Production of Germanium and Gallium Concentrates for Industrial Processes

Award No. DE-FE0032124

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Microbeam Technologies, Inc.

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
October 25 - 27, 2022

Project Overview

Funding

- DOE share: $199,921
- Cost share: $51,550
- Total project cost: $251,471

Overall Period of Performance

- January 1, 2022 to March 31, 2023

Overall Project Objective

- This project is aimed at developing a concept to extract, separate, recover and purify germanium and gallium from lignite carbon-ore rare earth element concentrates.

Project Overview

Project Participants

- Project Team:
  - Microbeam Technologies Inc. (Lead)
  - University of North Dakota (Nolan Theaker and Brittany Rew)
  - Dennis James (consultant)
- Support From:
  - US DOE National Energy Technology Laboratory (NETL)
  - North American Coal Corporation
  - North Dakota Industrial Commission
- Advisors
  - Lattice Materials - Ge product manufacturer
  - Ga refiner and product producer
  - Barr Engineering – Review technical and economic assessment

Dennis James Consulting

Technology Background

Technology Combined with 1–3-ton/day CM Facility

Element	Price (US$/kg)	Concentration (mg/kg)	Percent Recovery	Recovered Amount[3] (lb/yr)	Value ($/yr)
Cerium[1]	$2	162.6	48.64%	158,131	$143,430
Cobalt[2]	$30	17.1	45.15%	16,028	$216,382
Dysprosium[1]	$250	12.9	55.28%	13,429	$1,522,543
Erbium[1]	$22	6.6	62.72%	7,701	$76,831
Europium[2]	$30	4.1	45.83%	3,541	$48,177
Gadolinium[1]	$23	16.4	55.28%	17,085	$178,211
Gallium[2]	$195	15.7	40.70%	14,025	$1,242,659
Germanium[2]	$919	16.4	42.94%	16,695	$6,965,892
Holmium[2]	$0	2.4	62.72%	2,818	$0
Lanthanum[1]	$2	69.0	51.44%	68,165	$61,828
Lutetium[2]	$0	0.8	62.72%	901	$0
Neodymium[1]	$42	82.9	45.83%	72,563	$1,382,148
Praseodymium[1]	$50	20.2	46.77%	18,063	$409,582
Samarium[1]	$16	18.0	45.83%	15,643	$0.0
Terbium[1]	$400	2.4	55.28%	2,460	$446,291
Thulium[2]	$0	0.9	62.72%	1,038	$0
Scandium[1]	$1,000	21.5	39.24%	21,193	$9,611,362
Ytterbium[2]	$0	5.6	62.72%	6,578	$0
Yttrium[1]	$6	50.8	64.28%	67,904	$184,772

[1]Value from DOE solicitation 89243320RFE000032 – given as oxides.
[2] December 2020 market price.
[3]Amounts are for the oxide form and estimated from bench-scale results and material balance calculations.

Ge/Ga - Abundance and Modes of Occurrence

- Organic and mineral associations
- Mine samples with up to 160 ppm Ge and 30 ppm Ga (dry basis)
- North Dakota Geological Survey – 724 ppm and 50 ppm (dry basis)

Germanium and Gallium Recovery

- Extracted and end up in the concentrate
- Chemical properties are significantly different than REE
- Opportunity to separate and concentrate

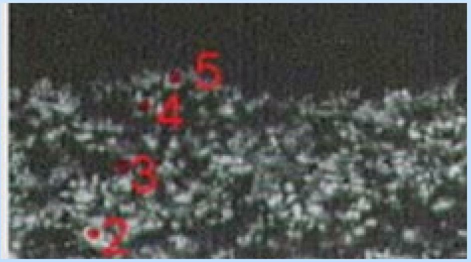
Technology Background

National Science Foundation Small Business Innovative Research Grant (SBIR) – Metalloid Recovery and Concentrating from Gasification Ash (2004-2007)

Idea – Originated from the analysis of ash related materials from an entrained-flow gasification system that was fired on coal. Detailed analysis revealed elevated levels of Ge.

NSF SBIR Project

- Phase I - Proof of concept that Ge could be separated and captured
- Phase II - Bench-scale Ge prototype recovery system was designed, constructed and tested constructed



Elemental Wt%

Fig. #	Point #	Description	S	Cr	Fe	Ni	Ge	O
	2	Inner layer	14.58	1.90	5.90	2.29	73.62	0.00
	3	Middle layer	6.30	0.00	0.00	0.00	80.83	11.83
	4	Middle layer	11.56	0.31	1.48	0.79	80.53	5.32
	5	Outer layer	14.70	0.00	0.98	0.00	83.32	0.00
	6	Outer layer	9.69	0.56	0.69	0.00	87.43	0.00

Technical Approach/Project Scope

- **Task 1.0 – Project Management and Planning --** Microbeam will coordinate activities in order to effectively accomplish the work. Microbeam will ensure that project plans, results, and decisions are appropriately documented, and project reporting and briefing requirements are satisfied.
- **Task 2.0 – Feed Stock Identification and Characterization --** Midstream REE concentrates will be characterized in detail to determine the abundance and forms of Ge and Ga.
- **Task 3.0 – Literature Review and Identify Industrial Applications --** The project team will develop a detailed literature review of technologies utilized to separate, concentrate, and refine Ge and Ga from conventional and non-conventional feedstocks. The project team will also identify industrial applications for the Ge and Ga.
- **Task 4.0 – Product Testing and Analysis --** Process flow diagrams (PFDs) will be developed to produce Ge and Ga in forms that are required to produce end products from the feedstock materials used in this project. The production route for the refined metal, salt, or oxide as required by the end user will be developed.
- **Task 5.0 – Market Analysis --** An analysis of the market regarding the current and future uses of Ge and Ga products will be conducted and an assessment of the potential of the quantity of Ge and Ga that can be produced from this process if scaled to a 1 to 3 tonne/day REE-CM production facility will be performed.

Technical Approach/Project Scope Milestones and Schedule

Task Number	Deliverable Title	Planned Completion Date	Date Completed
1	Project Management Plan	1/31/22	X
1	Kick-off meeting	3/31/22	X
1	Chemical characterization or analytical data if generated in Phase 1	3/31/23	
1	Technical Report	3/31/23	
2	Feedstock Identification	1/30/22	X
2	Feedstock Characterization	1/31/23	
3	Teaming Plan	1/31/23	
3	Technical Research Plan	1/31/23	
3	Purity Estimates	12/31/22	
4	Process Flow Diagrams/Bench Testing	3/31/23	
4	Identification of Quantities of Resource Needed	3/31/23	
5	Preliminary Technical Economic Assessment	3/31/23	

Technical Approach/Project Scope - Success Criteria

<u>End of Phase I Success Criteria</u> 1) Identification of lignite feedstocks that are rich in Ge and Ga, 2) Determination of the abundance and form of Ge and Ga in the lignite coal-derived rare earth element concentrates, 3) Development of a conceptual design of a process to produce high purity Ge and Ga products that meets industry specifications, and 4) A market analysis that shows the need for a domestic source of Ge and Ga.

<u>End of Phase II Success Criteria</u>

Demonstrated ability to produce +90% pure Ge and Ga oxides/salts/metals in a laboratory- or bench-scale facility.

<u>End of Phase III Success Criteria</u>

Demonstrated technical and economic feasibility of Phase II laboratory- and bench-scale testing.

<u>End of Phase IV Success Criteria</u>

Design an integrated process for recovery of Ge and Ga for a 1-3 Tonnes MREE as oxides or salts per day plant that is integrated with downstream manufacturing of products for consumers.

Technical Approach/Project Scope - Deliverables

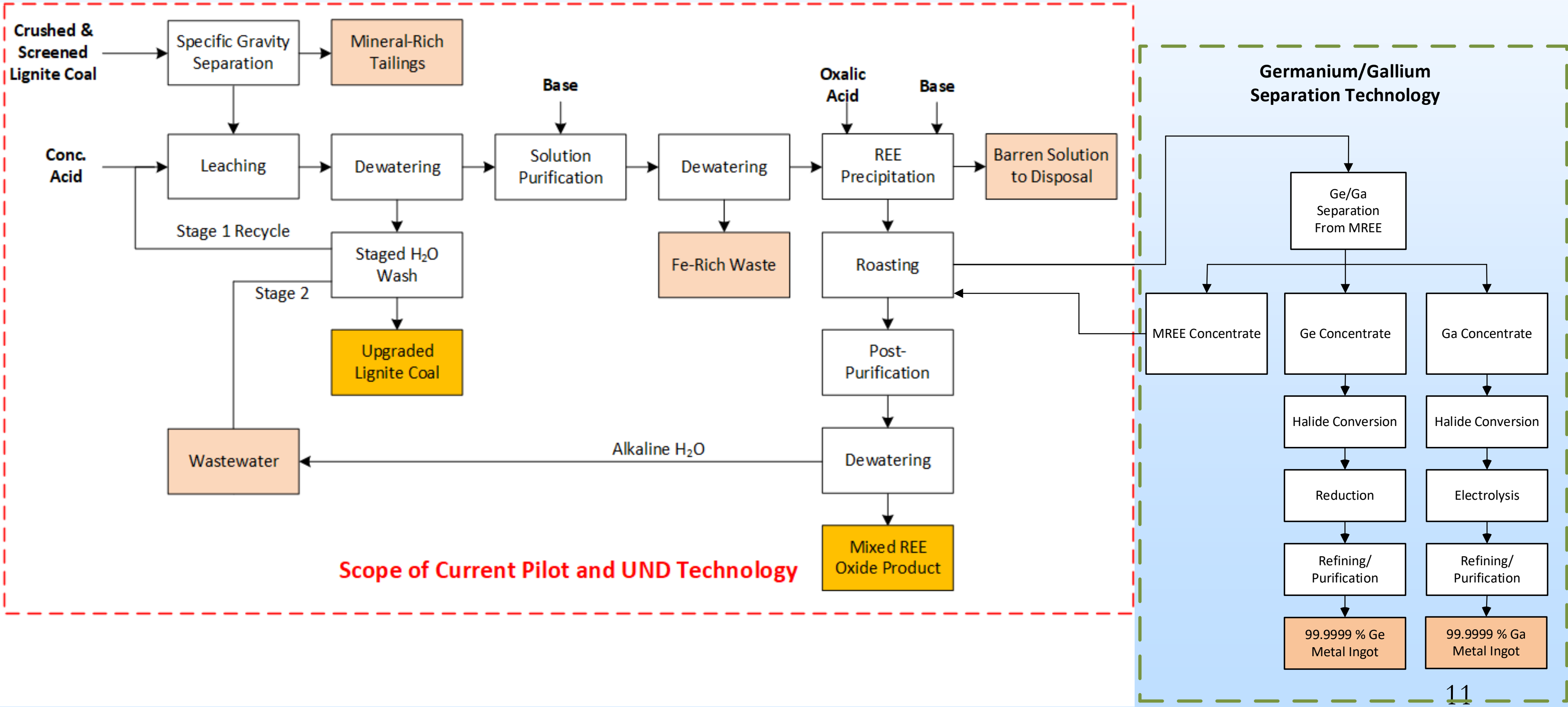
- **Teaming Plan:** A coal-based or alternate resource supplier, pilot-scale MREO/MRES and/or CM facility operator, advanced separation and purification and reduction to metal process developers, and an industrial partner(s).
- **Technical Research Plan:** A complete and detailed plan will be developed.
- **Purity Estimates:** An estimate of the purity obtainable.
- **Process Flow Diagrams:** An entire production process from mixed rare earth oxides/salts (MREO/MRES) to refined metal, and/or production of CM materials.
- **Resource Quantities:** Identification of quantities of resource (e.g., MREO/MRES) needed, and quantities of refined product to be produced if the project were scaled to a pilot project.
- **Analytical Data:** Analytical chemical characterization data generated in Phase 1 will be provided to DOE.
- Phase 1 Final Technical Report.

Technical Approach/Project Scope – Risks and Mitigation Strategy

Perceived Risk	Risk Rating: Probability	Risk Rating: Impact	Risk Rating: Overall	Mitigation/Response Strategy
	(Low, Med, High)			
Financial Risks:				
Cost of Materials	Low	Med	Low	Review cost of materials and identify alternatives as needed
Underestimate level of effort required to complete the work	Low	High	Med	Continually track costs and schedule
Cost Schedule Risks:				
Cost tracking	Low	High	Low	Assign responsibility for managing cost. Dedicated program resource manager for project management. Utilization of Project cost tracking system.
Scheduling/ meeting milestones	Low	High	Low	Planning system and communication implementation
Technical Scope Risks:				
Availability of a range of coal samples	Low	Medium	Low	Project team will work closely with NACC to identify coal samples for testing.
Ge and Ga concentrations after processing are low	Low	High	Low	Project team has identified multiple sources of coal to provide a range of Ge and Ga concentrations
Consistency of midstream samples provided	Low	Medium	Low	Project team has knowledge in the REE concentration process that will allow for troubleshooting of the process to identify issues
Management planning and oversight risks:				
Personnel availability	Low	High	Low	Utilize the large base of personnel expertise at MTI and UND, including engineers, operations, management, scientists, analytical chemists, technicians, fabricators and electricians.
Equipment Availability	Low	High	Low	The team has identified back up pieces of equipment to conduct the necessary analysis if needed
Communication	Low	High	Low	Coordinate and schedule meetings
ES&H				
Processing waste	Low	Low	Low	Current process does not use harmful chemicals and has waste procedures in place for materials that will be used

Technical Approach/Project Scope

The technology involves the separation of Ge/Ga from the MREE to produce +90 percent pure germanium and gallium metals from REE concentrates derived from carbon-ore



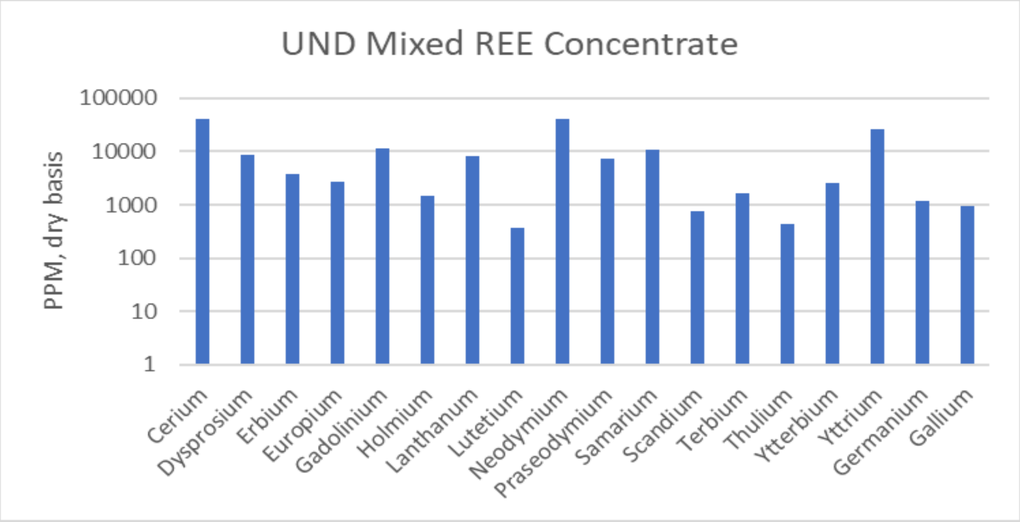
Progress and Current Status of Project

Task 2.0 Feedstock Identification and Characterization

University of North Dakota REE Concentrate – Bench System-Oxalate form

Fresh Feed (%)							
C	16.200	TiO_2	0.008	P_2O_5	0.100	Nd_2O_3	6.813
H	1.830	Tm_2O_3	0.071	SO_3	0.114	Lu_2O_3	0.060
N	0.200	Ga_2O_3	0.178	Yb_2O_3	0.421	Sm_2O_3	1.796
S	0.130	GeO_2	0.235	K_2O	0.021	EuO	0.417
O	42.520	Y_2O_3	4.705	CaO	6.627	Gd_2O_3	1.860
Na_2O	2.157	BaO	0.064	Sc_2O_3	0.167	Tb_2O_3	0.265
MgO	0.000	La_2O_3	1.354	ThO_2	0.028	Dy_2O_3	1.397
Al_2O_3	0.343	CeO_2	7.236	UO_2	0.003	Ho_2O_3	0.233
SiO_2	0.663	Pr_2O_3	1.254	As_2O_3	0.128	Er_2O_3	0.601

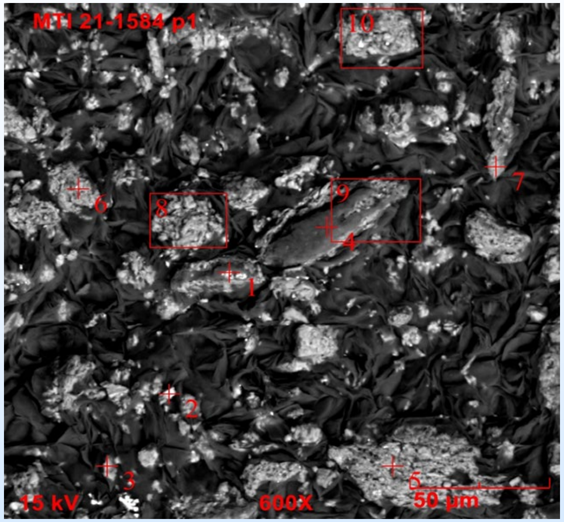
- University of North Dakota Pilot Plant
  -REE concentrate is extracted from North Dakota Carbon Ore



Progress and Current Status of Project – Lignite Feedstock – Modes of Occurrence

MTI 21-1584 Lignite Associated Sample

- Ga and Ge both present
- Minerals – mixed iron magnesium -rich aluminosilicates
- Mineral – pyrite oxidation product – gypsum/aluminosilicate
- Other elements – Ni, Cu, Zn, Ba



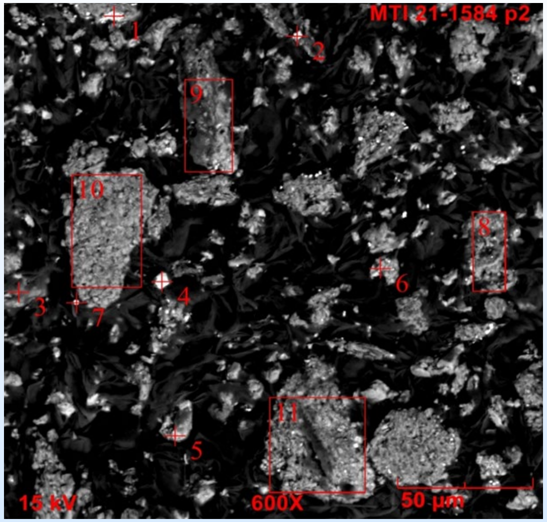
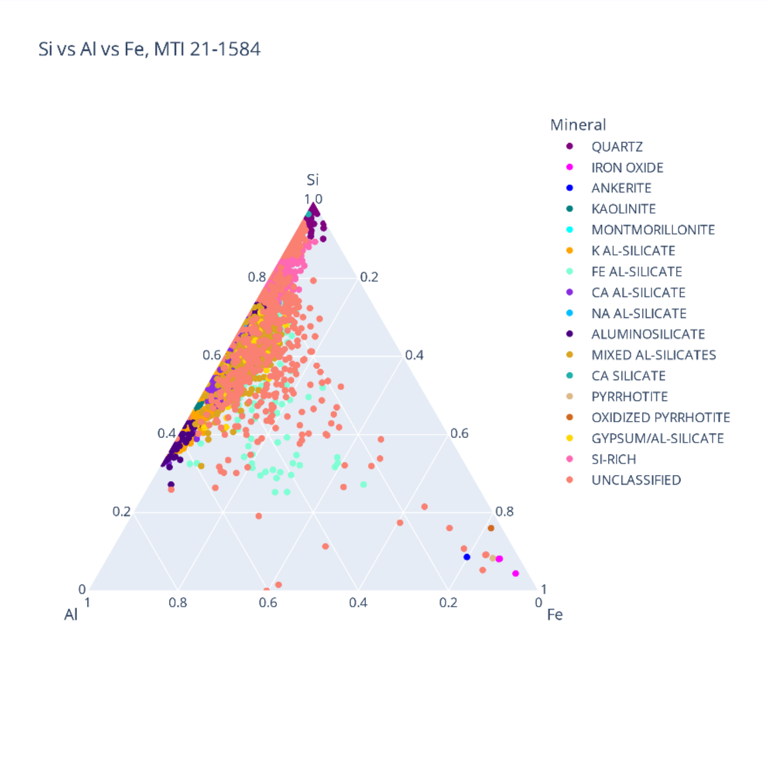
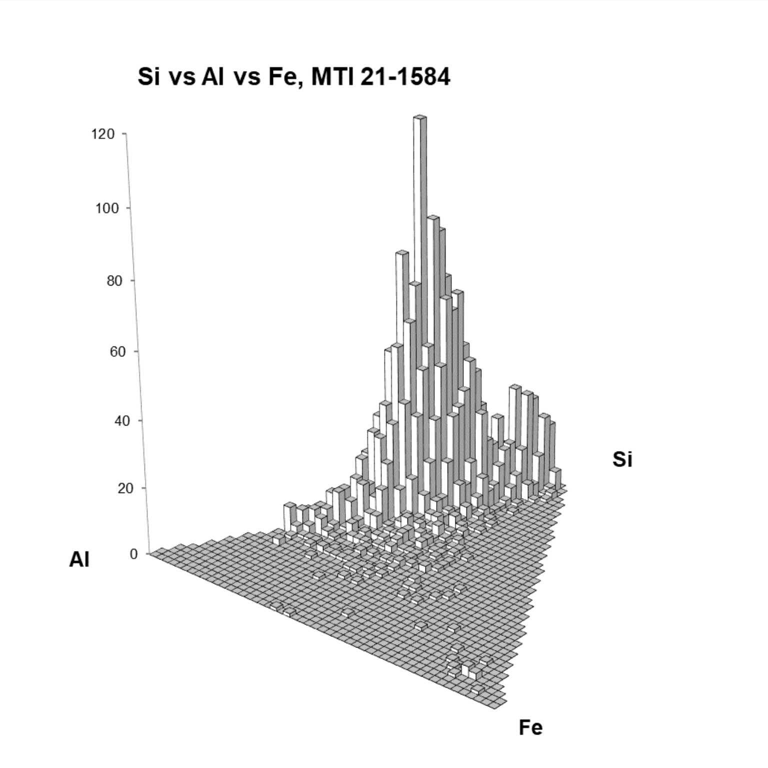


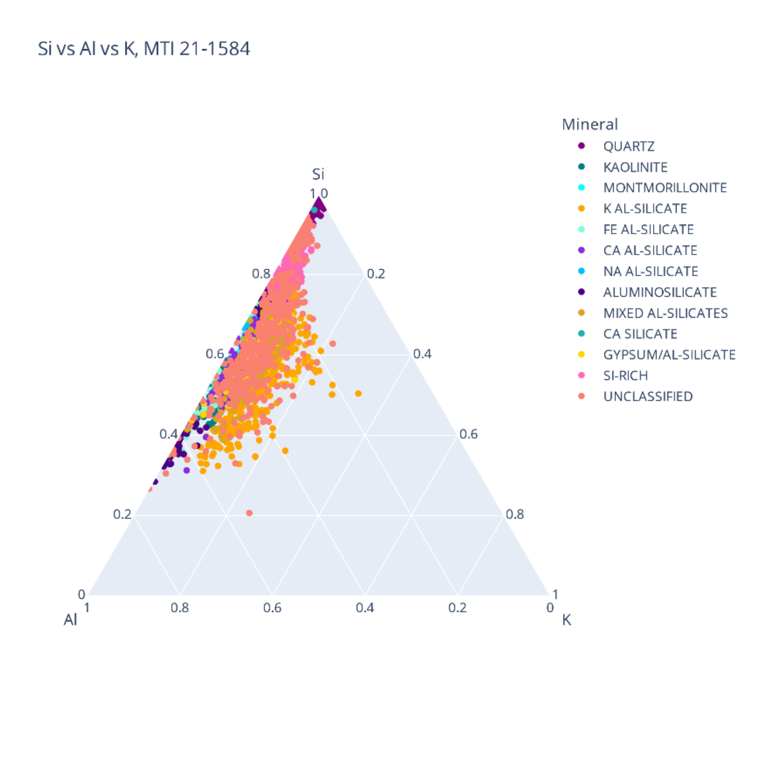
Fig.	Pt.	Description	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	Cu	Zn	Ga	Ge	Ba	O
1	1	Bright particle	2.0	5.7	7.1	12.9	2.0	24.6	1.4	18.8	6.3	2.2	0.4	0.3	0.9	0.4	0.6	0.8	13.3
	2	Bright particle	0.1	1.0	14.1	54.3	0.3	5.0	7.3	2.9	0.1	10.6	0.2	0.2	0.5	0.5	0.8	0.6	0.9
	3	Medium gray particle	0.9	11.6	18.0	23.8	2.8	2.9	1.5	10.8	0.0	4.3	0.8	2.2	2.8	3.3	4.8	5.1	3.1
	4	Dark particle	2.8	4.9	2.0	8.6	0.0	15.3	0.4	11.1	1.6	2.5	0.1	0.1	0.9	0.2	0.3	0.3	48.7
	5	Gray matrix	0.3	1.8	14.7	52.3	0.0	3.7	7.4	3.9	1.0	6.0	0.1	0.3	0.2	0.4	1.3	0.7	5.5
	6	Bright inclusion	0.5	7.3	18.5	41.3	3.3	2.5	4.3	2.6	0.1	4.3	0.8	0.5	1.3	3.4	4.0	1.4	2.3
	7	Gray matrix	0.0	9.3	9.9	19.4	0.3	0.7	1.1	2.6	0.0	11.6	2.9	3.1	3.5	7.5	11.0	7.0	5.2
	8	Area Scan	0.3	3.7	11.8	38.5	0.0	0.5	3.0	6.1	0.4	3.6	0.1	0.1	0.3	0.3	0.4	0.3	32.6
	9	Area Scan	0.6	2.0	12.7	35.2	0.0	2.0	3.8	3.6	0.5	2.9	0.1	0.1	0.3	0.3	0.5	0.0	35.2
	10	Area Scan	0.3	2.2	10.4	38.3	0.0	1.6	3.1	5.7	0.3	3.5	0.1	0.0	0.2	0.3	0.2	0.1	33.8
2	1	Bright particle	0.2	0.7	4.5	13.4	0.0	38.1	1.3	0.8	0.0	33.0	0.0	0.0	0.1	0.1	0.3	0.2	7.2
	2	Bright particle	0.1	0.2	0.5	1.1	0.1	52.7	0.1	0.3	0.0	39.0	0.0	0.1	0.1	0.0	0.2	0.3	5.2
	3	Medium gray particle	0.2	2.6	14.9	61.9	0.0	0.3	6.2	3.7	0.3	4.4	0.3	0.2	0.2	0.4	0.6	0.5	3.2
	4	Bright particle	0.1	0.2	0.3	0.8	0.1	53.2	0.1	0.2	0.0	39.7	0.0	0.1	0.0	0.0	0.2	0.2	4.7
	5	Light gray particle	0.0	13.2	1.2	2.6	0.0	0.0	0.4	33.2	0.0	4.4	0.0	0.0	0.1	0.2	0.2	0.0	44.3
	6	Light gray particle	0.3	5.4	13.4	30.1	0.0	0.1	3.4	11.1	0.2	4.7	0.1	0.1	0.1	0.2	0.4	0.1	30.2
	7	Bright particle	0.0	0.2	0.7	1.8	0.1	44.3	0.2	0.3	0.0	49.4	0.0	0.1	0.1	0.2	0.1	0.1	2.4
	8	Area Scan	0.2	4.5	12.5	35.5	0.0	1.8	3.7	7.5	0.3	4.1	0.0	0.1	0.1	0.2	0.2	0.2	29.0
	9	Area Scan	0.9	2.2	11.2	33.5	0.0	4.4	3.1	3.3	0.9	3.2	0.0	0.2	0.9	0.2	0.3	0.2	35.5
	10	Area Scan	0.3	1.8	15.3	42.9	0.0	0.0	4.7	0.5	0.4	3.4	0.1	0.0	0.4	0.2	0.3	0.2	29.5
	11	Area Scan	0.4	2.2	13.0	37.7	0.0	1.6	3.9	3.0	0.4	3.7	0.1	0.1	0.7	0.2	0.2	0.1	32.6

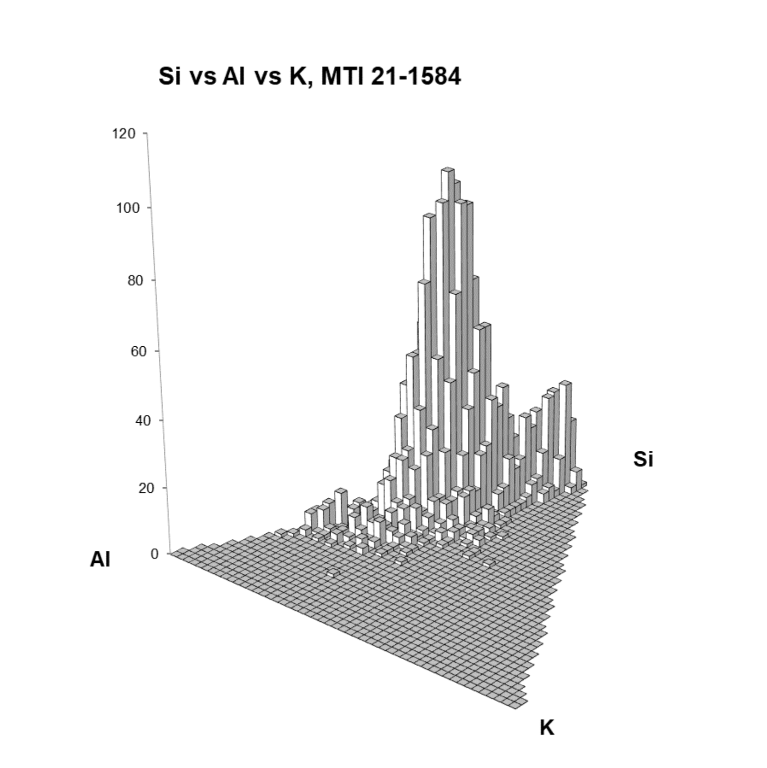
Progress and Current Status of Project – Lignite Feedstock – Modes of Occurrence- CCSEM – Particle Typing



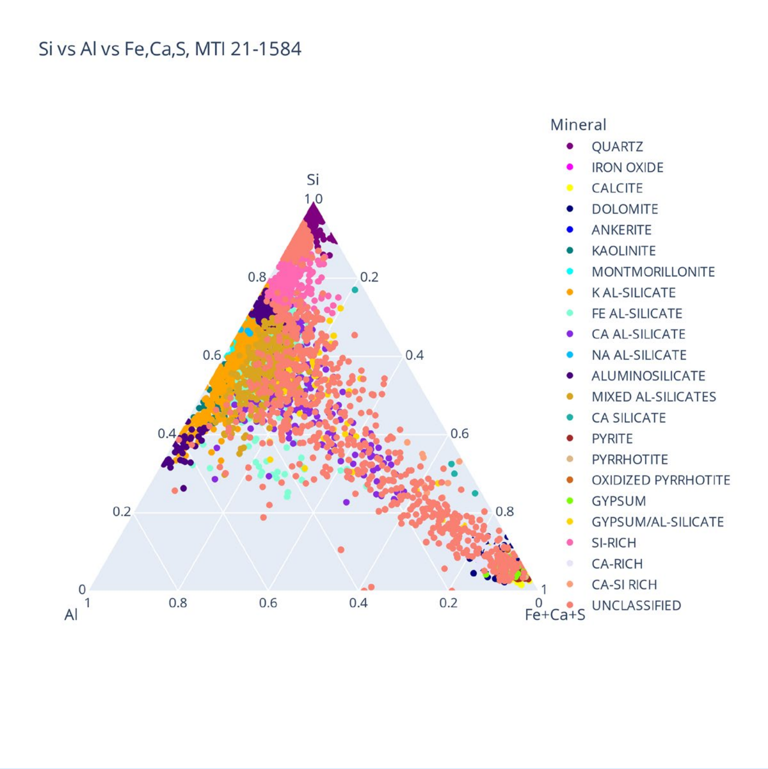


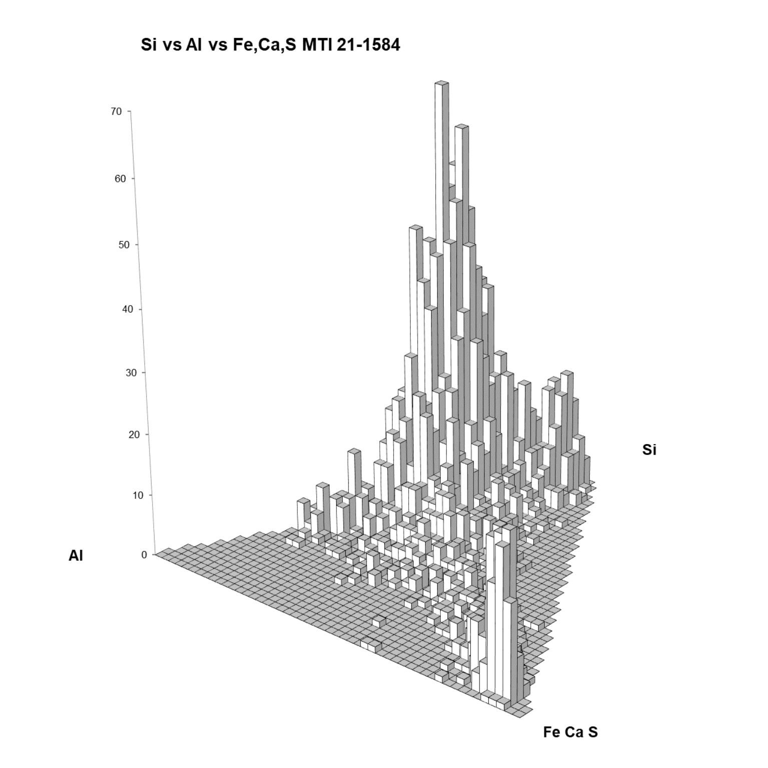
Progress and Current Status of Project – Lignite Feedstock – Modes of Occurrence





Progress and Current Status of Project – Lignite Feedstock – Modes of Occurrence





Progress and Current Status of Project – Lignite Feedstock – Extractable Ge and Ga

- High ash
  - Acid solubility – 20 to 40%
- Low ash
  - Acid solubility -- 40 to 60%
- Additional samples for testing – NACC offered samples of DryFine™ product and reject stream

Progress and Current Status of Project

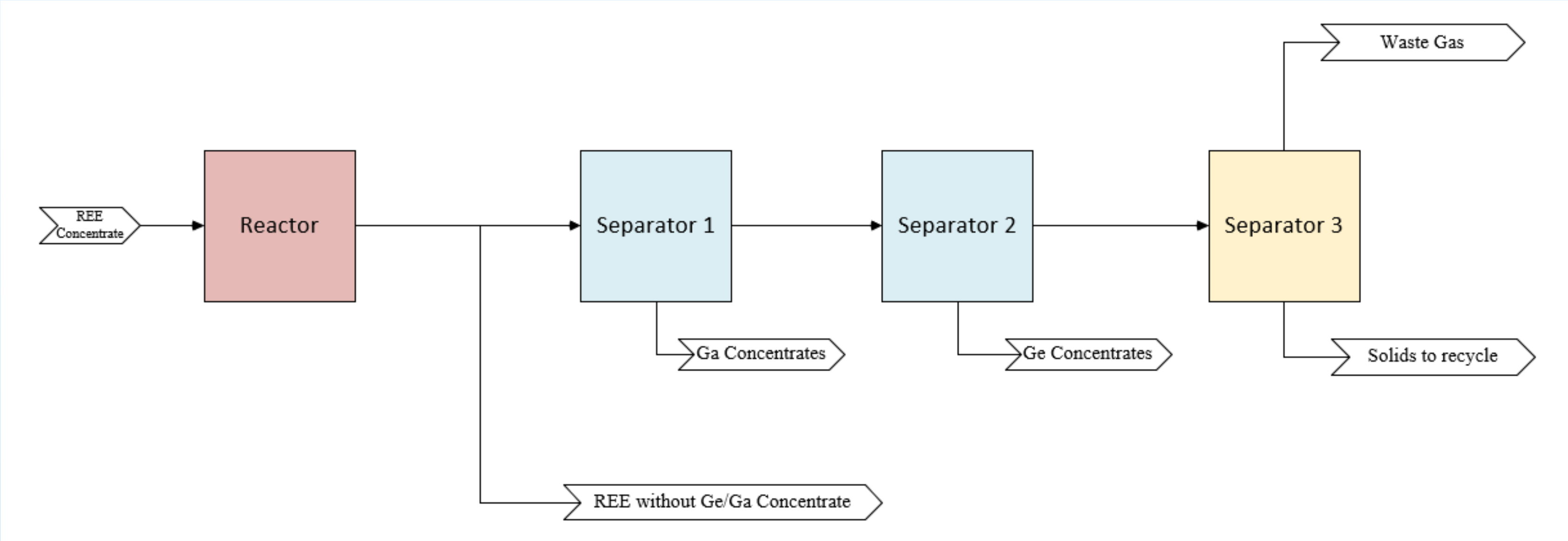
Task 3.0 – Literature Review and Identify Industrial Applications

- Review of industrial applications has been completed
- Example - Lattice Materials applications are summarized.

Progress and Current Status of Project – Task 4. Product Testing and Analysis

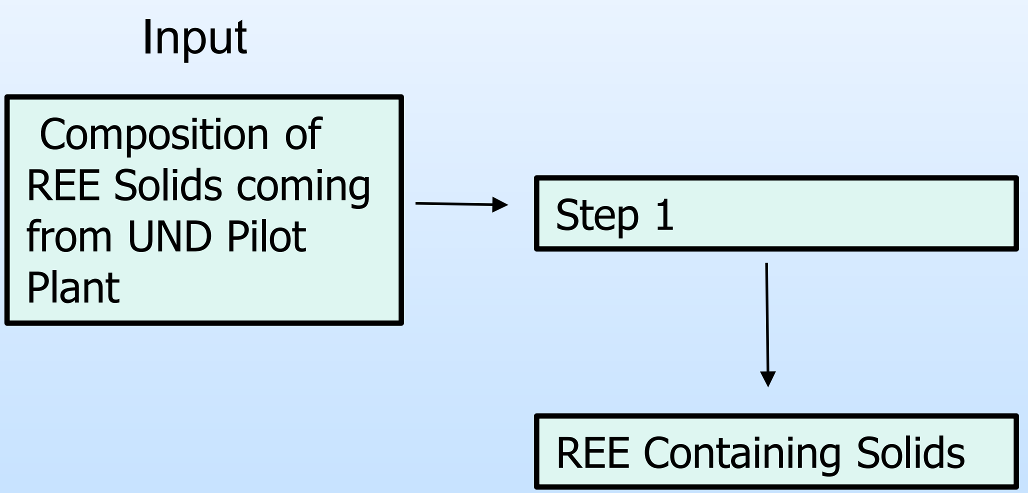
Process flow diagrams (PFDs) are being developed to produce Ge and Ga in forms that are required to produce end products from the feedstock materials used in this project. The production route for the refined metal, salt, or oxide as required by the end user will be developed.

Processing Step 1



Progress and Current Status of Project – Task 4. Product Testing and Analysis

Modeling: Step1 Separation from MREE Stream Composition



Compound	wt%
GeO	15.045
Ga2O	10.324
Ga2O3	3.900
Ga2S	0.643
GeS	0.309
Ga	0.009
GaH	0.001
K	1.497
H2O	13.556
NaOH	4.451
Na	13.440
NaH	0.056
(NaOH)2	0.031
Na2	0.061
CaO	0.510
BaOH	0.120

Progress and Current Status of Project – Task 4. Product Testing and Analysis

Modeling: Step 2 Ga and Ge Separation

Stream from Step 1 → Ga - Stream → Ge - Stream

Compound	wt%
Ga2O3	80.812
NaOH	18.342
Na2S	0.830
La2O3	0.003
Nd2O3	0.0001
CaO	0.008
BaO	0.005

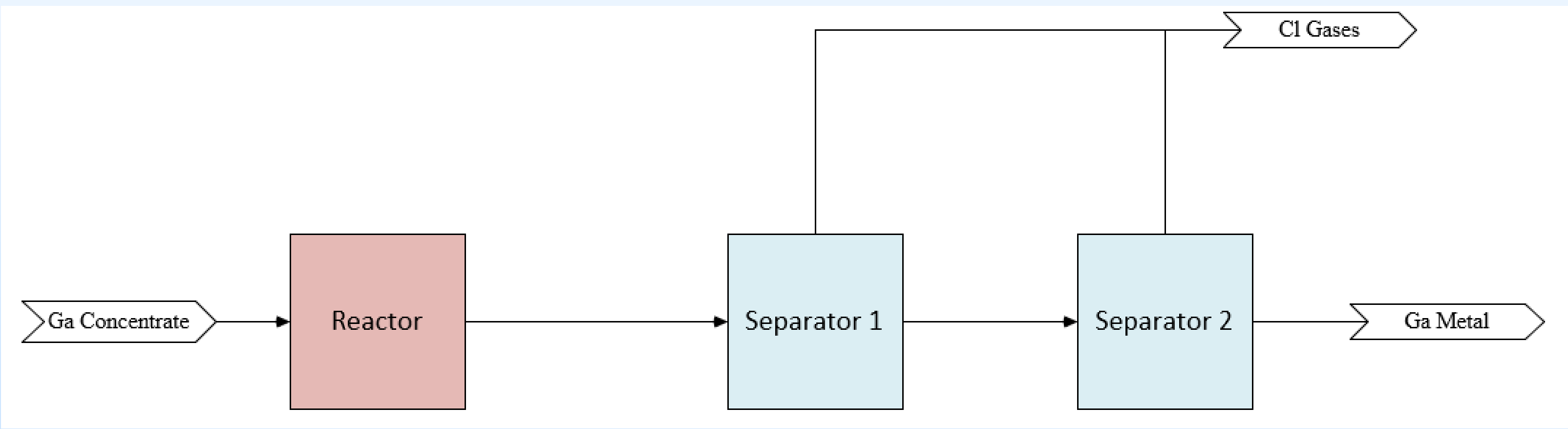
Gallium Refining

Compound	wt%
GeO	88.930
Ga2O3	0.265
KOH	6.397
NaOH	3.805
Na2S	0.584
La2O3	0.008
Nd2O3	0.0002
CaO	0.007
BaO	0.003

Germanium Refining

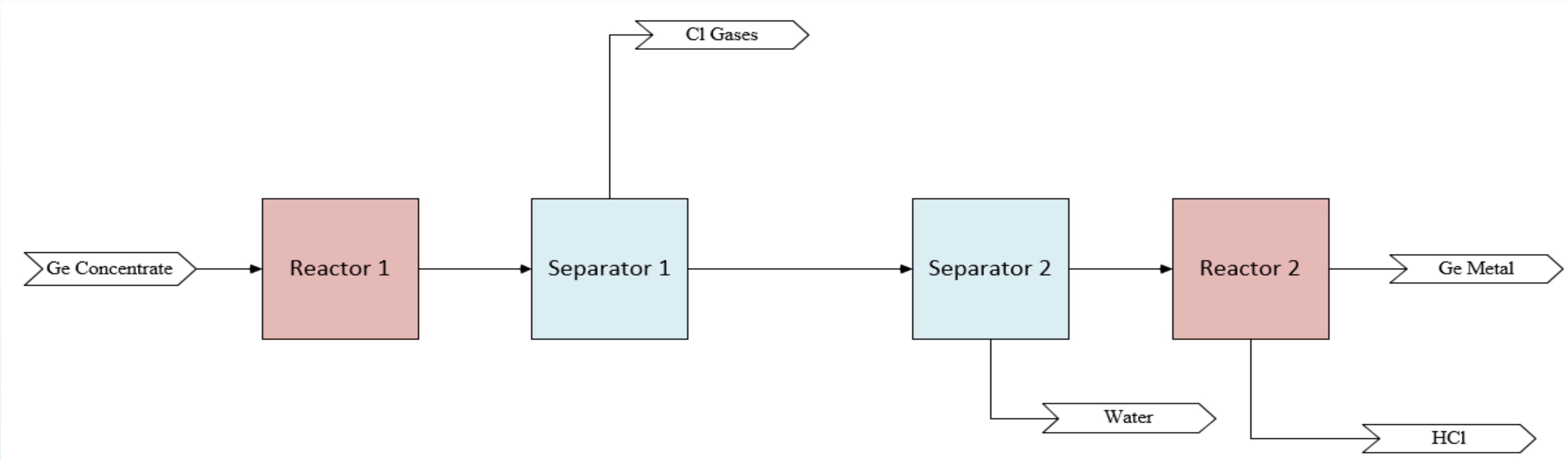
Progress and Current Status of Project – Task 4. Product Testing and Analysis

Processing Step 3 for Ga Metal (99.9%)



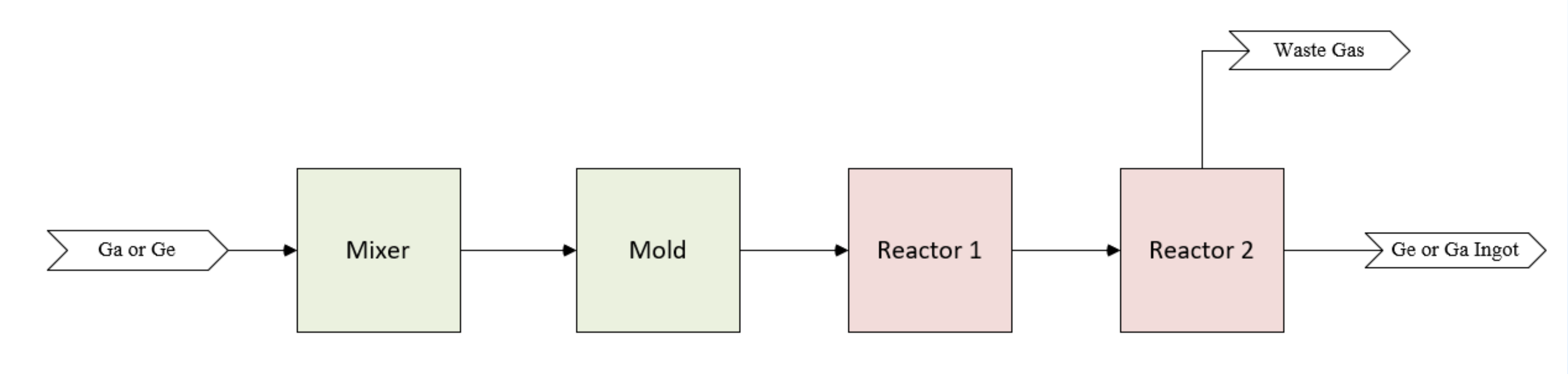
Progress and Current Status of Project – Task 4. Product Testing and Analysis

Processing Step 3 for Ge Metal (99.9%)



Progress and Current Status of Project – Task 4. Product Testing and Analysis

Processing Step 4 for High Purity Metal (99.9999%)



Plans for future testing/development/ commercialization

- Current Project
  - -Characterize feedstocks behavior on bench unit
  - -Finalize process flow diagrams
  - -Teaming plan for next phase
  - -Research plan for next phase
  - -Market analysis
- Next Project – Pilot System
  - -Develop PIDs
  - -Purchase, fabricate and install technology into University of North Dakota REE Pilot Plant
- Future Projects
  - -Scale technology upwards to commercial 1-3 ton/day critical mineral facility

Summary Slide

- Feedstock characterization
  - MREE concentrate from UND bench system has low levels of impurities that impact the properties of Ge and Ga Concentrates
  - Variable lignite carbon ore feedstock – range of extractability
- Product purity target is 99.9999% - meet Lattice materials needs
- Process flow diagrams have been drafted and will be finalized
- Testing of MREE concentrate from pilot will be used to corroborate modeling

Questions

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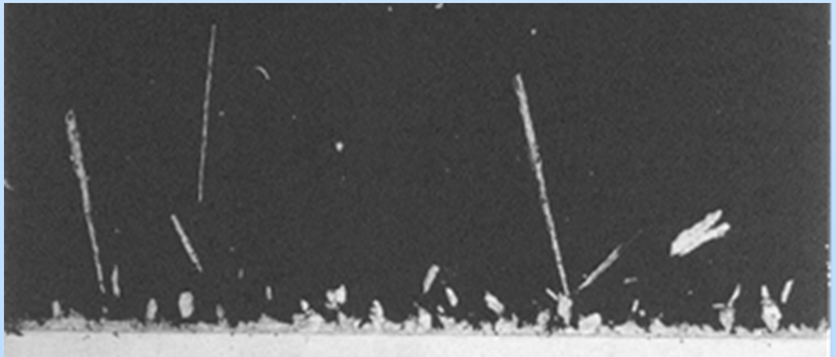
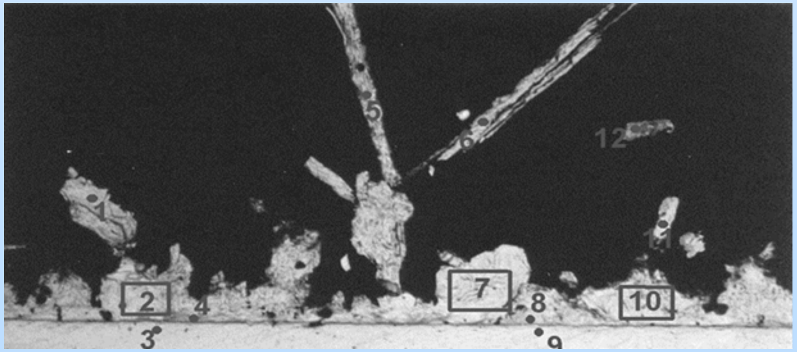
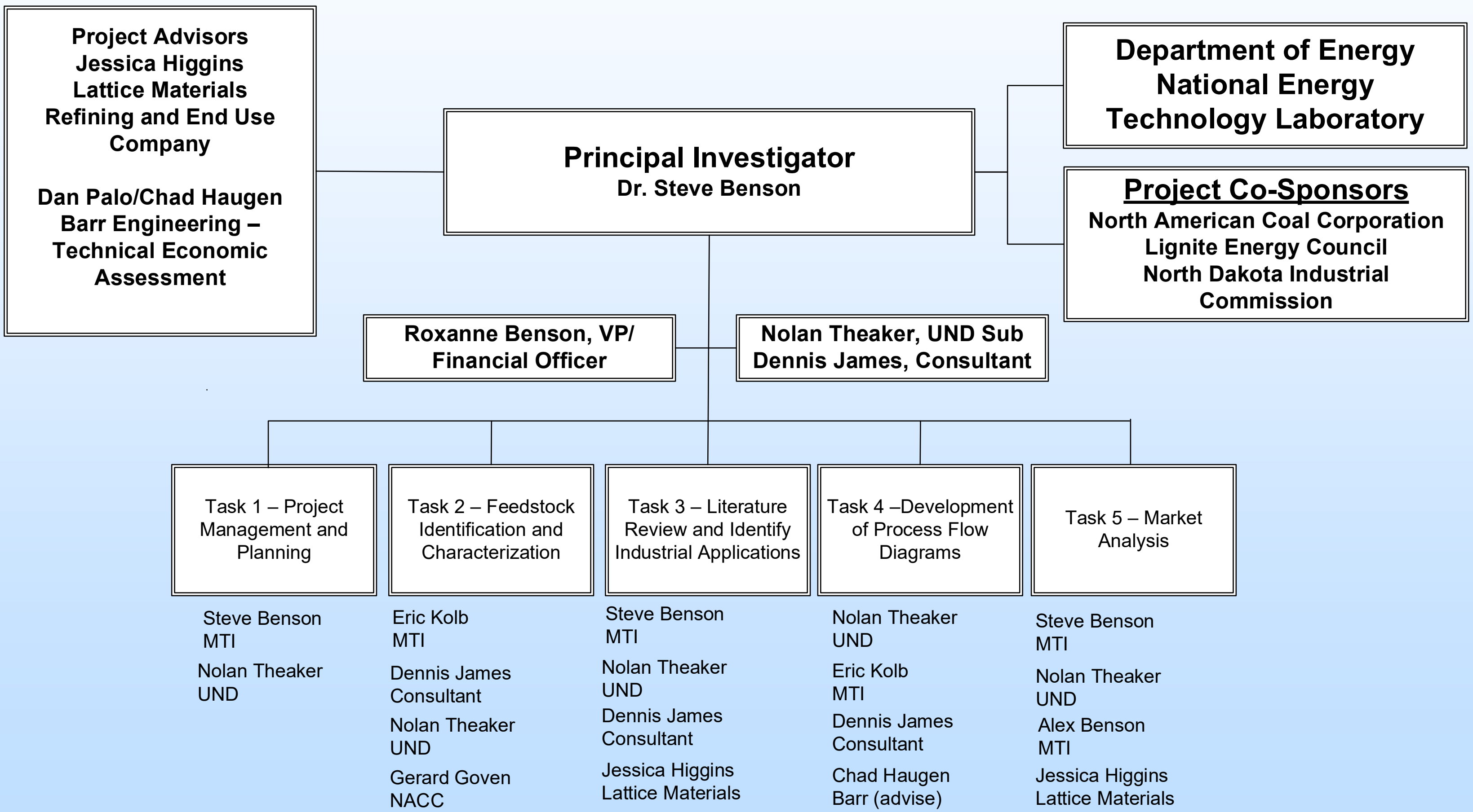
MICROBEAM TECHNOLOGIES, INC.



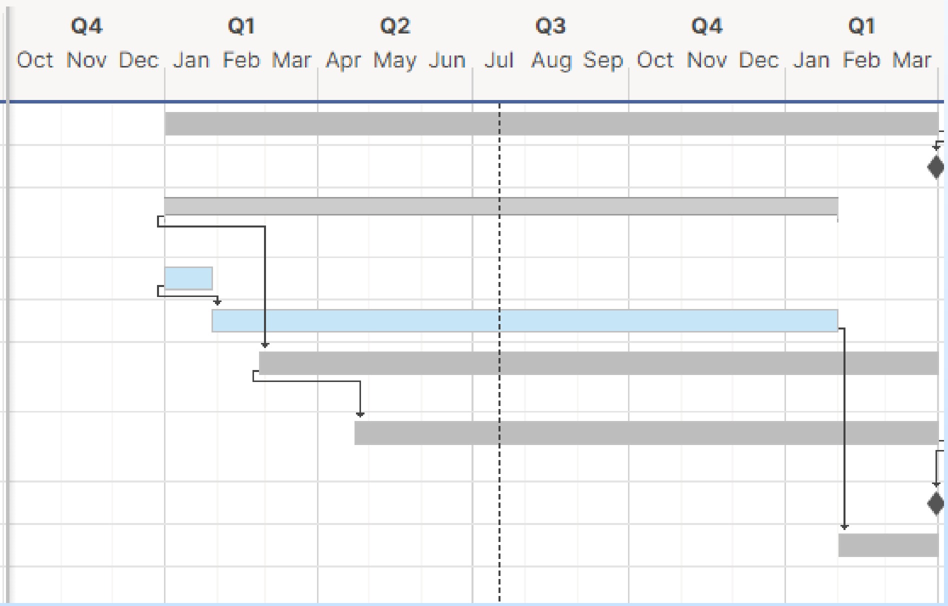


Organization Chart



Gantt Chart

Task Name	Duration	Start	Finish
Task 1. Project Management and Planning	326d	01/01/22	03/31/23
Phase 1 Technical Report	~0	03/31/23	03/31/23
Task 2. Feedstock Identification and Characterization	283d	12/31/21	01/31/23
Feedstock Identification	21d	12/31/21	01/28/22
Feedstock Characterization	263d	01/28/22	01/31/23
Task 3. Literature Review and Identify Industrial Applications	286d	02/25/22	03/31/23
Task 4. Development of Process Flow Diagrams	246d	04/22/22	03/31/23
Deliverable - Process Flow Diagram	~0	03/31/23	03/31/23
Task 5. Market Analysis	43d	02/01/23	03/31/23



Overall Project Objective

- This effort is aimed at achieving major (>50%) domestic production of these energy-critical elements utilizing easily accessible (usable within 4-5 years) resources.