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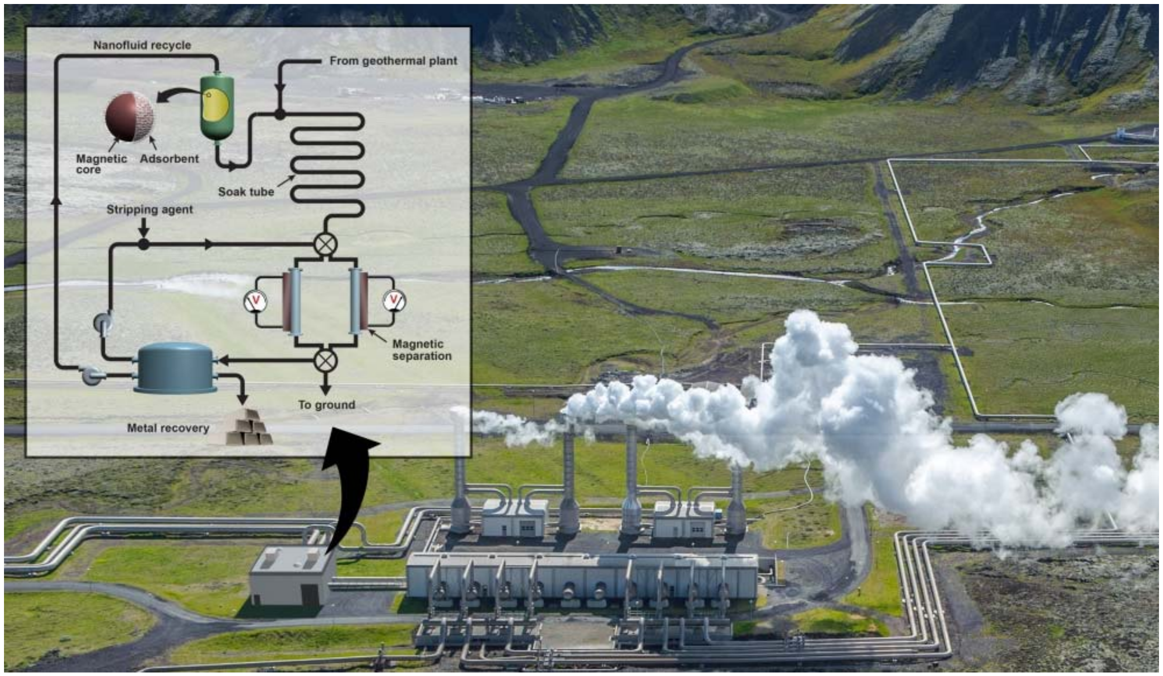
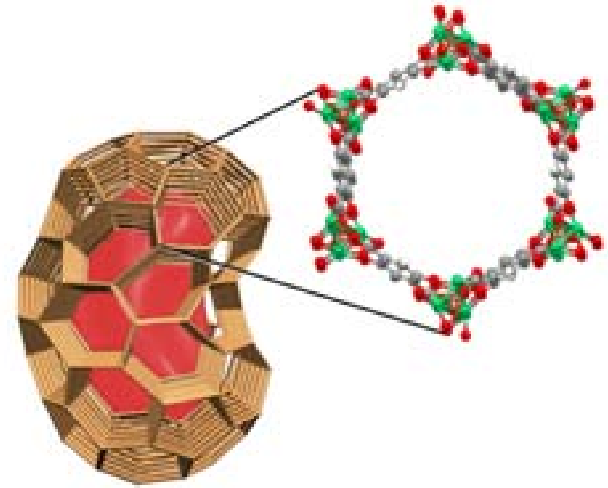




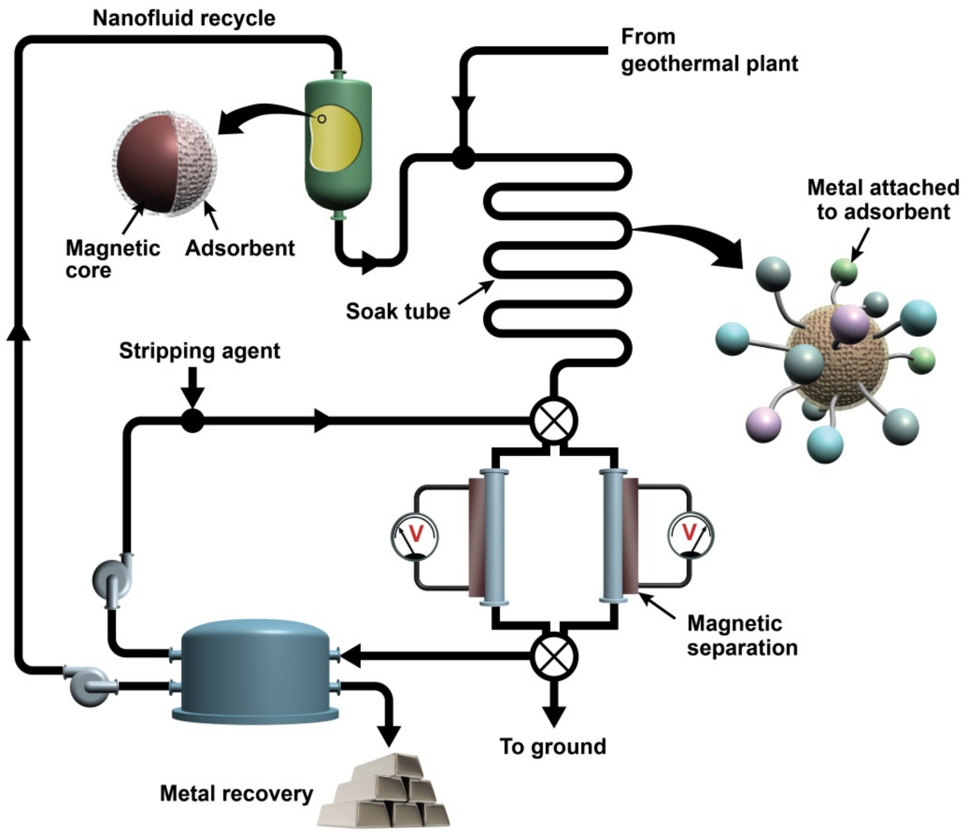
Demonstrating a Magnetic Nanofluid Separation Process for Rare Earth Extraction from Geothermal Fluids

B. Peter McGrail
Pacific Northwest National Laboratory

Mineral Recovery

Relevance to Industry Needs and GTO Objectives

- REEs are critical materials central to many industrial, commercial, and military applications
- World market supply is presently >90% sourced from China
- Opportunity to provide value add revenue stream for geothermal plants worldwide
- Nanoparticles provide high surface area and excess of chelating sites for REE extraction at low (ppb) concentrations
- Use of nanofluid avoids packed beds with large pressure drop, size, capital, and operating costs
- Magnetic core allows for simple and low energy use separator
- Achieve 90% REE removal efficiency at a fraction of production costs using conventional technologies



Scientific/Technical Approach

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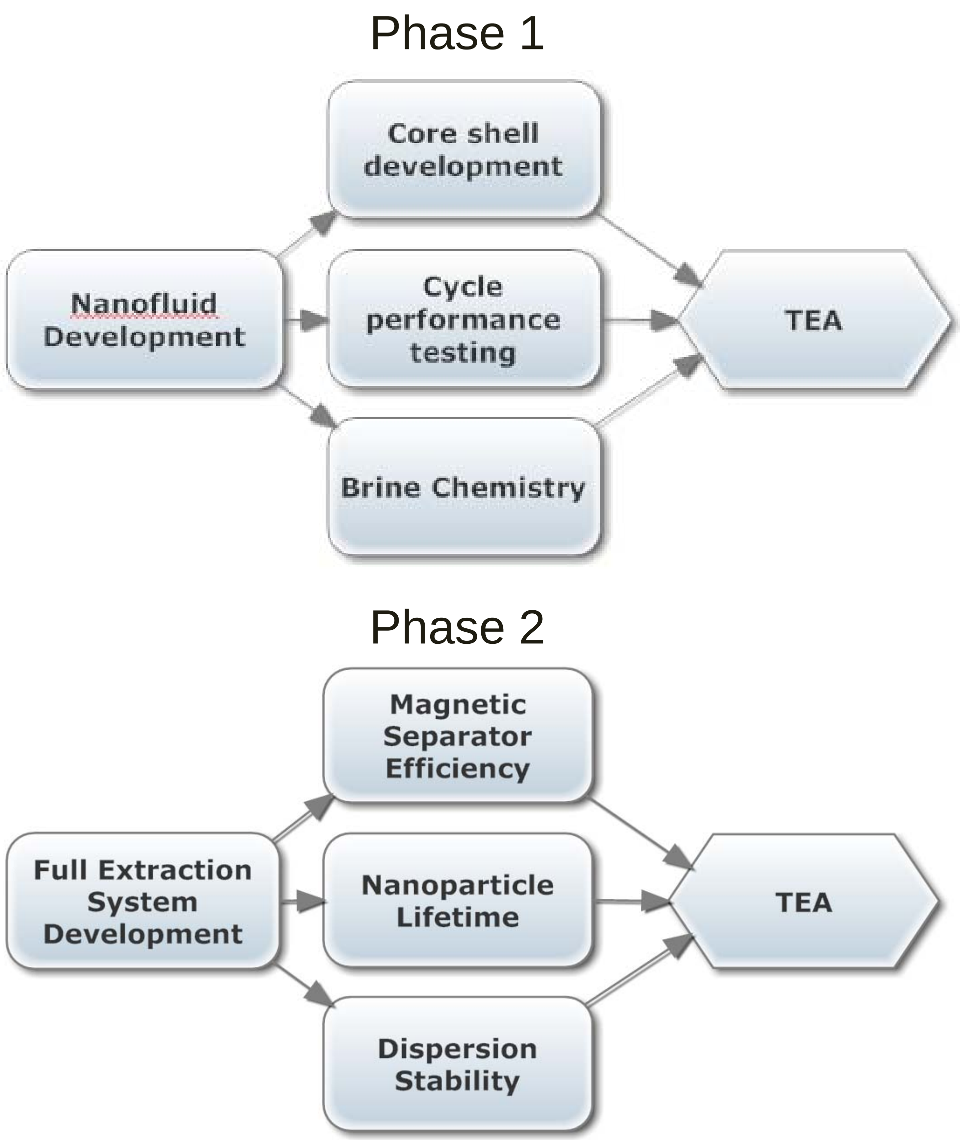
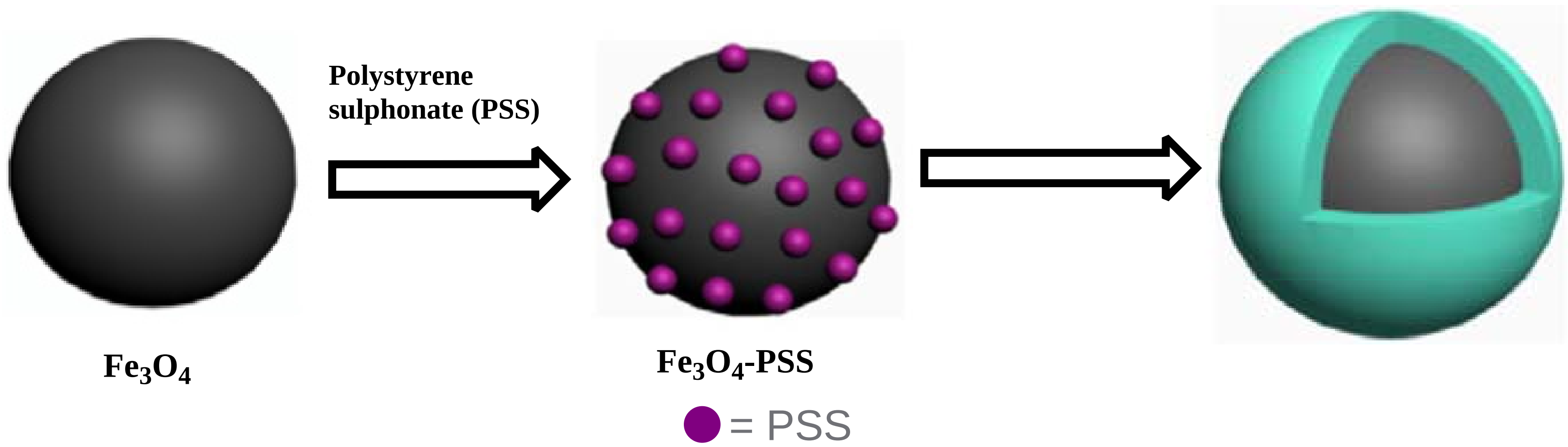
- Phase 1 produced effective core-shell REE sorbents for transition into Phase 2 testing
- Focus of Phase 2 is on full system cycle testing to support design and detailed cost analysis for commercial-scale implementation
  - Effectiveness of magnetic separator
  - Recycle performance of nanoparticle sorbent
- Techno-economic analysis updated throughout project for process assessment and go/no-go decision point at end of Phase 2 BP1 (scheduled for January 2018)



Core-Shell Nanoparticle Synthesis



Controlling the MOF thickness:

MOF@Magnetic Core	Fe_3O_4	In salt	IMD
F-InMOF-1@Fe_3O_4	1	1	4
F-InMOF-2@Fe_3O_4	1	1	3
F-InMOF-4@Fe_3O_4	1	1	2
F-InMOF-6@Fe_3O_4	1	1	1

F-InMOF@Fe_3O_4 Sample Characterization

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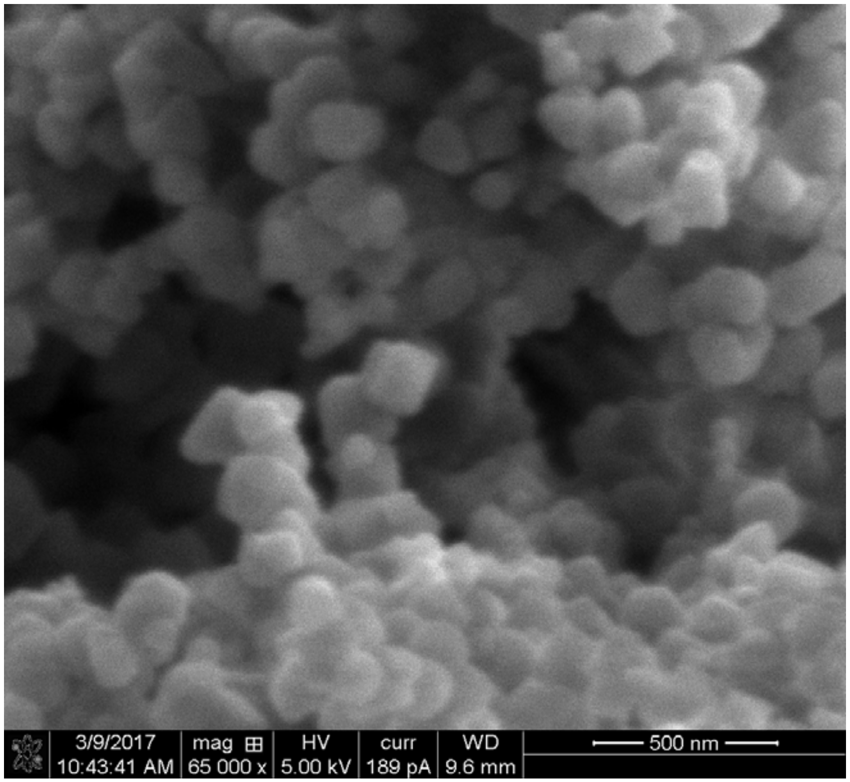
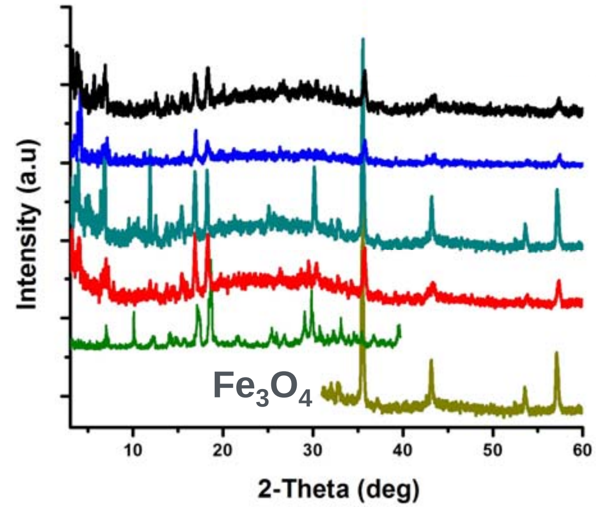
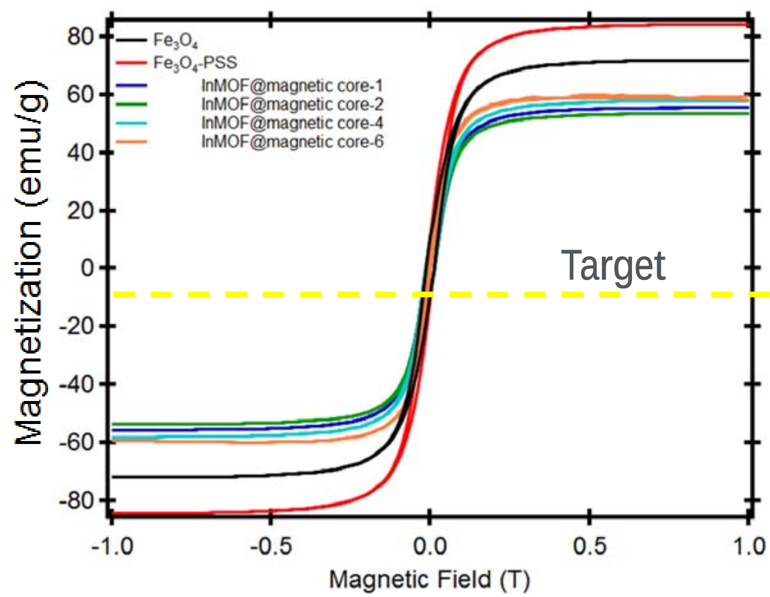
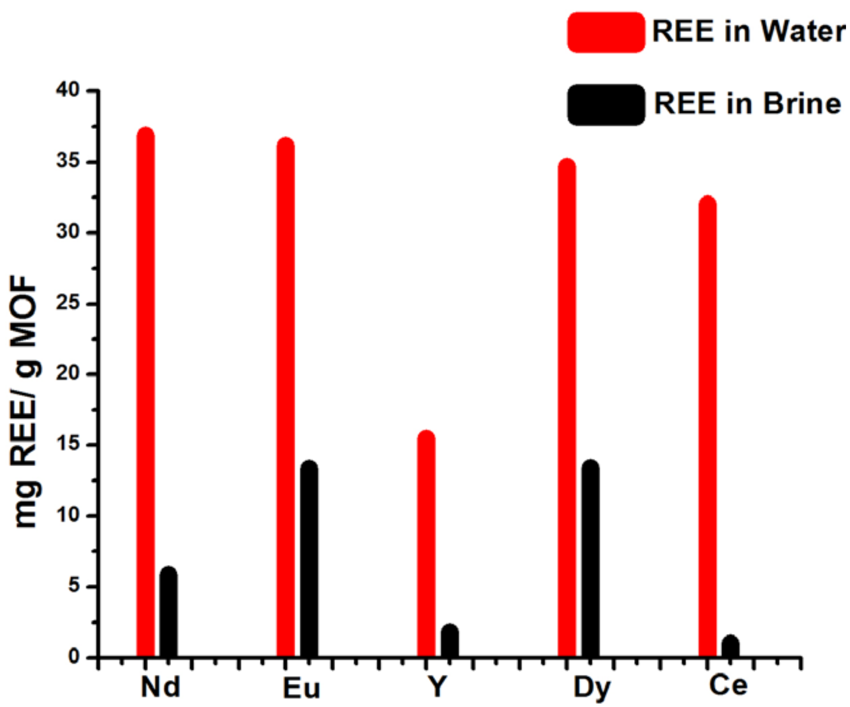




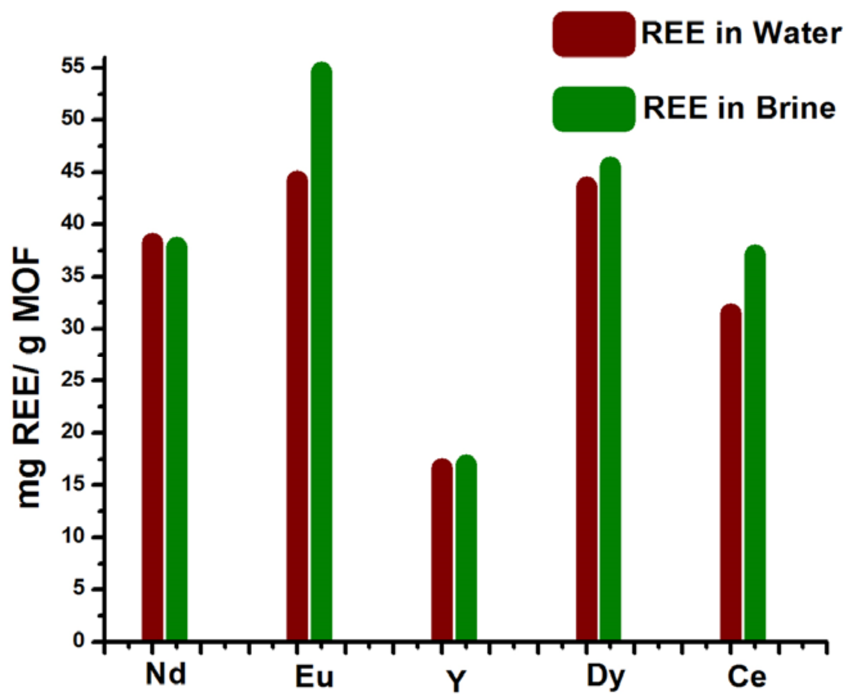


Sorption Performance

MIL-101 $SO_3@Fe_3O_4$



F-InMOF@Fe3O4



Salton Sea Case Study

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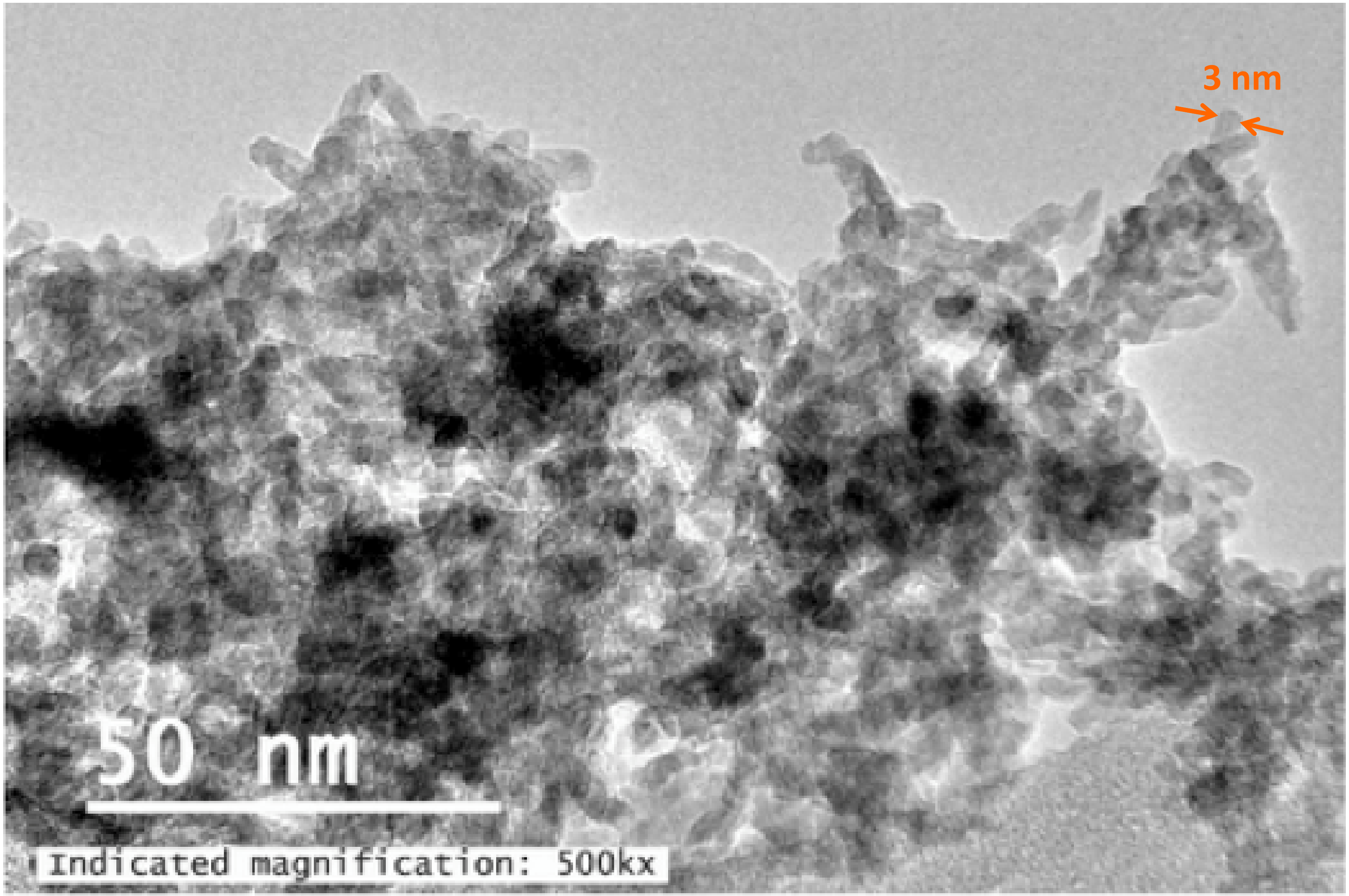
- PI was contacted by Principals engaged in Salton Sea geothermal project in January 2017
  - Found out about us through media reports
  - Interested in understanding technology potential for their operations
- 1 L brine sample sent to PNNL and has been analyzed
  - ICP-OES shows potentially attractive Mn content (2300 ppm)
  - ICP-MS shows 160 ppb Eu -> 10X values we are using in our TEA
  - Comprehensive nanoparticle analysis completed by Mike Hochella (VT)

Brine sample taken from well head at Salton Sea geothermal project

Akaganeite in Salton Sea geothermal brine



Split Sample Analysis

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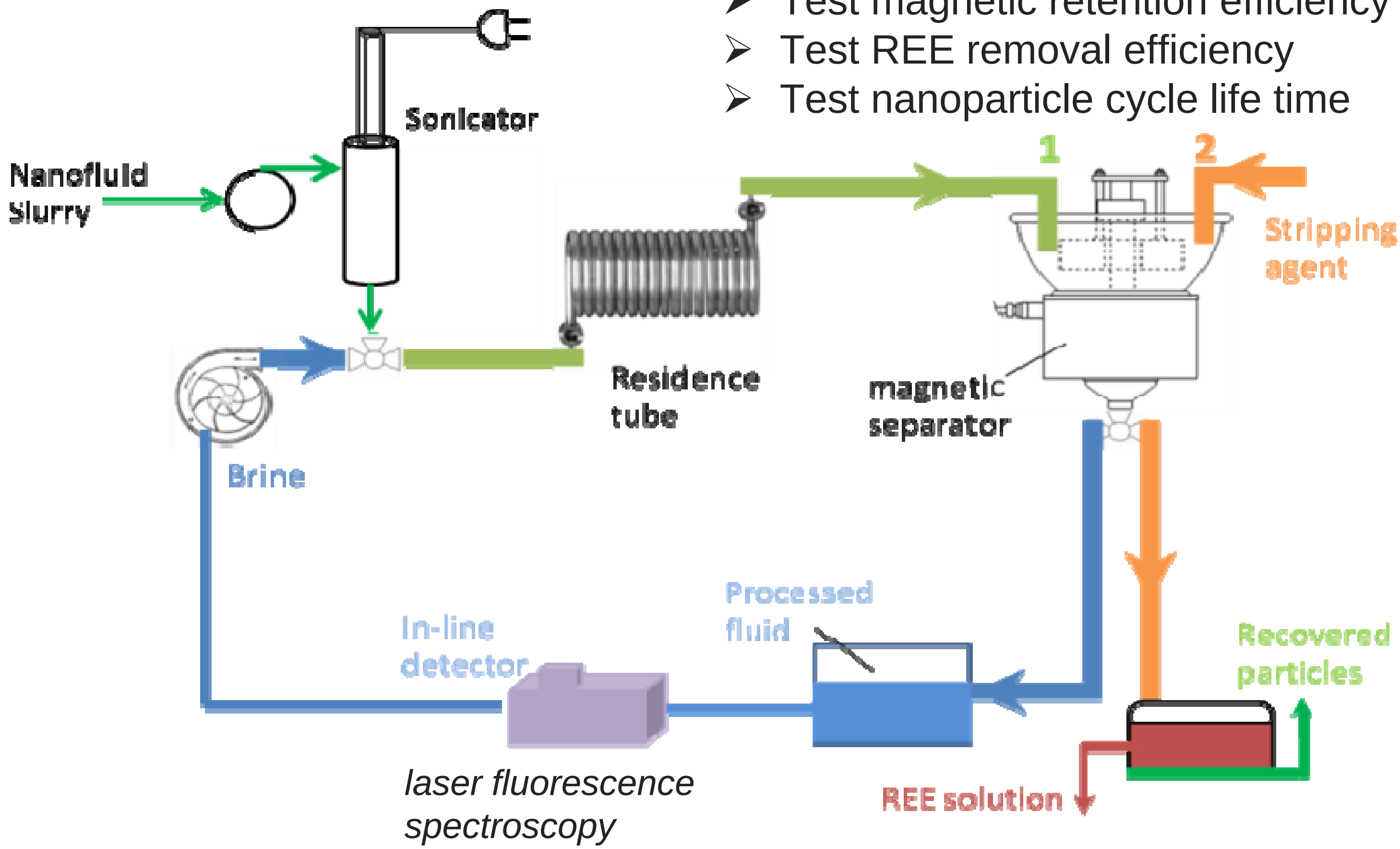
ICP-MS / ICP-AES

		PNNL	Clear 1	Clear 1	Clear 2	supernatant 1	supernatant 1	supernatant 2	sediment1	sediment 1	sediment2	Mixture
	Al	1348	0.49		0.94	0.44		0.63	0.04		0	1.61
	Na	70640	52955		51707	52236		51090	600		714	69570
	Cu	3.45	3.6		2.8	2.9		2.7	0.03		0.06	2.8
	Li	337.2										
	K	30940	21079		19811	20690		19637	227		287	20686
PPM	Ca	43920	34560		32325	33955		32044	374		443	34010
	Mg	62.9	47.3		44.6	46.4		43.6	0.52		0.52	46.6
	Sr	1002	585		538	568		534	6.3		9.6	614
	Mn	2283.3	1816	1437	1706	1779	1417	1695	19.6	18.9	27.1	1781
	Zn	638	655		621	646		605	7.3		12.9	643
	Cd	0.45	0.01		0.05	0.01		0.06	0		0	3.01
	Fe	1978	1400	1117	1243	1358	1092	1234	25.7	24.8	19.6	2606
	Dy	11.2										
	Eu	160.8	10.3	<11	8	10.8	<11	8	0.13	<11	0.21	208.9
PPB	Ce	22.2	4.27	<19	6.71	4.98	<19	6.71	0.1	<19	0.03	8.42
	Y	43.3										
	Nd	11.7	0.86	<19	0	0.83	<19	0	0	<19	0.01	1.69

Clear 1:	Top juice of brine sample with seating time t1
Clear 2:	Top juice of brine sample with seating time t2
supernatant 1:	Supernatant of Clear 1 after 3 hours centrifugation at 200,000 xg
supernatant 2:	Supernatant of Clear 2 after 48 hours centrifugation at 200,000 xg
sediment 1:	sediment (including small amount of supernatant 1) of Clear 1 after 3 hours centrifugation at 200,000 xg
sediment 2:	sediment (including small amount of supernatant 1) of Clear 2 after 48 hours centrifugation at 200,000 xg
Mixture:	A mixture of brine and sediment after shaking the brine bottle, undisolved part in 5% HNO3 was filtered by 0.45 um

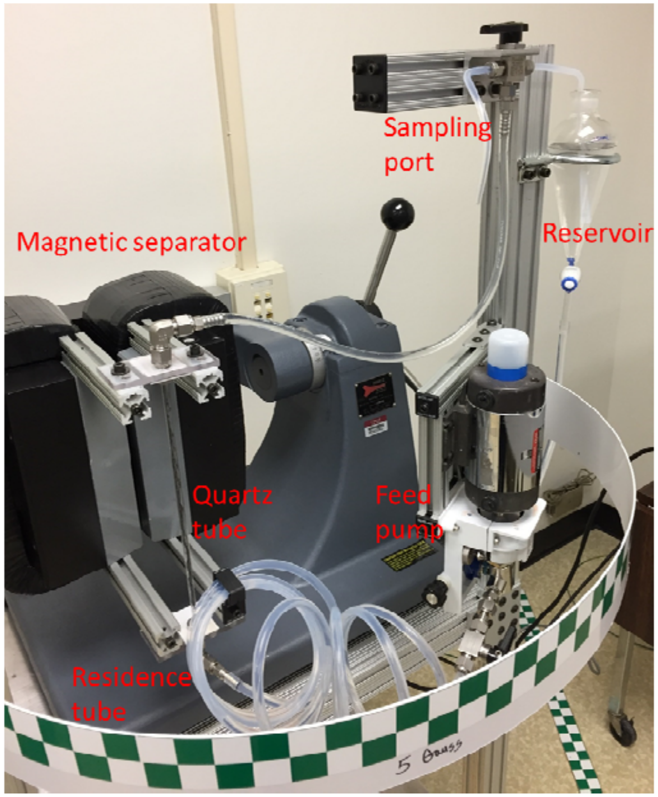
Magnetic Separator Test Loop System

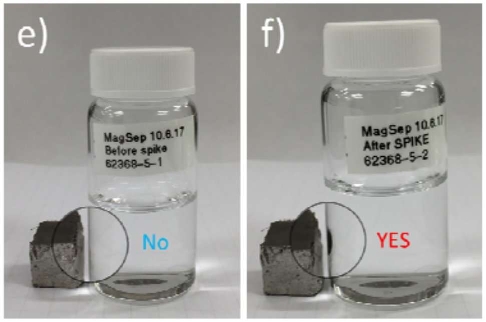
- Demonstrate continuous process
- Test magnetic retention efficiency
- Test REE removal efficiency
- Test nanoparticle cycle life time

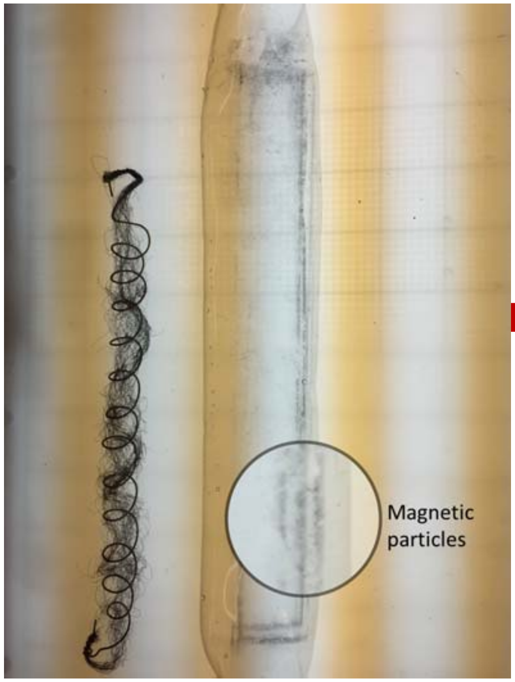


Key variables: flow rate (velocity and residence time in the separator), temperature
Key results: the concentration change of nanoparticles exiting the separator

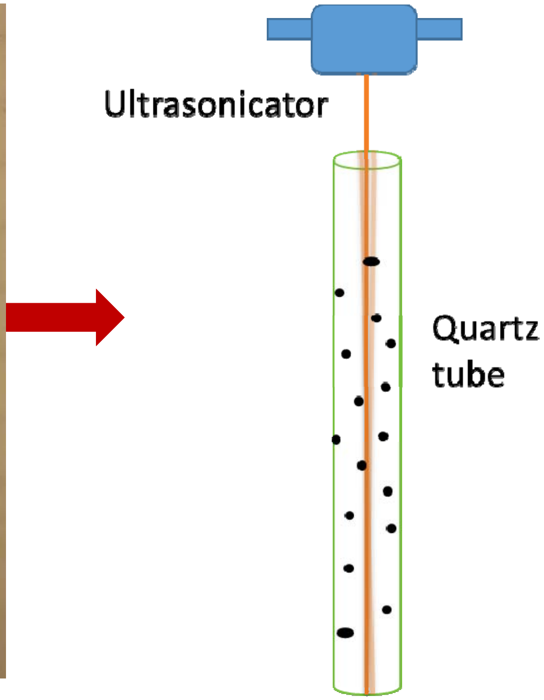
Magnetic Separator Test Loop System







Compaction of the magnetic particles on plastic tube walls under 2 Tesla field strength resulted in poor re-dispersion



Re-dispersion improved significantly in rigid quartz tube. Addition of sonicator and reduced magnetic field strength will be investigated to realize reversible capture of the magnetic particles.

Techno-economic analysis

- Milestone 4.1 Select external metrics of REE concentration and pricing and generate baseline parameters for IRR calculation.

Parameter		Ce	Dy	Eu	Nd	Y
Recovery Efficiency	90%					
Brine Flow Rate (gal/min)*	6800					
Metal Concentration in Brine (ppb)		384	27	7	167	300
Metal Production Rate (kg/yr)	11837	5136	361	94	2234	4012
Metal Sales Price $/kg		10	485	1038	79	54

The market prices for REEs (Free on Board price from China) were estimated using the average prices in 2016 and early 2017. The concentrations of REEs were updated using the average of estimated concentrations from both the crust and chondrite. The brine production rate was estimated based on a 20 MW geothermal power plant.

Techno-economic analysis

- Milestone 4.2 Update techno-economic analysis of nanofluid extraction system based on test loop data on REE extraction efficiency and updated MOF sorbent costs.

Reaction	Yield
Fe_3O_4 synthesis	90%
MOF synthesis	60%
DETA modified MOF@Fe_3O_4	75%

- The IRR was updated to reflect the new cost of adsorbents and updated equipment cost.
- The IRR is still above 15% with the assumptions in the calculation model for the DETA modified In-MOF. The yields can be improved in the future.
- The lifetime of the adsorbent and the extraction efficiency in the test loop will be evaluated in the near future to update the IRR to complete the M4.2.

Parameters				
FCI				$ 765,525
TCI				$ 972,217
Debt		45%		
Equity		55%		
Interest on debt		4.3%	Y2017	
Preferred dividend rate		0.00%		
Repayment term of debt		10	years	
Capital Expenditure Period		3	years	
completion in year	0	0%		
completion in year	1	10%		
completion in year	2	60%		
completion in year	3	30%		
completion in year	4	0%		
completion in year	5	0%		
Operation begins at year		4		
Operational Period		30	years	
Ramp Up Period				
capacity in year	4	100%		
capacity in year	5	100%		
capacity in year	6	100%		
Escalation of O&M, fuel, revs		3.00%		
Discount rate		10.00%		
Capital Cost Escalation prior to operation		0.397%		
Capital Depreciation period		20	years	
Depreciation X-declining balance		150%		
Corporate Tax Rate (fed+state)		38%		
Effective Annual Rate of Equity				
Cost of Capital				
Cost-Year Dollars		2015		
WACC		9.86%		
IRROE		**15.8%**		

DETA modified In-MOF

Technical Accomplishments and Progress

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SOPO Task #	Milestone/Deliverable Description	Original Planned Start Date	Original Planned Completion Date	Actual Completion Date	% Complete
1.1.1	Demonstrate attainment of nanoparticle magnetic saturation of 10 A m^2 kg^{-1} or greater.	1/5/2017	3/31/2017	2/28/2017	100%
1.2.1	Determine synthesis conditions required to produce core-shell sorbent particles	4/1/2017	6/31/2017	4/28/2017	100%
2.1.1	Nanofluid injector system keeps nanoparticle size distribution within ±25% of original distribution	7/1/2017	9/30/2017	9/30/2017	100%
2.2.1	Sorbent functionalized with polymer keeps nanoparticle size distribution within ±25% of original distribution in static tests	10/1/2016	12/31/2016	12/31/2016	100%
2.2.2	Upload data obtained under this task to the GDR per the DMP	10/1/2016	2/28/2017	4/30/2017	100%
3.1	Issue journal article on nanofluid extraction process	4/1/2017	06/31/2017	6/30/2017	100%
3.2	Nanoparticle lifetime projected at 3000 h or greater from cycle tests	7/1/2017	9/30/2017	11/30/2017	50%
4.1	Select external metrics of REE concentration and pricing and generate baseline parameters for IRR calculation	10/1/2016	12/31/2016	12/30/2016	100%
4.2	Update techno-economic analysis of nanofluid extraction system based on test loop data on REE extraction efficiency and updated MOF sorbent costs	7/1/2017	9/30/2017	11/30/2017	50%

Technical Accomplishments and Progress

- Presentations
  - Liu, J., P. K.Thallapally, B. P. McGrail, S. K. Nune, S. K. Elsaidi, D. Banerjee, Z. Nie, S. R. Jambovane, M. I. Nandasiri, and L. Kovarik, “Magnetic Nanofluid for Rare Earth Extraction from Geothermal Fluids,” AIChE Annual Meeting, San Francisco, California, 2016.
  - McGrail, B. P., P. K. Thallapally, J. Liu, and S. K. Nune, “Magnetic Nanofluid for Rare Earth Extraction from Geothermal Fluids,“ Australian Earth Sciences Convention, Adelaide, Australia, 2016.
- Publications
  - Elsaidi, S. K., M. Sinnwell, D. Banerjee, D. Debasis, A. Devaraj, R Kukkadapu, T. Droubay, Z. Nie, L. Libor, V. Murugesan, Vijayakumar; Manandhar, S. Nandasiri, B. P. McGrail, and P. K. Thallapally. 2017. “Reduced Magnetism in Core-Shell Magnetite@MOF Composites.” *Nano Letters (In Press).*
  - De, S., M. I. Nandasiri, H. T. Schaef, B. P. McGrail, S. K. Nune, and J. L. Lutkenhaus. 2017. "Water-Based Assembly of Polymer-Metal Organic Framework (MOF) Functional Coatings." *Advanced Materials Interfaces* **4**(2), 10.1002
  - Elsaidi, S. K., M. H. Mohamed, J. S. Loring, B. P. McGrail, and P. K. Thallapally. 2016. "Coordination Covalent Frameworks: A New Route for Synthesis and Expansion of Functional Porous Materials." *ACS Applied Materials & Interfaces* **8**(42):28424-28427.

Research Collaboration and Technology Transfer

- Working with InnaVenture LLC to implement synthesis conditions for core-shell MOF sorbents in their pilot-scale reactor system under exclusive IP license from PNNL
- Extension to REE extraction work in progress for application at Salton Sea geothermal project
- Initiated collaboration with partners in Kenya geothermal project
- In discussions with several companies managing produced waters from oil/gas and mining waste water operations

Future Directions & Summary

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Future Directions

- Complete planned test loop system performance tests
- Work with S.G. Frantz to develop commercial scale design for separator system
- Extend testing/analysis results to additional non-REE elements
- Continue to foster contacts with geothermal and oil/gas producers to seek out deployment and commercialization opportunities

Summary

- Project is on track to deliver a transformational technology for mineral extraction from produced waters
- Illustrates ability to rapidly advance new high performance materials into practical application
- Sorbent materials so far have exceeded performance requirements in terms of REE selectivity and retention of magnetic properties with MOF shell
- Test loop system is delivering critical operational experience with continuous separation and nanoparticle recycling that is very limited in the literature on magnetic separators