

**INFLUENCE OF TEMPERATURE ON NICKEL SORPTION ON CLAY MINERAL AND OXIDE SURFACES.** K. G. Scheckel<sup>1</sup> and D. L. Sparks<sup>1</sup>, <sup>1</sup>University of Delaware, 147 Townsend Hall, Newark DE 19717-1303, USA.

**Introduction:** Many kinetic studies have shown that sorption of metals on natural materials results in the formation of metal precipitates. However, the influence of temperature on the kinetic formation of these metal precipitates has not been studied. The effect of temperature on reaction rates is well known and important in understanding reaction mechanisms. For most reactions, the increase in rate with increasing temperature is nonlinear and reaction-rate data obeyed the Arrhenius equation:  $k = Ae^{-E_a/RT}$ .

Energies of activation below 42 kJ mol<sup>-1</sup> generally indicate diffusion-controlled processes and higher values represent chemical reaction processes [1]. For example,  $E_a$  values for gibbsite dissolution in various acid solutions ranged from 59 to 67 kJ mol<sup>-1</sup> [2] while pesticide sorption on humic acid had an  $E_a$  value of 6.7 kJ mol<sup>-1</sup> [3].

Additionally, one can determine the enthalpy, entropy, and free energy of formation by applying the Eyring equation  $k = (k_bT/h) e^{-\Delta G^\ddagger/RT} = (k_bT/h) e^{-\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$ .

**Materials and Methods:** Pyrophyllite and talc were employed in this research because they show very little deviation from the chemical formula of an ideal 2:1 clay. The structural difference between talc and pyrophyllite is that talc possesses three Mg<sup>2+</sup> in its octahedral position while pyrophyllite has two Al<sup>3+</sup> in the octahedral position. By using talc, Al<sup>3+</sup> will not be present in solution which is believed to be the driving mechanism behind the formation of mixed metal-Al surface precipitates. In addition, amorphous silica (SiO<sub>2</sub>) (Zeofree<sup>®</sup> 5112), gibbsite (Al(OH)<sub>3</sub>), and a stoichiometric combination of amorphous silica and gibbsite in similar molar ratios to pyrophyllite were employed. Silica (tetrahedral) and gibbsite (octahedral) make up the basic building blocks of phyllosilicate minerals.

For kinetic sorption studies, an initial Ni solution concentration of 3 mM (I = 0.1 M (NaNO<sub>3</sub>), T = 9°, 25°, and 35° C), which was undersaturated with respect to the thermodynamic solubility product of β-Ni(OH)<sub>2</sub> [4], was reacted with a 10 g/L suspension of each of the minerals employing a pH-stat (pH 7.5) batch technique. The systems were purged with N<sub>2</sub> to eliminate CO<sub>2</sub>.

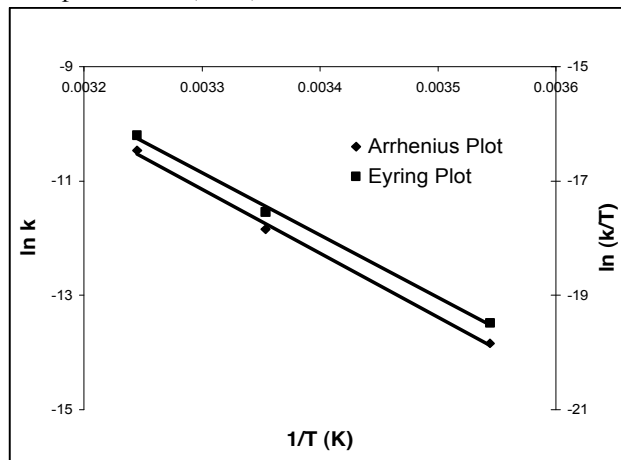
**Results:** First-order kinetic plots of the sorption data yielded rate constants ( $k$ ) used in determining temperature related parameters. Arrhenius and Eyring plots (Figure 1) of the rate constants resulted in good linear fits with  $E_a$  and  $\Delta H^\ddagger$  extrapolated from the slopes of the curves and  $A$  and  $\Delta S^\ddagger$  calculated from the intercepts.

From the free energy relationship,  $\Delta G^\ddagger$  was determined.

These data (Table 1) suggest a surface-controlled or associative mechanism for sorption based on the large  $E_a$  and negative  $\Delta S^\ddagger$  values. Additionally, the large  $E_a$  values are within the range of mineral formation which supports previous findings of nickel precipitation on these mineral and oxide surfaces.

**Conclusions:** Sorption of nickel on the mineral phases results in the formation of mixed Ni-Al precipitates on pyrophyllite, gibbsite, and gibbsite/silica mixture and β-Ni(OH)<sub>2</sub>-like products on talc and silica. By conducting temperature studies, we have shown that nickel sorption on these surfaces is surface controlled as demonstrated by the large  $E_a$  and negative  $\Delta S^\ddagger$  values.

**References:** [1] Sparks D.L. (1985) *Adv. Agron.* 38, 231–266. [2] Bloom P.R. and Erich M. S. (1987) *Soil Sci. Soc. Am. J.*, 51, 1131–1136. [3] Khan S. U. (1973) *Can. J. Soil Sci.*, 53, 429–479. [4] Scheidegger A. M. and Sparks D. L. (1996) *Chem. Geol.*, 132, 157–164.



**Figure 1.** Arrhenius and Eyring plots of first order rate constants of nickel sorption on pyrophyllite at various temperatures.

SURFACE	$E_a$ (kJ/mol)	$A$ (s <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol)	$\Delta G^\ddagger$ (kJ/mol) @ 25°C
Pyrophyllite	93.05	1.59E+11	90.60	-38.70	102.23
Talc	95.35	1.75E+11	92.90	-37.91	104.20
Silica	111.47	6.10E+11	109.02	-27.51	117.22
Gibbsite	123.71	4.05E+11	121.26	-30.90	130.47
Gibbsite/Silica	95.09	4.54E+11	92.64	-29.96	101.57

**Table 1.** Summary of reaction parameters derived from the Arrhenius and Eyring equations for Ni sorption on clay mineral and oxide surfaces.