ENVIRONMENTAL REMEDIATION APPLICATIONS OF GEOTHERMAL CALCIUM SILICATES

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ABSTRACT

The deposition of amorphous silica from geothermal brines within pipework and reinjection wells is a significant problem, which limits the effectiveness of geothermal resource utilisation. We have developed a method to remove this silica from the geothermal brine as a nanostructured calcium silicate hydrate. In addition to preventing the formation of silica scale, the recovered material has several potential useful applications, including environmental remediation of various metal and other inorganic species.

The material, which may also be prepared from synthetic silica sources, has a moderately high surface area of up to 400 m^2 g^{-1}. The calcium component of the silicate is chemically active and reacts rapidly with anions such as phosphate to form insoluble calcium phosphate phases. Additionally, hydroxide is released as the silicate reacts with water. This, in turn will react with many heavy metal cations, forming insoluble hydroxide species. In both cases, these insoluble products are retained within the silicate material.

The high surface area and the reactivity of the calcium within the silicate make this a promising material for the remediation of environmental pollution. The uptake capacity of the silicate towards metal ions, such as copper or iron is 5-10 mmol metal per gram of silicate. The silicate is also capable of removing phosphate from eutrophic water sources, where the phosphate concentration becomes problematic at concentrations less than 10 µmol dm^{-3}. When removing phosphate from more concentrated sources, the silicate has an uptake capacity of 5 mmol phosphate per gram of silicate. The resulting phosphate-containing product has potential for application as a fertilizer.

The uptake characteristics and potential applications of both synthetic and geothermal-derived versions of this calcium silicate in environmental remediation will be discussed.

1. INTRODUCTION

Contamination of the natural environment by anthropogenic inorganic pollutants is a major sociological concern. Sites exhibiting historic contamination, e.g. old municipal refuse facilities or mining sites, are particularly problematic, as these locations often lack effective pollution containment controls for the toxic metals in the leachate (Longe and Enekwechi 2007). Intensive agricultural operations can also cause environmental contamination in the form of run-off containing elevated levels of nutrients such as phosphate and nitrate. When this run-off enters waterways, these elevated levels of nutrients can cause eutrophication, in which the excess phosphate promotes microorganism growth and causes oxygen depletion. This in turn decreases the biodiversity of the contaminated area.

In both cases, these types of pollution are characterised by being diffuse, rather than point contamination sources, with the pollutants of concern present at relatively low concentrations, but in excess of the level likely to cause adverse environmental effects. For example, the New Zealand water quality guidelines (ANZECC 2000) set trigger levels where 95% of aquatic species are likely to be unaffected at < 0.1 µmol dm^{-3} for heavy metals and ~ 0.3 µmol dm^{-3} for phosphate species (variable depending on the specific ecosystem).

In the ideal case, remediation strategies for dealing with this pollution must be low cost. Remediation of phosphate-rich eutrophic waters includes the use of phosphate immobilisation agents, containing, e.g. Ca^{2+} or La^{3+} to precipitate the phosphate (Yin et al. 2017). Bio-based adsorbent materials (Pantano et al. 2017) and aeration strategies (Harris et al. 2015) are also used to counteract eutrophication.

Organic pollutants in leachate are often treated by electro- or photochemical oxidation to reduce the toxicity of the pollutants (Moreira et al. 2016). However, inorganic pollutants such as heavy metals are better treated by adsorption processes. Mojiri et al. (2016), for example, have demonstrated a removal of heavy metals from landfill leachate by a combination of zeolite adsorbents and bioaccumulation by plant species. We have previously developed a nanostructured calcium silicate hydrate material (NCaSilH), which has the capacity to act as an adsorbent for both phosphate and cationic toxic heavy metal species.

Our previous preparation of NCaSilH has been conducted via a controlled precipitation reaction between calcium hydroxide and a suitable silica source (Johnston et al. 2008). The resulting precipitate contains particles a few tens of microns in size, each consisting of a porous network of interlocked silicate platelets. When the material is prepared from a commercial sodium silicate, diluted to a SiO_2 concentration of approximately 1 mol dm^{-3} (6 wt.%), the synthetic material (sNCaSilH) has an atomic Ca:Si ratio of 0.8:1. It possesses a high surface area (~ 400 m^2 g^{-1}) and adsorption capacity for either water (~ 400 wt.%) or oil (~ 400 wt.%). The calcium within the structure is loosely bound to the NCaSilH, and will react with water, liberating both calcium and increasing the pH of the contacted water. These properties can be usefully exploited by using the NCaSilH as an adsorbent for species having insoluble hydroxide or calcium salts. This includes many metal species, including most heavy metals such as copper, which form insoluble hydroxides, and the nutrient phosphate, which forms insoluble calcium phosphates.

Previous adsorption studies concerning sNCaSilH have shown an uptake capacity of 5-10 mmol g^{-1} for copper and other metal species in simulated mining leachate (Borrmann et al. 2011), and up to 5 mmol g^{-1} for phosphate (Cairns et al.

2014). When the adsorption studies are conducted at elevated metal concentrations, the final products of the copper sorption are often crystalline minerals in the form of $Cu_2(OH)_3X$, e.g. raoulite [$Cu_2(OH)_3(NO_3)$] or brochantite [$Cu_4(OH)_6(SO_4)$], depending on the loading (Barassi 2012). These are useful as feedstock minerals in copper smelting processes, allowing the adsorbed metal species to be recycled. When low concentration metal feedstock is used, no crystalline metal phases are present in the spent sorbate.

When phosphate is the target sorbate, the sNCaSilH has been shown to work for very dilute phosphate sources (< 10 µmol dm^{-3}), typical of those encountered in eutrophic surface waters (Cairns et al. 2013).

A downside when using synthetic silicate sources in the preparation of the NCaSilH, is that cost limits its potential application as a sorbent for diffuse environmental contamination. The added expense of the synthetic silicate source means that sNCaSilH compares unfavourably to natural mineral-based sorbents in such applications.

Recently (Borrmann et al. 2017), we have been operating a pilot-scale trial whereby dissolved silica is removed from geothermal brine, in the form of a geothermal calcium silicate hydrate (gNCaSilH). The primary aim of this pilot-scale trial is the removal of dissolved minerals, and a corresponding reduction of scale formation. The gNCaSilH is effectively a by-product of these trials. Therefore, it can be obtained more cost-effectively than would be possible from synthetic commercial silicate sources. However, the pilot-plant operation parameters attempt to form NCaSilH with the minimum calcium content, while still removing the most dissolved silica from the brine and obtaining maximum separation efficiency of the NCaSilH product. As such, the gNCaSilH is not optimised with respect to increased calcium content and high surface area which are more desirable in sorbent applications. The concentration of the silicate source used in preparation also differs significantly, 6 wt.% SiO_2 for sNCaSilH, compared to 0.1 – 0.05 wt.% SiO_2 for gNCaSilH. This paper compares the sorption characteristics of gNCaSilH with those previously obtained for sNCaSilH for copper and phosphate salts.

2. MATERIALS AND METHODS

gNCaSilH was obtained from the separator of the pilot plant mentioned earlier on 20 February 2018. The plant was supplied by a geothermal brine feed from the Wairakei geothermal field in the Taupo Volcanic Zone, New Zealand. It was vacuum filtered, rinsed with distilled water, and dried at 120 °C. Elemental analysis of this gNCaSilH by X-ray Energy Dispersive Spectroscopy (EDS) provided an atomic Ca:Si ratio of 0.6:1. sNCaSilH was prepared according to the method described by Johnston et al. (2008) (rapid addition of a calcium hydroxide slurry to a solution of sodium silicate). Using this preparation technique provides an atomic Ca:Si ratio of 0.8:1. Batch adsorption tests were undertaken at 20 ± 1 °C. A stock solution containing the adsorbate of interest $CuSO_4.5H_2O$ (1.8 mmol dm^{-3}) or KH_2PO_4 (1.0 mmol dm^{-3}) was prepared from analytical grade reagents, and 1.00 dm^3 was transferred to a flask. NCaSilH (1.00 g) was added to this flask under vigorous stirring. Constant stirring was maintained throughout the experiment. Subsamples of 10 cm^3 were withdrawn at intervals, immediately filtered through a 0.45 µm membrane, and stored for elemental analysis. The pH of the reaction was recorded at the time of subsampling. At the conclusion of the sorption experiment, the solids were recovered by filtration.

Electron microscopy, EDS analysis (JEOL JSM 6610-LA) and X-ray diffraction (Panalytical X'PERT Pro MPD, using a Cu K_α radiation source) were used to analyse the silicate materials used in this study.

Quantification of metal species (Cu, Ca) was undertaken by flame atomic absorption spectroscopy (Thermo Scientific iCE3500). Phosphate was quantified spectroscopically (UV-vis) employing the molybdenum blue method (Greenberg et al. 1995).

This batch adsorption procedure, and concentrations chosen were similar to those previously described for sNCaSilH (Borrmann et al. 2011, Cairns et al. 2014).

3. RESULTS

A comparison of the X-ray diffraction patterns of the synthetic and geothermal NCaSilH samples is given in Figure 1. The geothermal sample was significantly more crystalline than the synthetic sample. In both cases, the primary reflection was present at ~ 29 °2θ. For the synthetic sample, this reflection was very weak and broad, and is typical of the diffraction pattern associated with many calcium silicate hydrate phases (Chen et al. 2004). For the geothermal sample, the only significant crystalline phases present were calcite, ($CaCO_3$) and portlandite ($Ca(OH)_2$).

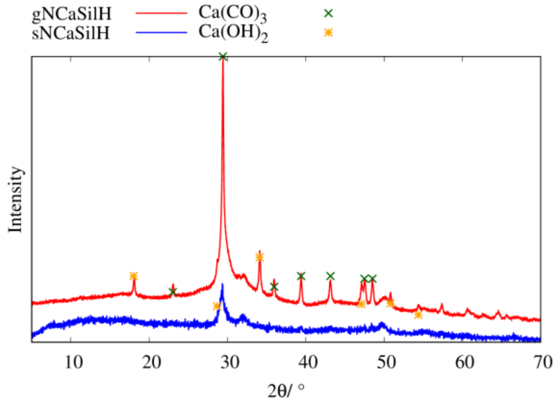

Figure 1: Powder x-ray diffraction comparison of synthetic and geothermal NCaSilH samples. Significant reflections of calcite [$Ca(CO)_3$] and portlandite [$Ca(OH)_2$] are indicated, scaled to the gNCaSilH pattern.

3.1 Copper Uptake

The copper adsorption properties of the gNCaSilH and sNCaSilH materials are presented in Figure 2, with the corresponding calcium release from both samples shown in Figure 3. In both cases, the uptake was rapid, with copper uptake exceeding > 99% within 30 minutes for both the synthetic and geothermal derivatives of NCaSilH. As mentioned earlier, the calcium component of the NCaSilH readily leaches into solution and results in an increase of solution pH-values. This behaviour was likewise observed for the gNCaSilH. The calcium release, and initial solution pH increase, occurred more rapidly with the synthetic variant of NCaSilH. This was expected, due to the initial higher calcium content of the synthetic sample. The solution pH remained acidic or neutral until all copper was removed from the solution. After this point, the solution pH increased as further calcium was leached from the NCaSilH material. Both variants of the NCaSilH showed good conformity to a pseudo-second order kinetic model for the removal of copper from solution. Pseudo-second order reaction kinetics are frequently encountered for batch uptake studies of dissolved species by a solid adsorbent (Ho and McKay 1999). This indicated that the rate limiting step was the chemical reaction of the copper with the NCaSilH, rather than diffusion of the metal species within the solution, which generally would exhibit first order kinetics.

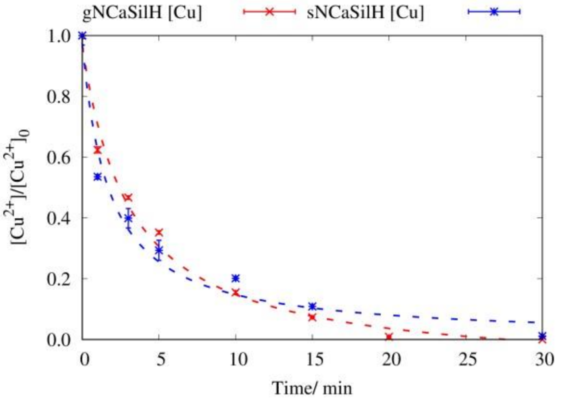

Figure 2: Copper adsorption by either geothermal or synthetic NCaSilH. An initial Cu^{2+} concentration of 1.8 mmol dm^{-3} was used, with data normalized to that initial value. Dashed lines indicate a pseudo-second order kinetic adsorption model fitted to the data.

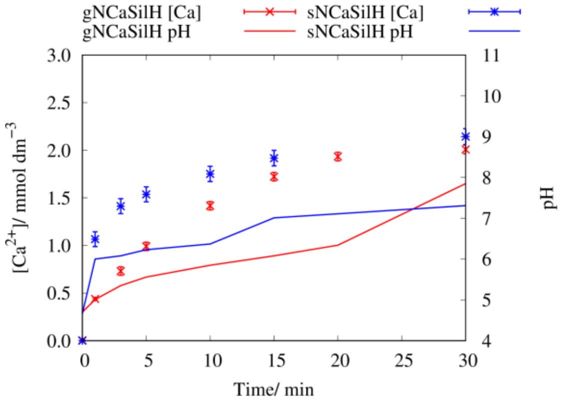

Figure 3: Calcium release by NCaSilH during copper adsorption. An initial Cu^{2+} concentration of 1.8 mmol dm^{-3} was used. Points indicate the concentration of Ca^{2+} released into solution, lines represent the change in solution pH during the adsorption process.

3.2 Phosphate Uptake

The phosphate adsorption properties of the gNCaSilH are presented in Figure 4. The synthetic sample exhibited faster absorption kinetics, likely due to the greater calcium content of the synthetic material. As with the copper uptake, the phosphate uptake was adequately modelled by a pseudo-second order kinetic model.

A comparison of the calcium release from the geothermal silicate sample for both copper and phosphate uptake is provided in Figure 5. During phosphate uptake, very little calcium was leached from the material. This was in contrast to the copper uptake studies, where significant quantities of calcium were leached. By contrast, the pH of solution during phosphate uptake very rapidly reached a value of 10, from an initial value of < pH 5, but the solution pH during copper uptake remained acidic while unbound copper was present in solution. In both cases, this was attributable to the reaction of the NCaSilH with water. The NCaSilH is sparingly soluble in water, liberating Ca^{2+} and OH^- ions. When copper was present, the liberated OH^- rapidly reacted with Cu^{2+}, maintaining a low solution pH, with the Ca^{2+} released into solution. During phosphate adsorption, the reverse situation occurred – Ca^{2+} reacted with phosphate, and the OH^- was not retained within the solid phases, but rather released, increasing the solution pH.

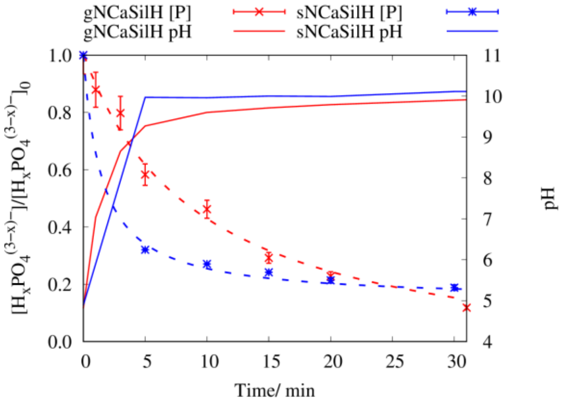

Figure 4: Phosphate adsorption by either geothermal or synthetic NCaSilH. An initial $H_2PO_4^-$ concentration of 1.0 mmol dm^{-3} was used, with data normalized to that initial value. Dashed lines indicate a pseudo-second order kinetic adsorption model fitted to the data. Solid lines indicate the change in solution pH during the uptake process.

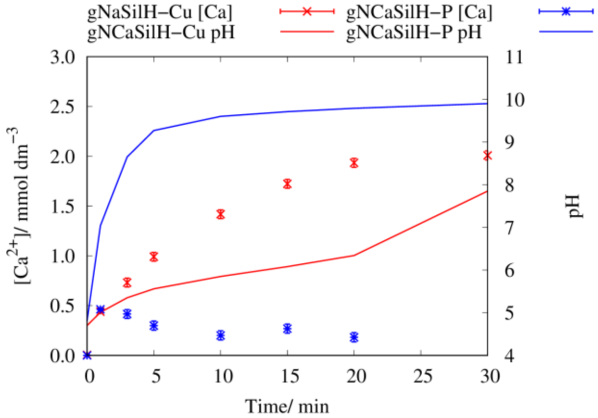

Figure 5: Calcium release by geothermal NCaSilH during copper or phosphate adsorption. Points indicate the concentration of Ca^{2+} released into solution, lines represent the change in solution pH during the adsorption process.

3.3 Microscopy

Scanning Electron Micrographs of the gNCaSilH product prior, and subsequent to uptake of either copper or phosphate are presented in Figure 6. The elemental distribution of silicon, calcium, and the adsorbed species is also shown for the samples. The electron micrographs were recorded in secondary electron imaging mode. In all cases, the morphology of the spent material after adsorption was very similar to that of the initial material, which displayed the open porous platelet network expected of NCaSilH. The materials retained their open porous structure following adsorption, and few morphologically distinct areas were observed.

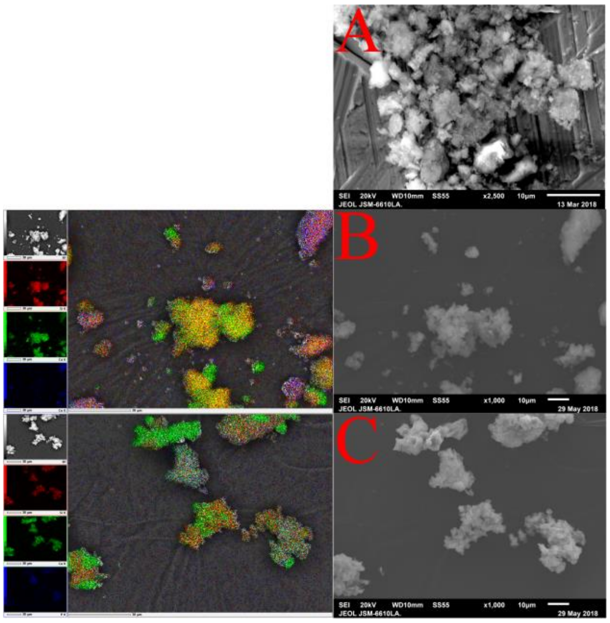

Figure 6: Electron micrographs (right) and elemental analysis (left) of gNCaSilH, before adsorption (A), or after copper (B) or phosphate (C) adsorption. The scale bar in the SEM images represents a distance of 10 µm. In the elemental analysis, Si is represented as red, Ca is represented as green and either Cu (image B), or P (image C) is represented as blue.

No reflections attributable to crystalline copper or phosphate phases were detected via XRD analysis of the spent material. This was the expected behaviour, as previous experience with copper uptake by sNCaSilH suggested that such phases do not occur until the initial copper concentration exceeds approximately 10 mmol dm^{-3} (Borrmann et al. 2011).

4. CONCLUSION

Previous studies with synthetic calcium silicate hydrate materials have shown that they possess properties suitable for uptake of a range of inorganic pollutants, particularly species exhibiting insoluble hydroxide or calcium salts, such as copper or phosphate. These synthetic materials were prepared with properties such as a high calcium content specifically targeted for pollutant uptake purposes. We have demonstrated that a calcium silicate hydrate obtained as a by-product of a geothermal scale-minimisation operation possesses comparable adsorption properties, despite minimising the calcium content of the material.

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REFERENCES

Australian and New Zealand Environment and Conservation Council (ANZECC), and Agriculture and Resource Management Council of Australia and New Zealand "Australian and New Zealand guidelines for fresh and marine water quality, volume 1" (2000), available at http://www.mfe.govt.nz/fresh-water/technical-guidance-and-guidelines/anzecc-2000-guidelines (accessed 3 August 2018)

Barassi, G. M. "A study of the uptake of Cu^{2+} by calcium silicate by batch and continuous reactors for potential commercialisation" *PhD Thesis, Victoria University of Wellington, N. Z.* (2013)

Borrmann, T., Cairns, M. J., Anderson, B. G., Höll, W. H., and Johnston, J. H. "Nano-structured calcium silicate as a sorbent in a study of artificial mining waste" *Int. J. Environ. Waste Manage.* 8, pp. 383 – 403. (2011).

Borrmann T., and Johnston J.H. "Transforming silica into silicate – pilot scale removal of problematic silica from geothermal brine." *GRC Trans.* 41, pp. 1322 – 1333. (2017).

Cairns, M. J., Krauss, C., and Johnston, J. H. "Recovery of phosphate from surface waters using a calcium silicate composite material for potential application in environmental remediation" *Technical Proceedings of the CTSI Cleantech Conference and Showcase*, pp. 252 – 255. (2013).

Cairns, M. J., and Borrmann, T. "Batch and continuous phosphate uptake studies employing a ferrimagnetic calcium silicate hydrate composite" *RCS Adv.* 4, pp. 53475 – 53483. (2014).

Chen, J. J., Thomas, J. J., Taylor, H. W. F., and Jennings, H. M. "Solubility and structure of calcium silicate hydrate" *Cem. Conc. Res.* 34, pp. 1499 – 1519. (2004).

Greenberg, A. E., Clesceri, L. S., and Eaton, A. D., Eds. "Standard methods for the examination of water and wastewater, 19th edition", (1995), *American Public Health Association,* Washington, D. C., U.S.A

Harris, L. A., Hodgkins, C. L. S., Day, M. C., Austin, D., Testa, J. M., Boynton, W., Van Der Tak, L., and Chen, N. W. "Optimizing recovery of eutrophic estuaries: impact of destratification and re-aeration on nutrient and dissolved oxygen dynamics" *Ecol. Eng.* 75, pp. 470 – 483. (2015).

Johnston, J. H., McFarlane, A. J., Borrmann, T., "Nano-structured silicate, functionalised forms thereof, preparation and uses", *US Patent Publication*, US/2008-0305027 A1, (2008)

Ho, Y. S., and McKay, G. "Pseudo-second order model for sorption processes" *Process Biochem.* 34, pp. 451 – 465. (1999).

Longe, E. O. and Enekwechi, L. O.; "Investigation on potential groundwater impacts and influence of local hydrogeology on natural attenuation of leachate at a municipal landfill" *Int. J. Environ. Sci. Tech.* 4, pp. 133 – 140 (2007)

Moreira, F. C., Soler, J., Fonseca, A., Saraiva, I., Boaventura, A. R., Brillas, E., and Vilar, V. J. P. "Electrochemical advanced oxidation processes for sanitary landfill leachate remediation: evaluation and operational variables" *Appl. Catal. B: Environ.* pp. 182, 161 – 171. (2016).

Mojiri, A., Ziyang, L., Tajuddin, R. M., Farraji, H., and Alifar, N. "Co-treatment of landfill leachate and municipal wastewater using the ZELIAC/zeolite constructed wetland system" *J. Environ. Manage.* 166, pp. 124 – 130. (2016).

Pantano, G., Ferreira, J. S., Aquino, F. W. B., Pereira-Filho, E. R., Mozeto, A. A., and Fadini, P. S. "Biosorbent, a promising material for remediation or eutrophic environments: studies in microcosm" *Environ. Sci. Pollut. Res.* 24, pp. 2685 – 2696. (2017).

Yin, H., Du, Y., Kong, M., and Liu, C. "Interactions of riverine suspended particulate matter with phosphorus inactivation agents across sediment-water interface and the implications for eutrophic lake restoration" *Chem. Eng. J.* 327, pp. 150 – 161. (2017)