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CONTROL TECHNOLOGY FOR IN-SITU OIL-SHALE RETORTS

P. Persoff and J.P. Fox

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CONTENTS

PREFACE

This is the final report of a four-year project conducted at Lawrence Berkeley Laboratory and the University of California at Berkeley from 1978 to 1982 to identify and evaluate environmental control technology for abandoned in-situ oil shale retorts. In this report, various candidate control technologies are considered and compared with respect to their potential ability to mitigate groundwater pollution from in-situ oil shale retorting. The project was terminated prematurely in response to a shift in national energy priorities, and considerable additional experimental and numerical work is required to evaluate these technologies satisfactorily. Therefore, important areas for future research are indicated, as appropriate.

Contributions were made by experts from several technical fields because of the interdisciplinary nature of the problem. A list of presentations, papers, and reports resulting from this project is given in Appendix A. Most of these are summarized briefly in this report, and the reader who needs more detail is referred to these publications, all of which are available from the Technical Information Department of Lawrence Berkeley Laboratory (telephone [415] 486-6782; FTS 451-6782).

ACKNOWLEDGMENTS

A problem as varied as this one could only be approached with contributions from experts in several fields. Appreciation is expressed to the following colleagues who have contributed their talents to this project:

Prof. Richard Goodman supervised the structural modeling work and the testing of experimental grouts. Joe L. Ratigan modeled subsidence over modified in-situ (MIS) retorts. Jess Albino and Glenn Boyce tested the grouts and the simulated grouted cores.

Prof. P.K. Mehta directed experimental work to enhance cementing in spent shale and to evaluate waste materials as grout ingredients. Ellis Cha and Eric Ko prepared the grout samples and tested spent shales for cementing properties. Prof. Milos Polivka offered valuable suggestions for the formulation of grouts.

William G. Hall and Gary L. Amy derived and verified mathematical models of spent shale leaching under the direction of Profs. Robert E. Selleck and Jerome F. Thomas.

Under the direction of Dr. T.N. Narasimhan, Neil Thomsen conducted experiments to determine the factors that limit penetration of spent shale grout through rubble, and Dr. Mohsen Mehran developed the numerical model of dewatering and reinvasion of abandoned retorts.

Dr. Christian G. Daughton critically reviewed this report and made helpful suggestions during its preparation.

ABSTRACT

The object of this study was to evaluate control technologies for groundwater pollution resulting from leaching of modified in-situ spent shale. Preliminary engineering analysis was used to identify control technologies which were technically feasible and cost-effective. Process modification, intentional leaching, and retort grouting were further evaluated using numerical modeling and experimental techniques.

Numerical simulation of the geohydrology at tracts C-a and C-b was used to determine the flow regime during and after processing, the amount of water available from dewatering, and the time scale of groundwater reinvasion. It was found that reinvasion would take over 200 years and that dewatering flows would probably be insufficient to satisfy water requirements for retort grouting.

The formulation of low-cost grouts based on surface-retorted spent shale was studied experimentally. A high-strength hydraulic cement was produced by calcining Lurgi spent shale with an equal amount of $CaCO_3$ at 1000 C for 1 hr. Heating Paraho or Lurgi spent shale at lower temperatures without added $CaCO_3$ enhanced setting properties but did not produce true hydraulic cements. Other low-cost grouts were developed using fly ash and gypsum. The permeability of these grouts varied with confining pressure and ranged as low as 4×10^{-7} cm/sec. Electrical conductivity measurements indicated that the leachate from a grouted retort would be more concentrated than that from an ungrouted retort, but the increase in concentration would be more than offset by the reduction in flow.

A standard flow-cone test used for grouting of preplaced aggregate concrete was used as the criterion for grout fluidity. This criterion was achieved by inclusion of either 33 percent sand or 0.25 percent lignosulfonate fluidizer in the grout. These grouts were found to be Casson fluids with yield stress values about 60 $dyne/cm^2$.

Intentional leaching of MIS retorts was evaluated by developing a mass-transfer model of the leaching process. The model was experimentally verified for total organic carbon and used to calculate that 2.1 to 3.4 pore volumes would be needed to reduce leachate concentrations to 10 percent of their initial value.

SUMMARY

Modified in-situ (MIS) oil shale retorting would result in degradation of groundwater quality if reinvading groundwaters were to leach the in-situ retorted shale. The objective of this work was to quantify the problem of groundwater pollution and to evaluate technologies for its control. This was accomplished by a review of the literature of allied fields (oil shale mineralogy and leaching, cement chemistry, construction grouting, Piceance Basin geohydrology), by numerical modeling, by experimental studies, and by engineering assessments of individual control technologies.

Numerical simulation of dewatering and reinvasion for a typical location showed that reinvasion would take over 200 years. Leachate transport away from the abandoned retorts would not occur during this time. At completion of reinvasion, flow through the retorts would transport leached solutes in aquifers toward surface streams. Transport to surface streams would take 130 to 1450 years after completion of reinvasion, depending upon location.

Based on reported experimental studies using actual and simulated MIS spent shale, the leachate would be alkaline and contain high concentrations of TDS, B, F, Pb, Se, V, phenols, and organic nitrogen, compared to existing groundwater quality. Affected groundwaters would have essentially the same composition as the leachate, but the concentrations in surface waters would be reduced by dilution.

The severity and extent of groundwater impacts would depend upon site-specific and process-specific factors. If local geohydrologic conditions are favorable, leachate transport could be reduced by low permeability of surrounding media.

The composition of leachate also would be affected by retort operating conditions. Review of the literature indicated that the most favorable conditions for leachate quality include retorting in an air-steam atmosphere with combustion of char, no use of recycle gas, and long residence time at high temperature to promote the formation of the silicate minerals in the diopside-augite series. Although these operating conditions are favorable, they are not sufficient to reduce all leachate constituents to safe levels. That these conditions can be achieved uniformly throughout a retort also has not been demonstrated.

Backfilling abandoned retorts with a grout based on surface-retorted shale appeared to be a technically feasible method to reduce the transport of leachate substantially. Grouting would require 200 to 270 gallons of water per barrel of oil recovered by MIS retorting. Candidate grouts based on Lurgi spent shale were prepared and tested for permeability and structural properties. These grouts are non-Newtonian fluids, with yield strengths of about 60 dyne/cm^2. Adequate fluidity is necessary to fill the entire retort from a small number of grout injection holes. This was achieved by inclusion of 0.25 percent lignosulfonate fluidizer in the grout. Addition of 10 percent fly ash or fly ash-gypsum cement increased the elastic modulus (stiffness) of the grout, but not sufficiently to allow the grouted retort to support the overburden and thus allow enhanced resource recovery. Permeability of grouts was measured by saturating the samples, placing them under confining pressure, and measuring the flow of water resulting from an

applied hydraulic gradient against a back pressure. Permeability of the grouts tested varied with confining pressure; permeabilities as low as 4×10^{-7} cm/sec were measured. Leachate from a grouted retort would be more concentrated than leachate from an ungrouted retort, because the grout, as well as the in-situ spent shale, would be available for leaching. However, electrical conductivity data for the leachates generated during permeability measurements indicate that the increase in concentration would be too small to offset the benefit of reduced flow through retorts.

Another proposed control technology is to intentionally leach the retorts, and treat the leachate for reuse. This would require at least 60 to 120 gallons of water per barrel of MIS oil recovered. This strategy would be effective for solutes which are mass-transfer-controlled, but not for solutes which are solubility-controlled. A mathematical model of mass-transfer-controlled leaching was verified for organic carbon. Some inorganic solutes, however, have been reported to be solubility-controlled, and the mechanism controlling concentrations of other inorganic solutes is not clear. Assuming that a treatment process for leachate can be demonstrated, it was found that treatment of 2.1 to 3.4 pore volumes of leachate appears to be adequate to reduce the concentration of total organic carbon in leachate to 10 percent of its initial value. Additional work is required to validate this technology for other solutes.

CHAPTER 1. INTRODUCTION

1.1 Oil Shale as a Fossil Energy Resource

Oil Shale of the western United States is a fine-grained, sedimentary marlstone containing up to 30 percent or more of a high-molecular-weight polymer called kerogen. The process of converting the solid kerogen to a liquid fuel similar to crude oil is called retorting, described below. For more detail on the nature of oil shale and retorting technology, refer to Yen (1976) or Sladek (1974-75).

The reasons for current interest in oil shale are that it produces a high quality middle distillate for transportation fuels, and the United States has the richest known reserves of oil shale. The H-C ratio of shale oil is much higher than that of coal-derived liquids, making it more valuable as a source of transportation fuels. The Green River Formation in Colorado, Wyoming, and Utah contains an estimated 1.8 trillion barrels of oil, of which an estimated 80 billion barrels can be recovered with current technology (Sladek, 1974-75).

1.2 Retorting Technology

Petroleum is believed to be formed by the degradation of kerogen under pressure and heat over geologic time. Retorting quickly accomplishes a similar oil production by the action of heat. Basically, retorting consists of anoxic heating of raw oil shale to a temperature of 450 C or higher. The shale oil emerges as a vapor or mist. The source of heat may be external or internal with respect to the retort. Hot gas may be passed through a packed bed of raw shale to raise it to the required temperature, or hot solids may contact a moving bed of raw shale. Alternatively, the residual carbon remaining on the shale after pyrolysis can be burned within the retort to produce heat.

Several technologies have been developed to retort raw shale and recover shale oil. It is convenient to divide them into surface and in-situ technologies. With surface retorting, the shale is mined, brought to the surface, and pyrolyzed in a vessel called a retort. For in-situ retorting, the oil shale is heated in its original underground formation after creating porosity and permeability to allow gas transport.

This report focuses on modified in-situ (MIS) technology. For MIS retorting, an underground retort is first prepared by mining out a fraction of the raw shale and then blasting the remainder into the mined-out void. Ideally, the raw shale remaining in the retort is broken into a uniform particle size, and the void space is distributed uniformly throughout the retort. Experimental MIS retorts have used void fractions of between 19 and 40 percent. Optimal conditions include a particle size of about 4 in. and uniform permeability so that gases flowing through the retort do not channel. The present inability of blasting techniques to achieve sufficiently uniform porosity and permeability is the main factor preventing MIS commercialization, and research in this area continues. For more detail on rubblization of retorts, see Britton (1980) and Ricketts (1980, 1982).

Heat for pyrolysis can be supplied by forcing externally heated gas through the retort, but current interest in MIS retorting is focused on methods in which heat is provided by burning char which remains on the shale after pyrolysis. A schematic of the process is shown in Figure 1-1. The top

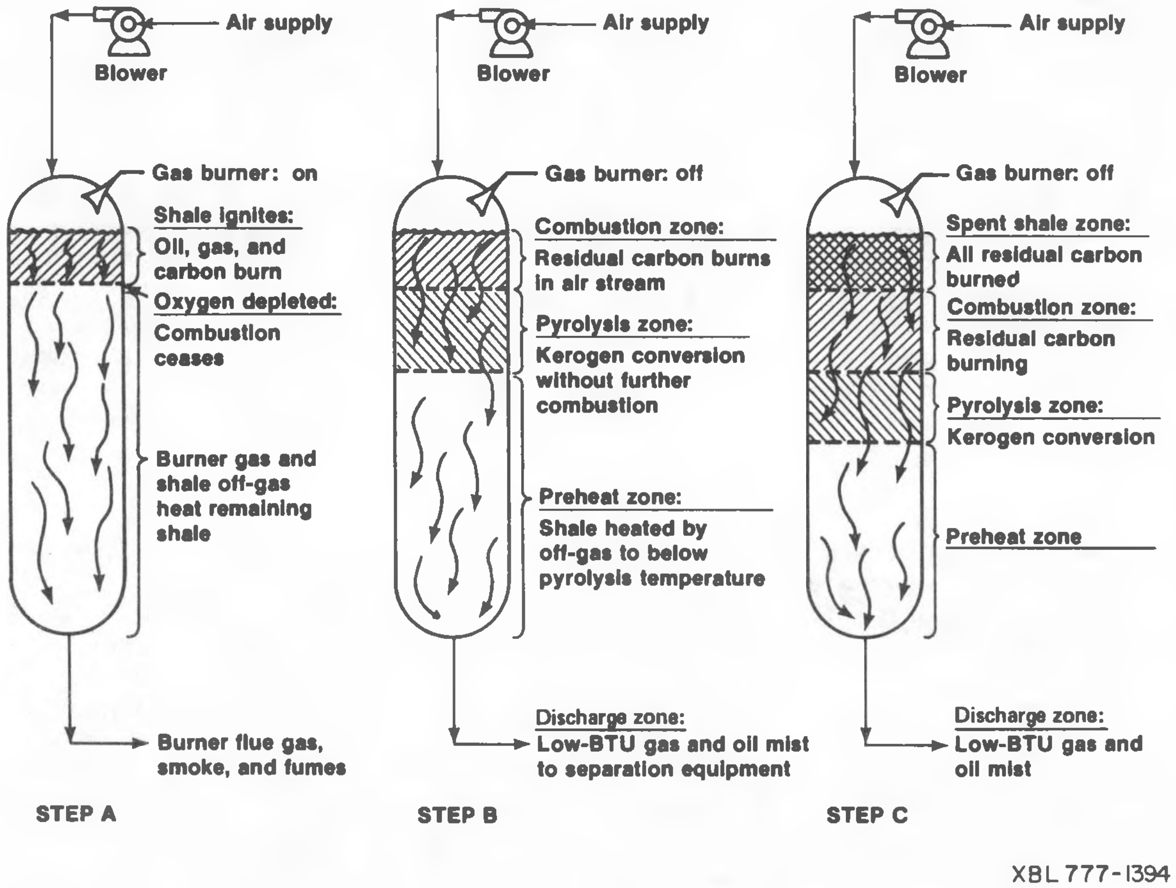

Figure 1-1. Schematic of in-situ retorting using internal combustion of char as the heat source. (Source: Sladek, 1975.)

of the rubblized shale column is first ignited using an external heat source with combustion air supplied by blowers distributed across the top of the retort so that air flow is uniform across the retort cross-section. Once the raw shale is ignited, the combustion is self-sustaining as long as air is supplied. As fuel is exhausted, the flame front moves down through the retort. The rate of progress of the flame front is controlled by the rate of air flow. For more information on ignition of MIS retorts, see Hommert (1982) or Berry et al. (1982). Below the flame front, an anoxic retorting zone is established in which raw shale reaches retorting temperature in an oxygen-starved atmosphere. Kerogen is pyrolyzed leaving behind char, which later serves to fuel the approaching high temperature flame front. When the retorting front reaches the bottom of the retort, air flow is shut off, the flame front is quenched, and the retort is abandoned. Cooling may be required, however, by blowing air or pumping water through the abandoned retort.

Resource recovery is typically higher in surface retorting than in in-situ retorting. Recoveries of over 90 percent of Fischer Assay are common in surface retorting, compared with up to 65 percent in field MIS experiments. This is primarily because the shale is mined and crushed to a small particle size (typically < 3 in.) before being fed to the surface retort while for MIS retorting, the particle size is much larger and the particle size and void distributions are not uniform throughout the retort, causing channeling of the retorting front. This can cause some of the raw shale to be left unretorted when the flame or reaction front reaches the bottom of the retort ("breaks through"), or it can cause oil recovered from large chunks to emerge behind the retorting front into an oxidizing atmosphere where it is burned in the retort and not recovered. Another inefficiency of in-situ retorting is poorer process control. Because of the low thermal conductivity of surrounding oil shale, temperatures higher than necessary for pyrolysis of kerogen are reached, and endothermic mineral reactions (decomposition of carbonates and other minerals) take place.

1.3 Environmental Problems of Surface and MIS Retorting

Water quality problems of surface and MIS retorting are mainly related to ultimate disposal of spent shale. Concerns include the transport of leached inorganic species, including Pb, B, F, Se, and V, and organic species, including phenols and organonitrogen compounds, into groundwater and surface waters. Current industrial plans for disposal of surface spent shale call for it to be moisturized (possibly with process waters that are difficult to dispose of otherwise), compacted, covered with stockpiled topsoil, and revegetated. Another option is to backfill spent shale into deep mines. For discussions of disposal techniques, see Holtz (1976), Redente et al. (1980), Earnest et al. (1978), or various development plans.

With MIS retorting, most of the spent shale remains in the abandoned retort, where it is vulnerable to leaching by reinvading groundwater. Another problem is that the retorts may intersect and connect aquifers of differing water qualities, causing poorer quality water to invade the better quality aquifer. These problems are discussed in detail in Chapter 2 of this report.

1.4 Scope of this Report

This report is concerned with critically assessing groundwater pollution problems associated with MIS retorting and examining proposed technologies and strategies for their control. Chapter 2 examines the effect of MIS retorting on groundwater quality. In Chapter 3, several proposed control technologies are briefly discussed, and preliminary cost estimates are presented for each. In Chapters 4 through 10, control technologies are considered in greater depth. These chapters report experimental and computational work that was done at Lawrence Berkeley Laboratory and the University of California at Berkeley in order to examine each of these technologies; work done elsewhere (by oil companies, other laboratories, and universities) also is reviewed. Chapter 4 discusses process control and Chapter 5 addresses intentional leaching. Chapters 6 through 10 focus on various aspects of retort grouting. Each chapter concludes with judgments on the possible efficacy of the control technology in question. Chapter 11 presents a comparison of the various control technologies studied and makes recommendations for further research.

CHAPTER 2. GROUNDWATER EFFECTS OF MODIFIED IN-SITU RETORTING

2.1 Introduction

To determine the need for control technology, a preliminary assessment was made of the probable effects of in-situ leaching on groundwater quality (Fox 1979, 1980). The areas in which additional research was needed also were indicated (Fox et al., 1980). Independent assessments of the problem also have been made (Robson and Saulnier, 1981; Slawson, 1980) and work is currently in progress at Denver Research Institute. The leaching process has been mathematically modeled (Amy, 1978; Hall, 1982) and the flow field in the vicinity of a field of MIS retorts has been modeled (Mehran et al. 1980, 1981). Laboratory studies have shown the effects of retorting conditions on leachate quality (Park et al., 1980; Kuo et al., 1979; Bethea et al., 1981; Peterson et al., 1982). Finally, cores recovered from actual experimental in-situ retorts have been characterized and leached (US DOE, 1980; Krause et al., 1980; Peterson et al., 1981). As a result of these and other studies, we are now in a better position to identify the factors controlling in-situ leaching, and we can predict effects within a narrower range than formerly, although we still do not know enough to state with certainty what the effects will be.

This chapter will review the above reports and others to refine the estimate originally made of the effects of in-situ spent shale leachates on groundwater and surface water quality. The environmental effects of dewatering during development are considered. These effects do not involve leaching and would occur regardless of any control technology considered here. The expected time-scale of groundwater reinvasion, leaching, and transport also is discussed. The likely composition of in-situ leachate, based upon leaching experiments on Occidental Oil Shale (Oxy) retort 3E cores, and others, is discussed. Finally, the probable environmental effects of uncontrolled leaching of abandoned MIS retorts by reinvading groundwater, and the need for controls, are discussed.

2.2 Groundwater Effects During MIS Development

During mining, retort preparation, and retorting, the area to be developed must be dewatered; sufficient water must be removed from the aquifers to lower the water table below the bottom of the retorts. Numerical modeling was used by Mehran et al. (1980) and by Golder Associates (1977) to simulate the effects of dewatering for MIS retorting. Mehran et al. (1980) found that the upper aquifer (presumably the source of base flow to surface streams) would be drawn down by as much as 31 m under Yellow Creek (5 km from tract C-a) after 30 years of operation and by as much as 100 m under Piceance Creek (3.5 km from tract C-b) after 60 years of operation. If the surface streams are indeed fed by the upper aquifer, their flows may cease for portions of their length. This may infringe upon existing water rights along these streams. Some developers are therefore considering using some of the pumped mine water for stream flow augmentation (Tipton and Kalmbach, 1977). Birman (1982) offered evidence, however, that surface streams are not hydraulically connected to the upper aquifer and would only be slightly affected. Field studies are required to resolve this issue.

Robson and Saulnier (1981) also calculated the effects of dewatering on groundwater quality due to alteration of the flow regime. These effects do not result from leaching, but from changes in quantity and direction of groundwater flow and transport of naturally occurring dissolved minerals by flowing groundwater. They calculated that a pumping rate of 5 ft^3/sec would be needed to dewater tract C-a, which would be balanced by decreases in base flow to Piceance Creek of 3 ft^3/sec and to Yellow Creek of 2 ft^3/sec; and a pumping rate of 15 ft^3/sec would be needed to dewater tract C-b, which would be balanced by a decrease in base flow to Piceance Creek of 15 ft^3/sec. Dewatering would cause low-salinity water in shallow aquifers to move downward. As a result, the salinity of water in deep aquifers (just above the saline zone) would decrease around the lease tracts and increase elsewhere. The groundwater discharging as base flow to Yellow and Piceance Creeks would be elevated in salinity, because less low-salinity water would be discharged. This would result in an increase in the salinity of base flow to Yellow Creek of about 200 mg/L (cumulative increase from the first point of groundwater discharge to a point two miles above its confluence with the White River) and an increase in the salinity of base flow to Piceance Creek of about 250 mg/L (cumulative increase from the first point of groundwater discharge to its confluence with the White River). Flows in these streams are approximately 80 percent base flow, so these increases would strongly influence the salinities of these surface streams. These increases can be compared with those caused by leaching, which are estimated in Table 2-2 below. The effects of dewatering should be estimated for each oil shale development site, whether surface or in-situ retorting is considered.

2.3 Time Scale of Groundwater Reinvasion and Leaching

When dewatering is terminated, groundwater will reinvade a retort site and leach soluble constituents from the spent shale. This material will be transported away from the site and may eventually be discharged into surface streams or wells. Estimates of the time required for groundwater to reinvade an MIS site and to transport the leachate away from the site to the nearest surface stream indicate that it may take over 1000 years before any leachate reaches surface waters. Transport of leachate away from a development site will be negligible while the retorts fill with reinvading groundwater. Mehran et al. (1980, 1981) modeled the reinvasion process numerically and found that, because of the low permeability of desaturated media and the enormous amount of water that must be replaced, this process would take centuries (see Figure 2-1). Calculations for tract C-b indicate that reinvasion would take more than 200 years. Eventually, a new steady-state groundwater regime would be established (barring other disturbances to the groundwater system) and water would flow through the abandoned retorts.

When reinvasion is complete, leachate may be transported away from the site. The area affected by the plume of polluted groundwater has been estimated by Robson and Saulnier (1980) and by Golder Associates (1977). These studies agree that the affected region will occupy all the area downgradient of the development tracts to the nearest surface stream. The rate at which this plume moves through the aquifer(s) has been estimated (Robson and Saulnier, 1980; Fox 1979, 1980). In the former work, the present rate of groundwater flow through the area was assumed to be restored after reinvasion. In the latter, the head difference between aquifers was assumed to be restored and the controlling permeability to be that of the aquifer receiving the leachate. A similar method was used by Denver Research Institute (1980). Since all these estimates arrived at similar numbers, they are probably as accurate as our estimates of aquifer permeability, and therefore adequate for prediction, subject to modification as field data improve. Field data must be obtained for any site under consideration. Based on these calculations, leachate is expected to reach the affected streams 130 to 1450 years after flow through retorts begins (Fox, 1980), which in turn could be centuries after abandonment.

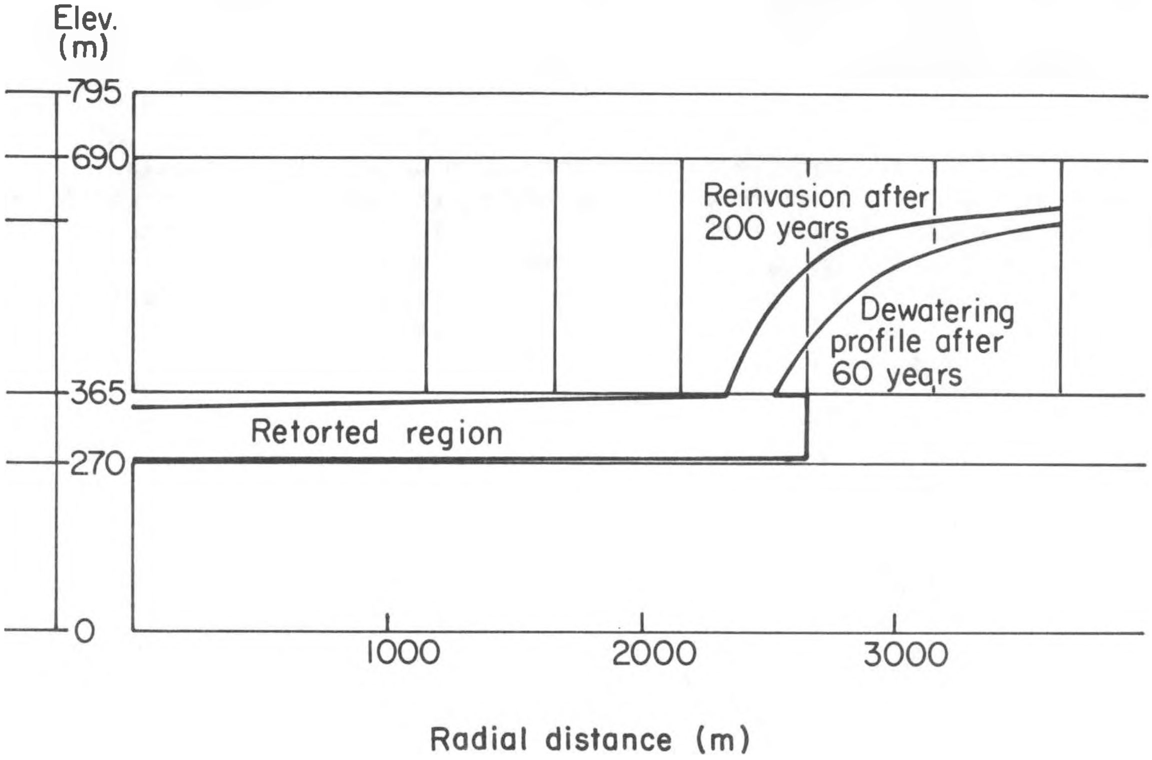

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Figure 2-1. Water table at tract C-b after 60 years of dewatering and after 200 years of reinvasion (reinvasion starts after 60 years). (Adapted from Mehran et al., 1980.)

2.4 Quality of In-Situ Leachates

Retorting conditions influence the quality of leachate; this will be discussed in Chapter 4. This chapter will focus on laboratory leaching data for material from Occidental Oil Shale (Oxy) retort 3, supplemented by data for Geokinetics and simulated in-situ spent shale. In reviewing these data, the reader is cautioned that the ability of laboratory leaching studies to simulate in-situ leaching is limited by many factors. Differences between field and laboratory leaching conditions include the quality of the leaching water, refluxing of water vaporized by contact with hot spent shale, rate of flow through columns, and liquid-to-solid ratio (LSR) of the leaching experiment. This last factor may be important. Laboratory experiments have generally used LSRs of 5 mL/g, while the LSR of an abandoned retort will be less than 1 (for calculations, see section 10.5.1). Several studies have shown that, in spent-shale leaching, the EC and concentration of several ions are inversely related to LSR (Fransway, 1980; Glaze, 1981; Silveira et al., 1978). Data presented by Fransway (1980) suggest that for Paraho spent shale, the EC and LSR are related by

$$EC = 14.46(LSR)^{-0.76}$$

i.e., a straight-line, log-log relationship. Assuming that a similar relationship applies to MIS retorts, decreasing the LSR by a factor of 5 would increase the concentration of the leachate by a factor of 3.4. This calculation is based upon data from laboratory leaching of small-particle-size Paraho spent shale and is only intended to demonstrate the possible magnitude of the error introduced by having LSR's in laboratory experiments much different from field conditions.

Contaminants of concern in leachates can be divided into organic species, salinity (measured as total dissolved solids, TDS), and trace elements. Each of these is considered.

2.4.1 Organic Compounds in In-Situ Spent Shale Leachate.

Organic compounds in MIS leachate have not been completely characterized for any sample. Organic compounds of concern include phenols and organonitrogen compounds, which have been observed in leachates from simulated in-situ spent shales (Amy, 1978; Hall, 1982). Polynuclear aromatics have been identified in surface-retorted shales, but not in MIS leachates.

Amy (1978) leached four types of simulated in-situ spent shale from the Lawrence Livermore National Laboratory 125-kg retort with distilled water and with a simulated groundwater at 20 and 80 C. The results of leaching 50 g of shale with 50 mL of each water for 30 days at 80 C are shown in Table 2-1. Mass leaching data (mg/100 g) in Table 2-1 can be converted to concentrations in the leachate (mg/L) by multiplying by 10. Thus, organic nitrogen in distilled water leachate from Type 1 shale was 0.4 mg/L and phenols, 0.23 mg/L. The phenol analyses do not include substituted phenols or phenols with more than one aromatic ring.

In another study, Hall (1982) studied the leaching of total organic carbon (TOC) from a simulated in-situ spent shale from the Laramie Energy Technology Center (LETC) 10-ton retort. He used batch and column studies to develop a mathematical model of organic carbon leaching. He also used GC/MS to identify organic compounds in the hexane extract of a single sample of leachate. The sample used for this characterization was obtained from a column run in which water flowed through the column for 7 days, and the column

Table 2-1. Organic Species in Leachates from Four Simulated In-Situ Spent Shales, Leached at 80 C with Distilled Water (DW) or Simulated Groundwater (SGW). (Data from Amy, 1978.)

	Type 1		Type 2		Type 3		Type 4	
Retorting conditions								
Source of heat	combustion		external		combustion		external	
Atmosphere	air + N_2		inert gas		air + recycle gas		inert gas	
Maximum temperature, C	750		510		935		460-535	
C initially present in solid phase, mg/100 g of shale	200		1800		2100		3900	
Leachate	SGW	DW	SGW	DW	SGW	DW	SGW	DW
TOC, mg/L	10	13	58	31	34	29	47	31
EC, mmho/cm	17	8	12	4	21	14.5	13.3	6
pH	11.6	11.5	9.1	8.1	11.9	12.5	9.2	8.0
TOC leached, mg/100 g of shale	1.0	1.3	5.8	3.1	3.4	2.9	4.7	3.1
Organic N leached, mg/100 g of shale	0.07	0.04	0.09	0.07	0.06	0.13	0.12	0.14
Phenols leached, mg/100 g of shale	--	0.023	--	0.030	--	0.015	--	0.035

remained quiescent for an additional 30 days before the sample was collected. Thus, the solutes present diffused from the interior of spent shale particles into the bulk liquid.

These simulated in-situ spent shales are not representative of well-burned spent shale expected from commercial MIS processes. However, they may be more representative of the incompletely burned, partly retorted, or even unretorted material expected at the bottom of an MIS retort. Special efforts should be made, in coring MIS retorts, to determine the extent of this "bottom plug" and to characterize it.

Table 2-1 indicates that in Amy's batch studies at 80 C, the equilibrium leachate TOC concentration ranged from 10 to 58 mg/L. In another batch study using LETC spent shale at 20 C, Hall (1982) found that the equilibrium leachate TOC concentration was 75 mg/L. Both investigators found that, in column studies, leachate TOC concentrations were initially high, ranging from 20 to 60 mg/L, and eventually decreased to less than 1 mg/L. For comparison, the average TOC of groundwaters in the vicinity of tracts C-a and C-b ranges from 6 to 23 mg/L (Fox, 1980). Thus, leachate in the first several pore volumes, which would be released over a 3- to 30-year period, would significantly increase the TOC in groundwaters. Leachate released after this initial pulse should have very low TOC concentrations, and thus it should not significantly increase groundwater TOC.

The potential significance of these organic compounds is uncertain because characterization data are scarce and because biological testing data (Ames assays, bioassays) are absent. Fractionation data reported by Amy (1978) indicate that sizeable quantities of basic, neutral, and acidic organic compounds were present in four simulated in-situ leachates. The only specific compounds or compound classes that have been identified in simulated in-situ leachates are phenolic and organonitrogen compounds.

The potential environmental significance of the organonitrogen compounds is uncertain. Amy (1978) reported that organic nitrogen concentrations ranged from 0.4 to 1.4 mg/L (Table 2-1), and Hall (1982) identified 3-methyl pyridine (0.002 mg/L) and several alkylpyridines (0.0018 mg/L). Riley et al. (1981) have reported that alkylpyridines are mobile in the hydrologic system common in oil shale regions. These concentrations are well below recommended environmental criteria (Cleland and Kingsbury, 1977), and none of the identified compounds has been reported as carcinogens or mutagens (Sax, 1981; McMahon et al., 1979). Significantly, unpublished characterization data for natural groundwaters from potential oil shale sites indicate that these waters naturally contain ppb-levels of pyridines, anilines, and other organonitrogen compounds (Spall, 1982) which are likely to be present in leachates.

The phenolics present in these leachates may be more important environmentally than the organonitrogen compounds. Amy (1978) reported that phenols ranged from 0.15 to 0.35 mg/L in leachates from four types of simulated in-situ spent shale. Hall (1982) identified phenol (0.005 mg/L), o-cresol (0.003 mg/L), p-cresol (0.02 mg/L), and two other alkylphenols in leachate from another simulated in-situ spent shale. Phenol is a priority pollutant and is included on the NIOSH list of suspected carcinogens (Sax, 1981). The US EPA has established a criterion of 0.001 mg/L to protect domestic water supplies and to protect against fish flesh tainting (US EPA, 1976). Since leachate concentrations, even following extensive leaching, exceed these recommended criteria, research should be directed at assessing the mobility of phenol in oil shale hydrologic systems.

2.4.2 TDS of Spent Shale Leachate. Salinity (measured as TDS) is of concern because at levels above 1000 mg/L, use of water for irrigation has adverse effects on many crops and requires careful management practices (US EPA, 1976). Salinity also is of concern for domestic water supply; the Clean Drinking Water Act (PL 93-523) requires that TDS be less than 500 mg/L. Salt leached into Piceance Basin groundwaters eventually reaches the Colorado River system, where salt levels are regulated by Compact (Fischer, 1980).

This chapter will focus on leaching experiments done on cores recovered from Occidental (Oxy) experimental MIS retort 3E that were reported by Peterson et al. (1981, 1982), and it will use those results in the framework established by Fox (1980) to calculate downstream effects of in-situ leaching.

In the leaching experiments of Peterson et al. (1981), the various sections of each core were ground to -100 mesh and leached with distilled water (liquid-to-solid ratio = 5). The water and solid were shaken for 48 hours, after which quasi-equilibrium was assumed to be established. It is assumed here that the leachates resulting from this experiment actually were in quasi-equilibrium with the solid. It is further assumed that these conditions are representative of those that would be encountered in the field. The effect of leaching with groundwater, rather than distilled water, is discussed below.

The electrical conductivity (EC) of the leachates ranged from 330 to 6990 µmho/cm, corresponding to TDS of approximately 230 to 4900 mg/L. The average of all sections in the core, weighted by core length, was 1860 and 2320 µmho/cm for the cores R3E2 and R3E3. A similar range in EC was noted for Geokinetics retort 1 core material (Krause et al., 1980). This suggests a typical TDS of 1500 mg/L for in-situ spent shale leachate. For comparison, the average TDS in groundwater in the vicinity of tracts C-a and C-b is 777 to 6190 mg/L (Fox, 1980). The leachate TDS can be added to the TDS of natural groundwater for a conservative estimate of the TDS of leachate leaving a retort. However, Peterson et al. (1982) and Bethea et al (1981) showed that leached ions enter into precipitation reactions with ions present in groundwater, reducing leachate TDS to less than the sum of distilled water leachate TDS and groundwater TDS, as calculated here.

Fox (1980) predicted TDS increases in surface streams resulting from the discharge of leachate as base flow. Those values were high because they were based on leachates from laboratory-retorted spent shales that were more similar to surface than to in-situ retorted materials. Using the figure of 1500 mg/L and applying the same method of analysis, the projected TDS in downstream surface streams is shown in Table 2-2. These increases would not occur for centuries after site abandonment. The calculations assume that the TDS of groundwater recharging surface streams near tracts C-a and C-b will be the same as that leaving the retort, that lower (or upper) aquifer water enters the retort, and that leachate is discharged to an upper aquifer which is hydraulically connected to the surface stream. Decreases in TDS at downstream stations are caused by dilution. TDS increases greater than 1500 mg/L are caused by leaching with high-TDS lower-aquifer water.

Table 2-2. Estimated Increase in TDS of Surface Waters of the Upper Colorado River Basin due to Discharge of MIS Leachates from Tracts C-a and C-b into Piceance and Yellow Creeks as Base Flow.

	Calculated increase in TDS, mg/L (based on leachate TDS = 1500 mg/L)	
Watercourse	Leaching with lower aquifer water	Leaching with upper aquifer water
Piceance Creek at White River	5272	1200
Yellow Creek at White River	1336	1200
White River near Watson, Utah	147	35
Green River near Green River, Utah	18	4
Colorado River near Lees Ferry, Arizona	6	1.5

2.4.3 Trace Element Concentrations in MIS Leachate. Peterson et al. (1981) analyzed leachates from Oxy cores R3E1, R3E2, and R3E3 for several trace elements, with the object of determining the mechanisms controlling leachate concentrations of various elements. They found that some elements are controlled by the solubility of minerals in the spent shale (primary solubility) and others by the solubility of solution products (secondary solubility). No controls were identified for many elements, and thus work is continuing. The controlling mechanisms for the various elements depend upon the spent shale mineralogy and leaching fluid (i.e., groundwater) composition. Because spent shale mineralogy is determined by processing conditions, this is discussed more fully in Chapter 4.

In the Oxy cores, certain elements were present in the leachate at levels exceeding water quality criteria for domestic water supply, agriculture, or stock watering. Table 2-3 (adapted from Peterson et al., 1982) shows that B, F, Fe, Li, Mn, Mo, Pb, Se, and V in leachate are high enough to cause concern. Peterson et al. (1982) concluded that groundwater quality will be altered in two ways: by aquifer interconnection and by actual spent shale leaching. In the first case, the elements which exceed water quality criteria after development already exceed water quality criteria under natural conditions (although by a smaller margin), and so the degradation resulting from aquifer interconnection would not affect the suitability of the water for beneficial uses. In the case of leaching of spent shale, most of the elements that are elevated in leachates already exceed water quality criteria in natural groundwaters. Only V, Se, and Pb were found to be elevated in leachate, but not in natural groundwaters. Of the elements studied to date, these represent the primary environmental concern from leaching of in-situ spent shale. Based on Table 2-3, control technologies will need to be applied to prevent transport of these elements into groundwaters. The calculations shown in Table 2-2 can be extended using the leachate composition data shown in Tables 2-3 to determine concentrations of trace elements in downstream surface waters.

The following chapter describes potential control technologies that were considered and presents preliminary cost estimates for each. Where other researchers have independently estimated costs for these control technologies, their estimates are reported for comparison.

Table 2-3. Concentrations of Selected Constituents in MIS Leachate and Piceance Creek Basin Groundwater (a).

		Pre-development groundwater quality		Estimated post-development groundwater quality (b)	
	Leachate (c) (mg/L)	C-a lower aquifer (mg/L)	C-b lower aquifer (mg/L)	C-a (mg/L)	C-b (mg/L)
B	2.72 (d,e,f)	0.84 (d)	36 (d,e,f,g)	3.5 (d,e,f)	39 (d,e,f,g)
F	8.0 (d,f,g)	14.7 (d,f,g)	21 (d,e,f,g)	23 (d,e,f,g)	29 (d,e,f,g)
Fe	0.134	0.78 (f)	0.8 (f)	0.91 (f)	0.93 (f)
Mn	0.016	0.075 (f)	0.13 (f,g)	0.09 (f)	0.15 (f,g)
Pb	0.168 (f,g)	--	0.03	--	0.2 (f,g)
Se	0.02 (f)	<0.01	0.004	0.02 (f)	0.02 (f)
V	0.51 (d,g)	<0.05	0.01	0.51 (d,g)	0.51 (d,g)
TDS	1500 (e,f)	1075 (e,f)	6190 (d,e,f)	2575 (d,e,f)	7690 (d,e,f)

(a) Table adapted from Peterson et al. (1982), except for TDS values, which were converted from EC measurements using a factor of 0.7. The water quality criteria for comparison are reported by Peterson et al. (1982). No domestic water supply criterion is reported for V; 500 mg/L was taken as the domestic water quality criterion for TDS.

(b) Calculated by adding concentration in distilled water leachate to concentration in lower aquifer groundwater, as reported by Fox (1980).

(c) Average concentrations in leachates from R3E2 and R3E3 cores.

(d) Exceeds standard for long-term irrigation.

(e) Exceeds standard for short-term irrigation.

(f) Exceeds standard for domestic water supply.

(g) Exceeds standard for livestock.

CHAPTER 3. POTENTIAL CONTROL TECHNOLOGIES CONSIDERED

3.1 Introduction

Based upon an assessment of groundwater quality effects of in-situ oil shale retorting (Fox 1979, 1980), some control technology was considered necessary to protect groundwater and surface water quality in the Piceance Basin. This need has been confirmed by more recent investigations, as reviewed in the preceding chapter. A survey of the literature was conducted to identify possible control technologies (Persoff and Fox, 1979). None of these control technologies, described below, is intended to eliminate completely the transport of leachables from abandoned retorts. Rather, the intent is to reduce the effects on groundwater quality to an acceptable level. Preliminary cost projections also were made in order to eliminate in advance any control technology that was obviously too costly to consider. Options eliminated on the basis of cost are discussed in Persoff and Fox (1979). Cost projections for control technologies initially considered to be economically feasible are presented at the end of this chapter (costs are in 1979 dollars), along with independent estimates made by other researchers.

3.2 Site Selection as a Control Technology

The potential for groundwater quality impacts is greater at some locations than at others. Raw shale mineralogy, groundwater quality, and permeability of the surrounding media all vary with location. The target oil shale resource at tracts C-a and C-b is below aquifers, but some MIS sites may be above aquifers in the unsaturated zone. From the point of view of groundwater quality protection, the most desirable conditions are:

1. The rate of flow of groundwater through abandoned retorts should be low, due either to low permeability of the surrounding media or to low hydraulic gradient.

2. The direction of flow through abandoned retorts (particularly if vertical) should be from higher to lower quality groundwater, e.g. downward on tract C-b. This would cause the least valuable water resource to bear the brunt of the degradation. Similarly, MIS retorting might be restricted to areas where groundwater quality is already low.

3. The aquifer receiving leachate should not be hydraulically connected to surface waters.

4. Proximate groundwaters should be unsuitable for beneficial uses (e.g., domestic supply, irrigation) and have no history or future prospect of extensive use.

The Naval Oil Shale Reserves Nos. 1 and 3 have been suggested as favorable locations where rich oil shale reserves are thick enough to accommodate MIS retorts (a continuous resource of at least 300 feet is required) without intersecting significant aquifers. Potential groundwater impacts of MIS retorting at this site should be evaluated using the hydrologic inventory recently published by TRW (1982).

No cost is associated with using site selection as a control technology.

3.3 Intentional Leaching as a Control Technology

Several experiments in which spent shale was leached, in batches or continuous-flow columns, showed that concentrations of many constituents decreased in successive pore volumes of leachate. This suggested that in-situ retorts could be intentionally leached with enough pore volumes to reduce concentrations of constituents of concern to acceptable levels; the leachate produced would be treated and reused for further leaching. For this approach to be feasible, the following conditions must exist:

1. Sufficient water must be available for the leaching.

2. Constituents of environmental concern must decrease in concentration through successive pore volumes. There also must be no subsequent increase in concentration resulting from pore diffusion of solutes to the particle surface.

3. The number of required pore volumes must be small enough to assure that treatment costs are acceptable.

4. A process must be demonstrated to treat the leachate. The volume of blowdown, brine, or reject streams must be small enough so that their disposal (say by evaporation from lined ponds) is not too costly. This requirement might be lifted if this stream could be codisposed with surface-retorted spent shale.

By way of preliminary evaluation, the case for leaching with two pore volumes and treating the leachate by reverse osmosis was examined. Costs developed for this scenario are presented in Table 3-1. Thode et al. (1981) recalculated costs for three and seven pore volumes of leaching using a counter-current mode of contacting spent shale and water. This resulted in lower costs because a smaller volume of water was treated.

Perhaps the most important condition is the second one. It is required that leachate concentrations remain low indefinitely. This may not be possible for all constituents because secondary solubility controls may be relaxed during the course of long-term leaching. In addition, studies by Stollenwerk (1980), using surface-retorted shales, suggest that solutes in the interior of intentionally-leached shale particles may diffuse to the surface during the time between intentional leaching and eventual groundwater reinvasion. These solutes would then be available for a second pulse of concentrated leachate. If this occurs for in-situ spent shale, intentional leaching will not be effective. However, if intentional leaching actually depletes the reservoir of soluble material, no second pulse would occur.

The water requirement for this technology may be a limiting factor. Thode et al. (1981) estimated that between 78 and 144 gal of water per barrel of oil recovered would be needed to prewet the in-situ spent shale and replace brine streams rejected from a treatment process. Only 50 to 70 percent of the water injected into a retort to leach it can be recovered. The rest remains in the interior pore space of spent shale. This water requirement for wetting in-situ spent shale is calculated in Chapter 6.

3.4 Reducing Flow of Groundwater Through Abandoned Retorts

For retorts which intersect aquifers (as do the planned retorts on tracts C-a and C-b), a possible means to control transport of leachates is to reduce the rate of flow of water through abandoned retorts. This can be done either

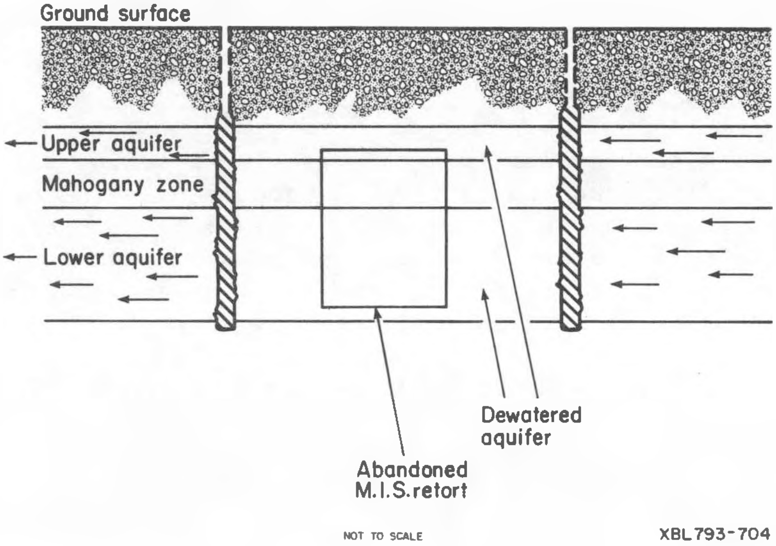


Figure 3-1. Proposed grout curtain constructed to surround a block of retorts in Piceance Creek Basin and cut off groundwater flow through abandoned retorts. Although only one retort is shown, many could be surrounded by such a curtain.

by cutting off flow in aquifers by forming a grout curtain around the development site, or by injecting grout into the abandoned retorts to reduce their permeability. Each of these is described briefly below.

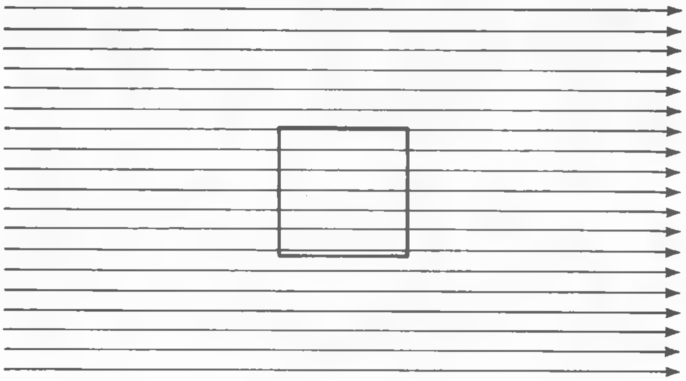
3.4.1 Grout Curtain around Development Site. Curtain grouting is an established technique used to cut off flow in aquifers. It has been conventionally used to prevent leaking of water under dams and also to prevent uplifting water pressures at the toe of dams. On a smaller scale, curtain grouting has been used to reduce groundwater inflow to excavations. The proposed application for in-situ retorts is shown in Figure 3-1. Grout curtains are formed in fractured rock by drilling a series of closely spaced parallel holes and injecting grout into the fractures. If fractures are wide enough, portland cement can be used (about $2 per cubic foot of grout); if not, a chemical grout with low viscosity must be used, which is more costly (about $10 per cubic foot). This technology is well established; however, the scale of this proposed operation exceeds anything previously done. In particular, the grout injection holes must be parallel through their entire length. Such accurate drilling at depths exceeding 1000 ft may be difficult to accomplish. Accurate cost projections for such an operation are extremely difficult, and field data are required to refine estimates.

3.4.2 Retort Grouting. Abandoned retorts will constitute a zone of very high permeability in a region of otherwise low permeability. As such, flowing groundwater will be channeled through them as shown schematically in Figure 3-2. The object of retort grouting is to reduce this permeability by filling the void space in the retorts with a grout. As shown in Chapter 6, any selected grout must be low in cost. This eliminates commercially available grouts such as portland cement or fly ash. Surface retorted spent shale, modified by small amounts of low-cost additives, may be suitable as a grouting material. Thus, the grouting operation becomes a hydraulic stowing operation for spent shale. Costs for retort grouting were developed on this basis. Because the distance of grout injection holes to be drilled is the major cost item, if grout injection can be accomplished from the air-injection level (the "attic space" or "plenum" above an in-situ retort), costs are much lower than if injection holes must be drilled from the surface. Spacing of holes and minimizing the number of holes while maintaining uniform grout injection is critical.

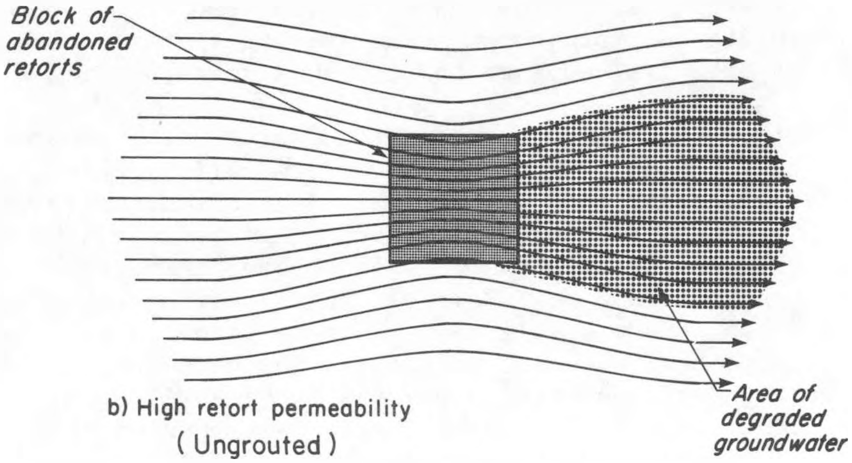
Chapter 6 gives more detail on the requirements for grouting. Because this control technology was the only one considered which not only addresses the problem of groundwater leaching of abandoned retorts, but also the problems of mixing of aquifers, subsidence, and low resource recovery (by supporting overburden and reducing the size of pillars needed between retorts), experimental work was directed at quantifying the structural requirements for retort grouting, and development and testing of candidate grouts. This experimental work is reported in Chapters 7 through 10.

3.5 Preliminary Cost Projections

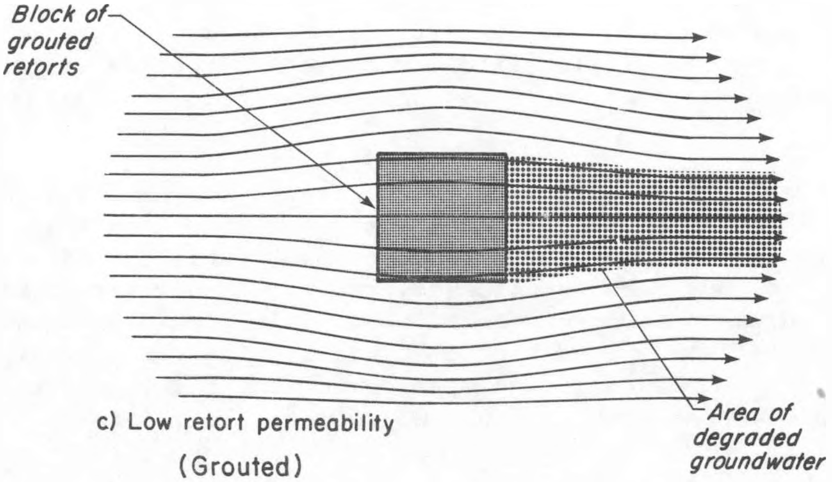
In order that research might be directed toward evaluation of control technologies which had the prospect of being cost-effective, preliminary costs were projected for each of the control technologies considered. Because the proposed technologies were unprecedented, numerous assumptions were necessary, which are summarized in Table 3-1. The detailed cost projections and assumptions are presented by Persoff and Fox (1979). In some cases, other researchers have ventured cost projections, which also are indicated in Table 3-1.



a) Predevelopment conditions



b) High retort permeability
(Ungrouted)



c) Low retort permeability
(Grouted)

XBL 826-825

Figure 3-2. Flow path of groundwater relative to abandoned MIS retorts with and without retort grouting.

Table 3-1. Preliminary Cost Projections for Candidate Control Technologies.

Control technology	Projected cost, $/bbl (a) C-a	C-b	Assumptions used to project costs
Retort Grouting with Spent Shale (b)	0.91	1.46	$2/ton to slurry and inject spent shale; $1/ton credit assumed for disposal of spent shale; 0.25% fluidizer included @ $0.15/lb $20/ft to drill injection holes; holes in square grid, 50 feet apart; Required water available at no cost; Drilling from ground surface.
	0.75	0.51	Same assumptions, but drilling and injecting from air-injection level.
Intentional Leaching (c)	0.67	0.59	Treating two pore volumes of leachate; Adequate water quality and quantity available at no cost; Treatment by reverse osmosis feasible (has not been demonstrated for MIS leachate) @ $1/1000 gal (approximately 60% of total cost); Disposal of 10% brine reject stream by evaporation from lined ponds (approximately 35% of total cost).
Construct Grout Curtain Around Block of 144 Retorts	0.74	2.85	Drilling grout injection holes on 5 ft centers from ground surface to bottom of lower aquifer; $20/ft for drilling; $3/ft^3 for grout material.

(a) Cost in 1979 dollars per barrel of oil recovered, including both surface retorting of mined shale and in-situ retorting. Tracts C-a and C-b were taken to indicate the effects of differing retort and overburden dimensions and differing retort void ratios. For C-a, retort dimensions of 300x150x750 ft were taken (LxWxH) with 450 ft of overburden and 40 percent voids in retort. For C-b, retort dimensions of 310x155x390 ft were taken with 1400 ft of overburden and 23 percent voids in retort. Shale grade was assumed 24 gal/ton, with 65 percent recovery by MIS retorting, and 100 percent recovery by surface retorting.

(b) Nevens et al. (1979) estimated, with different assumptions, a cost of $0.30 per barrel for MIS retort grouting.

(c) Thode et al. (1981) showed that volume of water could be reduced substantially by using multistage, counter-current leaching. This would reduce volume of water to be treated and increase the treatment cost per 1000 gal.

CHAPTER 4. PROCESS MODIFICATION AS A CONTROL TECHNOLOGY

4.1 Introduction

As indicated in Chapter 2, retorting conditions influence the amount of residual organic carbon on spent shale and also the spent shale mineralogy. Since these factors in turn influence the quality of leachate, process control may be used to produce a spent shale whose leachate would be less likely to degrade groundwater. In this chapter, literature on the effects of process variables (maximum temperature, time at temperature, and atmosphere) on MIS spent shale mineralogy is reviewed. Then literature on the effects of spent shale mineralogy on leachate composition is reviewed. Finally, the feasibility of process control to control the quality of leachate is discussed.

This review suggests that process modification may not be satisfactory for improving leachate quality or leachate release rates. The concentration of many ions in MIS leachates are inversely related, and a decrease in one leads to an increase in others. The presently anticipated retorting conditions for MIS processes generally decrease the concentration of many major ions and increase the concentration of certain minor ions, such as F and V. Thus, modifying process conditions cannot simultaneously reduce the concentration of all important constituents. This review does suggest areas worthy of further study. Heat losses from near-surface retorts result in more soluble spent shales. Thus, methods to reduce heat losses should be explored. The bottom plug in MIS retorts is a potential source of highly concentrated leachates, and methods should be explored to eliminate this zone from MIS retorts.

4.2 Effect of Retorting Temperature, Time of Exposure, and Atmosphere on Spent Shale Mineralogy

As shown in Figure 1-1, during MIS retorting with internal combustion of char, several temperature zones progress downward through the retort. Different mineralogical reactions occur in each zone, depending upon maximum temperature, time at temperature, and gaseous environment. In the pyrolysis zone, oil shale is heated to 450-500 C in an anoxic atmosphere. In this zone, kerogen is pyrolized to shale oil, and residual carbon (char) remains on the spent shale. In the combustion zone, temperatures may reach 1000 C in the presence of oxygen, and the residual char is burned off the spent shale. As the char is exhausted, the combustion zone moves downward, and the spent shale is cooled somewhat by inlet gases flowing past it. The residence time in the various temperature zones is controlled by the rate of retorting and the rate of cooling down of the spent shale after the combustion zone has passed. The rate of retorting refers to the rate of advance of the pyrolysis zone. This rate may range from 1 to 10 ft/day; the smaller value is typical of the Oxy MIS process. Retorting rate is controlled by the sweep gas velocity. The rate of cooling of the spent shale after passage of the combustion zone is controlled by the rate of air flow through the retort (convective cooling) and by the temperature, heat capacity, and thermal conductivity of the surrounding rock (conductive cooling). The inlet gas is air, probably with some diluent. If recycle gas (retort offgas) is used as the diluent, organic compounds in the recycle gas may be adsorbed on spent shale above the combustion zone. If steam is the diluent, steam will be present in all zones.

4.2.1 Mineral Reactions During Retorting. The major minerals present in Green River oil shale are quartz and carbonates. Nahcolite and dawsonite are also major minerals in the north-central part of the Piceance Creek Basin.

4.2.1.1 **Carbonate Decomposition Reactions.** Nahcolite and dawsonite decompose below the pyrolysis temperature. Other minerals are stable at this temperature and do not react until reached by the combustion zone. The carbonate minerals, dolomite and ankerite, decompose in the range 600 to 750 C to yield calcite and oxides of Fe and Mg. Calcite decomposes at a higher temperature, 600 to 900 C, to yield CaO.

The formation of oxides in MIS spent shale is important because they result in high TDS and pH in leachate (the pH of a saturated lime solution at 80 C is 12.4).

4.2.1.2 **Silication reactions.** The oxides formed by decomposition of carbonates can react with quartz to form silicate minerals. These reactions are important because the silicate minerals are much less soluble, and they result in leachates with lower TDS and pH. Frequently observed silicate minerals are akermanite, forsterite, and diopside. These reactions occur at higher temperatures than the decomposition reactions. Park et al. (1980) retorted Logan Wash oil shale at various temperatures for long periods of time (23 to 85 days). At higher temperatures, conversion to silicates was more complete. No calcite was detected by x-ray diffraction (XRD) above 700 C, and no quartz was detected above 1060 C. Akermanite was the major mineral present at 800 C, but at higher temperatures, diopside became the major mineral present. At 1200 C, diopside was the only mineral detected by XRD. This is significant because, as shown below, akermanite is more soluble than diopside.

4.2.2 Effect of Retorting Atmosphere. Campbell and Taylor (1978) showed that steam injected into the retort catalyzes the formation of silicate minerals and that the carbonate minerals could react directly with silica to form silicates without going through the oxide step. Injection of steam into retorts is proposed as a means to control the rate of advance of the flame front by diluting the air flow and to modulate temperatures.

4.3 Effect of Spent Shale Mineralogy on Inorganic Composition of Leachate

Smith et al. (1978) suggested that silication reactions would result in formation of insoluble minerals. It was hypothesized that the formation of silicates would prevent leaching not only of the major elements but also of trace elements. Leaching of major elements would be suppressed by the low solubility of the mineral forms; leaching of minor elements would be suppressed by their incorporation into the mineral structure.

This section will review various experimental data which illustrate the control of leachate TDS and pH by silication reactions in the spent shale. In general, with increasing temperature, the original carbonate minerals calcite and dolomite first decompose to form oxides, which then react with silica to form silicates. As retorting temperature increases, leachate TDS and pH first increase with the formation of oxides, and then decrease with formation of silicates.

Bethea et al. (1981) retorted oil shale at three temperatures, simulating in situ retorting, and then leached the resulting spent shale. Conductivity, total dissolved solids (TDS), and pH of the leachate were highest for spent shale which had been retorted at 780 C and were lower for spent shale which was retorted at 430 or 1000 C. Longer residence time at 780 C reduced the amount of leachable material. Low leachate TDS was correlated with either no mineralogical change (430 C) or with formation of silicates (1000 C). Large concentrations of leachate TDS was correlated with decomposition of original carbonates to form oxides. High pH of leachates from shale retorted at 780 C suppressed the solubilities of Ca and Mg.

Park et al. (1980) leached Logan Wash oil shale which had been retorted at various temperatures for long periods of time. Concentrations of major ions in the leachate (Ca, Mg, Si, and SO_4) had minima at 600 C and 1000 C and maxima at 700-800 C and 1100 C. The low solubility at 600 C appears to be related to a peak in the mineral periclase (MgO) and the high solubility at 700-800 C to a peak in the mineral akermanite. These results suggest that leachate concentrations are controlled by mineral phases.

Recently, examination of cores from experimental in-situ retorts has confirmed the hypothesis of major elements being immobilized by formation of silicates. Minor elements, however, were not immobilized. Peterson et al. (1982) examined cores from Oxy retort 3E. By correlating the suites of minerals present in the core sections, they were able to identify retort zones which had been exposed to higher or lower temperatures. Minerals formed after retorting due to injection of water or recycle gas into the retort also were identified.

The recovered cores also were leached. It was found that the formation of silicate minerals does suppress the leaching of major ions, and it results in lower leachate TDS. They concluded that the major ions are controlled by the mineral phases present in the spent shale, but that some minor elements are controlled by the solubility products of their respective minerals that precipitate from solution. For example, F ion concentration is controlled by the solubility product of fluorite (CaF_2); the supply of Ca ion, in turn, is controlled by the mineral residence of Ca. If retorting conditions promote the formation of Ca silicates, then the concentration of Ca ion in the leachate will decrease, but as a result, the concentration of F ion will rise. Formation of silicate minerals to control the leaching of major ions (and thus TDS) actually releases controls on minor elements that are subject to secondary controls. No control was identified for the solubility of some minor elements; it was presumed that availability of the element to solution (not solubility control) was controlling. Limitation by availability to solution is equivalent to control by mass transfer from the interior of particles to the bulk solution phase; this leaching process has been modeled as described in Chapter 5. For these elements, intentional leaching may be effective in reducing concentrations in leachate.

Spent-shale cores in which the major mineral was diopside-augite released smaller amounts of minor elements to leachates than cores in which akermanite-gehlenite was the major mineral. This suggests that the minor elements can replace the major elements in the diopside-augite structure, but not as easily in the akermanite-gehlenite structure (the pairs of minerals named are end members of a series of solid solutions). Park et al. (1980) did not report concentrations of minor elements, but found that leachate concentrations of major elements were also lower from spent shale in which diopside, rather than akermanite, was the major phase.

Krause et al. (1980) analyzed and leached trench samples that had been recovered from Geokinetics in-situ retort no. 1. Free lime was detected, suggesting either that insufficient quartz was present to consume all the lime by silication reactions, or that residence time at high temperatures was not long enough for silication reactions to go to completion. Significant quantities of glasses also were detected, suggesting rapid cooling. This is consistent with a retort located near the ground surface. Glasses are generally more soluble than the equivalent crystalline solids, and thus, they would lead to higher TDS in leachates. This suggests that slow cooling, such as occurs in deep MIS retorts, is beneficial to control leaching. Mason and Sinks (1982) examined recovered cores from a later Geokinetics retort (no. 16). They identified six lithologic zones, ranging from undisturbed rock to retorted, melted rock. A portion of the spent shale did not undergo silication reactions. Although in both the Geokinetics and Occidental processes the flame front advances through the retort at approximately 1 ft/day, the Geokinetics retort, being near the surface and even connected by fractures to the atmosphere, apparently loses heat too rapidly for complete silication of spent shale near the upper surface of the retort.

4.4 Effect of Retorting Atmosphere on Organic Composition of Leachates

Amy (1978) found that when recycle gas was included in the retorting atmosphere, more organic carbon was found in the leachate. The mechanism suggested for this was sorption of the organic species from the recycle gas to the cool spent shale above the combustion front. This suggests that recycle gas should not be used in MIS retorting. Recent experiments at tracts C-a and C-b have not used recycle gas.

4.5 Feasibility of Process Modification for Environmental Control

For process modification to be an effective control technology, two conditions must exist. First, there must exist some set of retorting conditions (i.e., time, temperature, and atmosphere) for which the leachate is acceptable. Second, these conditions must apply to essentially all the oil shale in the retort. The first of these requirements is discussed in section 4.5.1. This section concludes that the recommended retorting conditions are sufficient to control leaching of TDS, pH, and major elements, but not certain minor elements of concern. The second requirement, uniformity of processing conditions, is discussed in section 4.5.2. That section concludes that uniformity of processing conditions has not been demonstrated by experimental retorts to date, and that the problem of the bottom plug cannot be ignored.

4.5.1 Control of Major and Minor Elements by Silicate Formation. The above review shows that retorting at high temperatures (1000 C) in the presence of steam for long periods of time, promotes the formation of silicate minerals. As indicated above, formation of silicates reduces concentrations of major elements in the leachate. However, controlling the major elements in the leachate releases controls on some of the minor elements. Therefore, formation of silicates by itself is not sufficient for groundwater quality protection. Formation of diopside-augite may be more effective, but has not been demonstrated and will be difficult to demonstrate before commercial production.

4.5.2 Uniformity of Processing Conditions throughout Retort. In MIS retorting with char combustion, the retort burn is stopped by discontinuing gas flow when the retorting front approaches the bottom of the retort. This is done to avoid having to handle very hot offgases. As a result, the bottom plug is never exposed to oxidizing conditions or to temperatures sufficiently high to cause silication reactions. This bottom plug will have different leaching characteristics from the rest of the retort, and will also contain species sorbed from the oil and gas phases.

In studies of cores recovered from Oxy retort 3E (US DOE, 1980), it was found that leachate from sections 17 and 18 of core R3E1 at the bottom of the retort was higher in pH, TDS, and organic carbon than leachate from other sections of the core. This suggests that it was exposed to less severe retorting conditions. Thus, leachate from the bottom plug may not be controlled by process modification.

For process control to be considered as a viable control technology, nearly all the shale in the retort must receive the same processing. In particular, all the spent shale must be oxidized to remove char and subjected to the temperature, time, and steam catalysis needed for conversion to diopside-augite. The degree of process control needed to accomplish this has not yet been demonstrated. Spent shale cores recovered from Oxy retort 3E were heterogeneous, and Oxy retorts 5 and 6 suffered from channeling which left some raw shale unretorted. Similar heterogeneity has been noted in Geokinetics cores material (Mason and Sinks, 1982) and leachates (Krause et al., 1980). This primarily results from heterogeneities in the shale bed, caused by nonuniform rubblization. It is presently unclear whether commercial retorts will achieve sufficient homogeneity to control leachate quality.

CHAPTER 5. INTENTIONAL LEACHING OF ABANDONED RETORTS

5.1 Introduction

Several studies (Amy, 1978; US DOE, 1980; Hall, 1982) have shown that when MIS spent shale is column leached, constituents in the leachate decrease fairly rapidly in successive pore volumes. This observed decrease in concentration suggests that intentional leaching of abandoned in-situ retorts may be a viable control strategy.

This could be exploited in the field by flooding the retorts and pumping the leachate to the surface for treatment. The treated water would then be used for additional leaching. The object of the process is not necessarily to remove most of the solutes of concern from the abandoned retort, but to reduce their concentration to acceptable levels. As shown in section 5.5, the latter goal can be achieved without removing most of the solute, if leachate concentration is mass-transfer-limited.

Thode et al. (1981) suggested a modification of the process. In counter-current multistage contacting, water would be passed through n retorts in succession. Clean water (from the treatment process) would first contact a retort which had already been leached by n-1 pore volumes, and then proceed to successively "dirtier" retorts, finally contacting a retort which had not been previously leached, before being raised to the surface for treatment.

Because the leachate would have high total dissolved solids (TDS), a demineralization process such as reverse osmosis would be necessary (Persoff and Fox, 1979; Thode et al., 1981). No treatability studies have been reported yet to demonstrate such a process.

Although treated water would be reused for leaching, there is a substantial requirement for make-up water. Intentional leaching would require 78 to 144 gallons of water per barrel of oil to saturate the in-situ spent shale and to replace rejected brine from the demineralization process. Losses to brine have been estimated to be between 16 and 20 gallons per barrel of oil for multistage leaching, and rehydration water has been estimated to be between 62 and 124 gallons per barrel for 25 and 50 percent porosity of the spent shale (Thode et al., 1981). Thus, the consumptive water requirement for intentional leaching is somewhat less than the consumptive water requirement for retort grouting (see Chapter 6). For comparison, the sum of all other consumptive water requirements for MIS retorting has been estimated at between 61 and 128 gallons per barrel (Fox, 1980). The disposal of the brine stream by evaporation represents a significant cost, because of the large area of lined ponds needed.

The amount of material that can be removed by intentional leaching and the concentration of various solutes depend upon the mechanisms that control the release of solutes from the solid phase (primary mechanisms) and those that control the concentration of solutes in the aqueous phase (secondary mechanisms). The initial release of solutes typically is governed by solubility of spent shale mineral phases, adsorption or ion exchange equilibria, and diffusion of solutes from the interior of spent shale particles to the surface. Aqueous-phase concentrations subsequently may be controlled by precipitation or readsorption.

Not all constituents may be simultaneously controlled using intentional leaching, because many mechanisms govern leachate composition. Preliminary experiments reported by Peterson et al. (1982) revealed that solubility controls may limit the application of this technique. They found that large soluble reservoirs of some elements, such as As, Li, Ni, Na, and Sr, remain after leaching and that secondary solubility controls on other elements, such as F, may limit the efficacy of this technique. However, other constituents, including TDS and TOC, which apparently are limited by mass transfer from the solid to the bulk liquid phase (Amy, 1978) may be reduced using this technique.

Additional experimental work is required to evaluate the ability of intentional leaching to reduce specific ions in complex physical systems. Thus continuous-flow laboratory experiments should be conducted to assess the suitability of this control technology for specific ions of interest (e.g., V, Pb, Se).

We have developed and validated a mass-transfer model that is suitable for evaluating intentional leaching as a control method for TOC. This same model could easily be extended to TDS, using available experimental data and the same mathematical framework. This model explains the general decrease in TOC with flow through a column of in-situ spent shale. This chapter will review this model and use it to estimate the number of pore volumes of water which would have to pass through an abandoned MIS retort to reduce the TOC concentration to 10 percent of its initial value.

5.2 The Physical Model of MIS Spent Shale Leaching

The abandoned in-situ retort was modeled as a fixed bed packed with spent shale particles. Bimodal porosity was assumed in which the void space is distributed between micro- and macropores. The micropores are contained within the particles and result from the pyrolysis of kerogen and decomposition of carbonate minerals. Macropores are defined as the space between the particles. Solute transport within micropores occurs by diffusive mechanisms only while transport in macropores is primarily by advective and dispersive mechanisms.

A typical column breakthrough curve (a plot of effluent solute concentration vs. time) is shown in Figure 5-1. Mass transfer is assumed to occur in three stages. Stage I takes place subsequent to the filling of the bed voids with water and prior to the passage of the first pore volume of leachate. Stages II and III start immediately following the passage of the first pore volume; stage II is initially dominant but later decays, leaving stage III transport as the only mechanism until the reservoir of leachable material is exhausted.

During stage I, soluble material is transported from the outer surfaces of particles to the macropores, and from the inner surfaces to the micropores. At the start of stages II and III, the concentration of solute in the leachate is uniform throughout the pore system. As soon as the concentration in the macropores drops because of advective flow, a concentration gradient develops along the micropores, and solute is removed by the stage II mechanism, which is assumed to be Fickian diffusion.

The column effluent becomes gradually more dilute as the solute present in the micropores during the first pore volume is exhausted. This decrease in effluent concentration gives the typical rapidly decreasing stage II break-through curve which has been noted by several observers.

As stage II solute is removed from the micropores and the liquid concentration therein drops, additional material is conveyed from the solid

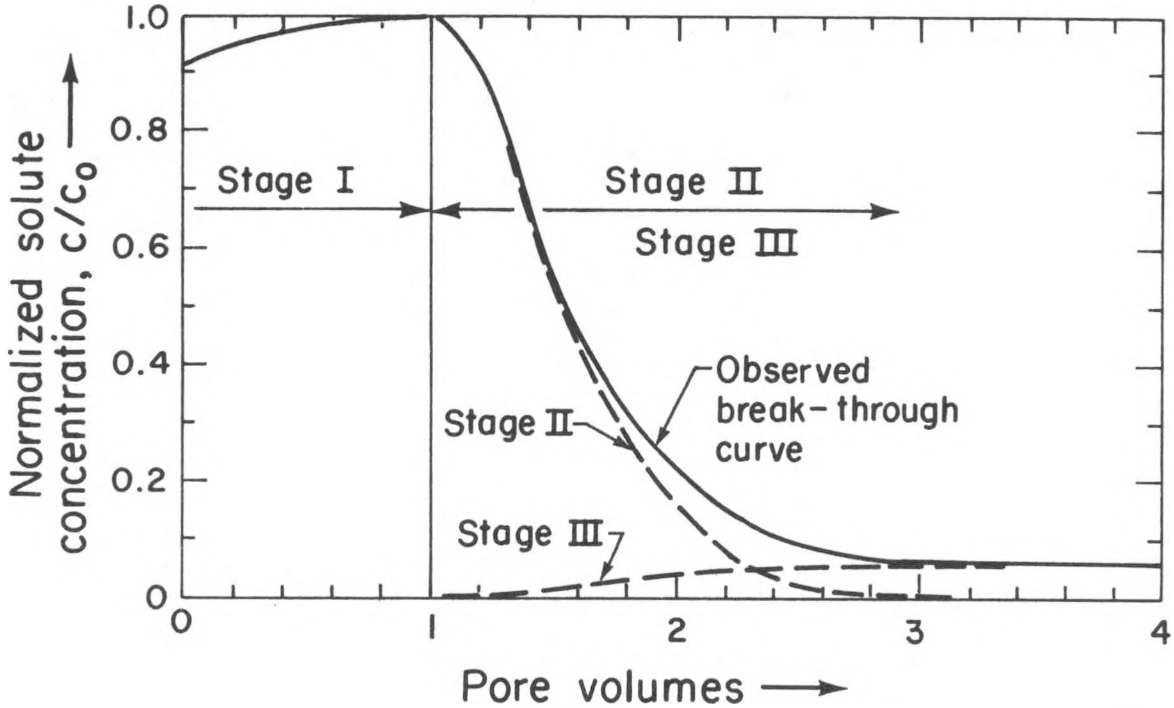


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Figure 5-1. Typical effluent concentration curve observed in column leaching experiments (Hall, 1982).

phase by stage III mechanisms. The mass-transfer rate of these mechanisms is much slower than that of stage II, as evidenced by the decrease in effluent concentration. If stage II mechanisms were rate-limiting, no such rapid decrease would be observed.

5.3 The Stage II Mathematical Model

Stages II and III were modeled separately (no model was developed for stage I). As noted above, stage II results in the rapid decrease in leachate concentration, and stage III represents the long tail. The spent shale particles were modeled as cylinders (Fig. 5-2). Solute transport occurs only in the pore planes normal to the axis of the cylinder. This agrees with the observation that raw and spent shale have distinct bedding planes along which fluid flow and transport occurs more readily. The mathematical development of the model is presented by Hall (1982) and is omitted here.

Solutions of the stage II model are presented in Figure 5-3 as dimensionless breakthrough curves in terms of the following parameters. ALPHAX is a dimensionless column length parameter:

$$\text{ALPHAX} = \frac{4\,D_m\,z}{m\,b^2\,U_p} \tag{5-1}$$

where D_m = diffusion coefficient, L^2T^{-1}
b = particle radius, L
z = distance in direction of flow, L
U_p = pore velocity, LT^{-1}
m = ratio of macropore volume to micropore volume.

TIME is a dimensionless time parameter:

$$\text{TIME} = \frac{\theta\,D_m}{b^2} \tag{5-2}$$

where $\theta = t - \frac{z}{U_p}$ = time after arrival of the first pore volume at a given location in the column, T.

TIME/ALPHAX is a dimensionless inverse velocity of flow through the column or retort.

$$\text{TIME/ALPHAX} = \frac{\theta\,m\,U_p}{4z} \tag{5-3}$$

The number of pore volumes, n_{pv}, is a function of TIME/ALPHAX.

$$n_{pv} = (\text{TIME/ALPHAX})(4/m) + 1 \tag{5-4}$$

The stage II model was verified by fitting breakthrough curves similar to those shown in Figure 5-3 to observed total organic carbon (TOC) column breakthrough data. Diffusion coefficients on the order of 10^{-5} cm^2/sec were calculated from the best-fit breakthrough curves. Diffusivities of this magnitude are typical of low concentrations of organic compounds in water, and

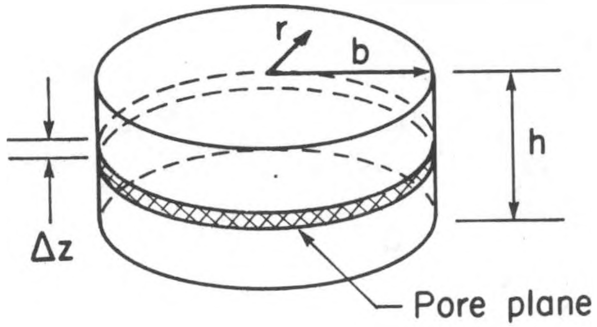

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Figure 5-2. Physical model of a spent shale particle (Hall, 1982).

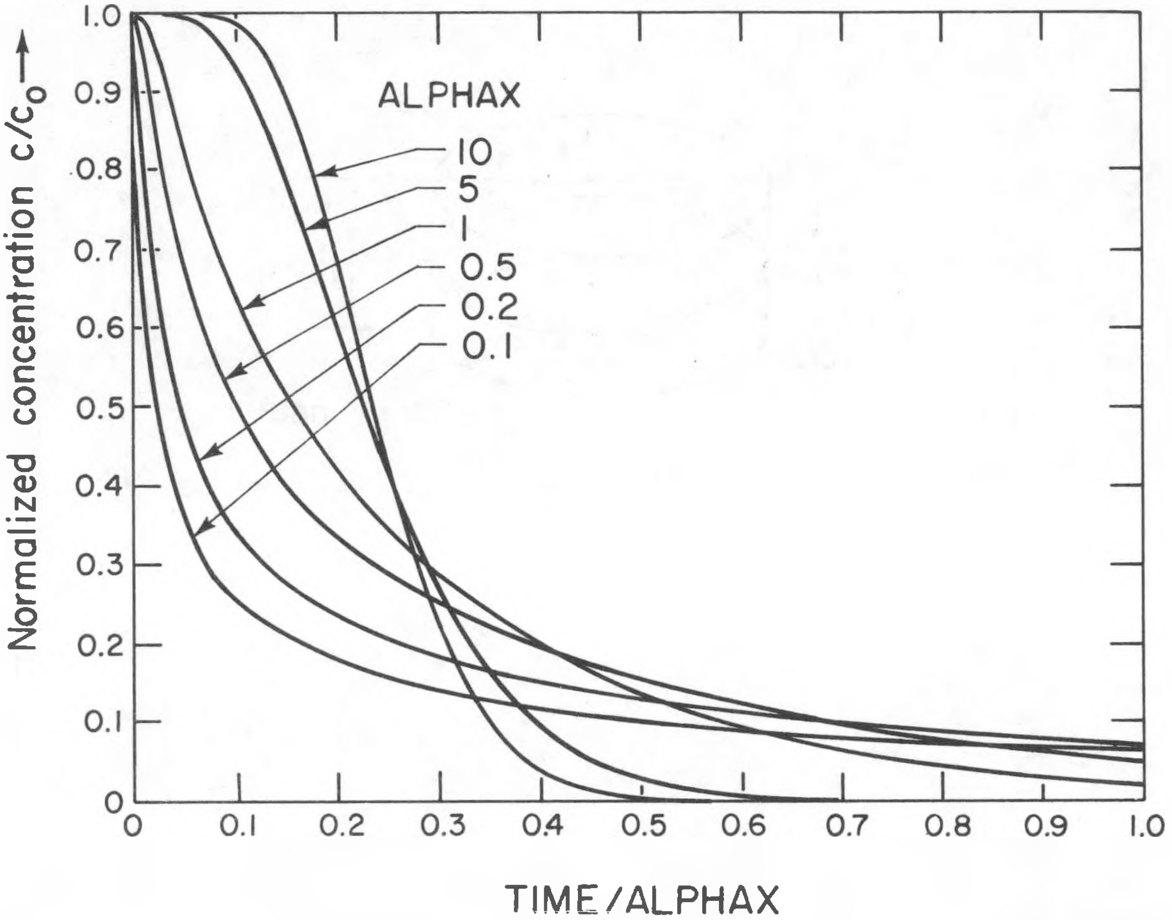

Figure 5-3. Plot of dimensionless breakthrough curves for ALPHAX values from 0.1 to 10 (Hall, 1982).

this was taken as evidence that the model was a reasonable representation of the leaching and transport process.

There was some evidence that dispersion caused by density gradients tended to distort the observed breakthrough curves, and thus the calculated diffusion coefficients contain a contribution from this dispersive mechanism.

5.4 Stage III Mathematical Model

The stage III mathematical model was derived from a mass balance of solute in the solid shale and in the leachate. The rate of TOC transport between phases in the extended tail where stage III mechanisms dominate was characterized by a mass transfer coefficient which was determined from long-term static leaching experiments. The model predicted TOC concentrations of less than 1 mg/L after the disappearance of stage II. A reasonable verification of this model against observed data was obtained.

5.5 Application of Leaching Models for Abandoned MIS Retorts

For any application of this model, it must be clearly understood that the models were validated only for TOC data derived from columns which were packed with a relatively uniform and small particle size of spent shale (i.e., less than 2.5 cm in diameter) and operated under laboratory conditions. In-situ spent shale in abandoned retorts will most probably have a much wider size range and also may be very chemically and physically heterogeneous. The presence of retorting gases, combustion products, and residual heat also will affect leaching mechanisms.

Two applications of this model will now be considered for illustrative purposes only. Using the data in Table 5-1, values of ALPHAX are calculated as shown, and compared to the solutions shown in Figure 5-3. Table 5-1 shows the required input data for tracts C-a and C-b, both for leaching by reinvading groundwater and for intentional leaching by pumping water through retorts. In the latter case, water is assumed to flow continuously through a single retort; countercurrent extraction as described by Thode et al. (1981) is not modeled.

The stage II model can be used to examine the effect of varying model parameters on the required number of pore volumes of leachate to reduce the effluent TOC concentration to a desired level. This analysis addresses only a portion of the problem. Leachates contain other soluble species, and a complete investigation must consider dissolved solids and individual organic and inorganic species which may be important environmentally. Additional work is recommended to address these other parameters.

For solubility-controlled species, effluent concentrations would be determined by equilibrium among ions in solution. Geochemical models are more appropriate for these ions. The stage II model is only applicable to those ions whose concentrations are limited by diffusion. Diffusion limitation may be the actual controlling factor for ions which Peterson et al. (1982) considered limited by availability of solute.

Extrapolation of the experimental data to field conditions is risky because the model was verified only distilled water and for much smaller particles than field retorts will contain. This estimate suggests, however, that after passage of two or three pore volumes, leachate TOC concentration would be decreased to 10 percent of its initial value. Almost all of the TOC would remain in the retort, available to slow stage III leaching.

Table 5-1. Estimation of the Number of Pore Volumes Required to Reduce Leachate Concentration to $c/c_o = 0.1$ for Groundwater Reinvasion and for Intentional Leaching at Tracts C-a and C-b.

Parameter	C-a	C-b
D_m, solute diffusivity, assumed, cm^2/sec	1.0×10^{-5}	1.0×10^{-5}
macroporosity (a,b)	0.40	0.23
microporosity (b,c)	0.18	0.23
m, ratio of macro- to microporosity	2.22	1.00
For Groundwater Reinvasion		
U_p, vertical velocity of flow through retort, cm/sec (d)	6.6×10^{-4}	4.30×10^{-5} to 1.35×10^{-4}
b, particle radius, cm	5.0	5.0
z, retort height, m	229	94
ALPHAX	25	350 to 111
value of TIME/ALPHAX at which $c/c_o = 0.1$ (e)	0.3	0.3
n_{pv}, number of pore volumes (f)	1.5	2.2
For Intentional Leaching		
U_p, vertical velocity of flow through retort, cm/sec (g)	1.55×10^{-2}	1.55×10^{-2}
ALPHAX	1.06	0.97
Value of TIME/ALPHAX at which $c/c_0 = 0.1$ (e)	0.6	0.6
n_{pv}, number of pore volumes (f)	2.1	3.4

(a) Based upon values reported for experimental MIS retorts.
(b) Macroporosity = (macropore volume)/(total volume). This is equivalent to the fraction of in-place raw shale which is mined out. Microporosity = (micropore volume)/(total volume).
(c) Microporosity = (0.3)(1 - macroporosity). That is, individual particles of spent shale have a porosity of 0.3. This value actually may be as high as 0.5; 0.3 is suggested by the data of Hall (1982).
(d) Estimated by Fox (1980, p. 203). Note that these velocities were calculated assuming that reinvasion is complete and a new hydrologic steady state has been established. Actually the first pore volume will fill up much more slowly.
(e) By interpolation or extrapolation in Figure 5-3. For infinite ALPHAX, the curve is a vertical line at TIME/ALPHAX = 0.25.
(f) From equation (5-4).
(g) Assuming one week to pump through a retort at tract C-b, as suggested by Thode et al. (1981).

It is important to note that calculations in Table 5-1 are for TOC, and similar calculations and models must be done for each constituent of interest. Recent work suggests that other constituents in leachate may be controlled by solid- and aqueous-phase products. In these cases, the number of pore volumes required to reduce leachate concentrations to $c/c_o = 0.1$ may be very much larger than calculated here for TOC, which is mass-transfer-controlled.

Studies are required to determine the effects of (1) leaching with groundwater, (2) long periods of time (greater than 100 years) that may pass between forced leaching and groundwater reinvasion, (3) field conditions such as trapped gases, elevated temperatures, and a bottom plug of different quality spent shale, and (4) multistaged leaching on system cost and efficiency. The second question is particularly important. During the long period after intentional leaching and before groundwater reinvasion, micropores will be full of water which may again become saturated with solute (if the reservoir of material was not depleted by intentional leaching). This would then be readily available for transport into the macropores, resulting in a second pulse of concentrated leachate. Studies by Stollenwerk (1980) indicate that this occurs for surface spent shales. This problem needs to be modeled and studied experimentally for in-situ spent shales.

Preliminary experiments have been conducted in which a single sample of MIS spent shale, recovered from Oxy retort R3E, was leached by three successive batches of water (Peterson et al., 1982). In these experiments, concentrations of some elements (including Ca, Mg, Si and F) remained constant, suggesting solubility controls, as discussed in Chapters 2 and 4. Concentrations of other elements (B, V, and Mo) decreased, suggesting exhaustion of available material, or limitation by mass transfer from the interior of the particle. For other elements, e.g., Fe, Pb, and Se, the trend was inconclusive. These data suggest that intentional leaching can reduce leachate concentrations of some constituents, but not of others. Further experimental work by these authors (in preparation) may clarify whether intentional leaching can be used to protect groundwater quality. If future results are favorable, then a treatment process must be demonstrated.

For materials that obey the mass-transfer model described here, stage II leaching only accounts for a small fraction of the total solute available. It is assumed that stage III leaching will continue until the reservoir of leachable material in the particles is exhausted. In the experimental work (Hall, 1982), the spent shale contained between 0.25 and 1.7 percent organic carbon, and the stage II curve usually accounted for only about 5 percent of this.

5.6 Conclusions

1. A mass-transfer model of the leaching of spent shale by distilled water has been verified for TOC. This model predicts that leachate concentration will decrease with flow, which has been observed for several solutes in leachate.

2. Similar modeling and experimental studies are needed for other constituents of interest and for groundwater-spent shale systems.

3. Leachate concentrations are reduced by the passage of a few pore volumes of water, but the majority of the solid-phase constituents remains in the spent shale. This material may be transported to the particle surface by pore diffusion and subsequently leached. This phenomenon should be studied

experimentally.

4. Calculations using the mass-transfer model indicate that TOC concentrations can be reduced to 10 percent of their initial values by intentional leaching with 2 to 4 pore volumes of water.

5. A treatment process must be demonstrated before intentional leaching can be considered a viable control technology.

6. The water requirements for intentional leaching are similar in magnitude to the sum of all other water requirements for MIS processing and may limit the use of this technology.

CHAPTER 6. RETORT GROUTING AS A CONTROL TECHNOLOGY

6.1 The Grouting Operation

The grouting of abandoned in-situ retorts would be of unprecedented scale. As presently envisioned, it has similarities to and differences from dam foundation grouting (in which cement slurries are injected into fractures in rock), preplaced aggregate concrete construction (in which sanded cement mortar is injected into gap-graded preplaced aggregate), and hydraulic stowing of mine wastes. The literature of these fields was reviewed as a preliminary step to cost projection (Persoff and Fox, 1979).

As discussed above, in situ retorts must be prewetted. This would be accomplished by flooding followed by drainage. It is assumed that the pillars between retorts are sufficiently strong to withstand the hydraulic loading on one side; if not, several retorts must be flooded at the same time. Only about 50 to 70 percent of the flooding water would be recoverable for grout production. The remainder would be retained in the saturated in-situ spent shale.

A proposed system for handling spent shale for the grouting operation is described by Nevens et al. (1979). Watson et al. (1982) also report experiments in grout development.

6.2 Criteria for Grouts for MIS Retorts

Qualitatively, a grout must meet the following criteria:

1. Fluidity must be sufficient to penetrate nearly all the macropores (spaces between rubble particles) in an abandoned retort, and the setting time must be long enough to allow grout penetration.

2. Permeability of the grouted retort must be sufficiently low to control transport of leachate within acceptable limits.

3. The contribution of the grout material itself to dissolved material in leachate must be small enough not to offset the benefit of reduced leaching flow. Related to this is the issue of grout permanence. The grout must degrade slowly enough to control leachate transport within acceptable limits.

4. The grout material must be cheap.

5. The grouted retort must have sufficient strength to satisfy structural requirements for subsidence prevention and, if possible, enhanced resource recovery.

6.3 Quantity of Grout Required

The analysis presented in Chapters 2 and 3 indicated that some control technology would probably be needed and that backfilling retorts with a cheap grout would probably be cost-acceptable. In principle, grout need only be applied to the outer surfaces of a retort to prevent the flow of groundwater through the retorts. In practice, however, the distribution of grouts through rubble is difficult to control. Therefore, it was concluded that the effectiveness of a grouting program would depend on filling the entire void space in the retort (macropores only, not micropores within particles left by pyrolysis of kerogen). For 25-gal/ton oil shale, with 65 percent recovery by in-situ retorting, 39 cubic feet of rock will be retorted per barrel of oil recovered; for 25 to 40 percent void volume, about 9 to 13 cubic feet of voids must be filled per barrel of oil recovered. Such a large requirement for grout material could be met only by on-site waste materials, such as surface-retorted spent shale. It is assumed that surface retorting would accompany any MIS project.

6.4 Water Requirement for Spent Shale Grouting

Water for grouting includes water for prewetting the in-situ spent shale and water for mixing the grout. In-situ retorted shale, being hot, dry, and porous, is very water-demanding. Nevens et al. (1977) found that 2.5 to 4 gallons of water per cubic foot were required to saturate simulated in-situ spent shale, corresponding to an internal porosity of 0.33 to 0.53. Hall (1982), studying spent shale from LETC run S-55, found an internal porosity ranging up to 0.50 and averaging 0.27. This internal pore space must be saturated with water before the retort can be grouted. Unsaturated in-situ spent shale will extract water from the grout and prevent it from flowing (the importance of water content of the grout to fluidity is discussed in Chapter 10). The quantity of water needed for grouting, expressed in gallons of water per barrel of oil recovered, can be calculated from

$$Q = \frac{\left([1-a]b\rho_w + a\rho_g\left[\frac{w}{1+w}\right]\right)\frac{1}{8.34}}{a\rho_s y r_s + (1-a)\rho_s y r_i}$$

where Q = water required for grouting, gal/bbl
a = porosity of the in-situ retort before retorting (original voids), $0.2 < a < 0.4$
b = porosity of in-situ spent shale, $b < 0.5$
w = water-solid ratio of grout, typically $w = 0.7$
ρ_w = density of water, $\rho_w = 62.4$ lb/ft^3
ρ_s = density of raw shale, typically $\rho_s = 140$ lb/ft^3
ρ_g = density of grout, typically $\rho_g = 100$ lb/ft^3 (this can be calculated for the grouts described in Chapter 10 using the density of spent shale, and agrees with observation)
y = oil yield from Fischer Assay, typically $y = 24$ gal/ton $= 0.00029$ bbl/lb
r_s = surface retorting recovery factor, typically $r_s = 0.9$
r_i = in-situ retorting recovery factor, typically $r_i = 0.65$

The water requirement for grouting can be calculated per barrel of oil recovered either counting recovery from surface retorting, or neglecting it (in which case substitute $r_s = 0$). For $a = 0.23$ (Oxy retort 5), the water requirement is 136 gal/bbl with surface recovery, and 198 gal/bbl without it. For $a = 0.40$ (Rio Blanco retort 0), the water requirement is slightly less, 132 gal/bbl with surface recovery, because although more grout needs to be placed, more of the shale is surface-retorted, with a higher recovery factor. Without surface recovery, it increases to 267 gal/bbl. These figures exceed all other consumptive uses of water in MIS processing. Fox (1980) indicated that water requirements for MIS retorting, excluding retort abandonment, would be between 61 and 128 gal/bbl. Lower water requirements were calculated from data presented by Nevens et al. (1979) for grout production (96 gal/bbl counting surface retorting, 136 gal/bbl not counting surface retorting, including water for prewetting spent shale). These figures were based on a water-to-solids ratio of 0.47, which appears to be too low to prepare an adequately fluid grout.

Substantial water requirements are evident. It is anticipated that in an actual grouting operation, mine water would be the source of water for retort prewetting and grout production. Estimated dewatering rates cover a wide range. Robson and Saulnier (1981) calculated long-term dewatering rates of 2200 and 6700 gpm at tracts C-a and C-b, respectively. Golder Associates (1977) estimated 9000 and 10,000 gpm, respectively, and Mehran et al. (1980) estimated 2500 to 22,000 for tract C-a and 14,000 gpm for tract C-b. For a grouting water requirement of 132 to 267 gal/bbl of oil, 4600 to 9300 gpm would be required to grout MIS retorts from a 50,000 bbl/day plant. Thus, the majority of the mine water would be required for retort grouting. It is unlikely that this quantity of water would be available for consumptive use since it is generally agreed that much of the mine water will have to be reinjected downdip or used to augment surface flows to maintain existing water rights. Thus, availability of water will be a serious issue for retort grouting. However, if large flows of mine water need to be disposed of, grouting may represent a convenient disposal option.

6.5 Retort Grouting Work Covered in this Report

Development and testing of grouts for retort abandonment constituted the major portion of experimental effort for this project; these studies are discussed in the following four chapters. Previously published work is summarized with reference to the original publication. Complete accounts are given where the work has not been published elsewhere.

Chapter 7 presents the results of structural analysis of grouted retorts which was done to determine whether spent shale grout could be designed to increase resource recovery by permitting retort design with smaller pillars or secondary blasting and retorting of pillars between grouted primary retorts.

Chapter 8 reports experiments to enhance the setting properties of Lurgi and Paraho spent shale by various postretorting heat treatments. This work includes development of a true hydraulic cement by heating a mixture of Lurgi spent shale and limestone.

Chapter 9 reports experimental work that was done to evaluate waste materials (fly ashes and waste gypsum) as potential grout ingredients.

Chapter 10 presents the procedure that was used to formulate Lurgi spent shale grouts and the results of structural and permeability tests. Conclusions about retort grouting are also presented in that chapter.

CHAPTER 7. STRUCTURAL ANALYSIS OF GROUTED RETORTS

7.1 Introduction

Resource recovery in vertical MIS retorting is severely limited by the structural requirement that pillars of intact rock be left in place between retorts. For example, the development plans for both tracts C-a and C-b call for pillars to occupy about 50 percent of the total area. We evaluated grouting of abandoned MIS retorts to improve resource recovery. If the strength and modulus of elasticity of the grouted retorts were great enough, retorts could be designed with smaller pillars or eventual secondary recovery of the pillars between grouted retorts could be done. To assess the feasibility of this prospect, and to define structural design criteria for grouted retorts, we undertook a project of numerical modeling of subsidence and stresses in grouted and ungrouted retorts.

In the preparation and firing of MIS retorts, intact rock is replaced by rubble-filled cavities of essentially zero strength and modulus of elasticity. If abandoned retorts are then grouted, the cavities are replaced by material of strength and modulus which are not zero, but which are still much less than those of the original intact rock. With the replacement of strong intact rock by relatively weak grouted retorts, the geometry of the retort-pillar-overburden system adjusts to reestablish equilibrium, possibly resulting in failure of some element of the system. The final equilibrium position is determined by the constitutive stress-strain relationships for the materials (overburden, raw shale, grouted retorts) under consideration. Before mining and blasting, the intact in-place oil shale, which later serves as the pillars between retorts, is subjected to an initial compressive stress due to the weight of overburden upon it. After rubblization of a portion of the in-place oil shale to form MIS retorts, the original weight of overburden is borne in compression by a smaller area of intact oil shale pillars, causing an increase in the compressive stress. The greater the percentage of area contained in retorts, the greater will be the increase in stress. Retorts are designed so that the compressive stress, although increased above natural conditions, does not exceed the failure limit for raw shale. Overburden material must span MIS retorts and is thus subjected to a bending moment. The greater the horizontal dimensions of the retorts, the greater will be the bending stress. Again, retorts are designed so that the increased bending stress does not exceed failure limits for overburden. It is clear that increasing the percentage of areal recovery increases the stresses to which pillars and overburden are subjected. Conversely, increasing the stiffness of the abandoned retorts, as by grouting, reduces these stresses.

Rock is not a uniform material, and many of its structural properties are determined by fractures and joints rather than by the material itself. Even the properties of the intact material are difficult to determine, so in practice, designs commonly employ a factor of safety (F.S.) of 3 or 5 to ensure that failure is avoided.

7.2 Modeling Approach

For this work, a finite element model was developed which calculated the geometric deformation and in-situ stresses for a series of backfilled cavities. The model is described by Ratigan (1980) and Ratigan and Goodman (1981), and a user's manual and program deck are available. The approach taken was to simulate the geometry and material properties of the system, calculate the stresses produced when grout of various modulus value is used to backfill the retorts, and compare the calculated stresses to the safe limits.

Four different retort/pillar geometries and four different primary/secondary recovery schemes were examined. Tract C-a geometry and material properties were simulated as shown in Figures 7-1 and 7-2 and Table 7-1. Subsidence calculated for this system is shown in Figure 7-3.

7.3 Calculated Overburden and Pillar Stresses in Primary and Secondary Recovery

Overburden and pillar stresses were calculated for various primary and secondary extraction schemes. Primary extraction refers to a scheme in which retorts are burned with no recovery of the pillars, as described in development plans for tracts C-a and C-b. Secondary extraction refers to additional recovery of oil by rubblizing the pillars between burned retorts to form additional retorts (secondary retorts). For this work, tract C-a conditions were used. Retorts were assumed square, with pillars of equal thickness on all four sides (four-way symmetry). Four models of retort/pillar geometry were examined as shown in Table 7-2: pillar widths of 50 and 150 ft, and retort widths of 100 and 300 ft. Three degrees of secondary extraction (recovery of pillars between primary retorts after primary retorts have been grouted) also were evaluated: Scheme I secondary extraction is recovery of pillars between the retorts in the "east-west" direction (Figure 7-4). Scheme II secondary extraction is recovery of pillars diagonally between retorts (Figure 7-5). Scheme III secondary extraction is recovery of pillars between retorts in both the "north-south" and "east-west" directions (Figure 7-6). For the four-way symmetric geometry studied, scheme III secondary extraction gave twice as much secondary recovery as scheme I. Table 7-2 presents the total areal extraction for the various combinations. Note that for geometries 3 and 4, with the same pillar/retort width ratio, the percentage extractions are the same. However, the stresses developed are different.

Forty-eight model runs were done, using the four geometries, four degrees of areal extraction (primary plus three secondary schemes), and three values of grouted retort elastic modulus (stiffness). Primary retorts were assumed to be grouted; secondary retorts were assumed to be ungrouted. For each of these runs, the pillar compressive stress and the overburden tension were calculated.

The results of the calculations are shown in Figures 7-7 through 7-9. Each figure shows the results for a different assumed value of grouted retort elastic modulus. Each curve represents a different retort/pillar geometry (Table 7-2). Ticks on the rising curves are the calculated percentage areal extraction, as summarized in Table 7-2. Horizontal lines in Figures 7-7 through 7-9 represent the maximum allowable stress, using factors of safety (F.S.) of 3, 5, or 10. For example, Figure 7-7 shows that, if retorts are grouted to a modulus of 50,000 psi, and geometry 4 is assumed (retorts 100 ft square with 50-ft pillars between them) primary extraction would only result in 44 percent areal extraction and would have factors of safety of 7 for overburden tension and 9.5 for pillar vertical stress. If we go to scheme III secondary extraction, the areal extraction would increase to 89 percent, but the factor of safety decreases to less than 3 for overburden tension, and to less than 5 for pillar vertical stress.

7.4 Conclusions

This work showed that the retort design proposed for tract C-a is sound. Subsidence over the center of a tract of 121 retorts in a square grid

Table 7-1. Material Properties Used in Subsidence Model Calculations.

Region	Material	Modulus (E) (psi)	Compressive Strength (C_o) (psi)
Overburden		2.35×10^6	---
Pillars	Raw oil shale	1.35×10^6	9500
Grouted retorts	In-situ spent shale, grouted	50×10^3	1000
		250×10^3	1000
		750×10^3	1000

Table 7-2. Percentage of Total Area Recovered for Combinations of Geometries and Secondary Recovery Schemes for which Stresses Were Calculated.

Geometry	Dimensions		Total area recovered (percent)			
	retort width (ft)	pillar width (ft)	primary only	primary plus scheme I secondary	primary plus scheme II secondary	primary plus scheme III secondary
1	100	150	16	40	52	64
2	300	50	73	86	76	98
3	300	150	44	67	56	89
4	100	50	44	67	56	89

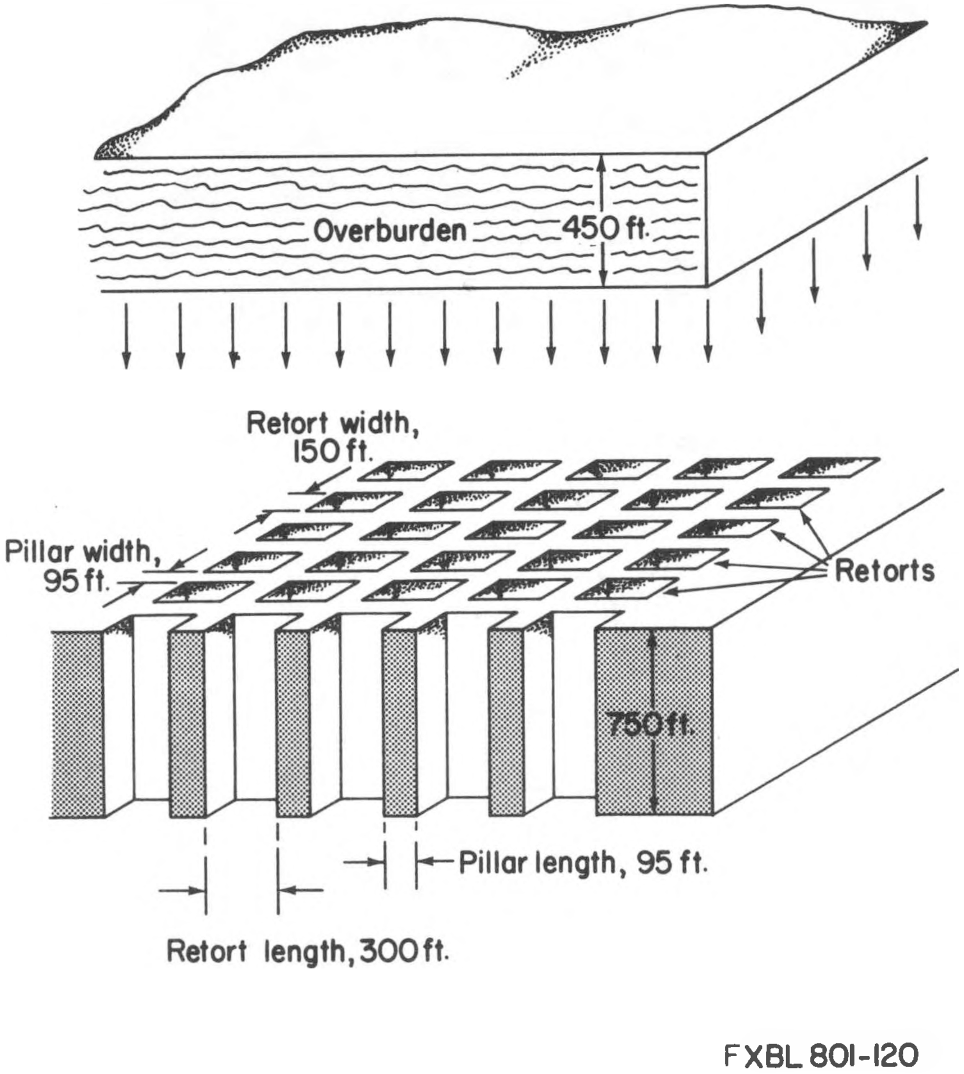

Figure 7-1. Retort, pillar, and overburden geometry used in subsidence modeling calculations. Dimensions are based on tract C-a.

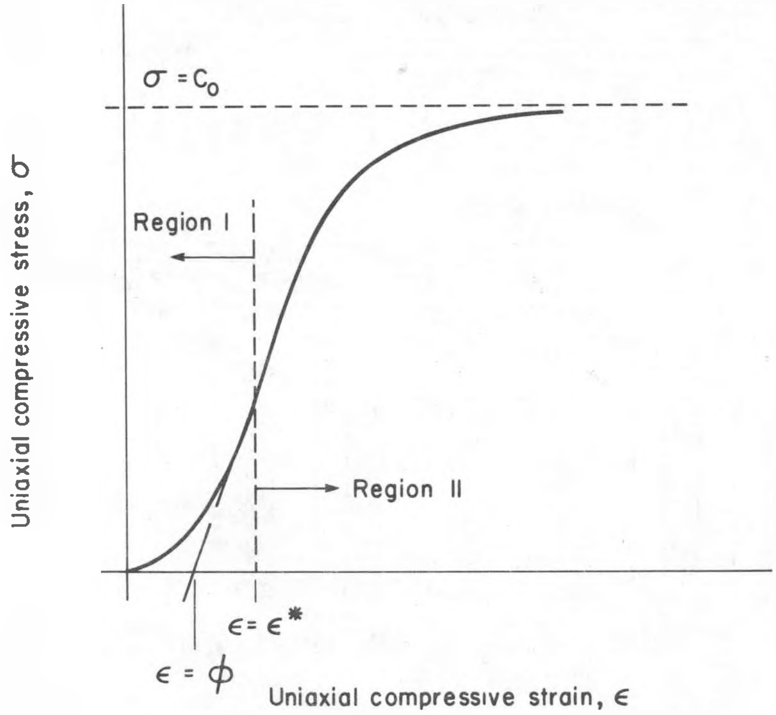

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Figure 7-2. Uniaxial stress-strain response assumed for pillars and grouted retorts (Ratigan and Goodman, 1981).

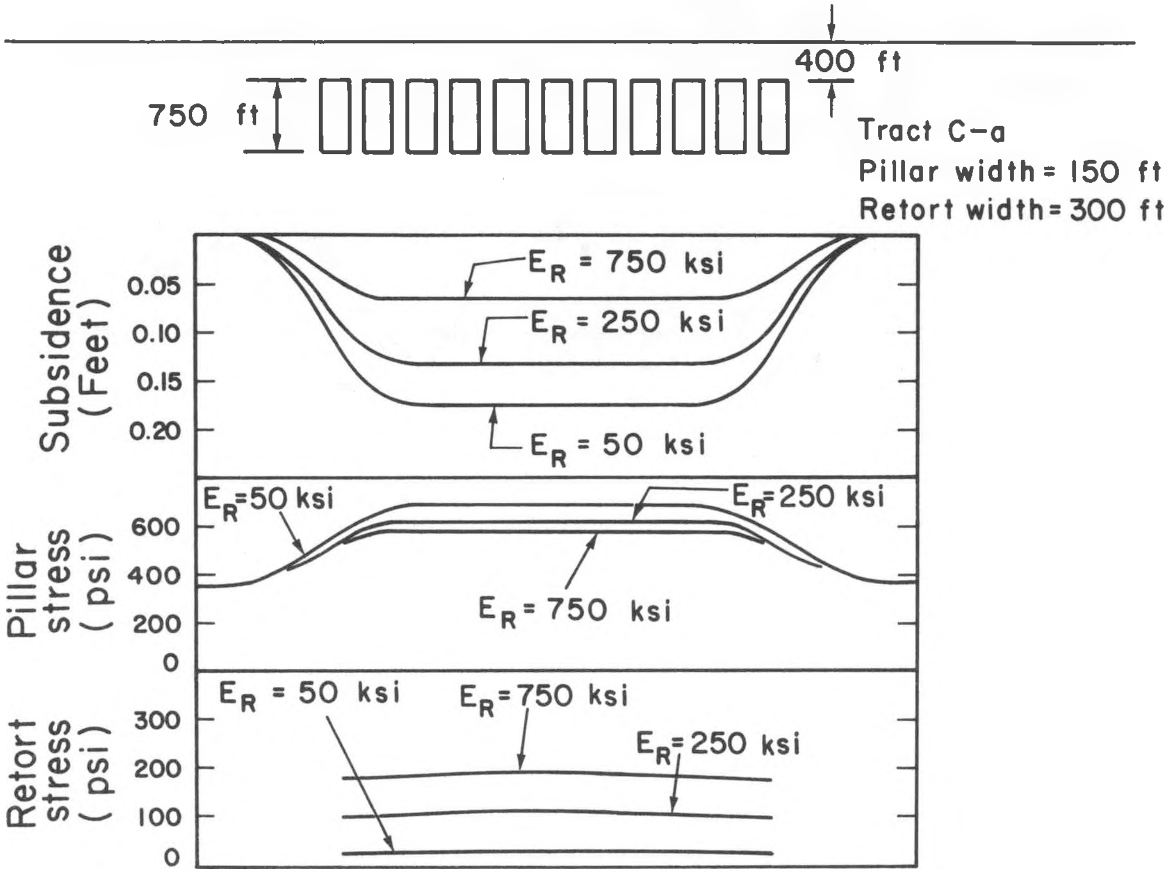

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Figure 7-3. Calculated subsidence and pillar and overburden stresses with three different values of grouted retort modulus of elasticity, primary recovery only.

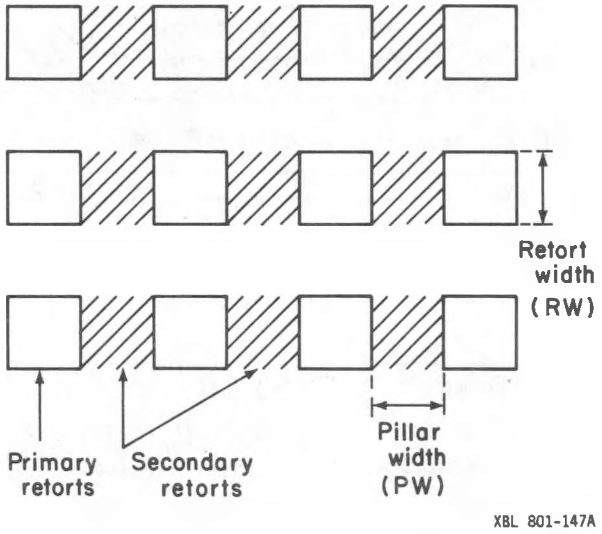

Figure 7-4. Definition sketch for scheme I secondary recovery.

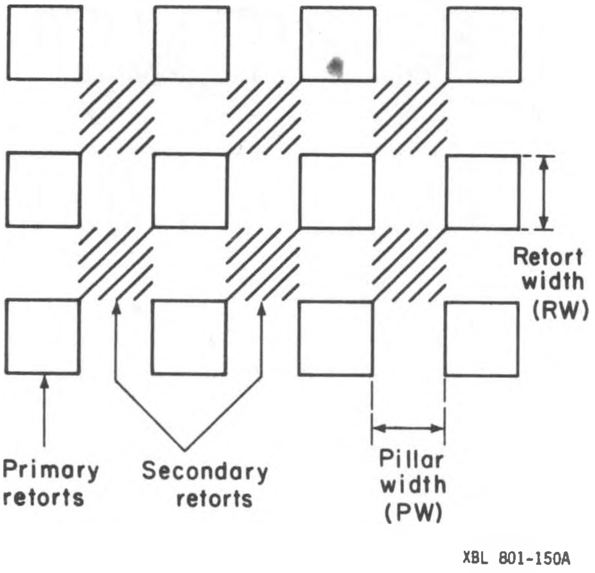

Figure 7-5. Definition sketch for scheme II secondary recovery.

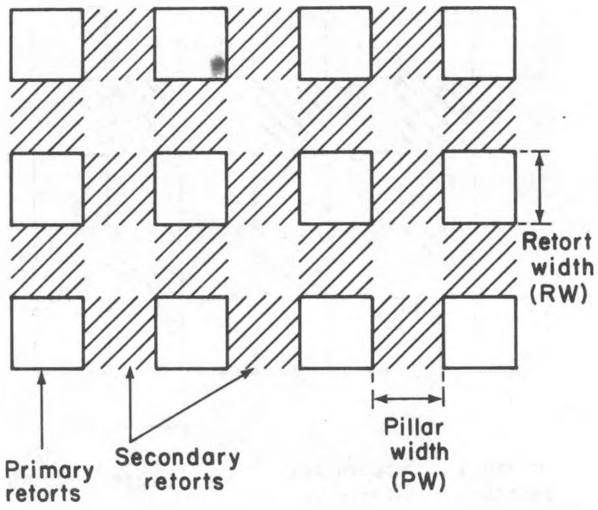

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Figure 7-6. Definition sketch for scheme III secondary recovery.

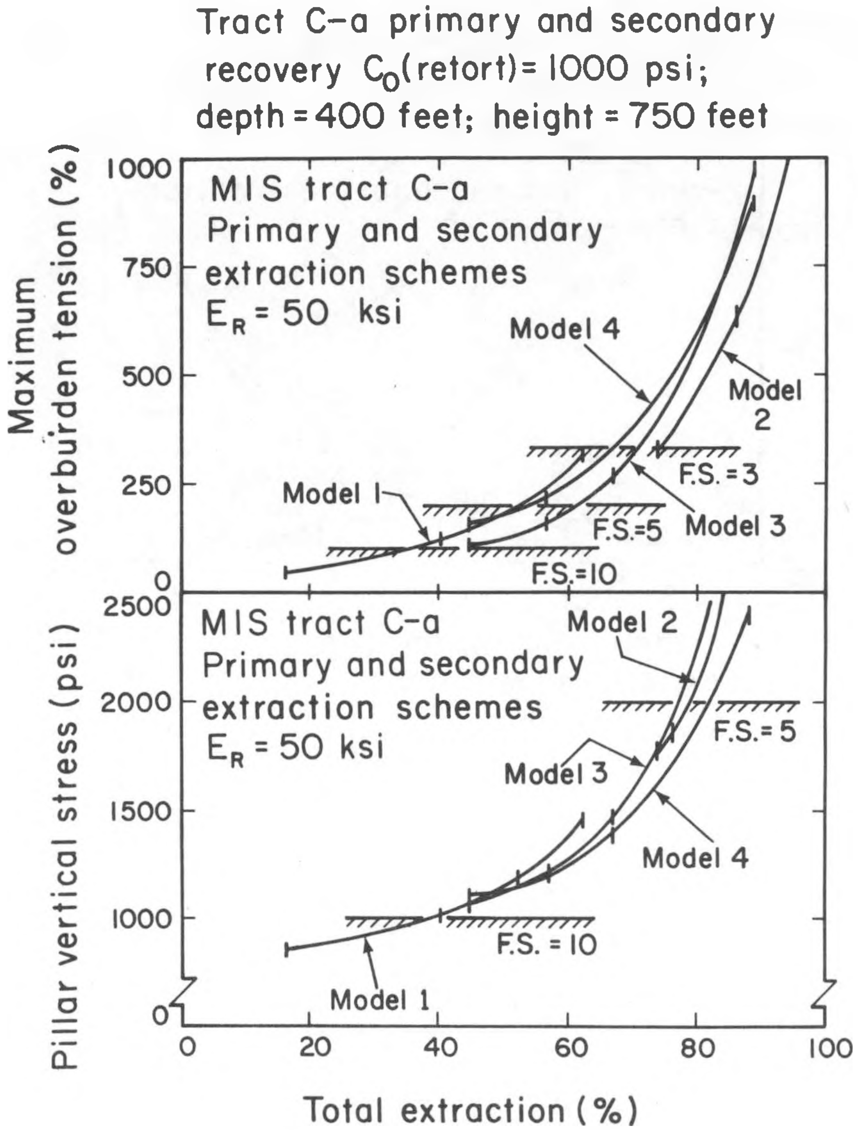

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Figure 7-7. Calculated variation of pillar vertical stress and maximum overburden tension with percent of total areal extraction. Each curve represents a different geometry as described in Table 7-1, and the ticks on each curve represent various degrees of primary and secondary recovery, as shown in Figures 7-4 through 7-6 and Table 7-1. Grouted retort modulus of elasticity = 50,000 psi.

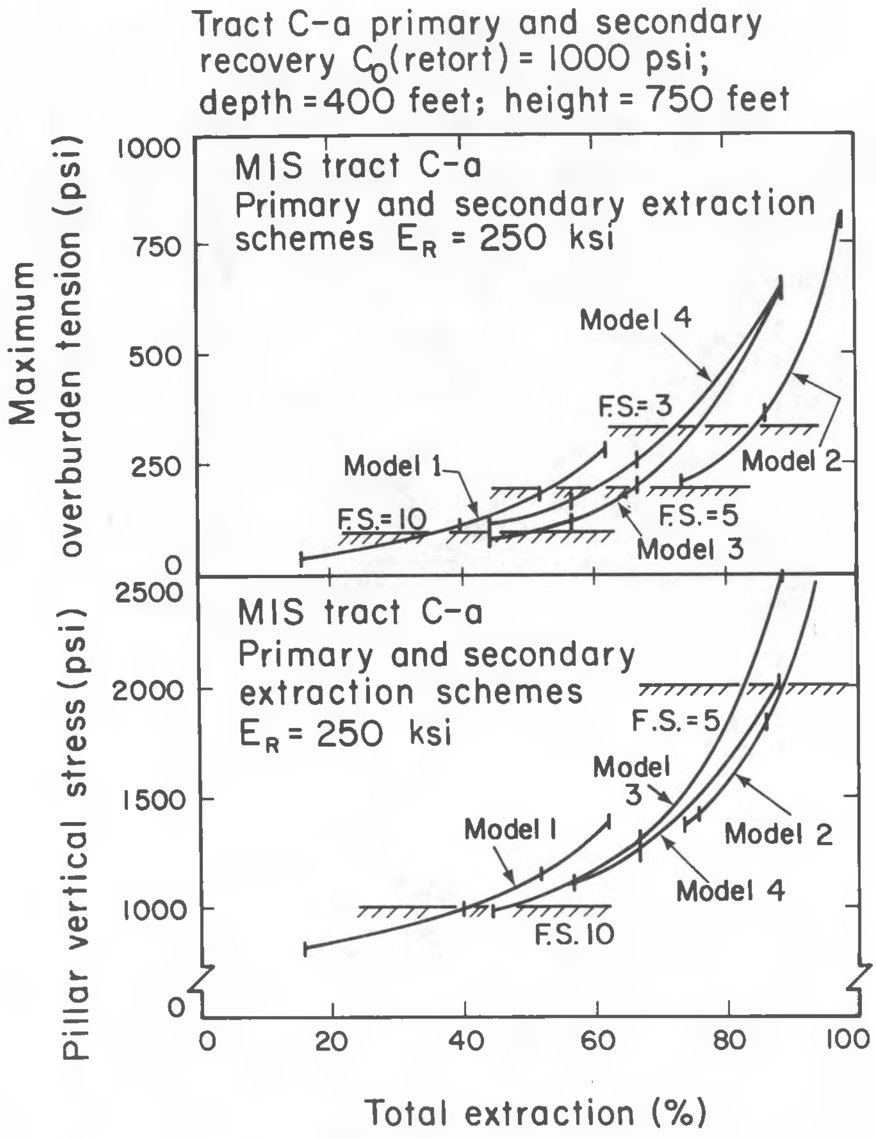

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Figure 7-8. Calculated variation of pillar vertical stress and maximum overburden tension with percent of total areal extraction. Each curve represents a different geometry as described in Table 7-1, and the ticks on each curve represent various degrees of primary and secondary recovery, as shown in Figures 7-4 through 7-6 and Table 7-1. Grouted retort modulus of elasticity = 250,000 psi.

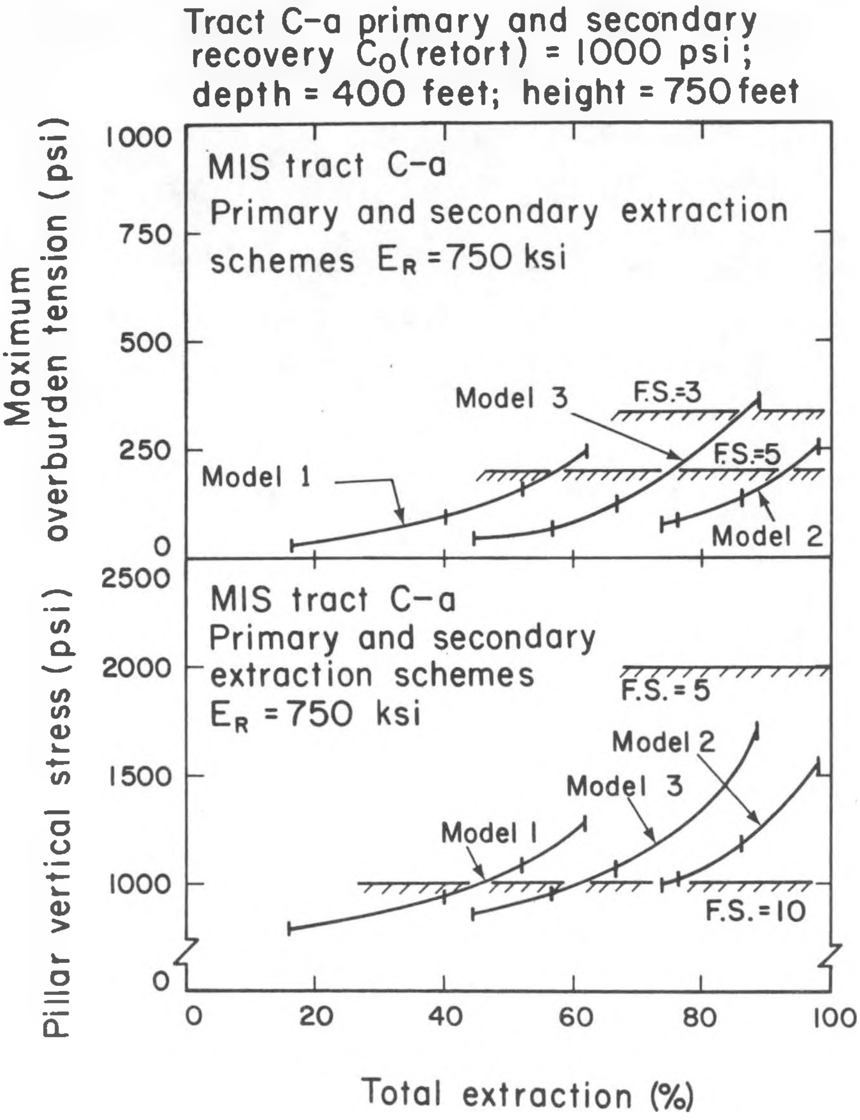

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Figure 7-9. Calculated variation of pillar vertical stress and maximum overburden tension with percent of total areal extraction. Each curve represents a different geometry as described in Table 7-1, and the ticks on each curve represent various degrees of primary and secondary recovery, as shown in Figures 7-4 through 7-6 and Table 7-1. Grouted retort modulus of elasticity = 750,000 psi.

was calculated to be less than 4 inches, even if not grouted. If grouted to a modulus of 750 ksi, the subsidence decreases to 1 inch, but this would not be worthwhile. This suggests that retort grouting is not important for structural stability of the abandoned retorts, and therefore permeability criteria should govern. For significant secondary recovery, grouted retort stiffness of at least 50 ksi would be needed. Tests of experimental spent shale grouts, as shown in Chapter 10, fell far short of this criterion. Therefore, secondary extraction of pillars for increased resource recovery is not possible with the spent shale grouts developed in this project.

CHAPTER 8. EXPERIMENTS TO IMPROVE THE SETTING AND CEMENTING PROPERTIES OF SPENT SHALE

8.1 Advantages of Cementing Properties in Grout Materials

Where the purpose of grouting is to control the flow of groundwater, cementing materials (defined below) are preferable to noncementing materials because they are stronger, less permeable, and more resistant to erosion and sediment transport. Historically, the first grouting material was a hydraulic cement similar to portland cement, and portland cement is presently the most commonly used grouting material. The large volume of voids to be filled makes portland cement, at $60/ton plus transportration costs, too expensive for backfilling abandoned in-situ retorts. Its cementing properties would be highly desirable, however, if they could be induced in spent shale, which is a waste material available on-site. Because of the high content of Si and Ca in raw and retorted Green River oil shale, we speculated that the retorted shale might have cementing properties (defined as the ability to react with water to produce a calcium silicate hydrate gel which gives strength) or pozzolanic properties (defined as the ability to react with lime and water to produce the same calcium silicate hydrate gel); or, alternatively, that these properties might be produced in the spent shale by heat treatment. A survey of the literature revealed that this process had been investigated previously for both Green River and other oil shales, both raw and spent, and that a process for the manufacture of portland cement from limestone and raw oil shale has been patented (Sellers and Chapin, 1959). Two cement plants in Colorado are currently producing portland cement from a low grade (2 to 2.5 gal/ton) oil shale and nondolomitic limestone. Retorted Estonian oil shale, which has a higher Ca and lower Mg content than Green River oil shale, has been used as an ingredient in blended cements (Kikas, 1968).

The setting properties of spent shale depend on the mineral composition and the retorting process. In general, setting is enhanced by retorting conditions that result in burning of most of the char (residual carbon remaining on the spent shale after pyrolysis) and decomposition of carbonate minerals to form oxides MgO and especially CaO (free lime), but not formation of calcium magnesium silicates. Formation of di- or tri- calcium silicates, which are portland cement compounds, would greatly enhance setting, but as shown below, this is unlikely to occur in Green River oil shales. The effect of retorting conditions on setting properties of the resulting spent shale is discussed by Farris (1979). The formation of free lime in Paraho spent shale is reported by Heistand (1978).

With the foregoing background in mind, tests were carried out to evaluate the suitability of Lurgi spent shale (LSS) as a cement or as an additive to blended cements and to determine how to modify spent shale to enhance its setting and hardening properties. This work (except section 8.3.3) was done in the laboratories of the Department of Civil Engineering, University of California at Berkeley, under the direction of Prof. P.K. Mehta. Standard ASTM tests for cement were used, modified only as necessary to apply the tests to spent shale or to use the tests with small quantities of sample. The tests used are listed in Table 8-1. Investigation was focused on LSS because this process has been under consideration to accompany MIS retorting at both tracts C-a and C-b, and because it meets the requirement of fine particle size. Other spent shales also were tested to determine the variability of properties.

Table 8-1. Tests Made on Spent Shale to Determine Cementing Properties.

Property tested	Test method	Test based on ASTM or other method	Modifications necessary (see notes)
Cementing	Compressive strength of mortar cubes	C 109	Higher water-cement ratio used (b)
Pozzolanic activity with portland cement	Strength comparison of mortar cubes with and without 35% replacement of cement by spent shale	C 311	None
Time of set	Resistance to penetration by standard Gillmore needle	C 266	Shallower test pat used (a)
Mineralogical analysis	X-ray diffraction		None
Elemental analysis	Nondispersive X-ray fluorescence	Hebert and Street, 1974	None
Free lime	Titration	C 114	None

(a) Modification necessitated by small size of sample or to conserve sample.

(b) Modification necessitated because properties of sample were different from those of portland cement.

8.2 Tests Made on Spent Shale as Received

A sample of approximately 70 kg of Lurgi spent shale (LSS) was graciously provided by the Standard Oil Company of Indiana. This material was Green River oil shale from the Colony Mine, which had been retorted at the Lurgi experimental retort in Germany. This particular sample was retorted in run 9, 1976, and collected in the electrostatic precipitator. As such, it represents the finest size fraction of spent shale from the Lurgi process. The properties of this sample are shown in Table 8-2.

Table 8-2. Properties of Lurgi Spent Shale as Received.

Mineralogical analysis(a)		Chemical analysis(b) (percent)		Particle size analysis(c) (percent)	
Quartz	present	Na_2O	2.3	> 0.0303 mm	0.6
Calcite	present	MgO	7.5	> 0.0179 mm	2.7
Dolomite	present	Al_2O_3	7.2	> 0.0100 mm	7.6
Feldspar	present	SiO_2	32.0	> 0.0066 mm	16.6
Free lime	not detected	CaO	21.8	> 0.00394 mm	42.3
		Fe_2O_3	2.7	< 0.00394 mm	57.7
		Loss on ignition (mainly carbonate)	20.0		
		Free lime	0.0		

(a) By x-ray diffraction.
(b) Elemental analysis by x-ray fluorescence.
(c) Analysis supplied by Lurgi.

8.2.1 Cementing Strength. The cementing properties of Lurgi spent shale as received were measured by ASTM C 109 (compressive strength of mortar cubes). In this test, 1 part of cement is mixed with 2.75 parts of standard sand and enough water to give a specified consistency (the desired consistency for this test is much too thick to pump as a grout). For portland cement, a water-solids ratio (WSR) of 0.4 is sufficient to prepare the mortar, but with LSS more water was needed. For ASTM C 109 tests, a WSR of 0.8 and a coarser sand (which reduces the amount of water needed) were used. Two-inch mortar cubes were molded and cured for 28 days at 73 F (23 C) under 100 percent relative humidity. In the standard test, the cubes are demolded after 3 days, but we found that the mortars made with spent shale could not be demolded without crumbling, so the cubes were left in the mold for the full 28-day cure. After 28 days, the cubes were tested to failure in a loading frame; LSS had a strength of only 72 psi. This indicated no significant cementing, and it confirms the mineralogical analysis by XRD which did not detect any cementitious compounds such as C_2S, C_3S, or C_3A*. Another surface-retorted spent shale, from the TOSCO hydrocarbon solids process (HSP), was tested similarly and gave a strength of 313 psi.

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*In cement chemists' shorthand C = CaO, S== SiO_2, A = Al_2O_3. Thus C_2S = Ca_2SiO_4.

8.2.2. Pozzolanic Activity with Portland Cement. Pozzolans are materials which are not cementing in themselves, but can react with CaO to form cementing compounds. Significant pozzolanic activity of spent shale would be of interest. The material could be marketed as a pozzolan or as an ingredient in blended cements, and also such pozzolanic activity could be exploited in grout development. Fly ashes described in Chapter 9 are marketed as pozzolans.

The standard test for pozzolanic activity (ASTM C 311) consists of running two tests for compressive strength of mortar cubes (ASTM C 109, described above), one with portland cement and the other with 35 percent of the cement replaced by the candidate pozzolan. In this test, accelerated curing for 28 days at 100 F (38 C) is used, because pozzolanic cements develop strength more slowly than portland cement. To qualify as a pozzolan, the strength of the 35 percent replacement cement must be at least 75 percent of the strength of the unblended cement. The ratio is called the index of pozzolanic activity with portland cement. The pozzolanic activity indices of Lurgi spent shale and HSP spent shale were 0.65 and 0.73, respectively. Both of these values are too low to qualify the materials used as pozzolans under ASTM C 311. In addition to pozzolanic activity index, other criteria including mineral analysis also would have to be met. The results from both the cementing and pozzolanic activity tests indicate that HSP is superior to LSS in these properties. The HSP process is currently under development, and the sample was not received until late in the project. Additional research to determine what value HSP may have as an ingredient in blended cement, or as the basis of a grout, are warranted.

8.3 Experiments to Enhance the Cementing Properties of Spent Shale

From the above results, it was clear that LSS as received had no significant cementing properties and only marginal pozzolanic properties. At this point, research was divided into two separate activities: (1) evaluation of as-received LSS in grouts (Chapter 10) and (2) evaluation of methods to enhance the cementing properties of LSS by appropriate postretorting heat treatments. The latter studies are discussed in this chapter.

Three series of experiments were conducted to enhance cementing properties. In the first, mixtures of spent shale and $CaCO_3$ in various ratios were calcined at temperatures ranging from 800 to 1000 C. The mixtures were heated in an autogenous atmosphere, i.e., evolved gases were not continuously removed. This work has been fully reported elsewhere (Mehta and Persoff, 1980; Mehta et al., 1980); a brief summary follows in section 8.3.1. Other experiments were done to improve the setting properties of Lurgi spent shale by heating it under various conditions without any added material; these experiments are reported in section 8.3.2. Finally, a patent application has been filed for a process to produce a hydraulic cement from raw Green River oil shale by retorting it under mild conditions and then heating it in steam (Mallon 1979a,b, 1982). We applied this process to Paraho spent shale, as reported in section 8.3.3.

8.3.1 Preparation of Hydraulic Cement from Lurgi Spent Shale with added $CaCO_3$. From the analysis of Lurgi spent shale (LSS) shown in Table 8-2, it was apparent that the minerals were primarily those present in raw shale. Higher temperatures would be needed to decompose the carbonate minerals. Preliminary experiments showed that when LSS was heated without added material, the carbonates decomposed to form the oxides MgO and CaO which reacted with the quartz present to form noncementing silicates such as akermanite, $Ca_2MgSi_2O_7$.

We hypothesized that addition of $CaCO_3$ could alter the composition of the raw mix to one more nearly approaching that of portland cement. This would favor the formation of cementing compounds rather than akermanite. Therefore two sets of experiments were conducted to determine the optimum temperature and level of $CaCO_3$ addition for formation of cementitious compounds. First, a 1:1 mixture of LSS and $CaCO_3$ was calcined at 900, 950, 1000, and 1100 C. The resulting clinkers were ground to powder, and the mineral composition and cementing properties were determined. Results of these tests are shown in Table 8-3. The strongest cement was produced at 1000 C.

In a second experiment, the calcining temperature was kept constant at 1000 C, and the $CaCO_3$-LSS ratio was varied. Results of this experiment are shown in Table 8-4 and Figure 8-1. Table 8-4 shows that the addition of $CaCO_3$ to the LSS prevented the formation of akermanite, a noncementing compound, and shifted the reaction equilibrium in favor of formation of cementing compounds β-C_2S and C_3A.

These results show that a true hydraulic cement can be produced by calcining LSS with an equal amount of $CaCO_3$. The strength of this cement is approximately two-thirds as great as portland cement. This work was reported in detail by Mehta and Persoff (1980).

8.3.2 Heat Treatment to Improve Cementing Properties of Lurgi Spent Shale Without Added $CaCO_3$. The addition of an equal amount of $CaCO_3$ to make a raw mix for cement manufacture would require transportation of such vast quantities of limestone as to make the process uneconomical for retort grouting. Therefore, additional experiments were done to determine what beneficial effects, from the point of view of cementing, could be obtained by heating the spent shale under various atmospheres with no added material. Table 8-4 shows that without any additional material, heating the spent shale in an autogenous atmosphere at 1000 C results in formation of akermanite, a noncementing Ca-Mg silicate. This would be predicted from the elemental composition of the spent shale as shown in Table 8-2. The ternary composition diagram in Figure 8-2 shows the weight ratios of Ca, Mg, and Si for various silicate minerals and for the spent shale and limestone mixtures. In solid-phase reactions, the reactants are not free to migrate and the local composition of the mixture determines the products formed. The favored product from heating of LSS is the nearest silicate product on the ternary diagram, in this instance, akermanite. Addition of $CaCO_3$ to the LSS moved the location toward the CaO vertex and promoted formation of β-C_2S, as shown in Table 8-4.

From the above considerations, it was apparent that, without changing the composition of the raw mix, any improvement in the cementing properties of the spent shale would not result from the formation of cementing compounds but rather from the formation of the oxides CaO and MgO, which can react with water to form crystalline hydroxides or with dissolved or atmospheric CO_2 to form carbonates. CaO also could react with pozzolanic components in the spent shale.

Accordingly, LSS was heated in controlled atmospheres at various temperatures for various times. A 5 gram sample of Lurgi spent shale was placed in a porcelain sample boat which was inserted into a 1-inch inside diameter, 1/8-inch thick wall mullite tube in a tube furnace. The atmospheres tested were no flowing gas (i.e., autogenous atmosphere), flowing nitrogen, or flowing steam. Steam was delivered to the mullite tube as shown in Figure 8-3.

Table 8-3. Mineralogical Analysis and Compressive Strength of Cement Made by Calcining a 1:1 Mixture by Weight of Lurgi Spent Shale and $CaCO_3$.

	Temperature of calcination			
	900 C	950 C	1000 C	1100 C
Minerals present (a)				
Akermanite	N	N	N	N
C_3S	N	N	N	N
β-C_2S	W	W	M	M
C_3A	W	W	W	W
$CaCO_3$	VS	S	W	N
Compressive strength after curing, psi (b)				
3 days	190	280	470	295
7 days	450	630	950	650
28 days	925	1400	2720	2100

(a) By x-ray diffraction; N=none, W=weak, M=medium, S=strong, V=very strong.
(b) By modified ASTM C 109.

Table 8-4. Mineralogical Analysis, Free Lime, and Compressive Strength of Cements Made by Calcining Various Proportions of CaCO3 and Lurgi Spent Shale for 1 hr at 1000 C.

	$CaCO_3$:Lurgi spent shale ratio by weight							
	2:1	1.75:1	1.5:1	1.25:1	1:1	0.75:1	0.5:1	0:1
Minerals present (a)								
$CaCO_3$	VS	VS	W	W	N	N	N	N
Akermanite	N	N	N	N	N	N	M	VS
C_3S	N	N	N	N	N	N	N	N
β-C_2S	W	W	M	M	M	M	W	N
C_3A	W	W	M	M	M	M	W	N
CaO	S	S	S	S	W	N	N	N
Free lime, % (b)	12.2	9.0	7.9	6.0	3.1	1.5	0.64	0
Compressive strength after curing, psi (c)								
3 days	120	250	140	170	340	375	poor	nil
7 days	380	630	390	395	670	455	poor	nil
28 days	840	1210	1200	890	2600	(d)	poor	nil
90 days	1310	1690	1910	1600	3340	(d)	poor	nil

(a) By x-ray diffraction; N=none, W=weak, M=medium, S=strong, V=very strong.
(b) By ASTM C 114.
(c) By modified ASTM C 109.
(d) Not determined.

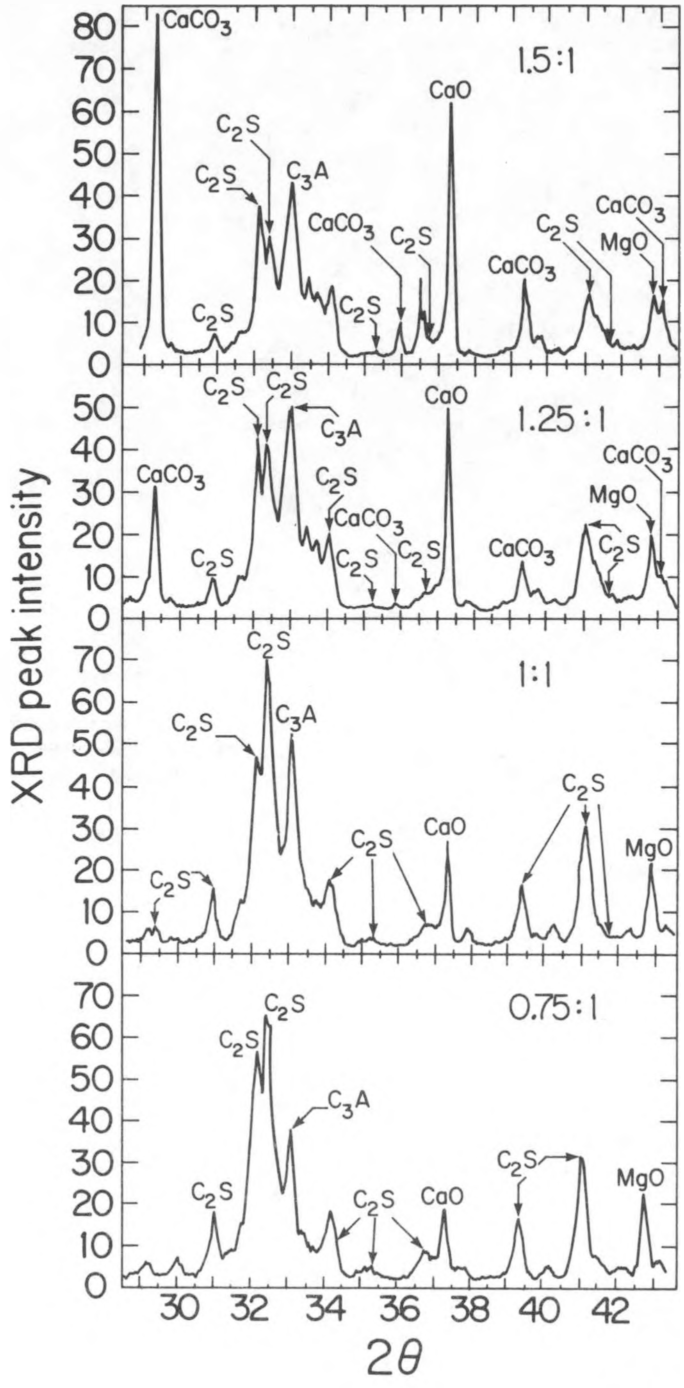

Figure 8-1. X-ray diffraction analysis of cements produced by calcining various proportions of $CaCO_3$ and Lurgi spent shale for 1 hr at 1000 C.

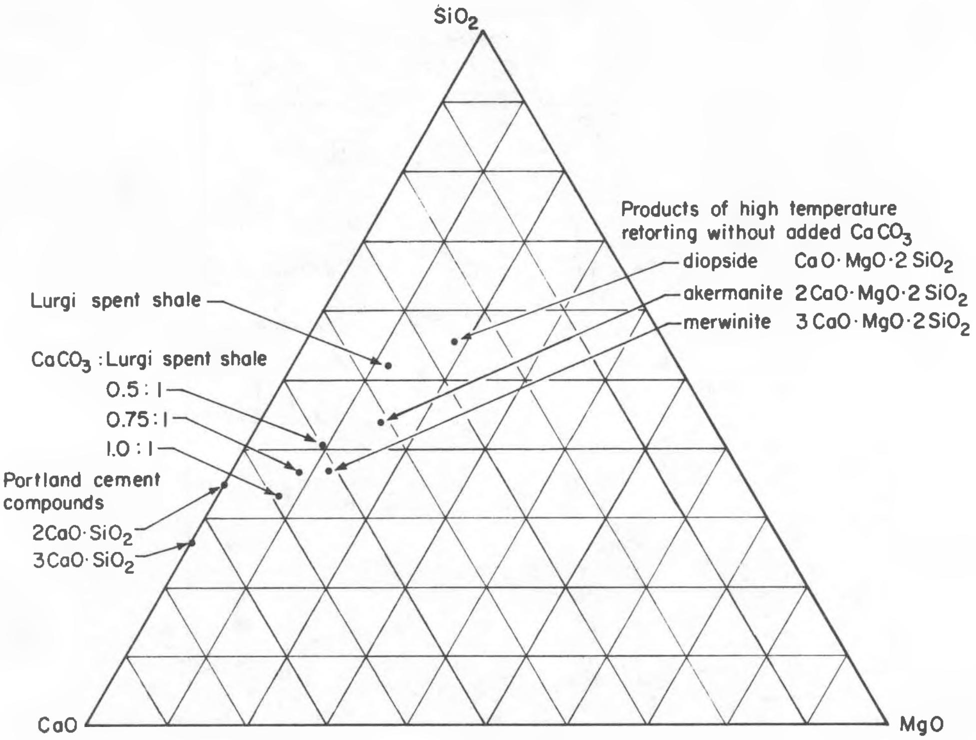

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Figure 8-2. Ternary composition diagram, showing the elemental compositions of Lurgi spent shale as received and with additions of $CaCO_3$, of silicate minerals formed by heating spent shale, and of portland cement compounds. The location of the point representing Lurgi spent shale is based on the elemental analysis shown in Table 8-2, ignoring minor elements.

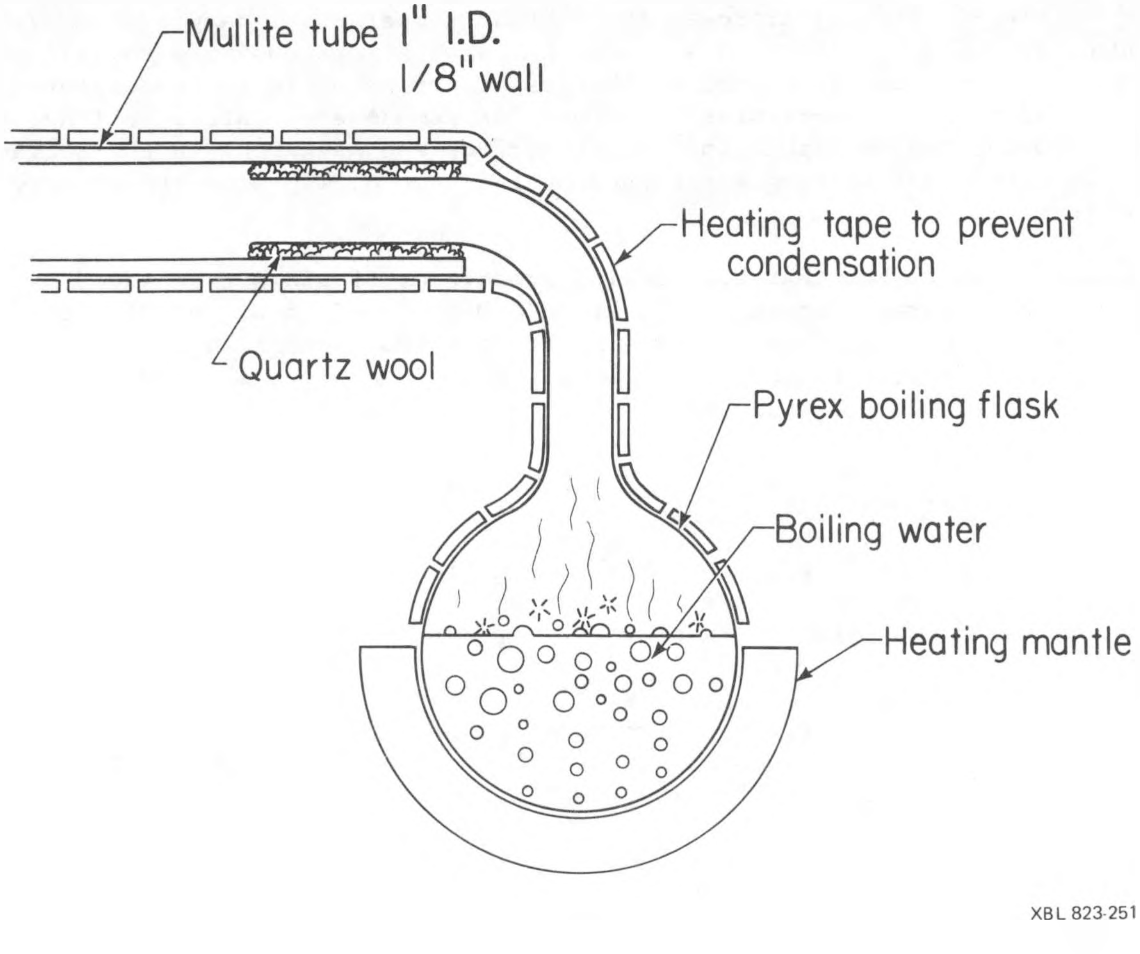

Figure 8-3. Method of delivering flowing steam to material under heat treatment.

Gas flow was continued during the cooling-down period. Samples were analyzed by ASTM C 114 for free lime and by XRD to identify mineralogical changes and were tested for time of set by a modification of ASTM method C 266 (time of set by Gillmore needle penetration). The modified setting test was done on a small pat (1/4 inch thick) rather than on the 1-inch thick pat stipulated by the method. This modification was needed because only 5 g of material could be prepared at a time. The powdered material was mixed with sufficient water to make a firm paste. Pats were cured at 73 F (23 C) in 100 percent relative humidity. Initial set is defined as the ability to support a needle which exerts a force of 1/4 lb over a circular area of 0.0018 in^2, without leaving an imprint. Final set is similarly defined as the ability to support a needle which exerts a force of 1 lb over an area of 0.00043 in^2.

The time-of-set, free lime, and XRD data are shown in Appendix B, Tables B-1 through B-3. Typical results, showing the progression of mineral phases during heating in flowing nitrogen for 1 hr at temperatures ranging from 700 to 950 C, are shown in Figure 8-4. Similar results were observed for all the experiments, with the mineralogical changes occurring at lower temperatures in steam and at higher temperatures in autogenous atmosphere. After setting, the samples developed a whitish color on the surface and just beneath the surface, which indicated that setting was caused by reaction of CaO with atmospheric CO_2 to form $CaCO_3$.

These results show that the setting properties of LSS are enhanced by heating under moderate conditions (1 hr at 800 or 850 C in air or nitrogen) to cause formation of free lime. They also suggest that retorting conditions which favor carbonate decomposition might result in a spent shale which would produce a stronger grout than LSS.

8.3.3 Experiments to Produce Hydraulic Cementing Compounds in Paraho Spent Shale by Heat Treatment with Steam. In a third set of experiments, we attempted to develop cementing properties in Paraho spent shale using a steam-heat treatment procedure developed by Mallon (1979, 1982). In our modification, Paraho spent shale (direct mode, run C-80-1, 1980) was used instead of raw shale, and the initial step of retorting at low temperature in an inert atmosphere was omitted. The conditions used in our experiments are summarized in Table 8-5. The purpose of using these various heat treatments was to determine whether strength was developed from silication reactions catalyzed by steam, from the presence of CaO, or from the products of carbonate decomposition in a flowing atmosphere which flushed away evolved CO_2.

The apparatus used for the heat treatments is shown in Figure 8-5. Spent shale was packed into a 1-in. inside diameter mullite tube. Quartz wool plugs held the material in place during the treatment. Maintaining the stability of the packed bed was important to avoid channelling of gases around, rather than through, the material. The mullite tube was heated in a tube furnace. In preliminary runs, two type K thermocouples were used to determine the temperature profile along the axis and wall of the tube. The maximum temperature was reached uniformly over a 2-in. long section of the tube, and flowing gas displaced the temperature profile slightly downstream. The wall thermocouple read about 10 C higher than the center line thermocouple. Since a uniform temperature exposure for the spent shale was desired, only the center 2 in. of the tube was loaded. This limited production to about 50 g per run. Temperature was measured with a single type K thermocouple placed at the wall, and manually controlled at 705 C. Flowing steam was delivered as for earlier experiments (Fig. 8-3).

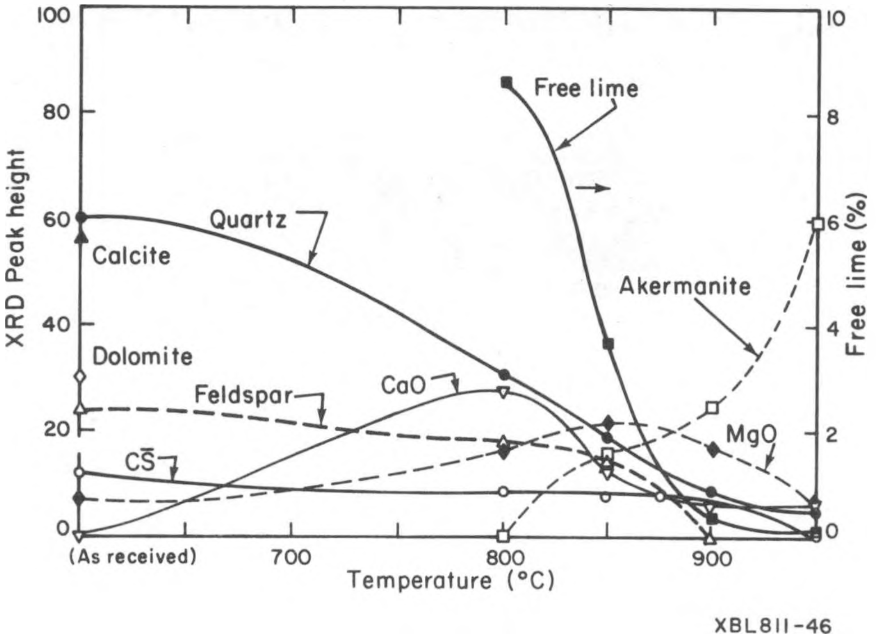

Figure 8-4. Mineral analysis of Lurgi spent shale after heating 1 hr in flowing nitrogen at various temperatures. CaO represents the XRD peak height; Free lime represents the weight percent free lime as determined by ASTM C 114.

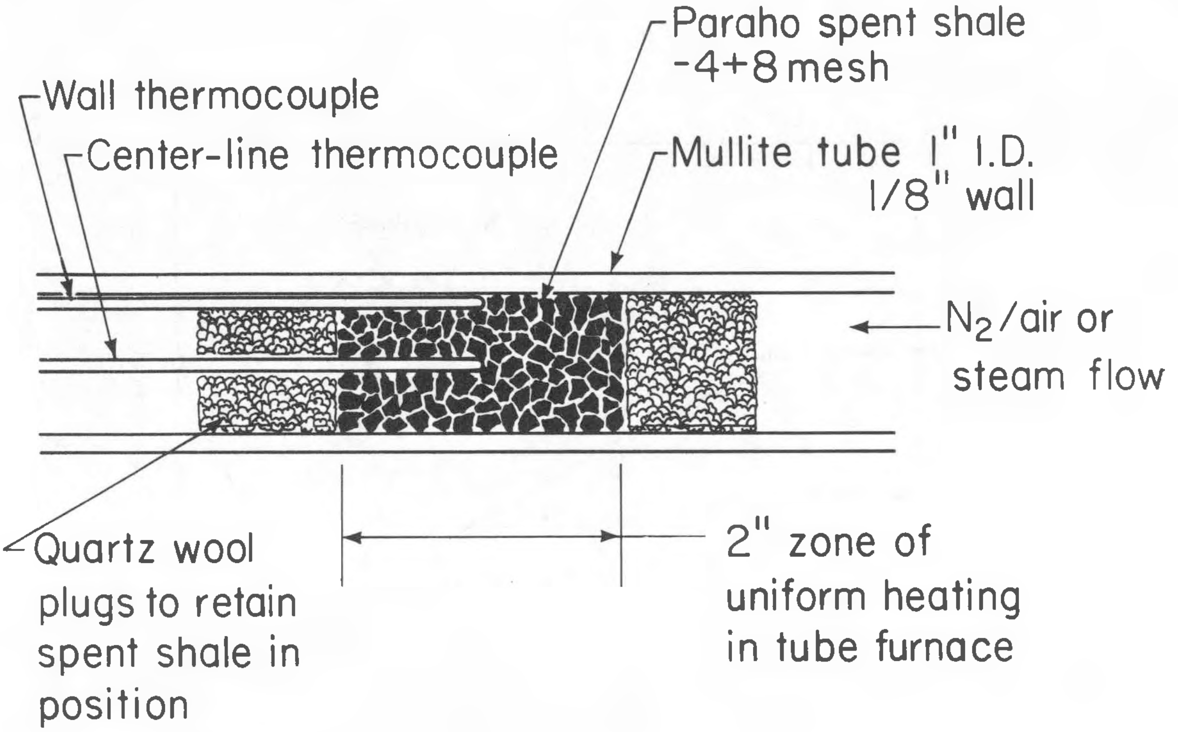

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Figure 8-5. Method of heating Paraho spent shale under controlled atmosphere.

Table 8-5. Preparation of Materials for Cementing Tests Using Paraho Spent Shale and Postretorting Procedure Modified from Mallon (1979).

Material	Steps in treatment process
S-1	• Paraho spent shale • ground to -200 mesh
S-2	• Paraho spent shale • crushed and sieved to -4 +8 mesh • heated in mullite tube below 550 C, in a flowing mixture of nitrogen and air, to burn off char • cooled in flowing nitrogen gas • ground to -200 mesh
S-3	• Paraho spent shale • crushed and sieved to -4 +8 mesh • heated in mullite tube below 550 C, in a flowing mixture of nitrogen and air, to burn off char • cooled in flowing nitrogen gas • 3 % CaO added • ground to -200 mesh
S-4	• Paraho spent shale • crushed and sieved to -4 +8 mesh • heated in mullite tube below 550 C, in a flowing mixture of nitrogen and air, to burn off char • gas flow changed to 100 % steam • temperature raised to 700 C • heated at 700 C, in flowing steam, for 70 min • cooled in flowing nitrogen gas • ground to -200 mesh
S-5	• Same as S-4, except heated in flowing nitrogen rather than flowing steam for 70 min at 700 C.

After loading the tube, the spent shale was heated as rapidly as possible in flowing nitrogen until it was hot enough to self-ignite (400 C). This typically required 20 minutes. Air was then added to the flowing nitrogen, and the external heat source (the tube furnace) was turned off. Combustion of residual organic carbon was indicated by a rise in the temperature while no external heat was supplied. By varying the air-nitrogen ratio, combustion was maintained below 550 C. The combustion step typically took between 15 and 20 minutes. For materials S-2 and S-3, the sample was then cooled in flowing nitrogen. For materials S-4 and S-5, the gas flow was than changed to steam or nitrogen, respectively, while the temperature was raised to 700 C. This temperature rise took between 30 and 40 minutes. The gas flow and temperature were maintained for 70 min at 700 C, after which the material was cooled to room temperature in flowing nitrogen.

Each batch of Paraho spent shale was weighed before and after treatment as a rough check on the observed mineral decomposition. Weight loss for both S-4 and S-5 was typically 13 percent, indicating either previous partial decomposition or incomplete decomposition of carbonate minerals. The ground materials were analyzed for free lime by ASTM C 114 and for minerals by XRD. Results of these analyses are presented in Table 8-6. The mineral analyses did not indicate the presence of any cementing compounds, and there was not enough material to use the standard test method for cementing strength, ASTM C 109 (compressive strength of mortar cubes). Therefore, in order to compare the materials for cementing, grouts were prepared with 0.8 water-solids ratio, mixed 3 minutes at 1300 rpm using a Jiffy mixer (Jiffy Co., Irvine, Calif.), and cast in 2-in. diameter by 4-in. high waxed cardboard cylinders. After curing for 70 days at 73 F (23 C) in 100 percent relative humidity, the samples were loaded to failure in a loading frame. The results of these tests are shown in Table 8-6.

Although temperatures did not exceed 550 C during the combustion of char, some of the dolomite decomposed. This is shown by the presence of periclase (MgO) in S-2, with an associated increase in height of the calcite peak. Further heating in either nitrogen or steam partly decomposed the calcite to free lime (S-4 and S-5), which was detected by XRD and ASTM C 114. No cementing compounds or silicates were detected by XRD. Strength development was apparently due to the presence of free lime. Although S-3 and S-4 had approximately the same lime content (3 percent), S-4 had higher strength. This may be related to the lime being produced by decomposition of calcite rather than being added as a reagent. While S-4 was heated in flowing steam, the best strength was obtained for S-5, which was heated in flowing nitrogen. Strengths measured were much lower than those reported by Mallon (1979a). Thus, it appears that while cementing products may be produced in raw shale by mild retorting followed by hydrothermal treatment, this cannot be done with Paraho spent shale.

8.4 Conclusions

1. Lurgi and Paraho spent shales are not hydraulic cements.

2. The setting property of Lurgi or Paraho spent shale is enhanced by heating to decompose carbonate minerals to form oxides MgO and CaO. Heating Lurgi spent shale in flowing nitrogen or air at 850 C for 1 hr accomplishes this. Heating Lurgi spent shale in steam at this temperature promotes formation of noncementing silicates (akermanite).

3. If the Ca:Si ratio of Lurgi spent shale is altered by adding an equal weight $CaCO_3$ to LSS, a true hydraulic cement can be produced by heating for 1 hr at 1000 C.

Table 8-6. Mineral Analysis of Paraho Spent Shale after Heat Treatment.

	XRD peak height			
Mineral analysis by XRD	S-1	S-2(a)	S-4(b)	S-5
Quartz(c)	100/41	100/30	100/27,100/29	100/31
Dolomite	60	69	0	0
Calcite	38	59	16,17,19	13
CaO	0	0	17,15, 7	22
Feldspar	25	28	31,48,40	33
MgO	0	24	27,27,33	24
Free lime by ASTM C 114	(d)	0.0	3.3,2.8,2.4	6.3
Time of Set by ASTM C 266				
Initial	(d)	1 day	8 min, 30 min	14 min
Final	(d)	7 day	10 hr, 30 hr	12 hr
Unconfined compressive strength, psi	(d)	35	232	337

(a) Mineral composition of S-3 was identical to S-2, except for addition of 3 percent free lime. Compressive strength of S-3 was 156 psi.

(b) XRD peak heights reported for 3 batches.

(c) Two peak heights are reported for quartz.

(d) Not determined.

CHAPTER 9. EVALUATION OF WASTE MATERIALS AS GROUT INGREDIENTS

9.1 Introduction

As indicated in Chapter 6, the large volume of voids to be filled in an abandoned in-situ retort requires that the grout materials be extremely inexpensive, such as waste materials from retorting or other processes. Utilization of waste materials also has the benefit of reducing a disposal problem. At the same time, transportation costs to the abandoned retorts requires that even waste materials, other than spent shale, be limited to a small fraction of the grout. Therefore, laboratory studies were undertaken to evaluate waste materials from the Utah-Colorado-Wyoming region as grout ingredients. This chapter reports the results of experiments to evaluate fly ash and waste gypsum.

9.2 Potential Value of Waste Materials as Grout Ingredients

Waste materials were considered which could increase the strength of the grout, or retard its setting. Fly ash (the fine ash from coal-burning power plants) is an obvious candidate as it is often used as a grout ingredient with portland cement, or even unmixed as a grout. Fly ash grouting is an established engineering practice, e.g., it is used to seal mine entrances (Murphy et al., 1968). Pozzolanic fly ash could react with any free lime present in the spent shale to form cementing compounds. (For definition of pozzolanic activity, see section 8.1). Fly ashes are classified according to mineral analysis by ASTM C 618. Class F fly ash is pozzolanic; class C fly ash is pozzolanic and also cementitious.

The cementitious properties of class C fly ash, in some cases, result from the presence of tricalcium aluminate (C3A). This compound also is present in portland cement; it is highly reactive and causes "flash set" unless its reactivity is retarded by addition of gypsum. About 5 percent gypsum is commonly added to portland cement specifically to prevent flash setting by reacting with C3A. Calcium sulfoaluminate hydrate (ettringite) is formed by the reaction of C_3A with gypsum and water, and it also contributes to the binding properties of the cement, increasing its strength. Therefore, gypsum tailings from phosphoric acid manufacture also were evaluated. Phosphoric acid is produced by the reaction between sulfuric acid and phosphate rock ($Ca_3(PO_4)_2$); gypsum tailings from this process are disposed of in slurry ponds. The materials evaluated are shown in Table 9-1.

9.3 Methods and Materials

Tests were conducted to determine the setting properties of the fly ashes. Waste gypsum was evaluated by comparing its performance to that of reagent gypsum. The test methods used were time of set (modified ASTM C 266) and compressive strength of mortar cubes (ASTM C 109). X-ray diffraction was used for mineral analysis of the fly ash and waste gypsum. The test methods are described in section 8.2.

Samples of fly ash were obtained from two power plants in Colorado (Craig plant, Craig, and Comanche plant, Pueblo) and from two in Wyoming (Jim Bridger plant, Rock Springs, and Wyodak plant, Gillette). The Craig plant is the nearest source of fly ash to the Piceance Basin, and the Jim Bridger plant is near the site of experimental true in-situ retorting work in Wyoming. The four fly ashes tested are all marketed as pozzolanic cement additives. Jim Bridger and Craig fly ash qualify under ASTM C 618 as Class F fly ashes, while

Table 9-1. Waste Materials (Other than Spent Shale) Evaluated as Grout Ingredients.

Waste material	Source	Delivered cost at Piceance Creek Basin(a)	Potential value in retort grouting	Tests used for evaluation
Class F fly ash	Craig Power Plant, Moffat Co. Colorado	\$30/ton	Pozzolanic activity	Time of set (ASTM C 266) Cementing strength (ASTM C 109)
Class C fly ash	Wyodak Power Plant, Gillette, Wyoming	\$54.50/ton	Pozzolanic activity, contains C_3A	Time of set (ASTM C 266) Cementing strength (ASTM C 109)
Class C fly ash	Comanche Power Plant, Pueblo, Colorado	\$31.50/ton	Pozzolanic activity, contains C_3A	Time of set (ASTM C 266) Cementing strength (ASTM C 109)
Waste gypsum	Gypsum tailings pond, Chevron Chemical Co., Magna, Utah	\$32/ton	Reacts with C_3A to form ettringite, retards flash set	Time of set (ASTM C 266) Cementing strength (ASTM C 109)

(a) Delivered costs are the sum of cost at plant and rail freight charges as quoted (Dunstan Laboratories, 1981).

the other two are Class C. Class F fly ashes are not cementitious, but they are pozzolanic; that is, they can react with lime to produce cementing calcium-silicate-hydrate (CSH) gel. Class C fly ashes have the additional property of being cementitious without addition of lime. Analysis by x-ray diffraction showed that Wyodak and Comanche fly ashes contain C_3A.

Waste gypsum was obtained from the gypsum slurry ponds of the Chevron Chemical Company's phosphoric acid plant at Magna, Utah (near Salt Lake City).

9.4 Strength Development of Fly Ash-Gypsum Mixtures

To evaluate Class C fly ashes as grout additives and determine the optimum level of gypsum addition, small amounts of reagent (not waste) gypsum were added to the fly ash, and the mixture tested for time of set (ASTM 266) and compressive strength of mortar cubes (ASTM C 109). These test methods are described in Chapter 8. The time of set and strength data are shown in Tables 9-2 and 9-3, respectively. Maximum strengths, over the tested range, occur at

Table 9-2. Time of Set of Wyodak Fly Ash (Class C) with Added Reagent Gypsum.

	Weight percent added gypsum		
	3	6	10
Initial set, min	20	20	16
Final set, min	60	90	160

Table 9-3. Compressive strength of fly ash-gypsum mixtures (ASTM C 109).

	Fly ash mortar compressive strength (psi)			
	Wyodak		Comanche	
	Test age (days)		Test age (days)	
Gypsum added, %	7	28	7	28
3	320	530	990	1000
6	680	890	580	640
10	610	1030	1240	1800

6 percent gypsum addition for Wyodak fly ash and 10 percent for Comanche fly ash. The greater strength of the Comanche fly ash is probably because it contains more C_3A than Wyodak.

The high calcium content of Class C fly ash suggested that it might replace limestone in the process for producing a hydraulic cement from spent shale described in section 8.3.1. A mixture of three parts Wyodak fly ash to one part Lurgi spent shale was calcined for 1 hr at 1000 C. The resulting product, however, was inferior to the as-received fly ash.

9.5 Evaluation of Retarders for Use with Class C Fly Ash

The cementing properties of Class C fly ash are ascribed to the presence of C_3A. This compound causes flash setting if a set retarder is not used. Accordingly, time of set measurements were made on Comanche fly ash with various set retarders, as shown in Table 9-4. Citric acid is known to be an effective retarder; gypsum is less effective, but increases the strength after setting. These results show that the waste gypsum is almost as effective as reagent gypsum to take advantage of the C_3A present in Class C fly ash.

Table 9-4. Strength and Time of Set of Comanche Fly Ash and Retarders.

		10% reagent gypsum	10% gypsum tailings	No gypsum
0.1 % citric acid	7 day strength, psi (a)	1625	1821	690
	28 day strength, psi	2075	2075	1040
	initial set, min (b)	8	--	31
	final set, min	15	--	38
No citric acid	7 day strength, psi	1240	1035	(c)
	28 day strength, psi	1800	1388	(c)
	90 day strength, psi	2180	--	(c)
	initial set, min	--	---	3
	final set, min	--	---	6

(a) Compressive strength of 2-inch mortar cubes (ASTM C 109).
(b) Time of set by modified Gillmore needle test (ASTM C 266).
(c) Unretarded fly ash set too quickly to prepare mortar cubes.

It is apparent from these results that a retarder would be necessary when preparing a grout with Class C fly ash and that use of gypsum would increase the strength of the grout. Waste gypsum appears to be almost as good as reagent gypsum for this purpose. Accordingly, test spent shale grouts were prepared with no fly ash, with 10 percent Class F fly ash, and with 9.5 percent Class C fly ash and 0.5 percent gypsum. Results of tests of these candidate grouts are presented in Chapter 10. The inclusion of 10 percent fly ash or 9.5 percent fly ash and 0.5 percent gypsum tailings in grout would increase the cost of grouting by approximately \$1.10/bbl of oil at tract C-a or \$0.66/bbl of oil at tract C-b. These costs are not included in Table 3-1. The difference between the two tracts results from the higher void fraction assumed for tract C-a.

9.6 Conclusions

1. A set retarder is needed if Class C fly ash is used as a grout ingredient, because of the presence of C_3A. Five percent gypsum is satisfactory as the set retarder, and it also increases the strength of mortars.

2. Waste gypsum can replace reagent gypsum in grouts made with Class C fly ash.

CHAPTER 10. FORMULATION AND TESTING OF SPENT SHALE GROUTS

10.1 Introduction

In Chapter 6, the reasons for selecting Lurgi spent shale (LSS) as a grouting material were discussed. In Chapter 8, the development of a hydraulic cement from LSS and $CaCO_3$ was described, and in Chapter 9, the inclusion of waste materials in the grout was discussed. This chapter will discuss the actual formulation of grouts based upon LSS and the testing of these grouts and of simulated grouted cores. The results of these tests will be presented and compared to the criteria for retort grouting which were listed in Chapter 6. They are repeated here:

1. Fluidity must be sufficient to penetrate nearly all the macropores (spaces between rubble particles) in an abandoned retort, and the setting time must be long enough to allow grout penetration.

2. Permeability of the grouted retort must be sufficiently low to control transport of leachate within acceptable limits.

3. The contribution of the grout material itself to dissolved material in the leachate must be small enough not to offset the benefit of reduced flow through retorts. Related to this is the issue of grout permanence. The grout must permanently retain its properties, or degrade slowly enough to control groundwater degradation caused by leaching within acceptable limits.

4. The grout material must be cheap.

5. The retort must have sufficient strength and stiffness to satisfy structural requirements for subsidence prevention, and, if possible, for enhanced resource recovery.

In experimental work to evaluate grouts made from LSS, two series of grouts were formulated to comply with the fluidity criterion while avoiding excessive bleeding (separation of a suspension by sedimentation to yield a clear supernatant). The specific criteria and methods used and experimental results are presented in section 10.2. Simulated grouted cores, containing coarse aggregate, and grout specimens, containing no coarse aggregate, were prepared and tested and compared to strength and permeability criteria. The test methods used and experimental results are presented in sections 10.3 and 10.4 for strength and permeability, respectively. The contribution of the grout material itself to solutes in leachate is discussed in section 10.5. The cost of grouting is discussed in section 10.6. Finally, in section 10.7, the results are summarized and conclusions drawn about the feasibility and efficacy of retort grouting.

10.2 Grout Fluidity and Bleeding Criteria

The formulation of grouts for injection into rubble is bound by two constraints that may be difficult to fulfill simultaneously. First, bleeding (separation of a suspension by sedimentation to yield a clear supernatant) must be as low as possible. Bleeding results in water-filled voids in the grouted mass. These could later act as conduits to pass water through grouted retorts. Second, the grout must be sufficiently fluid to maximize penetration through the voids of the rubble. The problem of grout penetration is discussed in detail in Appendix D.

Briefly, particulate grouts, such as spent shale grouts, are non-Newtonian fluids, in contrast to solution grouts, which are Newtonian. The penetration of non-Newtonian fluids into small pores is limited by the pore diameter, the pressure gradient, and the "yield stress" of the grout. Yield stress is the shear stress which must be applied to a fluid to make it flow (the yield stress of Newtonian fluids is zero). It may be thought of as contributing to the apparent viscosity of the grout. Other factors being equal, bleeding increases with water-solids ratio (WSR) and yield stress decreases. Thus, the objective is to formulate a grout that has a low enough yield stress without unacceptable bleeding.

Yield stress was not used directly as a criterion for grout formulation. Rather, the criterion for fluidity used in grout formula design was that the time of efflux through a standard Corps of Engineers grout flow cone be between 18 and 22 sec. Experience with intrusion grouting of preplaced aggregate concrete has shown this to be a realistic requirement (du Plessis, 1970; Crosby, 1971; American Concrete Institute, 1969). Grouts meeting this criterion were found to have yield stress values of approximately 60 dyne/cm^2. Theoretically, this is well below the limit for complete penetration in an abandoned MIS retort, as discussed in Appendix D.

Bleeding was measured on 250 mL of undisturbed grout after 4 hr in a graduated cylinder; the criterion for stability was that bleeding be less than 2 percent of the total volume. Preliminary experiments indicated that with only LSS and water, a WSR of 0.8 was the greatest that could be managed without bleeding of the grout. This ratio, however, yielded a grout too thick to pass through the flow cone.

Modification of the grout formula was therefore necessary. In construction grouting, two approaches are available to increase the fluidity of grout without increasing the WSR. One is to replace a portion (about one-third) of the spent shale with sand. This may be thought of as reducing the wetted surface area of the particles, by replacing spent shale particles with relatively coarse sand grains; or as increasing the WSR. The other approach is the use of organic fluidizers, which, when added in small amounts, reduce the apparent viscosity of suspensions. Several classes of fluidizers are available and are used in the construction industry to reduce the water requirement of grouts or mortars; attention here is directed to the lignosulfonate fluidizers, which are the least expensive of these fluidizers.

10.2.1 Grout Formulation. Accordingly, two series of grouts were prepared and tested. In the first (arbitrarily designated series Q), one-third of the spent shale was replaced by -30 +50 mesh (0.297-0.595 mm) sand. In the second (series R), 0.25 or 0.5 percent by weight of solids lignosulfonate fluidizer was used. The Lurgi spent shale (LSS) is described in section 8.2.

The use of -30 +50 mesh sand in series Q grouts was assumed to simulate the effect of using raw shale fines rejected from crushing of raw shale, overburden, or other mine waste. Grout will penetrate only through pores with diameters that are three times the diameter of the 95 percentile grout particle (Herndon and Lenahan, 1976). Therefore the sanded series Q grouts could not penetrate through pores smaller than about 1.8 mm. Because the spaces between chunks of in-situ spent shale in an abandoned retort may be this size, it was considered preferable to have a grout containing no sand, and series R grouts were formulated without sand. Thus, commercially available fluidizers were used in series R grouts. The formulae for the two series of grouts are shown in Tables 10-1 and 10-2.

Table 10-1. Sanded Spent Shale Grouts (Series Q).

	Q-0	Q-1	Q-3	Q-4	Q-5
Lurgi spent shale, g	100	100	100	100	100
Sand -30 +50 mesh, g	50	50	50	50	50
Portland cement, g	0	3.75	0	0	0
Lurgi spent shale cement, g (a)	0	0	3.75	7.5	15
Simulated groundwater, mL (b)	88.0	95.3	93.3	106.8	135.0
Water-to-solids ratio (WSR)	0.59	0.62	0.61	0.68	0.82
Flow cone time, sec	21	20	21	20	23

(a) $CaCO_3$-Lurgi spent shale ratio 0.9, calcined 1 hr at 1000 C, 5 percent reagent gypsum added. This cement had a 28-day strength of 528 psi; stronger cement can be made by increasing the $CaCO_3$-LSS ratio to 1.0 (see section 8.3.1).

(b) 0.61 g $NaHCO_3$ and 0.88 g Na_2SO_4 added to distilled water to simulate native groundwater.

Table 10-2. Spent Shale Grouts Containing Lignosulfonate Fluidizers (Series R).

	R-1	R-2	R-3	R-4	R-5
Lurgi spent shale, g	100	100	100	90	90
Class F fly ash, g (a)	0	0	0	0	10
Class C fly ash, g (b)	0	0	0	9.5	0
Reagent gypsum, g	0	0	0	0.5	0
Lignosulfonate fluidizer CZ-503, g	0.50	0.25	0	0	0
Lignosulfonate fluidizer CZ-512, g	0	0	0.25	0.25	0.25
Distilled water, mL	69.4	74.6	71.8	68.9	63.3
Water-to-solids ratio (WSR)	0.69	0.74	0.72	0.69	0.63
Flow cone time, sec	17	16	18	22	22

(a) From Craig power plant, Moffat County, Colorado.
(b) From Wyodak power plant, Gillette, Wyoming.

10.2.2 Method of Mixing. For both series of grouts, all ingredients were blended as dry solids (including the fluidizers, which were supplied as powders). The combined dry ingredients were then mixed with the least amount of water that would make a grout sufficiently fluid to pass through the flow cone. Water was then added in increments to reduce the time of efflux through the flow cone to the target value. Figure 10-1 shows how the flow cone time of efflux decreased with incremental additions of water for the series R grouts tested.

An important difference between the two series of grouts was the method of mixing. Series Q grouts were mixed following ASTM C-305, which is the method prescribed for mixing mortars. Grouts were mixed in a Hobart mixer (Hobart Co., Dayton, Ohio) at 125 rpm for 30 sec initially and after each addition of water. In preparing series R grouts, however, it was found that the time of efflux through the flow cone was less if the grouts were mixed at 1300 rpm for 3 min using a Jiffy mixer (Jiffy Co., Irvine, CA). Series R grouts were therefore mixed at 1300 rpm for 3 min initially and after each incremental addition of water. All grouts were tested for bleeding. For two of the grouts, rheologic measurements were made with a Contraves rheometer, model 15-T.

10.2.3 Results and Discussion. Bleeding was less than 2 percent for all the grouts tested. The flow cone time data shown in Figure 10-1 and Tables 10-1 and 10-2 indicate that the grouts met the fluidity criterion. Rheologic data indicated that the grouts were Casson fluids with yield stress values of about 60 dyne/cm^2. The penetration of grouts through porous media is discussed in Appendix D. These grouts would be able to penetrate all the macrovoids of an MIS retort from a small number of injection holes.

10.3 Strength of Simulated Grouted Cores

Consolidated drained triaxial tests were done on R-series grouts to determine the response of grouted retorts to long-term loading. Triaxial testing served two purposes. The data were needed to predict the ability of grouted retorts to support the overburden and to predict the confining pressure that would be experienced by a grouted retort; the latter value influences the permeability as shown in Section 10.4.3. Consolidated drained tests were considered to best simulate the long-term condition, because any increase in pore pressure would have had time to dissipate.

10.3.1 Structural Criteria for Grouted Retorts. The calculations presented in Chapter 7 indicate that the modulus of elasticity would be the controlling structural parameter for enhanced resource recovery. For a significant increase in the allowable areal extraction, the elastic modulus of grouted retorts must exceed 50,000 psi. For prevention of subsidence (given the conservative retort designs published in development plans), retort grouting was found not to be necessary. For more complete structural characterization of the simulated grouted cores, other parameters including unconfined compressive strength, angle of internal friction, and cohesion also were measured in uniaxial and triaxial compressive strength tests.

10.3.2 Sample Preparation. Specimens for structural tests were prepared with grout and aggregate to simulate grouted in-situ spent shale. The aggregate used was simulated in-situ spent shale from Laramie Energy Technology Center's 10-ton retort run S-55; this shale was crushed and sieved to -3/8 +1/4 inch, saturated with water and surface dried. In preliminary work, we tried to pump the grout into preplaced aggregate but found that we could not eliminate trapped air by this method. Therefore, we followed ASTM C 31 for the

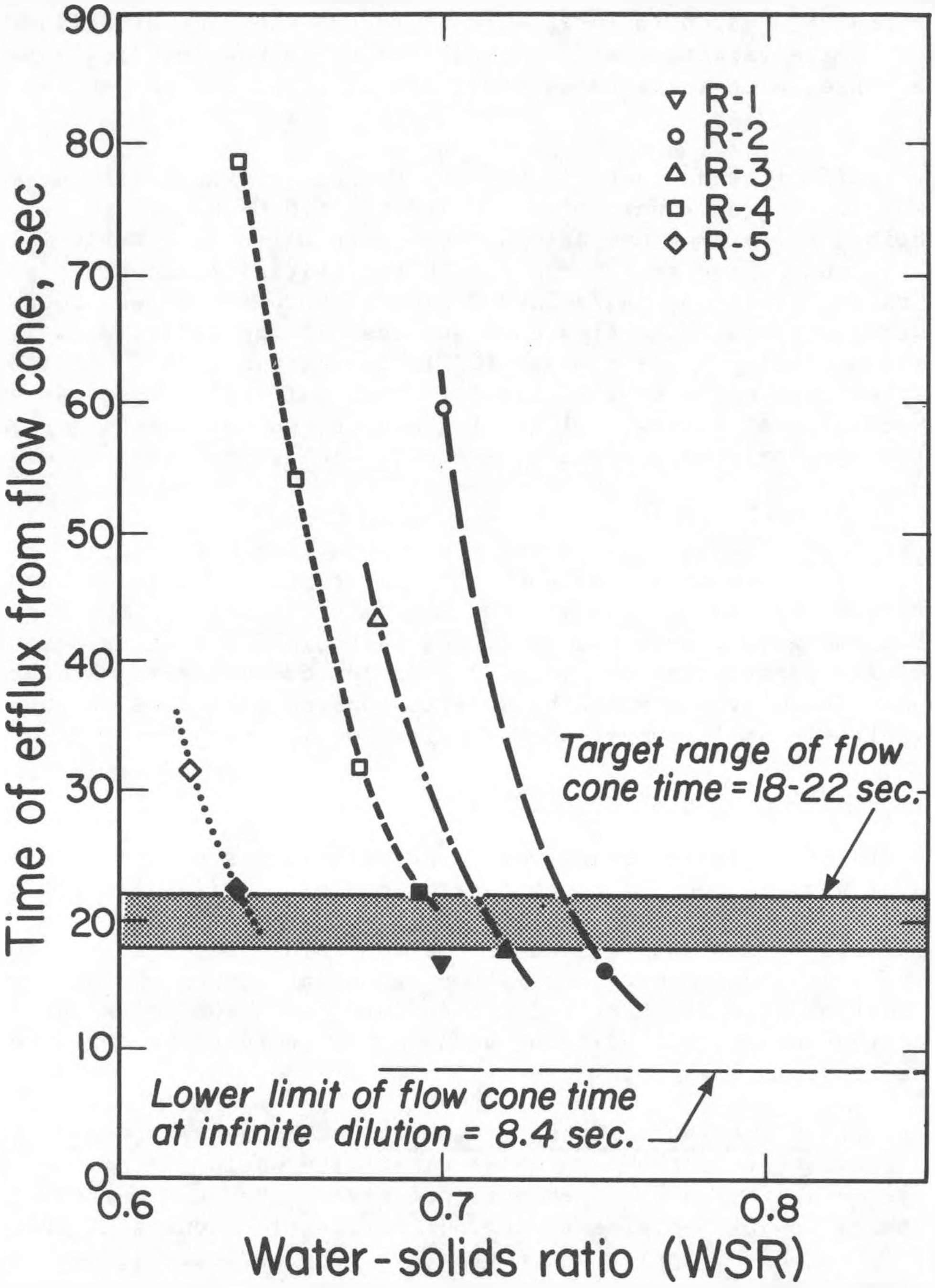

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Figure 10-1. Relationship between water-to-solids ratio (WSR) and flow-cone time for series R grouts. Solid points represent the final composition of the grouts (see Table 10-2).

preparation of test specimens. The grout and aggregate were mixed in a bowl and packed into the mold in three lifts, each lift being rodded 25 times with a 0.25-inch rod to eliminate trapped air. Waxed cardboard cylinder molds were used because the samples were expected to be so weak that they would be damaged by removing a metal mold. The samples were cured at 73 F (23 C) in 100 percent humidity for 5 to 7 months. This range of cure times was necessary because all grouts were prepared and cast over a one-week period, while testing took much longer, up to a week per sample. The aggregate occupied about 50 percent of the total sample volume, compared with 60 to 80 percent theoretically occupied by MIS spent shale.

Series Q grouts were mixed using a simulated ground water to explore the possibility that precipitation reactions would occur between ions in the mixing water and ions leached from the spent shale, increasing strength. When no such precipitation was noted (crystal formation was not observed by scanning electron microscope examination of the cured grouts), series R was mixed using distilled water. In both series of grouts, emphasis was placed upon maximum use of spent shale; only a minimum of cement or fly ash was added (up to 10 percent) to increase the strength.

10.3.3 Consolidated Drained Triaxial Tests. For consolidated drained triaxial tests, specimens must have flat and parallel ends. Usually, these are produced by trimming soil specimens with a knife, or capping rock or concrete specimens with a molten sulfur capping compound, which is then trimmed to the exact circumference of the sample. Neither technique could be used in these tests. Trimming the sample with a knife would dislodge pieces of aggregate and damage the specimen. The capping compound is stronger than the simulated grouted core; therefore trimming the caps also would damage the specimen. A novel capping technique was devised. Without removing the sample from the waxed cardboard cylinders in which it was cast, the bottom of the cylinder was removed, leaving both ends open. The sample then was placed in a Lucite mold with flat parallel end cavities into which Hydrostone, a proprietary plaster (US Gypsum, Chicago, IL), was injected. This eliminated the need to trim the end caps. For unconfined compressive strength tests, in which the sample was not jacketed, there was no need to trim the end caps, so sulfur capping compound was used.

The test method is described by Houston (1980). The samples were saturated under a vacuum and encased in filter paper and flexible membranes for the consolidated drained triaxial test. Consolidated drained tests were done at 40 and 80 psi. Uniaxial tests also were done (i.e., 0 psig confining pressure).

10.3.4 Results and Discussion. The maximum axial stress, corresponding to the failure point in both uniaxial and triaxial tests, for each grout-aggregate combination, was plotted against confining pressure (Fig. 10-2). The cohesion (c) and angle of internal friction (ϕ) were determined from the slopes and intercepts of the curves in Figure 10-2 using the relationships

$$\frac{d\sigma_{1_f}}{d\sigma_2} = \tan^2(45^\circ + \frac{\phi}{2})$$

$$q = 2c \tan(45^\circ + \frac{\phi}{2})$$

where σ_{1_f} = axial stress at failure,(psi)

σ_2 = confining pressure (psi)

c = cohesion (psi)

q = unconfined compressive strength, the y-intercept (psi)

ϕ = angle of internal friction.

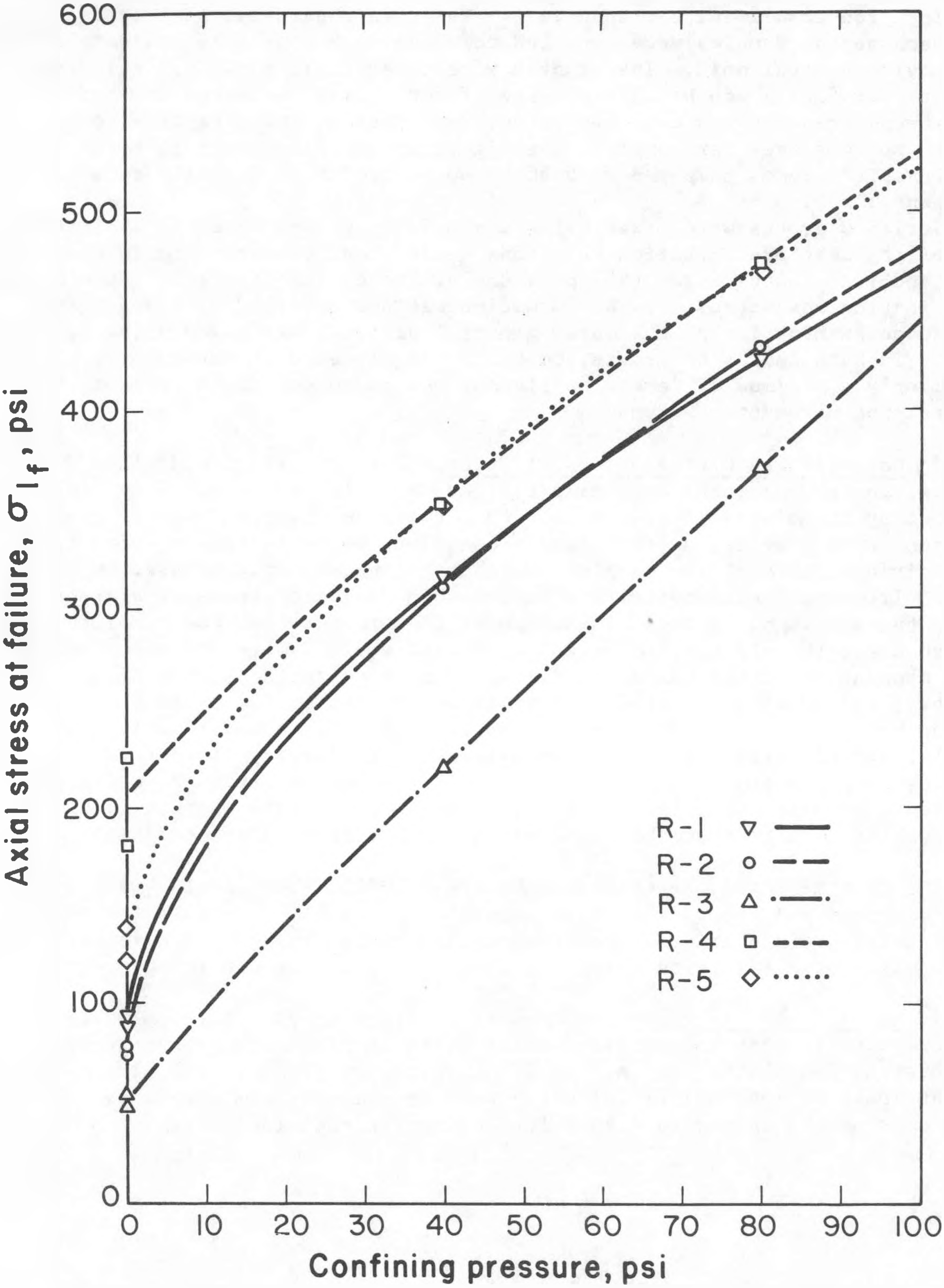

Figure 10-2. Relationship between confining pressure and axial load at failure (σ_{1f}) for simulated grouted cores. Curves are fit to data points by power law.

Because the curves are not linear, the average value of $\frac{d\sigma_{1_f}}{d\sigma_2}$ in the range 0 to 40 psi confining pressure was used to determine ϕ. The modulus of elasticity was determined from the maximum slope of the plot (not shown) of deviator stress vs. strain. The strain was zeroed after the confining pressure was applied. The values of the structural parameters are summarized in Table 10-3. For comparison, Watson et al. (1982) prepared grouts from a combination of Lurgi spent shale collected in the electrostatic precipitator and cyclone. The unconfined strengths of grout samples without coarse aggregate after curing 28 days were 87 psi and 110 psi for grout with no cement and 15 kg/m^3 portland cement, respectively.

The structural properties of the grouted cores (modulus, cohesion, and unconfined compressive strength) can be related to the grout formulae and to the way permeability of the grouts varied with confining pressure. As shown in Table 10-3, addition of portland cement or LSS cement increased the unconfined compressive strength of the sanded (series Q) grouts. Grouts made without sand had higher unconfined compressive strength than those made with sand. Addition of 10 percent fly ash to the grout substantially increased the unconfined compressive strength and cohesion. The increase in strength was greater with Class C fly ash and gypsum (a combination which is not only a pozzolan but a true hydraulic cement) than with Class F fly ash (which is a pozzolan but not a cement). It is not clear whether the strength increase in R-5 over R-3 is due to pozzolanic reaction with a trace of free lime, some other reaction, or to a lower water-solids ratio (WSR).

The fluidizer used also apparently contributed to the strength. Grout R-3, with 0.25 percent CZ-512, had an unconfined compressive strength of 51 psi, while R-2, made with 0.25 percent CZ-503 and a slightly higher WSR had an unconfined compressive strength of 77 psi (percentages refer to dry weight basis). Grout R-1, made with 0.5 percent CZ-503 and slightly lower WSR, had still higher strength. These data indicate that the use of CZ-503 enhances the strength of grouts compared to the use of CZ-512. The choice of lignosulfonate fluidizer also influences the permeability of the grout strongly, as shown below.

In Chapter 7, subsidence model calculations were reported for various assumed stiffnesses (as defined by elastic modulus values) of grouted retorts ranging from 0 (i.e., no grout) to 750,000 psi. These calculations indicated that little increased resource recovery would be possible if grouted retort stiffness is less than 50 ksi. Comparison of the results in Table 10-3 with these calculations shows that none of the grouts tested is sufficiently stiff to provide overburden support to appreciably increase resource recovery. Simulated grouted cores using grout R-4 did have a modulus of elasticity of 51 ksi when tested unconfined, but a lower modulus when tested under confining pressures, suggesting that the higher value could not be used in design. Therefore retort grouting with these spent shale grouts cannot enhance resource recovery. The calculations presented in Chapter 7 also showed that, for the dimensions and material properties used, subsidence would not be a problem, whether retorts were grouted or not.

10.4 Permeability

The definitions of permeability and hydraulic conductivity are presented in Appendix C along with the theory of their measurement. The two terms are not equivalent; permeability has units of L^2 while hydraulic conductivity has units of LT^{-1}. However, the word "permeability" is commonly used in

Table 10-3. Structural Parameters of Simulated Grouted Cores.

Grout	Unconfined compressive strength, psi(a)	Cohesion, psi(b)	Angle of internal friction, degrees(b)	Modulus of elasticity, ksi, at confining pressure		
				0 psi(a)	40 psi(c)	80 psi(c)
R-1	93	19	47	16	14	10
R-2	77	15	48	9	18	12
R-3	51	12	42	9	10	10
R-4	203	55	38	51	23	30
R-5	131	27	47	33	21	26
Q-0	30					
Q-1	81	(Triaxial tests not done on Q-series grouts)				
Q-3	34					
Q-4	52					
Q-5	90					

(a) Data from uniaxial (unconfined) compressive strength tests.
(b) Data from analysis of uniaxial and triaxial (confined) compressive strength tests.
(c) Data from triaxial (confined) compressive strength tests.

both senses. In this chapter, the word "permeability" will be used although, strictly speaking, "hydraulic conductivity" would be more correct. Conversion between the two systems of expression is presented in Appendix C.

10.4.1 Permeability Criteria. The criterion for grout permeability is that the rate of flow through grouted retorts be reduced enough to control the transport of leached contaminants to within acceptable limits. As discussed in sections 10.4.3 and 10.4.4, the required permeability depends upon the quality of leachate emerging from grouted retorts. In the absence of definitive leachate quality data, the permeability criterion was set at 10^{-6} cm/sec, as suggested by Golder Associates (1977).

10.4.2 Permeability Test Methods. Grout samples for permeability measurements were prepared by pouring the fluid grout into waxed cardboard cylinders, 2 inches in diameter by 4 inches high. No aggregate was included, because it was assumed the permeability of a grouted retort would be controlled by the permeability of the grout (the continuous phase) rather than that of the MIS spent shale (the discontinuous phase). Waxed cardboard cylinder molds were used because the samples were expected to be so weak that they would be damaged by removing a metal mold. The samples were cured at 73 F (23 C) in 100 percent humidity for 5 to 7 months. This range of cure times was necessary because all grouts were prepared and cast over a one-week period, while testing took much longer, up to a week per sample.

The method of permeability measurement is described in detail, with necessary theory, in Appendix C. A brief description is given here. The mold was stripped from the specimen, which was then encased in a flexible membrane and saturated by immersion in deaired water under a vacuum for 10 days. It was then placed under the desired confining pressure in a Bureau of Reclamation triaxial-load cell. The confining pressure was equal in all directions. The permeability measuring system is shown schematically in Figure 10-3; more detail is presented in Appendix C.

Permeability was measured at confining pressures of 60, 120, and 240 psi. A hydraulic gradient was applied across the length of the sample against a back pressure of 20 psi. Permeability was measured at hydraulic gradients of 250, 340, and 420 ft/ft. Upstream and back pressures were maintained by air pressure over reservoirs of deaired water. The flow of water through the specimen against the backpressure was determined using a volume-change device which was specially designed to measure small flows into a pressurized reservoir. When the volume of permeate approached the capacity of the pressurized reservoir, the reservoir was isolated from the system and the permeate collected for measurement of electrical conductivity using a YSI conductivity meter.

10.4.3 Results and Discussion of Experimental Data. Results of permeability measurements on series Q and R grouts made at three confining pressures are shown in Figures 10-4 and 10-5. For comparison, LSS grouts developed by Watson et al. (1982) had permeabilities of 5×10^{-7} and 4.5×10^{-7} cm/sec.

For all grouts, as confining pressure increases, permeability decreases. This suggests that the grouts consolidate under confining pressure, forming a denser, more compact structure with smaller pores. This interpretation is supported by the fact that grouts R-4 and R-5, which have higher moduli of elasticity than the other R-series grouts (see Table 10-3), also have lines of lesser slope in Figure 10-5; because they were stiffer they consolidated less, and permeability decreased less.

Choice of fluidizer also influences grout permeability. As noted above, grouts made with CZ-503 were somewhat stronger than those made with CZ-512. Figure 10-5 shows that these grouts had much lower permeability than any of the grouts made with with CZ-512, with or without fly ash. Both CZ-512 and CZ-503 are refined waste sulfite pulping liquors; they consist primarily of sodium salts of lignosulfonic acid. The main difference between them is that in CZ-503, residual sugars are present which have been removed from CZ-512. These sugars are removed because if they are used with portland cement, they retard the setting of the cement undesirably. For a noncementitious grout such as the R-series grouts, this is not a problem, so the fluidizers need not be desugared. Figure 10-1 shows that CZ-512 is a more effective fluidizer than CZ-503 (for example, grout R-3, made with CZ-512, reached adequate fluidity with a lower WSR than grout R-2, which was identical except that it was made with CZ-503). The apparent explanation for this is simply that CZ-512 has more of the active ingredient, sugars having been removed. However, the retention of the sugars apparently decreases the permeability and increases the unconfined compressive strength of the grouts. This is only a hypothesis and should be confirmed by tests on grouts made with other desugared and nondesugared fluidizers.

This work shows that, for grouts which are compliant enough to consolidate under confining pressure (which includes all grouts tested), higher modulus prevents development of low permeability. Since none of these grouts is strong enough to provide increased resource recovery, the best approach seems to be to design for lowest permeability. Thus, the best grout

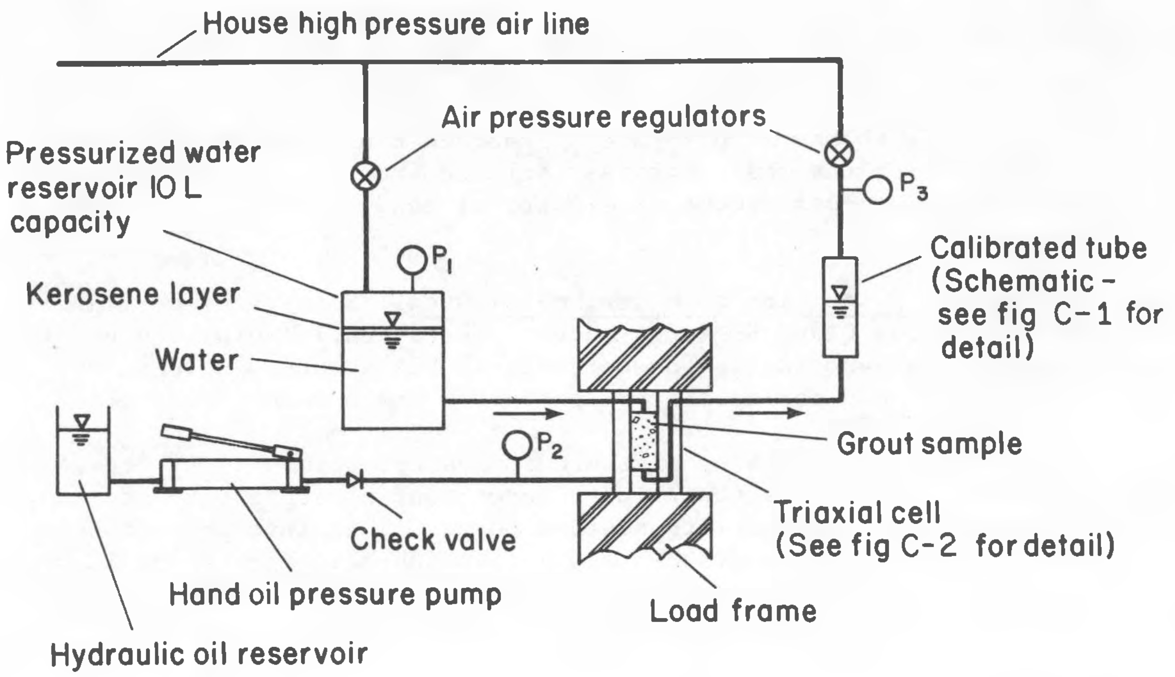

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Figure 10-3. Permeability measuring system used for series R grouts. P_1 = upstream pressure, P_3 = back pressure, P_2 = confining pressure. Hydraulic gradient = $(P_1 - P_3)$/(sample length). For series Q grouts, flow was into a burette at atmospheric pressure rather than into a pressurized reservoir.

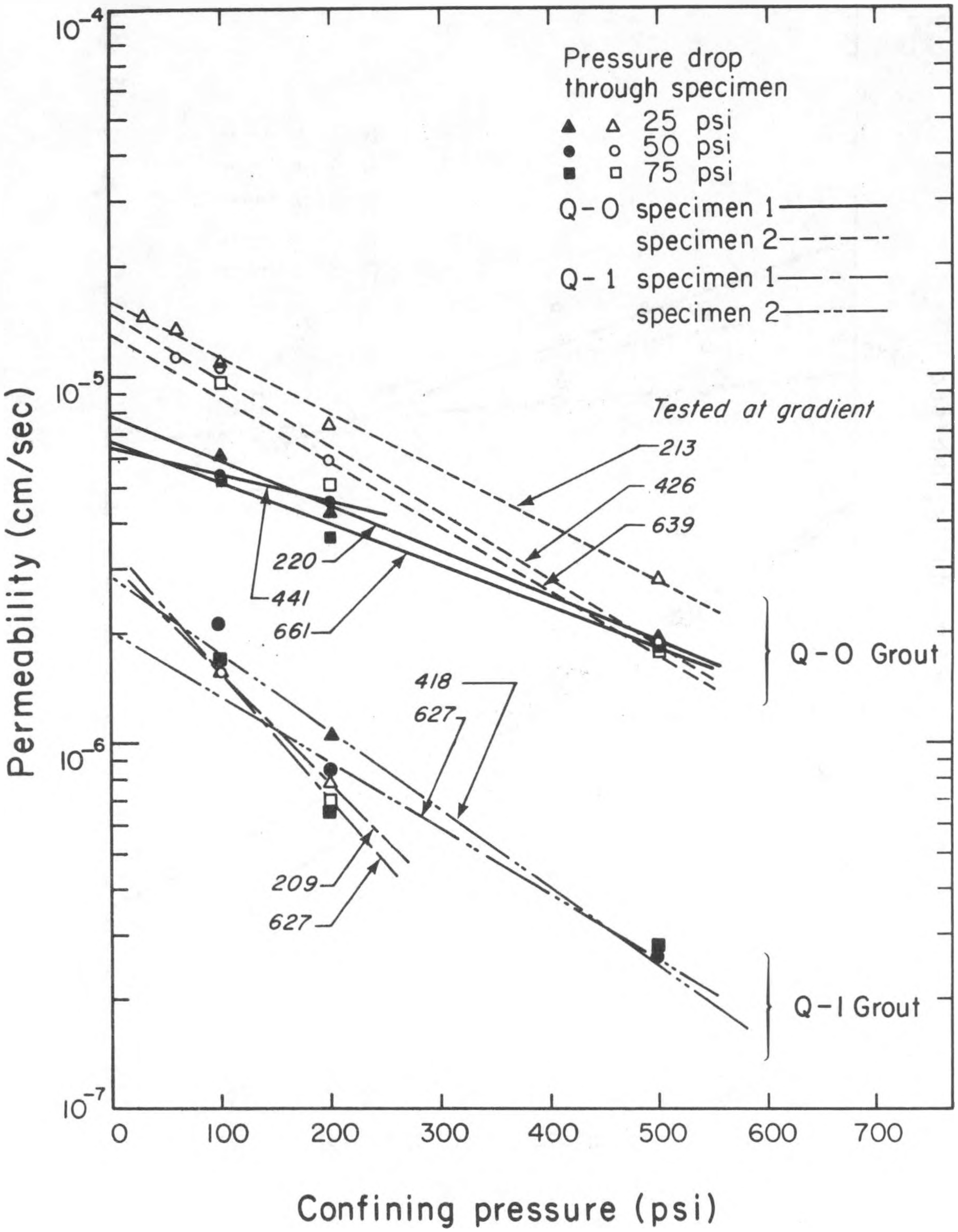

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Figure 10-4. Variation of permeability with confining pressure and hydraulic gradient for sanded grouts Q-0 (no cement) and Q-1 (2.5 percent portland cement).

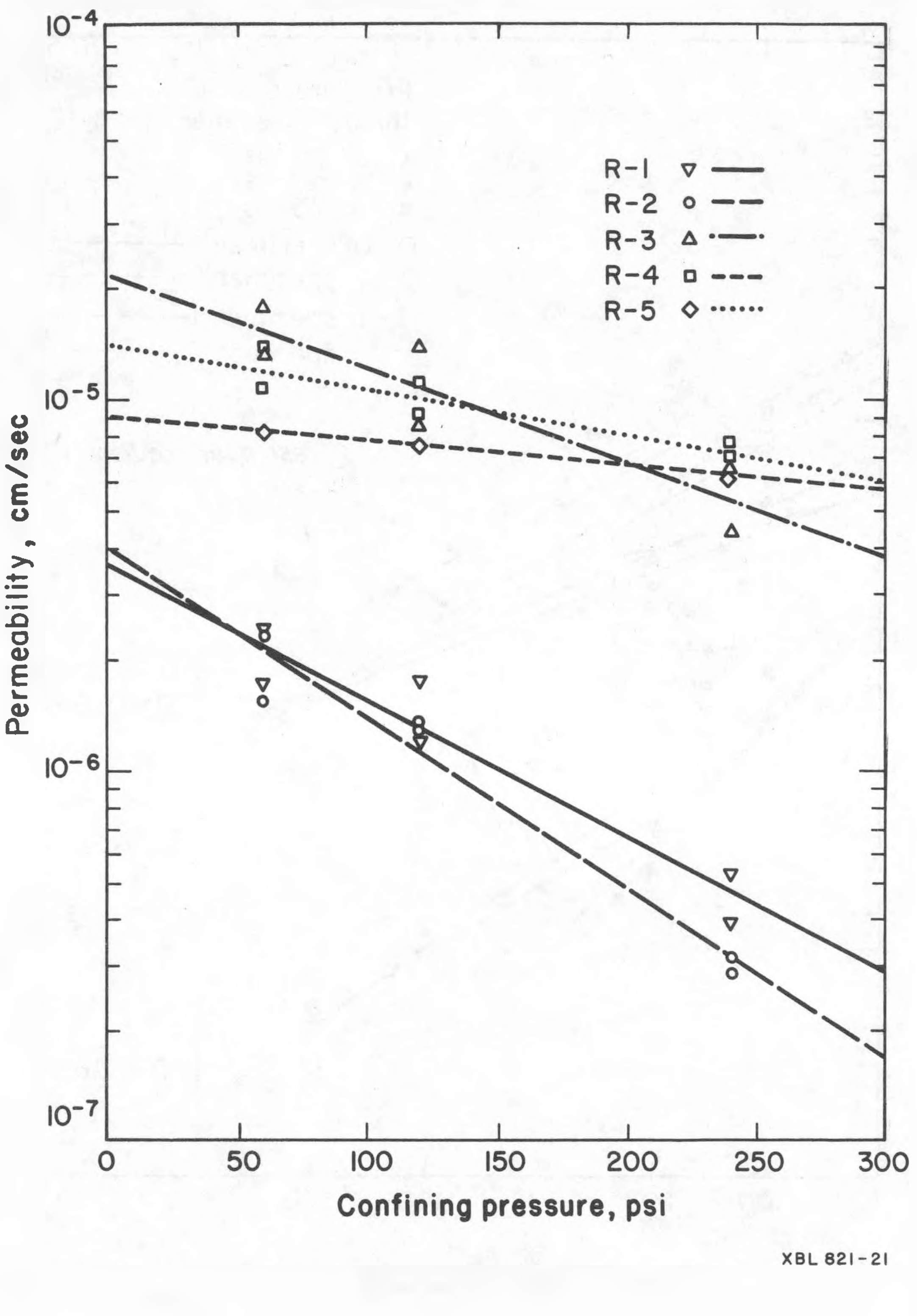

Figure 10-5. Variation of permeability with confining pressure for series R grouts containing lignosulfonate fluidizer.

of those tested here is R-1 or R-2, using fluidizer CZ-503 and no fly ash. Since the effect of the fluidizer choice is so important, other fluidizers should be screened. Variation between batches also may be important.

10.4.4. Comparison of Grout Permeability to Criteria. In this section, we will calculate the reduction in flow that will occur if MIS retorts such as those proposed by Rio Blanco Oil Shale Project and Occidental Oil Shale at tracts C-b and C-a, respectively, are backfilled with grout R-2. We will do this by using Figure 10-5 to estimate the permeability of grouted retorts. These values will then be compared to the permeability of undisturbed aquifers in the area.

Figures 10-4 and 10-5 show the variation of grout permeability with confining pressure. The actual confining pressure in a grouted retort will vary over the height of the retort. We use the average permeability over the retort height in our calculations. We conservatively assume that the overburden is supported only by the pillars and not by the grouted retort, so the confining pressure on the grout is its own hydrostatic pressure. Thus, at the top of the retort, there would be zero confining pressure, and at the bottom, the confining pressure would be given by the product of the grout density and the retort height. The grout densities measured for series R grouts were all approximately 100 lb/ft^3, corresponding to a pressure of 215 psi at the bottom of a 310-ft-tall retort (tract C-b) or 520 psi at the bottom of a 750 ft tall retort (tract C-a). For these conditions, retorts at tract C-b backfilled with grout R-2 would have permeability ranging over approximately one order of magnitude, from $4x10^{-7}$ to $4x10^{-6}$ cm/sec. At tract C-a, the range would extend to lower permeabilities, because of greater confining pressure in the retort. However, rather than extrapolate the experimental data beyond the range of confining pressure studied, we will use the same permeability values for tract C-a as for C-b, making the calculations conservative for tract C-a (Table 10-4).

The adequacy of these permeabilities depends on the effect of permeability reduction on both leachate concentration and flow through the retort. Ideally we would like to reduce the mass (m) of soluble constituents that is released from an abandoned MIS retort, where $m = cQ$. However, concentration (c) is inversely related to permeability, while flow (Q) is directly related. Thus, as the permeability is reduced by backfilling with a grout, the flow is reduced and the concentration is increased.

The reduction in flow is estimated in this section. Then, in section 10.5, we will estimate the effect of grouting on leachate quality. Ideally, a solute transport model, such as that used by Robson and Saulnier (1981), should be used for these calculations. However, there are presently inadequate data for such sophisticated calculations, and we instead will use a simple estimation procedure advanced by Fox (1980).

In Fox's work, it was assumed that retorts were in contact with both upper and lower aquifers, that flow was vertical through the retorts, and that the permeability of the aquifers controlled the rate of flow through the retorts. In order to reduce the rate of flow through the retort, the permeability of the grouted retort must be less than the permeability of either the upper or lower aquifer. Table 10-4 summarizes the permeabilities of the upper and lower aquifers at tracts C-a and C-b and the factor by which flow through the grouted retorts would be reduced for various values of grouted retort permeability.

Table 10-4. Reduction of Flow Through Retorts Resulting from Various Values of Retort Permeability.

	Tract C-a	Tract C-b
Permeability of upper aquifer, cm/sec(a)	5.3×10^{-4}	1.8×10^{-4} to 2.8×10^{-4}
Permeability of lower aquifer, cm/sec(a)	15.2×10^{-4}	0.4×10^{-4} to 1.1×10^{-4}
Factor by which rate of flow is reduced(b)		
grouted, permeability = 4×10^{-7}	1325	88 to 263
grouted, permeability = 1×10^{-7}	530	35 to 105
grouted, permeability = 4×10^{-6}	133	9 to 26

(a) Permeabilities of aquifers reported by Fox (1980), p. 203.

(b) This factor is the ratio of the permeability of the upper or lower aquifer (whichever is less) to the permeability of the grouted retort.

Table 10-4 shows that, assuming flow through retorts is vertical, the permeability of grouted retorts should be low enough to reduce the flow through the retorts substantially. The reduction of flow results from the permeability of the grouted retort being less than that of the upper or lower aquifer, whichever controls. The factor of reduction is less at tract C-b, where flow through retorts would apparently be controlled by the lower aquifer, which is itself of low permeability. As shown in section 10.5.1, these reductions are large enough to ensure that the mass of soluble material released from a grouted retort will be less than from an ungrouted retort.

10.5 Solubility of Grout Material

The contribution of the grout material itself to dissolved material in the leachate must be small enough not to offset the benefit of reduced flow through retorts. The objective this criterion is to assure that the grout does not adversely increase the concentration of constituents of concern in the leachate and surrounding groundwaters. Since the low-cost grouts that must be used for retort backfilling are not hydraulic cements, they will dissolve slowly in flowing groundwater. The effect of this dissolution on leachate quality depends on the composition of the leach water and spent shale (i.e., the surface retorting process used), on the ratio of injected grout to in-situ spent shale, and on the liquid-to-solid ratio (LSR) in the grouted retort.

The specification of such a criterion would require policy decisions on the maximum allowable increase in the concentration of various dissolved species in groundwaters. This has not been specifically determined by Colorado, Utah, or Wyoming. It also requires a substantial amount of scientific information on variables that affect leachate composition. In particular, information is required on the effect of groundwater quality and liquid-to-solid ratio on leachate composition from ungrouted MIS spent shale, from proposed grouts, and from combinations of the two. Since adequate information is not available, it is not possible to propose a definitive criterion for grout solubility. However, we have obtained limited data on the quality of leachates from our low-cost Lurgi spent shale grouts. The following section presents those data and qualitatively discusses its implications for effect on leachate quality.

10.5.1 Electrical Conductivity of Permeates. The primary purpose of grouting is to reduce the leaching of in-situ spent shale. The grouting operation will serve as a disposal mechanism for surface-retorted spent shale as well as reducing the flow of water through the retort. Water which does migrate through a grouted retort will leach not only the MIS spent shale but also the grout. For this reason, we obtained water quality data on the permeates that were produced in the permeability measurements.

In the permeability test, water that percolates through the specimen was exposed to a considerable length of stainless steel tubing and fittings, porous stones, and rubber jackets, as well as to the sample itself. The water also contacted dyed kerosene, both before and after the sample. For these reasons, sophisticated analysis of the permeates was not attempted. Gross increases in electrical conductivity, however, could not have resulted from contamination by the system. Electrical conductivity (EC) of the permeates was measured using a YSI Model 31 conductivity meter after they were removed from the volume change device (Fig. C-1). The total volume of permeate available varied between 0.1 and 1.5 L, depending on the permeability of the sample and the length of the test. For all samples, the porosity of the grout (before consolidation in the test) was about 0.67.

The EC of the permeate as a function of pore volume is shown in Figure 10-6. This figure also shows electrical conductivity measurements of leachates produced by column leaching of section 1 of core R3E1 from Oxy retort 3E (US DOE, 1980). Analysis of this material by x-ray diffraction showed only akermanite and diopside (Peterson et al., 1982) which indicates that the silication reactions described in section 4.2.1.2 were essentially complete for this material. Other sections of this core had less complete silication, and leachates from the other sections showed higher EC (US DOE, 1980).

Leachate concentrations from a grouted retort will likely be higher than from an ungrouted retort for two reasons: the added presence of finely divided surface-retorted spent shale grout material and the decreased liquid-to-solid ratio (LSR) in a grouted retort, compared to an ungrouted retort. Surface retorted spent shales are generally more soluble than MIS spent shale (Peterson et al., 1982) and also exhibit substantial variability in solubility. Several studies also have shown that, in spent shale leaching, the EC and concentration of several ions are inversely related to LSR (Fransway, 1980; Glaze, 1981; Silveira et al., 1978). The LSR of a grouted or ungrouted retort can be calculated from

$$\mathrm{LSR} = \frac{ae + (1-a)b}{\rho_g[a(1-e)] + \rho_s[(1-a)(1-b)]}$$

where a = porosity of the in-situ retort before retorting (original voids), $0.2 < a < 0.4$
b = porosity of the in-situ spent shale, $b < 0.5$
e = porosity of the grout, for R-series grouts $e = 0.67$
ρ_g = density of the spent shale grout material, typically $\rho_g = 2.65$
ρ_s = density of the MIS spent shale, typically $\rho_s = 2.65$.

For an ungrouted retort, substitute $e = 1$. Substituting the typical values, $b = 0.5$ and $a = 0.40$ for tract C-a or 0.23 for tract C-b, we calculate that the

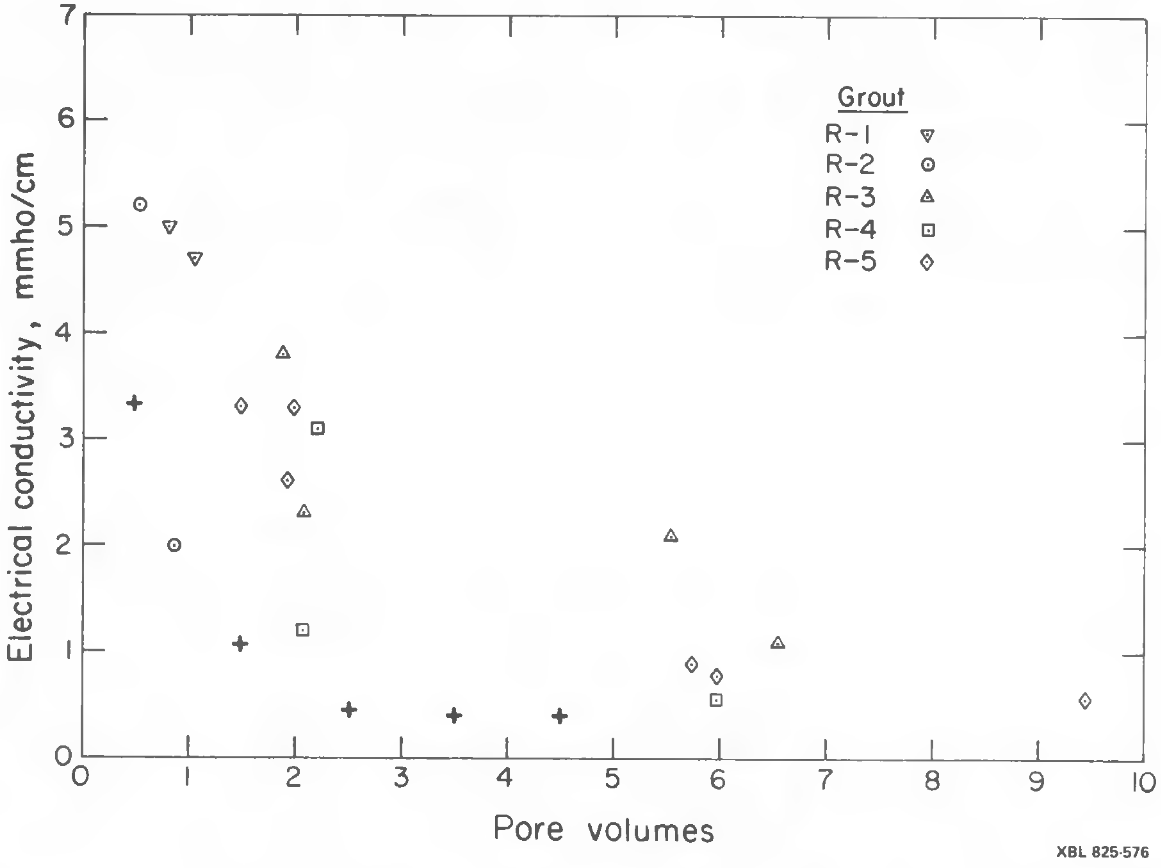

Figure 10-6. Decrease in electrical conductivity of permeates from series R grouts with cumulative flow through samples during permeability tests. Data are also shown (+) for section 1 of core R3E1 (data from US DOE, 1980).

LSR of an ungrouted retort is 0.88 at tract C-a or 0.60 at tract C-b. The corresponding values for grouted retorts are 0.50 and 0.44, respectively. Thus, grouting a retort reduces the LSR by 43 or 27 percent. This reduction in the LSR may affect the concentration of leachate from the retort. Data presented by Fransway (1980) suggest that for Paraho spent shale, the EC and LSR are related by

$$EC = 14.46(LSR)^{-0.76}$$

i.e., a straight line log-log relationship. Assuming that a similar relationship applies to MIS retorts, a reduction of 27 or 44 percent in the LSR would result in an increase in EC of 27 or 53 percent, respectively. This calculation is based upon data from laboratory leaching of small particle size Paraho spent shale and is only intended to demonstrate the possible magnitude of the effect of reducing the LSR (by grouting) on leachate quality. The chemical difference between the MIS spent shale and the grout material will probably be more important than the reduction in LSR due to grouting.

Spent shale grouting of abandoned retorts balances a decrease in leachate volume against an increase in leachate strength. To be effective, the factor by which flow is reduced must be greater than that by which concentration is increased. The data in Figure 10-6 suggest that leachate from a retort grouted with Lurgi spent shale would have TDS approximately three times as high as leachate from an ungrouted retort, depending upon the nature and relative amounts of in-situ- and surface-retorted spent shale. For grouting to produce a net reduction in the mass of TDS discharged into groundwaters and surface streams, therefore, the flow through abandoned retorts should be reduced by a factor greater than 3. The data presented in Table 10-4 indicate that flow may be reduced by factors of 9 to 1325 (depending on site-specific conditions). This suggests that retort grouting will successfully reduce the mass of TDS (and probably other soluble constituents) released from an abandoned retort.

10.6 Estimated Cost of Retort Grouting

Persoff and Fox (1979) estimated the cost of grouting abandoned MIS retorts. For that estimate, it was assumed that spent shale could be ground (if necessary), slurried, and injected into the retort for \$2 per ton. Additionally, a credit of \$1 per ton was taken for disposal of the spent shale. Drilling costs (\$20/ft through overburden, \$10/ft through rubble) were substantial if the air level ("plenum" or "attic space") above the retort could not be used as a grouting gallery. Sufficient water also was assumed available at no cost. Costs, in 1979 dollars per barrel of oil recovered, including both surface and in-situ produced oil, were estimated at \$0.49 or \$0.65 for tract C-a for grouting from the air level or ground surface, respectively, and \$0.35 or \$1.30 for tract C-b. The differences reflect the deeper overburden and smaller void fraction at tract C-b. (Costs shown in Table 3-1 are greater because they include the cost of fluidizer).

Table 10-5 calculates the increase in these costs for inclusion of 10 percent fly ash or 0.25 percent fluidizer. The use of fly ash increases the grout cost by \$0.66 to \$1.10 per barrel, while the cost of lignosulfonate fluidizer increases it by \$0.16 to \$0.27 per barrel. The total cost of grouting, including both fly ash and fluidizer, is \$1.86 to \$2.02 at tract C-a, and \$1.17 to \$2.12 at tract C-b. While the acceptable limit for environmental protection costs is an economic decision to be made by the operator, the cost of retort grouting appears to be reasonable (less than 10 percent of the value of the oil), if the stated assumptions are confirmed.

Table 10-5. Estimated Increase in Cost of Grouting One Retort Resulting from Inclusion of Fly Ash or Fluidizer.

	Tract C-a	Tract C-b
Grout material placed, tons(a)	358,000	114,000
Fly ash placed, tons(b)	35,800	11,400
Cost of fly ash, delivered, @ $30/ton	$1,074,000	$342,000
Decrease in credit for spent shale disposal, @ $1/ton	$35,800	$11,400
Increase in cost resulting from inclusion of 10 percent fly ash, $/retort	$1,110,000	$353,000
Oil recovered, bbl/retort(a)	1,010,000	530,000
Increase in cost resulting from inclusion of 10 percent fly ash, $/bbl	$1.10	$0.66
Fluidizer placed, tons(c)	895	285
Cost of fluidizer, delivered, @ $0.15/lb	$268,500	$85,500
Increase in cost resulting from inclusion of 0.25 percent fluidizer, $/bbl	$0.27	$0.16

(a) From Persoff and Fox, 1979, p. 88.
(b) 10 percent replacement of spent shale by fly ash.
(c) 0.25 percent fluidizer added to fly ash.

10.7 Conclusions

1. A grout prepared by mixing Lurgi spent shale and water cannot meet criteria of both fluidity and non-bleeding. However, if 0.25 percent lignosulfonate fluidizer is added, or one-third of the spent shale is replaced by -30 +50 mesh sand, both criteria can be met.

2. Mixing at high speed (1300 rpm) favors grout fluidity.

3. Grouts tested in this project were non-Newtonian fluids. They fit the Casson model with yield stress values about 60 dyne/cm^2.

4. The modulus of elasticity of simulated grouted cores tested is too low to permit enhanced resource recovery by retorting pillars.

5. The permeability of these grouts decreases in an approximately logarithmic manner with increased confining pressure, due to consolidation of the grout under confining pressure.

6. The decrease in permeability due to increase in confining pressure is greatest for those grouts with the smallest modulus of elasticity.

7. Assuming that grout penetration through rubble is essentially complete, and assuming that flow through retorts would be vertical, grout R-2 would reduce the flow through retorts by a factor between 9 and 1300. The factor of reduction depends on the properties of the aquifers and the degree to which grout permeability is reduced by consolidation in the retort.

8. Retort backfilling with a noncementitious grout based on surface spent shale may be expected to increase the concentration of many dissolved substances in leachates, compared to the ungrouted case. However, the relatively larger reduction in flow (factor of 9 to 1300), compared to the increase in concentration (factor of 3) should result in an overall reduction in the mass of dissolved material that is released from a grouted retort.

9. Waste materials used to improve the properties of spent shale grouts may be expected to increase the cost of grouting by about $0.82 to $1.37 per barrel of oil.

CHAPTER 11. COMPARISON OF CONTROL TECHNOLOGIES

11.1 Introduction

This chapter will briefly review the principal conclusions drawn in Chapters 2 through 10. Then, the relative advantages and disadvantages of each of the control technologies considered will be discussed. Finally, recommendations for further research to resolve uncertainties are presented.

11.2 Relative Merits of Control Technologies

Table 11-1 summarizes the state of knowledge for the and various retort abandonment strategies considered in this report. Criteria are needed to select control technology for MIS retorts. The choice will depend on the answers to several questions, which include technical, regulatory, and policy issues. Technical questions are discussed in section 11.4, and research is recommended to resolve uncertainties. Important policy questions which need to be addressed include: (1) What increase in concentration above background levels is acceptable for total dissolved solids (TDS), specific ions, total organic carbon, and specific organic compounds in affected groundwaters, local surface streams, various points in the Colorado River System? (2) How can effects that are expected to occur in the distant future be fairly and effectively regulated today? (3) What total MIS development is expected? (4) What degree of uncertainty is acceptable in estimates of pollutant transport?

This report does not attempt to answer any of the preceding policy questions. It does attempt to provide information which can lead to selection of a control technology once the preceding questions have been answered. Depending upon the priorities adopted by regulators (for example, whether it is more important to protect local groundwater or downstream surface waters; or whether it is more important to control the quality of leachate or its rate of flow; or whether it is more important to protect water quality in the short term (100 years) or the long term (1000 years)), different control technology options may be preferred. The following discussion addresses these questions.

11.3 Evaluation of Specific Control Technologies

11.3.1 No Control Technology. A decision to use no control technology should be based upon the following arguments (these arguments represent positions that might be taken, not positions taken by the authors): (1) Local groundwaters are little used and already of low quality. (2) Expected quality of MIS leachate is such that degradation of local groundwaters would not affect their suitability for beneficial use. (3) Time scale of reinvasion and leachate transport is so slow that the effects can be neglected (this issue is especially controversial). (4) Because of dilution in the Colorado River system, effects downstream will be minor.

If the "no control" option is recommended, the following points must also be considered: (1) Uncertainties in the chemical quality of leachate and in the time scale of reinvasion and leachate transport must be reduced by further experimental work. (2) The effects calculated in Chapter 2 assume the existence of only two MIS projects at tracts C-a and C-b; if these projects grow from their present sizes, or if additional projects are planned, then the effects will be greater.

Table 11-1. Effects of Control Technologies.

NO CONTROL TECHNOLOGY (BASE CASE)

For the purposes of this discussion, the base case consists of 50,000 bbl/day MIS plants located at tract C-a and C-b. The assumed MIS technology is similar to that proposed by Occidental Oil Shale, Inc., and it includes a retorting rate of 1 ft/day in a steam/air atmosphere. No postretorting treatment is assumed.

Leachate quality

Leachate would have TDS of approximately 1500 mg/L and elevated concentrations of certain trace elements and trace organics (Tables 2-1, 2-3).

Rate of flow through retorts

If flow is vertical between aquifers, rate of flow estimated between 45 to 680 ft/yr, controlled by local aquifer permeabilities and hydraulic gradients (see Table 5-1). If flow velocities are horizontal, they will be essentially unchanged from predevelopment conditions, 4 to 160 ft/yr.

Effect on local groundwater

The entire region downdip of the MIS tract to the surface stream which receives base flow from the affected aquifer(s) would be degraded. The solute front would advance at 20 to 160 ft/yr.

Effect on surface streams

Increases in TDS concentration are estimated in Table 2-2; similar increases in trace elements and organics can be estimated from Tables 2-1 and 2-3. Concentrations of all leached solutes would be reduced downstream by dilution, as shown in Table 2-2.

Time scale of effects

No leachate would leave the MIS tract until reinvasion by groundwater is complete; estimated time for this would be 200 years at tract C-b. Time for solute front to reach surface streams would be 130 to 1450 years beyond this (Fox, 1980).

SITE SELECTION (COMPARED TO BASE CASE)

Leachate quality

Same as base case.

Rate of flow through retorts

Rate of flow through retorts is controlled by permeability of surrounding media and local hydraulic gradients. Selection of sites in regions of low permeability or low gradients would reduce flow through retorts proportionally.

Effect on local groundwater

Effect would be the same as for base case, except that rate of advance of solute front would be reduced.

Effect on surface streams

Volumetric rate of flow of degraded groundwater would be reduced, therefore effects on surface streams would be reduced proportionally. No effect would occur if sites were identified where aquifers are not connected hydraulically to surface streams.

Time scale of effects

Rate of groundwater reinvasion and solute transport are controlled by permeability of surrounding media and local hydraulic gradient. Selection of sites in regions of low permeability would extend the amount of time required for reinvasion; selection of sites in regions of low permeability and low hydraulic gradient would slow the rate of advance of the solute front.

Water required

None. However, if sites are "dry," dewatering flows may be inadequate for process requirements.

PROCESS MODIFICATION (COMPARED TO BASE CASE)

Leachate quality

If retorting conditions are optimized and postretorting treatments are selected to encourage formation of silicate minerals in the diopside-augite series, TDS of leachate will be reduced. Some trace elements may be controlled by incorporation in the diopside-augite lattice structure; others probably will not be. A major difficulty is the present inability to control retorting conditions so that spent shale is uniform and well-burned throughout the retort.

Rate of flow through retorts

Same as base case.

Effect on local groundwater

Degradation of local groundwaters will be reduced.

Effect on surface streams

Effects on surface streams would be reduced.

Time scale of effects

Same as base case.

Water required

No additional water would be required, but steam must be used in retorting.

INTENTIONAL LEACHING (COMPARED TO BASE CASE)

Leachate quality

For solutes which are controlled by mass transfer, including organic carbon, concentrations in leachate could be reduced by any desired factor by leaching with a specified number of pore volumes. Calculations suggest that four pore volumes are sufficient to effect a 90 percent reduction in organic carbon. Some solutes are controlled by other mechanisms and would not be reduced by intentional leaching.

Rate of flow through retorts

Same as base case.

Effect on local groundwater

Concentrations of mass-transfer controlled solutes would be reduced.

Effect on surface streams

Concentrations of mass-transfer controlled solutes in surface streams would be reduced.

Time scale of effects

The time required for reinvasion of groundwater would be reduced, perhaps by one-third to one-half, because the MIS spent shale would be saturated.

Water required

Water for saturation of the MIS spent shale and to make up the brine stream rejected from the treatment process would amount to 78 to 144 gallons per barrel of oil recovered by MIS retorting. High quality water probably would be required.

Table 11-1. Effects of Control Technologies (continued).

RETORT GROUTING (COMPARED TO BASE CASE)

<u>Leachate quality</u>

Leachate quality would change because surface spent shale grout as well as MIS spent shale would be leached. Decreased liquid-to-solid ratio would increase concentrations of constituents which are mass-transfer-controlled. Data in Figure 10-6 suggest that TDS would be increased. Effects on specific elements or compounds are not known.

<u>Rate of flow through retorts</u>

Rate of flow through retorts would be sharply reduced. It is assumed that permeability of aquifers controls flow through retorts. If flow is vertical between aquifers at different heads, preliminary calculations in section 10.4.4 indicate flow reduction by a factor of 9 or 1300 at tracts C-b and C-a, respectively. If flow is horizontal, then flow reduction is due to alteration in the two-dimensional flow net as shown in Figure 3-2. Factor of reduction in this case is not known, but probably still substantial.

<u>Effect on local groundwater</u>

Concentrations of many solutes may be elevated compared to base case; rate of advance of solute front would be sharply reduced proportionally to reduction of flow rate through retorts.

<u>Effect on surface streams</u>

Less leachate would reach surface streams, but it might be more concentrated in some solutes. The net effect would depend upon the product of the reduction in flow and the increase in concentration. Effects would be delayed because of slower rate of advance of solute front through aquifers.

<u>Time scale of effects</u>

The time required for reinvasion would be reduced, because the MIS spent shale would be saturated and the voids filled with a saturated grout. However, the rate of advance of leachate through aquifers would be slower, because of reduced rate of flow through retorts.

<u>Water required</u>

Water required to prewet spent shale and to prepare grout amounts to 200 to 270 gallons per barrel of oil. Water quality for grouting is not critical, but could affect the quality of leachate.

GROUT CURTAIN (COMPARED TO BASE CASE)

<u>Leachate quality</u>

Same as base case.

<u>Rate of flow through retorts</u>

If a grout curtain can be formed, flow through retorts would be reduced. The factor of reduction is not known; it would depend upon the permeability of the grout curtain and the permeability of the aquifer.

<u>Effect on local groundwater</u>

Eventual degradation of groundwater downdip of development site would be the same as the base case, except that the rate of advance of the solute front would be reduced proportionally to the reduction in flow through the retorts.

<u>Effect on surface streams</u>

Effects on surface streams would be reduced proportionally to reduction in flow through retorts.

<u>Time scale of effects</u>

Reinvasion would be slower because grout curtains cut off aquifers. Rate of advance of solute front through aquifers would be reduced proportionally to reduction in rate of flow through retorts.

<u>Water required</u>

Water is required for grouting. The requirement (not estimated here) would be much less than for retort grouting because the amount of grout to be placed is much smaller and MIS spent shale would not have to be prewetted.

11.3.2 Site Selection. The occurrence and time scale of reinvasion and leachate transport is determined primarily by the hydrologic properties of the aquifers adjacent to MIS retorts. Fracture patterns are particularly important. A thorough review of the geohydrology and oil shale resources of the Piceance Creek Basin should be conducted to identify sites where reinvasion and leachate transport would be slow; then the analysis appropriate to "no control" should be applied.

11.3.3 Process Modification. From the discussion in Chapter 4, the retorting process can be controlled to encourage formation of silicates, particularly minerals in the diopside-augite series, which would reduce the TDS of leachate. However, minor elements (notably F) are not controlled. For process control to be selected as the control technology, two conditions must be satisfied. First, the mineralogy of "optimally processed" MIS spent shale must be confirmed. Analysis of the leachate also must show that the reduction in leachate TDS and major elements is sufficiently large, and the expected increase in minor elements is sufficiently small, to meet the desired leachate quality standards. Second, it must be demonstrated that spent shale is uniform throughout the retort. This would require better retort rubblization techniques (to control channeling) and also would require some technique to manage the "bottom plug," underground sump, and allied mining works of the retort. At present, neither of these problems has been solved.

11.3.4 Intentional Leaching. A decision to use intentional leaching should be based upon the following arguments: (1) An adequate water supply, treatment process, and brine disposal system are available. (2) The leachate quality (after n pore volumes) is acceptable. (3) Local groundwater quality is protected in the long term.

For intentional leaching to be the control technology of choice, it must be demonstrated that the concentrations of all constituents of concern are reduced to acceptable levels within the number of pore volumes which are to be treated. As discussed in Chapter 5, solutes which are limited by mass transfer will be reduced. This includes total organic carbon and TDS, but probably not certain trace elements, such as F. It also must be demonstrated that leachate concentrations do not subsequently increase (during the time interval between intentional leaching and eventual reinvasion) because of solute diffusion from the interior of spent shale particles to the surface.

It has been assumed in this report that a process to treat the leachate will be available. However, this may not be a routine matter because the leachate will be saturated with some minerals, and removal of water by a demineralization process such as reverse osmosis will result in supersaturation, possibly causing fouling of membranes by precipitates. This problem is especially acute when it is desired to recover a large proportion of the water for reuse. Fouling of membranes by precipitates has been controlled by addition of complexing agents, but these may add significantly to the cost of the process. Control of membrane fouling also may be achieved by exploiting the kinetics of precipitation to delay precipitation until the brine is removed from the membrane module.

Intentional leaching would consume a large amount of water (78 to 144 gal/bbl of oil) to replace brine and to rehydrate MIS spent shale. Acceptable quality for this water is unknown, but a low TDS water probably will be required. Therefore, if intentional leaching is to be considered as a control technology, adequate water supply for leaching must be assured.

Finally, as a result of saturating the MIS spent shale, the reinvasion process would be accelerated. Reinvasion is slow primarily because of the large volume of voids to be filled with water and the slow rate of delivery of water to the abandoned retorts (limited by the reduced permeability of desaturated aquifers). Resaturating the spent shale would replace about one-third to one-half of the water needed to complete reinvasion; it will also reduce the amount of time for reinvasion.

11.3.5 Retort Grouting. Retort grouting would reduce the flow of groundwater through retorts by reducing their permeability, and at the same time increase the concentration of leachate. The actual factor by which flow through the retorts would be reduced depends upon the flow regime (horizontally through retorts penetrating only one aquifer or vertically through retorts penetrating two aquifers at different heads). Flow reduction has not been calculated for the former case; in the latter case, a simple analysis presented in section 10.4 indicates flow reduction by a large factor (e.g., 9 to 1300).

At the same time, the leachate concentrations would be increased. The only cost-effective material for grouting is surface-retorted spent shale, which, in most cases, is more soluble than MIS spent shale. Grouting reduces the liquid-to-solid ratio (LSR) in an abandoned retort (compared to an ungrouted retort), which also would increase the leachate concentrations. Data presented in Figure 10-6 suggest that the increase in TDS would not offset the flow reduction caused by retort grouting.

The water requirements for grouting, estimated to be 200-270 gallons per barrel of oil recovered by MIS retorting, are substantial and may present an obstacle to retort grouting. Unlike intentional leaching, the water quality requirement is not critical, but if process wastewaters are used, the effect on leachate quality must be taken into account.

11.3.6 Grout Curtain. Using a grout curtain as a control technology to cut off flow in aquifers has been considered only superficially in this report. The major unresolved question is whether such a grout curtain could be formed.

11.4 Research Needed for More Complete Evaluation of Candidate Control Technologies

Research conducted under this project has produced some important data and concepts for evaluation of control technologies. As indicated above, the choice of control technology is partly dependent upon management decisions. However, large areas of uncertainty remain which should be resolved before any of these control technologies can be recommended for use. At the same time, experimental MIS retorts exist which will be abandoned, and some decisions must be made for their management. The best use of these retorts is as research tools to develop the additional data needed. This section presents research recommendations for each of the control technologies considered. Research recommendations are summarized in Table 11-2.

11.4.1 No Action (Base Case). Better information is needed to characterize leachate quality and leachate transport. Research is currently in progress to characterize leachates from the Oxy R3 cores; attention should be directed to organic compounds and trace elements (high priority). Analyses of solute transport presented in this report (Chapter 2) are rough; the current state of the art permits more sophisticated analysis. This activity is given a high

Table 11-2. Recommended Research.

1. Base case	1.1 Characterize MIS spent shale and leachate from existing MIS retorts, especially for trace elements and organics (high)(a).
	1.2 Develop improved models of leachate formation and solute transport, incorporating fracture flow, retardation of solutes by aquifer media, and chemical reactions and kinetics (high)(b).
	1.3 Resolve question of hydraulic connection between aquifers and surface streams, and between upper and lower aquifers by retorts (high).
2. Site selection	2.1 Critically review existing data and collection of new data to select sites for MIS retorting, using (1.2) above (medium).
3. Process control	3.1 Demonstrate uniform retorting conditions throughout retort (low).
	3.2 Evaluate effect of bottom plug, underground sump, and mining works on leachate quality (medium).
4. Intentional leaching	4.1 Critically assess water availability (high).
	4.2 Develop better understanding of mechanisms controlling solute concentrations (high) (a).
	4.3 Conduct sequential or column leaching experiments to demonstrate decrease in concentrations (high)(a).
	4.4 If results of 4.3 are favorable, demonstrate treatment process (medium).
5. Retort grouting	5.1 Critically assess water availability (high).
	5.2 Develop improved leachate flow models to determine factor by which flow through retorts can be reduced (medium).
	5.3 Demonstrate of penetration of grout through rubble in an experimental retort (medium)(c).
	5.4 Characterize leachate from a grouted core (high).
6. Grout curtain	6.1 Develop improved leachate flow models to determine factor by which flow through retorts can be reduced (medium).
	6.2 If results of (6.1) are favorable, prepare detailed cost estimate with field studies to determine feasibility (low).

(a) Research currently in progress at Los Alamos Scientific Laboratory
(b) Research currently in progress at Denver Research Institute
(c) Research currently in progress at Rio Blanco Oil Shale Company

priority because the long period of delay before the effects of leaching are felt downstream appears to be an important factor. Analysis to date has considered the Piceance Creek Basin aquifers as idealized porous media, when they are known to be fractured media. This may have caused an underestimate of the velocity of solute transport. Solute retardation by sorption on aquifer media also has been ignored. These two factors should be included in future analyses (high priority).

11.4.2 Site Selection. A combined hydrologic-resource evaluation of potential MIS sites should be conducted to identify those which are more favorable for MIS retorting than tracts C-a and C-b (medium priority).

11.4.3 Process Control. It should be demonstrated that uniform retorting conditions can be achieved throughout a retort (low priority). Work is required to evaluate the leaching properties of the bottom plug, underground sump, and allied mining works. The relative importance of these sources of leachate should be evaluated (medium priority).

11.4.4 Intentional Leaching. Sequential leaching experiments are currently in progress to identify elements which can be reduced by intentional leaching. If results of these experiments are favorable, and if water requirements can be met, treatability experiments are recommended. The emphasis must be on recovery of most of the leachate (i.e., a brine reject stream of 25 percent or less) and the most difficult problem appears to be avoiding fouling of reverse-osmosis membranes (high priority if preliminary results are favorable).

11.4.5 Retort grouting. Water requirements for grouting may be the limiting factor. Whether these can be met should first be evaluated. Ways to reduce these also should be examined. Studies are required to determine the effect of retort grouting on leachate concentration, resulting from reduction of the liquid-solid ratio in the grouted retort and inclusion of waste material. Cores from field retorts should be grouted with a grout similar to R-2 and leached, with similar ungrouted cores leached as controls (high priority if water requirements can be met).

11.4.6 Grout curtain. Field studies are apt to be expensive. Solute transport modeling with grout curtains in place should be done. If results are favorable, field studies to establish feasibility are recommended (low priority).

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APPENDIX B. MINERALOGICAL ANALYSIS OF LURGI SPENT SHALE AFTER HEATING IN VARIOUS ATMOSPHERES FOR VARIOUS TIMES AND TEMPERATURES

Five grams of Lurgi spent shale was placed in a porcelain sample boat and heated in a mullite tube in a tube furnace. Heating was at 700, 800, 850, 900, or 950 C; for 1, 2, or 4 hr; in flowing steam, flowing nitrogen, or autogenous atmosphere (no flowing gas). The material was cooled in the same atmosphere. Samples were analyzed for minerals by x-ray diffraction, and for free lime by ASTM C 114.

Table B-1. XRD Peak Heights of Lurgi Spent Shale Heated in Flowing Nitrogen.

			Time and temperature of heating														
			700 C			800 C			850 C			900 C			950 C		
Mineral	Bragg angle, 2θ	As received	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr
Quartz	26.6	60	--	--	--	31	31	21	19	17	13	12	9	6	5	5	2
Feldspar	27.9	24	--	--	--	18	20	15	15	11	9	0	0	0	0	0	0
Anhydrite	25.4	12	--	--	--	9	9	5	8	6	9	8	9	5	0	0	0
MgO	42.9	7	--	--	--	18	18	19	22	21	16	17	8	8	7	6	0
CaO	37.4	0	--	--	--	28	15	7	13	9	4	6	7	8	7	9	10
Dolomite	30.9	30	--	--	--	0	0	0	0	0	0	0	0	0	0	0	0
Calcite	29.4	56	--	--	--	0	0	0	0	0	0	0	0	0	0	0	0
C_3A	33.15	0	--	--	--	0	0	0	0	0	0	0	0	0	0	0	0
β-C_2S	33.2	0	--	--	--	0	0	0	0	0	0	0	0	0	0	0	0
Akermanite	31.3	0	--	--	--	0	0	10	16	14	26	25	51	76	60	80	100
Free lime, %, C 114		0.0	--	--	--	8.6	7.9	4.6	3.7	2.1	0.2	0.4	0.1	0.3	0.1	0.1	0.0

Table B-2. XRD Peak Heights of Lurgi Spent Shale Heated in Flowing Steam.

			Time and temperature of heating														
			700 C			800 C			850 C			900 C			950 C		
Mineral	Bragg angle, 2θ	As received	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr
Quartz	26.6	60	8	14	5	8	8	0	0	0	0	0	0	0	0	0	0
Feldspar	27.9	24	19	21	14	15	16	11	7	8	0	0	0	0	0	0	0
Anhydrite	25.4	12	10	12	13	10	11	10	7	9	7	7	8	6	6	6	0
MgO	42.9	7	7	9	0	6	6	0	0	0	0	0	0	0	0	0	0
CaO	37.4	0	5	6	5	7	7	7	8	8	9	9	9	9	9	0	0
Dolomite	30.9	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Calcite	29.4	56	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_3A	33.15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\beta-C_2S$	33.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Akermanite	31.3	0	40	17	52	55	60	83	95	100	100	100	100	100	100	100	100
Free lime, %, C 114		0.0	0.7	1.6	0.9	0.4	0.7	0.2	0.1	0.2	0.0	0.1	0.1	0.0	0.0	0.0	0.0

Table B-3. XRD Peak Heights of Lurgi Spent Shale Heated Without Flowing Gas.

			Time and temperature of heating														
			700 C			800 C			850 C			900 C			950 C		
Mineral	Bragg angle, 2θ	As received	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr
Quartz	26.6	60	59	--	--	32	28	20	24	20	17	14	9	6	8	4	4
Feldspar	27.9	24	27	--	--	22	20	15	18	17	13	9	0	0	0	0	0
Anhydrite	25.4	12	15	--	--	16	17	17	16	17	14	14	8	7	8	5	0
MgO	42.9	7	13	--	--	19	18	19	19	18	18	19	10	3	7	0	0
CaO	37.4	0	17	--	--	24	15	18	20	9	4	4	0	0	6	0	0
Dolomite	30.9	30	0	--	--	0	0	0	0	0	0	0	0	0	0	0	0
Calcite	29.4	56	37	--	--	0	0	0	0	0	0	0	0	0	0	0	0
C_3A	33.15	0	0	--	--	0	0	0	0	0	0	0	0	0	0	0	0
β-C_2S	33.2	0	0	--	--	0	0	0	0	0	0	0	0	0	0	0	0
Akermanite	31.3	0	0	--	--	8	7	12	10	13	17	23	42	68	58	78	88
Free lime, %, C 114		0.0	--	--	--	8.4	8.0	3.3	6.2	2.8	1.2	0.6	0.5	0.5	0.3	0.1	0.0

APPENDIX C. PERMEABILITY MEASUREMENT

Theory of Permeability Measurement

Permeability is defined as the property of a porous material which characterizes the ease with which a fluid may be made to flow through it by an applied pressure gradient. Darcy's Law defines permeability in terms of measurable quantities

$$Q = (kA/\mu)(\Delta P/L) \tag{C-1}$$

where Q = volumetric flow rate through cross-sectional area A, L^3T^{-1}
k = permeability, L^2
A = area perpendicular to direction of flow, L^2
$\Delta P/L$ = pressure gradient, $ML^{-2}T^{-2}$
μ = viscosity of the fluid, $ML^{-1}T^{-1}$.

An equivalent and more commonly stated form of Darcy's Law is

$$Q = KiA \tag{C-2}$$

where K = hydraulic conductivity, LT^{-1} (so called because of the analogy with electrical conductivity).
i = hydraulic gradient, dimensionless.

When equation (C-2) is used, the value of hydraulic conductivity K depends upon the fluid. Thus does not appear in the equation. Hydraulic gradient, i, is a dimensionless pressure gradient where pressure has been replaced by the height of an equivalent column of fluid (head, units of length).

Permeability, k, is a property of the porous medium only, while hydraulic conductivity, K, is also a property of the fluid. They are related by

$$K = kg\rho/\mu. \tag{C-3}$$

If the fluid and temperature are taken as water at 20 C, k and K can be related by

$$1 \text{ cm}^2 = 9.804 \times 10^4 \text{ cm/sec}.$$

Another unit for permeability in common use is the darcy

$$1 \text{ darcy} = 9.862 \times 10^{-9} \text{ cm}^2.$$

Because hydraulic conductivity is the mode of expression in common use by geohydrologists this form is used in the body of this report, where it is referred to as permeability.

Factors Affecting Permeability. The permeability of a saturated material is determined by the porosity (defined as void volume per total volume, dimensionless) and wetted pore surface area (defined as surface area per volume, L^{-1}). For a grout material, two other factors, saturation and confining pressure, have major impact upon the permeability measured in any test. Saturation determines whether all the pores are available to transmit test. Saturation determines whether all the pores are available to transmit fluid, and confining pressure influences the porosity.

A material is said to be fully saturated if all the pore space is filled with fluid. Saturation, S, is the fraction of pore space filled with fluid. If S is less than 100 percent, some of the fluid has been replaced by air. Air bubbles block flow paths, rendering the material effectively less permeable. This effect has two important consequences. First, a numerical model of a system undergoing desaturation must account for this effect; that is, permeability should be adjusted in response to loss of saturation. Second, laboratory measurement of permeability must be done at a known value of saturation, preferably complete saturation.

Grout placed underground is subject to the confining pressure of overburden and surrounding rock. When placed under a confining pressure, the grout will consolidate. Pore water will be forced out of the grout into surrounding materials, porosity will be reduced, grout solid particles will be in closer contact, and permeability will be reduced. Therefore any permeability measurements on grouts must be made at the expected confining pressure in service, or at a range of confining pressures.

As shown in Chapter 7, the confining pressure in a grouted retort depends upon the modulus of elasticity of the grouted retort (other factors, such as dimensions and host rock properties, being equal).

Method of Permeability Measurement

The method used to measure the hydraulic conductivity of the grouts was to place the sample, fully saturated, in a triaxial pressure cell. The specimen was then subjected to the desired confining pressure in all directions ($\sigma_1 = \sigma_2 = \sigma_3$). A hydraulic gradient was applied across the sample, and the hydraulic conductivity measured by equation (C-2).

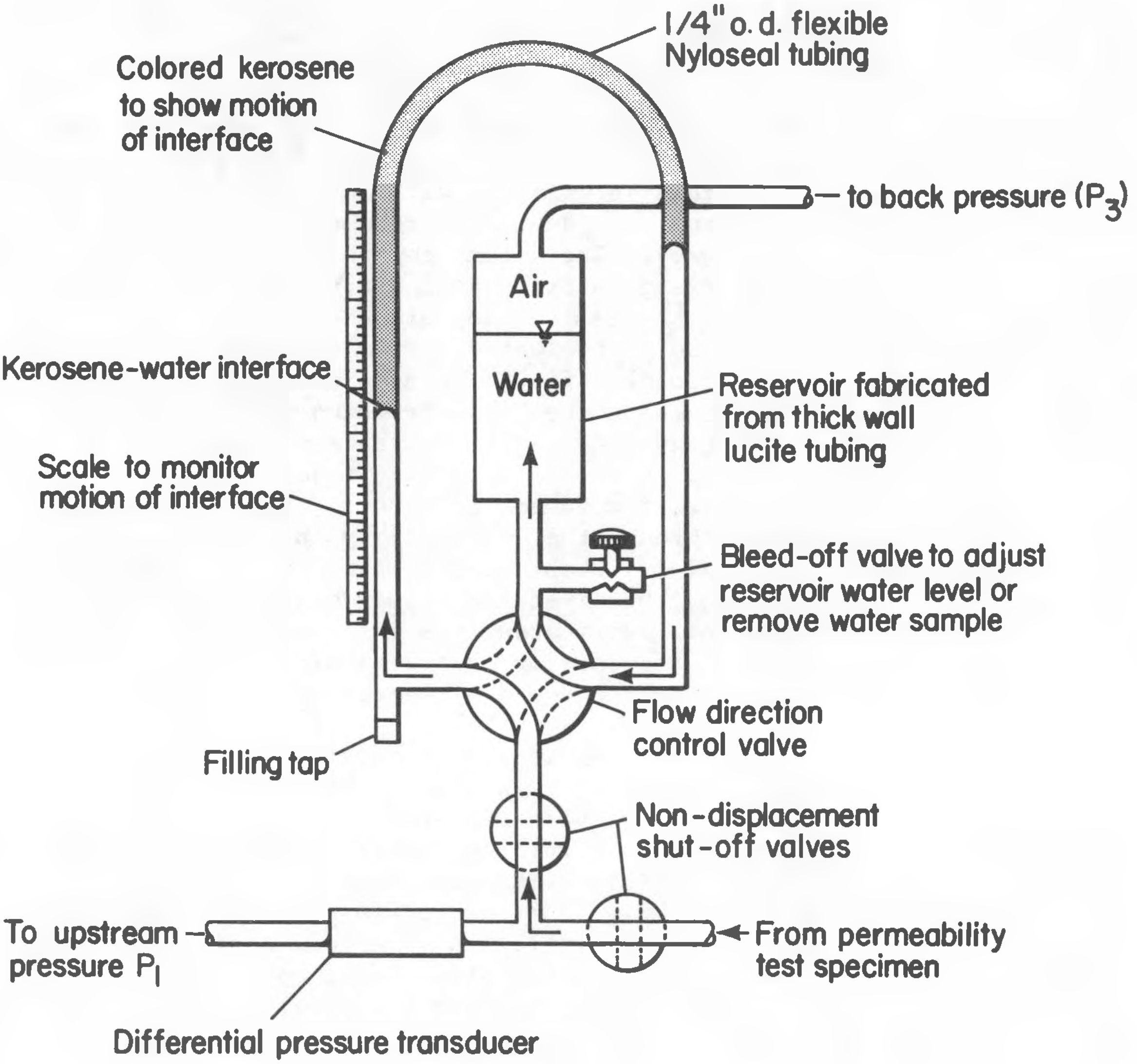
The hydraulic gradient used to induce flow for hydraulic conductivity measurement can be imposed against any desired back pressure, for example, 50 to 40 psi or equivalently 10 psi to zero. In theory, the flow through the sample would be the same in each instance, as long as the upstream pressure is less than the confining pressure. If the water contains dissolved gases, however, these will degas as the pressure decreases, causing desaturation and erroneous low values of hydraulic conductivity. In the first series of grouts tested (series Q), the back pressure was atmospheric pressure. Turbidity in the effluent water indicated that degassing occurred; for the second series, (series R) flow was measured against a positive back pressure.

Apparatus. The apparatus used in this experiment is a modification of that used by Ohnishi (1973), with flow measurement using a volume-change device developed by Chan and Duncan (1966). The permeability measuring system used for series R grouts is shown in Figure 10-3 in the body of this report. Desired water pressure and back pressure were maintained by air pressure regulators on the house high pressure air line. This produced the desired hydraulic gradient across the sample. Desired confining pressure around the sample was maintained by a hand pump and check valve. Hydraulic oil was used as the confining fluid. This exerted confining pressure in the two horizontal directions. To maintain a hydrostatic state of stress on the sample (compressive stress equal in all directions), a loading frame was used to apply a vertical stress equal to the confining pressure. The sample was isolated from the confining fluid by a flexible membrane.

Flow Measurement System. Two different flow measurement systems were used, depending on whether the flow was measured against a zero or positive back pressure. For flow against zero back pressure (atmospheric pressure), a burette was used to measure the flow rate. The time for passage of any volume of water up to 10 mL could be measured. The slight increase in back pressure due to the rise in the water level was considered negligible when compared with the upstream pressure (i.e., change in the pressure gradient was negligible). This flow measurement system was used for series Q grouts. For flow against a positive back pressure, flow was measured using a volume change device developed by Chan and Duncan (1966) (Fig. C-1).

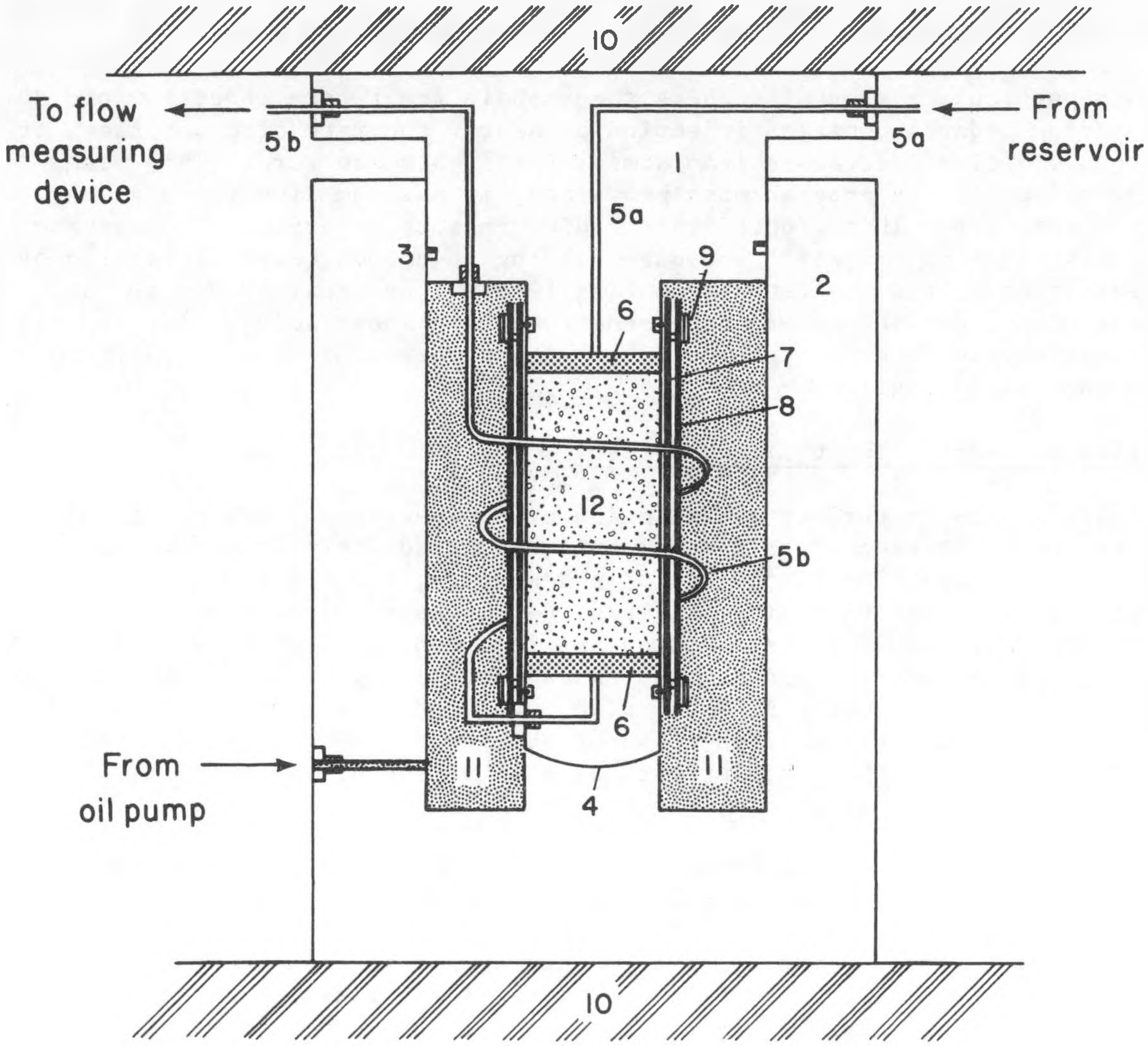
To measure low permeabilities, small flows must be accurately metered as they flow into a pressurized container. If the container is large, accurate estimation of the quantity of fluid entering is difficult, while if it is small, the container is filled too soon and must frequently be emptied (connected to atmospheric pressure). The volume change device developed by Chan and Duncan (1966) solves this problem by alternating the water flow direction through a narrow tube. An immiscible colored fluid (kerosene dyed with Sudan Red) is displaced ahead of the water. From displacement of the interface between the water and colored fluid during timed intervals, the flow rate can be accurately measured. When the flow-direction control valve is set as shown by the solid lines in Figure C-1, the interface moves upward in the calibrated section of the tubing. When the interface reaches the top of the calibrated section, the direction of movement is reversed (without changing the direction of flow of water through the specimen) by changing the setting of the flow-direction control valve. When the interface reaches the bottom of the calibrated section of tubing, the direction of movement is again reversed. A pressurized reservoir fabricated from thick-walled Lucite tubing receives the flow continuously. Pressure in the reservoir is maintained by an air-pressure regulator connected to the house high-pressure air line.

Triaxial Compression Cell. The triaxial compression cell maintained the samples under a uniform confining pressure in the two horizontal directions (Fig. C-2). Confining pressure in the vertical direction equal to the lateral confining pressure was maintained by an Instron-type load frame (Fig. 10-3) The sample was enclosed in two flexible waterproof jackets cut from bicycle inner tubes, which isolated the sample from the confining fluid while allowing the pressure to be transmitted to the sample. A spherical dome on the lower head fitted a spherical socket in the bottom of the cell body. This ensured that no bending stress would result when the vertical axial stress was applied to the sample by the load frame. Porous stones at each end of the sample distributed flow over the entire cross sectional area.



XBL 821-52

Figure C-1. Volume change device used to measure flow into a pressurized reservoir (Chan and Duncan, 1966).



XBL 821-35

1. Head of triaxial cell
2. Body of triaxial cell
3. Piston ring
4. Spherical socket

5a. Stainless steel sample line from reservoir (P_1)

5b. Stainless steel sample line to flow measuring device (P_3)

6. Porous stones at each end of sample
7. Inner flexible membrane jacket
8. Outer flexible membrane jacket
9. Hose clamps bear on O-rings
10. Load frame to provide axial stress
11. Hydraulic oil confining fluid (P_2)
12. Grout sample under test

Figure C-2. Triaxial compression cell used to maintain confining pressure on grout samples during permeability measurements.

APPENDIX D. PENETRATION OF NON-NEWTONIAN FLUIDS THROUGH RUBBLE

When particulate grouts (such as spent shale grout) are injected into a porous medium under a constant injection pressure, the rate of grout flow, or "take" (volume/time) decreases from some initial value to zero. This means that the radius of the grouted mass grows to some maximum size for a given injection pressure. This grouted mass radius in turn determines the maximum hole spacing for the project. Because drilling injection holes appears to be the greatest cost item for retort grouting (Persoff and Fox, 1979), it is important that the distance of grout penetration be known accurately, and also that this distance be great enough to keep the number of required injection holes economically small.

Limitation of Penetration by Yield Stress

Fluids are characterized as Newtonian or non-Newtonian, depending upon the relationship between shear rate and velocity gradient. If these two quantities are proportional, the fluid is Newtonian, and the constant of proportionality is the viscosity (see Fig. D-1). Particulate grouts are, in general, non-Newtonian. Two non-Newtonian fluid models often used to describe particulate grouts are the Bingham and Casson models (Fig. D-1). Bingham and Casson fluids, besides being non-Newtonian, are characterized by a "yield stress". This is a minimum value of shear stress that must be applied before the fluid will flow. The yield stress, as will be shown, is the critical parameter determining distance of penetration.

Figure D-2 shows the distribution of stress and velocity for a Newtonian fluid flowing in a horizontal circular tube. Figure D-3 shows the distribution for a Bingham fluid. The fluid travels as a central plug, which is not sheared (velocity gradient = zero) carried by an annular cylinder in shear. In both Figures D-2 and D-3, the slope of the line which plots shear stress against radial position in the tube is directly proportional to the pressure gradient in the tube.

In Figure D-3, as the pressure gradient decreases, the central plug expands toward the walls of the tube. Finally, when the pressure gradient reaches a critical value (G_c) the plug fills the entire tube, velocity is zero everywhere in the tube, and flow ceases. As grout is injected from a point source of constant pressure, and the grout front travels outward, the pressure gradient is constantly decreasing. Thus we have an expression for the limit of penetration: grout continues to flow until it reaches a distance such that the pressure gradient is equal to the critical gradient; then flow stops. The critical gradient is given by

$$G_c = 2\tau_y/R \qquad \text{(D-1)}$$

where G_c = critical pressure gradient
τ_y = yield stress
R = pore radius.

This analysis can only apply to non-Newtonian fluids that have a yield stress. For Newtonian fluids, the fluid never stops flowing as long as the pressure gradient is greater than zero.

As shown in Figure D-3, the critical gradient depends upon the yield stress of the fluid and the diameter of the cylindrical pore. To predict penetration of grouts through irregular pore spaces, one approach is to approximate the entire rubble volume by a single effective pore radius. Based upon descriptions of the rubblization techniques and the resulting fractured oil shale, an effective pore diameter of 1 mm appears to be appropriate. The yield stress of grouts R-3 and R-4 were measured at approximately 60 dyne/cm^2. Substituting these values in equation (D-1) gives G_c = 1200 dyne/cm^2. The injection pressure of a column of grout is given by

$$P = \rho g h \tag{D-2}$$

where P = grout injection pressure
ρ = grout density
h = height of grout column
g = acceleration of gravity = 980 cm/sec^2.

For a grout density of 1.5 g/cm^3, and a column height of 150 m (approximately the depth of overburden at tract C-b), the injection pressure is approximately 2.2×10^7 dyne/cm^2. The critical gradient is the ratio of the injection pressure to the distance of ultimate penetration. Thus for this example, the distance of ultimate penetration is approximately 180 m. This is well in excess of the distance of penetration (25 m) which was assumed for the preliminary cost estimate (Persoff and Fox, 1979). Thus the series Q and R grouts, which were formulated to meet standard criteria for grouting in prepacked aggregate, should penetrate quite well in MIS rubble.

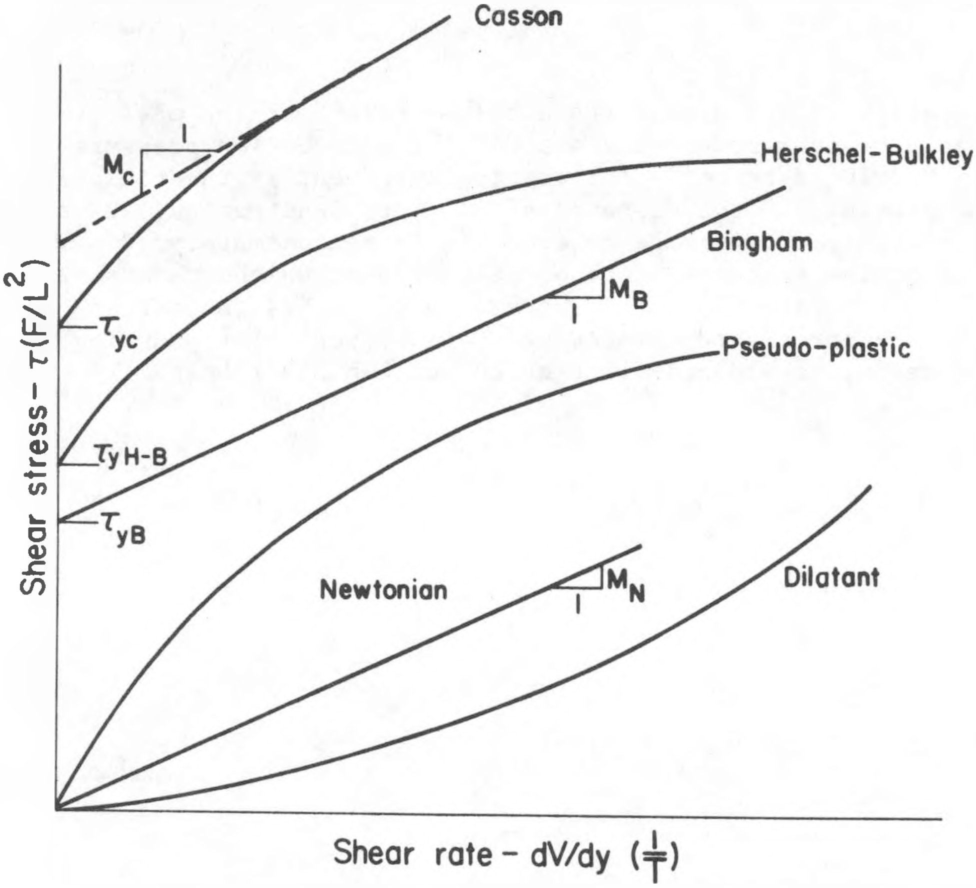


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Figure D-1. Flow curves for Newtonian and non-Newtonian fluids.

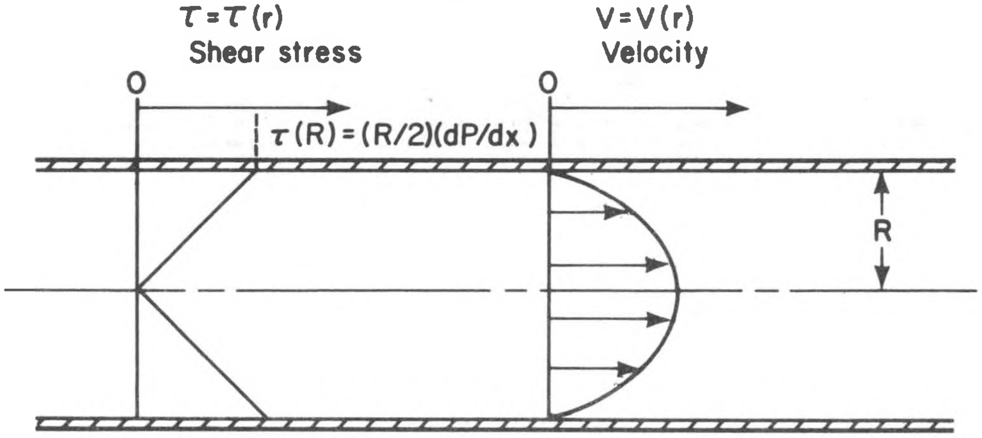

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Figure D-2. Newtonian flow in a straight, circular, horizontal tube.

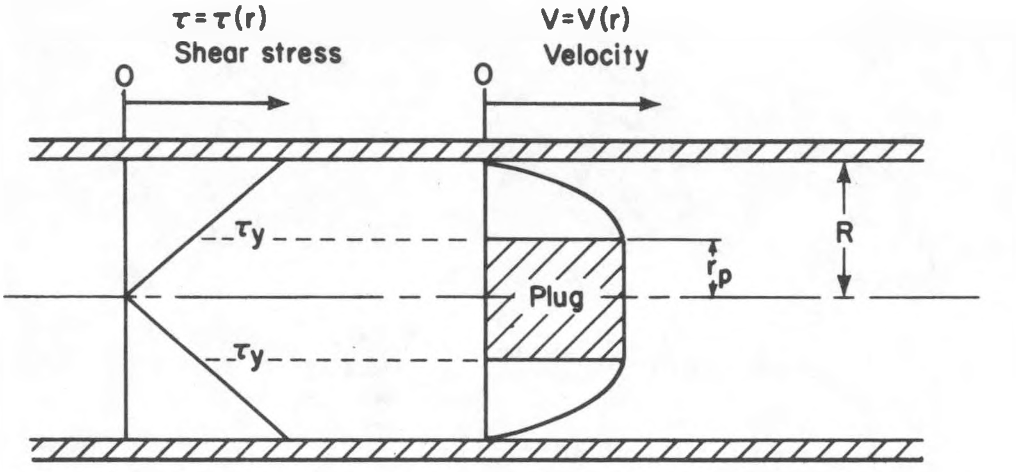

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Figure D-3. Non-Newtonian flow in a straight, circular, horizontal tube. An unsheared cylinder is developed in the center of the tube because the shear stress is this zone is less than τ_y. The radius of the unsheared cylinder is

$$r_c = 2\tau_y/G$$

where $G = dP/dL$ is the pressure gradient. If $R = r_c$, flow ceases. Conversely, for a given τ_y and R, there is a critical pressure gradient, given by

$$G_c = 2\tau_y/R$$