Microwave Pretreatment of Critical Mineral Sources

Project #FWP-1022420

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Project Overview

- **Funding :** DOE / FWP-1022420
- **Overall Project Performance Dates:** 07/2023-03/2024
- **Project Participants:** Christina Wildfire, Ashraf Abedin, Charles Henkel
- **Overall Project Objectives:** Evaluate microwave pretreatment on metalliferous black shales and mafic/ultramafic rock to improve pathways for solvent extraction. Microwave pretreatment will study the effect of surface area, crack formation throughout structure, energy utilization, and heating efficiency of organics and sulfide compounds within the rock structure.
- **Relevance to FECM REE-CMM Program:** Microwave pretreatment can provide a water free process to improve recovery of critical minerals in an energy efficient manner by providing microstructure pathways for traditional recovery methods (leaching).

Project Overview

- **Technology Readiness Level (TRL):** Move from TRL 2 to TRL 3 over the course of the project.
- **Interdependence on Additional EY23 NETL RIC FWP Tasks:** Guidance and input on appropriate rock formations for study from Tasks 6.0 and 7.0.
- **Anticipated Licensing, Patent Application, Commercialization Potential:** Previous patent has been issued on the use of this process for coal fly ash and it is anticipated that the expansion of this research could result in additional IP. Potential for adaption for in situ recovery processes and technology development.

Technology Background

Motivation: Microwave-assisted pretreatment of coal fly ash for extraction of rare-earth elements (REE)

- A MW-assisted pretreatment technique was developed to improve the extraction of REE from coal fly ash solid waste by NETL.
  - No solvents needed for pre-treatment
  - MW created cracks in glassy matrix containing REEs
  - Increased REE recovery yields by 83%
  - Pre-treatment time less than 10 min

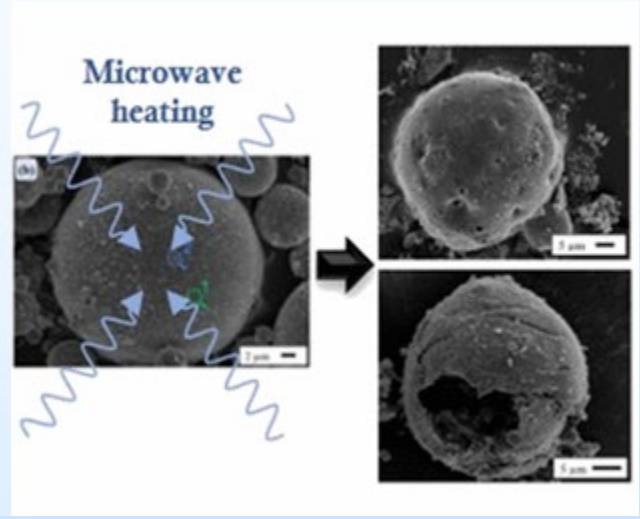


Figure: MW heating to extract REE from coal fly ash

Ref: Energy Fuels 2019, 33, 11, 12083–12095

Technology Background

Current goal: CM sources to screen

- Coal & coal underclays (previous work on fly ash)
- Metalliferous black shales
- Mafic/ultramafic rocks

Metalliferous black shales: Targeting vanadium associated with organic matter and authigenic clays.

Mafic/ultramafic rocks: Targeting nickel/cobalt/chromium located in the mineral structure.

Current extraction process is limited by inefficacy and solution access due to density of matrix material.

Problem statement:

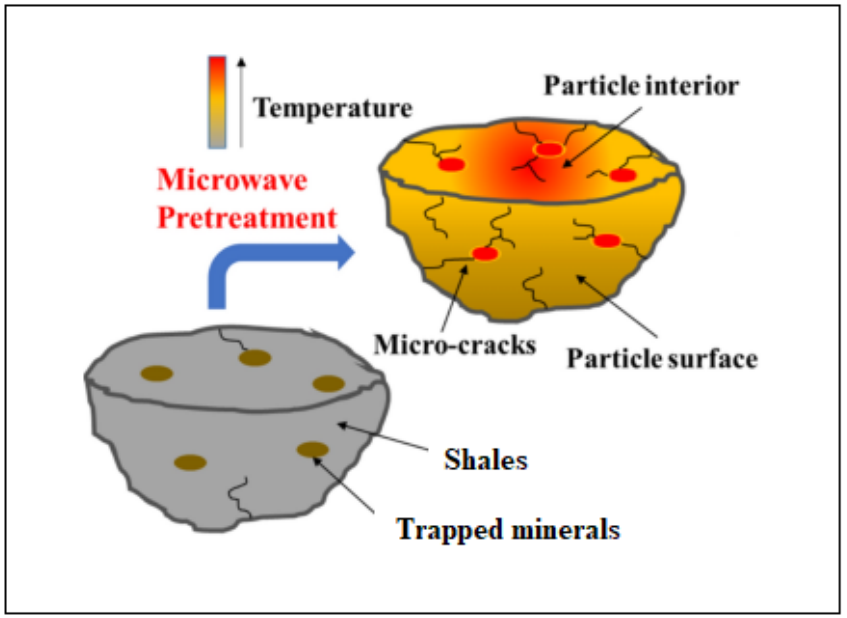
- What is the efficacy of microwave heating for CM sources?
- Can these be fractured to improve **leachability and accessibility**?

Technology Background

Microwave assisted comminution for minerals processing

- Comminution (grinding) commonly used as pre-treatment before leaching processes
  - Energy intensive
  - Small particle sizes needed for most leaching processes to access CMs

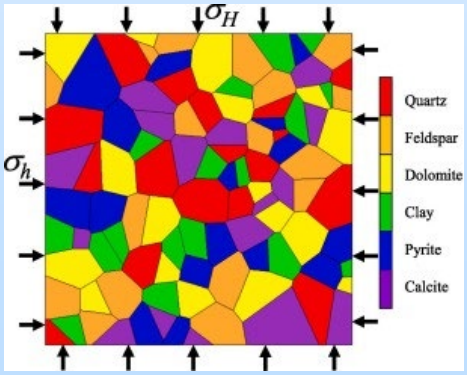
- MW can be used as pretreatment to create **thermal stress fractures** alongside grain boundaries
  - Can lower energy use
  - Has been used as pre-treatment to grinding steps industrially
  - Increase accessibility to CMs



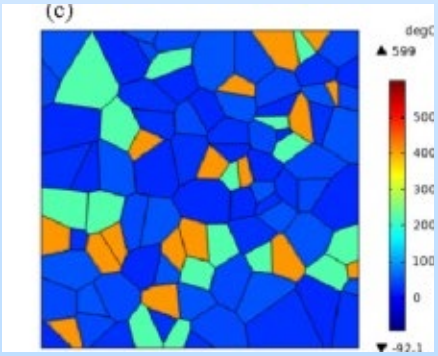
Technology Background

Microwave mineral pre-treatment

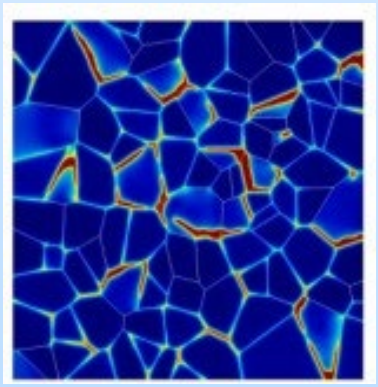
- Process does not involve solutions of any kind (**unlike** MW digestion)
- Method uses the direct interaction of the microwaves with each mineral phase to create thermal expansion within the ores
- Minerals like quartz, and limestones do not heat in microwaves while CM containing pyrite and organic phases heat rapidly
- Can create intergranular and transgranular cracking within the ores which makes recovery methods more effective
- Can operate in a continuous manner with conveyer belt reactors or subsurface



Simulated Shale



Heating of each phase under MW



Stress points and crack sites

https://doi.org/10.1016/j.engfracmech.2022.108665

Technology Background

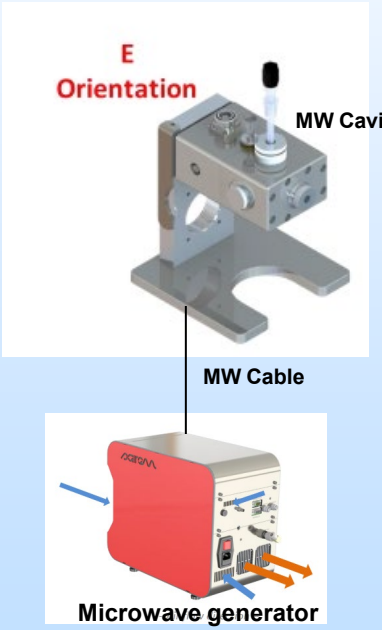
Microwave mineral pre-treatment

Advantages	Disadvantages/Challenges
Rapid heating of minerals	Equipment and installation costs
Process modularity	Penetration depth limitations
Quick operations (on/off)	Dependency on sample's dielectric property
Process electrification	
Selective heating of target metals	
Increased CM yield	
Allows processing of samples of large size distributions	

Operational goals include optimization of process parameters (MW power, exposure time, heating technique, MW modes etc.) to induce sufficient cracking that results in pore exposure.

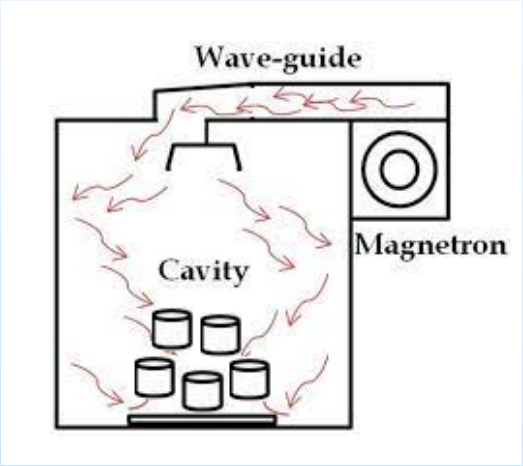
Technical Approach: Different MW Reactors

Single mode
(Fixed Temperature)



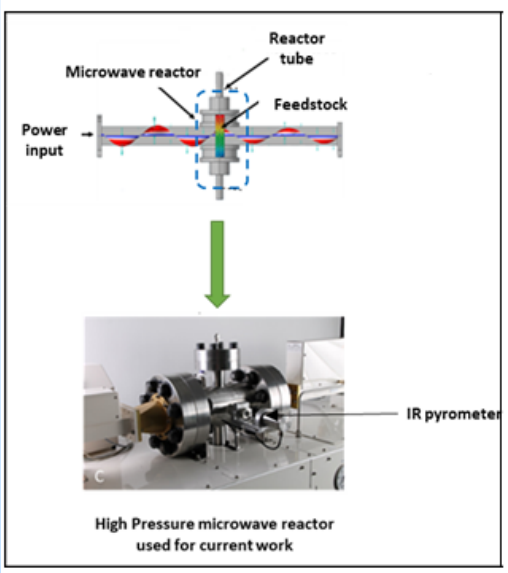
400-700℃ runs, max power 200 W

Multi mode
(Fixed Power)



1000 W constant power, 2-5 minutes runs

Single mode
(Pulsed power)



Pulsed power, 70% duty cycle, 5 mins

Project Scope and Progress

03/31/2024

Project Deliverables

1. Develop dielectric property library of common ores and minerals from literature and from direct measurements for critical mineral source selection for microwave processing.

2. Provide process optimization for input power, processing time, and reactive gas for surface area enhancement to critical mineral sources

3. Microwave pre-treatment methods allow for improved recovery of critical minerals by increasing pore structure by 25%

4. Provide report on microwave processing parameters on CM ore sources to identify optimal CM sources for microwave pretreatment

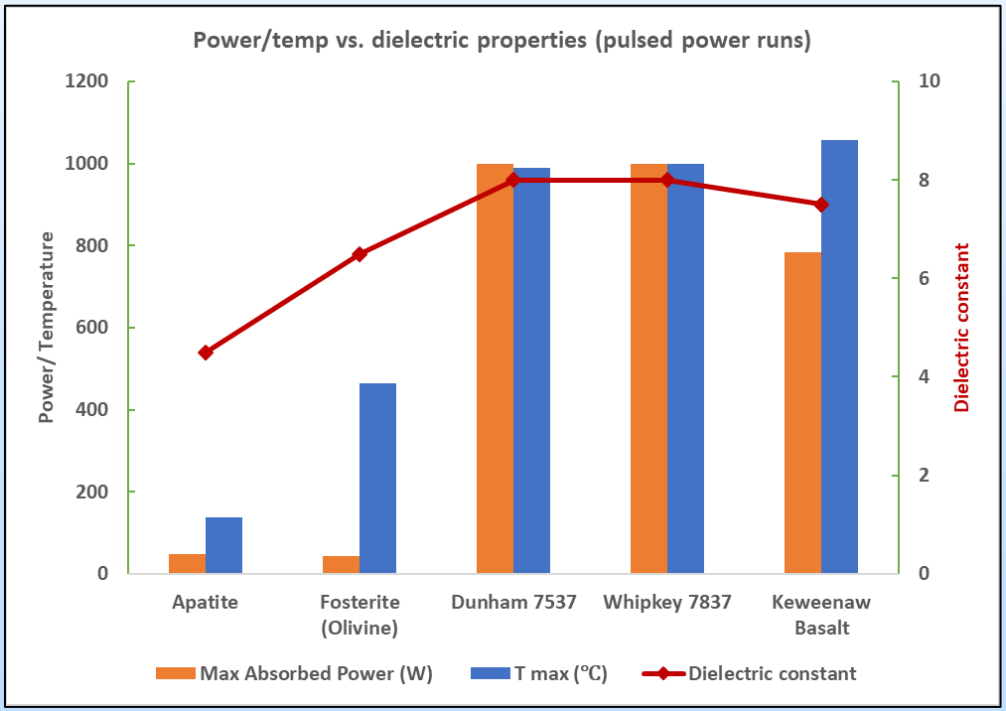
Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	01. Develop dielectric property library of common ores and minerals from literature and from direct measurements for critical mineral source selection for microwave processing.	3/31/2024	01	**Ongoing**

- We have compiled the dielectric properties of minerals selected for this task from literature review.
- High temperature direct measurement of dielectric property will be carried out using the current high temperature dielectric measurement system (HRTEM) being developed at NETL MGN.

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	01. Develop dielectric property library of common ores and minerals from literature and from direct measurements for critical mineral source selection for microwave processing.	3/31/2024	01	**Ongoing**



- Dielectric properties show susceptibility of minerals under MW heating.
- The *higher* the dielectric constant, the *more* is the ability for the sample to conserve microwave energy.
- Shales heat better under MW due to their higher dielectric constants.

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	02. Provide process optimization for input power, processing time, and reactive gas for surface area enhancement to critical mineral sources.	3/31/2024	02	**Completed**

To optimize process parameters, the CM Task 19 team used three different MW reactor over the 8-month project period and compared the results to study maximum surface area enhancement for CM sources.

Parameters	Single mode	Multimode	Pulsed power mode
Sample (s)	single	multiple	single
Temperature	400-700℃	Variable	Up to 1000℃
Exposure time	10 mins	2-5 mins	5 mins
Power	200 W max	1000 W fixed	1000 W, 70% duty cycle
Cracking effect (BET)	low	moderate	high (phase change)

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	03. Microwave pre-treatment methods allow for improved recovery of critical minerals by increasing pore structure by 25%.	3/31/2024	03	Completed

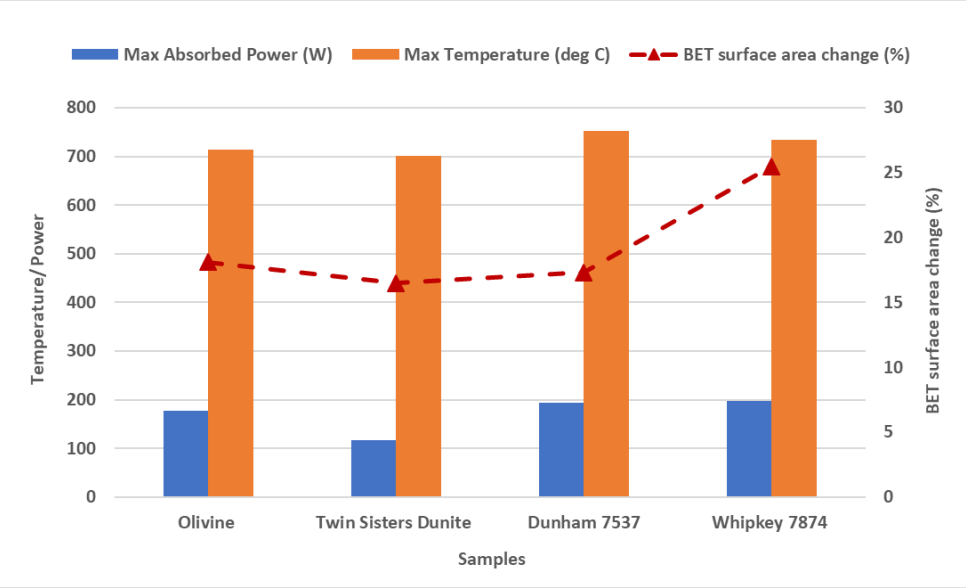
- After carrying out the microwave treatment of the selected minerals, the CM team has **successfully demonstrated** that microwave pre-treatment methods can increase certain shales and mafic rocks' pore structures by **at least 25% or higher** (confirmed by BET).
- Depending on the dielectric properties, MW power and exposure time, the metal inclusions within the minerals heat up by absorbing MW energy.

Characterizations: SEM and Optical Microscopy imaging to be used to confirm the changes observed during the BET surface area measurement.

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	03. Microwave pre-treatment methods allow for improved recovery of critical minerals by increasing pore structure by 25%.	3/31/2024	03	Completed

Results: Single mode MW reactor



- Shales absorbed more MW power vs. ultramafic rocks
- This resulted is greater change (20-25%) in surface area in shales, indicating more cracking.

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	03. Microwave pre-treatment methods allow for improved recovery of critical minerals by increasing pore structure by 25%.	3/31/2024	03	Completed

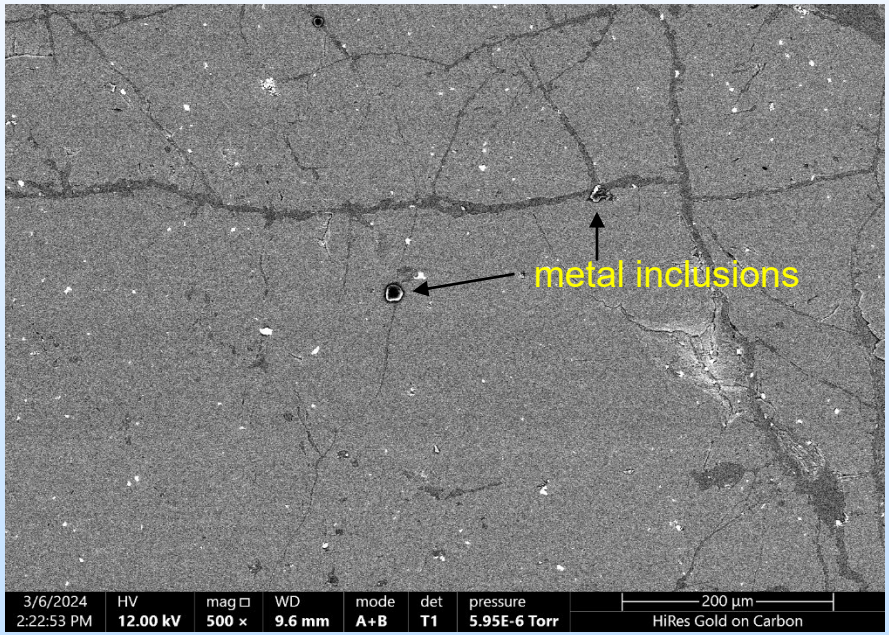
BET results
Multimode (1000 W) MW reactor

Classes	Minerals	BET surface area increase (%)	Pore volume increase (%)
Shales	Dunham 7537	37.1	41.1
	Boggess 7987	263.1	146.1
Ultramafic	Olivine Jackson NY	19.7	3.6
	Forsterite	98.8	152.1

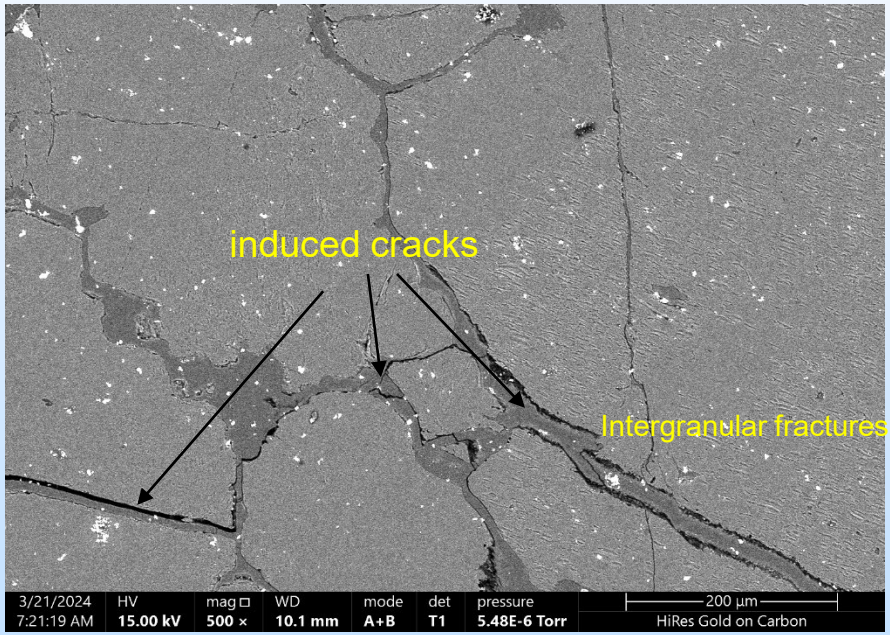
- Greater change in surface area observed for higher MW power input in multimode reactor (both shales and ultramafics) vs. single mode fixed temp reactor.

Progress and Current Status of Project

SEM imaging results : Serpentine (Multimode 1000 W MW reactor)



Serpentine untreated



Serpentine MW treated

- Intergranular fractures observed after 5 min of MW treatment at 1000 W

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	03. Microwave pre-treatment methods allow for improved recovery of critical minerals by increasing pore structure by 25%.	3/31/2024	03	Completed

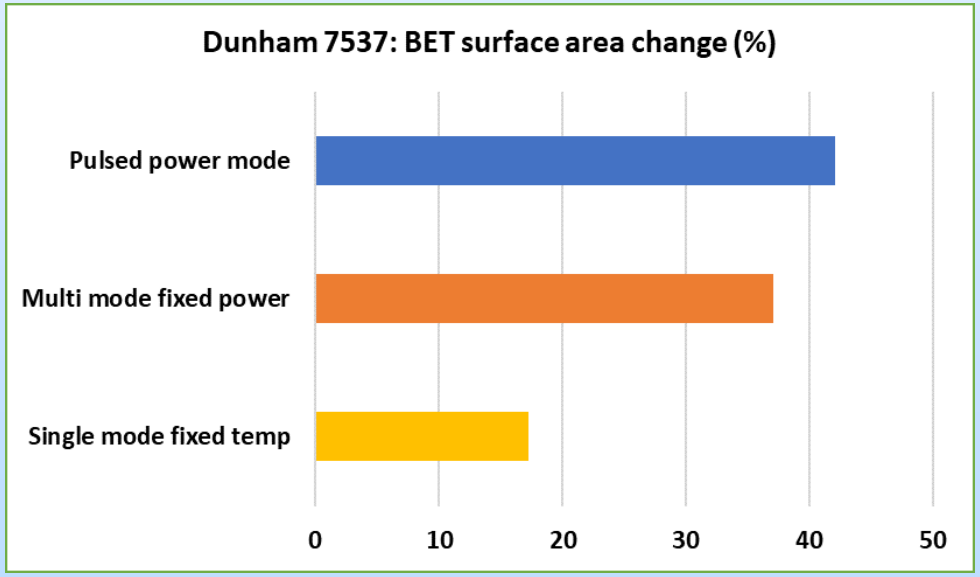
BET results (March 2024)
Pulsed power mode MW reactor

Classes	Minerals	BET surface area increase (%)
Shales	Dunham 7537	42.1
	Whipkey 7874	76.8
Ultramafic	Olivine Jackson NY	Characterization ongoing
	Forsterite	Characterization ongoing

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	03. Microwave pre-treatment methods allow for improved recovery of critical minerals by increasing pore structure by 25%.	3/31/2024	03	Completed

Change in surface area for different MW modes: Dunham 7537 shale



- Power is directly related to increase in surface area
- Pulsed power perform better compared to fixed power mode for higher pore exposure

Progress and Current Status of Project

Task	NETL Deliverable	NETL Due Date	DelID	Progress
019	04. Provide report on microwave processing parameters on CM ore sources to identify optimal CM sources for microwave pretreatment.	3/31/2024	04	Completed

- This report includes a summary of works already completed for microwave pretreatment of mineral samples to optimize the processing parameters including-
    - Process heating temperature
    - Power input
    - Minerals particle size
    - Processing time
    - Dielectric properties database

- The quarterly reports contribute to the continuous efforts of the compilation of the final report to identify the optimal CM sources for microwave pretreatment.

Future goals

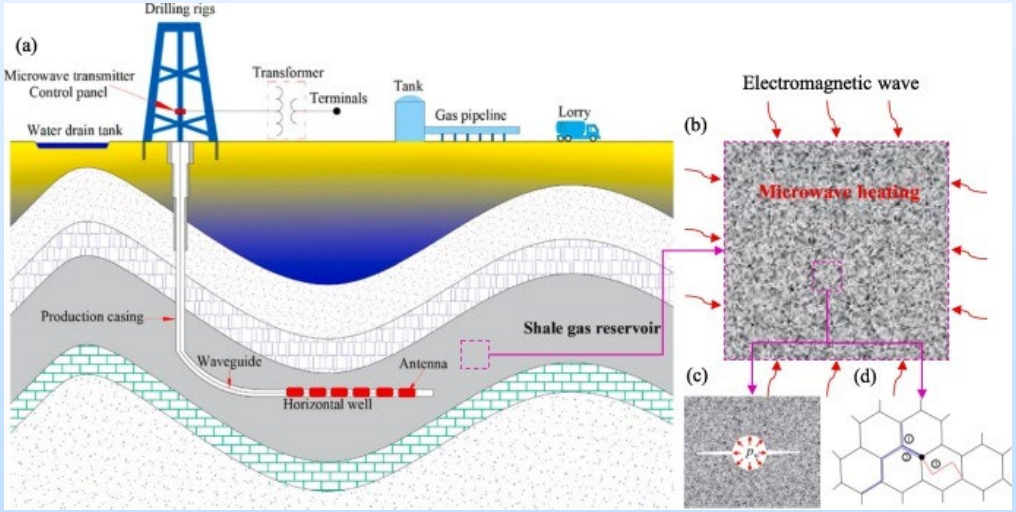
Plans for future works in this project include-

- Pairing the data and findings from Task 19 with the leaching and extraction efforts carried out by **CM Task 6** and **Task 7**.
- Expand CM sources used in study and have feedback loop with leaching.
- Continue to build the dielectric property database of minerals and share on public platform for community outreach.
- Continue BET measurements and SEM data analysis for all selected samples to study intergranular and transgranular cracking.
- Scale-up the pre-treatment process using a continuous feed microwave reactor (long term goal).

Future goals

Synergistic Efforts

- Microwave is being investigated for enhanced subsurface oil recovery by fracturing shales via scale-up efforts.
- Multiple pilot projects underway for mineral pre-treatment to reduce energy needs for grinding and pretreatment.



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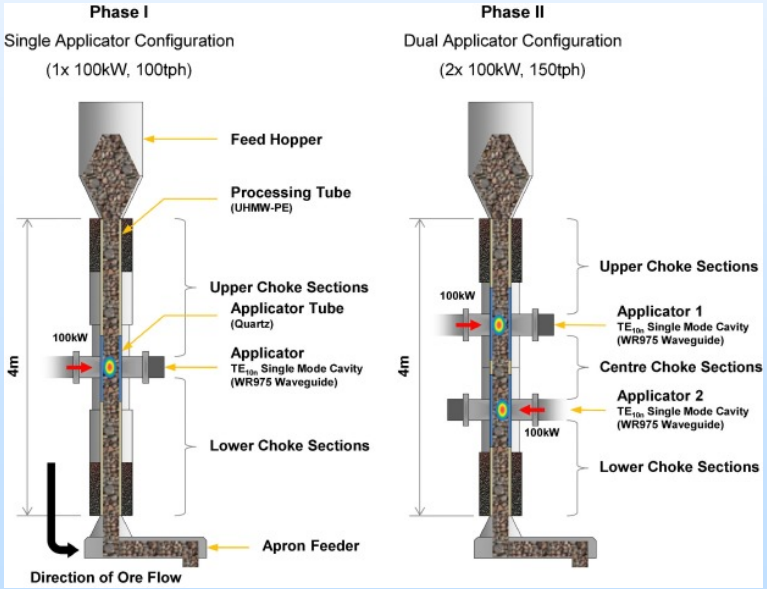


https://doi.org/10.1016/j.mineng.2017.03.006

Outreach and Workforce Development Efforts

Outreach –

- The CM Task 19 team is currently building a database with dielectric loss property at atmospheric and elevated temperature that will be shared in public platform eventually to establish community outreach.
- The team plans to present the research in national and local conferences to share the findings with scientific community.

Workforce Development –

The team is currently developing a high temperature dielectric loss property measurement technique that can be automated to measure multiple samples on batch mode, along with training NETL researchers on this unique capability.

Research summary

For the CM Task 19, the researchers carried out the following to support the NETL deliverables:

- Reported the dielectric properties through intensive literature reviews.
- Reduced the minerals to different sizes before heating under microwaves. Used (1) single-mode (2) multimodal MW reactor and (3) Pulsed power mode MW reactor - to study the parametric effect of microwave susceptibility, temperature, exposure time, and power on minerals.
- Carried out BET and SEM analysis on the minerals to detect changes in surface due to MW exposure.
- Compiled and submitted a report on the findings of CM efforts to NETL.

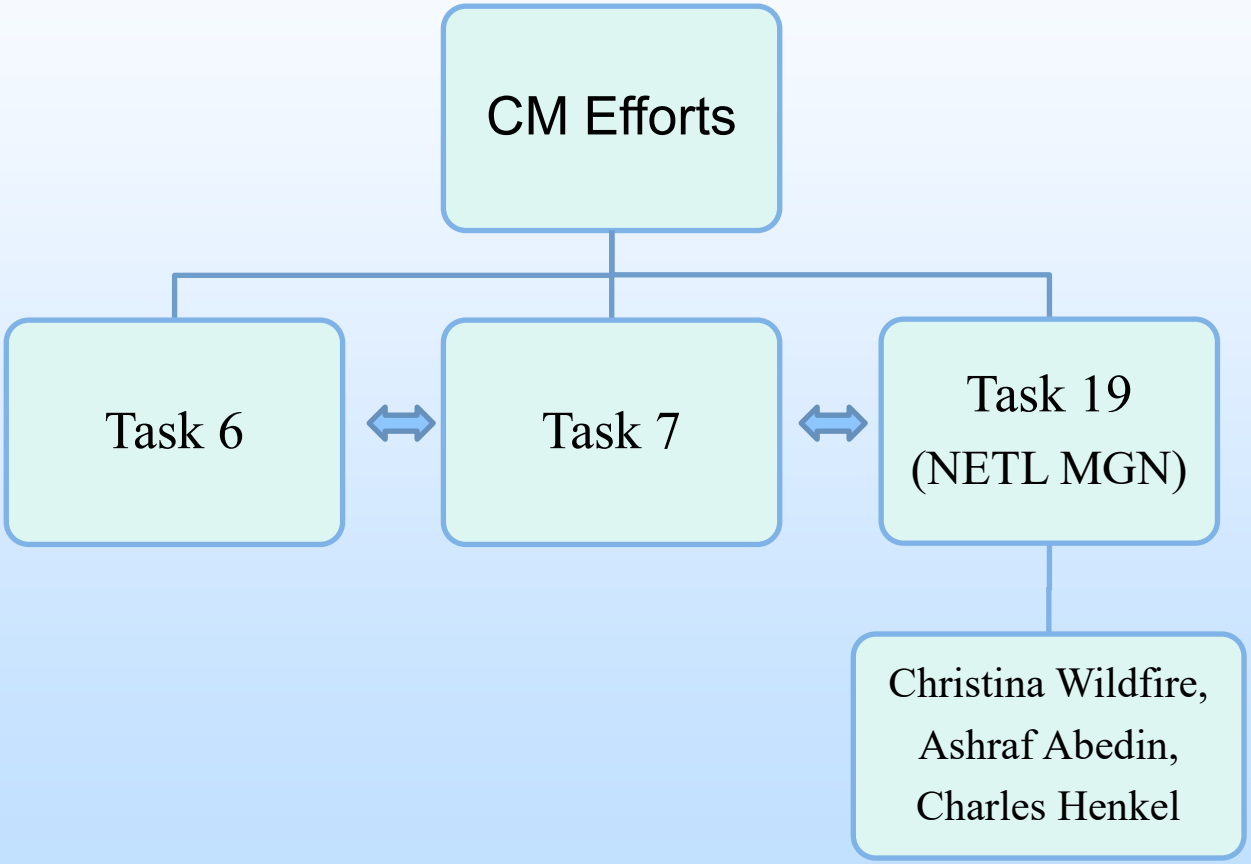
Work to do:

- Complete full set of MW treated minerals analysis via BET and SEM imaging.
- Complete measuring the dielectric properties of minerals and share the database for community outreach.
- Share the results from Task 19 with Task 6 and 7 for leaching and extraction efforts and support FECM long term CM goals (next phase).

Appendix

- MW: microwave reactor
- Cavity: sample chamber covered under microwave heating
- Magnetron: microwave generator
- Comminution: pretreatment of minerals to promote liberation of the valuable from the gangue minerals.
- Modes, single vs. multi: In single mode reactors, only one reactor vessel can be irradiated; multimode reactors may accommodate several vessels at once.
- Dielectric property: The dielectric loss is used to heat elements in the microwave field, and the heating effect is determined by the dielectric constant-ε of the material.
- IR pyrometer: to measure temperature of the surface of the microwave cavity and adjust power supply of the microwave generator according to the set temperature.

Organization Chart



Critical Minerals Task 19: Project Gantt Chart