Measurement of clay surface areas by polyvinylpyrrolidone (PVP) sorption: A new method for quantifying illite and smectite abundance

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Abstract

A new method has been developed for quantifying smectite abundance in bulk samples by sorbing polyvinylpyrrolidone (PVP) on smectite particles dispersed in aqueous solution. Sorption density of PVP-55K on a wide range of smectites, illites and kaolinites is ~0.99 mg/m^2, which corresponds to ~0.72 g of PVP-55K per gram of montmorillonite. PVP sorption on smectites is independent of layer charge and solution pH. PVP sorption on SiO_2, Fe_2O_3 and ZnO normalized to the BET surface area are similar to the sorption densities on smectites. □-Al_2O_3, amorphous $Al(OH)_3$ and gibbsite exhibit no PVP sorption over a wide range of pH, and sorption of PVP by organics is minimal. The insensitivity of PVP sorption densities to mineral layer charge, solution pH and mineral surface charge indicates that PVP sorption is not localized at charged sites, but is controlled by more broadly distributed sorbtion mechanisms such as Van der Waal's interactions and/or hydrogen bonding. Smectites have very large surface areas when dispersed as single unit cell thick particles (~725 m^2/g) and usually dominate the total surface areas of natural samples in which smectites are present. In this case, smectite abundance is directly proportional to PVP sorption. For some samples, however, the accurate quantification of smectite abundance by PVP sorption may require minor corrections for PVP uptake by other

phases, principally illite and kaolinite. Quantitative XRD can be combined with PVP uptake measurements to uniquely determine the smectite concentration in such samples.

Introduction

Smectitic minerals may have a dramatic, sometimes dominate effect on the physical and chemical properties of soils and sediments because of their high surface areas, high cation exchange capacities and swelling properties. However, the quantification of smectite minerals in sediments has remained problematic (Srodon et al., 2001). The first fundamental question in such studies is “What is a smectite?”. This question has been a popular philosophical topic among clay mineralogists. A traditional mineralogic definition, based on chemistry and structure, is difficult to apply both because smectite has a wide range of possible compositions and a variable structure that depends on hydration state, and because of the practical difficulty of isolating a single pure clay phase from a mixture for accurate chemical analysis. In fact, compositional variability between and within individual smectite particles may mean that smectitic minerals actually defy the strict definition of a phase (May et al., 1986). Before the work of Nadeau (1984, 1985) and those who followed, a practical working definition of smectites was any 2:1 clay mineral that swells to 17 Å when exposed to ethylene glycol vapor. However, this functional definition has become increasingly problematic as additional work has shown that illite-smectite mixed layer clays can be dispersed into fundamental particles. When in a dispersed state, the illite particles display only a 10 Å XRD peak (Eberl et al., 1998). However, when dried, the interfaces between the reassembled illite particles can be X-ray coherent, and yield layers that expand to 17 Å in ethylene glycol. Thus, a sample of “pure illite” particles can produce the characteristic smectite swelling with glycolation, even though strictly speaking, no smectite is present. We suggest that a more accurate working definition of a “smectite” is a 2:1 clay which, when Na saturated, can be dispersed into single unit-cell-thick particles in aqueous solution. This is the definition of a “smectite” used in this work. As will be shown, the ability to separate the unit cell layers of a clay largely correlates with chemistries found within the more traditional definition of “smectite” group minerals. Where as the dispersion criteria is a useful and a practical definition of smectite, it should be noted that the ability to disperse smectite fundamental particles in the laboratory does not necessarily imply anything about the smectite to illite reaction mechanism or the presence or absence of larger authigenic smectite/illite aggregates in sedimentary rocks.

Na-saturated smectite particles can be dispersed as single unit cell thick (~1 nm) particles in solution. It is the surface area of these particles which will be easily accessible to solution, and which will control the physical and chemical properties of smectites in saturated environments. However, we found X-ray diffraction (XRD) an inappropriate method for quantifying the amount of these smectite particles. Completely dispersed smectite particles have no (00ℓ) XRD peak, because the single unit cells do not have a repeat distance in the *c* direction (Eberl et al., 1998). The a-b plane of smectites generate XRD peaks [particularly the 060 reflection], but these peaks closely overlap with illites and micas, which are nearly ubiquitous in natural samples. When smectites and illites are dried, the particles are easily deformed by strong surface interactions to form highly oriented and coherent aggregates of illite/smectite crystals (Blum, 1994) which generate the commonly observed (00ℓ) diffraction peaks by interparticle diffraction (Nadeau, et al., 1984). However, in complex mixtures containing minerals in addition to smectite, both the “stacking” efficiency and the crystal orientation relative to the X-ray beam become highly variable with the shape and composition of the other mineral particles (fig. 1), making quantification of smectites using the (00ℓ) XRD peaks inaccurate.

During sorption of inert gases in a dry environment, (i.e. using N_2, Kr or various organic vapors by the Brunnuer, Emmet and Teller (BET) method) the gas does not access the “internal” surface between coherently stacked crystals, and therefore, grossly underestimates the smectite surface area that is exposed to solution (Alymore and Quirk, 1967). Smectites also may be quantified by measurement of the cation exchange capacity (CEC). However, the CEC of smectites can vary by a factor of two, leading to a similar error in using cation exchange capacity to quantify smectite abundance. In addition, other minerals and organic matter may also contribute to the CEC in an unquantifiable manner.

The sorption of ethylene glycol monoethyl ether (EGME) has been suggested as a technique to quantify smectite abundance (Cihacek and Bremer, 1975; Chiou and Rutherford, 1997; Quirk and Murry, 1999; Kennedy et al., 2002). However, recent work (Chiou and Rutherford, 1997; Rutherford et al., 1997) has shown that sorption of EGME is highly dependent on the EGME partial pressure, exchangeable cation and layer charge, as well as on void sizes and organic carbon content. We argue that the determination of smectite abundance by the sorption of polyvinylpyrrolidone (PVP) avoids many the problems discussed above.

Polyvinylpyrrolidone (PVP, CA#9003-39-8) is a widely used industrial surfactant, emulsifier and adhesive, with applications including hair spray, textile dye stripping, extender for blood plasma, ink-jet printing, tablet binder in pharmaceuticals, and the adhesive at both ends of toilet paper rolls. PVP polymers are synthesized from the monomer shown in fig. 2. PVP is available in a variety of chain lengths with molecular weights (MW) ranging from 10K to 1200K, which corresponds to chains of about 90 to 11,000 monomers.

PVP has been widely investigated as a surfactant. Frances (1973) and Levy and Frances (1975a) first studied the sorption behavior of PVP on montmorillonites, and Levy and Frances (1975b) proposed using an XRD technique utilizing intercalated PVP to quantify the amount of montmorillonite in a sample in the presence of other swelling clays, such as vermiculite. The nature of PVP binding to montmorillonite surfaces has also been studied by Gultek et al. (2001), Sequaris et al. (2000), and Sequaris et al. (2002). There have been studies of PVP sorption on silica by Cohen, et al. (1984), Esumi and Oyama (1993), Gun'ko et al. (2002), and Thibaut et al. (2000), on alumina by Otsuka and Esumi (1994), Esumi et al. (1994) and Esumi et al. (2000), on kaolinite by Israel et al. (2001), and on zirconium by Rovira-Bru et al. (2001). There have also been more general studies of the binding configuration and structure of PVP both on surfaces and in solution [Barnett et al. (1981); Gargallo et al. (1993); Misselyn-Bauduin et al. (2001); Smith et al. (1996); and Sun and King, (1996)]. Most of these studies were broadly aimed at understanding how PVP sorption can be used to modify colloid particle surfaces for better dispersion during industrial applications. Recently PVP 10K has been used to intercalate illite fundamental particles for XRD analysis (Eberl et al., 1996,1998; Uhlik et al., 2000). When the PVP/clay suspension is evaporated, the PVP widely separates the illite particles, eliminating interparticle diffraction, and allowing the quantification of illite particle thicknesses from the broadening of the (001) peak.

Methods

Bulk samples may be analyzed, and it is not necessary to isolate the clay fraction.

For surface area determination by PVP, the sample is typically Na saturated with 1 M NaCl twice to assure complete saturation and dispersion of smectite particles, and then washed to remove all soluble salts which might interfere with measurement of PVP concentration by weight. Dialysis bags with a molecular weight pore size of 10K are effective for both removing residual NaCl and any other low molecular weight soluble material which might be present in the sample, while retaining all the clay particles. However, it is necessary to use special treatments to remove semi-soluble salts such as gypsum prior to Na-saturation, because these salts will continue to dissolve slowly, and will not permit the clay to become Na-saturated. To remove gypsum, we use long dialysis times and pass the dialysis water through an exchange column to remove the calcium ions released from the gypsum.

Procedure --

1) A 15 ml centrifuge tube with lid is weighed, and then ~50 mg of dry smectitic clay (or any other sample with the mass adjusted so that the bulk sample has a total surface area of ~40 m^2) is weighed into the centrifuge tube. A replicate determination is routinely made with a sample ~_twice??? the mass of the first determination. 2) About 5 ml of water is added, and the sample is thoroughly dispersed with an ultrasonic probe. The tube is then weighed, ~1 ml of ~10% PVP 55K is added, and the tube is reweighed.

3) The sample is then shaken overnight, and centrifuged until the solids are completely separated from the solution. We usually use ~4 hours at 10,000 rpm.

4) A sample vial is weighed with the lid, solution is decanted from the centrifuge tube into the vial, closed and weighed. The vial is then dried at 85ºC overnight, capped immediately after being removed from the oven, and reweighed when cooled.

The mass of PVP sorbed on the sample then is calculated as the difference between the mass of PVP added to the centrifuge tube and the mass of PVP remaining in solution after the sorption reaction, as calculated from the measured PVP concentration, and the original amount of solution in tube (determined by mass). All masses are determined ±0.0001 g.

***Procedure Comments* --**

There is considerable latitude in the amount of sample that can be used, but it is difficult to effectively suspend 40 m^2 of surface area when analyzing low surface area (<50 m^2/g) samples such as kaolinite or silica. A sample size of 1 g per 5 ml water seems like a practical limit for fine material (<2 μm), but larger masses of high silt or sand samples can be accommodated. The amount of PVP solution added can be adjusted for low or high surface area samples to maintain a nearly constant final PVP concentration in solution. This precaution retains sensitivity in the analysis while remaining on the flat portion of the sorption isotherm. PVP uptake on the Wyoming and Belle Fourche low-charge smectites and the RM30 illite was measured with both with and without overnight shaking. Samples with immediate centrifugation (i.e. no shaking) sorbed >90% of the PVP sorbed overnight, so the PVP sorption kinetics are fast. However, sorption kinetics was not investigated for a wide spectrum of materials, and samples were routinely shaken overnight to assure complete sorption.

Settling of single unit cell thick smectite particles is difficult, and requires considerable centrifugation time. However, PVP sorbed on the clay surfaces prevents flocculation by traditional techniques such as adding methanol or acetone, increasing the ionic strength or manipulation of solution pH. As a result, we relied on high speed centrifugation to remove the clays from solution. Undoubtedly, some small clay particles will remain suspended in solution. However, the error introduced is proportional to the fraction of clay remaining in solution. By using different centrifuge times up to 48 hrs, we concluded that as long as the solutions appeared completely clear to the eye, the error introduced by any incomplete settling of a few fine particles was «1% of the PVP sorbed. Many previous studies have used UV sorption to measure the PVP concentrations in solution, which would be much simpler than gravimetric analysis. However, we found that the UV sorption spectra were extremely sensitive to residual colloids in solution. Because of the difficulty in removing all the smectite particles, we found this analytical method did not produce reliable and reproducible PVP concentrations for smectite containing samples.

Another practical problem is that PVP will hydrate after it is removed from the oven, gaining several wt.% of water over ~5 days, and this can lead to a large uncertainty in the calculation of the mass of PVP sorbed. The rate of PVP weight gain by hydration is initially rapid, decreasing dramatically after about 1 hour, but continuing for days at a slow rate. Therefore, it is important to keep the samples isolated from the atmosphere, and measure the mass soon after the vials cool. We also found that polystyrene vials had the smallest change in mass with heating and cooling, smaller than glass or polyethylene, and yielded more reproducible results. It may also take longer than expected to dehydrate the PVP in the oven, and it is necessary to heat the samples for at least several hours after they appear dry.

Preparation of PVP reagent –

Typically, ~50 g of 55K PVP reagent is dissolved in ~400 ml of distilled water. PVP has a nearly infinite solubility in water, but the dissolution kinetics can be very slow. The beaker is usually stirred and gently heated on a hot plate for several hours. PVP of all molecular weights seemed stable up to at least 120º C, and the reported melting point of PVP-55K is >300º C. The solution is then transferred to a volumetric flask, cooled to room temperature, and diluted to 500 ml. The PVP solutions are stable indefinitely if sterile, but are subject to biodegradation. Therefore, solutions usually were refrigerated to retard colonization if they were stored for more then a few days. Each batch of PVP reagent must be individually calibrated, typically by evaporating multiple aliquots of 1 to 10 ml of solution at 85º C as in step 4 of the sample procedure. Reproducibility is generally <±0.2%, and yields a final solution between 9.4 and 9.5 wt.% PVP, indicating the initial reagent is ~5 wt.% water.

Determination of sample specific surface areas -

In examining the behavior of PVP sorbed on minerals, and in the development and validation of the PVP sorption method, it is critical to have some independent measure of the mineral surface area in order to evaluate the sorption density. As elaborated in the introduction, there is no other reliable technique for determination of smectite surface area. However, because we know the geometry of the smectite crystals, we can calculate a theoretical surface area. Elementary smectite crystals are 1 nm thick, and from TEM (Nadeau, 1985) and AFM (Blum, 1994) observations they have diameters from ~0.1 to 2 μm. Using the lower bound of 0.1 μm for the diameter, the edges are calculated to contribute <2% of the surface area. Therefore, we can treat smectite as an infinitely large sheet 1 nm thick for the calculation of surface area. Although the chemistry of smectites may vary greatly, the structure is always very similar to muscovite, and consequently we can use the molar volume (V_{mol}) of muscovite [140.71 cm^3/mol (Robie et al., 1979)] as V_{mol} for all smectites. This volume neglects interlayer swelling by hydration, but this is appropriate because we consistently exclude the interlayer water in both the chemistry and the volume assumptions. The surface area of a smectite therefore is:

$$SA = \frac{2\,V_{mol}}{h\,F_{wt}} \qquad (1)$$

where SA is the specific surface area (defined as surface area/mass), h is the thickness of the crystal (for muscovite and smectites h = 1 nm), and F_{wt} is the formula weight of the mineral (~373 g for the Belle Fourche). For a typical montmorillonite, this formula yields a specific surface area of ~755 m^2/g. However, this SA is calculated for dehydrated smectite. Montmorillonite which is oven dried at 105° C still retains about 4.0 wt.% interlayer water (determined by heating at 300º C overnight) but the effective SA remains the same. This additional water reduces the specific surface area of a smectite sample weighed in air by about 4%, to ~725 m^2/g for a typical montmorillonite. The latter surface area, measured F_{wt} and eq (1) are used to calculate the SA of many of the smectites shown in Table 1.

For pure illite, surface areas also are calculated using eq. (1), except that h is taken as the mean crystallite thickness determined using the MudMaster program (Eberl et al., 1996), which analyzes XRD peak shapes to determine crystallite size distributions. For all the minerals except smectite and illite, the BET surface area was used to check the PVP method. BET surface area was measured by sorbing and desorbing N_2 from the surface. These samples all have a more blocky morphology without significant coherent stacking and interparticle diffraction. Consequently, it is assumed that in the dried samples, N_2 which has a diameter similar to that of a water molecule, has access to the same surfaces which are accessed by solution after aqueous dispersion.

Results

Sorption on Smectites -

A sorption isotherm for the Belle Fourche bentonite (a low charge smectite) is shown in figure 3 for PVP-10K and -55K. The general shape of the isotherms are consistent with the sorption of PVP on the clay surface, with a well defined surface saturation plateau at 0.61 g and 0.72 g of PVP sorbed per gram of clay (g/g) for PVP-10K and PVP-55K, respectively. The sorption isotherms are not fitted well by either a theoretical Langmuir or Freundlich isotherm, as is evident by the non-linearity of either a reciprocal or log-log plot, respectively (not shown). Nevertheless, there is a wide range of solution PVP concentrations at which the amount of PVP sorption is nearly constant. Throughout this range of solution PVP concentration, the amount of PVP sorbed is proportional to the amount of clay present, but independent of the solution composition.

There is also a trend of slightly greater PVP sorption with increasing polymer chain length which is observed over a range of PVP molecular weights from 10K (0.61 g/g) to 360K (0.76 g/g). The mass of PVP sorbed per unit mass (or SA) increases only slightly (~20%) as the polymer chain length increases by a factor of 36, indicating that the area per polymer unit (fig. 2) remains nearly constant. This observation is consistent with a conceptual model in which the PVP chains are lying on the surface, and not analogous to detergent molecules which are arranged perpendicular to the surface.

The unbonded electron pairs on either the amine or the carbonyl groups located on the five member ring might be expected to act as a weak Lewis bases. However, PVP does not appear to protonate significantly in the near-neutral pH region. A solution of 1% PVP-10K was titrated with HCL and NaOH. The solution neutralized 92 μeq of charge per g of PVP-10K between pH 5 and pH 9, which corresponds to about 1 charge per polymer chain. In practice, the PVP does not significantly buffer the solution pH. The pH of a 1 wt.% PVP solution is ~8.5, but the pH of the final suspension is controlled primarily by the surface chemistry of the sample, which in turn often reflects the last solution to which the sample was exposed.

Shifting the solution pH (by the addition of NH_4OH or HCl, which should be lost in the vapor phase when evaporated) had no discernible effect on the amount of PVP sorbed on smectites, at least in the pH range from 6 to 10 (fig. 4). There does appear to be some effect of low pH on PVP sorption, but this is most likely an experimental artifact. As hydrochloric acid is added to the suspension, protons substitute for Na^+ on the smectite exchange sites, releasing Na^+ to solution. When the solution is evaporated the Na^+ is retained as NaCl. This salt gives the appearance of a greater mass of PVP in solution, and therefore less PVP is calculated as sorbed on the clay. Differences in the fixed charge of the smectite (Table 1) also had no discernible effect on the PVP sorption density in the range from 0.3 to 0.8 charges per half formula unit, nor does it appear to be affected by whether or not the charge is in tetrahedral or octahedral layers. This insensitivity to layer charge is particularly evident by the similar PVP uptake of the Wyoming and Belle Fourche low-charge smectites, and the Cheto, Kinney and Outay high-charge smectites (Table 1).

A major issue in designing a technique using PVP to measure smectite surface areas was the effect of the suspension density (g clay/ ml water). The higher the solid to solution ratio, the greater the sensitivity of the technique, since a greater proportion of the PVP in solution is sorbed. Low charge smectites, such as the Belle Fourche and Wyoming bentonites had very little dependence on the suspension density (fig 5). However, high charge smectites such as the Cheto and Kinney displayed a strong dependence on suspension density. The cause of this solid/solution ratio effect is not understood, but is generally consistent with the higher charge smectites having a greater tendency to form aggregates in solution before the PVP is added. However, the PVP sorption of the high charge smectites is very reproducible, and is not strongly dependent on the time the solution sits between ultrasonic dispersion and addition of the PVP. This observation would suggest that it is a subpopulation of particles which tend to aggregate quickly, rather than a highly time dependent phenomenon.

The abundance of low-charge versus high-charge smectites in most natural environments is not known, because this is a quantity which can only be determined accurately on pure samples, usually from bentonites or hydrothermal veins. These environments, although economically important, are not representative of most natural sediments. Differences in dispersion caused by charge density differences could lead to considerable uncertainty in the surface area determination of unknown samples by PVP sorption. However, it was found that mixtures of low and high charge smectites do not vary their sorption properties in a simple linear mixing (Fig. 5) as might be expected. The addition of 50% low charge smectite to 50% high charge smectite results in PVP sorption behavior nearly identical to that of a pure low charge sample. Thus, the solution density should not be a significant effect for samples that contain <50% high-charge smectite. This assumption can be tested by measuring two different sample masses which should yield the same PVP sorption density, and this procedure is recommended for samples of unknown composition.

XRD evidence for the thickness of sorbed PVP -

XRD patterns for smectite solutions with different solid-to-solution ratios (fig. 6) reveals some insight into the difference in behavior of low-charge and high-charge smectites. It is important to remember that fig. 6 reflects smectite orientations after evaporation, and not in solution. All smectites dispersed in PVP solutions with a small solid-to-solution ratio (SSR) had no XRD (00ℓ) diffraction peaks. Such XRD patterns show only the smectite structure factor and weak and broad reflections from the PVP matrix. This is consistent with the observations of Eberl et al. (1998) for a dilute suspension of Kinney smectite in PVP. The lack of diffraction peaks in dilute solutions indicates that the smectites are dispersed as single unit cell crystals with enough excess PVP between the particles after evaporation to completely eliminate interparticle diffraction. However, as the solid-to-solution ratio increases, the low-charge and high-charge smectites display different behaviors. For example, the Belle Fourche has no XRD peaks until a SSR of ~14 mg/ml, at which point a peak appears at ~34.5 Å along with its higher orders. At such low angles, the Lorentz polarization factor (L_p) has a significant effect on peak shapes and positions. All d-spacings where determined after L_p removal, although fig. 6 shows the uncorrected XRD patterns. The peak at 34.5 Å increases in intensity with increasing SSR until ~50 mg/ml, beyond which the intensity continues to increase, but the peak position also moves to larger angles, reaching 27 Å at a SSR of 100 mg/ml, and the higher angle reflections become less rational.

In contrast to the Belle Fourche sample, the Cheto high-charge smectite has a very weak peak at ~23 Å at the lowest SSR of 1 mg/ml, which is detectable only at a greatly expanded scale from that used in fig. 6b. The 23 Å peak increases in intensity with increasing SSR, and shifts to slightly higher angles, approaching 22 Å at a SSR of 100 mg/ml. The Kinney, also a high charge smectite, has a behavior intermediate between the Belle Fourche and Cheto (not shown in fig. 6). At a low SSR, the Kinney smectite has a weak peak at ~31 Å, which increases in intensity as the SSR increases. At an SSR of 30 mg/ml the peak begins to shift to a progressively lower d-spacing, finally reaching ~23 Å at a SSR of 100 mg/ml. The multiples of the high-angle peaks initially become more irrational as the peak position moves away from 31 Å, and then become more rational again as the peak position approaches 23 Å.

The most rational XRD patterns in fig. 6 probably represent the best approximation of the thickness of the descrete repeat distances within the smectite/PVP mixed layering. While none of the patterns is completely rational, fig 7 shows the XRD patterns of the most rational XRD patterns from the Cheto and Belle Fouche smectites (50 mg/l and 60 mg/l, respecitively) corrected for the Lorentz polarization factor. These patterns suggest a repeat distance of 22.6 A for the Cheto and 30.5 A for the Belle Fouch.

These XRD observations can be explained by a simple structure, with stacking of 14.2 Å smectite crystals [a 9.2 Å 2:1 silicate layer + two 2.5 Å layers due to the Na saturated and hydrated surfaces] with either one or two 8.4 Å thick PVP interlayers. The conceptual model is shown in figure 8. At low SSR values, all the clays have a tightly bound 8.4 Å layer of PVP sorbed on their surfaces, but there is sufficient unbound PVP in solution to widely separate the clay crystals, yielding no XRD peak (i.e. only the structure factor is visible) when dried. In the case of Belle Fourche, as the SSR increases and the clay particles become more closely packed, some crystals begin to align, creating interparticle diffraction with a ~30.5 Å periodicity. Basically, as the number of particles increases and the amount of PVP in solution stays nearly constant, there is less PVP between each particle to disrupt interparticle diffraction. Since the amount of PVP sorption on each surface remains at ~8.4 Å, these interparticle associations, if present in solution, would not effect the amount of PVP taken up from solution. This picture is consistent with the observation that the PVP sorption on Belle Fourche is not changed by SSR's below ~50 mg/ml (fig. 5). We also can compare this uptake to the computed thickness of the sorbed PVP layer based on the observed uptake from solution (fig. 3). Assuming the hydrated smectite particles have a density of 2.4 g/cm^3 and a thickness of 14.2 Å, and the PVP layer has a density of 1.2 g/cm^3, the PVP surface layer is calculated from the PVP uptake of 0.72 g/g to have a thickness of 10.6 Å, in fairly good agreement with the XRD thickness of 8.4 Å.

As the SSR of the Belle Fourche increases to above ~50 mg/ml, some interlayers have only one layer of PVP between smectite 2:1 layers. This uptake produces a spacing of 22.6 Å, which causes the shift of the 30.5 Å peak to smaller apparent spacings with a loss in rationality of the multiple d-spacings, typical behavior of randomly interstratified mixed-layer clay (Moore and Reynolds, 1989). Formation of 22.6 Å aggregates in solution would produce a reduced PVP uptake, because two surfaces share one PVP layer, with each surface being effectively only 50% covered. This model is consistent with the reduced PVP uptake by Belle Fourche at SSR's above ~50 mg/ml (fig. 5).

In contrast to the Belle Fourche, the Cheto starts with a few 22.6 Å aggregates even at an SSR of 1mg/ml, and the number of aggregates increases quickly with increasing SSR. This behavior is consistent with the formation of 22.6 Å aggregates in solution, which explains why the uptake of PVP on the Cheto appears to be strongly dependent on the SSR even at low SSR values. The shift of peak positions to <22.6 Å at the highest SSR's may indicate the interstratification of 14.2 Å interlayers with no intercalated PVP at the highest clay concentrations. The Kinney at first forms 30.5 Å aggregates, but progressively moves toward 22.6 Å at higher SSR's much more quickly than the Belle Fourche, with a randomly interstratified structure during the transition.

Thus, the uptake of PVP from solution as a function of SSR (fig. 5) is consistent with the XRD evidence, and it appears that the XRD patterns reflect aggregates of clay crystals which formed in solution. We propose an explanation for these observations, based on the relative rates of PVP sorption versus particle aggregation. The clay particles are dispersed in solution prior to the addition of PVP, as evidenced by all smectites being nearly completely dispersed at low SSR's. Once the PVP solution is added, the PVP must sorb to all the clay surfaces before the particles aggregate. If this occurs, then there is an 8.4 Å PVP layer on all the surfaces, and the PVP uptake from solution is independent of the SSR. However, if the smectite particles associate before completion of the PVP sorption, then some clay particles may end up sharing a PVP layer with an adjacent particle, forming the 22.6 Å structure. As the SSR of the suspension increases, the mean distance between particles in solution decreases, increasing the likelihood of particles associating before PVP sorption is complete, and favoring the formation of the 22.6 Å structure. It seems reasonable that high-charge smectites would have a greater propensity to aggregate than low-charge smectites, and would be more sensitive to the SSR.

Illite and Vermiculite -

Natural sediments usually contain a complex mixture of clay minerals; therefore it is important to investigate the effects of a broader spectrum of minerals on PVP uptake. Illites are the other clay mineral with a high surface area present in many soils and sediments. Illites have a structure very similar to smectites, except that the fundamental particles are ≥2 unit cells thick, and interior (00ℓ) interfaces are fixed by potassium ions that cannot be readily cation exchanged or expanded by ultrasonic dispersion, ethylene glycol or EGME. The exterior (00ℓ) surfaces of the illites should behave in a similar manner as smectites, and the exterior unit cells of illites are thought to have a chemistry and fixed charge that are similar to low-charge smectites (Srodon et al., 1992). Sorption of PVP on a range of different illites (Table 1) is consistent with this conceptual model. When normalized to illite surface area determined by MudMaster (Eberl et al., 1996), illites have the same PVP sorption density and behavior as low-charge smectites.

The specific surface areas (m^2/g) of illites can at most be 50% that of smectite (assuming all the illite crystals are 2 unit cells thick, e.g., a rectorite), and the surface area decreases rapidly as the illite particles increase in thickness (SA μ 1/T). PVP sorption on two different rectorites, in which most of the particles are 2 nm thick, is shown in Table 1, and is about half the value of smectites on g/g basis, as would be expected if the particles are 2 unit cells thick. When illite particles reach a mean thickness of 12 nm, they will have a specific surface area ~8.3% that of smectites. Thus, if illite is abundant it may contribute significantly to the amount of PVP sorbed by a sample, and in samples with a low abundance of smectite mixed with a large amount of thin illites, illite may dominate the PVP sorption. Therefore, it is necessary to correct PVP-based measurements of smectite abundance for illite in samples where significant illite is present, as will be discussed later.

The behavior of vermiculites presents a middle ground between the behavior of illite and smectite. The interlayer cations in vermiculites are exchangeable, but are not swollen by ethylene glycol, and vermiculite is not dispersed into “fundamental” particles. Rather, vermiculites maintain “large” crystals with a low external surface area, but with the interlayers accessible for cation exchange. It appears that PVP does not enter the vermiculite interlayers (Table 2), and that vermiculites are not a significant source of PVP sorption.

Oxides -

Sorption of PVP on amorphous (fumed) silica is shown in figure 9a, and has a similar sorption density as smectite and illite surfaces (Table 1). These data are consistent with the PVP sorption data of Thibaut, et al. (2000) and Cohen et al. (1984). We did not measure quartz, because grinding to a sufficiently fine grain size to detect PVP sorption produced abundant amorphous material. Presumably, quartz would act in manner similarly to amorphous silica, since the local surface chemistry of amorphous SiO_2 and quartz are similar, and PVP sorption appears insensitive to the detailed surface structure. In natural samples, quartz may be high in abundance but with low surface area, and even highly pitted quartz will contribute insignificantly to the surface area in comparison to smectite.

In contrast to amorphous silica, _-Al_2O_3 sorbed no PVP (fig. 9b). The point of zero charge (PZC) of ??_-Al_2O_3 is near pH 8.5 (Huang and Stumm, 1973). Changing the solution pH on either side of the PZC to create a positively and negatively charged ??_-Al_2O_3 surfaces had no effect on the lack of PVP sorption. The apparent increasingly negative values for ??-Al_2O_3 PVP uptake at low and high pH are thought to be an artifact, the result of Al_2O_3 dissolution which increases the mass of solids in solution. Minimal PVP sorption to alumina surface has also been reported by Otsuka and Esumi (1994) and Esumi et al. (2000). Similar to ?? _-Al_2O_3, gibbsite and amorphous $Al(OH)_3$ showed no PVP sorption, and it appears that aluminum oxyhydroxides are not a significant contribution to PVP uptake. However, hematite (Fe_2O_3) showed PVP uptake equivalent to the silicates on a per surface area basis (Table 1).

Kaolinite -

Kaolinite presents a somewhat different situation from smectite and illite. For any kaolinite crystal, one surface should be an octahedral Al-OH surface and the other side a tetrahedral Si-O-Si surface. Based on the oxide analysis, we would expect that PVP would sorb on the tetrahedral side and not on the octahedral side, producing a PVP sorption per unit surface area (g PVP/m^2) that is one half that of smectites and illite. Kaolinite uptake of PVP (fig. 10) is near the detection limit for this technique, but it appears that kaolinite sorbs PVP in a similar manner and at the same surface density as smectites and other minerals, in contradiction with our expectation. Bonding between kaolinite layers is weak, and previous AFM observations have shown that vigorous ultrasonic treatment can generate some 7 Å thick kaolinite crystallites (Blum and Eberl, 1992). Qualitatively, these single-layer crystals appeared to be a very small fraction of the total sample, but, there was concern that our experimental procedure could be increasing the amount of kaolinite surface area present in the sample. If ultrasonic dispersion doubled the kaolinite surface area, then the apparent sorption of PVP on both surfaces of the kaolinite based on the BET surface area could be explained. Figure 11 shows that increasing the duration of ultrasonic treatment of the kaolinite had no impact on the amount of PVP sorbed, and that this procedure does not distort the results. However, grinding the kaolinite in a McCrone mill (a variety of vibrating rod mill) does systematically increase the PVP uptake by the sample, presumably by grinding of the kaolinite to a finer grain size, and thus, increasing the surface area.

Organic Matter -

A final consideration for natural samples is the effect of organic matter on PVP sorption. One end-member for organic carbon is activated carbon, which has a very high and reactive surface area (883 m^2/g). PVP did sorb on activated carbon with an average density of 0.12 mg/m^2, significant but much lower than the value of ~1 mg/m^2 for silicates. The most likely explanation is that PVP sorbed on to activated carbon at about the same density as on silicates. However, a large portion of the activated carbon surface area is internal, as is obvious from its silt size particles which have a surface area actually higher than smectites. Apparently, many of these pores are small enough that PVP-55K cannot access the interior. However, the internal porosity would be accessed by N_2, and thus, the sorption density based on N_2 BET surface areas appears low.

Consequently, organic carbon has the potential to uptake PVP. However, shales and sediments are rarely more than a few wt. % organic carbon, and natural organic material typically has surface areas that are orders of magnitude smaller than activated carbon. For example, a Florida (Pahokee) peat (an International Humic Substances Society source material), is highly reactive natural organic material with a large surface area, but it has a small apparently negative uptake of PVP. The dissolved organic matter imparted a dark yellow-brown color to the PVP solution, consistent with an increase in dissolved organic matter (DOC) in solution, and with the apparent negative PVP uptake. This experiment indicates that even with a thourghly water-washed sample, the PVP in solution solubilized (presumably by complexation) more organic matter than PVP was sorbed on the organic surfaces. We have also observed that some organic-rich shales also impart a dark brown color to the PVP solution, indicating the solubilization of organic matter. It appears that the major caveat for organic rich samples may not be the uptake of PVP by the organics, but the potential solubilization of DOC by the PVP measurement procedure. It may, therefore, be advantageous to wash organic rich samples with an organic solvent or destroy reactive organic matter with peroxide before the PVP analysis of organic rich samples, but this approach was not thoroughly investigated. An advantage of PVP uptake by organic carbon may be that organics sorbed to the clay surfaces will not greatly effect the measured surface areas of the clays, and should not interfere with smectite abundance measurements.

Discussion

The nature of PVP sorption -

The conceptual model for PVP sorption on silicates can be constrained based on the observations reported earlier. The insensitivity of the absolute mass of PVP sorbed on chain length indicates the PVP chains are lying parallel to the silicate surface, so that the area covered per polymer is approximately proportional to the polymer length. The large area covered by each PVP polymer, coupled with the apparent lack of sensitivity of PVP sorption to the details of surface chemistry, layer charge or solution pH, suggest the interaction between adjacent PVP chains is a major factor in the formation of the surface layer. However, there is no indication of the addition of more than an ~11 Å thick layer of PVP to the surface [ALEX-SHOULD THIS BE 8.4Å??], suggesting the surface also plays an important role in the formation of the PVP layer, and that this is not a surface precipitation type process. The XRD peaks at 23.5 and 34.5 Å (fig. 6) also suggest that the sorbed layer is relatively uniform in thickness, because a variability in the thickness of the PVP layer between particles would not produce a coherent XRD peak. The observations are all consistent with the sorption of a monolayer of PVP chains on the surface, although we have no direct evidence as to the organization of PVP within the sorbed layer. The reason why the Si-OH surface of fumed silica sorbs PVP but the Al-OH surface of gibbsite (or □-Al_2O_3) does not sorb PVP still awaits explanation.

Accuracy of PVP uptake as a measure of surface area -

The results have already illustrated some of the difficulties in constraining the accuracy of a PVP uptake measurement as a measure of surface area. Table 1 presents data from a wide range of materials. However, the only parameter directly describing PVP sorption is grams of PVP sorbed per gram of sample. The repeatability of measurement is generally (with several caveats discussed below) very good, and almost always better than ±5% for smectite-rich samples. However, this quantity is difficult to evaluate independently. In looking at the sorption per unit surface area, we can easily compare values, but these quantities incorporate errors in the surface area determinations, which are potentially numerous and significant. We certainly can compare the results of different smectites. At least theoretically, the only difference the specific surface areas of the different smectites is the difference in density resulting from variations in the chemical composition of the unit cell. In general, the smectites shown in Table 1 are in good agreement, clustering around 0.72 g/g. However, the purity of any smectite sample which has not been extensively characterized is always suspect, and "impurities" can usually be invoked as an explanation for PVP uptake numbers below 0.72 g/g. For example, the Glen Silver Pit smectite in Table 1 has a PVP uptake of 0.50 g/g, which could easily be explained by contamination with a small amount of amorphous material, illite, or another silicate. One encouraging aspect of the smectite data in Table 1 is that no samples yielded a PVP uptake significantly greater than 0.72 g/g.

The determination of illite surface areas are all dependent upon the MudMaster analysis. The use of MudMaster as a technique for determining illite surface areas appears to be valid (Eberl et al., 1998; Dudek et al., 2002), but the accuracy is still difficult to constrain. The question of the illite sample "purity" also introduces an uncertainty for many illite samples. Finally, the use N_2 surface areas for the non-clays for comparison with PVP surface areas is justifiable, but as suggested by the measurements of activated carbon, the surface area accessible to N_2 with a MW of 28 and PVP with a MW of 55,000 are not necessarily equivalent, especially if there is considerable internal microporosity. Despite all these caveats, we see a relatively consistent result of about 0.99 mg of PVP 55K sorbed per m^2 of surface area on a range of smectites, illites, silica and other materials (Table 1). This consistency gives confidence that PVP uptake can be used to accurately quantify silicate mineral surface area.

Quantitative measurement of smectite abundance -

To quantify the amount of smectite in a complex mixture, it is necessary to know how much PVP has been sorbed by other phases, such as illite, kaolinite, quartz and feldspars. However, non-phyllosilicate minerals rarely make up a significant portion of the <2 μm fraction of natural samples and their surface areas are very small. Therefore non-clays contribute very little to the total sample surface area. For example, in a sample which is 1 wt.% smectite and 99 wt.% 2 μm diameter spheres (ρ =2.8 g/cm^3), the smectite would account for 88% of the total surface area. If the spheres are 5 μm, 1 wt% smectite would account for >95% of the surface area. Even in fine-grained natural samples, the non-clays will rarely contribute significantly to the total surface area if smectite is present, and can be ignored. An exception may be ferrihydrite, which may occur in abundance near active redox interfaces, such as outflows from sulfide rich tailings piles. Ferrihydrite has a highly variable surface area, initially up to several hundred m^2/g, but decreases rapidly with recrystallization over a period of days to weeks. The presence of ferrihydrite could therefore complicate any PVP analysis, and may require removal by selective dissolution before a meaningful PVP uptake measurements can be performed.

Illite and kaolinite generally have surface areas only a fraction of that of smectites, but they may still contribute a significant proportion of the surface area and PVP uptake if smectite is present in only small proportion. Thus, the surface area attributable to smectite in a sample can be calculated as:

$$SA^{*}_{sample} = (SA^{*}_{kaolinite})(M_{kaolinite}) + (SA^{*}_{illite})(M_{illite}) + (SA^{*}_{smectite})(M_{smectite}) \qquad \text{(eq. 2)}$$

where M is mass fraction of the mineral in the sample, and SA^{*} is the specific surface area. Equation 2 must then solved for $M_{smectite}$.

SA_{total} is determined experimentally as:

$$SA^{*}_{sample}\left[\frac{m^2}{g}\right] = \frac{mass\ of\ PVP\ uptake\ [g/g]}{9.9 \times 10^{-4}\ [g/m^2]} \qquad \text{(eq. 3)}$$

alex-note the change in the above equation

The SA* of smectite was calculated earlier from the molar volume and formula weight to be ~725 m^2/g. The wt% kaolinite in the sample can be determined using the quantitative XRD techniques of Srodon et al. (2001) and Eberl (2003) . The specific surface area of the kaolinite in the sample is unknown and must be estimated. The surface areas of kaolinites do not vary as greatly as illites; and are generally near 25 m^2/g for poorly crystallized kaolinites, with well ordered kaolinites slightly lower, as low as 10 m^2/g. Thus, SA_{total} is ~30 times more sensitive to the abundance of smectite than kaolinite. In most cases the total kaolinite correction is small, and the uncertainties in the kaolinite surface areas are not significant.

SA^{*}_{illite} can be calculated from the crystal size distribution obtained from the (001) XRD peak shape using MudMaster measurements, as described earlier. The wt.% of illite in the sample can not be determined separately from smectite using the quantitative XRD techniques of

Srodon et al. (2001), but the wt.% of illite plus smectite ($M_{ill+smec}$) can be determined (from the from the integrated intensity of the 060 reflection of a randomly oriented sample in comparison with an internal standard). Thus, one can substitute [$M_{ill+smec}$ - $M_{smectite}$] for [M_{illite}] in equation 2, and solve for $M_{smectite}$.

$$M_{smectite} = \frac{SA^{*}_{Total} - SA^{*}_{kaolinite} M_{kaolinite} - SA^{*}_{illite} M_{Ill+smec}}{755 - SA^{*}_{Illite}} \qquad \text{(eq. 4)}$$

Thus, eq. 4 can be used to determine the mass of smectite in a sample, even in the presence of significant amounts of illite and kaolinite.

Analyses of several artificial mixtures are shown in figure 12. Mixtures were made by combining measured amounts of Belle Fourche smectite (montmorillonite, SA=725 m^2/g), Dry Branch kaolinite (SA=14.0 m^2/g by BET), RM30 illite (mean particle thickness of 11.6 nm and surface area of 63 m^2/g by MudMaster) and quartz (ground in a shatter box; assumed SA<< 1 m^2/g). The mixtures were divided into 5 series, with smectite varying between 5% and 80% in each series. We can calculate the specific surface area of each mixture by using the surface areas of the components in the proper proportions. We then used the measured PVP uptake and eq. 3 to calculate a sample specific surface area, and used eq. 4 to determine the smectite content of the sample. As would be expected, the non-smectite components had the largest relative impact on the specific surface area when samples had small smectite concentrations and/or large illite content. Both figures 12a and 12b show good linear correlations between measured and predicted values, with a slope of ~1. The components all appear to act independently in suspension, with no interaction or aggregation which impacts the PVP uptake. These experiments indicates both the validity and sensitivity of the approach outlined in equations 1 and 2 which uses PVP uptake by complex mixtures to determine the smectite content of samples. However, we used purified components which can be dispersed easily. Cements in natural samples, might effect the ability to disperse clays, and possibly impact the PVP uptake. This is not an issue we have investigated, but chemical treatments described by Jackson (1985) can remove cements prior to PVP analysis.

Applications of the PVP technique -

Because smectites have a significant influence on the properties of many natural and synthetic materials, both as a major phase and a minor contaminant, there are a large number of potential problems for which the ability to quantitatively measure smectite abundance would be helpful. Several applications that are immediately apparent include; a) the characterization of petroleum reservoirs and cap rocks, and reaction paths within sedimentary basins, b) prediction of the geotechnical properties of soils and rocks, particularly the detection of swelling potential in soils, c) the characterization of bentonites and other clays for application in ceramics, paper, drilling fluids and liners, and d) determining the provenance of sediments in fluvial and lacustrine systems.

Conclusions

The uptake of polyvinylpyrrolidone (PVP) while dispersed in solution yields an accurate measure of the surface area of silicate minerals. The sorbed PVP layer is ~11 Å 8.4 Å???? thick, and corresponds to ~0.99 mg 55K PVP per m^2 of surface area. Sodium saturated smectites can be readily dispersed as single unit cell crystals, and they tend to dominate sample surface areas. Therefore, PVP uptake (0.72 g PVP per g smectite) can be used to quantify the abundance of smectitic minerals in a sample. Quantitative XRD techniques can be used to further refine the measurement of smectite abundance by correcting the sample for illite and kaolinite surface areas.

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Table 1 – PVP uptake measurement of various minerals.

Sample	Mineral	PVP-55K uptake (g/g)	Surface Area (m^2/g)	PVP Surface Area (m^2/g)	PVP-55K uptake (mg/m^2)
Belle Fourche	montmorillonite	0.72[a]	725[b]	725	0.99
Belle Fourche (Ca-sat.)	montmorillonite	0.44	725[b]	443	0.61
Wyoming "B"	montmorillonite	0.71	725[b]	715	0.98
Wyoming B (Ca-sat.)	montmorillonite	0.46	725[b]	463	0.63
Kinney	high charge smectite	0.71	752[b]	715	0.98
SAz-1 (Cheto)	high charge smectite	0.71	717[b]	715	0.99
SAz-1 (Cheto) (Ca-sat.)	high charge smectite	0.33	717[b]	332	0.46
Hectorite	Li-smectite	0.72	725[c]	725	0.99
Camp Berteau	montmorillonite	0.71	725[c]	715	0.98
Red Hill	montmorillonite	0.72	725[c]	725	0.99
Bates Park Montana	montmorillonite	0.64	725[c]	644	0.88
Glen Silver Pit, Idaho	montmorillonite	0.50	725[c]	503	0.69
Fe smectite	nontronite	0.64	654[d]	644	0.98
Saute Loupe	nontronite	0.65	654[d]	655	0.99
Amargosa	sepiolite	0.34		342	
IMV	sepiolite	0.23		232	
Arkansas Rectorite		0.36	363[c]	363	0.99
Slovakia K-rectorite		0.35	363[c]	352	0.96
Wyoming "C"	montmorillonite	0.71	725[c]	715	0.98
Dry Branch	kaolinite	0.012	14.0[e]	12	0.86
KGa 1	kaolinite	0.0089	10.0[e]	9	0.89
KGa 2	kaolinite	0.018	22.6[e]	18	0.82
Libby	Vermiculite	0.005			small
SG4	illite	0.034	35[f]	34	0.97
RM30 (Na sat)	illite	0.071	63[f]	71	1.13
RM30 (Ca sat)	illite	0.073	63[f]	74	1.16
Marblehead	illite	0.105	117[f]	106	0.90
Fithian, Illinois	illite	0.074	176[f]	75	0.42 or 8%[h]
3M3	illite	0.51	201[g]	514	61% smectite[h]
IM5	illite	0.31	148[g]	312	29% smectite[h]
activated carbon	reagent	0.11	883[e]	111	0.12
Florida peat	humic standard	-0.017			
Fe_2O_3	hematite	0.0103	10.5[e]	10	0.98
fumed SiO_2	amorphous	0.13	280[e]	131	0.46
$Al(OH)_3$	amorphous	0.0014			~0
$Al(OH)_3$	synthetic gibbsite	-0.003	0.09[e]		~0
□-Al_2O_3	reagent	0.0016	175[e]		~0
ZnO	reagent	0.0025	3.83[e]		0.65

[a] The uptake of PVP-10K, 40K and 360K are approximately 0.61, 0.68 and 0.76 g/g, respectively.
[b] Calculated based on measured chemistry, the molar volume of muscovite and 1 nm thick crystals.
[c] Estimated surface area (see text).
[d] Calculated assuming a composition of $NaFe_4Si_{7.34}Al_{0.66}O_{20}(OH)_4$, an ideal nontronite.
[e] N_2 BET surface area.
[f] Computed from illite particle thickness distributions based on MudMaster XRD measurements.
[g] Surface areas measured by MudMaster (XRD). However, these samples are very thin illites which probably contain single unit cell smectite particles which are not detected by XRD.
[h] The % smectite is computed based on measured PVP uptake and the MudMaster surface area for the illite component.

Figure Captions

Figure 1 - The planar faces of smectite particles in dried samples have strong attractive forces with most silicate minerals, which easily deform the crystals to the underlying surface. A good analogy is "vacuum packing" the sample. Figure 1 illustrates a) the high degree of smectite conformation and orientation in samples with high smectite contents, and b) the lower and variable degree of coherent smectite stacking and orientation in mixtures containing other minerals in addition to smectites.

Figure 2 – Chemical structure of the polyvinylpyrrolidone (PVP) monomer.

Figure 3 – Sorption isotherm of 55K and 10K PVP on Belle Fourche smectite.

Figure 4 – The effect of solution pH on the sorption of PVP-K55 on Belle Fourche smectite.

Figure 5 – The effect of solid to solution ratio on PVP-K55 uptake.

Figure 6 – XRD patterns of a) Belle Fourche low charge montmorillonite, and b) Cheto high charge montmorillonite. Each trace is labeled with the solid to solution ratio, followed by the positions of the first and second peaks as determined from L_p corrected traces (not shown). Baselines of the patterns have been offset to add clarity.

Figure 7 – Cheto (50 mg/l) and Belle Fouche (60 mg/l) XRD patterns corrected for the Lorentz polarization factor. The Cheto pattern has a near rational repeat distance at 22.6 Å, and the Belle Fouch at 30.5 Å.

Figure 8 – Proposed structure for generating the 30.5 Å and 22.6 Å repeat distances observed in XRD patterns (figures 6 and 7).

Figure 9 – PVP uptake by SiO_2 and γ-Al_2O_3 as a function of solution pH.

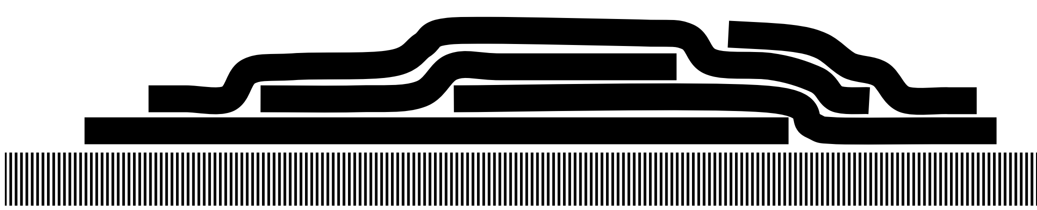
Figure 10 – PVP sorption isotherm for Dry Branch kaolinite.

Figure 11 – The effect of ultrasonic dispersion and grinding (McCrone mill in methanol) pretreatments on the amount of PVP uptake on Dry Branch kaolinite.

Figure 12 – The first three mixtures are variable amounts of smectite with the remaining portion of the sample containing a single additional phase. Recipe 1 is variable amounts of smectite with the remainder divided equally between kaolinite and illite. Recipe 2 is smectite plus 20% each kaolinite and illite with the remainder quartz, except 80% smectite, which has 10% each of kaolinite and illite. a) The surface area measured by PVP uptake versus the surface area predicted from the composition of the sample and the independently determined surface areas of the components. b) The composition of the smectite measured in the samples by PVP uptake as a function of the amount of smectite mass added to the sample.

Fig. 1

a)



b)

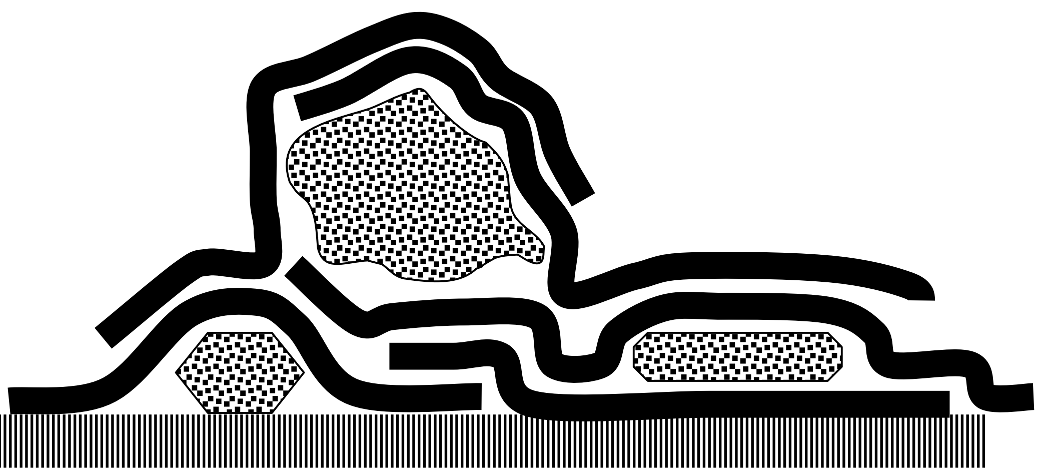
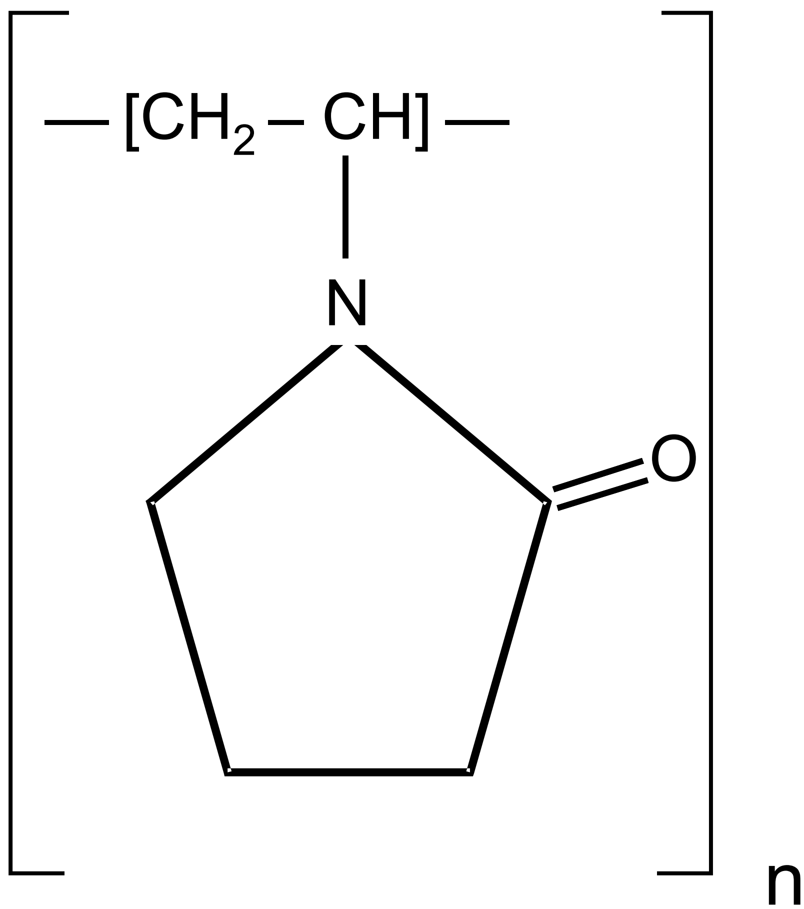
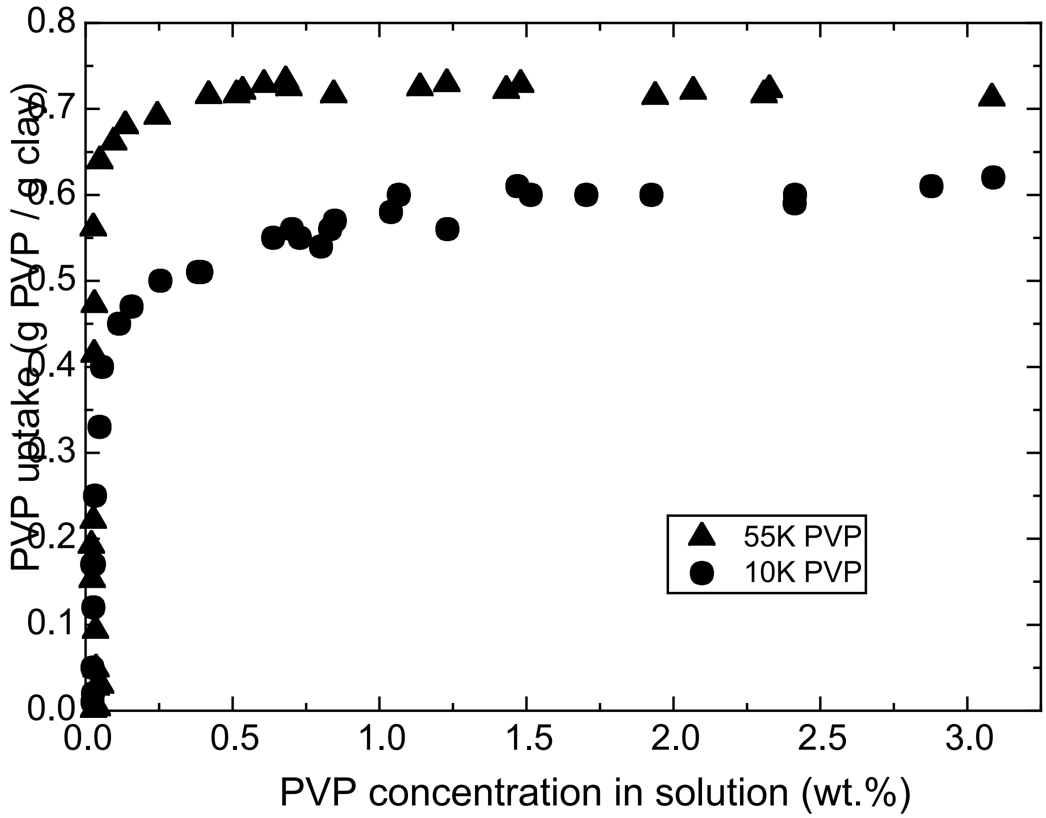


Fig. 2

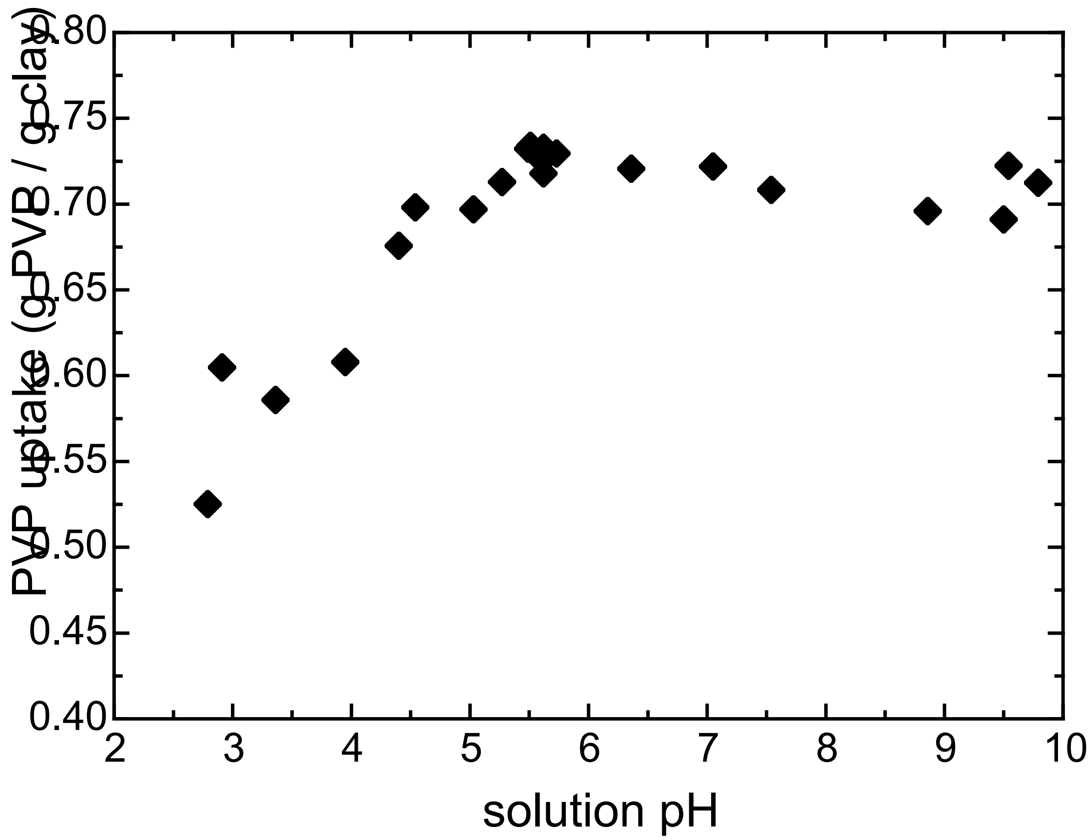




0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
PVP uptake (g PVP / g clay)
PVP concentration in solution (wt.%)
55K PVP
10K PVP

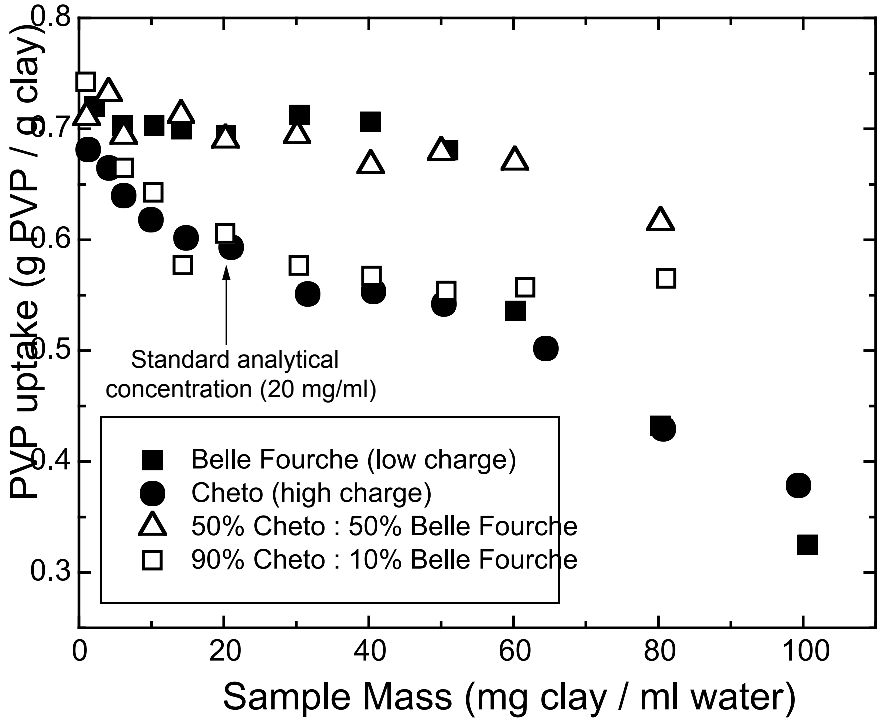
Fig. 3

Fig. 4



PVP uptake (g PVP / g clay)
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
2
3
4
5
6
7
8
9
10
solution pH

Fig. 5



PVP uptake (g PVP / g clay)
0.8
0.7
0.6
0.5
0.4
0.3
0
20
40
60
80
100
Sample Mass (mg clay / ml water)
Standard analytical
concentration (20 mg/ml)
Belle Fourche (low charge)
Cheto (high charge)
50% Cheto : 50% Belle Fourche
90% Cheto : 10% Belle Fourche

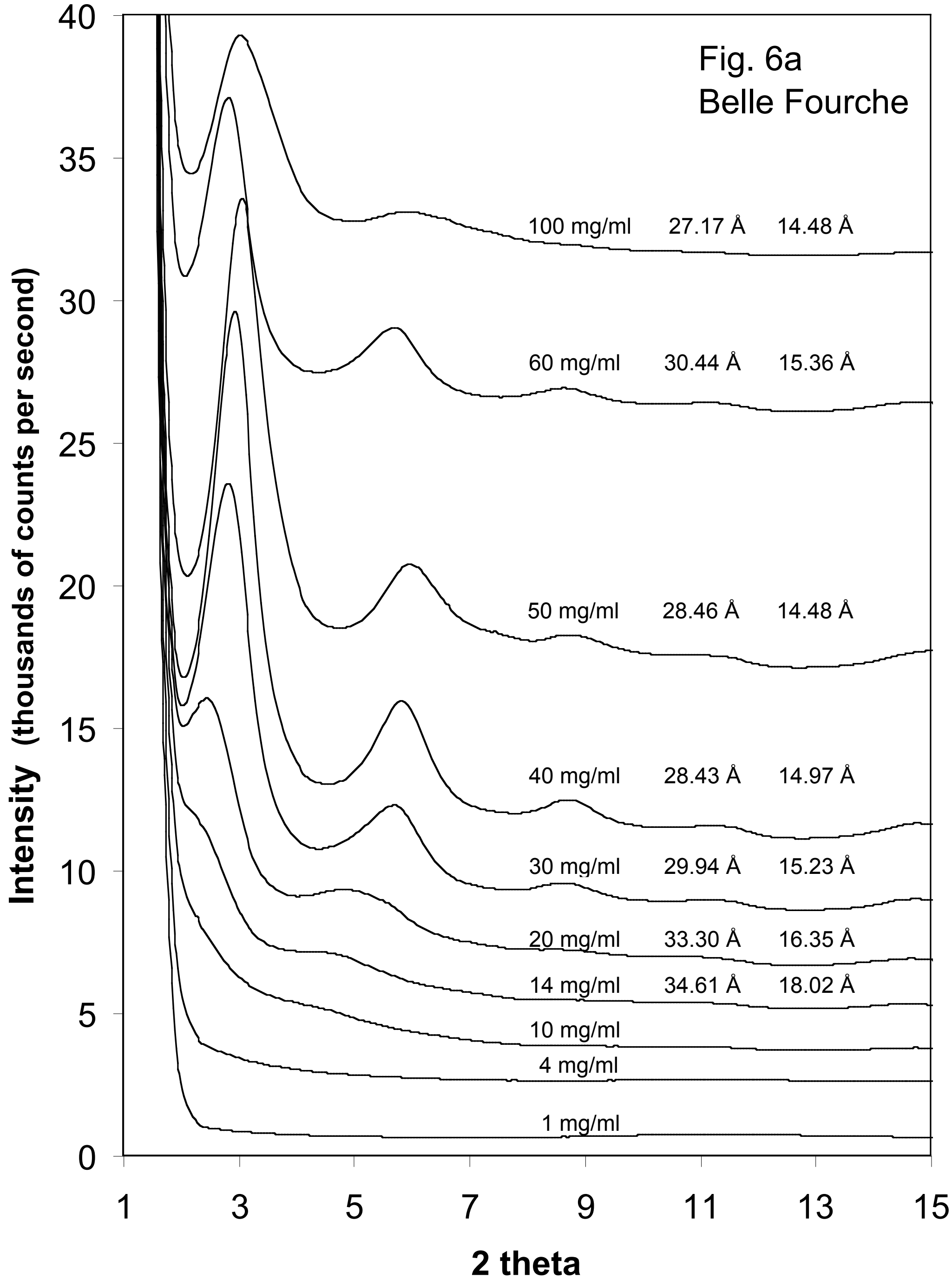


Fig. 6a
Belle Fourche
100 mg/ml 27.17 Å 14.48 Å
60 mg/ml 30.44 Å 15.36 Å
50 mg/ml 28.46 Å 14.48 Å
40 mg/ml 28.43 Å 14.97 Å
30 mg/ml 29.94 Å 15.23 Å
20 mg/ml 33.30 Å 16.35 Å
14 mg/ml 34.61 Å 18.02 Å
10 mg/ml
4 mg/ml
1 mg/ml
Intensity (thousands of counts per second)
0
5
10
15
20
25
30
35
40
2 theta
1
3
5
7
9
11
13
15

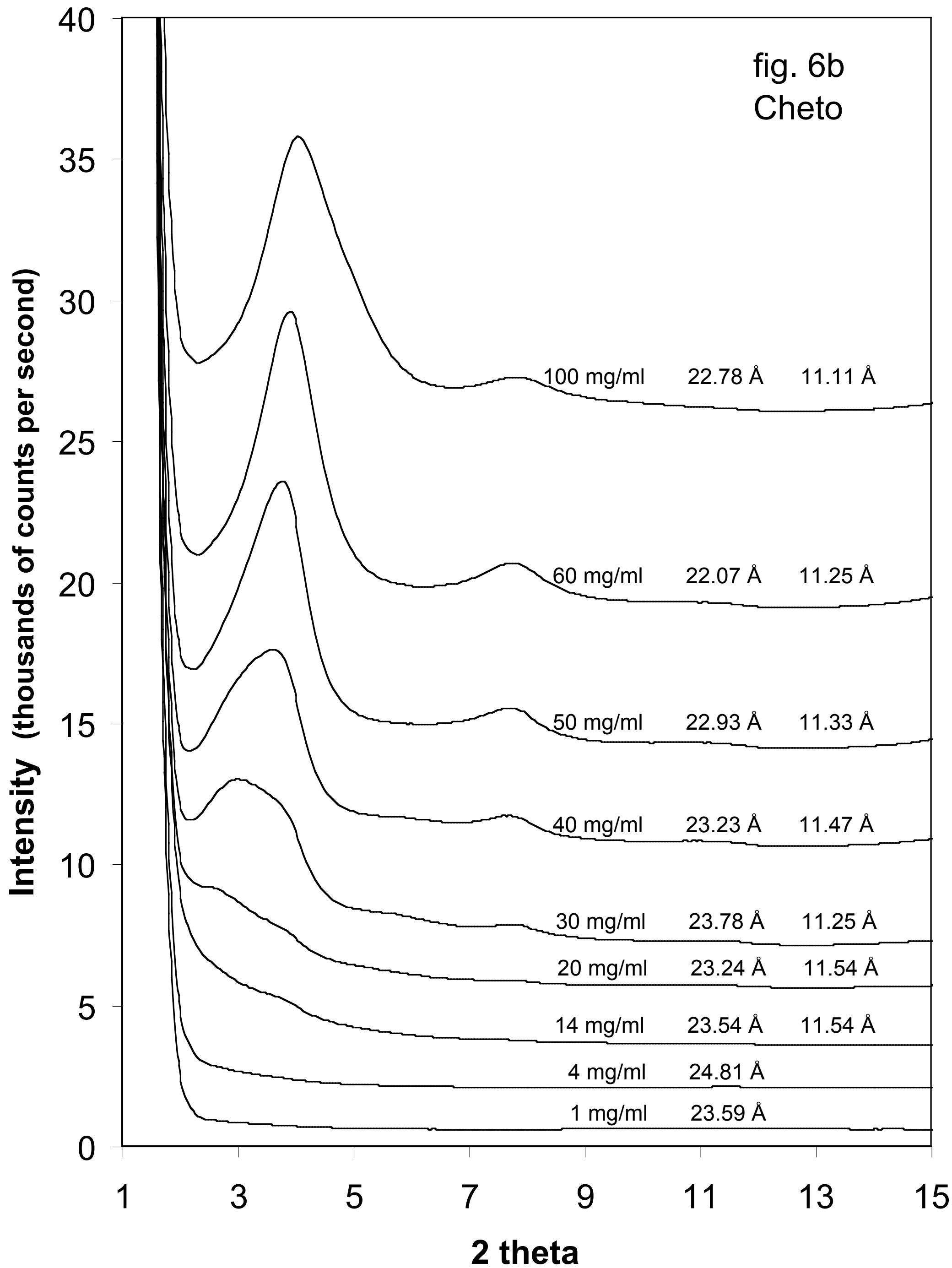
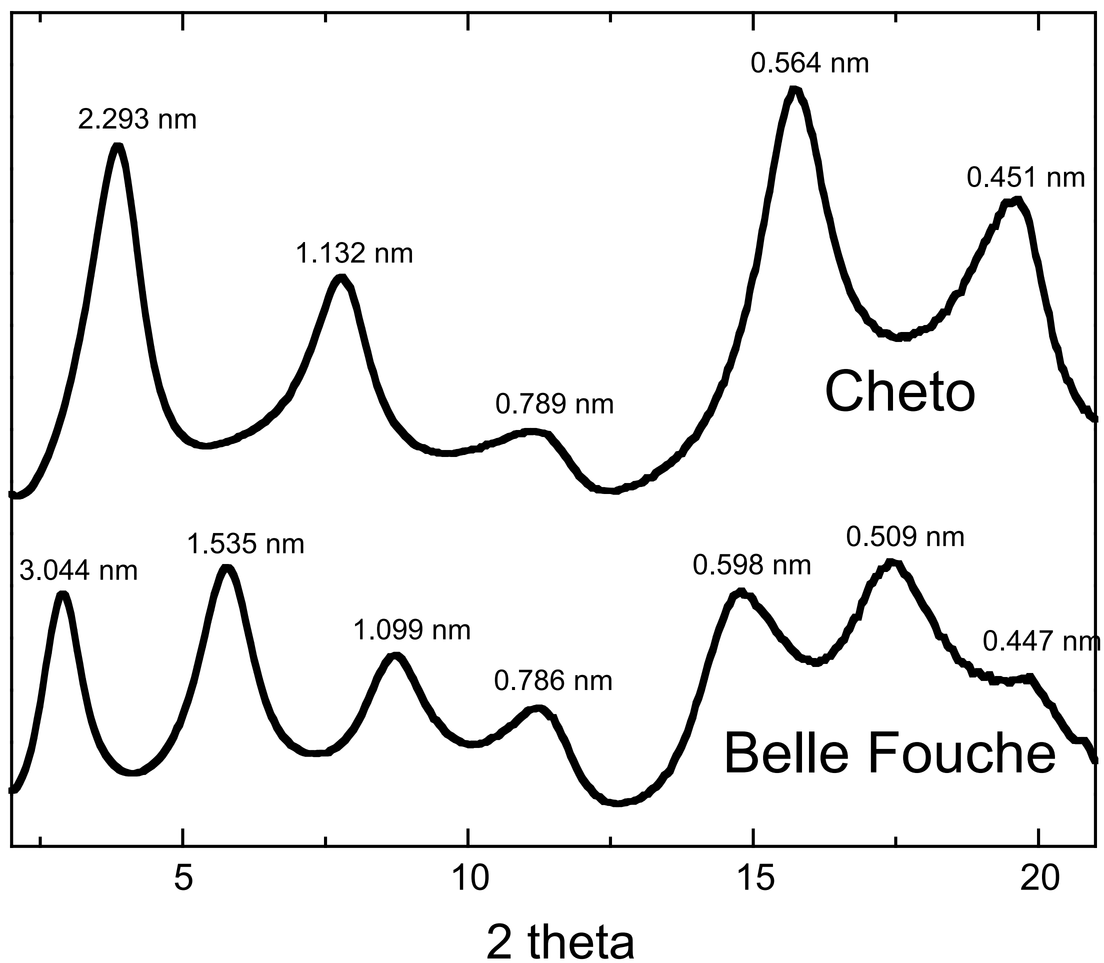


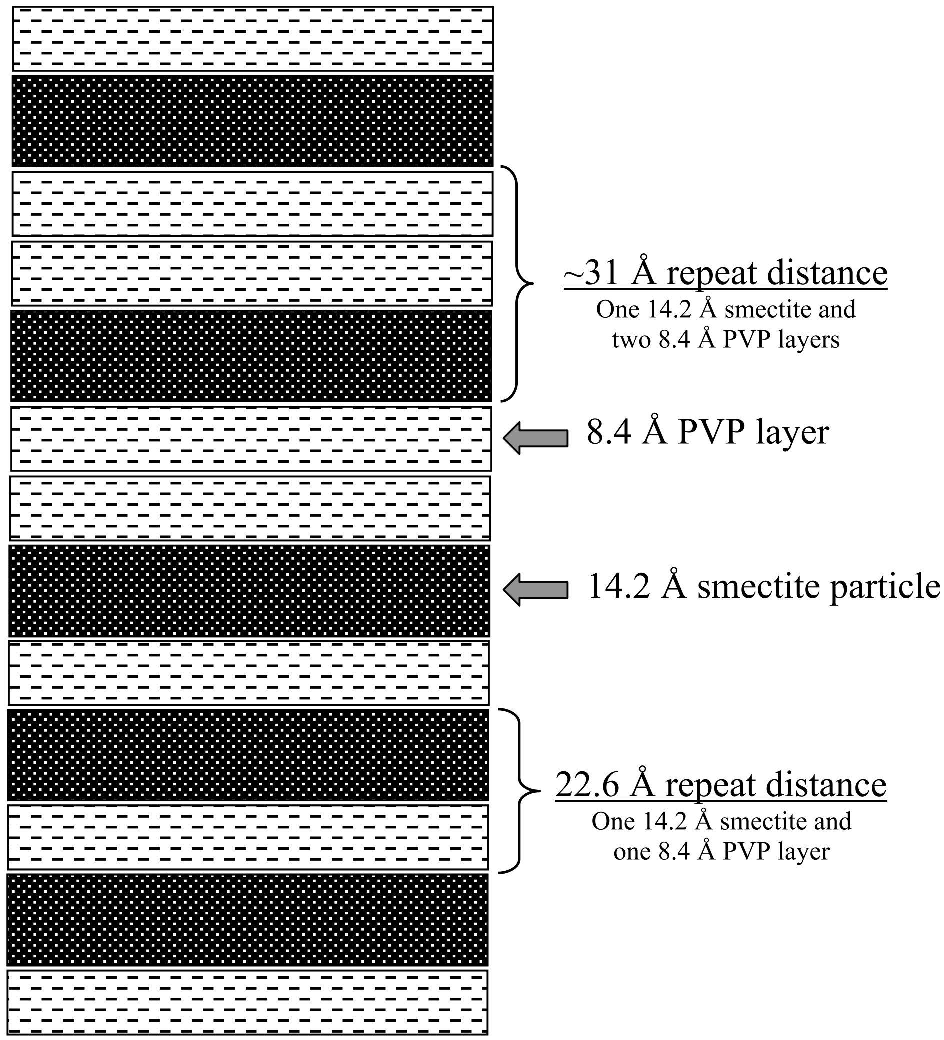
fig. 6b
Cheto
Intensity (thousands of counts per second)
2 theta
100 mg/ml 22.78 Å 11.11 Å
60 mg/ml 22.07 Å 11.25 Å
50 mg/ml 22.93 Å 11.33 Å
40 mg/ml 23.23 Å 11.47 Å
30 mg/ml 23.78 Å 11.25 Å
20 mg/ml 23.24 Å 11.54 Å
14 mg/ml 23.54 Å 11.54 Å
4 mg/ml 24.81 Å
1 mg/ml 23.59 Å
0
5
10
15
20
25
30
35
40
1
3
5
7
9
11
13
15

Fig. 7*(new)*



0.564 nm
2.293 nm
0.451 nm
1.132 nm
Cheto
0.789 nm
1.535 nm
0.509 nm
3.044 nm
0.598 nm
1.099 nm
0.447 nm
0.786 nm
Belle Fouche
5
10
15
20
2 theta

Fig. 8


~31 Å repeat distance
One 14.2 Å smectite and
two 8.4 Å PVP layers
8.4 Å PVP layer
14.2 Å smectite particle
22.6 Å repeat distance
One 14.2 Å smectite and
one 8.4 Å PVP layer

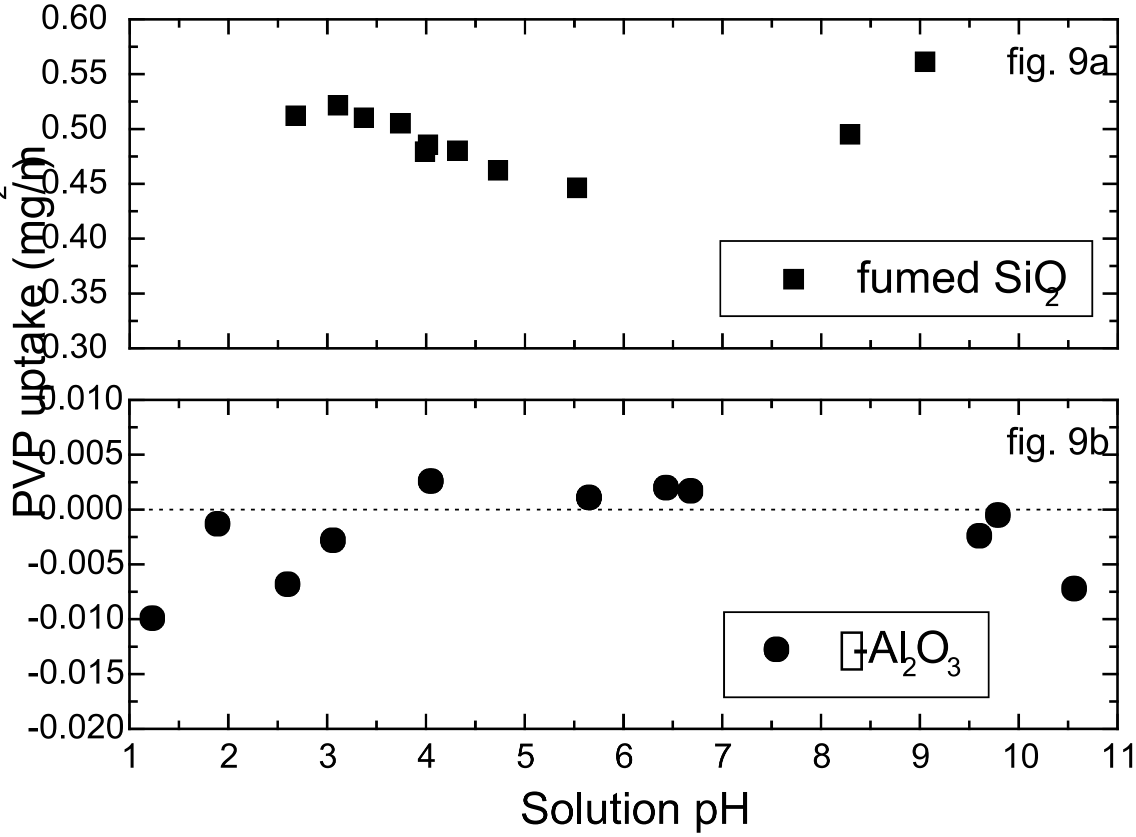
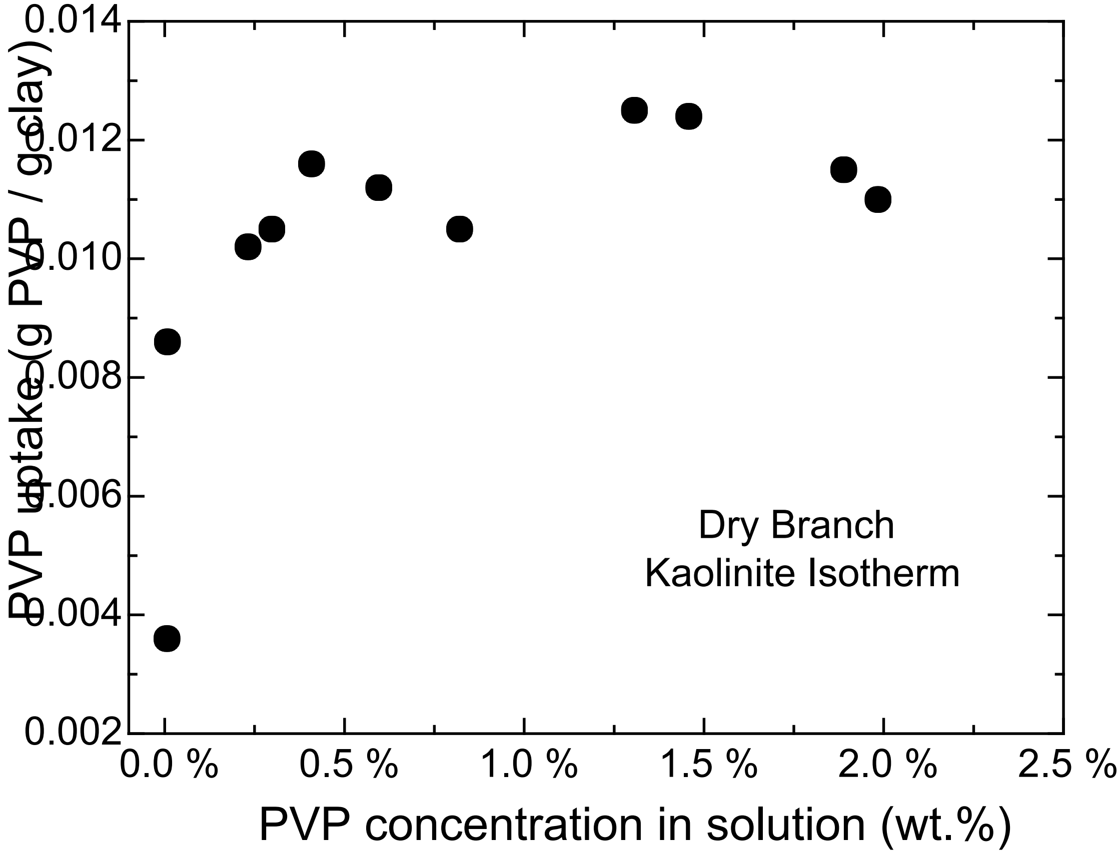


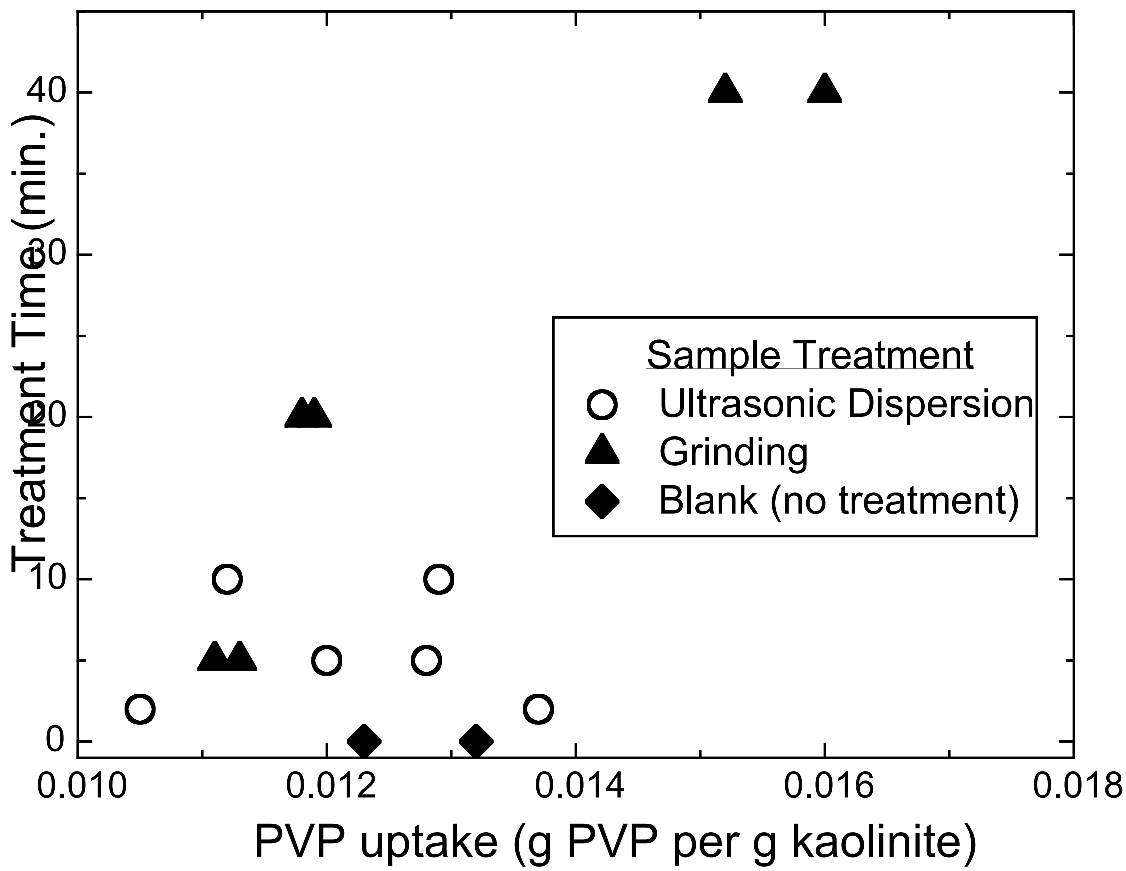
fig. 9a
fumed SiO2
fig. 9b
-Al2O3
PVP uptake (mg/m2)
Solution pH
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.010
0.005
0.000
-0.005
-0.010
-0.015
-0.020
1
2
3
4
5
6
7
8
9
10
11

Fig. 10



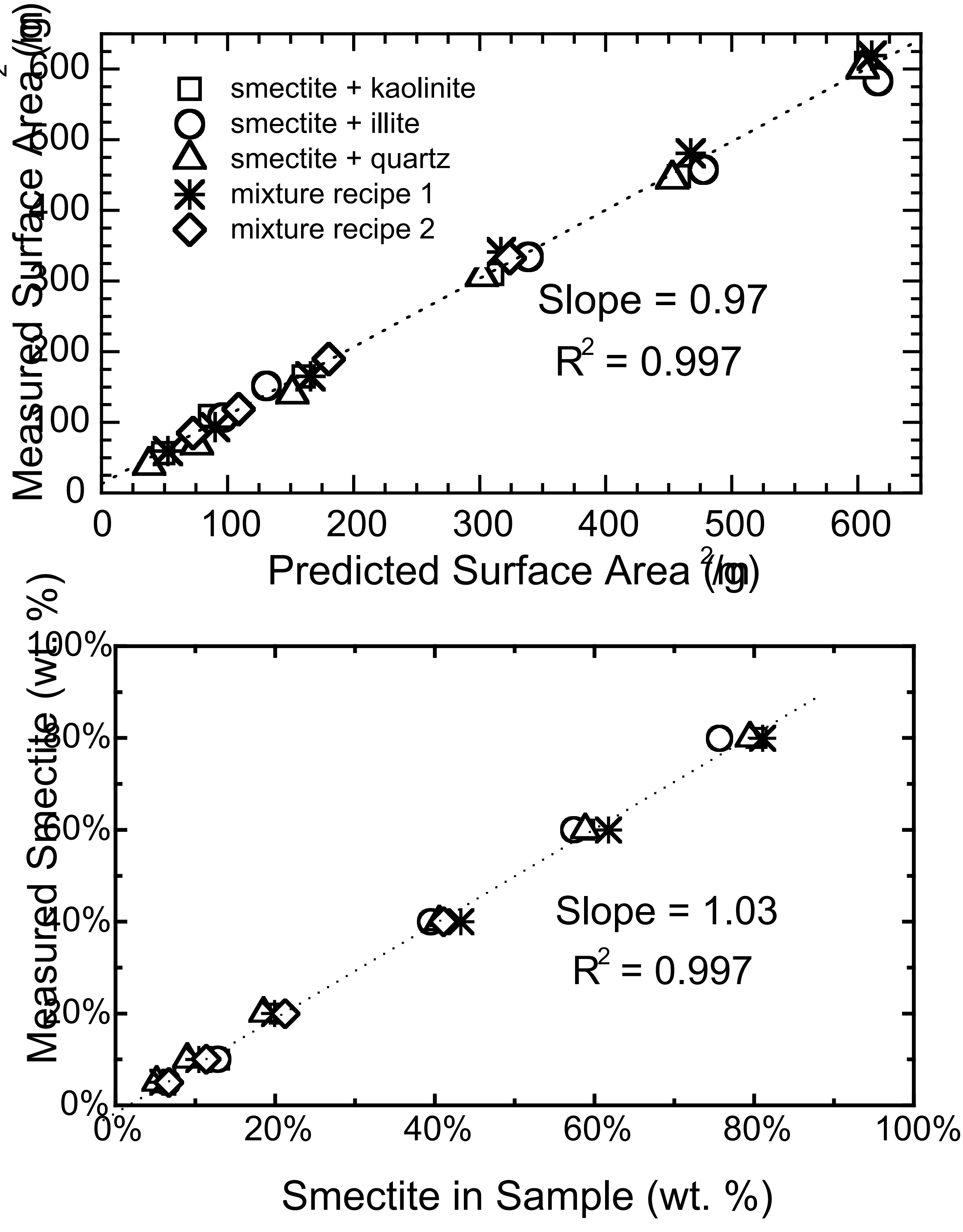
PVP uptake (g PVP / g clay)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.0 %
0.5 %
1.0 %
1.5 %
2.0 %
2.5 %
PVP concentration in solution (wt.%)
Dry Branch
Kaolinite Isotherm

Fig. 11



Treatment Time (min.)
40
30
20
10
0
0.010
0.012
0.014
0.016
0.018
PVP uptake (g PVP per g kaolinite)
Sample Treatment
Ultrasonic Dispersion
Grinding
Blank (no treatment)

Figure 12


smectite + kaolinite
smectite + illite
smectite + quartz
mixture recipe 1
mixture recipe 2
Slope = 0.97
R2 = 0.997
Measured Surface Area (m2/g)
Predicted Surface Area (m2/g)
0
100
200
300
400
500
600
Slope = 1.03
R2 = 0.997
Measured Smectite (wt. %)
Smectite in Sample (wt. %)
0%
20%
40%
60%
80%
100%