Waterproofing and Strengthening Volcanic Tuff in Waste Repositories

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ABSTRACT

Waste repositories from surface trenches and shafts at Los Alamos to drilled tunnels at Yucca Mountain are being built in volcanic Tuff, a soft compacted material that is permeable to water and air. US Department of Energy documents on repository design identify the primary design goal of "*preventing water from reaching the waste canisters, dissolving the canisters and carrying the radioactive waste particles away from the repository*". Designers expect to achieve this by use of multiple barriers along with careful placement of the repository both well above the water table and well above the ground level in a mountain. Though repositories are located in areas that have a historically dry climate to minimize the impact of rainfall infiltration, global warming phenomena may have the potential to alter regional climate patterns – potentially leading to higher infiltration rates.

Conventional methods of sealing fractures within volcanic tuff may not be sufficiently robust or long lived to isolate a repository shaft from water for the required duration. A new grouting technology based on molten wax shows significant promise for producing the kind of long term sealing performance required. Molten wax is capable of permeating a significant distance through volcanic tuff, as well as sealing fractures by permeation that is thermally dependent instead of chemically or time dependent. The wax wicks into and saturates tuff even if no fractures are present, but penetrates and fills only the heated area. Heated portions of the rock fill like a vessel. The taffy-like wax has been shown to waterproof the tuff, and significantly increase its resistance to fracture. This wax was used in 2004 for grouting of buried radioactive beryllium waste at the Idaho National Laboratory, chiefly to stop the water based corrosion reactions of the waste. The thermoplastic material contains no water and does not dry out or change with age. Recent studies indicate that this kind of wax material may be inherently resistant to bio-degradation.

INTRODUCTION

Radioactive waste disposal sites in the southwestern United States are typically located in a type of soft rock known as volcanic tuff. As these sites are investigated, fractures and faults are often found that reduce the long-term integrity of a waste disposal facility that must sequester the waste for many thousands of years [1, 2]. Sealing flaws or water leaks in rock is traditionally done by grouting in civil construction. However for nuclear waste applications, traditional grouts have some problematic limitations. Over thousands of years, the rock formations to be sealed are not static; but move and flex in ways that create new crack systems [2, 3]. It is impossible to seal cracks that do not even exist yet, and difficult to repair such leaks after waste internment. Cement grouts tend to be brittle and are themselves subject to chemical degradation over very long time periods. Malleable grouts, such as bentonite clay and chemical grouts are typically based on water and shrink when they dry out. Grouts based on polyurethane and other foaming grouts are too viscous to flow into cracks and not much is known about their ability to endure thousands of years. Cement and bentonite grouts contain particulates and cannot permeate into small fractures. Even chemical permeation grouts that are not much more viscous than water are limited because their emplacement is controlled by pressure and set time; and it is difficult to assure effective grout emplacement. These grouts cannot be placed in a carefully controlled and verifiable manner, and their performance is difficult to predict and monitor. In 2004 the authors were challenged to come up with a means of grouting fractured tuff that would produce a “perfect” seal that would endure for thousands of years. To do this a new type of grout was needed that could not only seal cracks and never dry out, but also prevent new cracks from forming in the brittle volcanic tuff rock. If such cracks were to from via unforeseen processes that occur in future millennia, then the technology would need to support rapid detection and repair of unforeseeable cracks and leaks.

Wax As a Grout

A special wax grout, developed for jet grouting of buried radioactive waste at the Idaho National Laboratory, was discovered to have unexpected applications in sealing waste repositories. When molten, the wax could flow through soil and rock that were only marginally permeable to water [4, 5]. Upon further study it was determined that the surface active properties of the wax, which allow the wax to displace water in jet grouted soil, also caused the wax to “wick”, by capillary action, through clay and rock. This wicking phenomenon occurs when the wax is a molten liquid but ceases when the wax cools to its congealing point. Upon cooling, the wax remains malleable but is highly impermeable to water and gas and has a sticky adhesive quality. These properties allow the material to be used as a highly effective waterproofing grout.

Thermal heat transfer, rather than chemical reactions, control the change from a permeating liquid to a waterproof wax solid. This allows a type and degree of placement control not possible with conventional grout. The distance from the injection point that the molten wax grout can travel may be limited by heat instead of pressure and viscosity. If a subterranean volume of soil is pre-heated, molten wax poured from the surface will flow into and saturate only the heated zone filling it like a cup without flowing away in an uncontrolled direction. This makes it possible to effectively waterproof a fixed volume of soil or rock, or create a waterproofed "panel" along a heated zone. It it is also possible to create barriers in fractured rock formations. The molten wax will flow only a limited distance into a fracture before it cools and seals off the fracture. The grout can soak through solid rock to reach and seal fractures that are not directly connected to the injection point.

Wax is a non-aqueous fluid that displaces water away from the surface of materials, and strongly inhibits the aqueous-phase geochemical reactions that normally occur in buried waste. This water-exclusion property was a key factor in the DOE's decision to use wax grout to seal the activated beryllium reactor blocks buried in the Idaho desert in 2004 [4, 6]. These intensely radioactive objects were subject to geochemical corrosion that released radioactive materials into the soil. Scientists determined that molten encapsulation of the waste with Waxfix 125 would be the best way to stop the chemical corrosion process and prevent water from contacting the waste [6]. More than 200 tons of Waxfix 125 was used to encapsulate the buried waste and stop the spread of contamination. In order for this encapsulation process to work effectively on buried waste, the wax must remain molten as it saturates the waste. This may be accomplished by heating the wax to a sufficiently high initial temperature or by pre-heating the waste itself. The relative volume of wax and the heat capacity of the waste/soil volume to be treated is also a factor in the design of such a project. If mistakes are made in the application, re-heating of the wax treated area, to more fully saturate the waste, may be done at a later date by driving heater pipes into the waste zone.

Wax Grout Durability

Wax is an ancient material that occurs naturally in near surface deposits as ozokerite and in rocks saturated with waxy material. Historically, wax was recovered by boiling these rocks in water. The durability of large masses of such natural wax in the environment is well established. Wax naturally occurs in some crude oil and tends to plug pipes and production equipment. Mineral wax, as well as insect and plant derived wax, have also been used as waterproofing, sealing, and preservative material since the beginning of recorded history. For example, even before 3000 BC, ancient Mesopotamians developed a wax-casting technology that reduced the amount of metal needed for bronze-working. Wax is a complex mixture that can be engineered to have different properties. Household wax such as common paraffin can be brittle, while more complex waxes, such as Waxfix 125, are more similar to synthetic ozokerite and contain multi-branched chains that make these materials malleable and resistant to degradation [4, 7-9]. Recent studies have shown that while most wax can be degraded and metabolized by certain bacteria in a laboratory under optimal conditions, the rate of progress for large underground masses is sufficiently slow that meeting 10,000-year design life for containments should not be an issue for the 1 meter thick barriers described herein [6]. Complex branched chain wax is significantly more resistant to biodegradation and can be modified with boron or other biocides to make it even more so.

Organic based grouts have not been widely considered for nuclear applications because of concerns about radiolysis generation of hydrogen or criticality concerns over neutron moderation [5]. While these factors should always be evaluated, they are unimportant in many cases. It should be noted that even cement grouts contain enough water to offer the potential for hydrogen generation and neutron moderation. Cement grout is permeable to hydrogen while wax is only marginally so. Hydrogen generated from exposure of large masses of wax to radiation is mostly retained within the wax matrix. However, since hydrogen generated on the wax surface may still escape, it is desirable not to allow a head space where gas could collect if the wax is used as a binder for the waste. Most wastes have far too low activity to generate significant gas. Waste such as uranium turnings, powders, contaminated soil, or resin beads, could be fully encapsulated with molten wax in a zero head space drum. Molten wax encapsulation effectively excludes water; rendering aqueous reactions inconsequential and preventing corrosion of the waste materials.

Toughening Tuff

Volcanic tuff is a soft fragile rock that is made of compacted volcanic ash. Massive tuff deposits cover many areas of New Mexico, such as the areas around Los Alamos and Yucca Mountain. Tuff is a low-density rock that is permeable to water and often contains small fractures that can channel water through it. Tuff is highly permeable to molten wax and has a low heat capacity and high void ratio; so wax will permeate a significant distance into the rock before losing enough heat to solidify. Small tuff samples obtained from the Los Alamos National Lab and treated with Waxfix 125 have show greatly increased crush and fracture resistance as compared to virgin tuff. In 2004 tests on permeation of molten wax through samples of volcanic Tuff from Los Alamos National Laboratory, it was noted that the normally fragile rock became significantly less fragile after being permeated by malleable Waxfix 125. It was observed that untreated samples from golf ball to baseball size are easily crushed under foot but that treated samples could not be crushed underfoot or even by driving over them with a car or being thrown down on the concrete. This was surprising given the relatively low strength of the malleable wax. Hitting the samples with a hammer dented the material locally but did not crush of fracture the entire sample.

To confirm this effect for this paper a quick scoping test was desired to confirm this effect. With only small amount of the original tuff sample remaining, making uniform core samples crushing them on a standard compressive strength tests was not feasible. Instead, a simple qualitative test was performed to confirm the 2004 observation. Ten samples of irregular size and shape between golf ball and baseball size were tested with half being treated with wax by sitting in a pan of molten wax overnight and then allowing the samples to drain and cool to 59C. The samples were placed on a concrete drive way and slowly run over three times with a light pickup truck at very slow speed. Four of the treated samples remained intact while the 5th one broke into three pieces. The pieces of the fifth sample were still stuck together also stuck to the concrete. All Five of the untreated samples were crushed to powder on the first pass.

In other tests, golf ball size irregular samples were placed in a sand bed and penetrated by a 5-millimeter diameter steel point tapering to a sharp point over a 15-millimeter length. The treated samples required between 50 and 70 kilograms force to break the sample. The untreated samples required between 30 and 60 kilograms force to break the samples indicating only a small improvement. All samples failed after about 15 millimeters of penetration with this crude method of evaluating tensile strength. This result indicated that while the wax does improve compressive strength, it might not have as much an effect on tensile strength. Since the malleable wax fills the porosity of the sample, this also may add to the net compressive strength.

Because the wax by itself is no stronger than the tuff, this increased material strength may result from a process where wax impregnation strengthens the tuff by allowing the rock to plastically deform under load – thereby preventing stress concentrations that would normally cause fracture at a much lower net loading. More quantitative research in this area is recommended, utilizing larger size samples with tuff from various formations.

If molten wax if poured into a new excavation in tuff, the wax will uniformly permeate a foot or two into the rock and then stop [10]. Wax will flow into fractures for a greater distance, and then these too will seal off. The wax will remain molten in a trench for significantly longer time because both the solidified wax and the tuff are thermal insulators [10]. If the remaining molten wax is then pumped back out of the trench, it will leave a lining of wax-impregnated tuff several feet thick. This wax-impregnated tuff is waterproof, fracture resistant and has a higher strength and toughness then the virgin tuff.

Sealing openings and shafts in volcanic tuff or salt domes with conventional grouts is difficult because the grout has difficulty bonding to the soft rock and the rigidity of the grout allows microscopic fractures to form that can enlarge over time. In contrast, molten wax grout flows some distance into a rock face and is able to stretch and deform without cracking. Conduits, shafts and sensor lines can be permanently sealed with molten wax. Molten wax penetrates microscopic fractures in salt beds, shale, limestone, clay, granite, and basalt allowing the grout to permeate into the rock formation [4].

Yucca Mountain Repository

Waste repository design often changes as site characteristics become better understood and policy goals change. When Yucca Mountain was first proposed, it was thought to be a very dry formation with little or no rainfall infiltration. Further study indicated that perched water zones and fracture systems in the rock exist that could allow rainfall to eventually reach the repository [2, 11, 12]. The current hot repository design plan for Yucca Mountain deals with this moisture issue by packing the waste so densely that the rock around and between the tunnel drifts becomes hot enough to boil away the small amounts of water expected to filter down into the repository. However, the climate change that will likely occur during the coming millennia can significantly change infiltration rates [11, 13]. In view of the possibility of radical climate change over time it is prudent to consider repository design strategies that can accommodate large changes in annual precipitation and subsequent water infiltration.

Thermal permeation grouting provides a new approach for constructing a hydraulic barrier in fractured rock or similar underground formations. Barriers may be constructed by drilling a row of closely spaced small diameter holes along the desired barrier. The holes are then heated and molten wax is introduced into the holes to permeate the rock within the heated zone and form a wall of overlapping cylindrical columns of wax-impregnated rock. One method of heating the holes is to simply circulate molten wax in them until they heat up to the desired overlap radius.

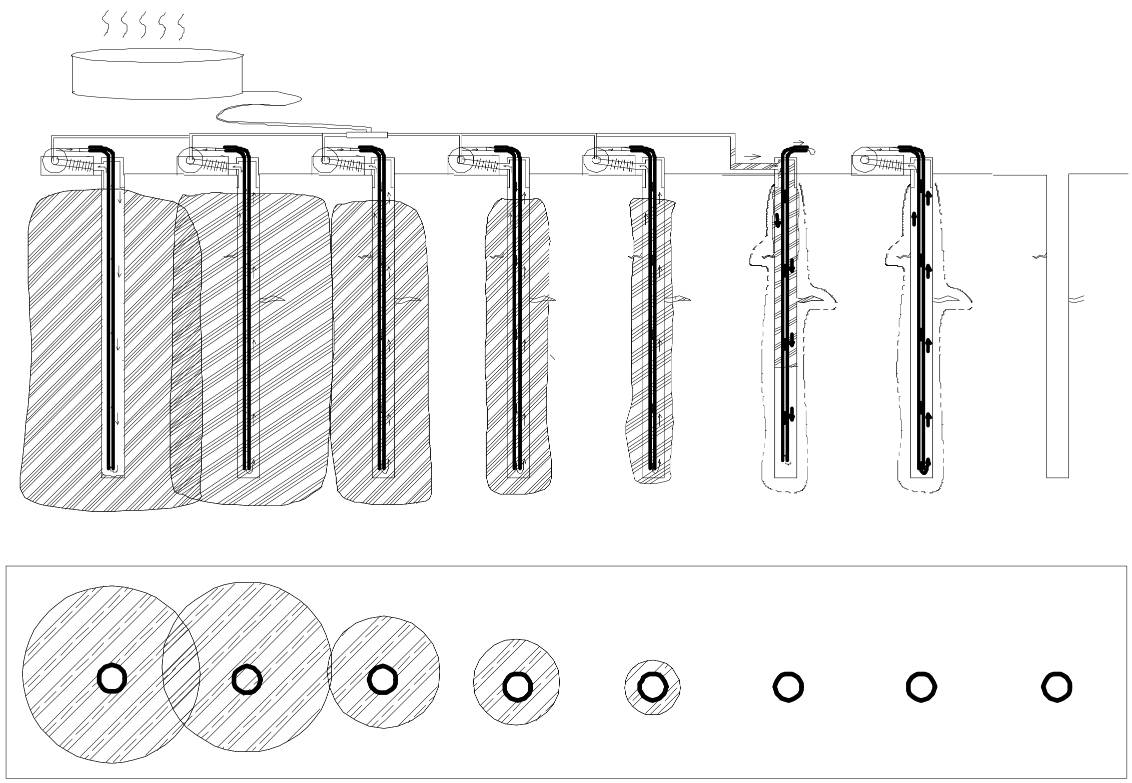
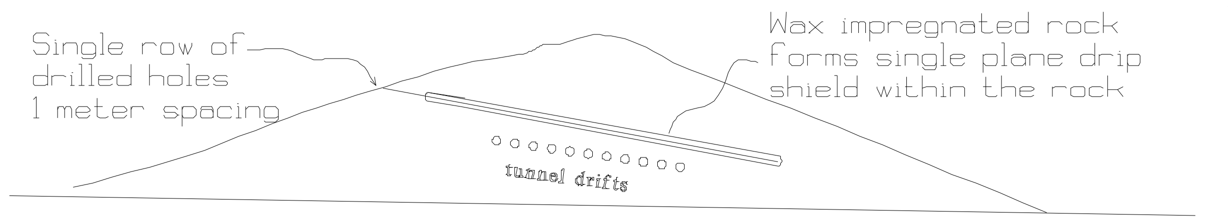


Fig. 1. Thermal permeation barrier formed in rock by circulation of molten wax in drilled boreholes until wax permeated zones overlap.

The wax thermal permeation grouting method performed in slant drilled holes may offer an additional means of mitigating water infiltration into the mountain. Impermeable roofs or “drip shields” could be formed in-situ in the rock above the repository to divert water away from the repository. Currently, titanium drip shields are planned within the tunnel. Wax grout may make it possible to form a more robust drip shield within the rock well above the tunnels by thermal permeation grouting. In-situ drip shields made by wax thermal permeation may be shaped in various “roof” configurations to channel water away from the repository. The malleable and sticky properties of the wax may allow a drip shield to be constructed across fault lines that continue to move. The wax-impregnated rock increases the ductility of the tuff and may also be able to automatically re-seal across shear planes.



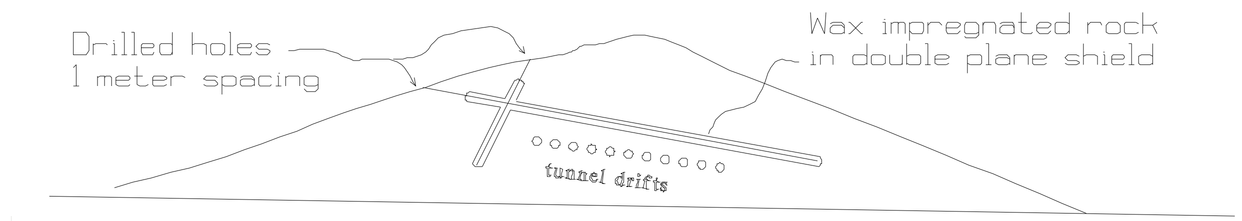


Fig. 2. Drip shield formed in-situ in rock above repository by thermal permeation grouting between a series of holes slant drilled from the surface.

The drip shield could be formed in-situ by drilling a series of holes on 1-meter centers along the desired plane of the barrier a hundred meters or more above the repository drifts. The closely spaced holes would be drilled dry and then treated with permeating wax grout to form a continuous waterproof roof over the repository area. After the small diameter holes are drilled, a tubing circulation pipe is inserted in every other hole and molten wax is circulated within the hole for 6 to 8 weeks. These holes are labeled “primary” and the ones in-between are “secondary”. The net wax and heat loss is measured and the wax reheated at the surface as it is circulated. As the wax is circulated, the tuff heats up around the radius of the primary holes and the wax permeates and fills the heated zone. Thermal imaging measurement instruments inserted periodically in the secondary holes verify that the heat is spreading uniformly from both adjacent primary holes. Instrument surveys of the uniformity of the hole spacing provide useful data but when the heat from the primary borehole reaches the secondary borehole we may be certain that the wax will reach it as well. Areas with reduced heat signature will be flagged for a longer heating cycle.

When the heated zone reaches a one-meter radius around the holes, wax will begin to flow into the secondary holes. When the molten wax begins to flow from the rock into the secondary hole, circulation pipes are also inserted in the secondary holes and molten wax is circulated within these holes also until the total heat loss and wax usage indicate that the barrier has reached the desired thickness. Data from the thermal logs and wax usage will allow us to calculate how long circulation must be continued in the secondary holes. The molten wax will be allowed to cool and seal the drilled holes. Once the wax is emplaced, geophysical monitoring can be used to help monitor barrier integrity.

The barrier will be a ridged shape since it is formed from overlapping cylindrical areas that are impregnated with wax. The down gradient shape of the ridges will serve to channel water away from the repository. Nominal thickness of the barrier would be between 1 and 2 meters. This drip shield barrier could be quite large covering the entire repository area rather than just one tunnel drift. The barrier can be emplaced at a distance from the waste canisters that is sufficient to prevent negative impacts from elevated temperatures or radiation. This in-situ drip shield within the matrix of the rock should be more durable than a metal shield within the tunnel and able to perform even if the average rainfall increases by an order of magnitude.

Sealing and Strengthening Tunnels In Tuff

Tunnels in volcanic tuff require significant mechanical reinforcement to maintain the stability of the tunnel. Rock bolts, supports, and wire mesh are necessary but all have a more limited life span than the tunnel design life. Many of the work areas of the Yucca mountain tunnels will never house waste but will still needed for access for a long time. Molten wax thermal permeation grouting provides an effective method of uniformly strengthening the tunnel walls in tuff. A movable fixture placed in the tunnel would allow a section of tunnel to be heated and permeated by circulating molten wax while still allowing travel through the tunnel.

In a cold repository design, tunnel walls made of volcanic tuff could be impregnated with wax up to 2 meters deep to create a more geologically durable and waterproof tunnel. The waste container packaging and its distance from the tunnel walls could prevent heating of the tunnels and radiolytic hydrogen generation. The wax impregnated tunnel walls could also be lined with other structural shield materials or the tunnels backfilled with crushed tuff that to shield the wax from long-term radiation exposure. In large tunnels a special tubular fixture would be used to treat the tunnel one section at a time operating behind the tunnel-boring machine. The wax treatment will produce a stronger and more durable tunnel wall as well as making it waterproof and gas tight. This treatment would also prevent radon gas from entering the tunnel drift. In some cases wax treatment may eliminate the need for rock bolts. If rock bolts are used, they could also be sealed with additional wax.

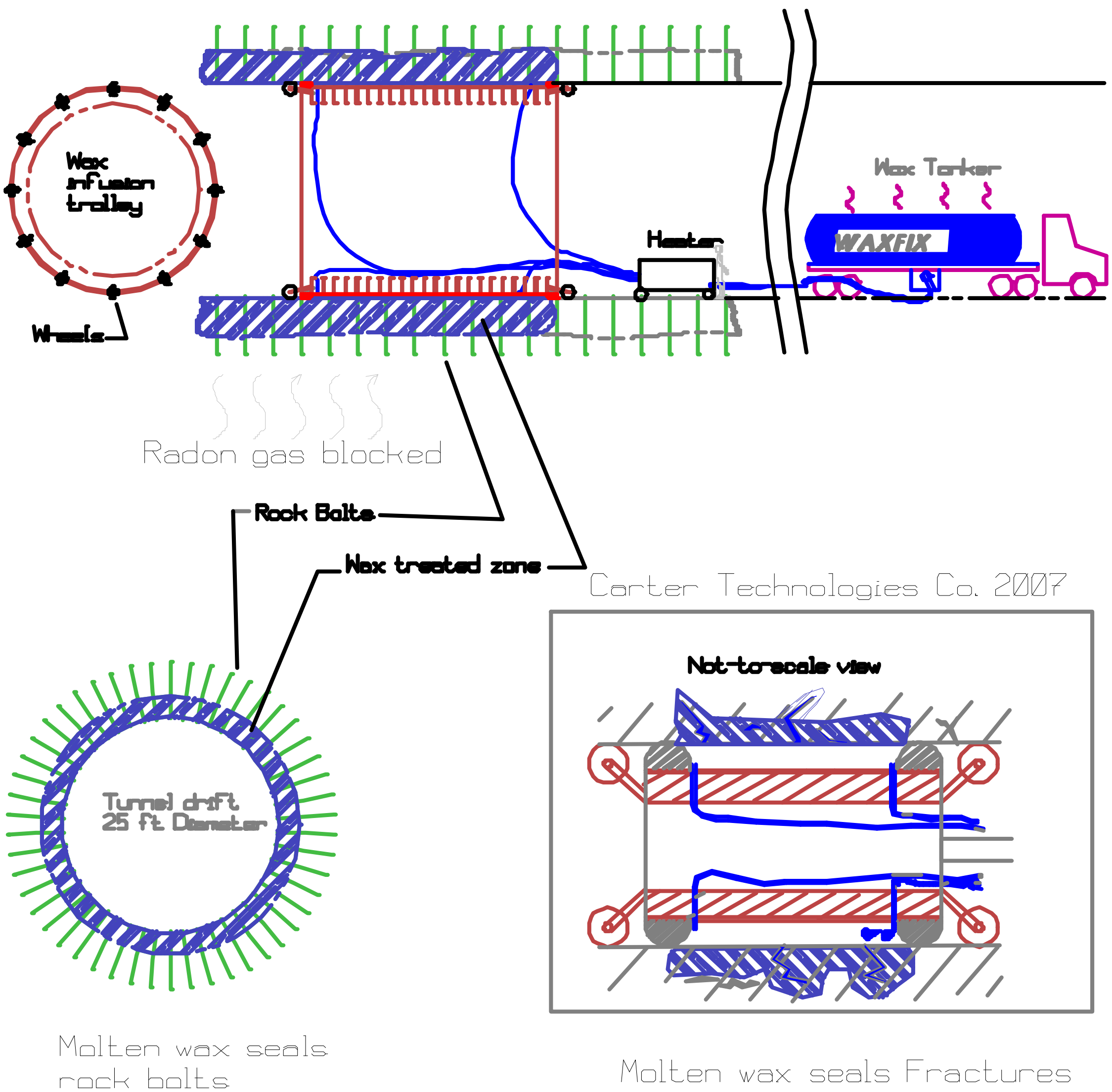


Fig. 3. Sealing and strengthening tunnels by impregnating with molten wax using a movable trolley with inflatable seals.

Waste Packaging

Transuranic waste packages emit only a small amount of radiation, but do so for a very long time. Corrosion of metal containers can occur even in a dry environment if there is water vapor in the air [14-16]. Metal encapsulated with molten wax at temperatures well above the boiling point of water are well protected from geochemical corrosion. The durability of the metal containers could be improved by encasing them directly in wax to prevent contact with moisture. A nominal wax thickness of 5 centimeters around a drum will provide long-term protection. Standard waste drums may be placed in an overpack drum. The space between the drums may be filled completely with malleable waterproof wax. For this application the wax would be designed with a higher melt point above 80C but it would still be a tough malleable material at the repository temperature.

Legacy Waste Trenches in Tuff

Wax treatment of an existing buried waste area generally requires that the waste be pre-heated so that the wax will remain molten as it permeates and saturates the waste. When radioactive waste repositories such as trenches and drilled shafts are filled, the waste is not compacted and the void space is significantly greater than the native tuff. In some cases trench waste can be treated and impregnated with molten wax without pre-heating the waste. A study performed for DOE in 2004 described a method for treating a particular waste trench at Los Alamos containing containerized waste [10]. The technique called for pipes to be driven along the edges of the trench to allow molten wax to be poured directly to the bottom of the trench. Wax would be installed in a series of lifts to prevent floating of the waste. Such a treatment would convert the entire trench into a flexible waterproof zone.

Some existing trench waste is randomly distributed with poor disposal documentation records. This type of trench can be treated in place by driving closed end heat pipes into the waste and heating the waste trench to 60 degrees Celsius. Molten wax is then allowed to enter the trench in lifts spreading out and saturating or encapsulating all the waste and soil in the trench.

Legacy Waste in Drilled Shafts

Drilled shafts in volcanic tuff and other soil types have often been used to dispose of waste that have no alternative disposal path [17]. This waste sometimes include activated metals and classified objects. The wastes are deposited and the shaft backfilled with crushed tuff. The long-term containment isolation of these shafts may be dramatically improved by saturating the shaft with molten wax. The preferred method is to pre-heat the shaft and soil before adding the molten wax. Heating means can be driven into the backfill or drilled around the perimeter of the shaft. The tuff is a thermal insulator so it does not require much power to slowly heat the earth to optimum temperature. There are commercial vendors in the soil thermal treatment business that have with the equipment to perform this work. After slowly heating the waste zone to approximately 60 degrees Celsius over a period of weeks. Molten wax is introduced from the surface or to the bottom of the shaft through one of the heater pipes. The molten wax will fill all the void space within the heated zone and for a waterproof durable mass.

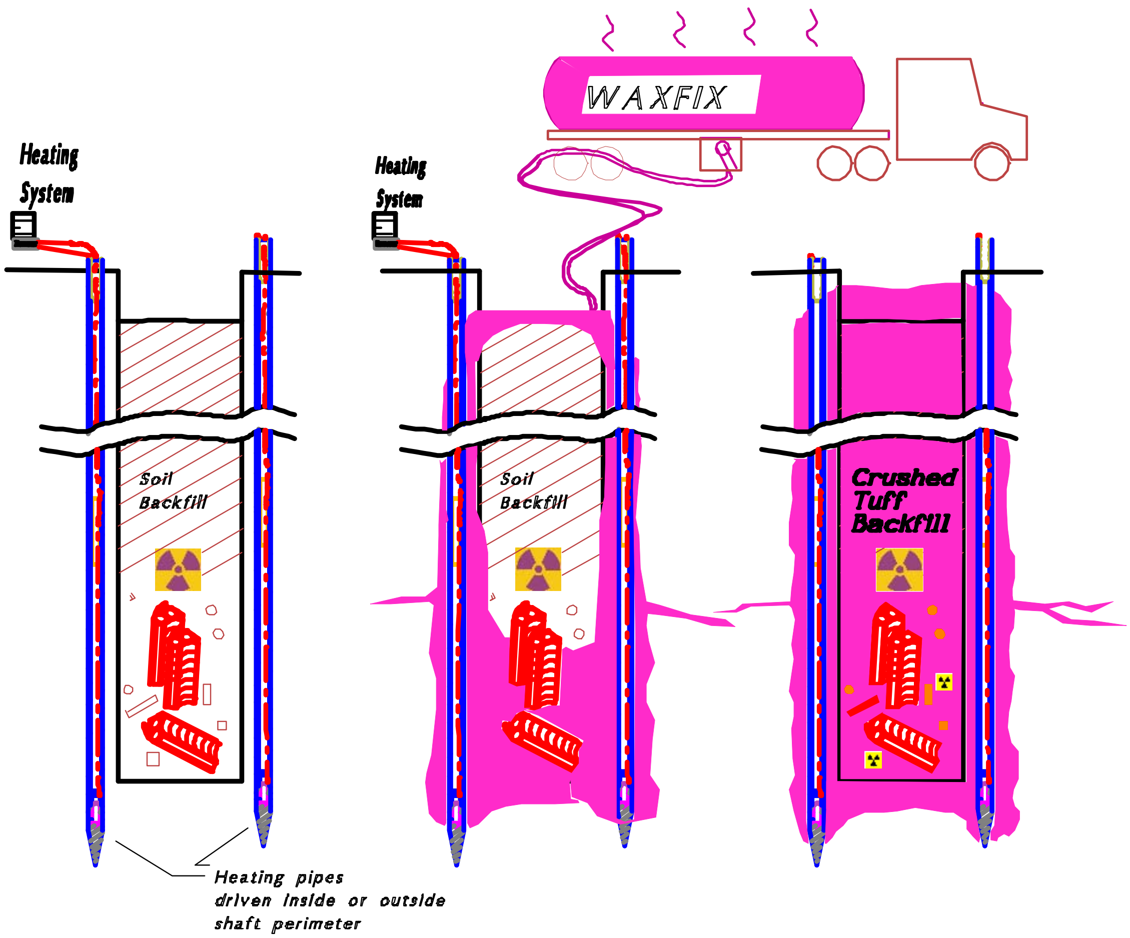


Fig. 4. Waterproofing legacy waste in drilled shaft by driving in heater pipes and allowing molten wax to permeate into the backfill soil. Heaters may be outside or inside of the original hole.

CONCLUSION

The new molten wax grouting concepts described in this paper will make it possible to significantly improve containment integrity of radioactive waste repositories, as well as existing legacy waste disposal sites in volcanic tuff formations. Molten wax offers exciting new ways to create waterproof barriers at great depth and to produce long lasting seals around both legacy and future waste disposal sites. The capability of wax impregnation to increase the resistance of tuff to future stress fractures combined with its malleability and potential to maintain a seal along an active fault line offer new engineering tools to increase the integrity of radioactive waste disposal solutions. The Idaho National Laboratory is currently using molten wax as a dust control system for decommissioning of underground piping from hot cells. The wax technology is owned by a small business enterprise so field deployment of these methods will probably occur only as client projects arise. Opportunities to discuss or demonstrate the capability of the technology in nuclear applications are welcome. Current commercialization efforts in this technology are focused on construction of 600-meter deep barriers in fractured rock to support dewatering and isolation of oil shale formations.

References

1. Tsang, C.F., *Linking Thermal, Hydrological and Mechanical Processes in Fractured Rocks.* Annual Review of Earth and Planetary Sciences, 1999. **27**: p. 359-384.
2. Bodvarsson, G.S., et al., *Overview of scientific investigations at Yucca Mountain—the potential repository for high-level nuclear waste.* J. Cont. Hydrology, 1999. **38**: p. 3-24.
3. Eckhardt, R.C.f., et al., *Yucca Mountain Looking ten thousand years into the future*, in *Los Alamos Science*. 2000. p. 464-494.
4. Hanson, D.J., et al., *Evaluation of the Durability of WAXFIX for Subsurface Applications*. 2004, ICP/EXT-04-00300. Idaho Completion Project: Idaho Falls, ID
5. Loomis, G.G., et al., *Final Results Report, In Situ Grouting Technology for Application in Buried Transuranic Waste Sites*. 2003, INEEL/EXT-02-00233. Idaho National Engineering and Environmental Laboratory: Idaho Falls, ID
6. Lopez, S.L., et al., *Summary Report for the OU 7-13/14 Early Actions Beryllium Encapsulation Project*. 2005, ICP/EXT-04-00646. Idaho Completion Project: Idaho Falls, ID
7. Jehlicka, J., H.G.M. Edwards, and S.E.J. Villar, *Raman spectroscopy of natural accumulated paraffins from rocks: Evenkite, ozokerite and hatchetine.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2007. **68**(4): p. 1143 -1148.
8. Tazaki, K., et al., *Hydrocarbon-degrading bacteria and paraffin from polluted seashores 9 years after the Nakhodka oil spill in the Sea of Japan.* 2006. **80**(3): p. 432-440.
9. Kawai, F., et al., *Comparative study on biodegradability of polyethylene wax by bacteria and fungi.* 2004. **86**(1): p. 105-114.
10. Carter, E.E., *Process for the excavation of buried waste*, in *United States Patent Office*. 2006, Carter, E.E.: United States.
11. Hinds, J.J., S.M. Ge, and C.J. Fridrich, *Numerical modeling of perched water under Yucca Mountain, Nevada.* 1999. **37**(4): p. 498-504.
12. Wu, Y.S., A.C. Ritcey, and G.S. Bodvarsson, *A modeling study of perched water phenomena in the unsaturated zone at Yucca Mountain.* 1999. **38**(1-3): p. 157-184.
13. Ritchey, A.C. and Y.S. Wu, *Evaluation of the effect of future climate change on the distribution and movement of moisture in the unsaturated zone at Yucca Mountain, NV.* J. Cont. Hydrology, 1999. **38**: p. 257-279.
14. Lee, S.G. and A.A. Solomon, *Localized corrosion of Alloy C22 nuclear waste canister material under limiting conditions.* 2006. **434**(1-2): p. 114-123.
15. He, X., D.S. Dunn, and A.A. Csontos, *Corrosion of similar and dissimilar metal crevices in the engineered barrier system of a potential nuclear waste repository.* 2007. **52**(27): p. 7556-7569.
16. Passarelli, A., et al., *Risk assessment of uniform and localized corrosion of alloy 22.* 2005. **36A**(5): p. 1121-1127.
17. Tempe, N.T., *Permanent underground repositories for radioactive waste.* Progress in Nuclear Energy, 2007. **49**: p. 365-374.