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Control Strategies for Abandoned In Situ Oil Shale Retorts

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CONTROL STRATEGIES FOR ABANDONED IN SITU OIL SHALE RETORTS

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ABSTRACT

In situ oil shale retorting may result in a number of environmental impacts including degradation of local surface and groundwaters, low resource recovery and subsidence. The target of present oil shale commercialization activities is the Mahogany zone in Colorado's Piceance Creek Basin. The principal oil shale resource in this area is surrounded by two confined aquifers. During mining and retorting, these aquifers are dewatered. When the site is abandoned, groundwater will reinvade the area and flow through the abandoned retorts, leaching potentially toxic or carcinogenic materials from the spent oil shale. This material may then be transported in local aquifers, withdrawn in wells or discharged into the Colorado River system as base flow.

Certain control technologies appear potentially able to protect groundwater quality at reasonable cost. These include designing retort blocks to include a hydraulic bypass around abandoned retorts (about $0.50/bbl), placing adsorbent clays in abandoned retorts to catch and hold leachable matter (about $0.50/bbl), collecting leachate and treating it on the surface (about $1.20/bbl), protecting abandoned retorts from leaching by placing a grout curtain around a block of abandoned retorts (about $2.00 to $3.00/bbl), or grouting abandoned retorts with spent shale (about $3 to $4/bbl).

ACKNOWLEDGMENT

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INTRODUCTION

Current industrial plans call for the development of lease tracts in the Piceance Creek Basin by modified in situ (MIS) retorting. Figure 1 shows in simplified form the relative positions of the rich oil shale layer (the Mahogany zone), fractured oil shale artesian aquifers, and MIS retorts.

During operation the aquifers will be dewatered. Following abandonment groundwater will re-invade the retorting area, leaching the in-situ spent shale, and transporting leached material into the aquifers. The worst case for aquifer disruption will occur when retorts are in contact with both aquifers at different heads. In this case there may be advective flow through the retorts, which would carry leached material into the aquifers. If contact is made with one aquifer only, transport of pollutants into the aquifer will not be advection, but only by diffusion, a much slower process. Since 80% of stream flow in Piceance Creek is base flow (i.e., the streams are groundwater fed), material leached by groundwater may eventually reach local surface streams.

The problem of aquifer and eventual surface stream pollution by leaching of modified in situ

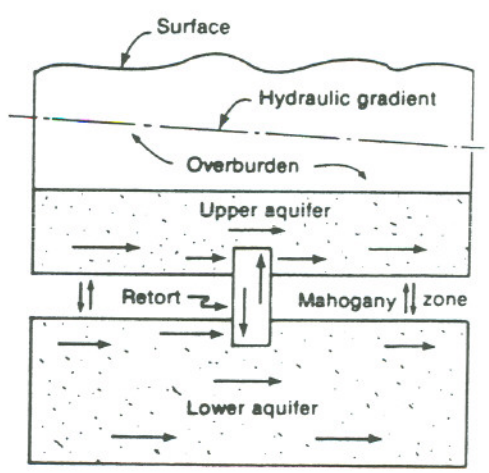

Figure 1. Schematic of retort-aquifer configuration in Piceance Basin. XBL 786-994

retorts in the Piceance Creek Basin has been quantified by Fox (1979). This study concluded that it could take centuries before significant groundwater degradation would occur due to the low flow velocities in many areas of the Piceance Creek Basin. However, the report pointed out that the potential long-term effects could be serious due to the critical issue of salinity in the Colorado River system and the slow self-purification properties of groundwater aquifers. Table 1 indicates that leachates could result in salinity increases in the Colorado River at Lees Ferry of from 0.3 - 50 mg/ℓ. A TDS increase of 50 mg/ℓ in the Colorado River would have a significant economic impact upon irrigated agriculture. The total economic loss due to Colorado River salinity increases is estimated to be $200,000 - 400,000 per year per mg/ℓ (1974 dollars) (Kleinman, 1974). Additionally, high concentrations of inorganic and organic materials may occur in aquifers or surface streams; some may be toxic or carcinogenic. In some areas of the Piceance Creek Basin, water quality of the lower aquifer is much worse than that of the upper aquifer. In these cases, contact between the two aquifers created by the retorts would permit degradation of the upper aquifer in the absence of leaching. Finally, resource recovery in MIS retorting is poor. Oil recovery is low and approximately 25% of the developed area must be left intact as pillars between retorts to support the overburden.

This paper will consider control technologies to prevent leaching of in-situ spent shale. Aquifer protection is the primary goal of these technologies, and strengthening of abandoned retorts is a secondary goal. Laboratory evaluation of these control technologies is currently under way at Lawrence Berkeley Laboratory; as the first stage of this study, the technical literature of related fields was reviewed. Conclusions and preliminary cost projections presented here are based upon that literature review (Persoff, 1979).

CONTROL TECHNOLOGIES

In situ leaching of spent shale can be prevented or mitigated using several different control strategies. These include selection of dry sites, isolation of the retorted area from the aquifers, intentional leaching, in-place adsorption of leachables and continuous dewatering. Some of these approaches will simultaneously address other environmental and technical issues, including subsidence, resource recovery and disposal of surface spent shales. Site selection may be adequate on a case-by-case

TABLE 1. The increase in TDS and TOC in surface waters of the upper Colorado River Basin due to the discharge of in situ leachates into Piceance Creek and Yellow Creek as base flow.

Watercourse	Average annual discharge (acre-ft/yr)	Maximum possible increase in TDS due to discharge of in situ leachate into Piceance Creek and Yellow Creek (mg/ℓ)	Maximum possible increase in Na due to discharge of in situ leachate into Piceance Creek and Yellow Creek (mg/ℓ)	Maximum possible increase in TOC due to discharge of in situ leachate into Piceance Creek and Yellow Creek (mg/ℓ)
Piceance Creek at White River	14,500	700 - 42,000	260 - 3,800	12 - 180
White River near Watson, Utah	532,000	20 - 1,270	8 - 110	0.4 - 5
Green River near Green River, Utah	4,427,000	3 - 150	1 - 14	< 0.05 - 0.7
Colorado River at Lees Ferry, Arizona	12,426,000	1 - 50	0.3 - 5	< 0.05 - 0.2

Ref: Fox, 1979.

basis but will have a limited area of applicability, as the target of MIS retorting, deep rich seams, is located in the center of the basin where groundwater abounds. Continuous dewatering is not economic and long-term custodial care would be required. The remaining options may be both technically and economically feasible and are discussed here.

Grout Individual Retorts

Retorts may be isolated from groundwaters by filling them with a material that is less permeable than the surrounding aquifers. This process, which is referred to here as grouting, involves partially or completely filling abandoned retorts with a material that will reduce permeability. If this material also enhances the strength of the retort, the risk of subsidence may be reduced and it may be feasible to retort the pillars to enhance resource recovery.

A wide variety of grouting materials are available, ranging in cost upward from soil-cement mixtures, at less than $1/ft^3 ($35/m^3) and neat portland cement, at about $2/ft^3 ($70/m^3), to chemical grouts with controllable gel times and viscosities, costing more than $20/ft^3 ($700/m^3). Even the cheapest commercially available grouting materials are too expensive for grouting abandoned retorts due to the large volumes that need to be filled. Oil shale is a low organic carbon resource and for each barrel (0.16 m^3) of oil extracted, 9 ft^3 (0.25 m^3) of voids remain to be filled (assuming a Fischer Assay of 24 gal/ton [100 ℓ/tonne], 65% recovery, and 20% voids in the retort; additional fine voids resulting from decomposition of kerogen are not considered groutable). Thus, cheap materials are required for grouting abandoned retorts.

Review of the literature suggests that spent shale may have properties which make it suitable for use as a grout. Spent shale from some retorts (Lurgi, TOSCO) is finely ground, and thus can be easily slurried and pumped. Investigators studying stability of spent shale disposal piles have found that the permeability of these piles is low and decreases with time and that compressive strengths increase with time. Unconfined compressive strengths up to 200 psi (1400 kN/m^2) were found for compacted Paraho spent shale (Woodward-Clyde, 1976), and up to 500 psi (3500 kN/m^2) for compacted TOSCO spent shale (Culbertson et al., 1970). This suggests that a cementing process, similar to that which occurs in lime stabilization of soils, occurs. Pozzolanic reactions, i.e., reactions between free lime [CaO or $Ca(OH)_2$] and active silica are known to occur. Pozzolanic activity (defined as the ability to react with free lime to form cohesive hydrates, e.g., tobermorite gel, which gives strength to portland cement) has been induced in shales and clays by heat treatment (Lea, 1971).

Retort grouting is the only candidate control technology that would simultaneously strengthen abandoned retorts and prevent leaching of spent shale. It would also reduce the problem of disposal of surface retorted spent shale and mixing of waters of the two aquifers. Design criteria for such a grouting operation have not been established, but they may include the following requirements:

(1) Low permeability of the grouted retort, probably on the order of 10^{-6} cm/sec.
(2) Sufficient strength to support the roof of the retort and permit the pillars (undisturbed rock between retorts) to be retorted afterwards. Compressive strengths of 1000 psi (7 kN/m^2) may be required.
(3) Long-term stability.

Two major technical problems remain to be solved for this technology to be successfully demonstrated. One is the preparation of a grout that would satisfy the criteria listed. The other is ensuring good penetration of the grout into the voids of an abandoned retort without incurring excessive drilling and injection costs.

Preparation of spent shale grout. In order to satisfy the design criteria, the grout will probably require that significant amounts of cohesive hydrates be formed. Unless this occurs, spent shale grout will be basically a silt, rather than a cement, grout. Adequate permeability reduction could be achieved by a silt grout, but probably not strength or permanence. Lack of permanence in a silt grout would be due to washing out of fines under the hydraulic gradient that may exist across an abandoned retort after reinvasion of groundwater.

For formation of cohesive hydrates, retorting conditions (or post-retorting treatment) must optimize both pozzolanic properties of spent shale and also formation of free lime [CaO or $Ca(OH)_2$].

Campbell (1978) studied mineralogical reactions during retorting and showed that the calcium content of raw shale, originally present as calcite ($CaCO_3$) or dolomite [$CaMg(CO_3)_2$], is largely converted to silicates which have no cementing value. Campbell's work suggests that at low CO_2 pressures and rapid heating rates, some free lime may be formed. Therefore it may be possible to operate a surface retort to optimize free lime formation. Research is required to define these operating conditions.

Another way to obtain cohesive hydrates in spent shale grout is to promote the formation of portland cement clinker compounds, e.g., tricalcium silicate (alite) or β-dicalcium silicate (belite). Addition of finely ground limestone either before retorting or before a post-retorting heat treatment step could produce these compounds. A temperature in the range of 1000°C would likely be required for this; thus, retorting conditions to optimize cementing properties would result in less efficient energy recovery.

Finally it may be economical to simply add a proportion of portland cement to the spent shale to improve its grouting properties.

Grout distribution. In usual soil grouting applications, grout is injected through closely spaced pipes, e.g., on 10-ft (3 m) centers. If this were done in grouting abandoned retorts, good penetration would be achieved, but the cost of drilling the injection holes would be high due to overburden depth. For retort grouting to be economical, grout holes must be drilled at some greater spacing [say 50 ft (15 m) on centers], and the grout must be able to penetrate the maximum distance between holes to fill the entire void space.

Penetration of grout through porous media depends on the properties of both the grout and the flow medium. For a grout with a defined setting time, the distance the grout can penetrate is the distance it can travel before it sets. The velocity of travel through pores is determined by the viscosity of the grout, or the apparent viscosity in the case of non-Newtonian grouts. Another factor limiting the penetration of particulate grouts, i.e., a spent shale grout, is the size of particles in suspension relative to the size of the pores. Shear strength of the fluid grout is also an important factor limiting penetration. In small pores, a greater pressure gradient is needed to overcome the shear strength of the grout. As grout injection proceeds, the injection pressure gradient which will cause flow of a grout with shear strength S through a pore of radius r is 2S/r (Raffle and Greenwood, 1961). Since the pressure gradient decreases with increasing distance from the point of injection, this limits the distance of penetration through fine pores. It appears that this last factor will be the most important factor limiting the flow of spent shale slurries through an abandoned retort. Therefore experimental work has focused on quantifying the shear strength of spent shale slurries, and the means to reduce it.

Additional complicating factors are the tendency of spent shale to absorb water and the complicated (and presently unknown) geometry of porosity in an abandoned retort. Nevens et al. (1977) found that simulated in-situ spent shale from the LETC 150 ton (135 tonne) retort absorbed up to 4 gal water/ft^3 (535 ℓ/m^3) and that for 2 in. (5 cm) cubes, most of this was absorbed within 5 min. Thus, if spent shale is not prewetted, any grout pumped through it would be dehydrated and its shear strength would increase.

Spent shale geometry in an abandoned retort may resemble that shown in figure 2. Pore distribution will include: (1) large voids (up to 3 cm and larger) where flow may be turbulent rather than laminar as is usually found in flow through porous media, (2) small voids between small pieces of rubble, (3) small voids between fragments of rubble that remain in close contact (such as where a block is broken into two pieces but the pieces are wedged together and cannot move apart), (4) cracks and fissures in retort walls, and (5) pores within rubble fragments remaining after pyrolysis of kerogen. The permeability of an abandoned retort has been estimated to be about 40 cm/sec, which is typical of a loose packed gravel. While it may be easy to fill the larger voids, which would certainly reduce the permeability by orders of magnitude,

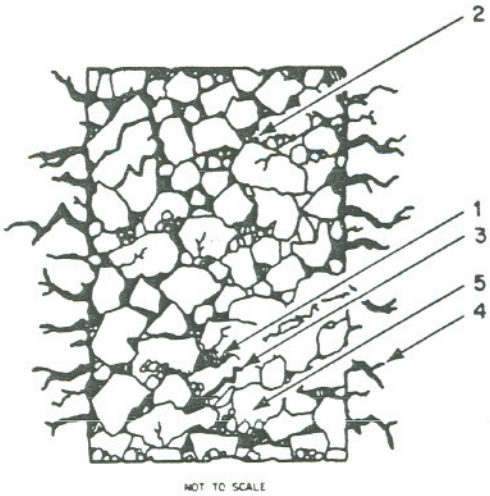

Figure 2. Schematic of porosity in an abandoned MIS retort. 1—Large voids between rubble blocks; 2—small voids between small pieces of rubble; 3—small voids where a block has broken but pieces cannot move apart; 4—cracks and fissures in retort walls; 5—micropores created by pyrolysis of kerogen. XBL 793-726

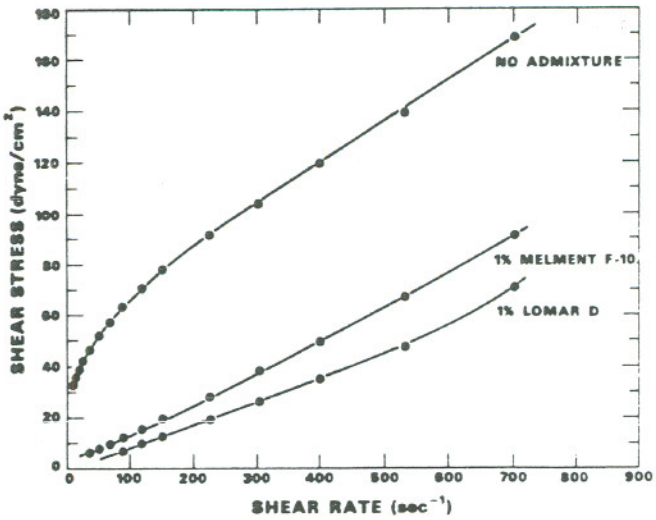

Figure 3. Viscosity-reducing effect of admixtures on spent shale slurries (45% solids). XBL 794-1187

permeability reduction necessary would almost certainly require filling of the smaller voids as well — probably all except the type (5) voids shown in figure 2.

Rheological properties of spent shale slurries. In grouting an abandoned retort, compromise must be reached between ease and completeness of grout penetration, which are favored by a high water-shale ratio, and strength and impermeability of the grout, which are favored by a low water-shale ratio. The situation is further complicated by the tendency of the spent shale in situ to absorb water and dehydrate the slurry being pumped through it. Preliminary measurements of rheological properties of spent shale grouts are presented in figure 3. Spent shale slurries studied here were non-Newtonian. Their flow characteristics (in the range of shear rates and water-shale ratios studied) are described by the Casson model (Casson, 1959):

$$F^{1/2} = a + bD^{1/2} \quad ,$$

where F = shear stress, dyne/cm^2

D = shear rate, sec^{-1}

a,b = constants.

This model was derived theoretically by considering the slurry of a suspension of rigid spheres in a Newtonian fluid. It is hypothesized that due to van der Waals attraction, chains of particles form, which are broken to shorter chains when the liquid is sheared. In figure 3 results are shown for a 45% solids slurry of Lurgi spent shale with and without addition of dispersant. The two dispersants tested were Lomar D (Diamond Shamrock Co.), sodium naphthalene sulfonate, and Melment F-10 (American Admixture Co.), a melamine-formaldehyde. Dispersants function by being adsorbed on the surface of particles in suspension, and preventing the formation of chains. As shown in figure 3, the addition of 1% by weight of shale of these dispersants changes the flow characteristics to quasi-Newtonian flow (Newtonian flow would be a straight line through the origin). The viscosity of the slurries with dispersants added are 130 cP and 90 cP for Melment F-10 and Lomar D, respectively. More important than the viscosity is the fact that the yield value (the stress that can be sustained by the grout without flowing) has been reduced from 25 dyne/cm^2 to less than 5 dyne/cm^2. This means that the grout, with dispersant added, can flow under a pressure gradient one-fifth as great as without. As a slurry flows through spent shale, its water-shale ratio will continuously decrease due to dehydration. Use of dispersants may be economical if grouts could penetrate farther and fewer injection holes would have to be drilled.

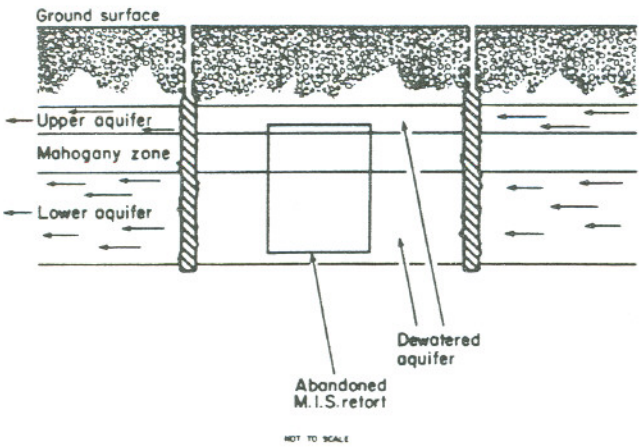

Figure 4. Schematic of grout curtain to prevent groundwater re-invasion of abandoned retorts. XBL 793-704

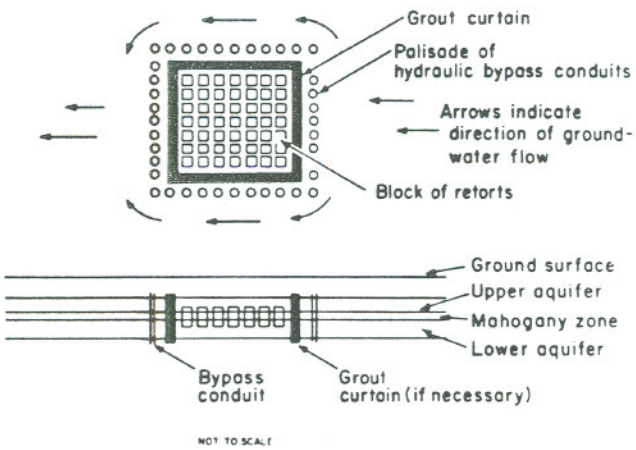

Figure 5. Schematic of hydraulic bypass around block of retorts. XBL 793-712

Hydrogeologic Modifications

Retorts may also be hydraulically isolated by surrounding a retorted area with a grout curtain or by providing a hydraulic bypass around the area.

Figure 4 shows a schematic of a grout curtain used in conjunction with an in situ retorting operation. A curtain of conventional grouting material such as portland cement would be formed around a large block of retorts. Flow through the area would be limited to leakage through the curtain which would be several orders of magnitude lower than would otherwise occur. The economic attractiveness of this approach requires that a large number of retorts (about 200-300) be surrounded by such a curtain. The technology of grout curtains is well established for smaller scale application. The application of this technology to large retort blocks may have some important technical limitations. Faults or fractures may limit the area which can be surrounded by a single grout curtain. Drilling and grouting at depths up to 1500 ft (450 m) may be technically difficult or costly.

Alternatively, flow through a retorted area may be limited by providing a hydraulic bypass around the area. If nine times as much groundwater flows through the bypass as through the retorts, pollutant transport will be reduced by a factor of ten. A hydraulic bypass arrangement could be a palisade of perforated pipes short-circuiting the lower to the upper aquifer, as shown schematically in figure 5. Alternatively, a grout curtain and hydraulic bypass could be used together.

Recover and Treat Leachate

Control technologies considered thus far have focused on retarding flow through the retorts. Another means of minimizing aquifer disruption is intentional leaching. Laboratory studies have shown that most of the leachable material is removed in the passage of the first few pore volumes of water. Thus, a finite amount of leachate can be pumped to the surface, treated, and disposed of. Figure 6 shows some experimental results for spent shale from the LETC 10-ton (9-tonne) retort. For shale particles in the size range 1/8 to 1/2 in. (0.3 to 1.3 cm), six pore volumes were required to remove most of the organic carbon (Fox et al., 1978). Similar results were obtained for salts leached

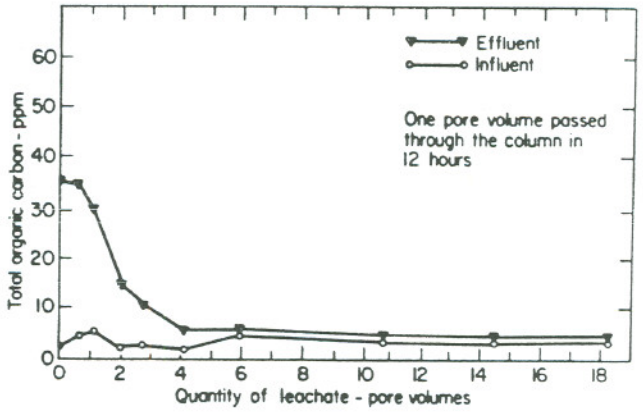

Figure 6. Progressive decrease in leachate strength — all organic carbon is leached by first six pore volumes. XBL 791-246

from TOSCO spent shale (Colorado State University, 1971). Thus after some limited volume of leachate is recovered and treated, additional leachate may enter the aquifers and pollutant transport will be minimal. Conventional technology is adequate to treat leachate. Adsorption on activated carbon followed by reverse osmosis would probably produce an effluent suitable for use or disposal (say by injection into aquifers). Other demineralization technologies, such as electrodialysis and ion exchange, are generally more costly for waters in the expected range of salinity.

The effect of particle size on the volume of leachate to be treated must be resolved before this technology can be applied. Another problem is the volume of brine (rejected from the reverse osmosis process) to be disposed of. The volume of brine to be disposed of is proportional to the volume and TDS of leachate treated. The maximum salt content in the brine (corresponding to the minimum brine volume) is about 60,000 mg/ℓ. Thus, assuming a leachate TDS of 6,000 mg/ℓ, about 10% of the leachate volume would end up as brine, requiring disposal by evaporation. To keep pace with a production rate of 100,000 bbl/day (16,000 m^3/day) of oil, 4.4×10^7 gal/day (1.7×10^5 m^3/day) of leachate would have to be treated. To evaporate 10% of this flow would require about 1,600 acres (650 hectares) of lined evaporation ponds.

It would theoretically be possible to allow re-invading groundwater to leach the retorts. The disadvantage of this is that control measures would only be implemented after retorting in an area had ceased, and would have to continue for a long period of time (on the order of 100 years).

Collecting leachate and treating it on the surface is limited by the large volumes to be handled and the rate at which it must be treated. An alternative is to treat the leachate in situ as it is formed. If adequate treatment of leachate can be achieved by adsorption only (no reverse osmosis step), then it may be feasible to inject an adsorbent into the retorts that would trap and hold leachable material in the retort. No technology for this has been demonstrated. However, some clays may display good adsorptive capacity for leachate contaminants.

Other Control Technologies

Other control technologies, such as managing polymerization reactions between components of retort water (aldehydes and amines or phenols for instance) or injecting a water-repellent coating into a retort are technologically remote and very costly. The control technologies described here appear feasible if the technical problems enumerated are resolved.

COST PROJECTIONS

At this stage, only rough cost projections can be made. The properties of the abandoned retorts and of the aquifers are not well known, nor have design criteria been established. However, it is useful to project costs approximately to focus attention on controls that have a potential for commercial application. Control costs in excess of about \$3/bbl (\$19/m^3) are not feasible and could seriously affect the economics of oil shale production. Table 2 summarizes unit costs for the various control technologies discussed and the assumptions upon which the cost projections have been based.

These cost figures are based upon the assumption of MIS retorting with 20% voids, a shale grade of 24 gal/ton (100 ℓ/tonne) and 65% recovery, plus other assumptions as noted specific to each control technology. Oil recovered from surface retorting is not considered; to include it, reduce the cost per barrel by 28%.

Retort/aquifer geometry from the detailed development plans (Gulf Oil Corp. and Standard Oil [Indiana], 1977 and Ashland Oil, Inc., and Occidental Oil Shale, Inc., 1977) for tracts C-a and C-b were used in these estimates. Costs for tract C-b are higher than for tract C-a due to the greater depth of overburden on tract C-b, and associated greater proportion of the costs due to drilling. For retort grouting (filling 100% of the voids), drilling injection holes amounted to 23% of the total cost for tract C-a, and 47% for C-b. This points up the importance of using a grout that can penetrate to substantial distances through fine voids, as doubling the distance of grout penetration would reduce the number of holes to be drilled by 75%.

While these cost projections are preliminary,

TABLE 2. Cost projections for control technologies.

Control technology	Technical problems to be resolved	Projected Cost, $/bbl		Cost assumptions
		Tract C-a	Tract C-b	
Grout abandoned retorts with spent shale slurry[a]	Development of spent shale with adequate cementing properties Distribution of grout through retort	2.70 (filling 100% of voids)	3.80	Grout injection holes on 50 foot centers $20/ft to drill injection holes $6/yd^3 to treat, slurry, and inject spent shale
		1.20 (filling 30% of voids)	2.35	
Construct grout curtain around block of retorts	Engineering feasibility of constructing grout curtain (not routine) Computer modeling to evaluate effectiveness	1.70	2.80	$13.50/ft^2 to construct grout curtain
Construct hydraulic bypass around block of retorts	Computer modeling to evaluate effectiveness	0.25	0.50	Bypass pipes placed around perimeter at 20-ft centers Pipe costs $30/ft, installed
Collect leachate and treat on surface by activated carbon and reverse osmosis	Disposal of brine. Volume of leachate that must be treated — depends on kinetics of leaching large blocks	1.20		Must treat 660 gal leachate per barrel of oil (=6 pore volumes) Pumping cost: $0.50/1000 gal Treatment cost: $1.20/1000 gal
Treat leachate in situ by injecting adsorbents into abandoned retorts	Still hypothetical — adsorption isotherms must be developed	0.50		No reduction in leachate TDS required — adsorbents remove only organics and heavy metals by ion exchange Adsorption on bentonite ($30/ton) 0.1 mg organic carbon leached per gram of spent shale 0.02 g organic carbon adsorbed per gram of adsorbent

[a]This control option may also strengthen abandoned retorts, permit additional resource recovery and allow disposal of part of the surface spent shale.

and require verification by laboratory and field data, they do indicate that environmental control may be economically feasible and that selection of control technology will be site specific.

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