REMOVING RADIOACTIVE CONTAMINATION FROM ION EXCHANGE RESINS USED IN DRINKING WATER TREATMENT

APRIL 3, 2007

James McMahon Dr. M. R. Collins

Department of Civil Engineering - University of New Hampshire

<u>Funded by:</u> United States Environmental Protection Agency (USEPA) New England Water Treatment Technology Assistance Center (WTTAC)

Presentation Outline

- Background
 - Chemistry/Radionuclides/Radium-226
- Radium-226 Treatment Processes
 - Ion Exchange Resins/Water Treatment
- Research Work Tasks
 - Resin Exhaustion Study
 - Resin Regeneration
 - Batch Studies
 - Column Study
 - Field Verification Study

Drinking Water Regulations for Radionuclides

- 1962 US Public Health Services DWS
 3 pCi/L Radium 226
- 1977 USEPA National Interim Prim. DWS
 5 pCi/L Combined Radium 226/228
- 2000 Radionuclide Rule USEPA

Regulated Contaminant	MCL	<u>MCLG</u>
Beta/photon emitters	4 mrem/year	0
Gross alpha particle	15 pCi/L	0
Combined Radium-226/228	5pCi/L	0
Uranium	30 ug/L	0

Treatment Options for Radium-226 in Drinking Water

- EPA Best Available Technologies (BAT)
 - Ion Exchange (IX)
 - Lime Softening
 - Reverse Osmosis
- Other Practices
 - Blending water sources to below standards
 - Find alternate well site

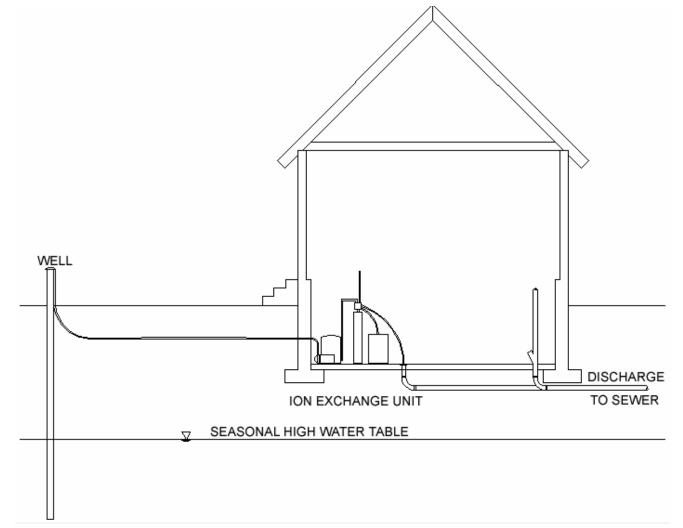
Radium-226 Treatment Using Ion Exchange Resin

- Raw water flows through treatment unit
- Exchanges Ion (Resin Exhaustion)
 2[RSO₃]Na⁺ + Ra² ≓ [2RSO₃]Ra²⁺ + 2Na⁺
- Backwash Cycle (Resin Regeneration)
 [2RSO₃]Ra²⁺ + 2Na⁺ ≈ 2[RSO₃]Na⁺ + Ra²⁺

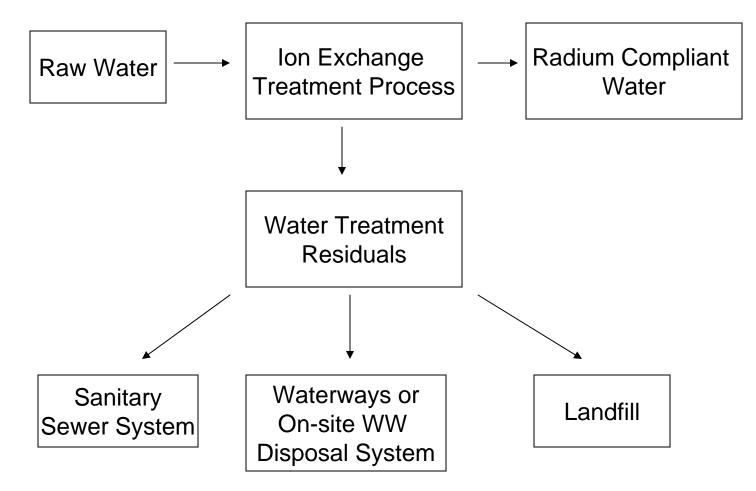
Cation Exchange Resin

- Effectiveness of IX Resin in Water Treatment based on:
 - Ion affinities
 - Ion concentrations
 - Abundance of oppositely charged sites on resin

Typical Home Ion Exchange Water Softening System Layout



Ion Exchange Waste Disposal Options Diagram



Project Specific Objectives

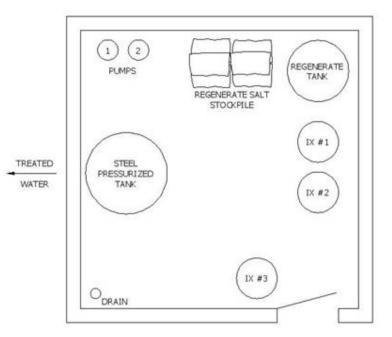
- Objective 1
 - Determine the extent of Radium-226 fouling on cation exchange resins
- Objective 2
 - Assess the amount of Radium-226 removal using various regenerate solutions and contact times
- Objective 3
 - Determine the Radium-226 ion-to-resin exposure time has on the Radium-226 removal process

Project Work Tasks Outline

- Objective 1
 - Resin Exhaustion Column Study
 - Treat water with high Ra-226 concentrations and accumulate Ra-226 on cation exchange resin for cleaning
- Objective 2
 - Resin Regeneration Batch Studies
 - Assess impact of cleaning variables on exhausted cation exchange resins
 - Resin Regeneration Column Study
 - Optimize most influential regeneration variables
- Objective 3
 - Field Assessment of Fouled Cation Exchange Resins
 - Compare optimized regeneration solution to resins which have been in operation for an extended period of time

Objective 1 - Resin Exhaustion Study Site Location & Layout

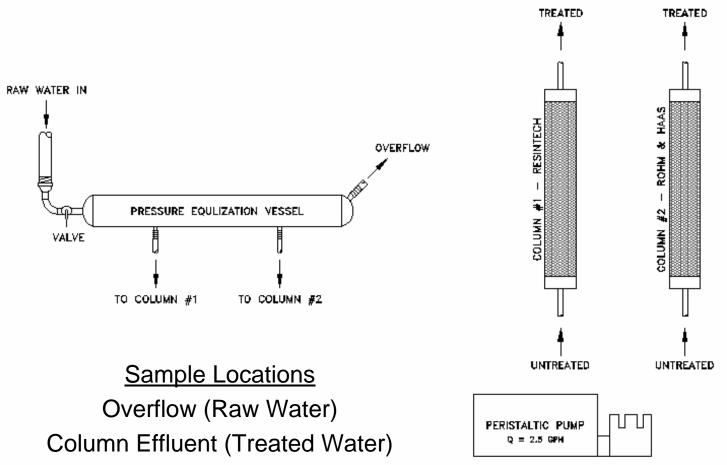




Water Treatment Building For Apartment Complex Pelham, NH

Treatment Building Layout

Objective 1 - Resin Exhaustion Study Column Layout



Objective 1 - Resin Exhaustion Study Sampling Event



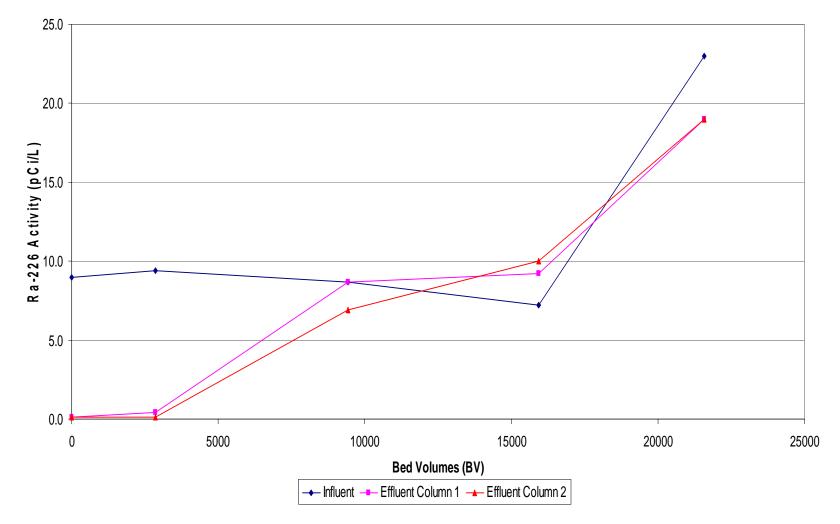
Sample Volumes 2 L (Radium-226) 14 mL (Metals)



Raw Water Data

Radium-226 (10.8 pCi/L) Calcium (150.3 mg/L) Magnesium (25.1 mg/L) Iron (2.2 mg/L)

Objective 1 - Resin Exhaustion Study Radium-226 Breakthrough Curve



Objective 1 - Resin Exhaustion Study Cation Accumulations on Resins

Summary Table - Column Setup 1 (40 Days)					
Item Units Resintech Rohm & Haas					
Radium-226	pCi/g	34.5	36.0		
Calcium	mg/g	48.4	8.0		
Magnesium	mg/g	3.0	1.1		
Iron	mg/g	1.0	0.5		

Summary Table - Column Setup 2 (28 Days)					
ltem	Units	Resintech	Rohm & Haas		
Radium-226	pCi/g	17.0	16.5		
Calcium	mg/g	16.4	9.7		
Magnesium	mg/g	1.7	1.4		
Iron	mg/g	0.1	0.3		

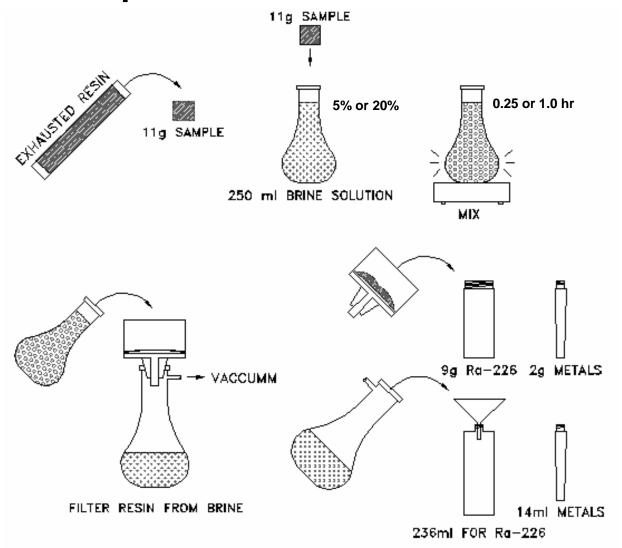
Note: All concentrations based on gram dry weight resin

Objective 2 - Resin Regeneration Batch Studies Experimental Approach

To assess various Regeneration Conditions

Sample	Brine Strength (% NaCl)	рН	Regenerate Contact Time (hr)	Ra-226 to Resin Exposure Time (days)
1	5	E E	0.25	
2		5.5	1.0	
3		0 5	0.25	
4		8.5	1.0	30 to 166
5	20	5.5	0.25	30 10 100
6		5.5 8.5	1.0	
7			0.25	
8			1.0	

Objective 2 - Resin Regeneration Batch Studies Experiment Procedure



Objective 2 - Resin Regeneration Batch Studies

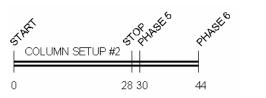


Phase 1

Sample	Brine Strength	pН		Exposure Time
	(% NaCl)	рп	Contact Time (hr)	(days)
1		5.5	0.25	
2	5	5.5	1	
3		8.5	0.25	
4		0.0	1	54
5		5.5	0.25	54
6	20	5.5	1	
7		8.5	0.25	
8		0.0	1	

Phase 2

Sample	Brine Strength	pН	Regenerate	Exposure Time
	(% NaCl)		Contact Time (hr)	(days)
9		5.5	0.25	
10	5	5.5	1	
11	5	8.5	0.25	
12		0.5	1	68
13		5.5	0.25	00
14	20	5.5	1	
15	20	8.5	0.25	
16		0.0	1	1



Phase 5

Sample	Brine Strength		Regenerate	Exposure Time
	(% NaCl)	рН	Contact Time (hr)	(days)
33		5.5	0.25	
34	5	5.5	1	
35	5	8.5	0.25	
36		0.5	1	30
37		5.5	0.25	
38	20	5.5	1	
39		8.5	0.25]
40		0.5	1	

Phase 3

Sample	Brine Strength	рН		Exposure Time
	(% NaCl)		Contact Time (hr)	(days)
17		5.5	0.25	
18	5	5.5	1	
19	5	8.5	0.25	
20		0.5	1	100
21		5.5	0.25	100
22	20	5.5	1	
23	20	8.5	0.25	
24		0.0	1]

Phase 4

Sample	Brine Strength	pН	Regenerate	Exposure Time
	(% NaCl)		Contact Time (hr)	(days)
25		5.5	0.25	
26	5	5.5	1	
27	5	8.5	0.25	
28		0.5	1	166
29	20	5.5	0.25	100
30		5.5	1	
31	20	8.5	0.25]
32		0.5	1	

Sample	Brine Strength	pН	Regenerate	Exposure Time
	(% NaCl)		Contact Time (hr)	(days)
41		5.5	0.25	
42	5	5.5	1	
43		8.5	0.25	
44		0.0	1	44
45		5.5	0.25	44
46	20	5.5	1	
47		8.5	0.25	
48		0.5	1	

Objective 2 - Resin Regeneration Batch Studies Photo Summary 1



Brine Solution & pH meter

Brine and Resin Samples

Objective 2 - Resin Regeneration Batch Studies Photo Summary 2



Samples on Mixing Table

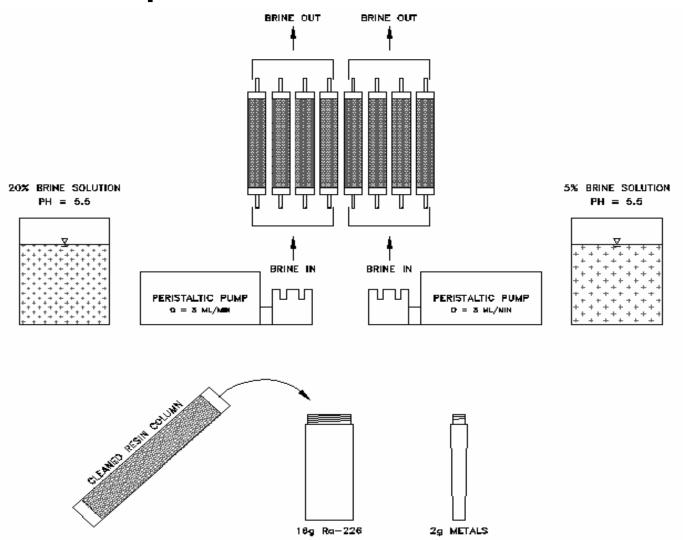
Sample Containers & Filter Setup

Objective 2 - Resin Regeneration Batch Studies Analysis of Variance Results

	Degrees			
	of	Sum of		%
Factors	Freedom	Squares	F Ratio	Contribution
Brine Strength	1	1.022	105.802**	46.0%
Resin Type	1	0.351	36.332 **	15.5%
Initial Radium-226 Resin Loading	1	0.239	24.751**	10.4%
Column Setups	1	0.183	18.980 **	7.9%
рН	1	0.075	7.817**	3.0%
Radium-226 Exposure Time	1	0.005	0.555**	N.S.
Brine Contact Time	1	0.000	0.01	N.S.
Error	64	0.618		17.1%

**Significant at 99% confidence interval N.S. = Factor Not Significant

Objective 2 - Resin Regeneration Column Study Experiment Procedure



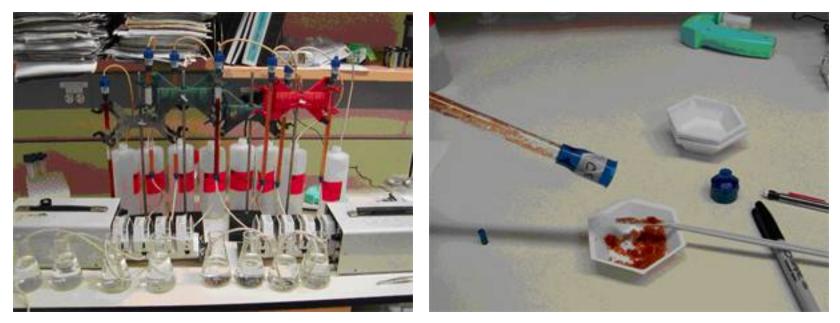
22

Objective 2 - Resin Regeneration Column Study Experimental Approach

Using the most influential variables from Batch Studies

Column	Resin	Pump	pН	<u>Brine</u> Strength	<u>Contact</u> Time (hr)	Flow Rate (mL/min)
1	Rohm & Haas				0.5	
2		1		5%	0.25	
3	Resintech	I		5%	0.5	
4			5.5		1	3 ml/min
5	Rohm & Haas		5.5	20%	0.5	5 111/11111
6		2			0.25	
7	Resintech	Z		2070	0.5	
8					1	

Objective 2 - Resin Regeneration Column Study Photo Summary



Column Setup

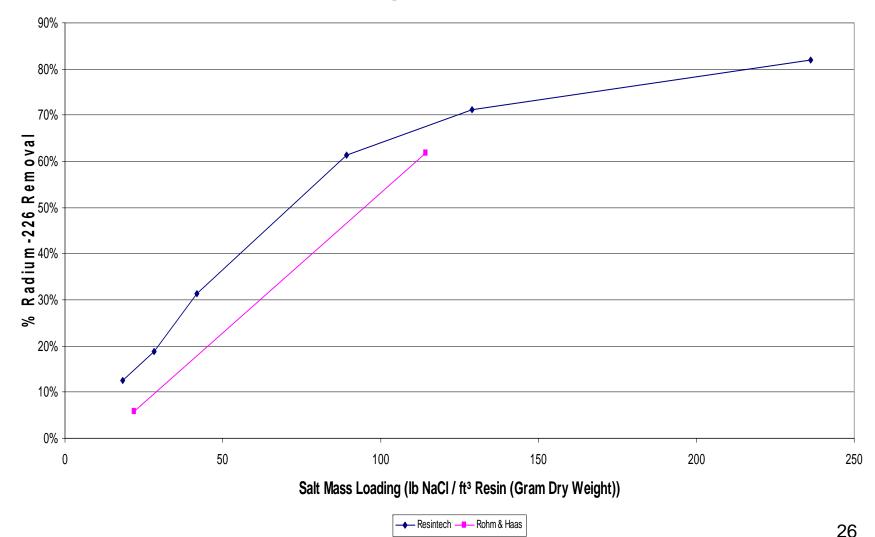
Resin Sample

Objective 2 - Resin Regeneration Column Study Analysis of Variance Results

	Degrees			
	of	Sum of		%
Factors	Freedom	Squares	F Ratio	Contribution
Brine Strength	1	142.629	472.894**	86.8%
Resin Type	1	7.526	24.953*	4.4%
Brine Contact Time	1	0.208	0.689	N.S.
Brine Volume	1	0.001	0.002	N.S.
Error	3	0.905		8.8%

*Significant at 95% confidence interval **Significant at 99% confidence interval N.S. = Factor Not Significant

Objective 2 - Resin Regeneration Column Study Salt Mass Loading vs. Ra-226 Removal

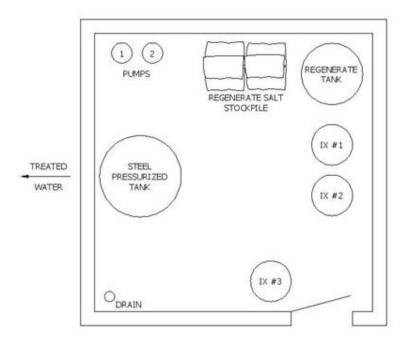


Objective 3 - Resin Regeneration Field Verification Study **Overview**

- Sample cation exchange resins in service for greater than 1 year:
 - Pelham, NH
 - Windham, NH
- Sample resin before and after cleaning
- Clean dirty resin using optimized regenerate solution from previous work
- Compare existing cleaning practices with the results

Objective 3 - Resin Regeneration Field Verification Study **Pelham Site Layout**





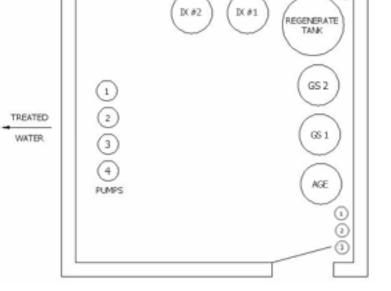
Water Treatment Building For Apartment Complex Pelham, NH

Existing Treatment Building Layout

Objective 3 - Resin Regeneration Field Verification Study Windham Site Layout



Water Treatment Building For Windham Public Water Windham, NH

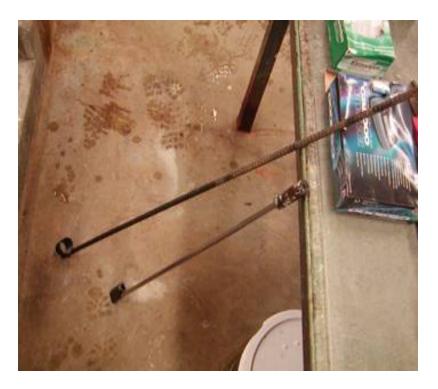


Existing Treatment Building Layout

Objective 3 - Resin Regeneration Field Verification Study Site Comparison

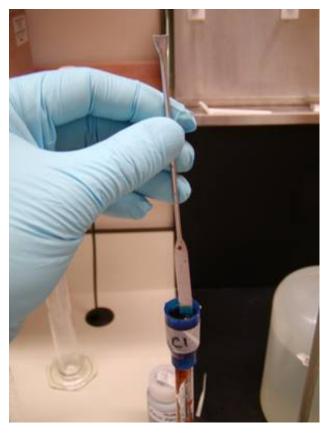
	Pelham, NH	Windham, NH
EPA ID	1852080	2542030
Date Installed	Jan-96	Nov-05
Treatment for	22 Apartments	Small Community (200 Connections)
Average Flow	2.4 gpm	80 gpm
Frequency of Backwash	2 days	1 day
Radium-226 (pCi/L)	10.4, 16	0.8 -4.4
Radium-228 (pCi/L)	0.1, 0.9	0.4
Gross Alpha (pCi/L)	0.6	4
Uranium (pCi/L)	27-81	30
Well Depth	575-625 ft	700-950 ft

Objective 3 - Resin Regeneration Field Verification Study Sample Locations

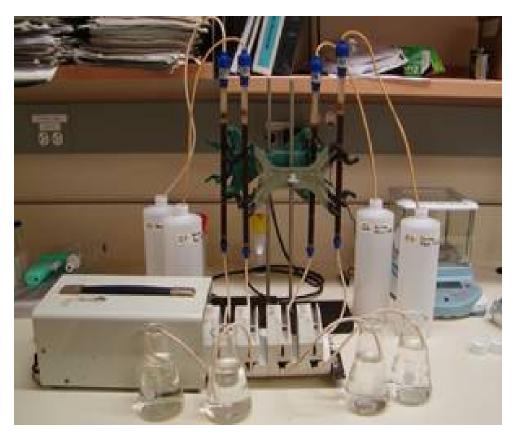


- Brine (500 mL)
 - Before Cleaning
 - After Cleaning
- Resin (200 g)
 - Before Cleaning
 - After Cleaning
- Raw Water (2L)
- Treated Water (2L)

Objective 3 - Resin Regeneration Field Verification Study Procedure Photo Summary



Adding Resin to Column



Column Setup

Objective 3 - Resin Regeneration Field Verification Study Sample Photo Summary





Brine Samples

Resin Samples

Conclusions

- Objective 1
 - Resin Exhaustion Study
 - Ra-226 buildup is possible on cation exchange resins and occurs past hardness breakthrough
- Objective 2
 - Resin Regeneration Batch Studies
 - Brine strength or salt concentration is most influential cleaning factor
 - Resin Regeneration Column Study
 - Higher salt mass resin loadings (Ib NaCl per ft³ resin) will more effectively clean cation exchange resins
 - Higher salt mass loadings show diminishing removals (non-linear relationship)
 - No Radium-226 removals greater than 85%
- Objective 3
 - Resin Regeneration Field Verification Study
 - Treatment plants with regular maintenance and consistent salt crock levels can extend the life expectancy and effectiveness of the ion exchange resin in drinking water treatment (hypothesis)

Recommendations

- Treatment Operators
 - Maintain high salt mass loading on resin to optimize regeneration and Radium-226 removal from cation exchange resins
- Designers
 - Consider space requirements for ease of maintenance for operators when designing treatment system layout
- Developers
 - Pursue other drinking water sources if groundwater contains excessively high levels of radionuclides

Questions?