PNNL-31328

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

This project demonstrated the technical viability of using tunable hydrothermal liquid (HTL) solutions to recover valuable minerals from a range of source materials. The effort focused upon rare earth elements (REE) and other minerals critical to the industrial security of the United States. This effort demonstrated, for the first time, that s, supercritical water (SCW) in particular, can:

- Extract critical and valuable minerals from a range of matrices ranging from rock ore to biomass.
- The process can be used to recover a wide range of minerals
- This novel extraction chemistry can be cheap, simple, and nontoxic/”green”
    - the chemical extraction uses water, the cheapest industrial acid (sulfuric), and simple salts (i.e., sodium sulfate). However, other acids, salts, and additives could be used as appropriate.

This Laboratory Directed Research and Development (LDRD) project identified that the process is complex with many interacting factors, but the benefits are significant if the complexities can be resolved. Challenges remain in the development of this technology and are described in this report. However, the results are positive, and commercial partners have already expressed interest. In summary, a novel, green, inexpensive mineral extraction process has been developed and demonstrated in a small batch reactor system. The effort provided information for an invention disclosure, proposal to DOE, and will support future business development efforts.

Summary

This project focuses on developing novel methods for mineral/critical material extraction from atypical sources using novel hydrothermal liquid (HTL) solutions and supercritical water (SCW) in particular. Improved methods for critical materials (rare earths, Mn, Co, Li, etc.) extraction and processing have been identified as a national priority. Enhanced processing methods, which enable recovery from a wider range of sources, benefit national security and impact numerous industries (advanced communications, manufacturing, food processing, etc.) and have many environmental processing applications. Consequently, this effort supports a broad range of DOE strategic objectives.

HTL/SCW chemistry provides several potential advantages for mineral extraction and recovery. The HTL environment can provide faster reaction kinetics, better penetration of solids for improved extraction, and unique redox conditions. HTLs also provide tunable extraction chemistry based upon changes in temperature, pressure, and chemical additives. In this effort we demonstrated, for the first time:

- HTL conditions can extract critical and valuable material from a range of matrices.
- A novel extraction chemistry that is cheap, simple, and nontoxic/"green" and applicable to the recovery of a wide range of minerals.
- The chemical reaction uses water, the cheapest industrial acid (sulfuric), and simple salts (i.e., sodium sulfate). However, other acids and salts could be used as appropriate.

The technology could be applied to a wide range of solids and slurries such as ores, waste products, coals, biological materials, etc. The byproducts from the process have been leached of metals (valuable and toxic) allowing them to be used safely as bulk materials for construction or composite materials.

The process has the disadvantages of requiring high temperatures and pressures needed for the reactions. However, conventional chemical reactors as well as nonconventional reactors, i.e. old oil wells, can easily enable these conditions. HTL/SCW chemical processing at the bottom of old fossil energy wells/boreholes is attractive since it reduces the cost of heating and pressurization. There is an enormous number of existing boreholes, but they may not be near the source materials sites inducing transportation costs for materials. The combination of HTL/SCW with geothermal resources has very intriguing potential.

The reaction HTL/SCW chemistry/extraction processes combined with phase changes result in complex and nonlinear conditions that are nontrivial to optimize, and significant work remains beyond proof of principle efforts. However, the HTL approach has the unique advantages including:

- Uses tunable and flexible extraction chemistry.
- Inexpensive and environmentally benign chemical reactants.
- the ability to be used on a wide range of source materials
- the ability to produce a wide range of minerals
- The ability to produce valuable mineral concentrates as well as nontoxic bulk materials for commercial use.

There are remaining challenges in the development of HTL/SCW technology. The chemistry is not simple, optimized, or fully developed. The high pressures and temperatures impose economic costs on the process and clever solutions, such as use existing deep fossil energy boreholes to provide the needed pressures and elevated temperatures, may help provide the conditions to make this technology economically viable.

Acknowledgments

The research described in this report was conducted under the Laboratory Directed Research and Development (LDRD) Program as a strategic investment at the Pacific Northwest National Laboratory (PNNL), a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Contents

1.0 Background

Technological innovations in advanced materials, electrical transportation systems, and renewable energy technologies are increasingly reliant on critical materials, such as rare earth elements (REEs), including scandium (Sc) and yttrium (Y), as well as the indispensable metals used in electronic applications such as copper (Cu) and nickel (Ni), which places increasing demand on mineral deposits with decreasing economic viability (U.S Geological Survey, 2020). The increased dependence of global communities on these materials means that supply chains are especially susceptible to disruptions and may become a risk to the “security and prosperity of the United States” (U.S. DOI, 2018). Maintaining robust supplies for the rapidly expanding use of REEs is a critical industrial challenge. The United States is currently 100% reliant on imports of Yttrium and Scandium as well as many REE metals (USGS, 2020). New environmentally friendly methods of recovery of these materials are needed to be used domestically. This effort explored the development of new hydrothermal methods to recover critical materials from unconventional sources. If successfully developed the technology could enable cost-effective domestic sources of critical materials from a variety of sources. The technology could also be used for cleaning toxic materials out of a range of challenging materials.

2.0 Alignment of Effort to DOE Mission Strategy

This project focused upon developing novel methods for mineral/critical material extraction from atypical sources using novel hydrothermal solutions. Improved methods for critical materials (rare earths, Mn, Co, Li, etc.) extraction and processing have been identified as a national priority by the Executive Branch as well as the DOE. Enhanced processing methods that enable recovery from a wider range of sources benefits national security and impacts numerous industries (advanced communications, manufacturing, food processing, etc.), and have many environmental processing applications. Consequently, this effort supports a broad range of DOE strategic objectives.

Technological innovations in advanced materials, electrical transportation systems, and renewable energy technologies are increasingly reliant on critical materials, such as rare earth elements (REEs), including scandium (Sc) and yttrium (Y), as well as the indispensable metals used in electronic applications such as copper (Cu) and nickel (Ni), which places increasing demand on mineral deposits with decreasing economic viability (U.S Geological Survey, 2020). The increased dependence of global communities on these materials means that supply chains are especially susceptible to disruptions and may become a risk to the “security and prosperity of the United States” (U.S. DOI, 2018). Maintaining robust supplies for the rapidly expanding use of REEs is a critical industrial challenge. The United States is currently 100% reliant on imports of Yttrium and Scandium as well as many REE metals (USGS, 2020).

This effort explored the development of new hydrothermal methods to recover critical materials from unconventional sources. If successful, the technology will provide cost effective domestic sources of critical materials.

3.0 Scientific Basis for Effort and Applications

This project established the baseline performance and technical viability of using near and supercritical water to recover valuable minerals from non-traditional sources. *This has not been previously demonstrated*. These methods support the concept for cost-effective recovery of REEs and other minerals using HTL/SCW conditions from primary and secondary sources without the cost and environmental issues of hard rock mining. This work has confirmed the technical feasibility of extracting rare earth elements and other minerals using PNNL's batch bench-scale HTL capabilities. PNNL also has several continuous flow HTL systems that include patent-protected features (US Patent 9,404,063) that facilitate ash/char removal at typical HTL operating conditions.

This approach could make mineral extraction of secondary mineral sources (e.g., kelp ash, bottom-ash, fly-ash, etc.) economically viable from a range of solids/sludges. This could be for mining, critical materials recovery, or remediation purposes. All the processes can be combined: for example, recovery of critical, valuable, and toxic metals from coal, coal fly ash, or mining waste. Valuable minerals are recovered, and the remaining particulate material cleaned of toxic metals, and potential organics, leaving clean bulk mater that can but used for bulk applications. This process would take waste piles and produce valuable minerals and low value but high-volume bulk materials with commercial applications. This would reduce legal, financial, and environmental risks for many materials from mining, energy productions, manufacturing etc. Experimental details are provided at the end of this report.

4.0 Technical Results and Discussion

Complex Chemistry

HTL mineral extraction involves complex chemistry as well as dynamic phase transformations. Figures 1-3 show the dynamic characteristics of HTL solutions.

Shown in Figure 1a below is the density of water as function of temperature and pressure. Density is a strong indicator of a solution's ability to dissolve and transport materials. Figure 1b shows the viscosity of water as function of temperature and pressure. Lower viscosities strongly impact reaction kinetics and heat transfer. Figure 2 shows the polar nature of water, as measured by the dielectric constant, as function to temperature. It can be observed that at lower temperatures water is a polar solvent we expect (higher dielectric constant) but at higher temperatures (with pressure) the polarity falls making the HTL more like an organic solvent complicating the extraction chemistry. The effects can be seen in Figure 3. The solubility of sodium sulfate in HTL water, which will be shown to be a key component in the process, can be seen to fall (counter intuitively) at higher temperatures. Clearly the properties of water under HTL/SCW conditions can be very dynamic and the chemical extractions and transport depend upon solution properties that are nonlinear.

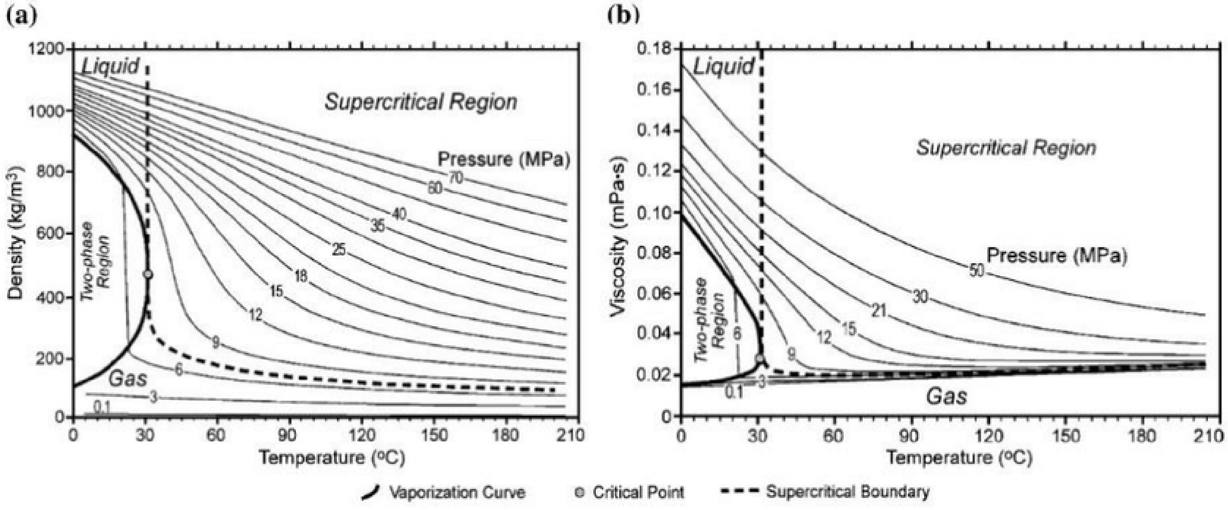

Figure 1. Shown in Figure 1a is the density of water as function of temperature and pressure. Density of a solution is strong indicator of a solutions ability to dissolve and transport materials. Figure 1b shows the viscosity of water as function of temperature and pressure. Lower viscosities strongly impact reaction kinetics and heat transfer. Clearly the properties of water as an HTL are very dynamic (from Tsar et. al., 2013; https://doi.org/10.3997/2214-4609.20130502).

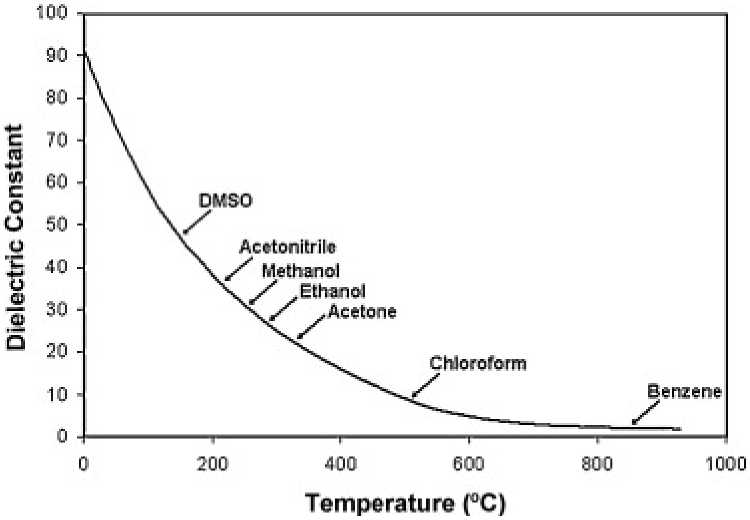

Figure 2. The polar nature of water, as measured by the dielectric constant, is shown as function of temperature. It can be observed that at lower temperatures water is a polar solvent as we expect (higher dielectric constant), but at higher temperatures (with pressure) the polarity falls making the HTL/SCW more like an organic solvent complicating the extraction chemistry (from *A Review of Subcritical Water as a Solvent and Its Utilization for the Processing of Hydrophobic Organic Compounds*, Carra et. al, https://doi.org/10.1016/j.cej.2011.06.007).

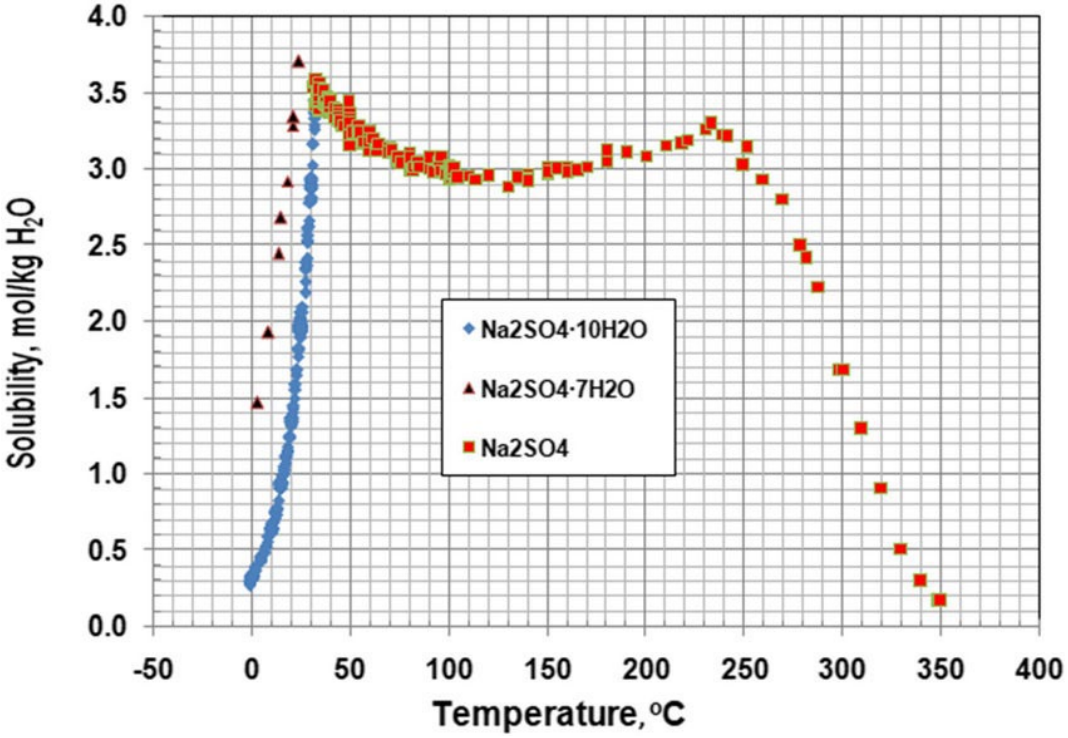

Figure 3. The solubility of sodium sulfate in HTL water which can be seen to fall, counter intuitively at higher temperatures. Consequently, extractions and transport depending upon this salt would first rise with temperature and then fall (from *Temperature Dependence of Mineral Solubility in Water. Part 3. Alkaline and Alkaline Earth Sulfates,* Journal of Physical and Chemical Reference Data **47**, 023101 (2018); https://doi.org/10.1063/1.5031951).

Effective HTL Extraction Chemistry—REEs and other Minerals from North Dakota Lignite Coal

Some of the various HTL extraction chemistries explored are shown in Table 1 for the REEs in North Dakota lignite coal. Initial work was done at ~1900 psi (operation variations 1800-2000 psi) and at ~335^0C (operational variations 330-350^0C). These conditions were chosen based upon previously effective HTL work at PNNL. Clearly 0.5M Na_2SO_4 + H_2SO_4 at pH ~3.3 was clearly the best condition. This solution is a combination of water, the cheapest industrial acid (sulfuric) and inexpensive salts (i.e., sodium sulfate). This is a novel, cheap, simple, nontoxic/"green" HTL extraction chemistry for a wide range of mineral recoveries. Other acids (i.e., nitrate and phosphoric) and salts could be utilized as needed. The addition of complexants would add cost but could significantly improve performance.

It must be pointed out that this is the first time effective mineral extraction with HTLs has been demonstrated. Extraction of Sc, Fe, Mn, Cu, Zn, Y, Ag, Au was also observed but data scatter on the new system made the results nonquantitative. Further, while the HTL extractions worked, the efficiency for this initial work was less than ideal. In *retrospect, operating at slightly lower temperatures, say 200^0C, should improve solubility and extraction performance* (see Figures 2 and 3). Future efforts to optimize reactions conditions (pressure and temperature) and chemistry (pH, additives, complexants) should enable high efficiency mineral extractions from a wide range of matrices.

Table 1. Percent extraction of REE from North Dakota lignite coal with Different HTL Extraction Chemistries at the nominal supercritical condition of 1900 psi and 335^0C

Element				**Percent Extraction**				
	DI Water	Ocean Water	H2SO4 pH 4	Na gluconate	Na gluconate + H_2SO_4	0.2M Na_2SO_4 + H_2SO_4	0.5M Na_2SO_4 + H_2SO_4	2M Na_2SO_4 + H_2SO_4
La	1	1	7	7	1	1	17	4
Ce	1	0	7	7	1	1	18	4
Pr	0	1	7	7	2	2	19	4
Nd	1	0	7	7	2	1	20	4
Sm	1	0	7	7	2	0	22	4
Eu	1	1	7	7	0	2	23	3
Gd	1	1	7	6	2	1	25	4
Tb	1	1	7	7	0	5	22	4
Dy	1	1	7	6	2	1	29	4
Ho	1	1	8	7	0	3	28	4
Er	1	1	9	7	3	2	34	8
Tm	1	1	8	7	0	13	20	6
Yb	1	0	8	7	5	4	39	4
Lu	2	0	9	7	0	18	20	5
pH	7	7.8	4	NA	0.1	3.3	3.3	NA

As described above, reducing the temperature to ~200^0C (with the 0.5M Na_2S0_4 and sulfuric acid reagent) is expected to substantial increase the extraction efficiency recovers (as per Figure 3 solubilities) shown in Table 1, Table 2, and Table 3 as well as extraction from ores.

Optimizing pressure (probably lower) to increase solution density and polarity of the HTL/SCW, should also improve extraction efficiency. Further, b*y reducing temperature and pressure the process becomes more economical and broadly appliable.*

Table 2 shows the results of several extraction chemistries for a larger range of minerals (again from North Dakota lignite coal). This initial work was done at ~1900 psi (operation variations 1800-2000 psi) and at ~335^{0}C (operational variations 330-350^{0}C). These conditions were chosen based upon Table 1 results and the acid and salt concentrations were increased in an effort to improve extraction efficiency. Table 2 shows a large number of minerals can be extracted. Due to its high value and similar chemistry the effective extraction of Sc in particularly important to enable economically viable REE processes. However, comparing Table 1 and 2 for the REE extraction efficiencies, it can clearly be seen that increasing chemical reactant concentrations was not effective and even counterproductive. While counterintuitive, the reasons for this are likely shown in Figure 3 with limited reactant solubility under at higher HTL temperatures and pressures. This clearly shows that the chemistry must be balanced with the physical HTL conditions and optimization of the process remains to be done. Performance can be improved with optimization of physical and chemical conditions in the HTL (as discussed above).

Table 2. Percent extraction of minerals from North Dakota lignite coal at the nominal supercritical condition of 1900 psi and 335^{0}C

Element	**0.5M Na_2SO_4 + 3M H_2SO_4**	**1 M Na_2SO_4 + 3M H_2SO_4**
Sc	26	100
Fe	18	0
Mn	100	0
Cu	46	66
Zn	76	11
Y	27	0
Ag	33	39
La	10	0
Ce	12	0
Pr	12	0
Nd	12	0
Sm	15	0
Eu	11	0
Gd	16	0
Tb	18	0
Dy	18	0
Ho	22	0
Er	21	0
Tm	27	0
Yb	20	0
Lu	17	0
Au	0	0
Pb	100	0

% extraction was corrected with processed blank

Table 3 shows the results of HTL extraction for REEs for different material types. This work was done at ~1900 psi (operation variations 1800-2000 psi) and at ~335^0C (operational variations 330-355^0C). The conditions chosen were not optimal in retrospect but based upon the best understanding at time the experiments were run. However, the results are valuable. Table 3 provides the following information:

1. The conditions used in Table 3 do not work well for North Dakota lignite coal. Tables 1 and 2 show better results and mineral recovery can clearly be better with other reaction conditions.
2. The conditions used in Table 3 do not work well for coal fly ash. Coal fly ash, a fired ceramic material, is a very difficult matrix to extract minerals from. However, a small fraction of the REEs were extracted. This suggests further work with HTL chemistry and condition may enable an effective extraction.
3. Despite less than optimal extraction conditions (based on Table 1 and 2 results) there was substantial REE recovery from Wyoming subbituminous coal. This is very promising. Why these conditions were more effective for subbituminous coal than lignite is not fully understood at this time.
4. Despite less than optimal extraction conditions (based on Table 1 and 2 results), there was substantial REE recovery from dried kelp mass. This is a very promising preliminary result for using HTLs to recover minerals from biomass sources. The power of HTLs to oxidize organic/biomasss into useful product, extract valuable organic material, as well as recover minerals could be a powerful and valuable chemical process.

Table 3. Percent extraction of REEs from selected matrices* with 2M Na_2S0_4 + H_2SO_4 at pH 3 at the nominal supercritical condition of 1900 psi and 335^0C

Element	**Percent Extraction**			
	North Dakota Lignite Coal	**Dry Kelp**	**Wyoming Subbituminous Coal**	**Coal Fly Ash**
La	4	21	43	3
Ce	4	21	40	4
Pr	4	23	30	4
Nd	4	20	36	3
Sm	4	3	33	3
Eu	3	11	20	1
Gd	4	19	32	2
Tb	4	13	26	2
Dy	4	16	24	2
Ho	4	20	23	3
Er	8	22	20	3
Tm	6	29	40	3
Yb	4	21	35	3
Lu	5	31	49	3

* sample composition details provided in Table 4

As described above we can improve our extraction efficiency, reducing the temperature to ~200^0C (with the 0.5M Na_2SO_4 and pH 3 sulfuric acid reagent), which is expected to substantial increase the extraction efficiency recoveries in Table 3. Optimizing pressure (probably lower) to increase solution density and polarity of the SCW, should also improve performance. *Improving* *performance by reducing temperature and pressure makes the process more economical and broadly appliable.*

HTL Extraction from Ores

We explored extraction of minerals from several ores from Idaho's Silver Valley near Kellogg, ID. These ores are rich in Zn, Pb, Cu, Ag and have some Au. Pure HTL water was unable to provide any useful extraction. However, an HTL composes of 1M Na_2SO_4 with 0.1 M H_2SO_4 did result in up to 60% recovery of Cu as well as some recovery of gold. Due to precipitating minerals the data scatter on this work was high. However, additional efforts should be able to define the HTL chemical conditions to enable extraction of all the valuable minerals. This process could be used with surface and provide more environmentally benign method for ore process or as an in-situ solution mining method. In-situ solution mining using HTLs could be very attractive]since it can be used very effectively with deep ore deposits (like those remaining in Silver Valley Idaho or the gold and platinum mines in South Africa) while minimizing environmental impact on the surface. The measured (via tradition acid digestion and ICP-MS analysis) metal concentrations in materials explored during the HTL efforts are shown in Table 4.

Table 4. Metal concentrations in materials explored

Element	**unit**	**Lignite Coal**	**Kelp**	**WY Coal B.06**	**Coal FlyAsh A (BEDFS*)**	**GRE Coal***	**NDSG Coal**	**NDSG Coal (rerun)**	**Silver Valley ID Ore A**	**Silver Valley ID Ore B**
Sc	ppm	22.5	61.8	28.7	85.2	202.4	99.4	29.2	8.9	5.3
Fe	ppm	15318	2240	188	34983	67706	47107	25987	28600	6877
Mn	ppm	14.3	66.8	4.9	206.2	715.2	45.8	21.1	1622.7	7579.6
Cu	ppm	55.0	22.7	32.5	158.2	111.0	114.0	66.1	473.6	85.3
Zn	ppm	27.8	16.8	405.3	88.5	130.4	64.5	36.5	1363.3	10161.2
Y	ppm	29.3	0.5	5.3	42.7	43.3	40.6	37.0	0.8	0.6
Ag	ppm	0.4	4.2	2.6	18.9	32.1	17.1	1.2	274.1	727.1
La	ppm	66.2	.7	5.9	36.7	34.7	67.0	84.1	0.8	0.3
Ce	ppm	162.7	1.3	13.1	77.8	69.4	158.9	185.4	0.5	0.8
Pr	ppm	19.3	0.1	1.7	9.0	7.6	18.6	21.9	0.1	0.1
Nd	ppm	81.4	0.6	6.7	38.2	30.6	78.6	88.6	0.3	0.8
Sm	ppm	17.4	0.8	1.2	7.8	6.0	16.6	19.0	0.2	0.4
Eu	ppm	3.8	0.03	0.3	0.2	2.0	3.6	4.3	0.3	0.5
Gd	ppm	15.5	0.1	1.3	7.9	6.5	14.6	16.7	0.2	0.3
Tb	ppm	1.9	0.01	0.2	1.0	8.8	1.8	2.2	0.03	0.04
Dy	ppm	10.1	0.08	1.1	6.5	5.7	9.5	10.9	0.2	0.2
Ho	ppm	1.6	0.02	0.2	1.2	1.1	1.5	1.8	0.03	0.02
Er	ppm	4.1	0.09	1.0	7.1	6.9	7.5	4.6	0.1	0.1
Tm	ppm	0.5	0.01	0.07	0.5	0.5	0.5	0.6	0.02	0.02
Yb	ppm	3.2	0.05	0.5	3.4	3.4	3.0	3.5	0.1	0.1
Lu	ppm	0.4	0.01	0.06	0.5	0.5	0.4	0.5	0.02	0.02
Au	*ppb*	7.5	96.4	15.3	52.6	39.1	25.0	15.1	123.7	23.3
Pb	ppm	18.6	1.2	2.8	20.4	34.9	15.0	16.9	911798	247996

* BEDFS FlyAsh = Basin Electric Dry Fork Station Fly Ash

GRE Coal Creek station Fly Ash

NDSG coal=20161109-L2-1 "H" bed, rerun=with prep blank subtracted (re-digest material as well)

System Analysis

During the exploration of hydrothermal liquid (HTL) recovery of REEs, critical materials and other minerals in this effort can be summarized with the following points.
HTL Advantages
The use of hydrothermal liquid (HTL) solution extraction processes for the recovery of minerals can provide major advantaged to current extraction methods. These advantages include:

- Cheap, simple, and nontoxic/"green" extraction chemistry for a wide range of mineral recoveries.
    - Water, the cheapest industrial acid (sulfuric) and salts (i.e., sodium sulfate).
    - Other acids (i.e., nitrate and phosphoric) and salts could be used.
- Tunable for specific mineral species via the controlled use of chemistry, temperature, pressure, the phased use of additives.
- HTL conditions provide:
    - faster reaction kinetics
    - better penetration of solids for improved extraction
    - unique redox conditions
- Can be applied to a wide range of solids and slurries
    - Rich ores, low grade ores, waste products, coals, biological material, environmental recovery/clean-up sites, etc.
    - Both mineral recover and clean-up of solids to allow them to be used as projects
        - i.e., silica a polymer additive or construction.
        - i.e. ,coal ash additive for construction materials or asphalt.
- Can be used to extract a wide range of minerals (demonstrated for rare earths, precious metals and industrial minerals).

HTL Challenges

The challenges for using hydrothermal liquid (HTL) solution extraction processes include:

- High pressure and temperature environments (such as boreholes) may not be near materials sites and may require drilling or transport of material.
- Normal pressured systems can be used as well but some of the economic cost advantages are lost.
- The extraction system is complex. Reaction chemistry/extraction processes involve a number of steps in a system with nonlinear phase changes. The result is a complex process with a number of interacting parameters.

Uniqueness of concepts pursued with effort

This process demonstrated, for the first time, that HTLs can be used for mineral extraction. A number of facets of the work were unique including:

- Novel green, cheap, mineral extraction, and separation method.
- Controlled HTL pressure, temperature and additives provide process tunability.
- Large solubility swings result in nonlinear chemical properties make extraction challenging.
- When (optionally) coupled with deep borehole technology (such as that provided by Pyrophase) we will have significantly reduced energy costs for processes requiring high temperatures and pressures for leaching of minerals. For every mile you dig beneath the Earth's surface, the temperature rises ~15^{0}F and the pressure increases simultaneously

at a rate of about 7,300 pounds per square inch. Older oil wells average 4,000-6,000 ft deep but can by over 30,000 ft deep.

A tremendous number of unused boreholes are available in many relevant areas. For example:

- Geothermal resources are often near mine sites.
- Many of the hundreds of thousands of played out hydraulic fracturing and oil bore holes near oil basins.

Reusing these holes is cost effective for bore hole owners—effective converting a remediation/closure site into production site again.

5.0 The Next Steps for HTL Mineral Extraction Research and Development

This project demonstrated that the HTL process can be an effective mineral recovery method. However, significant efforts remain to develop this technology into an efficient and economically viable process. Areas of advantageous future work include:

- Exploring other reactant chemistries (acids, salts, and complexants). These should be researched as there may be compositions that increase total recoveries and reduce reaction times.
- A key next incremental step is to evaluate extractions across a range of pressures, lower temperatures (~200^{0}C), and with the Na_2SO_4 and sulfuric acid reagent. This should produce higher recoveries at more economic conditions.
- Better measurement approaches. Future testing will benefit from analytical lessons learned in the effort and provide better process measurements of the complicated dynamic chemistries and precipitation processes.
- Integration with in-line micropillar separators for controlled particle separation (as minerals precipitate due to falling temperature and pressures) could be very powerful but has not yet been demonstrated.
- Future work needs to demonstrate the selective dissolution and transport of minerals which will be very important for many industrial applications.
- Complete preliminary technoeconomic analysis for selected applications.
- Explore using low geothermal sources a low-cost heat source.
- Better methods of handling high concentrations of inorganic solids at high temperatures and pressures are challenging.
- Complete key technology/extraction demonstrations to interest commercial partners and agencies funding the next stage of research.

6.0 Commercialization and Business Growth Opportunities

Approximately 10,000 tons/yr of potential domestic REE and other critical elements (here REE+) is locked up in waste, making the REE inaccessible with current technology. For example, 550,000 tons/yr of kaolin-process tailings (k-grit) contain almost 500 ppm of the EERE targeted elements: Nd, Pr, Dy, Tb, Sm, Co, Li, Mn and Sc. With a 75% utilization of available waste and a conservative 60% recovery efficiency, 225 tons annually can be concentrated from just one of the many potential feedstocks. Furthermore, decades of waste are stored in settling ponds, with ~16M tons of k-grit alone, yielding ~7,500 tons of REE concentrate. Concentrated materials from the waste (with ~75 ppm Sc) is valued at ~$200/kg, which can net ~$750M/yr in revenue for involved companies. Another example is the waste from the phosphate mines in Florida by Mosaic Company. Mosaic has over 1.7 *billion* tons of phosphogypsum by-product stored (in a piles that make the highest “mountains” in the state). Some of the waste is over 50 ppm REE and has other valuable minerals as well. It must be realized that the recovery of REE’s (and other metals, many of the toxic) from waste turns the liabilities of environmental management into a profit source for the industries. These activities could ignite a new economic sector that utilizes emerging downstream technologies to domestically produce REEs, making the US a global leader in sustainable energy solutions.

This project complements existing and future research and commercialization efforts related to the extraction of critical materials from various sources including petroleum, coal, mining leachates, seawater, and biomass. It relates to several available technologies including those in the chem/bio-processing portfolio and the mesofluidic separator device. PNNL currently has collaborations with SoCal Gas and the California Energy Commission on the separation and removal of minerals/chemicals/particles from geothermal brines. The results of this effort may support and facilitate future funding opportunities and/or commercialization effort with companies such as PyroPhase, ReExtract, Thiele Kaolin Company, Mosaic Minerals and more. One particular research/commercialization opportunity includes the DOE Commercial Technology Fund.

The results from this project have supported the development of IP and an IDR has been filed. Additional research opportunities are anticipated.

7.0 Experimental System

Testing Approach

All experiments were carried out in high pressure batch, stirred reactors. Water, mineral bearing materials, and additives were added to a cleaned, stirred reactor rated for elevated temperatures and pressures. After the addition of the components of interest, the system was heated with constant agitation to the desired temperature. The system pressure was determined by the vapor pressure of water at a given temperature. While at temperature and pressure, the liquid stream was sampled through a dip tube with a frit on it. An experimental diagram in shown in Figure 4. Shortly after sampling, HCl was added to the mixture to reduce the extent of precipitation after sampling.

Digestion and analysis

Analytical work was carried out with an ICP-MS. Samples were acid stabilized before analysis. Some samples were further acid digested before assay if particles or precipitation was suspected or observed. In general, 1 g of the colloidal sample was weighed and digested with 1-2 mL Conc HNO_3 then ultrasonicated for 1 hour. Then the dissolved sample solution was diluted with 2% acid solution (HNO_3 and HCl) and analyzed with ICP-MS (X-series, Thermo-Fisher Inc., England). Some samples that were not completely dissolved with Conc HNO_3 , then were digested with Conc HNO_3/HF and heated at 120^0 C for 1 -8 hours prior analyzed with ICP-MS. A 1ml of hydrogen peroxide was also applied to achieve complete dissolution of the particles in some cases. The analysis was performed with triplicates, and the final data from ICP-MS were subtracted from the prepared blank solutions.

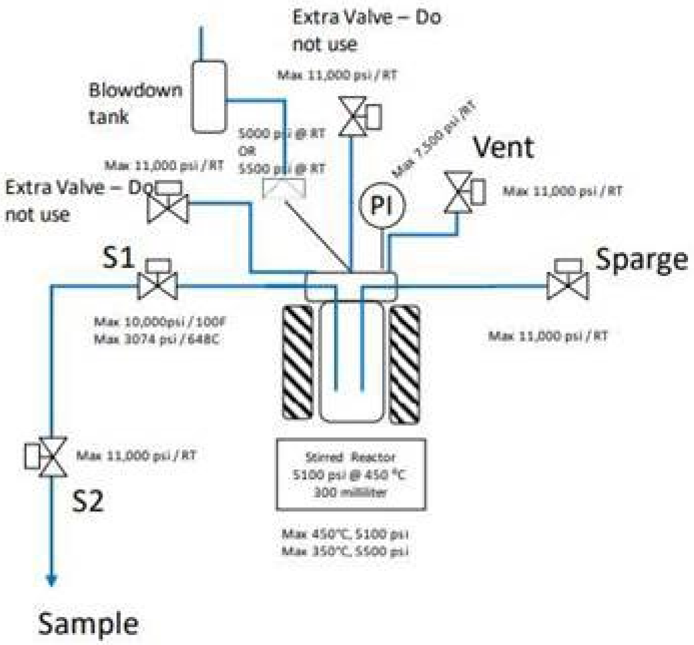

Figure 4. A diagram of the experimental system utilized the extraction minerals with HTLs/SCW. The core is a high pressure batch stirred reactors. Water, mineral bearing materials, and additives were added to a cleaned, stirred reactor rated for elevated temperatures and pressures.

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