Behaviour of natural zeolites used for the treatment of simulated and actual coal seam gas water

Graeme J. Millar*, Sara J. Couperthwaite, Kemal Alyuz

Institute for Future Environments, Science and Engineering Faculty, Queensland University of Technology (QUT), Brisbane, Queensland, Australia

ABSTRACT

Coal seam gas operations produce significant quantities of associated water which often require demineralization. Ion exchange with natural zeolites has been proposed as a possible approach. The interaction of natural zeolites with solutions of sodium chloride and sodium bicarbonate in addition to coal seam gas water is not clear. Hence, we investigated ion exchange kinetics, equilibrium, and column behaviour of an Australian natural zeolite. Kinetic tests suggested that the pseudo first order equation best simulated the data. Intraparticle diffusion was part of the rate limiting step and more than one diffusion process controlled the overall rate of sodium ion uptake. Using a constant mass of zeolite and variable concentration of either sodium chloride or sodium bicarbonate resulted in a convex isotherm which was fitted by a Langmuir model. However, using a variable mass of zeolite and constant concentration of sodium ions revealed that the exchange of sodium ions with the zeolite surface sites was in fact unfavourable. Sodium ion exchange from bicarbonate solutions (10.3 g Na/kg zeolite) was preferred relative to exchange from sodium chloride solutions (6.4 g Na/kg zeolite). The formation of calcium carbonate species was proposed to explain the observed behaviour. Column studies of coal seam gas water showed that natural zeolite had limited ability to reduce the concentration of sodium ions (loading 2.1 g Na/kg zeolite) with rapid breakthrough observed. It was concluded that natural zeolites may not be suitable for the removal of cations from coal seam gas water without improvement of their physical properties.

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1. Introduction

In recent times, the coal seam gas (CSG) industry has grown considerably and will continue to do so over the forthcoming years [1–3]. As the gas which is mainly composed of methane is normally held in place in the coal seam by water pressure, when drilling commences water is expelled over the life of the well. The water volume produced is not constant with the main quantity being removed in the initial few months of well operation and a decline in production being evident until the end of the gas extraction. Notably, the produced water contains dissolved salts with the main cation present being sodium [4–6]. The level of total dissolved solids (TDS) varies from well to well and gas field to gas field with concentrations ranging from 200 to 10,000 mg/L [7]. Produced water represents a significant resource to countries such as Australia which is among the driest places on Earth. Consequently, there is a distinct need to find technical solutions which can cost effectively treat CSG produced water to a state where it is acceptable for beneficial reuse in applications such as irrigation. Reverse osmosis and ion exchange are the two options which have received the most attention commercially [8–10].

With regards to ion exchange, synthetic resins and natural zeolites appear to be of the most practical interest. Resins can be used for desalination of the coal seam gas water [11] or for the softening of associated water prior to a reverse osmosis stage [12–14]. On the other hand, natural zeolites have mainly been examined for the removal of cations such as sodium from coal seam gas water. The Vance group [15–17] have investigated the treatment of produced water from the Powder River Basin using a range of natural zeolite minerals. For example, Zhao et al. [17] studied two clinoptilolite materials and one calcium exchanged chabazite mineral in order to determine their ability to treat synthetic CSG produced water. Interestingly, the chabazite did not significantly exchange sodium ions from solution whereas the clinoptilolite was successful in loading sodium to 9.6–12.3 mg/g and reducing the sodium adsorption ratio (SAR) value of the produced water from as high as 60.2 to less than 10. Initial economic evaluation of the process suggested that the costs involved may be acceptable for commercial usage. A subsequent report by Ganjegunte et al. [15] used actual CSG produced water from the Powder River Basin in the USA and verified that clinoptilolite could again successfully reduce SAR values to less than 10 (which allowed the water to be used for irrigation). Zhao et al. [16] proposed an innovative treatment process wherein the CSG produced water treatment using zeolites was integrated with the "softening" of hard water. The logic behind this idea was that the standard regeneration process using calcium chloride, in itself creates a brine stream which may be difficult to dispose of. Therefore, if natural zeolite was sequentially used to treat hard water (which loads the zeolite with calcium and magnesium ions) and then CSG produced water (which exchanges the loaded calcium and magnesium ions with sodium ions) then the overall process may become more economical. Huang and Natrajan [18] have also reported research involving natural zeolites to remove sodium ions from CSG produced water. The usable sodium ion exchange capacity was discovered to be relatively low with a value of 0.1 meq/g and as a consequence the economic feasibility calculations indicated that the zeolite based process may be significantly more expensive than deep well reinjection. Albeit, it was also pointed out that if the usable sodium exchange capacity could be increased to 1 meq/g then the costs would be comparable between the two outlined methods.

Australia not only has a growing coal seam gas industry but also substantial natural zeolite deposits. Based upon the aforementioned studies, zeolites do appear to have some potential for ion exchange treatment of CSG produced water to reduce SAR values to the point where the water is suitable for irrigation. However, as yet there have been minimal literature reports of Australian zeolite samples having been investigated to determine their effectiveness in removing sodium ions from CSG waters or the treatment of Australian CSG water compositions using zeolite minerals [19]. Moreover, complications concerning the methodology to interpret ion exchange behaviour have been recently reported [20]. In particular, it was noted that the bottle-point method used to generate exchange isotherms was critical in determining the nature of the profile observed. Previously reported research in this area all used the "constant mass" bottle-point method [15–17] instead of the recommended "constant solution normality" approach [20]. In addition, it is not clear at present what the difference in exchange behaviour is between aqueous solutions of sodium chloride and sodium bicarbonate and natural zeolite. As outlined above, the latter two salts represent the major fraction of dissolved species in coal seam gas water, and their relative abundance is highly dependent upon the source of the associated water [5]. Hence, an understanding of the influence of CSG water composition upon ion exchange performance is required.

Therefore, this paper presents data regarding the application of Australian natural zeolite for ion exchange treatment of both simulated and actual CSG water samples. A series of kinetic, equilibrium and column studies were conducted with the aim of gaining an insight into the feasibility and challenges to overcome if natural zeolites are to be used to treat coal seam gas water.

2. Materials and methods

2.1. Zeolites

Samples of natural zeolite were obtained from Castle Mountain Zeolites (CMZ) in Australia. Prior to use these materials were carefully washed in deionized water to remove excess dust and debris and dried overnight at 110 °C. Analysis of the zeolite sample indicated it was primarily composed of clinoptilolite in accord with previous literature [21]. The mesh size employed in this study was 1–2 mm. The 12-membered rings in clinoptilolite typically are about 0.4 nm in diameter depending upon the nature of any pre-treatment and identity of the exchanging cations on the zeolite lattice [22]. The chemical composition of the zeolite was found to be 12.28 wt% alumina and 71.59 wt% silica with 2.84 wt% CaO, 2.06 wt% Na_2O, 1,17 wt% K_2O and 0.88 wt% MgO as determined by X-ray fluorescence measurements [23].

2.2. Kinetic studies

2.2.1. Pseudo first order
Lagergren [24] derived the following pseudo first order model which has been extensively used in sorption studies:

$$\frac{dqt}{dt} = k_1(q_e - q_t) \tag{1}$$

Integration of Eq. (1) with boundary conditions t = 0 to t = t and q = 0 to q = q_t gives Equation (2).

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{2}$$

2.2.2. Pseudo second order
Ho [25] and Ho and McKay [26] emphasised the relevance of pseudo second order kinetic models for sorption studies. The theoretical basis for such models has been confirmed by Azizian [27] and can be expressed as Eq. (3).

$$\frac{dq}{dt} = k_2(q_{e-}q_t)^2 \tag{3}$$

Integration of Eq. (3) with boundary conditions t = 0 to t and q = 0 to q_t produces Eq. (4)

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

2.2.3. Intraparticle diffusion − weber morris
The role of intraparticle diffusion upon rates of exchange processes can be interpreted using the Weber and Morris [28] model [Eq. (5)].

$$q_t = k_i t^{0.5} + C \tag{5}$$

Where C relates to the boundary layer thickness.

2.3. Batch equilibrium ion exchange

Sorption isotherms are typically generated by placing a sorbent material of mass (m) in a sealed vessel along with a measured volume of a liquid (V) with an initial concentration (C_o, mg/L) of the