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A Study on the Formulation of Natural Zeolites

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Abstract – Zeolites are based on aluminosilicate (aluminium (Al), silicon (Si) and oxygen (O)) minerals, containing H2O and metals of the alkaline and alkaline earth groups; their empirical formula is M2/nO•Al2O3•ySiO2•wH2O, in which n = cation valence, y = 2 to infinity, and w = the water molecules within the framework's channels. The crystalline structure of zeolites is based on AlO4 and SiO4 tetrahedra that connect to one another through oxygen bonds.

The Al and Si tetrahedra are the primary building units (PBU) of the zeolite structure, and the connections between these form the secondary building units (SBU) that then repeat infinitely in a three-dimensional structure.

Keywords: Zeolite, Framework, Structure

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INTRODUCTION

The different combinations in which the rings and channels interconnect are responsible for the vast number of zeolite frameworks that have been identified. Framework types (or groups) are organised according to "corner-sharing network of tetrahedrally coordinated atoms", meaning that the frameworks formed by different combinations designate each group, regardless of the extra-framework chemistry.

The ion selectivity of an ion exchange process involving zeolite is based at least in part on the size of the ions in the fluid, i.e. the zeolite will most likely retain those which are not too large that they cannot enter the channels and pores, nor too small that they will flush through the framework, hence the term "molecular sieve" defining zeolites. Over 230 framework type codes (including 60 natural zeolites) can be found in the International Zeolite Association (IZA) Database classified by a three-letter code, generated mostly from the name of the material type (e.g. heulandite (HEU), edingtonite (EDI), faujasite (FAU), etc.

The channel system in the zeolite's structure allows free cations to be exchanged for cations in a solution. The ion exchange process is reversible, i.e. the cations captured in the zeolite structure can be released back into another solution when that solution contains an excess of a more favourable cation. For example, clinoptilolite is commonly used for ammonium removal and can be recovered after the zeolite is exhausted (loading is at capacity) by flushing a highly concentrated sodium chloride solution through the media.

Even though NH4 + is preferred the high concentration of Na+ induces a concentration flux reaction, meaning that the difference in concentration dislocates the equilibrium and the sodium cations dislodge the ammonium cations from the framework taking their place. This is known as regeneration, the sodium cations replace the ammonium in the zeolite and the media can be used again; other regenerant used includes NaOH, HCl and H2SO4.

This regeneration ability is an important feature of zeolitic materials, which in addition to extending their life cycle allows the recovery of cations of interest which would otherwise be eliminated from the system. The spent NaCl regenerant is loaded with ammonium (ammonium chloride (NH4 + Cl-)) and it is possible to use this latter solution as a fertiliser. A number of methods are available to recover the ammonium, including ammonia stripping (with previous pH elevation), precipitation as struvite (NH4MgPO4·6H2O), electrolysis and biological conversion.

Zeolites form in hydrothermal conditions found in nature and occur in geological deposits such as volcanic and sedimentary rocks and tuffs. The origin of the zeolite-rich (or zeolitic) rock influences the mineral composition of zeolite. The discovery of zeolites dates back to 1756, when Crönstedt first noticed the peculiar behaviour of the mineral appearing to boil upon being heated; indicating a porous nature. Due to their unique porous properties, they are now used in a variety of applications that consume an estimated 2.5 to 3 million tonnes globally.

The crystal structure of clinoptilolite is classified as part of the heulandite (HEU) group

(Ca0.5,Sr0.5,Ba0.5,Mg0.5,Na,K)9(H2O)24|[Al9 Si27 O72].

FORMULATION OF NATURAL ZEOLITES

Heulandite and clinoptilolite are natural zeolites with the same crystal structure (monoclinic, space group C2/m), however they have different water and cation distributions in the framework. According to the International Zeolite Association (IZA) [58] there has been (and still is) some discussion around the nomenclature of these minerals, since both have the same crystal structure and morphology. The difference between the two is set on the silicon to aluminium ratio (Si/Al), whereby a Si/Al smaller than 4 defines heulandite and Si/Al greater than 4, clinoptilolite.

When compared to synthetic materials, natural zeolites do not possess the highest capacity for ion uptake from solution. Resins and synthetic zeolites have higher capacity and kinetics, albeit at times, at the cost of lower selectivity. Natural zeolites, as previously described, are found in nature embedded in tuffs and rocks and as such, their use is inherently impacted by other components of the rock, and their composition may vary even within the same deposit [65]. Interest in synthesising zeolites goes as far back as the 1800s when St Claire Deville allegedly produced levynite in laboratory in 1862.

To achieve better capacity and efficiency with natural zeolites, several modifications have been reported, such as microwave, exchange with solutions of specific cations or calcination [38]. In the case of clinoptilolite, treating the mineral with specific solutions (brines, acids, bases and surfactants) is known to enhance its efficiency for specific pollutants.

The treatments modify the zeolite's properties and characteristics as a result of cation relocation within the structure; the cation migration impacts the openings and pore sizes in the framework, altering the zeolite's selectivity, exchange capacities and other features. For instance, the modification of clinoptilolite with Fe(II) has been reported to increase the material's capacity to remove Cr(VI) while maintaining the physical characteristics (particle size and hydraulic conductivity).

Clinoptilolite treated with NaCl shows an increase of 34 % in Pb2+ and 33 % in NH4 + removal, whereas when treated with NaCl + NaOH the increase in NH4 + uptake increased to 45 %. Ding compared their modifications of natural zeolite by NaCl and by NaCl + calcination, and observed a 1.5 fold increase in ammonium removal rate with both modifications. In addition to the improvement in kinetics and reported a 40 % higher capacity for ammonium adsorption after the NaCl modification and 50 % after the NaCl + calcination process.

Zeolites and laterite ores are of interest for application in stormwater filters due to a combination of their availability, effectiveness, and low cost. However, there exists a lack of information regarding key performance parameters such as the hydraulic conductivity.

Tests were conducted upon a series of different size ranges of granular zeolite and laterite ore in a column arrangement. It was found that Standard Test Methodology issued by ASTM International were not representative of the system studied.

Consequently, a number of methods were procured. Two were deemed as sufficiently representative of the field conditions. In relation to the hydraulic conductivity measurements, it was found that two approaches have been previously used which differed in terms of the Δh reference point. Hence, data was reported for both calculation methods. The results showed that larger media grain sizes produced higher hydraulic conductivity values and that settling and saturation periods impacted the results. The calculation of hydraulic conductivity by the tailwater Δh reference point demonstrated insensitivity to bed height changes. Conversely, when calculated by the media top Δh reference, the height of the media bed proved to have a significant influence upon hydraulic conductivity values. The type of media employed was found to have minimal influence on the hydraulic conductivity, wherein the much denser laterite samples had the same hydraulic conductivity as their zeolite counterparts.

DISCUSSION

The removal rate of pollutants is dependent upon properties of the media such as affinity for specific species, particle size, density, and hydraulic conductivity. Hydraulic conductivity (k) is a property of aggregate materials and soils that can be defined as "the ease with which water moves through an aquifer".

Stormwater filters are subject to a surprising level of complexity and often, studies have not encompassed the entire situation. The impact of media particle size is one such example where knowledge gaps are present, as the majority of hydraulic conductivity studies have been related to soils and relatively fine materials (on the scale of µm) such as clays, silt and loam.

Hydraulic conductivity is an essential design parameter in filters and yet there is minimal literature regarding the influence of testing methods, especially for coarse grain media. The bulk of literature and standard test methods is focused on the hydraulic conductivity of soils and sand filters. Therefore, this study focued on the determination of the applicability of certified standard test methodology for coarser grained materials such as zeolites and laterite ore.

The primary aim was to determine the relevance of existing models to media tests in a column environment which approximated practical situations.

In practical applications, the zeolite/laterite media filters are typically preceded by various treatment stages which are designed specifically for retaining solids, grease and oils, particulates and hydrocarbons. Therefore, tap water was considered representative of such a pre-treated water sample and as such was selected as the permeant liquid for the testing of zeolite and laterite. Tap water also conformed with the guidelines for permeant liquid requirements described in ASTM-D5856-95 and ASTM-D5084−10.

The top of the column was kept open and the flow downwards through the sample was due to the force of gravity alone. The time elapsed during the flow from one point to the next (Δt) was measured with a laboratory stopwatch with 0.01 s precision. The volume of water (V) discharged during the test was measured with a 1 L glass measuring cylinder with a precision of 10 ml. The head losses were measured using a tape measure with a precision of 0.01 m.

With respect to the constant head method, the hydraulic head is kept constant; conversely on the falling head method, the hydraulic head decreases as the permeant flows through the media. Thus, different equations are employed to each test type to correct for the head loss measurements. Darcy's law is the basis to hydraulic conductivity and permeability calculations with many derivations described which accommodate different systems and conditions.

For the constant head equation, the head loss features as an average value since the flow rate is constant; the flow measurement is made based on the outflow of the system, for instance by mass. Meanwhile, in the falling head equation (a derivation of Darcy's law), head loss appears as the ratio between initial and final head losses, in this case measured by the difference in the height of liquid above the media bed.

Furthermore, the falling head method is mostly applied to fine media (like silts and clays), with low hydraulic conductivities; for instance, within ASTM International's Test Methods, the falling head technique is used for hydraulic conductivities lower than 10-4 m/s . Generally, the system for the falling head test consists of a permeameter cell (where the media is contained) with a stand pipe connected directly above it (where the permeant is stored).

The measurement of the head loss is made by the height of the liquid on the stand pipe, which normally is much smaller in diameter than the permeameter cell. For materials with higher hydraulic conductivity, the falling head test can still be used but the higher flow rate requires adjustment of the stand pipe size so that the measurement is possible.

For the intended filter application, although the media is relatively coarse (up to 1.0 to 3.2 mm) and the hydraulic conductivity is expected to be in the order of 1 x 10-2 m/s, the constant head test is not realistic, given that the filter is subject to intermittent flows. Therefore, in order to achieve adequate measurements in this study, the stand pipe was virtually scaled up to the same size as the permeameter.

In practice, the stand pipe was eliminated by the use of a long column, whereby media cell and permeant liquid pipe were one and the same. Similarly, other methods for hydraulic conductivity measurement are available to cover other scenarios and situations such as the constant volume and the constant rate of flow.

Within the falling head method, there are other variations to consider such as the permeameter or system type and the pressure on the system outlet, namely the tailwater elevation. Different equations apply to each tailwater condition. On ASTM's methods procured for this study, the tailwater is at either constant or rising elevation, that is to say that the outlet flow is directed to a collection vessel, thus exerting backpressure on the system outlet.

Upon considering the test methods to employ, it was found that no standard methodology applied directly to the stormwater filter cartridge of interest. International standard methods (ASTM) provided several approaches for different ranges of k, materials and pressure conditions. The filter system was designed to operate under specific criteria, which the hydraulic conductivity test must satisfactorily reflect. Therefore, the following set of necessary conditions defined the testing configuration and methodology: (1) predicted hydraulic conductivity range; (2) intermittent flow operation; (3) filter cartridge open to atmospheric pressure; (4) the media was fully saturated; and, (5) the tailwater pressure was constant. The constant tailwater test with the outflow freely exiting the system, although not particularly described by ASTM, is commonly found in publications on soil testing and development of hydraulic conductivity permeameter systems.

Given the open character of the filter and the intermittent flow presented to it, a constant-head test was possibly not truly representative of the real situation; whereas a falling head test appeared more realistic. The expected hydraulic conductivity was actually a design value, under which the filter was expected to perform in order to cope with the predicted runoff flows it would be exposed to, which was is in the order of 1 x 10-2 m/s.

CONCLUSION

Natural zeolite and laterite ore proposed for the stormwater filter were characterised in order to understand their physical properties prior to hydraulic conductivity testing. The natural zeolite used in this study had been pre-treated by the supplier in order to replace a fraction of the calcium ions which dominated the exchange sites of the “as mined” material by sodium ions; this material is known as Na+ modified natural zeolite. Hydraulic conductivity testing was performed on zeolite and laterite ore samples as received, dried and re-sieved. Mineralogical composition analysis was performed on dried, micronized zeolite and laterite ore samples.

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