

MEASURING SURFACE CHEMICAL PROPERTIES OF SOIL USING FLOW CALORIMETRY¹

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Flow calorimetry, which is ideally suited for measuring reactions occurring at the liquid/solid interface, has been used to study the surface chemistry of many types of solids, but little use of it has been made in the study of surface reactions of soils. The purpose of this study was to demonstrate the application of flow calorimetry to the study of two fundamental soil chemical processes, namely cation exchange and phosphate sorption. Surface horizon samples of a Typic Acrorthox and a Typic Tropohumult from Puerto Rico, a strong acid cation exchange resin (Dowex 50W-8), and an amorphous $\text{Al}(\text{OH})_3$ were used. Heats for K/Ca exchange on the Dowex resin and the Oxisol, and K/Na exchange on the Ultisol, were consistent with literature values that were obtained using conventional batch calorimetry or derived from the temperature dependence of the exchange constant. Although peak areas associated with a given pair of exchange reactions were equal, peak shapes were generally not equivalent, indicating differences in the rate at which the two reactions occurred. For example, Ca displacing exchangeable K occurred more rapidly than the reverse reaction on the Dowex resin. The reaction of phosphate with the Ultisol and amorphous $\text{Al}(\text{OH})_3$ was exothermic. Exposure of the soil to several cycles of phosphate was sufficient to saturate the sorption sites, as evidenced by the loss of a detectable heat signal. However, phosphate reactive sites were regenerated by flushing the column with a salt solution at pH 10. Precipitation of Al-phosphate was shown to be endothermic, confirming that precipitation was not the primary mechanism for phosphate sorption in this study. The results of this study show that flow calorimetry can provide valuable information about surface chemical reactions in soils that cannot be obtained readily by other methods. (Soil Science 2002;167:782-790)

Key words: Phosphate sorption, ion-exchange, heat of adsorption.

CALORIMETRY provides a direct, quantitative measure of the heat involved in a reaction. This measured heat is related to a change in enthalpy, a fundamental property of the system that can provide information about the chemical processes taking place.

Flow calorimetry is ideally suited for mea-

suring interactions occurring at the liquid/solid interface. A typical flow calorimeter consists of a column holding 50 to 100 mg of a solid through which a carrier liquid is passed. A chemical or physical interaction between the solid and a component added to the carrier liquid results in a temperature change that can be related quantitatively to the heat of the reaction. Flow calorimetry has the following advantages over conventional batch calorimetry (Steinberg, 1981): i) flow calorimetry can resolve a complex series of reactions that occur more or less simultaneously but at different rates; ii) multiple adsorption/desorption cycles can be applied to the same sample, allowing reversible and irreversible processes to be distinguished; iii) changes that occur

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in the surface properties of the solid as a result of specific treatments or aging effects can be quantified; and iv) when both the amount of adsorption and its associated heat are measured, information about surface heterogeneity can be obtained.

Flow calorimetry has been used to study the surface chemistry of many types of solids (Canham and Groszek, 1992; Steinberg, 1981; Schneider et al., 1997; Groszek and Partyka, 1993; Noll, 1987; Meziani et al., 1997; Taraba, 1990), but little use has been made of it in the study of surface reactions of soils. Questions about some of the basic chemical processes that are involved in soils. While sorption isotherms have traditionally been used to obtain information about the rate and amount of solute sorbed over time, they give no insight into the mechanism by which sorption occurs (Sposito, 1984). Although enthalpies of adsorption on soil have been derived from temperature dependence of the sorption isotherm, in some instances the conclusions have been contradictory. The purpose of this paper is to summarize briefly the literature for two fundamental soil chemical processes, ion exchange and phosphate sorption, and to demonstrate the application of flow calorimetry to the study of these two processes in soils.

METHODS AND MATERIALS

Instrumentation

Several inexpensive flow calorimeters for measuring heats of adsorption from solution onto solids were constructed in our lab. Approximately 50 mg of soil were placed inside a small column (Fig. 1), and solutions containing reactive species were forced through the column using a total pressure drop of about 100 cm of water. Flow rates were controlled with a precision needle valve at

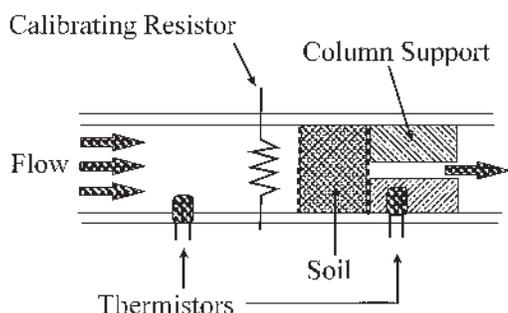


Fig. 1. Schematic of column, thermistors, and calibrating resistor used in the flow calorimeter.

the outlet side of the calorimeter and were generally constant to within a few $\mu\text{L min}^{-1}$ during a day's run. Typical flow rates were in the range of 0.25 to 0.35 mL min^{-1} . Assuming that water saturated soil requires a gravimetric water content of about 0.20, 50 mg of soil would have a pore volume (PV) equal to about 0.01 mL. Thus, typical flow rates for this study corresponded to about 25 to 35 PVs min^{-1} . Run times varied between 20 min and 1 h, depending on the time required for the signal to return to the baseline. Thus, endothermic and exothermic peaks corresponded to between 500 and 2000 PVs.

A pair of thermistors, one upstream and the other downstream from the soil column, formed one half of an electronic bridge and sensed temperature changes in the solution as it passed through the column. A change in solution temperature produced a differential output voltage from the bridge. This differential voltage was fed into an instrumentation amplifier, and the amplified signal was fed into a computer for processing. The system possessed high sensitivity, low thermal drift, and a good signal to noise ratio.

Peak areas were obtained by integrating the signal (volts) numerically over time. This time averaged peak area (V min) was converted to a flow rate averaged peak area (V mL) by multiplying by the average flow rate. This was measured for each peak by collecting the effluent volume and dividing by the time over which the volume was collected. Peak areas were converted to energy units (Joules) by comparison with peaks generated with a calibrating resistor located within the flow stream and immediately upstream from the column (Fig. 1). Voltage and current for the heat pulses were measured, and the heat input was then calculated from the relation $Q \text{ (Joules)} = V A t$, where V is voltage, A is amperage, and t is time, in seconds, that the resistor was energized.

The column assembly with thermistors and calibrating resistor was sealed inside a 500 mL polyethylene bottle, and the bottle was placed in a 50 L insulated container, filled with water, at room temperature. The water bath provided good thermal stability against ambient temperature changes and generally resulted in baselines with negligible drift.

Soils

The 0 to 15 cm depths of an Oxisol and an Ultisol from Puerto Rico were air dried and sieved to an aggregate size between 0.25 and 0.50 mm before being used in this study. The Oxisol

TABLE 1
Mineralogical and chemical properties of the two Puerto Rican soils

Soil	Organic matter		CEC cmol _c kg ⁻¹	Total Fe + Al g kg ⁻¹	Clay mineralogy ¹	Texture ² g kg ⁻¹	Surface area (m ² g ⁻¹)
	g kg ⁻¹	pH					
Oxisol	40.5	4.9	3.1	287	k>go>gi=q	100 340 560	41.9
Ultisol	18.6	4.7	11.0	86	k>q>s>go>m	120 290 590	37.8

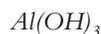
¹k - kaolinite, gi - gibbsite, go - goethite, q - quartz, s - smectite, m - mica

²Sand-Silt-Clay

(clayey, oxidic, isohyperthermic Typic Acrorothox) was found near Mayaguez, and the Ultisol (clayey, mixed, isohyperthermic Typic Tropohumult) was taken from the central mountainous area near Corozal. Mineralogical and chemical properties of these soils were obtained using standard methods and are presented in Table 1 (Appel and Ma, 2002).

Cation Exchange Resin

A 50 to 100 mesh Dowex 50W 8 strong acid cation exchange resin was also used. It was initially in the H⁺ form and had an exchange capacity of 5.0 mmol_c g⁻¹ dry weight.



This material was obtained by titrating a solution of AlCl₃ with NaOH to pH 6 and allowing the suspension to stand overnight. The solid was separated from the solution phase by centrifugation and dried in an oven overnight at 70 °C. X ray diffraction of the dried residue showed it to be noncrystalline.

RESULTS AND DISCUSSION

Sensitivity and Precision of Heat Measurements

A typical peak to peak noise level for the flow calorimeters used in this study was 5 mV or less. The thermistors had a nominal resistance of 10 kΩ at 25 °C and a temperature coefficient of resistance of about -400Ω °C⁻¹. Assuming an acceptable signal to noise ratio for peak detection to be about 5, and using the measured gain for the instrumentation amplifier, the calculated sensitivity for the flow calorimeter corresponded to a temperature change of about 10⁻⁴ °C. This is higher than that for a true microcalorimeter, which can detect a temperature change on the order of about 10⁻⁵ °C (Steinberg, 1981).

Figure 2 shows peak areas that were generated by 30 mJ heat pulses and plotted as a function of flow rate. Peak areas obviously depended on flow rate. This dependence was taken into account when comparing heat data obtained at dif-

ferent flow rates by applying a correction factor that was based on the linear relationship in Fig. 2.

Heat pulses for calibrating the instrument generally ranged from about 5 mJ to more than 100 mJ in size, corresponding to times of 2 to 45 s for energizing the calibrating resistor. Calibrating resistors were 22 kΩ and were energized at about 7.5 V. Figure 3 shows a series of heat pulses and the associated calibration curve, the latter corrected for differences in flow rate. Linear regression of heat pulse peak areas versus energy input consistently gave $R^2 > 0.99$.

Precision for replicated heat pulses generally resulted in coefficients of variation that were less than 5%. Precision for exothermic and endothermic peaks obtained on a single soil column were of a magnitude similar to that for heat pulses. Pre-

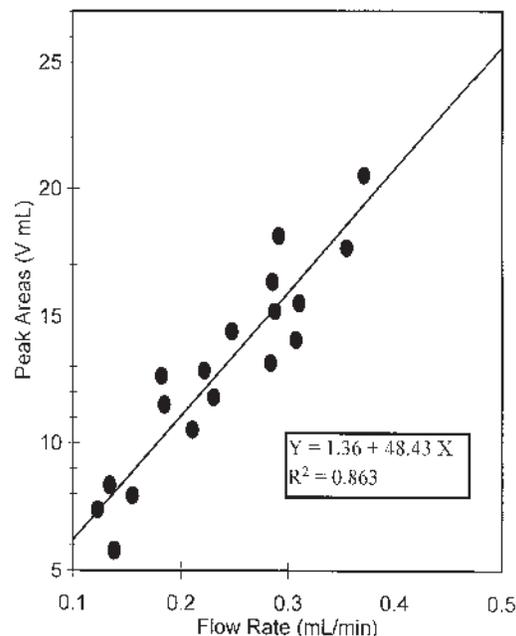


Fig. 2. Relationship between peak area and solution flow rate.

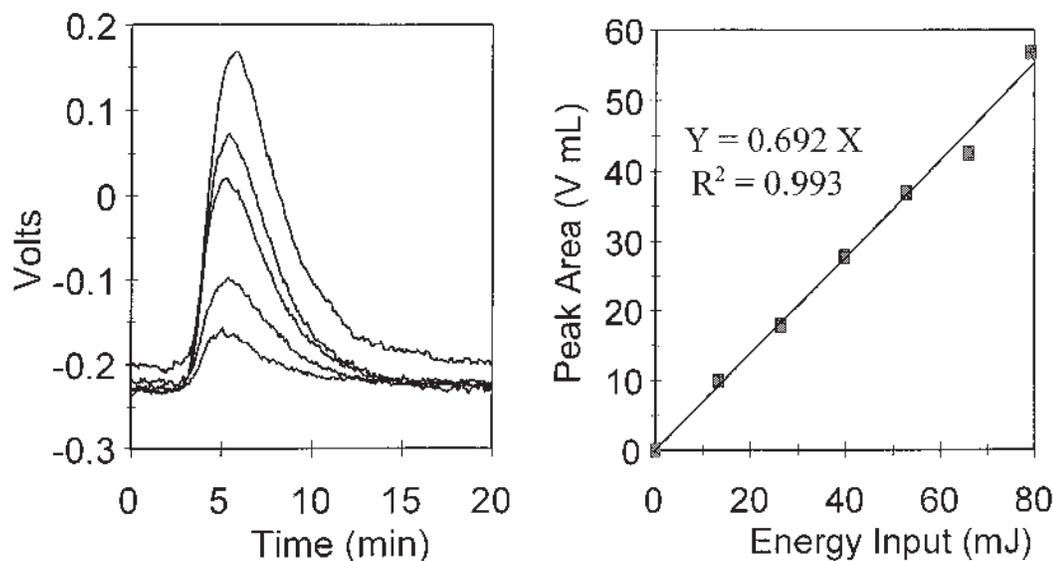


Fig. 3. Peaks obtained with various size heat pulses and the associated calibration curve.

cision obtained with replicated samples over periods of several months using different flow calorimeters and obtained with different operators was generally less than 15%. Because of their small size, reproducibility from sample to sample will depend strongly on sample homogeneity. In the case of the two Puerto Rican soils, use of 0.25 to 0.50 mm aggregates apparently resulted in a reasonably homogeneous material.

Ion Exchange

Using a crude calorimeter fitted with thermometers, Coleman (1952) observed heats of exchange for alkali and alkaline earth cations on exchange resins that were typically in the range of 4 to 13 kJ mol_c^{-1} . Gaines and Thomas (1953) described a method for deriving thermodynamic exchange constants from selectivity coefficients. Using the temperature dependence of the exchange constant, the standard enthalpy of exchange, ΔH° , can be calculated using the relation, $(\frac{d \ln K}{dT}) = \frac{\Delta H^\circ}{RT^2}$. In several instances, enthalpies derived using this relation have compared well with calorimetric values, although the standard enthalpy change, ΔH° , is not measured directly by calorimetry. Laudelout et al. (1968) corrected their calorimetric values to standard state conditions and found that they agreed well with values derived from the temperature dependence of $\ln K$. In the case of NH_4/Ca exchange on Camp Berteau montmo-

illonite, the corrected calorimetric value was 10.5 kJ mol_c^{-1} , and the one derived from temperature dependence was 11.3 kJ mol_c^{-1} . Heats of exchange on soils and clay minerals generally follow the lyotropic series: $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$; $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ (Gast, 1972; Gast et al., 1969; Laudelout et al., 1968). Because the forces of attraction are predominantly electrostatic, the preference of the clay for cations of the same charge increases as their hydrated radii decrease. As a result of its carboxylate content, soil organic matter can exhibit properties of a strong field exchanger, reversing the selectivity for some cations as given by the lyotropic series (Juo and Barber, 1969).

Figure 4 shows the results for K/Ca exchange that we obtained on Dowex resin using flow calorimetry. The resin was initially K saturated using 50 mM KCl. When the solution was changed to 25 mM CaCl_2 , an endotherm corresponding to the displacement of exchangeable K by Ca was observed. When the solution was switched back to KCl, an exotherm corresponding to the displacement of exchangeable Ca was observed. The two peaks in Fig. 4 are equal in area, as expected for a reversible ion exchange reaction. The quantity of heat associated with the peaks was 26 mJ mg^{-1} , which is equivalent to 10.4 kJ mol_c^{-1} for K/Ca exchange on this Dowex material. Coleman (1952) reported values of 10.5 and 11.3 kJ mol_c^{-1} for K/Ca exchange on Amberlite cation

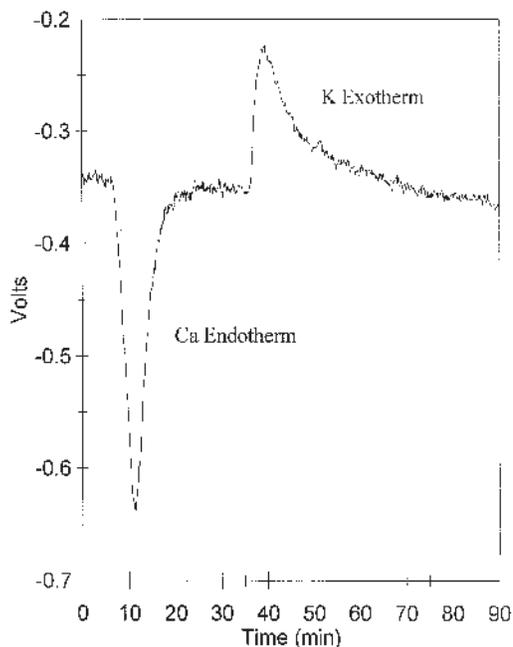


Fig. 4. Heats of K/Ca exchange obtained using 6.2 mg of Dowex 50W-8 exchange resin.

exchange resins IR120 and IR100, respectively. He also found that Ca replacing exchangeable K was endothermic.

Figure 5 shows K/Ca exchange on a sample of the Oxisol. The two peak areas each measured 0.47 mJ mg^{-1} of soil, which corresponds to a heat of exchange of $7.8 \text{ kJ mol}_c^{-1}$. Figure 6 shows K/Na exchange on the Ultisol. These two peaks measured 0.82 mJ mg^{-1} , which corresponds to $7.5 \text{ kJ mol}_c^{-1}$. These heats of exchange are similar to values reported for soils and clays that were obtained using conventional batch calorimeters or derived from temperature dependence of the exchange constant. For example, Gast (1972) reported calorimetric heats of exchange for alkali metal cations on Chambers montmorillonite ranging from a high of $10.4 \text{ kJ mol}_c^{-1}$ for Li/Cs exchange, to a low of $0.4 \text{ kJ mol}_c^{-1}$ for Li/Na exchange. Deist and Talibudeen (1967) reported standard state enthalpies for K/Ca exchange on five soils in which the clay fraction was dominated by 2:1 layer silicates. Their ΔH° values ranged from 3.8 to 35 kJ mol_c^{-1} . Udo (1978) derived the standard state enthalpy for K/Ca exchange on a kaolinitic soil clay and reported the value of 54 kJ mol_c^{-1} . Sparks and Jardine (1981) used a kinetic approach to derive K/Ca exchange constants at several

temperatures for a soil whose clay fraction was dominated by vermiculite, chloritized vermiculite, and mica. The temperature dependence of these exchange constants yielded standard enthalpies of exchange of 7.1 and $5.6 \text{ kJ mol}_c^{-1}$ for samples from the A and B horizons, respectively. Thus results obtained from flow calorimetry for ion exchange are consistent with those obtained using other methods.

Although the peak areas in Fig. 4 are equal, the peak shapes are different, indicating that the rates of exchange were not the same for the two displacement reactions. The lower peak maximum and the greater tailing for the K exotherm compared with the Ca endotherm in Fig. 4 indicate that K displaced exchangeable Ca at a slower rate than the reverse reaction. In contrast, K/Ca exchange on the Oxisol (Fig. 5) showed no evidence that the rates of exchange for these two cations were different. Exchange of K/Na on the Ultisol (Fig. 6) exhibited considerable disparity in peak shapes, indicating that Na had difficulty replacing exchangeable K. Sparks and Jardine (1981) observed a slower rate of K desorption from soil than that for K adsorption (K/Ca exchange) and attributed this to greater activation energy for desorption. Their soil contained ver

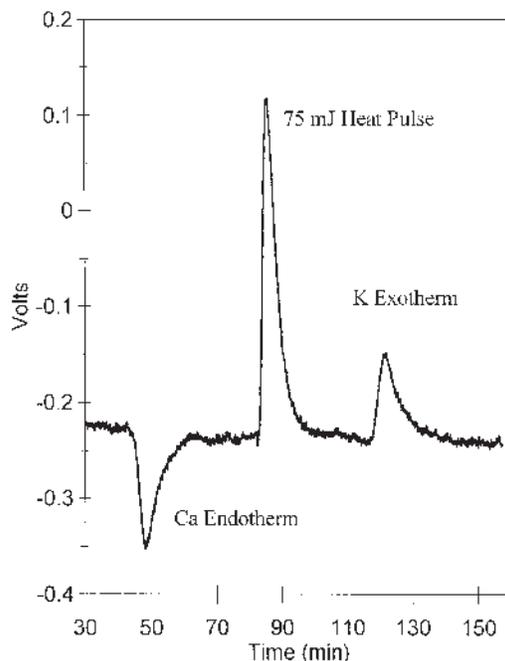


Fig. 5. Heats of K/Ca exchange obtained using 68.4 mg of Oxisol.

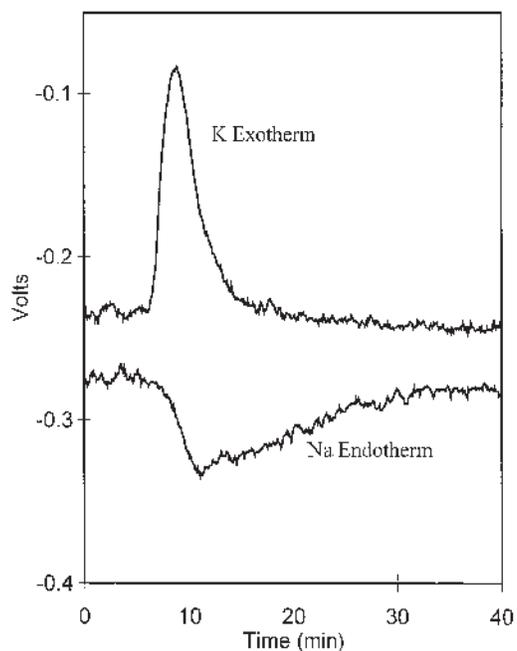


Fig. 6. Heats of K/Na exchange obtained using 57.2 mg of Ultisol.

miculite, and the rate limitation was ascribed to partial collapse of the 2:1 layer silicate following K saturation. Calorimetric studies of K/Na exchange on a high charge smectite in our lab showed peaks of considerably different shape as a result of kinetics. The peaks were also unequal in area because of some irreversibility in the ion exchange process (data not shown). The calorimetric data suggested that Na was unable to displace exchangeable K completely, presumably because of its inability to expand the lattice spacing following K saturation. This conclusion was confirmed by X ray diffraction analysis (data not shown), which showed that the K saturated smectite did not fully expand on subsequent treatment with NaCl.

Phosphate Sorption

Phosphate sorption by soils typically exhibits an initial, rapid uptake phase, thought to be a ligand exchange reaction, followed by a much slower rate of uptake that may continue for weeks or months. This slow uptake is thought to be the result of one or more of the following processes: i) diffusion to less accessible sites within pores of solid aggregates (Willet et al., 1988; Cabrera et al., 1981; Parfitt, 1989; Madrid and de Arambarri, 1985; Lookman et al., 1994); ii) penetration into

the amorphous Fe and/or Al oxides by solid state diffusion (van Riemsdijk and de Haan, 1981; van Riemsdijk et al., 1984; Barrow, 1983); and iii) precipitation with metals derived by dissolution of the soil matrix (Aulenbach and Meisheng, 1988; Lookman et al., 1994; Martin et al., 1988; Nanzyo, 1984, 1986; Pierzynski et al., 1990).

Malati et al. (1993) reported that phosphate sorption on kaolinite, mica, and anatase at $\text{pH} < 5$ was endothermic and generally in the range of $+10$ to $+15 \text{ kJ mol}^{-1}$. However, at $\text{pH} 7$, phosphate sorption by kaolinite was exothermic and similar in energy to hydrogen bonding. The endothermic heats were derived from the energy terms in the Langmuir equations used to describe their sorption isotherms. Hundal (1988) reported that phosphate sorption by a clay loam soil was endothermic based on results obtained by applying the Clapeyron equation to liquid/solid phase equilibrium. The isosteric heat of adsorption varied with surface coverage, ranging from about 9.2 kJ mol^{-1} to about 18 kJ mol^{-1} . Muljadi et al. (1966a) found that an increase in temperature increased phosphate sorption by kaolinite, gibbsite, and pseudoboehmite but that this increase was largely the result of an irreversible increase in the number of sorption sites. The heat of reaction between 200 mL of $0.1 \text{ M KH}_2\text{PO}_4$ and 20 g of K saturated kaolinite was less than the sensitivity of their calorimeter, $0.2 \text{ kcal mol}^{-1}$, leading them to conclude that the driving force for phosphate sorption by these materials was essentially entropic. Contrary to the above, Barrow (1983) and Froelich (1988) presented data that indicated that phosphate sorption was exothermic since an increase in temperature decreased phosphate sorption. Halter and Pfeifer (2001) reported that sorption of arsenate, an oxyanion chemically similar to phosphate, by $\alpha \text{ Al}_2\text{O}_3$ also decreased with increasing temperature.

Figure 7 shows calorimetric results obtained for a sample of the Ultisol that was initially equilibrated with a solution of 50 mM NaCl . Curve 1 resulted when this solution was changed to one in which 3 mmol L^{-1} of the NaCl had been replaced with NaH_2PO_4 (i.e., keeping the total Na concentration at 50 mM). The reaction of phosphate with the soil was exothermic, 0.42 mJ mg^{-1} . Returning to the original NaCl solution after the NaH_2PO_4 treatment produced no heat signal (data not shown), indicating that the peak observed with NaH_2PO_4 was not caused by reversible $\text{Cl}/\text{H}_2\text{PO}_4$ exchange. Curve 2 in Fig. 7 was obtained during the second cycle of NaH_2PO_4 treatment and yielded 0.21 mJ mg^{-1} .

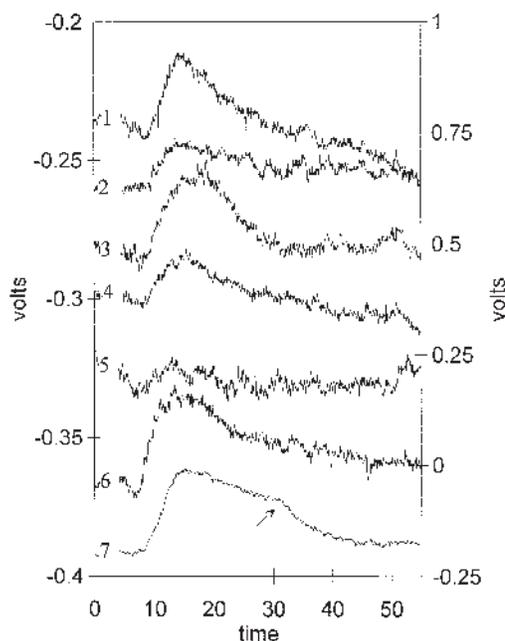


Fig. 7. Heats of reaction of phosphate on Ultisol (Curves 1 through 6) and amorphous $\text{Al}(\text{OH})_3$ (Curve 7). Curves 1 through 6 are read on the left-hand scale; Curve 7 on the right-hand scale. The arrow on Curve 7 indicates a change from phosphate solution back to NaCl.

The $\text{NaCl}/\text{NaH}_2\text{PO}_4$ solution had been adjusted to the same pH (5.8) as the NaCl. Reversibility of phosphate sorption with pH has been observed (Muljadi et al., 1966b). To determine whether the phosphate reactive sites on the Ultisol could be regenerated, the soil was treated with 50 mM NaCl to which sufficient Na_2CO_3 had been added to obtain a pH of 10. The reaction of the pH 10 solution with soil was endothermic (data not shown). Changing the solution back to NaCl, pH 5.8, produced no detectable heat signal. When the soil was then exposed to phosphate, an exotherm larger than that obtained in the first phosphate cycle was observed, 0.64 mJ mg^{-1} (Curve 3). Curve 4 shows the heat of reaction obtained in the fourth phosphate treatment cycle, which measured 0.21 mJ mg^{-1} . By the fifth cycle (Curve 5), the phosphate reaction was essentially undetectable, indicating that phosphate had reacted with all of the available sorption sites. The soil was then given a second pH 10 treatment followed by NaCl pH 5.8, and this was followed by the sixth phosphate treatment cycle. The heat generated during the sixth phosphate cycle was identical to that fol-

lowing the first pH 10 treatment, 0.64 mJ mg^{-1} (Curve 6), suggesting that the second pH 10 treatment had regenerated the same number of phosphate reactive sites as the first pH 10 treatment. The reaction of phosphate with amorphous $\text{Al}(\text{OH})_3$ (Curve 7) was also exothermic, suggesting that amorphous $\text{Al}(\text{OH})_3$ could have been responsible, at least in part, for the exothermic phosphate reaction in the Ultisol.

The reaction between phosphate and $\text{Al}(\text{OH})_3$ can be described as $\text{Al}(\text{OH})_{3(\text{crystalline})} + \text{PO}_4^{-3} = \text{AlPO}_{4(\text{crystalline})} + 3\text{OH}^-$ and, under standard state conditions, is endothermic, $+129 \text{ kJ mol}^{-1}$ (Wagman et al., 1982). The direct precipitation of Al^{+3} with phosphate is also endothermic under standard state conditions, $+75 \text{ kJ mol}^{-1}$ (Wagman et al., 1982). To verify that precipitation of Al phosphate was endothermic under our column conditions, the heat of reaction was measured when exchangeable Al was displaced from the Dowex resin, first by 50 mM KCl (exchange only) and then by 50 mM KH_2PO_4 (exchange plus precipitation). Curve 1 in Fig. 8 shows the exotherm that resulted when KCl displaced exchangeable Al from the Dowex resin. Curve 2 was obtained when the same

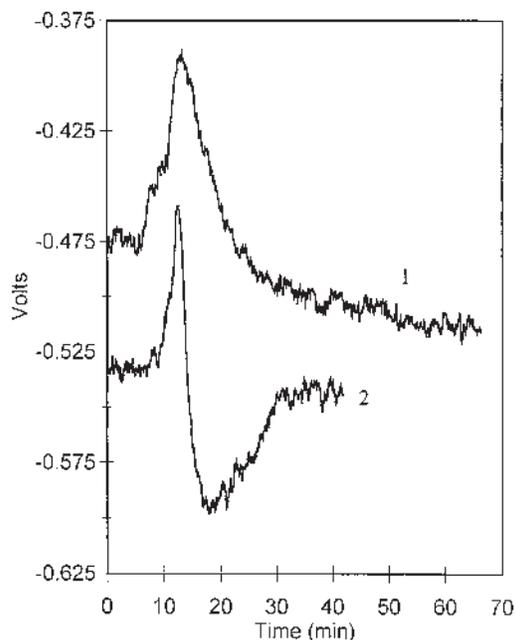


Fig. 8. Heat obtained by displacing exchangeable Al on 5.2 mg Dowex 50W-8 resin with KCl (Curve 1) and that obtained by displacing the Al with KH_2PO_4 (Curve 2).

Dowex column was resaturated with Al (by flushing with 10 mM AlCl_3 , pH 4) and the exchangeable Al displaced using KH_2PO_4 . The reaction was initially exothermic, consistent with K/Al exchange. However, the reaction shifted to endothermic, consistent with a secondary Al phosphate precipitation. The delayed start of the endothermic reaction would be expected since the Al concentration in solution must increase sufficiently after the onset of K/Al exchange to induce Al phosphate precipitation. However, once precipitation began, it proceeded rapidly and continued until all of the Al had been exchanged from the resin. The fact that precipitation of Al phosphate was endothermic whereas the reaction of phosphate with soil and $\text{Al}(\text{OH})_3$ was exothermic shows that precipitation was not the primary mechanism for phosphate sorption in this study.

An alternative to a precipitation mechanism is ligand exchange. If the exothermic reaction of phosphate with soil is the result of ligand exchange only, then ligand exchange is a slower reaction than ion exchange. For example, K displacement of exchangeable Ca and Na was complete in both soils in less than 20 min (Figs. 5 and 6). Phosphate sorption on the Ultisol took three 30 to 40 min cycles for a total of more than 100 min (Fig. 7). In the case of $\text{Al}(\text{OH})_3$, the reaction was still going strong after 20 min and would have required considerably longer exposure to saturate the sorption capacity (Fig. 7). It is possible that phosphate sorption begins as a fairly rapid ligand exchange reaction but is followed by a slower secondary reaction. This secondary reaction could be a diffusion limited process involving sites of limited accessibility on the surface or penetration into the interior of amorphous oxides/hydroxides. Either explanation could explain the slow evolution of heat accompanying phosphate sorption. A definitive explanation for the exothermic phosphate reaction will require additional information such as the amount of phosphate sorbed, pH and compositional changes in the effluent during sorption, and chemical and physical analysis of the solid phase after reacting with phosphate.

SUMMARY AND CONCLUSIONS

A simple, inexpensive flow calorimeter has been used to measure heats of reaction in soil. It uses a pair of thermistors to monitor changes in temperature of a solution as it flows through a column containing 50 to 100 mg of soil. A change in solution temperature generates a signal

that is amplified and fed into a computer for processing. The calorimeter exhibits high sensitivity, low thermal drift, and good signal to noise ratio.

The flow calorimeter was used to study two important soil chemical processes, cation exchange and phosphate sorption. Heats for K/Ca exchange measured by flow calorimetry were consistent with values that have been reported for other soils, clays, and cation exchange resins. In addition to heats of exchange, flow calorimetry provided insight into the kinetics of the exchange process. K displacing exchangeable Ca occurred more slowly than the reverse reaction on Dowex resin, whereas the rates were similar for K/Ca exchange on the Oxisol. Na experienced considerable difficulty in replacing exchangeable K from the Ultisol, which contained some expandable 2:1 layer silicate clay.

The reaction of phosphate with Ultisol and amorphous $\text{Al}(\text{OH})_3$ was exothermic. In the Ultisol, the phosphate exotherm decreased in magnitude with consecutive phosphate cycles and was essentially gone after three cycles. However, reactive sites were regenerated by treating the soil with a solution at pH 10, showing that the phosphate reaction was reversible with pH. The precipitation of Al phosphate was endothermic, showing that precipitation was not the primary mechanism for phosphate sorption in this study. The results of this investigation show that flow calorimetry can provide useful information about surface chemical reactions in soils that cannot readily be obtained by other methods. Used in conjunction with other techniques, it should help improve our understanding of many important soil chemical processes.

REFERENCES

- Appel, C., and L. Ma. 2002. Concentration, pH, and surface charge effects on Cd and Pb sorption in three tropical soils. *J. Environ. Qual.* 31:581-589.
- Aulenbach, D. B., and N. Meisheng. 1988. Studies on the mechanism of phosphorus removal from treated wastewater by sand. *J. Water Pollut. Control Fed.* 60:2089-2094.
- Barrow, N. J. 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. *J. Soil Sci.* 34:733-750.
- Cabrera, F., P. de Arambarri, L. Madrid, and G. G. Toca. 1981. Desorption of phosphorus from iron oxide in relation to pH and porosity. *Geoderma* 26:203-216.
- Canham, L. T., and A. J. Groszek. 1992. Characterization of microporous Si by flow calorimetry: Comparison with a hydrophobic SiO_2 molecular sieve. *J. Appl. Phys.* 72:1558-1565.

- Coleman, N. T. 1952. A thermochemical approach to the study of ion exchange. *Soil Sci.* 74:115-125.
- Deist, J., and O. Talibudeen. 1967. Thermodynamics of K-Ca exchange in soils. *J. Soil Sci.* 18:138-148.
- Froelich, P. N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnol. Oceanogr.* 33:649-668.
- Gaines, Jr., G. L., and H. C. Thomas. 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21:714-718.
- Gast, R. G., R. van Bladel, and K. B. Deshpande. 1969. Standard heats and entropies of exchange for alkali metal cations on Wyoming bentonite. *Soil Sci. Soc. Am. Proc.* 33:661-664.
- Gast, R. G. 1972. Alkali metal cation exchange on Chambers montmorillonite. *Soil Sci. Soc. Am. Proc.* 36:14-19.
- Groszek, A. J., and S. Partyka. 1993. Measurements of hydrophobic and hydrophilic surface sites by flow microcalorimetry. *Langmuir* 9:2721-2725.
- Halter, W. E., and H. R. Pfeifer. 2001. Arsenic(V) adsorption onto α - Al_2O_3 between 25 and 70 °C. *Appl. Geochem.* 16:793-802.
- Hundal, H. S. 1988. A mechanism of phosphate adsorption on Narrabri medium clay loam soil. *J. Agric. Sci.* 111:155-159.
- Juo, A. S. R., and S. A. Barber. 1969. An explanation for the variability in Sr-Ca exchange selectivity of soils, clays, and humic acid. *Soil Sci. Soc. Am. Proc.* 33:360-363.
- Laudelout, H., R. van Bladel, G. H. Bolt, and A. L. Page. 1968. Thermodynamics of heterovalent cation exchange reactions in a montmorillonite clay. *Faraday Soc. Trans.* 64:1477-1488.
- Lookman, R., P. Grobet, R. Merckx, and K. Vlassak. 1994. Phosphate sorption by synthetic amorphous aluminum hydroxides: A ^{27}Al and ^{31}P solid state MAS NMR spectroscopy study. *Eur. J. Soil Sci.* 45:37-44.
- Madrid, L., and P. de Arambarri. 1985. Adsorption of phosphate by two iron oxides in relation to their porosity. *J. Soil Sci.* 36:523-530.
- Malati, A. M., R. A. Fassam, and I. R. Henderson. 1993. Mechanism of phosphate interaction with two reference clays and an anatase pigment. *J. Chem. Technol. Biotechnol.* 58:387-389.
- Martin, R. R., R. St. C. Smart, and K. Tazaki. 1988. Direct observation of phosphate precipitation in the goethite/phosphate system. *Soil Sci. Soc. Am. J.* 52:1492-1500.
- Meziani, M. J., J. Zajac, D. J. Jones, J. Roziere, and S. Partyka. 1997. Surface characterization of mesoporous silicaluminates of the MCM 41 type: Evaluation of polar surface sites using flow calorimetry, adsorption of a cationic surfactant as a function of pore size and aluminum content. *Langmuir* 13:5409-5417.
- Muljadi, D., A. M. Posner, and J. P. Quirk. 1966a. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part III: The effect of temperature on adsorption. *J. Soil Sci.* 17:238-247.
- Muljadi, D., A. M. Posner, and J. P. Quirk. 1966b. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part I: The isotherms and the effect of pH on adsorption. *J. Soil Sci.* 17:212-227.
- Nanzyo, M. 1984. Diffuse reflectance infrared spectra of phosphate sorbed on alumina gel. *J. Soil Sci.* 35:63-69.
- Nanzyo, M. 1986. Infrared spectra of phosphate sorbed on iron hydroxide gel and the sorption products. *Soil Sci. Plant Nutr.* 32:51-58.
- Noll, L. A. 1987. Adsorption calorimetry of surfactant interactions with minerals. *Colloids Surf.* 26:43-54.
- Parfitt, R. L. 1989. Phosphate reactions with natural allophane, ferrihydrite, and goethite. *J. Soil Sci.* 40:359-369.
- Pierzynski, G. M., T. J. Logan, S. J. Traina, and J. M. Bingham. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: a) Quantitative analysis of phosphorus rich particles, b) Descriptions of phosphorus rich particles, and c) Solubility equilibria. *Soil Sci. Soc. Am. J.* 54:1576-1595.
- Schneider, S., F. Simon, D. Pleul, and H. J. Jacobasch. 1997. Flow sorption calorimetry, a powerful tool to investigate the acid base character of organic polymer surfaces. *Fresenius' J. Anal. Chem.* 358:244-247.
- Sparks, D. L., and P. M. Jardine. 1981. Thermodynamics of potassium exchange in soil using a kinetics approach. *Soil Sci. Soc. Am. J.* 45:1094-1099.
- Sposito, G. 1984. *The Surface Chemistry of Soils.* Clarendon Press, New York.
- Steinberg, G. 1981. What you can do with surface calorimetry. *Chemtech* 11:730-737.
- Taraba, B. 1990. Reversible and irreversible interaction of oxygen with coal using pulse flow calorimetry. *Fuel* 69:1191-1199.
- Udo, E. J. 1978. Thermodynamics of potassium calcium and magnesium calcium exchange reactions on a kaolinitic soil clay. *Soil Sci. Soc. Am. J.* 42:556-560.
- van Riemsdijk, W. H., and F. A. M. de Haan. 1981. Reaction of orthophosphate with a sandy soil at constant supersaturation. *Soil Sci. Soc. Am. J.* 45:261-266.
- van Riemsdijk, W. H., L. J. M. Boumans, and F. A. M. de Haan. 1984. Phosphate sorption by soils: I. A model for phosphate reaction with metal oxides in soil. *Soil Sci. Soc. Am. J.* 48:537-541.
- Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall. 1982. *The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units.* *J. Phys. Chem. Ref. Data*, vol. 11, suppl. 2. American Chemical Society and the American Institute of Physics for the National Bureau of Standards, Washington, DC.
- Willet, I. R., C. J. Chartres, and T. T. Nguyen. 1988. Migration of phosphate into aggregated particles of ferrihydrite. *J. Soil Sci.* 39:275-282.