Fluidized-Bed Reactor to Study Physico-Chemical Kinetics in Heterogeneous Soils and Sediments

2.1 INTRODUCTION

Chemical reactivity assessments of unconsolidated geosolids as sediments or soils (hereafter sediments) are typically performed by batch or column experiments. Within well-mixed batch reactors fluid and solids interact in a homogeneous suspension, while within column reactors the packed solid matrix interacts with the passing fluid. The main disadvantage of the batch reactor type is the build-up of reaction products and depletion of reactants. This transient state of chemical conditions complicates the assessment of kinetic controls (Chou and Wollast, 1984). Column experiments come closest to simulating hydrogeochemical processes under natural flow conditions. However, chemical gradients across the column and physically controlled kinetics, such as inter-aggregate and film diffusion, complicate the assessment of chemical reaction kinetics during column experiments.

Fluidized-bed reactors are a hybrid of column and batch reactors, in that aqueous chemical conditions can be kept constant while maintaining a well-mixed system and minimizing physical control on reaction kinetics. Unlike batch reactors, however, used, fluidized-bed reactors have been used rarely for sediment reactivity experiments. Some applied the fluidized-bed technique in weathering studies using particles with narrow grain size ranges (Chou and Wollast, 1984; Postma, 1990; van Hees et al., 2002), while (Griffioen, 1999) performed fluidized-bed experiments on aquifer sediments to study the biodegradation of organic contaminants.

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Here, fluidization is defined as the suspension of grains by a sufficiently fast upward flow through a granular bed (e.g. Leeder, 1982; Viessman and Hammer, 1998) and occurs when the upward flow velocity in the reactor overcomes the gravitational force on the solid grain particles (Fig. 2.1). Fluidized-bed reactors are widely used in chemical and biological engineering for chemical and physical production or treatment processes. In these reactors, the carrier or sorbent particles used are typically of uniform size and density. Therefore, the wide range of particle sizes and densities in natural sediments is an important difference with most industrial applications of fluidization.

![Fluidized-Bed Reactor Diagram](image)

**Figure 2.1** Conceptual Fluidized-Bed Reactor containing uniform particles. Degree of Bed Expansion (DBE) as related to upward flow velocity ($V_f$).

Not only do sediment particles exhibit a variety of particle sizes and densities, they also differ in physico-chemical reactivity. While in batch experiments all particles are retained within the reactor, fluidization can result in the loss of particles from the reactor. Minimization of particle loss due to elutriation is therefore important.
to prevent bias of experimental results. Additionally, reduction of particle elutriation may prevent technical problems due to clogging of tubing or filters.

Here, the hydrodynamical behavior of sandy sediments is studied during fluidization to determine how fluidized-bed reactors can be used in biogeochemical kinetic experiments. An experimental fluidized-bed reactor is designed and built considering specifically both the wide range in hydrodynamic behavior of sediment particles and experimental requirements.

Figure 2.2 Nomograph of settling velocities (m/s) as a function of particle size and density according to Stokes’ law (Eq. 2.1). Lines represent equal settling velocities according to Equation 2.2. Reynolds’ number <1 correspond roughly to settling velocities below 0.01 m/s. As an example, common sedimentary particles with various densities and sizes (Table 2.1) are plotted for an equal settling velocity of 0.001 m/s. Symbol size represents relative linear diameter. Shaded area represents an example range of the particles that can be fluidized by the reactor designed.

### 2.2 Theoretical Background

Settling velocity is the main particle characteristic that determines its behavior during fluidization. Sediment particles exhibit a variety of particle sizes and densities, resulting in a wide range of settling velocities (Fig. 2.2). Stokes’ law describes the dependency of unhindered terminal particle settling velocities ($V_g$) on the basis of their diameters ($d_p$ in m) and densities ($\rho_p$ in kg/m$^3$) under laminar flow conditions:

$$
V_g = \frac{gd_p^2(\rho_p - \rho_w)}{18\mu}
$$

*Equation 2.1*
where $\rho_w$ is the density of water, $\mu$ is the dynamic viscosity of water (1 mPa.s) and $g$ the gravitational acceleration (9.81 m/s$^2$).

Table 2.1

According to Stokes’ law, these examples of quartz and potentially redox-reactive sedimentary particles have a settling velocity of 1 mm/s and illustrates the interaction between density and particle size, as shown in Figure 2.4. Density data obtained from (Tyson, 1995).

<table>
<thead>
<tr>
<th>Species</th>
<th>Density (Kg/m$^3$)</th>
<th>Particle Diameter (µm)</th>
<th>Settling Velocity (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pollen</td>
<td>1100</td>
<td>135</td>
<td>1</td>
</tr>
<tr>
<td>Jet</td>
<td>1300</td>
<td>78</td>
<td>1</td>
</tr>
<tr>
<td>Anthracite</td>
<td>1600</td>
<td>55</td>
<td>1</td>
</tr>
<tr>
<td>Quartz</td>
<td>2650</td>
<td>33</td>
<td>1</td>
</tr>
<tr>
<td>Pyrite</td>
<td>4800</td>
<td>22</td>
<td>1</td>
</tr>
</tbody>
</table>

On the basis of Stokes’ law, particles of different densities and size have identical settling velocities (Fig. 2.2) when:

$$\frac{\rho_1 - \rho_w}{\rho_2 - \rho_w} = \left(\frac{d_2}{d_1}\right)^2$$

Equation 2.2

where subscript 1 and subscript 2 refer to particle type 1 and 2, respectively.

When the Reynolds number ($V_s \rho_v d_p / \mu$) increases above 1, the error in the absolute value of calculated settling velocities increases, owing to turbulent effects. Additionally, Stokes’ law does not account for effects of shape and roughness. Nevertheless, Stokes’ law-like behavior has been observed for settling porous sediment aggregates with a Reynolds number up to 11 (Van der Lee, 2000; Wu and Lee, 1998).

Under laminar flow conditions, Stokes’ law is used directly to describe either settling or fluidization behavior of a sufficiently isolated particle. However, the physical interaction of neighboring particles in a fluidized-bed results in a loss of kinetic energy. Moreover, the particle concentration in the bed affects the space for the upward fluid to flow through and thus influences the effective flow velocity. Therefore, the minimum flow velocity ($V_{f_{\text{min}}}$) required to fluidize a certain set of particles depends on porosity ($\varepsilon$) as follows;

$$V_{f_{\text{min}}} = \varepsilon^n V_s$$

Equation 2.3

where $n$ is a function of particle characteristics and flow regime as described in engineering textbooks or specialized publications (e.g. Godard and Richardson, 1969;
Richardson and da S. Jeronimo, 1979; Viessman and Hammer, 1998). For the practical purpose of this study we assume Stokes’ law and porosity only (i.e. n=1, Eq. 2.3).

2.2.1 Geo-scientific Applications of Fluidized-bed Reactors

Resuspension of sediment and intense mixing within the water column occurs in deltaic and continental systems. These natural dynamic conditions resemble those of fluidized-bed reactors and result in the efficient mineralization of sedimentary organic matter (Aller, 1998; Aller et al., 1996). Therefore, fluidization is not only a valuable experimental technique. It has also the potential to simulate the specific physico-chemical conditions during intense reworking, re-suspension and liquefaction of sediments.

Fluidized-bed reactors have been applied for various environmental and geochemical research purposes. Most studies have used such reactors mainly in the context of wastewater engineering because the high degree of mixing of the water and solid phase minimizes physical limitations and favors microbial growth processes. For example, a fluidized-bed reactor allows high substrate loadings to enrich slow growing solid-phase-associated biomass on sparingly soluble polyaromatic hydrocarbons (Rockne and Strand, 1998). Furthermore, during the bioremediation of contaminated water the recirculation of the water phase may dilute the influent contaminant concentration below a toxic level that allows its degradation (Langwaldt and Puhakka, 2000). Abiotic studies used fluidized bed reactors to study mineral dissolution to enable the maintenance of a constant undersaturation in the aqueous phase with respect to the mineral under study (Chou and Wollast, 1984). The control of pH on dissolution kinetics was tested by the possibility of instantly changing the acidity of the influent without disturbing the solid phase. Clearly, the use of a fluidized-bed reactor enables to evaluate the effect of various chemical conditions on the (bio)geochemical process of interest, by an instant change of the influent composition without manipulation of the solid phase.

An alternative application of sediment fluidization is hydrodynamic separation. Hydrodynamic separation of fine sediments fractions has been achieved using
SPLITT-fractionation (Contado et al., 1997; Keil et al., 1994). Unfortunately, this technique is not applicable for coarser (> 100µm) size fractions due to technical limitations. Hydrodynamic separation of coarser grained particles can be achieved by a sequence of widening elutriation columns (Nicholas and Walling, 1996; Walling and Woodward, 1993). Alternatively, fluidization is used for hydrodynamic separation as shown for binary particle mixtures (Rasul et al., 2000) and offers the advantage that flow velocity is a continuous variable.

### 2.3 Material and Methods

Grain size fractions of crushed silicate rock, taken from a previous study on the dissolution kinetics of olivine (Jonckbloedt, 1998), were obtained by wet-sieving 2 kg of sand for 20 min, using 20 cm diameter sieves and a sieve machine (Retsch Vibro). The sieved fractions were subsequently ultrasonically treated to remove adhering fines. Grain size distributions of the particle fractions and sediments were determined with a Laser Particle Sizer (Malvern Series 2600).

Fluidization experiments were performed with different size fractions of silicate sand (Table 2.1). The particles had a packed porosity of 0.39 and a density of 2.9 kg.m\(^{-3}\) as determined using standard techniques (Goudie, 1990). Experiments were performed in graded glass columns of 30 cm height (internal \(\varnothing\) 5.7 cm) with a bottom glass filter to evenly distribute the upward water flow from a water faucet. Velocity measurements were determined using a stopwatch.

Elutriation experiments were performed using the graded class columns described above. After each experiment, elutriates and residues were collected after which their particle size distributions were determined. A 1:1 weight mixture of the 63–150 and the 150–500 µm sieve fractions served as starting material. This mixture was exposed to the upward flow velocity (1.6 cm/s) that was required to totally elutriate the 63–150 µm sieve fraction. The collected elutriate of this mixture at this flow velocity was exposed to a halved upward flow velocity of 8 mm/s. In addition, a sample taken from a sandy soil in the eastern part of the Netherlands was exposed to this upward flow velocity.
Figure 2.3 Behavior of the particle size fractions 63–150 µm, 150–500 µm, 500–2000 µm and >2000 µm during fluidization experiments. Solid lines represent the predicted behavior using Stokes’ law (Eq. 2.1). Dashed lines represent the predicted behavior using the empirical model developed by (Gibbs et al., 1971). Both predictions were corrected for porosity using Equation 2.3. Porosity of 0.39 at DBE=1, density 2900 kg/m³.

2.4 RESULTS AND DISCUSSION

Sieve fractions of crushed silicate rock were used to study the hydrodynamic behavior of sediments during fluidization. Firstly, the relation between upward flow velocity \( V_f \) and the degree of bed expansion (DBE, Fig. 2.1) is discussed. Secondly, the relation between upward flow velocity and the elutriation of particles is assessed. Finally, the design of the fluidized-bed reactor is presented.

2.4.1 Fluidization Behavior of Sieved Particle Size Fractions

The increase of upward flow velocities resulted in a smooth progressive expansion of the bed for the two finest fractions (Fig. 2.3). This indicated homogeneous fluidized-bed conditions during the fluidization experiments. The
minimum upward effective flow velocities through the bed needed for fluidization of the 63–150 µm fraction is similar to the settling velocity of their finest end member as predicted by Stokes’ law (Eq. 2.1). With increasing flow velocities, the Reynolds number increases and Stokes’ law is no longer valid. Therefore, the fluidization velocity of the 150–500 µm particle sieve fractions is better described by an empirical relationship derived for silicate-density particles by (Gibbs et al., 1971). Fluidization of the two coarsest fractions required very turbulent flow conditions and these fractions could not be stably fluidized under the experimental conditions.

The elutriation experiments performed on the silicate sand fraction and a natural soil sample showed that, at a certain upward flow velocity, the finest particles are flushed out of the column while keeping a range of larger sized particle fluidized (Fig. 2.4). At an upward flow velocity of 16 mm/s, the sieve fraction 63–150 µm was completely flushed out of the column. When exposing the 63–500 µm mixture (Fig. 2.4a) to the same upward flow velocity the particle size distributions of the resulting elutriated and residual fractions were very similar to that of the original 63–150 µm and 150–500 µm sieve fractions (Fig. 2.4b).

When the particle fraction elutriated at 16 mm/s and the bulk soil was exposed to an upward flow velocity of 8 mm/s, particles with an average size of 100 µm were flushed out in both samples (Fig 4c). The particle size distribution of the elutriated material was very similar in both samples, considering the differences in material composition. The particle size distributions of both residue fractions were dissimilar. This is mainly due to the presence of coarser particles in the original soil sample.

The elutriation experiments show that the technical challenge of fluidizing a complete sediment sample is to keep the heavier and larger particles fluidized while preventing the lighter and smaller particles to escape the fluidized-bed column. A practical solution to this problem is to decrease the upward flow velocity in the upper part of the column by increasing the cross-sectional area of the column. For example, doubling the internal diameter of the reactor produces a four-fold increase in its cross-sectional area and a similar reduction in upward flow velocity.
2.4.2 Design of Fluidized-bed Reactor

A fluidized-bed reactor was designed and built for the specific purpose of kinetic sediment experiments (Fig. 2.5). The reactor has a volume of 1 liter with a diameter of 1 cm in the lower part of the reactor and a diameter of 12 cm in the upper part. The small reactor volume enables both high liquid mixing and refresh rates. Moreover, the 12-fold increase in cross-sectional diameter from the bottom to the top of the column results in a large retention capacity of sedimentary particles, since the decrease in upward flow velocity allows for a 144-fold range in particle settling velocities. Additionally, the minimum flow velocity to fluidize the particle in the lower part of the reactor depends on the porosity of the fluidized-bed (Eq. 3).

Assuming a porosity of 0.25 (DBE=1) in the lower part of the fluidized-bed, even a
maximum range in settling velocities of 576-fold is achieved. For example, sediment particles with a settling velocity of 5.76 cm/s (~200 µm quartz grains) can be fluidized, while retaining sediment particles with a settling velocity of 0.1 mm/s, which corresponds roughly to quartz grains of 10 µm (Fig. 2.2).

Figure 2.5  Fluidized-bed reactor design

Characteristic upward velocities needed to fluidize sediments range from 0.001 to 0.01 m/s (Fig. 2.2). This requires a combined flux from the influent and recirculation pumps of about 5–50 ml/min. Despite the strong radius increase in the upper part of the fluidized-bed reactor, the relatively small total reactor volume of one liter allows for fast response with hydraulic retention times smaller than one day and recirculation rates of several times per hour. Moreover, the steep internal angle (61°) of the glass column prevents significant deposition of fine particles on the reactor walls.

In addition to these experimental requirements regarding sediment particle characteristics and flow conditions, reactors may be used to study biogeochemical processes that require anoxia. Therefore, the fluidized-bed reactor consists of glass and the main tubing consists of stainless steel with gastight connections (Serto). Peristaltic pumps instead of piston pumps were used to add and recirculate the aqueous solution, since they allow the transfer of unfiltered solutions. To minimize the potential for oxygen diffusion into the system, Tygon tubing (Tygon LFL,
Fluidized-Bed Reactor

Masterflex) was used in the peristaltic pumps because of its low gas permeability of $0.79 \times 10^{-10}$ m$^2$.s$^{-1}$ (Kjeldsen, 1993).

2.5 CONCLUSIONS

Sediments contain potentially reactive particles that cover a wide range in size and density. To be able to retain this variety of representative particles, a fluidized-bed reactor for sediments was developed on the basis of observed hydrodynamical behavior during fluidization. This fluidized-bed reactor is suitable for sediment studies on biogeochemical kinetics under minimized physical kinetic limitations. The reactor is suitable for both oxic and anoxic experimental conditions.

References


