SULFATE REMOVAL FROM WATER PRODUCED DURING CO_2 ENHANCED OIL RECOVERY, COAL-BED METHANE RECOVERY, AND MINING OPERATIONS USING ANION EXCHANGE RESINS

BY

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THESIS

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ABSTRACT

Limited freshwater resources and expected increases in water demand are causing electric utilities to explore more non-traditional water sources, such as produced water from CO_2 enhanced oil recovery (EOR), coal-bed methane recovery, and mining operations. Electric utilities, including coal-fired power plants, are the second largest users of freshwater in the United States. Produced water from EOR is variable in composition; it is dominated by high total dissolved solids composed mainly of sodium and chloride ions, on the order of 100,000 mg/L, and also high sulfate concentrations (up to 900 mg/L). Dissolved sulfate can cause stress corrosion cracking in steam turbine blades at concentrations as low as 8 mg/L. A certain level of treatment must be done before reuse in power plants is a viable option.

This study focuses on sulfate removal from synthetic produced water and produced water from EOR and mining operations in the Illinois Basin using anion exchange resins. Equilibrium batch studies were conducted to compare commercially available strong base and weak base anion exchange resins of different type. Our results indicate that for optimal sulfate removal in high chloride solutions, (i.) weak base resins perform better than strong base resins, (ii.) resins with an epoxy polyamine matrix perform better than those with a divinylbenzene matrix, and (iii.) resins with secondary/tertiary amines perform better than those with pyridine functionality, and even better than those with quaternary ammonium. Reasons for better performance among resins include more closely spaced anion exchange sites and less steric hindrance. Sorption isotherms showed that weak base resins, pretreated with hydrochloric acid, significantly outperformed strong base resins, which had negligible sulfate removal at typical resin loadings. Resin titration curves coupled with experimental data were used to identify optimal pretreatment conditions for the weak base resins studied. Our results suggest that sulfate removal significantly decreases above 10,000 mg/L chloride, and that more moles of sulfate can be removed at high chloride concentrations when the chloride:sulfate ratio is lower. Sulfate removal was challenging for produced water from EOR and mining operations, with 576 and 918 mg/L sulfate, and 87,364 and 13,009 mg/L chloride, respectively. Measured sulfate removals were 8 and 70%, respectively. For practical use, weak base resins were able to be regenerated and their large retardation values allow for reasonable reactor dimensions.

ACKNOWLEDGEMENTS

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CHAPTER 1: INTRODUCTION

1.1 PROJECT BACKGROUND

The current study is a result of collaboration between the Illinois State Geological Survey and University of Illinois at Urbana-Champaign, and represents a contribution to the project *Reuse of Produced Water from CO_2-EOR, Coal-Bed Methane, and Coal Mine by Power Plants*. This contribution focuses on the treatment of produced water using anion exchange resins for the removal of sulfate, and ultimate reuse in power plants.

1.2 PRODUCED WATER BACKGROUND

1.2.1 DEFINITION AND SOURCES

Any water that is brought to the surface during fossil fuel extraction is considered produced water. Produced water is by far the largest volume byproduct or waste stream associated with oil and gas production [1]. Sources of produced water relevant to this study include CO_2 enhanced oil recovery (EOR), coal-bed methane recovery (CBM), and mining operations.

1.2.2 QUANTITY AND QUALITY

After conventional extraction methods have been completed, water and carbon dioxide can be injected into an oil field to recover up to 10 percent of the remaining oil. This method of extraction is referred to as EOR. Produced water volume increases during the life cycle of a well, and during EOR as much as 10 to 100 barrels of water are produced for each barrel of crude oil recovered [1]. Recent American Petroleum Institute (API) studies have shown that an estimated 71% of this produced water is re-injected for enhanced recovery and 21% is re-injected for disposal [2]. For 2002, total produced water generation was estimated at 14 billion bbls which shows the importance of produced water management [1].

Coalbed methane recovery is a process where removal of the formation water reduces the reservoir pressure and causes natural gas in the coal seams to migrate to collection wells [3]. Unlike EOR, the largest amount of water is produced early in the life cycle of the well. Water quantity varies from basin to basin, but water to gas ratios are typically between 0.03-2.75 bbl/1000 ft^3. CBM produced water volume is estimated at 4 billion bbl annually in the United States, and one Wyoming CBM operation manages 1.5 million bbl of produced water per day from over 12,000 wells. Produced water is one of the most significant issues facing CBM development [4, 5].

Active and inactive coal mining operations also offer a source of produced water. A mine in White County, Illinois produces about 432,000 gallons per day and the void spaces of abandoned underground coal mines in the Illinois Basin total more than 5.3 billion cubic yards [6]. These void spaces can hold vast quantities of water resources.

Produced water is variable in composition, but generally EOR produces water with elevated total dissolved solids (TDS) comparable to CBM. TDS in EOR is on the order of 100,000 mg/L, and is composed mainly of sodium and chloride ions. Both sources have shown high levels of sulfate, up to 900 mg/L. Interestingly, some produced water from CBM has been shown to meet federal drinking water standards [7]. Water quality data from produced water sources in the Illinois Basin are shown in Table 1.

Table 1- Produced water quality from the Illinois State Geological Survey [6]

Sample	Fluoride (mg/L)	Chloride (mg/L)	Bromide (mg/L)	Sulfate (mg/L)	Total Organic Carbon (mg/L)	TDS mg/L	Ammonia (ppm N)	pH
Main 1	21	10400	28		508	19000	4	7.0
Main 2		12400	27		14		0	6.9
Main 3		12000	33		11		0	7.2
Union Bowman 1		8880	45	48	6			7.0
Louden 1-EOR		60300	95		8	102000	25	6.9
Louden 2-EOR		58300	90		6		25	6.1
Louden 3-EOR		58100	90		7		24	6.2
Louden 4-EOR	2	1	< 0.5	2	0			
Dale 1-EOR		74900	123	60	20	127000	32	6.6
Dale 2-EOR		65800	110	100	7		36	6.6
Sugar Creek		14000	71	32	15	25300	5	6.2
Galatia 1-Coal Mine		9490	30	200	8	18000	6	7.8
Galatia 2-Coal Mine		9940	32	200	13		4	7.2
Millenium 1		8200	26	150	15	16000	8	7.5

Pattiki		10800	35	160	1		5	7.6
Royal Falcon 1-Coal Mine	2	21	1	5	1	522	0	8.0
Royal Falcon 2-Coal Mine	2	700	2	100	2	2860	0	7.8
Royal Falcon 3-Coal Mine	2	1060	3	110	1	1590	0	7.8
Royal Falcon 4-Coal Mine	2	0	< 0.5	< 0.5	0		0	
ACT		10400	37	< 0.5	7	25000	11	7.6
Pioneer 1-CBM		16000	40		2	27700	9	7.3
Pioneer 2-CBM		17100	46		1		10	7.6
Pioneer 3-CBM		19000	49		1		12	7.7
Pulse 1	3	139	2	1	0	1960	1	8.7
Pulse 2	5	44	1	25	1	1310	0	8.8
Pulse 3	5	149	2	46	3	1340	0	8.6

Table 1 cont.

1.2.3 USE OF PRODUCED WATER IN POWER PLANTS

Thermal power plants use very large amounts of water. The cooling system uses the largest volume of water at a plant, and water is also needed for the boiler system and wet flue gas desulfurization unit. Each process has its own water quality requirements but most produced water may not be used directly in any process without treatment. The primary concerns are scaling and corrosion of construction materials due to dissolved solids in the water.

Sulfate has been found to cause pitting and stress corrosion cracking in stainless steel steam turbine blades. Reported concentrations in the steam that induce this behavior are less than 20 parts per million (ppm) sulfate [8, 9]. The number cycles of concentration for a cooling tower system may be limited by precipitation of calcium sulfate.

Prior to use at a power plant, most produced water must be desalinated. For TDS values less than 60,000 mg/L, reverse osmosis is the most cost effective treatment option. Thermal desalination must be used for waters with greater values of TDS. Additional treatment processes may be needed if initial sulfate concentrations are large. This project investigates the use of ion exchange for sulfate removal.

1.3 ANION EXCHANGE

1.3.1 THEORY

Ion exchange is an established treatment technology for the removal of common anions and cations from water. Synthetic anion exchange resins have ionizable groups that become charged upon loading with exchangeable anions such as chloride and hydroxide, which exchange with more favorable anions in solution. Typical ionizable groups include quaternary ammonium and amine groups [10]. Strong base (equ. 1) [11] and weak base (equ. 2) [12] anion exchange resins for sulfate can be represented as follows:

$$2\ RCl + SO_4^{2-} <=> R_2SO_4 + 2\ Cl- \qquad \text{(equ. 1)}$$

$$2\ RHCl + SO_4^{2-} <=> (RH)_2SO_4 + 2\ Cl- \qquad \text{(equ. 2)}$$

where R is the ion exchange radical. The dilute solution anion selectivity sequence for strong base resins is [10]:

$$SO_4^{2-} > I^- > NO_3^- > CrO_4^{2-} > Br^- > Cl^- > OH^-$$

Note that OH^- will shift to the left for weak base resins.

1.3.2 COMMERCIAL ANION EXCHANGE RESINS

Six commercially available anion exchange resins were chosen to compare the influence of resin type, matrix, functionality, and exchangeable groups on removing sulfate in produced water. Commercial anion exchange resins are separated into two categories: weak base resins and strong base resins. Weak base resins typically have secondary or tertiary amine groups which readily accept protons to give them their functionality; they operate only at low pH. Strong base resins typically have quaternary ammonium groups and function independently of pH. Strong base resins are further classified into Type 1 and Type 2. Strong base Type 1 resins are the most basic, and typically incorporate hydrophobic $-CH_3$ groups around the ammonium nitrogen [13]. Strong base Type 2 resins are produced by reaction with dimethylethanolamine, which results in an electron withdrawing, hydrophilic $–C_2H_4OH$ group attached to the ammonium nitrogen, making Type 2 resins less basic than Type 1 [13, 14]. Studies have shown that, though bulkier, the Type 2 resins (compared to Type 1 resins) more strongly prefer sulfate over the more hydrophobic nitrate anion [14].

The resin matrices studied include polystyrene/divinylbenzene (DVB), acrylic/DVB, and epoxy polyamine. DVB was utilized in the matrix for both strong and weak base resins but the epoxy polyamine was strictly weak base. Clifford [14] argues that resin matrix is the most significant factor in determining selectivity between monovalent and divalent anions. Clifford's results suggest that the most divalent anion selective resins have fixed pairs of closely spaced charged amines. Epoxy polyamine matrices are made of a mix of secondary and tertiary amines, which inherently result in more closely spaced charges as compared to bulky polystyrene/DVB matrices. DVB matrices are also more hydrophobic than the epoxy polyamine matrices. Sulfate is a bulky, divalent anion that is very stable in solution. Table 2 shows that sulfate has a very high free energy of hydration compared to other common anions, which results in it being extremely hydrophilic [15]. From this, we infer that sulfate would greatly prefer anion exchange resins with less bulky and more hydrophilic matrices.

Boari [12] demonstrated that throughout different bulk salinities, sulfate selectivity was also based on the resins functional groups as follows:

resins with primary amine functional groups > secondary > tertiary > quaternary

This suggests that resin matrices with large functional groups, such as the quaternary ammonium groups of strong base resins, reduce the natural selectivity towards multi-valent ions due to steric hindrance and/or amine spacing. Presently, most commercially available weak base and strong base anion exchange resins contain tertiary and quaternary functionality, respectively, but some weak base resins offer both secondary and tertiary functionality.

Anion exchange resins can be regenerated once they reach their uptake capacity. The recommended regenerant for strong base resins is a 2 to 6% NaCl, or NaOH, solution depending on which ion the resin is exchanging, Cl^- or OH^-, respectively [16]. This translates to 12,156 to 36,473 mg/L Cl^-, which is on the same order of magnitude as chloride concentrations in produced water. Weak base resins use 6% NaOH solution for regeneration [17].

Table 2- Free energies of hydration for common anions in aqueous solution [15]

Anion	ΔG_h (kJ/mol)
ClO_4^-	-205
NO_3^-	-300
HCO_3^-	-335
Cl^-	-340
SO_4^{2-}	-1295

1.4 RESEARCH OBJECTIVES

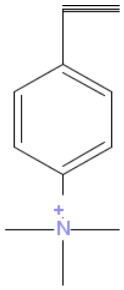
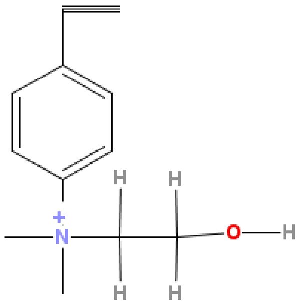
Specific research objectives are as follows: (i.) compare commercially available strong base and weak base anion exchange resins ability to remove sulfate in high chloride solutions, (ii.) determine at what critical chloride concentrations sulfate removal is hindered, and (iii.) gain insight into factors affecting sulfate removal in real produced water and engineering implications. Results from this study should help aid the selection of anion exchange resins for removing sulfate in produced water.

CHAPTER 2: METHODOLOGY

2.1 REAGENTS

Six commercially available anion exchange resins were studied. The following resins were provided by Resin Tech, Inc.: WBG-30, SBG1, SBG1-OH, SBG2, and SBACR-HP. Reilly Industries, Inc. Reillex$^{\text{TM}}$ 402 (R402) was purchased from Sigma Aldrich. Table 3 presents the characteristics of each resin used in this study. Sulfate, chloride, and potassium hydroxide (KOH) stock solutions were prepared with sodium sulfate (Na_2SO_4), sodium chloride (NaCl), and KOH, respectively, each with greater than 95% purity and purchased from Fisher Scientific. Nanopure water (>17.8 MΩ·cm-1; Barnstead Nanopure system) was used for all experiments and stock solutions. Trace metal grade hydrochloric acid (HCl) from Fisher Scientific was used for weak base resin pretreatment and titrations. Produced water samples from Dale and Galatia were obtained from the Illinois State Geological Survey, and Tables 1 and 6 show their composition. N_2 gas (99.9%) was purchased from Matheson Tri-Gas (Joliet, IL).

Table 3- Resin characteristics

Resin Name	Type	Matrix	Functional Groups	Exchange Group	Repeating Structure
SBG1	*Strong Base, Type 1	Poly-styrene DVB	Quaternary amine	Cl-	
SBG2	*Strong Base, Type 2	Poly-styrene DVB	Quaternary amine	Cl-	

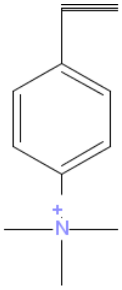
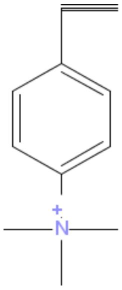
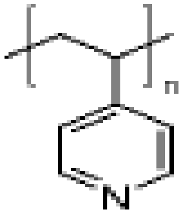
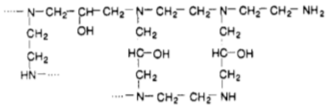
SBG1-OH	*Strong Base, Type 1	Poly-styrene DVB	Quaternary amine	OH-	
SBACR	*Strong Base, Type 1	acrylic, DVB	Quaternary amine	Cl-	
R402	**Weak Base	25% DVB	pyridine	Cl-	
WBG-30	**Weak Base	Epoxy poly-amine	Secondary/ tertiary amine	Cl-	 [18]

Table 3 cont.

*Strong base resins have Cl^- or OH^- exchange groups loaded on resin as received.

**Weak base resins arrive in free base form and must be pretreated to load Cl^- exchange group on resin.

2.2 BATCH EQULIBRIUM EXPERIMENT PROTOCOL

Batch equilibrium experiments were conducted for each anion exchange resin. All batch experiments were conducted in 120 milliliter (ml) glass serum bottles (Wheaton Industries Inc.) filled with 100 ml of aqueous solution (i.e. nanopure water, sulfate and chloride stock). A one ml sample was then taken and analyzed to represent initial solution conditions. Resin was then added to solution, and a 20 mm septum stopper (Bellco Glass, Inc.) and 20 mm aluminum seal (Fisher Scientific) were used to seal the serum bottle. Solution concentrations and resin loadings varied depending on the experiment. Sealed serum bottles were secured in a gyratory shaker water bath (New Brunswick Scientific, Model G76D), which continuously shook the resins at 219 rpm at 25 +/- 0.1 degrees Celsius. One ml samples were taken at selected time points over a 24 hour period to determine the equilibrium time.

Batch equilibrium experiments were performed using synthetic produced water solutions with varying chloride and sulfate concentrations, and pH. Resin loadings were varied from 0.001 to 1,000 grams of resin per liter of solution (g_{resin}/L) to obtain sorption isotherms. Strong base resins were used as received and weak base resins were pretreated as described below. The pH was adjusted with KOH to pH 7.8 for strong base resins to model actual produced water samples. Note that strong base resin performance does not vary with pH. After a pretreated weak base resin was added to solution, the pH dropped to pH 3.5, which is necessary for the resin to remain protonated.

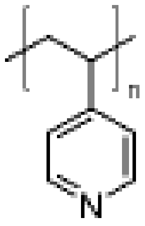
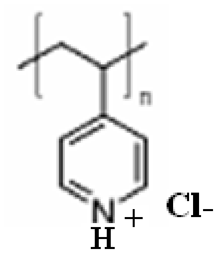
2.3 ACID TITRATIONS

Acid titrations were performed with non-pretreated weak base resins, WBG-30 and R402, and the strong base resin, SBG1. The titrations indicate proton uptake capacity and are used to estimate proton concentration ranges for resin pretreatment. One hundred ml of 10,000 mg/L chloride solution was prepared in a 250 ml three neck flask to represent the ionic strength in batch isotherm experiments. The three necks were filled with a pH meter, a nitrogen gas line, and a rubber stopper, respectively. The solution was continuously stirred using a magnetic stir bar, and continuously sparged with nitrogen gas to eliminate the influence of carbon dioxide buffering. After one hour, one gram of resin was added to the solution and allowed to equilibrate. Increments of 1 M HCl were added to the solution and allowed to equilibrate, which took between one and twenty minutes. The pH meter was calibrated using 10,000 mg/L chloride standards at pH 4, 7, and 10.

2.4 RESIN PRETREATMENT EFFECTS ON SULFATE UPTAKE

The purpose of pretreatment was to functionalize the weak base resins, WBG-30 and R402, which were obtained in free base form. Functionalization is illustrated in Table 4 for the R402 resin; the pyridine gains a positive charge after addition of a proton, which then attracts the chloride. The resin was pretreated with 0.001, 0.01, or 0.1 moles H+ per gram of resin by soaking in the appropriate amount of 1M HCl stock for two hours on a shaker table. The resin was then washed 10 times with 30 ml npw per 2.5 grams of resin before being vacuum dried (WBG-30), or oven dried (R402) at 40 degrees Celsius, to the original weight. The purpose for drying the resins was to know the exact resin loading without water weight and to eliminate the possibility of diluting the sample solutions thus this step may not be necessary for actual application. The pretreated resins were used in batch equilibrium experiments.

Table 4- Weak base anion exchange resin (R402) before and after acid pre-treatment

Free base form before pre-treatment	After pre-treatment
	

2.5 CHLORIDE INFLUENCE ON SULFATE UPTAKE

Initial chloride concentrations were also varied during batch equilibrium experiments to determine the influence of chloride on sulfate uptake. Synthetic produced water solutions were prepared with 100, 1,000, 10,000 and 40,000 mg/L chloride and 200 mg/L sulfate concentrations. Pretreated weak base resins were used at a resin loading of 10 g_{resin}/L.

2.6 SYNTHETIC AND REAL PRODUCED WATER ISOTHERMS FOR DALE AND GALATIA

Batch equilibrium experiments were performed with synthetic and real produced water solutions using pretreated weak base resins. Real produced water from Dale and Galatia was compared to synthetic produced water of the same sulfate and chloride concentrations.

Measured concentrations were as follows, 576 and 918 mg/L sulfate, and 87,364 and 13,009 mg/L chloride for Dale and Galatia, respectively. Resin loadings were varied from 0.1 to 100 g_{resin}/L to obtain sorption isotherms for each weak base resin.

2.7 RESIN REGENERATION

Pretreated WBG-30 resin from real Galatia batch equilibrium experiments at 50 gram/L resin loading was used to determine the resins ability to be regenerated. After the initial batch equilibrium experiment, the real Galatia (100 ml) was drained from the serum bottle and 100 ml of regenerant (6% NaOH) was added. The serum bottle with regenerant and resin where placed in the water shaker bath for 1 hour at 25+/- 0.1 degrees Celsius and rotation at 219 rpm. The regenerant concentration and contact time where as directed by the resin manufacturer [17]. The resin was then washed 10 times with 30 ml npw per 2.5 grams of resin before being re-pretreated with HCl as described above. After re-pretreatment, the resin was then washed with npw before being vacuum dried to the original weight. This describes one full regeneration cycle, after which the resin is ready for the next batch equilibrium experiment with a new volume of real Galatia.

2.8 DATA ANALYSIS

Sulfate sorption data was modeled using a linear isotherm (equ. 3), and linearized Freundlich (equ. 4) and Langmuir (equ. 5) isotherms as follows:

$$C_d = K_d\, C_w \qquad \text{(equ. 3)}$$

$$\log C_d = (1/n)\log C_w + \log K_f \qquad \text{(equ. 4)}$$

$$1/C_d = (1/(K_L C_{Smax}))(1/C_w) + (1/C_{Smax}) \qquad \text{(equ. 5)}$$

where:

C_d = adsorption capacity at equilibrium = ($mg_{SO4\ sorbed}/kg_{resin}$)

C_w = equilibrium sulfate concentration = (mg/L)

K_d = distribution coefficient = (L/kg_{resin}) = slope of linear fit of Figure 6

n = Freundlich constant related to the sorption intensity of a sorbent = inverse of slope in Figure 7

K_f = Freundlich constant related to the sorption capacity = antilog of y-intercept in Figure 7

K_L = Langmuir constant = (L/kg_{resin}) = inverse slope of Figure 8 multiplied by ($1/C_{Smax}$)

C_{Smax}= maximum adsorption capacity = ($mg_{SO4\ sorbed}/kg_{resin}$) = inverse of y-intercept in Figure 8

2.9 ENGINEERING IMPLICATIONS

The retardation factor was calculated for WBG-30 and R402 at each chloride concentration from sorption data as follows:

$$R = 1 + (p_b / n)K_d \qquad \text{(equ. 6)}$$

where:

K_d = distribution coefficient = (L/kg_{resin}) from sorption data (i.e., Figure 4 in results)

n = porosity (assume n = 0.33)

p_b = bulk density = 0.6139 kg/L (WBG-30) and 0.5051 kg/L (R402)

2.10 ANALYTICAL TECHNIQUES

For all batch experiments, concentrations of sulfate and chloride were analyzed using ion chromatography (IC; Dionex ICS-2000; Dionex IonPac AS18 column; 32 mM KOH eluent; 1.2 mL/min eluent flow rate). Calibration curves indicated a detection limit of less than 1 ppm sulfate. To protect the IC column, Dale and Galatia water samples were filtered with a 0.45um syringe filter before ion chromatography analysis for sulfate and chloride.

CHAPTER 3: RESULTS AND DISCUSSION

3.1 RESIN PRETREATMENT

Acid titration curves for both weak base resins (WBG-30 and R402), the strong base resin (SBG1), and water are shown in Figure 1. Results indicate that the weak base resins took up protons until 0.1 moles H+ were added to the solution. By taking the difference between the pH of the water curve and the weak base resin curves, we estimated that WBG-30 and R402 have proton uptake capacities of 0.033 and 0.082 moles H+ per gram of resin, respectively, as shown in sample calculation 1. The strong base resin, SBG1, took up no protons since it followed the water curve throughout the titration. These acid titrations motivated us to pretreat the weak base resins with 0.001, 0.01, and 0.1 moles H+ per gram of resin to identify optimal acid pretreatment conditions.

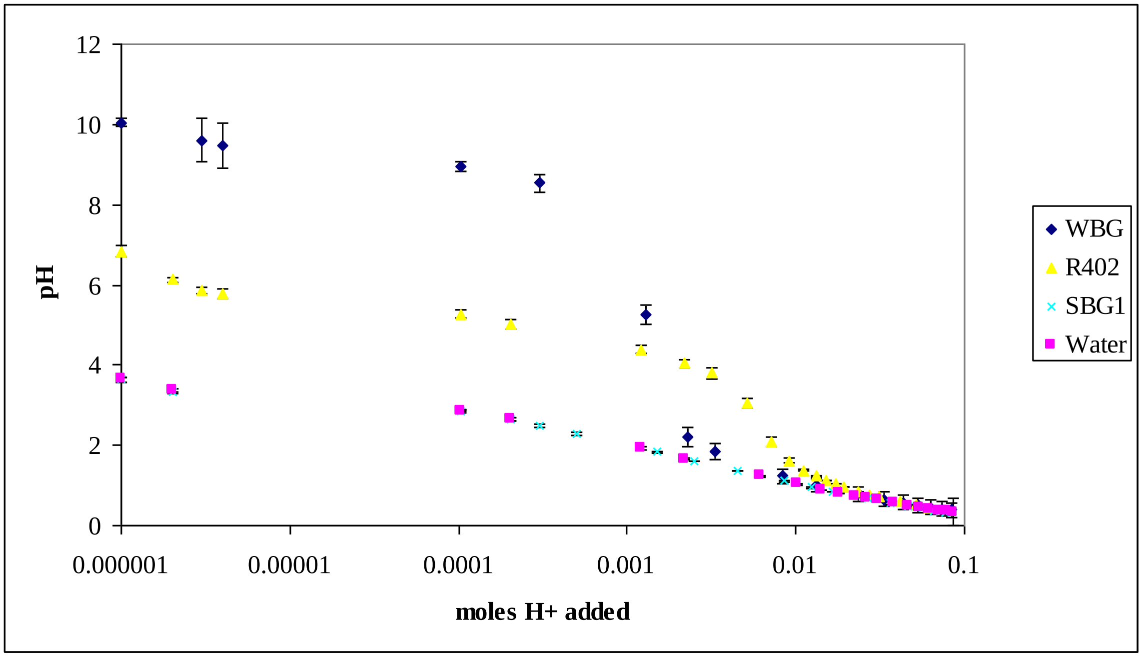


Figure 1- Acid titration curves for weak base (WBG-30, R402) and strong base (SBG1) anion exchange resins

Acid pretreatment effects on removal of 200 mg/L of sulfate from water containing 10,000 mg/L chloride are shown in Figure 2. Up to 85% improvement in sulfate removal was observed for resins pretreated with 0.01 or 0.1 moles H+ per gram of resin; in comparison, only 8% removal of sulfate was observed for resins pretreated with 0.001 moles H+ per gram of resin. Values of pH for different levels of resin pretreatment are shown in Table 5. After the pretreated resin was added to solution, the pH remained constant during the 24 hour batch equilibrium experiment for R402 at all resin pretreatment conditions (i.e., from 0.001 to 0.1 moles H+ per gram of resin). We observed that the pH increased during the 24 hour batch equilibrium experiment for WBG-30 at the 0.001 level of pretreatment which indicated that the resin still had proton uptake capacity and was not fully protonated. The pH decreased during the 24 hour experiment for the 0.01 and 0.1 levels of pretreatment using WBG-30 meaning that the initial equilibrium was not fully established. Overall, we observe a high equilibrium pH at the 0.001 level of pretreatment, in contrast to the 0.01 and 0.1 levels of pretreatment for both weak base resins. We attribute this to the poor sulfate removal at the 0.001 level of pretreatment.

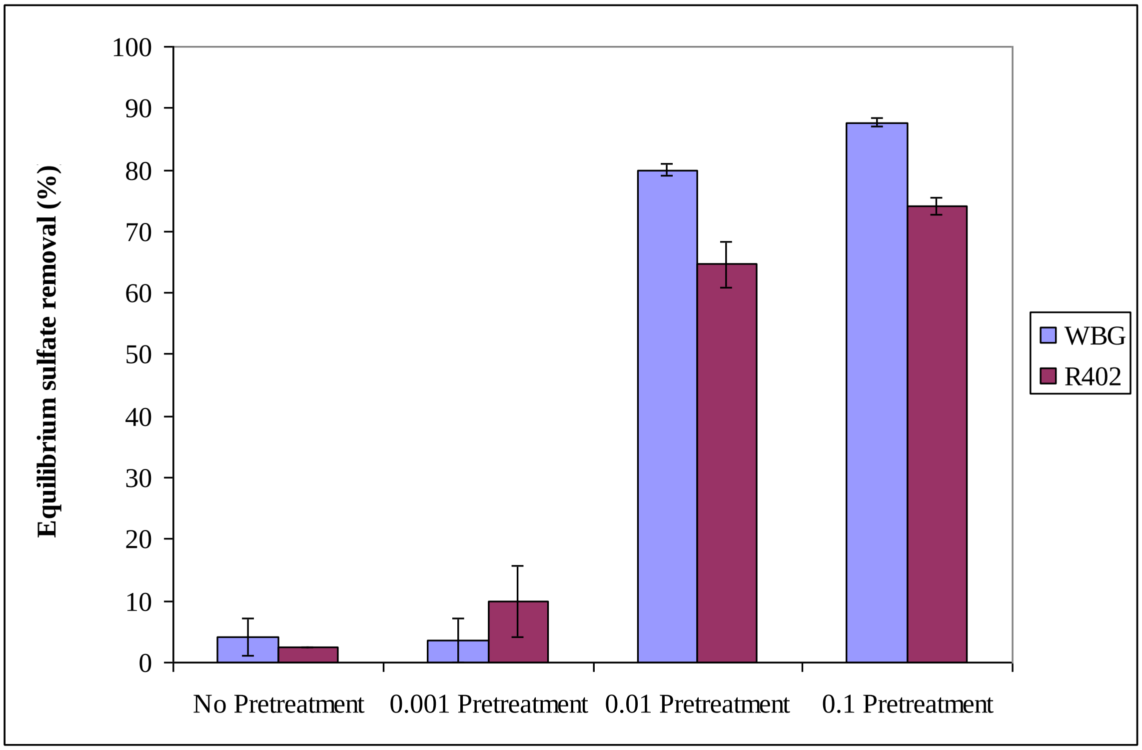


Figure 2- Effects of resin pretreatment on sulfate uptake for weak base resins
[Initial conditions: 200 mg/L sulfate, 10,000 mg/L chloride, 10 g/L resin loading]

Table 5- pH measurements during resin pretreatment batch equilibrium experiments

Resin	Pretreatment (moles H+/g_{resin})	Initial pH before resin added	Initial pH after resin added	24 hr pH
WBG-30	None	6.15	10.6	10.93
WBG-30	0.001	6.19	6.66	8.61
WBG-30	0.01	6.18	4.10	3.45
WBG-30	0.1	6.19	3.58	2.66
R402	None	6.42	8.66	9.26
R402	0.001	6.21	5.4	5.32
R402	0.01	6.19	3.76	3.76

R402	0.1	6.12	3.55	3.49

Table 5 cont.

3.2 EVALUATION OF ALTERNATIVE RESINS

Sorption isotherms for sulfate in the presence of 10,000 mg/L chloride for the six anion exchange resins are shown in Figure 3. Since weak base resins operate only at low pH and strong base resins function independent of pH, the experimental pH ranges differed between the two. The strong base resins were run at typical produced water pH ranges of pH 7.9+/-0.2 and weak base resins were run at pH 3.6. The pretreated weak base resins, WBG-30 and R402, markedly outperform all strong base resins. The weak base resins have secondary/tertiary amine functional groups or a pyridine group, which resulted in less steric hindrance compared to the quaternary functional groups of the strong base resins. This is in agreement with Boari [12], who also showed that resins with secondary/tertiary amine functional groups preferred sulfate over resins with quaternary functional groups. Additionally, the suggested regenerant for strong base resins is a concentrated (i.e., >12,000 mg/L) chloride solution [16]; this provides further insights into why strong base resins remove very little sulfate. Based on these isotherm results, the remainder of the study was carried out using pretreated weak base resins, WBG-30 and R402.

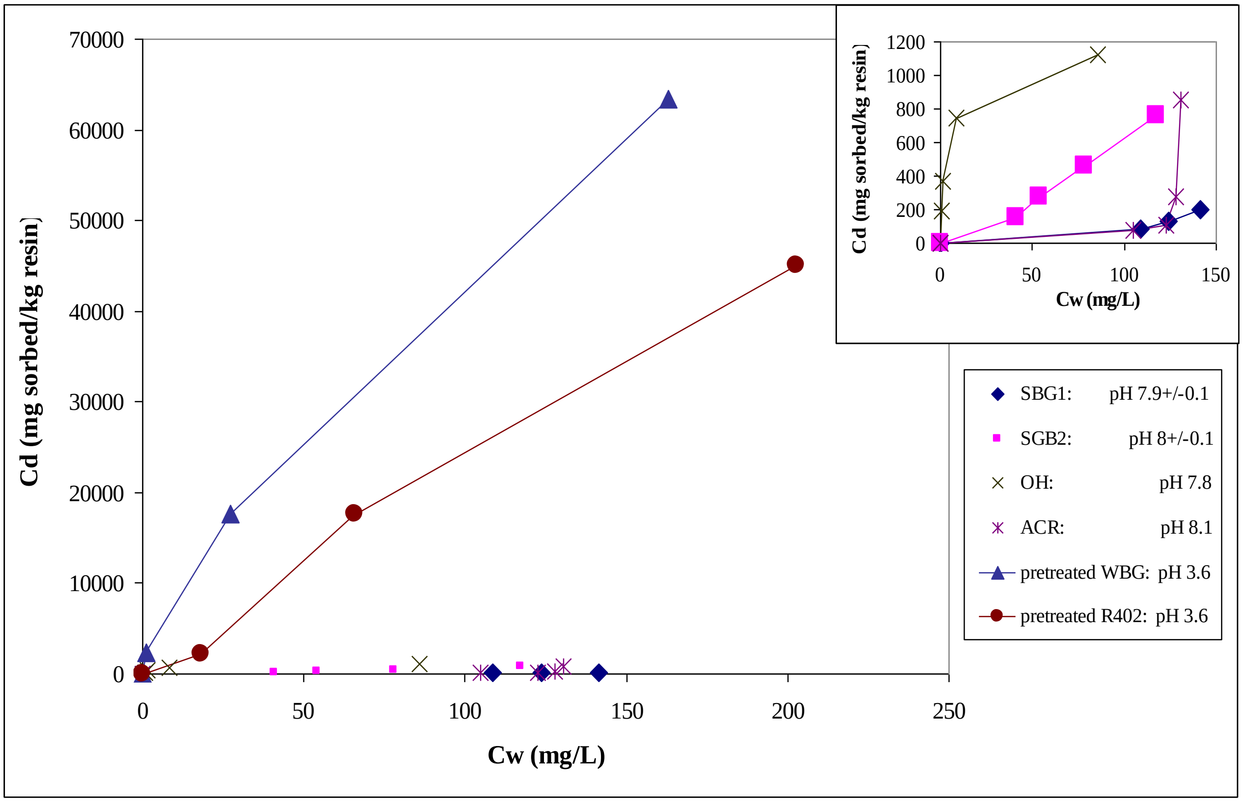


Figure 3- Sorption isotherms for commercially available weak base and strong base anion exchange resins. Inset plot shows strong base resin isotherms expanded.
[Initial conditions: 200 mg/L sulfate, 10,000 mg/L chloride, 10 g/L resin loading]

As shown in the inset plot in Figure 3, we see that the resin that used a hydroxide exchange group (SBG-OH) instead of a chloride exchange group had the greatest performance among the strong base resins. This result is in agreement with the typical anion selectivity sequence [10]. Between Type 1 and Type 2 strong base resins, we observe that the Type 2 resin had better performance. In the case of the Type 2 resin, the functional group ($–C_2H_4OH$) is bulkier than Type 1 resin ($-CH_3$), but is more hydrophilic. This supports our assertion that sulfate would rather interact with a more hydrophilic resin.

Between the weak base resins, we argue that WBG-30 outperformed R402 due to its resin matrix and functional group. Sulfate is divalent and interacts with two anion exchange sites. The epoxy polyamine matrix of WBG-30 allows for more closely spaced exchange sites which promote exchange with divalent anions, compared to R402’s DVB matrix that has further spaced exchange sites [14]. The WBG-30 resin also utilizes a secondary/tertiary functional group which has less steric hindrance than R402’s pyridine functional group.

3.3 CHLORIDE EFFECTS ON SULFATE REMOVAL

Batch studies were used to determine the effect of chloride concentration on sulfate removal as shown in Figure 4. Sulfate removal was 99+/- 0.5% for both weak base resins at 500 and 1,500 mg/L chloride. We observe that at 10,000 mg/L chloride, sulfate removal drops to 73 and 87% for R402 and WBG-30, respectively, and drops to below 40% at concentrations above 40,000 mg/L chloride. Overall, we confirmed that sulfate removal decreases as chloride concentrations increase, but this result also suggests that there is a threshold chloride:sulfate ratio that must be achieved for the sulfate ion to be preferred.

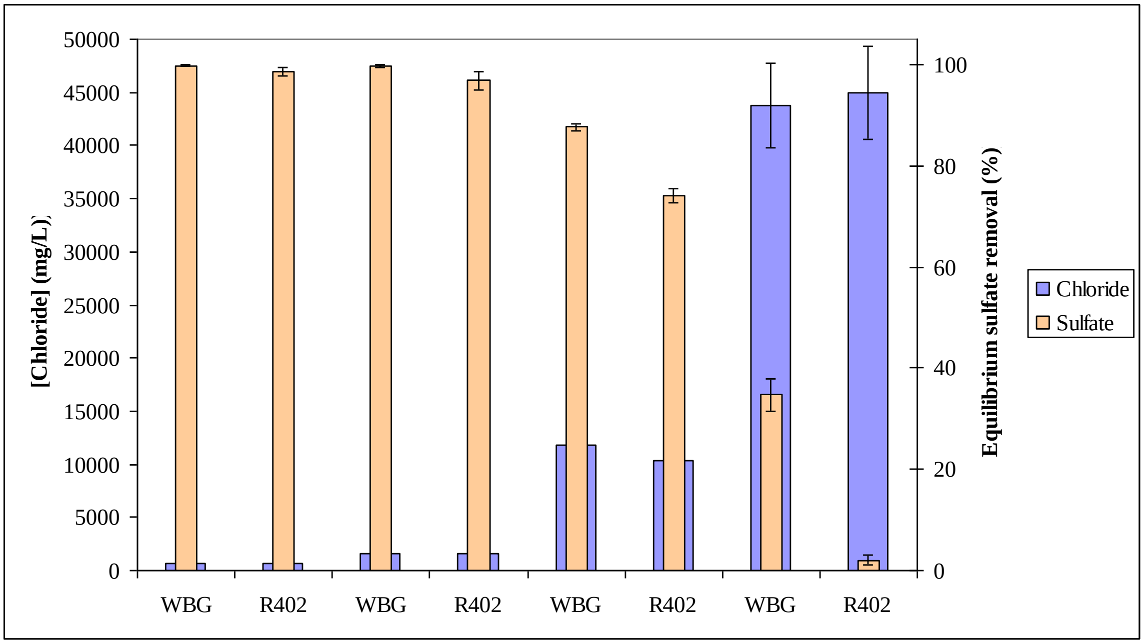


Figure 4- Chloride effects on sulfate uptake
[Initial conditions: 200 mg/L sulfate, 10 g/L resin loading, 0.1 mole H+/g resin pretreatment, pH 3-3.5]

3.4 SYNTHETIC VERSUS REAL PRODUCED WATER

Produced waters from enhanced oil recovery (Dale) and coal mining operations (Galatia) were analyzed for sulfate and chloride and then batch studies were conducted with weak base anion exchange resins as shown in Table 6 and Figure 5, respectively. Chloride concentrations for Dale average 87,364 mg/L and are approximately 150 times higher than sulfate concentrations. Sulfate removal for Dale was only 8+/-2% and 2.7+/-2% for WBG-30 and R402, respectively. Chloride concentrations for Galatia average 13,009 mg/L and are approximately 14 times higher than sulfate. More sulfate removal was observed for Galatia, 69.3+/-0.1% and 45.9+/-0.3% for

WBG-30 and R402, respectively. We again argue that WBG-30 outperformed R402 due to its epoxy polyamine matrix and R402's bulkier and less hydrophilic DVB matrix.

From Figure 5 we observed that the pH drops from pH 7.5+/-0.5 to pH 3.5+/-0.5 after the pretreated weak base resins were initially added to Dale and Galatia which means that protons were released from the resins. As shown in sample calculation 2, we measured that the weak base resins lose between 0.2 to 1.5% of their total proton uptake capacities during this initial pH change and thus their anion exchange capabilities were not significantly diminished.

Table 6- Produced water quality for Dale and Galatia

Source	Chloride (mg/L)	Sulfate (mg/L)	pH
Dale	87,364	576	7.9
Galatia	13,009	918	7.1

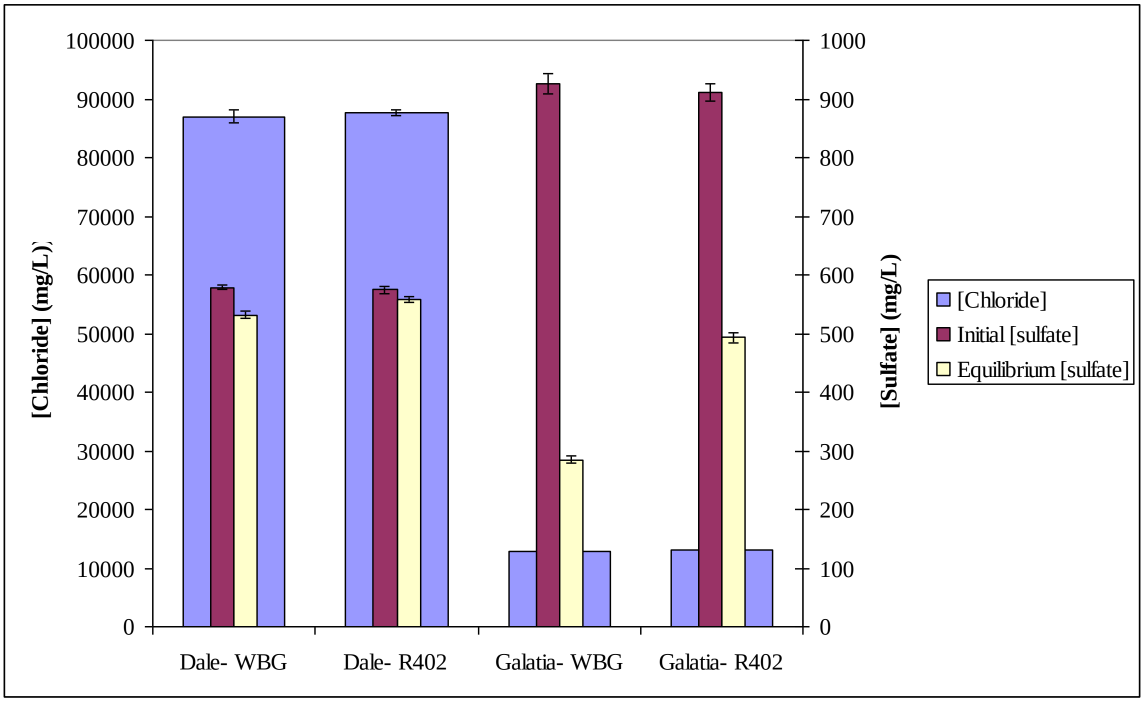


Figure 5- Sulfate removal for Dale and Galatia using weak base anion exchange resins
[Initial conditions: 10g/L resin loading, 0.1 mole H+/g resin pretreatment]
[Galatia: final pH 3.64(3.87) for WBG(R402); Dale: final pH 3.17(4.17) for WBG(R402)]

Synthetic produced water solutions consisting of the same chloride and sulfate concentrations as Galatia produced water were evaluated. Sulfate removal from synthetic produced water was within 3 and 10% of the sulfate removal from real produced water for WBG-30 and R402, respectively. Since the synthetic and real produced water had statistically insignificant differences in sulfate removal, sulfate and chloride appear to be the dominant anions in solution with no complications from competing anions.

Sorption isotherm data are plotted in Figures 6 thru 8 for both synthetic and real Galatia. Constants for linearized Freundlich and Langmuir isotherms are shown in Table 7. As expected, isotherm constants are significantly higher for WBG-30 compared to R402. The Galatia isotherm data appear to fit the Freundlich and Langmuir isotherms ($R^2 > 0.99$) better than the linear isotherm ($R^2 > 0.93$). The Freundlich and Langmuir isotherm fits are similar. Less than 20% sulfate removal was seen for Dale at a resin loading of up to 100 g/L, thus making isotherm fitting impractical.

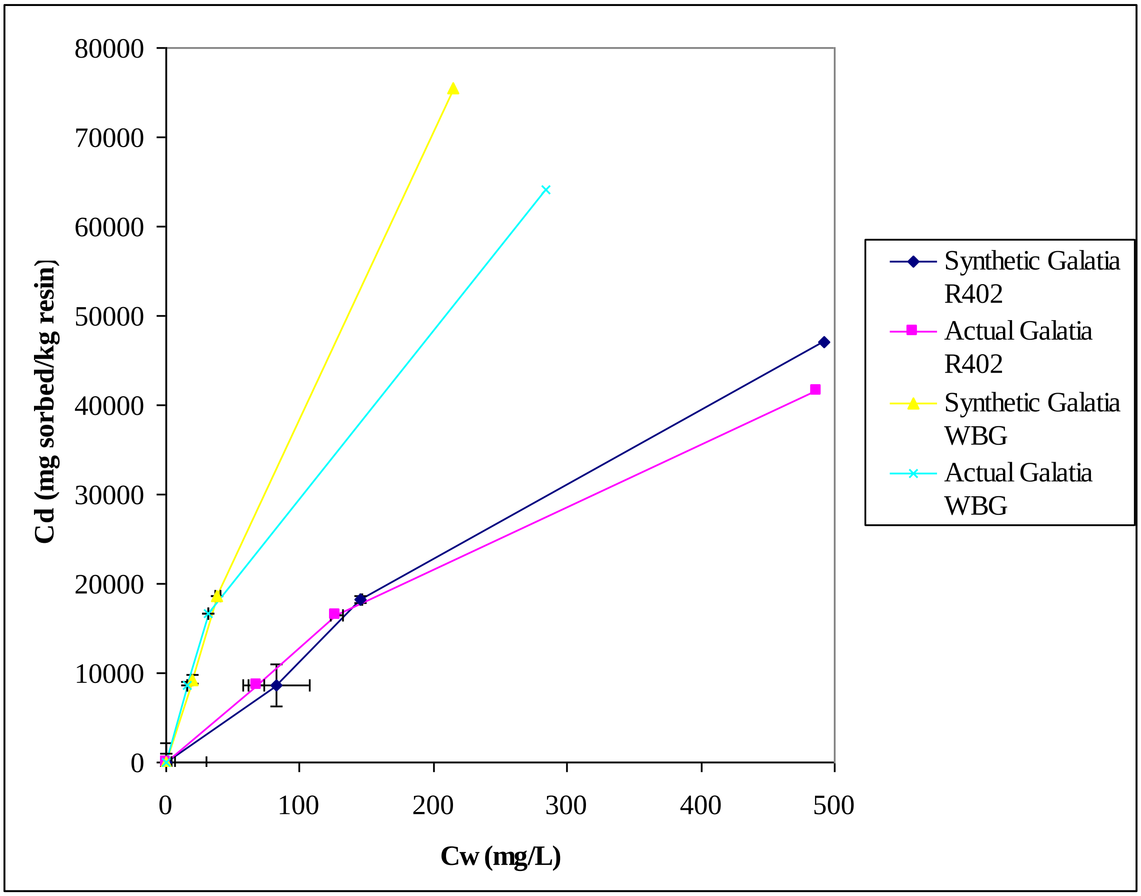


Figure 6- Sorption isotherms for synthetic and real Galatia using weak base anion exchange resins

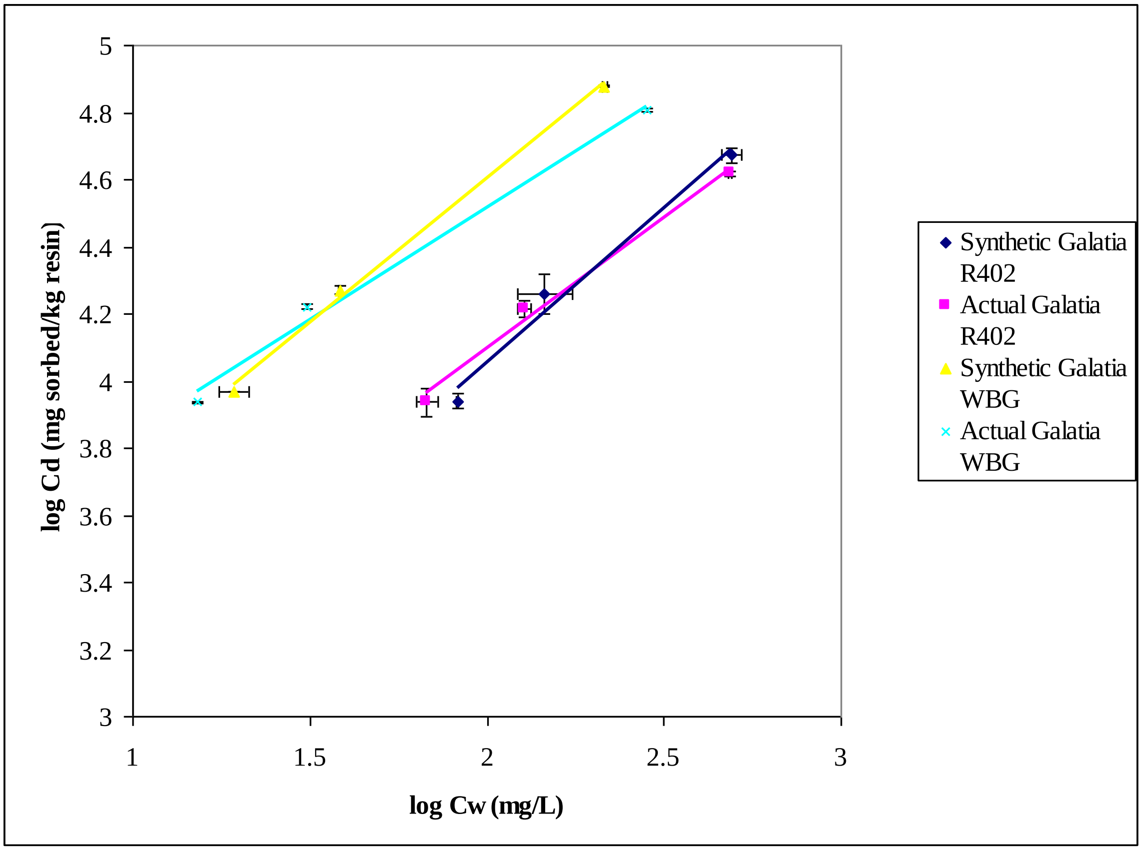


Figure 7- Freundlich isotherms for synthetic and real Galatia using weak base anion exchange resins

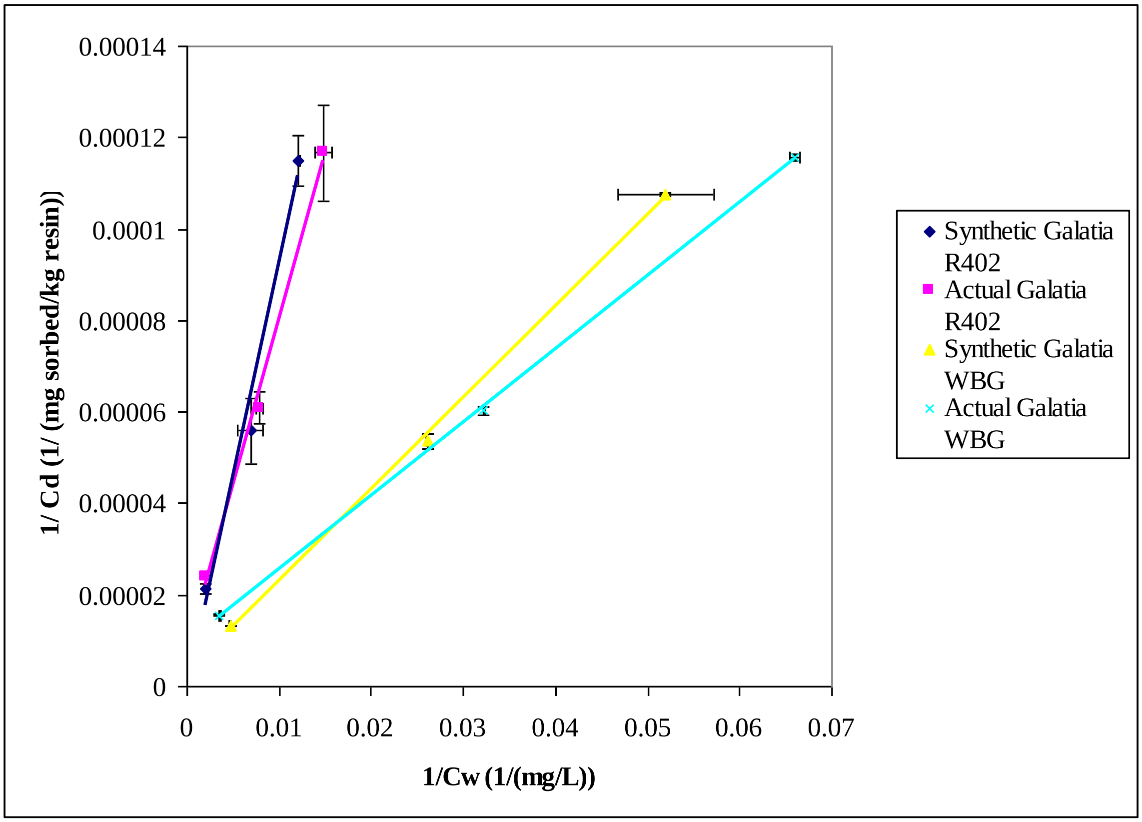


Figure 8- Langmuir isotherms for synthetic and real Galatia using weak base anion exchange resins

Table 7- Isotherm constants

		Isotherm							
		C_d vs. C_w (linear fit)		$\log C_d$ vs. $\log C_w$			$1/C_d$ vs. $1/C_w$		
Source Water	Resin	K_d	R^2	K_f	1/n	R^2	K_L	C_{Smax}	R^2
Synthetic Galatia	WBG	357.8	0.988	766.3	0.859	0.997	0.001540	325013	0.999
	R402	98.0	0.978	166.4	0.917	0.982	-0.000122	882690	0.984
Actual Galatia	WBG	230.7	0.935	1520.2	0.667	0.992	0.005874	106065	0.999
	R402	88.9	0.939	343.7	0.780	0.990	0.000986	139001	0.996

We notice an interesting phenomenon in Figure 9, when we compare sulfate removal for waters with different fractions of sulfate but similar chloride concentrations. Real Galatia has 13,009 mg/L chloride and a chloride:sulfate ratio of 38; similarly, synthetic water from Figure 4 has10,000 mg/L chloride but a chloride:sulfate ratio of 160. As shown in sample calculation 3, we observed 3.6 and 2.9 times more moles of sulfate removed for WBG-30 and R402, respectively, for the real Galatia. From this result, we conclude that the chloride concentration may not be the only factor affecting sulfate removal, but also the chloride:sulfate ratio, since as this ratio decreases we see more moles of sulfate removed.

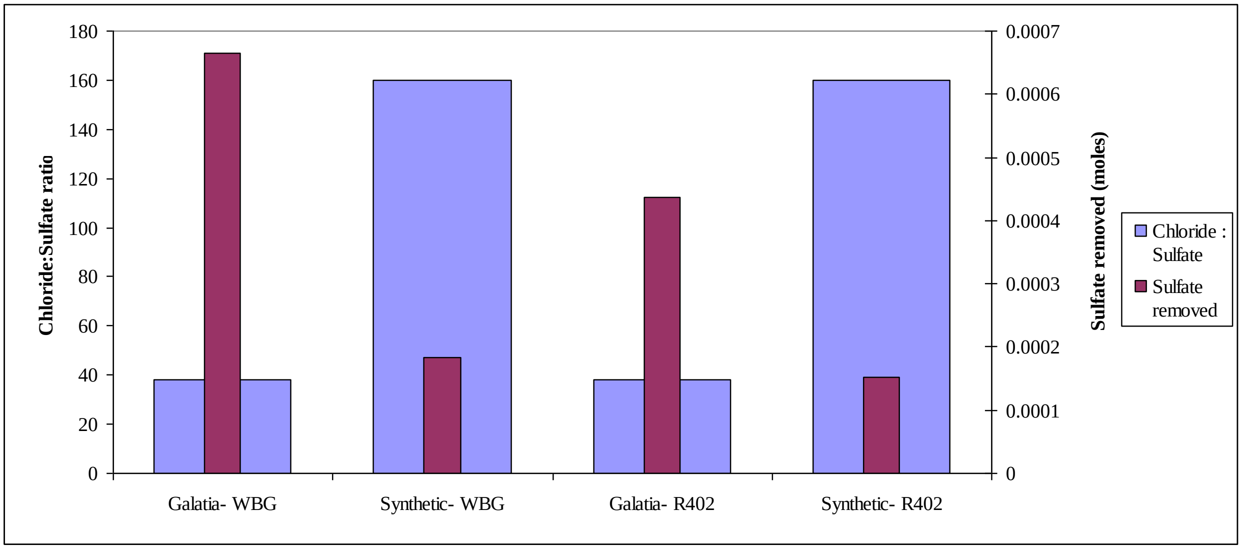


Figure 9- Sulfate removal for waters with similar chloride concentrations but differing chloride:sulfate ratios using weak base resins
[Initial conditions: 13,009 and 10,000 mg/L chloride, and 918 and 200 mg/L sulfate for real Galatia and synthetic water, respectively; 10 g/L resin loading]

3.5 RESIN REGENERATION

The ability for a resin to be regenerated is a key element in determining whether it can be useful in practical application. Batch experiments with real Galatia were conducted with WBG-30. Weak base resins are typically regenerated by raising the pH, which causes the nitrogen sites to de-protonate and release sulfate anions.. As shown in Figure 10, the resin was subjected to three regeneration cycles using a 6% NaOH solution as the regenerant. The resin was pretreated after each regeneration cycle. Sulfate removal differed by less than 0.2% between each regeneration, showing that WBG-30 can easily be regenerated without compromising performance.

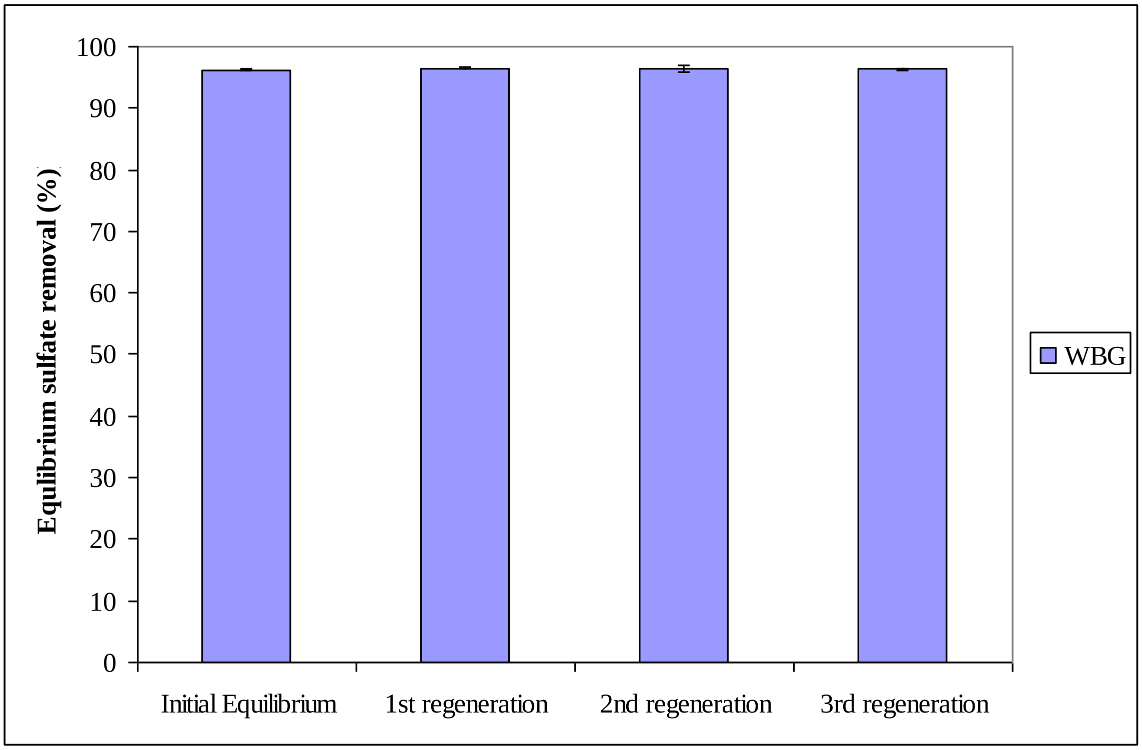


Figure 10- Regeneration cycles for WBG-30
[Initial conditions: real Galatia, 50g/L resin loading, 0.1 mole H+/g resin pretreatment]

3.6 ENGINEERING IMPLICATIONS

To gain a better understanding of the feasibility of using anion exchange resins, we can calculate retardation factors (R) from isotherm K_d values, resin bulk density, and resin porosity in a packed bed. Assuming plug flow, we can estimate the reactor volume needed to treat produced water entering a power plant. For example, if R equals 430, we estimate that the resin can treat 430 bed volumes before sulfate breakthrough. Table 8 shows R values for synthetic and real Galatia calculated using the K_d from Table 7. If we assume we can supplement power plant water demand with 1 MGD from produced water sources and we want to regenerate the resin once per day, a reactor treating real Galatia using WBG-30 would have the dimensions (length x width x height) of 7 feet x 7 feet x 6.5 feet. The suggested service flow rate for WBG-30 from the manufacturer is 2 to 4 gpm/ft^3, which corresponds to a service flow rate of 0.9 to 1.8 MGD using the previous reactor dimensions [19]. If we assume resin regeneration occurs once per week, the reactor dimensions increase to 13 feet x 13 feet x 13 feet, which corresponds to a service flow rate of 6.3 to 12.7 MGD. For both conditions, the service flow rate is well within the 1 MGD water usage at the power plant. Example calculations are shown in sample calculation 4.

Table 8- Retardation values for weak base anion exchange resins

Source Water	Resin	R
Synthetic Galatia	WBG	666.6
	R402	150.9
Actual Galatia	WBG	430.1
	R402	137.1

The dependence of R on chloride concentrations is shown in Figure 11, where R is calculated from K_d values obtained in Figure 4. As expected, R markedly decreases at chloride concentrations greater than 40,000 mg/L, which corresponds to the resins inability to remove sulfate in the presence of high chloride concentrations.

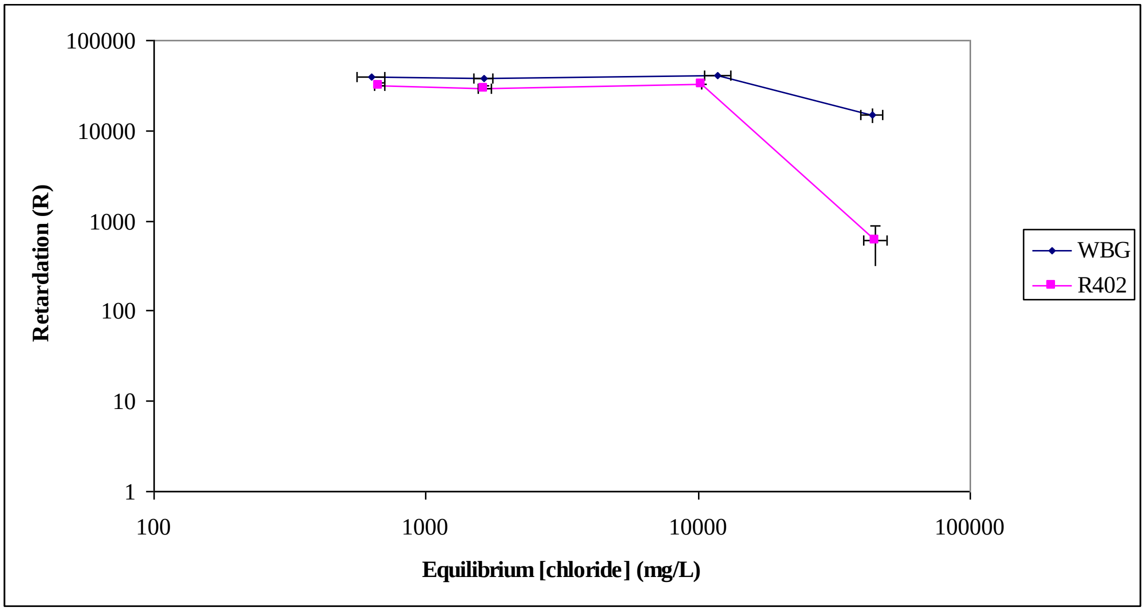


Figure 11- Chloride effect on retardation (R)
[Conditions: Constant 200 mg/L sulfate and 10 g/L resin loading]

Pretreated weak base resins initially drop the pH of real produced water from pH 7.5+/-0.5 to pH 3.5+/-0.5 by releasing protons. This release was shown in sample calculation 2 to insignificantly reduce the anion exchange capability of the resins in batch equilibrium experiments but the long term effects we not studied. It could be favorable to drop the pH of incoming produced water to pH 3.5+/-0.5 before entering an anion exchange reactor so that the resin does not have to release any protons.

CHAPTER 4: CONCLUSION

Our results support that for optimum sulfate removal in high chloride solutions, characteristics desired in an anion exchange resin are as follows: (i.) type- weak base > strong base, (ii.) resin matrix- epoxy polyamine > DVB, and (iii.) functional group- secondary/tertiary amine > pyridine > quaternary ammonium. Weak base resins significantly outperformed strong base resins but must be pretreated with HCl and operated at low pH. Among the weak base resins, WBG-30 consistently showed 15 to 25% higher sulfate removal than R402 throughout the study, which can arguably be attributed to its resin matrix and functional groups.

Our results suggest that sulfate removal significantly decreases above 40,000 mg/L chloride and that more moles of sulfate can be removed at high chloride concentrations when the chloride:sulfate ratio is lower. We found that chloride and sulfate were dominant in solution and no other anions were competing for ion exchange sites in the real produced water. For practical use, weak base resins were able to be regenerated and their large retardation values allow for reasonable reactor dimensions.

CHAPTER 5: SAMPLE CALCULATIONS

5.1 SAMPLE CALCULATIONS

Sample Calculation 1

Given:

$V_{reactor,\ initial}$ = 100 ml = 0.1 L

M_{resin} = 1 g WBG-30

$[H^+] = 10^{-pH}$

Titrating with 1M HCl

Objective:

Find proton uptake capacity for WBG-30

HCl added = 0.001 ml of 1M HCl

Accumulated HCl = initial HCl (moles) + HCl added (moles) = 0 + (0.001 ml)*(1 mole HCl/L)*(L/1000 ml) = 0.000001 moles H^+

$[H^+]_{Theoretical}$ = (Accumulated HCl(moles))/($V_{reactor,\ initial}$ + Accumulated HCl(L)) = (0.000001 moles H^+)/(0.1 L + 0.001 ml (L/1000 ml)) = 9.99E$^-$6 M

$pH_{Theoretical}$ = -log($[H^+]_{Theoretical}$) = -log(9.99E$^-$6 M) = 5.0

$pH_{Measured}$ = 10.05

$[H^+]_{Measured} = 10^{-pH} = 10^{-10.05}$ = 8.9125E$^-$11 M

$H^+_{Measured}$ (moles) = $[H^+]_{Measured}$*($V_{reactor,\ initial}$ + Accumulated HCl(L)) = 8.9125E$^-$11 M*(0.1L + 0.001 ml (L/1000 ml)) = 8.9126E$^-$12 moles

Proton uptake = Accumulated HCl (moles) – $H^+_{Measured}$ (moles) = 0.000001 - 8.9126E$^-$12 = **9.99E$^-$7 moles H^+**

Proton uptake capacity = Summation of proton uptake for each HCl addition

Sample Calculation 2

Given:

Proton uptake capacity = 0.082 moles $H^+/g_{\ R402}$

$pH_{initial,Dale}$ = 7.9

$pH_{final,Dale}$ = 3.94

Objective:

Find proton uptake capacity lost due to initial pH decrease. Increments of 10M HCl were added to 100 ml Dale until pH 3.94 was reached.

$V_{HCl\ added}$ = 0.017 ml = 0.000017 L HCl

H^{+}_{added} (moles) = 0.000017 L HCl*(10 moles/L) = 0.00017 moles H^{+}

% of resin capacity lost = (0.00017 moles H^{+}/0.082 moles H^{+})*100 = **0.21%**

Sample Calculation 3

Given:

87.66% sulfate removal in synthetic 200 mg/L sulfate and 11,818 mg/L chloride water

100 ml batch reactor, 1 gram WBG-30 resin

Objective: Find moles of sulfate removed and initial chloride to sulfate ratio

(200 mg/L sulfate)*(g/1,000 mg)*(mole sulfate/96 g sulfate)*(0.1 L) = 0.000208 moles sulfate initially

(11,818 mg/L chloride)*(g/1,000 mg)*(mole chloride/35.5 g chloride)*(0.1 L) = 0.03329 moles chloride initially

Chloride:sulfate = 0.03329 moles chloride initially / 0.000208 moles sulfate initially = 160

(0.8766)*(200 mg/L sulfate)*(g/1,000 mg)*(mole sulfate/96 g sulfate)*(0.1 L) = 0.000183 moles sulfate removed

Sample Calculation 4

Given:

$Q_{power\ plant}$ = Power plant water usage = 1 MGD

Suggested resin service flow rate = 2 to 4 gpm/ft^3

Real Galatia using WBG-30, R = 430 from Table 8

1 resin regeneration per day

Objective: Size reactor and check to make sure we are within the suggested service flow rate

$Q_{power\ plant}$ = 1 MGD (1 ft^3/ 7.48 gallons) = 133,690 ft^3/day

1 resin regeneration per day = 430 bed volumes treated per day

Reactor Volume (Bed Volume) = $Q_{power\ plant}$ / R = (133,690 ft^3/day) / (430 bed volumes/day) = 311 ft^3/bed volume

Reactor dimensions = **7 x 7 x 6.5** = 318.5 ft^3

$Q_{suggested}$ = (Reactor Volume)*(Suggested service flow rate) = (318.5 ft^3)*(2 gpm/ft^3)*(60 min/hr)*(24 hr/day) = 917,280 gallons/day

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