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Selective Silica Separations from Waste Water using Ion-exchange Media

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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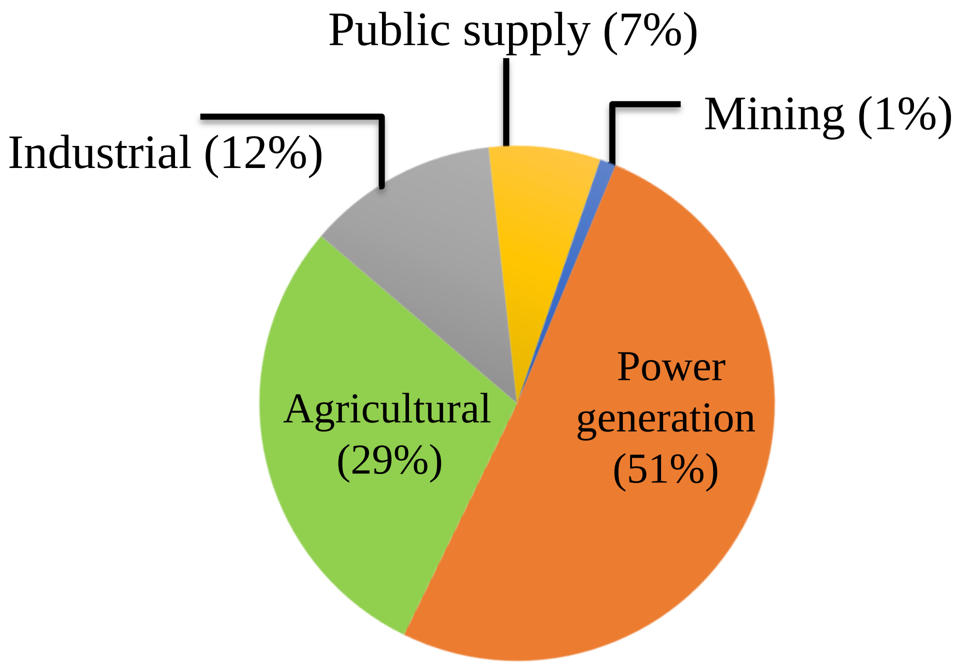
Outline

- Current silica removal methods limitation
- Hydrotalcite (HTC) structure
- Batch testing of silica removal by Hydrotalcite (HTC)
- Single path flow through (SPFT) results of silica removal
- Regeneration of HTC
- Techno-economic analysis of silica removal by HTC
- Ongoing studies

Fresh Water Consumption in the U.S.

- **Project Goal:**
  Developed low cost, energy efficient materials for silica removal from impaired waters



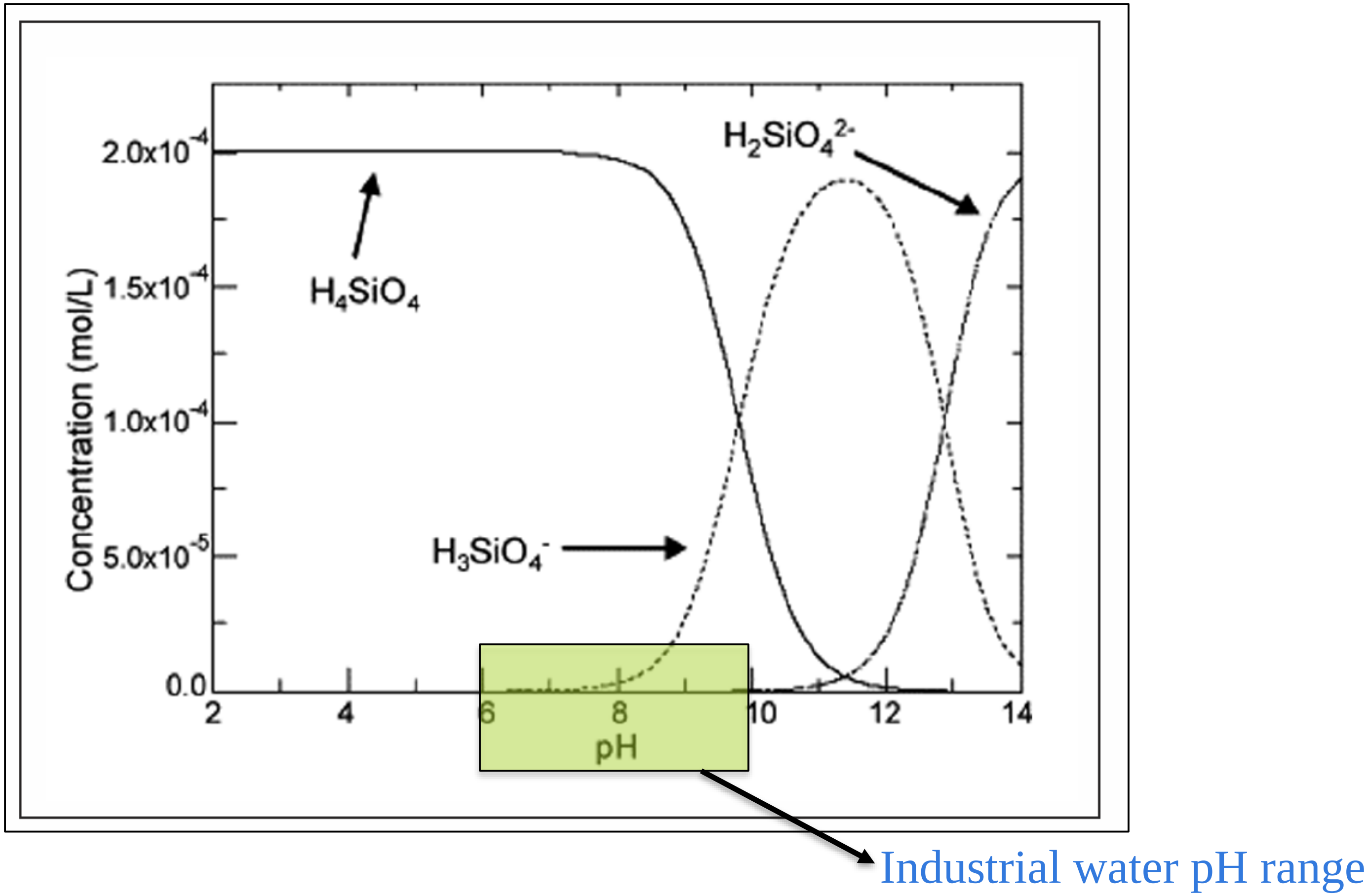
Fresh water withdrawal in the U.S.[1]

Mineral silica scales

- Thermoelectric power generation is the largest user of fresh water in the US, at ~180 million gallons/day (half of all water withdrawn daily).[1]
- Reclamation of impaired waters for thermoelectric power generation at inland sites ~1.5 – 2.5x the cost of freshwater, in part because of high cost of silica removal.[2]

1. http://water.usgs.gov/edu/wateruse-total.html
2. EPRI (Electric Power Research Institute) , Report 1005359, 2003

Chemistry of Dissolved Silica



- Silica exists either as particulate or anions based on pH[1]
- Removal technology needs to be pH specific for silica species
- Development focus is for low energy technology that avoids costly pH swing

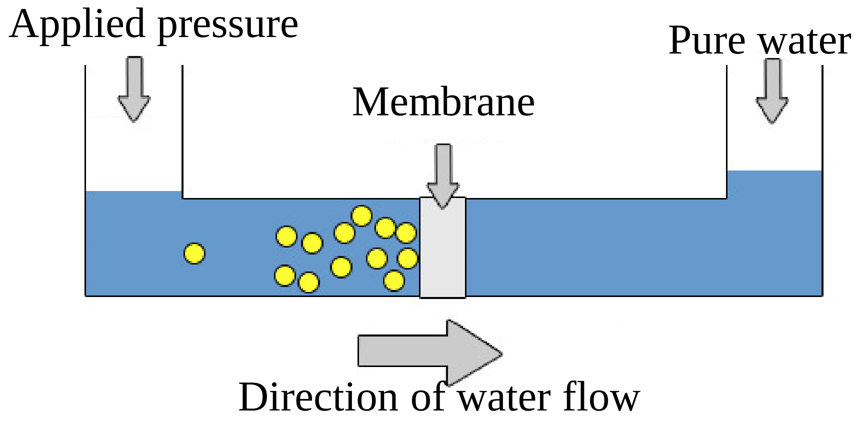
1. Latour, I.; Miranda, R.; Blanco, A.. Environmental Science and Pollution Research 2015, 23, 3707-3717

Current Silica Removal Methods Limitation

I. Reverse Osmosis

Drawbacks:

- High pressures are needed to maintain flow
- Membrane rapidly loses efficacy[1]



II. Ion exchange

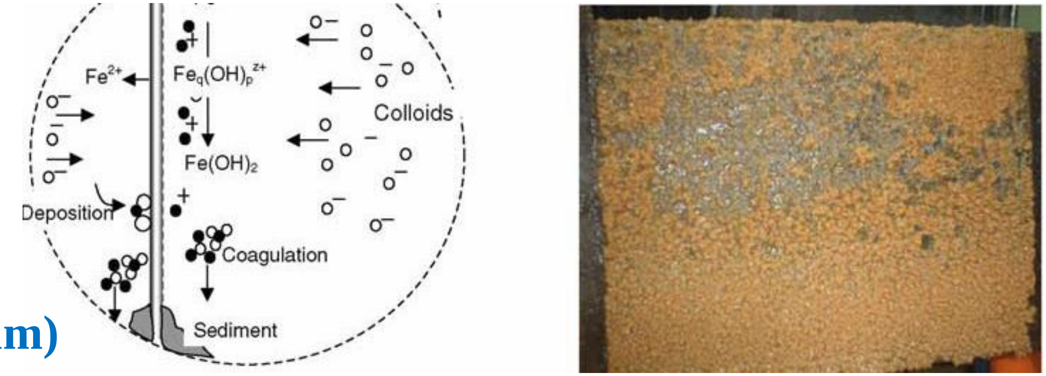
Drawbacks:

- Sulfate and chloride are competing ions.
- pH above 9.5 is required to facilitate dissociation of silicic acid.[1]

III. Electro-Coagulation

Drawback:

- High electrical cost[1]



Electro-Coagulation

IV. Co-Precipitation (eg, with Magnesium)

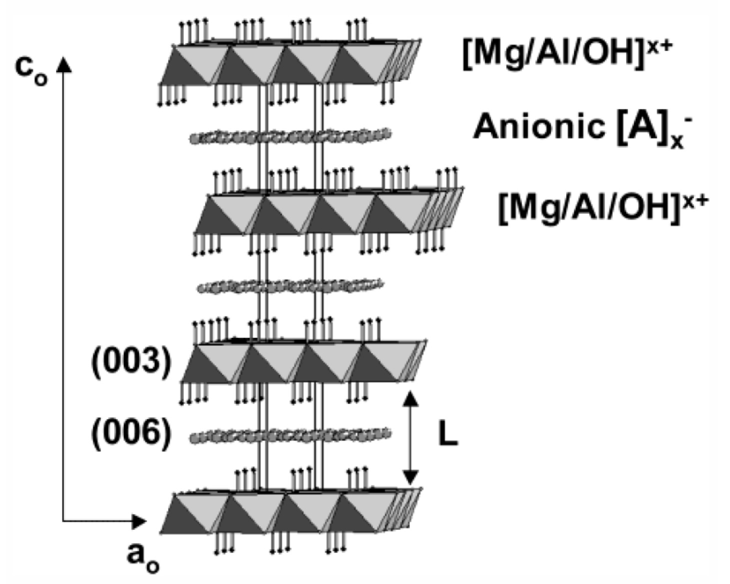
Drawbacks:

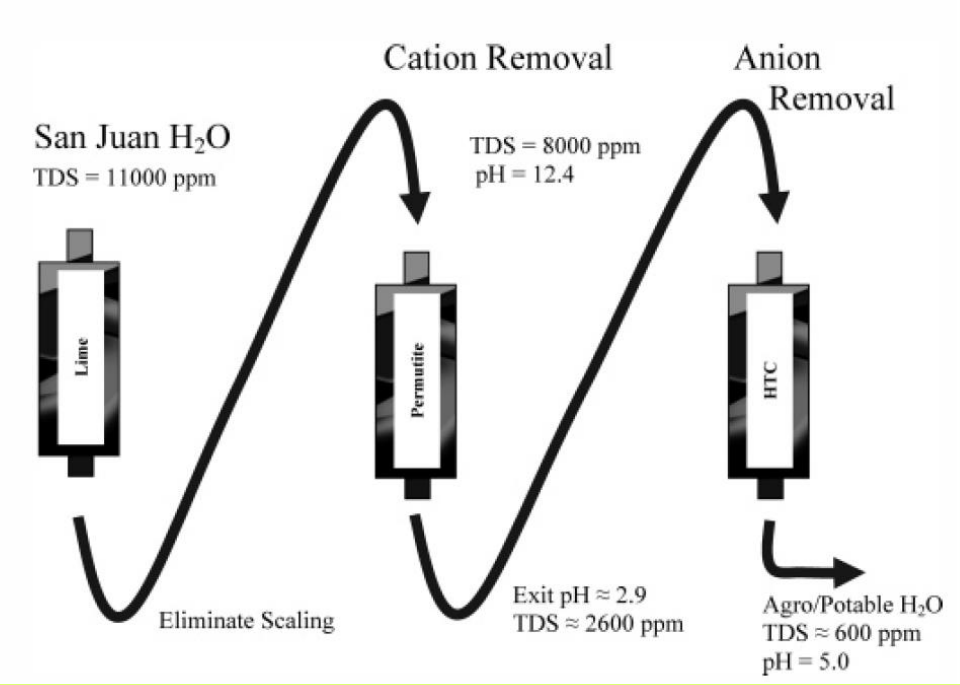
- High chemical use
- Remaining metal residual in the treated water[1]

1. Stephen Booth, Melinda Friedman, Silica white paper report, June 2014, Confluence engineering

Hydrotalcite (HTC) for Water Purification

- Hydrotalcite (HTC): $Mg_6Al_2(OH)_{16}(CO_3).4H_2O$
- Earlier studies Nenoff, et.al.[1-2] used HTC for low energy, high selectivity, anion exchange in brackish water desalination





- **HTC as an ion-exchange material:**
  - Environmentally friendly
  - Highly selective
  - Robust and inexpensive
  - Easy to regenerate

1. Bontchev, R. P.; Liu, S.; Voigt, J.A.; Krumhansl, J. K.; Nenoff, T. M. Chem. Mater., 2003, 15, 3669
2. Pless, J. D; Krumhansl, J.; Voigt, J.; Moore, D.; Axness, M.; Phillips, M.L.F; Nenoff, T. M.,Ind. Eng.Chem. Research, 2006, 45, 4752-4756.

Experimental and Characterization Techniques

Experimental Methods

- Calcination of HTC at 550 °C in the air furnace for 2h
- Adding 25-125 mg HTC to 50 ml of test water for batch testing
- Shaking the solution for given times
- Centrifuging the solution for 15 mins (5000 rpm)

Water Compositions

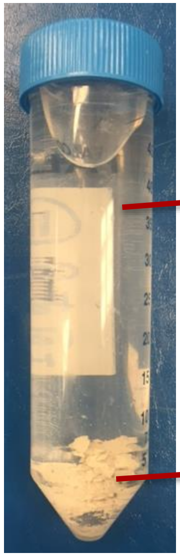
Cooling Tower Water: SiO_2 : 122 ppm; Cl^- : 80 ppm; SO_4^{-2} : 132 ppm

Simulated California Central Valley:[1] SiO_2: 150 ppm; Cl^- : 10386 ppm; SO_4^{-2} : 15695 ppm

Synthetic Produced Water: SiO_2: 50 ppm; Cl^- : 4700 ppm; SO_4^{-2} : 156 ppm

Water Characterization Methods

- pH of solution
- Silica concentration by Optical Hach method 8185
- Anion (Cl^-, SO_4^{-2}, …) concentrations by Ion Chromatography (IC).
- Cation (Mg^{+2}, Ca^{+2}, …) concentrations by ICP-MS.

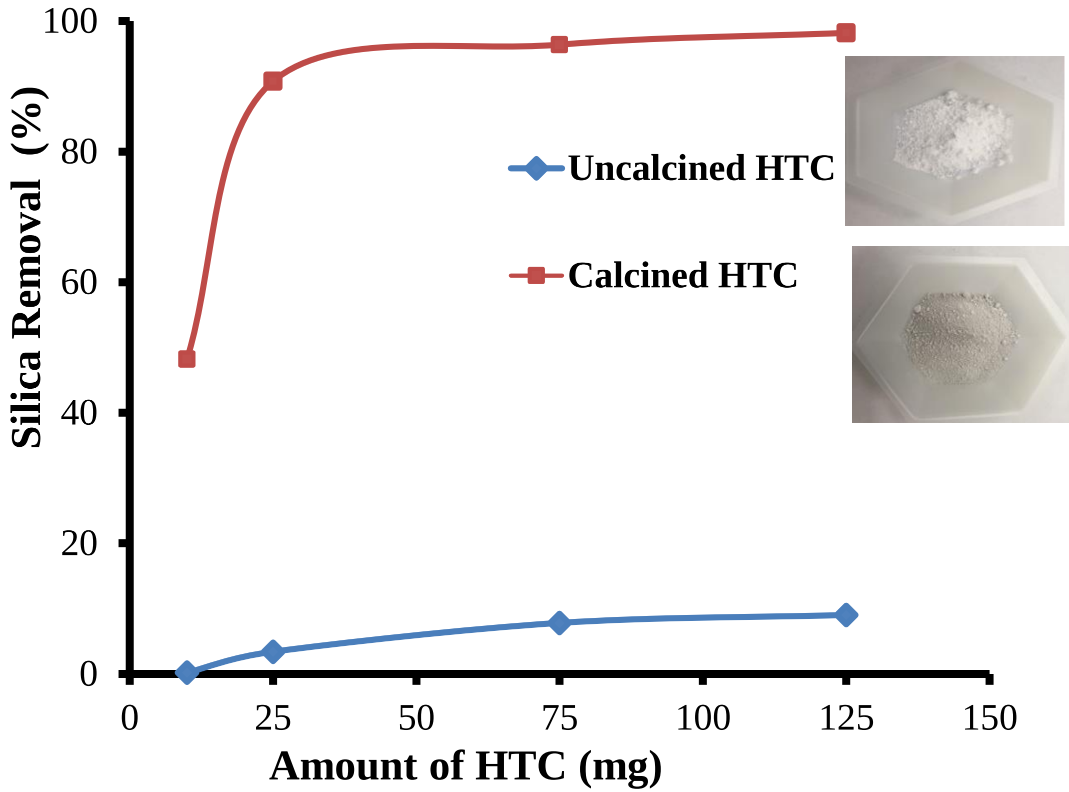


Test water after silica removal process

HTC after ion-exchange

1) California Energy Commission, Use of Degraded Water Sources as Cooling Water in Power Plants, P500-03-110, Electric Power Institute, Oct 2003, p. 3-4. URL: http://www.energy.ca.gov/reports/2004-02-23_500-03-110.PDF

Experimental:
Batch Testing of Silica Removal by Hydrotalcite (HTC)

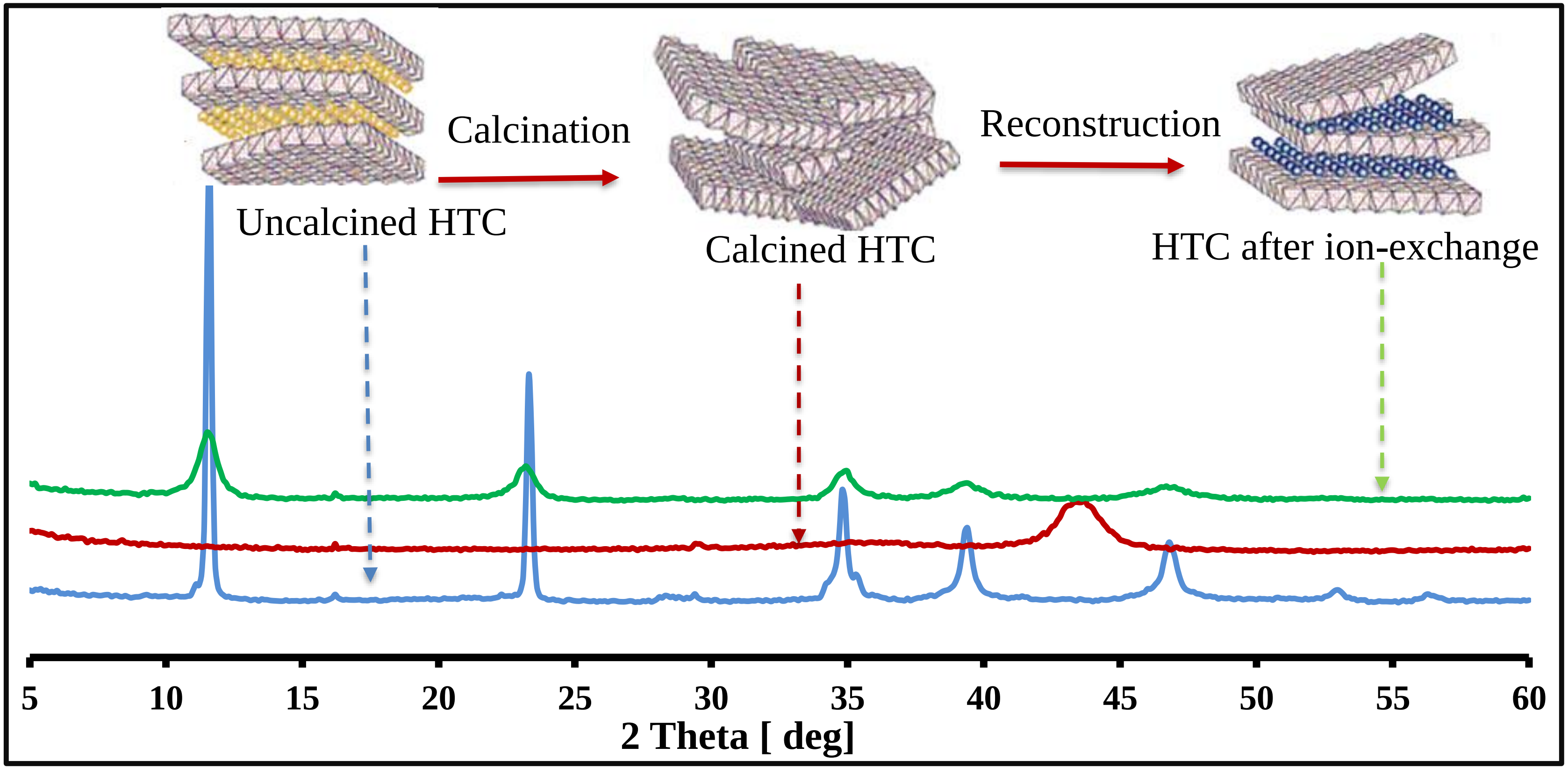


Experimental setup
Synthetic Produced Water:
pH 7.8, 25 °C, 50ml, 50 ppm SiO_2

- Calcined HTC has much higher silica adsorption than uncalcined HTC
- Optimum silica removal (~95%) at 75 or 125 mg of calcined HTC

1. Sasan, K.; Brady, P.V.; Krumhansl, J. L.; Nenoff, T. M. *Journal of Water Process Engineering*. 2017, Accepted
2. Nenoff, T. M.; Sasan, K.; Brady, P.V.; Krumhansl, J. L.; pending US patent, SD14053.0/S146025, 2016.

Why Does HTC work in Anion Exchange: Reconstruction of Hydrotalcite (HTC), XRD



Uncalcined HTC → **Calcined HTC**

$Mg_6Al_2(OH)_{16}(CO_3).\ 4H_2O \rightarrow 5\ MgO.\ MgAl_2O_4 + CO_2 + H_2O$

	Uncalcined HTC	Calcined HTC
Surface area	12 m^2/g	138 m^2/g
Average particle size	487.2 nm	43.3 nm

Silicate Anion Adsorption during Reconstruction of Hydrotalcite (HTC)

- **Step I**. The generation of OH^- ions during reconstruction of the calcined HTC to the original HTC structure

Calcined HTC

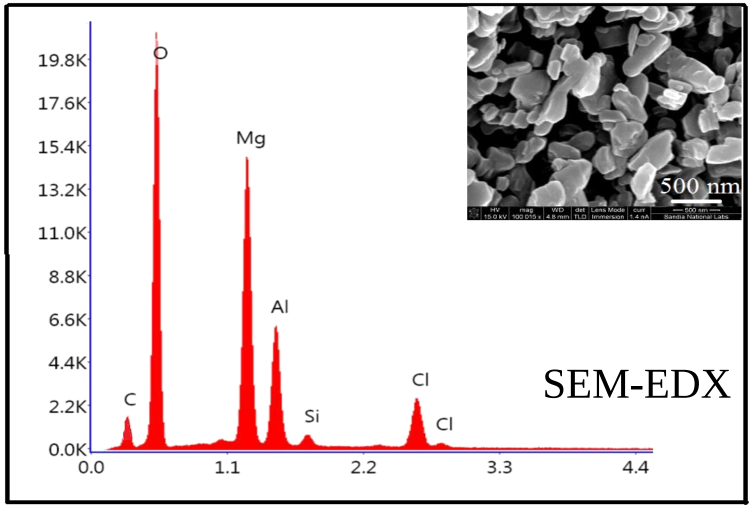
$$\underbrace{5MgO \,.\, MgAl_2O_4}_{\text{Calcined HTC}} + 13H_2O + 2Cl^- \longrightarrow Mg_6Al_2(OH)_{16}Cl_2.4H_2O + 2OH^-$$

- **Step II**. At a pH > 9.5, most of the silica is in ionic form as $H_3SiO_4^-$ and confined in the HTC

Calcined HTC

$$\underbrace{5MgO \,.\, MgAl_2O_4}_{\text{Calcined HTC}} + 13\,H_2O + H_3SiO_4^- \longrightarrow Mg_6Al_2(OH)_{16}\,(H_3SiO_4)_x.4HO_2 + 2OH^-$$

Presence of Si and Cl are Confirmed by SEM-EDX



High Selectivity of Hydrotalcite (HTC) for Silica Removal

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Experimental setup

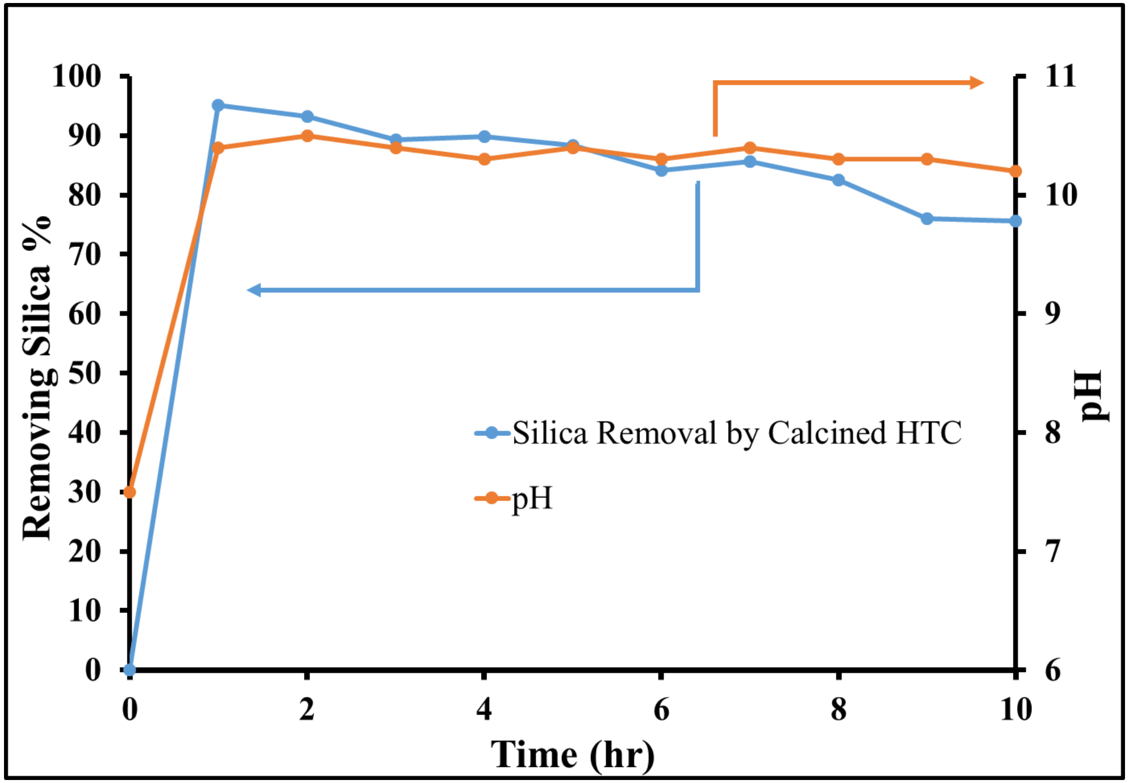
- Using NaCl or Na_2SO_4 as sulfate and chloride sources
- Synthetic Produced Water (pH 7.8, 25 °C, 50ml, 50 ppm SiO_2)
- 125 mg calcined HTC

Sample #	Sample ratio Silica: Sulfate	Removed Silica (%)
1	1:1	99.0%
2	1:5	97.0%
3	1:10	95.8%
4	1:15	95.2%
5	1:20	94.8%

Sample #	Sample ratio Silica: Chloride	Removed Silica (%)
1	1:1	99.0%
2	1:5	98.8%
3	1:10	98.5%
4	1:15	97.9%
5	1:20	97.6%

The silica adsorption by calcined HTC remain high even with presence of competing ions such as Cl^- and SO_4^{2-}

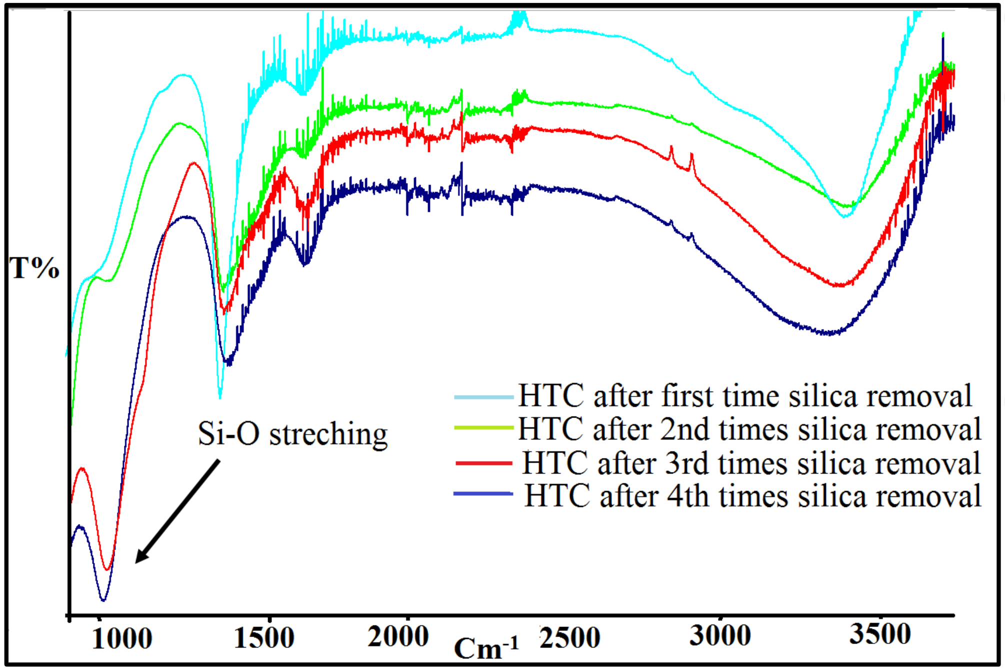
Single Path Flow Through (SPFT) Results of Silica Removal



Experimental setup
Synthetic Produced Water
pH 7.8, 25 °C, 0.5 L, 50 ppm SiO_2
Calcined HTC: 200 mg
Flow rate: 0.15 ml min^{-1}
Hydraulic Residence Time (HRT): 7 mins

- SPFT tests confirmed to rapid uptake of silica during column filtration.

Regeneration of HTC



HTC Samples	Removed Silica (%)
Calcined HTC for first time	97.5%
Calcined HTC for 2nd times	96.4%
Calcined HTC for 3rd times	95.3%
Calcined HTC for 4th times	65.4%

Experimental setup

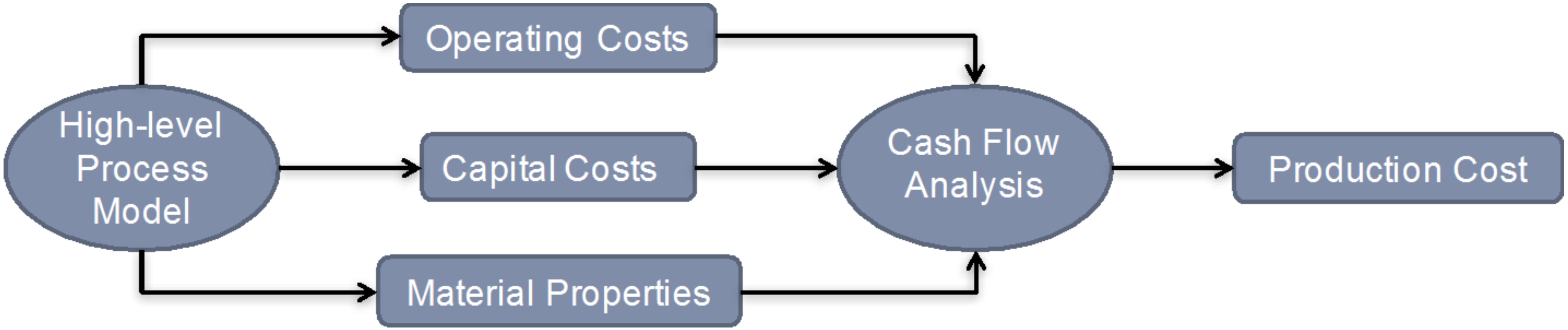
Synthetic Produced Water:

pH 7.8, 25 °C, 50 ml, 50 ppm SiO_2

125 mg HTC

- The average silica removal for 4 regeneration cycles of HTC is 88.6%
- After calcination and reused of this composition of HTC:
  Formation of Si-O (stretching peak at ~ 1070 cm^{-1})

Techno-economic Analysis Combines Simple Process Models and Cash Flow Analysis



➢ Parameters[1]

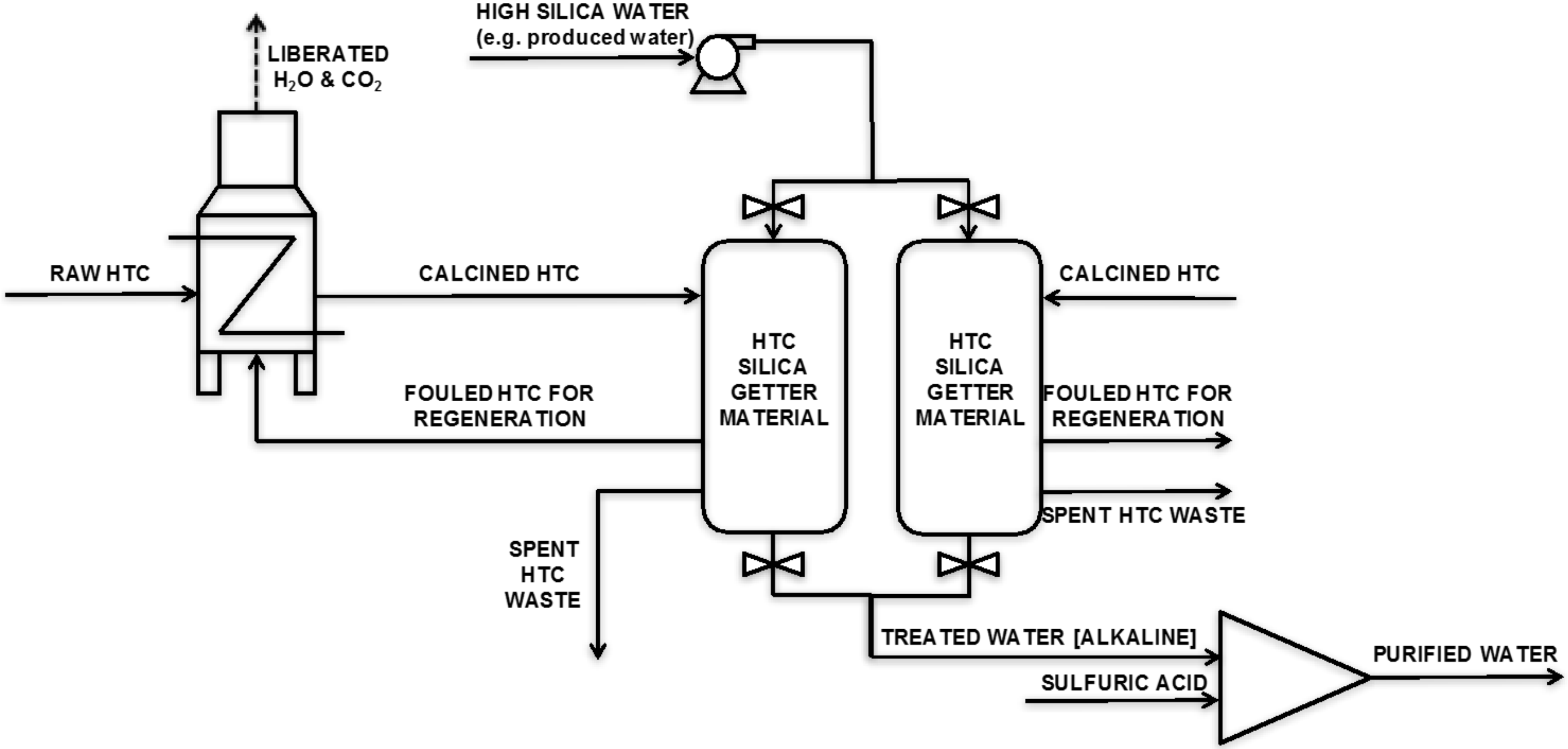
- Getter properties are derived from laboratory experiments and measurements
- Costs are derived from prevailing market prices or vendor quotation
- Process variables were adapted from a 2003 Electric Power Research Institute (EPRI) study[2]

➢ Technical Details

- Process model and cash flow model are constructed in Microsoft® Excel
- The models can be employed in Monte Carlo (MC) analyses

1. B. Heimer, S. Paap and T.M. Nenoff, ; Technical Advance for US patent : SD14295, 2016; "*Techno-economic analysis tool for industrial water treatment processes*"
2. J. Maulbetsch; EPRI report, Palo Alto, CA, 2003; "*Use of Degraded Water Sources as Cooling Water in Power Plants*"

Techno-economic Analysis: Process Flow Diagram



- The figure shows the flow of material through an industrial scale silica removal process.

Techno-economic Analysis: Treatment Cost as F(Parameters)

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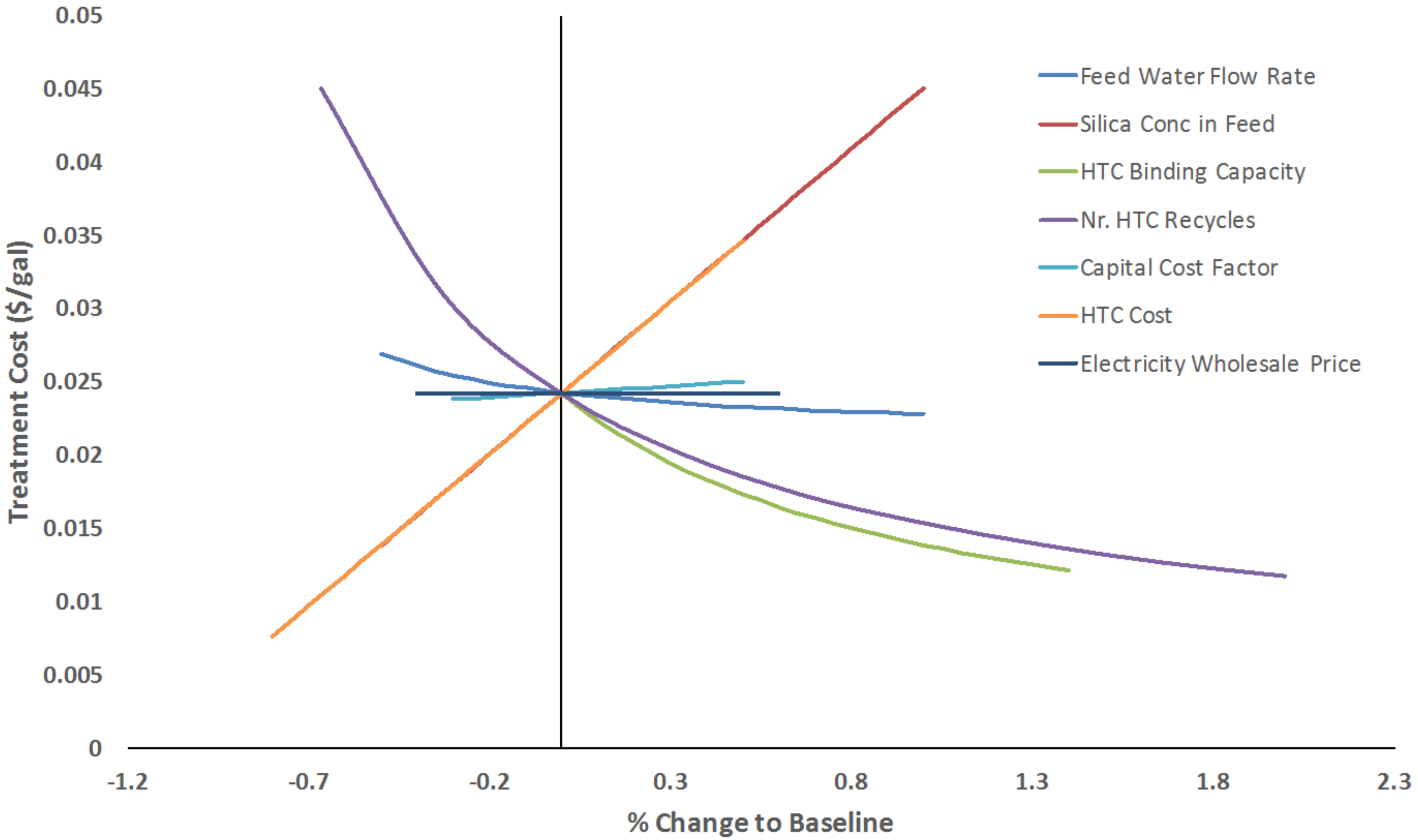
Process Parameters			Lower Cost Bound	Baseline	Upper Cost Bound	Units
	Feed water	Flow rate	1928	1928	1928	gal/min
		Silica loading	120	120	120	mg silica/L H_2O
	Getter properties	HTC Binding Capacity	120	48.8	50	mg silica/g HTC
		Nr. of HTC Recycles	9	3	1	#
	Capital Costs	Capital cost factor	0.7	1	1.5	$
Variable Operating Cost Parameters						
	Raw Materials Costs	HTC	$1.00	$5.00	$5.00	$/kg
		Sulfuric acid	$0.09	$0.09	$0.09	$/kg
		Natural gas	$0.27	$0.27	$0.27	$/kg
		Electricity wholesale price	$0.03	$0.05	$0.08	$/kWh
Model Outputs						
	Water Treatment Cost		$0.004	$0.025	$0.046	$/gal
			$0.17	$1.05	$1.93	$/bbl

- The cost silica removal may range from $0.17 to as much as $1.93/bbl depending on the actual value of each parameter.

Sensitivity Analysis: Parameter Variation



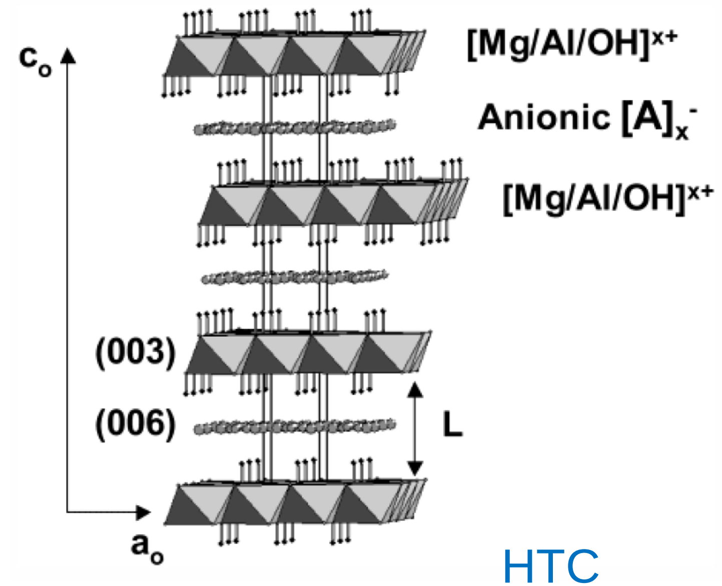
- The treatment cost is a much stronger function of the number of HTC recycles, HTC cost, and the silica concentration in the feed water.

Ongoing Studies

- Scale up[1]

- Combine the HTC with other silica removal methods (e.g. precipitation) to reduce cost and increase efficiency

- Techno-economic analysis:
  Process-level calculations and overall economic analysis to establish process cost targets, sorbent lifetimes and lifecycle costs (e.g. waste disposal).



HTC

1. Dr. Howe group, Department of Civil Engineering, University of New Mexico

Conclusion

- Selective silica removal from aqueous solutions using calcined Hydrotalcite phase (HTC) of composition: 5MgO; $MgAl_2O_4$
- Successfully silica removal batch testing with HTC on single component and complex aqueous streams, in particular cooling tower water with competing ions (SO_4^{2-}, HCO_3^-, Cl^-)
- In water solutions with 50 ppm silica, 75 mg calcined HTC effectively removes ~95% dissolved silica from the cooling tower water.
- This non-optimized HTC phase can be regenerated and reused up to 4 times
- The uptake of silica remain high even with competing ions such as Cl^- and SO_4^{2-}
- Techno-economic analysis indicated that the cost silica removal may range from $0.17 to as much as $1.93/bbl

1. Sasan, K.; Brady, P.V.; Krumhansl, J. L.; Nenoff, T. M. *Journal of Water Process Engineering*. 2017, Accepted
2. Nenoff, T. M.; Sasan, K.; Brady, P.V.; Krumhansl, J. L.; pending US patent, SD14053.0/S146025, 2016.
3. B. Heimer, S. Paap and T.M. Nenoff.; Technical Advance for US patent : SD14295, 2016; "*Techno-economic analysis tool for industrial water treatment processes*"

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