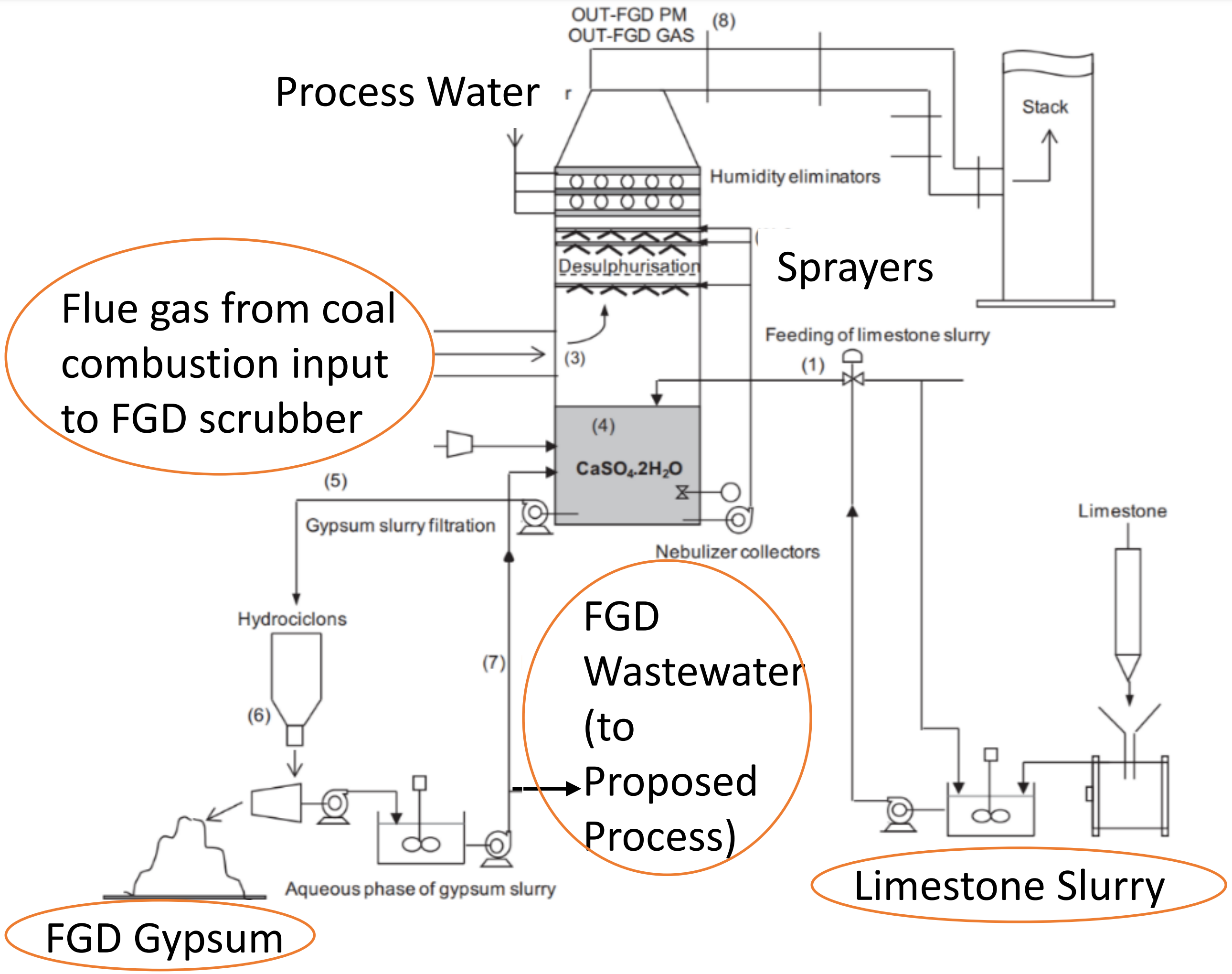
Project Description

Current Practice: Wet FGD process



Typical Example of wet FGD process (Cordoba, 2015)

Average FGD wastewater: 451,000 gal/d

Project Objectives

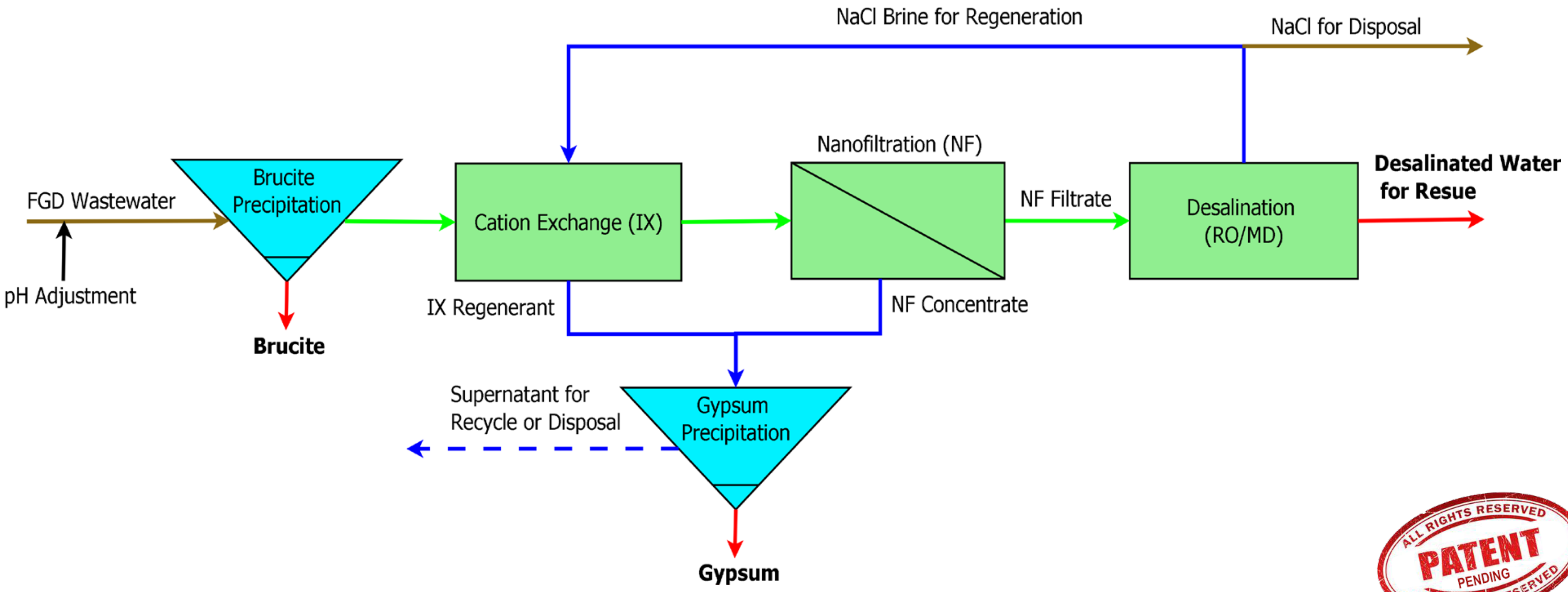
1) Recover wastewater from the FGD process for subsequent reuse.

2) Recover marketable commodities (gypsum ($CaSO_4 \cdot 2H_2O$) and brucite ($Mg(OH_2)$)), from FGD wastewater for commercial sale.

3) Treat FGD wastewater to remove regulated constituents including As, Hg, NO_3^-, and Se.

4) Reduce the volume and mass of waste requiring disposal from FGD wastewater.

Proposed Treatment Train

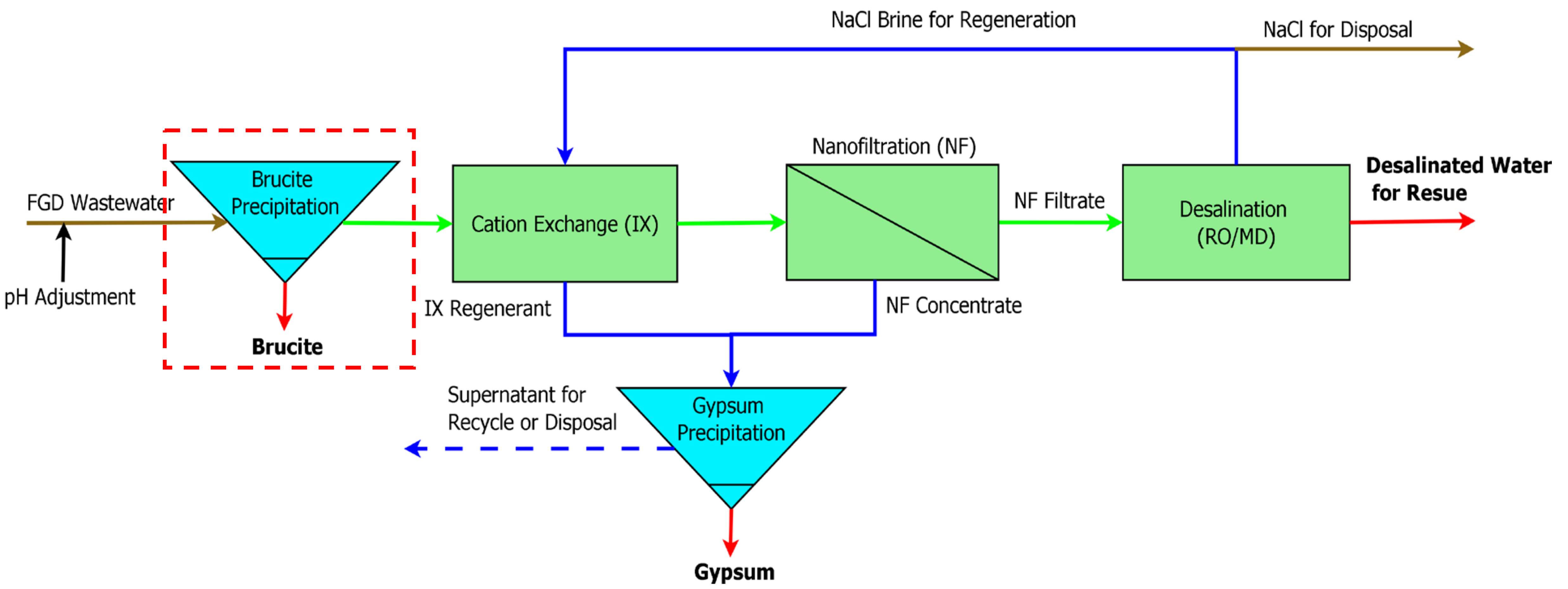


Project Update

Project Components

1. Magnesium Hydroxide Precipitation
2. Ion Exchange for Calcium Removal
3. Nanofiltration for Sulfate Removal
4. Gypsum Precipitation

Magnesium Hydroxide Precipitation



Magnesium Hydroxide Precipitation

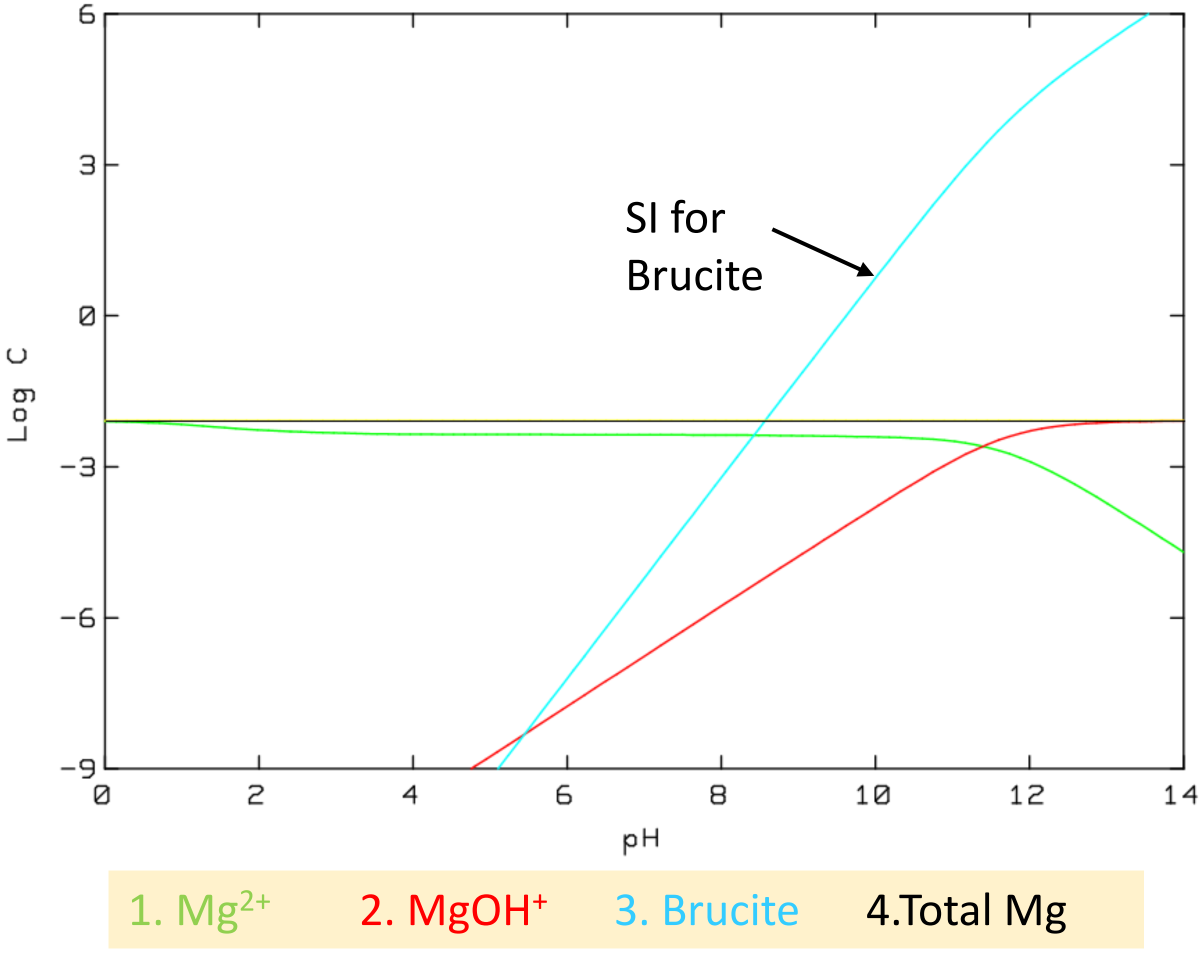
Principles

- In aqueous systems, the free Mg^{2+} ions react with hydroxide ions to form $Mg(OH)_2$ precipitates

- $Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$;

  $pK_{sp} = 10.45$

  $$K_{sp} = [Mg^{2+}][OH^-]^2$$



Magnesium Hydroxide Precipitation

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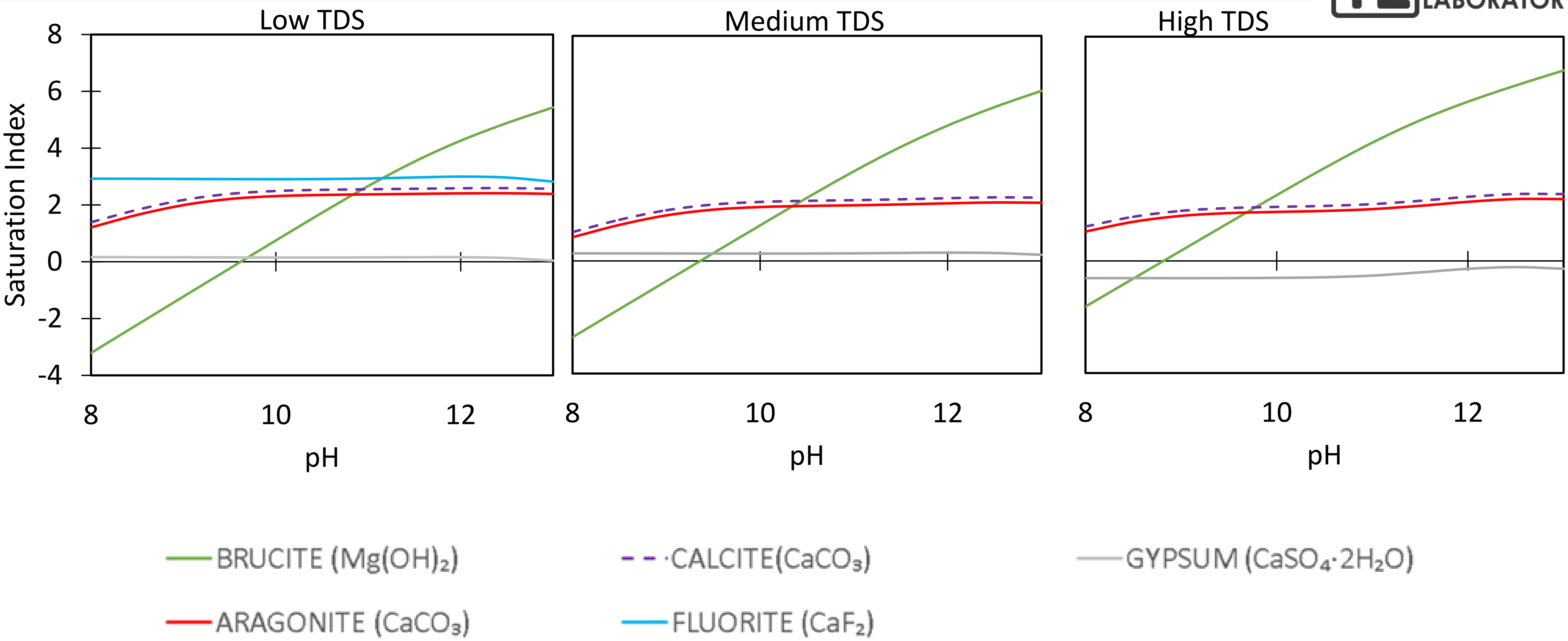
Waste Water Composition (from EPRI,2006)

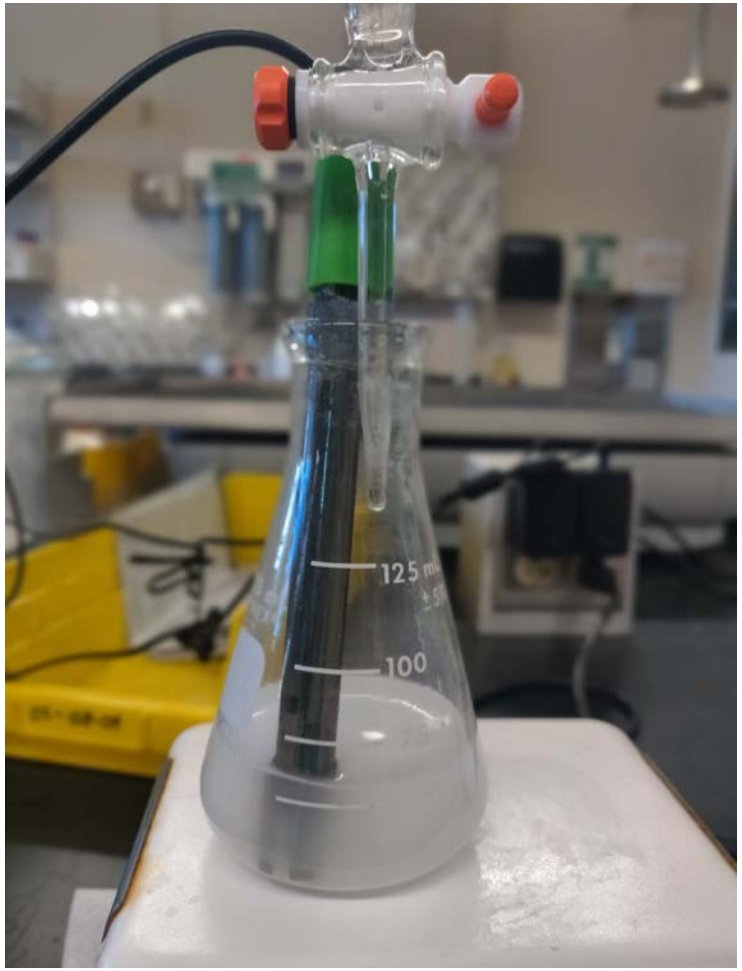
Ions	Site Y, Low TDS	Site U, Medium TDS	Site P, High TDS
	Conc (mg/L)	Conc (mg/L)	Conc (mg/L)
Na^+	450	2540	6680
Ca^{2+}	730	660	4240
Mg^{2+}	200	850	4510
F^-	50	0	0
Cl^-	1290	4300	29200
SO_4^{2-}	1480	4340	2180
HCO_3^-	150	100	280
TDS	**4340**	**12790**	**47080**

MINEQL+ Modeling



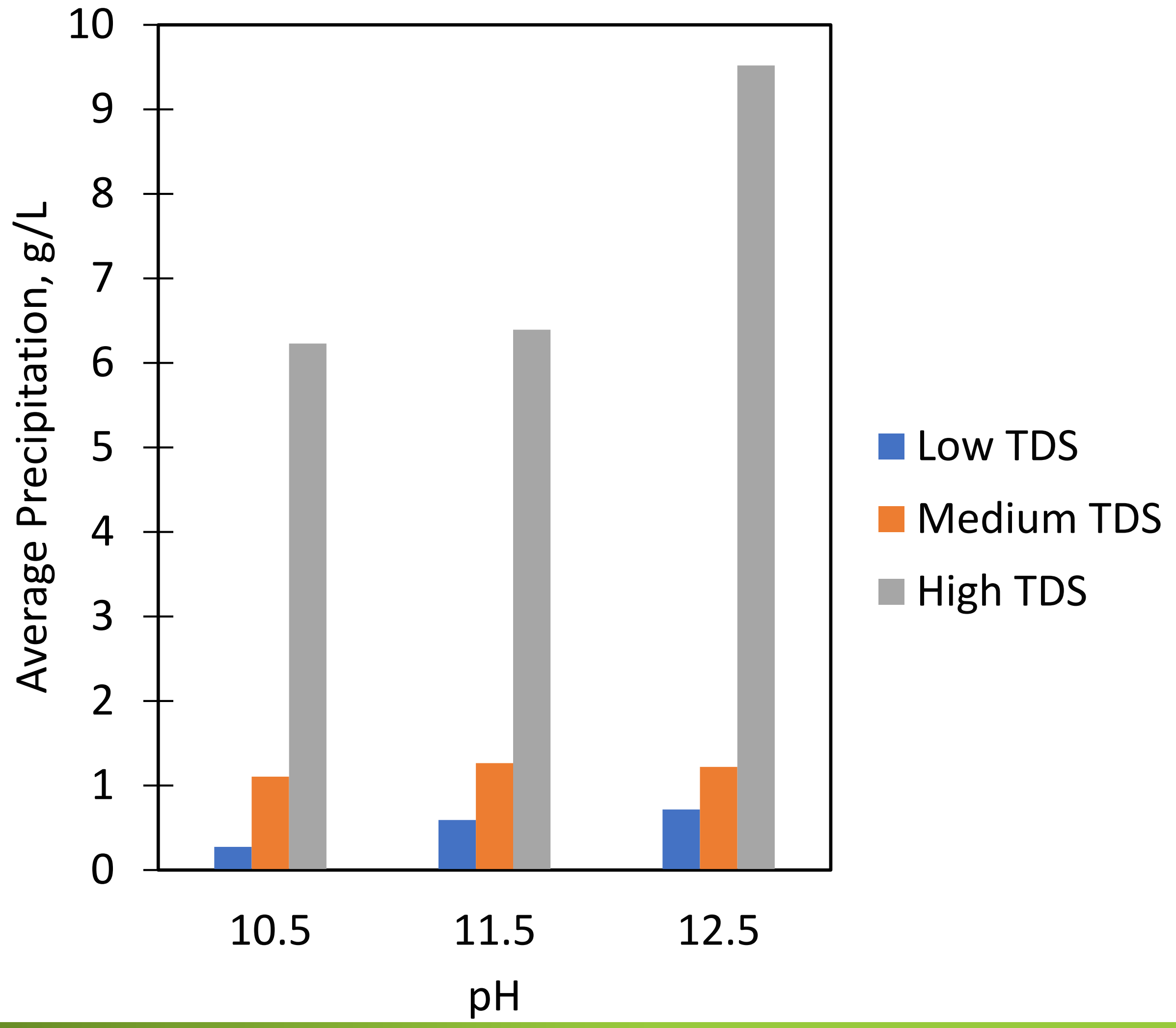
Experimental Procedure

- pH range: 10.5, 11.5 & 12.5
- Filtrate analysis: ICP-OES (Inductively coupled plasma - optical emission spectrometry)
- Precipitate analysis: dissolved in 2% nitric acid; ICP-OES
- Solids analysis: XRD & SEM-EDX



Magnesium Hydroxide Precipitation

Results

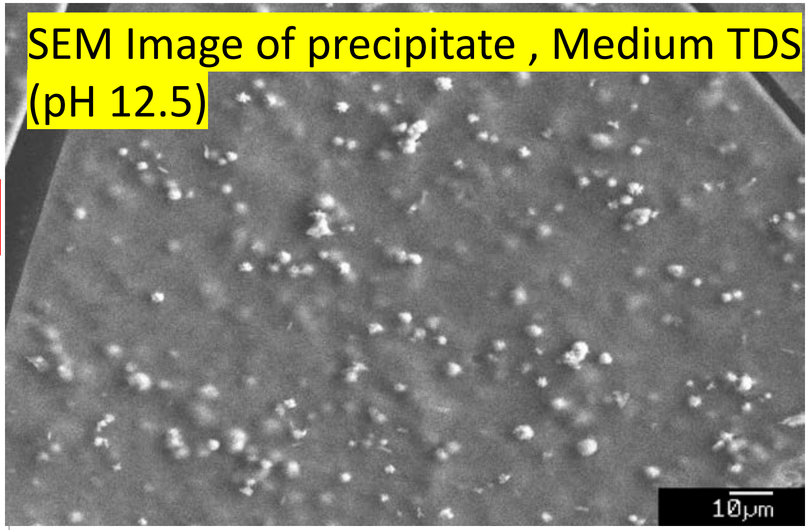


Cations	pH	Removal		
		Low TDS (%)	Medium TDS(%)	High TDS(%)
Ca	10.5	5	16	12
	11.5	29	11	7
	12.5	35	24	69
Mg	10.5	16	80	85
	11.5	**100**	**84**	**96**
	12.5	**100**	**98**	**100**

Solids Analysis

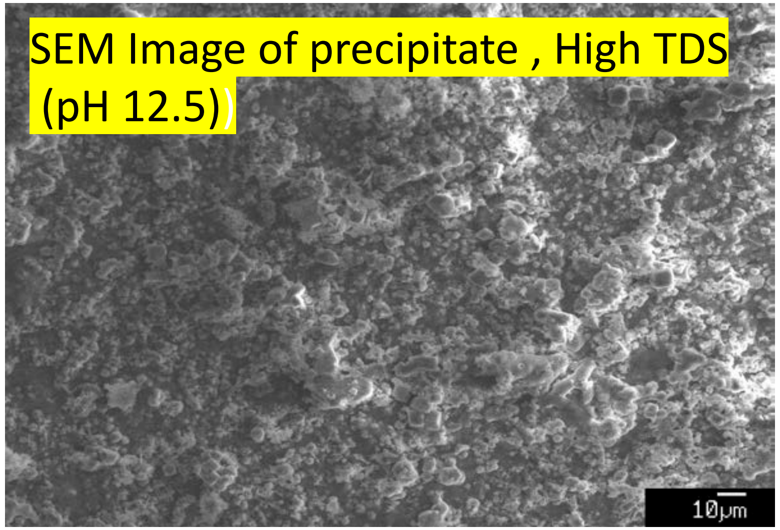
% of different phases in precipitate from XRD

	10.5	11.5	12.5
Phase ID	Weight%		
Aragonite • $CaCO_3$	0	0	0
Brucite • $Mg(OH)_2$	**86**	**95**	**94**
Calcite • $CaCO_3$	1	3	5
Gypsum • $CaSO_4 \cdot 2H_2O$	14	2	1
Portlandite • $Ca(OH)_2$	0	0	0



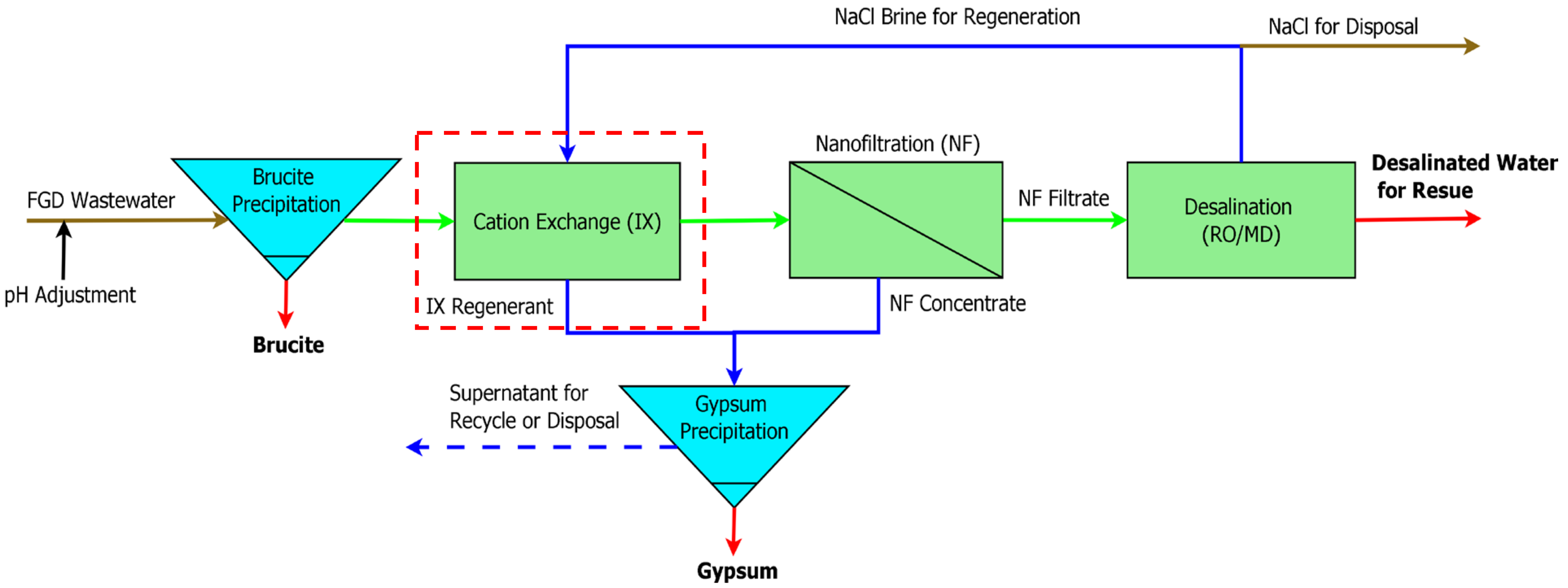
Medium TDS

	10.5	11.5	12.5
Phase ID	Weight%		
Aragonite • $CaCO_3$	3	1	5
Brucite • $Mg(OH)_2$	**91**	**93**	**48**
Calcite • $CaCO_3$	3	6	9
Gypsum • $CaSO_4 \cdot 2H_2O$	4	0	30
Portlandite • $Ca(OH)_2$	0	0	9



High TDS

Ion Exchange



Principles of Ion Exchange

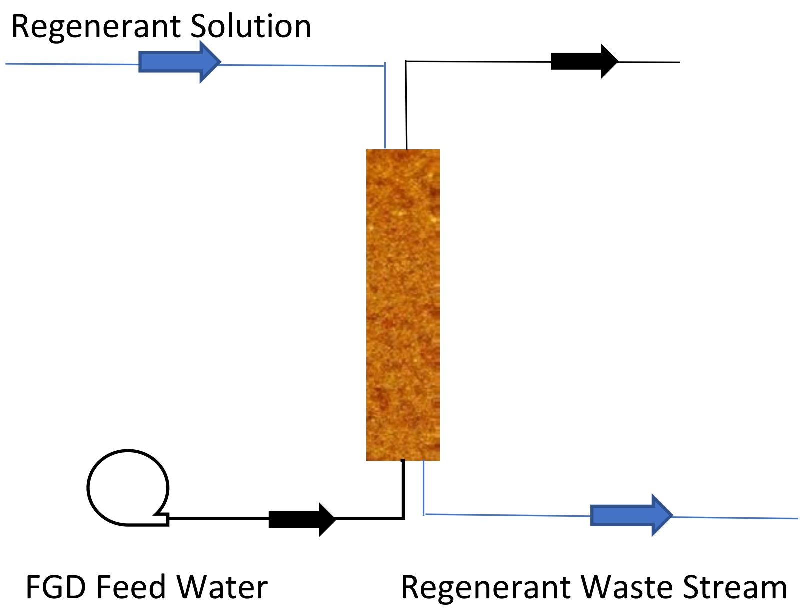
Objectives

- To remove calcium from the solution to precipitate gypsum
- To determine the threshold up to which IX can be used
- To design effective feed and regeneration conditions

Principle

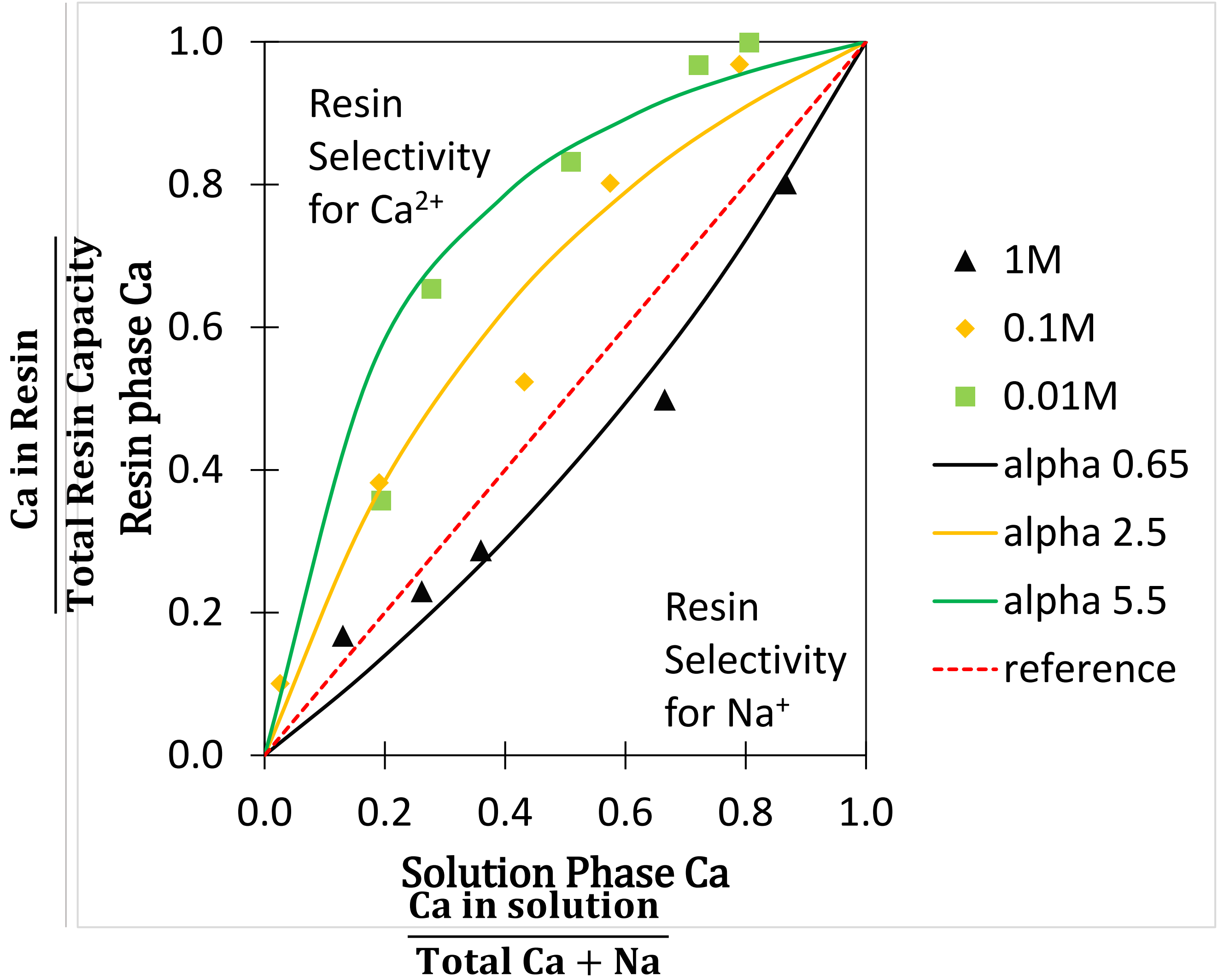
$2(R\text{-}Na) + Ca^{2+} = R_2\text{-}Ca + 2Na^{+}$

Resin used: Purolite SSTC60 Resin



Batch Experiments

Experimental determination of selectivity



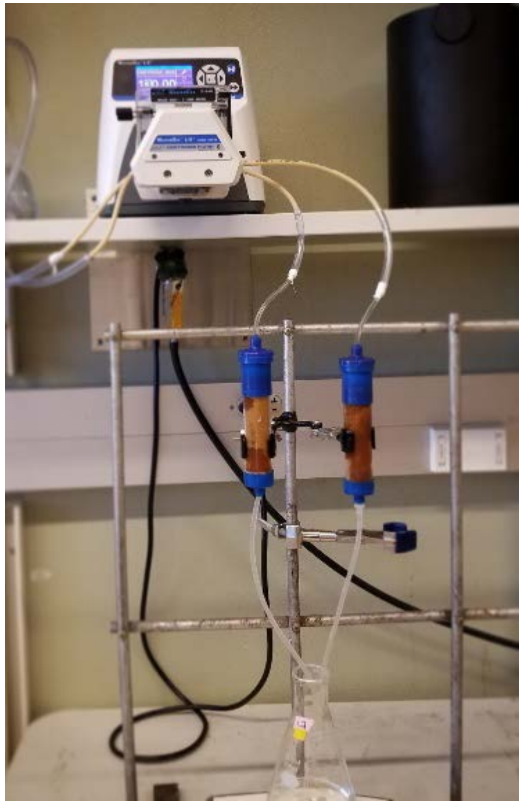
- Batch experiments carried out on varying ionic strength
- Solutions with resins were placed on shaker table
- Analytical method: ICP-OES

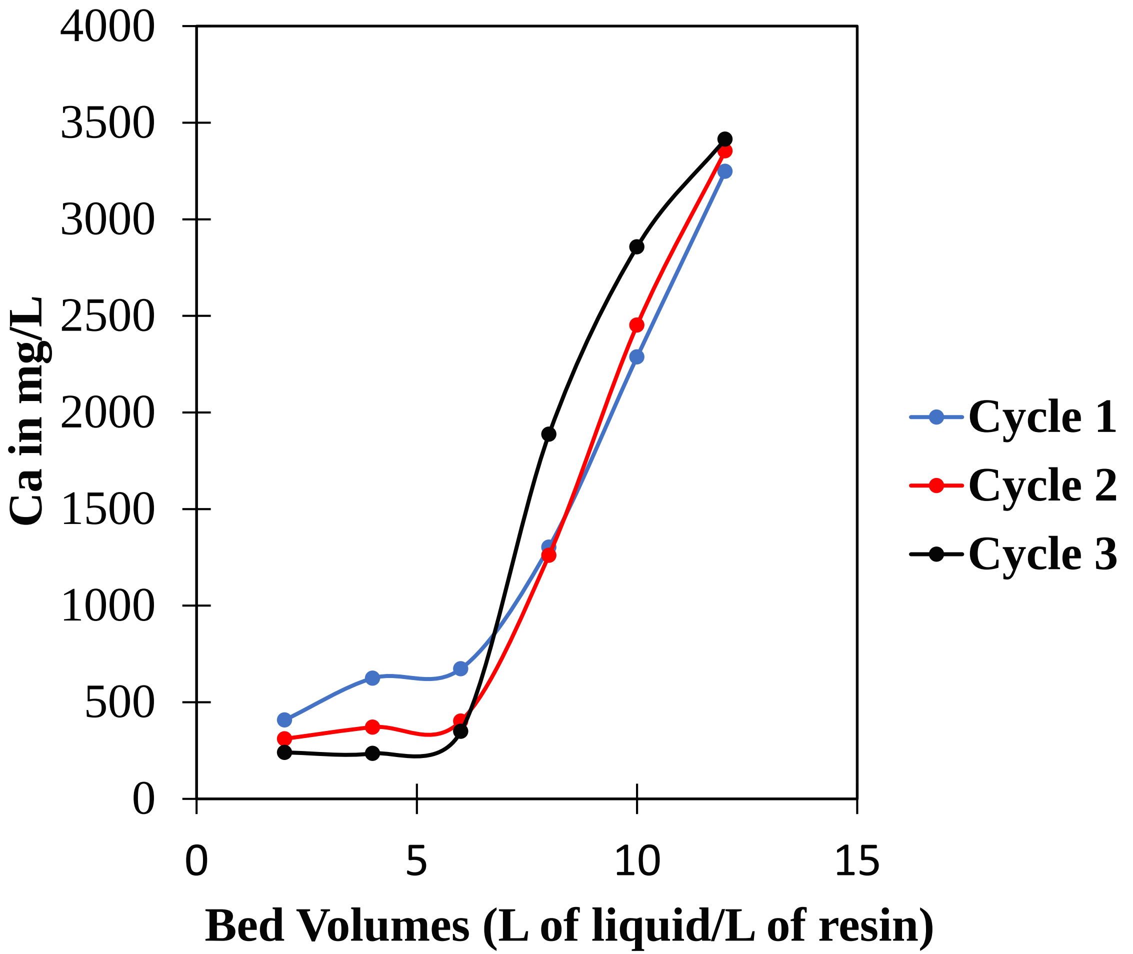
Column Experiments

To determine the bed volumes required to exhaustion

Methods

- Duplicate columns were used
- Samples taken at multiple BVs
- Analytical method: ICP-OES
- EBCT (empty-bed contact time) = 5 minutes
- Feed rate 10mL/min





Feed Water Exhaustion for Medium TDS

Regeneration for Ion Exchange

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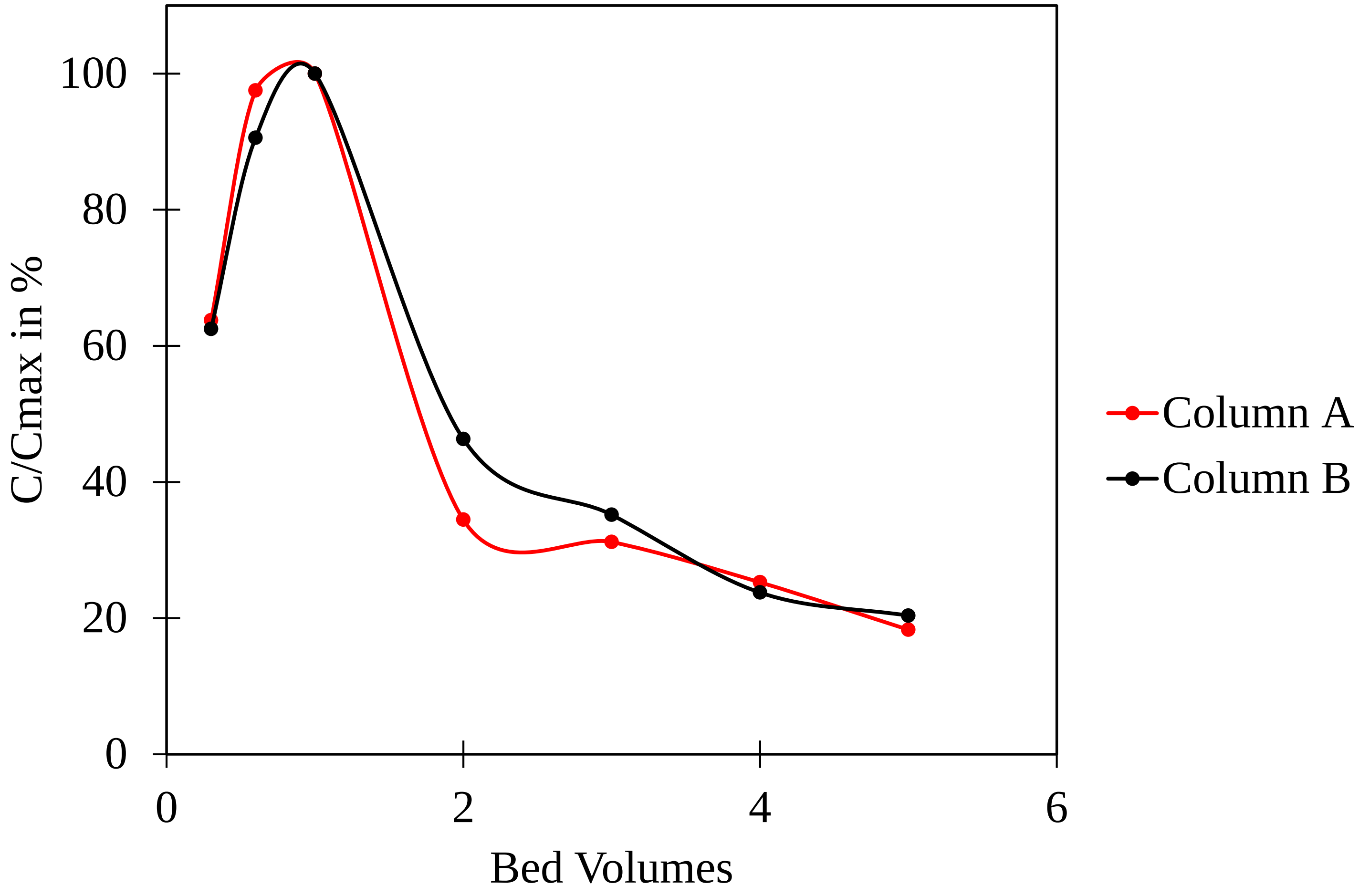
Methods

- Regeneration rate: 2.5mL/min
- R_2-Ca + 2Na^+ = 2(R-Na) + Ca^{2+}
- Regenerant: 10% NaCl Solution
- Analytical method: ICP-OES



Determination of Ionic Strength Cutoff for Ion Exchange

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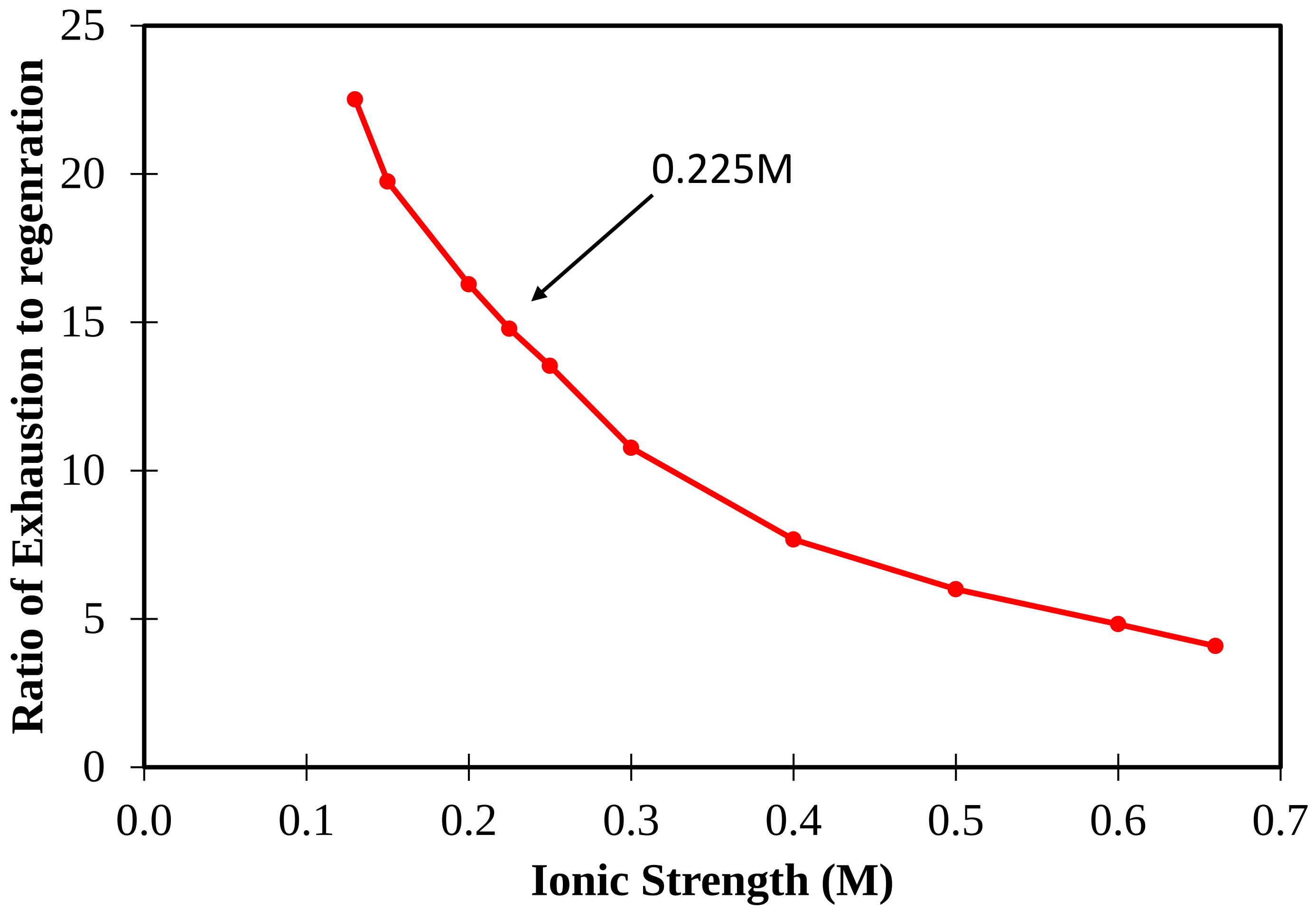
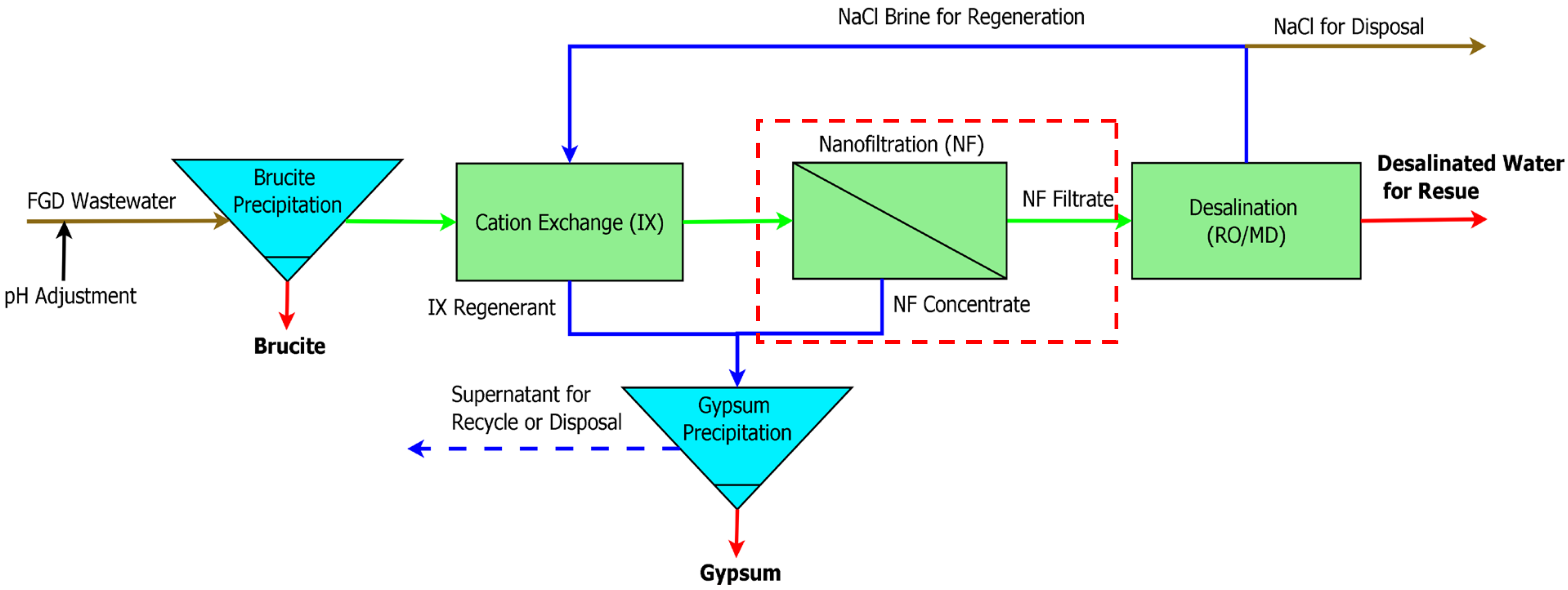
Wastewater	TDS Concentration in mg/L	BVs for Feed Exhaustion	BVs for regeneration	Ratio of BV required for Feed Exhaustion /BV required for Regeneration
Low TDS	5890	65	2	**32.5**
Medium TDS	28800	12	2	**6**
High TDS	52600	6	2	**3**

Determination of Ionic Strength Cutoff for Ion Exchange

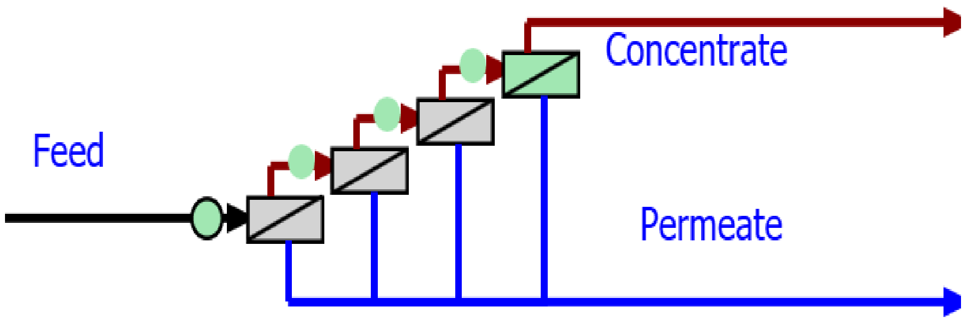


- For practical operation, minimum practical ratio of feed water exhaustion to regeneration is around 15: 1
- 0.225M ionic strength is 10000-10500mg/L

Nanofiltration



Principles of Nanofiltration

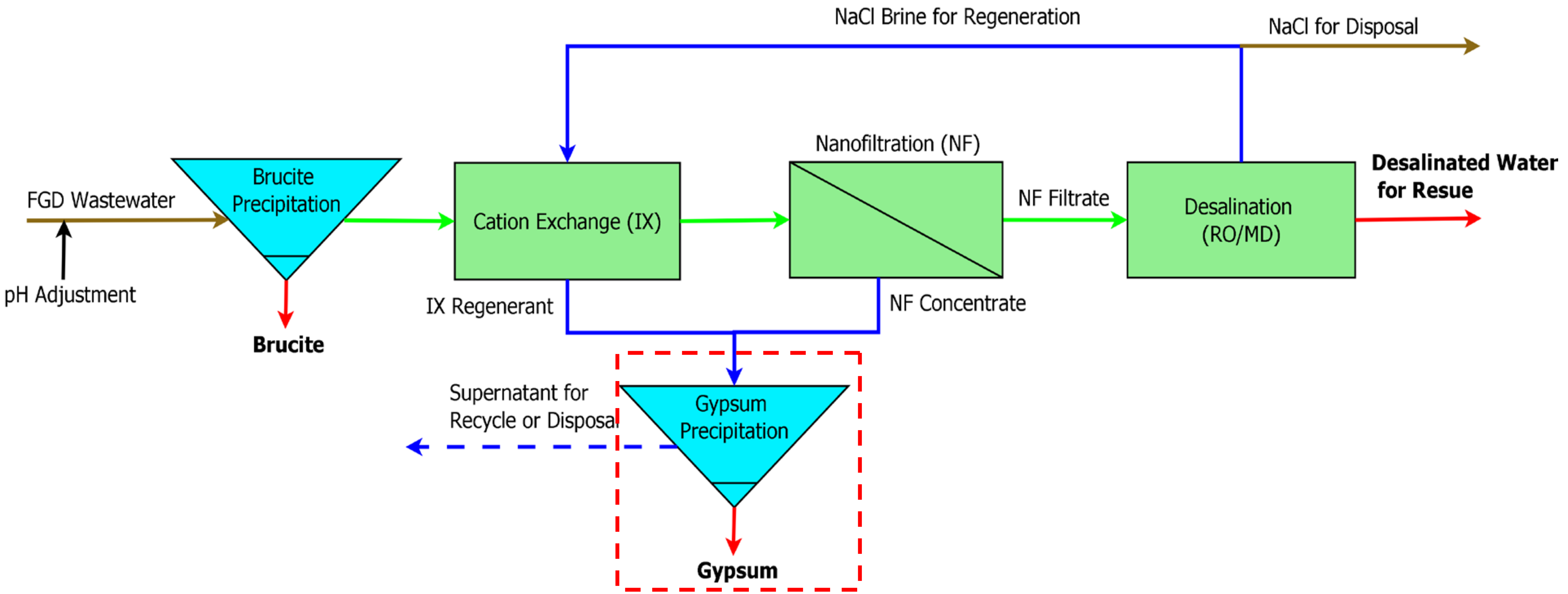


- **Design Objective:** High rejection of Sulfate and low rejection of Sodium and Chloride
- NF membrane used for modelling: **NF 270-400-34i** Dow Water & Process Solutions
- Modelling software used: Water Application Value Engine **(WAVE)** software by Dow

Modelling of Nanofiltration

No. of Stages	Wastewater	Feed Total Dissolved Solids (mg/L)	RO Recovery (%)	Rejection		
				Cl^- Rejection (%)	SO_4^{2-} Rejection (%)	Na^+ Rejection (%)
3	Low TDS	6320	**91**	22	**96**	56
4	Medium TDS	12500	**90**	19	**95**	55

Gypsum Precipitation

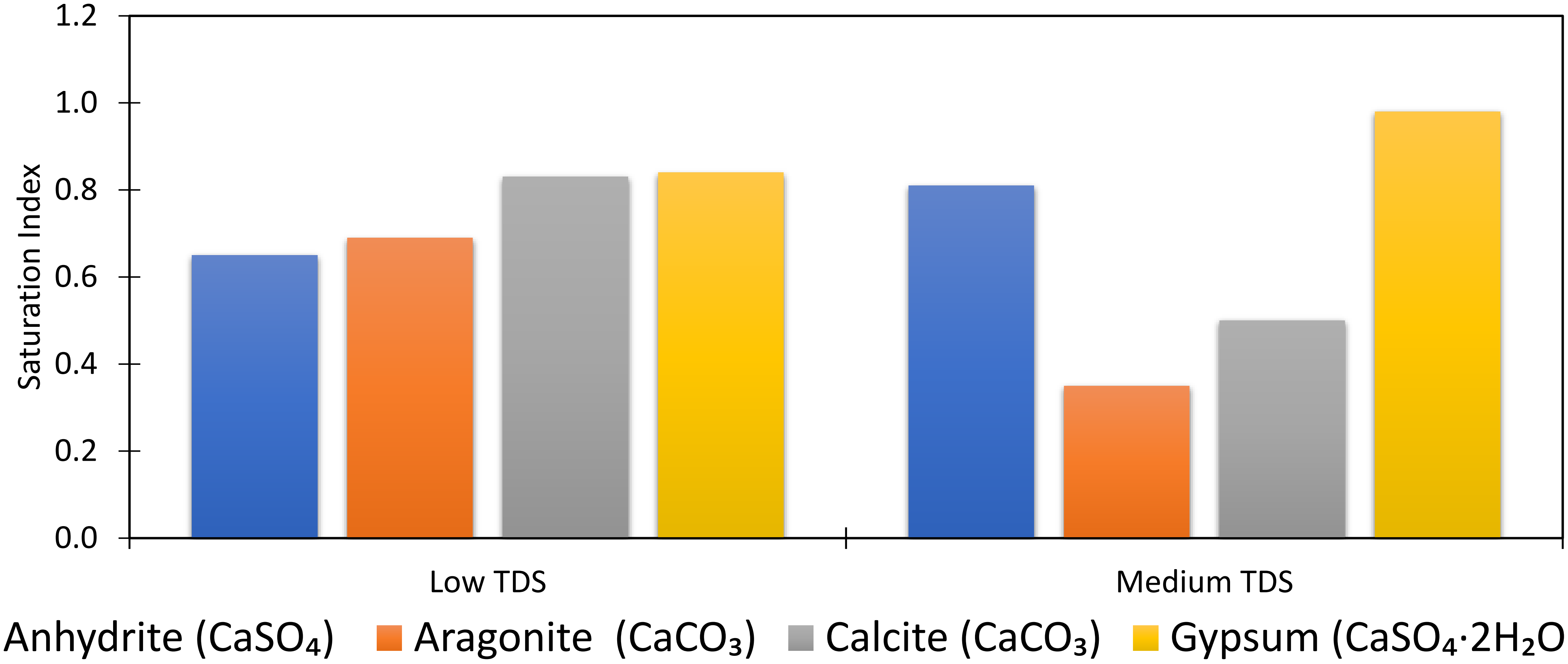


Gypsum Precipitation

Ions	Low TDS, mg/L			Medium TDS, mg/L		
	IX Regenerant	NF Concentrate	Mix	IX Regenerant	NF Concentrate	Mix
Na^+	21300	11500	16400	24400	33000	28700
Ca^{2+}	**15500**	**0**	**7800**	**9300**	**0**	**4630**
Mg^{2+}	0	0	0	2100	0	1070
Alk.	120	150	130	120	100	110
Cl^-	60300	7100	33700	60200	19800	40100
SO_4^{2-}	**0**	**14300**	**7100**	**0**	**41800**	**21000**
		TDS	**65130**		**TDS**	**95610**

IX Regenerate & NF Concentrate Mix

PHREEQC Analysis



Future Work

- Experimental verification of Nanofiltration modelling
- Experimental verification of Gypsum modelling
- Experiments on removal of trace contaminants from each component

Preparing Project for Next Steps

Market Benefits/Assessment

- Provide economic incentives to coal fired power plants
- Recovery of water back into the power plants
- Decrease the amount to waste to be disposed/hauled
- Magnesium hydroxide is a commodity which can be used for medical purposes, antibacterial agent and chemical neutralizer
- Gypsum can be used for making wall board

Preparing Project for Next Steps

Technology-to-Market Path

- Patent has been filed; Mineral Recovery Enhanced Desalination (MRED) Process for Desalination and Recovery of Commodity Minerals
- Treatment technology can be used for other water and wastewater treatment industries

Concluding Remarks

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- The treatment process has economic and environmental benefits to fossil energy
- Major components of the project have been modelled and experimentally proven
- The limitation of ion exchange is it cannot be used for solutions of ionic strength greater than 0.225 M (~10000 mg/L)

Acknowledgment

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DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

CIVIL, CONSTRUCTION & ENVIRONMENTAL ENGINEERING

CENTER FOR WATER & THE ENVIRONMENT