SYNTHESIS, STRUCTURE AND PERFORMANCE OF CALCIUM SILICATE ION EXCHANGERS FROM RECYCLED CONTAINER GLASS

Nichola J. COLEMAN[*], **Qiu LI**[**], **Atiya RAZA**[*]

[*] School of Science, University of Greenwich, Chatham Maritime, Kent, ME4 4TB, UK;
    nj_coleman@yahoo.co.uk
[**] School of Civil Engineering, University of Leeds, Leeds, LS2 9JT, UK.

Abstract: Numerous technical, economic and societal factors limit the recycling of waste soda-lime-silica glass back into the primary production process and accordingly alternative applications for this material are sought. This study demonstrates that waste soda-lime-silica container glass is a suitable feedstock material for the production of tobermorite, a calcium silicate cation exchanger. Tobermorites were synthesised at 100 °C from stoichiometric mixtures of container glass and lime under alkaline hydrothermal conditions. Increasing concentrations of sodium hydroxide (between 1.0 M and 4.0 M) in the reaction mixture promoted the formation and crystallisation of tobermorite, and also resulted in greater fragmentation of the silicate chains along the b-axis direction. The maximum removal capacities of these tobermorite specimens for Cd^{2+} (441 mg g^{-1}) and Zn^{2+} (122 mg g^{-1}) compared well with those of other waste-derived sorbents. Superior Cd^{2+}- and Zn^{2+}-uptake capacities and kinetics were observed for the least crystalline tobermorite specimen, indicating that stacking defects facilitate the transport and exchange of cations within the lattice.

Keywords: tobermorite, sorbent, hydrothermal synthesis, cullet, recycling, ion-exchange

Introduction

Discarded soda-lime-silica glass containers constitute a significant and increasing proportion of the urban waste stream in every developed nation (Pontikes et al., 2007). The reuse and recycling potential of waste container glass (cullet) back into the primary production process is limited by a range of political, societal and technical obstacles (Coleman, 2011). In response to this problem, a variety of research projects has been carried out to identify alternative applications for waste cullet as a secondary feedstock in the production of aggregates, concretes, ceramics, abrasives and water filtration media (Ayadi et al., 2011; Coleman, 2011; Korkosz et al., 2012; Matteucci et al., 2002; Park et al., 2002).

Tobermorites are a family of naturally occurring calcium silicate hydrate minerals which are also readily synthesised under hydrothermal conditions between 80 and 225 °C (Coleman, 2005; El-Hemaly et al., 1977; Nelson and Kalousek, 1977). Their structure comprises a double Ca-O sheet bound on both sides by anionic wollastonite-like silicate chains running along the *b*-axis, as indicated in Fig. 1. The interlayer region houses labile charge-balancing cations and water molecules. Members of this family are characterised in terms of the length of their *c*-axis, which is dependent on the number of water molecules *per* unit formula. There are three principal polytypes of this mineral, *viz*. 14, 11 and 9 Å tobermorite, whose names relate to the approximate d-spacings of their (0 0 2) Bragg reflections.

11 Å tobermorite ($Ca_2Si_6O_{16}(OH)_2.4H_2O$) is of particular interest as it is the primary binder in autoclaved cements and also functions as a basic catalyst for organic synthesis and as an adsorbent for carbon dioxide and aqueous heavy metal contaminants (Al-Wakeel et al., 2001; El-Hemaly et al., 1977; Komarneni et al., 1986; Lima et al., 2008; Reinik et al., 2011). 11 Å tobermorite specimens exhibit a range of thermal behaviour: those which convert to 9 Å tobermorite at ~300 °C by the loss of molecular water are referred to as 'normal' tobermorites; whereas those which do not are described as 'anomalous' (El-Hemaly et al., 1977).
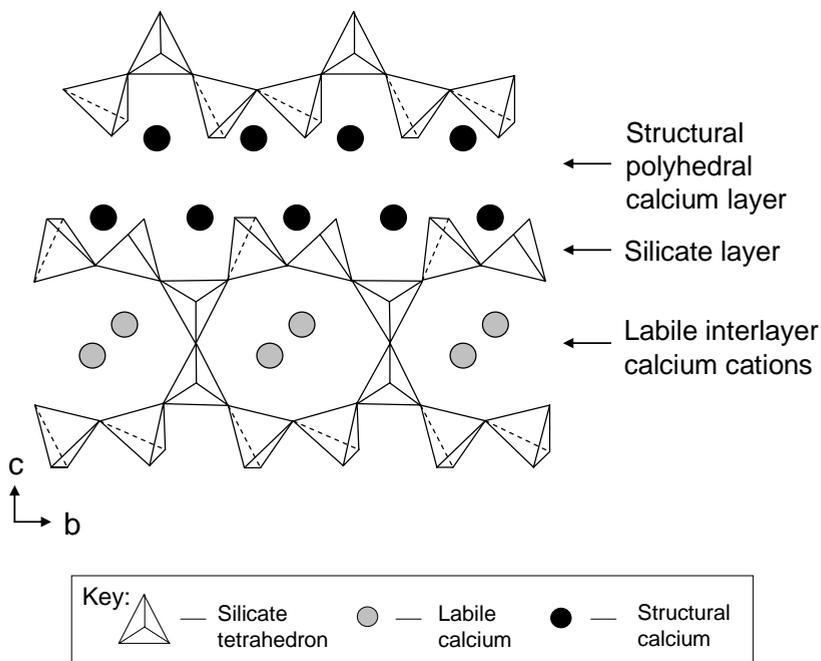

Fig. 1. Projection of 11 Å tobermorite in the *bc*-plane

The synthesis of 11 Å tobermorites reported in the literature has generally been carried out using analytical grade reagents such as sodium silicate and fumed silica; however, more recently, tobermorites have been prepared from industrial waste materials such as oil shale ash, cement kiln dust and paper recycling residue (Coleman, 2005; Coleman et al., 2009; Reinik et al. 2011). Recent research has also demonstrated that it is possible to prepare 11 Å tobermorite from waste container glass and that this material is an effective sorbent for divalent lead and cadmium ions (Coleman, 2011).

In the present study, waste soda-lime-silica container glass was used as the silicate feedstock for the hydrothermal synthesis of 11 Å tobermorites at 100 °C under conditions of varying alkalinity. The structures of the tobermorite products were analysed by powder X-ray diffraction (XRD) and solid-state ^{29}Si nuclear magnetic resonance spectroscopy (NMR). The relationship between structure and ion-exchange behaviour was explored *via* batch sorption of divalent cadmium and zinc ions.

Materials and methods

Materials, synthesis and characterisation

Flint soda-lime-silica glass (SLSG) containers were collected from the urban waste stream in Rochester, Kent, UK, and milled to pass 125 µm. An oxide analysis of the SLSG, obtained by X-ray fluorescence spectroscopy (XRF) at the Materials Research Institute, Sheffield Hallam University, Sheffield, UK, is given in Table 1.

Reaction mixture compositions and synthesis regimes are summarised in Table 2. All syntheses were carried out in triplicate by heating at 100 ºC in hermetically sealed PTFE reaction vessels under autogenous pressure for 7 days. Samples Tob-1, Tob-2 and Tob-4 were prepared from mixtures of 3.5 g of SLSG and 1.5 g of CaO in 60 cm^3 of 1.0 M, 2.0 M and 4.0 M sodium hydroxide solution, respectively. The products of each synthesis were washed with deionised water to pH ~7 and dried to constant mass in air at 40 ºC. Oxide analyses for each of the SLSG-derived tobermorite products are given in Table 1.

The reaction products were analysed by powder XRD using a Siemens Kristalloflex 810 X-ray diffractometer. To determine whether the tobermorite products exhibited normal or anomalous thermal behaviour, the samples were heated to 300 ºC for 10 hours in air and re-analysed by powder XRD.

The silicate structures of the tobermorite products were analysed by solid state ^{29}Si NMR, as described elsewhere (Coleman and Brassington, 2003). The free induction decay profiles were processed by Delta software (provided by JEOL) to obtain spectra which were then analysed and deconvoluted using Igor Pro software.

Table 1. Composition of SLSG and tobermorite products

Oxide Component	SLSG (mass %)	Tob-1 (mass %)	Tob-2 (mass %)	Tob-4 (mass %)
SiO_2	72.1	40.12	43.15	41.76
Na_2O	13.4	5.44	3.44	3.16
CaO	11.3	28.76	31.42	32.52
MgO	1.30	0.56	0.91	0.64
Al_2O_3	1.14	0.68	0.91	0.76
K_2O	0.39	0.10	0.04	0.04
SO_3	0.21	0.28	0.13	0.13
Fe_2O_3	0.08	0.04	0.04	0.04
TiO_2	0.05	Nil	Nil	Nil
Mn_3O_4	0.03	Nil	Nil	Nil
Loss on ignition	Nil	23.76	19.84	20.72

Table 2. Reaction conditions and mixture compositions

Sample	Reaction conditions	Si : Ca : Al : Na molar ratios
Tob-1	100 °C, 168 h, 1.0 M $NaOH_{(aq)}$	1.00 : 0.80 : 0.02 : 1.79
Tob-2	100 °C, 168 h, 2.0 M $NaOH_{(aq)}$	1.00 : 0.80 : 0.02 : 3.21
Tob-4	100 °C, 168 h, 4.0 M $NaOH_{(aq)}$	1.00 : 0.80 : 0.02 : 6.07

Notation used to describe the silicate structure of the tobermorites is such that the symbol Q represents one SiO_4^{4-} tetrahedron and a superscript denotes the number of other Q units to which it is bonded. Substitution of Q units by tetrahedra other than SiO_4^{4-} is indicated in parentheses, for example, a mid-chain SiO_4^{4-} unit linked to one other SiO_4^{4-} unit and one AlO_4^{5-} unit would be represented as $Q^2(1Al)$.

The silicate chain configurations of the SLSG-derived tobermorite products were evaluated in terms of their 'mean chain length' (MCL). MCL is a measure of the average number of tetrahedra linked along the *b*-axis direction between breaks in the chain, and is given by (Richardson and Groves, 1997):

$$MCL = \frac{2\left(Q^1 + Q^2 + Q^3 + \frac{3}{2}\left[Q^2(1Al) + Q^3(1Al)\right]\right)}{Q^1} \tag{1}$$

where, in this instance, Q^n symbols represent the relative intensities of the deconvoluted [29]Si resonances arising from the associated silicate tetrahedra.

The specific surface areas of the tobermorite products were determined according to ISO 9277:1995(E) by nitrogen gas sorption at 77.4 K using a Micromeritics Gemini VI analyser.

Batch sorption of Cd^{2+} and Zn^{2+}

The uptake of $Cd^{2+}_{(aq)}$ and $Zn^{2+}_{(aq)}$ by Tob-1, Tob-2 and Tob-4 was determined by single metal batch sorption at 25 °C. In each case, 50 mg of tobermorite product were contacted with 200 cm^3 of metal nitrate solution at an approximate metal concentration of 0.5 mM in screw-capped polypropylene bottles. Contact times for specimens were between 1 and 168 hours, after which, the supernatant liquors were recovered by centrifugation at 3000 rpm and analysed by atomic absorption spectrophotometry using a Pye Unicam SP 9 spectrophotometer. Each experiment was carried out in triplicate and the relative standard deviations of the mean metal-uptake data were lower than 5% in all cases.

Results and discussion

Characterisation of SLSG

The major oxide components of SLSG used in this study (listed in Table 1) are in the system SiO_2-Na_2O-CaO-MgO-Al_2O_3 in proportions which are typical of container cullet (Park et al., 2002). K_2O, SO_3, Fe_2O_3, TiO_2 and Mn_3O_4 are also present at concentrations below 0.5% by mass. The ^{29}Si NMR spectrum of SLSG (Fig. 2(a)) shows a broad asymmetric signal of maximum intensity at ~-95 ppm with a shoulder to high field which is consistent with a range of amorphous Q^1 to Q^4 silicate units comprising a predominance of Q^3 species. Powder X-ray diffraction analysis (not shown) also confirmed that SLSG is amorphous.\

Preparation and characterisation of SLSG-derived tobermorites

Powder XRD diffraction patterns of the SLSG-derived tobermorite products are shown in Fig. 3(a-c) and closely resemble those of phase-pure 11 Å tobermorites reported in the literature which have been prepared from reagent grade materials (Al-Wakeel et al., 2001; Mitsuda and Taylor, 1975). The comparatively broad and weak (0 0 2) basal reflection and poor resolution of the (2 2 0) and (2 2 2) reflections (at 2θ = 28.9° and 29.9°, respectively) in the XRD pattern of Tob-1 indicate that this specimen is less crystalline that its counterparts, Tob-2 and Tob-4, which were produced under conditions of increasing alkalinity (Fig. 3(a-c)). All SLSG-derived tobermorite products exhibited 'normal' thermal behaviour in that they dehydrated to form 9 Å tobermorite when heated to 300 °C (Fig. 3(d-f)). This finding is in agreement with those of other researchers who report that relatively low reaction temperatures (< 140 °C) and short processing times (< 14 days) generally give rise to normal tobermorite (El-Hemaly et al., 1977).
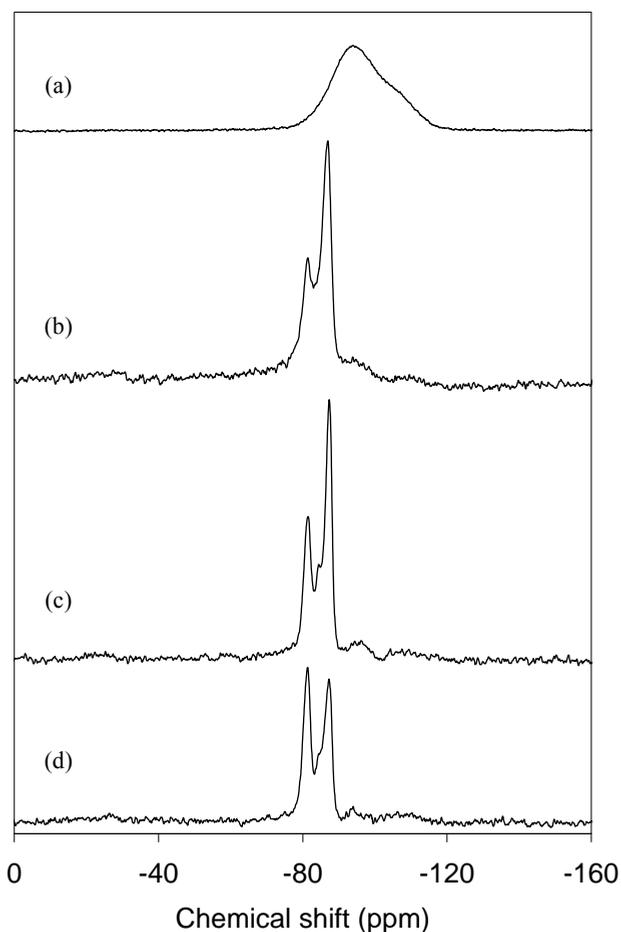
Fig. 2. ^{29}Si NMR spectra of (a) SLSG, (b) Tob-1, (c) Tob-2 and (d) Tob-4

The ^{29}Si NMR spectra of samples Tob-1, Tob-2 and Tob-4 (Fig. 2(b-d)) are consistent with the presence of crystalline phase-pure 11 Å tobermorites (Komarneni et al., 1985; Wieker et al., 1982). Terminal Q^1 silicate tetrahedra of the wollastonite-like chains and isolated silicate dimers are denoted by resonances at -81.6 ppm. Mid-chain Q^2 tetrahedra give rise to the resonances at -87.4 ppm and the low field shoulder at -85.2 ppm is assigned to Q^2(1Al) species. The low intensity signals at ~95 ppm arise from bridging Q^3 species and minor proportions of residual SLSG may also contribute to the signals in this region of the spectrum. The mean silicate chain lengths (MCL) of the SLSG-derived tobermorite products are listed in Table 3 and indicate that MCL decreases from 18.5 to 4.1 units as the sodium hydroxide concentration of the hydrothermal system is increased from 1.0 M to 4.0 M. Nitrogen gas sorption analysis demonstrated that the BET specific surface areas of the tobermorite products were also

influenced by the alkalinity of the reaction mixture (Table 3). These data, and those obtained by other researchers (Reinik et al., 2011), indicate that specific surface area tends to decrease as a function of increasing pH of the reaction mixture.
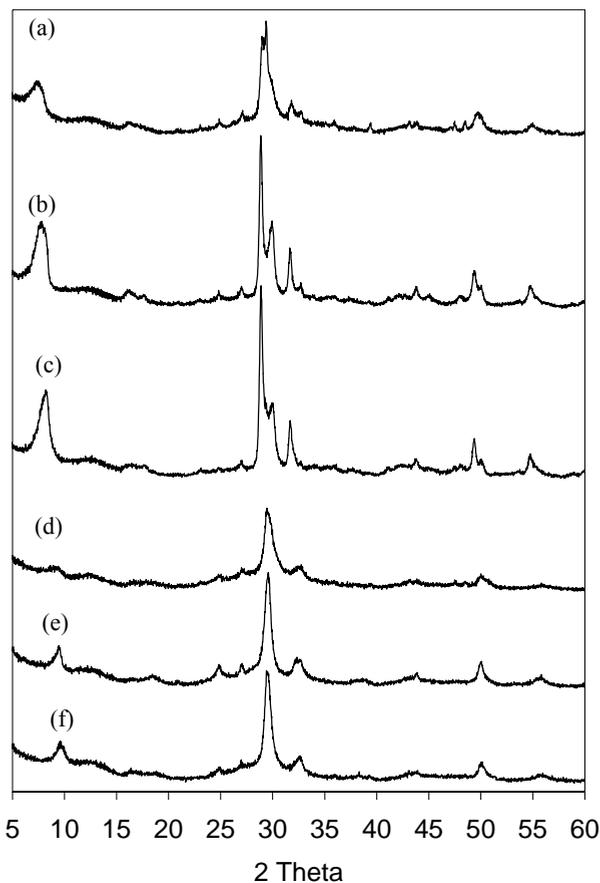

Fig. 3. Powder XRD patterns of SLSG-derived tobermorites (a) Tob-1, (b) Tob-2, (c) Tob-4; and tobermorite after heating at 300 °C (d) Tob-1, (e) Tob-2, (f) Tob-4

Table 3. Mean silicate chain length (MCL), BET specific surface area and metal ion uptake data for tobermorite products

Sample	MCL	Surface area	Cd^{2+}-uptake at 168 h		Zn^{2+}-uptake at 168 h	
		(m^2g^{-1})	$(mg\ g^{-1})$	$(mg\ m^{-2})$	$(mg\ g^{-1})$	$(mg\ m^{-2})$
Tob-1	18.5	16.1 ± 0.2	441	27.4	122	7.58
Tob-2	5.7	27.1 ± 0.3	374	13.8	96	3.54
Tob-4	4.1	26.0 ± 0.4	325	12.5	78	3.00

This study has demonstrated that phase-pure 11 Å tobermorites can be synthesised from a stoicheiometrically appropriate mixture of SLSG and calcium oxide *via* one-step hydrothermal processing at 100 °C under alkaline conditions. Unlike many industrial and municipal waste materials, SLSG does not require pre-treatment such as leaching or chemical conditioning prior to use. This research has also revealed that increasing concentrations of sodium hydroxide in this hydrothermal system increase the degree of crystallinity and surface area, yet reduce the average silicate chain length of the resulting product.

Mitsuda and Taylor observed that the development of tobermorite proceeds *via* the formation of a poorly structured calcium silicate hydrate gel phase (C-S-H) similar to that found in hydrating cement (Mitsuda and Taylor, 1975). This observation was subsequently confirmed in a real-time synchrotron study, which revealed that the first hydrothermal reaction product formed during tobermorite synthesis is a C-S-H gel with good periodicity in the *ab*-plane and poor organisation parallel to the *c*-axis (Shaw et al., 2000). Other studies have indicated that increasing alkalinity generally enhances the rate of tobermorite formation; whereas, increasing concentrations of Na^+ ions are reported to stabilise the intermediate C-S-H gel phase and impede the development of the tobermorite product (Nocun-Wczelik, 1999; Shaw et al., 2000). SLSG-derived tobermorites confirm these observations, as increasing sodium hydroxide concentrations resulted in an enhanced reaction rate (i.e. superior crystallinity) at the expense of mean silicate chain length.

Batch sorption of Cd^{2+} and Zn^{2+} ions

The sorption profiles for the removal of Cd^{2+} and Zn^{2+} ions from single metal nitrate solutions by Tob-1, Tob-2 and Tob-4 under batch conditions are shown in Fig. 4. The uptakes of Cd^{2+} and Zn^{2+} after 168 hours as functions of mass and of BET surface area are also listed in Table 3. These data demonstrate that the rates and extents of sorption of both Cd^{2+} and Zn^{2+} ions by the SLSG-derived tobermorites are of the following order: Tob-1 > Tob-2 > Tob-4.

Despite a steadily increasing body of data, the mechanisms and extents of ion exchange reactions between heavy metal cations and 11 Å tobermorites remain disputed. For example, Komarneni et al. (1986 and 1988) report that essentially all of the Ca^{2+} ions within the tobermorite structure can be exchanged for Co^{2+} or Ni^{2+} ions; whereas, in a similar investigation, Shrivastava and Glasser (Shrivastava and Glasser, 1986) found that fewer than 20% of the total Ca^{2+} ion content was available for exchange by these heavy metal cations. It is clear that these and other such discrepancies arise from differences in structural features which have not been identified to date. Indeed, very little is presently known of the relationship between tobermorite structure and ion exchange behaviour.
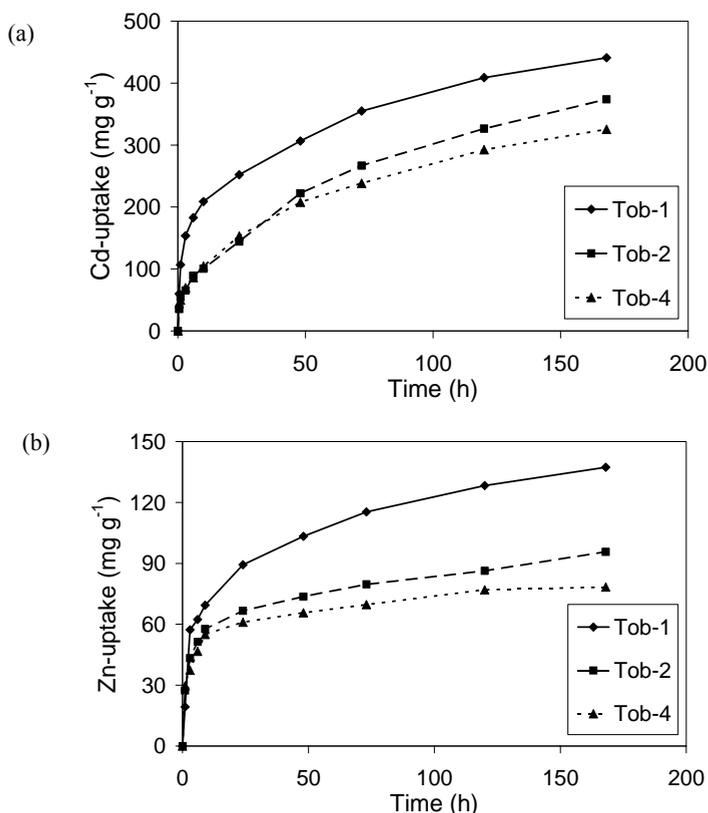
Fig. 4. The uptake of (a) Cd^{2+} ions and (b) Zn^{2+} ions by SLSG-derived tobermorites

The results obtained in this investigation indicate that low crystallinity, specifically arising from stacking disorders, assists the transport and ion-exchange of Cd^{2+} and Zn^{2+} ions within the tobermorite lattice. Conversely, these findings have also demonstrated that structural defects arising from breaks along the silicate chains do not facilitate these transport and ion-exchange processes.

Table 4. Cd^{2+} and Zn^{2+} sorption capacities for a range of waste-derived sorbents

Sorbent	Cd^{2+}-uptake (mg g^{-1})	Zn^{2+}-uptake (mg g^{-1})	Reference
Red mud	68	133	Vaclavikova et al. (2005)
Modified chestnut shell	10.14	9.26	Vázquez et al. (2012)
Bone char	53.6	33.0	Choy and McKay (2005)
Papaya wood	19.99	14.44	Saeed et al. (2005)
Rice husk	16.7	8.14	Krishnani et al. (2008)

For comparison, the maximum Cd^{2+} and Zn^{2+} sorption capacities for a range of waste-derived sorbents are listed in Table 4 (Choy and McKay, 2005; Krishnani et al., 2008; Saeed et al., 2005; Vaclavikova et al., 2005; Vazquez et al., 2012). It should be noted that the original data were reported in a variety of units which have been converted to mg g^{-1} for convenience. In general, the sorption capacity of SLSG-derived tobermorites for both metal cations compares favourably with those of other waste materials such as bone char, papaya wood, rice husk and modified chestnut shells; however, their performance was inferior to that of red mud with respect to the removal of Zn^{2+} ions. Further work is now in progress to more fully characterise the ion-exchange properties and potential for post-use regeneration of SLSG-derived tobermorite sorbents.

Conclusions

The findings of this study have demonstrated that waste soda-lime-silica container glass is a suitable feedstock material for the one-step hydrothermal synthesis of ion-exchangeable tobermorites. Unlike many industrial wastes, discarded container glass does not require leaching or chemical pre-treatment prior to use in this application.

All tobermorites synthesised at 100 °C from stoicheiometric mixtures of waste glass, lime and sodium hydroxide solution were structurally similar to those prepared from analytical grade reagents and exhibited normal thermal behaviour. Increasing concentrations of sodium hydroxide (between 1.0 M and 4.0 M) in the reaction mixture promoted the formation and crystallisation of tobermorite, although also resulted in greater fragmentation of the silicate chains along the b-axis direction. Superior Cd^{2+} and Zn^{2+} ion-exchange capacities and kinetics were observed for the least crystalline tobermorite specimen, indicating that stacking defects in the c-axis direction facilitate the transport and exchange of cations within the lattice.

References

AL-WAKEEL E.I., EL-KORASHY S.A., EL-HEMALY S.A.S., RIZK M.A., 2001, *Divalent Ion Uptake of Heavy Metal Cations by (Aluminum plus Alkali Metals)-Substituted Synthetic 1.1 nm-Tobermorites*, J. Mater. Sci. 36, 2405-2415.

AYADI A., STITI N., BOUMCHEDDA K., RENNAI H., LERARI Y., 2011, *Elaboration and Characterization of Porous Granules Based on Waste Glass*, Powder Technol. 208, 423-426.

CHOY K.K.H., MCKAY G., 2005, *Sorption of Cadmium, Copper and Zinc Ions onto Bone Char using Crank Diffusion Model*, Chemosphere 60, 1141-1150.

COLEMAN N.J., BRASSINGTON D.S., 2003, *Synthesis of Al-substituted 11 Å Tobermorite from Newsprint Recycling Residue: a Feasibility Study*, Mater. Res. Bull. 38, 485-497.

COLEMAN N.J., 2005, *Synthesis, Structure and Ion Exchange Properties of 11 Å Tobermorites from Newsprint Recycling Residue*, Mater. Res. Bull., 40, 2000–2013.

COLEMAN N.J., TRICE C.J., NICHOLSON J.W., 2009, *11 Å Tobermorite from Cement Bypass Dust and Waste Container Glass: a Feasibility Study*, Int. J. Miner. Process. 93, 73-78.

COLEMAN N.J., 2011, *11 Å Tobermorite Ion Exchanger from Recycled Container Glass*, Int. J. Environ. Waste Manage. 8, 366–382.

EL-HEMALY S.A.S., MITSUDA T., TAYLOR H.F.W., 1977, *Synthesis of Normal and Anomalous Tobermorites*, Cem. Concr. Res., 7, 429–438.

KOMARNENI S., ROY R., ROY D.M., FYFE C.A., KENNEDY G.J., BOTHNER-BY A.A., DADOK J., CHESNICK A.S., 1985, ^{27}Al *and* ^{29}Si *Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy of Al-substituted Tobermorites*, J. Mater. Sci. 20, 4209–4214.

KOMARNENI S., ROY R., ROY D.M., 1986, *Pseudomorphism in Xonotlite and Tobermorite with* Co^{2+} *and* Ni^{2+} *Exchange for* Ca^{2+} *at 25 °C*, Cem. Concr. Res. 16, 47–58.

KOMARNENI S., BREVAL E., ROY R., ROY D.M., 1988, *Reactions of Some Calcium Silicates with Metal Cations*, Cem. Concr. Res. 18, 204–220.

KORKOSZ A., PTASZYNSKA A., HANEL A., NIEWIADOMSKI M., 2012, *Cullet as a Filter Medium for Swimming Pool Water Treatment*, Physicochem. Probl. Miner. Process. 48, 295–301.

KRISHNANI K.K., MENG X., CHRISTODOULATOS C., BODDU V.M., 2008, *Biosorption Mechanism of Nine Different Heavy Metals onto Biomatrix from Rice Husk*, J. Hazard. Mater. 153, 1222–1234.

LIMA S., DIAS A.S., LIN Z., BRANDÃO P., FERREIRA P., PILLINGER M., ROCHA J., CALVINO-CASILDA V., VALENTE A.A., 2008, *Isomerization of D-Glucose to D-Fructose over Metallosilicate Solid Bases*, Appl. Catal. A: General. 339, 21–27.

MATTEUCCI F., DONDI M., GUARINI G., 2002, *Effect of Soda-Lime Glass on Sintering and Technological Properties of Porcelain Stoneware Tiles*, Ceram. Int. 28, 873–880.

MITSUDA T., TAYLOR H.F.W., 1975, *Influence of Aluminium on the Conversion of Calcium Silicate Hydrate Gels into 11 Å Tobermorite at 90 °C and 120 °C*, Cem. Concr. Res. 5, 203–210.

NELSON E.B., KALOUSEK G.L., 1977, *Effects of* Na_2O *on Calcium Silicate Hydrates at Elevated Temperatures*, Cem. Concr. Res. 7, 687–694.

NOCUŃ-WCZELIK W., 1999, *Effect of Na and Al on the Phase Composition and Morphology of Autoclaved Calcium Silicate Hydrates*, Cem. Concr. Res. 29, 1759–1767.

PARK S.B., LEE B.C., KIM K.H., 2002, *Studies on Mechanical Properties of Concrete Containing Waste Glass Aggregate*, Cem. Concr. Res. 34, 2181–2189.

PONTIKES Y., ESPOSITO L., TUCCI A., ANGELOPOULOS G.N., 2007, *Thermal Behaviour of Clays for Traditional Ceramics with Soda-Lime-Silica Waste Glass Admixture*, J. Eur. Ceram. Soc. 27, 1657–1663.

REINIK J., HEINMAA I., KIRSO U., KALLASTE T., RITAMÄKI J., BOSTRÖM D., PONGRÁCZ E., HUUTANEN M., LARSSON W., KEISKI R., KORDÁS K., MIKKOLA J-P., 2011, *Alkaline Modified Oil Shale Fly Ash: Optimal Synthesis Conditions and Preliminary Tests on* CO_2, J. Hazard. Mater. 196, 180–186.

RICHARDSON I.G., GROVES G.W., 1997, *The Structure of the Calcium Silicate Hydrate Phases Present in Hardened Pastes of White Portland Cement/Blast Furnace Slag Blends*, J. Mater. Sci. 32, 4793–4802.

SAEED A., AKHTER M.W., IQBAL M., 2005, *Removal and Recovery of Heavy Metals from Aqueous Solution Using Papaya Wood as a New Biosorbent*, Sep. Purif. Technol. 45, 25–31.

SHAW S., CLARK S.M., HENDERSON C.M.B., 2000, *Hydrothermal Formation of the Calcium Silicate Hydrates, Tobermorite* $(Ca_5Si_6O_{16}(OH)_2.4H_2O)$ *and Xonotlite* $(Ca_6Si_6O_{17}(OH)_2)$*: an In Situ Synchrotron Study*, Chem. Geol. 167, 129–140.

SHRIVASTAVA O.P., GLASSER F.P., 1986, *Ion-Exchange Properties of 11-Å Tobermorite*, React. Solids 2, 261–268.

VACLAVIKOVA M., MISAELIDES P., GALLIOS G., JAKABSKY S., HREDZAK S., 2005, *Removal of Cadmium, Zinc, Copper and Lead by Red Mud, an Iron Oxides Containing Hydrometallurgical Waste*, Studies in Surface Science and Catalysis 155, 517–525.

VAZQUEZ G., MOSQUERA O., FREIRE M.S., ANTORRENA G., GONZALEZ-ALVAREZ J., 2012, *Alkaline Pre-Treatment of Waste Chestnut Shell from a Food Industry to Enhance Cadmium, Copper, Lead and Zinc Ions Removal*, Chem. Eng. J. 184, 147–155.

WIEKER W., GRIMMER A-R., WINKLER A., MÄGI M., TARMAK M., LIPPMA E., 1982, *Solid-State High-Resolution ^{29}Si NMR Spectroscopy of Synthetic 14 Å, 11 Å and 9 Å Tobermorites*, Cem. Concr. Res. 12, 333–339.