## Summary

Small particles suspended in injection waters may cause more severe permeability damages than larger ones. In addition, the deposition kinetics increases as velocity decreases so that substantial permeability damages are expected at large distances from injection wells where remediation is questionnable.

This paper reports the main results of lab experiments carried out using very well-characterized systems. Colloidal particles were submicron monodispersed hydrophilic latexes and polydispersed sharpedged mineral particles. Porous media were obtained by packing sharp-edged grains of different sizes, giving a well-known microstructure. Water injections were performed at different flow rates and salinities. The laws of deposition kinetics which governs the depth of formation damage were determined under an adimensional form, including prefactors, for the case of weak or strong energy barriers between particles and pore surface. At intermediate salinity, real surfaces behaves as heterogeneous.

By extending a formation damage model based on a detailed physics to include surface heterogeneity of pore surface, a very good agreement between simulations and experimental results is obtained, giving confidence that the physics included in the model is pertinent. This model is thus a good tool to obtain in a practical case the parameters needed to predict injectivity damages.

## Introduction

Injection and re-injection of produced waters become an important issue with respect to environmental protection and profitability. Recently, laboratory (1) and field (2) observations confirmed the theoretical prediction that small micronic-size particles suspended in injection waters may cause severe injectivity decline. Indeed, in contrast with large particles which form remediable external cake, small particles can penetrate at large distances from injection wells where remediation is questionnable. In addition, injectivity decline may be very slow and thus not detected soon enough to be prevented.

In this paper are reported the results of a laboratory study aimed at determining the basic laws of deposition for stable small particles much smaller than pore throats, i.e. when there is no pore throat bridging. The experiments have been carried out in well-defined conditions so that deposition kinetics laws could be fully determined (including numerical prefactors) as a function of grain Peclet number and of pore wall-particle interaction energy (varying with salinity). The analysis of the results, using a permeability damage model based on a reliable physics at pore scale, shows that real pore surfaces are always heterogeneous in term of surface energy. When this heterogeneity is taken into account in the PARIS model (3) a very good agreement is found between experiments and model predictions. That gives useful tools to elaborate a lab methodology for injectivity prediction.

## Background

Permeability damage by retention of particles supended in injection waters has been analysed (1) as consisting in four more or less overlapping steps: 1) deposition onto grain and pore throat surfaces 2) formation of mono or multiparticle (4) bridges accross pore throats, followed by retention upstream from bridges 3) intemal cake building when non-percolation threshold is reached near the entrance of porous medium 4) external cake formation. The Paris model takes into account these four steps and uses the Grain and Pore Throat (GPT) model (5) to describe pore microstructure.

Pore surface deposition is of the utmost importance not only because it can affect significantly the permeability but also because it is a prerequisite for pore bridging and internal cake formation. Indeed, non-depositing particles smaller than pore throats move through porous media without affecting permeability. Since suspended particles and pore surface are usually negatively charged in the pH range prevailing in field conditions, the driving force for surface deposition in the convective diffusive regime comes only from van der Waals attraction, while the excess of positive charges in the gap between particles and pore surface creates an energy barrier which reduce deposition kinetics.

Deposition occurs in two stages 1) the particle transfer from the bulk to the interfacial region or interaction layer by convection and diffusion and 2) the attachment occuring by diffusion over the possible energy barrier. The deposition flux onto a collector is always anisotropic, being maximum onto the upstream side and decreasing as the azimuthal angle with flow direction increases. When collectors are packed to form in a porous medium, this anisotrpy is still increased further. This essential feature of deposition kinetics has been introduced in the Paris model as described in Ref. 3 and 6.

As soon as 1962, Levich (7) proposed the diffusion layer concept to solve the problem of mass transfer to an isolated sphere. This approximation is valid when $\mathrm{a} \ll \delta_{\mathrm{D}} \ll \mathrm{a}_{\mathrm{s}}$ where a and $\mathrm{a}_{\mathrm{s}}$ are particle and sphere radii respectively and $\delta_{\mathrm{d}}$ is the diffusion layer thickness $\delta_{\mathrm{d}}=\mathrm{a}_{\mathrm{g}} \mathrm{Pe}^{-1 / 3} . \mathrm{Pe}$ is the Peclet number $\mathrm{Pe}=2 \mathrm{Ua} / \mathrm{D}$ where U is flow velocity and D the particle diffusion coefficient.

In the absence of an energy barrier between particles and the sphere, the collection efficiency $\eta_{0}$, i.e. the collected-to-incident particle flux, has been calculated:
for an isolated sphere:

$$
\begin{align*}
\eta_{0} & =4 \mathrm{Pe}^{-2 / 3}  \tag{1}\\
\eta_{0} & =12.4 \mathrm{Pe}^{-2 / 3} \tag{2}
\end{align*}
$$

and sphere packs:
The increase in the prefactor from 4 to 12.4 comes from the change in velocity profile due to packing. The value of 12.4 is calculated by using the sphere-in-cell Happel model (8) for a porosity of $40 \%$, but other approaches gives similar results as well as experiments (9). For sharp-edged grain packs the prefactor in Equation (2) must be determined by experiments, using the relation:

$$
\begin{equation*}
\eta_{o}=-\mathrm{N}^{-1} \ln \mathrm{C} / \mathrm{Co}=-\frac{4 \mathrm{a}_{\mathrm{g}}}{3(1-\emptyset) \mathrm{L}} \ln \mathrm{C} / \mathrm{Co} \tag{3}
\end{equation*}
$$

where N is the number of successive grains on the pack length $\mathrm{L}, \varnothing$ is porosity and $\mathrm{C} / \mathrm{Co}$ the reduced outlet concentration, extrapolated for 1 PV injected, ensuring that deposition occurred on bare grains.

In presence of an energy barrier, Spielman and Friedlander (10), using the interaction force boundary layer approximation (IFBLA), calculated the collection efficiency $\eta$ for a sphere:

$$
\begin{equation*}
\eta=\alpha \eta_{o}=\frac{\beta}{1+\beta} \eta_{0} \quad \text { with } \quad \beta \approx 1.42 \alpha_{p c} \mathrm{Pe}_{\mathrm{s}}^{-1 / 3} \tag{4}
\end{equation*}
$$

where $\alpha_{\mathrm{pc}}$ is the physicochemical collision efficiency between particles and pore surface, $\mathrm{Pe}_{S}$ the surface Peclet number defined in Ref. 3 and 6: Pes $=\left(\mathrm{a}_{\mathrm{p}} / \mathrm{ag}_{\mathrm{g}}\right)^{3} \mathrm{Pe} \mathrm{g}$ and $\alpha$ is the collection efficiency factor.

In the convective diffusion regime, $\mathrm{Pe}_{S}<1$ so that $\eta$ follows the $-2 / 3$ power law dependence, as long as $\alpha$ is not too small. When $\alpha$ becomes small enough for $\beta$ to be much smaller than 1 , then $\eta \alpha \mathrm{Pe}_{\mathrm{g}}^{-1}$, i.e varies as the inverse of velocity. The Equation (4), which must be valid for porous media with a prefactor A characterizing pore structure, determines two regimes: the diffusion limited deposition (DLD) for $\beta \gg 1$ and reaction limited deposition (RLD) for $\beta \ll 1$. When Pes $>1$, the hydrodynamic forces reduces energy barriers between particles and pore surface, thus increasing deposition kinetics $(4,6,11)$.

More detailed informations on both experimental and modelling aspects may be found in Ref. 12.

## Materials and Methods

## 1. Porous media

Silicon carbide (SiC) grains having sharp-edged shape (characteristic of ground homogeneous materials, similar to that of detrital sands) but different sizes ( 30 and $150 \mu \mathrm{~m}$ ) were used to pack granular beds with the same pore microstructure ( 5 ) and porosity ( $\varnothing=40 \%$ ) but different permeabilities (respectively 0.48 and $12 \mu \mathrm{~m}^{2}$ ).

The SiC grains were washed extensively using 1 M HCl to remove metalic impurities (mainly iron) and then treated for 8 hours in presence of air at elevated temperature ( 350 or $800^{\circ} \mathrm{C}$ ) to ensure two different and reproducible oxidation state. After treatment, the surface bears different fractions of silanol groups, giving negative charges at $\mathrm{pH}>2.5$. In some experiments, the SiC grains were sonicated in distilled water to extract very fine particles (coming from the grinding). During sonication, the grains were subjected to attrition which removes to some extent oxidation layer in some areas. In these zones, the Hamaker constant is higher and the surface is less charged, leading to less repulsive surface forces.

## 2) Colloidal particles

Both mineral and organic particles were used in this work.. The organic particles are monodisperse surfactant-free polystyrene latexes bearing a hairy layer of grafted acryclic acid (CML latexes from IDC), the characteristics of which are described elsewhere (13). Their mean hydrodynamic diameters in
0.5 and 1 M NaCl are close to 245 nm . The mineral particles are SiC grindinded fines initially sticked on SiC grains and then collected by sonication. Their mean size in 190 nm but they are strongly polydisperse and sharp-edged. Both SiC and latexes particles were stable in the aqueous dispersions used

## 3) Experimental procedures

The SiC grains were packed inside small pyrex cylinders. The porous media pore volumes were determined by using a tracer injection (potassium iodide). The latex suspensions were obtained by simple dilution of the concentrated stock suspensions in electrolyte solutions previously prepared using electrolyte ( NaCl ) analytical grade reagent and high quality distilled deionised water. During latex injection at constant flow rate , the pressure drop accross the porous medium and the outlet particle concentration were monitored as a function of time. The pressure drop was measured using both home made very accurate oil/water manometers or transducers while the outler latex concentration was obtained with a very high accuracy ( 0.1 ppm ) from in-line turbidity measurements using an UV spectrometer.

## Results and Discussion

## 1) Deposition and Pore Surface Heterogeneity

The figure 1 shows the characteristic shape of the reduced outlet concentration (ROC) curve for deposition on an heterogeneous surface ( SiC fines in SiC grains treated at $800^{\circ} \mathrm{C}$ but subjected to attrition). At the beginning (region 1 on Fig. 1), the ROC results from the deposition on both the weakly repulsive fractions of the surface (created by attrition during sonication) and on the less attractive ones (strongly oxidized at $800^{\circ} \mathrm{C}$ ). The increase in ROC in region 1 is due to the progressive coverage of these weakly repulsive zones by more repulsive fines. The strong increase in ROC in region 2 corresponds to the saturation of these zones. In region 3, a plateau is reached which charracterizes the deposition on both previously weakly repulsive but saturated zones and possible deposition on still bare but strongly repulsive oxidized zones. Note that after 300 PV injected only $1 \%$ of the pore surface has been covered in this experiment.

The figure 2 shows the deposition of CML latexes at $10^{-2} \mathrm{M} \mathrm{NaCl}$ on packed SiC grains subjected to different treatments. There is strictly no deposition onto non-sonicated SiC grains treated at $800^{\circ} \mathrm{C}$ (curve 1). On SiC treated at $350^{\circ} \mathrm{C}$, there is a small fraction of weakly repulsive zones (oxidation efficiency depends on the angle of the grinding fractures with SiC cristal faces). When SiC grains have been treated at $350^{\circ} \mathrm{C}$ and sonicated, the attrition has created additional weakly repulsives zones (curve 3 ).
2) Deposition Kinetics and Fluid Velocity

The figure 3 shows the power law dependence of deposition kinetics. The collection efficiency per grain $\eta$ calculated from Equation (4) is plotted in $\log -\log$ coordinates as a function of grain Peclet number Peg.

The power law exponent at 1 M NaCl (open squares) is -0.61 , i.e. slightly smaller than the theoretical value $-2 / 3$. However, the measurements were carried out on the same pack, beginning by the highest flow rate. Thus, the subsequent measurements were made on non-strictly bare grains, thus giving underestimated values for both $\eta$ and the power law exponent. This conjecture is confirmed by experiments carried out at 0.5 M NaCl (open circles), where successive points have been obtained taking the mean value between measurements made in decreasing and then increasing flow rate. Assuming that deposition amounts were similar during the decrease and the increase in flow rates, we expect the mean curve should have the right slope. Effectively, we found -0.67 , as expected theoretically.

The prefactor in the kinetic equation for sharp-edged grains was determined four times in our experiments giving values between 23.5 and 24.7 with a mean value of 24 . Knowing this value gives the possibility of calculating $\alpha_{\mathrm{pc}}$ and thus the energy barrier between particles and surface.

The figure 4 shows that two deposition regimes (DLD and RLD), may be found when deposition occurs on a surface which behaves as heterogeneous. In our experimental conditions, heterogeneity is revealed at medium salinity ( 0.05 M NaCl ). The curve shows the velocity dependence of the effective grain collection efficiency $\eta_{\mathrm{e}}$. When deposition occurs mainly on the less repulsive zones (curve 1 ), the measured slope is -0.63 close to that expected for DLD regime. Note that the effective prefactor is $\mathrm{A}_{\mathrm{e}}=$ 0.95 , giving a first estimation of the fraction $f$ of less repulsive zones $f=0.95 / 24=4 \%$. When these zones have been covered and thus behave as strongly repulsive, we obtain the $\eta_{\mathrm{e}}$ on the more repulsive zones (curve 2), with a slope equal to -0.93 , very close to -1 , the value expected for the RLD regime.

## 3) Modelling Surface Deposition in Porous Media

The three main results deduced from experiments described above, i.e. 1) the prefactor in deposition kinetic equation $A=24$ for sharp-edged grains 2 ) the heterogeneity in pore surface potential and 3) the power law dependence corresponding to this heterogeneity using Equation (3) with the right prefactor A, have been introduced in the Paris model.

When the surface behave as homogeneous, i.e. at high ionic strength ( 1 M NaCl ), the model predicts very accurately deposition kinetics, i.e. the variations of both reduced outlet concentration $\mathrm{C} / \mathrm{Co}$ and permeability reduction ko/k as a function of the number of pore volumes injected (Fig. 5). In this case, there is no need of any adjustable parameter.

When the surface behave as heterogeneous, i.e. at intermediate ionic strength ( 0.1 M NaCl ), the agreement is also quite good (Fig. 6). However there is three parameters to be determined by experiments: the fraction $f$ of less repulsive surface area (here $\mathrm{f}=0.4$ ) and the particle/surface grain collection efficiency factors $\alpha$ on less and more repulsive surfaces respectively (here $\alpha_{1}=0.2$ and $\alpha_{2}=$ 0.00315 ). Note that a even better agreement for $\mathrm{k} / \mathrm{ko}$ could be obtained by taking a particle diameter increased from 1 M NaCl to 0.1 M NaCl (12), but this was not justified considering the accuracy of $\mathrm{ko} / \mathrm{k}$ measurements.

## Conclusions

New basic results concerning the kinetics of deposition of small particles onto heterogeneous pore surfaces have been derived from experiments carried out in well-defined and controlled conditions:

1) The kinetic law of deposition in the purely attractive case has been carefully determined including the prefactor corresponding to packs of sharp-edged grains and the power law dependence of flow velocity under the adimensional form of grain collection efficiency vs Peclet number.
2) The power law dependence of deposition kinetics when there is a significant energy barrier between particles and pore surface has been determined experimentally, in agreement with previous theoretical predictions.
3) The effects of pore surface heterogeneity have been observed and analyzed. Heterogeneity affects drastically the deposition kinetics and its consequences on permeability damage.
4) After introduction of pore surface heterogeneity in the Paris model, a very good agreement is obtained between experimental results and model predictions.

In practical applications, tests similar to that described in this paper using field cores and injection water must be performed and analyzed with Paris model to get parameters for evaluating a possible injectivity decline.

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Fig.1: Deposition of SiC fines on a 30 $\mu \mathrm{m} \operatorname{SiC}$ grain pack at 0.003 M NaCl : treatment at $800^{\circ} \mathrm{C}$ with attrition.


Fig.3: Effects of velocity on deposition kinetics at high ionic strength (SiC 150 $\mu \mathrm{m}$ treated at $350^{\circ} \mathrm{C}$ without attrition).


Fig.2: Deposition of latex particles on 30 $\mu \mathrm{m} \mathrm{SiC}$ grain packs: $800^{\circ} \mathrm{C}$ without attrition (1), $350^{\circ} \mathrm{C}$ without (2) and with (3) attrition.


Fig.4:Evidence of two deposition kinetic regimes at medium ionic strength on heterogeneous surfaces ( $\mathrm{SiC} 350^{\circ} \mathrm{C}$ without attrition).


Fig.5: Experimental data (symbols) vs Paris model predictions (full lines) for deposition onto surface behaving as homogeneous (1M NaC).


Fig.6: Experimental data (symbols) vs Paris model predictions (full lines) for deposition onto surface behaving as heterogeneous ( 0.1 M NaCl ).

