EVALUATION OF MAGNETIC NANO-ADSORBENTS FOR SELECTIVELY REMOVING METALS OF VALUE FROM REVERSE OSMOSIS REJECT STREAMS

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Overview

- **Introduction and background information**
  - Coalbed Methane (CBM) produced water
  - Desalination Using Reverse Osmosis (RO)
  - Magnetic nanoparticles having tailored surface chemistries
- **Experimental Approach**
  - Synthesis and modification of magnetic nano-adsorbents
  - Applications
  - Cost Benefit Analysis
- **Preliminary Conclusions**
  - Future research directions

Introduction and Background

Coalbed Methane Produced Water

Production:

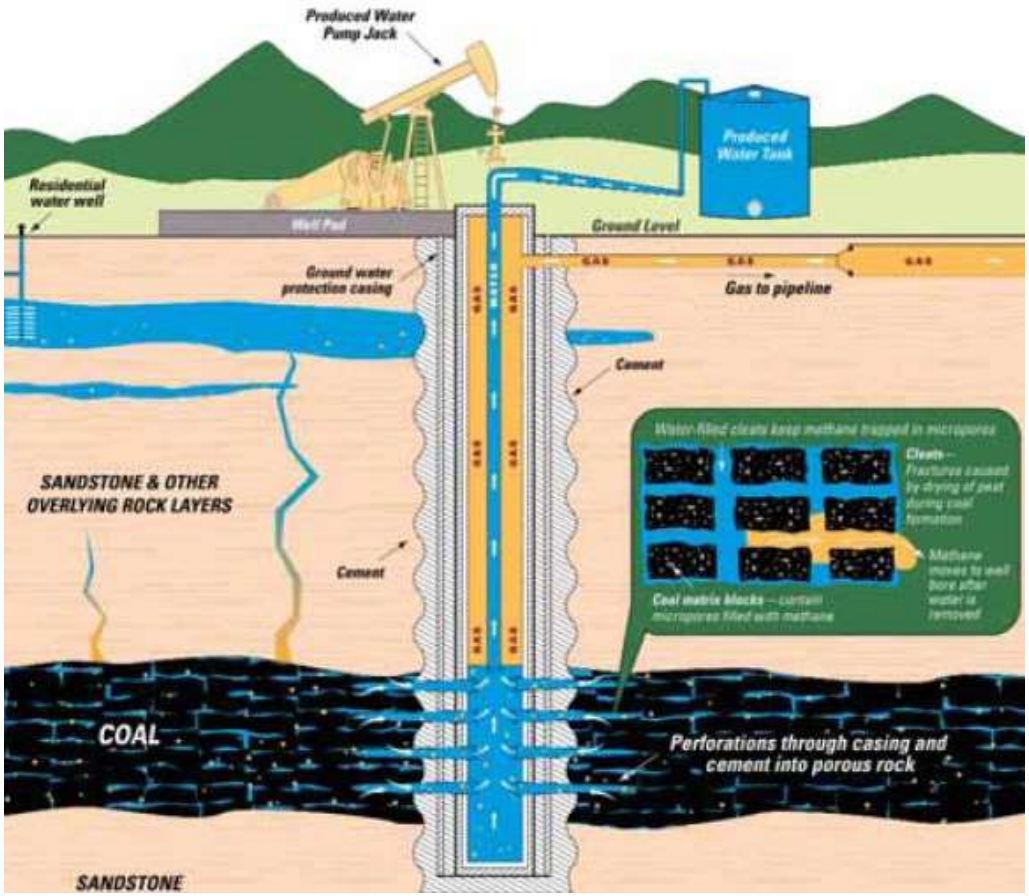
Produced during extraction of Coalbed Methane (CBM)

Volumes:

U.S. CBM production can generate between1.6-2.6 bgd

A single CBM well can produce as much 3,500 gpd

Powder River Basin produces as much as 100 mgd



Coalbed Methane Produced Water

Inorganic Constituents:

Minerals

Salts

High TDS

Organic Constituents:

Oil and grease

BTEX compounds

phenols

	Produced Water, US		Seawater	
Constituent	**Low, mg/L**	**High, mg/L**	**Low, mg/L**	**High, mg/L**
Calcium (Ca^{2+})	ND	74,000	400	700
Magnesium (Mg^{2+})	60	130	1,400	1,550
Sodium (Na^{+})	ND	150,000	12,000	12,000
Sulfate (SO_4^{2-})	ND	15,000	2,400	2,670
Bicarbonate (HCO_3^{-})	ND	15,000	120	140
Chloride	ND	250,000	21,000	23,000
TDS	1,000	400,000	18,000	48,000

(ND) Not Detected, (TDS) Total Dissolved Solids

Coalbed Methane Produced Water

Composition: Potential constituents of value

Source	Li µg/L	Mo µg/L	Sn µg/L	Ni µg/L	Cu µg/L
1	-	2.9	-	-	24.2
2	2340	-	-	96.1	97.5
3	-	4.1	5.5	-	29
4	208	-	5.5	35.4	28.6
5	4100	-	-	-	-
6	-	2.9	-	-	19.7
7	-	2.5	-	-	24.2
8	-	2.9	-	-	19.7

Possible Element Recovery?

Constituent	Average Market Value (February 2011) US$/g	US$/lb
Li	0.066	30.00
Mo	0.035	16.00
Sn	0.032	14.50
Ni	0.029	13.00
Cu	0.010	4.50

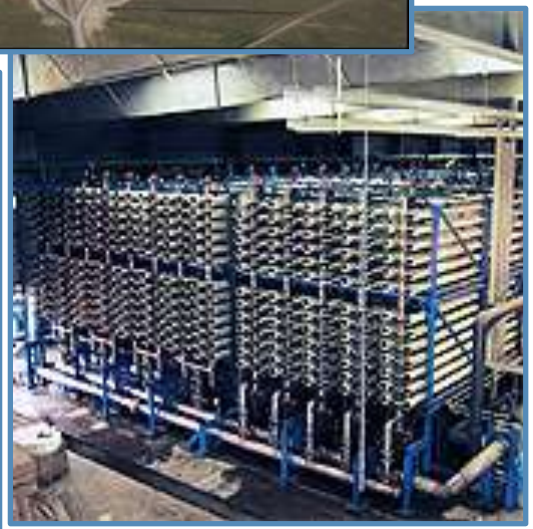
Coalbed Methane Produced Water

Disposal Options:

- Evaporation Ponds
- Deep well injection
- Land application
- Constructed wetlands
- Surface water discharge

Treatment / Desalination

- Reverse Osmosis
- Mechanical evaporation
- Ion exchange



Reverse Osmosis (RO)

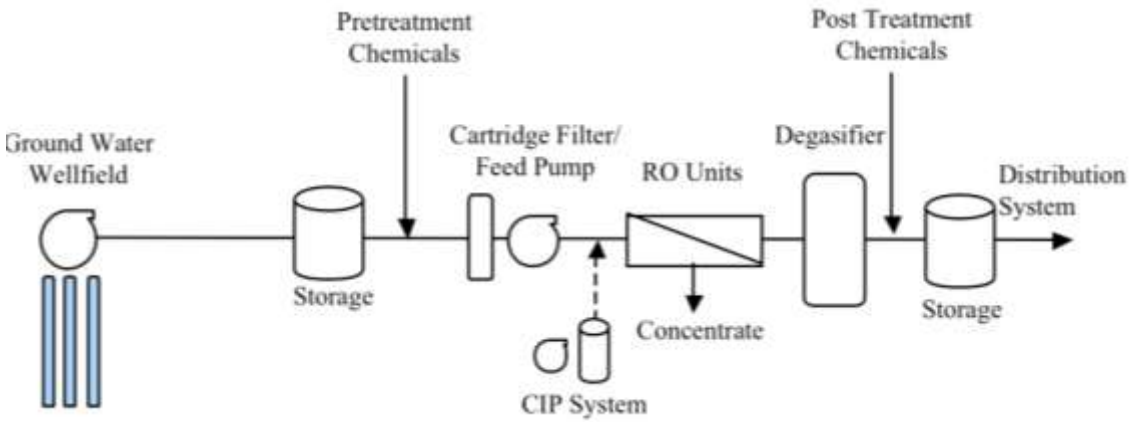
Operation:

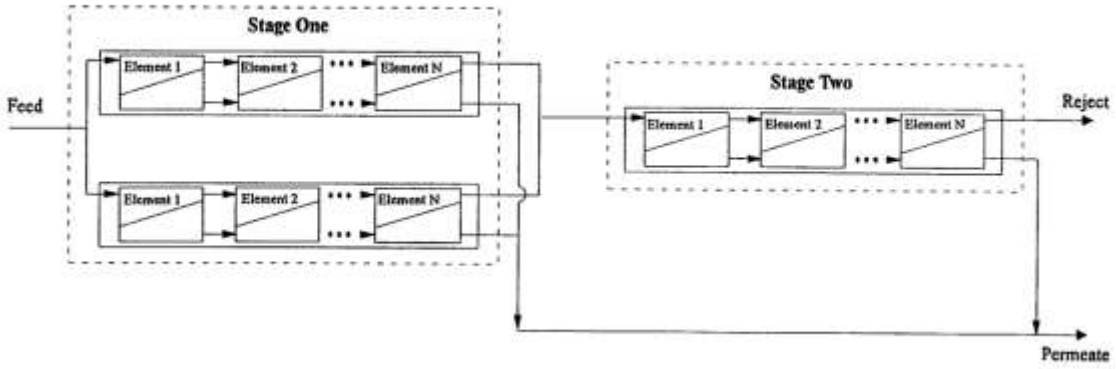
High Pressure Membrane Process

Removal by Differences in Diffusion

Multi-Stage System

Typically 2-3 stages (RO train)



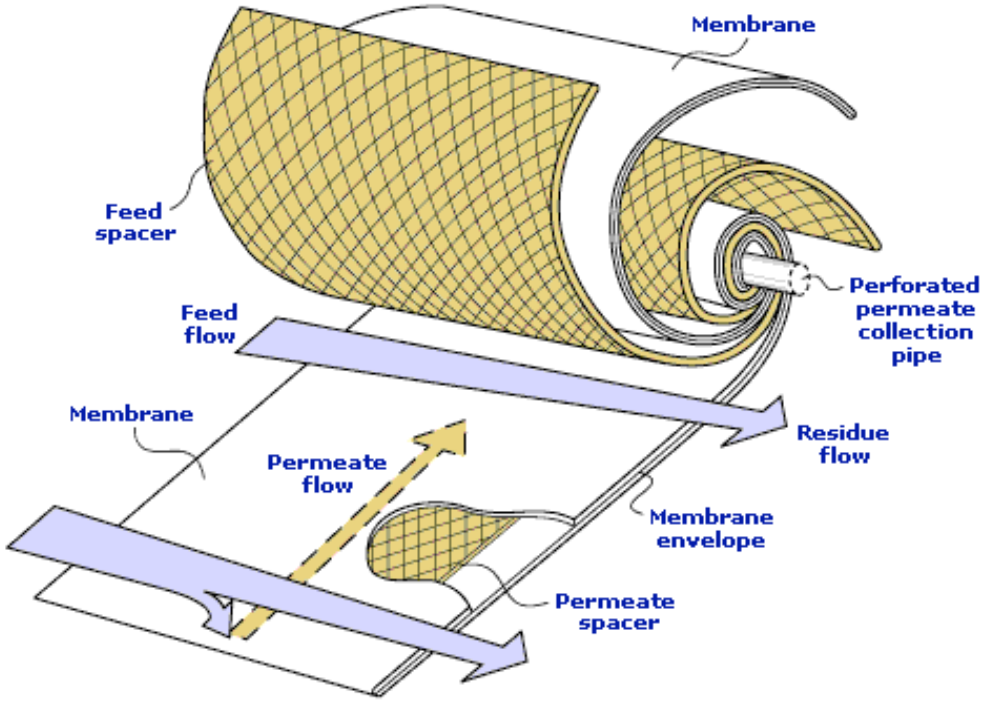


Reverse Osmosis (RO)

Challenges:

Membrane Fouling (Ca^{2+}, Mg^{2+}, SO_4^{2-})

Generation of Concentrated Waste Stream



$$Cf = \frac{1}{1 - Rf}$$

Where:

C_f= Concentration factor

R_f=Recovery factor

Magnetic Nanoparticles

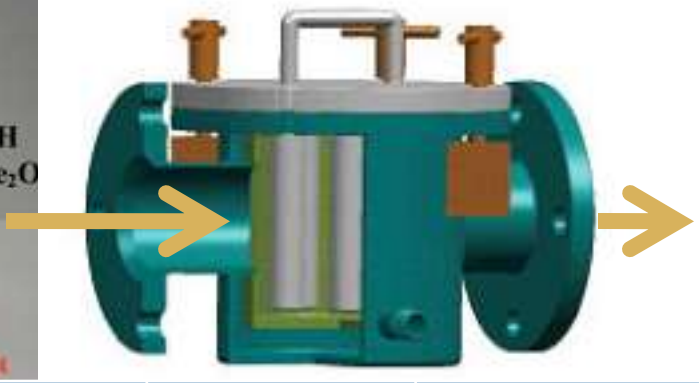
Useful Characteristics:

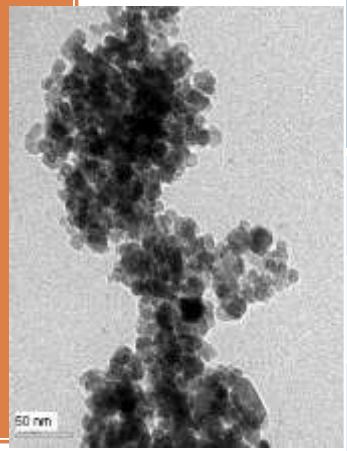
1-100 nm particle diameter

High surface area to volume ratio (specific surface area)

Ability to tailor surface chemistry to selectively remove contaminants

Can be removed with a magnet





Particle Size, nm	Specific Surface Area, m^2/g	Adsorption Capacity, mg As(III)/g Fe_3O_4
11.72	99	114.8
20	60	29.1
300	4	1.6
1,000	0.9	0.2

Surface Coatings

Desired Characteristics:

Hydrophilic

High Charge Density

Selectivity for certain ions:

Ca^{2+}, Mg^{2+},SO_4^{2-}, Li^+

Nanoparticle used	Coating	Constituent Removed/Recovered	Reference
Fe_3O_4 (Magnetite)	Humic Acid	Mercury, Lead, Copper, Cadmium	Liu et al. 2008
Fe_3O_4 (Magnetite)	DMSA	Mercury	Yantasee et al, 2007
Fe_3O_4 (Magnetite)	Chitosan	Gold, Cobalt, Copper, Nickel, Lead	Chang and Chen, 2005, Chang et al., 2006, Tran et al., 2010
Fe_3O_4 (Magnetite)	NTH	Platinum, Palladium	Uheida et al., 2006
γ-Fe_2O_3 (Maghemite)	δ-FeOOH	Chromium	Hu et al., 2007

dimercaptosuccinic acid (DMSA), nonylthiourea (NTH), Feroxyhyte (δ-FeOOH)

Research Objectives

- Research potential magnetic nano-adsorbents:
  - Magnetite, Maghemite
- Research potential surface coatings
  - Potentially removes desired dissolved ions from CBM produced water
- Cost/Benefit Analysis
  - Potential value in recovering constituents from CBM produced water

Experimental Approach

Synthesis

- **Options:**
  - Many options
  - Coprecipitation chosen
    - Most common and least complicated
    - Most economic and energy efficient
- **Procedure:**
  - Coprecipitation of Fe^{3+} and Fe^{2+} ions to form magnetite
  - Oxidation to produce maghemite

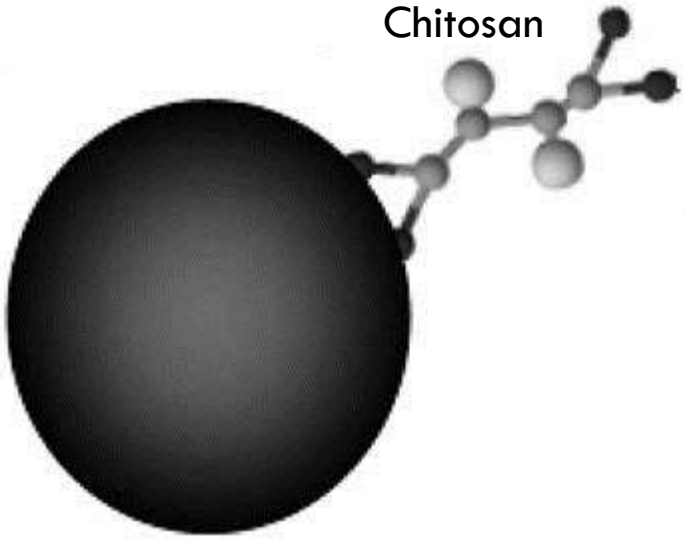
Surface Coatings

Potential Coatings:

- DMSA- dimercaptosuccinic acid
- EDTA- ethylenediaminetetraacetic acid
- Chitosan

Based on selectivity of certain ions:

- Ca^{2+}, Mg^{2+},SO_4^{2-}, Li^+



Surface Coating:
DMSA, EDTA, Chitosan

Magnetic Adsorbent:
Magnetite, Maghemite

Applications

Current Applications:

Removal of toxins:
- Arsenic
- Chromium
- Mercury
- Lead

Recovery of constituents of value:
- Gold
- Platinum
- Molybdenum
- Copper
- Nickel

Nanoparticle used	Constituent Removed (toxin)	Constituent Recovered (value)
Fe_3O_4 (Magnetite)	Arsenic, Chromium, Mercury, Lead	Gold, Platinum, Copper, Nickel,
γ-Fe_2O_3 (Maghemite)	Arsenic, Chromium	Molybdenum

Applications

Potential Applications:

- Decrease surface fouling (due to scaling) of RO membranes
  - Remove: Ca^{2+}, Mg^{2+}, SO_4^{2-}
- Recover constituents of potential value from CBM produced water
  - Recover: Lithium, Molybdenum, Tin, Nickel, Copper

Preliminary Conclusions

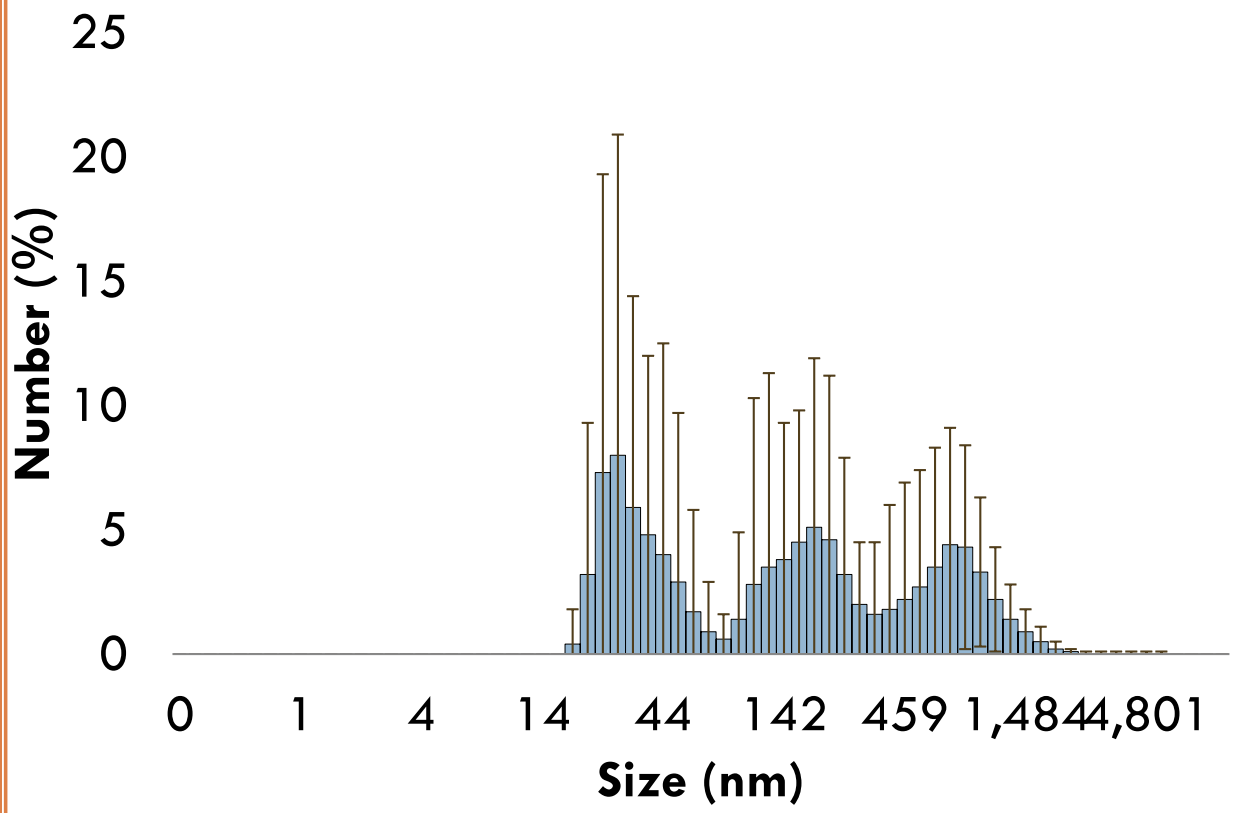
Results

Original size:
106 nm

Original composition:
magnetite

Measured size:
33 (peak 1)
156 (peak 2)
1521 (peak 3)

Possible oxidation to maghemite



Results

Constituent	Average Concentration, WY (µg/L)
Lithium (Li)	2,220
Molybdenum (Mo)	3
Tin (Sn)	6
Nickel (Ni)	66

Average CBM produced water generated in WY	
million gallons per day	billion gallons per year
57.8	21.0

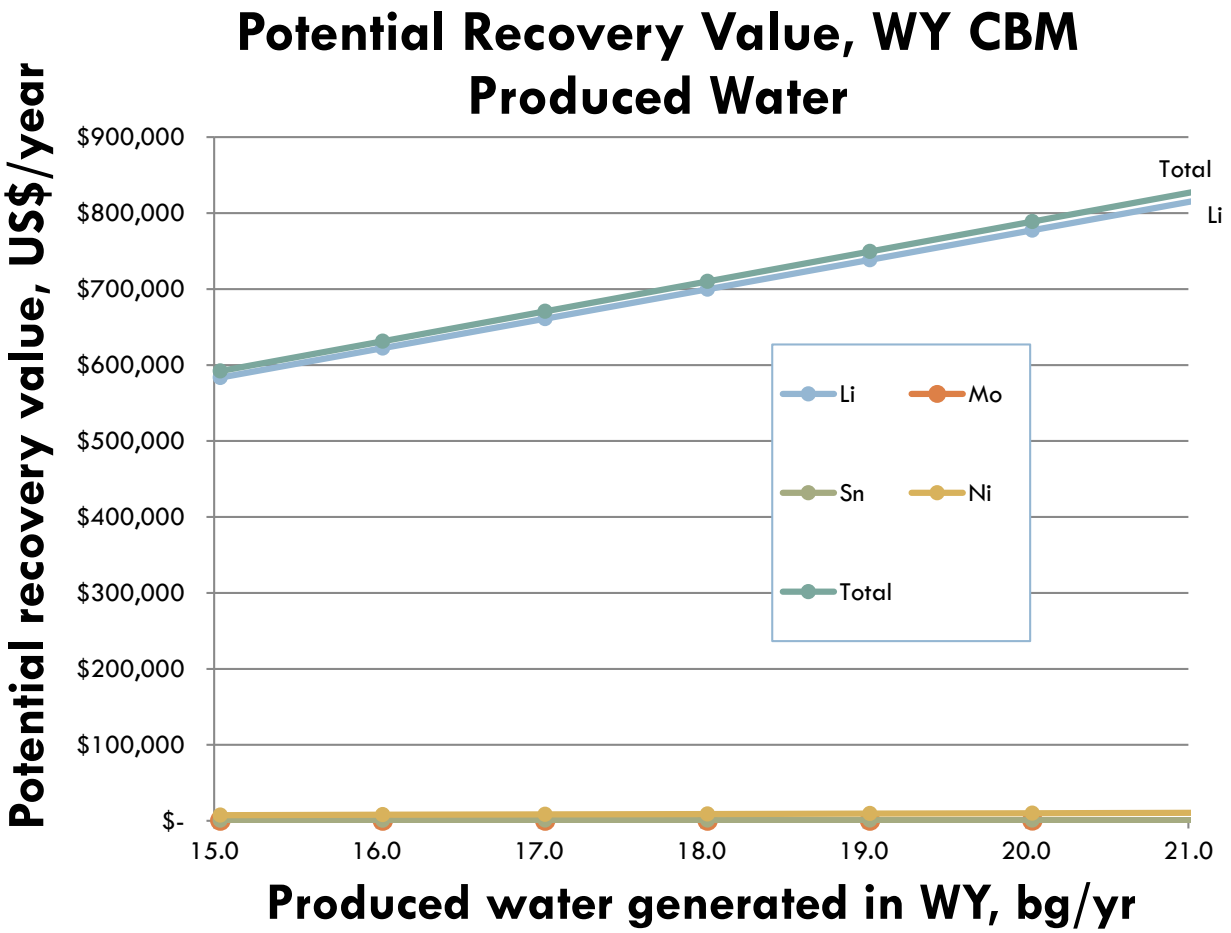
Results

Assumptions:

100% recovery of constituent

Conclusion:

Potential value in recovering constituents from CBM produced water



Conclusions

- **Maghemite chosen over Magnetite**
  - Further oxidation not a concern
- **Surface Coating**
  - DMSA, EDTA, chitosan
- **Potential value in recovering constituents from CBM produced water**
  - Lithium

Future Research

- **Synthesis and surface modification of Maghemite (magnetic nano-adsorbents)**
  - Optimize size and stability of nanoparticles
  - Maximize theoretical adsorption capacity
- **Adsorption Tests**
  - Measure adsorption capacity in fluidized reactor configuration
  - Evaluate regeneration of nano-adsorbents
  - Quantify recovery of dissolved metals as a function of RO recovery and solution chemistry

Questions?

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