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## PRACTICAL APPLICATIONS FOR CLAY-DERIVED ZEOLITE N: AN AMMONIUM-SELECTIVE ION EXCHANGER FOR INDUSTRY USE

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Over the past ten years, scaled-up utilisation of a previously under-exploited zeolite, Zeolite N<sup>1</sup>, has been demonstrated for selective ion exchange of ammonium and other ions in aqueous environments. As with many zeolite syntheses, the required source material should contain predictable levels of aluminium and silicon and, for full-scale industrial applications, kaolin and/or montmorillonite serve such a purpose. Field, pilot and commercial scale trials of kaolin-derived Zeolite N have focused on applications in agriculture and water treatment as these sectors are primary producers or users of ammonium. The format for the material – as fine powders, granules or extrudates – depends on the specific application albeit each has been evaluated.

Zeolite N is a convenient, stable framework within which appropriate ions such as K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> are transferred from one medium to another based on chemical equilibria of the specific environment. The type zeolite, produced by either low temperature ambient<sup>2</sup> or hydrothermal<sup>3</sup> conditions, is potassic with the specific formula: |K<sub>10</sub>(H<sub>2</sub>O)<sub>8</sub>Cl<sub>2</sub>| [Al<sub>12</sub>Si<sub>12</sub>O<sub>40</sub>] - EDI<sup>4</sup>. Other compositional forms of Zeolite N, which allow for cation and anion substitution such as |K<sub>>8</sub>Na<sub><2</sub>(H<sub>2</sub>O)<sub>8</sub>X<sub>2</sub>| [Al<sub>12</sub>Si<sub>12</sub>O<sub>40</sub>] where X=I, Br, F, NO<sub>x</sub>, are also known<sup>3</sup>. The exchanged form of Zeolite N, for example when used in agricultural processes<sup>5</sup>, is of the form |K- (NH<sub>4</sub>) (H<sub>2</sub>O)<sub>8</sub>Cl<sub>2</sub>| [Al<sub>12</sub>Si<sub>12</sub>O<sub>40</sub>].

At production scale, bulk density of the powder is ~0.3 g/cm<sup>3</sup>, with average particle size ~2.5 μm, pH~10.8 (in 20% slurry) and average brightness L=94.9. Granules or beads for fixed bed reactors are prepared as 1.6mm–3.0mm size fraction with 9wt% to 15wt% sodium silicate binder. In general, the cation exchange capacity (CEC) of Zeolite N powder produced from kaolin is greater than 500meq/100g (or ~65g NH<sub>4</sub><sup>+</sup> per kg zeolite). In beads or granules, this capacity is reduced by the quantity of binder and in practice, results in effective loadings of between 45–55g NH<sub>4</sub><sup>+</sup> per kg zeolite<sup>6,7</sup>.

Fertilisers based on ammonium can often be inefficiently utilised by horticultural crops or high-value applications<sup>5</sup> (e.g. golf turf), particularly when grown on low quality or sandy soils. In some environments, the lost nitrogen in highly leached soils can be an environmental hazard or may constrain use of aquifers<sup>5</sup>. Glasshouse trials show that plants grown in sandy soils with moderate levels of Zeolite N powder reduced the loss of added ammonium by 90% compared with an unamended soil<sup>5</sup>. An added advantage of a Zeolite N amendment is that exchanged potassium is released into soil solution and is available to plants<sup>8</sup>.

Pilot plant and commercial use of Zeolite N is demonstrated for wastewater sidestreams in sewage treatment plants<sup>6,7</sup> and for treatment of mature landfill leachate solutions. A range of ammonium ion concentrations from <10mg/L to >600mg/L have been reduced to defined breakthrough conditions by ion exchange using Zeolite N, often in the presence of competing

cations such as Na, Ca, Mg, and Fe. These applications are in fixed bed reactors using beads or extrudates as described above and with pre-treatment to reduce total suspended solids to < 100mg/L. Generic sites for which Zeolite N has been used to reduce ammonium concentrations to target levels include: digester sidestream and tertiary flows from wastewater treatment plants; mature landfill leachates and stormwater run-off.

Use of Zeolite N to treat anaerobic digester sidestreams resolves a significant operational problem by reducing overall nutrient load in the effluent<sup>7</sup>. However, the dominant market for this type of product is more likely to be focused on streams with 50mg/L < [NH<sub>4</sub><sup>+</sup>] < 250mg/L and little or no BOD. These waste streams are common in manufacturing plants, mature landfills and smaller sewage treatment plants. Regeneration of the media is simply effected *via* caustic or caustic + salt solutions and can result in beneficial re-use of the ammonium by-product. Ammonium exchange efficiency after many cycles of regeneration is retained with limited loss of loading capacity on subsequent cycles<sup>6,9</sup>.

Other applications have been trialled with this robust material and include comparisons with natural zeolites and Zeolite A. In these latter cases, the selectivity for ammonium ion is compromised by a larger pore size that exchanges more readily with divalent ions. The effective pore size for Zeolite N is <0.3 nm compared with 0.41 nm for Zeolite A. For fixed bed reactors under similar conditions, Zeolite N reduces ammonium to a specific breakthrough value through ion exchange by factors of more than ten compared with natural zeolite and a factor of three times that of Zeolite A. In all applications, Zeolite N loading capacity for ammonium is significantly higher than natural zeolites<sup>5-10</sup>.

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