Hydroxyl and Sulfate Radical Scavenging by Solid Phase Mineral Species

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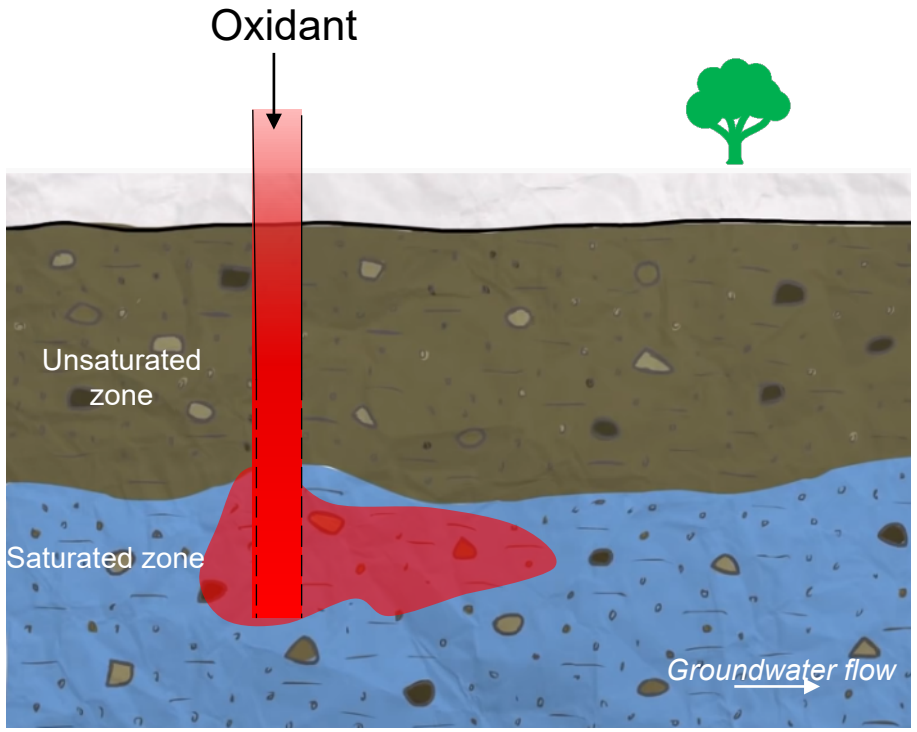
Problem statement



A simplified schematic of oxidant delivery into the contaminated aquifer.

OXIDANTS:
Persulfate, $S_2O_8^{2-}$ (PS)
Hydrogen peroxide, H_2O_2

- Treatment of contaminated water
- Activated oxidants generate •R ($SO_4^{\bullet-}$, •OH)
- $SO_4^{\bullet-}$/•OH highly effective: transform contaminants to form less toxic products

BUT: $SO_4^{\bullet-}$/•OH unselective and react with non-target species (scavengers); limiting treatment efficiency; possibly incomplete contaminant(s) removal

Fate of •R reaction by means of kinetic analysis

Contaminant ← preferred ·R ($SO_4^{\bullet-}$/•OH) → Scavengers (aqueous, solid)

Example	$k_{SO_4^{\bullet-}}$	c	
1,4-dioxane + $SO_4^{\bullet-}$ →…	4.1×10^{7} 1/M s*	1.1×10^{-5} M	Estimate of $SO_4^{\bullet-}$ reaction
HCO_3^- + $SO_4^{\bullet-}$ →…	$9.1\ 10^{6}$ 1/M s*	1.6×10^{-3} M	
$S_2O_8^{2-}$ + $SO_4^{\bullet-}$ + → …	$6.1\ 10^{5}$ 1/M s*	4.2×10^{-2} M	
$S_{\equiv,i}$ + $SO_4^{\bullet-}$ → …	Not available		no estimate

→ Develop kinetic analysis and laboratory methods to determine the rate of surface radical scavenging

*Neta et al., 1988

Kinetic model – calculation of $k_{\equiv S}$

$d[\bullet R]/dt = P_{\bullet R} - C_{\bullet R}$

$C_{\bullet R} \sim P_{\bullet R}$ (QSSA)

$C_{\bullet R} = Rp + Rs + R_{\equiv S}$

$Rp = k_{\bullet R,P}\,[P]\,[\bullet R]_{SS}$

$Rp = k'\,[P]$

$R_S = \Sigma_{i=1}^{n} k_i\,[S_i]\,[\bullet R]_{SS}$

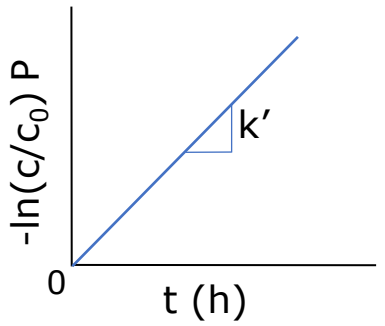
$Rs = k_S\,[\bullet R]_{SS}$

$R_{\equiv S} = \Sigma_{i=1}^{n} k_{\equiv,i}\,[S_{\equiv,i}]\,S_A\,m_S\,[\bullet R]_{SS}$

$R_{\equiv S} = k_{\equiv S}\,S_A\,m_S\,[\bullet R]_{SS}$

$[\bullet R]_{SS} = k'/k_{\bullet R,P}$

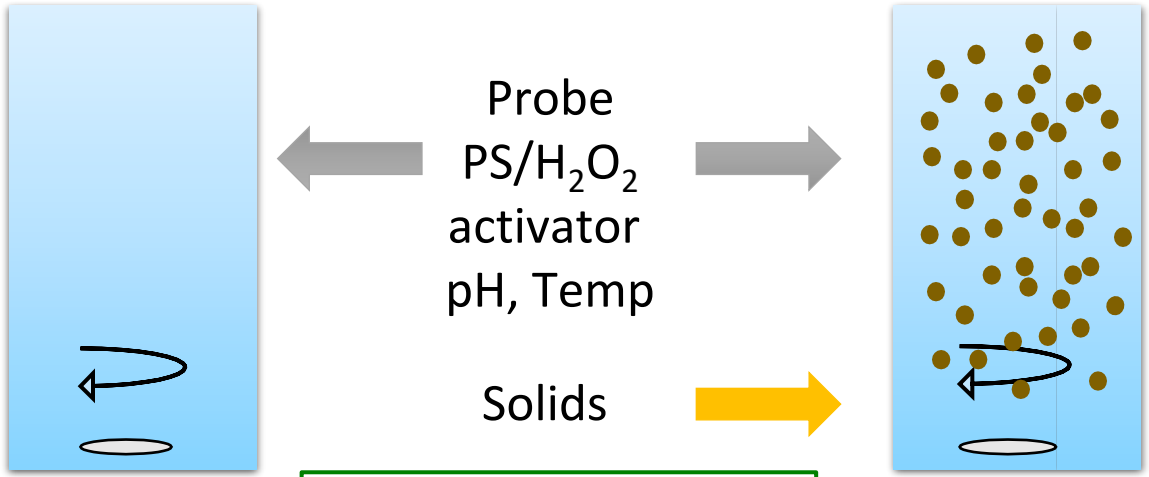
- All reactants have equal access to •R (•R = $SO_4^{\bullet -}$ or •OH)
- $k_{\bullet R,P}$ and k_i = known 2nd order rate constant for probe and aqueous scavengers, respectively
- k' = observed rate of probe decay (experimentally)



Experimental approach – determining k'

homogeneous

heterogeneous



$$P_{\bullet R,hom} = P_{\bullet R,het}$$

Parameters:

Probe: RhB (λ=556 nm);

Activator:

PS: UV, T → $SO_4^{\bullet-}$

H_2O_2: UV, Fe^{3+} → •OH;

Solids: alumina (2.3 m^2/g), silica (1.5 m^2/g), MMT (82.2 m^2/g)

Solids: 1) React minimally with oxidant, no •R formation
2) React with oxidant, but no •R formation

Experimental approach – controls

Determine fate of the reactants

Controls define the reaction system!

RhB

- Solid + RhB (pH, no sorption)
- Oxidant (PS/H_2O_2) + RhB (no oxidation)

Oxidants (PS, H_2O_2)

- Solid + Oxidant ($k'_{oxidant}$)
- Solid + Oxidant + RhB (k'_{RhB}, $k'_{oxidant}$)
- Activator + Oxidant ($k'_{oxidant}$)

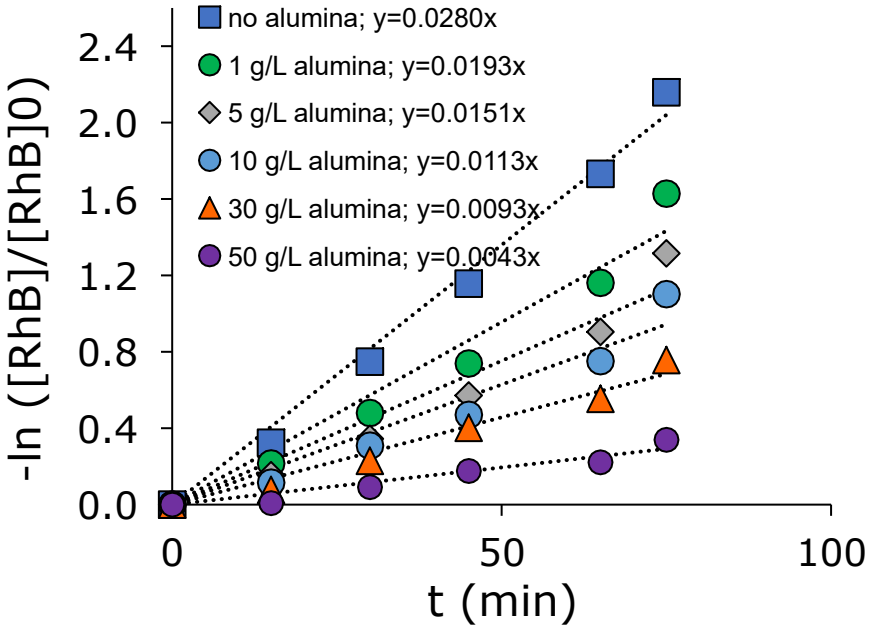
$$P_{\bullet R,hom} = P_{\bullet R,het}$$

Dissolved species (S_i)

- Leachate + Oxidant + RhB (no RhB oxidation?)

Impact of alumina on RhB oxidation

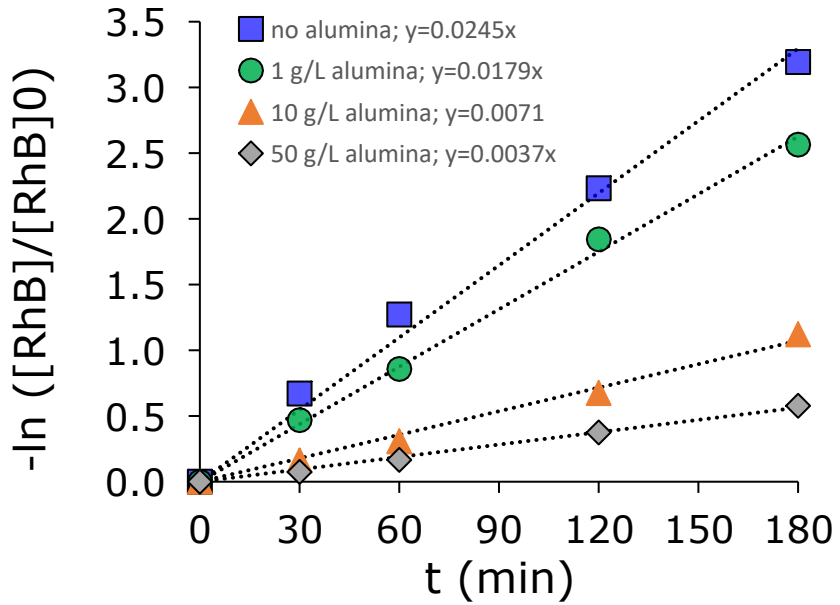
UV-PS → $SO_4^{\bullet-}$



$$[SO_4^{\bullet-}]_{ss} = \frac{k'_{RhB}}{k_{SO_4^{\bullet-},RhB}}$$

λ=365 nm; $[RhB]_0$=5 mg/L, 0.01 mM; $[PS]_0$=500 mg/L, 2.1 mM; [alumina]=0-50 g/L; pH_{start}=6.0, pH_{end}=4.5.

UV-H_2O_2 → •OH



$$[\bullet OH]_{ss} = \frac{k'_{RhB}}{k_{\bullet OH,RhB}}$$

λ=365 nm; $[RhB]_0$=0.01 mM; $[H_2O_2]_0$=29.4 mM; [alumina]=1-50 g/L; pH_{start}=6.8, pH_{end}=6.0.

Deriving the $k_{\equiv S}$

homogeneous:

$$P_{\bullet R,0} = k_{\bullet R,RhB}\,[RhB]\,[\bullet R]_{SS,0} + k_S\,[\bullet R]_{SS,0}$$

heterogeneous:

$$P_{\bullet R,10} = k_{\bullet R,RhB}\,[RhB]\,[\bullet R]_{SS,0} + k_S\,[\bullet R]_{SS,10} + k_{\equiv S}\,S_A\,m_{S,10}\,[\bullet R]_{SS,10}$$

$$P_{\bullet R,0} = P_{\bullet R,10}$$

Set equal, solving for $k_{\equiv S}$:

$$k_{\equiv S} = \frac{([\bullet R]_{SS,0}\,(k_{\bullet R,RhB}\,[RhB] + k_S)) - ([\bullet R]_{SS,10}\,(k_{\bullet R,RhB}\,[RhB] + k_S))}{S_A\,m_{S,10}\,[\bullet OH]_{SS,10}}$$

$\bullet R = SO_4^{\bullet -}$ or $\bullet OH$

Estimates of $k_{\equiv S}$ for selected minerals

System	n	[alumina] (g/L)	$k_{\equiv S}$ ($1/m^2$ s)
UV-H_2O_2	11	1-50	7.45×10^6
Fe-H_2O_2	10	1-50	3.92×10^6
UV-APS	15	1-50	2.42×10^4
T-APS	8	1-10	2.03×10^4

System	n	[MMT] (g/L)	$k_{\equiv S}$ ($1/m^2$ s)
UV-H_2O_2	8	1-50	$\leq 4.22\times10^5$

System	n	[silica] (g/L)	$k_{\equiv S}$ ($1/m^2$ s)
UV-H_2O_2	2	1-10	4.50×10^6
Fe-H_2O_2	10	1-30	2.85×10^6

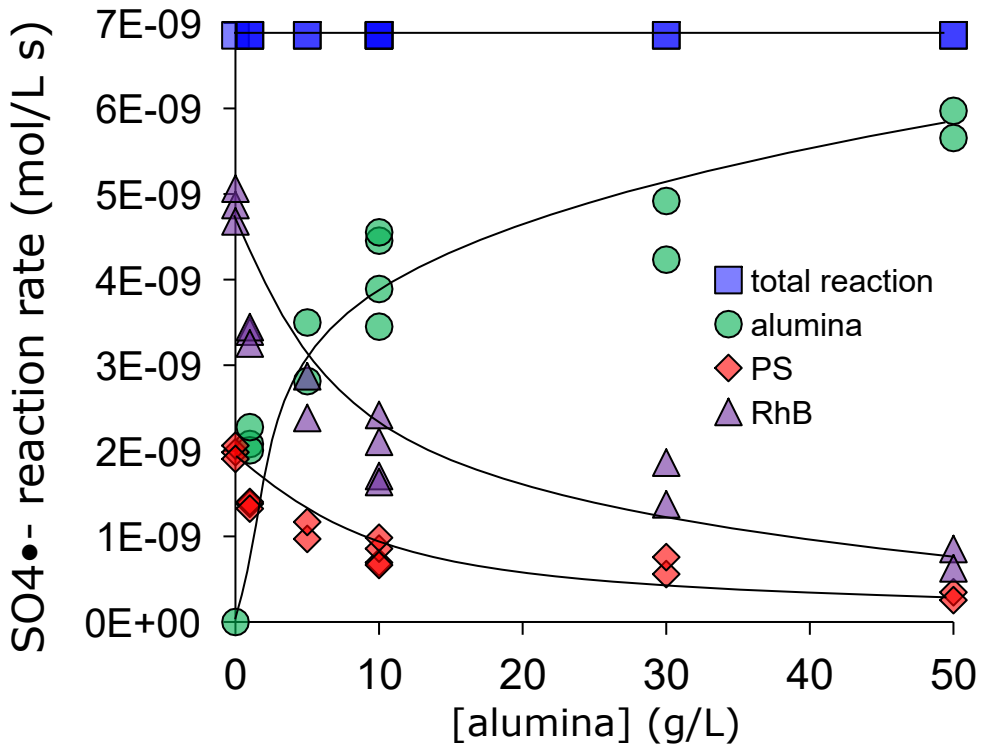
Mechanism of $k_{\equiv S}$ is not yet well understood;

- Si and Al in their highest oxidation state;
- surface OH^- groups and surface defect sites could play a role in •R scavenging (Flockhart, 1970; Suh et al., 2000; Konecny, 2001).

Contaminant ← preferred ·R → Scavengers (aqueous, solid)

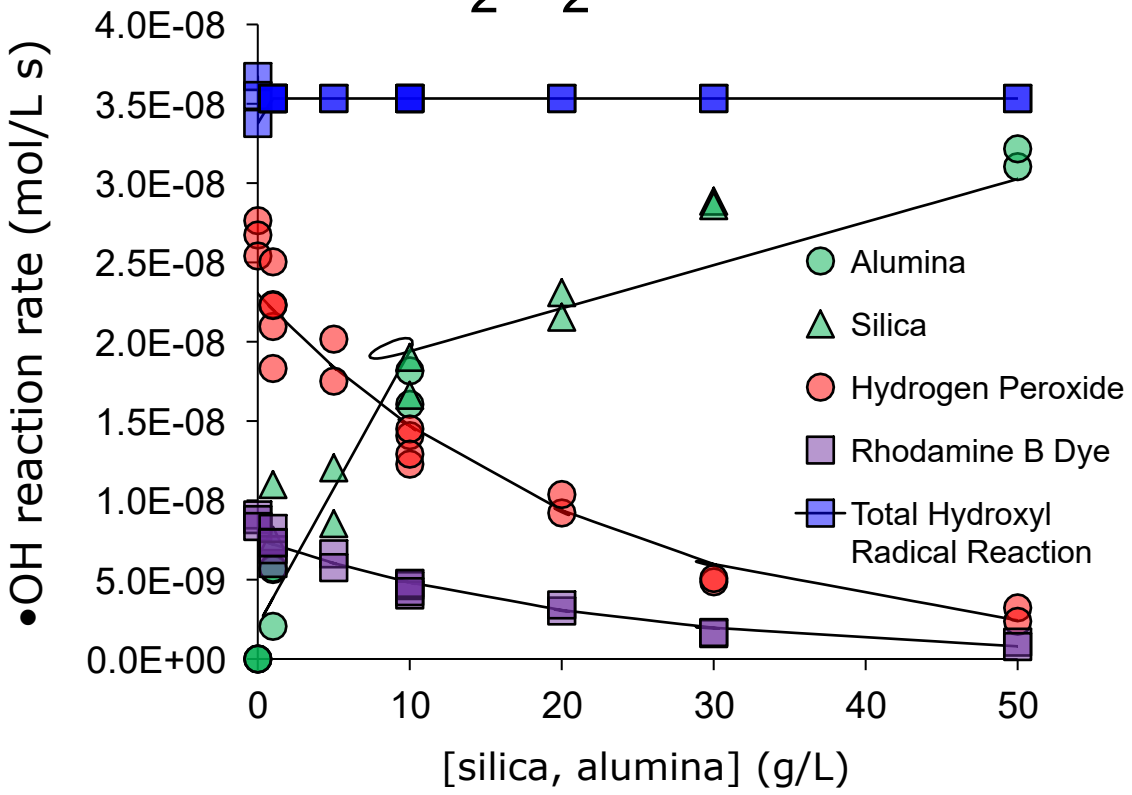
$SO_4^{\bullet-}$/•OH

UV-PS → $SO_4^{\bullet-}$



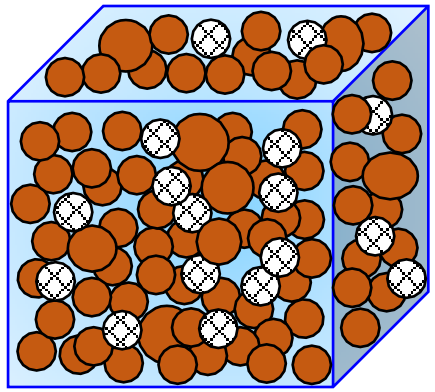
λ=365 nm; UV-PS; $[RhB]_0$=0.01 mM; $[PS]_0$=2.1 mM; [alumina]=0-50 g/L; pH_{start}=6.0, pH_{end}=4.5.

Fe^{3+}-H_2O_2 → •OH



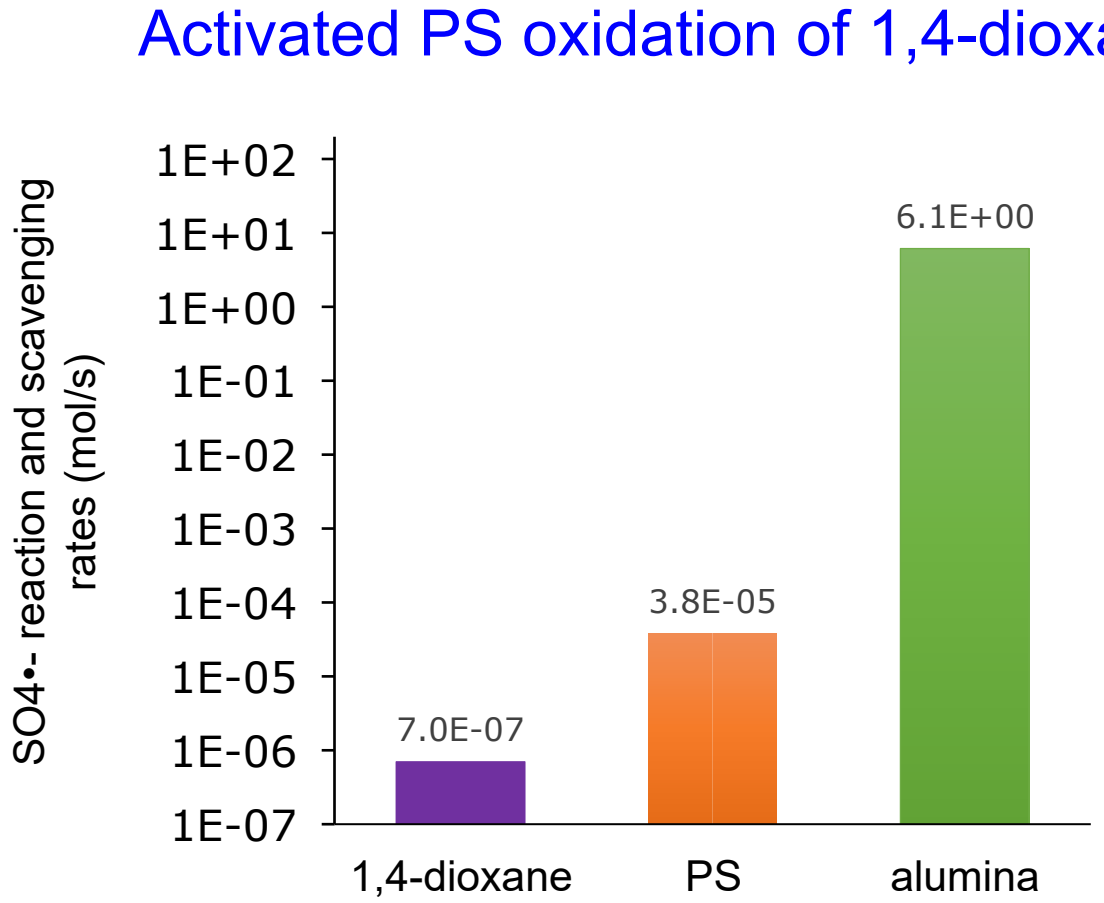
Fe-H_2O_2; $[RhB]_0$=0.01 mM; $[H_2O_2]_0$=29.4 mM; [alumina]=1-50 g/L; [silica]=1-30 g/L pH_{start}=6.0, pH_{end}=3.5.

Environmental implications



Parameters:

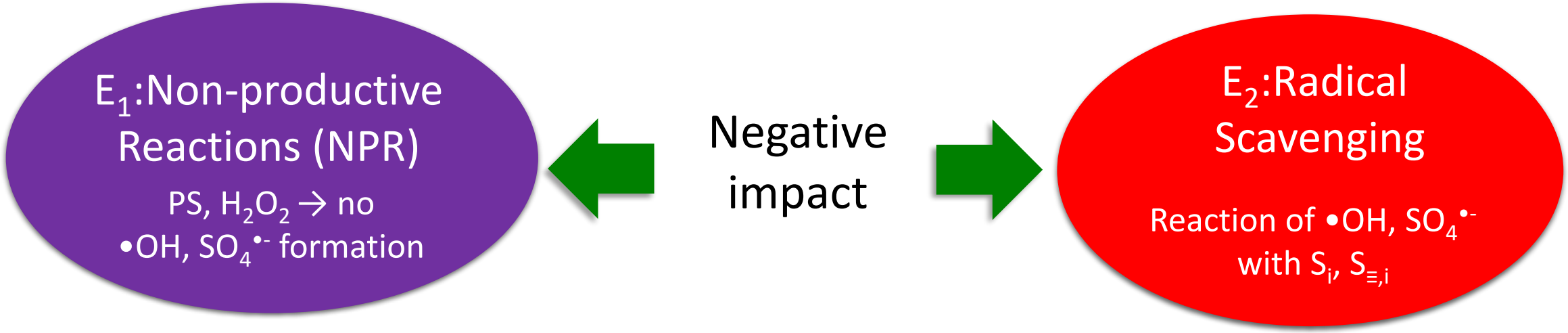
total volume=1 m^3, ρ_{bulk}=1.6 g/cm^3,
porosity (η)=0.3,
[alumina]=7 wt.%,
$k_{\equiv S}$=4.42×10^4 $1/m^2$ s,
$[PS]_0$=4.2×10^{-2} M,
$k_{SO4^{\bullet-},PS}$=6.1×10^5 1/M s,
$[1,4\text{-dioxane}]_0$=1.13×10^{-5} M,
$k_{SO4^{\bullet-},1,4\text{-dioxane}}$=4.1×$10^7$ 1/M s,
$[SO_4^{\bullet-}]_{SS}$=5×10^{-12} M (assumed)
equal access to $SO_4^{\bullet-}$



A simplified example of $k_{\equiv S}$ utilization in predicting reaction rate of $SO_4^{\bullet-}$ with contaminant (1,4-dioxane), PS and solids (alumina) in oxidative treatment systems.

Process efficiency

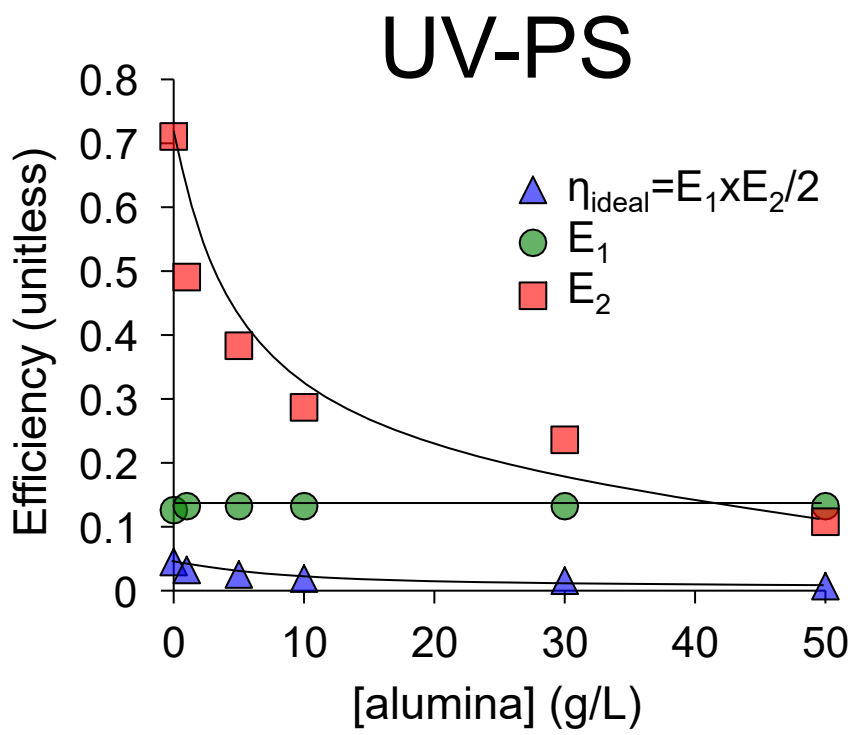
Overall efficiency: $\eta = E_1 \times E_2 = \frac{k_{probe}\,[probe]}{k_{oxidant}\,[oxidant]}$

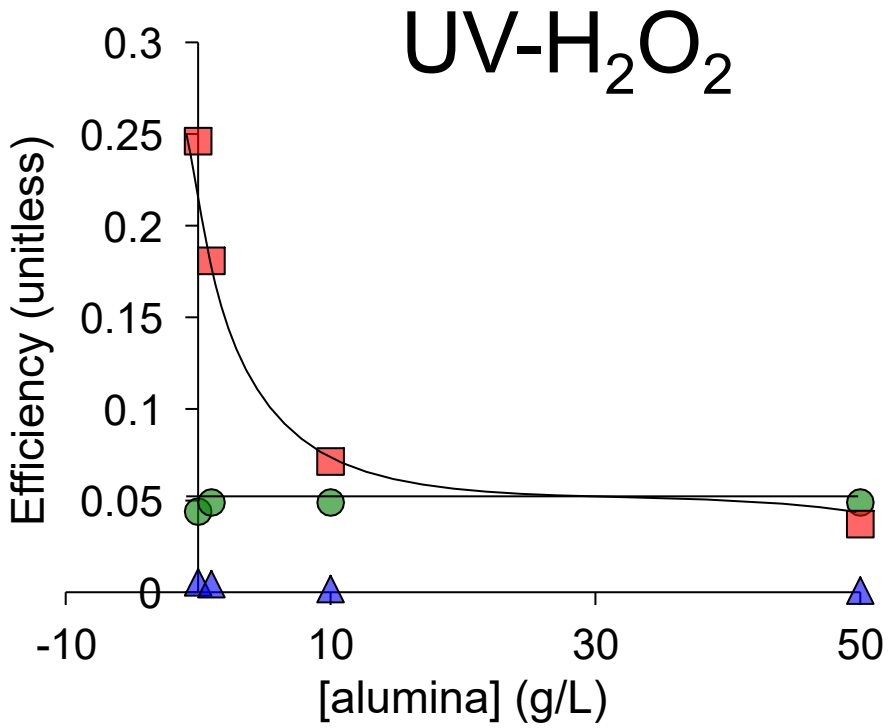


$E_1 = \frac{\text{Overall rate of radical production}}{\text{Rate of oxidant reaction}}$

$E_2 = \frac{\text{Rate of radical reaction with probe}}{\text{Overall rate of radical production}}$

Efficiency in UV-PS and UV-H_2O_2





$$k_{R\bullet,RhB}\,[RhB] = k_{R\bullet,OX}\,[OX]$$

R• = $SO_4^{\bullet-}$ or •OH; OX = PS or H_2O_2

UV-PS; $[RhB]_0$=0.01 mM; $[PS]_0$=2.1 mM; [alumina]=1-50 g/L; pH_{start}=6.0, pH_{end}=4.5.

UV-H_2O_2; $[RhB]_0$=0.01 mM; $[H_2O_2]_0$=29.4 mM; [alumina]=1-50 g/L; pH_{start}=6.8, pH_{end}=6.0.

In conclusion

- Competition kinetic model and laboratory methods were developed to establish $k_{\equiv S}$
- The $k_{\equiv S}$ was determined for alumina, silica, MMT
- Reaction between •R and the solids tested was much more significant than aqueous phase reactions
- Mitigation of surface scavenging has a great potential to improve in situ treatment with persulfate/hydrogen peroxide

K.R. Crincoli, S.G. Huling. Contrasting hydrogen peroxide- and persulfate-driven oxidation systems: Impact of radical scavenging on treatment efficiency. Chem. Eng. J., 2021, 126404.

K.R. Crincoli, C. Green, S.G. Huling. Sulfate radical scavenging by mineral surfaces in persulfate-driven oxidation systems: reaction rate constants and implications. Environ. Sci. Technol., 2020, 54, 3, 1955-1962.

K.R. Crincoli, S.G. Huling. Hydroxyl radical scavenging by solid mineral surfaces in oxidative treatment systems: rate constants and implications. Wat. Res., 2020, 169, 115240.

Thank you!