Efficient Removal of Perchlorate (ClO_4^-) From Contaminated Water by Highly Selective, Regenerable Bifunctional Resins

Baohua Gu and Gilbert M. Brown

Environmental Sciences Division
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6036

Contact: *Dr. B. Gu; Ph: (865)-574-7286; E-mail: b26@ornl.gov*

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Background

- Perchlorate (ClO_4^-) contamination is a wide-spread problem and has been detected in ground or surface water in 14 states (Urbansky 1998; Damian and Pontius, 1999).
- ClO_4^- exceedingly mobile and stable in underground aquifers and surface water.
- Remediation technologies are limited.

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Comparison of Treatment Technologies

	Advantages	Disadvantages
Bioremediation Technology	▪ Practical and economical ▪ Effective for treatment at relatively high concentrations (e.g., above 10 mg/L)	▪ Need a highly reducing environment and a continual feed of nutrients ▪ Other electron acceptors in groundwater and soil ▪ Not suitable for treatment of water plumes with only slightly contaminated ClO_4^-. ▪ Slow reactions and living microorganisms
Conventional Ion Exchange	▪ Effective and able to remove ClO_4^- below detection limit (<4 ppb) ▪ Fast reaction and simple operation ▪ Can be operated at a high flow rate	▪ Competition by other anions (e.g., NO_3^-, Cl^-, $SO_4^=$, HCO_3^-) ▪ Large quantities of waste brine generation ▪ Remineralization may be needed ▪ Regeneration problems with selective resins
Reverse Osmosis	▪ Effective	▪ Fouling of the membranes ▪ Remineralization may be needed ▪ High capital cost and impractical
Chemical Reduction	▪ A possible alternative ▪ May work well with highly concentrated ClO_4^- in a small volume	▪ Relatively slow reduction process ▪ Addition of chemicals ▪ May generate toxic byproducts
Chemical Precipitation	▪ May work well with highly concentrated ClO_4^- in a small volume (e.g., nitron and K^+) ▪ Fast reactions	▪ Addition of chemicals ▪ Impractical for large-scale treatment

Reference: Urbansky 1998, Biorem. J. 2:81-95; Damian and Pontius 1999, Environ. Prot. pp. 24-31.

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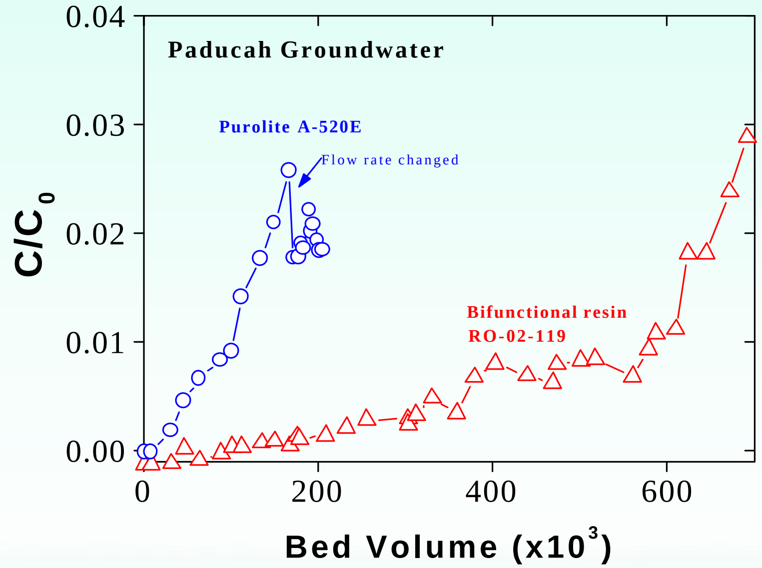
Treatment by Highly Selective, Regenerable Resins

- Under DOE sponsorship, bifunctional anion exchange resins developed for pertechnetate (TcO_4^-) removal at ppt levels.
- Bifunctional resins consist of quaternary ammonium groups with both large (C_6) and small (C_2) alkyl groups resulting in high selectivity and good exchange kinetics.
- Demonstrated to be highly efficient in removing low-levels of TcO_4^- from groundwater at Paducah, KY (with an initial TcO_4^- concentration ~ 0.1 ppb (or ~0.7 nmol/L).



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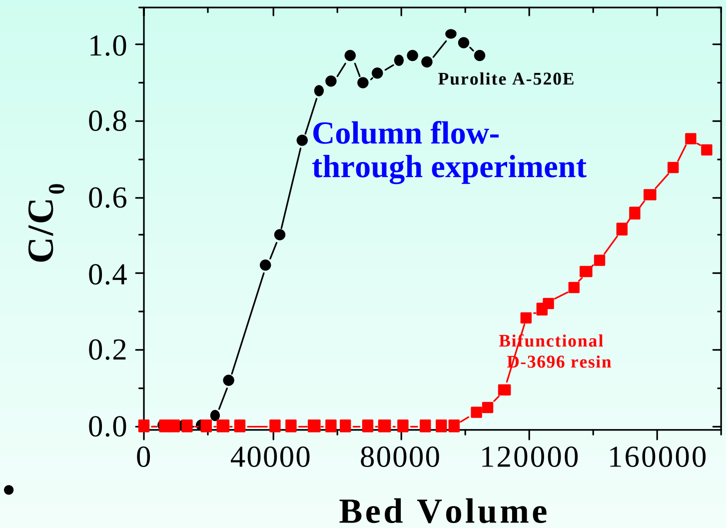
Treatment by Highly Selective, Regenerable Resins

- **Perchlorate (ClO_4^-) behaves similarly as pertechnetate (TcO_4^-) – both are large, poorly hydrated anions.**

- **Bifunctional resins were also demonstrated to be highly effective in removing low-levels of ClO_4^- from groundwater in northern California (with an initial ClO_4^- concentration ~ 50 ppb).**



- **Bifunctional resins can be regenerated using the innovative sequential chemical displacement technique (*patent pending*).**

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Objectives

- Selective sorption (or partitioning) of ClO_4^- on bifunctional resins and the treatment processes.
- Column flow-through experiments and field evaluation.
- Regeneration of bifunctional resins (loaded with ClO_4^-) – theory and experimental results.

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Synthetic Resins

- **Bifunctional resins (or BiQuat):**
  - **RO-02-119 – with trihexylamine/triethylamine functional groups; Synthesized at the Univ. of Tennessee, Knoxville.**
  - **D-3696 – with trihexylamine/triethylamine functional groups; Scale-up version by Purolite International, Inc.**

- **Commercial monofunctional resins:**
  - **Purolite A-520E – with triethylamine functional groups (by Purolite International).**
  - **Sybron SR-6 – with tributylamine functional groups (by Sybron Chemicals, Inc.).**

Experimental

Batch Sorption Experiments

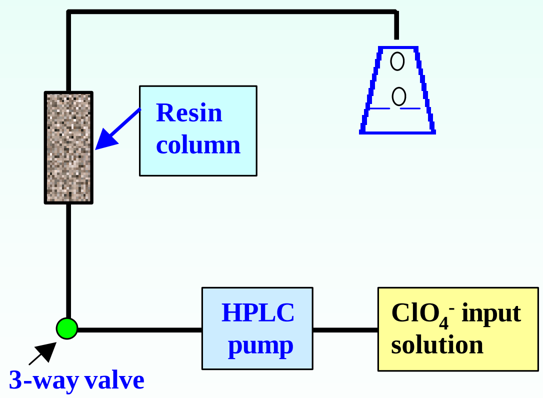
- **Sorption and selectivity coefficient:**

$$K_d = \frac{ClO_4^- \text{ sorbed on resin (mg/g)}}{ClO_4^- \text{ in solution (mg/mL)}} \quad \text{(mL/g)}$$

- **Initial ClO_4^- concentration: 1,000 – 200,000 ppb (or mg/L).**

Column Flow-Through Experiments

- **Flow rate: ~17 BV/min in laboratory;**
  ~2 BV/min in field.
- **Influent ClO_4^- concentration:**
  1,000 or 10,000 ppb in lab;
  ~50 ppb in field.



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Experimental (water chemistry)

Property	Synthetic water (lab test)	Groundwater (field test)
Cl^- (mg/L)	106	7.0
F^- (mg/L)	0	0
NO_3^- (mg/L)	31	61.2
$SO_4^=$ (mg/L)	49	14.9
HCO_3^- (mg/L)	183	98.6
ClO_4^- (µg/L)	1,000 – 10,000	~50
pH	8.3	6.9

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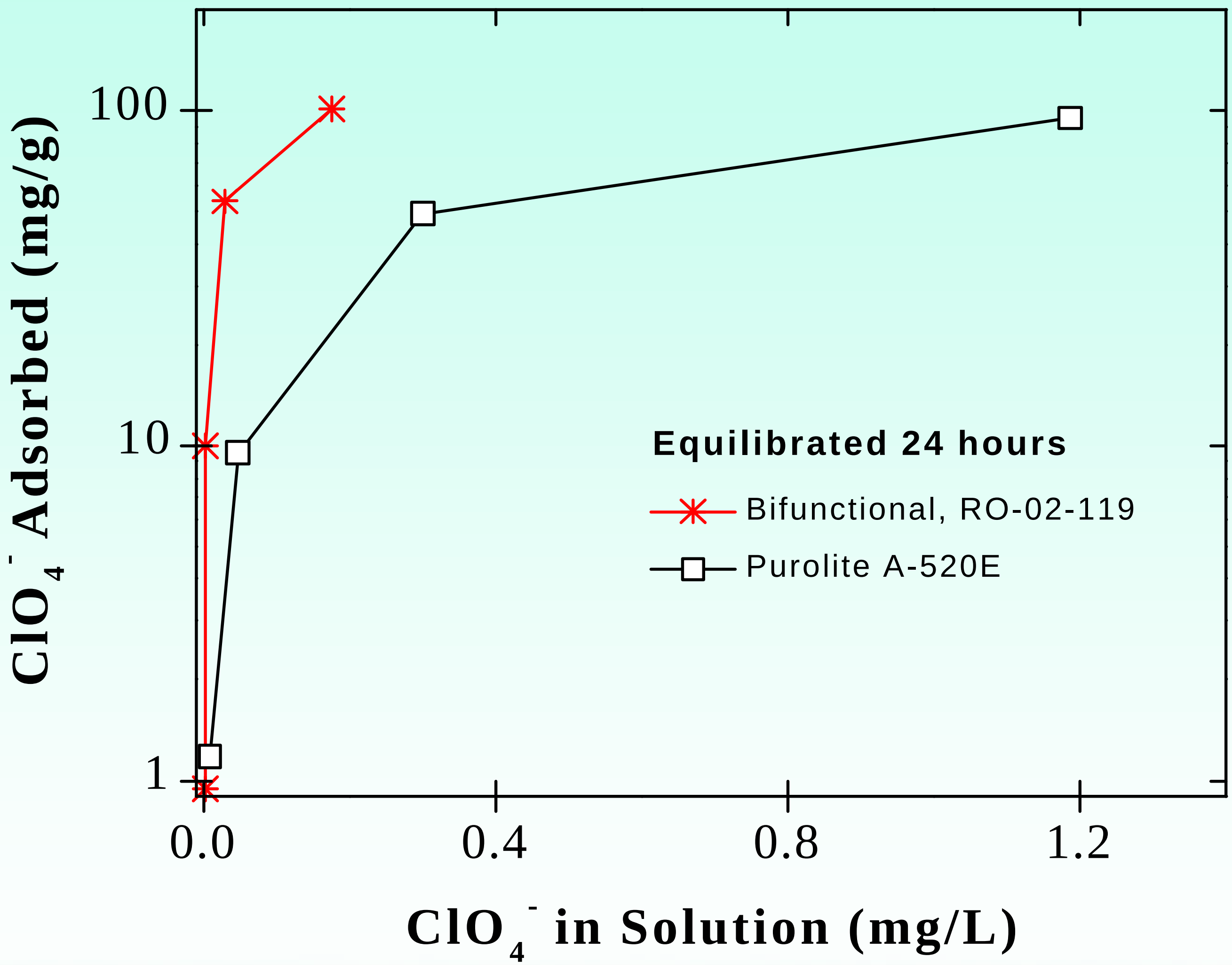
ClO_4^- Sorption on Synthetic Resins



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Perchlorate Selectivity Coefficients (K_d) on Synthetic Resins

(C_0 = 10 mg/L ClO_4^-)

RESIN	1-h Kd (mL/g)	24-h Kd (mL/g)	168-h Kd (mL/g)
Bifunctional anion exchange resins			
RO-02-119	285,000	>3,330,000	>3,330,000
Purolite D-3696*	164,800	1,877,000	1,842,000
Commercial anion exchange resins			
Purolite® A-520E	97,000	203,000	217,000
Sybron® SR-6	65,000	250,000	282,000

* Purolite D-3696 is a scale-up version of ORNL bifunctional resin made by Purolite International, Inc.

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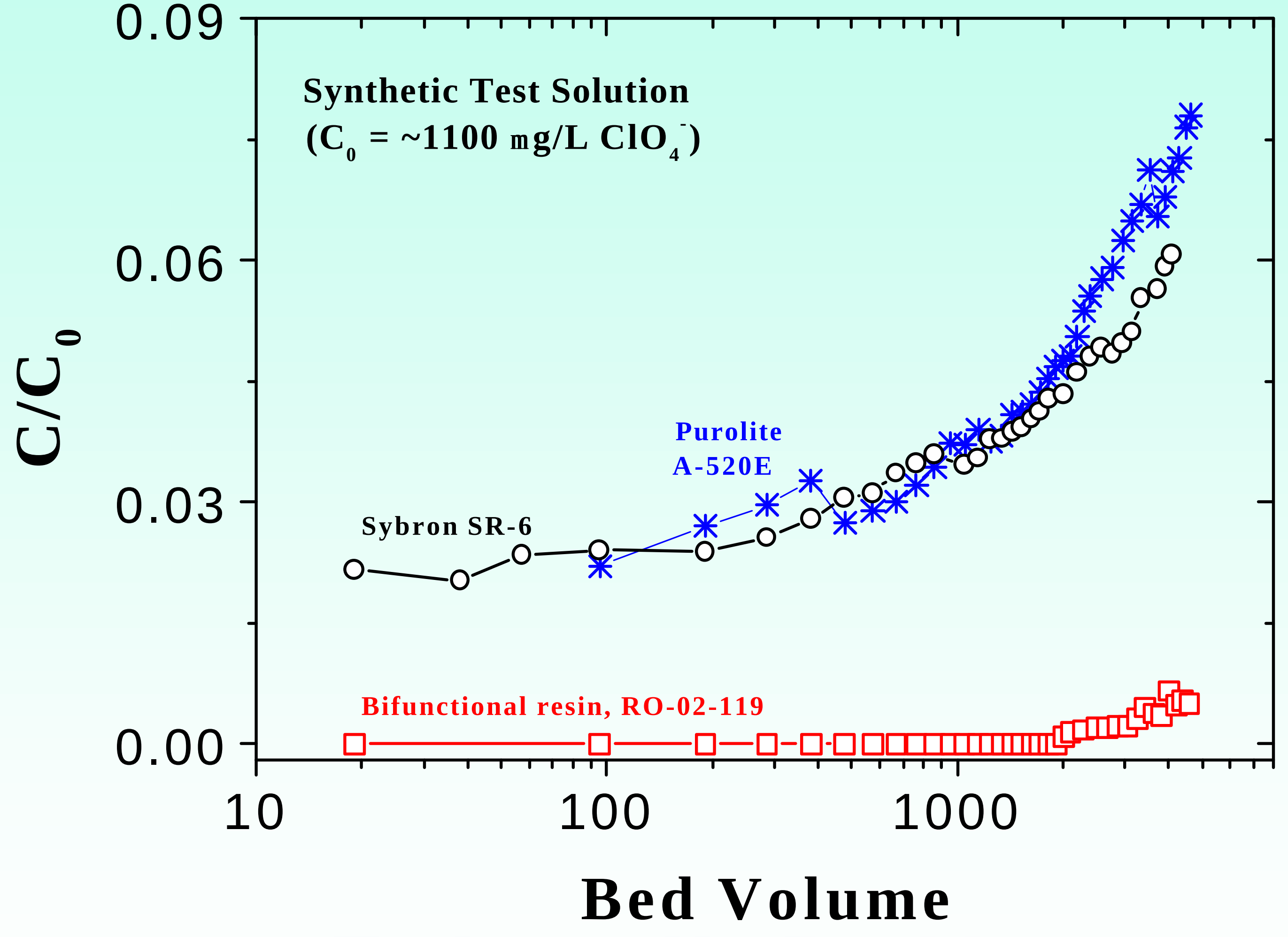
ClO_4^- Breakthrough in Laboratory Column Flow-Through Experiment



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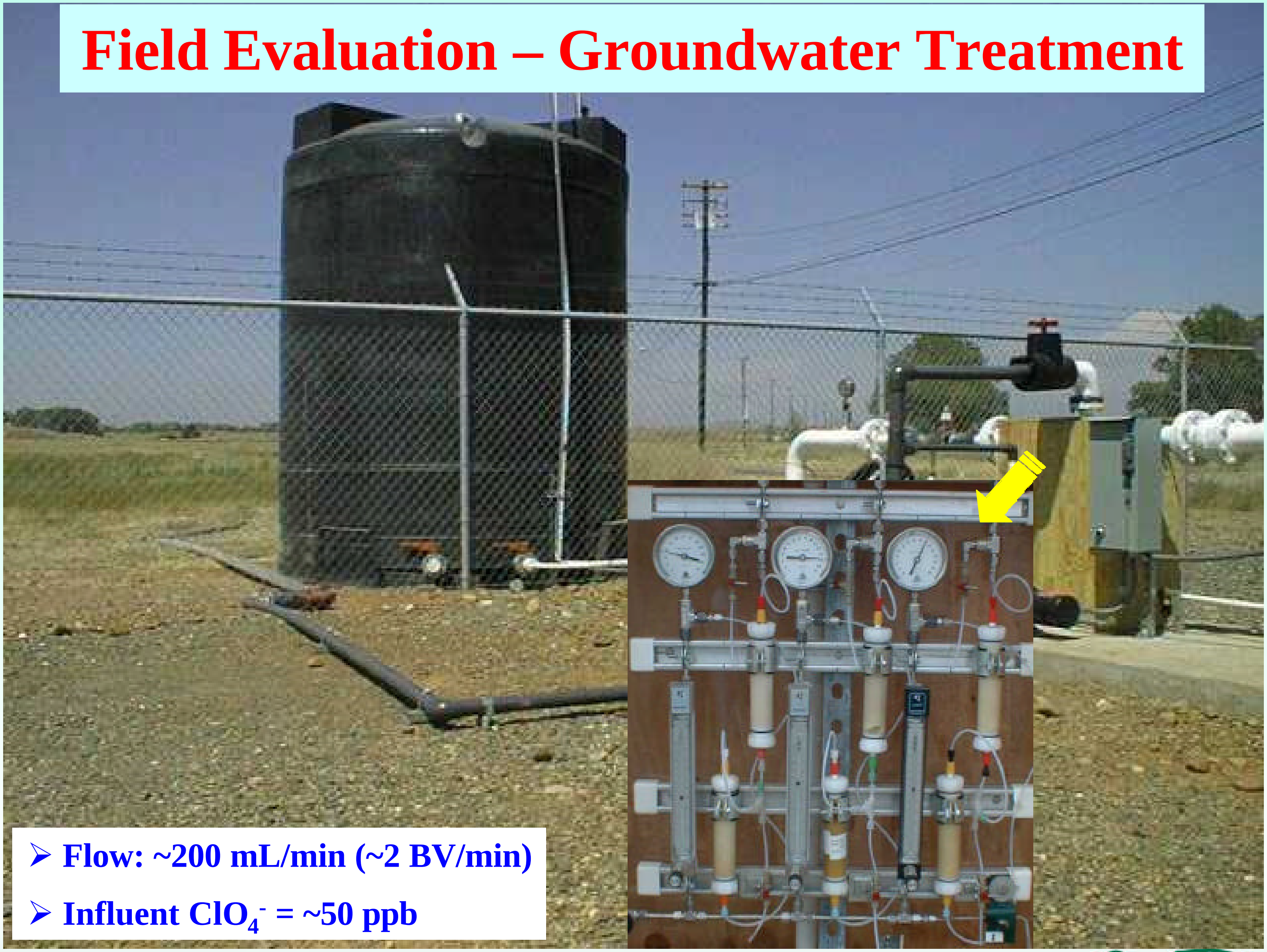
Field Evaluation – Groundwater Treatment



- Flow: ~200 mL/min (~2 BV/min)
- Influent ClO_4^- = ~50 ppb

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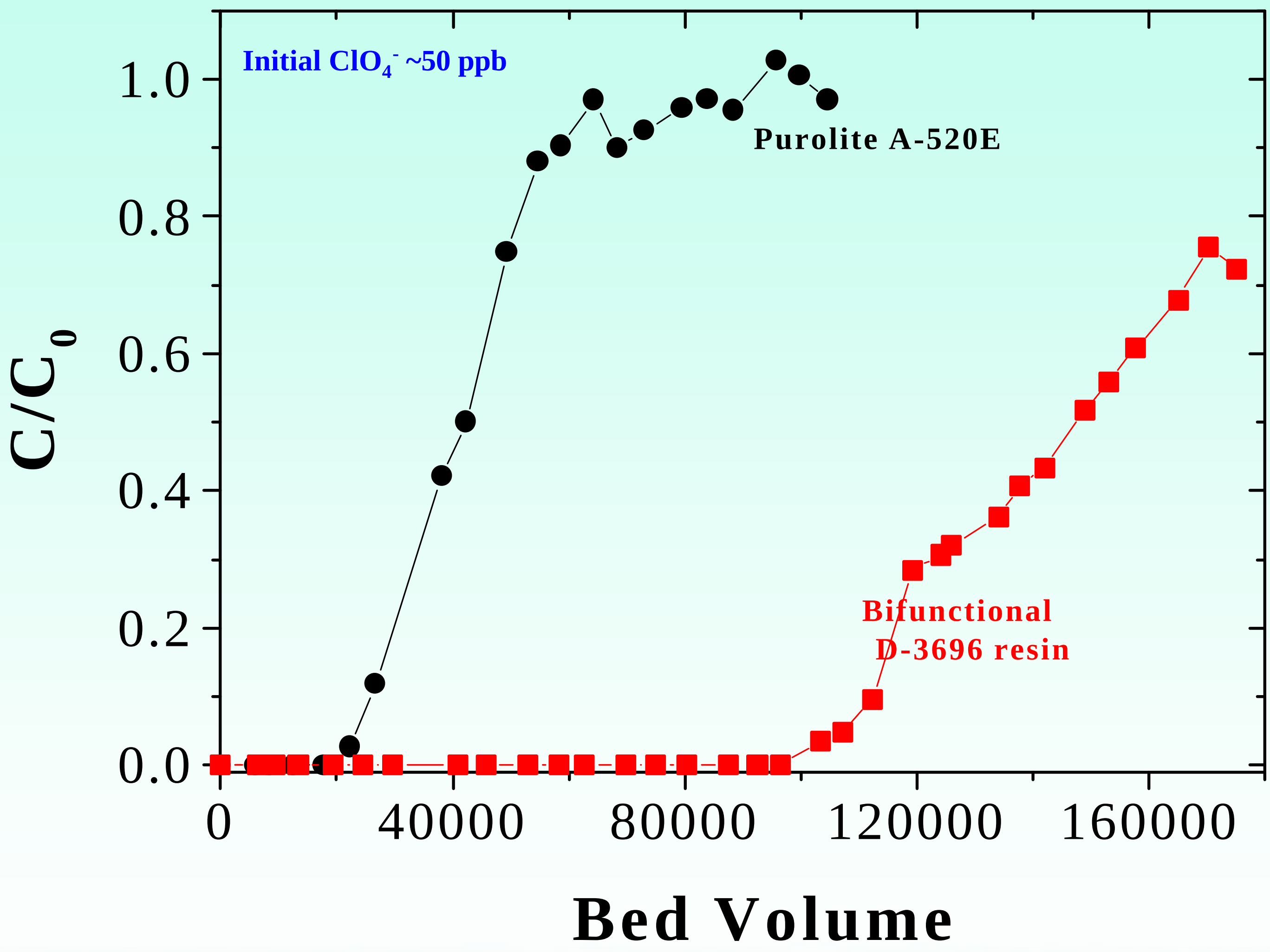
Treatment of ClO_4^--Contaminated Groundwater in Northern California



- Treated ~110,000 bed volumes of groundwater in ~40 days.
- Less than 10% breakthrough of ClO_4^- occurred.
- Flow rate ~ 2 bed volumes min^{-1}.
- No pretreatment is necessary.

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Resin Regeneration

- **Conventional Regeneration**
  - **Washing with a brine (~12% NaCl) for non-selective resins.**
  - **ClO_4^- loading often less than 0.5% of the exchange capacity on non-selective resins because of the competition and partitioning by other anions (*Loading* → K_d*C).**
  - **Regeneration questionable because >99.5% of the exchange sites loaded with other anions (HCO_3^-, NO_3^-, Cl^-, $SO_4^=$ …).**
  - **A mass balance must be obtained to evaluate the regeneration efficiency.**
  - **Regeneration by brine is ineffective for selective resins such as Purolite A-520E and bifunctional resins.**

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Regeneration by Tetrachloroferrate ($FeCl_4^-$)

(Patent pending)

- $FeCl_4^-$ formed in ferric chloride solutions ($FeCl_3 + Cl^- \rightarrow FeCl_4^-$).
- $FeCl_4^-$ is also a large, poorly hydrated anion and strongly sorbed by selective anion exchange resins.
- $FeCl_4^-$ effectively displaces ClO_4^- sorbed on resins.

- However, $FeCl_4^-$ readily dissociates in dilute HCl solutions:

$$FeCl_4^- \rightarrow FeCl_3 + Cl^-$$

$$FeCl_4^- \rightarrow FeCl_2^+ + 2Cl^-$$

……

- Positively-charged Fe species are readily eluted off the resin bed by electrostatic repulsion, whereas Cl^- remaining on the resin bed by charge balance, thereby regenerating the resin to its original state.

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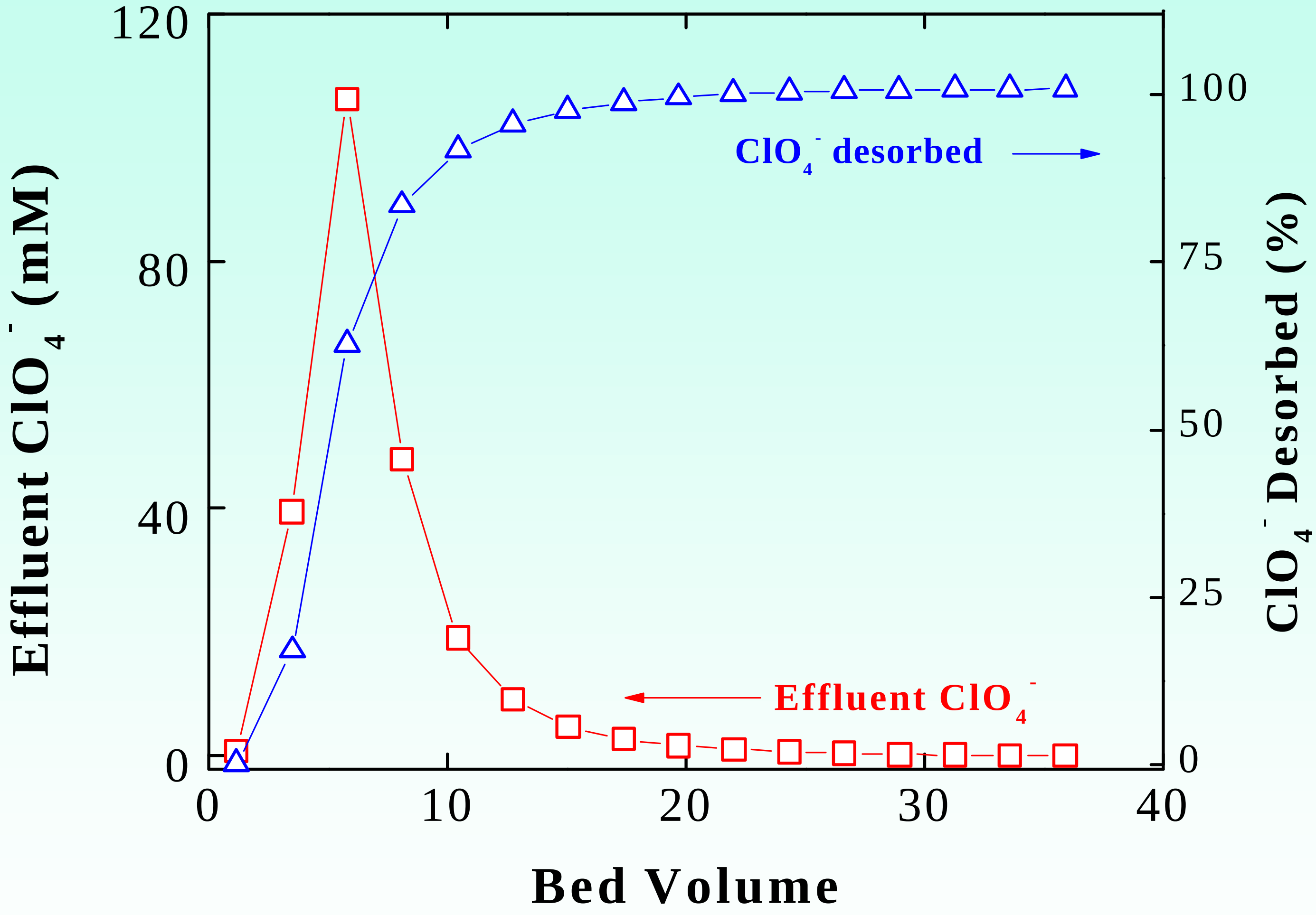
Regeneration Efficiency and Mass-Balance Analysis of Displaced ClO_4^- by $FeCl_4^-$



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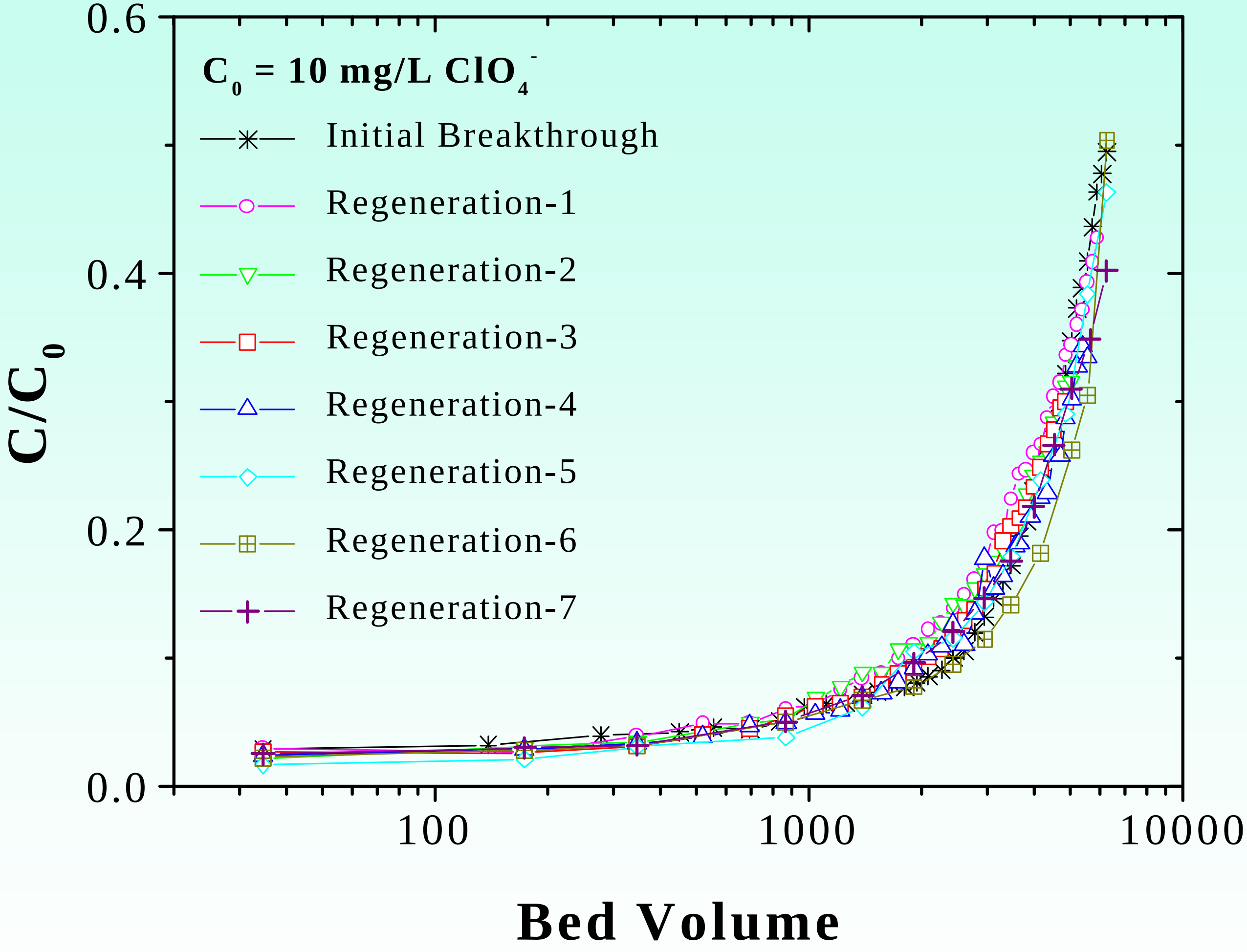
Resin Performance After Repeated Regeneration



- **No decrease in resin performance after repeated ClO_4^- loading and regeneration cycles (7 cycles).**
- **Performed with D-3696 resin column (10x22 mm), Flow = 17 BV/min, and Initial ClO_4^- = 10 mg/L.**

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Comparison of Ion-Exchange Treatment Technologies

Conventional Ion Exchange (Non-selective resin, brine regeneration)	New Technology (Highly Selective, Regenerable Resins)
▪ Effective and able to remove ClO_4^- below detection limit (<4 ppb). ▪ Inefficient (ClO_4^- loading <0.5%) because of the Competition by other anions (e.g., NO_3^-, Cl^-, $SO_4^=$, HCO_3^-). ▪ Less effective at low ClO_4^- concentration levels in groundwater. ▪ Require frequent regeneration. ▪ Generate large quantities of secondary waste brine (with ClO_4^-). ▪ Remineralization may be needed. ▪ High operational and waste disposal costs. **Conclusion: Unattractive** *(Urbansky 1998, 1999; Damian and Pontius 1999; Batista et al. 2000)*	▪ Effective and able to remove ClO_4^- below detection limit (<4 ppb). ▪ Efficient because of its high selectivity (ClO_4^- loading capacity ~ K_d*C). ▪ No changes in groundwater chemistry, and no remineralization is needed. ▪ Last longer and require less regeneration cycles. ▪ Particularly effective in removing low levels of ClO_4^- (at ppb levels). ▪ Effective regeneration by $FeCl_4^-$ with a good mass balance and recovery of ClO_4^-. ▪ Regenerant solution can be reused and $FeCl_3$ can be precipitated out for waste minimization. ▪ ClO_4^- can be co-precipitated out from the highly concentrated regenerant solution with KOH. ▪ Reduced overall operational and waste disposal cost.

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Summary

- Bifunctional resins were demonstrated to have superior selectivity for perchlorate sorption in both laboratory and field tests.
- A single-step treatment process (because of its high selectivity); No pretreatment (e.g., carbon or nanofilter) is necessary.
- Bifunctional resin is particularly effective in removing ClO_4^- at low or trace concentrations.
- New regeneration technology has been developed for selective anion exchange resins (for reduced operational and waste disposal costs).
- Can be operated at a high flow rate, typically at 2 – 4 BV/min (e.g., a 6x4 ft treatment column may be operated at 1000 – 3000 gpm).
- A combination of highly selective anion exchange resins and the new regeneration technology may offer a promising treatment technology for remediating ClO_4^- contaminated water.

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