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Chlorine Absorption In S(IV) Solutions

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Chlorine Absorption in S(IV) Solutions

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Abstract

The rate of chlorine (Cl_2) absorption into aqueous sulfite/bisulfite [S(IV)] solutions was measured at ambient temperature using a highly characterized stirred cell reactor. The reactor media were 0 to 10 mM S(IV) with pH ranging from 3.5 to 8.5. Experiments were performed using 20 to 300 ppm Cl_2 in nitrogen (N_2). Chlorine absorption was modeled using the theory of mass transfer with chemical reaction. Chlorine reacts quickly with S(IV) to form chloride and sulfate. Chlorine absorption is enhanced by increasing pH and S(IV) concentration. The rate constant for the reaction of chlorine with S(IV) was too rapid to be precisely measured using the existing stirred cell reactor, due to mass transfer limitations. However, the most probable value of the rate constant was determined to be 2×10^9 L/mol-s.

These results are relevant in the simultaneous removal of chlorine, sulfur dioxide (SO_2), and elemental mercury (Hg) from flue gas. The developed model shows that good removal of both chlorine and mercury should be possible with the injection of 1 to 10 ppm chlorine to an existing limestone slurry scrubber. These results may also be applicable to scrubber design for removal of chlorine in the pulp and paper and other industries.

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Nomenclature

A	gas/liquid contact area (m^2)
A^-	generic anion
C_{Cl_2}	concentration of chlorine in liquid (mol/L = M = kmol/m^3)
$[Cl^-]$	concentration of chloride in liquid (M)
D_{Cl_2}	diffusion coefficient for chlorine in water (m^2/s)
D_{Hg}	diffusion coefficient for mercury in water (m^2/s)
$D_{S(IV)}$	diffusion coefficient for S(IV) in water (m^2/s)
E	enhancement factor (dimensionless)
FC	mass flow controller
Φ	reactant stoichiometric coefficient (dimensionless)
G	gas flow rate to reactor (m^3/s)
HA	generic acid
H_{Cl_2}	Henry's law constant for chlorine (atm-m^3/kmol)
H_{Hg}	Henry's law constant for mercury (atm-m^3/kmol)
IMS	ion mobility spectrometry
K	equilibrium constant
k_g	individual gas film mass transfer coefficient (kmol/s-atm-m^2)
k^o_{L,Cl_2}	individual physical liquid film mass transfer coefficient for chlorine (m/s)
K_{OG}	overall gas phase mass transfer coefficient (kmol/s-atm-m^2)
$k_{1,H2O}$	first order rate constant for chlorine hydrolysis reaction (s^{-1})
$k_{2,buf}$	second order rate constant for chlorine/buffer reaction (L/mol-s)
$k_{2,Hg}$	second order rate constant for mercury/chlorine reaction (L/mol-s)
$k_{2,S(IV)}$	second order rate constant for chlorine/S(IV) reaction (L/mol-s)
$k_{2,OH}$	second order rate constant for chlorine/hydroxide reaction (L/mol-s)
N_{Cl_2}	flux of chlorine (kmol/m^2-s)
N_g	number of gas phase mass transfer units, defined as k_gA/G (dimensionless)
n_g	gas phase agitation rate (rpm)
n_L	liquid phase agitation rate (rpm)
P_{Cl_2}	partial pressure of chlorine (atm)
$P^*_{Cl_2,b}$	partial pressure of chlorine in equilibrium with chlorine in bulk liquid (atm)
pK_a	negative logarithm of acid dissociation constant
R	gas constant (8.205 x 10^{-5} m^3-atm/mol-°C)
t	time (s)
T	temperature (°C)

V	reactor volume (m^3)
y_{Hg}	mole fraction of mercury in the gas phase (dimensionless)

Subscripts

b	in bulk
i	at gas/liquid interface
in	inlet
init	initial
out	outlet
T	total