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Porosity and Permeability of Round Top Mountain Rhyolite (Texas, USA) Favor Coarse Crush Size for Rare Earth Element Heap Leach

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Abstract: Water-saturation porosity and dye-penetration permeability measurements of Round Top Mountain rhyolite confirm that a ½-inch (13-mm) crush size would permit efficient acid heap leaching of yttrium and heavy rare earth elements (YHREEs) hosted in yttrofluorite, a YHREE-substituted variety of fluorite. Laboratory acid leaching has extracted up to 90% of the YHREEs. The bulk insoluble gangue mineralogy of the rhyolite, 90% to 95% quartz and feldspars, assures low acid consumption. Different crush sizes were weighed, soaked in water, and reweighed over time to determine water-penetration estimated porosity. Typical porosities were 1% to 2% for gray and 3% to 8% for pink varieties of Round Top rhyolite. The same samples were re-tested after soaking in dilute sulfuric to simulate heap leaching effects. Post-leach porosity favorably increased 15% in pink and 50% in gray varieties, due to internal mineral dissolution. Next, drops of water-based writing ink were placed on rhyolite slabs up to ~10 mm thick, and monitored over time for visual dye breakthrough to the lower side. Ink penetration through 0.5 to 2.5-mm-thick slabs was rapid, with breakthrough in minutes to a few hours. Pink rhyolite breakthrough was faster than gray. Thicker slabs, 4 to 10 mm, took hours to three days for breakthrough. Porosity and permeability of the Round Top rhyolite and acid solubility of the yttrofluorite host should permit liberation of YHREEs from the bulk rock by inexpensive heap leaching at a coarse and inexpensive nominal ½-inch (13-mm) crush size. The rate-limiting step in heap leach extraction would be diffusion of acid into, and back-diffusion of dissolution products out of, the crushed particles. The exceptional porosity and permeability that we document at Round Top suggest that there may be other crystalline rock deposits that economically can be exploited by a coarse-crush bulk heap leach approach.

Keywords: heavy rare earth elements; yttrofluorite; heap leach; yttrium; dysprosium; YHREE; rhyolite; Round Top

1. Introduction

Yttrium and the heavy rare earth elements (YHREEs) are vital components of the materials in the optical, electronic, and mechanical products that define 21st Century technologies [1]. Virtually, all YHREEs currently are sourced from the famed south China ionic clay deposits [2]. Taxation, regulatory policies, and environmental degradation are challenges to the steady supply of those elements. Expanded demand for select YHREEs might exceed supply in the future. Thus, there is a global search for alternative sources beyond China, driven by these factors, as well as by trade policies and economic considerations [3,4].

Round Top Mountain in Hudspeth County, west Texas, USA, is a surface-exposed peraluminous ($Al_2O_3 > Na_2O + K_2O + CaO$) rhyolite laccolith, a mushroom-shaped igneous intrusion. The mountain is roughly 2 km in diameter and over 1200 m high, with a rhyolite mass estimated at some 1.5 billion tonnes (Figure 1) [5]. The rock is enriched in rare earth elements (REEs) in excess of 500 ppm, of which the economically desirable heavy REEs and yttrium (YHREEs) comprise approximately 72%. The rhyolite intrusion is Late Eocene in age, dated radiometrically at 36 Ma (million years) [6]. Although originally emplaced at shallow depth beneath the Earth's surface, subsequent erosion of the overlying strata has left this rock, more resistant to gradual weathering, as a prominent topographic feature. Thus, there is little or no overburden that would need to be removed to commence surface mining by blasting, moving, crushing, and stacking operations to prepare a heap leach pad.

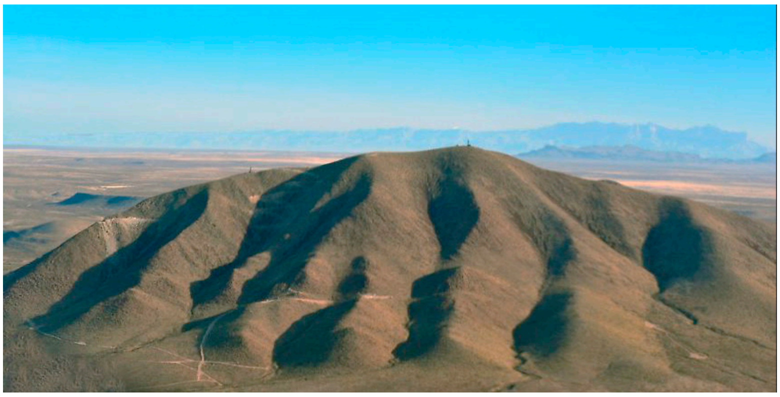


Figure 1. Round Top Mountain yttrium and the heavy rare earth elements (YHREE) deposit, Hudspeth County, west Texas, USA. Virtually the entire mountain, extending a short distance into the subsurface, is mineralized. Note drill rig on peak for scale.

Round Top is enriched in a suite of incompatible elements, those that are due to their ionic radius and charge are not easily incorporated into common igneous rock-forming minerals. At Round Top, these include YHREEs, light REEs (LREEs), Sn, Be, Li, Cs, Rb, U, Th, Ga, Nb, and Ta. Although a number of REE-bearing minerals have been reported in the deposit, synchrotron-based X-ray absorption spectroscopy documented that yttrofluorite hosts essentially all of the YHREEs [7]. Yttrofluorite is a variety of the common mineral fluorite (CaF_2, isometric) in which the trivalent (3+) Y and HREEs substitute for ~5% to 30% of the bivalent Ca^{2+} cations, yielding the formula $(Ca_{1-x},Y,HREE_x)F_{2+x}$ [8]. No other yttrofluorite-hosted YHREE deposit has yet been described; the Round Top Mountain deposit mineralogy at present appears to be unique.

Mineralization is pervasive and homogeneous through the laccolith, with the exception of the rhyolite margins, where mineralizing fluids interacted with the enclosing country rock and concentrated or diluted various elements. YHREE mineralization occurred via pervasive deposition from late stage (end of the magma cooling and solidification) fluorine-enriched fluid, in which the incompatible elements had concentrated [5,9,10].

The target YHREE-containing yttrofluorite occurs in the fine-grained matrix or groundmass of the rhyolite. Large crystals (up to perhaps 250 μm in diameter) of feldspars and quartz formed during early slow cooling, and were encased in a fine-grained matrix that formed during rapid cooling when the magma was emplaced near the Earth's surface. Most of the yttrofluorite grains range from perhaps 10 to 1 μm or less in diameter. The small size of the target yttrofluorite grains renders such conventional physical beneficiation techniques as froth flotation, gravity separation, magnetic separation, *etc.* uneconomical, chiefly, due to the extremely fine, and perhaps unachievable, particle size required to liberate the minuscule yttrofluorite crystals by sequential crushing, grinding, and milling. Nonetheless, yttrofluorite is soluble in dilute sulfuric acid and thus the deposit potentially could be exploited by heap leaching [11].

The Round Top deposit is situated on land owned by the State of Texas, currently leased by Texas Rare Earth Resources, Inc. (TRER, Sierra Blanca, TX, USA), a publically traded (US stock ticker TRER) mining exploration and development company. TRER has issued preliminary plans to extract the YHREEs, LREEs, and byproduct U, and possibly Be and Li, via low-cost heap leaching with dilute sulfuric acid [12,13].

In a heap leach operation, mineralized rock is blasted and crushed (and ground or milled to a fine particle size, if required), then placed in a large shallow pit previously lined with an impermeable barrier of clay or synthetic material. Crushed rock is stacked to a height of perhaps 10 m, and then irrigated from above with the solvent (in this case it would be dilute sulfuric acid). The leach solution percolates down through the pile, wetting surfaces of the particles. The solution reacts with both the external surface of the crushed particles, and with the interior of the particles by infiltrating and saturating their contained micropore system. Leach solution is collected from the pit bottom, recharged with acid as needed, and recirculated or drawn off for removal of dissolved target and waste ions in an adjacent chemical processing plant [14].

Bench scale column test leaching of composite samples of Round Top rhyolite with dilute sulfuric acid yielded recoveries of up to 90% of the YHREEs at various crush sizes up to 0.5 inches (~13 mm) [13]. This observation suggests that the acid solvent solution is able to penetrate to the centers of such grains, as well as permeate most of the rock volume of the particle to achieve the nearly complete YHREE recoveries observed in the laboratory. These petrophysical qualities of the rhyolite are thus crucial to scaling the proposed leaching process from bench studies to pilot plant to industrial field operations.

This petrophysical study examines the porosity and micro-permeability of the Round Top rhyolite at a scale, roughly 5 to 10 mm or pebble sized, similar to anticipated heap leach crush sizes. Large voids and fluid paths, such as faults and joints in the massive rock (meter to km scale, boulder to outcrop size), are not germane to the proposed crushing and heap leach operations and thus were not examined. Note that use of the term micro-permeability reflects that the relevant fluid pathways in the crushed material occur chiefly at a micrometer (μm) or smaller scale.

Porosity is defined as the volume of contained void space expressed as a fraction or percent of the total rock volume. This percentage varies dramatically with rock type and individual occurrence; some sedimentary rocks can exhibit 40% or more porosity, whereas igneous rocks, such as granite and rhyolite, typically have porosities in the low single digit range [15–20]. For most crystalline rocks (*i.e.*, igneous and metamorphic groups), porosity values are low due to formation of the rock at high temperatures and/or pressures. In some igneous rock commercial deposits, the mineralizing hydrothermal solutions enhanced the original porosity and permeability.

Permeability is the ability of a rock to transmit fluids, typically water, gas, or oil. Unless extensively fractured, most crystalline rocks exhibit low permeabilities [19,21]. Thus, a slab of unbroken granite can be suitable for use as a kitchen counter top but does require a synthetic sealant to prevent minor penetration and staining.

In the petroleum industry, porosity and permeability are conventionally measured by the injection of mercury into a rock specimen under increasing pressure [22]. Although this technique is appropriate for the ambient pressures several or more kilometers deep in the Earth's subsurface, it is not relevant to the mild surface conditions in a heap leach. To simulate anticipated heap leach conditions, we therefore designed experiments based on penetration of water and water-based ink into our rock under Earth-surface temperature and atmospheric pressure. The experiments thus simulate anticipated heap leach conditions (aqueous solutions, ambient temperature and pressure).

2. Materials and Methods

2.1. Rhyolite Samples

Two colors, pink and gray, dominate the rhyolite found at Round Top. Previous investigators have described 4 or 5 colors (pink, red, purple, gray, and tan, the latter of limited volume and occurring only in places at the borders of the deposit), with no formal distinctions; here, we use pink to include pink, red, and purple hues (Figure 2) [5,9,10]. Samples of the two colors are similar in elemental composition, with the pink hue resulting from the partial oxidation or rusting of magnetite (Fe_3O_4, isometric) grains [5,9,10,23]. In Round Top Mountain, there are no sharp boundaries between these colors and intermediate shades are common. Because the oxidation may have been controlled by, and/or also altered, porosity and permeability, samples of both colors were tested and compared.

Figure 2. Polished blocks and specimens of pink (including red and purple hues) and gray varieties of Round Top Mountain rhyolite. Note sub-mm size of the mineral grains. Scale = 16 cm.

Samples for analysis were taken from a large (several hundred kg), well-mixed composite of material recovered from numerous reverse circulation bore holes drilled at scattered sites across the deposit [13]. Crush sizes and size ranges were produced by conventional sieve separations or visual inspection and selection of particles on appropriately sized printed measurement grids.

2.2. Porosity Measurements

A total of 15 pink and 15 gray samples were chosen by hand from crushed material based on estimated size. Samples were divided into three particle size categories with 5 samples each: 5 mm × 5 mm (visual grid inspection), 5 to10 mm (sieved), and 10 mm (visual grid). Sample sets, after weighing (between 5 and 11 g), were placed into 50-mL beakers containing a mixture of nine parts de-ionized water and one part tap water (to neutralize pH while limiting dissolved solids), covered, and allowed to soak.

Pre- and post-soak sample weights served to determine the mass of water that penetrated the samples during a 3-week period of immersion. The volume of pore space filled in this process was derived from the added water mass (with the calculation taking into account, of course, the respective densities of water and rhyolite). In order to accurately measure the gain in mass due to water infiltration of the interior pore space of each sample, but not due to water clinging on the exterior of the particle. It was imperative to dry the surface of the sample, while retaining the interior moisture. This was accomplished by quickly blowing air on the rock surface until it was visually dry. Dried samples exhibited a characteristic rough and dusty appearance, in contrast to the shiny clean surface when wet. Inasmuch as some interior moisture could be lost in this process, the weight gain and calculated porosity (more precisely stated, the estimated porosity) thus obtained can be considered a minimum. Nonetheless, repeated measures over time and examination and comparison of 5 multiple samples confirm the accuracy of the technique for determination of estimated porosity. Weights for all samples were recorded after 1, 2, 4, 8, 13, and 21 days.

Next, the Round Top samples were dried for 2 days. Then, samples were placed into beakers with 80 mL of 4.25% (v/v) H_2SO_4 and left on a shaker table for 3 weeks. This simulates the initial, and most productive (the period during which most of the YHREEs are released), stage of the heap leach process, which would actually continue for up to 2 to 3 months. After 3 weeks, samples were rinsed 3 times with water and transferred into a clean beaker. Samples were again left to soak for 24 h in the same type of water used for the porosity measurements to allow the diffusion of residual acid from the interior of the samples. This procedure was repeated twice. Samples were then removed from the water bath and left to air dry for 24 h before recording the new current dry weight. This weight was used to quantify the effects of the acid treatment in a second round of "post-acid-leach" porosity experiments. This procedure to simulate the heap leach would document anticipated increases in porosity due to the corrosive action of the acid. Note, of course, that under the field conditions of an industrial heap leach operation, increases in porosity would occur over considerably longer time scales than those modeled here at bench scale.

2.3. Permeability Measurements

Both pink and gray samples of Round Top rhyolite were cut into parallel-sided slabs at staged thicknesses of up to 10 mm with the use of a low-speed circular saw with a diamond blade (Buehler Isomet™, Lake Bluff, IL, USA) and/or a coarse diamond grinding wheel. A single drop of consumer fountain pen ink (Parker Quink™, Newhaven, UK, washable blue) was placed on each slab and penetration breakthrough to the underside was tracked over time by observing the slab bottom in a mirror placed below the slabs (Figure 3). To prevent the ink drop from spreading laterally, and even bleeding down the sides of the sample slab, prior to placement of the drop, a small barrier ring was created on the slab surface with quick-drying clear fingernail polish. The ink was refreshed as needed, and water added when evaporation was seen to have concentrated and thickened the ink.

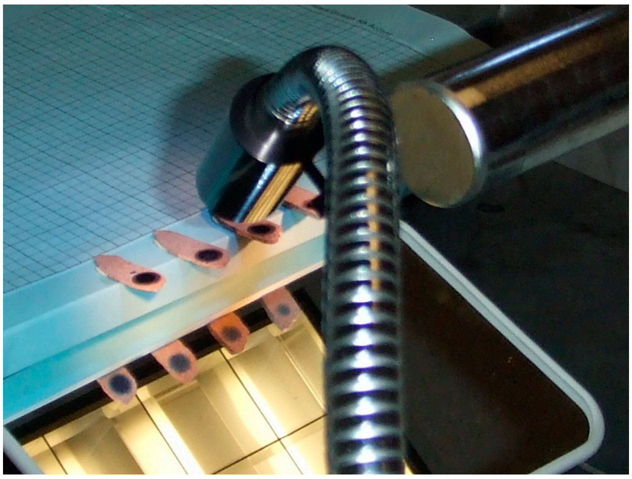


Figure 3. Experimental setup to permit simultaneous observation of ink applied to tops of slabs and image in mirror, angled below, of breakthrough ink on the undersides of slabs. Metal gooseneck piece in foreground is a high-intensity lamp.

Some thicker samples (>2.5 mm), particularly of the gray variety, were found to require up to 2 to 3 days for penetration. Therefore, a shallow (<1 mm deep) dimple was drilled into the upper surface to permit placement of a larger drop of ink. The samples were then placed into an airtight box containing water in open beakers that would maintain a high ambient humidity (Figure 4). This would slow evaporation and drying of the ink, which could clog the micropores and invalidate the experiment. Additional ink was added as it was lost to both evaporation and penetration of the rock. Penetration breakthrough and spread were documented photographically and time-recorded for the thin slabs.

Figure 4. Drops of fountain pen ink being applied to thick slabs of rhyolite in the open humidifying box. Beakers of water to maintain humidity visible at the bottom of box.

3. Results

3.1. Pre-Acid-Leach Porosity

In the first set of trials (pre-acid leach), the pink rhyolites displayed overall higher porosities than the gray rhyolites, for all particle sizes (Figure 5a). Variation among the five individual particles measured in each experimental set was more pronounced for the pink rhyolites than for the grays. These two observations suggest that the magnetite (and possibly other minerals) oxidation reactions that created the pink color also created additional porosity and/or additional micro-permeability that permitted better penetration of the water in our experiments. Similarly, the magnetite oxidation might have been controlled by the prior distribution of permeability and porosity in the nearly solidified rhyolite.

For each of the two individual colors, variation in porosity between particle sizes was relatively minor. We examined different sizes because of the possibility that potential errors in the surface drying process might be correlated with the different surface-area-to-volume ratio inherent in different particle sizes. A further consideration was the possibility that in larger particle sizes (imagine, at the extreme, a boulder) penetration of water to interior porosity might be extremely slow or even impossible, yielding a lower measured water-mass-gain porosity, or that smaller sizes might expose more internal pore space. The data indicate that none of these potential effects was a significant problem in the range of particle sizes tested.

The flattening of the curves of porosity *versus* time (Figure 5a) demonstrates that water saturation of the particles was approached in two to five days. The flattening is more pronounced for the pink rhyolites; some of the gray rhyolites appear to have absorbed minor additional quantities of water throughout the experimental period (slight positive slope to three weeks). The longer saturation time for the gray rhyolite is consistent with their lower porosity.

The largest water gain occurred during the first day, an effect confirmed in the permeability studies (Section 3.3.), where mm-scale dye penetration was observed at a time scale of minutes to a few days.

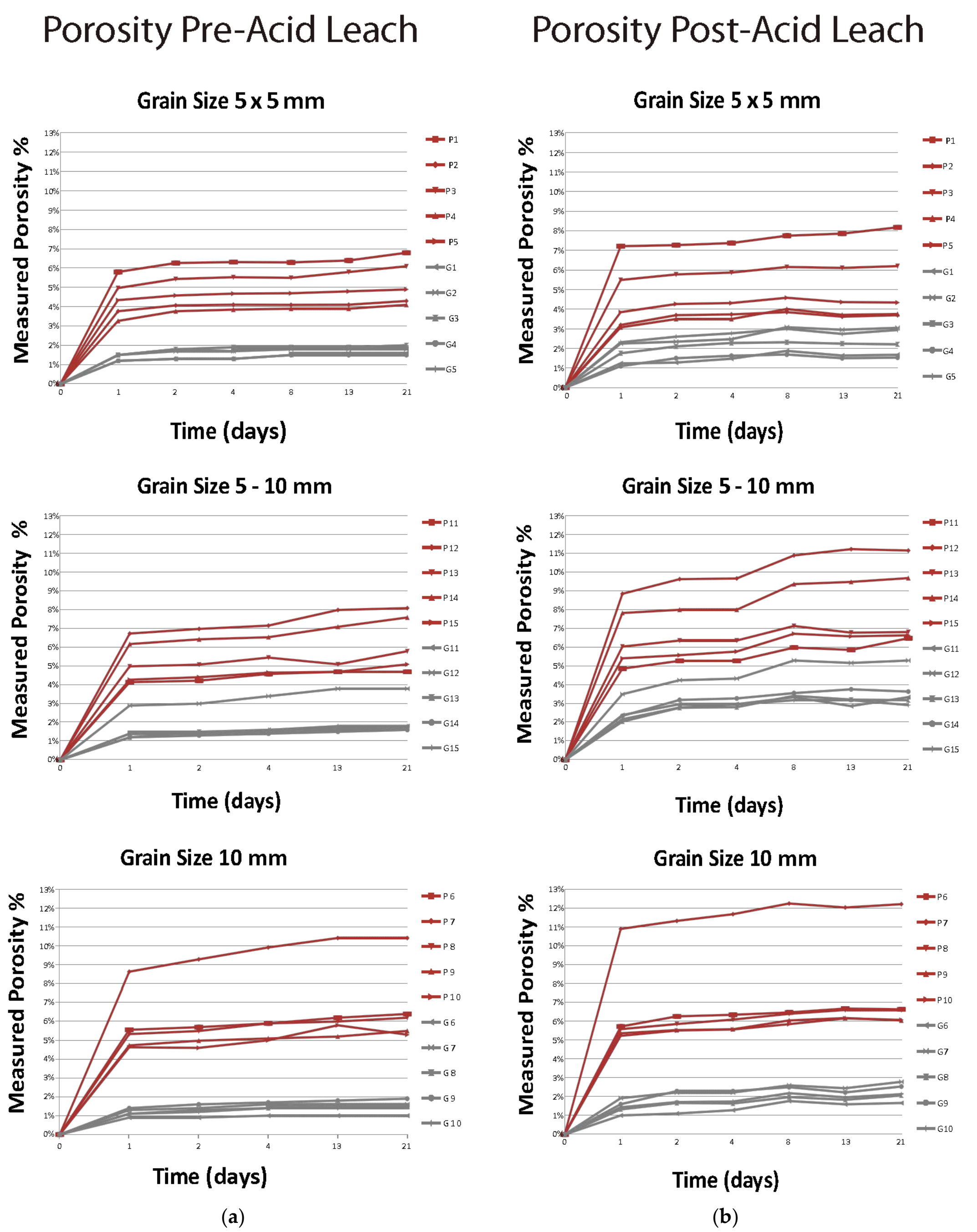


Figure 5. Estimated porosity measurements: (**a**) Pre-acid leach experiments; (**b**) Post-acid leach experiments. Red lines = pink samples; Gray lines = gray samples.

3.2. Post-Acid-Leach Porosity

In the second trial, porosities are seen to have increased overall after leaching with dilute sulfuric acid (Figure 5b). Further, the spread of the data, as seen in the vertical separation of the individual curves, is also greater. This is consistent with the addition of a new variable, the degree of interior corrosion by the acid leach, which potentially increases variation in the data. As in the first set of trials, the pink rhyolites exhibit higher overall porosities than the gray suite.

Interestingly, the approach to water saturation appears consistently to be approximately one week, about twice as long as observed in the pre-acid-leach experiments. This suggests the creation of additional micro-pores by mineral dissolution during the leaching period, which then require additional time to fill.

No porosity trends relative to grain size were evident; the 5 to 10 mm exhibited the highest overall porosities.

The pink rhyolites (all 15 samples used in the study) exhibited an average 15% increase in final porosity (21st day observation) from 6.1% pre-leach to 7.0% post-leach (Figure 6). The gray rhyolites (15 samples) averaged a 50% increase in final porosity, from 1.8% before leaching to 2.7% after leaching.

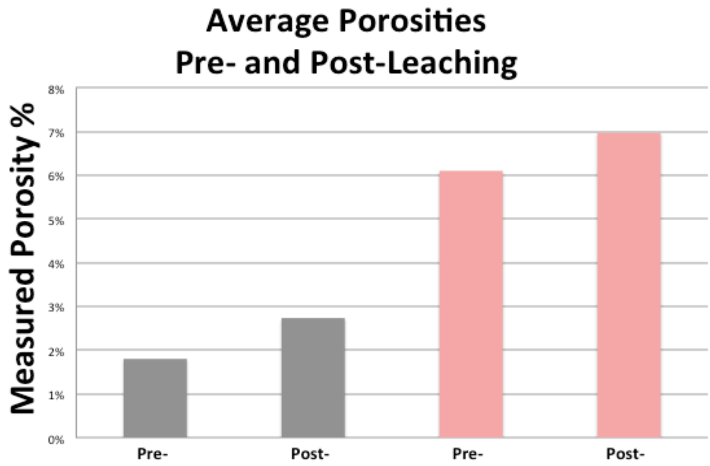


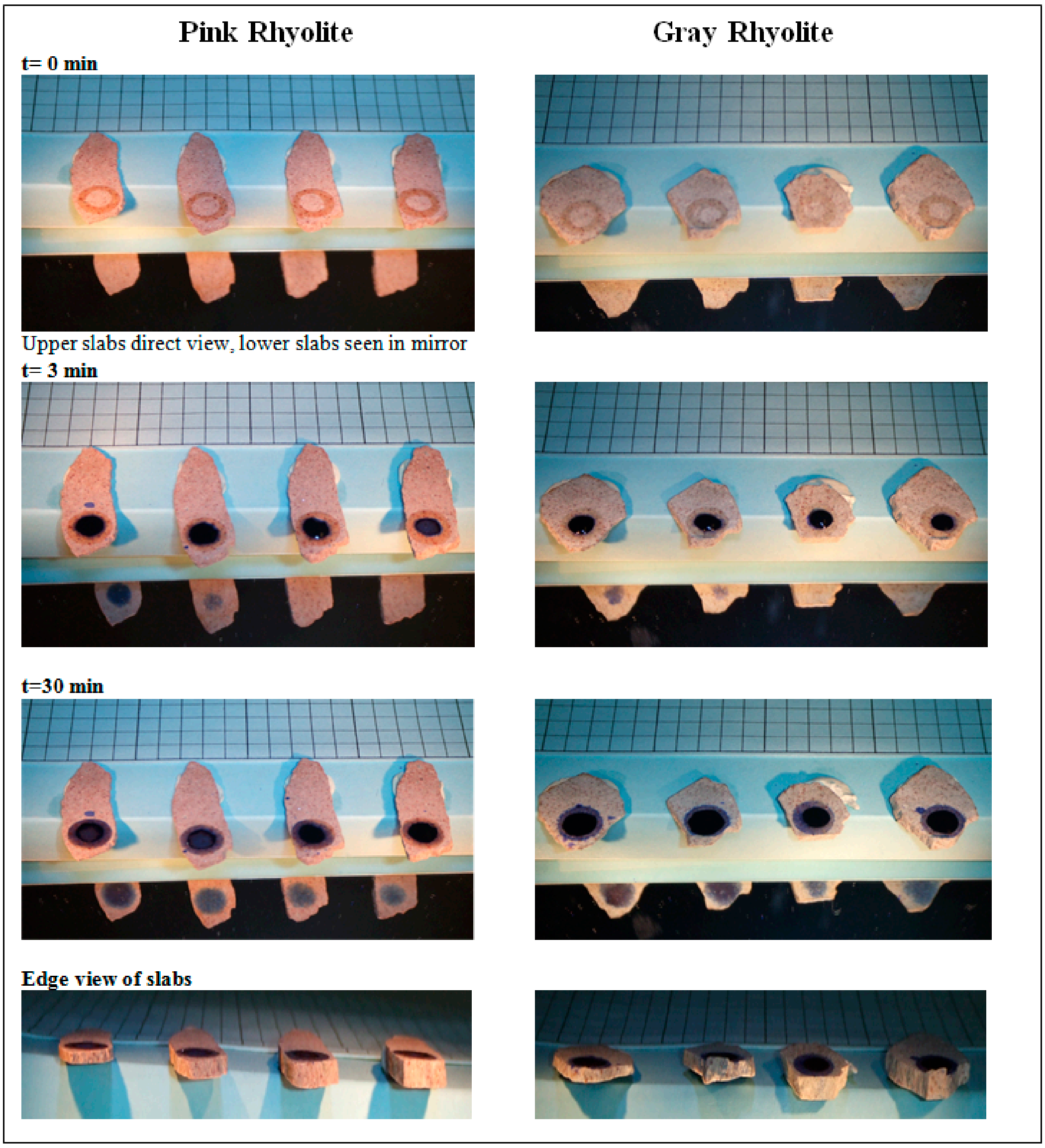
Figure 6. Average (15 samples per color) porosity pre- and post-leaching, showing an increase in porosity after sulfuric acid dissolution. Gray bars represent gray samples; red bars represent pink samples.

3.3. *Permeability*

Penetration of both the pink and gray rhyolites was rapid, and sequential in time with slab thickness (Figure 7). Within 30 min, breakthrough of the ink on all the pink and the gray rhyolite slabs with thickness to 2.5 mm had occurred. Greater thickness, 3 to 10 mm, took up to three days for breakthrough (Figure 8). This is consistent with the two to three days for the similarly sized porosity samples to approach water saturation. Of special significance is the observation that this initial penetration was focused, that is, the initial ink stain penetrations on the slab bottoms were circular and similar in size to those placed on the slab top. Lateral spreading of the ink at the lower surface of the slabs is only evident at some time well after initial breakthrough. This indicates that the fluid pathways from the top of the slabs to their bottoms were relatively direct. In light of this, it is evident that the micro-pore system in these rhyolites is pervasive and isotropic, with no evidence of preferred orientation of the fluid pathways. On the thick slabs, ink permeation is visible on the sides of many of the blocks, consistent with continued ink spreading during the longer time duration of these experiments.

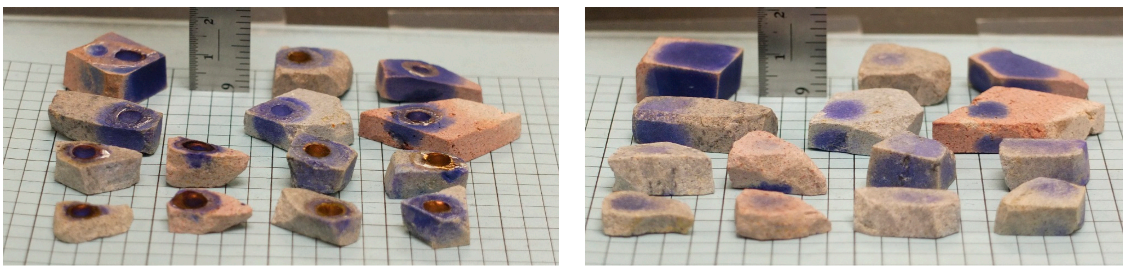
One cautionary note: Once the ink penetrates to the bottom of the slab, it gradually spreads outwards from the transporting pore systems, migrating along the open lower surface. Thus, the ink-stained surface gives the appearance of a denser and more pervasive saturation than actually exists in the interior of the slab. Nonetheless, the stain indicates the general area reached by the micro-pore system in the rhyolite slab.

In general, the pink variety of rhyolites exhibited more favorable permeability than the gray rhyolite. This was particularly noticeable in tests of the thicker slabs (5 to 10 mm). Pink specimens typically required 6 to 24 h for breakthrough, whereas the grays required as long as three days for penetration.



(**a**) (**b**)

Figure 7. Timed ink penetration of rhyolite slabs to determine permeability. Boxes = 0.5 cm. (**a**) Pink rhyolite; (**b**) Gray rhyolite. Circles seen at t = 0 are the ridges created by nail polish, which serve to contain and restrain the ink.



(**a**) (**b**)

Figure 8. (**a**) Top surface of thick slabs with ink dimples; (**b**) Bottom surface of slabs showing ink breakthrough. Exposure times from six hours to three days. Top row of samples, left to right: pink, gray pink; Second row: gray, gray pink; Third row: gray, pink, gray, gray; Bottom row: gray, pink, gray, gray.

4. Discussion

4.1. Significance of Round Top Rhyolite Porosity and Permeability

The porosities measured on the Round Top rhyolite samples exceed those of such related rocks as granite, typically reported at 1% or less. Equally important, all samples proved visibly permeable, with rapid penetration and saturation of the particles. These properties contribute to the feasibility of heap leaching at a nominal crush size of ½ inch (13 mm). If the rock were not porous and permeable, it would be necessary to grind or mill to a much finer particle size for the acid to access the minuscule, scattered yttrofluorite target grains. Such mechanical processing would involve considerable expense, in capital equipment, operating costs, and complexity of design. Further, finer particle sizes can lead to jamming of the fluid pathways of the percolating leach fluid, resulting in incomplete exposure of some particles and lower YHREE recoveries.

The ink penetration permeability study demonstrated rapid particle penetration on samples up to 10 mm thick. This suggests that a crush particle 20 mm thick would be efficiently saturated by entry of the solution from all sides of the particle (10 mm radius). Thus, a ½ inch crush size is well within the range of successful testing in this study. It is important to realize that the loci of the YHREEs within the rhyolite apparently are closely associated with the primary porosity of the rock. The minerals hosting the YHREEs and associated incompatible elements were precipitated from a fluorine-rich vapor phase in the final stage of cooling of the magma. These last-stage minerals formed in the space that the vapor phase occupied, and in the pore space opened as the F-vapor corroded pre-existing feldspar crystals [10]. Consequent to this quirk of the rhyolite's genesis, a leach solution entering the micropores of a crush particle will contact most of the target yttrofluorite grains. Very few yttrofluorite grains can be expected to be "locked" in a matrix of acid-insoluble minerals, e.g., quartz and feldspar. This apparent geometric association of porosity and target yttrofluorite contributes significantly to the exceptional recoveries, up to 90%, encountered in both bottle roll and column test heap leach experiments at bench scale [13].

4.2. Heap Leach Efficiency: Pink vs. Gray Rhyolite Varieties

The better performance characteristics of the pink rhyolite in porosity and permeability tests suggests that a heap leach with material solely of this color could achieve faster and perhaps more thorough YHREE recoveries. The distribution of these two varieties in Round Top Mountain would permit selective mining of either color variety. Overall, pink dominates the upper portion of the mountain, gray the center, and pink the lower part. To extract primarily pink, one could mine the deposit from the top, or mine the lower slopes from the level of the surrounding desert. Given the huge size of the mountain, mining solely the pink could be carried out for many decades—tens and tens of years.

Alternatively, the rate of leaching in the heap pile could be slowed or moderated by the judicious mixing of pink and gray rhyolite. Such an approach could be an option if the leach is designed with separate piles, where the leach solution is shunted between different sections to regulate the concentration of ions delivered to the chemical recovery plant. Continuous delivery of a final leach solution of constant composition to the chemical plant is essential to its efficient operation.

4.3. Ionic Diffusion: Rate-Limiting Step for Round Top Heap Leach

The porosity and permeability experiments described herein are consistent with laboratory-scale sulfuric acid leaching experiments described elsewhere, and with unpublished data [13]. Initial dissolution of rare earths and other elements is rapid, with YHREE recoveries of ~33%, in the first 24 h, depending on acid strength and particle size. In bottle roll tests recoveries of 50% to 75% were achieved with 4-mm-diameter particles in one week, and 75% with 10-mm-diameter particles in two weeks. Nonetheless, REE recoveries were observed to increase, albeit with diminishing returns, with continued immersion in acid solution over the course of several to many weeks. Final recoveries of up to 90% for the target YHREEs were achieved in approximately 10 weeks in both bottle roll and column tests.

The time lapse between initial dissolution of YHREEs and near-complete dissolution indicates that transport of acid to the interiors of the particles, and back-transport of the YHREEs out of the particles, is an important rate-limiting step in the leaching process. On the one hand, the permeability breakthrough data and the porosity saturation data indicate that aqueous solutions pass into the rhyolite rapidly, typically taking less than three days to penetrate to the center of a 13-mm-diameter particle (the anticipated crush size for the heap leach). On the other hand, it is obvious that efficient two-way advective transport of the leach solution into and out of the grains is not possible due to the micron to sub-micron dimension of the cracks through which such transport apparently occurs. There is no drive mechanism to push the leach solution in and then back out of these micro-cracks. At crack widths of this scale, capillary force dominates gravity force, and flow through or in and out of the particles does not proceed at economically favorable time scales. Diffusion of acid into the pores and back-diffusion of YHREE and other dissolved species out of the pores will be the most important drive mechanism for YHREE extraction in the heap leach. It is anticipated that diffusion thus will be the rate limiting step in the process. The dynamics of two-way diffusion between aqueous solutions in cracks in rock particle interiors and an external buffering solution has been described in detail in the literature [24].

4.4. Unconventional Opportunity to Heap Leach Coarse-Crushed Crystalline Rock

Bulk heap leaching of relatively unaltered crystalline rock is not a conventional mineral resource extraction technique. Typically, only carefully selected high-grade areas of hard rock mineral deposits are ever mined, crushed and heap leached. Bulk crystalline deposits occasionally can be crushed to a fine particle size and heap leached, e.g., the 5-mm crush size at the Etango uranium project [25]. The exceptional porosity and permeability for a crystalline rock that we documented at Round Top present the opportunity to heap leach the bulk deposit at a coarse crush size. This finding suggests that there may be other crystalline rock deposits that economically can be exploited for rare earths and other elements by a similar strategy.

5. Conclusions

(1) Water-saturation porosity of Round Top rhyolite ranged from 1%–10%, with the pink variety consistently higher than the gray variety.

(2) Water penetration and saturation was rapid, with most occurring within one day, and nearly complete in two to three days.

(3) Porosity increased 15% (pinks) to 50% (grays) after a three-week dilute sulfuric acid leach.

(4) Ink-penetration permeability was rapid (minutes to hours) for slabs up to 2.5 mm. Thicker slabs, to 10 mm, took as much as several days. Pink rhyolite was consistently more permeable than gray rhyolite.

(5) The rate-limiting step for YHREE recovery in the anticipated heap leach is expected to be diffusion of fresh acid from the dripping heap leach solution into the solution-saturated micropores, and back-diffusion of dissolved elements out of the pores.

In light of these findings, the ½-inch (13 mm) crush size proposed by Texas Rare Earth Resources, Inc. for their heap leach design appears sound, and even conservative. Further, the conclusions suggest that bulk coarse-crush heap leaching of other crystalline rock deposits with favorable porosity and permeability may be economical.

The ultimate success of the proposed Round Top Mountain YHREE heap leach will depend not just on the favorable estimated porosity and permeability documented here. Such other factors as wetting of the particles, clay formation or release, presence of fines, chemical reactivity leading to precipitation of secondary compounds, *etc.* all will play a role [26–29]. Typical heap leach recoveries for such ore deposits as copper porphyries are in the 60% range, significantly less than the 90% achieved in laboratory scale column tests of Round Top rhyolite. This suggests that tall column field scale tests are a logical next step in evaluating and "de-risking" heap leaching of the Round Top deposit.

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Author Contributions: Nicholas Pingitore conceived and designed the experiments; Lorraine Negron and Nicholas Pingitore performed the experiments; Nicholas Pingitore and Lorraine Negron analyzed the data; Daniel Gorski contributed reagents/materials/analysis tools; Nicholas Pingitore and Lorraine Negron wrote the paper.

Conflicts of Interest: Lorraine Negron declares no conflict of interest. She has not received any compensation from the contracts that supported this research. Nicholas Pingitore serves on the Board of Directors of Texas Rare Earth Resources (TRER). He is not and has never been an employee of TRER, nor has he received any compensation from the research contracts that supported this research. Daniel Gorski is the CEO of TRER and serves on its Board of Directors. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

YHREEs: yttrium and heavy rare earth elements;
REEs: rare earth elements;
LREEs: light rare earth elements;
HREEs: heavy rare earth elements;
TRER: Texas Rare Earth Resources.

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