first-order kinetic model does not fit and that the illitization process may be more than temperature dependent (Figure 3-4). Figure 3-4 does show, however, that within the time frame of interest to repository sealing, i.e., far less than 20 million years, the first-order kinetic model fits the data reasonably well. This evidence, therefore, suggests significant collapse of smectite clay layers (30 percent collapsed) would occur at almost 10 million years at 110°C. This interpretation, however, must be tempered by the fact that reaction rates are controlled by possibly
Figure 3-3. Illite/smectite expandabilities in natural mixed-layer clays versus the temperature of the formation in which they occur.
Figure 3-4. Illite/smectite expandabilities for selected Gulf Coast shales as related to age.

REFERENCE HOWARD, 1980
several physico-chemical factors, which are largely unknown, and which may not pertain to seal environments in repository sites.

The chemistry of the interstitial fluids also plays a significant role in the rates of illitization. Within intercalated sandstones and shales buried at the same depth, with equal present-day temperatures and equal thermal history inferred from sedimentation rates, the I/S clays found in sandstone laminae are more expandable than those found in adjacent shale laminae (Howard, 1981). This may be the result of greater salinity in the sand pore waters. The presence of abundant Na⁺ and Ca²⁺ in the interlayer positions in the smectites effectively competes with K⁺ and retards the illitization reaction. Also, the greater organic acid content of shales relative to sandstones, may enhance the breakdown of potassium feldspars and increase the activity of potassium in pore water (Crossey et al., 1986). The potassium may increase illitization rates in the shale. The transformation of smectite to a nonexpandable illite is also the subject of many experimental studies. Results from this work reveal that the extent of reaction, or the percentage of illite layers intergrown in the smectite, is dependent upon temperature, duration of run, the nature of the interlayer cation, and fluid composition (Eberl and Hower, 1976; Eberl, 1978). A K-beidellite (a montmorillonite-group clay generally free of Mg or Fe in the octahedral sites) glass formed from standard Ludox gel procedures and reacted at temperatures between 250° and 400°C for up to nine months was altered to a mixed-layer illite/smectite clay. The extent of reaction as a function of time was identified on a
series of first-order-kinetic plots, so that the slopes of the various isothermal lines are equal to rate constants for the illitization reaction (Figure 3-5). An Arrhenius plot of these rate constants against the inverse of temperature also produces a straight line, the slope of which is a function of the activation energy. For a K-beidellite reacting to illite, an activation energy of 19.4 kcal/mole is obtained, large enough to suggest that breaking of Si-Al-O bonds within the lattice is a necessary step in the illitization process (Eberl and Hower, 1976). This high activation energy probably represents the energy required to break bonds in the tetrahedral layers so that Al$^{3+}$ can substitute for Si$^{4+}$ and increase the negative structural charge.

The high temperature rate constants obtained in this experimental study can be extrapolated to lower temperatures; consequently "run durations" measured in years can be obtained by means of the calculated activation energies and the first order Arrhenius equation (Figure 3-6). The rates thus obtained are significantly faster than those observed in nature, i.e., at 90°C a smectite would collapse to 20 percent expandable I/S clay in less than one million years. By contrast, the Gulf Coast Miocene sediments at 80°C have reacted only to 50 percent expandable I/S clay in 25 million years. This contradiction led the authors and may subsequent investigators to conclude that the degree of I/S expandability is determined by prevailing P-T conditions rather than the length of time the clay had to react (Eberl and Hower, 1976; Weaver, 1979).
Figure 3-5. Extent of reaction for a beidellite composition glass reacting to illite as a function of time (slope of each isotherm provides a rate constant for the illitization reaction), at 200 MPa (29,000 psi).
Figure 3-6. Relationship between temperature and the time for the illitization reaction of a beidellite composition glass calculated from experimentally determined rate constants (Figure 3-5), at 200 MPa (29,000 psi).

REFERENCE: EBERL AND HOWER, 1976
Eberl and Hower (1976) also recognize that the presence of Na\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\) in the interstitial fluids all have the effect of retarding reaction rates, which would permit their results to be consistent with either a kinetic or equilibrium interpretation. The effect of additional Na\(^+\) in the interstitial fluids on reducing the rate of silica removal from smectites illustrates the effect interstitial water chemistry can have on illitization reactions (Lahann and Robertson, 1980).

Howard and Roy (1985) performed hydrothermal alteration experiments using Na-montmorillonite and two artificial basaltic groundwaters (low K\(^+\); one with Ca\(^{2+}\), one without Ca\(^{2+}\)). Their results indicated the potential growth of nonexpandable layers may be as high as 30 percent (150°C, 180 days) to 40 percent (250°C, 180 days), if K\(^+\) is present in sufficient quantity. Other cations in solution appear to inhibit layer collapse and formation of mixed layer (illite-smectite) clay. Reaction rates measured from these experiments are faster than those extrapolated to lower temperatures based on the work of Eberl and Hower (1976).

The reasons for this result are uncertain, but may include surface-area effects. The study recognized that in low permeability seals, for example, clay mineral alteration rates may well be lower than in experimental systems where the supply and removal of constituents is relatively uninhibited.

The energy required to dehydrate the interlayer cations found in smectites is inversely correlated with rates of illitization in hydrothermal studies.
(Eberl, 1978). The dehydration energy available to a clay corresponds to the negative structural charge created by substitution within primarily the tetrahedral sheet; therefore, the low charge deficiency associated with smectites is insufficient to dehydrate any interlayer cations and the layer remains completely expanded. As the layer charge is increased by lattice substitution, cations with low dehydration energies (e.g., potassium) are dehydrated, and the layer collapses forming an illite. The presence of other alkali and alkaline earth cations with higher hydration energies in the interlayer positions requires greater layer charge deficiencies, or higher temperatures to collapse the expandable smectite layers. The implication for natural clay assemblages is that the presence of these high hydration energy cations can effectively retard any illitization reaction when compared to a smectite with $K^+$ already in the interlayer positions.

Thermodynamic calculations indicate that smectites like other clays are stable at surface conditions when compared to their component oxides in solution (Tardy and Garrels, 1974). However, when compared to free energies calculated for illite, smectite is the unstable phase at surface conditions, and at elevated temperatures. The implication is that smectites will eventually alter to illite under diagenetic conditions even though the rates at which the reaction proceeds cannot be determined from thermodynamic data.

Like illites, the variable composition of smectites results in a fairly diffuse and uncertain stability field on various activity-activity diagrams.
Smectites generally inhabit a field close to amorphous silica saturation extending over a fairly wide alkali/H$^+$ ratio (Figure 3-7).

Smectites are ubiquitous at and near the earth's surface in soil zones, on the ocean floor, as an authigenic cement in shallow-buried sandstones and shales, and even in certain hydrothermal zones. However, in many of these cases, the smectites under consideration are not pure phases, but contain a small percentage of other clay layers interstratified within the smectite packet. Closer investigation of many soil and diagenetic smectites indicates that they contain a small percentage of nonexpandable layers. The only pure smectites appear to be associated with freshly devitrified volcanic glass in recent bentonites, recent authigenic cement in very porous sandstones, and recent hydrothermal alteration products. Given enough time it is likely that even these examples would begin to incorporate other layers within the smectite clay.

At this time there is no overall kinetic expression to explain the illitization reaction; at best there are several elementary expressions which focus on individual steps, e.g., the release of Si$^{4+}$, and the diffusion of K$^+$. Despite the lack of consensus on whether illitization is a kinetic or equilibrium phenomenon, the expected response of smectite clay to the elevated temperatures anticipated in a repository is for it to partially collapse to an I/S clay. The extent of this collapse and the rate at which it does this will be dependent on whether kinetic rates or equilibrium exert the greater influence.
REFERENCE: GARRELS AND CHRIST, 1965

Figure 3-7. Stability relationship diagrams for several common low-temperature clay minerals calculated for the activity of several cations (K⁺, Na⁺, Mg²⁺, H⁺) against silica activity, at 25°C, 1 atmosphere.
In summary, therefore, the longevity of smectite clays appears to be dependent upon several factors. Smectite stability is enhanced in silica-rich environments and low temperatures. Assuming that the kinetic model is correct, and utilizing the kinetic diagrams produced by Eberl and Hower (1976), a smectite would collapse to a virtually all illite I/S clay at temperatures below 100°C within $10^4$-10$^5$ years. Note, however, that the results of Howard and Roy (1985) suggest faster reaction rates may pertain at these temperatures. The presence of interstitial fluids high in alkali and alkaline earth cations other than K$^+$, and interlayer, or exchange, cations other than K$^+$ reduce the rate and extent of illitization of smectites. The magnitude of the retarding effect of other interstitial cations in the pore fluids is uncertain at this time. For example, a first-order kinetic model appears to fit Gulf Coast data relating the extent of illitization with the age of sediments. This model predicts only about 10 percent collapsed layers would occur in smectites at 110°C at the end of $10^6$ years. Apparently, many environmental factors (heating rates, maximum temperature, and fluid chemistry) strongly affect the illitization reaction under natural circumstances and could control the stability of smectite clay minerals under repository conditions. Of concern, though, is the recognition that many of the physical and chemical properties of even a slightly illitic I/S clay may vary from those associated with a pure Na-bentonite.

3.3.2.4 Effects Due to Radiation

Incorporation of clays in seals, such as fracture seals near waste packages, that are intended to
contact and sorb long-lived radionuclides requires that the clays remain stable and functional for long time periods. The exposure of the clays to ionizing radiation, particularly the radiation from sorbed radionuclides, may also decrease their long-term stability.

A study by Haire and Beall (1979) was restricted to the morphologic effect on kaolinite and palygorskite (attapulgite) by a strong alpha radiation source* sorbed on the clays. Morphologic effects (porosity, pitting, fragmentation of plates, and clumping of rods) were evident, and the rate and severity at which they appeared were directly related to the strength of the alpha source. Clays loaded to only a small fraction of their sorptive capacity remained apparently unchanged after several weeks, but with radionuclides sorbed to capacity, the clays rapidly showed evidence of disruption. In addition, the palygorskite which has a far greater sorptive capacity, showed much greater radiation damage in a given time. An important conclusion of this work was that the sorption of Es-253, as measured from the radionuclide concentration in brine carrier fluids, remained unaffected by the disruption of the sorbent. It must be noted, however, that the sorption mechanism under these conditions was not determined. The Es may be retained on the clay, or may occur in an unknown insoluble and centrifugeable phase. The experiment provides no evidence

*Es-253, $6 \times 10^{10}$ alpha/minute-microgram or 6.6MeV alpha radiation; this alpha source is very high with respect to decay energy of individual radionuclides in waste inventories, but not large with respect to the decay energy of the entire waste inventories.
for either possibility, and the relevance of this result to other clay minerals and radionuclides is unknown.

The potential for crystallographic, and thereby behavioral changes in clays due to irradiation by sorbed sources may be estimated by exposure of clay materials to radiation from external sources. The morphological effects of an electron beam and gamma irradiation on quartz and kaolinite have been investigated (Spitsyn et al., 1980). The radiation treatment (Co-60, 2.6 Mrad gamma/hr) resulted in the formation of clumps from an initially evenly dispersed and evenly size-distributed kaolinite sample. The electron beam (accelerating voltage, $E_0 = 100$ kev, time = ?) caused surficial pitting of the kaolinite crystals, and the clay crystals became anhedral. Nonetheless, no structural changes were apparent in the X-ray diffraction of the sample. A volume increase in the surface layers of the kaolinite may have occurred due to irradiation, although the causative mechanism for this phenomenon was not determined. Krumhansl (1982) also showed no crystallographic changes occurred in smectite (from bentonite) exposed to $10^{10}$ rads of $^{60}$Co gamma radiation.

No firm conclusions can be made based upon existing data for the irradiation effects on clays. Apparently, clays are not immune to crystallographic disruption from strong radiation sources. Long-term effects due to irradiation by nuclides in a repository and the effects on the functional properties of a clay seal or backfill are currently unknown.
Other components in earthen seals. Other components of an earthen seal material may also be altered under repository conditions. Quartz, for example, is likely to occur in such materials either as an accessory mineral in bentonite or as noncohesive additive to clay-rich materials. At low temperatures and pH between 4 and 10, quartz is very stable. Increased temperatures will increase quartz solubility; however, Pusch et al. (1985), explain that temperatures up to 100°C should cause little alteration of seal materials properties due to quartz dissolution and subsequent silica precipitation upon cooling. Long-term transport of silica from a fracture seal at elevated temperatures may increase porosity in the seal. This effect on seal integrity has not been widely examined.

3.4 SUMMARY OF PROGRAM OF RESEARCH FOR PRIORITY SEAL MATERIALS

The priority seal materials have been selected because sufficient evidence has been generated to show they can be effective seal materials, and because any uncertainties they present can be surmounted through practical research programs. Sealing issues, however, require resolution before final seal designs can be devised for a nuclear waste repository.

Table 3-3 summarizes the sealing issues and a proposed approach for addressing issues for the candidate materials. The issues may be resolved through:

- Laboratory testing
- Field testing
- Analytical studies and modeling.
Table 3-3. Summary of general issues for priority grouting materials for fracture sealing

<table>
<thead>
<tr>
<th>Issue</th>
<th>Proposed Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Define materials performance requirements.</td>
<td>Perform modeling of seal performance under several release scenarios including site geology, site hydrology, site geochemistry, repository design and (in situ conditions) site performance regulatory criteria (if any) to determine seal performance requirements for hydraulic conductivity, retardation potential, performance longevity, mechanical properties. Performance requirements are site specific based on (1), select cementitious materials and additives likely to produce desirable characteristics using test data and industry literature; priority should be given to inexpensive, available materials.</td>
</tr>
<tr>
<td>(2) Select starting materials and prepare mix design(s); characterize selected materials.</td>
<td>Determine limited range in which design parameters may be varied from literature. Perform trial mixes and preliminary laboratory tests (e.g., viscosity, penetrability, bleed, strength, hydraulic conductivity); select mix(es) based on (1) for further study.</td>
</tr>
<tr>
<td>(3) Select key materials properties and determine materials performance with respect to performance with respect to performance requirements; optimize materials properties.</td>
<td>Select key properties of grout based on (1) and devise test program. Perform standard laboratory tests to evaluate properties of selected materials. Materials properties may include:</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
</tr>
<tr>
<td></td>
<td>Bleed</td>
</tr>
<tr>
<td></td>
<td>Penetrability/set time</td>
</tr>
<tr>
<td></td>
<td>Hydraulic conductivity</td>
</tr>
</tbody>
</table>
Table 3-3. Summary of general issues for priority grouting materials for fracture sealing (continued)

<table>
<thead>
<tr>
<th>Issue</th>
<th>Proposed Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3) (Continued)</td>
<td>Based on (1), establish the longevity requirements for grout performance; longevity requirements will be site-specific and probably specific to individual seals, materials, seal functions, or locations within the facility; estimate long-term compatibility to performance of grout in host environment through real-time and accelerated laboratory testing of grout materials; perform geochemical modeling, thermodynamic and kinetic calculations to estimate types and rates of materials alteration and consequences on performance; host environment includes host rock, ground water, waste, adjacent seals, backfills, waste package, temperature and pressure conditions.</td>
</tr>
<tr>
<td>(4) Establish longevity requirements for grout and determine materials performance longevity (stability).</td>
<td>Interface hydraulic conductivity Unconfined/confined compressive strength Thermal expansion Tensile strength (flexural) Shear strength/erodability</td>
</tr>
<tr>
<td>(5) Determine effects of grout material, emplacement, or alteration products on radionuclide mobility.</td>
<td>Perform laboratory solubility and sorption testing using selected grout materials, alteration products (4), and altered ground water compositions and key radionuclides or analogs.</td>
</tr>
</tbody>
</table>

SKB:135-Sec3
### Table 3-3. Summary of general issues for priority grouting materials for fracture sealing (continued)

<table>
<thead>
<tr>
<th>Issue</th>
<th>Proposed Approach</th>
</tr>
</thead>
</table>
| (6) Confirm material's emplaceability and emplacement equipment; optimize grout emplacement. | Perform field tests in test facilities comparable to repository conditions; determine:  
  - Grout delivery rates  
  - Penetration of grout as a function of grout type, equipment, nature of fracture (e.g., aperture, tortuosity, etc.); perform post-test analysis (including destructive tests) to determine:  
    - Uniformity of grout penetration  
    - Permeability of treated fractures. |
Laboratory testing may include bench scale tests. Table 3-3 lists the potential approaches that currently appear most significant. Final selection of technical approaches to issue resolution will be included in future research planning activities. Test planning will include equipment and test location selection, optional methods evaluations, and test/analysis procedure development.

The technical approach to seal materials research and the priorities for testing and analyses are individual to specific sealing programs, sites, and in situ conditions. The approach shown in Table 3-3 is generic, but notes where site specific matters are most critical; e.g., definition of seal performance requirements, definition of longevity requirements, and tests to be performed. The overall approach, however, should apply in all seal material development programs:

- Determine performance requirements of grouts
- Select materials and formulæ that appear likely to meet performance requirements, and characterize starting materials
- Select key (or priority) materials properties and determine materials performance; optimize materials performance with respect to performance requirements
- Establish longevity requirements for seal performance and determine materials longevity (stability) under in situ repository conditions
- Determine any effects of grout materials, their emplacement, or alteration products on radionuclide mobility
- Confirm materials emplaceability and emplacement equipment performance in situ and optimize grout emplacement.
3.5 EMPLACEMENT CONSIDERATIONS

Materials performance characteristics primarily dictate seal materials selection and design. In addition, emplacement considerations and emplacement methodology may also affect the design and selection of seal materials. The special requirements of grouting fine fractures in rock have been summarized by Pusch et al. (1985), Pusch (1986), Gray (1986) and references cited in those reports. This section briefly summarizes the effects of emplacement considerations on materials selection for fracture sealing. Emplacement methods are described in Section 4.

3.5.1 Cementitious Materials

In general, the grain size of particulate grouting materials must be about 0.1-0.4 the size of the aperture of the fracture to penetrate the fracture successfully (Karol, 1982b). Common cementitious grouts have been shown to penetrate into fractures only a small fraction of a meter if the fracture aperture is 0.3 mm or smaller (Pusch et al., 1985). Both the Swedish (Pusch, 1986) and the Canadian programs (Gray, 1986; Ballivy, 1986; Aitcin, 1986) are investigating the performance of finer grind cements such as reground sulphate resistant portland cements and Geochem, microfine grouting material (MC-500) that has penetration abilities similar to chemical grouts (Shimoda and Ohmori, 1982).

Expressing the fineness of cements in terms of specific surface area, as measured by the Blaine
permeameter, Gray (1986) described sulfate-resistant portland cements and expansive cements that have been reground to yield cements with finenesses of 600 to 670 m²/kg, respectively (normal value ~300 m²/kg). The influence of the finer grain size on the rheological and setting properties of cement/water mixtures (Aitcin, 1986) shows that fine-grained cements tend to have higher viscosity for a given w/c (or higher w/c is required to produce a low viscosity paste with fine-grained cements). This effect is pronounced with Geochem grouting material, but not as pronounced in finer-grained samples of Type 50 (ASTM Type V) or API Type K (expansive) cements. The w/c of the Geochem mix was about 40-60 percent higher (0.72) than in the portland cement mixes (0.45 to 0.55, without silica fume) for 12 second flow cone time. In general, the finer-grained cements tend to set (initial and final) faster than coarser grinds of the same cement based on mixes of approximately the same initial viscosity. Geochem, however, does not fit this general pattern, being slower to set than the reground portland cement materials, although it is considerably finer grained. Aitcin (1986) noted that regrinding has a tendency to cause mineral segregation because of the variable hardness of the particles.

Penetration of grouts generally increases as the viscosity of the grout decreases. In cementitious slurries, viscosity can be reduced by increasing the w/c ratio. If fluid, high w/c grouts are used, bentonite may be added to enhance the homogeneity of a cementitious grout suspension by providing a higher density fluid, and it will help to reduce bleed ("stabilization").
As described earlier, however, the w/c ratio affects several properties of the grout and should be kept as low as possible to maintain:

- Low hydraulic conductivity
- High strength
- High bond strength
- Low bleed
- Low shrinkage

Materials with w/c ratios of about 0.5 become difficult to inject in fractures finer than about 0.5 mm aperture (Pusch, 1986) using standard grouting methods because the viscosity of the paste becomes relatively high. Table 3-4, for example, shows the viscous properties of neat cement grouts as a function of w/c. Below w/c = 0.5, viscosity increases rapidly. Much thinner grouts are more commonly used in grouting practice e.g., w/c = 3 to 10, (Pusch, 1986). Studies have been completed by Lau and Crawford (1986) which show that two plasticizers, naphthalene sulphonate (NS-200) and sulphonated naphthalene formaldehyde concentrate (Lomar-D), will decrease the viscosity of rapid hardening portland cement at w/c < 0.6. The homogeneity of the mixtures is also improved. The data indicate that NS-200 and Lomar-D are required in proportions of up to 7.5 percent by dry mass of cement to be effective. Tests have been completed which show that a third, lignin-sulphonate based superplasticizer, trade name Dical, will be effective with sulfate-resistant portland cement in proportions of less than one percent by dry mass cement (Ballivy, 1986). Studies are in progress to examine the effects of this material on grouts in their fresh and cured states (Gray, 1986).
Table 3-4. Shear strength and plastic viscosity of neat cement grouts

<table>
<thead>
<tr>
<th>w/c</th>
<th>Shear Strength (dynes/cm²)</th>
<th>Plastic Viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>3840</td>
<td>4.03</td>
</tr>
<tr>
<td>0.4</td>
<td>670</td>
<td>0.90</td>
</tr>
<tr>
<td>0.5</td>
<td>230</td>
<td>0.37</td>
</tr>
<tr>
<td>0.6</td>
<td>120</td>
<td>0.20</td>
</tr>
<tr>
<td>0.7</td>
<td>70</td>
<td>0.13</td>
</tr>
<tr>
<td>1.0</td>
<td>29</td>
<td>0.06</td>
</tr>
<tr>
<td>2.0</td>
<td>10</td>
<td>0.025</td>
</tr>
<tr>
<td>5.0</td>
<td>5.3</td>
<td>0.014</td>
</tr>
<tr>
<td>10.00</td>
<td>4.3</td>
<td>0.012</td>
</tr>
<tr>
<td>20.00</td>
<td>3.9</td>
<td>0.011</td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
<td>0.010</td>
</tr>
<tr>
<td>Ref: Littlejohn, 1982</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Although lower viscosity grouts show improved penetration and rate of delivery to a fracture, as viscosity is decreased there is a well-documented tendency for the grout to flow into a fracture along irregular fingers. Low viscosity grouts tend to be unable to push water out of the fracture but to mingle with it. The void space in the fractures is poorly filled and the grouting proves ineffective. Thus, there is a practical limit to reducing the viscosity of grout as a means to penetrate saturated fractures.

3.5.2 Earthen Materials

Clay grouts generally incorporate only fine-grained particulates. The majority of the particulates are clay size unless admixtures, such as cement or silt, are present. Clay grouts and chemical grouts (pure solutions that usually contain no particulates) penetrate fractures finer than 0.3 mm more
effectively than ordinary cement grouts. Clay grouts require water contents on the same order as their liquid limits to be successfully emplaced by standard grouting technology (Pusch et al., 1985). For Na-bentonite, the water content will be about 300 wt% or more to achieve the required liquidity. Water content in excess of the liquid limit reduces viscosity of bentonite grouts and makes them easier to emplace. High water contents, however, tend to exhaust the swelling capacity of the smectites in the bentonite, and the hydraulic conductivity of the resultant fracture seals tends to be higher than in clay grout seals formulated with lower water contents. The erosion resistance of these "low density" (high water content) clay grouts is not as satisfactory as denser clay grouts because the thixotropic property (the ability to set or gel and increase in shear strength when undisturbed) of the clay grout is also diminished. The high water content limits the development of an extensive flocculated clay fabric that would tend to hold the clay particles together. Means to overcome erosion of clay grouts are discussed in Section 3.2.2

3.6 FORMULATIONS OF PRIORITY MATERIALS

Section 2.4 includes a summary of performance criteria for the materials for sealing fractured rock in a mined nuclear waste repository. Based on these criteria, priority materials were selected from among several possible materials for use in fracture sealing and described in greater detail. These materials have been selected for priority study and for use in field and laboratory tests. The priority seal materials are:
• Cementitious materials
• Earthen materials, particularly bentonite.

### 3.6.1 Cementitious Materials

Cementitious materials offer several valuable properties to repository sealing. These are:

- Low permeability
- Potential for long-term performance, if emplaced under good quality control and not exposed to environments known to degrade these materials
- High strength or, with proper mix design, a degree of flexibility.

Priority cementitious grouts include the following components:

- Portland cement or a reground portland cement or other fine-grained cement product
- Pozzolan, such as silica fume
- Plasticizer
- Expansive additive, and other additives, as necessary.

The type of cement used will depend on local conditions; e.g., if sulfate or acid conditions are present. For grouting large-aperture fractures, ordinary portland cement is expected to be serviceable. For fine aperture fractures, ultrafine-grained cements will be required. In order to produce a material with adequate hydraulic conductivity and strength, pozzolanic additives and low water:cement ratios appear necessary. Plasticizers will help reduce the viscosity of grouts formulated with low water:cement ratios. Expansive additives
will help preserve a strong, low hydraulic conductivity bond between the grout and the host rock by preventing shrinkage due to curing and drying. Other additives, such as accelerators, air entrainment additives, or clays may be required to meet specific performance or emplacement needs.

The chemical longevity of cementitious materials appears to be enhanced by the use of pozzolanic additives, low water:cement ratios, and high quality emplacement techniques that help reduce the porosity and permeability of the final material. The rate and amount of leaching from cementitious materials tends to be lower when porosity and permeability are low.

The longevity of cementitious grouts can be further assured if the emplacement environment is well-characterized and the material design is adjusted for conditions known to limit the service lifetime of portland cement-based materials. These conditions include high sulfate, acid, CO₂, or elevated temperatures. For example, poorly crystalline C-S-H phases in cementitious materials cured at low temperatures undergo phase transformations around 100°C which may increase the porosity of the material and thereby reduce the longevity of the material. This factor may be offset somewhat by the greater thermodynamic stability of C-S-H phases resulting from the transformation and possible increased strength of the material due to the transformation of C-S-H phases in the cementitious gel to more crystalline C-S-H phases or tobermorite.
The mechanical stability of cementitious materials is optimized by the use of pozzolans, high strength aggregate (if any), and low water: cement ratios. Cementitious materials can withstand the compressive stresses that are likely to occur in situ in a mined nuclear waste repository in crystalline rock and should be well-suited under these conditions. Cementitious materials and their bonds with host materials tend to be weakest under tension. Thermal or mechanical stresses that place tension across a bond in a fracture seal, for example, may cause the fracture to reopen after grouting with cementitious grout. The cement has no ability to re-heal or re-cement after fracturing. Thus, cementitious grouts appear least suitable under tensile stress.

3.6.2 Earthen Materials

Earthen materials, particularly clays are considered widely applicable, high-priority materials for repository sealing. Clays possess many favorable properties that support their priority consideration. The priority earthen materials for study as fracture sealing grouts include:

- Commercial Na-bentonite
- Bentonite with small proportions of cement and fine- and/or coarse-grained, noncohesive and noncementitious admixtures.

Na-bentonite provides several desirable properties; e.g., low hydraulic conductivity, swelling capacity and self-healing of fractures, and emplaceability. For example, a clay grout consisting of bentonite (substantially the Na form) and water, at its

SKB:135-Sec3
liquid limit (sufficient water to inject the material), achieves hydraulic conductivity of about $10^{-7} - 10^{-8}$ cm/sec (Chan, 1982; Pusch et al., 1985). Higher water content, or the Ca form may result in higher hydraulic conductivity grout. The addition of small amounts of cement or coarser grained materials may impart greater erosion resistance to the bentonite, perhaps at the sacrifice of emplaceability in the finer aperture fractures.

There appears to be little evidence that substantial alteration of the crystal structure of smectites will occur under repository conditions that do not greatly exceed 100°C or include extremely high or low pH groundwater. Cation exchange in sodium smectite is likely to occur if groundwater contains cations, such as calcium, with a strong preference relative to sodium for exchange sites. The introduction of calcium in exchange sites will increase permeability of the clay but may improve its mechanical properties, particularly with regard to erosion under high hydraulic gradients.

Clay-poor earthen materials can possess substantial confined compressive strength and the addition of substantial clay fraction may decrease the strength of the material. The addition of clay, however, imparts plasticity to the material, and, in the case of bentonite, a fracture-healing ability upon contact with water. Thus, clay-rich seals may resist the effects of in situ stresses by plastic deformation or self-healing any fractures that occur (e.g., during a desiccation period) by swelling upon the reintroduction of water (Pusch et al., 1985).
Investigations (e.g., Yong et al., 1986) have shown that other pure clay minerals (e.g., kaolinite and illite) and mixtures of clay minerals and other clay sized materials (materials such as rock flour with particle sizes of less than two microns) can possess hydraulic conductivities as low as $10^{-8}$ cm/sec and through sorption can retard the rate of radionuclide migration. The results show that montmorillonite generally sorbs radionuclides more efficiently than most other minerals. These material studies indicate that, by virtue of lower hydraulic conductivity, higher sorptive capacity for radionuclides, lower chemical diffusion coefficients, and an ability to swell, bentonite appears to be the most favored clay mineral for sealing fractured rock near a nuclear waste disposal vault.

3.6.3 Description of Likely Compositional Ranges

Table 3-5 contains a summary of the materials and compositional ranges of materials that are being studied or have been recommended for further study in participants' sealing research programs. Most data are derived from the Swedish and Canadian programs which have the most advance research programs for fractured rock sealing. Several materials in addition to those listed have been mentioned in terms of fracture sealing, particularly cements and additives for cement. The references shown in the Table include lists of these alternate materials.
Table 3-5. Compositional ranges of candidate sealing materials in current sealing programs

**CEMENTITIOUS GROUTS**

<table>
<thead>
<tr>
<th>Cement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Class A (Type I, CSA Type 10)</td>
<td>Gray, 1986</td>
</tr>
<tr>
<td>2. Class B (Type II, CSA Type 20)</td>
<td>Gray, 1986</td>
</tr>
<tr>
<td>3. Class C (Type III, CSA Type 30)</td>
<td>Gray, 1986; Roy et al., 1983</td>
</tr>
<tr>
<td>4. Class H (standard oil well cement)</td>
<td>Roy et al., 1983</td>
</tr>
<tr>
<td>5. Class K (expansive cement)</td>
<td>Gulick, 1978; Ballivy, 1986; Aitcin, 1986</td>
</tr>
<tr>
<td>6. Other sulphate resistant portland cement (Type V, CSA Type 50)</td>
<td>Gray, 1986; Ballivy, 1986; Aitcin, 1986</td>
</tr>
<tr>
<td>8. MC-500, fine grained grouting cement</td>
<td>Gray, 1986; Ballivy, 1986; Aitcin, 1986</td>
</tr>
<tr>
<td>9. Gypsum-free cement</td>
<td>Pusch, 1986</td>
</tr>
</tbody>
</table>
Table 3-5. Compositional ranges of candidate sealing materials in current sealing programs (Continued)

CEMENTITIOUS GROUTS (Continued)

<table>
<thead>
<tr>
<th>Additives</th>
<th>Proportions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pozzolans</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Silica fume</td>
<td>0-10 wt%</td>
<td>Ballivy, 1986; Aitcin, 1986</td>
</tr>
<tr>
<td>b. Silica flour (with lime)</td>
<td></td>
<td>Pusch, 1986</td>
</tr>
<tr>
<td>2. Plasticizers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Napthalene sulphonate</td>
<td>up to 7.5% by dry mass</td>
<td>Gray, 1986</td>
</tr>
<tr>
<td>b. Sulphonated napthalene formaldehyde</td>
<td>up to 7.5% by dry mass</td>
<td>Gray, 1986</td>
</tr>
<tr>
<td>c. Lignin sulphonate (Dical)</td>
<td>&lt;1% by dry mass</td>
<td>Gray, 1986; Ballivy, 1986; Aitcin, 1986</td>
</tr>
<tr>
<td>3. Accelerators (as needed)</td>
<td>1-3% by dry weight</td>
<td>Gray, 1986</td>
</tr>
<tr>
<td>CaCl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Expansive additives</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(not including Type K cement)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. aluminum powder</td>
<td>0.005 wt %</td>
<td>Ballivy, 1986; Aitcin, 1986</td>
</tr>
<tr>
<td>b. gypsum, hemihydrate</td>
<td>5-10 wt %</td>
<td>Roy et al., 1983</td>
</tr>
<tr>
<td>5. Clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Na-bentonite</td>
<td>2-5% cement weight</td>
<td>Pirhonen, 1986</td>
</tr>
<tr>
<td>b. Ca-bentonite</td>
<td></td>
<td>McCombie and Knecht, 1986</td>
</tr>
<tr>
<td>water:cement ratio</td>
<td>0.6 – 0.4</td>
<td>Pusch, 1986</td>
</tr>
<tr>
<td></td>
<td>(generally &gt;0.5)</td>
<td></td>
</tr>
</tbody>
</table>
Table 3-5. Compositional ranges of candidate sealing materials in current sealing programs
(Continued)

**EARTHEN MATERIAL GROUTS**

<table>
<thead>
<tr>
<th>PROPORTION</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Bentonite grout</td>
<td>Pusch, 1986</td>
</tr>
<tr>
<td>Na-bentonite</td>
<td>50 - 75%</td>
</tr>
<tr>
<td>Sand (~50)μm quartz</td>
<td>25 - 50%</td>
</tr>
<tr>
<td>Water</td>
<td>150 - 400% optimum (500-600% may be required)</td>
</tr>
<tr>
<td>B. Bentonite grout</td>
<td>Pusch, 1986</td>
</tr>
<tr>
<td>Na-bentonite</td>
<td>100%</td>
</tr>
<tr>
<td>Water</td>
<td>&lt;500%</td>
</tr>
<tr>
<td>C. Bentonite grout</td>
<td>Pusch, 1986</td>
</tr>
<tr>
<td>Ca-bentonite</td>
<td>100%</td>
</tr>
<tr>
<td>Water</td>
<td></td>
</tr>
</tbody>
</table>

**EARTHEN/CEMENT MIXTURE GROUTS**

<table>
<thead>
<tr>
<th>PROPORTION</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Clay-cement grout</td>
<td>Pusch et al., 1985</td>
</tr>
<tr>
<td>Commercial Na-bentonite</td>
<td>75%</td>
</tr>
<tr>
<td>Quartz filler (~50)μm</td>
<td>15%</td>
</tr>
<tr>
<td>Cement (~75)μm, low alkali</td>
<td>10%</td>
</tr>
<tr>
<td>Water</td>
<td>400%</td>
</tr>
<tr>
<td>Commercial Na- or Ca-bentonite</td>
<td>Chan, 1986</td>
</tr>
<tr>
<td>CSA Type 10 cement</td>
<td>15 - 34%</td>
</tr>
<tr>
<td>Silica fume</td>
<td>5 - 8%</td>
</tr>
<tr>
<td>Water</td>
<td>0 - 2%</td>
</tr>
<tr>
<td>B. Silt grout</td>
<td>Pusch et al., 1985</td>
</tr>
<tr>
<td>Silt</td>
<td>75 - 95%</td>
</tr>
<tr>
<td>Cement</td>
<td>0.5% by weight</td>
</tr>
<tr>
<td>Clay</td>
<td>0.2 - 0.05%</td>
</tr>
</tbody>
</table>
Table 3-5. Compositional ranges of candidate sealing materials in current sealing programs (Continued)

**CHEMICAL GROUTS**

**NOTE:** Not recommended in Canadian, Swiss, and U.S. Programs.

<table>
<thead>
<tr>
<th>A. Sodium silicate grout</th>
<th>Pusch, 1986</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynagroat (aluminate + NaOH solution)</td>
<td>2.2%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>20.0%</td>
</tr>
<tr>
<td>Water (neutral to slightly acid)</td>
<td>77.8%</td>
</tr>
</tbody>
</table>
Emplacement of seals, including materials handling and transport, and quality control of the emplaced material, will be key to the successful operation and closure of a repository. Considerations for emplacement include:

- Emplacement technology that can be used with priority sealing materials to achieve adequate seal performance
- Practical limits on emplacement technology
- Quality control of emplaced seals.

The literature related to emplacement of seals, in general, is extensive. A number of references related to general seal emplacement methods are cited by ONWI (1980) and Meyer and Howard (1983). This discussion will review research on grouting fractured or damaged rock for nuclear waste repositories. More extensive reviews of grouting technology, in general, are found in Pusch et al. (1985) and Gray (1986) and references cited in these reports.

4.1 FRACTURE SEALING METHODS

The general purpose in sealing or grouting fractures in host rock for nuclear waste repositories is to restore the bulk permeability of the host formation to a value close to its undisturbed permeability for a specified (presumably long) period of time. Grouting will require that materials possessing certain desirable characteristics will be emplaced in fractures, some of which may have very narrow apertures (0.1 mm or less).
To meet the overall goals of the grouting operation, the materials will possess low hydraulic conductivity and a high degree of chemical and physical stability in the emplaced environment. Thus, the emplacement technique must operate using selected materials (priority sealing materials), causing no additional damage to the host rock, and meeting the space, logistical, and practical limitations likely to prevail in a mined nuclear waste repository.

The fracture grouting methods that may prove useful in repository sealing include:

- Injection of grout slurry at high pressures
- Electrophoresis
- Dynamic injection.

Pressure Injection. Injection of grout slurries under pressure can be applied to both priority grout materials, cementitious and clay grouts, as well as to chemical grouts, and bitumen currently considered lower priority material groups. Usually grout is introduced into the fractures in the rock under pressure through a packed-off interval of a borehole or other opening. The grouting operation requires mixing and blending tanks, pumps, a power source, packers, and connecting hoses, valves and fittings [see Department of the Army (1973) for illustrations and descriptions].

The applied pressure is usually in the range of 0.5-2.0 MPa (Pusch, 1986). The pressure must overcome any hydraulic pressure on groundwater residing in the fracture and push the water from voids that will be filled by grout. The applied pressure provides the shear stress that forces the grout to flow through a tortuous fracture. Pressure can be increased to improve the penetration of
grouts, including coarse-grained materials. The maximum pressure that can be applied varies from site to site depending on in situ confining stresses (e.g., Pirhonen, 1986), but excess pressure will result in increasing the aperture of existing fractures or increasing the number of fractures in the rock being grouted. The probability of damaging the host rock severely limits the maximum pressure that can be applied.

**Electrophoresis.** Electrophoresis has been studied by Pusch (1978c) and Pusch et al. (1985) and may be effective in emplacing clays in fine fractures in rock. The principal of electrophoresis is to drive clays through fractures under a static electric potential. Laboratory tests proved good penetration (up to one meter) of montmorillonite through irregular fractures using electrophoresis (Pusch, 1978c). A field test (Pusch et al., 1985) proved less successful, with variable sealing of fractures. A key practical disadvantage to electrophoresis, as presently configured, may be the need to drill additional holes for electrodes which may present sealing problems of their own. Electrophoresis may be effectively applied under select circumstances but continued research appears necessary.

"Dynamic Injection". Recent reports by Pusch (1986) and Pusch et al. (1985), describe a novel injection technique named "dynamic injection" in which a constant pressure is placed on the grout slurry, not unlike ordinary pressure grouting, on which are superimposed shear waves induced by percussion. A similar technique, using ultrasonic waves, has been demonstrated in shallow environments at a quarry in Japan (Kameda, 1983). The
dynamic injection technique can be applied to
cementitious and clay grouts and is designed to
overcome the penetration limits caused by the high
viscosity of grouts that otherwise possess
desirable properties. The shear imparted to the
grout by the percussion reduces the tendency for
cementitious and clay grouts to thicken during
injection into the fracture, and helps to keep silt
size particles suspended.

The method has been laboratory and field tested.
Figure 4-1 shows the grouting operation configura­
tion of Pusch et al. (1985). These tests have
demonstrated that clay grouts containing water at
the liquid limits and possessing good thixotropic
behavior, high swelling capacity, low hydraulic
conductivity, and some degree of erosion resistance
can penetrate apertures as small as 0.1 mm several
decimeters or even meters. In the same series of
tests, cementitious grout prepared at a low
water:cement ratio (0.5) was emplaced with
penetration in excess of 0.5 m.

Pusch et al. (1985) have field tested the method
using sodium bentonite prepared at its liquid
limit. These tests, in granite at Stripa, proved
the method to be effective in sealing fractures.
As expected, however, at in situ high hydraulic
gradients, the clay grout was not effective as a
barrier to groundwater flow, probably due to
erosion.

Special Methods to Produce Effective Fracture
Seals. Special means to produce effective fracture
seals entail using emplacement techniques such as
pressure or dynamic injection with a sequence of
materials designed to overcome potential problems
currently recognized in sealing with one material
Figure 4-1. Principle for injecting rock with "dynamic injection technique".
A) percussion drilling machine, B) steel cylinder, C) slurry container, D) transducer F) valves, G) air pressure, I) borehole, 2) packer, 3) high-pressure hose, 4) valve

Pusch et al., 1985
or type of material alone. For example, Tokonami (personal communication, 1987) describes current efforts to emplace cementitious grout which would be followed by a clay (bentonite) grout in a single fracture seal. The cementitious grout provides high erosion resistance during the resaturation phase of the repository during which hydraulic gradients through fractures may be greatest. Over the long term the cementitious grouts may be chemically altered, (for example, by dissolution) and become nonfunctional, or in situ stresses may cause fracturing of the grout, particularly if tensile stresses occur. At the time when the cementitious grout becomes ineffective, hydraulic gradients will presumably be reduced to almost negligible values; i.e., following resaturation of the repository. Thus, the clay grout, with its lower erosion resistance but good hydrologic, chemical stability, plastic, and fracture healing properties, will provide long-term, effective sealing. Research in specially-designed emplacement of fracture grouts is ongoing in most of the participants' repository sealing programs.

4.2 LIMITATIONS IMPOSED BY REPOSITORY DESIGN

Several of the limitations on fracture seal emplacement have been briefly mentioned in previous sections. Other considerations that bear on the practicality and selection of emplacement methods are imposed by the repository (or test facility) design itself. These are briefly described in this section. The significance of these considerations will vary from one facility to another.

The repository design will impose limits on the available space for grouting equipment and, if
necessary, drilling equipment. This is not expected to present serious consequences on grout emplacement methods mentioned in Section 4.1. These methods have been employed in tunnels, either in industrial/civil projects or in repository sealing programs (Pusch et al., 1985). Space limitations have not affected the equipment selected, the methods utilized, or the results of the grouting operations. Subsurface drilling equipment is standard in mining and tunneling, and drilling should not be severely affected by space limitations.

Grouting operations that produce excessive heat or require high energy input present practical obstacles. Repository design incorporates ventilation and power systems, and these limit the allowable heat output and power requirements of the emplacement methods. Experience has shown these considerations have not affected grouting operations; however, extensive grouting programs have not been performed in repositories or in repository test facilities. Full-scale grouting operations will take these considerations into account.

4.3 EMPLACEMENT TEST CONSIDERATIONS

Practical issues must be identified and resolved prior to performing full-scale in situ tests of fracture sealing technology. Items to be included are:

- Selection of injection technique
- Selection of fractured rock type and location
- Selection of candidate materials for each test
A key preliminary activity will entail selection of the most suitable grout injection technique(s), and operation principles, and to construct or obtain practical equipment. Pilot tests may be employed to verify the suitability of the selected injection technique(s). Pilot tests may be followed by large scale sealing tests in waste deposition holes, fractured rock zones, and in seal zones.

The selection of suitable locations for the sealing test is of particular importance. More than one test site may be necessary to verify methods and procedures under a variety of conditions, such as underground design, in situ stress and hydrologic conditions, rock type, and the nature of the fractures. The number of repeat tests required to assure the grouting operations will result in reproducible seals and seal performance will be determined.

4.3.1 Selection of Injection Techniques

A strong emphasis of early testing is the development of effective grout techniques. Thus, conventional injection (grouting) which implies that the grout is pressed into fractures under a static pressure in the range of 0.5-2 MPa, is not sufficient to bring in cement or clay suspensions in fractures with a physical aperture that is smaller than 0.1 mm. This aperture may represent the upper end of the spectrum of fracture widths.
that will be dealt with in sealing fractures intersecting waste emplacement boreholes in high quality granitic rock. To some extent this can be solved by reducing the viscosity of the grout, but its sealing properties may thereby become insufficient.

A very promising way of improving the penetrability of cements and clays as well as other particulate materials is the "dynamic injection technique", described by Pusch et al. (1985) and summarized in Section 4.1, or the similar ultrasonic vibration method described by Kameda (1983). Both procedures are based on the principle in which vibratory motions are superimposed on the static injection pressure and each has proven effective in emplacing cementitious and clay grouts in narrow apperture openings. At this time both methods merit consideration in injection technology development.

4.3.2 Selection of Fractured Rock Type

The repository sealing program will determine which types of fractures are significant to meeting repository performance goals and determine locations for performing tests within individual facilities (candidate repository or test facility). Each program may concentrate on different grouting requirements; e.g., sealing of major water-bearing fractures intersecting waste emplacement boreholes. An example of such fractures is shown in Figure 4-2.

In addition, grouting of crushed rock zones that are intersected by repository tunnels is also of great importance if required as part of the temporary sealing to prevent severe water inflow in
Figure 4-2. Major fractures in heater hole no. 1 of the Buffer Mass Test at Stripa
the construction period or if required in permanent seal designs as part of decommissioning a nuclear waste repository. Suitable rock zones will be identified in test facilities for pilot or demonstration tests.

4.3.3 Selection of Candidate Material

The priority materials discussed in Section 3 are recommended candidates for use in individual tests. The selection of appropriate materials for each test or type of host rock/fracture must be completed as part of individual test planning efforts.

Clay grouts may be suitable for sealing fractures in the "near-field" rock intersecting waste emplacement boreholes because they may retain their flexibility and sealing functions during any temperature-induced change in aperture that the fractures may undergo in a real repository. However, the potential loss of plasticity or alteration of the clay may degrade the performance of clay seals and may require the use of alternate seal materials. In addition, clay grouts may be subject to severe erosion due to hydraulic gradients in situ. For this reason, both clay, cementitious, and a combination of these grout materials, in sequence, may be examined. For very small aperture fractures, cementitious grouts will require fine-grained cement.

Standard cementitious grouts may be most suitable for sealing fractures with wide aperture and high seepage rates. Cementitious grouts or a cement-clay sequential grouting operation may be included in crushed rock zone sealing tests.
4.3.4 Space Requirements

Two major points need to be considered regarding space requirements for performing in situ grouting tests: 1) the dimensions of the shafts and drifts available to bring in and handle the equipment for injection, and 2) the spacing and orientation of boreholes for grouting and the space requirements for installing these boreholes. For example, there appear to be two options for grouting fractures extending from heater holes. One is to drill an array of small diameter boreholes around the heater hole for injection of grout. The second option would entail injecting grout from the heater hole itself by using a special megapacker (Figure 4-3). Space requirements will not present serious constraints on the feasibility of grouting or testing grouting method options if the need for grouting is clearly recognized and test facility designs are reviewed and altered, as necessary, to be in conformance with expected space requirements.

4.4.5 Thermal Considerations

The grouting operations for all tests will most likely take place at normal rock temperatures at any test facility. The testing of the seals should also be conducted at these temperatures. Further investigations are required to determine whether the effects of the heating/cooling process on the performance of the grout emplaced around waste emplacement boreholes can be included in the test plans. A possible means of simulating the heating effects is to insert a tightly fitting heater in the sealed hole and produce a heat pulse of sufficient magnitude and duration. This would be a very valuable option for thermo-mechanical testing.
Figure 4-3. Prototype for sealing of Buffer-Mass Test heater holes. The grout is injected through the 1" tube, fills the space between the rubber sealings (R) and enters fractures which are exposed in the rock (F).
of grouts and modeling work that may be incorporated in repository development programs.

4.3.6 Monitoring of Injection Test

Documentation of the function and efficiency of the seals is, of course, fundamental. The properties or quantities that may be determined and the corresponding monitoring principles are listed below:

<table>
<thead>
<tr>
<th>QUANTITY</th>
<th>RECORDING PRINCIPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Flow of water through defined rock structure before sealing</td>
<td>Precision flow meter for recording flux of injected water</td>
</tr>
<tr>
<td>b. Flow of water through defined rock structure after sealing (also after heat pulse if possible)</td>
<td>Precision flow meter for recording flux of injected water</td>
</tr>
<tr>
<td>c. Injected amount of grout</td>
<td>Direct measurement of material retained in the grout cylinder after injection. Also special precision flow meter at the point of injection</td>
</tr>
<tr>
<td>d. Identification of grout flow passages</td>
<td>Acoustic emission or radar technique. Tracer technique</td>
</tr>
<tr>
<td>e. Fracture aperture changes in the course of grouting (also during and after heat pulse if possible)</td>
<td>Extensometers</td>
</tr>
</tbody>
</table>

---
4.3.7 Post-test Sampling Concepts

There may be valuable information to be gained by determining the location of the injected grout and its physical state after the termination of the tests. Any sampling may be designed so that the degree of homogeneity of the grout can be visualized, and so that representative specimens can be extracted for physical and chemical analysis.

The following quantities and possible means of investigating them may be of particular interest.

<table>
<thead>
<tr>
<th>QUANTITY</th>
<th>OPERATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Location and distribution of grout</td>
<td>Break-up of the rock.</td>
</tr>
<tr>
<td></td>
<td>Microscopic examination of samples</td>
</tr>
<tr>
<td>b. Homogeneity of the grout</td>
<td>Determination of water content and grain size distribution or degree of segregation using standard lab procedures</td>
</tr>
<tr>
<td>c. Grout-rock interface and interaction</td>
<td>Break-up of the rock.</td>
</tr>
<tr>
<td></td>
<td>Microscopic examination of samples</td>
</tr>
</tbody>
</table>

Nondestructive methods to test grouting quality may be included, if available, prior to destructive sampling for comparison and evaluation of the validity of the nondestructive techniques.
5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The principal conclusions of the state-of-the-art report on fracture sealing for mined nuclear waste repositories, particularly those sited in crystalline (i.e., granitic) rock are:

- Seals, including fracture seals, may be used to limit groundwater flow into and away from a nuclear waste repository and to limit the release of radionuclides that may be transported by groundwater movement.

- Seals, if required to achieve repository performance or desirable from a performance standpoint, should have as long service life as possible; the primary means to assure long-term sealing functions is to assure long-term stability of the materials selected for sealing.

- Seal materials selection and seal design will depend on quantitative sealing criteria; these criteria have not been established and probably cannot be established generically; each repository will have different sealing criteria and individually selected seal materials and designs.

- In light of the above, however, the priority fracture seal materials, i.e., bentonite grouts and cementitious grouts and their mixtures, will probably be widely applicable and will meet sealing requirements that may be imposed by any of the participants' repository programs.

5.2 RECOMMENDATIONS

Based on the state-of-the-art of fractured rock sealing presented by the participants,
recommendations for research, conceptual development, and outstanding issues resolution are:

- Establish sealing criteria for fracture seals; these will provide an "index" by which materials and emplacement methods, as well as trial grouting operations can be evaluated.

- Continue research directed toward improved grout penetration and grouting efficiency, including study of new products, grain size gradation effects, and fracture pretreatment.

- Continue research on materials longevity under repository conditions; cementitious materials present the greatest uncertainties with respect to longevity and should be considered with priority; emphasis must be placed on the compatibility between seal materials and seal degradation occurring because of the juxtaposition of different sealing materials.

- Consider dynamic injection a priority emplacement technique because of its effectiveness and applicability to both priority materials groups; continued research should include equipment development and its effects on host rock integrity, permeability, etc.

- Develop nondestructive seal quality control procedures to test the efficacy of a grouting operation and the penetration of grout in fractures.
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GLOSSARY OF TERMS RELATING TO GROUTING
(API, 1969; Meyer and Howard, 1983; Gray, 1986)

Absorption - The assimilation of fluids into interstices.

Accelerator - A material which increases the rate at which chemical reactions occur; materials that shorten the gel time or set time of and increase the early strength of grouts or cementitious materials.

Activator - A material which causes a catalyst to begin its function.

Additive - Any material other than the basic components of a grout system; in cementitious systems refers to materials other than cement and water added after manufacture of the cement to modify its properties.

Adhesion - Bond strength between unlike materials.

Adsorption - The attachment of water molecules or ions to the surface of particles.

Aggregate - As a grouting material, relatively inert granular material, such as sand, gravel, slag, crushed stone, etc. "Fine aggregate" is material that will pass a 0.25 inch screen; "coarse aggregate" is material that will not pass a 0.25 inch screen. Aggregate is mixed with a cementing agent (such as portland cement and water) to form a grout material.

Alkali Aggregate Reaction - A chemical reaction between Na₂O and K₂O in the cement and certain silicate minerals in the cement and certain silicate minerals in the aggregate, which causes expansion resulting in weakening and cracking of portland cement grout. See Reactive Aggregate.
Base - Main component in a grout system.

Batch - Quantity of grout mixed at one time.

Bearing Capacity - The maximum stress a soil or rock will support without excessive settlement or failure.

Bentonite - A clay derived from the alteration and devitrification of sialic volcanic glasses composed principally of clay minerals of the montmorillonite group, characterized by high absorption and a very large volume change with setting or drying; typically, containing small portions of quartz and other silicates, calcite, and gypsum.

Binder - Anything which causes cohesion in loosely assembled substances, such as clay or cement.

Blaine Fineness - The fineness of powdered materials such as cement and pozzolans, expressed as surface area usually in square centimeters per gram.

Bleed - The free water released from newly placed grout.

Bleeding - (water gain) The autogeneous flow of mixing water within, or its separation from newly placed grout caused by the settling of the solid materials within the mass.

Bleeding Rate - The rate at which water is released from grout by bleeding.

Bond Strength - Resistance to separation of set grout from other materials with which it is in contact; a collective expression for all forces such as adhesion, friction, and longitudinal shear.
Catalyst - A material which initiates or enhances a chemical reaction.

Catalyst System - Those materials which, in combination, cause chemical reactions to begin. Catalyst systems normally consist of an initiator (catalyst) and an activator.

Cation - An ion that moves, or would move toward a cathode; hence nearly always synonymous with positive ion.

Cation Exchange (Capacity) - Ability for loosely bonded cations in a solid, crystal or reactive substrate to be replaced by cations in an associated solution; the mass of a given cation that can be taken up by a material by cation exchange or the equivalents of cations that can be taken up by a material by cation exchange.

Cement - Powdered clinker, formed by heating siliceous calcium carbonate that is interground with gypsum, available in several types or classes providing different properties; a plastic paste formed by mixing powdered cement with water with or without additives; the act of emplacing a cementitious material.

Chemical Grout - Any grouting material characterized by being a pure solution; no particles in suspension, (cf., Particulate Grout).

Chemical Grout System - Any mixture of materials used for grouting purposes in which all elements of the system are pure solutions (no particles in suspension).

Clay - Common usage in engineering and soil science, refers to any fine-grained (predominantly less than 0.002 mm), earthen, more-or-less plastic material containing a substantial proportion of clay minerals.
Clay Mineral - Usually fine-grained, hydrous aluminio or magnesium silicates with a platy or fibrous habit due to regular interlayers of octahedrally or tetrahedrally coordinated cations. Clays frequently absorb water and usually display compositional variability due to cation substitution and ion exchange. The layer charge on clay sheets is lower than in micas, frequently permitting ion substitution and expansion of the interlayer spacing. Heating tends to drive off adsorbed or interlayer water. Clay minerals are often found in fine-grained aggregates, which are plastic upon addition of water. Fibrous clays are less common than platy clays.

Cohesion - Shearing resistance of a soil mass relatively independent of soil loads.

Colloid - A substance composed of particles so finely divided that they do not settle out of a suspension. True colloid range from 5 to 800 millimicrometers in size.

Colloidal Grout - A grout in which the dispersed solid particles remain in suspension (colloids).

Concrete - A cementitious material usually emplaced as a slurry consisting of cementitious binder and relatively inert fine aggregate, and coarse aggregate.

Concrete, Preplaced Aggregate - Concrete produced by placing coarse aggregate in a form and then injecting a portland cement-sand or resin grout to fill the interstices.

Consistency - The relative mobility or ability of freshly mixed mortar or grout to flow; the usual measurements are slump for stiff mixtures and flow for more fluid grouts.
Core - A cylindrical sample of hardened grout, concrete, rock or grouted deposits, usually obtained by means of a core drill.

Creep - Time-dependent plastic or viscoelastic deformation due to load.

Cure - The enhancement of properties of a grout, with time by controlling conditions (temperature, humidity, etc.) after mixing and emplacement.

Cure Time - The interval between combining all grout ingredients or the formation of a gel and development of a substantial proportion (~90 percent) its optimum properties, such as strength; in cementitious systems, the period after mixing during which moisture is strictly controlled and minimized.

Deformability - A measure of the change in shape or volume of a material under stress.

Direct Shear Test - A shear test in which soil under an applied normal load is stressed to failure by moving one section of the soil container (shear box) relative to the other section.

Dispersing Agent - An additive which promotes dispersion of particulate grout ingredients by reduction of inter-particle attraction.

Drill - A machine or piece of equipment designed to penetrate earth and/or rock formations.

Elastic Modulus - See Young's Modulus.
Elasticity - The property of a material to return to its original size and shape when load is removed after being deformed.

Emulsifier - A substance which modifies the surface tension of colloidal droplets, keeping them from coalescing, and keeping them suspended.

Emulsion - A system containing dispersed colloidal droplets.

Endothermic - Pertaining to a reaction which occurs with the absorption of heat.

Epoxy - A multi-component resin grout which usually provides very high, tensile, compressive and bond strengths.

Exchangable Cation - In clays, a monovalent or divalent cation which is electrostatically bound between weakly negative charged aluminosilicate sheets, and which can be substituted by other cations dissolved in associated fluids under certain physiochemical conditions. The cation exchange capacity of a clay is a measure of the ability of a clay to substitute its cations, and is usually measured in milliequivalents per unit mass of clay.

Exothermic - Pertaining to a reaction which occurs with the evolution of heat.

Expansive Cement - A cement designed to increase in volume or have minimal volume loss during cure (also shrinkage-compensating cement).

Extender - An additive whose primary purpose is to increase total grout bulk or volume.

Fineness - A measure of particle-size distribution.
Flow Cone - A device for measurement of grout consistency in which a predetermined volume of grout is permitted to escape through a precisely sized orifice, the time of efflux (flow factor) being used as the indication of consistency.

Fluidifier - An additive employed in grout to increase flowability without changing water content (also plasticizer, superplasticizer, water reducer, high-level water reducer).

Fly Ash - The finely divided residue resulting from the combustion of ground or powdered coal and which is transported from the firebox through the boiler by flue gases; used as a pozzolanic (q.v.) additive in portland cement based materials.

Fracture - A break or crack in a rock mass, regardless of size, aperture, condition or orientation.

Gel - The condition where a liquid grout begins to exhibit measurable shear strength.

Gel Time - The measured time interval between the mixing of a grout system and the formation of a gel.

Grout - In soil and rock grouting, a material injected into a soil or rock formation to change the physical characteristics of the formation, such as permeability or strength.

Groutability - The ability of a formation to accept grout.

Grout Mix - The constituents of a grout; e.g., for a neat cement grout, the volume ratio of water to dry cement. The cement portion is customarily taken as being unity. Thus a 5:1 mix would contain five cubic feet of water for each sack (cubic foot) of dry cement.
Grout Take - The measured quantity of grout injected into a unit volume of formation, or a unit length of grout hole.

Hardener - In a two component epoxy or resin, the chemical component which causes the base component to cure.

Heat of Hydration - Heat evolved by exothermic (q.v.) chemical reactions with water, such as that evolved during the setting and hardening of portland cement.

High Alumina Cement - Material in which monocalcium aluminate is the primary cementitious constituent that, when mixed with water, forms refractory material that resists thermal shock and wide temperature changes; generally applicable in conditions that experience wide thermal cycles and conditions above 300°C.

Hydration - Formation of a compound by combining water with some other substance.

Hydraulic Cement - A material whose cementitious properties are activated by the addition of water.

Hydraulic Conductivity - A measure of the ability of a soil to transmit water flow, numerically equal to the gross velocity of flow (or flow volume per unit time per area) divided by the hydraulic gradient. Its units are velocity, commonly centimeters per second.

Hydrostatic Head - The height of water which would exist above a given point due to water fluid pressure.

Illite - Dioctahedral (rarer trioctahedral), monoclinic clay mineral group, in which clay sheets or layers of octahedrally coordinated cations (Al^{3+}, usually) sandwiched
between SiO$_4$ tetrahedra linked in hexagonal networks. Like muscovite, illites contain interlayer potassium ions, although in illite these are coordinated to relatively weakly negatively charged clay layers. The presence of the bound interlayer potassium ions prevents significant expansion of the crystal structure and ion exchange capacity in illites. Illites dominate in sedimentary formations and hydrothermal environments. They may occur due to alteration of clays during diagenesis. Illite formation is favored by alkaline conditions when aluminum and potassium are available.

Inert - Not participating in any fashion in chemical reactions.

Inhibitor - A material which stops or slows a chemical reaction from occurring.

Injectability - See Grourability.

In Situ - Applied to a rock or soil when occurring in the situation in which it is naturally formed or deposited; in repository sealing, refers to seal zone conditions, including geologic, geochemical, stress and thermal conditions during the operations period through the performance lifetime requirement of seals.

Interstitial - Occurring between the grains or in the pores in rock or soil.

Joint - A fracture or parting in a rock mass. Joints usually occur in sets with common orientation or in regular patterns. The term also refers to a single length, or to the juncture between two connected lengths of casing, drill rod, or grout pipe.
Kaolinite - Triclinic or monoclinic dioctahedral clay, usually white in color, occurring in massive aggregates; each clay sheet is composed of gibbsite-like sheets composed of aluminum octahedrally coordinated with oxygen and (OH)\(^{-}\) ions coordinated with Si\(_4\)O\(_{10}\) tetrahedra in a hexagonal array.

The chemistry of kaolinite \([\{Al_4(Si_4O_{10})(OH)_8\}\]\) shows little variation. There is little ion substitution in the clay structure. There is little or no layer charge on clay sheets, but kaolinite does not swell upon application of water, or have a large cation exchange capacity, as many other clay minerals do. Kaolinite occurs as a hydrothermal alteration or weathering product of feldspar and other silicates. Its occurrence appears to be favored by alteration of siliceous rocks under acid (or nonalkaline) conditions (Grim, 1953; Deer et al., 1966). Polymorphs include dickite and nacrite. Halloysite is a hydrated form which displays swelling properties and a significant ion-exchange capacity.

Liquid Limit - The minimum water content of a soil or clay in weight percent of the solids, at which the shear strength of the material is very small and the material behaves as a liquid; one of the Atterberg limits (see PLASTIC LIMIT).

Liquefaction - Instantaneous formation of "quick" (fluid) conditions due to shock loading (seismic, explosives, etc.).

Matrix - A material in which particles are embedded, i.e., the cement paste in which the fine aggregate particles of a grout are embedded.

Mixed-Layer Clays - Clays which contain usually two different minerals which are randomly or regularly interstratified. The properties and behavior of mixed layer clays generally reflect the constituent minerals and their relative proportions. Mixed layer clays occur due to
diagenetic effects or hydrothermal reactions. Illite-smectite, kaolinite-smectite, and chlorite-smectite commonly occur in mixed layers.

Moisture Content - Also called water content. The ratio, expressed as a percentage, of the weight of water in a given soil mass to the weight of solid particles.

Neat Cement Grout - A mixture of hydraulic cement and water without any added aggregate or filler materials; may or may not contain additives.

Newtonian Fluid - A fluid in which viscosity is not a function of the rate of shear.

Packer - A device inserted into a hole in which grout is to be injected which acts to isolate a particular interval in the hole and prevent return of the grout around the injection pipe; usually an expandable device actuated mechanically, hydraulically, or pneumatically.

Particle-Size Distribution - The distribution by weight of particles or granular material among various sizes; usually expressed in terms of cumulative percentages larger or smaller than each of a series of diameters (sieve openings) or the percentages between certain ranges of diameters (sieve openings).

Particulate Grout - Any grouting material characterized by having undissolved (insoluble) particles in suspension (cf., Chemical Grout).

Penetrability - A grout property descriptive of its ability to fill a porous mass. Primarily a function of lubricity and viscosity.
Permeability - An intrinsic property of a porous medium which is an index of the rate at which a liquid can flow through the pores, measured in darcys (dimension \( L^2 \)).

\( \text{pH} \) - A measure of hydrogen ion activity in a solution. A \( \text{pH} \) of 7 indicates a neutral solution such as pure water. A \( \text{pH} \) of less than 7 indicates acidity and a \( \text{pH} \) of greater than 7 indicates alkalinity.

Plastic Limit - The minimum water content at which a clay or soil exhibits plasticity; one of the Atterberg limits (see Liquid Limit).

Plasticizer - A material that increases plasticity and reduces viscosity of a grout, cement paste, or mortar without addition of water (syn. fluidifier superplasticizer, water reducer, high-level water reducer).

Porosity - The ratio of the volume of voids in a material to the total volume of the material including the voids, usually expressed as a percentage.

Portland Cement - A hydraulic cement based on calcium silicates, calcium aluminates and ferrites that are combined with calcium sulfate in manufacture.

Pozzolan - A siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Proprietary - Made and marketed by one having the exclusive right to manufacture and sell; privately owned and managed; frequently entailing components or formulii that are privately held.
Pumpability - A measure of the properties of a particular grout mix to be pumped as controlled by the equipment being used, the formation being injected, and the engineering objective limitations.

Reactant - A material which reacts chemically with the base component of a grout system.

Reactive Aggregate - An aggregate containing siliceous material (usually in amorphous or crypto-crystalline state) which will react chemically with free alkali in the cement. Usually results in expansion of the hardened material, frequently of damaging extent.

Refusal - When the rate of grout take is low, or zero, at a given pressure.

Resin - A material which usually constitutes the base of an organic grout system.

Resin Grout - A grout system composed of essentially resinous materials such as epoxys, polyesters, and urethanes. (In Europe, refers to any chemical grout system regardless of chemical origin.)

Retarder - A material which slows the rate at which chemical reactions occur.

Sand - Specifically, soil particles with a grain size ranging from 0.076 mm to 2.0 mm. Loosely, fine aggregate component of grout - may include particle finer than 0.053 mm; consist chiefly of quartz of other silicates, but may include carbonates and rock fragments.
Segregation - The differential concentration of the components of mixed grout, resulting in nonuniform proportions in the mass.

Self-Stressing Grout - Expansive-cement grout in which the expansion induces compressive stress in grout if the expansion movement is restrained.

Set - The condition reached by a cement paste, or grout when it has lost plasticity to an arbitrary degree, usually measured in terms of resistance to penetration or deformation; initial set refers to first stiffening; final set refers to an attainment of significant rigidity.

Setting Shrinkage - A reduction in volume of grout prior to the final set of cement caused by bleeding, by the decrease in volume due to the chemical combination of water with cement, or by syneresis.

Set Time - A term defining (1) the hardening time of portland cement or (2) the gel time for a chemical grout.

Shrinkage-Compensating - A characteristic of grout made using an expansive cement in which volume increase, if restrained, induces compressive stresses which are intended to offset the tendency of drying shrinkage to induce tensile stresses. See Self-Stressing Grout.

Silt - Soil particles with grains in the range from 5 to 53 micrometers.

Slump - A measure of consistency of freshly mixed concrete or grout.

Slurry Grout - A fluid mixture of solids such as cement, sand, or clays in water.
Slurry Trench - A trench which is kept filled with a bentonite slurry during the excavation process to stabilize the walls of the trench.

Smectite (Montmorillonite Group) - Monoclinic dioctahedral and trioctahedral clays. Principal dioctahedral smectites include montmorillonite (commonly $\frac{1}{2}(\text{Ca}, \text{Na})_{0.7}(\text{Al}, \text{Mg}, \text{Fe})_4 (\text{SiAl})_8 (\text{OH})_4 \times n\text{H}_2\text{O}$), beidellite (an aluminous $\text{VIAl}^{+3}$ and $\text{IVAl}^{+3}$) montmorillonite) and nontronite (a ferric iron-rich $\text{IVFe}^{+3}$ montmorillonite). Trioctahedral smectites include $\frac{1}{2}(\text{Ca}, \text{Na})_{0.7}(\text{Mg}, \text{Fe})_6 (\text{SiAl})_8 (\text{OH})_4 \times \text{H}_2\text{O}$, hectorite (a $\text{VILi}^+$ - rich saponite), and sauconite (a $\text{VIZn}^{+2}$ - rich saponite). All are so-called swelling clays, whose crystal structures expand to admit water and organic liquids. All have significant ion exchange capacities. Because the interlayer cation is frequently substituted, smectites may carry H, Li, Be, Mg, K, Rb, Sr, Cs, and Ba ions as well as Na$^+$ and Ca$^{2+}$ in the interlayer sites. There is a small anionic charge on the clay layers which is balanced by the interlayer cations. Water and organic liquids are readily absorbed between layers, the quantity of which is influenced somewhat by the interlayer cation species. Smectites occur as weathering and hydrothermal alteration products of acidic ash (bentonite). Calcium montmorillonite is more common than the sodic form. Smectites occur in hydrothermal assemblages also. The availability of Mg and Ca and alkaline conditions, and the absence of K during weathering of basic igneous rocks also favor smectite formation.

Sorption - The major emphasis in this report is upon radionuclide sorption. Common usage indicates sorption as any mechanism by which a solid (sorber or sorbent) removes species from associated fluids (liquids or gases). Mechanisms may include absorption, adsorption, ion exchange,
chemical reactions (precipitation), and filtration. This common usage arose because the effects of individual mechanisms have not been regularly studied in experiments regarding radionuclide-clay interaction.

Sulfate Resistance - Ability of portland cement-based materials to resist chemical attack by solution or soils high in dissolved sulfate; common aggressive sulphates are those of Na, Mg and, to a lesser extent, Ca; generally results in production of calciumsulfoaluminate ("ettringite") and other expansive phases that can result in disintegration of the emplaced material. Sulfate resistance is enhanced by decreasing calcium and aluminate content of the cement [C₃A (3CaO-Al₂O₃), and C₃S (3CaO-SiO₂) compounds], use of pozzolanic additives, and use of low water:cement ratios in mix, air entrainment, and avoidance of CaCl₂ additive as an accelerator.

Suspension - A mixture of liquid and solid materials.

Suspension Agent - An additive which decreases the settlement rate of particles in liquid.

Syneresis - The exudation of liquid (generally water) from a set gel which is not stressed, due to the tightening of the grout material structure.

Take - See Grout Take.

Toxic - A poisonous material

True Solution - One in which the components are 100 percent dissolved in the base solvent.

Ultra Fine Grouting Material - Cementitious material with a mean grain diameter of 4 micrometers and a maximum grain diameter of 10 micrometers.
Unconfined Compressive Strength - The force per unit area at which an unconfined prismatic or cylindrical specimen of material will fail in a simple compression test without lateral support (syn., uniaxial compressive strength).

Viscosity - The internal fluid resistance of a substance which makes it resist a tendency to flow under shear stress.

Void Ratio - The ratio of the volume of voids divided by the volume of solids in a given volume of soil or rock.

Waste Disposal Holes - Large diameter boreholes drilled into the floor or ribs (walls) of waste disposal rooms in a mined nuclear waste repository; designed to accept the waste, canisters, overpacks, containers, other buffers and materials including the waste package.

Water-Cement Ratio - The ratio of the weight of water to the weight of portland cement in a cement grout or concrete mix. See GROUT MIX.

Water Gain - See Bleeding.

Young's Modulus - Also called elastic modulus. The ratio of axial stress on a test specimen required to produce a unit of axial strain; limited to materials having a linear stress-strain relationship over the range of loading.
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