Reply to Comment on Breakdown of Colloid Filtration Theory: Role of the Secondary Energy Minimum and Surface Charge Heterogeneities

We thank Johnson and Li for their interest in our article describing systematic experimental studies to identify the key mechanisms causing deviation from classical colloid filtration theory (CFT). Here, we address the specific points raised by Johnson and Li and provide additional details regarding our earlier publication. In brief, we believe that their comments result from some misinterpretations of our work.

**Collector versus Particle Heterogeneity.** Johnson and Li argue that the observed deviation from CFT must be caused by heterogeneity in the surface characteristics of the particle population. We agree that particle heterogeneity must contribute to the observed deposition behavior. However, it is interesting that even when the particle population exhibits considerable variability in surface characteristics (represented as a normal distribution in the particle deposition rate) the observed deposition behavior does not always necessarily deviate from that predicted by CFT. For example, in Figure 2 of ref 3 we show that the deposition behavior of a particle population with a normally distributed deposition rate (curve b) is nearly identical to that of a particle population with a single (constant) deposition rate (curve a). In these calculations, the coefficient of variation for the distributed particle population was relatively high (25%) yet did not result in any noticeable difference in the spatial distribution of suspended or retained particles. A normal distribution in the particle deposition rate is used to describe the occurrence of population heterogeneity. Thus, these results demonstrate how even in the presence of heterogeneities in the particle population, the observed particle deposition behavior may be in good agreement with CFT.

It is important to note that we do not attribute the deviation from CFT solely to the presence of collector surface charge heterogeneity as implied by Johnson and Li. Rather, in our several publications on the subject, we have repeatedly indicated that the breakdown of classical CFT is caused by the occurrence of a wide distribution (e.g., bimodal) in the interactions (or interaction energy profiles) between particles and collectors. A distribution in interaction energies between particles and collectors will give rise to a distribution in particle deposition rates. This wide distribution in particle—collector interaction energies may arise from a combination of several factors, including particle and collector surface charge heterogeneity. In our published work, we demonstrated and discussed how these factors can give rise to three deposition mechanisms causing the breakdown of CFT: (i) a fraction of particles may be retained in a relatively deep secondary energy well, (ii) some particles may overcome the repulsive energy barrier and deposit in the primary energy well, and (iii) some particles may deposit under favorable conditions. This concept is well described by the schematic diagram (Figure 4) in ref 5 and the related discussion.

The combined influence of the above-mentioned three deposition mechanisms will give rise to an apparently distributed particle population. In our previous publications, we avoided the use of the term “population heterogeneity” to describe the observed phenomenon. This was purposely done to avoid confusion with regards to readers attributing the observed deviation behavior solely to inherent physical or chemical heterogeneities of the particle population. Rather, to make our point clear, we refer to “the concurrent existence of both favorable and unfavorable chemical—colloidal interactions”. In our discussion above of the calculations in Figure 2 of ref 3, we indicated that in certain systems consisting of homogeneous collectors and heterogeneous particles (e.g., normally distributed deposition rates) the resulting deposition behavior may be in good agreement with CFT. However, in the case where both particles and collectors exhibit normal distributions in surface properties (e.g., in zeta potential), the resulting interaction (proportional to the product of two Gaussian distributions) will be asymmetric and can result in a deviation from CFT (see Figure 2, curve c, in ref 3 with a related discussion). These calculations demonstrate how the influence of minor heterogeneities in the particle population can be amplified in the presence of collector heterogeneity, giving rise to a wider distribution in particle deposition rates. In this case, although collector heterogeneity is evenly distributed in the porous matrix, we now have a system with particle population exhibiting a wider distribution in deposition rates.

**Even versus Uneven Distribution of Fast and Slow Deposition.** In the Supporting Information, Johnson and Li present basic equations used to describe particle deposition behavior for two general cases: (i) porous medium (collector) heterogeneity (i.e., an even distribution of fast and slow deposition sites) and (ii) population heterogeneity (i.e., an uneven distribution of fast and slow deposition sites). They also show plots of calculated profiles of suspended and retained particles based on these simple formulations. We recognize that the particle deposition behavior observed in our experiments must be represented by an “uneven” distribution of fast and slow deposition rates because an even distribution of deposition rates will clearly result in an exponential decay in particle concentration with distance. In fact, this is the approach we take in developing our dual deposition mode (DDM) model. This model is based on the recognition that population heterogeneity drives the observed overall particle deposition behavior, as discussed by Johnson and Li. As indicated in the previous section, the combined influence of the three deposition mechanisms depicted in Figure 4 of ref 5 gives rise to a uneven distribution in particle—collector interaction energies. This distribution in interaction energies is driven by the presence of population heterogeneity.

It was never our intention to suggest that the deposition behavior observed in our experiments could be attributed to an even distribution of particle deposition rates. In particular, we do not claim that there exist fast and slow deposition sites that are evenly distributed across the packed porous media. Such an even distribution of

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deposition sites would clearly give rise to an exponential decay in particle concentration as mentioned previously. Furthermore, we have not suggested that “the fast deposition mechanisms are located up-gradient of the slow deposition mechanisms”. This is a misinterpretation of our analysis where we actually describe how the steep slope at the top end of the column reflects the contribution of the particles depositing at a fast rate.

Also in the Supporting Information, Johnson and Li suggest that the measured retained profiles in ref 2 show near-exponential decay. Actually, most of the measured spatial distributions of retained colloids do not exhibit exponential behavior, except for certain cases where the experimental results are in good agreement with CFT (e.g., at the highest ionic strengths). This nonexponential behavior is not very obvious in Figures 2 and 10 of ref 2 because of the scale of the plots, which results in the compression of the profiles. However, the curvature (or two distinct slopes) of most measured retained profiles is quite evident when plotted over a narrower range (e.g., in Figure 7 of ref 2 and Figure 2 of ref 5).

**Contribution of Secondary Minimum Deposition.**

In our previous work, we proposed and demonstrated the influence of secondary minimum deposition on the observed breakdown of CFT. By conducting experiments using three differently sized particles, we showed how the degree of deviation from CFT diminishes when we eliminate the contribution of secondary minimum deposition (Figure 11 in ref 2). If particle surface charge heterogeneity were the sole cause of the observed deviation from CFT, then this would still not explain the results shown in Figure 11 of ref 2.

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