Soil remediation after radioactive contamination Study of illite clay extraction by dispersed air flotation in a new instrumented column

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Soil remediation after radioactive contamination: Study of illite clay extraction by dispersed air flotation in a new instrumented column

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ABSTRACT
A new instrumented flotation column that is halfway between the pilot and the lab scale is presented. This installation works in continuous mode and allows both bubble size distribution and gas hold up measurement in the slurry. In the present study, it was used in the context of clay extraction. The final objective was to employ this flotation process for radioactive soil remediation. Data were interpreted using a two-zone model based on mass balance. A cationic surfactant (TTAB) is able to adsorb on the negatively charged clay particles surface and modifies the hydrophobicity to different extents depending on the employed TTAB quantity. We looked at the influence of TTAB/clay mass ratio on flotation performances, bubble size distribution and gas hold up. Consistent and reproducible data were obtained. The flotation rate constant increases with the TTAB/illite ratio whereas bubble size decreases. Gas hold up measurements underlined an accumulation of small bubbles at the highest TTAB/illite ratio tested due to their small buoyancy.

Keywords: bubble, clay, column, particulate flotation, remediation

INTRODUCTION
After a nuclear accident like the one of Fukushima Daiichi in 2011, radioactive cesium aerosols are emitted (Miyamoto, Yasuda et al. 2014) and transported by wind and rain water to the neighboring soils surface. Cesium is then solubilized in water (Tanaka, Sakaguchi et al. 2012) and can penetrate in the soils. Clays are micrometric phyllosilicate minerals that are present in most of the soils (ex: 9 to 40% in Japanese paddy soils (Nakao, Ogasawara et al. 2014)). These minerals, and especially the varieties called illite and vermiculite, contain adsorption sites located on layer edges on which cesium ions can selectively sorb in presence of other competing ions like sodium or calcium (Sawhney 1972). Furthermore, adsorption is known to be nearly irreversible and very resistant to washing. (Bostick, Vairavamurthy et al. 2002) Thus, the objective of the work was to find a process to selectively extract these contaminated clay particles to reduce the radiological activity of the remaining soil fraction and allow its use for human activities.

Particulate flotation was thought of as good option because of its reduced cost and modularity. (Faure and Messalier 2012). Furthermore, clay particles are negatively charged at neutral pH and a cationic surfactant can be used to modify their surface hydrophobicity. Prior to large scale flotation experiments and to get a good understanding of the system behavior, a new instrumented flotation column working in continuous mode was developed. This column has the originality of being halfway between a pilot scale unit and a lab scale unit. Experiments can be easily multiplied to study the influence of different parameters like the air flow or the collector concentration. The bubble size in the aerated suspension and the gas hold up can also be measured.

First, the flotation column and its instrumentation will be described and then the flotation model based on a mass balance that was used to interpret data will be presented. Finally, an example of application on the flotation of natural illite clay will be given. The influence of the collector mass ratio relatively to the mass of clay on flotation performances, gas hold up and bubble size will be studied.

METHODS

New instrumented flotation column

Global description

A schematic description of the continuous flotation column is presented in figure 1.

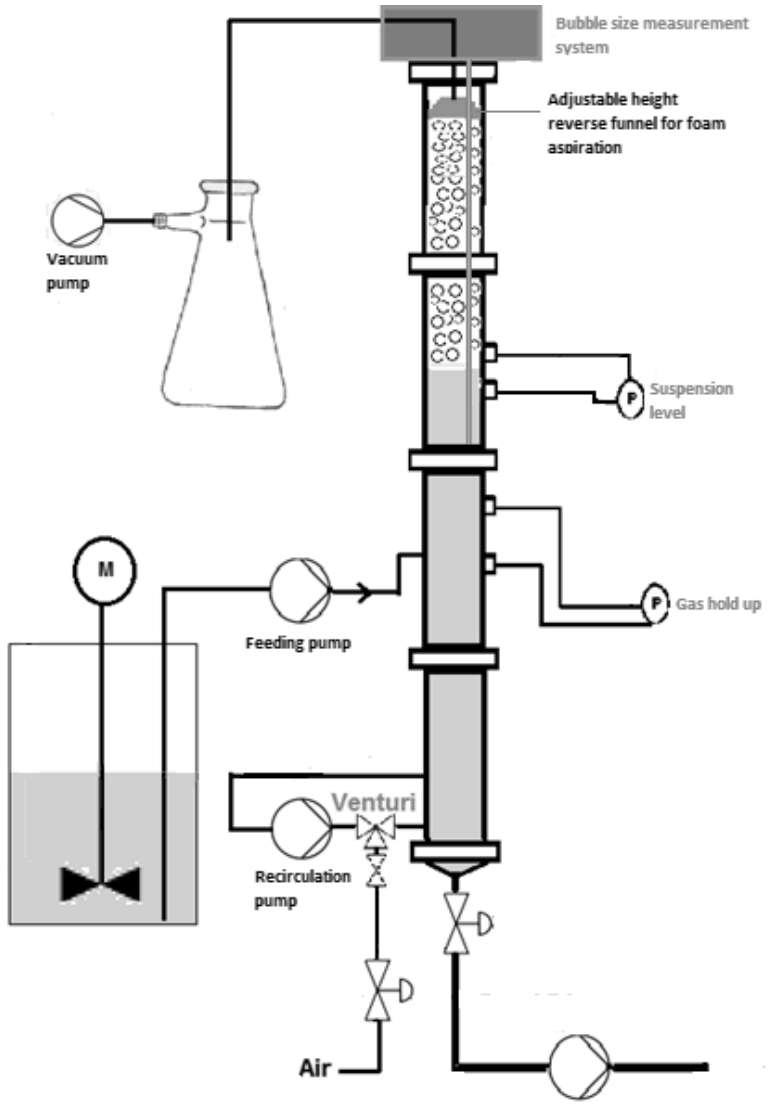

Figure 1: Schematic representation of the continuous flotation column

The column is 160 cm high and has a diameter of 8 cm. Air bubbles are injected at the bottom of the column in a 15 cm height aeration region thanks to a tangential Venturi aerator (diameter: 4 mm). The clay suspension was recirculated at a flow of 11 L min^{-1} through the aerator and the air flow was controlled by a mass flow meter. Two cross-shaped baffles were placed at 2.5 cm above and below air injection point in order to avoid the formation of a vortex and bubble axial clustering. Clay pulp was injected at a height of 60 cm and had a counter-current contact with rising air bubbles. The collection region had a fixed height of 81 cm and it was controlled by a differential pressure sensor (Deltabar S, ENDRESS+HAUSER,

Germany) linked, through a computer interface, to a discharge electrovalve for the regulation of the floated pulp flow. The froth was collected with a reverse funnel connected to a vacuum pump. The funnel height was adjusted to modify the froth residence time in the column before removal. Gas hold up was determined with a differential pressure sensor (Deltabar S, ENDRESS+HAUSER, Germany) located in the collection region. The two pressure gauges were separated by 10 cm and calibration was performed on tap water without aeration. The gas hold-up $\boldsymbol{\varepsilon_g}$ was calculated using the following formula:

$$\boldsymbol{\varepsilon_g = \frac{\Delta P - (\rho_{water} - \rho_{pulp}) \times g \times d}{\rho_{pulp} \times g \times d}} \quad \textbf{(Equation 1)}$$

where ΔP is the differential pressure, ρ_{water} is water density, ρ_{pulp} is the pulp density (determined by dry extract), g is acceleration constant and d is the distance between pressure gauges (i.e. 10 cm).

Bubble size measurement

The air bubble size in the collection region was determined using an intrusive bubble sampling technique (Randall, Goodall et al. 1989; Grau and Heiskanen 2002) constituted of a 1 cm diameter and 80 cm long pipe filled with deionized water and 4 mg L^{-1} of TTAB (non-coalescing liquid) that is immersed in the pulp. The free TTAB concentration was determined using adsorption data from a previous study (Chapelain, Faure et al. 2016). It corresponds to the concentration of unadsorbed TTAB at a TTAB/illite ratio of 0.9%. Bubbles are conveyed up to a lighted viewing chamber on which is directed a high speed camera (see figure 2). Image analysis was made by a "home-made" Labview application and gave a bubble size distribution in number.

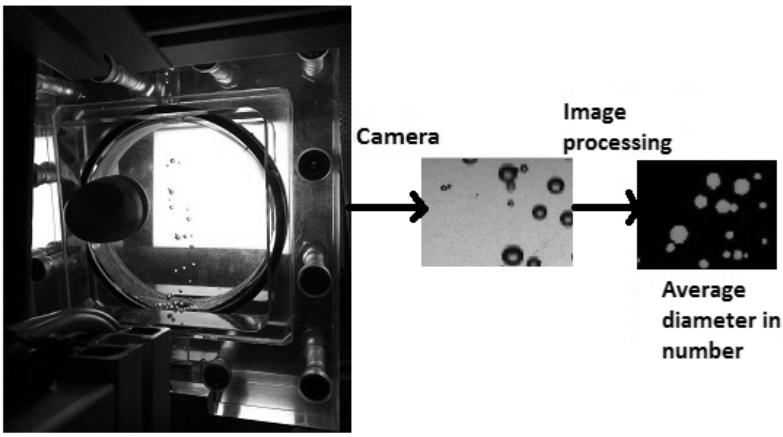

Figure 2 : Schematic representation of bubble size measurement set up

Experimental procedure

Materials

Natural illite clay was provided by the company Argile Du Velay (Saint Paulien, France). It is characterized by a broad size distribution between few micrometres to about 70 µm (D_{50} = 12.5 µm). Tetradecyltrimethyl ammonium bromide (TTAB) cationic surfactant was obtained from Fluka with a 98% purity.

Protocol

The feed pulp (30 L) was prepared 30 min before starting the experiment and was kept under continuous stirring. It contained a concentration of 50 g L^{-1} of clay and varying TTAB/illite ratios defined as:

$$\mathbf{TTAB/_{illite}\ ratio} = \frac{\textbf{mass of TTAB in the pulp}}{\textbf{mass of clay in the pulp}} \times \mathbf{100}\ \textbf{(Equation 2)}$$

The pulp feed flow (Q_1) was fixed at 0.5 L min^{-1} for all experiments. The gas hold up ε_g was unstable during the first minutes of experiment (when the column was in unsteady conditions) so data acquisition started only after 10 minutes. Four different froth heights were successively tested during each experiment. The froth was collected during 10 minutes at each height and weighed.

Clay concentration in floated pulp and froth by drying

Clay concentration in the floated pulp and in the froth was determined by dry extract. Samples were dried at 60 °C during 24 h.

The volume liquid fraction $\varepsilon_{wh\,exp}$ in the froth was calculated at each froth height h with the hypothesis that all injected gas was conserved:

$$\boldsymbol{\varepsilon_{wh\,exp}} = \frac{\boldsymbol{Q_{water}}}{\boldsymbol{Q_{water}+Q_{air}+Q_{clay}}}\ \textbf{(Equation 3)}$$

where Q_n represents the volume flow (L min^{-1}) of water, air and clay.

Flotation model

The two-zone flotation model used in this study takes into account three transport phenomena occurring in the aerated pulp and the froth: true flotation, entrainment and drainage. Micro-scale phenomena (ex: collision, capture and attachment probability (Bloom and Heindel 1997), Plateau border geometry (Haffner, Khidas et al. 2015)) are neglected to simplify the mathematical approach. A similar model was used in the past for paper deinking (Beneventi, Allix et al. 2008; Beneventi, Allix et al. 2009; Allix, Zeno et al. 2011).

A perfectly stirred flotation cell containing a fixed volume V of pulp with a particle concentration c which is stable overtime is considered in this modelling approach, as presented in figure 3.

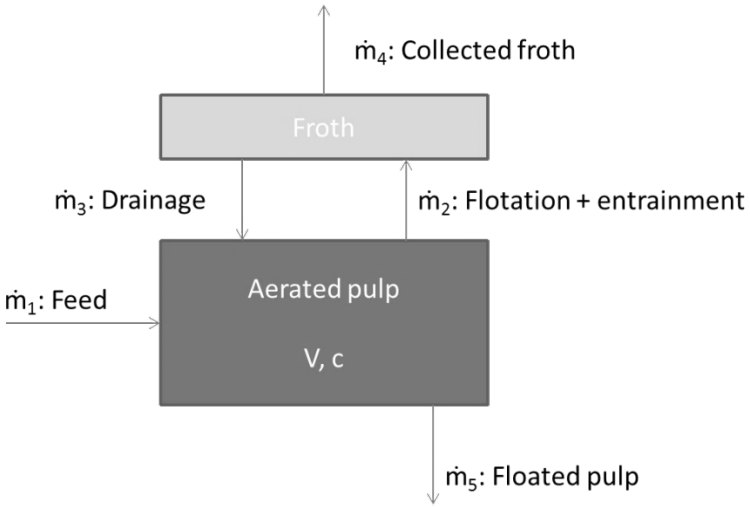

Figure 3 : Schematic representation of mass flows $\dot{m}_n$ involved in flotation in a two-zone model.

The global mass balance is equal to zero because the system has reached its equilibrium:

$$\dot{m}_1 + \dot{m}_3 - (\dot{m}_2 + \dot{m}_5) = V.\frac{\boldsymbol{dc}}{\boldsymbol{dt}} = 0$$

$$\Leftrightarrow \dot{m}_1 + \delta \cdot \left(\frac{c.k.V}{Q_{air} \cdot \varepsilon_{w0}} + \varphi . c\right) . Q_{air} . \varepsilon_{w0} \left(1 - exp(-L_d . t) - E/\varepsilon_{w0}\right) - \left((k . V + \varphi . Q_{air} . \varepsilon_{w0}) c + (Q_1 - Q_{air} . (\varepsilon_{w0} . exp(-L_d . t) + E) . c\right) = 0$$ (**Equation 4**)

With δ the particle drainage coefficient, k the flotation rate constant (min^{-1}), ε_{w0} the liquid fraction in the froth at the interface between the aerated pulp and the froth, φ the concentration ratio due to entrainment defined as c_f/c with c_f the particle concentration in the wake of air bubbles. (Johnson 1972) L_d (min^{-1}) is the froth drainage constant and E an associated constant. These last two parameters were described in a previous study. (Chapelain, Faure et al. 2016)

k and δ were calculated by solving the equation 4 at 4 to 6 different foam heights (or foam residence time t). φ was estimated from the literature and the experimental data. The detailed description of φ estimation will be given in a future paper.

RESULTS AND DISCUSSION

The tested TTAB/illite ratios varied between 0.6 and 1.2%. Previous studies on the adsorption isotherm of TTAB on illite and zeta potential showed that in this range of ratios the surface is not totally covered with TTAB and is still negatively charged. (Chapelain, Faure et al. 2016)

Influence of TTAB/illite mass ratio on flotation performances

In figure 4 are presented the results of the liquid fraction measurements at different froth residence time and TTAB/illite ratios.

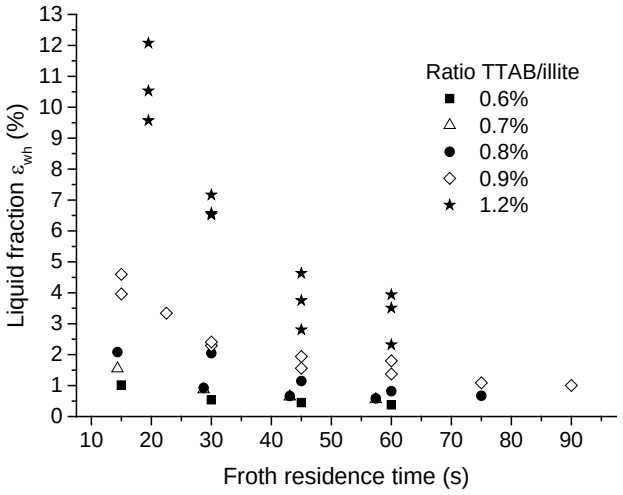

Figure 4: Evolution of the liquid fraction ε_{wh} in the froth with the froth residence time t

Overall, the froth was sufficiently humid to be vacuumed on the top of the column and the liquid fraction increased with the TTAB/illite ratio especially from the ratio 0.9%. The froth became humid above this TTAB/illite ratio. Nevertheless, it appeared that the liquid fraction decreases strongly with time whereas it was nearly stable between the ratios 0.6 to 0.8%. The evolution of the flotation rate constant k is presented in figure **5.**

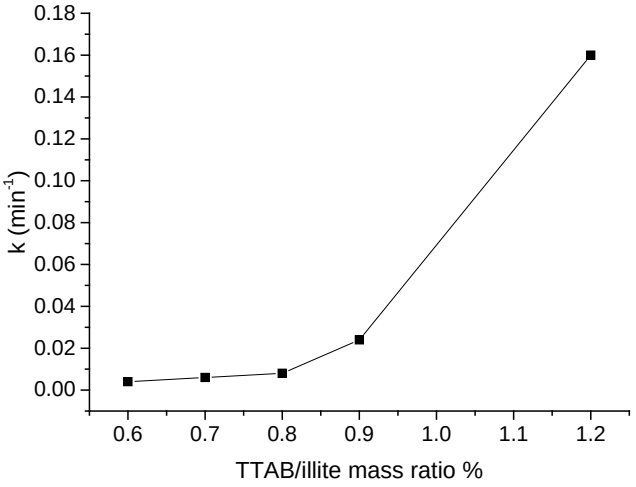

Figure 5: Evolution of the flotation rate constant k with the TTAB/illite ratio

As expected, k increases with the TTAB/illite ratio because the flotation is favored when the surface hydrophobicity increases. The increase is especially strong for the ratios 0.9% and 1.2%. Therefore, froths became at the same time more humid and charged when the TTAB/illite ratio increases. These two contributions are interrelated because the high clay content promotes froth stability and hence a higher liquid fraction.

Evolution of gas hold up and bubble size

In figure 6 and figure 7 are shown the results of gas hold up and bubble size measurements during the flotation experiments.

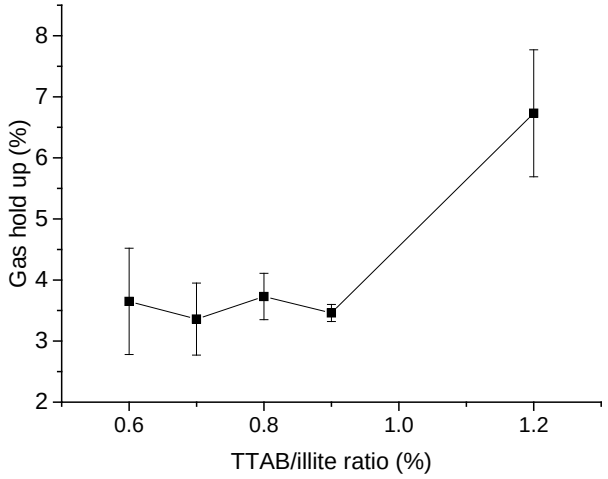

Figure 6: Evolution of gas hold up with the TTAB/illite ratio

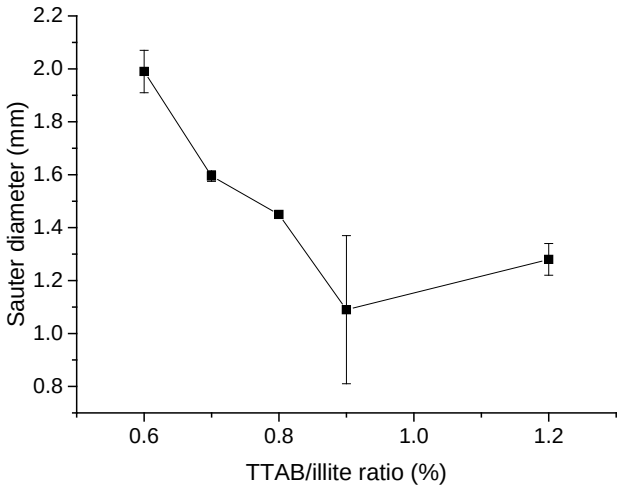

Figure 7: Evolution of bubble Sauter diameter with the TTAB/illite ratio

Bubble size decreased with TTAB/illite ratio from 2 mm to 1.2 mm and it was associated with a rise of gas hold up for the point at 1.2% only. Bubble size decreased because the density of adsorbed particles on bubbles has increased and these particles have a stabilizing effect on the air water interface (Binks 2002). The interfacial tension decreases and allows the formation of smaller bubbles that develop a larger surface area. Thus, it is known that there is a correlation between the bubble surface area expressed as a flux (m^2 s^{-1}) and the flotation rate constant k (Gorain, Franzidis et al. 1997). The strong increase of gas hold up observed at the TTAB/illite ratio of 1.2% may be due to air bubbles accumulation in the column because small bubbles are subject to a smaller buoyant force than big bubbles.

CONCLUSIONS

A new instrumented flotation column that is halfway between the pilot and the lab scale was presented. This installation works in continuous mode and allows both bubble size and gas hold up measurement. Froth humidity permitted its collect by vacuum. Consistent and reproducible results were obtained when looking at the influence of the TTAB/illite ratio on the liquid fraction of the froth, bubble size and gas hold up. It was shown that a two-zone model based on mass balance could be used to estimate the flotation rate constant.

A future paper will present the application of this experimental strategy to study the influence of air flow, clay granulometry and clay concentration on clay extraction.

ACKNOWLEDGEMENTS

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