Clemson Hydrogeology Symposium

Design and Feasibility of Using Acid to Dissolve Carbonate Rock Formations for Creating Storage Caverns

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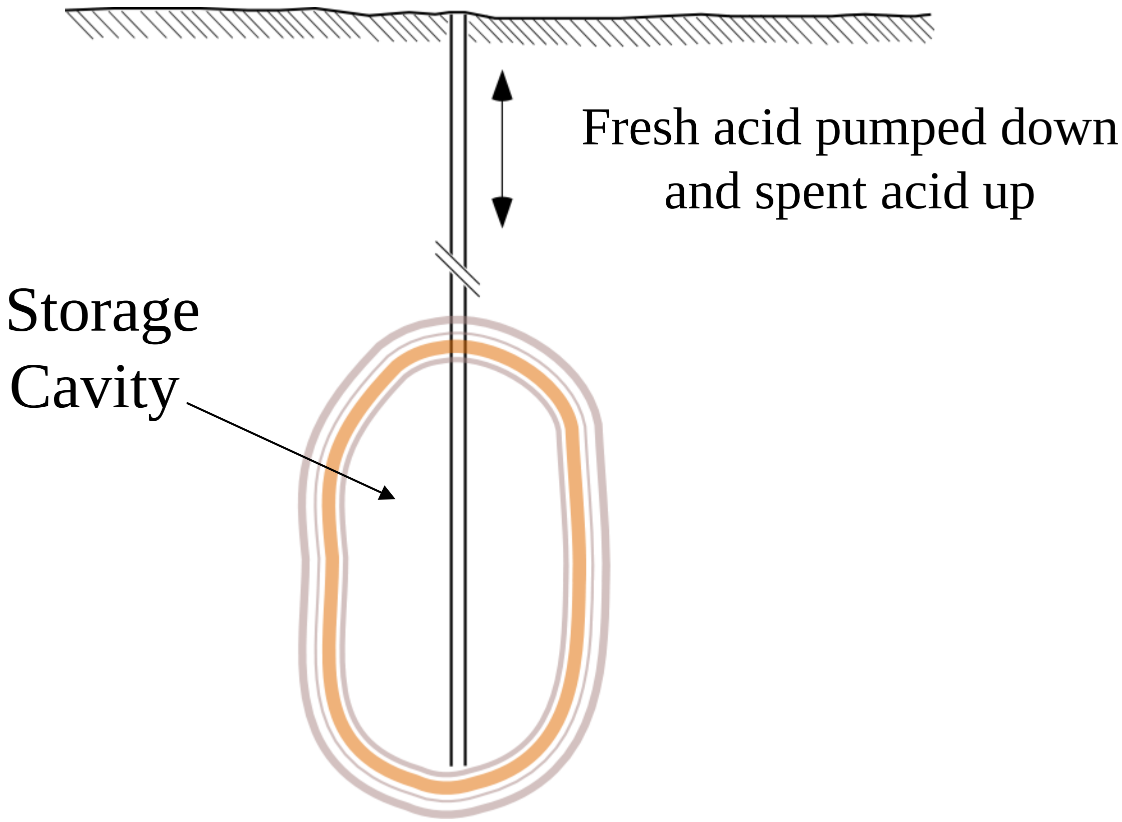
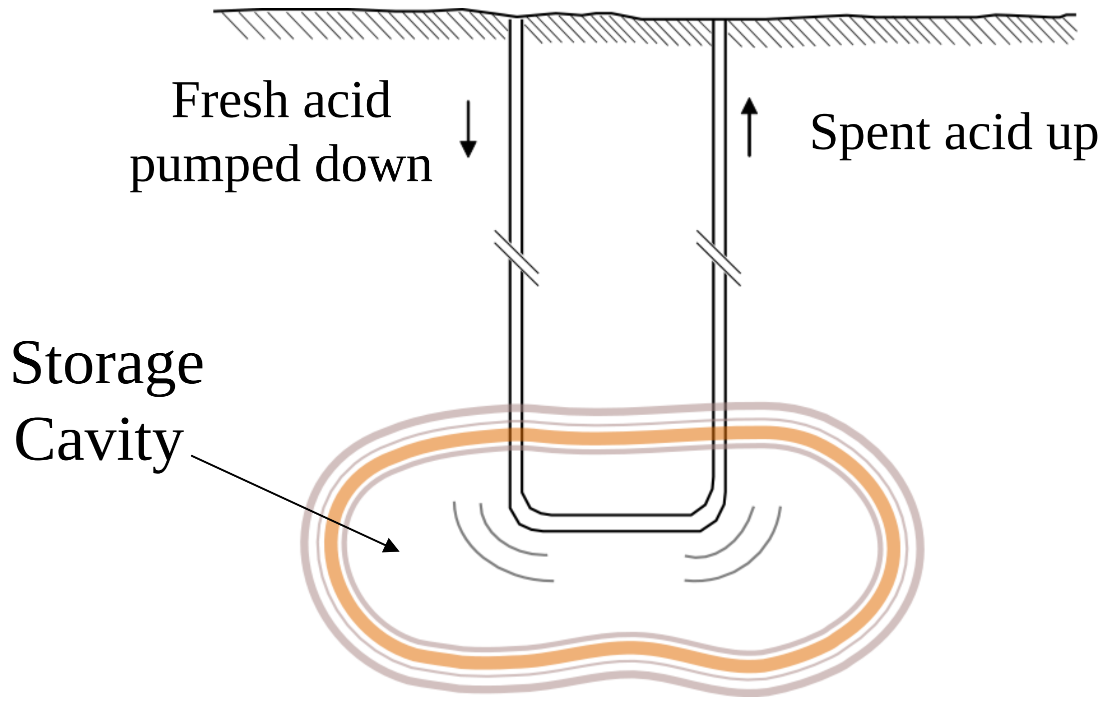
Concept – Create Storage Cavern

- Identify suitable site – select well location(s) and drilling depth
- Drill well(s) into carbonate rock formation
- Fracture the rock, if needed
- Inject acid to dissolve the rock and create storage cavern
- Remove reaction products and dispose of fluid

One-Well Design



Two-Well Design



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Acid Dissolution of Limestone

$$HX(aq) + CaCO_3(s) \leftrightarrow CaX_2(aq) + H_2CO_3(aq)$$

General Comments

- Fast reaction rates
- Reaction equilibria favor products
- Mass transfer limited process

Process Feasibility and Cost

Analyze requirements for creating gas storage volume via acid dissolution of limestone:

- Examine various depth and thickness scenarios
- Estimate volume of void space required for various target storage capacities
- Identify most suitable type of acid
- Estimate volume and cost of acid required
- Identify and determine market value of dissolution products
- Examine options for waste treatment
- Identify regions where technology could be implemented

Factors in Selecting Optimal Acid

- acid cost and availability
- aqueous solubility of resulting calcium salts
- acid and/or salt toxicity
- waste remediation considerations
- corrosion characteristics
- dissolution reaction rate
- dissolution reaction equilibrium constant
- prior use in related mining or gas storage applications

Listed Acid Prices: Dec. 2003

Acid	Current Sale Price $ US / ton (wt % acid)	Acid Cost per Pound of Limestone Dissolved, $ US
*ortho*phosphoric acid (H_3PO_4)	2.7 (52%, farm grade)	0.005
sulfuric acid (H_2SO_4)	25 (100%)	0.012
hydrochloric (HCl)	68 (22 °Be, 34%)[a]	0.075
nitric acid (HNO_3)	215 (40 °Be, 68%)[a]	0.199
formic acid (HCOOH)	451 (85%)	0.244
acetic acid (CH_3COOH)	910 (95%)	0.575
3-hydroxypropionic acid ($C_3H_6O_3$)	1100 (95%)[b]	0.918
citric acid ($C_6H_8O_7$)	940 (98%)	0.921
hydrobromic acid (HBr)	1120 (48%)	1.886

a. Sp.gr. = 145/(145-Baume).

b. Projected sales price in 2006 (Cargill).

Source: Chemical Market Reporter

Calcium Salt Solubility

Acid	Calcium Salt	Calcium Salt Solubility in Water (g/l)
hydrobromic acid (HBr)	calcium bromide ($CaBr_2$)	1420
nitric acid (HNO_3)	calcium nitrate ($Ca(NO_3)_2$)	1212
3-hydroxypropionic acid ($C_3H_6O_3$)	calcium hydroxypropionate ($Ca(C_3H_6O_3)_2$)	1000
hydrochloric (HCl)	calcium chloride ($CaCl_2$)	745
acetic acid (CH_3COOH)	calcium acetate ($Ca(C_2H_3O_2)_2$)	374
formic acid (HCOOH)	calcium formate ($Ca(CHO_2)_2$)	162
*ortho*phosphoric acid (H_3PO_4)	calcium *ortho*phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$)	18
sulfuric acid (H_2SO_4)	calcium sulfate (anhydrite, $CaSO_4$)	2
citric acid ($C_6H_8O_7$)	calcium citrate ($Ca_3(C_6H_5O_7)_2 \cdot 4H_2O$)	1

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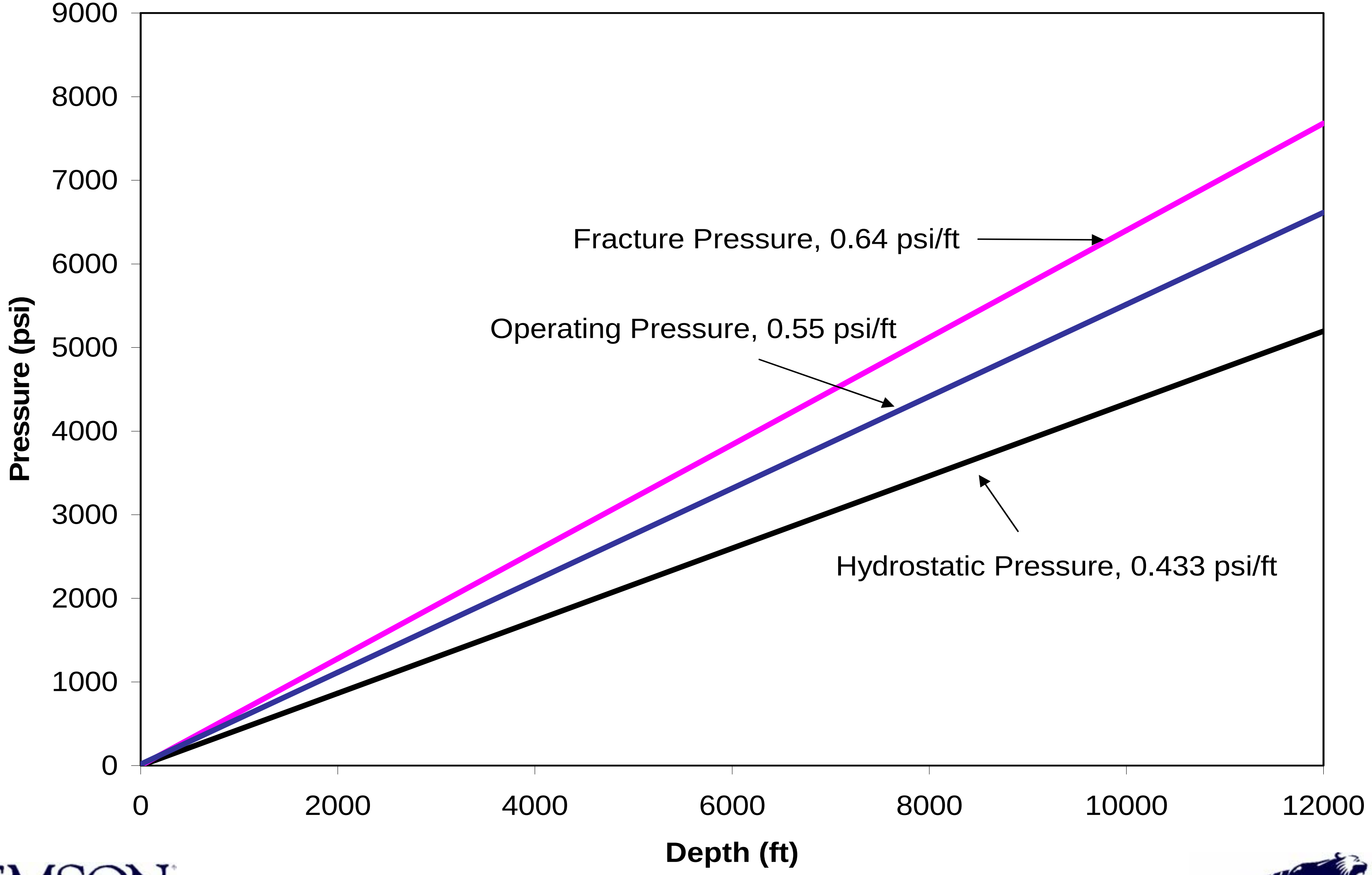
Gas Storage Operating Pressures



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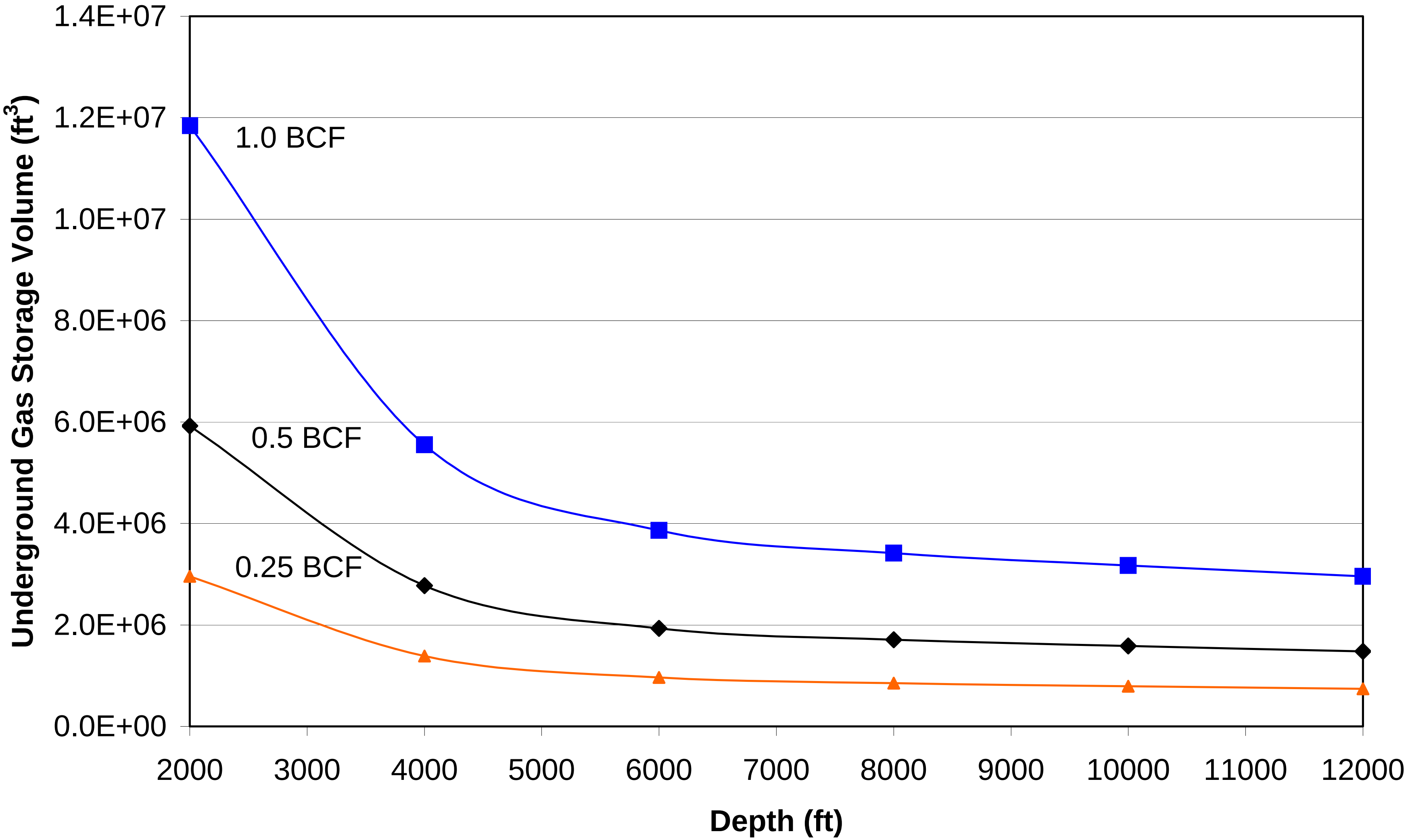
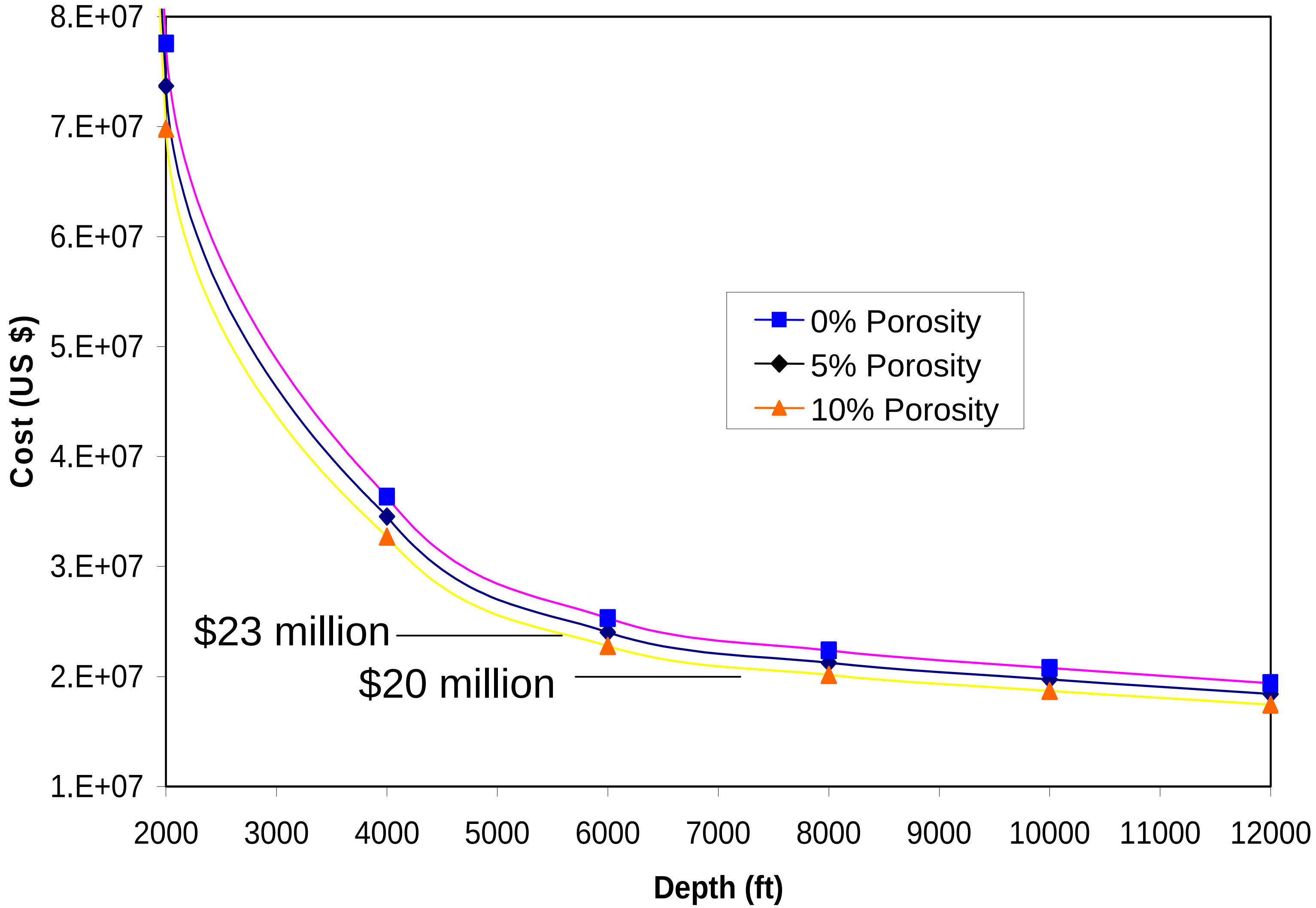
Rock Volume to Dissolve



Hydrochloric Acid Cost: 0.5 BCF



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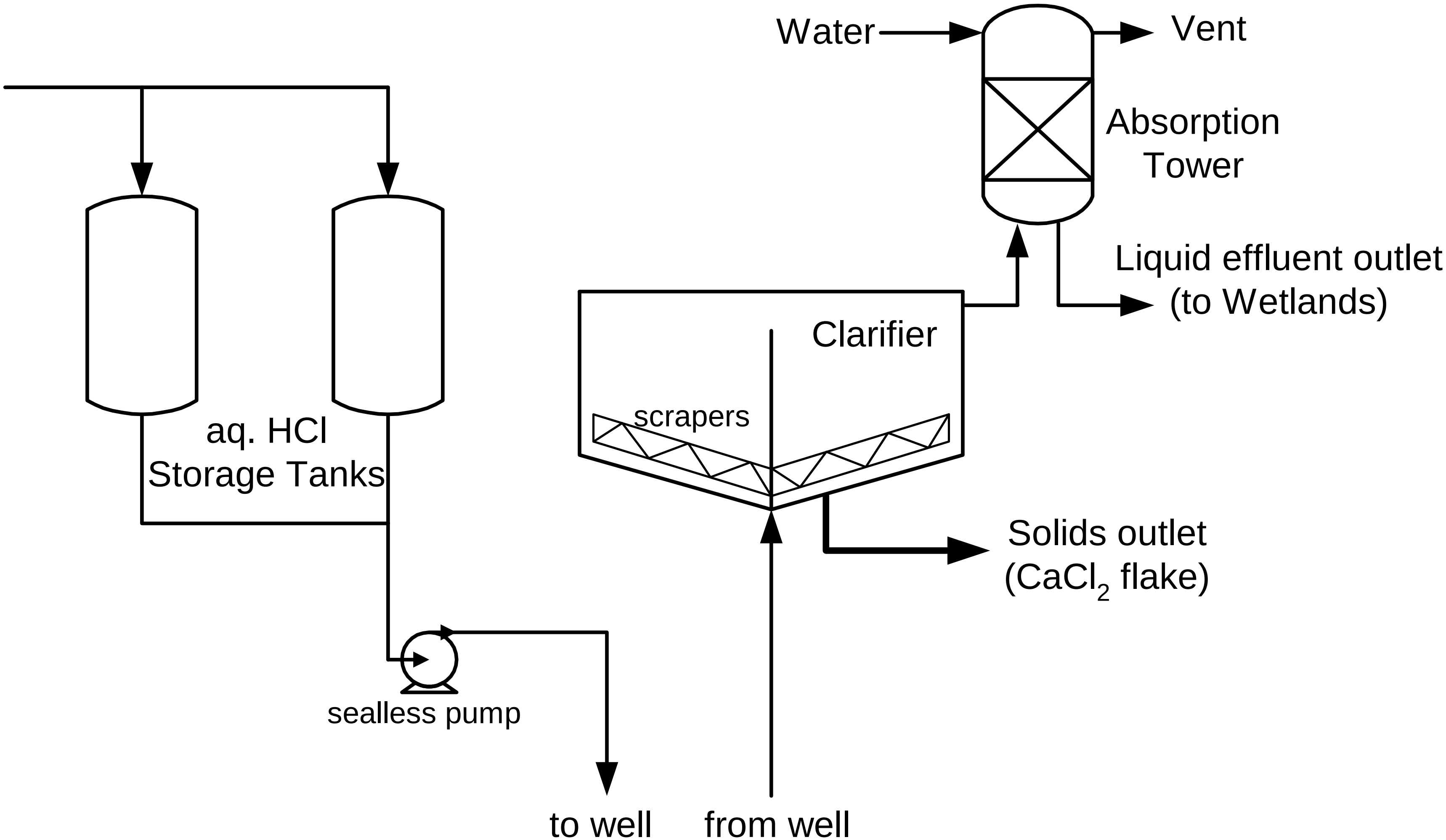
Schematic: Dissolution Process



Capital Investment: Direct Costs

Operation	**Lang Factors, Solid-Liquid**	**Cost ($ US)**
Direct Costs		
Purchased equipment	100	799,640
Installation	39	311,860
Instrumentation	13	103,953
Piping	31	247,888
Electrical	10	79,964
Buildings	29	231,896
Yard Improvements	10	79,964
Service facilities	55	439,802
Land	2	15,993

Capital Investment: Indirect Costs

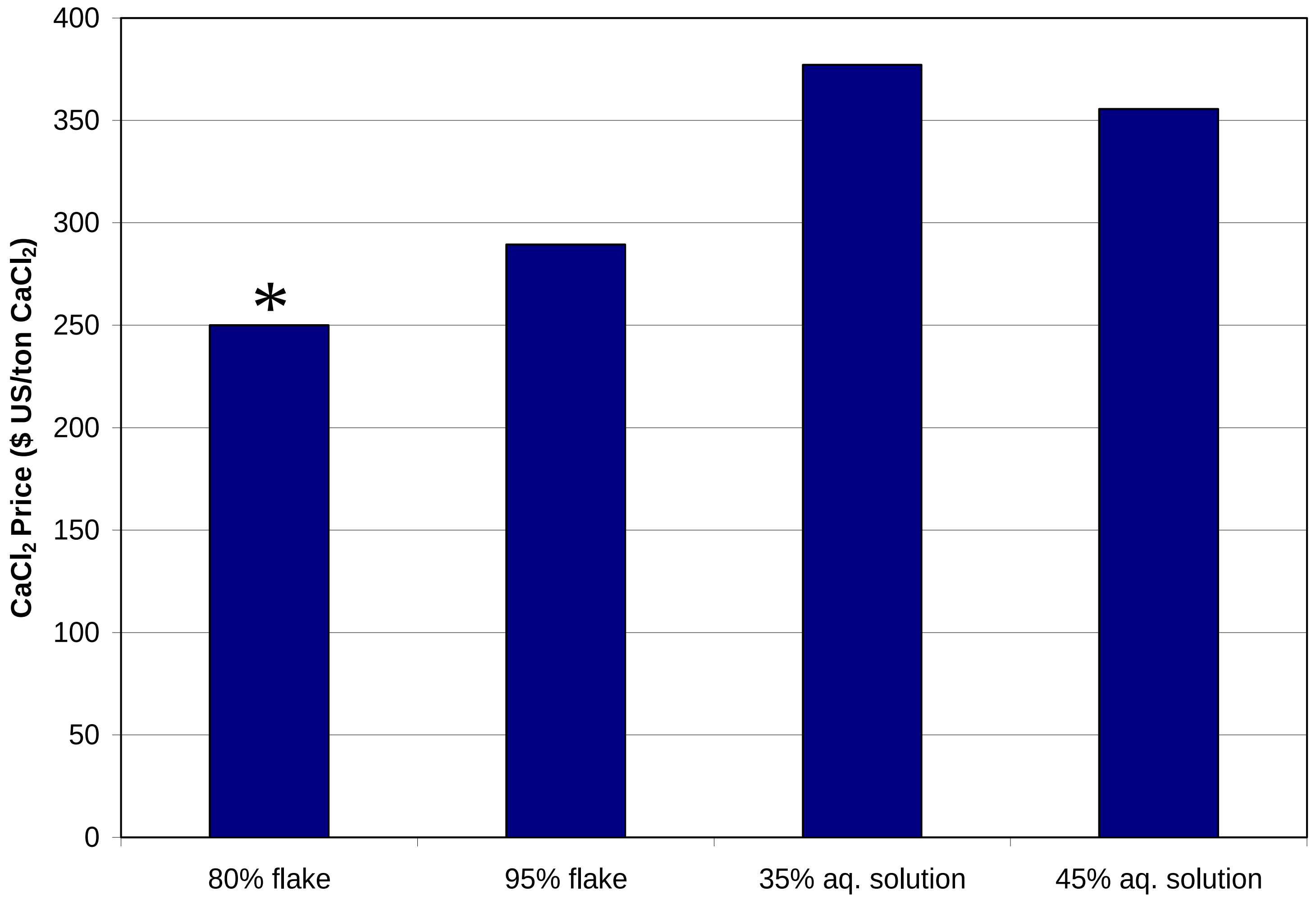
Operation	Lang Factors, Solid-Liquid	Cost ($ US)
Indirect Costs		
Engineering & Supervision	32	255,885
Construction expenses	34	271,878
Contractor's fee	18	143,935
Contingency	36	287,871
Total Fixed Capital Investment	**407**	**3,270,529**

Well Costs: Drilling and Fracturing (Two-Well Design)

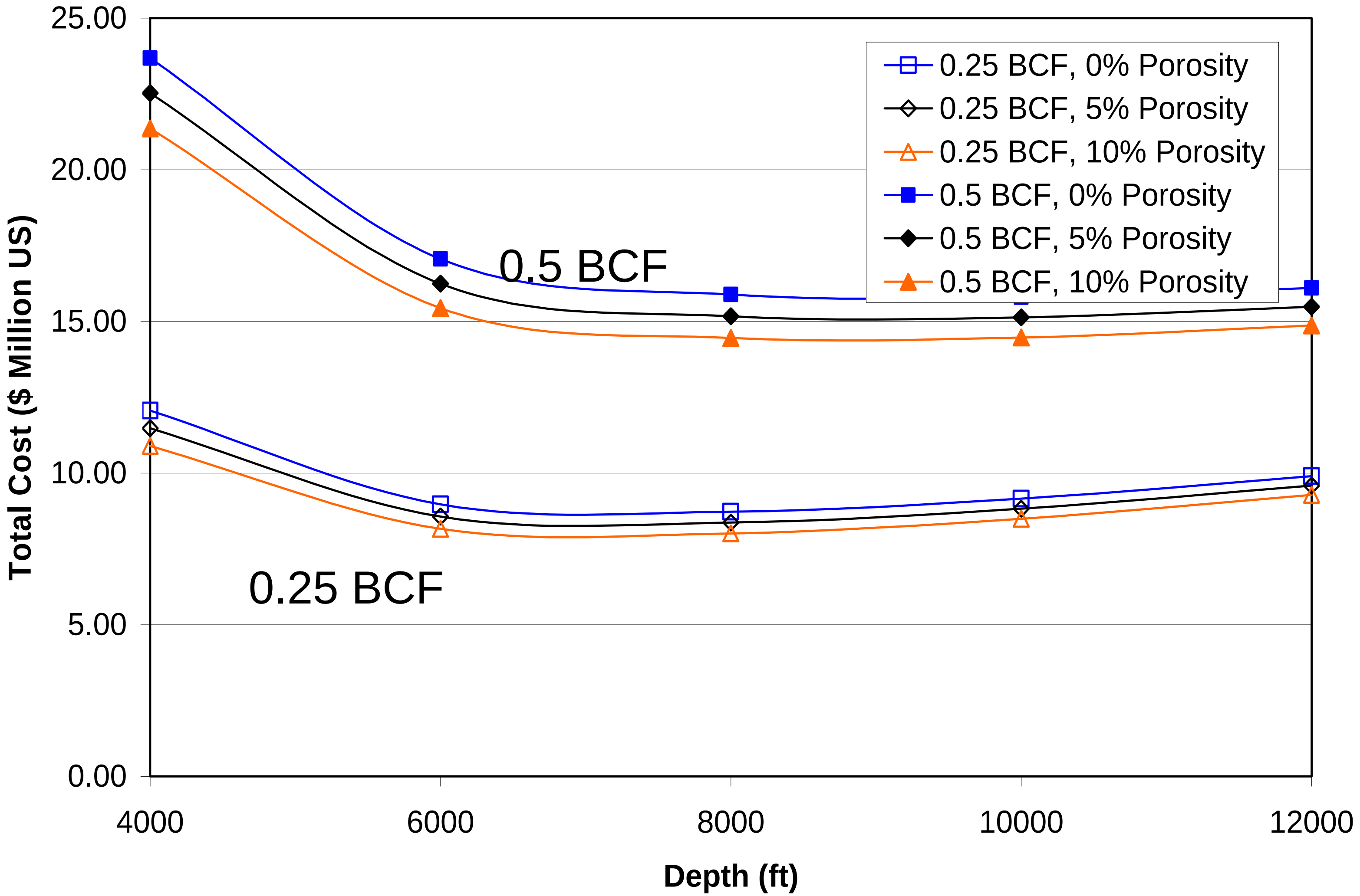
Total Depth (ft)	Completed Well[a]	Construction Well[b]	Additional Completed Costs		
			Horizontal Connection[c]	Acid Fracturing[d]	Hydraulic Fracturing[e]
4,000	$250,000	$150,000	$50,000	$20,000	$30,000
8,000	$1,000,000	$500,000	$100,000	$100,000	$75,000
12,000	$2,500,000	$1,000,000	$150,000	$150,000	$200,000

a. Completed injection/withdrawal storage well. Eastern US area. Seven inch high deliverability flow string to bottom.
b. Additional slim hole well to assist in cavity building. Flow string set at total depth.
c. Directionally drilled connection between wells at total depth.
d. Five thousand gallon gelled acid breakdown to initiate cavity building process.
e. Hydraulic fracture with proppant to initiate/accelerate cavity building process.

Calcium Chloride Pricing

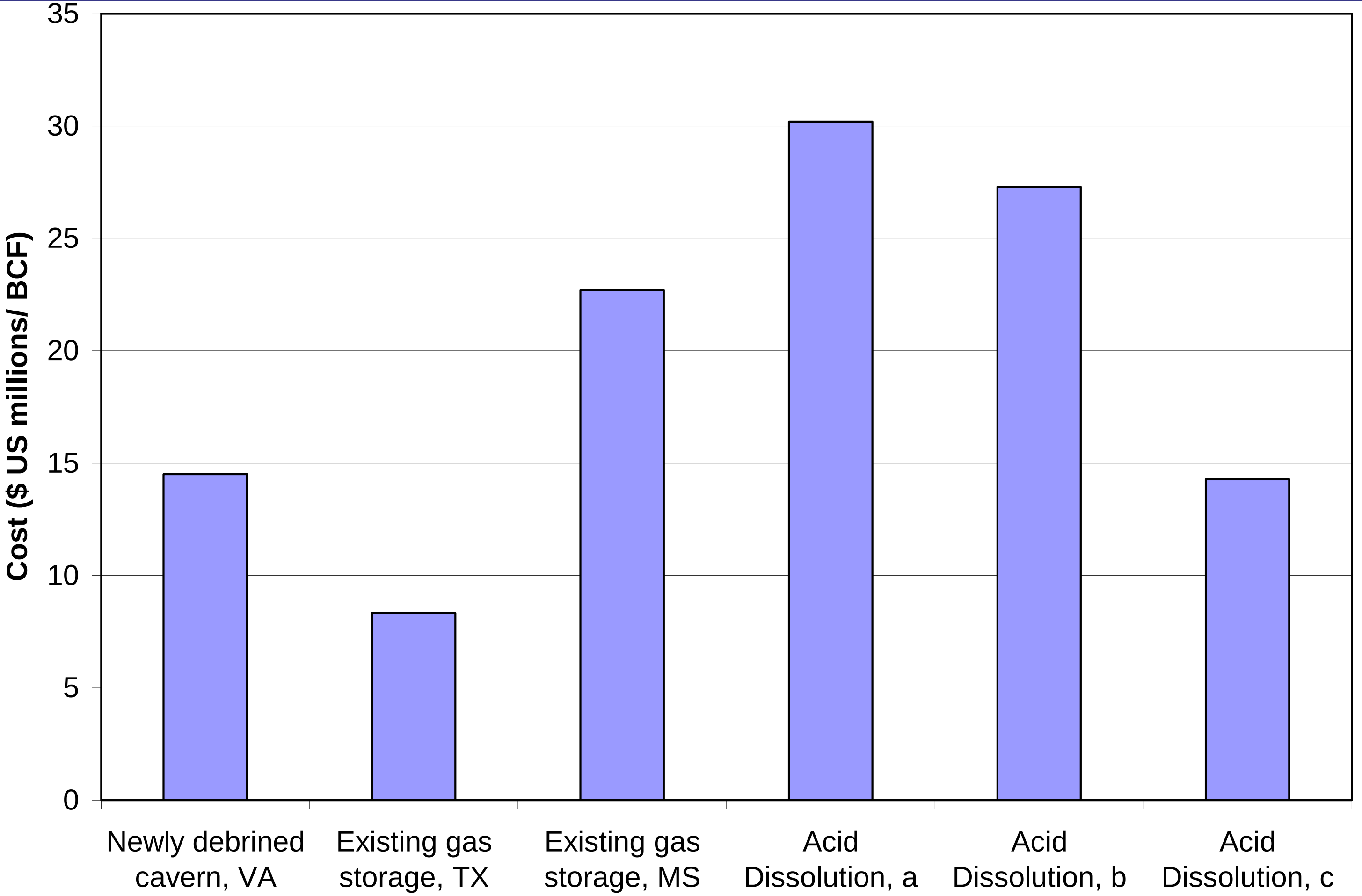


Estimated Cost



Assumes catalog list price for HCl;
sale of 75% calcium chloride, 80% flake

Cost Comparison – Construction of Underground Storage



a.1 BCF, 0% Porosity, Listed Acid Cost, 75% $CaCl_2$ sold, 8000 ft.

b.1 BCF, 10% Porosity, Listed Acid Cost, 75% $CaCl_2$ sold, 8000 ft.

c.1 BCF, 5% Porosity, 65% of Listed Acid Cost, 75% $CaCl_2$ sold, 8000 ft.

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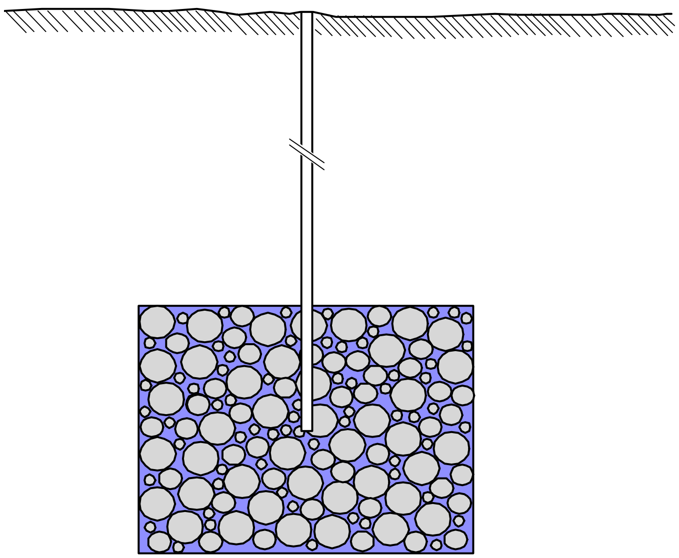
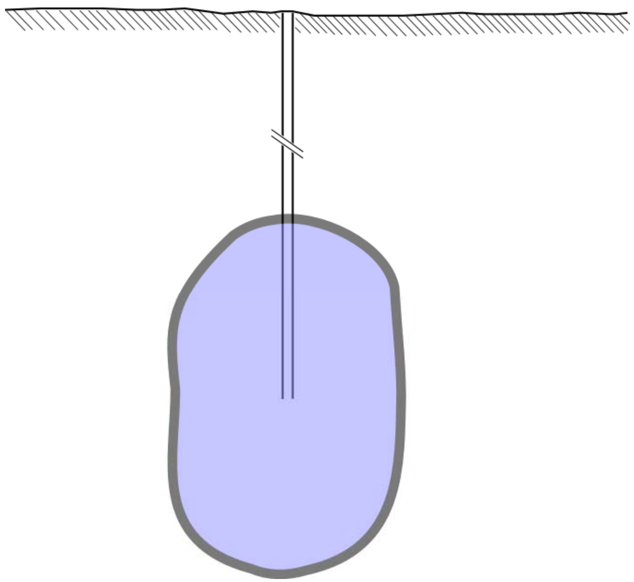
Characteristics of Underground Storage

- Converted oil & gas fields
- Converted aquifers



- Cavern storage (including carbonate cavern storage)



✓ High deliverability
✓ High cycling frequency
✓ Low cushion gas

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Conclusions

- The process of creating storage cavities by acid dissolution of carbonate rock appears feasible based on preliminary economic analysis.
- Results of cost comparison with other types of storage are favorable.
- Carbonate rock of sufficient thickness and depth is present in numerous areas.
- Advantages:
  - High deliverability
  - High cycling frequency
  - Low cushion gas
  - Wide geographic availability
  - Open new market areas

Project Support

- Funded by the U.S. Department of Energy through the National Energy Technology Laboratory, Morgantown, WV.
- James R. Ammer, Project Manager, USDOE